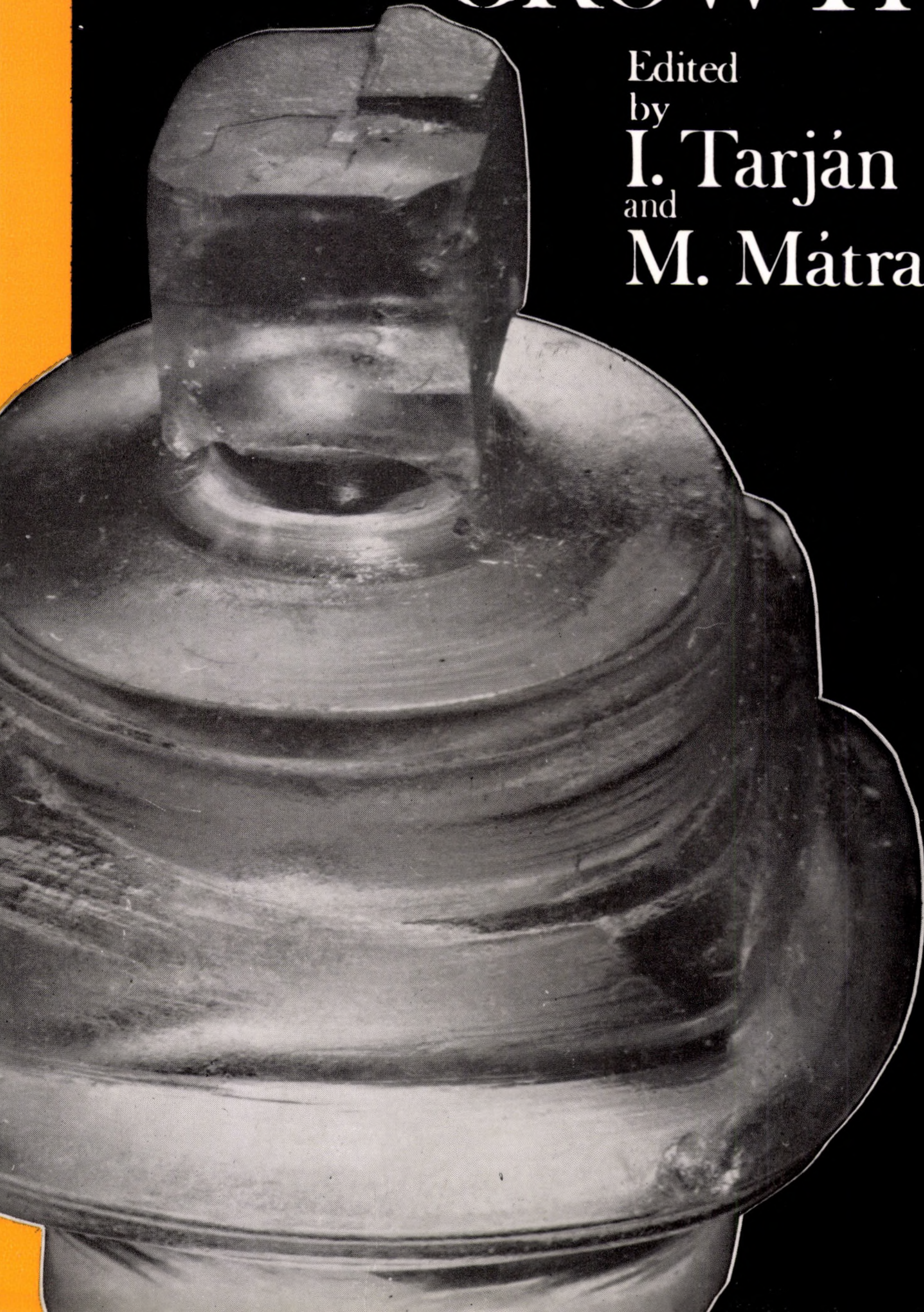
Laboratory Manual on CRYSTAL GROWTH

Edited
by
I. Tarján
and
M. Mátrai



Laboratory Manual on CRYSTAL GROWTH

Laboratory Manual on Crystal Growth is a modest attempt at furthering the study of crystal growth and the knowledge of the various growth methods.

From the aim of the manual it follows that the theoretical problems of crystal growth are not discussed, concerning them only a few brief remarks are made. The Bibliography provides a useful coverage of the theoretical background. The experiments described in the volume are written by specialists in the respective fields. The various growth apparatuses are shown in a great number of figures. Photographs of several crystals grown by the methods described, are also given. It is hoped that *Laboratory Manual on Crystal Growth* will prove to be a useful instrument in teaching crystallography at university level.

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AKADÉMIAI KIADÓ
BUDAPEST
By arrangement with
UNESCO

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CRYSTAL GROWTH

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DR. I. TARJÁN
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AKADÉMIAI KIADÓ, BUDAPEST 1972
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TRANSLATED
BY
DR Z. MORLIN

DRAWINGS
BY
DR A. SÁRMAY

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PREFACE

A frequent request from crystallographers at the various international meetings has been for a text-book suitable for teaching crystallography at university level. *Laboratory Manual on Crystal Growth* is a modest attempt to fulfil this need.

The aim of the authors is to assist in carrying out laboratory experiments, to further the study of crystal growth and the knowledge of the various growth methods. Whilst it is not the purpose of this manual to deal with theoretical questions, nevertheless, some remarks do occasionally appear, and the Bibliography provides a useful coverage of the theoretical background. No stress is laid either on methods serving to control the quality (e.g. purity, perfection) of the grown crystals or on those to measure various physical (e.g. electronic or optical) properties important from the practical point of view. These problems, especially the general and the basic methods of quality control, should be dealt with in a separate book.

Concrete and practical instructions aim to make the exercises easier. Should the experiments fail to give satisfactory results or the grown crystals be poor in quality, the actual environment conditions, the materials used in the growth equipment, impurities in the starting material or other factors difficult to control, may be held responsible for that. Consequently, prolonged experiments may be necessary before the desired result is obtained.

A knowledge of experimental techniques in a great number of other fields—such as the handling of microscopes, the preparation of microphotographs and of samples for electron microscopical studies, the calibration of thermocouples, titration, and several of the usual chemical procedures—is necessary for carrying out these exercises. None of the techniques and procedures is described in detail and attention is drawn only to such circumstances that deviate from the usual methods.

Although many of the exercises can be carried out using simple equipment and devices, more complicated experiments requiring more costly pieces of apparatus are also included. Simple home-made sets of instruments for experiments that are easy to carry out are described, while for more complicated experiments merely mention is made of the devices (such as thermoregulators, more complicated resistance furnaces, induction furnaces, etc.) required for obtaining satisfactory results.

The various exercises require different lengths of time. Whilst some can be performed within a few hours, others require a periodic time control and/or observation for several days. Some are suitable for an independent task (e.g. as part of a thesis) as well as for selecting details from them which need only a relatively short time to be carried out.

Some of the materials used in the experiments are good models or rather cheap and easily obtainable (e.g. alkali halides), whilst others are important basic materials for practical application (e.g. Ge, InSb).

It was considered important that the various chapters should be written by specialists in these fields and this explains the relatively large number of contributors.

References are included in the Bibliography, and in order to keep down the size of the manual only monographs and proceedings of international congresses on crystal growth are quoted; papers are quoted only if figures or data are taken over from them.

The authors and editors wish to add that they welcome any comments or advice from the reader which may serve to improve this manual.

Finally, the editors wish to express their gratitude to the Science Teaching Division of UNESCO, especially to Professor N. Joel, for the support and continuous interest manifested at the preparatory phase of this book. Our thanks are also due to Dr Gy. Turchányi and Dr S. Ujhelyi for the careful revision of the text.

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Dr I. Tarján
and
M. Mátrai

CONTRIBUTORS

I. Bertóti	(II.2.2.3; II.2.3.2; II. 3.2.1)
J. Gémesi	(I.6.1.3; I.13.1.1; II.1.1.1; II.1.1.5; II.1.2.2; II.1.3.1; II.1.4.2; II.1.4.3; II.5)
Dr J. Giber	(II.2.2.5; II.3.2.2)
M. Hársy	(II.1.5.1; II.1.5.2; II.1.5.3; II.3.1.3)
Dr E. Hartmann	(I.6.1.4; I.7; I.8; I.9.1; I.9.2; I.9.3.1; I.13.1.2; I.13.3)
B. Jeszenszky	(I.5.3; I.10)
Dr F. Kardos	(I.12; II.2.1.4)
Dr J. Kiss	(II.1.1.4; II.1.2.1; II.1.4)
G. Konczos	(I.11.1.1; II.2.1.1; II.2.2.2; II.5)
Dr Ö. Lendvay	(II.1.5; II.2.2.3; II.2.3.2; II. 3.1.3; II.3.2.1; II.5)
Dr L. Malicskó	(I.1.1.1; I.2; I.3; I.4; I.5.1; I.5.2; I.6.1.1; I.6.1.2; II.1.1.3)
Dr Z. Morlin	(I.11.1)
J. Paitz	(II.2.1.1; II.2.2.2)
Dr I. Tarján	(II.1.6; II.4)
Dr Gy. Turchányi	(I.9.3.2; I.9.3.3; II.2.1.2; II.2.3.1; II.5)
Dr S. Ujhelyi	(I.1.2; I.1.3.1; II.2.1.3; II.2.2.1; II.3.1.1; II.3.1.2)
Dr R. Voszka	(II.2.2.4)
F. Wilwerger	(I.11.2)
Dr Gy. Zimonyi	(I.13.2; II.1.6)

PART ONE

BASIC PHENOMENA

I.1. SOLUBILITY OF CRYSTALLINE MATERIAL IN LIQUID SOLVENTS

Solutions are mixtures either in the solid or in the liquid state. A saturated solution contains the maximum amount of material which can be dissolved and its concentration is the saturation concentration. The solubility of a material in a solvent is characterized by its saturation concentration, the value of which depends upon the temperature at constant pressure (Table I.I). The temperature at which a solution of given concentration becomes saturated is the saturation temperature.

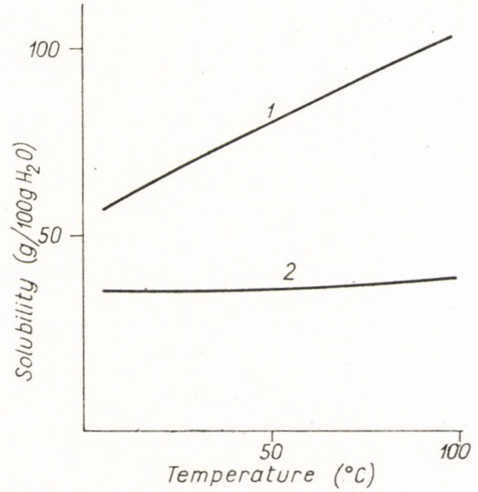

Fig. I.1.1 Temperature dependence of solubility in water
1 KBr; *2* NaCl

Solubility usually increases with increasing temperature, though there are some materials whose solubilities remain constant or even decrease with the increase of temperature (Fig. I.1.1). The solubility may be influenced by impurity in the starting materials and the pH value of the solvent.

TABLE I.I

Crystalline properties and solubility in water at various

Abbreviations:

dh.	= dihydrate	cl.	= colourless	gr.	= green
ph.	= pentahydrate	pu.	= purple	b.	= blue
anhydr.	= anhydride	w.	= white		

Material	Molecular weight	Temperature (°C)			
		0	10	20	30
					Solubility
$AgNO_3$	169.89	122	170	222	300
$BaSO_4$	233.42	1.15×10^{-4}	2.0×10^{-4}	2.4×10^{-4}	2.85×10^{-4}
$CdCl_2$ (anhydr.)	183.32	49.39	55.58	—	—
$CuCl_2$ (anhydr.)	134.48	41.4	42.45	43.5	44.55
$CuSO_4$ (anhydr.)	159.63	14.3	17.4	20.7	25.0
KBr	119.02	53.5	59.5	65.2	70.6
KCl	74.56	27.6	31.0	34.0	37.0
KI	166.02	127.5	136	144	152
$KMnO_4$	158.03	2.83	4.4	6.4	9.0
$MgSO_4 \cdot 7H_2O$	246.49	—	23.6	26.2	29
NH_4Br	97.96	60.6	68.0	75.5	83.2
NH_4Cl	53.50	29.4	33.3	37.2	41.4
NH_4I	144.96	154.2	163.2	172.3	181.4
NaCl	58.45	35.7	35.8	36.0	36.3
$NaNO_3$	85.01	73	80	88	96
$PbCl_2$	278.12	0.6728	—	0.99	1.20
$Pb(NO_3)_2$	331.22	38.8	48.3	56.5	66
$KAl(SO_4)_2 \cdot 12H_2O$	474.38	3.0	4.0	5.9	8.39

I.1.1. Determination of Saturation Temperature of Solution with a Given Concentration

A known quantity of the material to be dissolved and a known volume (or mass) of the solvent are sealed in an ampoule which is put in a liquid bath of constant temperature. From this point one may proceed along two different lines. If the solid material does not dissolve completely the exact temperature of complete dissolution may be determined by changing (usually increasing) the temperature gradually. In the case of an unsaturated solution the temperature at which the first crystals appear may be determined by a gradual change (usually decrease) of the temperature. In the application of this method supercooling may cause a serious error in the determination of the critical temperature. This error may be decreased by shaking the ampoule from time to time.

*temperatures of some crystalline materials**

m. = monoclinic
tr. = triclinic
r. = orthorhombic
trig. = trigonal
c. = cubic
dip. = dipyramidal
pin. = pinacoidal
pr. = prismatic
h. = hexahedron
o. = octahedron

Temperature °C							Crystal system and form, colour
40	50	60	70	80	90	100	
(gsalt/100 g H_2O)							
376	455	525	—	669	—	952	r. cl.
—	—	—	—	—	—	—	r. dip. w.
—	—	—	—	—	—	—	c. cl.
45.6	46.65	47.7	—	49.8	—	51.9	r. dh. gn.
28.5	33.3	40.0	—	55.0	—	75.4	tr. pin. ph. b.
75.5	80.2	85.5	90.0	95.0	99.2	104.0	c. h. cl.
40.0	42.6	45.5	48.3	51.1	54.0	56.7	c. h. cl.
160	168	176	184	192	200	208	c. cl.
12.56	16.89	22.2	—	—	—	—	r. pr. pu.
31.3	—	—	—	—	—	—	r. (m.) cl.
91.1	99.2	107.8	116.8	126	135.6	145.6	c. cl.
45.8	50.4	55.2	60.2	65.6	71.3	77.3	c. o. cl.
190.5	199.6	208.9	218.7	228.8	—	250.3	c. cl.
36.6	37.0	37.3	37.8	38.4	39.0	39.8	c. h. cl.
104	114	124	—	148	—	180	trig. cl.
1.45	1.70	1.98	—	2.62	—	3.34	r. w.
75	85	95	—	115	—	138.8	c. cl.
11.7	17.0	24.75	40.0	71.0	109.0	—	c. o. cl.

Handbook of Chemistry and Physics (1933): Chem. Rubber Publ. Co., Cleveland, 18th ed., pp. 272–397, 44–55; and H. Römpp (1958): *Chemielexikon*. Bd. I–II, 4 Aufl., Francklische Verlagshandlung, Stuttgart

I.1.1.1. Saturation temperature of KBr solutions

Approximately 7 g dry, pulverized reagent grade potassium bromide is added to 10 ml distilled water in a carefully purified and dried ampoule or test-tube. After sealing, the tube is put into a water bath, pre-heated to about 28° C, and kept there for half an hour. The tube is shaken every two–three minutes without taking it out of the bath. During this process a great part of the crystalline material becomes dissolved. The temperature is raised at a rate of 0.8–1.2° C/hour, and the temperature at which the last crystals fully dissolve is observed. This temperature, which in our case is about 32° C, is the saturation temperature.

The determination of the saturation temperature is more exact if the temperature is raised very slowly. The measurement takes about 4–5 hours in the described way. (The saturation temperature should be read at the point at which the last crystals disappear.)

I.1.2. Measurement of Saturation Concentration

The solvent and the excess crystalline material to be dissolved are kept in a vessel held at constant temperature. When equilibrium has been reached a sample is taken from the solution and its concentration determined. The best way of taking a sample is to take out an exactly defined volume with the aid of a pipette without changing the temperature of the solution. The measurement of the concentration of solutions may be carried out in various ways. The concentrations of concentrated solutions used for crystal growth are usually determined by an analytical chemical (gravimetric or volumetric) method. The proper method should be selected in accordance with the material under investigation.

I.1.2.1. Solubility of $NH_4H_2PO_4$ (ADP)

40 g ADP and 20 ml water are put into a saturating vessel of approximately 100 ml volume (Fig. I.1.2). The vessel is placed into a liquid thermostat set at 35° C. The mixture should be stirred with a mechanical stirrer or by continuously shaking the vessel itself. The temperature values on a thermometer placed in the saturating vessel should be taken as solution temperatures. If the material has been previously ground to fine powder the saturation process will be completed within an hour. Then, after stopping the stirring, 2 ml of the solution is transferred by a pipette into a 100 ml measuring flask. In order to avoid taking up crystals lying at the bottom of the vessel a 2.0–2.5 cm long glass tube loosely filled with dry cotton must be connected to the end of the pipette with the aid of a short rubber tube. It is better to withdraw excess solution into the pipette, and let the surplus run out after the removal of the rubber and glass tube. If the solution in the pipette cools, some material may crystallize in it. In order to avoid this the pipette must be kept before use in an air-conditioned thermostat at a temperature of 35–36° C.

The 2 ml solution is made up to the mark of the measuring flask, and after vigorous stirring 10 ml of the diluted solution is poured into a 200 ml beaker. In order to precipitate the phosphate ions of the solution in a measurable quantity a precipitating solution is prepared beforehand by dissolving 10 g reagent grade crystalline magnesium sulphate ($MgSO_4 \cdot 7H_2O$) and 5 g reagent grade ammonium chloride (NH_4Cl) in 100 ml distilled water. To the original solution are added 2.5 g reagent grade NH_4Cl, 10 ml 10% NH_4OH solution, and 80 ml distilled water. The solution so obtained is heated to 80–90° C. At this temperature 0.5 ml precipitating solution is added dropwise to the solution with constant stirring which is continued until the precipitate, at first fleecy and rather difficult to filter, recrystallizes forming large crystals which are easy to filter. The process of recrystallization takes 10 minutes. After this a further 10 ml precipitating solution is added to the precipitate and after vigorous stirring the mixture is left to cool down slowly. After approximately 24 hours the precipitate is transferred to an analytical G4 glass filter previously weighed on a balance with an accuracy of 0.1 mg. Every crystal adhering to the beaker is washed into the filter funnel with 50 ml 1% ammonium hydroxide solution. In order to speed up the drying process the funnel and the precipitate in it are washed three times with approximately 3 ml alcohol, air is sucked through the system with a water pump for a short time, and finally the system is kept at room temperature in air for about half an hour. During this procedure all the water and alcohol evaporate from the surface of the precipitate.

The combined weight of the glass filter and precipitate is measured (the accuracy of measurement should be 0.1 mg) and the drying is continued.

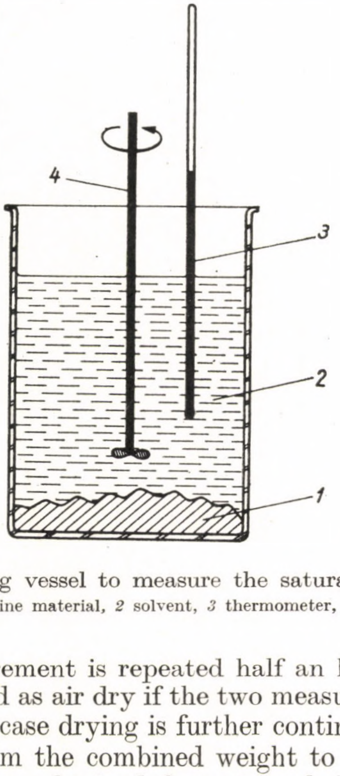

Fig. I.1.2 Saturating vessel to measure the saturation concentration
1 crystalline material, *2* solvent, *3* thermometer, *4* mixer

The gravimetric measurement is repeated half an hour later and the precipitate may be regarded as air dry if the two measurements yield the same value. If this is not the case drying is further continued. The weight of the funnel is subtracted from the combined weight to give the weight of the precipitate. If this latter, obtained from 0.2 ml ADP solution saturated at 35° C (as determined by the previous gravimetry), is multiplied by 500 the result refers to 100 ml solution. The precipitate is $MgNH_4PO_4 \cdot 6H_2O$ with a molecular weight of 245.48 g which is stoichiometrically equivalent to 115.08 g ADP; this means that 1 g $MgNH_4PO_4 \cdot 6H_2O$ is obtained from 0.4688 g ADP. If the value determined previously is multiplied by 0.4688, the ADP content of 100 ml ADP solution saturated at 35° C is obtained. An error arises in the determination if the pipette is not calibrated to 35° C (which is usually the case). This error, however, is not very significant and may consequently be neglected.

I.1.3. Temperature Dependence of Solubility

Solubilities of materials depend on temperature to various degrees. This fact is important in practice not only from the view-point of purification but also because one method of growing crystals from solution involves a slow decrease of the temperature of the saturated solution.

The temperature dependence of solubility as related to 100 ml solvent is not suitable for the study of this phenomenon, since—because of the thermal expansion of the solvent (and to a lesser degree of the dissolved material)—it does not refer to solvents of identical masses. Consequently, for a comparison of the experimental results the data obtained must be related to the mass of dissolved material (g) per 100 ml solvent of identical temperature, or to the mass of dissolved material (g) per 100 g solvent (in the case of very exact measurements the thermal expansion of the dissolved material and the volume changes due to dissolution must also be considered).

I.1.3.1. Temperature dependence of KBr solubility

The determination of the concentration of saturated potassium bromide solution is carried out with the aid of a 0.25 M $AgNO_3$ solution; 8.4945 g crystalline reagent grade $AgNO_3$ is put into a 200 ml measuring flask and dissolved in about 100 ml distilled water; the flask is made up to the mark with distilled water; 10 ml 5% K_2CrO_4 solution is used as indicator.

50 g powdered reagent grade KBr and 40 ml distilled water are placed in a 100 ml saturating vessel (Fig. I.1.2), which is kept in a liquid thermostat at 80° C, and shaken continuously. When the solution has become saturated 1 ml of it is transferred by a pipette into a 200 ml flask. If some crystals precipitate during this procedure, they must also be washed into the flask with 2–3 ml distilled water. The solution is diluted to 50 ml and 1 ml K_2CrO_4 indicator solution is added. With continuous stirring 0.25 M $AgNO_3$ solution is dripped in from a 50 ml burette until one drop of the $AgNO_3$ causes the change of the colour of the solution from yellow to red owing to the formation of silver chromate. When in spite of stirring the red colour persists the volume of the measuring solution used to obtain the stable coloration is read off. From the value obtained the KBr concentration of a 1 ml sample may be calculated. As an example let us suppose that the measuring solution was 10 ml 0.25 M $AgNO_3$ solution which is equivalent to 10 ml 0.25 M KBr solution; this contains $10 \times 0.25 \times 10^{-3} \times 119 = 0.2975$ g KBr. In our case this quantity is dissolved in 1 cm^3 saturated solution.

After the first sample has been taken, the temperature of the liquid thermostat is adjusted to 60° C. When the solution, which must be permanently agitated in the thermostat, has attained this temperature the next sample is prepared similarly. The pipette and the attached glass tube are washed and dried, fresh dry cotton wool is put into the glass tube and the solubility is determined for solutions saturated at 40, 20 and 0° C, too. The results multiplied by 100 yield the solubility of KBr (in weight to volume per cent) at the given temperature.

I.2. NUCLEATION IN SOLUTION

A solution is said to be supersaturated if its concentration at a given temperature is greater than its saturation concentration (C_s; Fig. I.2.1). Supersaturation may be obtained either by decreasing the temperature of the solution, or by evaporation. The following quantities characterize the state of supersaturation.

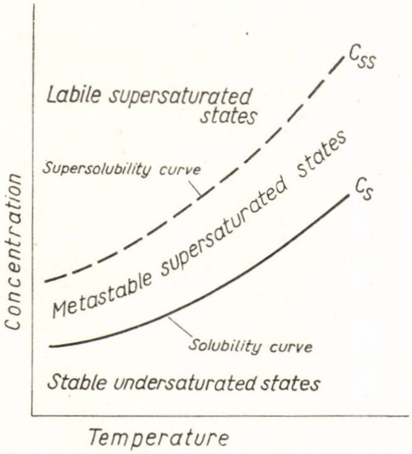

Fig. I.2.1 Temperature dependence of saturation concentration (C_s) and of supersolubility (C_{ss})

(a) Undercooling: $\Delta T = T_s - T$ (T_s = saturation temperature of solution, T = actual temperature of solution, and $T_s > T$).

(b) Absolute supersaturation: $\Delta C = C - C_s$ (C = actual and C_s = saturation concentration at a given temperature, $C > C_s$).

(c) Relative supersaturation: $\sigma = \Delta C/C_s$.

(d) Logarithmic supersaturation: $S = \ln(C/C_s) = \ln(1 + \sigma)$.

Supersaturated solutions are unstable because crystals may easily form in them. The process of crystallization starts with the local association of the molecules (ions) of the dissolved material, which leads to the formation of embryos. The embryos below a certain size, the critical size, may eventually dissolve again. Once the critical size is reached they become stable nuclei, and start growing.

The process of nucleation may be characterized by the rate of nucleation (I), which is defined as the number of nuclei formed per unit time in unit volume. The quantity I satisfies the following equation:

$$I = K \exp(-A/kT),$$

where A is the work necessary to form a nucleus (the activation energy necessary to form a nucleus of the critical size), T is the actual temperature, k is Boltzmann's constant and K is a constant factor. In the case of a system of given composition the activation energy A is a monotonously decreasing function of the supersaturation, and this explains the fact that I increases with the increase of the supersaturation (or undercooling).

The process of nucleation is usually also characterized by the introduction, i.e. incubation, time τ. This is the time that passes until the formation of the first nucleus in the supersaturated solution. A large rate of nucleation means a small τ value. If the supersaturation is less than a certain critical value (this depends upon the quality of the various components of the solutions, e.g. its purity), the incubation time may become very long, in fact so long that in solutions free of any disturbing effects (e.g. electric or magnetic field, mechanical influence, etc.) no nucleation ('spontaneous nucleation') can be found in a finite time of observation. The solution in such circumstances is in a metastable state. (In laboratory practice the 'finite' time interval may be 10 minutes.) If the supersaturation of the solution exceeds a critical value, the so-called metastable limit (supersolubility C_{ss}; Fig. I.2.1), spontaneous nucleation commences in a finite time interval.

I.2.1. Relation between Incubation Time and Undercooling

A solution of known saturation temperature is sealed in an ampoule and placed in a transparent vessel of adjustable temperature (Fig. I.2.2). The temperature of the solution should be controlled with a thermometer placed near to the ampoule. The solution is heated a few degrees above its saturation temperature and left to undercool to the desired degree; the time necessary for the appearance of the first small crystal nucleus is measured. The incubation time decreases rapidly with the increase of the degree of undercooling. The vessel and ampoule are illuminated from the side so that the developing small crystal can be seen clearly. Although the pressure in the ampoule changes during the experiment this effect may be neglected.

I.2.1.1. Relation between incubation time and undercooling in the case of KBr solutions

About 20 ml KBr solution saturated at a temperature of 70° C is sealed in a thick-walled test tube which is put into a water bath at 80° C. In order to speed up the dissolution the test tube is shaken from time to time without taking it out of the water bath. After full dissolution the temperature is decreased to 65° C. If the solution is fairly pure no spontaneous nucleation starts within 10 minutes. The solution is again heated up to 80° C, then cooled to 60° C. Spontaneous nucleation may still not be observed within 10 minutes (even in the case of 10–15° C undercooling). Various increasing undercooling values are set, and the dependence of the incubation time upon the degree of undercooling is determined (Fig. I.2.3 gives some experimental results). The incubation time must be measured from the moment when the thermometer attains the desired undercooling temperature.

If the undercooling is adjusted to a value at which no spontaneous nucleation can be observed within 10 minutes, an avalanche-like nucleation

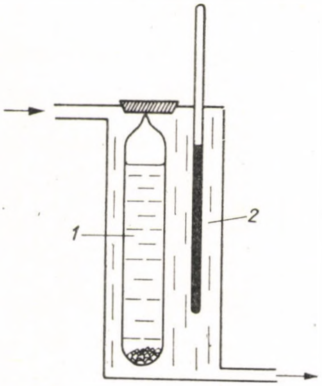

Fig. I.2.2 Device to investigate the dependence of incubation time on undercooling

1 ampoule containing the solution, *2* thermometer

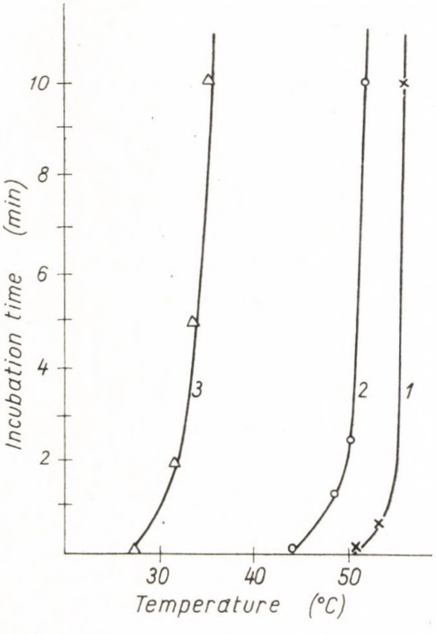

Fig. I.2.3 Dependence of incubation time on undercooling for KBr solutions saturated at various temperatures

1 76.5° C, *2* 70.0° C, *3* 53.2° C

may set in if the test tube is shaken or knocked gently. Besides block-like crystals, thin crystal plates, and also whiskers develop in experiments of this type (for a more detailed description see I.7.1.2). The dependence of the incubation time upon the degree of undercooling (Fig. I.2.3) is determined with the aid of a solution of given saturation temperature. Similar experiments may be carried out with solutions of other crystalline materials dissolved in various solvents.

I.2.1.2. Approximate determination of KBr supersolubility curve

Aqueous KBr solutions of various saturation temperatures are prepared in test tubes. The experiment described in I.2.1.1 is performed with each solution, and the temperature dependence of the incubation time [$\tau(t)$] determined. The $\tau(t)$ functions of the various solutions may be represented by a set of curves similar to those in Fig. I.2.3. As has been pointed out in the introduction to I.2, the metastable limit at a given temperature is determined by the highest concentration of a supersaturated solution at which no nucleation takes place within a finite time.

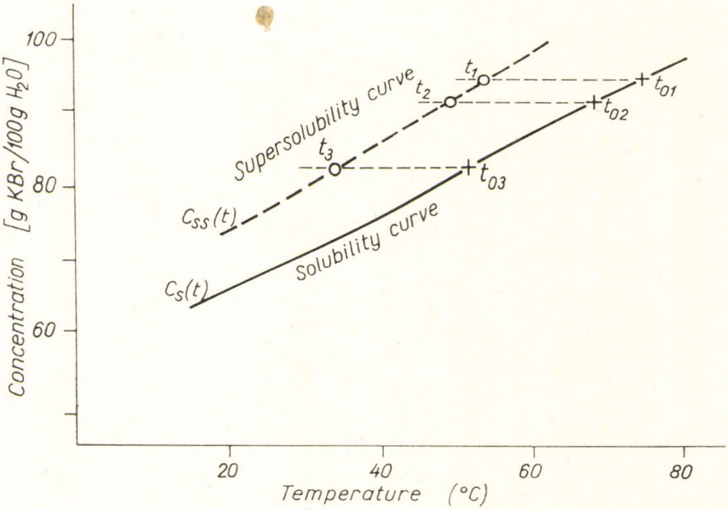

Fig. I.2.4 Approximate determination of KBr supersolubility curve
From the data of Fig. 1.2.3

An observation period of 10 minutes is taken as finite time. From the $\tau_1(t)$, $\tau_2(t)$, $\tau_3(t)$ . . . incubation time–temperature curves of Fig. I.2.3 for the solutions saturated at temperatures of t_{01}, t_{02}, t_{03}, . . ., the temperatures t_1, t_2, t_3, . . . at which no nuclei appear within 10 minutes are determined graphically. The points at temperatures t_1, t_2, t_3, . . . on the straight lines drawn parallel to the t axis from the points of the $C_s(t)$ solubility curve relating to the temperatures t_{01}, t_{02}, t_{03}, . . ., give the points of the supersolubility curve $C_{ss}(t)$. As an example consider the $\tau(t)$ curves of Fig. I.2.3.

The t values are

$t_{01} = 76.5°\,C$ $\quad$ $t_1 = 54.8°\,C$
$t_{02} = 70.0°\,C$ $\quad$ $t_2 = 50.5°\,C$
$t_{03} = 53.2°\,C$ $\quad$ $t_3 = 34.0°\,C$

With the aid of Table I.I the KBr solubility curve $[C_s(t)]$ is drawn. The above data give the supersolubility curve $C_{ss}(t)$ presented in Fig. I.2.4. By increasing the time of observation the metastable limit may be determined more exactly. According to what has been said in the introduction this more exact curve should lie below the curve of the Figure.

I.3. RELATION BETWEEN SOLUBILITY AND SIZE OF CRYSTALS

Solubility, i.e. the saturation concentration C_r, of crystals, depends upon the size of the dissolving crystals (r; Fig. I.3.1). Saturation concentration increases with decreasing crystal size. Solutions may be prepared which are supersaturated for larger crystals, and still not saturated for smaller ones, and consequently the larger crystals grow while the smaller ones dissolve. Size dependence is valid only for crystals smaller than a few microns. For crystals of larger size saturation concentration is independent of the size of crystals.

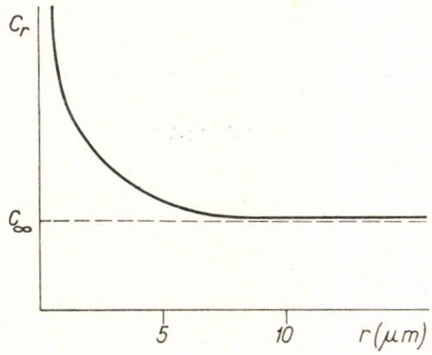

Fig. I.3.1 Crystal-size dependence of saturation concentration

According to theoretical considerations the following relationship exists between the saturation concentration of crystals with sizes much larger than 10 μm (C_∞) and the saturation concentration (C_r) of crystals of size $r < 10$ μm (e.g. spherical crystals with radius r) at temperature T:

$$C_r = C_\infty \exp\ (\eta/Tr),$$

where $\eta = \gamma M\beta/R\varrho$ is a constant depending on material and shape of crystals; γ is specific surface energy of the crystal in solution, M is molecular weight, ϱ is density, R is gas constant and β is form factor.

I.3.1. Growth of Average Crystal Size in Solutions Containing Crystals of Various Dimensions

In these experiments it is practicable to use a rotating crystallization equipment (Fig. I.3.2). The saturated solution *1* and the crystalline material *2* are in a 300–400 ml stemmed cylinder *3* with an external diameter of 5–10 cm and a wall thickness of 2–3 mm. The cylinder is covered with a rubber-packed plexi lid *4*. The lid supports two mixing rods *5* reaching into the cylinder. The crystallization cylinder can be sealed hermetically with the aid of a 1 cm thick plexi disc *6* the same size as the lid, and three screw rods *8* fitted with butterfly-nuts *7*. The crystallization cylinder revolves at 1–2 revolutions per second on a horizontal axis; for the purpose of sampling the cylinder must be opened from time to time. During the experiment, which may take a long time (occasionally days), the solution is kept at the desired temperature; the rotation of the cylinder ensures adequate mixing. In order to determine the average crystal size, crystals should be taken, for example, daily for sampling.

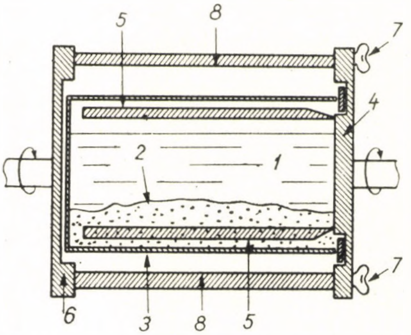

Fig. I.3.2 Rotating crystallization equipment

I.3.1.1. Growth of average crystal size in KBr solution

About 250 ml KBr solution saturated previously at the desired temperature is prepared in a crystallization cylinder and approximately 100 g dehydrated powdered reagent grade KBr is added to it. The cylinder is sealed and put together with the rotating device into a thermostat stabilized at the desired temperature. With continuous stirring the solution is kept at a steady temperature for 6–8 days. Samples are taken from the granules at least daily, the crystalline material is washed with alcohol, and dried on filter paper, and the size of the crystals is determined. This may be done as follows. A small quantity of dried granules is put on a slide, the total weight of the crystals is measured with an analytical balance, and the number of crystals is counted under a microscope directly or by projection. From these data the average grain size may be calculated. After 4–5 days larger grains become visible to the naked eye.

Larger crystals suitable for further experiments may also be obtained by the described method. The crystallization cylinder is opened after about a week's tempering, and the largest grains (1–2 mm in size) are selected and dried on filter paper. The solution is filtered from the rest of smaller crystals, and fresh fine-grained KBr powder is put into the filtered solution. Selected larger grains are placed into the solution, the cylinder is sealed, and the solution kept at a constant temperature for about another week, during which period the larger grains act as seeds and grow. If this process is repeated several times single crystals of several millimeters may grow.

Since solubility depends not only on crystal size but also on temperature, the growth process may be accelerated by periodically alternating the temperature around the selected value (e.g. with a period of a few hours and an amplitude of 1–2° C). With experiments carried out at room temperature no thermostat will be necessary if the daily natural fluctuation of the temperature is not more than 2–3° C. Temperature fluctuation usually deteriorates the structure of crystals grown. The experiments, similarly as described with KBr, may be carried out with other crystalline materials too.

I.4. INHOMOGENEITIES OF SOLUTION CLOSE TO GROWING OR DISSOLVING CRYSTALS

Crystals grow in their supersaturated solution. The concentration of the solution close to the growing surface is lower than that far from it (Fig. I.4.1). As a consequence, a diffusion field (layer) develops in the solution around the crystal in which the molecules (ions) of the dissolved material diffuse to the crystal to replace the molecules (ions) already built into the lattice. Crystal growth is usually accompanied by heat liberation (quite rarely by heat extraction), and consequently a 'heat-diffusion field' builds up between the crystal and its surroundings.

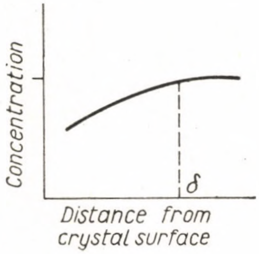

Fig. I.4.1 Variation of solution concentration with the distance from the crystal surface

In the case of stationary growth conditions the thickness of the diffusion layer (δ) developed along a crystal face remains constant with the order of magnitude of 100 μm in an unstirred solution.

Crystals in contact with their unsaturated solution dissolve. The diffusion processes for dissolution run in the opposite direction to those for growing.

I.4.1. Study of Inhomogeneities

Inhomogeneities caused by concentration- and temperature-gradients are reflected in the refractive indices of the solution. The regions of various refractive indices deflect the light passing through the solution to various extents. This can be observed with the naked eye. For the purposes of demonstration a well-contrasting picture may be obtained by illuminating the solution in a parallel-walled cell with a pinhole source of light, and observing the silhouette on a screen (Schlieren method). Inhomogeneities can be seen on the picture as darker and lighter patches or lines. The more point-like the light source and the greater the distance between light source and screen, the higher is the sensitivity of the method. It is advisable to put the cell half-way between light source and screen.

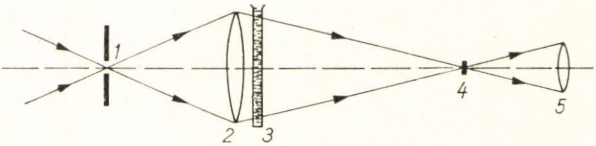

Fig. I.4.2 Schlieren projection

Another arrangement, which is a suitable version of the dark-field illumination, is demonstrated in Fig. I.4.2. The light source is a small circular diaphragm *1*, which is illuminated with the focused light of a point-like source of light. The narrow cell *3* is placed in front of the condenser lens *2*. An image of the cell is projected by a projector lens *5* onto a distant screen. An important part of the equipment is the small opaque disc *4*, which excludes the direct rays of the light source, and transmits only those rays which are deflected by inhomogeneities. The inhomogeneities show up in the picture as light patches or lines in an otherwise dark background (Schlieren projection).

I.4.1.1. Observation of inhomogeneities in $Pb(NO_3)_2$ solution by the Schlieren method

A $Pb(NO_3)_2$ solution is prepared which is saturated at a temperature of about 10° C higher than room temperature.* The solution is poured into

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* On dissolving in water $Pb(NO_3)_2$ hydrolyses and the solution becomes opalescent. In order to avoid this undesired effect 1–2 M HNO_3 solution is used as a solvent.

a 5–50 ml glass cell, and a small 5–10 mm crystal (granulated crystals are also suitable) is put into the bottom of the cell. The cell is placed in the equipment shown in Fig. I.4.2 or in a simpler shadow-projecting system. On cooling the solution becomes supersaturated, and the crystal in the cell starts growing. As a result of the ensuing concentration and temperature differences complicated heat and concentration flows set in. In the Schlieren picture light and dark lines characteristic of the laminar and turbulent flow become visible (Fig. I.4.3). As a state of equilibrium between crysta and solution is approached, the contrast in the picture decreases and it becomes poorer in detail. When equilibrium is attained the picture becomes homogeneous. If observations are to be carried out with dissolving crystals the starting solution must be saturated at a few degrees below room temperature.

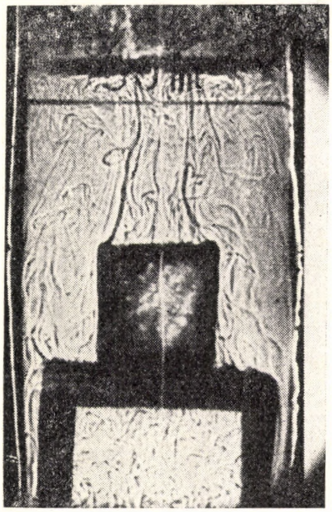

Fig. I.4.3 Schlieren photograph of a KBr crystal growing in solution (M: 0.8×)

Owing to complexities of flow relations the picture obtained with this simple method is not suitable for quantitative evaluation, but may be used for example for the exact control of the saturation of solutions. The study of the concentration distribution may be carried out with the aid of a phase contrast or an interference microscope.

I.4.1.2. Microscopical investigation of the diffusion field round a growing $KMnO_4$ crystal

A few ml aqueous solution of $KMnO_4$ saturated at room temperature is prepared. A drop of the solution is placed with a pipette in the centre of a microscope slide, and left to evaporate until a few, small, columnar crystals develop. The evaporation may be accelerated by warming the slide gently on a gas flame or with a hair drier. After the drop is more or less dry a further drop of the solution is added to it and covered with a cover-slip. It is warmed up again slightly, the slide put immediately under the micro-scope, and a relatively large, preferably solitary crystallite is selected. With a magnification of about 100 the dissolution of the nucleus, due to warming up, and the development of a round dark patch around it may easily be observed. On cooling the solution becomes supersaturated, and the crystal grows rapidly. A relatively light patch becomes visible around

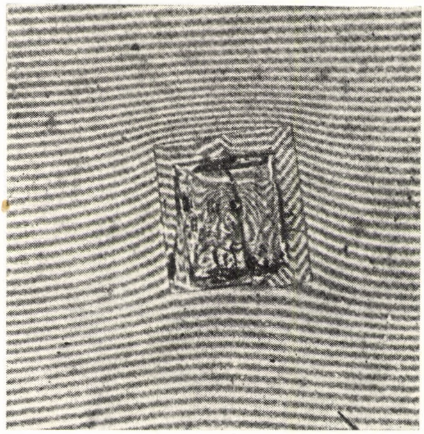

Fig. I.4.4 Deflection of the parallel interference lines in the diffusion field round a $NaClO_3$ crystal growing in solution*

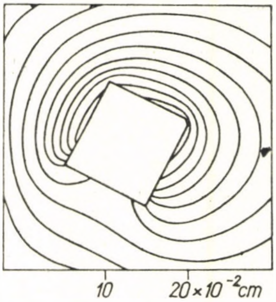

Fig. I.4.5 Equal-concentration contours in the diffusion field round a growing crystal of $NaClO_3$

Contours drawn at concentration intervals of 0.246 g $NaClO_3$/100 g solution*

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* C. W. Bunn (1959): Crystal growth. *Disc. of the Faraday Soc. No. 5, 1949*, Butterworth Sci. Publ., London, p. 132.

the growing crystal. With the aid of an ocular micrometer the thickness of the dark and light layers, i.e. the thickness of the diffusion layers may be estimated. On changing the growth velocity the thickness of the diffusion layers also changes.

Information on the concentration distribution in the diffusion field may be obtained by photometrically measuring the optical density of the microgram taken of one single crystal and its surroundings. In this way the equal-concentration lines can be approximately determined.

More exact information on the concentration distribution may be obtained with the aid of an interference microscope. The parallel lines of interference corresponding to identical optical paths become deflected in the part of the solution close to the crystal (Fig. I.4.4). From this deviation the concentration distribution can be determined using the well-known laws of optics. Figure I.4.5 represents the equal-concentration lines of the diffusion area round a $NaClO_3$ crystal growing in an aqueous solution.

I.5. GROWTH MECHANISM; EFFECT OF SUPERSATURATION ON GROWTH RATE

According to Kossel, in the case of very small supersaturation, i.e. in the case of a very slow crystal growth, the probability of the building-in of the components is greater at that point of the surface where the energy liberated by the deposition is greater. For instance, in the case of a crystal of the sodium chloride type the energy E liberated by the deposition of one ion—i.e. the binding energy of the deposited ion—may be written for any point on any crystal face in the following form:

$$E = \alpha \frac{q^2}{a} ,$$

where a is the distance between the centres of two adjacent lattice elements, q represents the charge of one ion, and α is a numerical factor depending upon the site of deposition. The different sites for deposition shown in Fig. I.5.1 are characterized by the following factors: $\alpha_1 = 0.247$, $\alpha_2 = 0.090$, $\alpha_3 = 0.066$, $\alpha_4 = 0.181$, $\alpha_5 = 0.494$, $\alpha_6 = 0.874$. The probability of deposition is the largest for the site of type *6*, and the smallest for type *3*.

According to Kossel, atomically flat faces (F-faces) grow in the following way. Among the sites of types *1*, *2* and *3* which occur on a flat surface, site *1* is energetically the most favourable position. Thus the deposition of a new layer starts usually at one corner (A in Fig. I.5.2). After this, ionic rows formed along the edges (B), and new rows join these progressing inwards on the surface (C). In this way atomic surface steps are formed along the corners and the edges, and these steps spread out over the whole surface. Since $\alpha_1 < \alpha_5 < \alpha_6$ the deposition of one ion on the corner is followed by a rapid spreading out of the new ionic layer. The growth rate of the crystal face is thus mainly governed by the rate of formation of a new layer and especially by the frequency of depositions in the corners. This is the Kossel rule.

Analogous considerations may be carried out for homeopolar crystals. For this type of crystal the deposition of a new layer starts at the central parts of the crystal face (site *3* in Fig. I.5.1), and the layer then spreads over the whole surface toward the corners and edges.

Kossel's theory does not give any quantitative description of the normal growth of the flat faces, and consequently only a qualitative experimental control of it is possible. The actual limiting faces of a crystal polyhedron can be flat faces (*F*-faces), stepped faces (*S*-faces) or kinked faces (*K*-faces) depending upon their orientation. In the last two cases (i.e. in the case of roughened faces) the building elements arriving at the face may find relatively easily energetically favourable sites for deposition (*6*-type sites). In the case of surfaces free of impurities these faces grow at a greater rate than the flat ones, and their rate of growth increases linearly with the relative supersaturation.

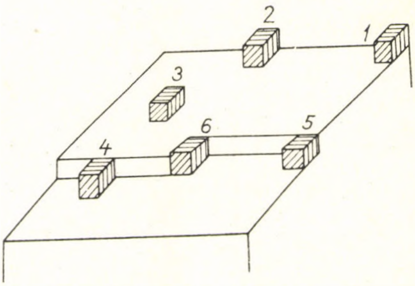

Fig. I.5.1 Sites of different types for deposition on a crystal surface

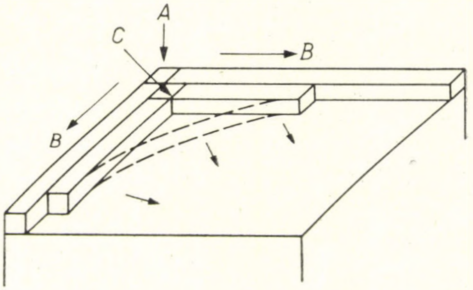

Fig. I.5.2 Development of a new atomic layer

In connection with the growth of atomically flat faces the Volmer–Brandes–Stranski–Kaishev theory comes to the following conclusions. Let us consider an atomically flat (100) face on an ideal cubic crystal. The crystal-forming elements (atoms, ions, or molecules) adsorbed from the surrounding solution form somewhere on the surface a small monomolecular crystalline island, a two-dimensional surface nucleus (Fig. I.5.3). If its dimension attains or even exceeds a critical value the two-dimensional crystal (i.e. its side boundary, the molecular surface step) becomes capable of growing along the face. The atomically flat (ideal) faces grow by the repeated development and spreading-out of these two-dimensional nuclei along the surface. The normal rate of growth of such faces is governed by the rate of formation of the two-dimensional nuclei. According to molecular kinetic considerations the normal rate of growth v may be written in the following form:

$$v = K \exp(-A_2/kT),$$

where K is a constant ('entropy factor'), A_2 is the work necessary to form a two-dimensional nucleus, k is Boltzmann's constant and T is the absolute temperature; A_2 is inversely proportional to the logarithmic supersaturation S. The growth of atomically flat faces in the described way may be expected only at higher supersaturation (theoretically at 25–50%).

The Burton–Cabrera–Frank theory of crystal growth assumes the existence of special crystal defects, especially screw dislocations, in the crystal. If a screw dislocation intersects the surface of an otherwise flat plane a step of monomolecular height will be created (Fig. I.5.4). The steps provide energetically favourable positions for a further deposition of crystal elements (positions of type *6* in the original Kossel theory). If the length of a step achieves a certain critical value (the size of the critical two-dimensional nucleus), the step becomes capable of growing along the surface. Owing to the special situation around a screw dislocation emerging on the surface (the face is a Riemann-surface) the original step creates new steps in the course of its growth (growth spiral). In this way the continuous growth of the respective plane is ensured. According to molecular kinetic considerations the normal growth rate of the face is related to the relative supersaturation σ by the following equation:

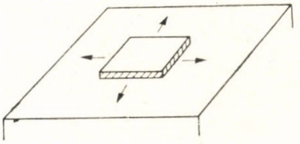

Fig. I.5.3 Two-dimensional surface nucleus

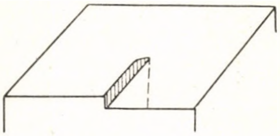

Fig. I.5.4 Atomic surface step advancing from the point of emergence of a crew dislocation

$$v = K'(\sigma^2/\sigma_1)\ \mathrm{th}(\sigma_1/\sigma),$$

where K' is a constant, and σ_1 is a certain critical relative supersaturation value depending on the characteristics of the substance and the conditions of growth; it varies between 10^{-3} and 10^{-1}. If $\sigma \ll \sigma_1$, $\mathrm{th}(\sigma_1/\sigma) \approx 1$ and $v(\sigma)$ becomes parabolic. If $\sigma \gg \sigma_1$, $\mathrm{th}(\sigma_1/\sigma) \approx \sigma_1/\sigma$ and one obtains a linear dependence of v on σ.

I.5.1. Microscopically Observable Phenomena Demonstrating Kossel Rules

I.5.1.1. Growth of $Na_2S_2O_3 \cdot 5H_2O$ crystals

A frame measuring internally about 1 cm^2 is prepared on a clean slide from strips of microscope cover plates, and a droplet of distilled water is placed in its centre. A small 2–5 mm $Na_2S_2O_3$ crystal is put into the droplet, and the slide is heated gently on a gas flame until the crystal melts. The water droplet is necessary to compensate for the water lost by the crystal on heating. The molten drop is covered with a preheated cover slip taking care that no air bubbles remain in the covered drop, and the slide is cooled to room temperature and put under the microscope. The molten drop becomes undercooled, and no crystallization sets in. (The drop may be kept in its undercooled state for days if it is not exposed to mechanical shocks.) The crystallization may be initiated for example by disturbing the edge of the drop with a needle. In this case small rhomboid-shaped crystals develop at the site of the disturbance and grow very rapidly. During growth the formation of a considerable number of new growth layers may be observed near to the corners of the crystals. The thickness of these layers amounts to a few μm. After the new layers are formed at the corners they run very rapidly along the edges of the already existing crystals. (The timing of this experiment is easy, and thus it is very convenient to demonstrate the layer growth in lectures.)

I.5.1.2. Growth of NH_2CSNH_2 crystal in solution drops

A drop of an aqueous solution of NH_2CSNH_2 (thiourea) saturated at room temperature is put on a microscope slide, and is investigated with a polarization microscope. As a result of evaporation small rhomboid-shaped crystals are formed. A well-developed specimen with sufficiently smooth faces is selected. The layers growing on the smooth surfaces become visible between crossed polaroids as coloured formations (birefringence). The movement of these layers along the edges and inwards on the faces is observable all the more because the growth is much slower than in the previous experiment with $Na_2S_2O_3$.

I.5.2. Study of Supersaturation Dependence of Crystal Growth

The investigation needs an optical microscope furnished with a heatable stage; this, however, can easily be made from a 5–7 mm thick copper or

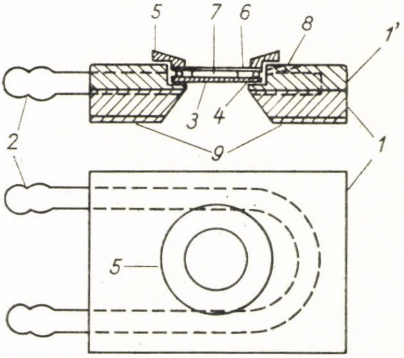

Fig. I.5.5 Heated microscope stage

brass plate (Fig. I.5.5). For this purpose two rectangular slabs with surfaces of 5×7 cm^2 (*1* and *1'*) are made with a U-shaped notch in each. In the cases of heating with an ultrathermostat or of electrical heating a metal-tube *2* or properly isolated electrical heating spirals, respectively, must be installed in the U-shaped ducts of the notches. A circular slide *3* is stuck (e.g. with Araldite cement) above the conic boring of the metal block and a sealing ring *4* is put on it. The cover slide *6* is clamped to the sealing ring with the aid of metal ring *5* screwed into the metal block. In this way the drop *7* becomes hermetically sealed. The temperature of the stage is measured with a thermocouple fitted into boring *8*. The stage must be covered with heat-insulating layer *9*.

I.5.2.1. Supersaturation dependence of KBr growth rate

The microscope stage is heated to about 50° C. A drop of KBr solution saturated at 50° C is put on the slide, and a small smooth-faced crystal cleaved from a larger single crystal is placed into the drop. The drop is sealed with the threaded cover of the stage and the temperature of the stage is changed until no growth or dissolution occurs in the course of an observation time of about 30–60 minutes. The temperature relating to this state may be considered the temperature of saturation T_1. The saturation concentration C_1 for this temperature is determined from Table I.I. The stage is now cooled to a lower temperature T_2 (e.g. 47° C) at which the saturation concentration is C_2. The relative supersaturation will be

$$\sigma = (C_1 - C_2)/C_2$$

With the aid of an ocular micrometer the 'displacement' of a selected plane of the crystal in a given time is measured.* From the measured values the rate of growth can be calculated. After the measurement of the rate of growth at the set supersaturation the original temperature T_1 is reset. When equilibrium has been reached one changes to a greater supercooling, and the rate of growth is again measured. In the same way more measurements are taken for various supersaturation values to determine the exact relationship between σ and v.

Naturally, the supersaturation dependence of the rate of growth of other crystalline materials may also be measured in this way.

I.5.3. Crystal Growth in the Presence of Screw Dislocations

As has been mentioned in the introductory section I.5, according to the Burton–Cabrera–Frank theory, screw dislocations already present in the crystal play a preferred role in the mechanism of crystal growth. Around

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* The time interval is chosen according to the microscopic observability of growth ncrement.

the screw dislocations emerging on the crystal surface, spiral-shaped surface steps (growth spirals) are formed. In this way the growth proceeds even at low supersaturation.

The spiral growth mechanism can be observed in many crystalline materials with an optical microscope as well as with an electron microscope. It is rather difficult to detect any system of steps of the height of a unit cell with an optical microscope; with an interference microscope, however, steps a few Å high are easily detectable. Nevertheless, there are a few simple cases where the spiral growth mechanism and the development of growth spirals can be observed with the aid of an optical microscope. Two exercises are described below; one refers to spiral growth, while the other gives an insight into the spiral mechanism of dissolution.

I.5.3.1. Observation of spiral growth of paraffin crystals

A few ml saturated solution of commercially available plate paraffin in ether or benzene is prepared in a flask with a ground glass stopper. The solution is shaken thoroughly, and left to stand for a few hours, after which it is again shaken vigorously. The solution contains small crystal plates visible to the naked eye. A drop of this solution is put on a microscope slide, and the edge of the drop is observed under an optical microscope in transmitted light at a magnification of 300. Lively motion can be seen in the drop. The small crystal plates push each other in the rapidly evaporating solvent, and thus observation of their surfaces is rather difficult. At the same time, however, new plates grow at the edge of the drop, and their surfaces are easily observed at a magnification of 500–600. Well-developed hexagonal spiral systems can be seen. In some cases the movement of layers with spiral contours starting from a source at the centre of the surface is visible. It is advisable to use a strong light source, and illuminate out of focus if a transmission microscope is used. (See the microphotographs in Figs I.5.6 and I.5.7.)

I.5.3.2 Observation of spirals developed on (100) surfaces of NaCl crystals by etching

The experiment to be described is extremely simple. The phenomenon—up to now not fully explored—is connected with screw dislocations emerging on the (100) surfaces of the crystal, and with the mechanism of growth and re-dissolution.

For purposes of the observation freshly-cleaved NaCl samples must be etched in 5 ml absolute ethanol to which a few drops of 0.1 N iodine solution have been added. The iodine solution should be made with absolute alcohol. The colour of the etching reagent, which must be kept in a jar with a cut glass stopper, is dark orange-red. A plane glass plate is put at the bottom of the jar. The low water content of the solution plays an important role. The alcohol takes up some water from the air, or eventually becomes

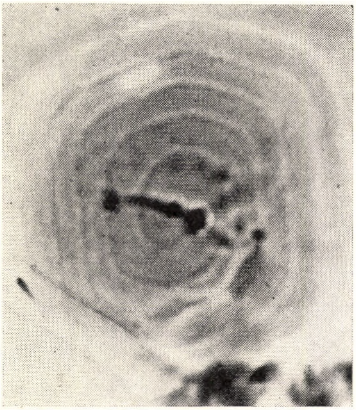

Fig. I.5.6 Growth spiral on a paraffin crystal plate grown from solution
The initially circular spiral step shows hexagonal symmetry (M: 500×)

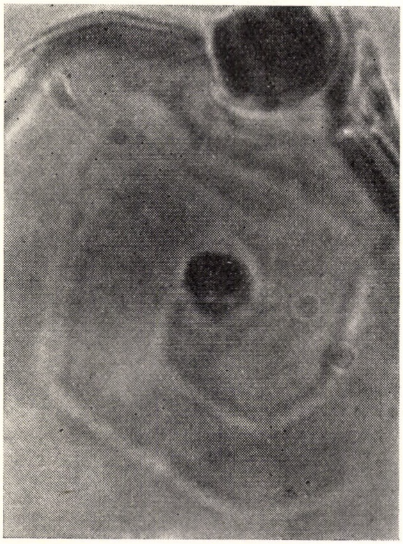

Fig. I.5.7 Combination of two spirals of the same type on the surface of a paraffin crystal plate grown from solution
The dark central part may be some impurity or a channel (M: 1000×)

contaminated by water by immersing the crystalline sample in it. The relative humidity of the environment should be low, otherwise it may spoil the freshly-cleaved surfaces. The sample is placed with its freshly-cleaved surface downwards on the glass plate in the jar containing the etchant, and left there at rest (static etching). After etching for 5, 15, 30, 60 or 120 minutes the sample is taken out with a pair of forceps, and dried on a soft filter paper by pressing it gently to the filter. Rinsing in absolute alcohol produces better resolved etch figures.

On investigating microscopically in transmitted light with a magnification of several hundreds the upper and bottom planes of the crystals will show different etch figures. If a short etching time is applied the well-known pyramid-shaped etch pits at the grain boundaries and on the glide planes can be observed. After a prolonged etching, however, no etch pits are visible on the bottom plane, and instead a new system of etch figures develops (Fig. I.5.8). Vicinal surfaces at the edges of the crystal show that several layers of the plane have become dissolved. The greatest part of the etched surface is covered with lamellae partly lying on each other. Engraving-like spirals, either single or in various combinations are observed

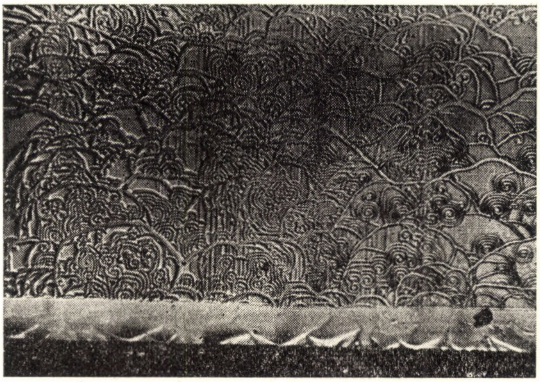

Fig. I.5.8 Etch figures on the (100) plane of a NaCl crystal
(M: 250×; etching time: 40 min)

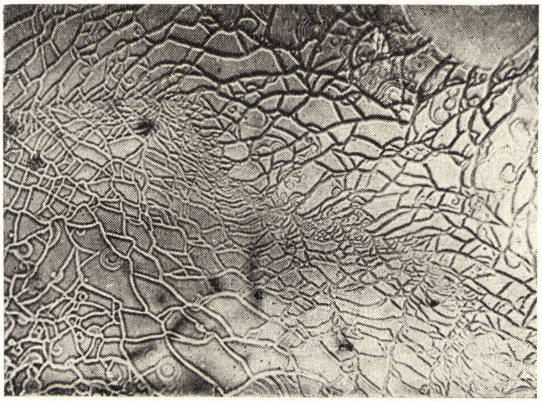

Fig. I.5.9 Etch figures with zig-zag grain boundaries on the (100) plane of a NaCl crystal
(M: 250×; etching time: 90 min)

on these lamellae. The glide lines due to the deformation of the crystals can also be seen, somewhat thickened. The microphotograph of Fig. I.5.9 shows another quite characteristic etch figure. The spirals are here rather scarce in relatively large areas without any structure. (Note, however, the zig-zag shaped grain boundaries.)

Fig. I.5.10 Single spiral configuration on the (100) plane of a NaCl crystal
(M: 1000×; etching time: 60 min)

Fig. I.5.11 Surface of a NaCl crystal with a few lamellae developed after etching of 40 min
(M: 500×)

Microgram I.5.10 shows one large spiral with various fine details, e.g. spiral-branching, steps along the single spiral arms, spirals of smaller dimensions, etc. Only a few lamella levels with spiral structures are seen in Fig. I.5.11. If this surface is investigated with the aid of an interference microscope the spiral structures turn out, in most cases, to be stepped above level. Sometimes, rather rarely, they are depressions (the step heights are in both cases of several 100–1000 Å). If the surfaces are etched with acetic acid, used generally in the case of NaCl (see I.10), etch pits are revealed at the centres of the spirals (Fig. I.5.12); of course etch pits may also develop in other parts of the surface depending upon the glide band system or the grain boundaries of the sample. The etching in acetic acid must be carried out very rapidly (in half a second) as otherwise the spirals are washed away. From these observations of double etching it may also be concluded that the spirals are connected with the dislocations of the crystal.

It should be noted that etching in iodine also develops spirals at the beginning of the process when the surface attacked by the etchant dissolves somewhat. The structures thus obtained, however, differ from the spiral figures developed in a later period of the etching process. This may be explained by a slow supersaturation of the etchant with NaCl which may eventually result in a deposition process after the first layers have become dissolved. Other similar observations are also reported.

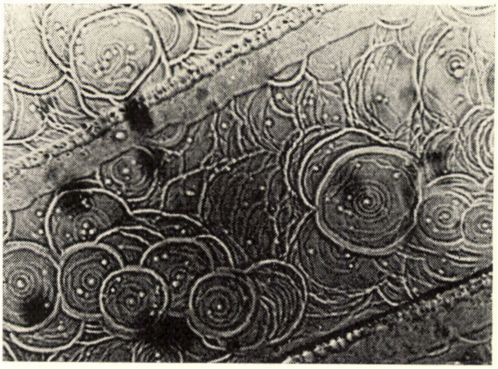

Fig. I.5.12 Double etching (NaCl crystal)

After etching in a reagent containing iodine for 120 min, the crystal is dried and re-etched in acetic acid for a wery short time (1/10 sec); bright spots in the centre are the usual pyramidal etch pits; similar weak spots can also be seen elsewhere (M: 500×)

I.6. GROWTH FORMS; CRYSTAL HABITS

Certain growth directions in growing crystals may be preferred to others. The shape of the growing crystal will be determined by the existence or lack of dominant growth directions. If the crystal grows mainly in one direction it assumes a whisker or column-like form. Crystals growing mainly along one plane become tabular or plate-like. Finally, crystals which grow nearly uniformly in all three dimensions are isometric and grow to blocks. All these forms are called polyhedral.

Dendritic crystals (dendrites) have branching, tree-like crystalline forms. Within each growth form, further variations in the shape of the crystals may be observed, e.g. a whisker may be straight or twisted, blocks and plates may be bounded by concave or convex surfaces, etc.

The relative magnitudes of the faces of various orientations may be different even in the case of identical chemical compositions. The habit of the crystals is determined by the dominant crystallographic faces of the crystal polyhedron. The shape and habit of a growing crystal are determined only partly by characteristic data of the lattice (lattice constant, forces acting between the elements building up the crystal, etc.), and partly by the lattice defects already existing in the growing crystal, and the conditions of growth (relative supersaturation, temperature, impurities, etc.).

The different crystallographic faces bounding the growing crystal grow under identical growth conditions, usually—but not necessarily—at various rates. The rates of growth of the various crystallographic faces depend, in addition to their orientation, on the temperature, the relative supersaturation of the solution, and the nature and concentration of the impurities present. The impurity molecules (atoms, ions) are adsorbed on the surface of the crystal. The extent of the adsorption depends upon the crystallographic orientation (the atomic structure of the face, the binding energy for adsorption, the number of positions available for adsorption, etc.). Thus the impurities will be adsorbed on the various faces to different extents. The adsorbed particles may be obstacles to the growth, but at the same time they may also promote the growth of various faces. On the one hand they may prevent the free advance of the growth layers on certain faces thereby decreasing the rate of growth; and on the other hand the impurities may also increase the probability of the formation of two-dimensional nuclei, and so the normal rate of growth of this face will be increased. As a result of these two effects the relative rates of growth of two adjacent faces may be very different in impure and in pure solutions. In the course of the growth of a given crystal some faces may appear while others disappear and thus the habit of the crystal may be changed (Table I.II). In the following, the geometrical conditions of the stability or the modification of the crystal habit are briefly summarized.

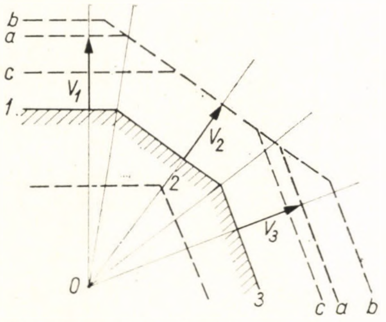

Fig. I.6.1 Growth of crystal faces

Let us consider the plane section of three adjacent crystal faces (lines *1*, *2*, *3* in Fig. I.6.1). Normals to these faces are drawn from the point *0* lying

TABLE I.II

Habit changes due to impurities in heteropolar crystals grown from aqueous solution

Substance	Impurity	Crystal polyhedron faces	References
KCl	—	100, hexahedron	Honigmann (1958)
	urea	411	
	bromobenzene aniline, phenol	Hexoctahedron	Kuznetsov (1954)
	Pb^{2+}	111, 100	Yamamoto (1938)
	Hg^{2+}	100, 111	
KBr	—	100, hexahedron	Yamamoto (1938)
	Pb^{2+}	111, 100	
	Ti^{4+}	100, 111, 110	
CsCl	—	100, 110, 111	Honigmann (1958)
	La^{3+}, Ce^{3+}, $6d^{3+}$	100	Yamamoto (1938)
NaCl	—	100, hexahedron	
	urea	100, 111, 110	Honigmann (1958)
	$HgCl_2$	100, 110	
	alanine	111	
	glycine	110	
$Pb(NO_3)_2$	—	111	Kuznetsov (1954)
	methylene blue	100	Buckley (1959)
$NaClO_3$	—	Cube	Kuznetsov (1954)
	Na_2SO_4	Tetrahedron	
$MgSO_4 \cdot 7H_2O$	—	Rhombic prismatic	Kuznetsov (1954)
	$Na_2B_4O_7 \cdot 10H_2O$	Tetrahedron	
$KAl(SO_4)_2 \cdot 10H_2O$	—	001, 111, 011, etc.	Honigmann (1958)
	KOH, Na_2CO_3	001	Buckley (1959)

H. E. Buckley (1959): *Crystal Growth.* Chapter X. J. Wiley and Sons, Inc., New York.
B. Honigmann (1958): *Gleichgewichts- und Wachstumsformen von Kristallen*, Table 4 in Chapter III. D. Steinkopff Verl., Darmstadt.
B. Д. Кузнецор, (1954): *Кристаллы и Кристаллизация.* Изд. Технико-теоячезкой Литературы, Москва, pp. 216–22
T. Yamamoto (1938): *Sci. Papers. Inst. Phys. Chem. Research (Tokyo)*, *35*, pp. 228–89.

in the interior of the crystal. In unit time the faces are displaced to position *a*. The normal growth rates of the faces are denoted by v_1, v_2 and v_3, respectively. The crystal shapes at every stage of growth remain similar to each other (i.e. the *growth form is stationary*) if the conditions $v_1/v_2 = K_1$, and $v_3/v_2 = K_2$ are fulfilled (K_1 and K_2 are constants depending on the orientation of the respective faces, and characteristic of the given crystalline material). If on the other hand $v_1 > K_1 v_2$ and $v_3 > K_2 v_2$ (position *b* in Fig. I.6.1) the size of plane *2 increases* in the course of growth whereas it decreases, and finally disappears, if $v_1 < K_1 v_2$ and $v_3 < K_2 v_2$ (position *c* in Fig. I.6.1). If a crystalline face grows at a greater rate than that given by the above conditions, the size of the face decreases and the face finally disappears. In the opposite case the face first appears, or more exactly it becomes observable, and afterwards continues to grow. Both cases may result in a modification of the habit.

I.6.1. Production of Various Growth Forms and Crystal Habits

I.6.1.1. Growth of variously shaped KBr crystals

A drop of KBr solution saturated at room temperature is put on a microscope slide. As a result of evaporation the drop becomes supersaturated within a few minutes, and mostly cube-shaped crystals will develop on the edges of the drop (Fig. I.6.2). If the evaporation is slow the cubic form of the crystals will be preserved during their further growth. (The rate of evaporation may be regulated by partially covering the drop, which for this purpose should be placed on a special concave slide.) The lamellar growth is easily observable on well-developed crystals. The several-micron-thick layers develop first usually in the corners, and then spread over the whole crystal face (cf. I.5). If the evaporation is fast the growth layers follow each other more rapidly, sometimes so quickly that the central parts of the growing crystal face cannot be filled up and as a result 'sand-glass'-like cubes, so-called skeletons are formed with their deeper parts toward the centre. (A more detailed discussion of these phenomena is given in I.8.) If the saturated solution is dropped onto a carefully prepared grease-free slide and smeared with a thin glass rod, a rapid (peaked) growth in the [110] direction may be observed in the rapidly evaporating solution film (Fig. I.6.3). This type of growth results in dendritic crystals (cf. I.8).

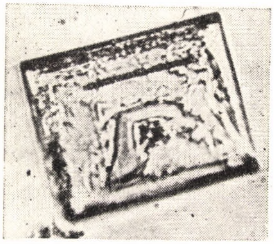

Fig. I.6.2 KBr crystal with surface layers
(M: 100×)

In order to produce and study plate-like crystals the solution drop on the slide is allowed to evaporate freely for about 5–10 minutes at room temperature (at a relative humidity of 30–50%) after the appearance of the first crystals. After this the centre of the drop is stirred with a thin glass rod: fine plate-like crystals develop. The 'one-dimensional' motion of the growth layers formed on the side faces of the plates developed can be studied with ease (Fig. I.6.4). The advance of a layer developed at one

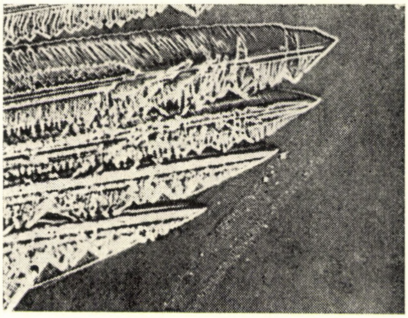

Fig. I.6.3 Dendritic KBr crystals
(M: 200×)

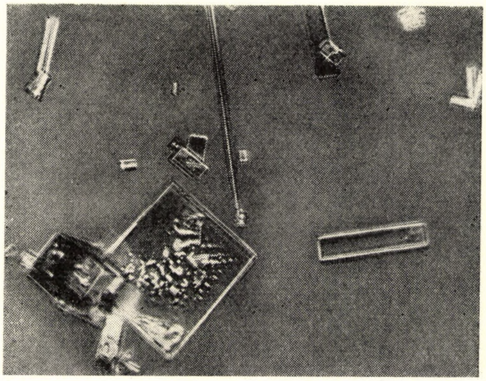

Fig. I.6.4 Variously shaped KBr crystals
(M: 150×)

corner is slowed down at the centre of the plane, and again becomes accelerated in the vicinity of the opposite corner (except if the layer becomes united with some earlier growth layer, thereby thickening). It may also be observed that the advance of thicker layers is usually slower, and is not uniform but shows considerable fluctuations.

In the cases described above whiskers too are developed; a more detailed discussion of these will be given in I.7.1.1. Further experiments to grow alkali halide crystals of various shapes are described in I.7.1.2.

I.6.1.2. Effect of lead impurities on the habit of KBr crystals growing in solution

Pure KBr solution (a few ml) saturated at slightly below room temperature is prepared, together with similar solutions doped with 100, 500, 1 000 and 5 000 ppm lead. For this purpose $PbCl_2$ or $Pb(NO_3)_2$ is used. One drop of each solution is put on a microscope slide and the drops are left to evaporate freely. The development and growth of crystals are clearly visible with a microscope. The habit of the crystals growing from the pure solution is hexahedral, and the dominant bounding faces are (100). With an increase of the lead content, (111) faces also appear in addition to the (100) faces; moreover they become dominant, and the crystal habit becomes octahedral. Kinetically this means that the rate of growth of the (111) faces is $v_{111} \leqq \sqrt{3}v_{100}$, where the equality sign refers to pure and the inequality sign to doped solutions. If one crystal face [e.g. the (100) face] is perpendicular to the optical axis of the microscope, the impurity concentration dependence of the v_{111}/v_{100} ratio may be approximately determined by simple geometrical considerations after measuring the change in the length of the edges.

I.6.1.3. Formation of $KNaC_4H_4O_6 \cdot 4H_2O$ (KNT) crystals from the melt and observation of their growth kinetics

Analytical grade KNT (Seignette salt) sieved to a crystal size of less than 0.1 mm is placed on a slide which is then transferred to a heated microscope stage. On warming the stage up to 100° C the KNT melts, the melt is transparent and as clear as water. The temperature is set to 70° C, and one point of the melt is observed with a magnification of 150–400. When the temperature falls below 80° C whiskers appear in the melt and within a few minutes cover the whole field of vision. If the temperature is set to 50° C, point-like crystals become visible among the whiskers. These point-like crystals grow at a high rate, the whiskers disappear, and soon the well-known rhombohemihedral domains of KNT become visible. If the cooling is fast enough some whiskers may remain frozen in among these domains.

The experiment may also be carried out without a heated stage. For this purpose a double-walled glass vessel in which the KNT melt is well observable at the applied magnification is put on the microscope slide. Suitably heated water is circulated in the double wall, its temperature being regulated with the aid of an ultrathermostat.

I.6.1.4. Crystallization of salol from the melt

A small quantity of salol (phenyl salicylate) is melted on a slide, and cooled slowly to below its melting point (42° C). The edge of the molten drop is touched lightly with a needle the tip of which has been previously slightly heated and subsequently immersed in crystalline salol powder. Crystallization starts at the point of inoculation, and—if the temperature of the undercooled melt is not less than 30° C—rhombus-shaped crystals appear and grow rapidly. Tetragonal spirals may also be observed on the crystal platelets; these may be explained by a screw dislocation growth mechanism. If the salol melt is cooled below 23° C, instead of rhombic, leaf-shaped crystals grow on the surface of the molten drop (Fig. I.6.5) at the point of inoculation. If on inoculation the temperature of the molten drop falls between 23° C and 30° C the platelets grow in transitional forms.

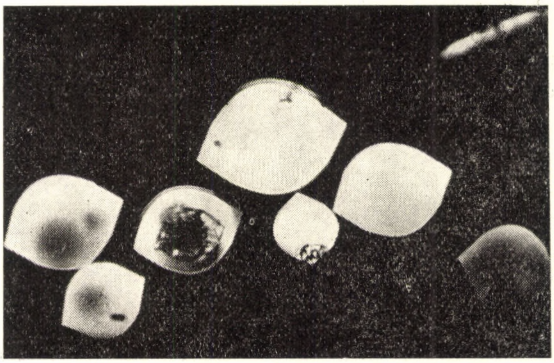

Fig. I.6.5 Formation of leaf-like crystals in a salol melt
(M: 100×)

I.7. GROWTH OF WHISKERS

Whiskers are single crystals in one direction much larger than in the others; their thickness usually amounts to a few microns. Although whiskers had already been known for some centuries, scientists became interested in them only when it was demonstrated with samples of various substances that their mechanical strength exceeds that of the bulk single crystals by 10–100 times; it sometimes even approaches the strength calculated theoretically for ideal crystal lattices. On the other hand, not only mechanical investigations but also magnetic, electrical and optical measurements, and oxidation and dissolution experiments indicate that the behaviour of whiskers differs in many cases from that of large bulk crystals.

Though natural whiskers too may sometimes be found, in general only artificially grown whiskers are of scientific interest. Whiskers may be grown from various materials: metals, metal oxides, salts, semiconductors, and organic compounds. The methods of growing also show great variety. They may be grown from melts, from solutions, from gels, by the condensation of vapours, and also from the solid state. This variety of growth methods also indicates that whiskers grow by various growth mechanisms, which are determined by screw dislocations, impurities and various external conditions acting either separately or together.

I.7.1. Growth of Alkali Halide Whiskers in Solution

I.7.1.1. Growth of KBr whiskers in solution drops; promotion and inhibition of whisker growth with various impurities

A KBr solution saturated at 40° C is prepared. One drop of it is put on a clean microscope slide with a pipette and the process of evaporation is observed with a stereomicroscope. In addition to cubic and prismatic larger crystals, thin platelets and whiskers also become visible. With proper illumination, as a result of interference these platelets and whiskers appear coloured. (The illumination of the drop should be carried out with a lamp movable in every direction.)

A KBr solution saturated at 40° C is doped with 1% $Pb(NO_3)_2$. A warm drop is placed on a slide and observed under a microscope. Neither platelets nor whiskers are formed in the doped solution on cooling or evaporating. The conclusion can be drawn that certain impurities, in the case of our experiment lead ions, inhibit the formation of whiskers. It is worth noting that transparent octahedral crystals are formed in place of cubic or prismatic crystals, i.e. the lead ions also change the shape of the bulk crystals (cf. I.6.1.2). At the edge of the drop dendritic crystal growth may be observed (cf. I.8.1.2).

Some impurities do not inhibit the formation of alkali halide whiskers, on the contrary, their presence promotes it; polyvinyl alcohol is an example of an impurity of this type. Again a KBr solution saturated at 40° C is prepared, this time not with distilled water but with a few hundredths per cent aqueous solution of polyvinyl alcohol. (The effectiveness of polyvinyl alcohols produced by various firms is different and thus an exact value of the polyvinyl alcohol concentration cannot be given in advance.) If one drop of this solution is examined under the microscope, practically only thin platelets and whiskers can be observed; with suitable illumination these will again be coloured as a result of interference.

There are also other impurities which inhibit or promote the growth of alkali halide whiskers though with less effectiveness than lead or polyvinyl alcohol. Some organic materials such as gelatin, sugars, or phenols have a promoting effect, while some cations such as Cd^{2+}, Mn^{2+}, Bi^{3+}, Sn^{2+} are effective inhibitors.

I.7.1.2. Formation of a large quantity of whiskers in KBr solutions by mechanical effects

The formation of a great number of platelets and whiskers in alkali halide solutions may be produced not only with suitable impurities but also by mechanical effects.

Thermometers are installed in two glass tubes with diameters of a few centimeters and lengths of 30 centimeters. The tubes are filled to two-thirds of their length with a KBr solution saturated at 70° C. Afterwards the tubes are hermetically sealed, and the KBr crystals dissolved completely by warming them in a water bath above 80° C. The tubes are then left to cool down in a quiet place. When the temperature inside the tubes has fallen to 68° C and some crystals have appeared in the bottom, one of the tubes is shaken vigorously, or tapped with a wooden hammer. The shaking (tapping) initiates a 'stormy' crystallization, and the hexahedral crystals grown in this process settle down within 1 or 2 minutes. A few minutes after this an increasing number of sparkling whiskers and thin platelets become visible. Their number increases steadily and the small crystals, in an avalanche-like process, fill the whole tube, resembling heavy snowfall (Fig. I.7.1). After this process which lasts 10–20 minutes the loose deposit fills up more than half the volume of the tube. In the undisturbed tube no avalanche process takes place during the cooling process, and afterwards much fewer, more densely packed and larger crystals may be observed in the bottom of the tube.

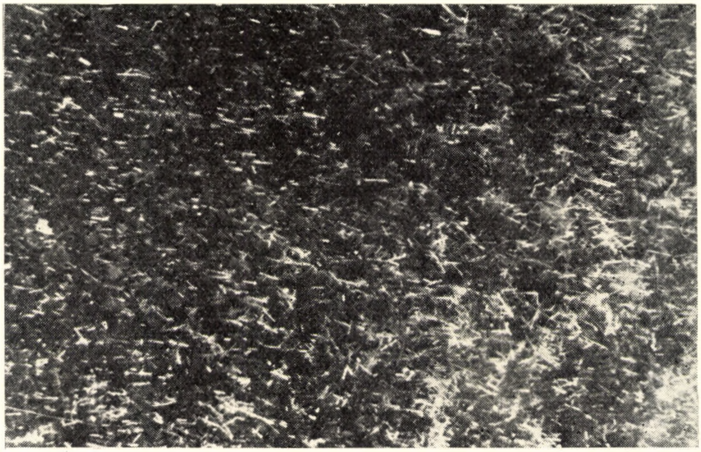

Fig. I.7.1 Avalanche-like development of whiskers in KBr solution (M: 2.5×)

It is advisable to repeat the experiment at various shaking temperatures. The time period between the first crystallization and the eruption of the avalanche is longer at lower shaking temperatures. The same experiment may also be made with KCl solutions. The presence of lead ions inhibits the avalanche formation in both KBr and KCl solutions. The above experiment is repeated with solutions doped with 0.1–10 ppm $PbCl_2$.

I.7.1.3. Growth of very long NaCl whiskers from solution

A few hundredths per cent polyvinyl alcohol solution is prepared. Since the effectiveness of the polyvinyl alcohol is unknown, it is advisable to prepare solutions of various concentrations and carry out the experiments

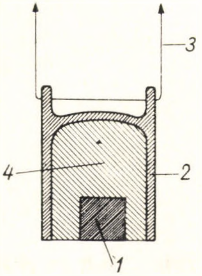

Fig. I.7.2 Suspension of a seed crystal
1 NaCl crystal, *2* glass bell, *3* Ag wire, *4* paraffin

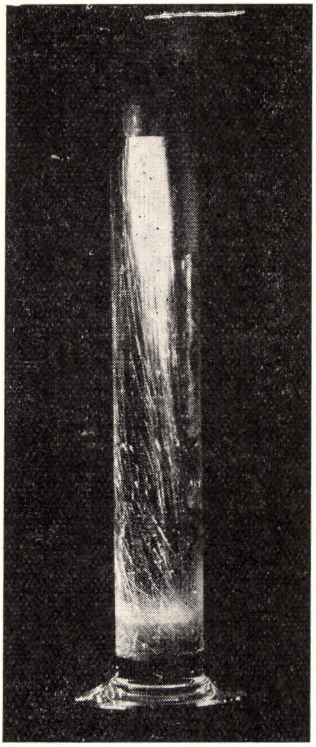

Fig. I.7.3 Bundle of NaCl whiskers grown in a solution containing polyvinyl alcohol as an additive
(Original size reduced by 2.5)

with each solution. NaCl is added to the aqueous solution of polyvinyl alcohol until the solution becomes saturated at 60° C; it is then heated to 70° C, and thereafter cooled slowly to room temperature. The solution is filtered into a 30–40 cm long glass cylinder with a diameter of a few centimeters. A freshly cleaved 1/4–1/2 cm^3 NaCl seed crystal surrounded by a small glass bell hanging on a silver wire and filled with solid paraffin (Fig. I.7.2) is hung in the cylinder. The purpose of the covering is to ensure that the whiskers grow only on the free bottom surface of the seed crystal which is previously polished slightly with emery paper. The glass cylinder is covered and put in an undisturbed place. The growth of whiskers soon begins at an average rate of 1 cm/day, and within a few weeks their length may reach 15–20 cm. The whisker-bundle looks as if the seed has grown a beard (Fig. I.7.3). With proper illumination some whiskers become visible as a row of shining points (Fig. I.7.4); this observation can be accounted for by the fact that the whiskers are twisted around their axes, and as a result the light is reflected only by certain parts of them. A long whisker is taken out by tearing it off the seed with a pair of forceps (care must be taken that no other whiskers should adhere). The structures grown on its surface are investigated under the microscope.

Fig. I.7.4 Straight and twisted NaCl whiskers
(M: 2.5×)

I.7.2. Growth of Whiskers on Porous Materials

For this type of experiment collodion membranes, cellophane, porcelain, faience or other burnt ceramics, etc. may be used. (The enamelled, glazed surfaces must be ground to expose the fine pores of the material.) Silica gel may also be used. With porous materials an introduction time of varying length is necessary before whisker formation commences; whiskers sometimes begin to grow within a few minutes, but sometimes days or even weeks may elapse before the first whiskers are seen.

I.7.2.1. Growth of KBr and LiF whiskers on collodion membranes

A collodion bag is prepared from a solution of collodion, alcohol and ether (4% collodion cotton in 2 parts alcohol + 8 parts ether by weight) in the following way. The collodion solution is poured into a clean test tube up to a height of 0.5–1 cm, and spread over the walls of the test tube by tilting and rotating the tube. After the evaporation of the alcohol and ether a thin collodion membrane is left on the walls of the test tube. The membrane is peeled off with the aid of forceps; care must be taken lest we should tear it. (As collodion and its alcohol–ether solution are inflammable, this experiment must be carried out with special care.)

The bag prepared as described is filled with a KBr solution saturated at room temperature, its opening is tied with thread, and it is hung up so that it does not touch any other object. Within a few minutes, mainly at the upper parts of the bag, KBr whiskers become visible which grow within an hour to a length of a few millimeters. The change of the length of the whiskers is observed microscopically during the growth; for the purpose of the observation some mark, e.g. some defect, is looked for on the growing whisker, and the change of its position with regard to the tip or base of the crystal is observed. It has been found from these experiments that in this method whiskers grow on their base. The rate of growth of the whisker is measured.

LiF whiskers can also be grown with this method. Since the solubility of LiF in water is rather low LiCl and KF solutions are first prepared. The concentrations of the solutions are such that when they are poured into the collodion bag the resulting double solution will be nearly saturated. Within a few days KCl whiskers will grow on the external surface of the bag whereas lithium fluoride whiskers develop on the inner side. Because of the fire hazard the collodion membranes must be destroyed after the experiment has been performed.

I.7.2.2. Growth of NaCl and other whiskers on ceramic plates

Ceramic plates are soaked with saturated NaCl solution. Some of the plates are put in vessels together with small cups filled with saturated NaCl solution. The vessels are covered with glass plates so that the inner part of the vessel is exposed to the air only through a small hole. The other ceramic plates soaked with NaCl solution are put in uncovered beakers. The humidity of the air surrounding the ceramic plates in this latter case is nearly identical to that of the laboratory. Straight whiskers 1–10 mm long will grow in the covered vessels while the growth of thin, wool-like crystals can be observed in the uncovered beakers. On illumination with white light the thinner whiskers appear coloured; they are often so thin that in the open air they constantly move, and become bent by their own weight.

If the pores of the ceramic plates contain much of the solution, first the well-known NaCl 'flowers' are seen; they frequently assemble to form thick bundles. The growth of whiskers begins only later. If the ceramic plates do not contain too much solution, only whiskers will grow. With this method whiskers can also be grown from other compounds, e.g. KCl, KBr, KI, NH_4Cl, $NaAl(SO_4)_2 \cdot 12H_2O$, $KAl(SO_4)_2 \cdot 12H_2O$, $NaClO_3$, $NaNO_3$, KH_2PO_4, KNO_3, $KClO_3$, $CuSO_4 \cdot 5H_2O$. The growth direction of the whiskers may be determined with the aid of Laue diagrams. The most frequent growth direction for NaCl whiskers is [100].

I.7.2.3. Growth of NaCl whiskers on cellophane, and the determination of their tensile strength

Cellophane membrane is washed in distilled water, dried, and stretched on a horizontal frame mounted on short legs. NaCl solution saturated at room temperature is poured onto the membrane, the frame with the membrane is put into a beaker, and a small glass vessel filled with saturated NaCl solution is placed on the bottom of the beaker. The beaker is almost completely covered with a glass plate to obtain a slow evaporation. Within a few days whiskers will grow generally on both sides of the cellophane membrane up to 3–4 cm in length (Fig. I.7.5). The usual thickness of the whiskers is 3–50 μm. The growth rate depends on the temperature and humidity in the laboratory.

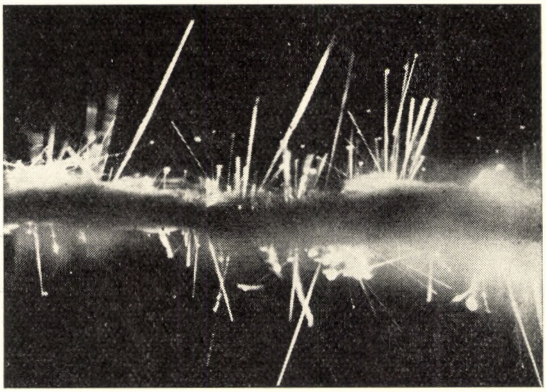

Fig. I.7.5 Whiskers grown on cellophane
(M: 1.5×)

It is worthwhile carrying out tensile strength measurements on the whiskers grown by the methods described. The experiments may be performed in the following simple way: a quartz fibre a few tenths of a millimeter thick is calibrated for bending. One tip of the whisker is stuck with diphenylcarbazide to the calibrated quartz fibre, and the other to a thicker glass rod. This glass rod is moved downwards with the aid of a micromanipulator while the bending of the calibrated quartz fibre is observed with a microscope (Fig. I.7.6). From the bending read at the moment of breaking of the whisker the tensile strength can be determined with the aid of the calibration diagram. The cross-section of the whisker (the value of which is necessary to determine the tensile strength) may be measured as follows: the whisker is stuck with plasticine onto a steel needle, and the needle is fastened onto a micromanipulator. With the micromanipulator the whisker is moved into a vertical position corresponding to the optical axis of the microscope. Since the NaCl whisker is a light-guide, with suitable manipulation of the mirror of the microscope the cross-section of the whisker becomes brighter than its surroundings. Thus the cross-sectional dimensions can be measured with the aid of an ocular micrometer. —With the apparatus described it can be proved that the tensile strength of the whiskers depends on their cross-sectional dimensions. (The thinner the whisker, the higher is its tensile strength.)

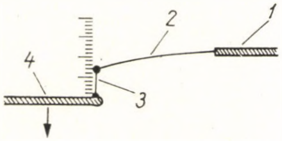

Fig. I.7.6 Measurement of the tensile stress of whiskers
1 fixed glass rod, *2* quartz fibre, *3* whisker, *4* glass rod manipulated with a micromanipulator

I.8. DENDRITIC AND SKELETAL CRYSTAL GROWTH

Crystals grow not only in the form of convex polyhedra. Sometimes, not infrequently, growth forms can be found where some of the bounding elements (planes, edges, corners) are missing. Such deficiently developed forms are among others the tree-like and moss-shaped crystals, the so-called dendrites (the word comes from the Greek 'dendron' which means tree; Fig. I.8.1). In the case of dendritic growth the main stem of the dendrite develops first. This advances rather quickly, and from it may grow branchings at angles determined by the crystal structure; from these branchings secondary branchings may develop (Fig. I.8.2). Sometimes, at the end of the dendritic growth the crystallizing material gradually fills up the space between the branches, and as a result—especially in the case of dendritic growth from the melt—the final forms may show a great variety.

Dendritic growth frequently takes place in the cases of rapid crystallization from strongly undercooled melts, supersaturated solutions or vapours. Furthermore, dendrites may be formed in crystallization in chemical reactions or electrolysis. Several theories have been worked out to explain the formation and growth of dendrites. Some theories regard dendritic growth as a transport problem, for if in the case of solutions the diffusion, or in the case of melts the heat-flow, is weak and inhomogeneous, some places (the corners) of the growing crystal are in a more preferred position to the rest, and this leads to a dendritic growth. According to other considerations, dendritic crystallization may be explained by the presence of impurities.

Fig. I.8.1 Silver dendrites
(M: 20×)

Skeletons are transitional forms between polyhedral and dendritic growth forms. With this type of growth, only the framework (skeleton) of the crystal will develop. The skeletons are single crystals, and under proper growth conditions may transform into the usual convex polyhedral crystals. A skeletal crystal form to be found in nature is the snowflake. Skeletons may also be found among the alkali halides grown from solution. In these crystals the corners and edges are more or less well developed, but instead of the faces of the hexahedron deep stepped pits are formed (Fig. I.8.3). The formation of skeletons may also be explained by the favourable situation of the corners and edges or by the effect of impurities.

The formation of dendrites and skeletons is usually considered harmful when large industrial single crystals are to be grown. On the other hand ribbon-like germanium dendrites are used in semiconducting devices because of their excellent surface properties.

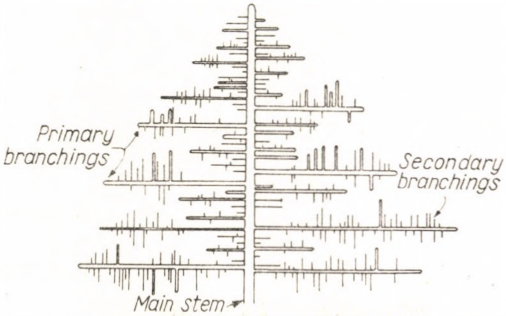

Fig. I.8.2 Schematic diagram of dendritic growth

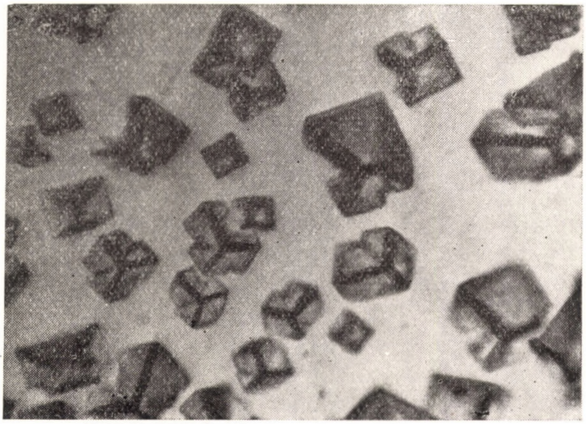

Fig. I.8.3 Skeletal KBr crystals
(M: 30×)

I.8.1. Growth of Dendrites from Solution

Some compounds readily crystallize in the dendritic form, e.g. NH_4Cl (sal-ammoniac). The presence of impurities in the solution may in some instances promote, and in others inhibit the formation of dendrites.

I.8.1.1. Dendritic crystallization of NH_4Cl from solution; inhibiting effect of impurities

A drop of NH_4Cl solution saturated at room temperature is put on a microscope slide, and the dendritic growth starting at the edge of the drop is observed with a stereomicroscope.

If the NH_4Cl solution is doped with $CdCl_2$ in a suitable concentration, instead of a dendritic growth the compound crystallizes in the polyhedral form. In order to obtain this result 1% $CdCl_2$ is dissolved in the NH_4Cl

solution saturated at room temperature. Under the stereomicroscope the growth of beautiful, mostly transparent polyhedral crystals can be observed. In this case only traces of a dendritic growth may be detected. Solutions of NH_4Cl doped in sequence with 0.8%, 0.6%, 0.4%, etc. $CdCl_2$ are prepared. The dendritic character of the crystallization becomes more and more pronounced with decreasing impurity concentration. The same experiment is repeated, but the NH_4Cl solution is doped with $FeCl_3$, $NiCl_2$, $CoCl_2$ or $CuCl_2$. These impurities also inhibit the formation of dendrites.

I.8.1.2. Growth of dendrites in thin layers of solution in the presence of impurities

A KBr solution saturated at about 40° C is prepared, and 1% $Pb(NO_3)_2$ is added to it. Inside a drop taken from this solution octahedral crystals will grow (see section I.6.1.2), whereas on the edges of the drop dendritic growth commences. The individual dendritic branches run forwards out of the drop like the fingers of the hand causing the drop to flatten more and more. In many cases the ends of the dendrites become elevated 1 or 2 mm above the slide. Without lead impurities, such dendritic growth can be observed only rarely in KBr solutions. It is worthwhile making the observations with a stereomicroscope.

I.8.2. Formation of Dendrites in Melt Drops

Dendrites formed on the solidification of transparent melt drops may be investigated in the following way: a loop 2–3 mm in diameter is made from a 0.3 mm thick platinum wire. Metal wires, 1 mm in diameter, soldered with silver at both ends of the loop support it, and also serve as leads for the heating current. In order to ensure a precise adjustment of the loop the supporting wires are mounted on a micromanipulator. The platinum wire can be heated with the aid of a transformer; the current of several amperes at a low voltage should be regulated with a variable transformer connected between the network and the low-voltage heating transformer. The loop is set in a vertical position, and a drop of the material to be investigated is melted onto the heated loop. The melting must be carried out carefully lest the drop should splash. If the current is decreased or switched off the drop solidifies. The crystallization process during the solidification may be observed with a horizontal microscope of low magnification (5–80×). Since in the case of low magnification the objective lens of the microscope is far from the crystallizing drop no cooling is necessary. By the horizontal positioning of the microscope the condensation of vapours from the molten drop onto the objective is avoided, and the observations can be carried out undisturbed. The drop can be illuminated in various ways. One possibility is to place another glowing platinum loop behind the molten drop. This second loop must be set so that the whole drop is illuminated uniformly. Another advantage of the use of a second platinum wire is that the crystallization starts later on the back part of the drop than on the front. Thus the rear crystallization does not disturb the observation of the crystal growth on the front side. The loop serving for illumination should be of platinum wire 0.5 mm in diameter.

I.8.2.1. Formation of NaCl dendrites in melt drops

The growth of NaCl dendrites may be studied with the method described above. NaCl is melted on the glowing platinum loop in such a quantity as to fill the loop completely with the melt drop. The current is switched off after a few seconds. On the surface of the drop four-branched star-like dendrites develop which grow together fairly quickly, although below them in the interior of the drop the dendritic growth can still be observed for a short time. The full solidification of the drop takes place within a few seconds. If the current is switched off immediately after the NaCl grains have melted, a layer consisting of a great number of small and thin crystals develops on the surface of the molten drop, while below this layer many sphere-like crystals grow which later assume a dendritic shape too.

Dendritic growth can also be studied without melting the NaCl grains fully. For this type of experiment the heating current should be decreased before the substance becomes fully molten. In this case, starting from the still solid parts of the sample, dendrites grow on the surface of the molten drop. The surface of the solidified NaCl grain is observed in reflected light. An incandescent lamp movable in every direction is used as light source. The surface of the solidified NaCl grain consists in many cases of plane faces in which two rows of holes, perpendicular to each other, are visible. The crystallographic orientation of these rows of holes may be established as follows. The NaCl grain on the platinum loop is heated to slightly below the melting point and paraffin oil is then poured onto it. The cracks forming on the plane face mark the [100] cleavage directions. From the angle between the cracks and the direction of the rows of holes the crystallographic orientation of the rows may be determined; it is found to be [110]. The same experiments can also be carried out with other alkali halides.

I.8.3. Growth of Dendrites from the Vapour Phase

I.8.3.1. Growth of NaCl dendrites from the vapour phase

For this type of experiment the apparatus described in I.8.2 may be used. The NaCl grain is melted on the platinum loop which, however, this time must be in a horizontal position. The other platinum loop used in the previous experiments for illumination is now not heated to incandescence, but to only a few hundred degrees. With the aid of a micromanipulator this latter loop is placed a few tenths of a millimeter under the molten NaCl drop. Within seconds moss-like crystals grow on the platinum wire.

Single dendrites and small skeletal crystals (with cube edges of about 0.5 mm) may also be grown from the vapour if the second platinum loop is made of a thin wire (diameter: 0.05–0.1 mm), placed about 1 mm from the

NaCl drop, and heated to several hundred degrees. Well-developed dendrites may be grown too on the NaCl grain placed on the platinum loop. The grain must not be molten, but heated to only slightly below the melting point. At this constant temperature, 'christmas-tree'-like dendrites grow within 2–3 hours on the whole grain and mainly round the platinum loop. The thickness of the dendritic branches depends upon temperature; at higher temperatures thinner branches develop. These dendrites undoubtedly grow from the vapour surrounding the hot NaCl grain, since the vapour pressure of NaCl is high even below the melting point. However, surface diffusion may also play an important role in the formation of dendrites.

I.8.4. Growth of Dendrites by Chemical Reactions

I.8.4.1. Formation of metal dendrites by chemical reactions

A small piece of zinc is flattened between two thick paper sheets to a thin foil 0.1–0.2 mm thick. A piece of a few mm^2 is cut from it and put on a microscope slide. With a pipette a few drops of 5% $AgNO_3$ solution are placed on the zinc sample, and it is covered with a coverslip. The growth of silver dendrites may be observed under the microscope and also with the naked eye (Fig. I.8.1). If possible a stereomicroscope should be used.

The same experiment is repeated using copper instead of zinc. Experiments are also carried out with more concentrated $AgNO_3$ solutions.—$Pb(NO_3)_2$ or $CuSO_4$ solution is dropped onto the zinc samples.

The above experiments should be repeated without covering the samples.

I.8.5. Growth of Metal Dendrites by Electrolysis

I.8.5.1. Growth of lead dendrites

A 50 ml glass cell with plane-parallel walls is filled with saturated lead acetate solution. Electrodes are placed in the cell as shown in Fig. I.8.4 and a current of about 0.1 A is applied. After the current is switched on, well-

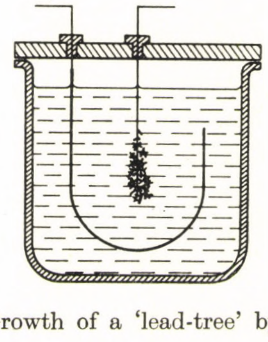

Fig. I.8.4 Growth of a 'lead-tree' by electrolysis developed, large lead dendrites grow on the cathode within a few minutes. The growth of loosely connected lead dendrites may be observed by a larger audience if the growth process is properly projected.

I.8.5.2. Growth of sodium dendrites in NaCl crystals

Electrolysis may also take place in the solid state. A NaCl crystal of approx. 1 cm^3 volume is put into an electrical furnace between a plate and a needle electrode. The furnace is heated to 600–700° C and a d.c. voltage of 100–200 V is applied for several minutes via the electrodes (the needle should be the cathode). After the current is switched off the crystal is removed from the furnace when well-developed sodium dendrites may be observed microscopically in the crystal (Fig. I.8.5).

Fig. I.8.5 Na dendrites in NaCl crystals heated in an electric field
(M: 150× ; by J. Kiss); (a) $\langle 110 \rangle$ oriented dendrites ($>600°$ C); (b) $\langle 100 \rangle$ oriented dendrites ($\sim 500°$ C)

I.8.6. Formation of Skeletal Crystals from Solution and from the Melt

I.8.6.1. Formation of skeletal KI crystals from solution

A KI solution saturated at 35° C is heated to 40–50° C, and drops of the solution are put on a microscope slide. Inside the drop skeletal crystals and aggregates of skeletal crystals will develop; the process is clearly seen under the microscope. If the microscope is focused on the surface of the drop reversed pyramid-shaped skeletal crystals swimming on the surface of the solution may be observed.

I.8.6.2. Growth of skeletal KBr crystals in solution

10 ml 92% ethyl alcohol is poured into a crystallization crucible and placed under a stereomicroscope. With a pipette two drops of KBr solution saturated at room temperature are added. It is advisable to let the drops fall into the alcohol at a distance of 0.5–1 cm from the objective of the microscope and not immediately below it. Immediately after the drops have been put into the alcohol the growth of skeletal KBr crystals may be observed at a magnification of 150. After the termination of the growth all the crystals grown in the crucible are examined. It can be seen that the crystals grown at a greater distance from the site of addition show the characteristics of the skeletal type of growth to a much greater degree.

The experiment is very sensitive to the water content of the alcohol. If the water content is a few per cent more than prescribed no skeletal growth takes place. Consequently it is better to start with an alcohol of low water content, and repeat the experiment with an increasing water content until the most favourable alcohol : water ratio is obtained. If the water content of the alcohol is very low extremely small snow-like precipitates will form when the KBr solution is dropped into the alcohol. At a too high water concentration well-developed cubes will grow.

I.8.6.3. Growth of skeletal bismuth crystals from the melt

A tightly fitting copper wire is put into a long glass tube. The lower part of the glass tube is inserted into a bismuth melt at melting temperature. If the heat conduction along the copper wire is good, bismuth crystals will grow on the tube. The tube is pulled very carefully out of the melt. If the crystals grown on the tube are investigated with a stereomicroscope at low magnification, a great number of intertwined skeletal crystals will be seen.

I.9. EPITAXIAL CRYSTAL GROWTH

An oriented crystal growth on another crystal surface is called epitaxial growth. An oriented overgrowth on the same single crystal is called auto-epitaxy. Epitaxial crystal growth may take place from any phase. The growth is simplest in the case of solutions, although this technique is rarely used in technology because of the following considerations: (a) many substances do not dissolve well in the usual solvents; (b) the solvent may influence the orientation of the growing crystals; (c) the solvent may dissolve the substrate crystal and this may lead to the formation of mixed crystals.

Growth from the vapour is a technique mainly used to produce semiconducting layers. The methods most frequently used are: condensation of an atomic beam in high vacuum and chemical transport reactions.

In the first method the substance is evaporated at high vacuum (10^{-8} torr), and the warmed substrate crystal is placed in the path of the vapour beam. If suitable experimental conditions are established, oriented single crystal layers grown by condensation will result from this procedure. In the case of the second method, some compound of the substance to be crystallized is led in the vapour phase over the substrate crystal, where the substance becomes deposited in the desired orientation either by thermal decomposition or by chemical reduction.

For a mutual epitaxy of metals an electrolytical separation method is frequently applied. — Epitaxial crystal growth may also take place from the melt. However, only few experiments have been carried out with this method.

There still exists no satisfactory theory which would explain all the features of epitaxial growth. The theories worked out to date are mainly phenomenological. The reason for this is that the binding energies and the binding forces acting between the lattices of the crystals growing together are still unknown. In the interpretation of epitaxial overgrowth much importance was first attributed to the equality of the lattice parameters in the plane of the overgrowth. More recent investigations, however, have proved that in some instances epitaxy may take place even in the case when the lattice parameters differ by 90 per cent. The close agreement of the lattice parameters is certainly advantageous, but it is not a necessary condition of epitaxial crystal growth.

Epitaxial crystal growth is of great practical importance. From some substances, e.g. from $NaNO_3$, large single crystals (with dimensions of a few centimeters) may be grown epitaxially on mica. The problems of producing artificial rain are also connected with epitaxial processes. Thin epitaxial layers play a further important role in the physics of semiconductors, in the microminiaturization of electrical devices and so on.

I.9.1. Epitaxial Crystal Growth from Solution

Epitaxial growth from solution may be suitably investigated with the aid of a microscope, preferably a stereomicroscope. One or two drops of the solution to be investigated are placed on the substrate (mother crystal), and the precipitation and growth of the crystals are observed at an appropriate magnification (50–400).

I.9.1.1. Epitaxial NaBr growth on NaCl crystal plates

One drop of a 20% NaBr solution is placed on a freshly cleaved surface of a NaCl crystal. If after the evaporation of the water the surface of the

NaCl crystal is observed at a magnification of 100–200, it can be seen that the NaBr crystals grown on the surface are oriented (Fig. I.9.1). The basal edges of the crystals grown are parallel to the side edges of the NaCl substrate.

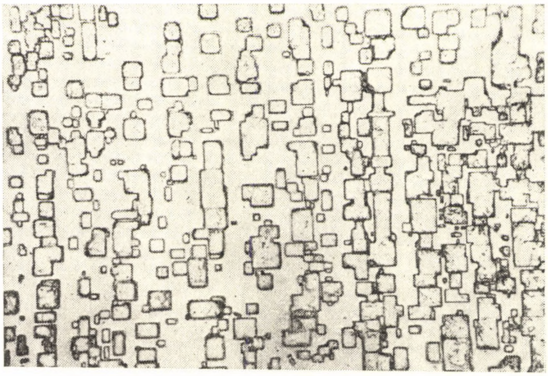

Fig. I.9.1 Epitaxy of NaBr on NaCl
(M: 100×)

I.9.1.2. Epitaxial KCl growth on NaCl crystal plates

The above experiment is repeated with saturated KCl solution. In the interior of the dried drop, larger not regularly oriented KCl crystals will also be found. During the drying of the drop one may observe at a magnification of 100–200 that the majority of the unoriented crystals are formed on the surface of the solution drop, and fall from there onto the substrate crystal.

I.9.1.3. Epitaxial $NaNO_3$ growth on $CaCO_3$ (calcite) crystals

A small piece is cleaved from a calcite crystal with a sharp knife. At cleaving the blade should be parallel to the basal plane of the crystal. Saturated $NaNO_3$ solution is dropped onto the freshly cleaved calcite surface. During the evaporation rhombohedral $NaNO_3$ crystals will grow oriented with their edges parallel to the edges of the substrate crystal.

I.9.1.4. Epitaxial KI growth on mica

One drop of saturated KI solution is put onto the freshly cleaved surface of a thin muscovite mica plate. Pyramids with trigonal bases or, frequently, truncated pyramids grow with base edges oriented parallel to each other on the surface of the mica. The equilateral triangles seem to prove that the oriented KI crystals grow with their (111) planes on the (001) pinacoid faces of the mica. Cubic crystals are formed on the surface of the solution drop and settle down on the mica irregularly.

One base edge of the oriented KI crystals is parallel to the (010) plane of symmetry of the mica. In order to prove this, a sharp needle is put on the cleavage plane of the mica normal to that plane, and hit gently. In this way a six-branched crack-star characteristic of mica will be formed, the largest branch of the star always being parallel to the (010) plane of symmetry.

I.9.1.5. Epitaxial alizarin growth on NaCl crystals

Alizarin is dissolved in a few ml benzene mixed with 0.1 ml absolute ethanol to obtain a clear, transparent, ochre solution. One drop of this solution is put onto a freshly cleaved NaCl surface; care is taken so that the drop may not reach the edges of the crystal.

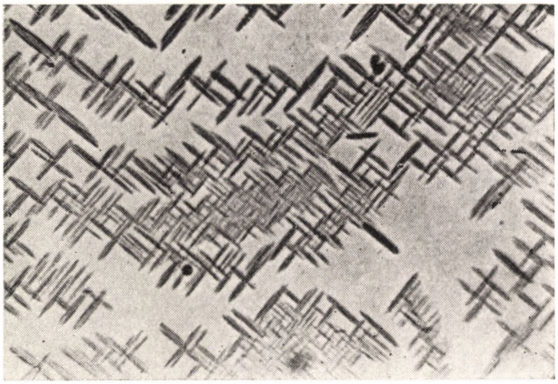

Fig. I.9.2 Epitaxy of alizarin on NaCl
(M: 300×)

On evaporation, the first needle-like alizarin crystals grow at the rim of the drop. After the first crystals are grown the drop becomes patulous as a result of the change in the surface tension, and soon dries up. At a magnification of 100–200 the needle-like alizarin crystals can be clearly seen. The crystals are oriented parallel or normal to each other (Fig. I.9.2). The alizarin crystals form an agle of 45° with the base edges of the NaCl crystals, that is they lie on the (001) planes of NaCl in the [110] and [$1\bar{1}0$] directions. In the case of too high concentration of the solution non-oriented alizarin crystals can also be found in the interior of the dried drop. These crystals grow in the solution itself, and only later become deposited on the NaCl surface.

I.9.1.6. Epitaxial alizarin growth on LiF crystals

One drop of alizarin dissolved in a benzene–alcohol mixture as described above is put onto a freshly cleaved face of a LiF crystal. The vast majority of the oriented alizarin crystals lie on the (001) plane of the LiF crystal in the [100] and [010] directions, but in some instances in the [110] and [$1\bar{1}0$] directions too. The lattice constants of alizarin correspond better to the lattice parameters of LiF in the [100] direction than to those in the [$1\bar{1}0$] direction (Table I.III).

TABLE I.III

*Epitaxy of alizarin on LiF**

Crystal	Planes growing together	Lattice parameters of planes growing together and their deviations			
Alizarin (rhombic)	(010)	$c_0 = 3.75$ Å	—	$a_0 = 21.0$ Å	—
LiF (cubic)	(001)	[110] : 5.64 Å	−34%	5×[1$\bar{1}$0] : 28.2 Å	−25%
	(001)	[100] : 4.02 Å	− 7%	5×[010] : 20.1 Å	+ 4%

* A. Neuhaus (1952): *Z. für Electrochemie 56*, p. 453.

I.9.2. Epitaxial Crystal Growth from the Melt

I.9.2.1. Epitaxial KBr growth on mica

A KBr crystal grain of a few mm^3 is put on a freshly cleaved thin mica plate. The mica plate is held with a pair of long forceps over a gas flame, and the KBr grain is melted. When the grain is molten (melting point 730° C) the mica plate is taken out of the flame. The molten drop solidifies rapidly, and as a result of the sudden cooling cracks. One can see with the naked eye, or at a magnification of 5–50 that the cracks form angles of 60° (Fig. I.9.3). The cleavage planes of cubic KBr are the {100} planes, and consequently the KBr crystal grows with its ($\bar{1}\bar{1}\bar{1}$) plane on the (001) cleavage plane of the mica. One crack direction is parallel to the (010) plane of symmetry of the mica (see I.9.1.4). The position of the K$^+$ ions on the contact plane of KBr and mica in the epitaxial growth is shown in

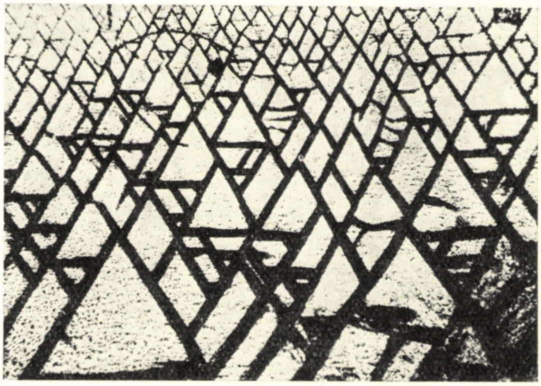

Fig. I.9.3 Cracks developed on KBr crystals grown epitaxially from the melt on mica
(M: 40×)

Fig. I.9.4.—If a new KBr grain is melted on the mica plate used in the previous experiment, the cracks formed after the solidification of this new drop are parallel to the cracks in the drop solidified in the first experiments.

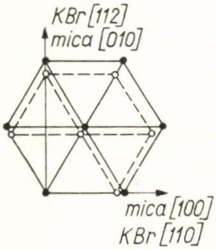

Fig. I.9.4 Position of K^+ ions in the plane of contact of KBr crystals grown epitaxially on mica

Position of K^+ ions on the (001) plane of the mica (●); position of K^+ ions on the $(\bar{1}\bar{1}\bar{1})$ plane of KBr according t
Palatnik and Papirov (○)*

I.9.3. Epitaxial Crystal Growth from the Vapour Phase

I.9.3.1. Epitaxial KBr growth on mica

A thin mica plate is cleaved almost entirely into two so that the pair of plates formed should not be fully disconnected. A few small KBr grains (with volumes of a few tenths of a mm^3 each) are put between the two plates. The mica is held with a pair of long forceps above a gas flame. When some of the KBr grains have melted the mica is taken out of the flame. If the upper mica plate is torn off, white smoke-like precipitates can be observed

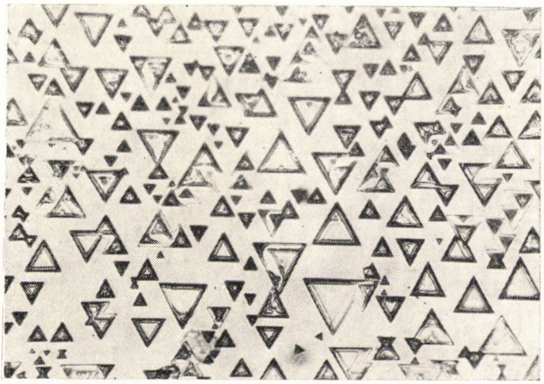

Fig. I.9.5 Epitaxy of KBr crystals grown from the vapour on mica
(M: 200×)

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*Л. Ш. Палатник, И. И. Папиров (1964): *Ориентированная кристаллизация* Изд. Металлургия, Москва with the naked eye. On investigation with the microscope at a 100-fold magnification oriented KBr crystals with equilateral triangular bases can be observed. The corresponding sides of the triangles are parallel to each other (Fig. I.9.5). With the impact experiment described in I.9.1.4 one can ascertain that one side of the triangles is parallel to the (010) plane of symmetry of the mica.

I.9.3.2. Autoepitaxial phenomena on the surface of heat-treated NaCl crystal plates

2–3 mm thick cleaved NaCl plates with a surface of 3×3 cm^2 are put into a 12 cm long porcelain crucible with a diameter of about 4 cm. The crucible should have a pointed bottom and a rim on top. The crystals should be arranged in the crucible according to Fig. I.9.6. After a prolonged heat-treatment (6–72 hours), during which the crucible must be kept covered, a great variety of autoepitaxially grown crystals will be observed on the surfaces, especially on the lower surfaces of the plates, and similar crystals also grow on the lid of the crucible. The small crystals and whiskers grow from NaCl condensed from the vapour phase.

Since NaCl crystals are hygroscopic, the crucible is opened in dry air at a humidity below 40% and replicas of the crystalline surfaces are prepared in the following way. Collodion is dissolved in isoamyl acetate, and a thin layer of the solution is poured onto the plates. The collodion membrane solidifies in about 12 hours. This longer method is advisable, though with the aid of an infrared lamp the membrane can be dried in twenty minutes. However, with this latter and faster method the membranes may become wrinkled. The dried collodion membrane is torn off with the aid of fine tweezers. Another suitable method of separating the collodion membrane from the crystal consists in immersing the specimen in water and dissolving the crystal; in this case, the collodion membranes float on the water surface and can be easily handled. The collodion replica so obtained is put on a microscope slide, and covered with a coverslip. This is fixed at its edges with paraffin (Figs I.9.7–10).

A microscopic investigation of the specimens provides the following observations.

(a) The surface figures become curved if the specimen has been heat-treated near the melting point; they become straight lines in the [100] direction after a heat-treatment at about 600° C; in the intermediate temperature range between 600° C and the melting point the lines are of the transitional [110] direction (Fig. I.9.11).

(b) The variety of structures with straight lines developed on the surface corresponds to configurations which may be expected from theoretical considerations (Fig. I.9.12); the lack of some theoretically expected figures may be attributed to impurities.

(c) The variety of the surface structures and the coexistence of figures corresponding to various temperatures (Fig. I.9.13) may be explained by the development of undercooled drops (Fig. I.9.14); an additional growth

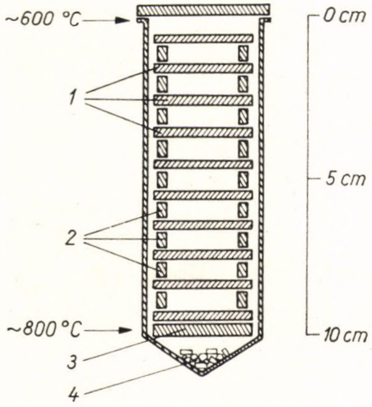

Fig. I.9.6 Assembly for the heat-treatment
1 NaCl crystal plates, *2* supports separating the plates, *3* porcelain, *4* NaCl crystal fragments

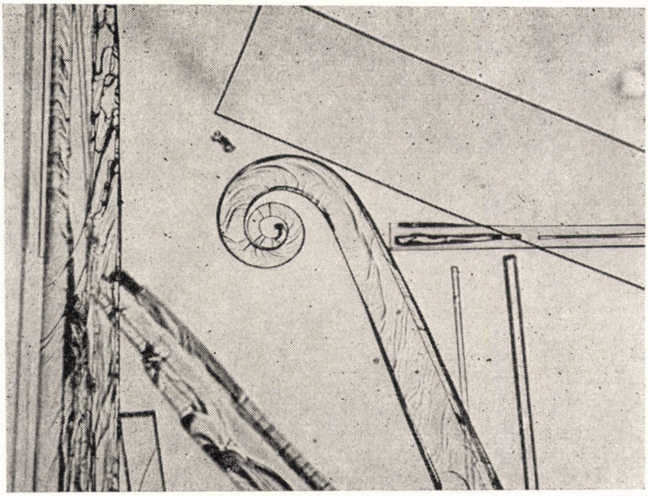

Fig. I.9.7 NaCl whiskers grown from the vapour
Spiral termination (part seen in the picture is about 2 mm long)

of these drops after their adherence to the plate may also be observed (Fig. I.9.15).

(d) If instead of the separating supports quartz crystal-plates are placed between two adjacent NaCl faces, the crystals developed on the quartz plates show surface configurations due to silicon impurities, especially if during the heat-treatment water vapour is streamed through the crucible (Fig. I.9.16).

(e) Surfaces with {110} or {111} planes can be obtained by sawing the samples in the desired directions; by a subsequent heat-treatment the surface characteristics of these faces are developed (Figs I.9.17 and I.9.18).

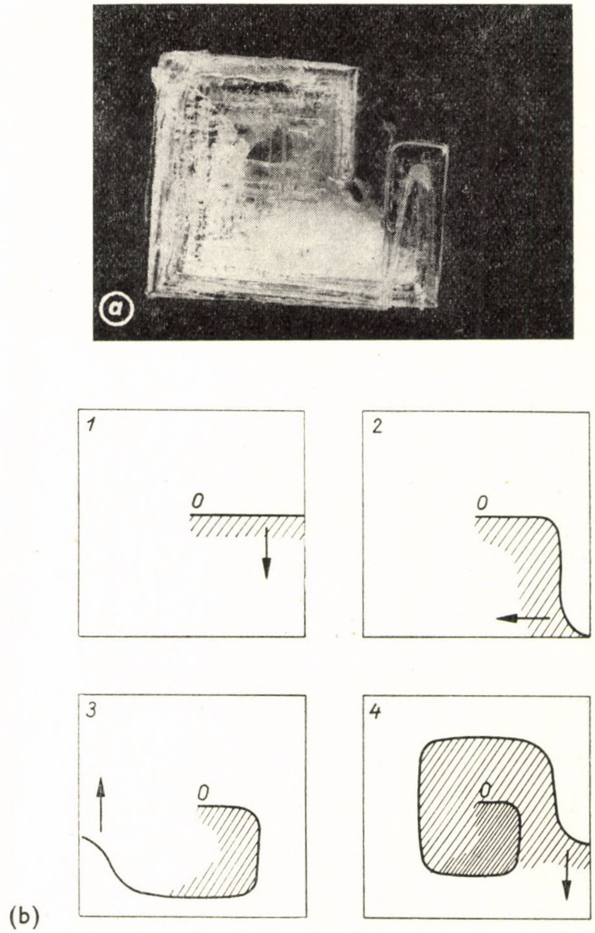

Fig. I.9.8 NaCl whisker grown from the vapour

(a) spiral cross-section of a truncated pyramid (original size 8×6 mm); (b) its development according to S. Amelinckx*

(f) If the plates are previously cut slightly at their corners, e.g. with a razor blade, during the heat-treatment characteristic configurations suitable for studying the growth mechanism will be formed in the cracks (Fig. I.9.19); especially interesting phenomena may be observed if collodion solution is poured into the cracks before the heat-treatment (Fig. I.9.20).

Investigations with other crystals (KCl, KBr, KI, NaI, etc.) yield similar results.

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* S. Amelinckx (1958): *Physica 24*, p. 390.

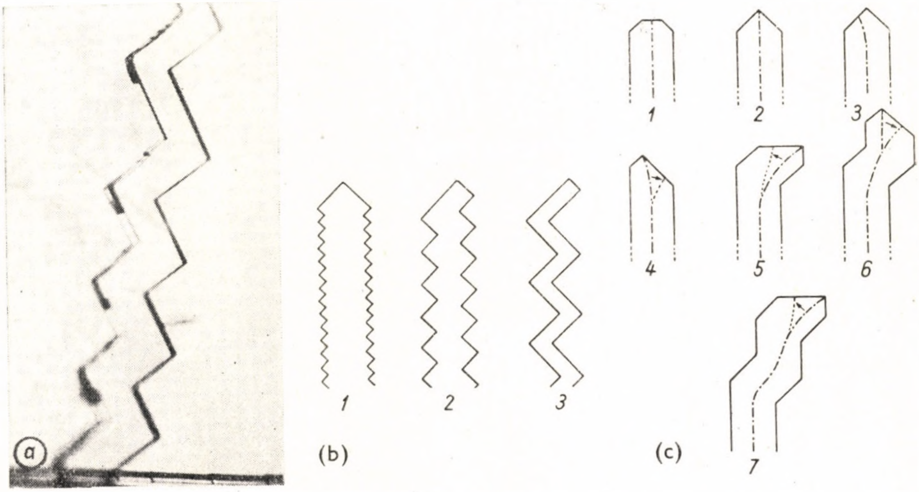

Fig. I.9.9

(a) Zig-zag-shaped NaCl whisker; (b, c) two possible explanations of formation; the latter according to S. Amelinckx*

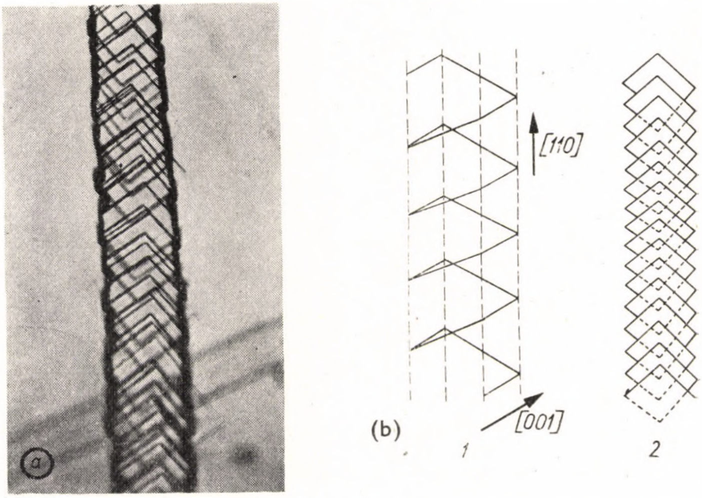

Fig. I.9.10

(a) Polygonized helical NaCl whisker (M: 60×); (b) *1* polygonized helix according to S. Amelinckx et al.,** *2* polygonized helix in another position

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* S. Amelinckx (1958): *Phil. Mag. 3* 8.
** S. Amelinckx, W. Bontinck and W. Maenhout-Van der Vorst (1957): *Physica 23*, p. 270.

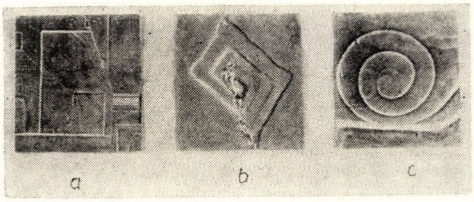

Fig. I.9.11

(a) Rectangular (M: 70×), (b) 'diagonal' (M: 100×), and (c) curved (M: 200×) spirals on the surface of NaCl crystals heat-treated at various temperatures

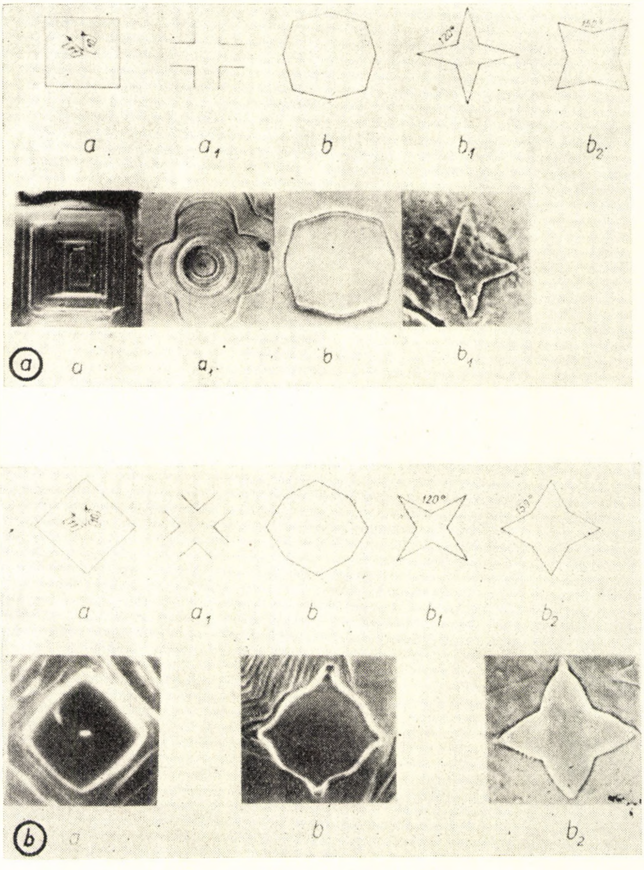

Fig. I.9.12

Comparison of autoepitaxially grown NaCl surface configurations and theoretically expected ideal geometrical forms

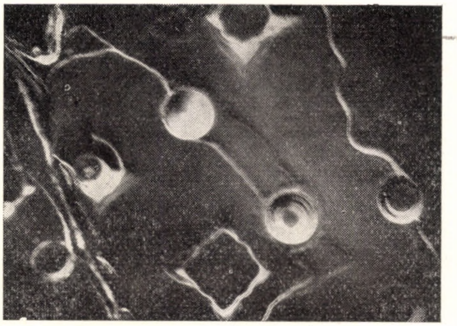

Fig. I.9.13 Simultaneous appearance of autoepitaxial growth forms corresponding to various temperatures
(M: 200×)

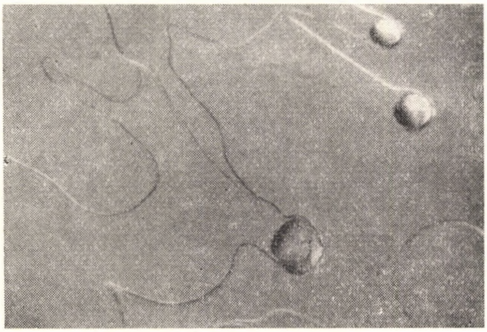

Fig. I.9.14 Undercooled drops on the surface of heat-treated NaCl crystals
(M: 100×)

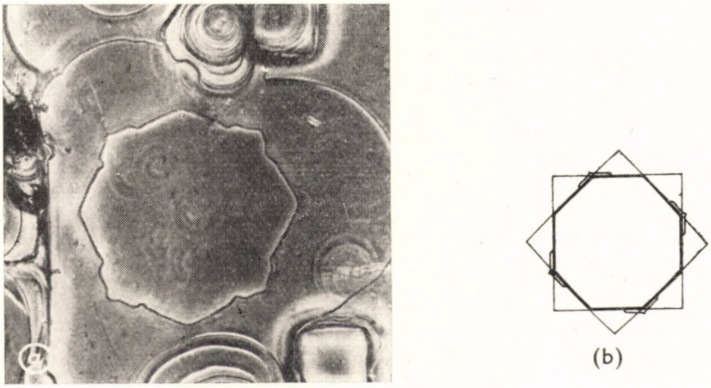

Fig. I.9.15 Phenomena in further growth of undercooled drops on the surface of heat-treated NaCl crystals
(M: 100×)

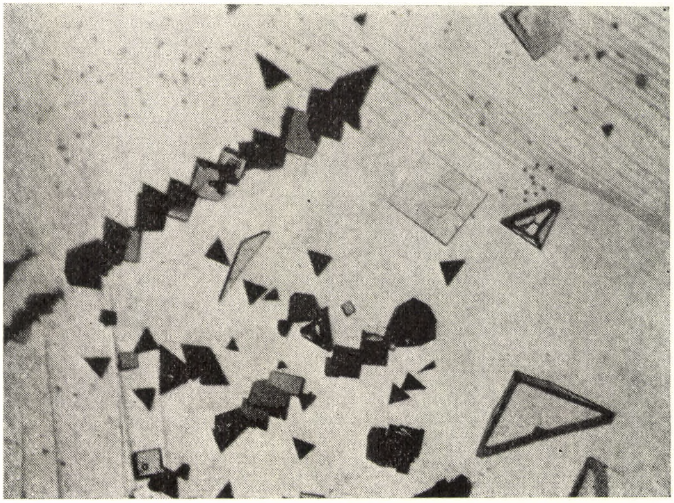

Fig. I.9.16 Small NaCl crystals grown from the vapour onto the surface of silica crystal plates
(M: 200×)

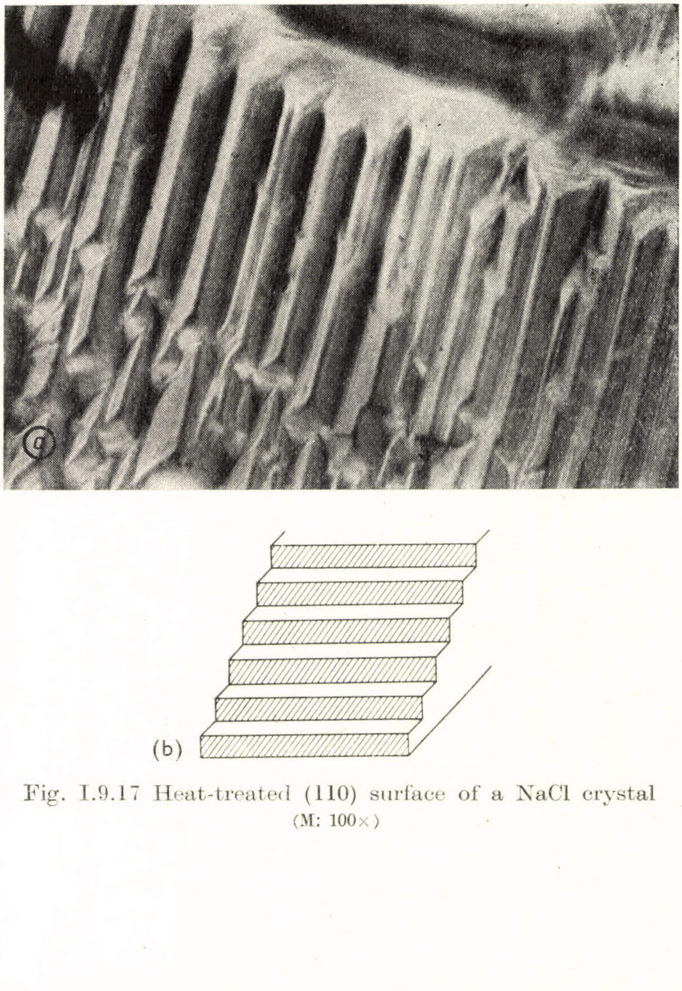

Fig. I.9.17 Heat-treated (110) surface of a NaCl crystal
(M: 100×)

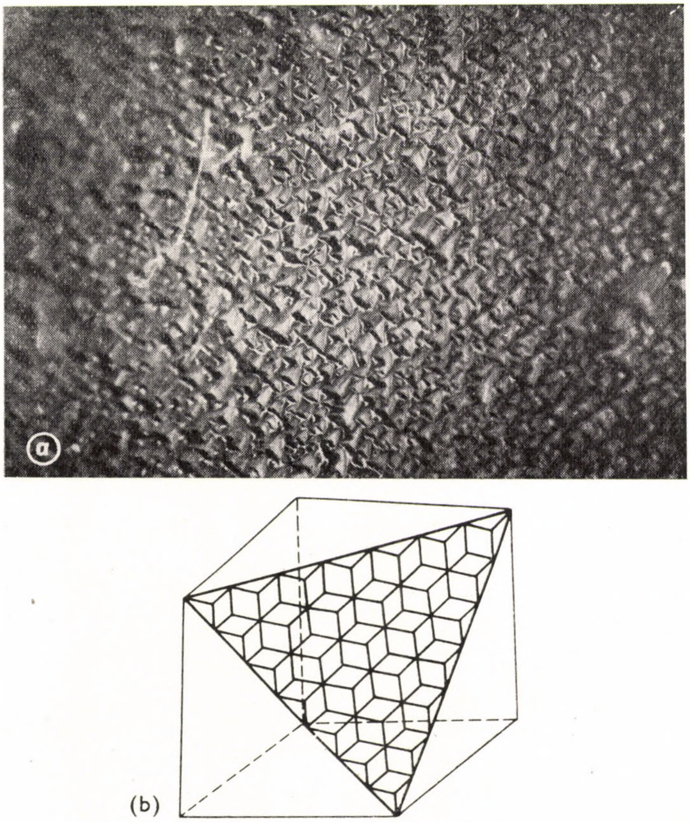

Fig. I.9.18 Heat-treated (111) surface of a NaCl crystal
(M: 100×)

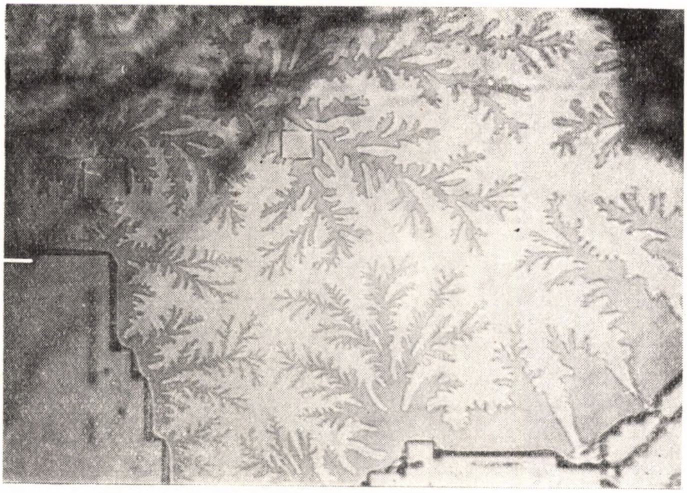

Fig. I.9.19 'Ice-flowers' developed in a crack of NaCl crystal during heat-treatment
(M: 100×)

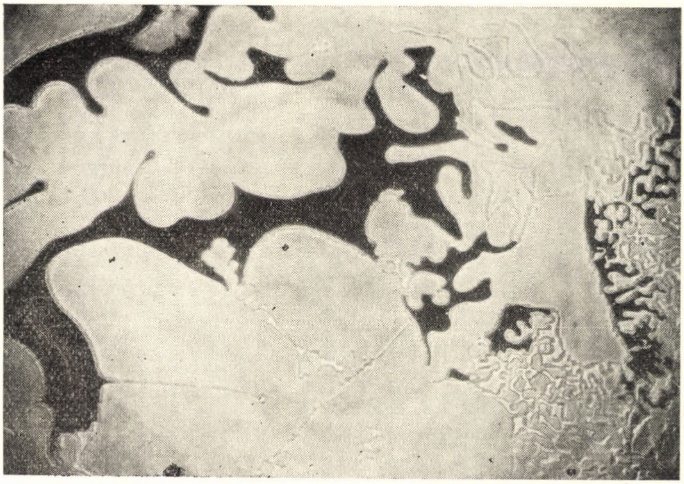

Fig. I.9.20 Phenomenon in a crack of a NaCl crystal during heat-treatment, if collodion dissolved in isoamyl acetate is placed in the crack previously
(M: 100×)

I.9.3.3. Autoepitaxial growth on the surface of locally deformed NaCl crystals

The tip of the crucible shown in Fig. I. 9.6 is ground until a small hole is formed so that a needle can be pushed through it. An iron cylinder of the same shape, weighing about 1 kg, is placed inside the crucible (the cylinder should have a pointed bottom). Into the tip of the cylinder is fastened a needle the end of which should protrude about 1/2 mm from the crucible. The crucible containing the iron cylinder is put into an electrical furnace, at the bottom of which a cleaved 2–3 mm thick NaCl plate with a surface of 3×3 cm^2 has previously been placed. The crucible with the iron cylinder is hung on a hook fastened to the lid of the furnace so that it can be moved upwards and downwards in the furnace. At the beginning of the experiment the hook with the crucible is lowered into the furnace so that the needle almost touches the crystal plate. By lowering the crucible the needle indents the surface of the crystal, deforming it locally. The distribution of the deformation is identical with that to be discussed in detail in I.10. By moving the crystal under the crucible and indenting again and again, one may create several local defects.

The crystal plate is indented at above 200° C, e.g. at 400° C, and afterwards the plate is put in the assembly shown in Fig. I.9.6 in the second or third row from the top with the indented surface downwards. If the treatment is carried out as previously, surface configurations as shown in Fig. I.9.21 will develop. The same procedure is repeated at various temperatures with plates of the same size cleaved from the same single crystal block. With the aid of a drawing mirror the outlines of the indentation and of the area disarranged by deformation and 'developed' by the heat-treatment are drawn. (The same magnification should always be used.) The areas on the drawings are determined with a planimeter, and their ratio is plotted as a function of temperature of the heat-treatment. This results in a curve similar to that in Fig. I.9.22. An analysis of the curve shows that the degree of deformation caused by a given indentation is not a simple function of deformation temperature.

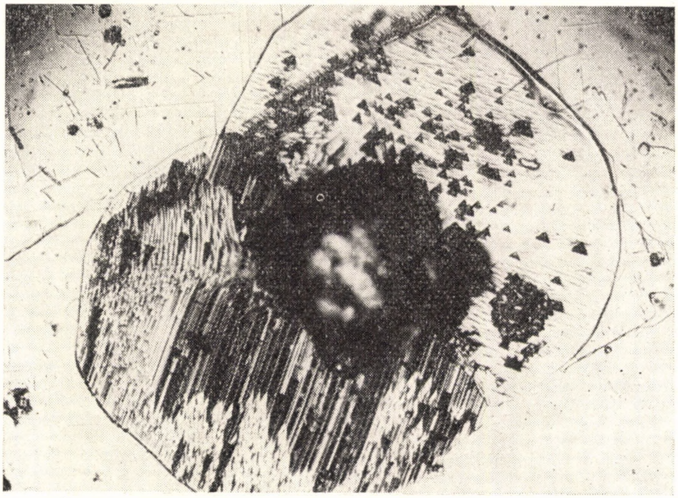

Fig. I.9.21 Surface forms around an indentation at 400° C after subsequent heat-treatment
(M: 100×)

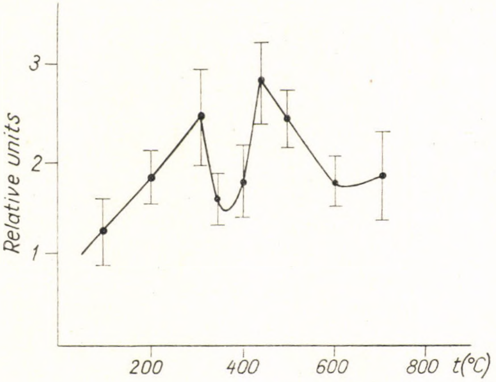

Fig. I.9.22 Area of heat-treated surface forms around point-like deformations in dependence of deformation temperature
Heat-treatment following deformation is carried out at the same temperature

I.10. CONTROL OF CRYSTAL QUALITY BY CHEMICAL ETCHING

Since the defects of the seed crystal grow into the new crystal, the defect structure of the seed crystal considerably influences the quality of the crystal growing from it. In order to control the seed, and to select the most suitable conditions for the growth, the heat-treatment and the processing of the grown crystals a periodic quality control of the growing crystals is important. The simplest method of this control consists in treating the surface of the crystal with some suitable chemical reagent: preferential etching. The treatment reveals the dislocations emerging on the surface. Since the efficiency of this treatment is extremely sensitive to the orientation and the condition of the surface, the dislocation structure cannot be revealed by this method in every crystal. As the method is still almost exclusively empirical, much effort is needed to find the most suitable conditions for the various substances. The etch figures can be investigated microscopically only if certain conditions are fulfilled, the most important of these being that the rate of dissolution along the surface (v_t) must not greatly exceed the rate of dissolution perpendicular to the surface (v_n) (Fig. I.10.1). Experience has shown that the ratio (v_t:v_n) should be at most 10. In order to obtain a favourable ratio, the solvent should contain a small amount of an inhibitor which decreases the rate of dissolution along the surface to the desired degree, probably by becoming deposited on the ledges of the dissolution terraces. With a suitable etching technique microscopically observable small grooves and etch pits are formed around the points of emergence of the dislocations usually oriented parallel to the crystallographic directions.

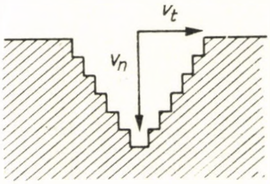

Fig. I.10.1 Schematic drawing in section of an etch pit
v_n rate of dissolution normal to the surface; v_t rate along the surface

The formation of the etch pits can be explained as follows. The lattice is distorted for a distance of a few atoms around the dislocations. As a result of the stress field generated by the deformation the lattice elements dissolve here more easily than in stress-free, undeformed areas. The etch pits are usually straight pyramids with polygonal bases, but oblique pyramids may also be found with various bases and heights. In one field of view, pits of two or three different sizes may usually be found. Some of the pits are stepped or terraced; these develop usually during a prolonged or repeated etching procedure. However, pits with one or two terraces, and flat-bottomed pits may be developed by applying the etchant only once and for a short time (Fig. I.10.2). The shape of an etch pit is closely related to the dislocation revealed by it. The straight pyramidal pits belong to dislocations emerging perpendicularly to the observed surface; the oblique, asymmetric etch pits are formed by dislocations emerging inclined with respect to the surface. The great majority of the dislocations are closely connected with

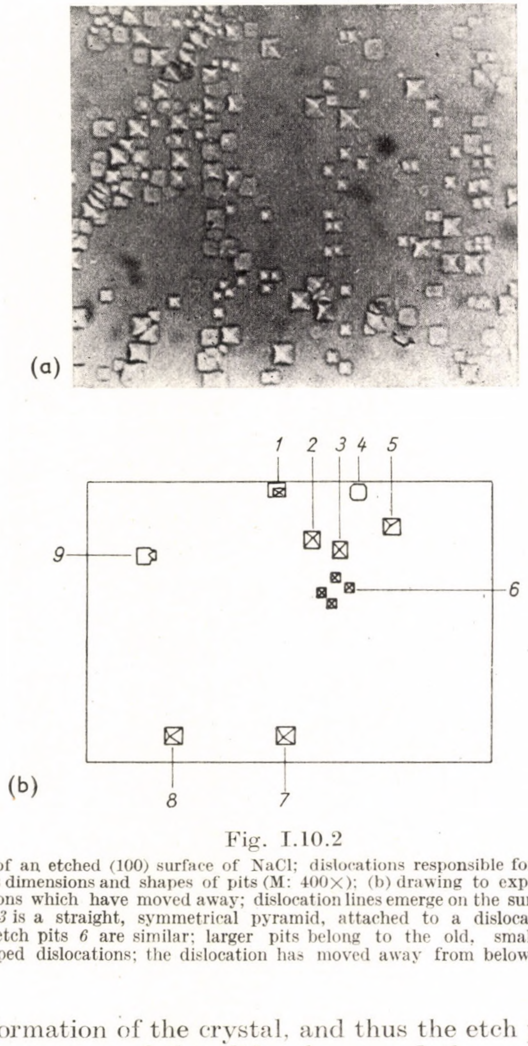

Fig. I.10.2

(a) Microphotograph of an etched (100) surface of NaCl; dislocations responsible for the etch pits are characterized by the various dimensions and shapes of pits (M: 400×); (b) drawing to explain the microphotograph; *1* and *9* are dislocations which have moved away; dislocation lines emerge on the surface in various directions at pits *2*, *5*, *7* and *8*; *3* is a straight, symmetrical pyramid, attached to a dislocation line being normal to the surface; smaller etch pits *6* are similar; larger pits belong to the old, smaller ones to the recently developed dislocations; the dislocation has moved away from below etch pit *4*

the plastic deformation of the crystal, and thus the etch pits are located in the line of intersection of the glide planes and the crystal surface (Fig. I.10.3a; Fig. I.10.3b shows schematically the etch pits created at the ends of dislocation loops). The etch figures show that the dislocations move during the etching process. The flat-bottomed pits already mentioned mark the former positions of the dislocations which have moved away from under this etch pit. Close to it, or sometimes within the original pit, the smaller, new pit can usually be found in an off-centre position (Figs I.10.4 and I.10.2). Damages of various origins may also create dislocation etch pits. Rosettes formed around an indentation for instance also belong to this type. Rosettes are rows of etch pits in various crystallographic directions (see a typical example in Fig. I.10.5).

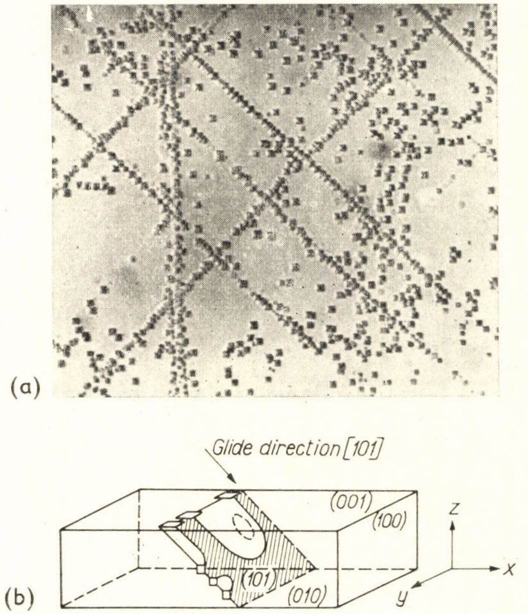

Fig. I.10.3

(a) Etch pits belonging to dislocations created when the sample was cleaved lie in the (100) glide bands, viz. in the ⟨110⟩ glide traces; etching time 10 sec., etchant $CH_3COOH+FeCl_3$ (M: 200×); (b) glide plane of NaCl with 3 dislocation loops and etch pits formed at the end of loops

Curved lines consisting of rows of individual etch pits, grain boundaries, may usually also be detected on the crystal surfaces. Some of these boundaries consist of symmetric pits loosely following each other, while in other cases the pits are strongly compressed along one diagonal (Fig. I.10.6); sometimes the pits are not resolved, and the curved lines give the impression of continuous grooves. These lines which usually do not follow any crystallographic direction belong to small or large angle ($>3°$) grain boundaries (Fig. I.10.5). If the surface is observed at low magnification, these lines form the so-called veined structure of the surface.

A given substance may be characterized by the densities of its grain boundaries and of its individual dislocations. The grain boundary density is measured as their length per unit surface, and the density of dislocations is expressed as their total length per unit volume of the substance. With the etching technique only the intersections of the dislocation lines with the surface, i.e. the etch pits, can be observed. In most cases it is quite satisfactory to give the number of these pits per unit surface. The value thus obtained is the apparent dislocation density. If the density is not too high the number of etch pits can be counted directly with the aid of a meshed ocular micrometer. The dislocations in the grain boundaries must also be

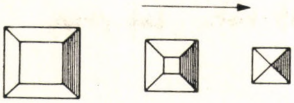

Fig. I.10.4 Etch pits of dislocations having moved away in two steps
The first two pits with flat bottoms are already empty, the third smallest pyramid-shaped pit shows the position of dislocations at the termination of etching

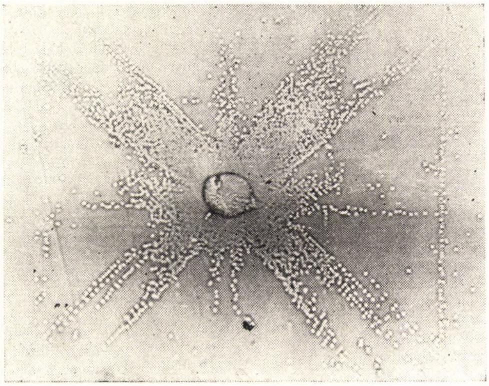

Fig. I.10.5 Rosettes produced by dislocation arrays
Indentation was made by letting a needle hanging on a thread fall onto the crystal surface (M: 400×)

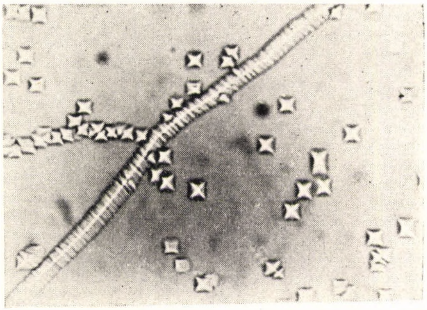

Fig. I.10.6 Block structure of sample
Revealed through a system of etch pits attached to the dislocations in the grain boundaries (M: 400×)

included in the counting. The dislocations in the large-angle grain boundaries cannot be counted in this way since they form a continuous groove (as can be seen in Fig. I.10.5).

The counting may also be carried out by taking a microphotograph of the surface and enlarging the picture. The number of dislocations may be decreased with appropriate heat-treatment followed by slow cooling; at the same time the dislocations in the grain boundaries may also be rearranged. In this way the number of dislocations in NaCl may be decreased to $10^4/\text{cm}^2$.

I.10.1. Investigation of Defect Structure of Alkali Halides by Chemical Etching

I.10.1.1. Etching of NaCl crystals with acetic acid

For the experiments NaCl single crystals cleaved to the dimensions of 3×5×10 mm should be used. The samples should be stored in covered Petri-dishes; 5–10 ml of 99.5% acetic acid is poured into a glass vessel with a cut glass cover and 10–15 ml absolute alcohol into another similar one. One of the crystals is taken out of the dish with a pair of forceps, cleaved in half with a razor blade and one of the cleaved plates put back into the dish; this will serve as a control specimen. The other half is dipped with its cleaved face downwards into the acetic acid, kept there for one second, taken out quickly and rinsed with absolute ethanol. In order to avoid the contamination of the alcohol with acetic acid the sample is shaken vigorously, and one corner of it is touched to absorbent filter paper before immersing it in the alcohol. Thus the paper practically 'pulls off' the rest of the etchant layer. The removal of the alcohol may be carried out in the same way. The sample is dried in an air flow, put on a microscope slide with the etched face upwards, and investigated at a magnification of 100×. The etching was sucessful if small, scattered, squared dots are visible on the otherwise smooth surface (Fig. I.10.7). The process is repeated at 5, 10, 60 and 120 sec etching times. With an etching time of 5 sec the etch pits are clearly observable at a magnification of 200×. The etch pits are best developed after a 60 sec etching time (using 99.5% acetic acid). (The contrast of the pictures can be improved by doping the acetic acid with $FeCl_3$.) In the case of other acetic acids the development of sufficiently large etch pits may take as long as 5 minutes.

The etch pits are square-based pyramids sunk into the surface the direction of their base edges being $[\langle 100 \rangle]$. It should be noted that the above time data are valid only if the samples are not moved in the etchant, the temperature is about 20° C, and the relative humidity in the laboratory is about 45%.

For the purpose of etching freshly cleaved crystals, preferably with clean cleavage surfaces, should always be used. In order to protect the crystals from humidity the cleavage and the etching should be carried out in a dry chamber. For the same reason the microscope is equipped with a breath-deflecting plate. In order to cleave blocks of several centimeters in diameter 15–30° chisels or a sharp scalpel are used; for crystals with a thickness of about 1 mm or less, new unused razor blades (preferably single-edged) should be employed. In cleaving, the edge of knife, the hammer handle and the direction of stroke should form a rectangular co-ordinate system (Fig. I.10.8). Thin plates may also be cleaved by simply pressing the knife or the razor blade in the desired direction. The cracking of the samples at an undesirable place is best avoided if they are halved. Defects (glide bands, scratches, cracks, indentations) introduced by the cleavage can be avoided after some practice.

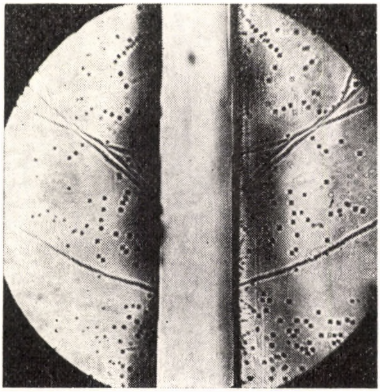

Fig. I.10.7 Etch figures of two parts of a crystal halved by cleavage are mirror images of each other

The microgram proves that the defects attached to etch pits are continuous within the sample (M: 100×)

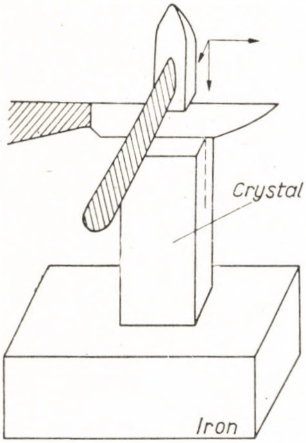

Fig. I.10.8 Right directions for the edge of cleaving knife and striking hammer in cleavage

If the etching of a not freshly cleaved surface is desired the surface must first be polished. For this purpose a polishing solution, e.g. 4 g $CaCl_2$+50 ml CH_3OH+10 ml H_2O is used. A slight agitation of the crystal in this solution removes the already existing etch pits. After rinsing and drying, the etching may be repeated.

I.10.1.2. Investigation of the defect structure of crystals in mechanical deformation

(a) The freshly cleaved surface of a NaCl crystal is punctured slightly with a thin glass rod, a sewing needle, or by shedding fine metal filings onto the surface of the crystal from various heights in vacuum in order to obtain extremely small indentations. After this deformation the crystal is etched for 30 sec (see experiment I.10.1.1). Around the indentations characteristic etch figures (the so-called rosettes) will become visible (Fig. I.10.5). The pits thus produced are smaller than the others. In the rosettes the etch pits may lie in six various types of plane (Fig. I.10.9), since at the point of indentation parts of the crystal move away creating intricately intersecting dislocation loops and the dislocations move on the six different planes. The etch figures are dissolved in the polishing solution, and the etching process is repeated. The dimensions, forms and positions of the dislocation loops may be followed microscopically down to their full depths. It is advisable to carry out this type of experiment with the most simple rosettes.

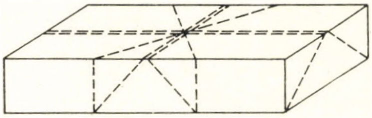

Fig. I.10.9 Structure of a rosette with the six possible glide planes

(b) Approximately 10–15 mm long, 2×2 mm NaCl bars are cleaved and put on 2 glass rods about 2 mm in diameter placed at a distance of 8–12 mm from each other. The centre of the crystal supported by the glass rods is pressed gently with a third glass rod (Fig. I.10.10). This bending is repeated on samples placed in the etchant. The etch pits of dislocations set in motion by deformation are shown in Fig. I.10.11 fitted together from three parts. The central band shows the etch figures on the crystal surface perpendicular to the axis of bending, while the upper and lower bands show etch figures produced on the upper and lower surfaces. After repeated attempts one may obtain a low degree of plastic deformation with the result that the crystalline surface is not overcrowded with etch figures. With only a slight bending, the etch lines inclined at 45° consisting of etch pits reach only the middle of the crystal.

The etch pits of dislocations created by the deformation are, similarly as the rosettes, smaller than those resulting from dislocations in grain boundaries or already present in the crystal before deformation.—If the bending test is to be carried out in the etchant a plane glass plate is put in the bottom of the vessel, and the supporting glass rods are stuck on it at various distances, thus the samples of various dimensions may be suitably placed on them (Fig. I.10.10b).

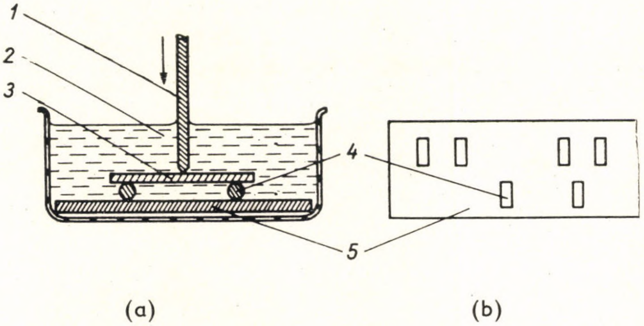

Fig. I.10.10 Production of plastic deformation during etching
1 glass pressing rod, *2* reagent (etchant), *3* NaCl crystal plate, *4* glass rods, *5* glass plate

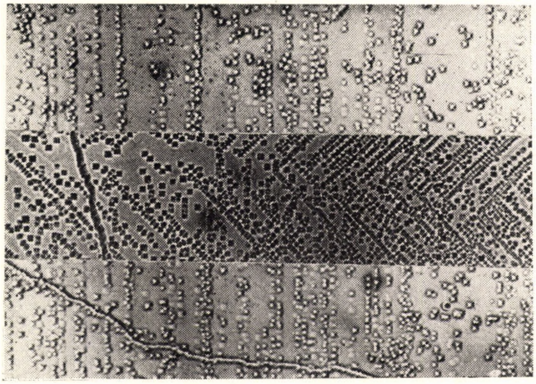

Fig. I.10.11 Etch figures of a bent crystal
On the crystal surfaces normal to the axis of bending (central part), and on the lower and upper surfaces of the sample (lower and upper parts) (M: 170×)

The above experiments are repeated with the following alterations. A crystal is put on the supporting glass rods already placed in the etchant, and pressed in the centre with a flat, wedged glass rod. The rod is left where it is, but the load is taken away for a short time (5–10 sec), then applied again. This second experiment is more difficult than the previous one, because the sample becomes more brittle as a result of 'work-hardening' caused by the first deformation. The etching process has already started at the dislocation loops emerging on the surface, which were created by the first deformation, when the sample is subjected to a new load. As a result new dislocations are created, and at the same time the 'old' ones continue to move. All this results in new, much smaller etch pits at the points of emergence of dislocations. One may also observe that the movement of dislocations in their glide plane may be stopped by a grain boundary. In this case the dislocation will start to move again only if the crystal is subjected to a new deformation (Fig. I.10.12). This also happens when the glide planes intersect each other.

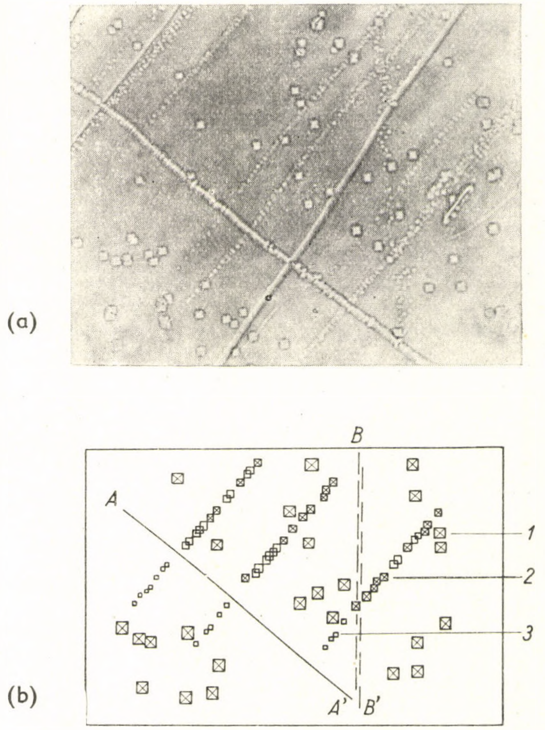

Fig. I.10.12
Etch figures after a double deformation

(a) between first and second deformations there was a pause of about 5 sec (M: 400×); (b) largest etch pits *1* relate to the grown-in dislocations; pits *2* to dislocations produced during the first deformation; and pits *3* to dislocations produced during the second deformation; grain boundary *AA'* restrains the movement of dislocations as well as the glide plane in section *BB'*

With bent samples the movement of dislocation loops may also be followed by the technique of repeated etching and polishing, and by identifying the same etch pits in the subsequent etch pictures.

1.10.1.3. Investigation by etching of phenomena in crystal growth from the melt

The seed crystal to be used when growing a crystal by the Kyropoulos method (see II.2.3.1) may be investigated by the method described above. The investigation should also include the counting of the individual dislocations. It is to be found out whether gliding took place or deformation bands were created on the cleavage of the seed crystal. The etch pictures of the five surfaces of the seed crystal, which come into contact with the melt are investigated. The etching also reveals dislocations created by indentations, scratches and microcracks. Most of these defects may be eliminated by melting the seed crystal slightly. Seeds with large angle grain boundaries, or strongly deformed ones, must not be used for crystal growth, since dislocations belonging to these defects may grow into the new crystal. Microphotographs of the various faces of the etched seed crystal are prepared. The most important defects are already visible on a micrograph of lower magnification surveying the whole plane.

In the second part of this experiment the bulk crystals grown in 1–2 hours are investigated. The bulk is cleaved perpendicularly to the direction of growth, and also parallel to it. The cleavage surfaces of the sample are etched, and the results compared with the etch figures obtained on the seed; the numbers (that is the order of magnitude of the number) of dislocations on both grown block and seed are compared. This type of investigation may also be carried out on surfaces cleaved perpendicularly to the axis of growth at consecutive distances of 2–3 mm; the locations of the grain boundaries on the successive cleavage surfaces are compared.

The investigation will show that the grain boundaries already existing in the seed are also present in the grown crystal block, sometimes in several sections for a distance of several centimeters.

The edges of the bulk usually consist of a great number of smaller blocks, which are separated by small and large angle grain boundaries. The formation of this block-like structure depends upon the temperature gradient and the rate at which the solidified part is pulled out from the melt. With faster pulling the crystal will be plastically deformed as a result of 'thermal shock', and this increases the dislocation density considerably; in the course of growth the dislocations appear in arrays in the grain boundaries. Some of the dislocations, however, remain 'frozen in'. Crystals cooled down to room temperature very slowly after the growth (e.g. in several hundred hours) contain much fewer dislocations and grain boundaries than crystals cooled down rapidly.

The investigation of quenched crystals by etching as a function of the quenching temperature of the medium where the quenching is carried out, or of other parameters, would be an interesting experiment but would require a long time.

I.11. CRYSTAL GROWTH IN THE SOLID STATE

Substances in the solid state are crystals. In a broader sense glass-like amorphous substances may also be regarded as solids, though from the structural point of view these are liquids of high viscosity. The notion of solid state will be used further on in this latter, broader sense.

If energy is communicated to a solid body many of its physical properties change. Thus for example polycrystalline metals harden on deformation, and soften on annealing following the deformation. The changes of the various physical properties are the result of complicated processes in the course of which the structure of the material may alter considerably. Of the possible processes only the following are more closely investigated here: the growth of individual crystal grains in a polycrystalline specimen at the expense of others; the formation of a new crystalline phase in crystalline and amorphous materials consisting of two or more components. The first phenomenon is called recrystallization, the latter crystallization by precipitation.

Recrystallization and precipitation can generally be observed in samples subjected to strong deformation and high temperature heat treatment (annealing). They can be carried out at the same time or in consecutive stages. The processes can be followed with the aid of an optical microscope, with X-ray techniques, or by measuring physical properties of the samples.

I.11.1. Recrystallization

I.11.1.1. Investigation of aluminium recrystallization

(1) 1–2 mm thick aluminium plates are deformed by rolling. The aluminium must be of technical purity, containing at least 0.05 % and at most 1% impurities. After rolling, 1–2 cm wide strips of arbitrary length are cut from the plates. The crystal grains are made visible by etching the aluminium strips with a 10% NaOH solution, and they are then rinsed with concentrated aqua regia. The samples are kept in both solutions for 1 minute each. (The data relating to the etching time and the concentrations of the etching reagents are only for general information. The optimum values should be established separately by experiment in each case, since the quality of etching depends upon the purity of the material used and upon the degree of deformation.) The grains developed by etching can be examined with the naked eye, with a magnifying glass, or with an optical microscope in reflected light at low magnification.

(2) In the following experiment the strips are annealed at about 600° C, and the change in the average grain dimensions due to annealing is observed. The heating is carried out in an electrical furnace. During the annealing process some of the grains start growing at the expense of others. The annealing is continued (for 20–30 minutes) until the grain growth has practically stopped. In order to observe the various stages of the grain growth, the heat

treatment is interrupted from time to time and the grains are made visible by repeated etching as described above. The average grain dimension (l) can be determined with the following formula

$$l = \sqrt{\frac{f}{n}}$$

where f is the field of view of the microscope, and n is the number of grains. The grains which are only partly in the field of view are counted in the calculations as half values.

(3) When the dimensions of the grains no longer change, the strips are deformed and annealed at various temperatures for a given time, and for various times at a given temperature. After annealing the samples are etched, and the average grain dimensions determined with the aid of an optical microscope. The average grain dimension depends upon the degree of the previous deformation and upon the temperature and duration of the annealing. For given annealing conditions maximum grain dimensions are obtained at a 'critical' value of the deformation (for example, for aluminium this value is 2–5%). On the other hand, for a given deformation the average grain dimensions are larger if the annealing is carried out at a higher temperature and for a longer time. A simple method of deforming by strain consists in gripping one end of the aluminium strip in a vice and pulling the free end with the aid of a plane catcher. The strips may be elongated by 1–10% of their original length.

(4) In another experiment, the samples instead of being strained are indented with a needle, and hence become strongly deformed at the point of indentation and in its surroundings. As a result a considerable grain growth can be observed during heat treatment.

(5) Recrystallization can be used to grow large single crystals (strain–anneal method of crystal growth). For this purpose an aluminium strip about 20 cm long and 1–2 cm wide is cut out, and deformed by rolling to 50–75%. After deformation the strip is pulled at a rate of 2–3 cm/minute through a tube furnace preheated to 600° C. After the heat treatment the samples are examined microscopically. The strips usually consist of randomly oriented grains with an average diameter of 0.05–0.1 mm. From the plates prepared as described previously 4–5 strips 15–20 cm in length are cut out, a tension of 2–4% is applied, and they are then annealed. Large single crystals, easily visible to the naked eye, grow during the annealing which is carried out in a horizontal, movable tube furnace. At one opening of the furnace a temperature gradient of approximately 40° C/cm must be set at a background temperature of about 630° C. The samples are placed on a ceramic or graphite support which is then put in a quartz tube running through the furnace. The annealing consists now in pulling the furnace over the samples with the aid of a driving unit at a rate of 0.5–20 cm/hour (note that the rate is considerably slower than previously). The heat treatment causing recrystallization may be regarded as terminated when the temperature gradient mentioned above has passed along the whole length of the samples,

which at the end of this process are again at room temperature. The experiment is successful if aluminium single crystals with diameters of 1–2 cm have grown (Fig. I.11.1), but sometimes the whole strip is a single crystal.

The relatively large temperature gradient at one end of the furnace can be obtained by a water-cooled copper spiral pipe pulled onto the quartz tube running through the furnace, and pushed directly to the opening of the furnace. The copper spiral should be fixed to the furnace so that it moves together with the furnace over the samples.

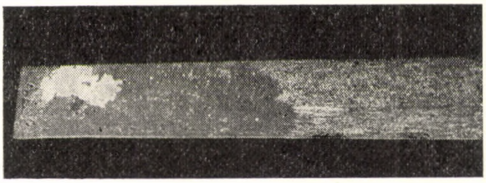

Fig. I.11.1 Photograph of a deformed and annealed aluminium plate
On the left is a polycrystalline, on the right a single crystalline region; bright area refers to a single crystal whose orientation deviates from its surroundings

Care should be taken when handling the aluminium strips after deformation, and before putting them into the furnace, so that any further unwanted deformation (e.g. by bending) may be avoided. In order to determine the optimum degree of deformation, a series of the above experiments is carried out with the same annealing temperature and time but with various straining loads, resulting in 2, 2.5, 3, 3.5, 4, 6, 8 and 10% deformations. The simultaneous effect of the deformation and the annealing is investigated by etching and with an optical microscope. Instead of using aluminium plates, the experiments may also be carried out with aluminium wires or rods, a few mm in diameter. If wires or rods are used the preliminary deformation consists of stretching instead of rolling.

I.11.1.2. Recrystallization of discs pressed from NaCl powder

(1) *Pulverizing and pressing.* P.a. grade NaCl dried for an hour at about 120° C and stored in an exsiccator is used. The polycrystalline material is pulverized vigorously in an agate mortar for about 10 minutes. The maximum grain size is about 50 μm. The pulverized material is put into a press tool made of stainless steel and the discs are pressed in a hydraulic press. Press tools are obtainable commercially; tools for making KBr discs for infrared spectroscopy can be applied with good results. No special requirements are needed regarding the hydraulic press machine. Quite satisfactory results are obtained with a hand-operated hydraulic press machine with a normal pressing power of between 1 000 and 20 000 kp/cm^2.

Good press tools can be made in the workshop from stainless steel (or from tool steel). Figure I.11.2 shows a simple tool in sections. The polycrystalline disc is produced in a cylindrical press mould between two dies. The pressure is transmitted by an anvil. An accessory cylinder with a somewhat larger diameter serves to press out the samples from the mould. For this purpose the mould should be put on the accessory and the sample pressed cautiously downwards with the press until the sample falls into the lower cylinder, the bottom of which should be lined with cotton wool. Both pressing dies fall down with the sample, but only rarely cause any damage to it. In order to obtain even sample surfaces, it is advisable to polish the surfaces of the pressing dies. After careful cleaning, the press tool is stored in a vacuum exsiccator.

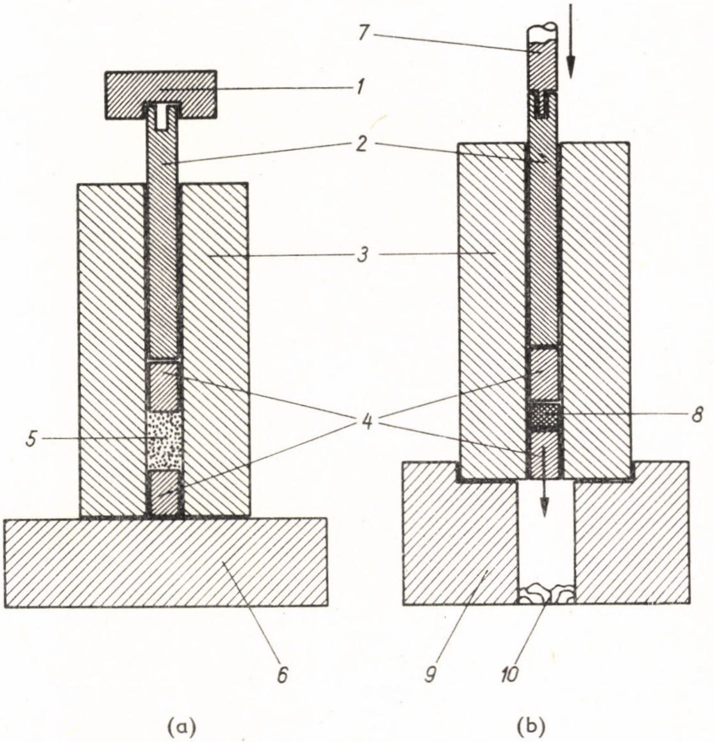

Fig. I.11.2 Press tool

(a) preparation of a disc; (b) pushing out of the disc; *1* upper die (cap), *2* press rod, *3* press cylinder, *4* steel dies, *5* crystalline powder, *6* underplate, *7* pushing rod, *8* disc, *9* accessory cylinder, *10* cotton wool

(2) *The pressure-dependent change of the grain dimensions at constant temperature.* Discs are prepared according to the method described previously at pressures of 2 000, 4 000, 6 000, 8 000 and 10 000 kp/cm^2 (pressing time: 1 minute). The polycrystalline discs obtained are put in ethanol. The small quantity of water present in the ethanol mainly attacks the grain boundaries, which thus become observable with an optical microscope; etching for 3–10 minutes usually yields satisfactory results. After carefully drying

them on filter paper it is advisable to polish the samples by rubbing them gently on a silk cloth or a piece of felt (or on the knuckle).

The average grain density of the surface decreases with increasing pressure (see Fig. I.11.3), which indicates an increase in the average grain dimension. The surface grain density is obtained from the ratio $n:f$, where f denotes the area of the field of view of the microscope and n is the number of grains counted in this area. The grains only partly in the field of vision are counted as half grains.

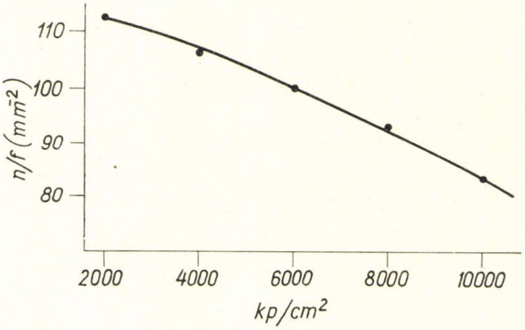

Fig. I.11.3 Curve of average surface grain density of discs prepared at 100° C

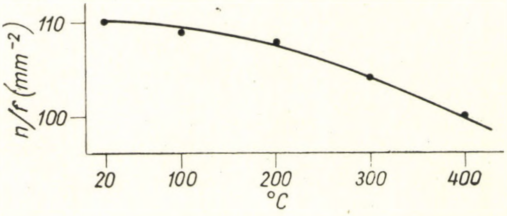

Fig. I.11.4 Curve of average surface grain density of discs prepared with a pressure of 3 000 kp/cm²

(3) *The temperature dependence of grain dimensions at a given pressure.* Discs are prepared as described above at various temperatures. The applied pressure is always the same, e.g. 3 000 kp/cm^2. The desired temperature can be attained by putting the press tool in an electrical furnace. The temperature is measured with a thermocouple placed in a hole drilled through the press cylinder. It should be noted that at lower pressing temperatures (say up to 400° C) the tool is usually not damaged. At higher temperatures, however, the tool anneals, resulting in a decrease in its resistance to pressure. Consequently, for this type of experiment it is advisable to work with tools made in the laboratory workshop and to have more than one at hand. The grains are made visible by etching and polishing as before. The

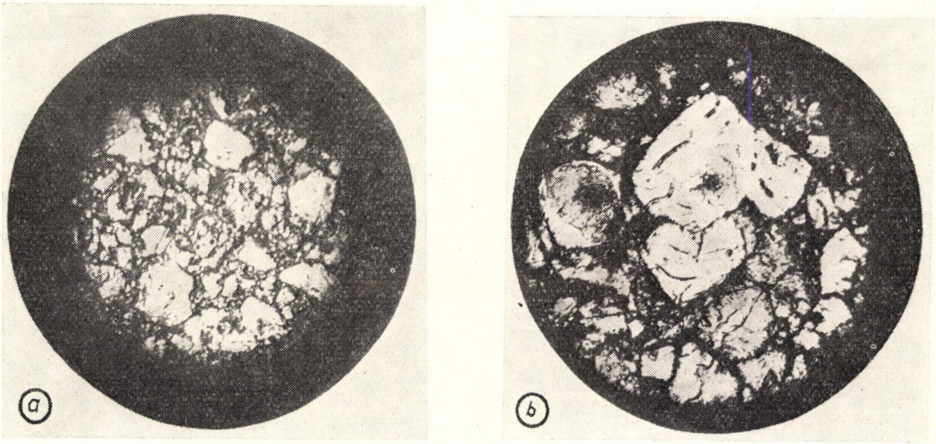

Fig. I.11.5 Etched NaCl discs
(a) pressing temperature 20° C, pressure 3 000 kp/cm^2; (b) pressing temperature 100° C, pressure 10000 kp/cm^2; pressing time 1 min in both cases
(M: 130×)

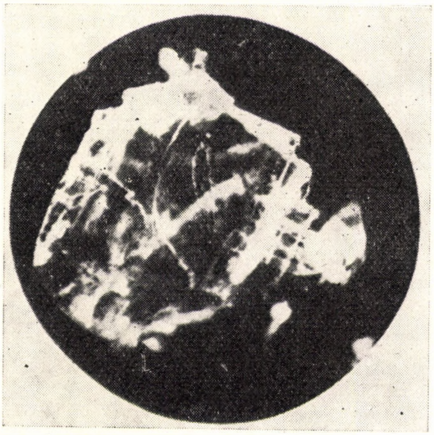

Fig. I.11.6 Single crystal prepared from NaCl discs
Pressing temperature 750° C, pressure 6 000 kp/cm^2; pressing time 60 min (the press tool became unusable after the experiment)
(M: 50×)

average surface grain density is determined with an optical microscope; it decreases with the increase in pressing temperature. This indicates an increase in the average grain dimensions (see Figs I.11.4–6).

I.11.2. Crystallization by Precipitation

I.11.2.1. Formation and investigation of crystals in silicate glasses

If the conditions are favourable crystals are formed in the melts of silicate glasses. The process takes place in a temperature interval depending upon the composition of the glass, and occurs if the glass is kept in this temperature interval for a long time. From the industrial viewpoint crystal precipitation is generally regarded as harmful, since it decreases the mechanical strength of the glasses; moreover it is aesthetically unfavourable.

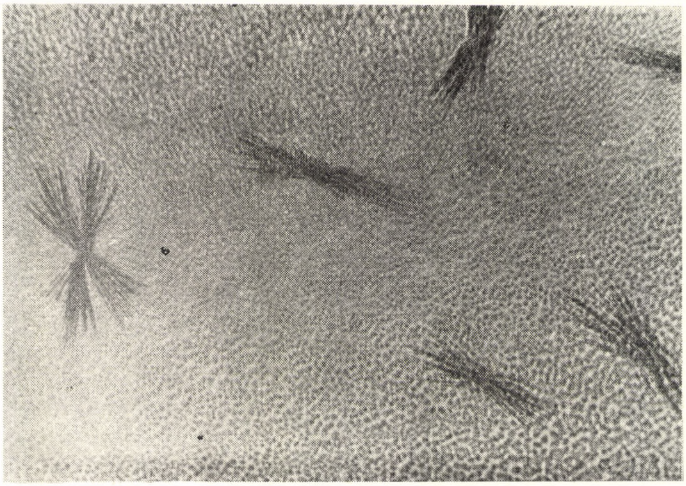

Fig. I.11.7 Pulled plate-glass annealed at 860–870° C for about 4 hours
Brush-like formations are devitrite crystals formed directly below small cristobalite crystal conglomerates grown on the surface (M: about 100×)

Various types of crystals may precipitate from the various types of glass; e.g. devitrite, various modifications of SiO_2, wollastonite. One of the best known and most thoroughly studied is devitrite, which forms mainly in calcium silicate glasses of great CaO content. This crystal precipitation is dominantly a fault of pulled plate-glass. The crystals form in the layers close to the glass surface during the development of the glass plate. If their dimension is 0.1–2.0 mm they resemble granulated sugar, and can be felt with the finger. In a more developed form the precipitate consists of an agglomeration of milky crystals resembling broken, sharp rocks. The devitrite crystal usually forms in a temperature interval of 725–1 000° C; its mineralogical composition is $Na_2SiO_3 \cdot 3CaSiO_3 \cdot 2SiO_2$ ($Na_2O \cdot 3CaO \cdot \cdot 6SiO_2$), and it crystallizes in the rhombic system. Morphologically the devitrite crystals are mainly brush-like formations (Fig. I.11.7), but long, thin felty whiskers crossing each other, thin prismatic needles and even fanshaped spherolites or dendrites may also be observed. A great number of spherolitic crystals are formed during the slow cooling of the glass which flows out of furnaces.

Of the crystalline modifications of SiO_2 mainly cristobalite is formed in plate-glass. The cristobalite crystals grow predominantly on the surface of glass during annealing (Fig. I.11.7).

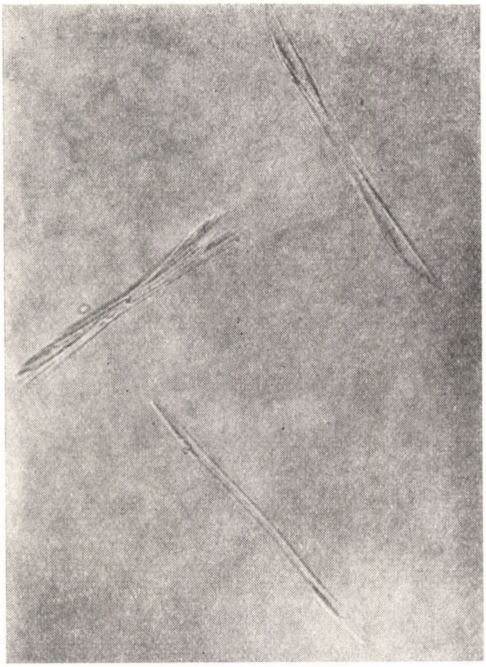

Fig. I.11.8 Separate devitrite crystals in surface layers of a pulled plate-glass

Time of annealing at 900° C approximately 4 hours; picture taken in transmission (M: about 100×)

(1) *Development of devitrite crystals in pulled plate-glass.* The 2–3 mm thick glass plate to be annealed is cleaned very carefully with a piece of soft cloth. From the faultless parts a few plates of about 40 × 14 mm are cut out, put on a porcelain (combustion) tray and the tray is placed in a furnace heated to 900° C. After an annealing time of 3–4 hours the samples are taken out of the furnace and left to cool down to room temperature. The crystals developed in the surface layers of the plates can be observed with the naked eye. More exact investigations are carried out with an optical microscope at a magnification of 100× (Fig. I.11.8).

For good observation the glass plates are covered with glycerine. The refractive index of glycerine is approximately equal to that of the cristobalite crystals developed on the surface, and thus their picture is blurred, while the devitrite crystals become more clearly visible.

Fig. I.11.9 A large quantity of devitrite crystals formed at 920–940° C within a few hours in the interior of pulled plate-glass

Picture taken of a polished 0.1–0.2 mm thick specimen in transmitted light (M: about 100×)

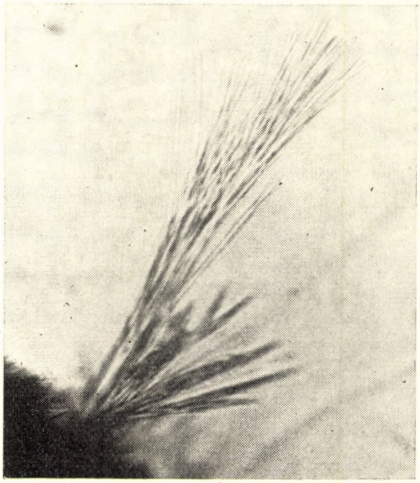

Fig. I.11.10 Devitrite crystals grown in pulled plate-glass adhering to a porcelain tray

Crystals grow from the surface on the porcelain; time of annealing at about 920° C approximately 4 hours; picture taken of a polished specimen in transmitted light (M: about 100×)

In order to investigate the crystals formed at a greater distance below the surface, the annealed plates are broken into pieces and the cleaved surfaces are investigated microscopically. The glass plates suitable for the above investigations must have such cleaved surfaces that are parallel to each other and normal to the original planes of the glass plate. If necessary the surface to be examined must be improved by polishing.

Also in order to study the crystals precipitated further away from the surface, thin polished sections are prepared from the glass. For this purpose one side of the plate must be polished with a very rapidly rotating diamond-disc. After this the sample is glued with Canada balsam to a microscope slide, and the other side is also polished. The thin sections are covered with Canada balsam and a glass cover, and placed under the microscope (Figs I.11.9 and I.11.10 show microphotographs of samples prepared in this way).

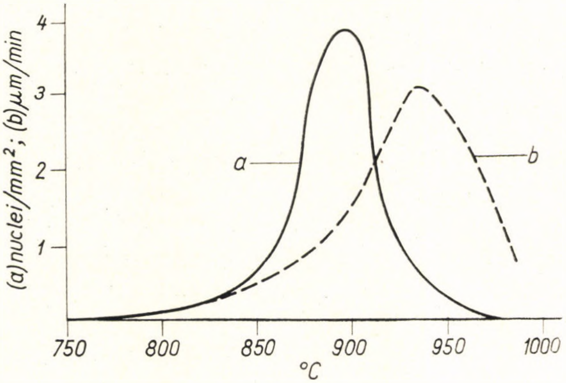

Fig. I.11.11

Dependence of the average embryo density (*a*) and the average rate of growth (*b*) on annealing temperature

(2) *Comparison of pulled plate-glasses of various origin.* From plate-glasses manufactured in various factories 4–6 cm^2 faultless pieces of intact surface are cut out. These samples are placed on porcelain trays and the trays put in a furnace pre-heated to about 870° C. After annealing for two hours the samples are taken out of the furnace and cooled down to room temperature. This cooling must be carried out at the same rate and under the same conditions for every sample. Afterwards the samples are investigated microscopically at a low magnification as in the previous experiment. The samples of various origin are compared by observing the devitrite crystals formed in the surface layers. Two sets of data must be determined: first the average numbers of crystals grown per unit surface in a given time (in this experiment: two hours); the second data refer to the rates of crystal growth as calculated from the average lengths of the crystals. The individual samples can be characterized by the products of these two values. It should be mentioned that annealing for a period of two hours results in the formation of 1–2 nuclei per mm^2, and the average growth rate is 0.5–1 μ/minute.

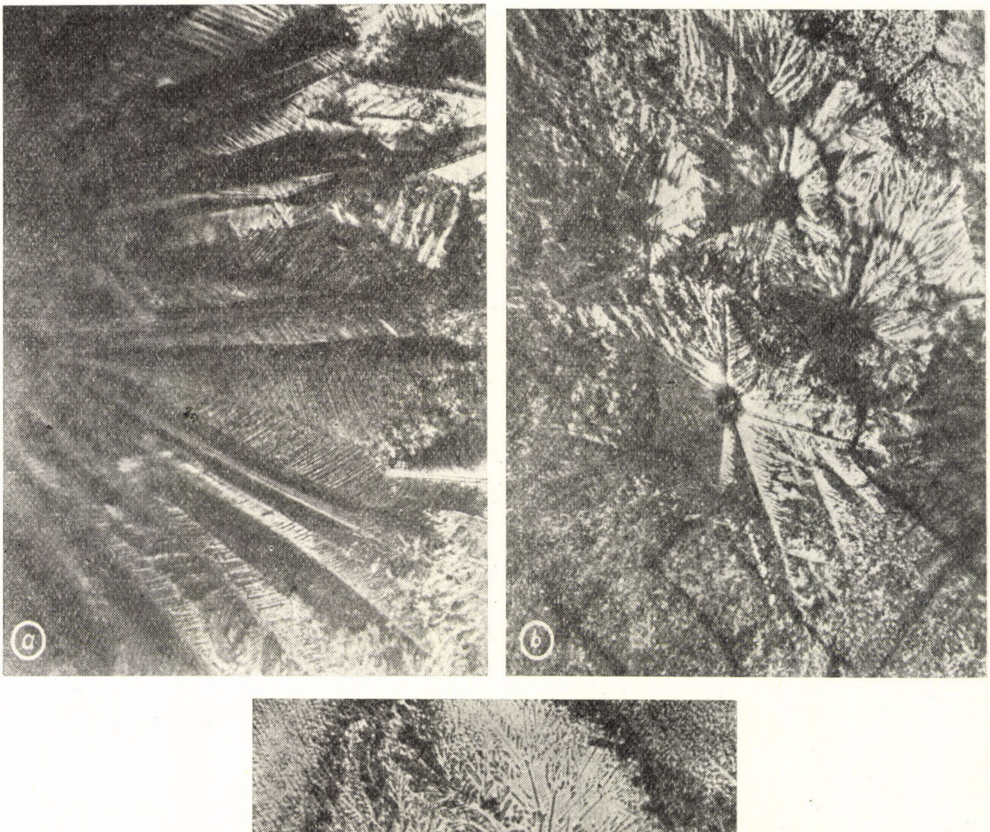

Fig. I.11.12 Cristobalite crystals

(a) and (b) grown on the surface of pulled plate-glass by cooling the samples in 5–6 hours from 1 000° C to 700° C; picture taken in reflected light (M: about 100×); (c) same as (b) but here the sample is covered with glycerine

The samples are placed under the microscope with the centres of their surfaces in the field of vision, since in this central region crystals formed in nearly one plane may be observed. If a cristobalitic devitrification of the surface disturbs the sharpness of the picture of devitrite crystals, the samples are covered with a thin layer of glycerine. A more complete picture of the crystallizing tendencies of samples of various origin may be obtained if annealing for a given time is carried out at various temperatures. In this case the temperature dependence of the average nucleus density and of the average crystal dimension can be demonstrated (see e.g. Fig. I.11.11).

(3) *Growth of cristobalite crystals on the surface of pulled plate-glasses.* When ordinary pulled plate-glass is annealed, the various crystalline modifications of SiO_2, and mainly cristobalite, are formed as already mentioned. The crystals grow on the surface of the glass. Well-developed crystals with definite orientation can be grown if the glass passes through the temperature range of crystallization at a low cooling rate. (Figure I.11.12 demonstrates those cases when the cristobalite crystals cover the whole surface of the glass.) A great number of small crystals are formed if the temperature range of crystallization is attained by an increase of the temperature, and if the samples are annealed at a relatively low temperature.

I.12. CRYSTAL GROWTH BY ELECTROLYSIS

Metals may be segregated from electrolytes containing them as cations by electrolytic methods. The segregation can be carried out from solution, from the melt, and in certain cases also from the solid phase (see experiment I.8.5.2). This method of segregation is generally called electroplating. The purpose of electroplating is usually to obtain a very thin continuous covering layer with a fine structure. In connection with crystal growth, however, the aim is the preparation of large single crystals. In the growth process the metal crystal to be enlarged by crystal growth is used as a cathode. It is most suitable to use the same metal for making the anode. The segregating metal ions are directed by the electric field to those places where they can fit into the already existing lattice. In order to study electrolytic crystal growth, as cathode is used one macroscopic single crystal which can be easily handled. The symmetry of the ion migration can be ensured with a spherical cathode which is surrounded by a spherical shell-shaped anode. Thus one may avoid (at least as far as the electric field is concerned) the formation of preferred sites where, as a result of very fast segregation, dendrites may be formed.

I.12.1. Crystal Growth by Electrolysis from the Melt

I.12.1.1. Formation of crystal surfaces on spherical silver crystals

As cathode *1* in the electrolysis tank (Fig. I.12.1) is used a silver single crystal sphere with a diameter of about 6 mm, with a stem about 30 mm long. A simple method of growing silver spheres is described in II.2.14. The anode *2* consists of two hollow hemispheres with hollow handles. The hemispheres together with their handles are pressed from a 1 mm thick silver plate; the sphere formed from the two halves has a diameter of 40 mm (the hemispheres are made by pressing, and not by soldering). To the stem of the cathode is welded the silver wire *3* a few tenths of a mm thick, of suitable length, and onto it is pulled the hard glass or porcelain tube *4* with a wall thickness of 0.5 mm and an internal diameter of 2.0–2.5 mm. The tube fits into the hollow handles of the anode hemispheres so that after the two halves are put together the handle forms one tube about 50 mm long containing the glass or porcelain tube with the wire in it. The length of this insulating tube is approximately 80 mm. The handles of the anode hemispheres are fastened with a silver wire which also serves as an electric contact. The diameter of the cylindrical electrolysis tank *5* is 5–10 mm larger than the diameter of the anode, and its height is about 70 mm. The tank is made of glass softening only at a high temperature (e.g. Jena hard glass, durane, ergon or pyrex). In the centre of the lid *6* there is a hole with a diameter of 6.0–6.5 mm to let through the handle. The gaps between the various parts of the equipment are stuffed with asbestos flakes.

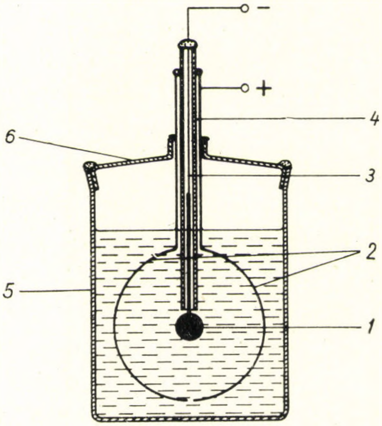

Fig. I.12.1 Electrolysis tank

Both cathode and anode may be made of 99.99% pure silver which can be obtained commercially either as a granulate or in the form of wires or plates. The purity of the electrolyte must be the same. The melts of $AgNO_3$, AgCl, AgBr, etc. are used as electrolytes, 'diluted' by adding e.g. KNO_3, KCl or KBr to them. The cathode and anode are cleaned by etching the metal surfaces slightly with diluted nitric acid which is then washed off with distilled water. Before the experiment the metal is heated for 10–20 hours at 800° C. During this heat treatment the possible stresses present in the single crystals to be used as cathode become relaxed. After the heat treatment the crystal surfaces must not be touched, and thus it is advisable to carry out the heat treatment with already mounted assemblies. The surface of the heat treated crystal is similar to surfaces etched with nitric acid but is somewhat brighter, and, of course, shows the characteristic single crystal line reflexes.

A 4 V accumulator is used as a current source. In electroplating processes the calculations are usually carried out for current densities. Since the surface of a 6 mm diameter sphere is approximately 1 cm^2, the current value read on the galvanometer is an approximate measure of the current density on the cathode. It is worth mentioning that, with a current density of 2×10^{-4} A/cm^2, one atomic layer per second precipitates.

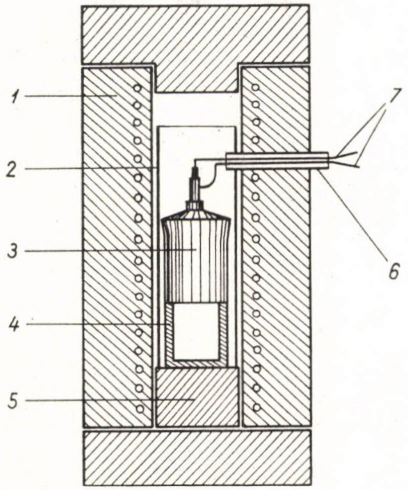

Fig. I.12.2 Schematic diagram of the growth apparatus

In the case of the electrolytes summarized in Table I.IV it is quite satisfactory to use a furnace (see *1* in Fig. I.12.2) which can be heated only up to 300° C. The furnace must be constructed (possibly from several parts) so

TABLE I.IV

Composition of electrolyte	Current density ($\times 10^{-5}$ A/cm^2)	Temperature (° C)	Time (h)	Developed forms
$AgNO_3$	10	220	480	{311} {100}
	300	220	16	{311}
	35	220	48	{311}
	35	220	120	{311} {100}
$AgNO_3$ (99%) + KNO_3 (1%)	35	220	144	{311} {100}
$AgNO_3$ (85%) + KNO_3 (15%)	35	200	216	{311} {100}
$AgNO_3$ (75%) + AgCl (25%)	18	240	192	{522} {100}
$AgNO_3$ (62%) + AgCl (38%)	8	260	240	{111} {100}

that a homogeneous temperature distribution develops in the tank. This homogeneous temperature distribution can be attained for example by the metal tube *2* placed in the furnace. The temperature is stabilized within ±1° C. In order to collect the electrolyte which will pour out should the tank *3* break, the porcelain or glass crucible *4* standing on the thermo-insulating block *5* is placed at the bottom of the furnace. The thermocouple (e.g. iron-constantan) can be inserted into the furnace through the same insulating tube *6* which also serves for the leads *7* (0.3 mm silver wires) connecting the electrodes with the circuit.

Fig. I.12.3 Crystal faces grown on a spherical silver single crystal

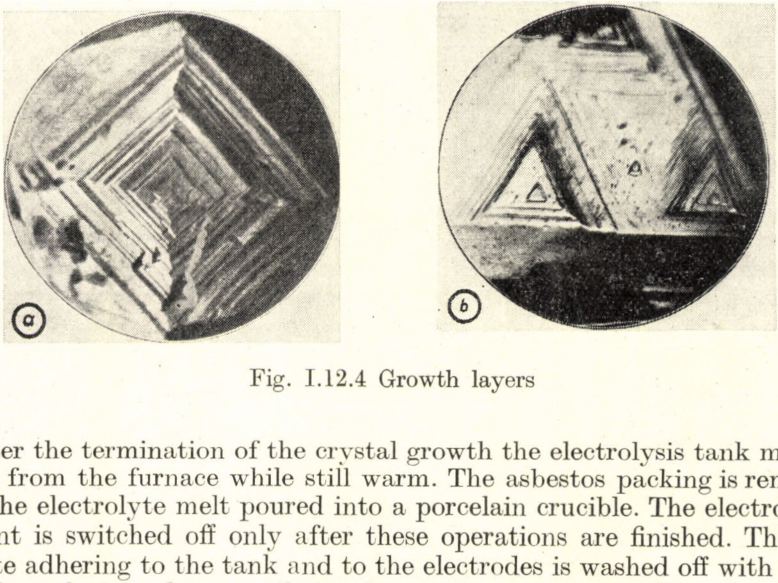

Fig. I.12.4 Growth layers

After the termination of the crystal growth the electrolysis tank must be lifted from the furnace while still warm. The asbestos packing is removed, and the electrolyte melt poured into a porcelain crucible. The electrolysing current is switched off only after these operations are finished. The electrolyte adhering to the tank and to the electrodes is washed off with water. The electrolysis tank can easily be placed into and removed from the furnace if it is surrounded with a hoop which has a handle reaching to the lid of the furnace.

The crystal surfaces developed during the electrolysis are in most cases smooth and well-reflecting, and consequently their Miller indices can easily be determined with a reflexion goniometer. However, in the case of a pure silver halide melt the quality of the grown sample is not always satisfactory; it is sometimes polycrystalline, consisting of several small (oriented) crystals. If halogen ions are present, the {311} surfaces will not develop under the given experimental conditions. Table I.IV contains the temperature of electrolysis, the melting points of the electrolytes being 20–25° C lower than these values.

Figure I.12.3 shows the planes which develop on spherical crystals; Fig. I.12.4a shows the (100) planes at a magnification of 15×. The growth layers are well visible. The side faces of the layers correspond to the {311} surfaces, and consequently the edges of the layers represent the lines of intersection of {100} and {311} planes. The growth layers developed on the (111) planes are shown in Fig. I.12.4b at a magnification of 80×; the sides of the layers correspond to the {311} planes.

I.12.2. Crystal Growth by Electrolysis from Solution

I.12.2.1. Development of crystal surfaces on spherical silver and copper crystals

The electrolysis tank is prepared according to experiment I.12.1.1. A cut glass lid is used and sealed with pizein instead of asbestos. The experiment is carried out at a temperature close to room temperature, e.g. with the electrolysis tank in a thermostat set at 25° C. The electrolyte solutions suggested are given in Table I.V. If a current density of 3–6 × 10^{-5} A/cm^2 is maintained the crystal faces appear within a few days, but their identification with a goniometer is possible only after a growth of 2 or 3 weeks. Table I.V also contains the crystalline forms which develop under the conditions mentioned above. The + signs indicate that the respective form is present only in 'traces'. Attention must be drawn to the fact that the growth proceeds well only if the solution contains the silver in the form of complex

TABLE I.V

Solution*		100	111	110	hk0	h11	hk1
0.2 N AgI,	2.4 N KI	+	—	—	—	211	521
Saturated AgBr,	4.2 N KBr	—	+	—	720	211	—
Saturated AgBr,	14.5 N NH_3	—	+	+	720	—	—
Saturated AgBr,	5.1 N NH_4Br	—	+	—	310	—	—
0.2 N AgCl,	14.5 N NH_3	+	+	+	—	—	—
Saturated AgCl,	5.6 N NH_4Cl	—	+	—	510	—	—
Saturated AgCl,	6.3 N $MgCl_2$	+	+	—	310	211	—
0.2 N Ag_20,	14.5 N NH_3	+	+	—	—	—	—

* The silver compound is dissolved in a complex-forming solution having the concentration indicated; sufficient silver compound is taken for the final solution to be either 0.2 N or saturated with respect to the complex silver ion.

ions. The Table refers to such solutions that can be prepared by dissolving otherwise insoluble silver salts in solutions of some easily soluble and complex forming salt.

Copper crystals (see Fig. I.12.5) can be grown electrolytically from solutions of copper salts. The procedure is as previously with silver. There is a definite difference between copper (I) and copper (II) compounds in so far as well-observable crystal planes grow only from the latter. In solutions of copper (I) compounds which also contain chloride and bromide ions, in addition to the octahedral forms which always become visible, more complicated forms (e.g. four-faced cubes, icositetrahedra, rhombododecahedra) can also be observed. The presence of I^-, CN^- or CH_3COO^- ions influences the crystal growth unfavourably. Good results may be obtained with electrolytes of the following compositions: 0.01–0.3 N CuCl + 20% KCl, 0.1 N CuCl + 15% KCl + 0.75 N HCl, 0.1–0.4 N CuBr + 40% KBr; KCl can be replaced by $MgCl_2$, $CaCl_2$ or $AlCl_3$ of similar concentration. (In these latter solutions the copper (I) compounds are present in complex form.) Current densities of $4–12 \times 10^{-5}$ A/cm^2 and $3–7 \times 10^{-5}$ A/cm^2 are suggested for chlorides and bromides, respectively. Well-developed crystal faces can be obtained at room temperature within a few weeks.

Fig. I.12.5 Crystal faces grown on a spherical copper single crystal
(E. Frankl, 1936: *Thesis*, Budapest)

I.13. MISCELLANEOUS

I.13.1. Crystal Textures

Crystal textures consist of whiskers or platelets of the same orientation. They are somewhat similar to electrets which, being dipoles, can be oriented in an electric field. However, the orientation of textures is obtained mechanically, and the polaroid plates which produce polarized light are also oriented mechanically; piezoelectric crystal textures are sometimes called electrical polaroids.

I.13.1.1. Preparation of $KNaC_4H_4O_6 \cdot 4H_2O$ (KNT) crystal textures

KNT (Seignette or Rochelle salt) crystallizes in the rhombohemihedric system. The crystals are very brittle and hygroscopic. Their practical importance is due to their piezoelectric properties. In spite of the fact that the piezoelectric constant of KNT crystal textures is about one order of magnitude smaller than that of the single crystal, the advantage of the crystal textures is that they can be produced in a short time, are easily processed, and are less sensitive to shaking or knocking. The samples made from the textures cannot be used as filters in electrical oscillating circuits, because their selectivity is not high enough (they have several eigen-frequencies), but they can be used quite well for other purposes such as electrical-mechanical transformers.

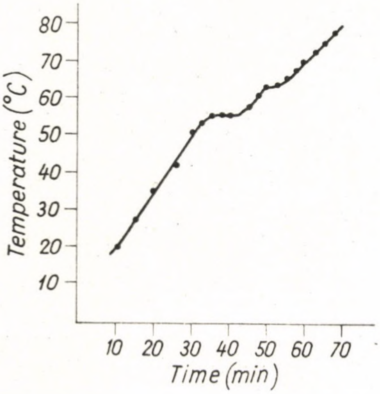

Fig. I.13.1 Heating diagram of KNT

Textures are produced from KNT melt. The polycrystalline starting material warmed in an open glass jar or porcelain crucible melts at 55° C. Within half an hour it loses most of its crystal water, and is transformed into a white powder. The transformation takes place according to the following equation:

$$4KNaC_4H_4O_6 \cdot 4H_2O = 2Na_2C_4H_4O_6 \cdot 2H_2O + 2K_2C_4H_4O_6 \cdot \frac{1}{2} H_2O + 11H_2O$$

If the heating rate is decreased below 0.5° C/minute, and the jar is covered during the heating process, the heating diagram shows an inflection at 63° C indicating another transformation (Fig. I.13.1). The water-clear melt becomes opaque at this temperature, and clears only on further heating. If the

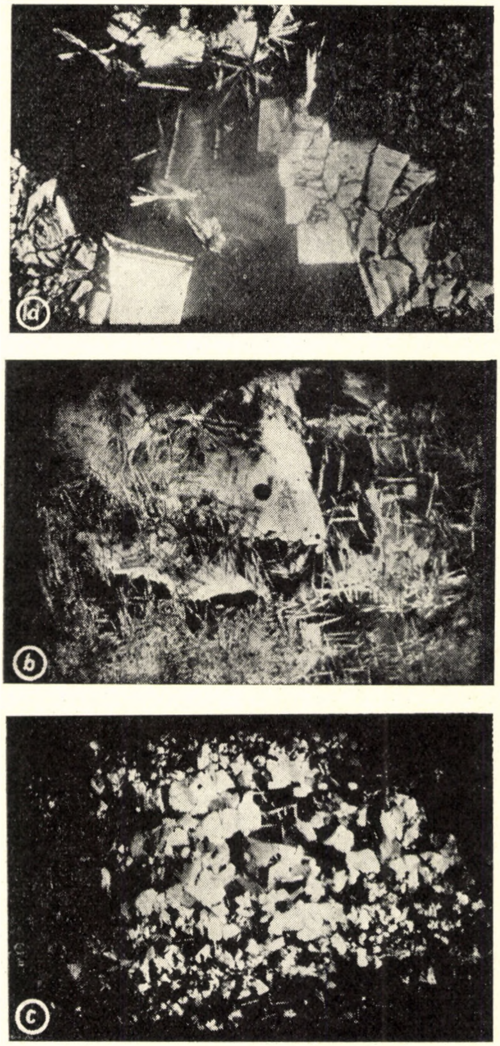

Fig. I.13.2
Frozen-in spherolites
(a) whiskers; (b) and (c) plates (M: 400×)

process is investigated under the microscope the formation of whiskers can be observed at 63° C. (It is advisable to put the crystals in a concave microscope slide and cover the melt with a cover glass.) At atmospheric pressure the KNT melt and the crystal water boil at 105° C, and the remaining solid material carbonizes at 117° C.

If the melt is cooled down rapidly to 10–20° C a very hard, white, partly glass-like material is produced. The solidification is a very slow process and may last several days. The material so obtained consists of the domatic modifications of the trigonal-scalenohedral form of frozen whiskers, spherolites and plates, which can be clearly observed in the microscope (Fig. I.13.2a, b, c). These latter forms become dominant if the melt is cooled down from a temperature above 63° C, e.g. from 80° C. The frozen-in crystals may be stored for years without any damage at a relative humidity of 70–80%.

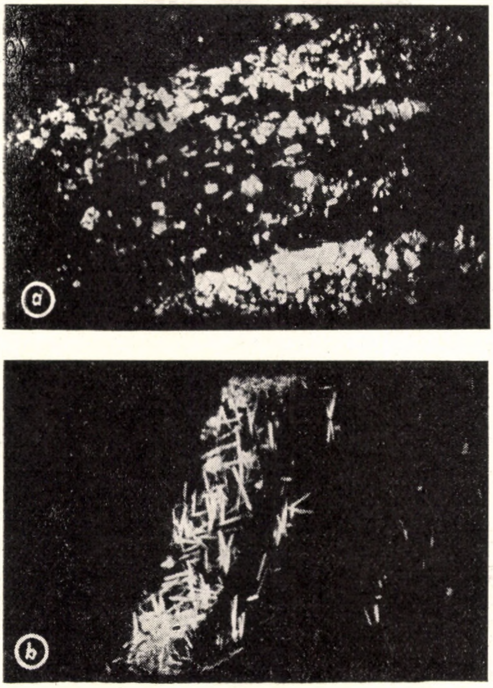

Fig. I.13.3
KNT crystal textures consisting of (a) plates and (b) whiskers
(M: 400×)

KNT melt can be easily supercooled and kept in a supercooled state at a temperature of 10–15° C for several minutes. The supercooled fluid is very viscous and may be used as a glue, for example to fix electrodes to piezoelectric crystal plates, or to glue the plates to each other.

The textures can be made from a rapidly cooled down melt in the following way. Approximately 200 g KNT is put in a beaker, which is covered and warmed in a water bath to 80° C. The resulting water-clear melt is spread with a fine brush onto a plastic, glass, or metal plate with parallel strokes of the brush. (The plastic used must not deform at the temperature of the melt.) Figure I.13.3 shows a crystal texture (several tenths of a mm thick) which was prepared with a single stroke of the brush on a microscope slide. The strokes are not necessarily straight lines. Wavy, or circular textures can be prepared too. The support used in the preparation of the textures is warmed by the hot melt, and thus the rate of cooling decreases. In order to avoid a too slow cooling, the support is cooled either by a cold air stream from below, or by blowing air onto its surface. If the cooling is satisfactory new layers can be put on the first one after 20–30 seconds. Those textures are best suited for mechanical-electrical transformers, whose consecutive layers are identically oriented.

The ready textures can in most cases be detached from their support with the aid of a sharp blade. If the supporting plate is thin (0.5–1 mm) the support must be carefully warmed to approximately 40° C before the sample is detached. In this case the crystal texture can be pushed off its support with the finger. The surface layer of the sample which is in contact with the support may be damaged during the warming up of the support. For this reason this bottom layer of the sample must be polished off with fine emery paper.

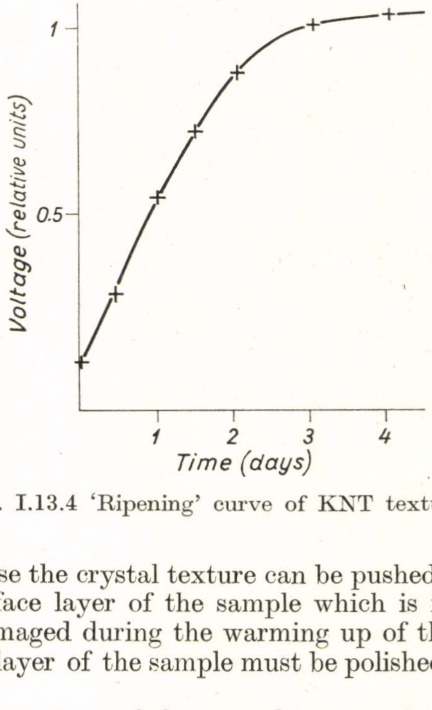

Fig. I.13.4 'Ripening' curve of KNT textures

The piezoelectric constant of the crystal textures increases for a certain time after hardening; this 'ripening' process terminates in about 4 days. It is advisable therefore to detach the samples from their support only 1 or 2 days after their preparation. The 'ripening' process of the textures can easily be followed if they are provided with electrodes (e.g. gold, silver, aluminium foils) connected to an oscilloscope. At certain time intervals a small (1 g) steel ball is dropped from about 10 cm onto the texture, and the voltage caused by the deformation is measured with the oscilloscope (Fig. I.13.4).

With the method described crystal plates of various shapes and dimensions may be prepared. It is advisable to select previously the shape and dimension of the support as in this case only the edges and upper surface of the plate must be polished. However, the final shape can also be developed from a larger plate by sawing and polishing. The polishing of parallel surfaces is better carried out with a polishing machine.

KNT crystal textures can be used for experimental purposes as well as for industrial applications. For instance the oscillations of metal (or plastic) plates may be studied by preparing a crystal texture on them as described above. A sample is made 1–2 tenths of a mm larger than the support to be studied. The edges are then polished off until the dimensions of the support are obtained. The upper surface of the crystalline layer must also be polished off so that it is bounded by plano-parallel faces. If metal plates are to be investigated, only one electrode is glued onto the upper face of the texture; in every other case a second electrode must also be fixed onto the support As an adhesive a supercooled KNT melt is used. After this the plate is fixed in a horizontal position at the appropriate points, and lycopodium powder is sprinkled on it. The electrodes are connected at the point of fixing to the output of an audio-frequency (or to an ultrasonic) generator. As a result of electrical excitation at the appropriate frequency the crystal textures make the support oscillate, and the lycopodium powder collects along the nodal lines (Chladni figures, Fig. I.13.5).

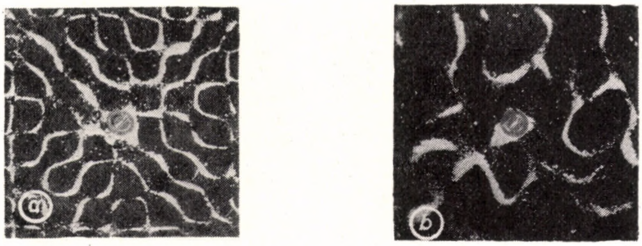

Fig. I.13.5 Chladni figures produced with the aid of crystal textures

The oscillations of buildings or pillars can be investigated by gluing the crystal plate provided with electrodes onto the point to be investigated, and connecting the electrodes to the oscilloscope.

I.13.1.2. Orthotropic crystallization of salol

If a drop of salol melt is covered with a cover glass, and after cooling is touched with a needle contaminated with salol crystals at the centre of one edge of the cover, the salol crystals grow radially from this point. If the needle is moved rapidly around the whole contour of the cover glass the crystals grow perpendicularly to the edges. Finally one obtains a crystalline aggregate as depicted in Fig. I.13.6. This growth type, where the growth direction is perpendicular to the line (or plane) where crystallization starts is called orthotropic.

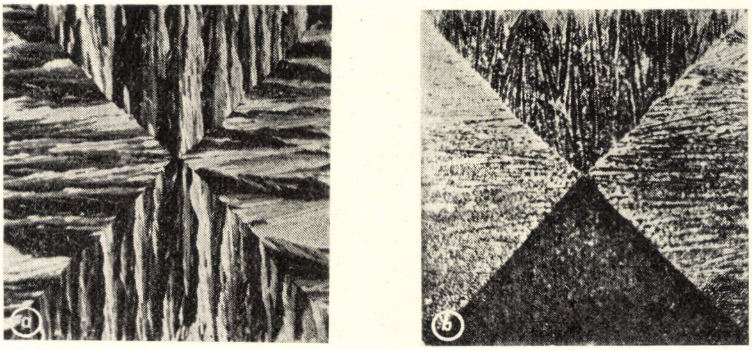

Fig. I.13.6 Orthotropically grown salol crystals
(a) in polarized light; (b) in natural light (M: 2.5×)

I.13.2. Investigation of Cement Crystals

The most important cement type, silicate or portland cement, is made by mixing a prescribed quantity of finely ground limestone with clay (marl), and heating the mixture at about 1450° C until shrinkage occurs. The greenish-grey, lumpy material thus produced is cement clinker or simply clinker. Cement is obtained by grinding the clinker (to which a few per cent of plaster-stone, gypsum, is added), and mixing it with water; the cement paste first gradually sets and then hardens to cement-stone.

The formation of clinker is the result of a process taking place in a four-component system (impurities which may be present in small quantities are neglected). The components are: $CaO–Al_2O_3–Fe_2O_3–SiO_2$. Besides the solid phase a melt is also produced at the heating temperature. The crystallization of so-called clinker minerals takes place in the melt. The properties of cement are determined by several factors, of which the relative quantities of the main clinker minerals, as well as the size of the crystals, play a decisive role. The four main minerals are: tricalcium silicate ($3CaO \cdot SiO_2$, Ca_3SiO_5, or briefly C_3S); β-dicalcium silicate ($2CaO \cdot SiO_2$, Ca_2SiO_4, or briefly C_2S); tetracalcium aluminate-ferrite ($4CaO \cdot Al_2O_3 \cdot Fe_2O_3$, $Ca_4Al_2. Fe_2O_{10}$, or briefly C_4AF), and finally tricalcium aluminate ($3CaO \cdot Al_2O_3$, $Ca_3Al_2O_6$, or briefly C_3A). With reference to cement, these minerals are called alite, belite (the β-modification of C_2S) and celite (which refers to minerals containing iron and aluminium compounds). Alite occurs in the largest percentage (37–60%), followed by belite (15–37%). The proportion of the minerals in the cement may be determined by chemical analysis; this yields the so-called potential composition. This, however, does not often correspond with the actual mineral composition, since crystallization during heating is usually imperfect, and minor impurities may also considerably influence the formation of crystals in the mixture. It is advisable, therefore, to determine the mineral composition of cement with the aid of a microscope.

In addition to the crystalline materials mentioned above, clinker cement also contains a glass-like phase whose composition may also vary depending upon those components which have crystallized from the melt.

The mixing of cement with water initiates hydrolysis by dissolution followed by hydration processes, during which new compounds, crystalline and gel-like hydrated products are formed (e.g. calcium hydroxide, calcium silicate hydrates, calcium hydroaluminates). The cement paste first sets by rather complicated physico-chemical processes, and gradually becomes stone-like by hardening. Though this latter process is very long (lasting for years), clinker minerals are always found in cement-stone in addition to new products.

It follows, therefore, that the problem to be investigated can be divided into two groups: crystallization of the clinker; crystallization processes taking place during the setting and hardening of cement.

I.13.2.1. Qualitative study of crystals formed in clinker

Clinker-lump obtained from a cement plant is used for the investigations. A suitable piece of clinker is selected and embedded in artificial resin, and after grinding, polishing and etching the specimen is investigated in a metallographic microscope.

(1) *Preparation of the ground sample.*—One side of a clinker granulate 1 cm in diameter is ground on emery-cloth, and the ground surface is cleaned thoroughly with the aid of a stiff brush to free it from dust. It is advisable to wash the ground surface with ethanol or some other water-free liquid which does not attack the clinker. The granulate is embedded into some unshrinkable artificial resin; this can be carried out in the following way. A piece about 3 cm long and 3 or 4 cm in diameter is cut off from a plastic tube. To one end of the 3 cm long piece is glued a circular plate made of tracing paper, and its inner side is coated thinly with vaseline. (If the cut surface of the tube is uneven it is first smoothed by grinding.) The clinker granulate is put into the vessel thus obtained (with its ground surface downwards), and artificial resin is poured onto it. The clinker granulates are porous, and consequently it is advisable to place the sample in a vacuum exsiccator; this is first evacuated and then air is admitted so that the pores of the sample become filled with resin. When the resin has hardened it is pushed out of the tube, which can thus be re-used.

The next step is to process the plane surface of the clinker-lump. For this purpose the disc-like specimen is ground first on coarse and then on increasingly finer grade emery-papers. Before the finer grade grinding is begun, the specimen is dusted and washed carefully in pure ethanol or isobutyl alcohol. If the clinker is very porous and the resin does not fill the pores sufficiently, granulates may break off during grinding. In order to avoid this unwanted effect the pores are filled with artificial resin.

Grinding may also be carried out on an iron disc 1 cm thick, with a diameter of about 20 cm, or on a glass plate, with grinding powder which must be pulpified with a liquid which does not contain water since water attacks the crystals of the clinker. Pure ethanol, isobutyl alcohol, or a mixture of

80% ethanol and 20% butylene glycol are most suitable for this purpose. Not only the specimen, but also the grinding disc must be cleaned when the change-over is made from a coarse grinding powder to a finer one. This cleaning must be carried out with exceptional care after the final grinding, since the grains of the grinding powder adhering to the specimen surface may seriously disturb the subsequent polishing process. It is advisable to use several grinding discs if a number of cement specimens are to be made. With grinding powder of a given grade the same disc, which should be stored separately, is always used.

Polishing is begun on a glass plate and continued on polishing paper. The surface of the glass plate must previously be made mat with fine grinding powder. By polishing first on glass, any damage to the polishing paper may be avoided. For this same purpose it is advisable to round off the edges of the disc-like specimen during grinding. (Polishing on felt is not advisable: no uniform surfaces are obtained, because felt hollows out the softer crystals of the clinker.) Polishing may be carried out with a good quality polishing paste containing diamond powder, or with some other suitable hard and fine powder (e.g. cerium oxide, aluminium oxide, or chromium oxide which must be carefully pulverized in an agate mortar). The liquid used for grinding is used for polishing. After polishing, the specimen is dried in a dry chamber at 60° C.

(2) *Etching.* — The crystals of the clinker minerals cannot be observed on the polished surface. However, they can be made visible by a proper etching technique, some details of which are given in the following. The etching reagents listed below give surfaces with the mineral components visible.

Double etchants:

		°C
10% KOH in distilled water	10 s	35
1% HNO_3 in ethanol	10 s	20
1% HNO_3 in ethanol	10 s	20
distilled water	2 min	20
1% HNO_3 in ethanol	10 s	20
10% KOH in distilled water	15 s	40

Single etchants:

		°C
1% HNO_3 in ethanol	10 s	20
concentrated hydrofluoric acid	1 s	20
1 N salicylic acid in ethanol	4 min	40

Before the sample is dipped in a new etchant, and after the etching is finished, the sample is rinsed with pure alcohol and dried in an air stream. The various regions of the etched surface have various colours; this, however, is not decisive in differentiating between the various clinker minerals. Thus, for instance, if the first double etchant is used some grains of alite are of a bluish or greenish colour, others are violet or yellow.

(3) *The study of clinker with an optical microscope.* — A metallographic microscope is used, and the investigation is begun at low magnification, gradually proceeding to higher magnifications. At low magnification, various regions (zones) related to the distribution of impurities incorporated during the annealing are observed. A typical zonal structure is shown in Fig. I.13.7.

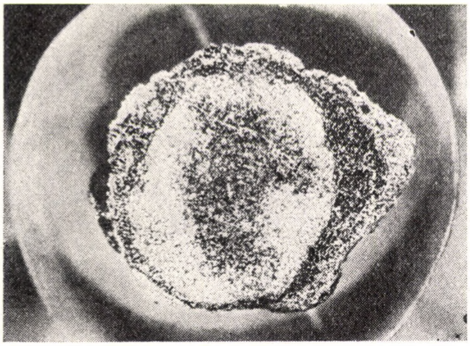

Fig. I.13.7 Clinker embedded in artificial resin and polished
Disc diameter is 3.5 cm

Fig. I.13.8 Alite crystals
Space between crystals is filled with celite and a glass-like phase (M: 270×)

The crystals of clinker minerals may be studied at a magnification of several hundreds. The crystals of the various minerals are usually evenly distributed, though sometimes smaller or larger zones may be found which consist mainly of alite or belite crystals (Figs I.13.8 and I.13.9). The crystal habit of alite in clinker has trigonal symmetry. The crystal structure of alite, however, is converted on cooling from the trigonal form to the monoclinic form. The belite crystal, the β-modification of calcium orthosilicate, also belongs to the monoclinic system. (The β-modification is stable in the temperature range of 675–1420° C, though it may exist in a metastable state at room temperature too.) The γ-modification of calcium orthosilicate, which is stable at high temperatures occurs only rarely. This modification is hexagonal and belongs to the glaserite type. The average size of alite crystals is larger than that of the belite grains. The former are angular, and frequently contain inclusions and cracks. Bands can sometimes be seen in the crystals, corresponding to growth layers. Belite crystals may be banded as well as granulated; they are usually rounded off.

The crystals of the celite group appear only rarely. The tricalcium aluminate crystal shown in Fig. I.13.10 crystallizes in the cubic system, and its lattice is similar to the perovskite structure.

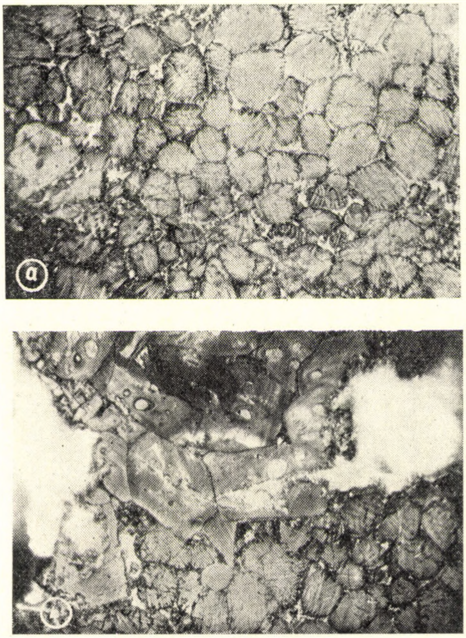

Fig. I.13.9
(a) belite crystals (M: 270×); (b) in the upper part of the picture alite, in the lower part belite (M: 270×)

(4) *Electron microscopical investigations.*—Only a few problems are mentioned in this section: problems which can be studied only with the aid of the high resolving power of an electron microscope. Such problems are the study of inclusions in alite crystals; the nature of the grainy layer structure observed at the boundaries of alite crystals and indicating the decomposition of these crystals; the structure and properties of whiskers grown on fast cooling; the transformation of the belite modification metastable at room temperature; the composition of celite; and the study of the glass-like phase.

For electronmicroscopical investigations, carefully polished and etched clinker surfaces are used (Figs I.13.11 and I.13.12). The surface region to be investigated electronmicroscopically is selected with the aid of an optical microscope, then marked by scratching with a diamond needle.

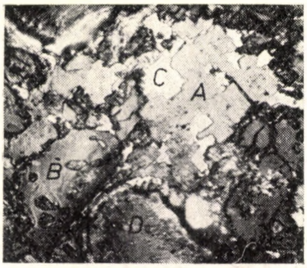

Fig. I.13.10 *A* Tricalcium aluminate crystal, *B* alite crystal, *C* glass-like phase, *D* artificial resin
(M: 525×)

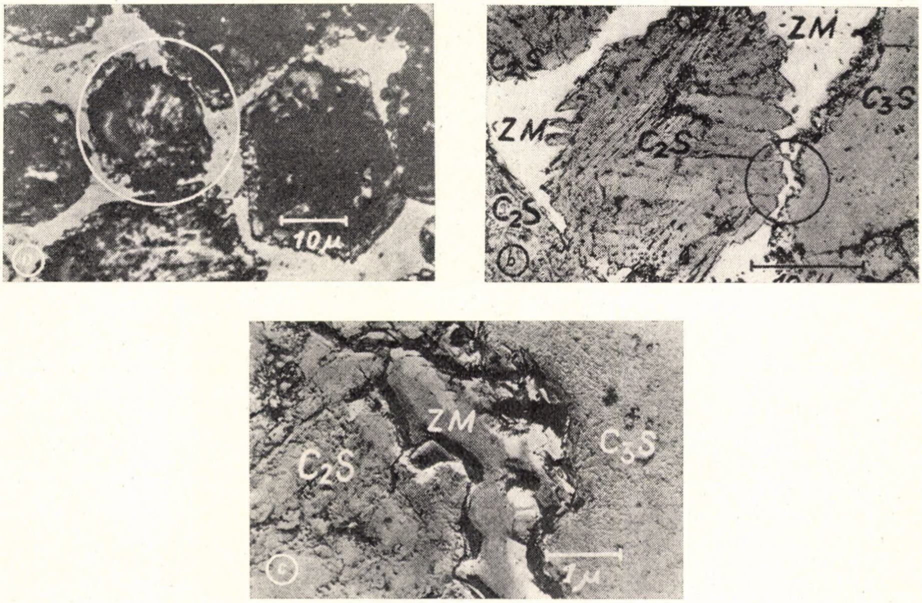

Fig. I.13.11 Micrograms of the polished and etched surface of a clinker grain*

(a) taken with optical microscope; (b) taken with electronmicroscope, detail of (a); (c) electronmicrogram, detail of (b); sample etched at 20° C with 1% HNO_3 solution for 10 s; in (b) and (c) the C_2S and C_3S crystals are easily distinguishable from each other, and from the intermediate material belonging to the celite group (*ZM*); characteristic structures of C_2S and C_3S crystals are well visible, but no well-defined information is given about the details of the intermediate material

A microphotograph is made of the marked zone. A two-stage replica of the specimen surface is prepared. Details of the preparation technique are not discussed, only its main features are mentioned. From the marked surface, with the aid of a suitable foil, a replica is prepared, shadowed, and carbon is evaporated onto it. The carbon film is reinforced with gold evaporated

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* Brunner, P. (1965): Eine Methode zur elektronenoptischen Abbildung von polierten Zementklinkeroberflächen. *Zement–Kalk–Gips 18*, pp. 247–52.

onto the film. The gold layer should be 1 μm thick. The foil is dissolved from the specimen on a microgrid, and the gold film is also removed. For this purpose about 0.15 g potassium cyanide is dissolved in 15–20 ml water and 3 drops of 30% hydrogen peroxide are added to the solution. The gold dissolves in this solution at room temperature within 30–60 minutes. The rate of dissolution can be increased by increasing the concentration of hydrogen peroxide.

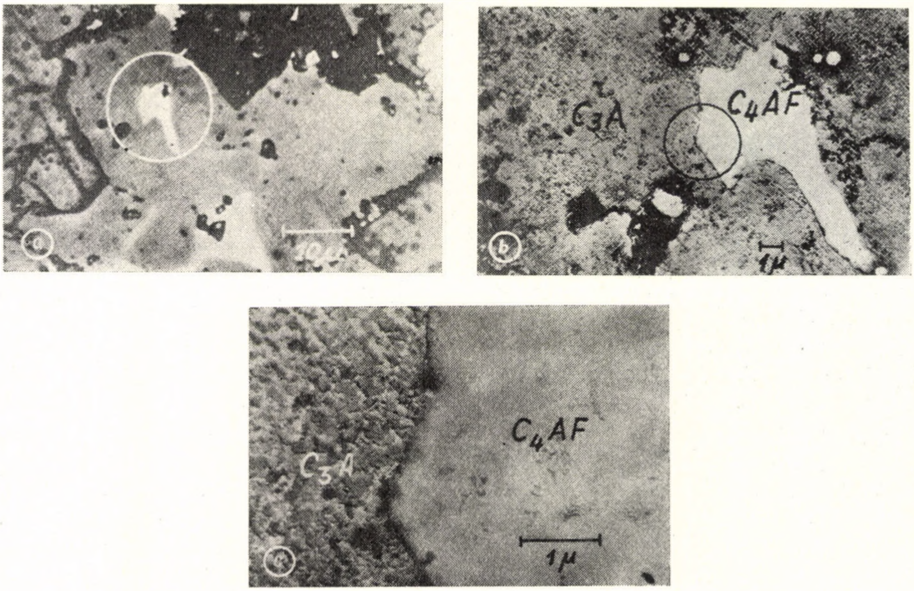

Fig. I.13.12 Micrograms of a polished and etched clinker grain*

(a) taken with an optical microscope; (b) electronmicrogram, detail of (a); (c) detail of picture (b); etching with a double etchant: 10% KOH solution, 35° C, 10 s; 1% HNO_3 solution, 20° C, 10 s. – In contrast to Fig. I.13.11, C_3A and C_4AF crystals belonging to the celite group are clearly distinguishable; in the case of C_3A a fine structure is also visible

Surfaces of rough structure may also be prepared for electronmicroscopical investigation. With these specimens, however, only a low magnification can be used. In this case the fracture surface of the clinker is shadowed directly and covered with a carbon film. The carbon film is reinforced with a 2% collodion solution. The reinforced film is scratched with a thin needle and cut into pieces along the scratches. Each piece should be approximately the same size as the microgrid. The specimen is put into a 1 : 1 hydrochloric acid solution. After 24 hours the hydrochloric acid is sucked off and hydrofluoric acid (diluted 15 : 2) is poured onto the specimen. The carbon film is detached from the surface of the clinker in 1–2 hours. It is put on a microgrid and the collodion dissolved from it with acetone.

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* Brunner, P. (1965): Eine Methode zur elektronenoptischen Abbildung von polierten Zementklinkeroberflächen. *Zement–Kalk–Gips 18*, pp. 247–52.

I.13.2.2. Quantitative microscopic analysis of clinker

The aim of this investigation is to determine the relative quantities of the more important mineral components of the sample. The samples to be investigated are prepared by selecting 2.0–2.5 mm pieces from the clinker-crushing by sieving. These selected grains are embedded in artificial resin as described previously. (One artificial resin disc contains several grains; the grains, however, are placed separately in the resin.) It is advisable to grind plano-parallel end faces of the resin disc. Thus, when moving the specimen under the microscope, the focus need not be changed.

There is more than one possibility for the determination of the ratio by volume of the minerals. The most frequently recommended method uses the integrating desk (Fig. I.13.13). This is an instrument which can be mounted onto the microscope stage, and which serves for the summation of distances. It consists of a small desk which can be moved with micrometer screws (micrometer or measuring spindles). The sample to be investigated is fastened to this desk. The distances are measured with the aid of six measuring screws. Different measuring screws are used for different crystal types. With these the specimen can be moved only backwards and forwards. Special screws serve to shift the specimen to the right or to the left.

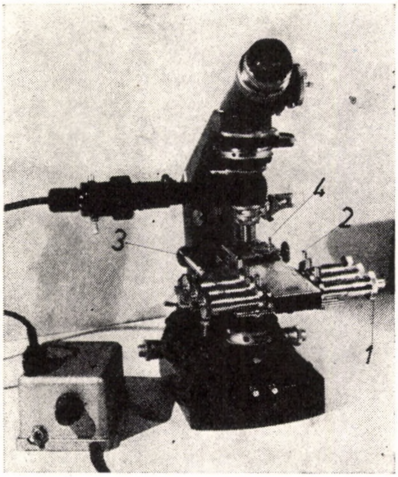

Fig. I.13.13 Polarization microscope with integrating desk
1 measuring screw, *2* clamp screw, *3* screw to shift the object sideways, *4* object clamp

A magnification greater than 600 is used. The method of measurement can be seen in Fig. I.13.14. The Figure shows the surface of a clinker grain, the dotted line denoting the area to be investigated. The upper left part of the Figure shows the view field of the microscope together with the cross hairs. If the measuring screws are rotated, the grain is moved in the direction indicated by the arrow. At the beginning of the measurement the intersection of the cross hairs is placed at the boundary of the crystal (alite in the picture) which is on the edge of the area to be measured (*A*). For the next step, the clamps are loosened, the measuring spindles brought to the 0.00 position, and the clamps fixed again. The measuring spindles to be used for the various crystal types are decided on. If one crystal type is predominant (e.g. alite in the case of the Figure) two measuring spindles are assigned for it. One measuring spindle is reserved for the 'empty' places filled with resin or polishing material. Now the actual measurement begins. The measuring screw (in our case the screw intended to measure the alite) is rotated to push the specimen until the intersection of the cross hairs is shifted from point *A* to point *A*'. In this way the length of the crystal along the distance *AA*' is obtained. The measurement is continued by rotating the screw which has been reserved for the mineral component adjacent to the component to be measured (or to an 'empty' place). Thus the measurement is carried out successively by rotating the corresponding spindles. The distances measured with the same spindle are integrated. If the lower boundary of the area *B* is reached the clamps are loosened. The desk then goes back automatically to its starting position. (The position of the measuring spindle on the screws does not change during this procedure.) The clamps are fastened and the desk, with the specimen on it, moved 0.5 mm sideways. The intersection of the cross hairs moves from point *A* to point *C*. The measurement is now carried out along the line *CD*. This procedure is continued until the whole area has been measured.

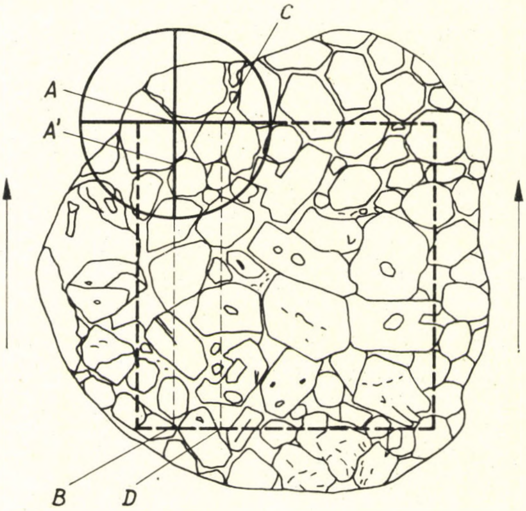

Fig. I.13.14 Schematic diagram for evaluation with the integrating desk

One obtains a correct picture of the percentage by volume of the clinker components if at least 10–20 grains are investigated. This means the measurement of a total distance of 100 mm. The relative volume of each mineral is given by the ratio of its length to the measured total length. The distances belonging to the 'empty' places are not included in the measured total length.

If the ratios by volume of the minerals are known, the ratios by weight can also be determined if the densities of the components are known. Some density values are:

C_3S	3.20 g cm^{-3}	C_3A	3.04 g cm^{-3}
C_2S	3.27 g cm^{-3}	C_4AF	3.77 g cm^{-3}

Since, in the case of a normal composition, the density values of the minerals present in the highest percentage do not differ greatly from each other, the ratios by weight are nearly equal to those by volume.

Another method of determining the ratio by volume of the minerals is the method of point counting. With the third method microphotographs of polished and etched samples are enlarged, and the areas of the various crystals (alite, belite, etc.) are measured with a planimeter.

1.13.2.3. Production of tricalcium aluminate and the study of its hydration in the presence of gypsum

The processes taking place during the setting and hardening of cement are not yet fully understood, and they are still undergoing scientific investigation. The investigations carried out with pure clinker minerals have yielded fundamental results. In the following section, only the hydration of tricalcium aluminate ($Ca_3Al_2O_6$, in brief notation C_3A) is discussed. For the investigations minerals produced in the laboratory are used, and in connection with this the laboratory production of other clinker minerals too is described.

(1) In order to obtain tricalcium aluminate adequate quantities of $CaCO_3$ and Al_2O_3 are mixed in the ratio $3CaO : Al_2O_3$. This mixture is heated to about 1 500° C, and during this process CaO is formed from $CaCO_3$. Both CaO and Al_2O_3 are in the solid phase at this temperature. The reaction in the solid state is more efficient if large surfaces of the reactants are in close contact, and therefore both $CaCO_3$ and Al_2O_3 are used in the form of fine powders; the powders are mixed and small cylinders 1–1.5 cm in diameter are pressed from the mixture at a pressure of a few hundred kp/cm^2. The heating of the samples is best carried out in an electric silite-resistor furnace. The pressed cylinders are either suspended from a platinum wire or placed on a platinum plate (the cylinders must not touch the furnace walls). The temperature in the furnace is measured either with a thermocouple or with an optical pyrometer. The temperature must not be allowed to rise above 1 500° C since the mixture melts incongruently at 1 535° C.

In order to promote and accelerate the reactions in the solid state the surfaces of the reacting materials in contact must be renewed from time to time. This is done by removing the cylinders from the furnace after heating for 3–4 hours, cooling down and pulverizing them again in an agate mortar. After this, cylinders are again pressed from the powder and are heated anew for 3–4 hours. If the pulverized substance is fine enough the reaction is complete after repeating the above process four times. The residual CaO can be dissolved with a mixture of acetoacetic ester and isobutanol. The dissolved quantity may be determined by titration.

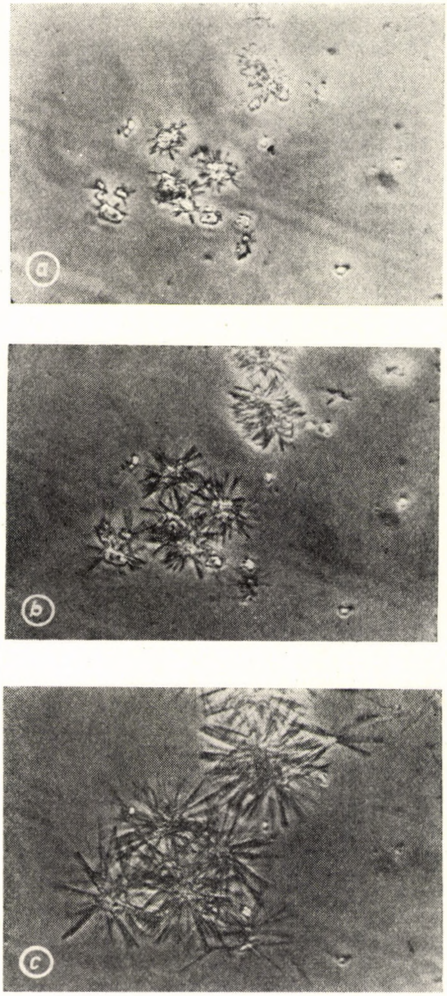

Fig. I.13.15 Growth of ettringite crystals after a 5 : 1 mixture of C_3A and gypsum has been brought into contact with water
(a) after about 0.5 min; (b) after 4 min; (c) after 10 min (M: 450×)

Tricalcium silicate (C_3S) and dicalcium silicate (C_2S) are similarly produced. As starting material, a mixture of $CaCO_3$ precipitates and finely crushed (milled) high purity sand is used; C_3S is heated to 1 600° C and C_2S to 1 500° C. The β-modification of C_2S can be produced only if the heated sample is quenched from approximately 1 000° C to room temperature. The stabilization of the β-modification is promoted by certain additives, e.g. 0.5% B_2O_3.

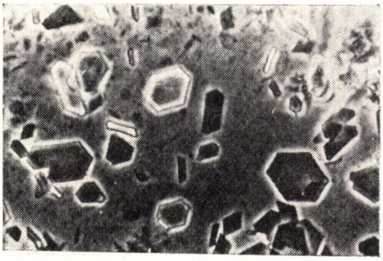

Fig. I.13.16 Hexagonal tricalcium aluminate monosulphate hydrate crystal plates
(M: ca. 450×)

(2) Crystallization processes taking place in the system $Ca_3Al_2O_6$–$CaSO_4$–H_2O.—Tricalcium aluminate, pulverized in an agate mortar, and gypsum are very carefully mixed in a 5 : 1 ratio. A thin, sparsely cohesive layer is sprinkled through a sieve onto a microscope slide (the average grain diameter should be less than 60 μm), and the layer is covered with a coverslip. The edges of the coverslip are glued to the slide with paraffin (or a mixture of wax and resin) so that only two diagonally opposite corners are left free. A drop of water is dripped onto one free corner and allowed to get between the slide and the coverslip. The surplus water is wiped off and the free corner is also glued to the slide. The specimen is investigated in a phase contrast microscope.

The following observations can be made: (a) At some places (where the gypsum concentration is large enough) hexagonal whiskers develop, starting from the grains, in radial arrangement. The whiskers are tricalcium aluminate trisulphate hydrate crystals ($Ca_3Al_2O_6 \cdot 3CaSO_4 \cdot 31H_2O$). A natural mineral of this composition, ettringite, is also known (Fig. I.13.15). With the concentrations given above, the whiskers appear within minutes. (b) At places where the $CaSO_4$ concentration is lower the formation of tricalcium aluminate monosulphate hydrate crystals ($Ca_3Al_2O_6 \cdot CaSO_4 \cdot 12H_2O$) can be observed. These crystals grow in the form of hexagonal plates (see Fig. I.13.16), and are clearly visible after 1–2 hours. (c) Tricalcium aluminate hexahydrate crystals ($Ca_3Al_2O_6 \cdot 6H_2O$), crystallizing in the cubic system, also grow from the solution (Fig. I.13.17). They can be observed on some parts of the specimen almost simultaneously with the appearance of the monosulphate hydrate.

The ratio of the above crystal types depends upon the tricalcium aluminate : gypsum ratio; this ratio, however, may change in time. The increase in the proportion of gypsum, for example, favours the formation of tricalcium aluminate trisulphate hydrate. If relatively little gypsum is present, the tricalcium aluminate trisulphate hydrate crystals formed in the first few minutes may later transform into tricalcium aluminate monosulphate hydrate.

Fig. I.13.17 Electronmicrogram of ettringite and cubic tricalcium aluminate hydrate crystals formed by the hydration of a C_3A and gypsum mixture (M: 2750×)

I. 13.3. Rhythmical Crystallization

I.13.3.1. Rhythmical crystallization of salol

The phenomenon of rhythmical crystallization may readily be demonstrated with salol. For this purpose a warmed ruling pen is filled with salol melt, and a line is drawn with it on a slightly matted glass plate. The glass plate is warmed and then allowed to cool to room temperature. Since salol can easily be undercooled, the melt on the glass begins to crystallize only when one point of the line is lightly touched with a needle previously contaminated with salol crystals. However, the crystallization which has started from this point will soon stop; the salol melt is withdrawn from the new crystals, and no crystal is formed on one section of the plate. At some distance, however, crystallization commences again (Fig. I.13.18).

I.13.3.2. Liesegang's rings

A few days before starting the experiment a 5% gelatine solution is prepared. On the day the experiment is begun, a mixture is prepared from the warmed gelatine solution (100 ml) and 5% potassium dichromate and citric acid solutions (2 ml and 1 ml, respectively). The mixture is poured out onto a glass plate to form a layer about 1 mm thick, and left to cool until the gelatine sets. A drop of 20% silver nitrate solution is placed at the centre of the layer. A few hours later concentric rings of fine-grained pre-

Fig. I.13.18 Rhythmical crystallization of salol on a mat glass plate
(M: 25×)

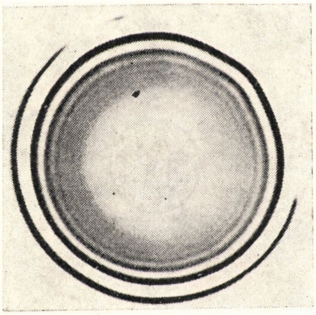

Fig. I.13.19 Liesegang's rings

cipitated silver bichromate will be obtained (Fig. I.13.19). It is advisable to carry out the experiment in a dark and cool room. Several trials may be necessary to get good results.

PART TWO

TECHNIQUES OF CRYSTAL GROWTH

The term good quality is quite frequently applied to the growth of large single crystals. A crystal may be considered good if it has no veils, and is clear with no inclusions, bubbles, cracks, constitutional stresses, twinned growth structures or any other growth faults; the crystal surfaces must be planar and smooth, without steps, and so on. Besides these general requirements there are also some special demands connected with the purpose of growing crystals. Accordingly, the crystals are semiconductors, piezoelectric crystals, or crystals with special mechanical, optical, electrical or electronoptical properties. The most important physical characteristics of a good quality crystal must also meet certain prescribed standards.

II.1. CRYSTAL GROWTH FROM SOLUTIONS

When the growth of crystals from solutions is considered, one usually thinks of processes where the material to be crystallized dissolves quite well in well-known solvents (notably in water) under ordinary conditions (at atmospheric pressure, temperatures close to room temperature, etc.). The most frequently used growth methods also refer to normal conditions.

Special methods of crystal growth from solution may be summarized as follows:

crystallization from melt solution (the solvent is for example the melt of some metal);

growth of crystals by electrolysis;

formation of crystals by diffusion and chemical reaction (the reacting components are brought into contact by diffusion in the solvent);

crystal growth at very high pressures (one type of this is hydrothermal synthesis).

In the following, the more simple cases of the growth of crystals from solution will be considered first. After this, growth from melt solution and hydrothermal synthesis, important and much used in practice, will be reviewed. The theoretically interesting but from the point of view of practice less important electrolytic and chemical growth methods will not be discussed here. (For electrolytic growth see I.12.)

Throughout this chapter the following abbreviations will be used:

KNT Potassium sodium tartrate (Seignette or Rochelle salt), $KNaC_4H_4O_6 \cdot 4H_2O$

ADP Ammonium dihydrogen phosphate, $NH_4H_2PO_4$
KDP Potassium dihydrogen phosphate, KH_2PO_4
EDT Ethylenediamine tartrate, $C_2H_4(NH_2)_2C_4H_6O_6$

(1) *Basic principles.* The growth of large, good-quality crystals from solutions usually takes place in two stages (periods). First a crystal nucleus must be formed (first stage), and this then grows in a new solution (sometimes again in more stages) to the desired dimensions. Both the formation of the nucleus and its further growth are based on the relation between solubility and temperature (Fig. II.1.1). The nuclei are obtained from unstable solutions, viz. from highly supersaturated solutions. The probability of spontaneous nucleation in this case is rather high. As a result of nucleation the concentration of the solution decreases. It is advisable to start with a solution which becomes metastable after the formation of a small number of nuclei. In the metastable state the already developed nuclei start growing without the formation of new ones. The best nuclei are selected and used in their original form, or suitable pieces are cleaved from them to grow the desired crystal. For the further growth of the seeds a metastable solution is used.

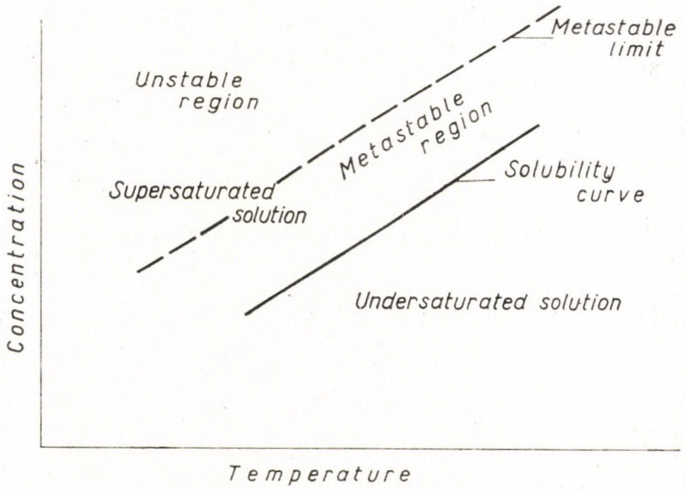

Fig. II.1.1 Temperature versus solubility

(2) *Production and preservation of supersaturation.* For the nucleation process and the growth of the formed nuclei one method of preparing a supersaturated solution and of preserving the required supersaturation is *the evaporation of the solvent* at constant temperature. The advantage of this method is the simple regulation of evaporation (e.g. by changing the number and dimensions of the vents on the lid of the crystallization vessel); thus, the growth rate too is regulated. In this case it is experimentally favourable to maintain a constant temperature. It is disadvantageous to

grow the crystal at temperatures considerably above room temperature, because if one takes out the produced crystal, sometimes measuring 10–20 cm, and the cooling down is rapid and irregular, stresses and cracks may develop in it. The method of evaporation should be used in preference to any other method when the solubility changes only slightly with temperature, or when the solubility increases with decreasing temperature.

In the cases when the solubility decreases rather quickly with decreasing temperature, the supersaturation can be ensured by a *constant decrease of temperature*. In most cases the initial temperature is above room temperature, and growth is finished when room temperature is attained. In this case the grown crystals are not subjected to any thermal shock when taken out of the crystallization equipment. This is certainly an advantage. The crystallization apparatus, however, is more complicated than in the case of evaporation, since the temperature must be decreased according to an exact programme.

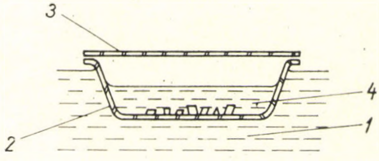

Fig. II.1.2 Production of seed crystals

1 water bath of the thermostat, *2* crystallization vessel, *3* perfectly or only partially closing lid, *4* supersaturated solution with the seed crystals

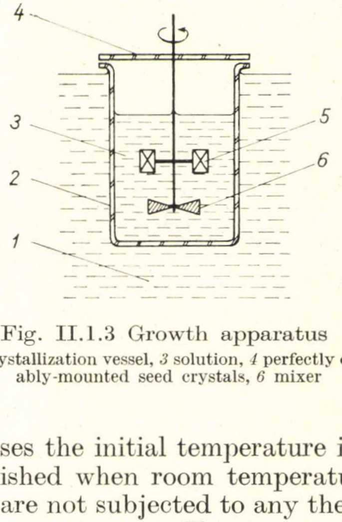

Fig. II.1.3 Growth apparatus

1 water bath of the thermostat, *2* crystallization vessel, *3* solution, *4* perfectly or only partially closing lid, *5* rotatably-mounted seed crystals, *6* mixer

The evaporation method and the methods based on the decrease of the temperature may be carried out in various ways. Figures II.1.2 and II.1.3 show only a few experimental features for general information.

The same equipment can usually be used for evaporation as well as for growing crystals by the method of decreasing the temperature. In the first case a loosely fitting lid must be applied, in the second one the lid should be tightly fitting. For the purpose of producing seeds a combination of both methods is frequently used to keep the rate of supersaturation constant. In this case the temperature is slowly decreased with a simultaneous slight evaporation.

Because of its great importance the *circulation method* is considered separately. It consists in a continuous substitution of the material precipitated from the solution (Fig. II.1.4). The equipment consists of two vessels: the crystal grows in one of them (the growth tank), while in the other one (solution make-up tank) the saturated solution is made. In the great majority of cases, when the solubility increases with temperature, the temperature of the make-up tank must be kept higher than that of the growth tank.

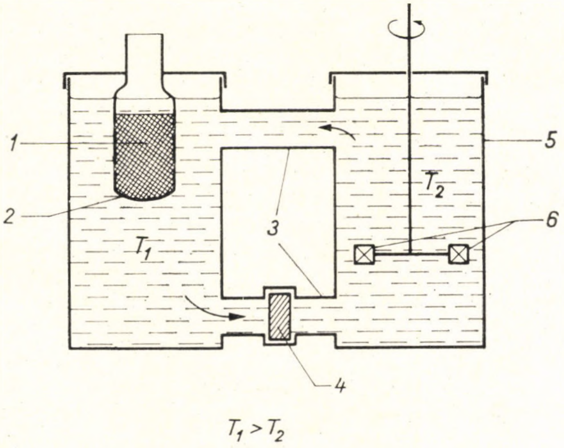

Fig. II.1.4 Circulation method

1 vessel for the solution supersaturated at temperature T_1, *2* polycrystalline material in a densely woven nylon sack, *3* connecting tubes, *4* pump, *5* growth vessel at temperature T_2, *6* growing crystals

The saturated solution made in the make-up tank is streamed over into the growth tank where owing to cooling it becomes supersaturated, and a part of the excess dissolved material precipitates on the seeds. The diluted solution is then streamed back into the make-up tank and is saturated again at the higher temperature. The circulation method has the advantage that the growth equipment operates at a constant temperature, and the possibility of continuous material substitution results in the economical production of large, good-quality single crystals.

(3) *Solvent, additives, purity.* Experience has shown that good crystal growth is obtained in the case of high solubility (at least a few mole %) and if there is a certain structural similarity between the solvent and the dissolved material. Thus the extremely good crystallization of alum from its aqueous solution is readily explained.

The growth rate increases with increasing supersaturation; consequently, it is advantageous to remain within the metastable zone at the highest possible supersaturation for which the crystal growth may still be regarded as perfect. The growth rate above which the crystal grows with defects is called the critical growth rate.

The critical growth rate increases with the increase of temperature, which means that at higher temperatures crystals of the same quality can be grown faster. The rate of supersaturation is usually adjusted so that at room temperature the growth rate does not exceed 0.1 cm/day. Even at this seemingly low value several hundred atomic layers per second become deposited on the new crystal.

The solubility, the metastable zone width and the critical growth rate may be increased by applying additives to the solution. For example several crystalline silver salts can be grown quite satisfactorily from their aqueous solutions if the quantity of dissolved material is increased as a result of complex formation following the addition of 10% ammonia solution ($NH_3 \cdot aq.$) to the solution. $Li_2SO_4 \cdot H_2O$ crystals grow strain-free if the pH of the solution is between 6.5 and 6.7. It is almost impossible to grow perfectly transparent sodium chloride crystals from pure aqueous solution; in the presence of for example 0.01 mole % Pb, however, large transparent crystals several centimeters long will grow.

TABLE II.I

Metal ions favourable in small quantities for crystal growth

Compound	Additives
$KBrO_3$	Pb
KCl	
KI	
KNO_3	
$LiCl \cdot H_2O$	Cd, Mn
$NaCl$	Pb, Mn
$NaNO_2$	Ca
$(NH_4)_2C_2O_4 \cdot H_2O$	Cu
NH_4Cl	Zr, Cd, Mn
$NH_4H_2PO_4$	Fe, Cr, Al
NH_4PO_3	Cd, Ca
$RbCl$	Pb

The presence of some metal ions in very small quantities (sometimes only in traces) favourably influences the growth of certain compounds from aqueous solutions (Table II.I). Some additives are known (e.g. glycerine, sugar) which exert a favourable effect on crystal growth, probably by changing the viscosity and surface tension of the solution, etc. However, it must be considered that the additives may change not only the conditions of crystal growth but the form, and the physical and chemical properties of the crystal as well. NaCl, for instance, in the presence of some organic compounds (e.g. carbamide, phenol, aniline) grows with octahedral faces. The additives compiled in Table II.I also change the form of the crystal concerned, usually by shifting it in some equidimensional direction. If an aqueous solution of $NH_4H_2PO_4$ is doped with 0.1% sulphuric acid the electrical conductivity of a crystal grown from this solution is higher by one order of magnitude than that of a crystal grown from the additive-free solution.

Naturally, crystal growth and the quality of the grown crystal may be influenced by impurities already present in the solution. The effect may be favourable in some cases, unfavourable in others. Since the exact detection of these impurities is a rather tiresome task, and in the case of traces it is difficult if not impossible, it is advisable to start with solutions which are as pure as possible and then apply the additives to the purified solution. Thus one can influence the circumstances of growth and the quality of the grown crystal in the required way.

(4) *Seed crystals.* Good quality crystals grow only from good seeds. A distinction must be made between growth flaws and mechanical defects in the seeds. Veils, inclusions, twinning, misorientation, etc. are growth defects, whereas mechanical defects are caused by cracks, notching (chipping), improper sawing, or polishing, etc. The growth defects may spread out during the further growing of the seed and may even multiply, consequently faulty, defective seeds must never be used. The mechanical defects, on the other hand, are usually harmless and may facilitate the deposition of new layers. The seeds should be carefully investigated before use (if necessary in polarized light). Those parts containing flaws must be sawn or broken off. In some cases only a properly sawn off part of the seed is used and not the whole seed.

(5) *Other factors.* The supersaturated solution should be made from a solution which is saturated at a given temperature. For this purpose grains of the material to be dissolved are put into a bag made of densely woven nylon, and immersed in the solvent. The solution is kept at a constant temperature for several hours, sometimes for 1–2 days. During this period continuous agitation is necessary. The saturation is easily controlled by measuring the density of the solution either with an areometer or by dropping a piece of crystal into the solution and measuring its weight. After saturation is reached the bag containing the superfluous material is removed from the solution. The still undissolved crystals and other solid particles must be carefully removed from the liquid, since these may become unwanted, spontaneous seeds (false seeds, parasite seeds, parasite crystals) disturbing the growth of the seeds adhering to them, or consuming part of the dissolved material and producing defective growth. In order to remove these unwanted pieces, the temperature of the solution is increased a few degrees above its original temperature, and the solution is filtered several times through a densely woven nylon filter.

The vessels used for the preparation of the solutions, and the tanks used for crystal growth are made of glass, plastic or chemically inert metals. The rods, frames and plates which serve to support the seed crystals are also made of these materials. Silk, metal or plastic threads are used to suspend the seeds (Fig. II.1.5).

Care must be taken lest the growth solution should become supersaturated before the required time. In order to avoid this the seeds should be heated up together with their supporting construction to the saturation temperature or to a few tenths of a degree above it before placing them in the solution. It is also suggested that the solution be somewhat below the saturation point when the growth equipment is assembled. This can easily be done either by raising the temperature slightly, or by adding a few drops of the solvent to the solution. Under these circumstances the seeds placed in the solution first dissolve slightly, and start growing only later when the solution has become supersaturated either by a decrease in temperature or by evaporation. The dissolution of the original surfaces of the seed creates suitable initial conditions for the growth, and favourably influences the quality of the grown crystal too.

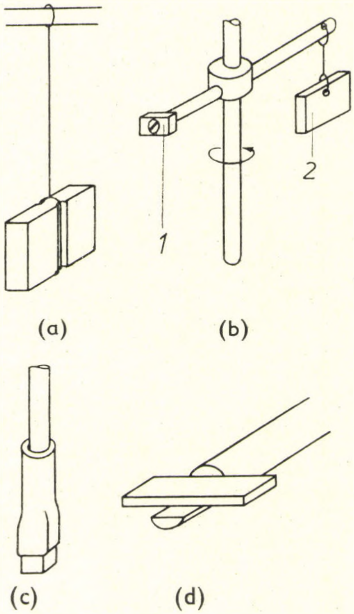

Fig. II.1.5 Fixing of seed crystals

(a) suspended by a silk, plastic or metal thread fixed to a plexi rod; (b) fixed to a rotatable plastic support with the plastic screw *1* or the metal wire *2*; (c) placed in a rubber tube; (d) glued (e.g. with lucite dissolved in chloroform) to a plastic rod

Growth often takes days, sometimes weeks. During this period much care must be taken to stabilize the temperature or to decrease it in a slow controlled way. If high standard crystal growth is desired a thermostat is used whose temperature can be stabilized within a few hundredths of a degree. If the growth proceeds by a decrease of the temperature, the rate of decrease should be a few tenths of a degree per day. The growth equipment must be protected by proper heat insulation from any abrupt temperature change occurring in its surroundings.

An important factor is the continuous agitation of the solution; this enhances the exchange of the depleted solution at the growth surface for the supersaturated solution from more distant regions. A small increase in the rate of agitation speeds up the growth process without producing defective growth. The agitation is most properly carried out with the aid of rotating shafts, or by revolving the seed crystal. If the viscosity of the solution is almost equal to the viscosity of water the suggested number of revolutions in a jar with a diameter of 30 cm is 20–30 revolutions per minute. In the case of strongly viscous liquids 5–10 revolutions per minute are sufficient. It is advisable to alter the direction of revolution every 2–5 minutes. Sudden changes of direction, however, must be avoided, since spontaneous nuclei (parasite seeds) may be produced as a result of unwanted turbulence. Similarly, to avoid any nucleation due to turbulence, care should be taken that even at the end of the growth process a distance of a few centimeters be maintained between the rotating shaft and the jar wall, i.e. between the moving and fixed parts of the equipment.

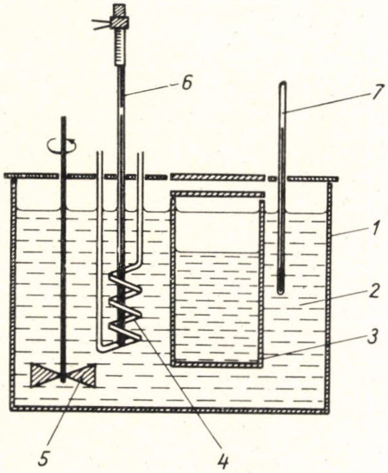

Fig. II.1.6 Home-made thermostat

1 glass or metal tank (10–20 l), *2* water bath, *3* crystallization tank (3 l) containing the solution, *4* heating resistor, *5* mixer, *6* contact thermometer, *7* control thermometer

As a result of local cooling (especially on the surface of the solution), the danger of the formation of spontaneous nuclei exists during the whole growth process. Their presence is troublesome because, as has already been pointed out, the spontaneously developed seeds may fall onto and adhere to the growing crystal thereby causing defective growth. In order to avoid this protecting plates or a fine net are placed above the growing crystals. Similarly, the heating can be adjusted so that the surface of the solution and the bottom of the crystallization tank are slightly warmed to dissolve parasite seeds on the surface or the bottom.

If the crystal growth is terminated above room temperature care must be taken in taking out the grown crystal from the growth apparatus. The best method is to replace the solution by some other liquid, e.g. chloroform, which is at the same temperature as the solution, immiscible with it, and does not dissolve the crystal. After this the system is slowly cooled to room temperature.

(6) *Temperature regulation.* Commercially available thermostats may be used for crystal growth. However, since temperature regulation is important, some of its features are discussed. Figure II.1.6 shows a home-made thermostat. The crystallization tank is separated from the water bath. Frequently, however, the crystallization tank is immersed directly in the water bath. Temperature regulation is carried out by using bimetal thermometers, thermistors, resistance thermometers or mercury contact thermometers. These latter have proved to be most reliable (see the Figure). Mercury contact thermometers work more reliably with currents of lower intensity. Therefore, the current must never be interrupted directly by the mercury contact, and instead a relay should be inserted into the thermometer circuit. The advantage of a thyratron or thyristor relay is obvious since these types do not contain any movable parts and thus may work without trouble over a period of weeks or even months (Fig. II.1.7). The anode voltage is supplied by the 220 V a.c. network. The anode and grid currents are fed by the battery A. If the temperature is less than desired, and thus the regulating thermometer circuit is not closed, that part of the battery which is connected to the grid circuit keeps the grid on a positive potential as related to the cathode; consequently, the anode current flows at its full intensity through the heating resistance R. If the thermometer circuit closes on the attainment of the desired temperature the potential of the grid as related to the cathode becomes negative. This in itself would not close the anode current, but since the anode voltage is supplied by an a.c. source, and the anode current breaks off anyway in each half period and does not start again after B begins to operate, this results in the permanent disconnection of the heating filament R. If the contact of the thermometer breaks off

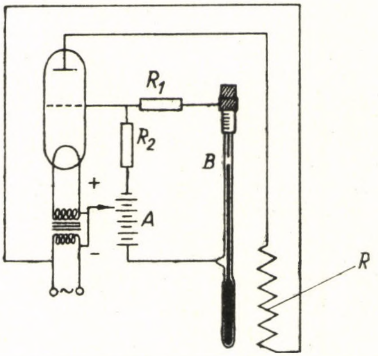

Fig. II.1.7 Thyratron relay

again on cooling the anode current of the thyratron begins to flow again thereby heating the filament. R_1 and R_2 are large resistors which decrease the grid current and also the current flowing through the thermometer to small values. With this system the temperature can be kept constant within a few hundredths of a degree.

The thermostat is frequently heated by two heaters, one of which, with a high heat capacity, is placed close to the mixer. This itself almost makes up for the natural heat loss of the thermostat. The other heater of low heat capacity is placed close to the regulating thermometer controlling the operation of this latter. If the crystallization is carried out by temperature decrease the metal filament of the control thermometer must be lowered either gradually or continuously. Thus the contact becomes closed at lower and lower temperatures. The continuous setting is achieved by a motor via a proper transmission.

II.1.1. Production of Seed Crystals

II.1.1.1. Production of $KNaC_4H_4O_6 \cdot 4H_2O$ (KNT) seed crystals

KNT belongs crystallographically to the rhombotetrahedral class of the orthorhombic system; its melting point is at about 42° C. The crystal dissolves quite well in water, its solubility increasing very rapidly with temperature (Fig. II.1.8). It is strongly hygroscopic, but loses its crystal water at low atmospheric humidity. The crystal is best stored in places where the relative humidity is kept at 50–70%. Its heat expansion is about one order of magnitude larger in the direction of axis c ($\approx 6 \times 10^{-5}$/degree) than in the other two directions ($\approx 7.8 \times 10^{-6}$/degree). This explains its great sensitivity to temperature changes; the crystals may crack from the heat generated by the human hand, and thus it is advisable to hold them with a pair of forceps wrapped in rubber. Seignette salt crystals are of practical value because of their piezoelectric properties, and are used as energy transformers in acoustic devices (e.g. as pick-ups).

(a) *Evaporation procedure.* About 500 ml solution saturated at room temperature is prepared and filtered through a paper filter or a densely woven plastic filter into a photographic tank. Since the solution is rather viscous at room temperature it is advisable to filter at a few degrees higher than this. In a few minutes a large number of crystals will be formed in the uncovered tank. If the solution is filtered several times one has to wait some time for the precipitation to begin, and in this case only a few crystals will be formed. The removal of the seed crystals, their drying, and their growth should be carried out as described in the following section.

(b) *The production of seed crystals by temperature decrease.* A solution, which is saturated at 5–7° C above room temperature, is prepared from about 200 ml distilled water. It is filtered twice at a temperature of 1–2° C above the saturation temperature, and left to cool in a covered tank placed in a water bath of the same temperature. The solution soon becomes unstable; a large number of pure rhombohemihedric structures (Fig. II.1.9a and c) and single crystals (Fig. II.1.9b) precipitate at the bottom of the tank. The shapes denoted by (a) and (b) are the most suitable ones for growth. As the size and number of the precipitated seeds increase they readily unite. In order to avoid this, the solution is poured off, the crystals are washed with distilled water, and then dried on filter paper. The larger, apparently faultless crystals are selected as seeds, and immersed as described above in a solution which is saturated at 28–30° C. This procedure can be repeated until large crystals measuring 1 cm are obtained.

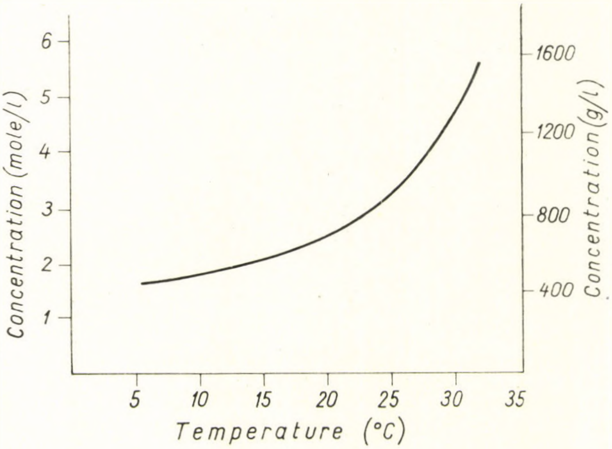

Fig. II.1.8 Temperature versus solubility diagram of KNT

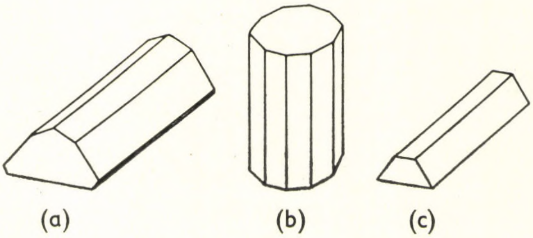

Fig. II.1.9 KNT seed crystal forms

II.1.1.2. Production of $KAl(SO_4)_2 \cdot 12H_2O$ seed crystals

$KAl(SO_4)_2 \cdot 12H_2O$ (alum) crystallizes in the cubic system, and dissolves quite well in water.

(a) *Evaporation method.* 500 ml solution saturated at room temperature is prepared from reagent grade alum, and the solution is filtered as described in the previous experiment, and poured into a photographic dish. Crystals clearly visible to the naked eye are formed within 25–30 min; these grow in a few hours to a size of 1–2 mm. At this stage the solution is filtered, the best octahedral samples are selected, placed in a new solution which has previously been filtered at least twice, and allowed to grow to the desired dimensions. In order to increase the rate of evaporation, dishes with large surfaces are used. The depth of the liquid should be about 6–8 mm.

(b) *Method of temperature decrease.* 500 ml solution saturated at 35° C is prepared, filtered several times, and its temperature decreased within an hour to 25° C. The crystals precipitated from the solution are selected according to method (a). If this process is repeated two or three times the selected crystals can be grown to the desired dimensions.

The crystal form can be greatly influenced by impurities (e.g. dyes). If 0.15 g brilliant blue is added to 500 ml saturated solution, instead of the octahedral form, the hexahedral becomes dominant. In this case crystals are frequently obtained on the hexahedral tips of which traces of the (111) planes can still be detected. A similar result is produced by adding 0.25 g Bismarck brown to the saturated solution.

II.1.1.3. Production of KCl seeds

(a) *Production of seeds by evaporation.* 200 ml distilled water made slightly acidic with hydrochloric acid (pH 4–5) is used as solvent; 500–1000 ppm lead in the form of $Pb(NO_3)_2$ or $PbCl_2$ is added to the solution which is then

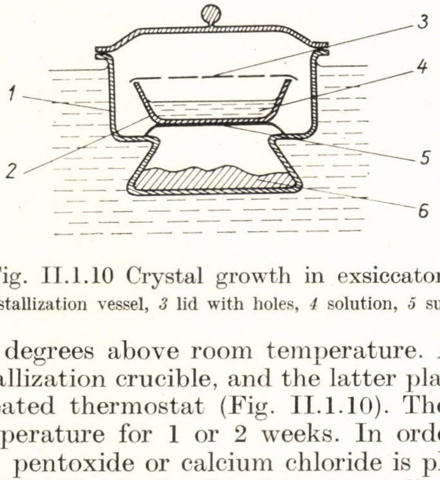

Fig. II.1.10 Crystal growth in exsiccator

1 exsiccator, *2* crystallization vessel, *3* lid with holes, *4* solution, *5* support, *6* absorbent

saturated at a few degrees above room temperature. After filtration it is poured into a crystallization crucible, and the latter placed in an exsiccator in a suitably preheated thermostat (Fig. II.1.10). The exsiccator is kept at the preset temperature for 1 or 2 weeks. In order to remove water vapour phosphorus pentoxide or calcium chloride is placed at the bottom of the exsiccator. The holes in the lid of the crystallization tank must be so adjusted that the rate of evaporation of water does not exceed 0.2 g/day. A few holes of 2–3 mm diameter satisfy this requirement. The solution is poured off from the grown seeds, and these are dried on filter paper. The best crystals are selected, and allowed to grow until they measure 0.8–1.0 cm. Because of the lead impurity the (100) faces grow faster than the (111) ones. As a result, instead of the hexahedral form usually obtained in pure solutions, the seeds grow in hexoctahedral or octahedral form. When the seeds are selected, preference should be given to crystals with (100) planes.

(b) *Production of seeds by temperature decrease.* 200 ml of the above solution, saturated at 28° C, is filtered into a crystallization tank of 300 ml volume. The latter is placed in a thermostat also set to 28° C (or a few tenths of a degree higher). The tank is covered, and its temperature decreased in 1–2 days to room temperature. If the temperature fluctuation of the laboratory is not more than 1–2 degrees it is quite satisfactory to put the crystallization tank into a 28° C water bath and then let it cool down. The suitable seeds are selected from among the grown crystals, and are grown to large crystals in the described way.

II.1.1.4. Production of $NH_4H_2PO_4$ (ADP) seeds

ADP crystallizes in the scalenohedral class of the tetragonal system (Fig. II.1.11). The *a* and *b* axes are normal to the side faces of the prism, and the *c* axis intersects the apices of the two pyramids. The density of the crystal is 1.804 g/cm^3 at room temperature. Its solubility (L_t; g/l) in distilled water in the temperature range between 20° C and 50° C can be expressed by the formula

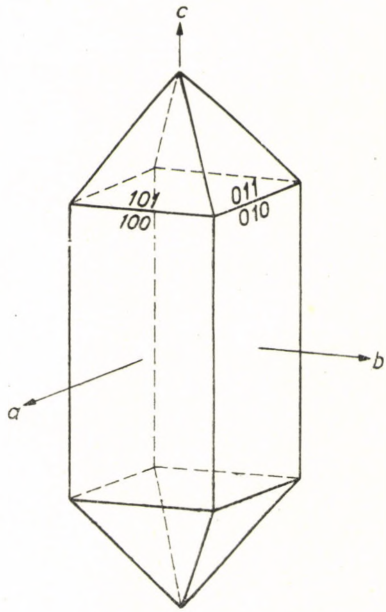

Fig. II.1.11 ADP crystal form

$$L_t = \alpha + \beta t$$

where *t* denotes the temperature in degres centigrade, and $\alpha = 180$ g/liter, $\beta = 4.55$ g/liter. When the crystals are stored it must be kept in mind that the crystal surfaces dissolve at above 90% relative humidity. The crystals are of practical value due to their piezoelectric properties, and they are used mainly to emit and receive underwater signals (sonar).

The seeds are usually produced by evaporation between 30° and 50° C from a supersaturated solution which is filtered several times. The pH of the saturated solution is 3.7. The cross-section normal to the *c* axis of the seeds grown by this method is usually disproportionately small. Addition of either NH_3 or $(NH_4)_2HPO_4$ to the solution increases its pH to 5 with the result that the rate of growth in the direction normal to the *c* axis is increased. The seeds are usually grown in several stages. Seeds about 5–8 mm long are grown first in a solution of pH 3.7, and then these seeds are grown in a solution of pH 5.0. In order to grow large single crystals, sections normal to the *c* axis are cut from crystals which already have a cross-section of several cm^2, and these sections are used as seeds.

II.1.1.5. Production of $C_2H_4(NH_2)_2C_4H_6O_6$ (EDT) seeds

The colourless EDT salt dissolves quite well in water. Its saturated solution is slightly acidic (pH 6.1). Near room temperature the compound has an anhydrous and also a monohydrous phase. The former is stable above 43° C, the latter below 40.6° C. Both phases may exist together (mixed phase) in the temperature range between 40.6° C and 43.0° C. The anhydrous phase is valuable technically because of its piezoelectric properties (it can be used for frequency stabilization in place of quartz). It belongs to the monoclinic-sphenoid crystal class (Fig. II.1.12). Anhydrous EDT crystals can be crystallized only in the small temperature range between 43° C and 50° C, since below 43° C the monohydrous phase develops. Above 50° C, on the other hand, the crystals become brown in the presence of oxygen, which indicates some chemical transformation.

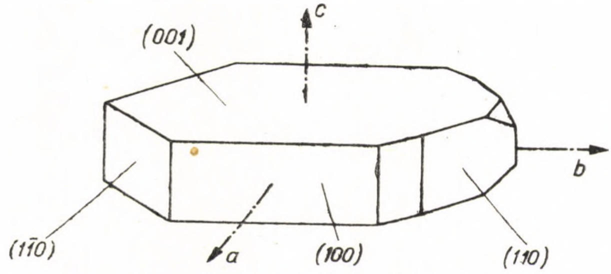

Fig. II.1.12 EDT crystal form

The seed crystals are produced in several stages, usually by the *evaporation method*. A solution saturated at 44° C is poured into a crystallization tank previously placed in a thermostat set to 44° C (the depth of the solution should be not more than 2–3 cm). The solution is covered with a lid with holes in it, the rate of evaporation being regulated by the number and dimension of the holes. A large number of small crystals measuring 1–2 mm is produced. The perfect ones are selected, and removed from the solution with a pair of rubber-covered forceps. The seeds are washed with distilled water, and placed to grow in a solution saturated at 44° C. This procedure is continued until seeds 1 cm in diameter are obtained.

If the seeds are to be produced by the method of temperature decrease one must be careful to keep the temperature of the solution below 50° C, and the growth must be terminated at 43° C. The crystals should be grown in a thermostat with a rate of temperature decrease of 1–2° C/day.

It is advisable to store the EDT crystals in a place of less than 80% relative humidity, or even better in an exsiccator above phosphorus pentoxide.

II.1.2. Crystal Growth by Evaporation

II.1.2.1. Growth of $KAl(SO_4)_2 \cdot 12H_2O$

The growth is carried out at room temperature with the apparatus shown in Fig. II.1.13. The solution, saturated at room temperature, and filtered several times at slightly above room temperature, is poured into the growth tank. In order to eliminate the harmful effects of rapid temperature changes in the surroundings, the tank is placed in a water bath, and is then covered with filter paper gripped between ring clamps. The rate of evaporation can be controlled either by changing the diameter of the opening covered with the filter paper, or by applying several sheets. The seed hangs on a silk thread. (For the production of seeds see II.1.1.2.)

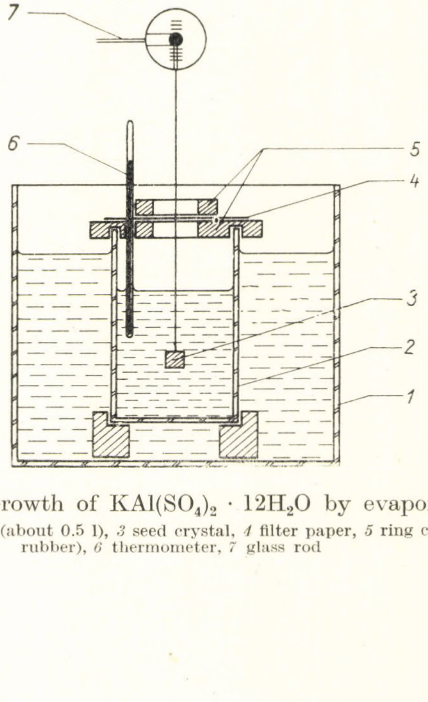

Fig. II.1.13 Growth of $KAl(SO_4)_2 \cdot 12H_2O$ by evaporation

1 tank (about 3 l), *2* growth tank (about 0.5 l), *3* seed crystal, *4* filter paper, *5* ring clamps (made e.g. of hard rubber), *6* thermometer, *7* glass rod

The equipment is suitable for measuring the rate of growth if the other end of the thread is connected to a dynamometer, e.g. a 20 cm long thin glass rod with a diameter of 0.2–0.3 mm. The bending of the rod is measured with the aid of a magnifying glass. The effects of the change of the laboratory temperature on the temperature of the solution and on the rate of growth are observed.

The experiment is carried out in a more exact way by using a thermostat instead of a simple water bath. In this case one starts with a solution which is saturated at a few degrees above room temperature, and the temperature of the thermostat is set accordingly. The temperature of the filtration is also increased. The rate of growth is measured at various rates of evaporation.

II.1.2.2. Growth of $KNaC_4H_4O_6 \cdot 4H_2O$ *(KNT)*

The growth equipment is shown schematically in Fig. II.1.14. The growth tank is placed, together with the crystal support, in a thermostat set to 28.5° C. A solution saturated at 28° C, and previously filtered at 33° C at least three times, is poured into the tank.

When the assembly has reached 28.5° C, the seed stored in another thermostat at about 28° C, is placed on the support by means of a pair of forceps covered with rubber. (For the preparation of the seed see experiment II.1.1.1.) After this, the protecting cover, which has also been stored at 28° C, is placed above the crystal. This cover protects the growing crystal from parasite crystals which may grow on the surface of the solution, and which on sinking may adhere to the crystal. Finally, the growth tank is covered with a lid. Vapour from the solution condenses on the colder lid, and the

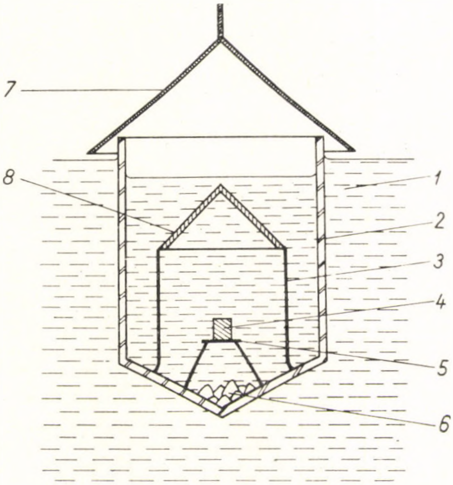

Fig. II.1.14 Growth of KNT by evaporation

1 water bath of the thermostat, *2* growth tank (1–2 l), *3* solution, *4* seed crystal, *5* small table, *6* parasite crystals, *7* funnel-shaped lid (fixed to the rim of the tank by three arms), *8* protecting cover supported by legs drops flow into the water of the thermostat through the slit between the lid and the rim of the tank. The parasite crystals which sink collect close to the pointed tip of the tank bottom where they can be dissolved by heating the bottom. With the above method crystals measuring 8–10 cm can be grown from a 1 cm seed within 10–15 days.

Seignette salt crystals are very sensitive to temperature changes, and the grown crystals easily crack if they are taken out of the solution at 28° C. Consequently, it is advisable to replace the solution first by some other liquid immiscible with it (e.g. chloroform) of the same temperature, and to let the crystals cool down in this liquid in 1 or 2 hours.

II.1.2.3. Growth of KCl

The same assembly used for growing the seed crystals is employed (see experiment II.1.1.3 and Fig. II.1.10). The crystallization tank of the assembly, however, must be properly prepared. The solution is prepared in a way similar to that used for growing the seeds. Figure II.1.15 shows the plastic frame supporting the seeds, and the cover protecting them against parasite seeds. Any premature supersaturation must be carefully avoided. For this reason the filtration as well as the storage of the growth tank and its accessories take place at about 1° C above the saturation temperature. The seeds are placed in the solution when the temperature of the growth assembly is only 0.1–0.2° C above the saturation temperature.

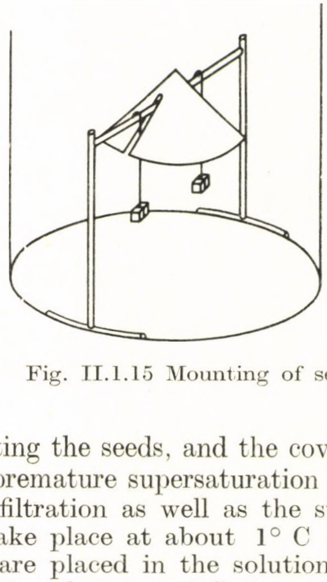

Fig. II.1.15 Mounting of seeds

II.1.3. Crystal Growth by Temperature Decrease

II.1.3.1. Growth of $KNaC_4H_4O_6 \cdot 4H_2O$ (KNT)

(a) One of the possible methods is shown in Fig. II.1.16. A solutio saturated at 35° C is warmed to 38° C and filtered (several times if necessary) into a 2–3 l container placed in a thermostat. The previously prepared seed crystals (see II.1.1.1) measuring approximately 1 cm are fixed to the plexi frame placed in the solution. (The most suitable seeds are rhombohemihedric half crystals.) During these operations the thermostat is kept at 35.2–35.5° C, and the saturation temperature of 35° C is set only after the seeds have been placed in the solution. The decrease of temperature is begun only a few hours later, first at a rate of 0.2° C/day; this may be increased later to the maximum rate of 0.5° C/day. The growth is terminated at room temperature. It is worth mentioning here that crystals measuring 3–4 cm grow in 5–6 days. The spontaneous nuclei growing on the surface of the liquid sink, and adhere to the growing crystals, causing defective growth. In order to avoid this unwanted side effect the growing crystals are covered with a metal or plastic cover.

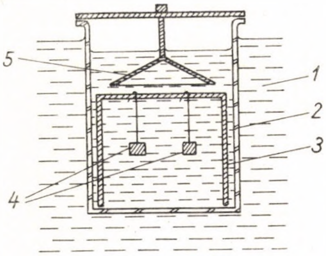

Fig. II.1.16 Growth of KNT (I)

1 water bath of thermostat, *2* crystallization tank with solution, *3* plexi frame to fix the seeds, *4* suspended seeds *5* screen fixed to the lid

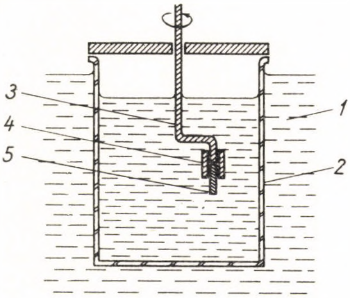

Fig. II.1.17 Growth of KNT (II)

1 water bath of thermostat, *2* crystallization tank containing the solution, *3* rotatable and bent plexi rod to fix the crystal, *4* rubber tube, *5* seed crystal

(b) Another method is shown in Fig. II.1.17. An important change compared with the method described above consists in the rotation of the growing crystal. The number of revolutions should be 40–60 per minute.

II.1.3.2. Growth of KCl

Suitable growth assemblies which may also be used to grow other crystals are shown in the following figures.

In connection with Fig. II.1.18 attention should drawn to two details: the shape of the lid and that of the bottom. The lid is usually cooler than the rest of the growth tank, and consequently the vapour of the solvent condenses on the inner surface of it. The drops collect in the deeper, inner parts of the conical lid and, on falling into the solution, decrease the supersaturation of its surface layers. In this way the formation of spontaneous nuclei is less likely just in the most critical place, right above the seed crystal. The extension formed at the bottom of the tank is also connected with parasite seeds. The crystals which sink to the bottom are collected in the extension and thereby disturb the growing crystal to a much smaller extent. It is advisable to place a heating element close to the extension to dissolve the parasite seeds collected in it.

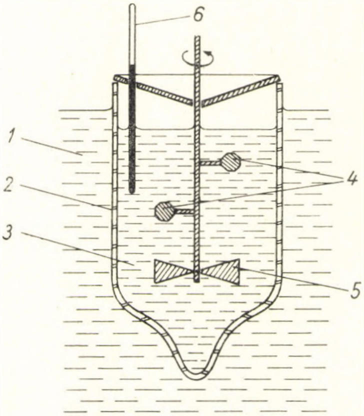

Fig. II.1.18 Growth of KCl by temperature decrease (I)
1 water bath of the thermostat, *2* growth tank (2–3 l), *3* solution, *4* seed crystals fixed on a rotatable support, *5* mixer, *6* thermometer

The equipment shown in Fig. II.1.19 is an assembly which in itself serves also as a thermostat. The temperature cannot be stabilized exactly, but nevertheless it can be controlled with an accuracy of ±0.1° C. The stirring of the solution is carried out with the aid of a bar magnet in a closed glass or plastic tube, which is rotated with a horseshoe magnet fixed to a small electromotor.

The solution for growing potassium chloride should be slightly acidic, as in the production of the seeds (see II.1.1.3), and should also contain 500–1000 ppm lead. The solution is saturated at 30° C, filtered at 31° C or 32° C, and finally poured into the growth tank which must be kept at 30° C. The seed crystals mounted on a proper support are put into the solution when its temperature is a few tenths of a degree above the saturation temperature. The immersion of the seed crystals in the solution is timed well if the surface layers of the seeds become dissolved while the system reaches a state of thermal equilibrium at 30° C. However, it may happen that the seeds are immersed in too hot a solution and become fully dissolved. This may be the case with the assembly of great heat capacity shown in Fig. II.1.18; there is less danger with the system of Fig. II.1.19. If the assembly of Fig. II.1.18 is used, it is suggested that a pipe coil connected to the water supply be put into the water bath of the thermostat, allowing cold water to flow through it to decrease the temperature of the system quickly to the saturation point. Even if the operation of the system is undisturbed it is kept at the saturation temperature for 1 or 2 hours, and the decrease of temperature is begun only after this period at a rate of a few tenths of a degree per day.

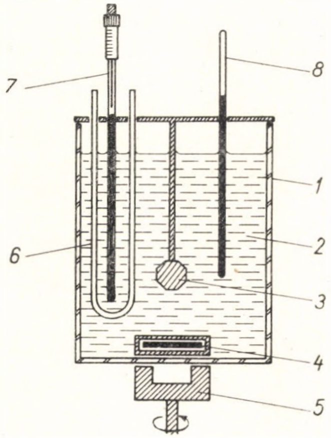

Fig. II.1.19 Growth of KCl by temperature decrease (II)

1 vessel (1–2 l), *2* solution, *3* seed fixed to a plastic rod, *4* magnet rod with glass or plastic cover, *5* rotatable horseshoe magnet, *6* U-shaped heating element, *7* regulating thermometer, *8* control thermometer

II.1.4. Circulation Method

II.1.4.1. Growth of $KAl(SO_4)_2 \cdot 12H_2O$ in a one-tank circulation system

A simple laboratory assembly is shown in Fig. II.1.20. Unlike the procedures described in the introduction to II.1, here only one container is used for the solution and growth. The upper part of it is at a higher, the lower part at a lower temperature. The polycrystalline starting material is placed in the upper, and the seed crystal in the lower part of the container. The circulation is based on the well-known fact that the density of a saturated solution of alum (or of many other crystals) increases with increasing temperature. The saturated solution of the upper, warmer part sinks to the colder bottom, where it becomes supersaturated, and part of the dissolved material precipitates, and becomes deposited on the seed. As a result the density of the solution around the seed decreases, the solution streams upwards to the warmer regions where it dissolves new material, and so on. In the assembly shown in the Figure the crystallization tank is a 15–20 cm long glass tube with a diameter of 3–4 cm. The bottom of the tube is

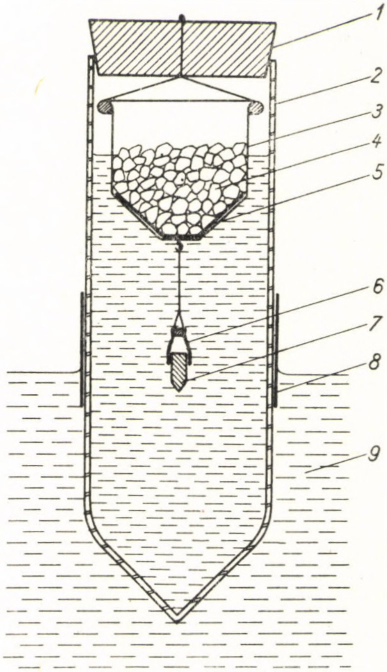

Fig. II.1.20 Growth of $KAl(SO_4)_2 \cdot 12H_2O$ by the circulation method
1 cork stopper, *2* crystallization vessel, *3* sack containing the material to be crystallized, *4* polycrystalline material, *5* funnel-shaped jar, *6* rubber tube, *7* seed crystal, *8* muslin cooling belt, *9* water bath

closed. The polycrystalline material is placed in a densely woven plastic net, in the bottom of which there is a funnel-shaped plastic jar. The diameter of the material holder must be 5–6 mm smaller than the diameter of the glass tube. The seed crystal is put in a rubber tube, and suspended by a silk thread from the holder.

The constant temperature difference between the surroundings of the material to be crystallized and the surroundings of the seed can be maintained in various ways. The most simple method is as follows. The crystallization glass tube is put in a water tank so that the water level of the tank does not reach the material holder. As a result of evaporation the water becomes 0.1–0.2° C colder than the surrounding air. This slight cooling is enough to start the flow of the solution. If, in order to accelerate the rate of growth, a larger temperature gradient is to be produced the crystallization tube is lowered into the water bath only until it reaches the level of the seed, as demonstrated in the Figure. At this height on the wall of the tube there is a belt made of some fine-textured material (e.g. muslin). The lower part of the belt must touch the water. The cooling effect of the water-evaporation from the belt develops a temperature difference of 1–2° C. The cooling effect and with it the temperature difference may be changed by varying the width of the belt. The experiment may be carried out as follows.

A solution saturated at room temperature is prepared. The material holder is filled with the compound to be crystallized, and the saturated solution is poured through it to wash out the smaller grains. Before the saturated solution is poured into the crystallization tube, either its temperature is raised a few tenths of a degree above the temperature of crystallization, or 1–2 cm^3 distilled water is added to it. In this way the formation of parasite seeds may be avoided. Then, the material holder and the seed fixed to it are immersed in the solution, and the mounted crystallization tube is put carefully into the water bath.

The system described above is less sensitive to the slow temperature changes of its surroundings, since to a certain degree it automatically regulates the rate of crystal growth. With any rise in the temperature, the concentration of the solution increases in the surroundings of the material holder as well as in the surroundings of the seed. Thus the supersaturation remains approximately constant. The situation is similar if the temperature decreases.

An improved modification of the above equipment is shown in Fig. II.1.21 (it is suggested that the various parts of the assembly should be made of plastic). The cylindrical tank *1* containing the polycrystalline material (material holder) has four windows, and is lined with light plastic gauze. A horizontal disc *3* in a thin-walled tube *2* is connected to the material holder; 6–8 small vertical tubes *4* with inner diameters of 1–1.5 mm are placed on the disc. The thread fixing the seed crystal reaches into the solution via a vertical tube *5* pulled through the centre of the disc. The crystallization tank is placed in a thermostat *6*. The necessary temperature gradient is produced by surrounding the material holder with a heating filament placed in a glass tube *7*. The filament is heated with constant power (10–20 W). The air layer *8* below the disc plays an important role in the development of the temperature gradient. This layer is formed when the disc is placed together with the material holder in the solution. The solution saturated in the higher temperature region above the disc streams through the small tubes into the lower, cooler parts of the growth tank. The solution of lower density and concentration streams back into the upper part of the tank through a slit between the crystallization tank and the thin-walled tube. The advantage of this assembly is that the growth can be carried out at various temperatures by setting the thermostat differently, and regulating the temperature of the heating filament.

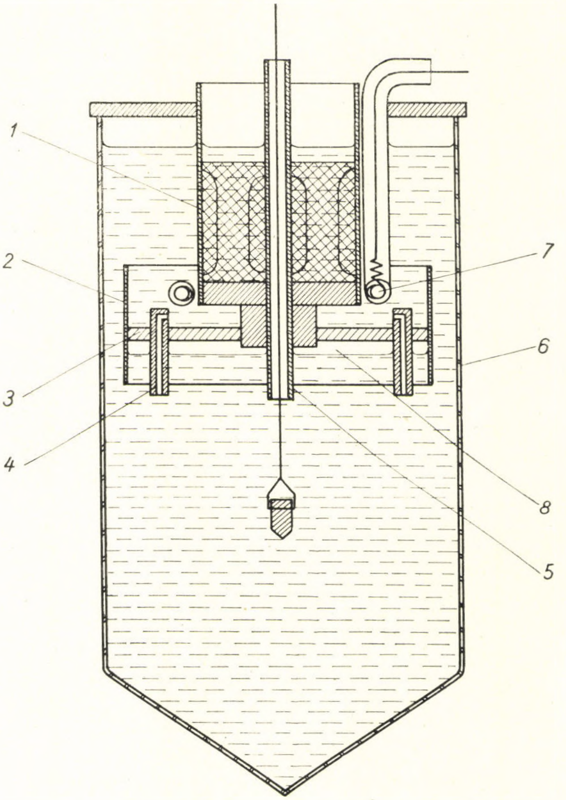

Fig. II.1.21 A variant of the single-tank circulation method
(half the original size)

II.1.4.2. Growth of $KNaC_4H_4O_6 \cdot 4H_2O$ (KNT) in a two-tank circulation system

The schematic diagram of the equipment can be seen in Fig. II.1.22. The temperature in the make-up tank is kept at a few tenths of a degree above the growth temperature. It is suggested that the growth be carried out at 29.7° C, and the saturation at 30° C.

The solution circulates spontaneously in the crystallization apparatus. This circulation develops for two reasons. First, the specific density of the solution increases with the concentration at a given temperature; and secondly, the specific density of the saturated Rochelle salt solution increases if its temperature is raised. As a result of these two facts, the solution saturated at the upper end of the make-up tank sinks down, and streams through the lower connecting tube into the colder growth tank. Here it becomes supersaturated, and the excess Rochelle salt precipitates.

As a result the concentration and specific density of the solution decrease, and thus it streams back into the make-up tank through the upper connecting tube where it again becomes saturated at a higher temperature, and so on.

The small bend at the end of the upper connecting tube in the make-up tank serves to retard back-streaming. The parts of the connecting tube outside the thermostat should only be sufficiently large to ensure safe connections. Even with the greatest care spontaneous nucleation may occur. This can be avoided either by wrapping the tubes in some heat insulating material, or by surrounding them with a heating filament and heating them so that their temperature does not fall below the temperature in the growth tank.

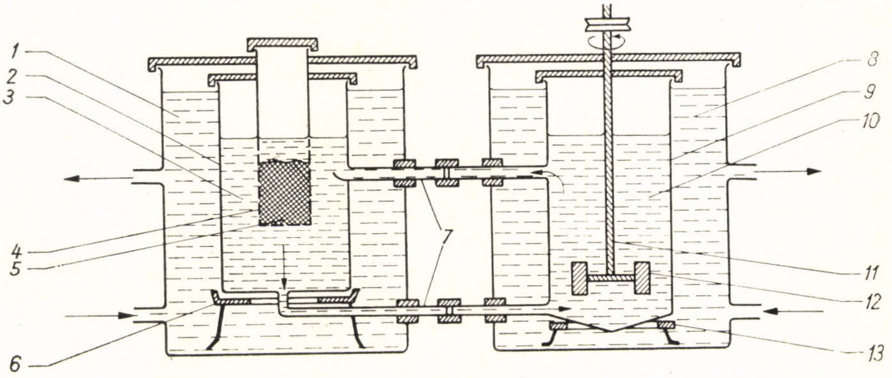

Fig. II.1.22 A two-tank circulation system to grow KNT crystals

1 water bath connected to the thermostat set to 30° C, *2* make-up tank (about 0.6 l), *3* saturated solution (30° C), *4* plastic support with holes lined with plastic net, *5* polycrystalline material, *6* stand, *7* heatable connecting tubes, *8* water bath connected to the thermostat set to 29.7° C, *9* growth tank (about 1 l), *10* saturated solution (29.7° C), *11* rotatable crystal support (1–2 revolutions per min), *12* seed crystal, *13* stand

Experimental procedure. — The temperature of the two thermostats is first set above the growth temperature, i.e. at 30–31° C in these experiments. Afterwards, solution saturated at 30° C is poured into the apparatus through the make-up tank. The seeds, preheated to 30° C, are put into the growth tank, the temperature of which is decreased gradually to the growth temperature, i.e. to 29.7° C. Simultaneously, the plastic holder filled with the material to be crystallized is lowered into the make-up tank, and the temperature of the latter is set to 30° C. (In the filling, the volume of the holder must also be considered.) When the grown crystals are taken out from the growth assembly, it must not be forgotten that Rochelle salt is rather sensitive to any temperature change, and the procedure described in II.1.2.2 should be followed. With this apparatus Rochelle salt crystals measuring 3–4 cm can be grown in 4–5 days (Fig. II.1.23). Naturally, other crystals may also be grown in the same assembly; for example, alum crystals measuring 2–3 cm grow in 2–3 weeks.

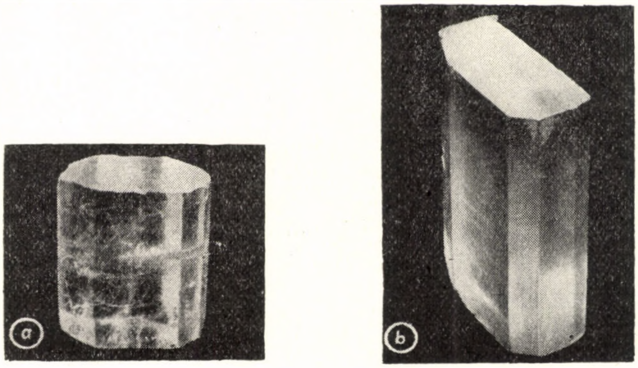

Fig. II.1.23 KNT crystals
(a) grown from a suspended and rotated seed; (b) grown from a supported seed

II.1.4.3. Growth of $C_2H_4(NH_2)_2C_4H_6O_6$ (EDT) in a three-tank circulation system (Walker–Kohman method)

This assembly differs from the previous system by the addition of a third container, the so-called holding tank. In order to remove small undissolved crystals and other solid particles, the saturated solution is filtered and allowed to flow into the holding tank. Its temperature is kept somewhat above the saturation temperature. The solution is stored in this tank, and flows from it into the lower temperature growth tank. Figure II.1.24 shows the suggested assembly. During the growth the make-up tank is kept at 45.2° C, the holding tank at 45.5° C, and the growth tank at 45° C. The temperature of these tanks is regulated by separate thermostats, as shown

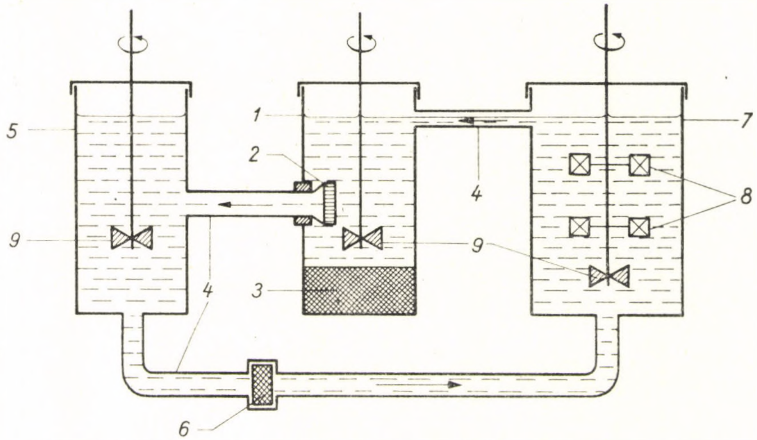

Fig. II.1.24 Growth of EDT by the Walker–Kohman method
1 solution make-up tank (3–5 l), *2* G-1 Jena (Pyrex) glass filter, *3* polycrystalline material, *4* heated connecting tubes, *5* holding tank (3–5 l), *6* membrane pump, *7* growth tank (3–5 l), *8* seed crystals, *9* mixer

in the Figure. In order to avoid any formation of parasite crystals the connecting tubes (mainly the one connecting the holding and the growth tank) should be heated, and kept at the temperature of the holding tank.

The growth procedure.—At the beginning of the experiment the temperature of the tanks is set to 46° C, and they are filled through the make-up tank with solution saturated at 45° C, and filtered several times. After filling, the temperature values are gradually set as given above. During setting the temperature the seeds mounted on their support are placed in the growth tank. (For the production of the seeds consult experiment II.1.1.5.) After this the make-up tank is filled with the material to be crystallized. In the assembly described 200–300 g crystals can be grown in a few months.

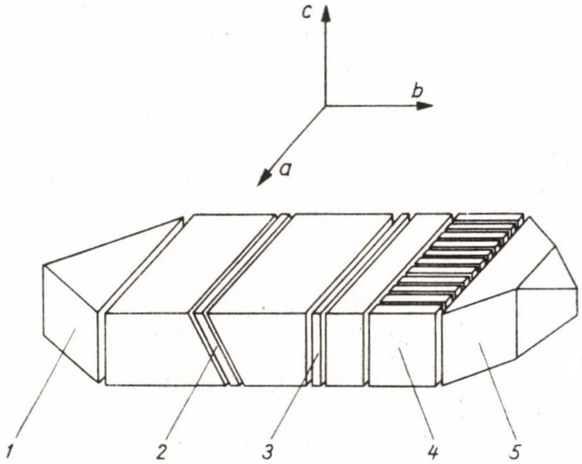

Fig. II.1.25 More important EDT sections

EDT crystals are very sensitive to any temperature change. Thus it is advisable to handle them with a pair of rubber-covered forceps. When large crystals are taken out of the tank, the solution is first replaced by chloroform of the same temperature. Only afterwards is the temperature decreased slowly to room temperature. Figure II.1.25 shows crystal sections which may be used as seeds or as piezo-cells. Section *1* may be used best as seed, whereas a section less good for this purpose is that denoted by *5*.

For piezoelectrical purposes, sections of small heat expansion and large piezoelectrical constants should be used; these are numbered *2*, *3*, and *4*. The angle between sections *2* and *b* is 10–20°. For piezoelectrical purposes it is also possible to use slices forming an angle with not only the *a*, but the *b* sections too. Figure II.1.26 demonstrates the various growth phases of EDT crystals. In this case the seed used was similar to that denoted by *1* in Fig. II.1.25. In order to grow larger, good quality crystals it is advisable to use appropriately cut faultless pieces of an already-grown crystal. (Figure II.1.27 shows crystals grown by the above method.)

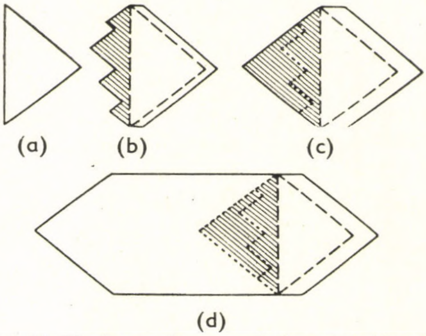

Fig. II.1.26 Various phases of the growth of EDT

(a) section which serves as seed (the tip points in the negative direction of axis); *b* (b)–(c) phases of completion; (d) completed and grown crystal

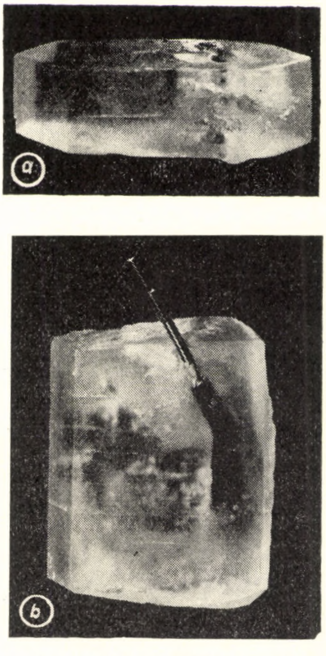

Fig. II.1.27 EDT crystals

(a) crystal grown from a solution of pH 6.1 (observe on the right side the veiled structure formed initially on the seed); (b) distorted crystal grown from a slightly acidic solution (the protruding metal rod served as a support for the seed)

II.1.5. Crystal Growth from Melt Solutions

The essence of crystallization from any melt solution consists in dissolving the material to be crystallized in a melt of different composition. The crystals are formed by a slow cooling of the melt. Thus, for example for crystallizing compounds of the type $A^{III}B^{V}$ which have important semiconducting properties, melts of metals with low melting points and low vapour pressures (Ga, In, Bi, Sn, etc.) may be used as solvents even at 1 000° C. For the purpose of crystallizing oxides, sulphides, titanates, and garnets of high melting point, so-called flux materials may be used as solvents with good results, e.g. halides and oxides of low melting point (PbO, $PbCl_2$, NaCl, etc.). In this latter case the growth is called crystal growth from molten salt solution, or flux growth.

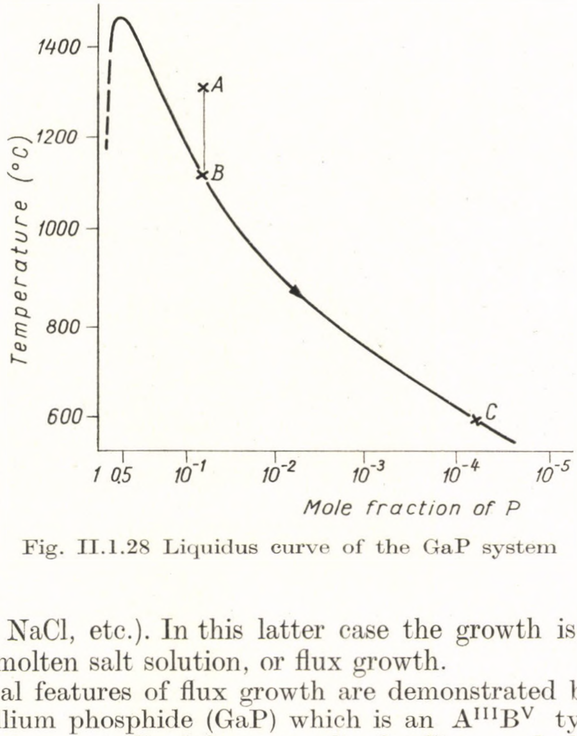

Fig. II.1.28 Liquidus curve of the GaP system

The principal features of flux growth are demonstrated by the crystallization of gallium phosphide (GaP) which is an $A^{III}B^{V}$ type compound. GaP may also be crystallized from a melt of gallium and phosphorus containing P in a non-stoichiometric proportion. Figure II.1.28 shows the liquidus curve of the GaP system. The abscissa of the diagram gives the composition of the melt, the ordinate the temperature at which crystallization begins at a given composition. Let the melt be in the state represented by A, in which the mole fraction of phosphorus is about 5×10^{-2} and the temperature is 1 300° C. On cooling, the formation of GaP begins at B, which corresponds to a temperature of 1100° C. As a result of the GaP formation the solvent becomes depleted of phosphorus, and thus any further crystallization occurs according to the liquidus curve at lower temperatures. Consequently, the nuclei grow if the temperature is continuously decreased. The change of the system is demonstrated by the *B–C* section of the diagram.

It should be noted that the liquidus curve has a maximum at the stoichiometric composition. Consequently, if one starts with a stoichiometric melt the crystallization will take place at a temperature higher than in the case of a non-stoichiometric composition; this means that the crystallization from a non-stoichiometric composition is more favourable from the point of view of experimental techniques.

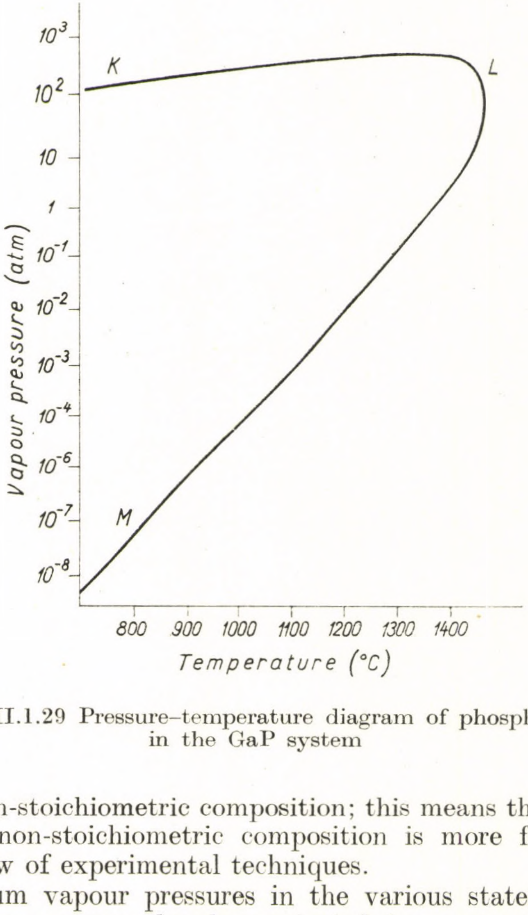

Fig. II.1.29 Pressure–temperature diagram of phosphorus in the GaP system

The equilibrium vapour pressures in the various states corresponding to the liquidus curve can be demonstrated in a pressure–temperature diagram (Fig. II.1.29). Of the two components phosphorus is the more volatile, and the total vapour pressure is practically equal to the partial vapour pressure of phosphorus. Let us consider the situation for example at 1100° C. As can be seen from the liquidus curve, two compositions are related to this temperature. One of them is poorer in phosphorus and richer in gallium, while the other one is just the reverse (in Fig. II.1.28 only the first type is shown in which the mole fraction of phosphorus is 5×10^{-2}). Accordingly, two values of equilibrium vapour pressure are found for this temperature of 1100° C, viz. 100 and 10^{-3} atmospheres. Since the situation is similar at any other temperature below L, the P–T diagrams consist of two branches, the upper branch (K–L) showing the equilibrium vapour pressure of the melt rich in phosphorus and partly depleted of gallium, and the lower branch (M–L) that of the melt partly depleted of phosphorus and rich in gallium. One single vapour pressure value only is related to the state corresponding to the maximum of the liquidus curve; this is represented by the point L. It is inconvenient to grow crystals from a stoichiometric melt, since in addition to the high temperature necessary, the vapour pressure of the melt is close to 100 atmospheres; in contrast, the growth can be carried out at vapour pressures lower by several orders of magnitude if a non-stoichiometric melt is used (e.g. if the melt contains only 5% of phosphorus the order of magnitude of the vapour pressure of the melt at 1100° C is only 10^{-3} atmosphere). This example demonstrates quite well the advantage of crystal growth from melt solutions: the growth of single crystals can be carried out at relatively low temperatures, and the problems connected with high pressure technology can be avoided.

II.1.5.1. Synthesis of GaP and its crystallization from gallium melt

GaP has a cubic structure with a sphalerite-type lattice; the crystals are orange coloured. The melting point is approximately 1 470° C, and the vapour pressure at this temperature is about 30 atmospheres. Owing to high temperature and high vapour pressure, the growth of GaP single crystals from a stoichiometric melt is difficult. GaP crystals can be grown in a simpler way from a melt solution which contains excess gallium. In this case the difficulties connected with high temperature and high vapour pressure can be avoided.

The technology of the crystal growth comprises several steps: (a) synthesis of the compound from its elements in silica ampoules sealed in vacuum at 400–550° C; (b) heating up of the ampoule to approximately 1 150° C; at this temperature the formed solid GaP dissolves in the excess gallium present; in order to promote the synthesis as well as the dissolution, the mixture must be vigorously agitated with the aid of a vibrator; (c) crystallization of GaP by cooling the melt solution; (d) separation of GaP crystals from the gallium metal.

Equipment and materials.—Electrical tube furnace which can be heated up to 1 200° C (Fig. II.1.30); vibrator (frequency: 50–100 s^{-1}, amplitude: 0.5 mm); temperature-regulator ensuring a cooling rate of 15–20° C/hour; vacuum assembly (10^{-4} torr); silica ampoule (Fig. II.1.31); filtration apparatus (Fig. II.1.32); gallium and red phosphorus of at least 99.9% purity.

Experimental procedure.—The silica ampoule is washed with a hot 1 : 1 mixture of hydrochloric and nitric acids, rinsed several times with distilled water, boiled in distilled water and dried in a drying oven at 120° C; 20 g molten gallium and 0.4 g red phosphorus are measured into the ampoule, and after its neck has been thinned it is sealed off at a vacuum of 10^{-4} torr. The gallium is most suitably melted with an infrared lamp at 35–40° C, and poured into the ampoule through a long plastic funnel. The use of the funnel is important since the gallium melt wets the silica, and would easily adhere to the neck of the ampoule without the funnel. During sealing off gallium oxide would form which attacks silica. A silica rod connected to the vibrator is sealed to the stump at the bottom of the silica ampoule. Since the ampoule must be placed in the homogeneous heat zone of the furnace, the length of the silica rod must be selected accordingly.

The gallium and the phosphorus sealed off in the ampoule must be heat-treated. For this purpose the furnace is heated at any chosen rate up to 400° C while the mixture is agitated vigorously by the vibrator. When this temperature is attained it should be increased gradually to 550° C during 3 hours. In this period the chemical reaction takes place between the gallium and the phosphorus. It must be stressed that agitation plays an extremely important role in the whole course of synthesis. If there is no agitation molten phosphorus will deposite on the surface of the gallium, and microcrystalline GaP will coat the surface of the gallium thus slowing down the reaction. The vapour pressure of the phosphorus not taking part in the reaction increases to several atmospheres at the temperature of the reaction, and this may lead to the explosion of the ampoule. The vigorous agitation ensures a free gallium surface; this shortens the reaction time, and the free phosphorus is consumed quickly, with the result that the vapour pressure within the ampoule does not increase to a dangerous level. The contents of the ampoule must not be heated directly to 1150° C since without the prior synthesis of the GaP at the lower temperature, the ampoule would explode.

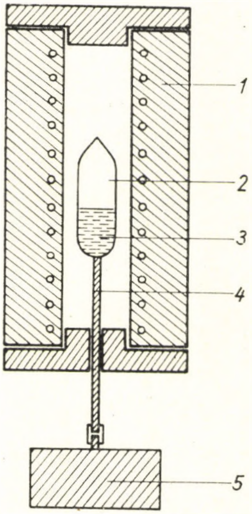

Fig. II.1.30 Apparatus used to grow GaP crystals
1 tube furnace, *2* silica ampoule, *3* melt solution, *4* quartz rod, *5* vibrator

In the procedure following synthesis the temperature of the ampoule containing the solid gallium phosphide and the excess gallium is raised at an arbitrary rate to about 1 150° C, and is kept there for about 1 hour. In this time the GaP becomes fully dissolved in the liquid gallium. To initiate the formation of GaP crystals the agitation must be stopped, and the temperature-regulator put into operation. The temperature of the ampoule is gradually decreased to 500° C at a rate of 10–20° C/hour. At 500° C the crystallization is practically completed. Afterwards the system is cooled at any rate to 30–40° C, the ampoule is taken out of the furnace, its tip is crushed, and its contents poured into a filtering funnel. (It is advisable to put adhesive tape around the ampoule before crushing its tip.) The gallium melt is drawn off from the GaP crystals and collected in a polyethylene container (if the melt solidifies in the course of this procedure, it is remelted under an infrared lamp). The gallium which remains adhered to the GaP crystals can be removed by shaking the crystals in 10% hydrochloric acid to which some drops of hydrogen peroxide have been added. The metallic gallium dissolves in this solution within a few minutes leaving behind GaP crystals with undamaged, shining surfaces. The crystals are dried after being washed in distilled water.

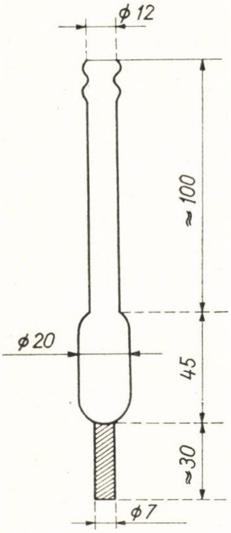

Fig. II.1.31 Silica ampoule, lower part showing the stump soldered to ampoule (sizes in mm)

Liquid gallium can be maintained in a supercooled state at room temperature for months, but it solidifies instantly on being shaken, or as a result of impurities which act as crystal nuclei. Consequently, if the closed ampoule is not opened immediately after the termination of the growth process, it should be stored in a horizontal position to avoid cracking which may occur when the gallium becomes solidified.

With the method described above, rhombus-shaped dendritic GaP crystal plates measuring 2×5×10 mm are obtained (Fig. II.1.33). The crystals are bounded mainly by {111} faces, and the main direction of growth is [112].

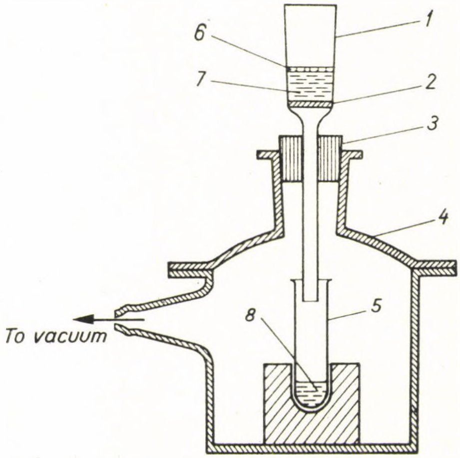

Fig. II.1.32 Filtration assembly

1 filtration funnel, *2* Jena (Pyrex) glass filter G-1 or G-2, *3* rubber stopper, *4* vacuum exsiccator, *5* polyethylene jar, *6* crystal, *7* metal melt, *8* filtered metal melt

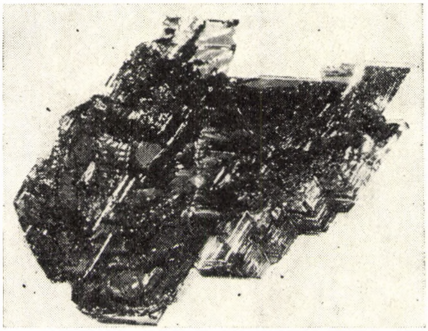

Fig. II.1.33 GaP crystal

II.1.5.2. Synthesis and crystallization of Ga_2S_2 from gallium melt

Ga_2S_2 is a yellow material with a band gap of 2.7 eV, and has so far been produced as a p- and n-type semiconductor. Its crystal structure is similar to that of graphite: it consists of a hexagonal layer lattice with the sequence sulphur–gallium–gallium–sulphur. These fourfold layers are normal to the axis *c* (Fig. II.1.34).* The adjacent sulphur layers are bound to each other only by van der Waals forces. As a result the plate-like crystals are elastic, like mica, and can be easily cleaved normal to the axis *c*.

The growth procedure, similarly as that for GaP, consists of several steps: (a) synthesis of Ga_2S_2 from its elements at a temperature of 400–550° C in a silica ampoule sealed off in a vacuum of 10^{-4} torr; (b) dissolution of Ga_2S_2 formed in the course of the synthesis in the gallium melt at about 1 150° C; in order to promote the synthesis and dissolution, the mixture must be vigorously agitated with a vibrator; (c) crystallization of Ga_2S_2 by cooling the melt solution; the suggested rate of cooling is 10–20° C/hour; (d) separation of the Ga_2S_2 crystals from the gallium metal.

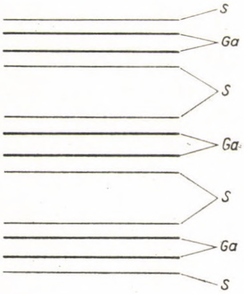

Fig. II.1.34 Layer structure of the Ga_2S_2 crystal

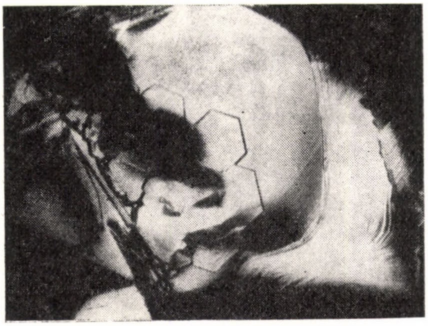

Fig. II.1.35 Ga_2S_2 crystals

The procedure is quite similar to the previous one, and the same assembly and accessories can be used. However, the separation of the grown Ga_2S_2 crystals from the Ga melt is different. This is carried out as follows. The ampoule is opened, and the Ga_2S_2 crystals floating on the surface of the gallium melt are taken out with a pair of plastic forceps. These crystals (and

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* Instead of Ga_2S_2, the notation GaS is frequently used; however, from a consideration of the crystal structure it is more correct to use the formula Ga_2S_2.

also those which have been caught on the filter) are put into a beaker containing 1% NaOH solution and approximately 10 ml mercury. The NaOH removes the oxide layer adhering to the crystal surfaces, while the gallium is removed by the mercury. The beaker is carefully shaken bringing the mercury into contact with both surfaces of the Ga_2S_2 plates. The metal is poured off from the crystals, these are transferred together with distilled water into another beaker, rinsed several times and dried. If necessary, the mercury treatment is repeated several times. — The average size of Ga_2S_2 crystals (flexible like mica) is 5×10×0.2 mm. The growth steps parallel to the hexagonal basal planes can be seen clearly (Fig. II.1.35).

II.1.5.3. Crystallization of ZnS in indium

ZnS is one of the best known luminescent materials. Its melting point under a pressure of 150 atm is approximately 1 850° C, under atmospheric pressure sublimation occurs at 1185° C. ZnS single crystals are usually grown by a chemical transport method in the temperature range of 1000–1400° C. If the material is to be crystallized from some metallic melt, mainly Ga, In, Tl, Sn, etc. melts are used. Although the crystals grown from the melt always contain 1% of the solvent, this method of growth is important because the grown crystals are comparatively free of oxygen or halide impurities. Two modifications of ZnS crystals are known, the hexagonal wurtzite, stable at higher temperatures, and the cubic sphalerite forming at lower temperatures. The temperature of transformation is approximately 1050° C, but this may be influenced to some extent by impurities. With most growth methods ZnS crystals of mixed structure are developed, i.e. the hexagonal and cubic phases are present simultaneously. If the crystals are grown from the metal melt, dendritic crystals of pure cubic structure are formed if the cooling rate does not exceed 30° C/hour (Fig. II.1.36).

For crystallization from an indium melt the same assembly can be used as was described in connection with experiment II.1.5.1 (see Figs II.1.30 and II.1.31), with the exception that, since the melting point of indium is 156° C, heatable filtration equipment must be used (Fig. II.1.37). Microcrystalline zinc sulphide, which has previously been heated in oxygen-free hydrogen sulphide at 900° C for an hour, is used as starting material. The experimental procedure is similar to that of experiment II.1.5.1, and consequently only the dissimilar features are mentioned here.

Twenty grams of indium, which is cut into small pieces, and 3 mole % zinc sulphide are measured into a clean, dry ampoule. The indium grains are first purified by washing them for 1 minute in 10% hydrochloric acid, then in distilled water, and finally in ethanol. The grains are best dried under an infrared lamp. The zinc sulphide is dried in a vacuum drying oven at 120° C for at least two hours before being placed in the ampoule. The time between the termination of these procedures and the sealing off of the ampoule should be as short as possible to avoid any contact with oxygen or humidity.

The sealed-off ampoule is placed in a furnace which is heated uniformly to 1150° C. (The vibrator is switched on at 200° C.) For the full dissolution of ZnS at 1150° C, approximately 30 minutes are needed. After this the vibrator is switched off, and the temperature of the furnace lowered at a rate of 10–20° C/hour to approximately 500° C. During this time the ZnS formation is terminated. Dendritic crystal plates grow to a size of 5×3×0.2 mm, and dendritic whiskers to a size of 2×2×10 mm.

The ampoule is taken out of the furnace at a temperature above the melting point of indium (at 200–300° C). In order to avoid any cracking of the silica ampoule by the solidifying metal, the ampoule is stored on an asbestos sheet in a horizontal position. Before the ampoule is broken, it is surrounded with adhesive tape. After the tip of the ampoule is removed, its indium content is melted in a drying oven, or on a gas flame, and the entire content of the ampoule is poured onto a heated filter. Care should be taken that the metal melt covers the whole filter surface.

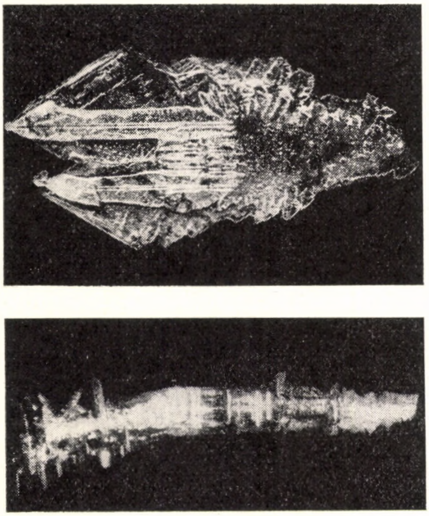


Fig. II.1.36 Dendritic ZnS crystals grown from gallium melt

Following the separation of the majority of the metal by filtration, the further purification of the ZnS crystals is carried out as follows. The crystals are carefully washed from the filter with mercury, and a small amount of 1% NaOH solution, into a 100 ml beaker. The beaker is slowly shaken so that all sides of the crystals come into contact with the mercury. The indium forms an amalgam which wets the grown crystals much less than does the indium melt. The mercury is poured into another beaker, and the remaining, almost pure crystals are washed with distilled water. The procedure must be continued (if necessary the mercury amalgam is replaced by fresh, pure mercury) until every ZnS crystal grown is recovered. Since the crystallization follows the so-called H dendritic mechanism, parallel to the main growth directions small holes and indium inclusions may be formed in the crystals. Owing to the unfavourable surface tension conditions the mercury cannot get into these channels, and thus a further purification method must be applied to separate the crystals entirely from the remaining indium. The dendrites are steeped for 24 hours in 5% $CuSO_4$ solution. The indium dissolves, and instead copper precipitates in the holes and gaps of the crystals. The copper can easily be dissolved in slightly alkaline KCN solution during 1 or 2 days. The KCN solution is neutralized by pouring it into a $KMnO_4$ solution. The ZnS crystals are washed with distilled water and dried.

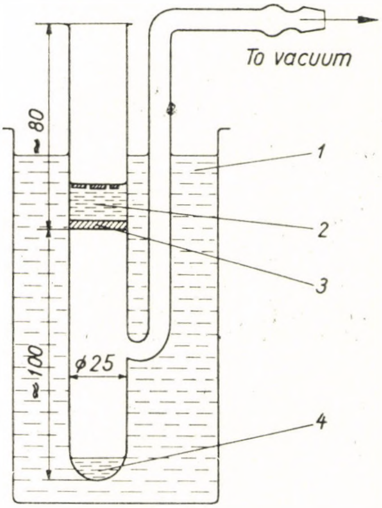


Fig. II.1.37 Glass filtration assembly heated by an oil bath (sizes in mm)
1 oil bath, *2* metal melt containing the crystals, *3* Jena (Pyrex) glass filter G-1 or G-2, *4* filtered metal melt

Note. When the starting mixture is prepared, instead of zinc sulphide an equivalent quantity of elementary zinc and sulphur in a proper stoichiometric ratio may be added to the indium. In this case, however, it must be taken into consideration that the vapour pressure of sulphur is very high compared with those of indium and zinc. Thus, during the heating, the ampoule may explode at a few hundred degrees. In order to avoid this it must be kept for a few hours at 400–500° C, when the sulphur reacts with the zinc forming zinc sulphide. In the final procedure—since elementary sulphur is no longer present—the temperature can be raised at any rate as in the previous experiment.

II.1.5.4. Production of ZnS single crystals by the flux method

A few physical characteristics of ZnS crystals have been mentioned in the previous section. When it is desired to apply the flux method, alkali halide, $PbCl_2$ or Ba_2ZnS_3 melts may be used. The growth can be carried out below

1000° C to obtain crystals of the sphalerite structure. While dendritic crystals usually grow in metal solutions, crystals grow from a flux (e.g. $PbCl_2$) with octahedral faces. Crystallization from fluxes (flux growth) may be carried out in a uniformly heated zone (similarly as the crystallization from indium melt), but it can also be carried out in an inhomogeneously heated zone. In the following, this latter method is described by discussing the crystallization of zinc sulphide in a $PbCl_2$ melt.

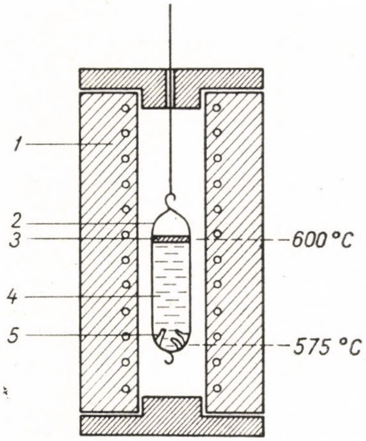


Fig. II.1.38 Apparatus to grow ZnS
1 electrical resistance furnace, *2* suspended quartz ampoule, *3* polycrystalline ZnS, *4* ZnS dissolved in $PbCl_2$ melt, *5* ZnS single crystals

A mixture containing $PbCl_2$ and ZnS is sealed off in a silica ampoule, and heated above 501° C. At this temperature $PbCl_2$ melts and dissolves partly the ZnS. Since the density of the solid ZnS is smaller than the density of the melt the undissolved excess ZnS floats on the surface of the liquid. If, starting from the surface, a downward negative temperature gradient is produced in the system, the solid ZnS on the surface of the melt gradually dissolves, and proceeds downwards by diffusion. In the lower, cooled regions of the ampoule the ZnS crystallizes, and adheres to the wall. This adherence prevents the crystals from getting to the surface of the flux.

Equipment. — Electrical resistance furnace, vacuum-assembly (10^{-4} torr), silica ampoule (its length is about 10 cm, diameter is 3 cm). The growth assembly (size of the furnace and ampoule, the quantity of the charge) must be designed so that the temperature of ZnS on the surface of the $PbCl_2$ melt is 600° C; the bottom of the ampoule is kept at 575° C (Fig. II.1.38).

Experimental procedure.—The ampoule is made of a silica tube sealed off at one end. The sealed tube is washed in a 1 : 1 mixture of hydrochloric and nitric acids, rinsed thoroughly with distilled water, and dried in a drying oven at about 120° C. The lead chloride and zinc sulphide are also dried at 120° C to constant weight. The charge depends on the diameter of the ampoule and the distance which develops in the heated furnace between the 600° C and 575° C isotherms. Lead chloride is first weighed into the ampoule, and then a zinc sulphide layer of 15 weight % is placed on it. The neck of the ampoule is narrowed, and sealed off in a vacuum of 10^{-4} torr. It is best if the free space left above the charge in the ampoule is not more than a few ml. The ampoule is placed in the furnace either by suspending it, or by supporting it from below. The furnace is heated, and kept at the prescribed temperature for 70–80 hours. The formation of crystals is observed with the aid of a mirror placed at an angle below the bottom opening of the furnace. After the completion of crystallization, the ampoule is quickly taken out of the furnace and allowed to cool down in an inverted position. In this way the greatest part of the $PbCl_2$ is separated from the ZnS crystals adhering to the walls of the ampoule. After the ampoule is broken the lead chloride can be dissolved in hot water. (The solubility of $PbCl_2$ in water at 120° C is 3.5 g/10 g H_2O.)

II.1.6. Hydrothermal Crystal Growth

The hydrothermal method consists in producing and growing crystals in an aqueous solution of high temperature ($>100°$ C) and high pressure corresponding to the vapour pressure of water or even at much higher pressures (sometimes several thousand atmospheres). This method has been used in the chemical industry for quite a long time. The further development and perfection, with the aim of obtaining large single crystals is, however, the result of much experimental work carried out mainly in the last two decades. A great number of different crystals can be grown solely by this method. Its advantages are summarized below when describing the growth of β-quartz. The β-modification of quartz is valuable since it is the only one which can be used as a piezo-cell. This modification is stable up to 575° C. Consequently, β-quartz can be grown only below this temperature, and growth from the melt or vapour is therefore out of the question. Any growth of β-quartz at lower temperatures (up to about 200° C) from some solution must also be excluded, since no solvent is known which dissolves it satisfactorily at such temperatures. Near the critical temperature of water (374.12° C), however, if proper pressure conditions are applied, β-quartz dissolves quite well in an alkaline solution or even in pure water. Thus the practical value of this method to grow large single crystals is considerable.

The disadvantage is that the growth process proceeds in a closed high-pressure vessel, and consequently cannot be observed. Thus the actual processes taking place can be deduced only from the initial conditions and the reaction products at the end of the experiment, when the grown crystals are at atmospheric pressure and have cooled down to room temperature. Some technical problems are presented by the expense and complexity involved in the design and construction of the growth equipment. The growth vessel is an autoclave with a well-fitting closure, containing the quantity of water or aqueous solution necessary to obtain the desired pressure at the growth temperature. The more important technical data are presented in the figures.

The shift of the liquid–vapour phase boundary for pure water, when the temperature in a vertical autoclave is raised, is shown in Fig. II.1.39, where the abscissa shows the temperature values, while the ordinate refers to the volume of the liquid phase expressed as a percentage of the inner volume of the autoclave. The curves obtained may be divided into two groups. The first group contains those where the liquid phase at room temperature (20° C) is less than 32.6% of the inner volume, and the second group those where it exceeds 32.6%. It can be seen from the Figure that with a charge of less than 32.6% the meniscus first rises, then falls abruptly, and disappears at the bottom of the autoclave before the critical temperature (374.12° C) is attained. For instance, with a charge of 10% the meniscus disappears at approximately 340° C; with a charge of 30% it disappears at about 372° C. At higher temperatures only the vapour phase exists. With charges of more than 32.6 %, the meniscus rises monotonously at a given temperature—e.g. with a charge of 60% at approximately 350° C, already below the critical temperature—until, on reaching the lid of the autoclave, it disappears. Consequently, in this case also there is only one phase present at the higher temperature. However, this is the liquid phase which at the critical temperature transforms into the vapour phase. The two sets of curves are separated from each other by the curve belonging to the 32.6% value. This curve represents that condition at which the meniscus persists all the time below the critical temperature; it disappears only at the critical temperature. — Figure II.1.39 also demonstrates the density relations at the various temperature values, giving the densities of the liquid and of the vapour phase.

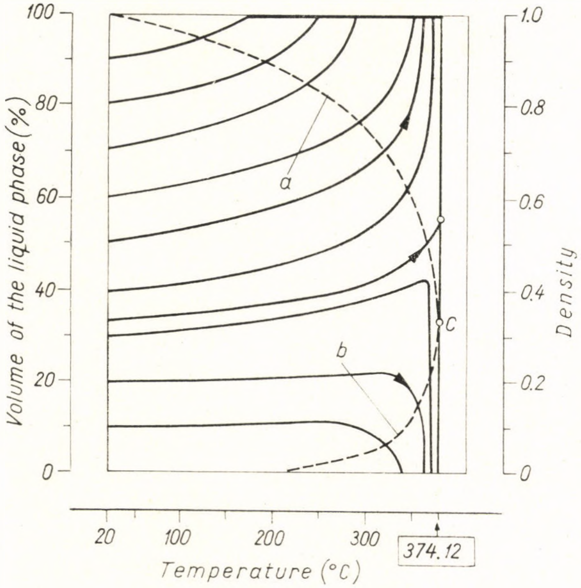


Fig. II.1.39

Temperature dependence of the volume of the liquid phase (expressed as a percentage of the inner volume of the autoclave) for various water charges (full line curves and left-side ordinate), and temperature dependence of densities; *a* liquid phase, *b* vapour phase (dotted curve and right-side ordinate) of density *C* at the critical temperature

This is shown by the dotted line which refers to the right-side ordinate of the Figure, the upper section giving the density of the liquid, the lower one that of the vapour phase.

Figure II.1.40 shows the temperature dependence of pressure inside the autoclave for various charges.

As previously, the charge (here pure water) is characterized by the volume of the liquid measured at room temperature, and is represented in Fig. II.1.40 as a percentage of the autoclave volume. The thicker full line extends to the critical temperature and represents the equilibrium pressure in the two-phase system. Disregarding the 32.6% charge, the two-phase system becomes a one-phase system already below the critical temperature; this is why the *T–P* curves become detached from the thick full line. The parting of the curves takes place at those temperatures where the system transforms into a one-phase system. The temperature values corresponding to the points of divergence are the same as those at which the curves of Fig. II.1.39 intersect the lower or the upper horizontal axis. The Figure is of practical use since with its aid that charge can be determined which is necessary to obtain a prescribed pressure in the autoclave at a prescribed temperature. Although the Figure refers to pure water, the data may also be used for dilute solutions since there are no essential deviations.

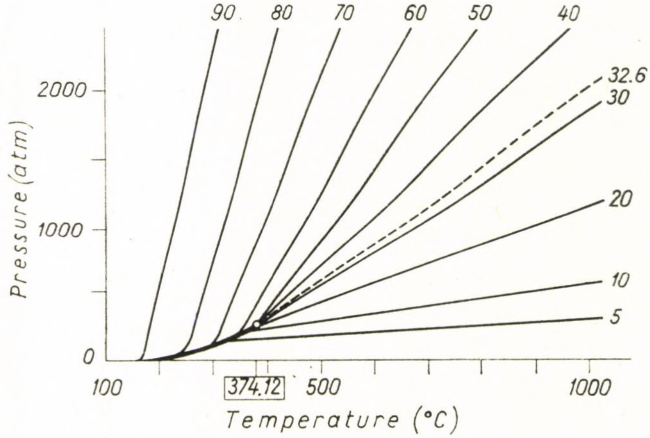


Fig. II.1.40 Temperature dependence of pressure for various charges

The autoclaves must be constructed from steel which possesses a high yield point at high temperatures and is resistant to corrosion. The wall thickness and the size of the autoclave are determined by the temperature and pressure to be used. Self-sealing autoclaves are also available commercially. Autoclaves with a volume not larger than 50–100 cm^3 may be made in the laboratory workshop. The various types shown in Fig. II.1.41 may be used successfully up to a temperature of 500° C and a pressure of approximately 1 500 atm.

Careful closing and sealing of the autoclave are always of great importance. The laying surfaces must be parallel to each other. In case *a* the screw caps should be tightened gradually, uniformly and in small steps.

For sealing, it is suggested to use 0.2–0.3 mm thick silver plates which are placed on the closing surface. These silver plates are softened by heating. Along concentric circles on the closing surface 0.2–0.3 mm deep furrows are grooved at equal distances (case *c* in the Figure). The laying surfaces of the seal discs are similarly developed. The soft silver plate is pressed into the grooves when the autoclave is closed. Thus a good sealing is obtained at temperatures of several hundred °C and even at pressures higher than 1 000 atmospheres. Before the autoclave is used the uniform bearing of the closing steel disc must be ascertained. This can be done by mixing fine (grade 600) emery powder with oil and smearing it uniformly on the edge of the disc. When the disc is replaced the laying surfaces are polished by twisting them from right to left. In the case of good bearing uniformly mat surfaces are obtained. After polishing the greasy emery powder is wiped off thoroughly with a dry cloth, and the surfaces are carefully cleaned with petrol or alcohol. If the autoclave is used repeatedly it is advisable to renew the closing plates in the described way.

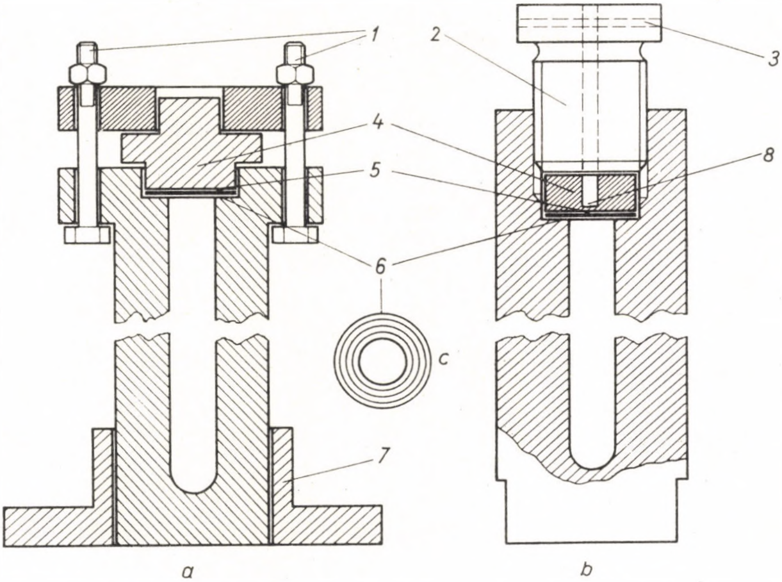


Fig. II.1.41 Autoclave types (length is e.g. 40 cm, otherwise the actual dimensions are four times the dimensions of the Figure)

a closing with the aid of 6–8 connecting screws *1*; *b* closing with a single screw *2*; it is fixed by a steel rod put through a transverse boring *3*; *c* the closing surface viewed from above; *1* connecting bolt, *2* fixing bolt, *3* transverse boring, *4* closing steel disc, *5* sealing silver plate, *6* closing surface, *7* support fixed to the table to prevent overturning, *8* safety diaphragm

A further important problem is the protection of the autoclave from explosion. There is always a danger of explosion even in the case of good construction if for example the furnace temperature increases unduly. Commercially available autoclaves are furnished with steel membranes which burst above a prescribed pressure, and the autoclave blows off without any serious damage. The home-made autoclaves constructed for high pressures must be furnished with a safety valve. Proper safeguard against explosion can be obtained for example by drilling a hole into the screw of the autoclave (Fig. II.1.41*b*), and thinning one part of the closing steel disc so that the thinned part will burst under any excess pressure. To give an example, a diaphragm of thickness 0.3 mm and diameter 3.3 mm made from steel of low carbon content bursts above a pressure of approximately 1 000 kp/mm^2.

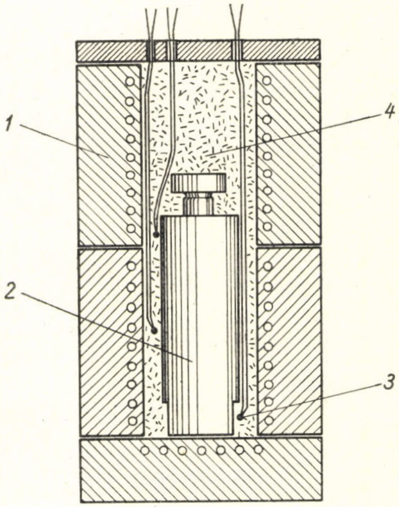


Fig. II.1.42 Position of autoclave in an electrical furnace
1 furnace, *2* autoclave, *3* thermocouple, *4* heat insulating filler (e.g. asbestos)

The autoclave can easily tip over during assembling. To avoid this, before mounting, it is put into a holder as shown in Fig. II.1.41*a*. The autoclave shown in Fig. II.1.41*b* must be prevented from rotating when the plug screw is drawn in. For this purpose the lower part of the cylindrical autoclave must be filed flat on the two opposite sides of its diameter, and pressed between parallel rails (or between vice grips).

The harmful effect of bases and acids is more pronounced at high temperatures. Consequently, the steel type used must be resistant to corrosion by alkaline and acidic solutions. Coating of the inner autoclave surfaces with a silver layer of appropriate thickness may also provide some protection against corrosion. Coating can be carried out by electrolysis, and before starting the process it is advisable to cover the surfaces with copper.

Figure II.1.42 demonstrates the position of the autoclave in an electrical resistance furnace.

Depending on the growth problem involved, the autoclave is either kept in its full length at the same temperature (isothermal method), or else a temperature gradient is produced along its length (temperature gradient method). In both cases it is best to use furnaces consisting of several parts. (The furnace shown in Fig. II.1.42 consists of three parts, two of them heating the sides and the third one the bottom.) The desired temperature values can be set by controlling the heating of the various furnace sections (e.g. with the aid of variable toroid transformers), and by changing the thickness of the heat insulating layer above the autoclave. Temperature measurements are usually made with thermocouples placed in insulating tubes, and fixed to the side of the vessel. In order to avoid any metallic contact, mica sheets are placed between the surface of the vessel and the solder of the thermocouple wires.

II.1.6.1. Growth of β-quartz by the hydrothermal method

(1) *Solubility of quartz in water.* The method is based on the solubility of crystalline quartz in water as demonstrated in Fig. II.1.43. The curves in the Figure show the temperature dependence of solubility if a known quantity of water is brought into a given volume (into the autoclave). The known water quantity, i.e. the charge, is characterized by the volume of the water measured at room temperature. The numbers written on the curves denote these volumes expressed as a percentage of the total voume available (the volume of the vessel).

The temperature dependence of solubility is given for instance by the curve AB_1C_1 for a 50% charge, while for a 71% charge it is desribed by AB_2C_2. At lower temperatures, where water is present in two phacses, solubility is demonstrated by the relevant section of the thick full line (e.g. AB_1, AB_2). At higher temperature values, when already only the vapour phase exists, solubility must be read from the curve-section corresponding to the given charge (e.g. B_1C_1, B_2C_2). These curve-sections start from the thick main line at the temperature where the water in the given volume becomes fully transformed into the vapour phase. The Figure demonstrates solubility only for relatively large charges which are important in practice. The given solubility curves are of two types. One type has a local maximum at 332° C, then decreases and only at higher temperatures increases monotonously. The second type increases monotonously throughout the whole temperature range. The first group comprises curves relating to a charge smaller than 62.5%, e.g. curve AB_1C_1 which increases up to 332° C, decreases in the range from 332° C to 365° C, and increases again only after this latter value is reached. The curves belonging to the second group are characteristic of charges above 62.5%, e.g. AB_2C_2.

(2) *Growth procedure.* In the method to be discussed below, instead of pure water a dilute alkaline solution is used as solvent. The information given by Fig. II.1.43 is quite satisfactory in this case too, since the solubility curves are similar to those of pure water, and the data deviate only slightly. The

bottom of the autoclave containing the dilute alkaline solution is kept at a higher, its upper part at a lower temperature. The nutrient quartz is placed on the hotter base of the vessel in the form of broken pieces, and the seeds are placed in the upper zone of the vessel (Fig. II.1.44). The solution which becomes saturated at the higher temperature streams upwards to the colder zone, where it becomes supersaturated. The precipitating SiO_2 deposits partly on the seeds. The solution depleted of silicon dioxide cools down, and sinks to the bottom; here at the prevailing higher temperature it again becomes saturated, and the process repeats itself. Thus the replenishment for continuous growth is accomplished by convection currents in the solution. This current is maintained by the temperature gradient. (Figure II.1.45 shows a quartz crystal grown by the hydrothermal method.)

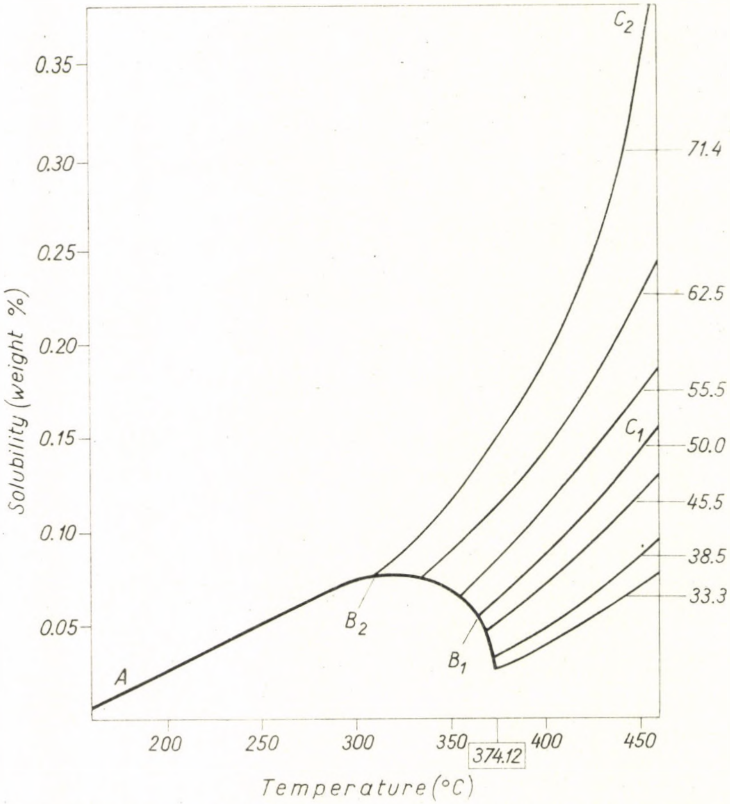


Fig. II.1.43 Temperature dependence of the solubility of quartz in water for several relatively large charges

(3) *Detailed instructions.* — (a) Preparation of seed crystals. Seed crystals are flawless crystal plates measuring about 6 × 6 × 2 mm. The usual faces are sections parallel to the prismatic (1010) or rhombohedral (1011) and (0111)

faces, and other sections normal to the axis. *c* For the purpose of processing the quartz crystals are glued with tar, sealing wax, or resin and beeswax to a piece of metal or wood. If there is no sawing machine, cutting may be carried out by hand; in this case a 0.5–0.7 mm thick brass plate fixed into a metal-saw frame is used. In sawing wet carborundum powder of medium (about 300) grade is employed. The crystal plates cut to the required size are polished with wet emery powder until each crystal face becomes uniformly mat. Grooves are made on the seed surfaces for the suspending wire. The seed crystals must be carefully cleaned. First the still adhering glue is removed (dissolved), then the crystals are put into hydrochloric acid, or a mixture of hydrochloric and nitric acids, and left standing for several hours. They are rinsed several times with distilled water and fixed with a silver wire of a few tenths mm diameter to a supporting frame also made of silver wire. The supporting frame with the seeds is put into approximately 10% NaOH solution, and kept there for several hours before being placed in the autoclave.

(b) Solvent and nutrient material. 0.5–1.0N NaOH solution is used. Small pieces of quartz debris or 'pure' quartzite may be used as nutrient. Before use the nutrient is cleaned in the same way as the seeds. The quartzite, however, is first broken up into pieces of about 5 mm, purified of dust, and boiled in concentrated hydrochloric acid for about an hour. Afterwards it is rinsed several times with boiling distilled water until no traces of chlorine are left. This can be controlled by adding a few drops of silver nitrate solution to the water; no chlorine traces are present if the water does not opalesce. For an autoclave with a volume of 60–70 cm^3, 5–7 g nutrient is needed.

(c) Solvent quantity and growth temperature. It is desirable to grow the crystals under conditions of relatively high solubility (Fig. II.1.43). Thus it is advisable to operate at a high temperature and with as much charge as possible. However, with too large charges and at high temperatures the technical difficulties increase. Thus, under the given circumstances, it seems to be best to compromise with an autoclave content of 70–80%, and to keep the temperature at approximately 400° C at the bottom of the autoclave, and at approximately 380° C in the upper part. Therefore, the autoclave must be made to withstand a pressure of 1 500 atmospheres.

Since the method discussed is based on the increase of solubility with increasing temperature, the temperature range in which solubility decreases while the temperature is increasing cannot be considered. In this temperature range the seed would dissolve instead of growing. However, even with smaller charges higher temperatures can be applied where solubility is already normal. The system passes through the zone of retrograde solubility in these cases too, but, if this is not very slow, it does not disturb the growth process; a slight dissolution of the seed surfaces is rather advantageous.

For the experiments small autoclaves are used which are simple to operate (Fig. II.1.41). For the dimensions of the autoclave we advise 3 cm inner diameter, 20 cm internal height, which means a volume of about 60 cm^3. The quantity of solution used in the autoclave is determined by its effective volume, but only 70–80% of this should be occupied. The effective volume of the autoclave is obtained by subtracting the volume of the nutrient and the seed crystals from the total volume.

(d) Operation of the autoclave. Much care must be taken to clean the inner surfaces of the autoclave. It is advisable to renew them before each use by polishing with increasingly fine wet carborundum polishing powder. For polishing a rotatable wooden rod fitted into the bore of the autoclave is used. After the autoclave has been polished, it is washed several times with distilled water and finally with alcohol, and heated as quickly as possible to 400° C to dry it. During heating-up the fresh metal surface becomes covered with a thin oxide layer resistant to chemical effects. It is a well-proved method to cover the renovated surface first with copper, and afterwards with silver by galvanization.

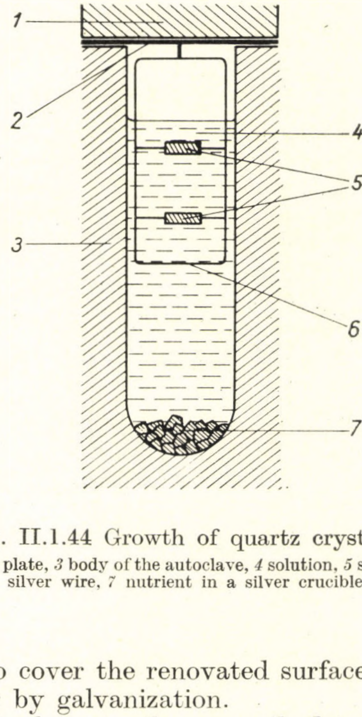


Fig. II.1.44 Growth of quartz crystals

1 closing steel disc, *2* sealing silver plate, *3* body of the autoclave, *4* solution, *5* seed crystals, *6* suspending frame of silver wire, *7* nutrient in a silver crucible

Heating up the autoclave to the prescribed temperature takes several hours. At the beginning of heating, a high temperature gradient should not be applied because an intensive flow in the solvent may carry along some powdery residual debris from the nutrient to the seed thereby causing defective crystal growth. At the termination of growth the autoclave is cooled down to room temperature in approximately a day by decreasing the heating current gradually.

It is sometimes difficult to open the autoclave. Any forcing may lead to the galling of the screws. If this happens the only thing to do is to saw off the top of the autoclave. Instead of applying force good results may be obtained by putting the autoclave in a hydraulic pressure apparatus. At the same time as it is attempted to loosen the screws, pressure is applied in the direction of its longitudinal axis.

It frequently occurs that the part of the nutrient not used up during the growth forms a rigid block adhering to the wall of the growth vessel. This block can easily be dissolved by pouring 10–20% sodium hydroxide solution into the autoclave so as to fill it to approximately one third of its volume; the solution is then boiled in the open autoclave. It is even better to place the nutrient in the autoclave in a small boat made of silver plates a few tenths of a mm thick.

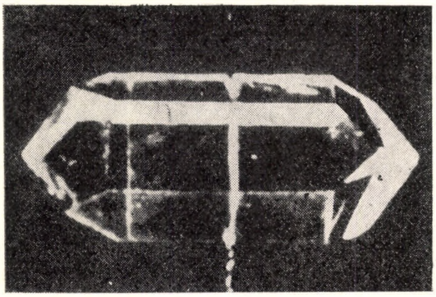


Fig. II.1.45 Quartz crystal

II.2. CRYSTAL GROWTH FROM THE MELT

Crystallization from the melt is one of the most generally used methods of obtaining relatively large single crystals in a short time. A great number of variants of this method have been developed and are usually named after the researchers who first applied them, e.g. Nacken, Bridgman, Czochralski, Kyropoulos, Stockbarger, Verneuil methods, etc. Each of these methods may be applied with good results to grow crystals from practically any type of material: ionic salts, oxides, metals, semiconductors, organic compounds. The various methods to be discussed are arranged in the following groups: (a) simple or normal freezing method; (b) zone melting; (c) crystal pulling.

The devices used in the above methods of crystal growth are discussed in more detail in II.5.

II.2.1. Normal Freezing (Simple Gradient Methods)

The methods to be discussed in this section consist in melting all of the material to be crystallized in a crystallization crucible; the crystal is then grown from the melt in the same crucible according to a given programme.

In the case of a *horizontal arrangement* (Fig. II.2.1) the material to be crystallized is put into a boat which is subsequently pushed into a heat insulating tube previously mounted in a tube furnace. After the entire material is melted, either the furnace is pushed away from the boat or the boat is pulled out of the furnace. This means that first only the temperature of one end of the boat falls below the melting point; solidification commences here, and gradually follows throughout the whole melt. The quality of the grown crystal depends a great deal upon the temperature gradient in which solidification takes place. In the simple case sketched here, this gradient develops close to the end of the furnace and can be influenced by regulating the heating current. In order to regulate the gradient and the temperature distribution more efficiently it is advisable to pull the boat into another space of regulated temperature instead of simply pulling it out into the open air. For this purpose a furnace consisting of two separately heatable parts with independent heating currents may be used. One part is heated above the melting point, and the other is kept just below it. The temperature gradient influencing the crystal growth develops in the surroundings of the contact between the two parts of the furnace.

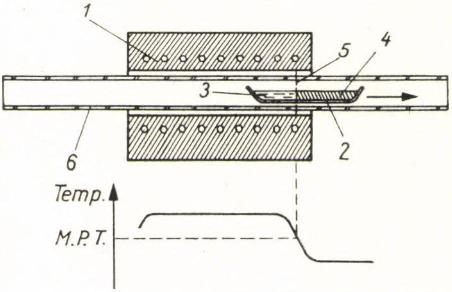


Fig. II.2.1 Schematic diagram of the horizontal freezing method; below: ideal temperature distribution

1 resistance furnace, *2* boat, *3* melt, *4* crystal, *5* isotherm belonging to the melting point, *6* heat insulating tube

Growth in a horizontal boat has several advantages. The shape and the dimensions of the boat can be varied, thus rendering possible the growth of crystals of various dimensions and forms. The growth of crystals of preferred orientation can easily be realized if the solidification of the melt starts from a seed of proper orientation placed in one end of the crystallization boat. Regulation of the temperature gradient and the rate of growth makes possible the study of various problems, such as the distribution of impurities or additives in the crystal in various conditions of solidification, the role of the factors influencing the formation of crystal defects, and so on.

In the case of *vertical methods* the material is put into a crucible with a conical or pointed end, and the crucible is placed in a vertical tube furnace. The simplest method after melting has taken place is to lower the crucible into the lower part of the furnace the temperature of which is below the melting point (Bridgman method). A more advanced method uses a double furnace in order to regulate the temperature gradient, and a ring-shaped baffle made of metal or some heat insulating material is placed between the two parts (Stockbarger's method; Fig. II.2.2).

Nucleation begins in the tip of the crucible in a comparatively small volume. It is advantageous if only a few seeds or one single seed is formed. In some cases it is necessary to work with crucibles with a capillary extension at the conical end. In this way only one seed inoculates the melt. By tilting the capillary the orientation of the growing grain can be selected. In order to obtain an oriented growth it is also possible to place a properly oriented seed into the capillary. The crucible is either suspended or supported. In this latter case the supporting rod can be pushed into the furnace from below. The rod's head must fit the conical end of the crucible (Fig. II.2.2).

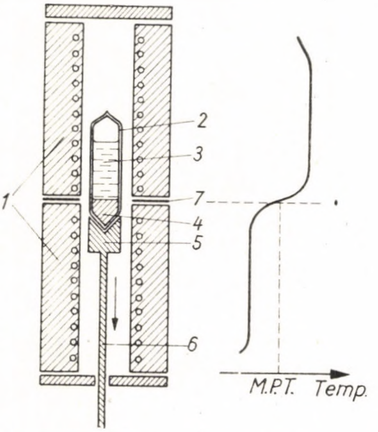


Fig. II.2.2 Left: schematic diagram of the vertical normal freezing method; right: ideal temperature distribution

1 resistance furnace assembled from two parts, *2* crucible, *3* melt, *4* crystal, *5* crucible support, *6* lowering rod, *7* baffle

Owing to the heat extraction of the rod the end of the crucible cools, and in this way a sufficiently high temperature gradient develops; this results in a nucleation localized to one point. The baffle is of manifold use; e.g. it increases the temperature gradient, or it produces nearly plane isothermal surfaces in the area of solidification.

In the Stöber method the crucible is kept immobile in the furnace, and the temperature is gradually decreased. With this method the temperature distribution of the furnace (usually consisting of several parts) must be regulated so that first the temprature of the tip of the crucible cools below the melting point. If the heating current is decreased further, gradually larger sections of the melt solidify until finally it becomes completely crystallized all along its length.

Many problems arise more pronouncedly in the case of a vertical assembly than with a horizontal one. The adherence of the grown crystal to the crucible wall may result in deformations, and in many instances in the cracking of the crystal or of the crucible. This method can be applied only with difficulty or not at all with materials which expand upon solidification. The problem may occasionally be solved by a proper selection of the crucible material, by coating the inner walls with some suitable layer (e.g. carbon), or by the use of specially shaped or thin-walled crucibles. In many cases the grown crystal is melted off the crucible wall by heating it quickly before cooling down to room temperature. In this case the crystal is dropped into a larger container by inverting the crucible, and cooled down there.

As regards the growth processes mentioned above the following considerations should be kept in mind: (1) In order to avoid any contamination of the melt, all the materials (material of the crucible, gas atmosphere in which the growth process takes place, etc.) with which the melt or its vapour may come into contact must be selected very carefully. (2) In order to minimize the possible reactions between the melt and the crucible and to avoid any accidental decomposition of the melt, the temperature of the melt must not be raised too much above the melting point. (3) Solidification must take place in a large temperature gradient to avoid constitutional supercooling. (4) The temperature gradient in the already solidified part should be small in order to avoid the formation of mechanical stresses. Especially with materials of high melting point it is advisable to keep the already solidified part just below the melting point until the crystallization of the whole sample has been completed. Afterwards the produced crystal should be cooled down to room temperature very slowly, meanwhile keeping its whole volume nearly at the same temperature, i.e. in a homogeneous heat-space. (5) The lower the rate of growth, the more perfect crystals can be obtained. On the other hand it is not advisable to apply too low rates of growth, partly because this increases the possibility of contamination and undesirable nucleation, and partly because it is not economical. (6) The impurity distribution in the crystals grown is generally inhomogeneous, because the impurity concentrations in the melt (C_l) and in the solid phase in contact with the melt (C_s) are usually different. If the distribution coefficient, $k = C_s/C_l$, is smaller than unity, the impurity concentration increases in the growth direction, while it decreases if the value of k is greater than unity. This means that for rod-shaped crystals the purest part is the end if $k > 1$, and the front part in the case of $k < 1$.

II.2.1.1. Growth of tin, cadmium and zinc single crystals by the horizontal gradient method

Polycrystalline metals of high grade (at least 99.9%) purity are used. An adequate quantity is melted in a silica crucible in air, and the melt is poured into a boat of the same shape as the boat that will later be used for the growth. The oxide layer is removed from the solidified metal surface with a 5 N hydrochloric acid solution. After this the metal is washed with distilled water and alcohol, and put into a boat of a semicircular or trapeze-shaped cross-section with the dimensions of $1.5 \times 2 \times 20$ cm. The growth apparatus is shown schematically in Fig. II.2.3.

Furnace *2* surrounding the 1 m long silica tube *1* with external diameter of 36 mm is placed on the movable support *3* by means of which it can be moved along the silica tube at various speeds. The temperature of the material to be crystallized is measured with the thermocouple *5* touching the boat *4*, while the temperature of the furnace is measured with another thermocouple *6* placed close to the heating coil. The external diameter of the furnace is 10 cm, and its length is 32 cm. The heating filament is a KANTHAL-A wire of 1 mm diameter. Fireclay powder serves as an insulating layer. The heating current of the furnace can be regulated by a variable transformer. The power demand of the furnace is 150 W at 600° C.

The growth process. The material is put, together with its thermocouple, into the furnace. The gas stream of 10 l/hour is switched on. Pure argon or nitrogen is used. The furnace is heated to 30–50° C above the melting point of the metal, which means in the case of tin 260° C, for cadmium 350° C and for zinc 450° C. After the temperature of the melt has reached this value the sample is kept in the molten state for about 30 minutes, after which the driving mechanism is switched on, and the furnace is 'pulled down' from the melt at a rate of about 0.5–10 cm/hour. In order to determine the optimal pulling rate growth experiments are made with the given metal at various pulling rates. After the termination of the growth process, it is checked by etching with a 5 N hydrochloric acid solution whether the sample has become a single crystal.

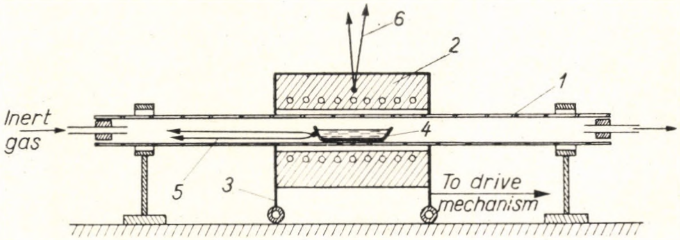


Fig. II.2.3 Equipment to grow metals of low melting point

II.2.1.2. Production of alkali halide single crystals by the vertical normal freezing method

A simple method is described for producing single crystals from the following compounds: NaCl (m.p. 801° C), KCl (m.p. 776° C), KBr (m.p. 730° C), KI (m.p. 723° C), NaI (m.p. 651° C).

Materials and apparatus. (a) Dry starting material. Approximately 200 g material is needed to grow one crystal in the manner described below.

(b) Porcelain crucible with a pointed bottom to grow 4 cm long single crystals with a diameter of approximately 4 cm (Fig. II.2.4).

(c) Resistance furnace (900–1 000 W) for growth, consisting of two parts with a double-walled coating (Fig. II.2.5). It is operated with stabilized voltage from the network. The growth space is protected from any rapid temperature changes in its surroundings by the circulation of cold water in

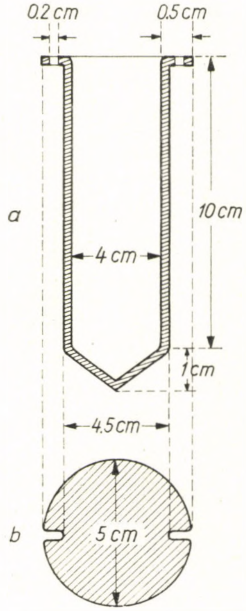


Fig. II.2.4

a Longitudinal section of a porcelain crucible, and *b* top-view of its cover; the two borings on the opposite sides of the rim, and the holes at the edge of the cover serve for pulling through the fixing wires

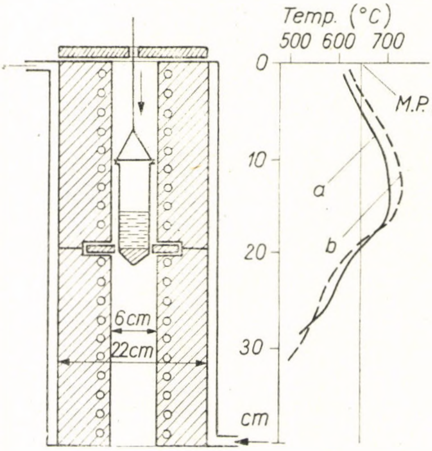


Fig. II.2.5 Left: schematic diagram of the growth furnace; right: longitudinal heat distribution of a furnace to grow NaI single crystals

a for an empty furnace; *b* for placing into the furnace a covered crucible filled with aluminium oxide powder to model the actual situation during the growth process (the thermocouple measuring the temperature is placed in the centre of the crucible, and is lowered with it) the double-walled coating. The furnace must be developed so that in the upper part—which must be at least as long as the crystal to be grown—the temperature is 30–60° C above the melting point, whereas in the lower, second part—also at least as long as the crystal— the temperature is 30–60° C below the melting point. This is proposed since it is advisable to keep the grown crystal in the lower part of the furnace at a temperature at which it is still plastic. A baffle (about 1 cm thick) made of heat insulating material must be placed between the two parts of the furnace.

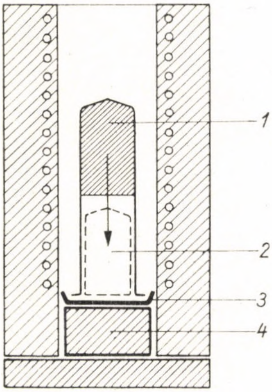
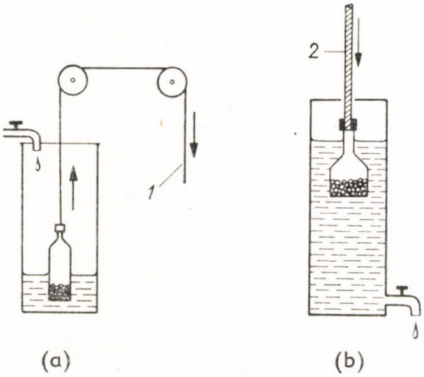


Fig. II.2.6 Melting furnace

1 crystal in its original position, *2* crystal after it has been melted off, *3* corundum dish to receive the melt flowing down, *4* insulating brick



(a) (b)

Fig. II.2.7 Simple assembly to lower the crucible

(a) suspended crucible; (b) supported crucible; *1* suspending thread, *2* supporting rod

(d) Tube furnace open at the top (but coverable if necessary) to melt off the crystal from the wall of the crucible (Fig. II.2.6). The furnace must be heatable to a temperature of 100° C above the melting point, and must be constructed so that the crucible can easily be lowered into or pulled out of it.

(e) A tube furnace to cool the grown crystal slowly to room temperature after it has been taken out of the crucible (annealing furnace). The furnace is closed at the bottom, and can be covered at the top. The construction is similar to that of the melting furnace, and it can be heated close to the melting point.

(f) Crucible-lowering device. A horizontal axis driven by a mechanical clock-work or by an electrical motor. Discs of various diameters can be mounted on the axis. The crucible is fixed with the aid of a KANTHAL wire (1 mm in diameter) to a cord over the disc. The rate of lowering is controlled by changing the number of revolutions, or the diameter of the disc. The wires used to suspend the crucible are straightened out by heating them under load to incandescence with electric current. A simple lowering device is shown in Fig. II.2.7a. The crucible is lowered at the same rate at which a shot-filled flask, floating on the water surface, rises. Figure II.2.7b depicts another variant of this device, where the crucible is supported from below.

Procedure. The crucible is filled with the dry, granulated material to be crystallized, covered and pulled into the upper part of the growth furnace. The heating current is switched on; 1 or 2 hours after the desired temperature is reached lowering of the crucible is begun. On melting, the fine granulated material collapses, and the melt fills only less than half of the crucible. The suggested rate of growth is 1–2 mm/hour. When approximately three-quarters of the crucible have entered the lower furnace part, it is pulled quickly out of the growth furnace, turned over with crucible tongs, and put into the preheated melting furnace. The crystal melts off from the crucible wall in a few minutes; the knock when it falls into the corundum dish below the crucible can be heard. After this the crucible is taken off the crystal, and the latter is placed into the homogeneous heat space of the annealing furnace and cooled down to room temperature in a day. The furnace is kept covered during this period as any removal of the furnace lid may result in the cracking of the crystal. The danger of cracking is greater at lower temperatures when the crystal is less plastic (e.g. around room temperature). For annealing, it is advisable to use a furnace with a very good heat insulation, i.e. a furnace with a high heat capacity, since in this case it is not necessary to decrease the heating current gradually; it is quite sufficient to switch off the current as soon as the crystal is placed in the furnace and the covering lid is put on it. As a result of the good heat insulation the crystal cools down to room temperature slowly together with the furnace.

It is not an absolute necessity to use three furnaces, since the growth furnace can also be used as a melting and annealing furnace if it can be turned over together with the crucible after the termination of the growth process; so melting off and annealing can be carried out in the same furnace.

A few additional remarks are made below, referring mainly to the growth of strongly hygroscopic materials. It is advisable to take them into consideration when growing for example thallium activated NaI crystals, used as gamma-ray detectors. [The description given below in (a) actually refers to these crystals. The addition under (c) is more general, and refers mainly to the construction of the furnaces.]

(a) Reagent grade sodium iodide is dissolved in distilled water, and the solution is made very slightly acidic by adding a small excess of HI. Complexone is added to the solution, which is filtered on active carbon in a glass filter into a porcelain jar. The jar is placed in a vacuum drier and evaporated at 150° C. The dried and powdered material is transferred to the crucible (Fig. II.2.4) containing 0.2–0.5 weight % thallium iodide. The crucible is covered with a lid and prepared for suspension. However, before the growth process, it is kept for another 24 hours at about 150° C in the vacuum drier. Before the crucible is taken out of the drier dry air is admitted; the crucible is taken out, and put quickly into the preheated growth furnace. It is lowered into the furnace at a rate of 1.5 mm/hour, and stopped when the molten layer above the grown crystal is 1 cm thick. This melt is relatively strongly contaminated, and must be poured off the crystal before the crucible is placed into the melting furnace. The remainder of the process is as described earlier.

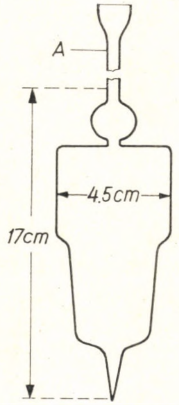


Fig. II.2.8 Silica jar for crystal growth and stress-free cooling

(b) The silica jar shown in Fig. II.2.8 can be used with some small alterations as a growth crucible. The jar is filled with the material to be crystallized through the funnel in the upper part. After this the jar is placed in a melting furnace with the funnel protruding from it. The funnel is cut off at *A* and the crucible connected to the vacuum system, which must be operated throughout the heating of the furnace. When the material has melted, the tube-like end part of the crucible connected so far to the vacuum system is sealed off. From the remaining sealed tube part a hook is formed to suspend the crucible. The crucible is pulled into the upper part of the preheated double growth furnace, and after about half an hour its lowering is begun. An advantage of the transparent silica crucible is that the first stage of crystal growth can be observed. For the purpose of observation a mirror is placed below the lower opening of the furnace. The phase boundary between the growing crystal and the melt can be seen well as soon as the solidification starting from the capillary reaches the broadening part of the crucible. The grown solid phase is a single crystal if the phase boundary is clear and smooth without angles or bends. If polycrystalline material has grown it is remelted and the growth process restarted. Crucible tips of various shapes determine the orientation of the growing crystal (Fig. II.2.9). In case (a) such crystals usually grow whose ⟨110⟩ direction is parallel to the crucible axis, in case (b) crystals whose ⟨100⟩ direction coincides with the crucible axis.

The procedure after the termination of the crystal growth is similar to that described above. The crucible is turned over, and put first into the melting furnace and then into the annealing furnace. The grown crystal fills only the narrower part of the crucible and thus on turning over it comes into the broader part where it cools down stress-free. The spherical part of the crucible serves to hold the melt formed in the melting off of the crystal from the crucible wall.

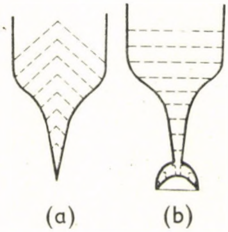


Fig. II.2.9 Various shapes of crucible tips
(a) simple tip; (b) indented spherical surface (dotted lines show the most frequent position of the {100} planes)

(c) For the purpose of the experiments described above, and also for numerous others, it is advantageous to use furnaces constructed from several parts. These are generally suitable since they can easily be reconstructed, while the electrical input and the temperature distribution can be changed too. The heating filaments in the furnace shown in Fig. II.2.10 are supported by cylinders of various internal diameters (e.g. 6, 8.5, 10 cm). The external surfaces of the cylinders have helical grooves to a depth of 1 cm, into which the coiled heating filament is put. The heating filament supports are surrounded by cylinders made of insulating material and of appropriate length (e.g. 2.5, 5, 10 cm). These cylinders fix the heating filaments and also tightly fasten together the filament supports placed on each other. On the various heating filament supports are installed the heating coils, which are drawn more or less apart, and made of wires of various lengths and diameters. Each coil can be heated independently. Rings of various internal diameters and thicknesses, and made either of some insulating material or metal, may be placed between the neighbouring cylinders. The insulating rings can also be heated. With the aid of these rings the temperature gradient can be regulated within a wide range. In order to increase the temperature gradient, circular rows of holes may be drilled in the grooved heating filament supports. The heat radiated by the filament acts directly through these holes.

If the development of a prescribed temperature distribution is required the following procedure is suggested. First the power demand of each heating element is estimated, and they are constructed accordingly. The furnace is assembled from these heating elements, and the temperature distribution within the furnace determined in the case of a given heating current. The distribution obtained usually differs from that desired. In order to obtain the prescribed temperature distribution it is advisable to feed each heating element separately with a variable transformer. With the aid of these transformers the input current values are changed until the desired temperature distribution is obtained. After this the furnace is dismounted, and the exact input of each heating element is measured. From a knowledge of these exact values the furnace may now be reconstructed so that by connecting the various elements the whole furnace can be operated with one variable transformer. Certain heating elements will probably have to be changed, the heating coils of others will have to be shortened or pulled apart, and so on. After this has been carried out, the furnace is again re-assembled in its final form.

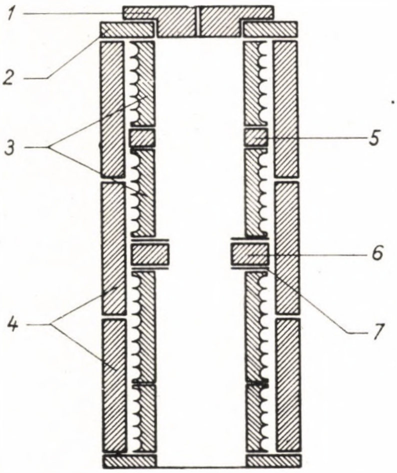


Fig. II.2.10 Furnace assembled from elements

1 lid, *2* closing ring, *3* heating filament support, *4* connecting cylinder, *5* distance ring, *6* insulator baffle, *7* metal baffle

II.2.1.3. Growth of anthracene single crystals by the vertical gradient method

Zone-refined anthracene which is used as starting material may be even further purified by sublimation (see also experiments II.2.2.1 and II.3.1.1). The polycrystalline material is pulverized to a fine powder in a clean porcelain or agate mortar, and put into the vessel shown in Fig. II.2.11. This vessel will later be converted into a crucible. In order to avoid any contamination (air-borne dust particles), pulverizing and filling should be carried out in a dry box or in some other dust-free space. The vessel should be made of duran or rasotherm, or some other glass, which is resistant to chemical effects, and which softens only at high temperatures. Before filling, the vessel is cleaned with a mixture of concentrated nitric acid (10%) and hydrochloric acid (90%), then washed with distilled water and dried. With continuous shaking the broader cylindrical part of the vessel is filled with anthracene, and then connected to a hydrogen container via a rubber stopper fitted into the funnel-shaped part.

The hydrogen gas may be obtained from pure zinc and reagent grade 25% hydrochloric acid, but must then be bubbled through a copper sulphate and a permanganate solution. It is simpler to obtain the hydrogen gas from an industrial gas container. In this latter case the gas should be passed through a gas chamber of constant pressure (corresponding to a 15 cm water column). To eliminate oxygen impurities from it, the hydrogen is passed through a silica tube filled with copper gauze along most of its length, and placed in a tube furnace heated to 600° C. The hydrogen is dried by passing it through a double cold-trap used in vacuum devices. One of the traps should be cooled with ice, the other with liquid air. The hydrogen flow removes the air and the adsorbed oxygen. To make this latter process more efficient the anthracene-filled vessel is put into a horizontal furnace which is heated gradually to the melting point of anthracene (208° C). When the anthracene has already become partly molten, the ends A and B of the vessel are sealed (Fig. II.2.11). A higher pressure inside the crucible than that outside would hamper the

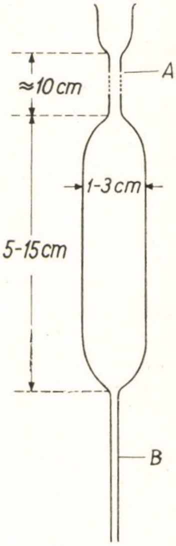


Fig. II.2.11 Glass vessel to grow anthracene crystals sealing. In order to avoid this unwanted side effect the thin glass pipe first at the hydrogen source side is pulled down, and then the other thin glass tube is soldered too (if possible within a few seconds). Care should be taken lest air should get into the vessel. A hook is formed on the end of the sealed tube. In this way a crucible is made which should be hung into the preheated crystallizing furnace (Fig. II.2.12). The lower extension of the crucible 'filters' the crystals growing from more than one seed, and thus it is highly probable that in the broadening part only a single crystal will grow. Since anthracene is predisposed to undercooling, it is advisable to form an extension several centimeters long, and even to give an S shape to it.

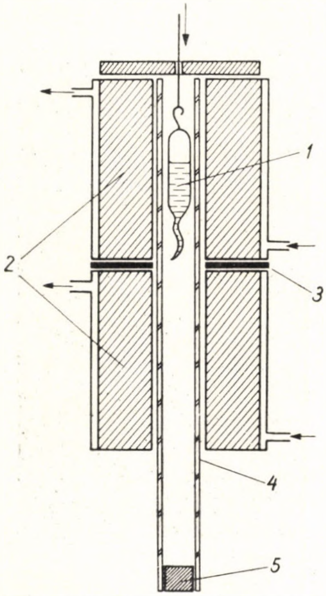


Fig. II.2.12 Assembly for growing anthracene crystals

1 suspended glass crucible with melt, *2* double furnace (with double-walled jacket for water cooling), *3* copper baffle, *4* glass tube, *5* rubber stopper

The vertical tube furnace consists of two parts. The heating of each part can be regulated separately. The tube furnace must be long enough to give room for the crucible and its extensions in each of the separated parts. The crucible is put first into the upper part of the furnace heated to 220–225° C. After the anthracene has melted completely the crucible is lowered at a rate of 0.6 mm/hour into the lower part of the furnace heated to 190–195° C. In order to obtain a steep temperature gradient the two parts of the furnace should be separated from each other by a baffle made of a 1.5 mm thick copper ring. The air-flow around the crucible may be decreased by inserting into the furnace a long glass tube fitting its walls. The upper end of the tube should be sealed with a ceramic disc, and the lower one extending down about 20–30 cm with a rubber stopper.

The time of growth depends upon the size of the crystal and lasts from 3 to 6 days. During this period the fluctuation of the furnace temperature must not exceed 0.02° C. This condition can be best ensured by using a stabilized heating current and a furnace with a double-walled jacket. Water of constant temperature should be circulated in the jacket.

When the crucible has reached the lower part of the furnace in its whole length the temperature is decreased very slowly at a constant rate (in several days) to room temperature. Even thus, the grown crystal—which cleaves rather well—may split into two or three pieces. When the crystal is being sawn and polished, care must be taken to avoid temperature differences of several degrees in it. During polishing the crystal is held with some heat insulating material because even the heat of the hand may cleave it. Sawing is best carried out with a thread moistened with cyclohexane.

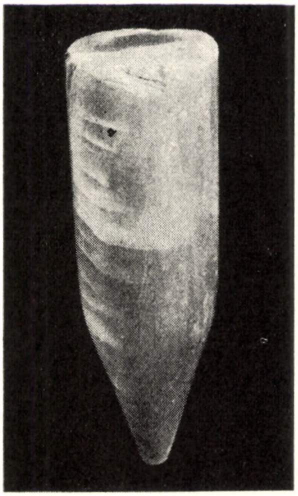


Fig. II.2.13 Anthracene crystal grown by the vertical gradient method
(on the left, cracks formed during cooling)

A crystal grown in the way described above is shown in Fig. II.2.13.

II.2.1.4. Growth of spherical silver crystals by the vertical gradient method

In order to study the development of various crystal forms experiments frequently proceed from spherical single crystals (see I.12.1.1 and I.12.2.1). For the purpose of growing spherical silver crystals, a dismountable graphite crucible is used in a vertical tube furnace heatable to 1 100° C. The growth space can be evacuated or filled with inert gas. The dismountable graphite crucible is about 60 mm long with a diameter of 10–12 mm (Fig. II.2.14). The spherical cavity moulded for the crystal has a diameter of 6 mm, and is connected with the funnel-shaped upper part of the crucible by a channel about 30 mm long and 1 mm in diameter. Approximately 1.7–1.8 g silver to be melted is placed in this upper part of the crucible. Silver of 99.99% purity is used; this can be obtained commercially in granulated, wire or plate form. It is advantageous to construct the crucible from anode graphite (also called Acheson graphite) because in this case crystallization starts with great probability from one single nucleus.

The electrically heated tube furnace is about 180 mm long with an internal diameter of 25–30 mm (see *1* in Fig. II.2.15). The length of the effective growth space, which is at 1 100° C, is 100 mm. The silica tube *2* about 450 mm long with a wall thickness of 3 mm and an internal diameter of 12–13 mm is placed in the furnace so that it protrudes about 80–85 mm at the upper end and 170–180 mm at the lower end. At the ground upper end of the silica tube can be placed the silica window *3* through which, with the aid of a mirror, the processes taking place within the furnace can be observed.

Fig. II.2.14 Dismountable graphite crucible to grow spherical crystals

If the window is sealed for example with pizein, the end of the tube must be surrounded with a pipe coil cooled with water to avoid the melting of the pizein. If Pyroceram cement (applied in the production of colour TV tubes) is used, the window can be heated up to 400° C without harming the vacuum sealing. The ground extension piece *4* is fitted to the lower end of the tube, which can be connected to a rotary vacuum pump. (To ensure a good sealing at the joint to the vacuum pump it is advisable to use silicone grease.) Lowering of the graphite crucible *5* can be carried out in various ways. One simple method is given in the following. The crucible is supported by the 100–110 mm long ceramic tube *6*, to the lower end of which is fastened the 80 mm long soft iron rod *7*, with a diameter of 8 mm and a weight of 30 g. The iron rod is the magnetic core of an electromagnet. The coil of the electromagnet *8* is suspended by metal wires *9*, and can be raised or lowered within a distance of 100 mm with the aid of a pulley. The counterweight at the other end of the wire over the pulley floats in water, and it rises with a rising water level while the coil sinks. The rate of sinking can be regulated by the rate of the water flow raising the level. Technical data of the coil: length 120 mm;

internal diameter 35 mm; external diameter 100 mm; the coil is made of 1 mm copper wire; it consists of 1 440 turns; current 3.5 A.

At the beginning of the experiment the crucible is fixed with the aid of the electromagnet in the centre of the furnace. After this the furnace is evacuated to 10^{-2} torr, and heated up to the melting point of silver. (The vacuum is measured for example with a Pirani gauge.) The lowering of the crucible begins only when the silver has melted and flowed down into the lower part of the crucible. This process is readily observable through the silica window. The advised rate of lowering is approximately 5 mm/minute. Under these conditions the growth is terminated after 20–25 minutes, and the furnace can be switched off. It is unnecessary to wait until the furnace cools down; the equipment can be dismounted at an elevated temperature of about 400° C. Air is first admitted into the system, the vacuum pump is disconnected, and the current of the electromagnet is switched off. The iron core, the ceramic tube and the crucible then fall out of the furnace. When

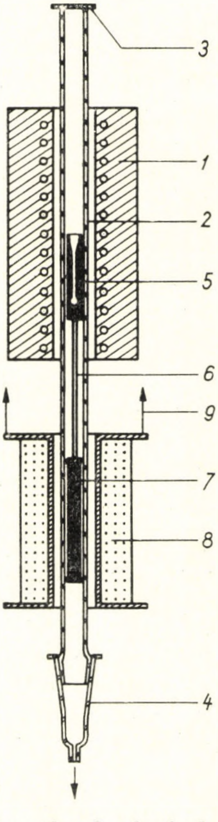


Fig. II.2.15 Growth of spherical silver crystals the crucible is dismounted the crystal sphere can be carefully pushed out with a metal rod about 0.8 mm in diameter applied at the funnel side of the crucible. If the crucible is handled with care it can be used for the growth of 20–30 samples.

The single crystal character of the silver sphere can be proved by etching. For this purpose the silver is kept at room temperature for a few seconds in 30% nitric acid and afterwards carefully rinsed in distilled water. As a result of etching, silky reflections appear which are characteristic of the single crystal. If the sphere consists of several grains, sharp, clearly observable contours are visible. The contours divide reflections of various orientations. The silver sphere is a single crystal only if, when it is looked from various directions, no sharp reflections can be detected.

II.2.2. Zone Melting

Zone melting is an extremely efficient method of purification. The method may also be used to grow crystals. The solid material to be zone melted should be placed in a boat, in an oblong crucible or in a tube sealed at both ends (Fig. II.2.16). The zone melting equipment may have a vertical or a horizontal lay-out. In both cases the sample is surrounded by a narrow ring-like heating element which is moved along it. Only one small section of the sample is melted, and this molten part travels together with the heating element.

Zone melting is efficient for purification if the impurity concentration in the melt (C_l) is different from the impurity concentration in the solid phase (C_s). Their ratio k is the distribution coefficient:

$$k = \frac{C_s}{C_l}$$

In most cases $C_s < C_l$, that is to say $k < 1$, and the impurities are carried along in the molten zone. If zone melting is repeated several times in the same direction the front part of the sample will become more and more pure, while the impurities accumulate at the other end.

In order to obtain an efficient purification, the following facts should be kept in mind. The zone length should be as small as possible. The most frequently used zone length varies between one tenth and one twentieth of the sample length. If the travel rate is too high the impurities in the molten zone are again incorporated into the solid phase on solidification before they can diffuse away from the fast moving zone-boundary into the inner parts of the zone. If on the other hand the travel rate of the zone is too small the compensation of the concentration differences by diffusion already begins during the purification procedure, with the result that the impurities diffuse back from the melt into the solid layers behind the zone. Consequently, the efficiency of zone-refining decreases at low travel rates as well as at high ones. The optimum travel rates for metals lie between 0.5 and 15 cm/h. In the case of several zone passes in the same direction increasingly pure material is obtained though in practice there is an upper limit to the purity obtainable; usually 20–30 passes are completed but in order to save time several passes can be carried out simultaneously with heaters placed at short distances from each other.

If single crystals are grown it is especially important to select crucible materials to which the melt does not adhere. Adhesion may result—especially in the case of vertical zone melting—in deformation or even in fracture. This danger can be reduced by moving the zone downwards in the case of materials expanding on melting, and upwards in the case of materials contracting in the liquid phase. With a horizontal lay-out the formation of a single crystal is ensured by starting the zone from a seed crystal placed in the end part of the boat. The same applies to a vertical lay-out, a single crystal being obtained if the zone travelling upwards is started from the appropriately shaped pointed end of the crucible or from a seed placed in the bottom of the crucible. This latter method, however, can be used only with restrictions because of the reasons discussed above. In order to avoid stresses and deformations, especially with materials of high melting point, it is advisable during the zone melting to keep the temperature of the whole growing sample somewhat below the melting point, and apply a separate, movable heater for the purposes of zone melting. The grown bar must be cooled down to room temperature slowly and uniformly throughout its total length. If the crystal growth immediately follows the purification of the material, i.e. if both processes are carried out in the same apparatus, the achieved purity can be preserved during crystal growth.

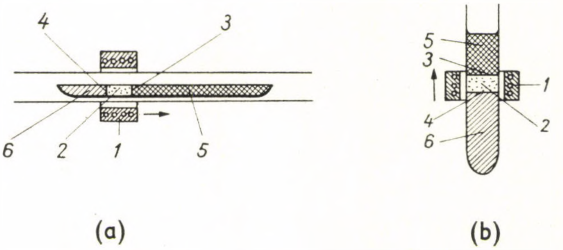


Fig. II.2.16 Zone melting

(a) Horizontal and (b) vertical zone melting; *1* heating element, *2* molten zone (arrow indicates direction of travel of the zone and at the same time the direction of impurity accumulation), *3* zone boundary on melting side of the zone, *4* zone boundary on solidifying side of the zone, *5* unmolten solid material, *6* zone-refined solid phase

An important variant of crystal growth by zone melting is the so-called *floating-zone method*. Its main feature is that a bar must be made of the material (e.g. by sintering), which is fixed only at the two ends, and the molten zone is held together by surface tension. As no crucible is used, the possibility of contamination is greatly decreased.

The advantage of growing crystals by zone melting is that it offers a relatively simple way of producing doped crystals containing deliberately admixed additives in given concentrations, within the required limits of error, and in a uniform distribution. This variant of zone melting is called *zone levelling*. The inhomogeneities of the concentration can be decreased in several ways. In one variant of zone levelling the zone is passed several times backwards and forwards along the rod-shaped ingot containing the additives. In another variant the zone is moved several times in the same direction around a closed ring-shaped sample. A procedure that proved successful in practice is to start with a pure material and place the additives in a given concentration in the molten zone, then to pass the zone several times along the sample. In this case too the zone is passed backwards and forwards along rod-shaped ingots and in the same direction around ring-shaped ones. The concentration of the additives is given here too by the equation $C_s = kC_l$, where C_l is the concentration in the molten zone, C_s the concentration in the solid phase, and k the distribution coefficient.

There are various methods of producing molten zones. The most simple one consists in surrounding the sample with a wire loop, a spiral or a strip of metal heated by electric current. Zones of short length, especially in the case of melting metals by the floating-zone method, are obtained by high frequency induction heating. A further advantage of this method is a continuous mixing of the melt by eddy currents induced in it; this prevents the accumulation of the impurities in the solidifying side of the zone. The radiation energy of incandescent lamps may also be used for the purpose of zone melting; the energy is focused with the aid of mirrors onto a small section of the sample to be melted. Finally, melting with cathode rays should be mentioned briefly. Electrons are obtained from a hot tungsten wire or tape cathode surrounding the sample ringwise. The sample itself is the anode. The electrons are accelerated with a voltage of a few kV, and are focused on the sample with a suitable electron-optical device.

II.2.2.1. Purification of anthracene by vertical zone melting

Even the purest anthracene supplied commercially contains tar impurities which deteriorate the fluorescence of single crystals prepared for scintillation purposes. Several methods are known for purifying anthracene crystals; we describe here zone refining carried out in a hydrogen atmosphere. For this purpose a 2 m long thermoduric glass tube of 1 cm internal diameter is used. One end of the tube is sealed off (Fig. II.2.17), washed with a mixture of concentrated sulphuric and nitric acids, rinsed thoroughly with distilled water, and dried. When dry the upper open end of the tube is stretched so that it may easily be sealed off later. A small funnel-shaped part is left in the extended part, and this is used to fill the tube with powdered anthracene. When the tube is filled up almost to the funnel, it is connected with the aid of a rubber stopper and two three-limb vacuum stopcocks to a rotary pump. One free limb is connected to an apparatus supplying pure, dry hydrogen (see experiment II.2.1.3) and the other one to an open mercury manometer. The tube is evacuated to 0.1 mm Hg, and filled with hydrogen by turning the key of the stopcock leading to the hydrogen supply. In order to eliminate any residual oxygen as completely as possible, the evacuation and filling are repeated three times. After this the tube filled with anthracene powder and hydrogen is heated carefully with a gas flame until the anthracene melts, and the melt runs down into the lower part of the inclined tube. The melt fills only less than half of the tube. After cooling, the stopper is removed from the funnel, and the empty part of the tube is again filled with anthracene powder. After the tube has been evacuated, and filled with hydrogen three times, the anthracene is melted as before. This process is repeated until the tube is filled with anthracene up to 15 cm from the upper end. After the last hydrogen filling the tube is evacuated, connected to the manometer and the hydrogen supply, filled with hydrogen to a pressure of 600 mm Hg, and the open end is sealed off. The manometer must also be filled with hydrogen, and evacuated several times before connecting it to the tube.

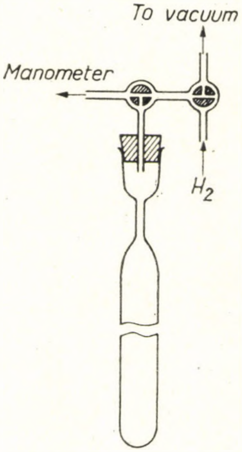


Fig. II.2.17 Filling of glass tube to grow anthracene

The tube is placed in a vertical position in four heating furnaces arranged above each other as shown in Fig. II.2.18. The distance between the neighbouring furnaces should be 5–7 cm. The lowest furnace surrounds the top part of the anthracene. Each furnace consists of heating coils made of wires of identical resistivity wound on 10 mm high ceramic rings. The diameter of these rings is 1–2 mm larger than the tube diameter. The furnaces should be connected to a stabilized voltage source. The heating is regulated so that the zone width is about 10 mm. The power demand of each furnace is about 50 W.

When the lowest furnace melts the top of the anthracene, the row of furnaces is lowered along the whole length of the tube at a rate of 2 mm/hour. One run means four zone passes. After the first run the furnace assembly is pulled back, and the process is repeated four times. The tar impurities accumulate in the melt and thus become concentrated towards the bottom of the tube. At the end of the last run the larger part of the anthracene is white (with a blue fluorescence), while towards the bottom of the tube its colour is first yellow, then brown, and finally black. After cooling, the 20–30 cm long lower tube end with the contaminated anthracene in it is cut off. The glass must be carefully broken off from the pure anthracene. If larger quantities of anthracene are purified, several tubes should be used; their furnace assemblies may be lowered from a common spindle.

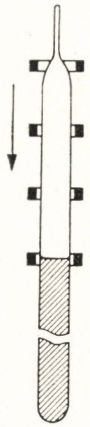


Fig. II.2.18 Apparatus for zone refining of anthracene
The arrow indicates the direction of motion of furnaces

II.2.2.2. Growth of tin crystals by zone melting in a horizontal boat

As regards the preparation of the polycrystalline material and the apparatus, this experiment is in many instances quite similar to experiment II.2.1.1. Consequently only the differences will be discussed here. With this method the growth starts from a seed cut off a single crystal, and placed at the relevant end of the tube (Fig. II.2.19). If a single crystal of given orientation is desired a properly oriented seed must be cut off. A thin-walled silica boat should be used. If the seed is large enough the boat may

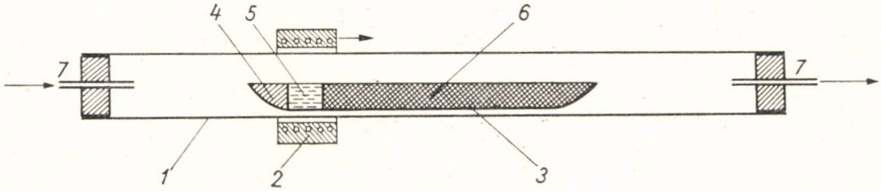


Fig. II.2.19 Growth of tin crystals by zone melting
1 silica tube (length 60 cm, outer diameter 3.6 cm), *2* heating coil (9 turns made of KANTHAL-A wire 2 mm in diameter, 7 V, 25 A), *3* silica boat (1.5×2×20 cm), *4* seed, *5* molten zone, *6* polycrystalline bar, *7* inlet and outlet of inert gas

have a uniform cross-section, but in the case of a small seed one end of the boat must be appropriately narrowed down. The crystallizing apparatus described in II.2.1.1 (Fig. II.2.3) is used but the tube furnace is removed, and the zone melting coil is placed on the movable support *3*. The coil consists of 9 turns of KANTHAL-A wire 2 mm in diameter, with an internal coil diameter of 3.8 cm. As power supply a stabilized voltage source is used, the heating power being 7 V and 25 A.

The growth should be carried out as follows. With a fret saw a piece about 2 cm long is cut off a tin single crystal, this will be the seed. The cut surface is polished with a set of graded emery papers. Before starting with the finer grade emery paper, the damaged layers are removed by etching with a 5 N hydrochloric acid solution. After the final polish the sample is once more etched in hydrochloric acid for at least 30 minutes. If the etching results in a smooth, homogeneous surface, the removal of the deformed surface is complete and the sample can be used as a seed. Instead of mechanical cutting it is better to use for example the more intricate chemical or electrochemical cutting methods which cause less deformation. The seed is placed close to the polycrystalline material in the silica boat, the boat put into the silica tube, and the gas flow (purified argon) is started. The heating coil is placed near the edge of the seed which is carefully melted to the polycrystalline rod by slow heating. The perfect merging of the two surfaces might be hindered by an oxide layer or some other factor. Therefore it is advisable to melt a layer of the seed at least some millimeters long. The pulling assembly is switched on (suggested pulling rate is 4 cm/hour). After the termination of crystal growth, it is checked by etching with 5 N hydrochloric acid solution whether a single crystal is obtained.

With this method other metals with low melting points (e.g. Cd, Zn, In) may also be grown (and purified).

II.2.2.3. Growth of InSb single crystals by horizontal zone melting

The zone melting method is frequently used to purify elementary (Ge, Si) and compound semi-conducting materials, or to grow single crystals from them. Purification and crystallization of an intermetallic compound InSb of the type $A^{III}B^{V}$ is as follows.

InSb crystallizes in a sphalerite type lattice. The compound can easily be produced by melting a mixture of the two components in the proper stoichiometric ratio. (The phase diagram of the system is shown in Fig. II.2.20.)

InSb crystals can be grown in any of their low index directions ($\langle 111\rangle$ $\langle 110\rangle\langle 100\rangle$), but they grow most easily in the $\langle 111\rangle$ one. There is a greater probability of twinning in the other two directions. Single crystals should be grown in a graphite or a graphitized silica boat (Fig. II.2.21). This type of boat is not wetted by the melt, and consequently the probability of the growth of a polycrystalline structure is small. Single crystals can thus be grown without seed. In order to obtain a crystal of uniform cross-section all along its length, the boat must be tilted. If the boat is horizontal the cross-section of the growing crystal will increase in the direction of the growth, because the density of the InSb melt is considerably greater than the density in the solid phase (6.48 g cm^{-3} and 5.74 g cm^{-3}), and as a result of this the material will be transported in the growth direction when the zone passes. The angle of tilt (Θ) at which material transport still does not occur can be calculated from elementary considerations. The formula is

$$\Theta = \tan^{-1} \frac{2h_0(1-\alpha)}{l}$$

where h_0 is the height of the solid phase, α is the ratio of the densities of the crystal and the melt at the melting point, and l is the length of the molten zone. The suitable angle of tilt should be set according to the above equation. The boat is put into a silica tube in which protecting gas can be circulated. Nitrogen or some inert gas free of oxygen and water vapour should be used. With this zone-melting furnace a 1–2 cm long zone can be produced with a maximum temperature of 600° C.

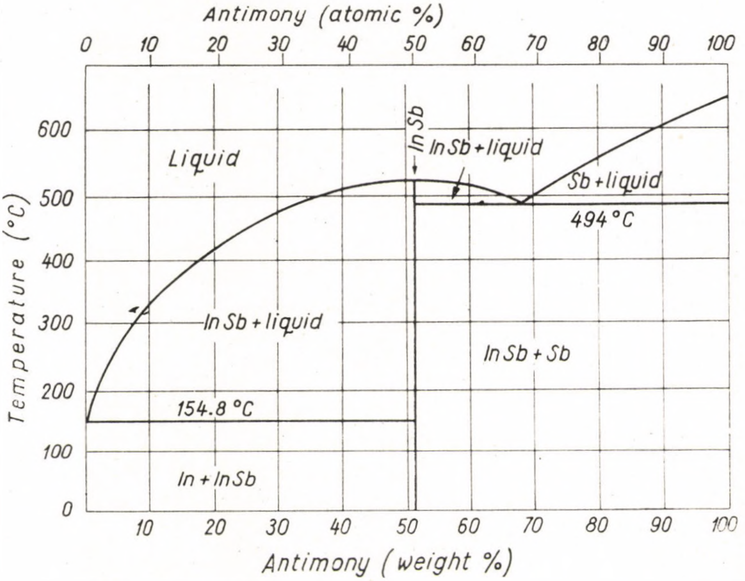


Fig. II.2.20 Phase diagram of the system InSb

Growth procedure. The boat with the InSb ingot is put into the zone-melting equipment. The protecting gas supply is switched on; a flow rate of 50–100 l/hour is suggested. The angle Θ calculated according to the above equation (e.g. $h_0 \approx 1$ cm, $l \approx 1$ cm, $\alpha \approx 0.885$ and $\Theta \approx 13°$) is then set so that the lower part of the boat is directed towards the gas inlet. The movable furnace is placed at the lower end of the boat, and after about 15 minutes heating is started. The heating power must be regulated to obtain a zone length of about 10–15 mm. After a period of 5–10 minutes for steady state conditions to be obtained, the driving mechanism of the furnace is switched on and the travel rate of the zone set to 1–3 cm/h. If the ingot is still polycrystalline after the zone has been passed, the process must be repeated at a lower rate. When zone melting is finished, heating is switched off, and the furnace stopped. The gas stream, however, must be kept on until the system cools to room temperature. The crystals obtained are suitable for texture and dislocation studies and for a study of their semiconducting properties.

If a properly shaped polycrystalline InSb ingot is not available, it may be produced in the following way. Into a clean, dry silica tube, one end of which is sealed, equivalent quantities of pure (e.g. 99.9%) metallic indium and antimony are measured. [To obtain a 10 cm long InSb ingot with a cross-section of 1 cm^2, 0.25 gram-atom (= 28.7 g) indium and 0.25 gram-atom (= 30.45 g) antimony are needed.] The radius of the silica tube must be equal to the radius of curvature of the boat. The tube should be long enough so that the molten In and Sb fill about one-third of its volume. In this way the ingot fits well into the boat. The tube is connected with a rubber vacuum pipe to a vacuum pump, and evacuated to a pressure of less than 10^{-3} mm Hg. After the desired vacuum is obtained, the tube is sealed off with a coal-gas-oxygen, or an oxyhydrogen flame, and put into the uniformly heated zone of a horizontal furnace. The molten material is kept for an hour at a temperature of 580° C. In order to complete the reaction, the contents of the tube are mixed by shaking without taking the tube out of the furnace. After annealing the warm tube is taken out, and put on a horizontal asbestos sheet. When it has cooled down to room temperature, the tube is carefully broken so that its contents do not become contaminated. It is advisable to use such a quantity of material that not only is the cross-section of the ingot equal to that of the boat but also their lengths are equal. In this case the ingot may be placed directly into the zone melting boat.

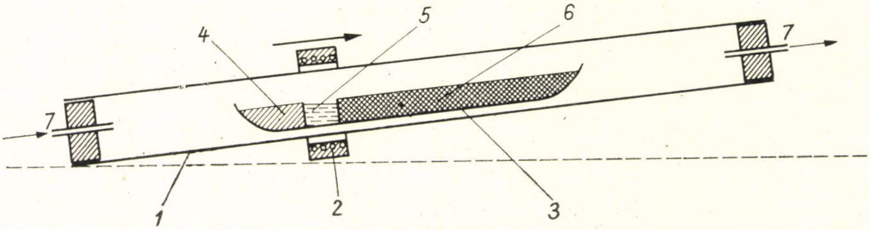


Fig. II.2.21 Apparatus for zone melting of InSb

1 silica tube (length is about 100 cm, diameter is 3–5 cm), *2* heating coil, *3* graphitized silica boat (length is 15–20 cm), *4* single crystal, *5* molten zone (length is about 1 cm), *6* polycrystalline bar, *7* inlet and outlet for inert gas

II.2.2.4. Growth of KCl crystals by vertical zone melting

The experiment consists of three consecutive stages, viz. (a) the polycrystalline material is melted, placed in a silica crucible, and the melt purified from impurities containing oxygen by the passage of CCl_4 vapour through it; (b) the upper end of the crucible is sealed off, and the melt cooled to room temperature; in this way a polycrystalline bar is obtained which will be purified by zone melting; (c) after about twenty zone passes the growth of the single crystal is started in the same apparatus but with a reduced zone speed.

A more detailed description of the procedure is as follows. The crucible used for purification purposes should be made of a 35–40 cm long silica tube with a diameter of about 2 cm. The surface of the silica tube must be even (mechanically drawn tubes are used). Uneven tubes cannot be used because the variable cross-section may lead to fracture during the zone melting. One end of the tube is rounded off, the other is provided with an 8–10 cm long tube with a diameter of about 8 mm (Fig. II.2.22). The crucible is purified by boiling for about 3 hours in concentrated nitric acid and sulphuric acid. After this it is rinsed first with isothermally distilled hydrochloric acid and then thoroughly with double-distilled water. The purified crucible is put into a 40–45 cm long tube furnace which is then heated up to about 1 000° C (case *a* in Fig. II.2.22); CCl_4 vapour in a 99.99% pure argon carrier gas stream is passed into the preheated crucible through its capillary. The CCl_4 vapour decomposes at this high temperature resulting in a thin carbon layer which covers the inner wall of the crucible. The decomposition products (some of them poisonous) must be removed through an efficient exhaust system. When a transparent carbon layer has formed, the crucible is removed from the furnace (the Ar + CCl_4 stream is continued),

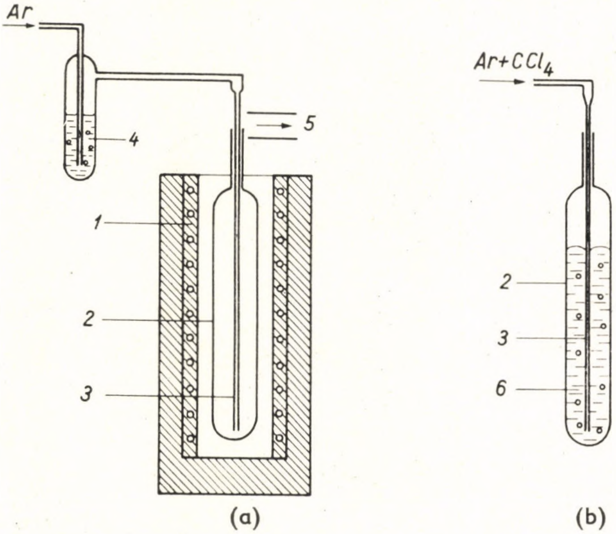


Fig. II.2.22 Apparatus for the removal of impurities containing oxygen from KCl

a) formation of a carbon layer on the inner wall of crucible; (b) purification of the melt; *1* furnace, *2* silica crucible, *3* silica capillary, *4* carbon tetrachloride, *5* exhaust, *6* melt cooled down, and filled with granulated potassium chloride. The crucible is put back into the furnace, and the potassium chloride melted in the presence of the Ar + CCl_4 stream. The gas is bubbled through the melt until its surface becomes convex (case *b* in Fig. II.2.22). In this second heating of the crucible a reaction takes place between the decomposing CCl_4 and the impurities containing oxygen (e.g. O_2, OH), and the gaseous reaction products (e.g. CO_2, HCl) are removed with the argon stream. This conclusion is drawn from the fact that the melt does not wet the silica. When the

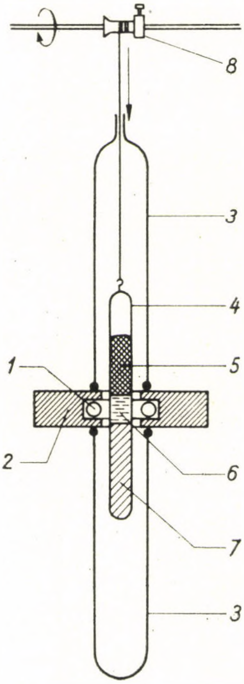


Fig. II.2.23 Zone melting of KCl

1 heating coil, *2* ceramic ring, *3* glass tubes, *4* sealed silica crucible, *5* polycrystalline bar, *6* molten zone, *7* single crystal, *8* lowering assembly

described procedure is finished, the capillary is taken out. The crucible containing the melt is sealed immediately and a hook is made from the silica extension remaining after the removal of the capillary. The melt is either put into the tube furnace, and cooled down together with the furnace to room temperature in about 24 hours, or the crucible with the melt is put into a 40–45 cm long preheated tube furnace, and lowered from this furnace into room temperature at a rate of 6 cm/h. The solidified matter in the latter case is much denser and better for the zone melting procedure. The preparation of the material, as described above, is correct if the solidified sample comes off the crucible wall at every point. Treatment with CCl_4

for only a short time, or a slow sealing of the crucible, results in sticking of the melt to the crucible wall. Sticking may also be caused by faulty sealing. Only well-prepared material can be used for crystallization by the zone melting method.

The zone melting furnace used for experiments (b) and (c) consists of a KANTHAL-Al coil embedded in a ceramic ring (Fig. II.2.23). The surface of the coil around the silica crucible is left free of ceramic. Protecting glass tubes placed above and below the surface decrease the heat loss, and protect against air eddies. The power demand of the furnace is 500–1000 W depending upon its heat insulation. The zone length should be about 25 mm. Since the dissipation of heat is different in the various positions of the crucible, the temperature must be regulated. The crucible is moved by applying for example an electrically driven control mechanism (rate of lowering about 60 mm/h, pulling back within 30 seconds). The crucible should be placed in a preheated furnace, and about 20 passes should be carried out. In the case of a relatively fast zone travel, gas inclusions are formed in the material. Consequently, the last pass must be slow; in this case, at a rate of 1–2 mm/h, the crystal grows free of inclusions. (See Fig. II.2.24.)

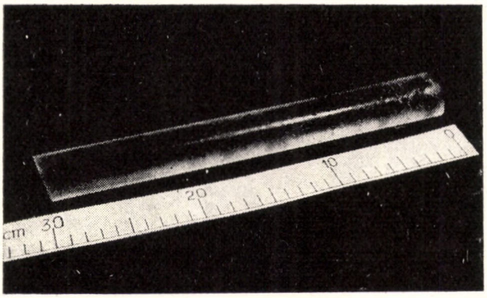


Fig. II.2.24 KCl crystal grown by zone melting

II.2.2.5. Production of germanium single crystals by the horizontal zone melting method

Germanium crystallizes in the diamond structure its melting point being 958.9° C. It is an important base material in the production of semiconducting devices. For these purposes the starting material is carefully zone-purified germanium. Five- or three-valent elements (usually antimony or indium) are incorporated in appropriate concentration into the four-valent germanium crystals. In this way germanium of the required specific conductivity may be obtained. In the first case the charge carriers are mainly electrons (n-type conduction), and in the second case defect electrons (p-type conduction). Germanium crystals are usually produced either by the horizontal zone refining method or by the Czochralski method. In the present case one variant of the former method is discussed.

(1) The purpose of the experiment is to produce *n*-type germanium single crystals with a specific resistivity of about 3 ohm cm at 20° C. Zone-refined polycrystalline germanium is used as base material. The growth is started from a purified single crystal seed. In the case of germanium crystals produced for semiconducting devices, the purity of the base material is usually characterized by its specific electrical resistivity. Germanium is satisfactorily pure for growth if its specific resistivity at 20° C is about 40 ohm cm· In the experiment to be described antimony doping is used.

(2) Growth procedure.—An example is given in Fig. II.2.25 where the rod to be grown has dimensions of $2 \times 2 \times 20$ cm and the length of the molten zone is 3 cm. The growth is carried out in a silica boat coated with soft amorphous carbon black (see below); the distribution of antimony is also shown. At the beginning of growth all of the additive is in the molten zone; however, as soon as the zone moves antimony also becomes incorporated into the single crystal growing behind the zone. If the zone is run once along the polycrystalline rod, the concentration of the additive in the single crystal may be calculated as a function of the distance from the seed using the following formula

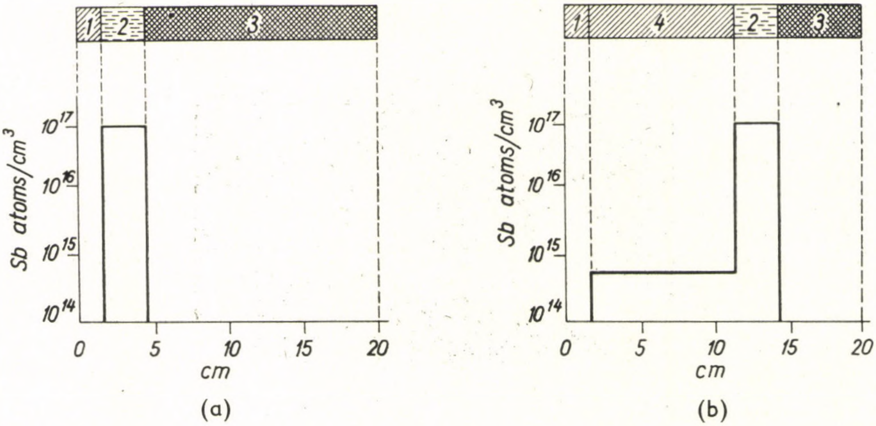


Fig. II.2.25 Diagram to growth procedure

(a) position of zone and distribution of additive at the beginning of growth; (b) position of zone and distribution of additive at some later time; *1* seed crystal, *2* molten zone, *3* polycrystal, *4* grown single crystal

$$C_s = k \cdot C_l e^{-k\frac{x}{l}}$$

where C_l is the initial additive concentration of the molten zone, C_s is the concentration of the additive in the single crystal at a distance x from the seed, l is the length of the molten zone, and k is the distribution coefficient. With increasing x values C_s decreases, but this decrease is smaller when the k values are small. For antimony $k \approx 5 \times 10^{-3}$, and consequently even in the case of a monocrystalline rod with a tenfold zone length the antimony concentration decreases only by 1%. According to the above relation this means that the antimony distribution is homogeneous within 1%. The horizontal straight line in Fig. II.2.25b indicating the concentration distribution in the single crystal part is accounted for by this relatively small change of concentration.

The quantity of antimony to be put into the zone may be determined with the aid of Fig. II.2.26. According to the Figure the specific resistivity of the germanium single crystal attains the prescribed value of 3 ohm cm if the concentration of the antimony atoms in the crystal is 5×10^{14} cm^{-3}. From this it follows that for $k = 0.005$ a concentration of 10^{17} cm^{-3} must be produced in the melt. Since the volume of the molten zone in the present case is $2 \times 2 \times 3$ cm^3 the zone must contain 1.2×10^{18} antimony atoms or 0.244 mg (the atomic weight of antimony is 122). Since considerable errors are likely to occur in the measuring and placing of such small quantities into the zone, the additives are used not in their elementary form but dissolved in germanium as so-called master ingots. In the present case it is advisable to use a master ingot of several times 10^{17} cm^{-3} concentration, and from this cut off a piece containing the amount of antimony necessary for the experiment. This piece is placed in the boat between the seed and the polycrystalline germanium. The experiment is begun by melting a zone

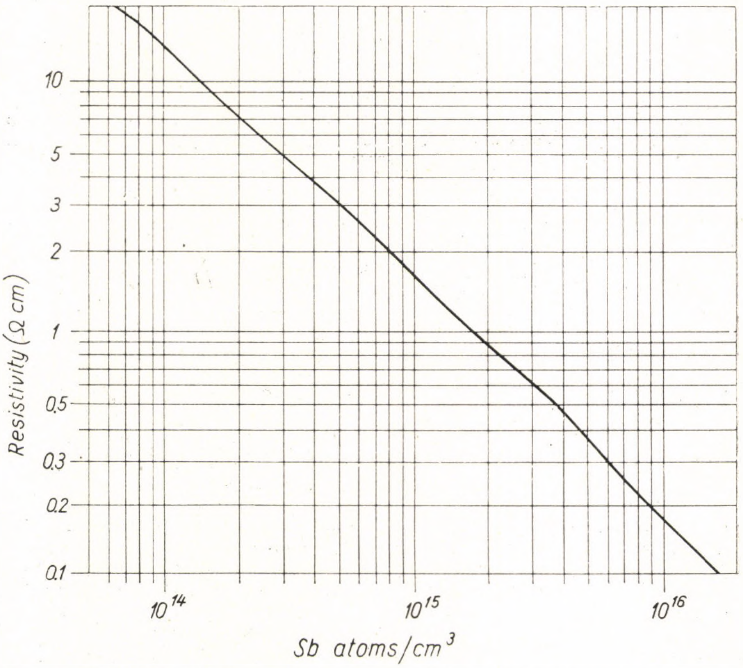


Fig. II.2.26 Empirical relation between concentration of antimony incorporated into the germanium and specific resistivity of germanium
Resistivity of indium-doped germanium with same indium concentration is about twice larger

which contains the master ingot, a part of the seed and the polycrystalline germanium. This is possible since the volume of the master ingot, because of its large antimony concentration, is smaller than the volume of the whole molten zone. In order to obtain a uniform antimony distribution in the melt the zone is held in its initial position for about 30 minutes, and only after this is the growth started. In the case of germanium crystals produced for semiconducting devices, seed crystals are used whose orientation ensures a crystal growth in the direction normal to the (111) face.

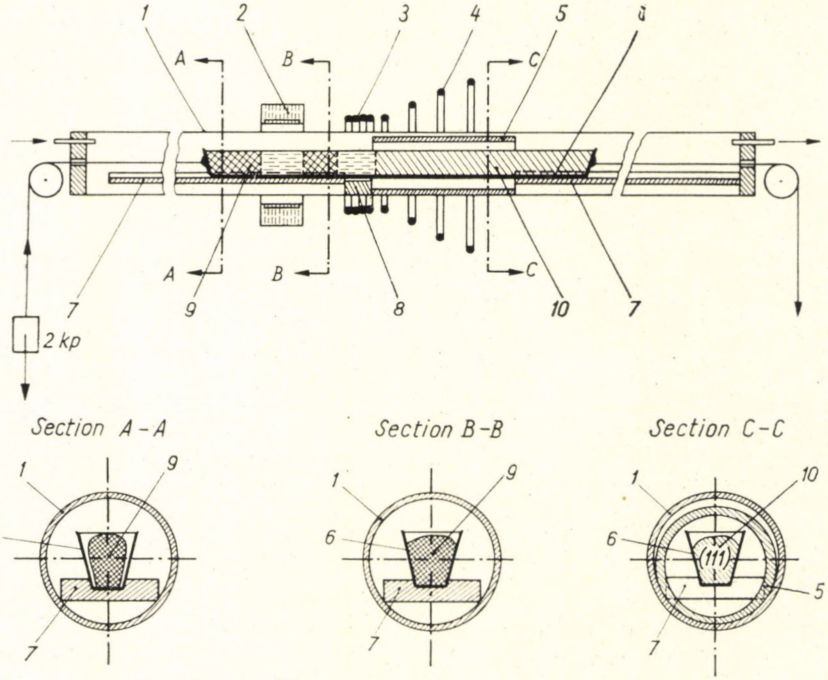


Fig. II.2.27 Diagram of the growth equipment

1 transparent silica tube (length is about 70 cm, internal diameter about 3 cm) with closed ends, flushed continuously with nitrogen containing 25% hydrogen, *2* resistance heater to fuse the polycrystal into the boat, *3* high frequency coil (about 500 kHz) heating the germanium directly; the eddy currents developed by the inductive heating agitate the melt, *4* high-frequency afterheating coil, *5* graphite tube heated by the afterheater ensuring the slow, uniform cooling of the grown crystal, *6* silica boat (length about 20 cm, internal width 10–12 mm, internal height about 12 mm), *7* graphite rails, *8* separating ceramics, which cannot be heated with a high-frequency generator, replacing the graphite rails placed below the coil *3*; *9* polycrystal, *10* single crystal

Figure II.2.27 shows the placing of the boat into the growth equipment. The zone is produced by means of inductive heating. The heating coil is fed by a generator working at 500 kHz with an output of about 10 kW. In order to obtain a constant temperature the output must be regulated with considerable care. Good quality crystals can be grown if the temperature gradient is relatively large at the growing surface (40–60° C/cm). A 3 : 1 N_2 and H_2 gas mixture is used as protective gas. It is important to free the protective gas from oxygen and water; it is advisable to use some catalytic system (e.g. the puri-dryer system) for this purpose. The first stage consists in freeing the gas mixture from its oxygen content by uniting the O_2 traces with hydrogen to form water at room temperature. At the next stage a molecular sieve adsorbs water traces produced at the first stage and still present in the gas. The dew-point of the purified gas must be below $-50°$ C. The velocity of the gas stream is set to about 40 l/hour. Before the growth procedure is started, the equipment is flushed with the protective gas for about 5 minutes. After this the gas streaming out of the equipment is burnt at the gas outlet.

Besides the coil producing the molten zone an afterheating coil is used which is also fed by a radio-frequency generator. The grown crystal is slowly cooled down in the heat zone of the afterheater to approximately 500° C. This temperature is the lowest limit of plastic deformation. In this way the defects produced by deformations due to thermal stresses are decreased.

During the growth process either the inductive coils fixed on a silica tube or the boat may be moved (pulled). The suggested rate of growth is 1 mm per minute. Thus, as a result of the high temperature gradient (40–60° C/cm) near the growing surface, constitutional undercooling may be avoided. The pulling of the heating coils is usually carried out by wheeling the supporting structure on rails, while the boat is moved by pulling it inside the growth tube (Fig. 2.27 shows this latter method). Much care must be taken to move both the boat and the coils uniformly. If the boat is moved for example, it should be made of a smooth-walled mechanically drawn silica tube, and pulled on polished graphite rails. Any risk of uneven movement or jerks may be avoided by pulling against a counterbalance of approximately 2 kg.

(3) Further practical advice. (a) The nucleus-forming effect of the boat wall can be decreased by coating it with a soft amorphous carbon black layer. The germanium melt does not wet this layer. The following procedure is suggested. First roughen the boat surface by sanding, then clean the surface obtained. The coating of soft carbon black is obtained by using a 2 : 1 toluene–ethanol mixture through which hydrogen is streamed. The gas mixture is passed through a suitably thinned silica tube and lit at its end. The roughened surface of the boat is treated until its surface becomes uniformly coated with carbon-black. The surface is sometimes covered with a hard carbon layer, which in turn is coated with soft carbon-black. The hard layer is best made of carbon used to make carbon film resistors.

(b) If the crystals are grown for semiconducting devices much care must be taken to avoid the formation of lattice defects. This can best be attained by a low growth rate. It should also be considered, however, that the dislocations of the seeds may grow into the new crystal, and that defects may also be produced by plastic deformation. The dislocation density of the seeds is determined by the etching technique [see paragraph (d) below]. Crystals with the lowest dislocation densities should be selected as seeds; the surface density should not be more than 3000–5000 dislocations per cm^2. New defects (dislocations) may be created by stresses due to a non-uniform cooling of the crystal. This can best be avoided by using the afterheating coil mentioned above. The afterheating considerably decreases the temperature difference between the interior of the crystal rod and the lateral surfaces (i.e. the radial temperature gradient). The crystal cools down mainly by longitudinal heat dissipation. In this direction, however, the temperature gradient is relatively small (5–10° C per cm) if afterheating is applied, and consequently no large plastic deformation occurs in the longitudinal direction.—Figure II.2.28 shows a crystal grown by zone melting.

(c) The seed crystal, the polycrystalline rod and the master ingot are degreased with CCl_4, and after drying kept in a so-called BS solution at approximately 75° C for 5 minutes. After this treatment the sample is rinsed with de-ionized water till it becomes acid-free (at least ten rinsings). Finally the samples are washed in ethanol and dried on filter paper. The BS solution contains 385 ml conc. HNO_3, 600 ml de-ionized water and 126 g tartaric acid. The silica utensils are cleaned with hot BS solution, de-ionized water and finally washed in ethanol. The coating of the silica boat with amorphous carbon-black is carried out only after this procedure.

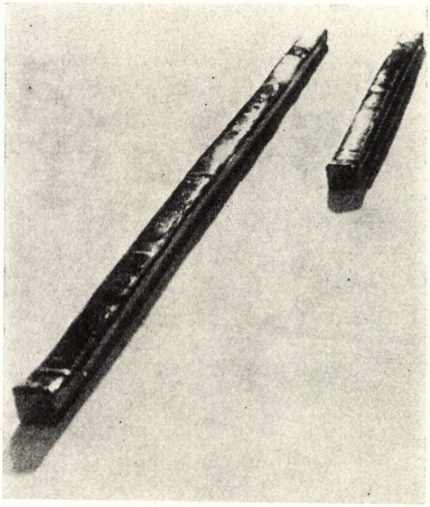


Fig. II.2.28 Germanium single crystal rods of trapezoidal cross-section
Length of larger piece is 90 cm, its cross-section is 5 cm²

(d) The etchants revealing the dislocations in germanium crystals produce regular etch pits only on one or two crystal faces: on the {111} and {100} planes. If the orientations of the examined surfaces deviate from the {111} and {100} planes the shapes of the etch pits are distorted, and from the distortion the degree of deviation may be determined.

In order to reveal the dislocations on the {111} planes the following procedure is suggested (see II.5). The polished crystal surfaces are cleaned as described previously, and then etched at 70° C with an etchant composed of 25 ml conc. HNO_3, 15 ml conc. HF and 25 ml glacial acetic acid (CP4–A etchant) for approximately one minute. After this the crystal is washed in de-ionized water, and boiled in Billig solution for 3 minutes.

During this latter procedure the already developed etch pits blacken, which makes their microscopic observation easier. The Billig solution is a 1 : 1 volume mixture of 14% $K_3Fe(CN)_6$ and 20% KOH solutions. The etch pits are clearly visible at a magnification of 50. In the case of {111} planes the etch pits to a good approximation are trigonal pyramids bounded by {322} planes. If the orientation of the etched surface is exactly {111} the contour of the pits is an equilateral triangle. In the case of a different orientation the pyramid is elongated according to its oblique cut. In this case isosceles triangles are usually visible. The orientation may be determined from the base-to-height ratio of the triangles. (Fig. II.2.29).

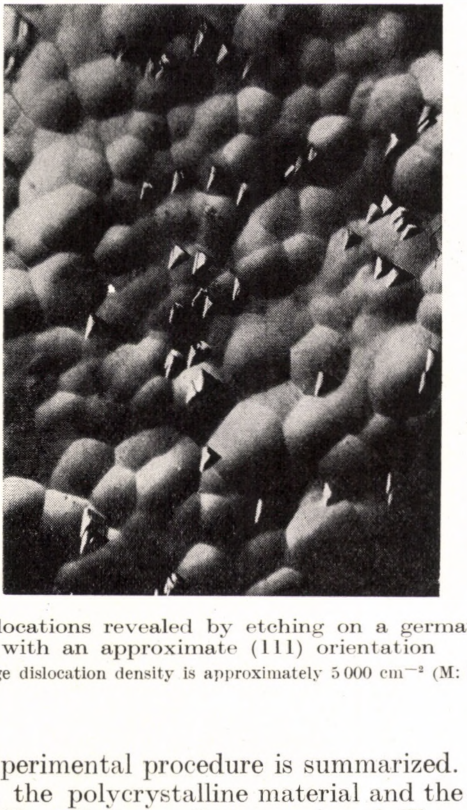


Fig. II.2.29 Dislocations revealed by etching on a germanium surface with an approximate (111) orientation

The average dislocation density is approximately 5 000 cm^{-2} (M: 200×)

(e) Finally the experimental procedure is summarized.

The seed crystal, the polycrystalline material and the master ingot are purified chemically. The silica utensils are prepared. The growth equipment is assembled, and the gas stream is started. The radio-frequency generator is switched on, and the molten zone is produced by fusing the seed crystal, the master ingot and the polycrystal. The speed of the pulling motor moving the heaters is set, and the growth is started. After the termination of the growth the pulling motor is stopped and the radio-frequency generator switched off. When the single crystal has cooled down to room temperature the gas stream is switched off.

II.2.3. Crystal Pulling

The method essentially consists in immersing a cooled crystal in the melt, and then pulling it out slowly (Fig. II.2.30). Care must be taken that the crystal remains in contact with the melt throughout the whole process. Thus the melt gradually becomes frozen onto the seed crystal. The method gives the impression of the crystal being pulled out of the melt. The variants of the method are named after the research workers who applied them first: the Czochralski and the Kyropoulos methods, the latter frequently also called the Nacken–Kyropoulos method. (Czochralski's name is most often mentioned in connection with the growth of metal crystals by pulling.) The main advantage of the method is that it does not require any growth vessel; its disadvantage, on the other hand, is connected with the fact that the control of the temperature gradient is rather limited.

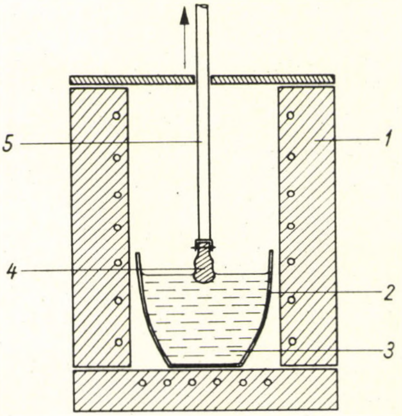


Fig. II.2.30 Pulling method

1 furnace (heating of sides and bottom can be regulated separately), *2* crucible, *3* melt, *4* seed crystal, *5* cooling tube

II.2.3.1. Growth of alkali halides from the melt by the Nacken–Kyropoulos method

As seeds are used some grown crystals, or, if there are no single crystals at hand, one of the small crystals frozen onto the bottom of the cooling tube immersed into the melt. Cooling tubes of low heat conductivity and rough surfaces are best used. For example, a silica tube cooled by an air-stream is quite appropriate (Fig. II.2.31). If necessary, some other crystal may also be used as seed if its lattice constant, and physical and chemical properties are similar to those of the crystal to be grown. For example good NaCl, or NaBr crystals can be grown by using PbS as seed. Alkali halides crystallize quite easily; thus seeds can be obtained by melting the granulated material in a crucible, letting the melt cool down slowly, and choosing larger grains from the polycrystalline material obtained.

The crucible material may be porcelain with an unglazed inner surface, aluminium oxide or platinum. A simple porcelain jar can also be used with quite satisfactory results. Alkali halide melts attack porcelain or aluminium oxide crucibles if the material is molten in air, and even platinum crucibles may become damaged. Thus a high standard growth technique demands the use of some inert gas.

Cooling, and consequently the rate of growth and the size of the grown crystal, depend greatly upon the fixing of the seed to the cooling tube. If the seed is not properly fixed to the tube the weight of the growing crystal may break off the seed. A simple method of fixing is to suspend the seed by a nickel wire from the end of the cooling tube. For this purpose grooves are made in the tube-end. It is customary to drill a hole through the seed, and pull the wire through it. A more reliable method is to grip the seed between for example nickel clamps (Fig. II.2.32). The diameter of the cooling tube and the thickness of the seed are usually only slightly different. The size of the grown crystal depends not only on the dimensions of the furnace and the crucible, but also on the thickness of the seed. In the case of a furnace with an internal diameter of 3–10 cm and a crucible of appropriate size, the seed crystal thickness is about 0.8–1.0 cm, and the diameter of the cooling tube is approximately the same. The rate of flow of the cooling water should be regulated so that the temperature of the water flowing out of the cooling tube is at most tepid. In order to obtain a uniform crystal growth it is advisable to rotate the seed at about 1 revolution/minute (Fig. II.2.33).

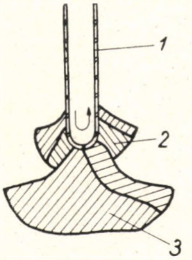


Fig. II.2.31 Preparation of seed crystals
1 silica cooling tube, *2* several crystals formed, *3* region used as seed

The growth process is as follows.

(a) The crucible is filled with dry crystal powder. On melting, the powder collapses, and the melt fills only half of the crucible volume. More crystal powder or small grains left over from a previous growth are added to the melt. Care must be taken to avoid any scattering of the crystalline material outside the crucible because alkali halide melts attack the heating filament. The melts of NaCl and KCl are transparent, whereas KBr, KI, NaI, and CsI decompose and their melts are dark. However, the crystals grown from them are again quite transparent. At the beginning of the growth process it is advisable to cover the crucible with half-rings which overlap each other like roof tiles. This cover protects the melt from contamination, and hinders the too early formation of parasite crystals on the surface of the melt. Later the rings can be removed, since their role is taken over by the growing crystal itself. The removal of the rings is also necessary because they impede too much the already decreased heat dissipation.

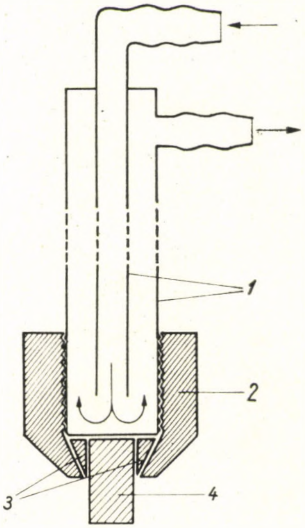


Fig. II.2.32 Fastening of the cooling tube and seed crystal

1 double-walled cooling tube of copper or nickel (length 20–25 cm, outer diameter 0.8–1.0 cm, arrows indicate direction of cooling water), *2* nickel socket connected to the cooling tube by a screw-thread, *3* nickel clamps, *4* seed crystal

(b) At the beginning of the experiment the temperature should be set so that the seed immersed in the melt first remelts to some extent. The actual growth should begin only after this. The seed is sometimes remelted until it is connected to the growing crystal only by a 'neck'. The surface of the melt must be well illuminated in order to see how deeply the seed is immersed in the melt. In this first phase of the growth the rotating device should not be operated. If the start is good the contours of the growing crystal appear in a few minutes around the seed. A sharp and continuous contour indicates the growth of a single crystal. If several crystals begin to grow the temperature of the furnace is increased to remelt them. Until some experience has been gained it is advisable to use seeds of a few centimeters in length. This allows for the start to be repeated several times. In fact a good result is determined by a good start.

(c) To continue with the growth either the temperature of the furnace is decreased, or the crystal is pulled out together with the cooling tube.

On decrease of the furnace temperature the crystal grows mainly in width; as a result of pulling it grows in length. The pulling may be either continuous or gradual, e.g. 1 mm every 5–10 minutes. During this process the growing crystal is observed, and the rate and the frequency of the pulling are chosen according to the development of the growth process. If the pulling is too fast the diameter of the crystal decreases, if too slow it increases.

In Fig. II.2.34 a crystal is shown which has obtained an elongated shape as a result of gradual pulling. It can be observed that the rate of pulling in three cases was relatively high. The growth usually begins with the growth of a crystal of large diameter and pulling is started only afterwards. The increase of the diameter is frequently accompanied by the formation of parasite crystals. This phenomenon limits the attainable diameter size. The parasites are formed on the walls of the crucible as a result of the decrease in heating, and they grow inwards. The original crystal can be grown only until it reaches the parasite crystals.

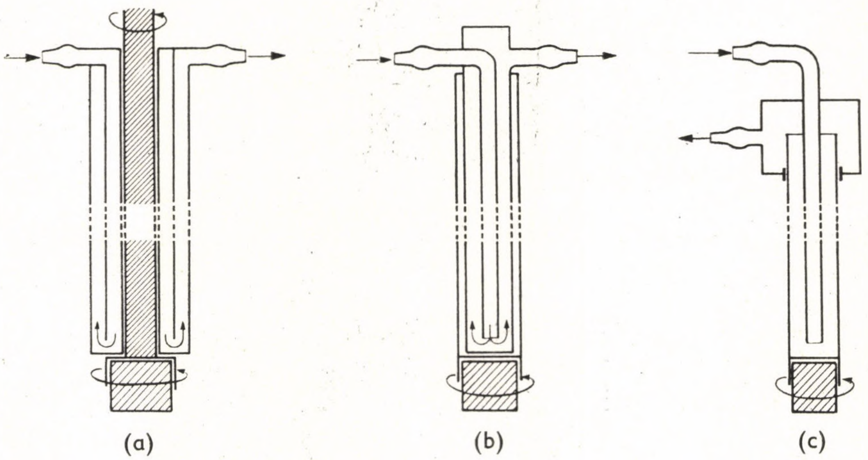


Fig. II.2.33 Various possibilities for rotation of the seed crystal

(a) rotatable rod reaching across the centre of the cooling tube; (b) rotatable metal socket pulled onto the cooling tube; (c) rotatable cooling tube

(d) The growth process may be considered complete at any stage. Afterwards follows the cooling of the grown crystal, which may be carried out in various ways; e.g. the crystal is taken out of the growing furnace as quickly as possible with the aid of the cooling tube, and put into the uniform temperature region of another furnace (annealing furnace) heated to a temperature slightly below the melting point of the crystal. The crystal is broken off immediately from the cooling tube, and the furnace is then covered and allowed to cool down slowly (in about a day) to room temperature (see Bridgman's method in II.2.1). The crucible still containing some melt is filled up with new dry crystalline material so that it may be used for a new growth. If this is not necessary, in order to avoid the cracking of the crucible, the molten salt is poured out and the empty crucible cooled. If an annealing furnace is not available and it is not necessary to save the crucible from cracking, the grown crystal can be cooled down in the growth furnace itself. In this case the crystal is slightly pulled out of the melt which is then frozen by a slow temperature decrease. After this the crystal is broken off from the cooling tube, and placed on the frozen melt. The cooling tube is taken out, the heating current switched off, and the furnace covered.

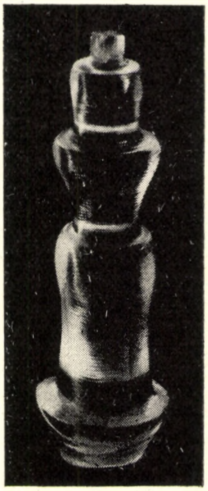


Fig. II.2.34 NaCl crystal grown with changing diameter

Top part is the seed crystal; truncated conical bottom shape is formed by freezing the melt which remained in the crucible to the crystal

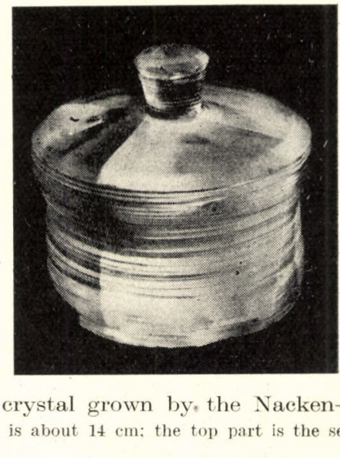


Fig. II.2.35 NaCl crystal grown by the Nacken–Kyropoulos method

Diameter is about 14 cm; the top part is the seed crystal

Crystals weighing several kilograms (Fig. II.2.35) can be grown only in large furnaces. It is enough in this case too to use a cooling tube of 2 cm diameter; however, in order to increase the diameter of the crystal, supplementary cooling must be applied. This can be done by lowering cooling rings parallel to the surface into the furnace, close to the surface of the growing crystal. To maintain the temperature gradient necessary for the crystal growth, the bottom of the furnace must be strongly heated.

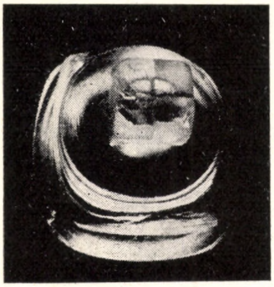


Fig. II.2.36 Alternation of cylindrical and prismatic growths of the same NaCl crystal

Note. Alkali halide crystals grown by the described method are usually cylindrical instead of having plane crystal faces. The reason for this is that the isothermal surfaces in the crystal growth furnace are of cylindrical symmetry. However, plane boundary faces corresponding to the orientation of the seed crystal can easily be developed (Fig. II.2.36) if, instead of the seed, the crucible is rotated, and is slightly shaken several times during each revolution.

II.2.3.2. Growth of InSb single crystals by the Czochralski method

With the Czochralski method InSb single crystals can be grown in the direction of any of the three low Miller indices. Good single crystals are obtained if the face of the seed touching the melt consists of Sb atoms ($\langle\bar{1}\bar{1}\bar{1}\rangle$ plane). If the orientation of the seed is different, twinning may occur. The growth equipment is a Czochralski single crystal pulling apparatus with gas flow (Fig. II.2.37). The rate of pulling is 1–10 cm/hour up to the maximum temperature of 600° C. The heatable crucible is equipped with a rotable seed holder which can be rotated at a rate of 30–60 revolutions/minute. For the growth process metallic In and Sb of sufficient purity (at least 99.9%), or polycrystalline InSb, and purified nitrogen, hydrogen or some inert gas are needed.

In order to obtain single crystals with a length of about 10 cm and a cross-section of 1 cm^2, 0.25 gram-atom (28.70 g) metallic indium and 0.25 gram-atom (30.45 g) metallic Sb, or 60 g polycrystalline InSb are measured into a crucible. The crucible is made of graphite or graphitized or sanded quartz. The crucible is first washed in hydrochloric + nitric acids, then in distilled water until it is acid-free, and is finally heated at 600° C for about 5–10 minutes in the same gas stream used during the growth. If polycrystalline material is used it is etched at room temperature in a 1 : 1 : 2 : 4 mixture of HF : : CH_3COOH : HNO_3 : H_2O for about 1 minute. During the etching process the material must be vigorously agitated to remove impurities adhering to the surface.

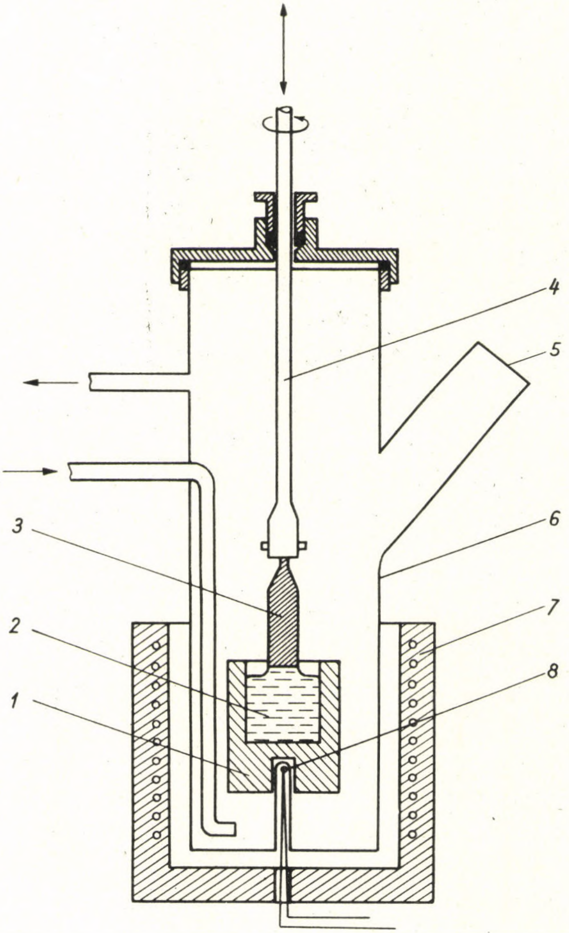


Fig. II.2.37 Apparatus used to grow InSb by the Czochralski method
1 graphite crucible, *2* melt, 3 seed crystal, *4* crystal holder, *5* window, *6* silica vessel, *7* furnace, *8* thermocouple

Before the seed is put into the holder its $\langle\overline{111}\rangle$ direction is determined by chemical etching or by X-ray diffractometry. The seeds are square prisms with a cross-section of 10–25 mm^2 and 50–60 mm in length. After the seed is clamped in its holder the rotating device is switched on to see if the clamping is centric. The rotation is stopped, the crystallization vessel closed, and the protecting gas flow switched on. The rate of the gas flow, depending upon the size of the equipment, is set to 100–200 liter/hour. After about 10 minutes the crucible heating is switched on. The seed must be placed a few centimeters above the rim of the crucible. If polycrystalline InSb is used, the material is heated up in 20 minutes to 540° C, slightly above its melting point.

If metallic indium and antimony are used the final temperature is 560° C. The InSb synthesis is finished if the melt is kept at this temperature for about 20 minutes. The melt is cooled in both cases by a slow decrease of the heating current until the first crystal—a parasite crystal—appears on the surface of the melt. The heat distribution of the equipment is well set if the parasite crystal appears in the centre of the crucible. After the appearance of the first crystal, the heating current is gradually increased until the crystal remelts. At this stage the rotating device is switched on, and the seed rotated at a rate of 40–100 revolutions/minute, and lowered until it is a few millimetres above the surface of the melt. In 2–3 minutes a temperature equilibrium is reached. The seed is lowered until it comes into contact with the surface of the melt. If the temperature (i.e. the heating power) is well set the melt wets the seed somewhat.

If the heating power is too small parasite crystals appear on the surface of the melt, starting from the seed. If the temperature is too high the melt creeps up too high on the seed thus melting it partly. This may result in the breaking off of the lower part of the seed. To avoid this the temperature is corrected in both cases by an appropriate setting of the heating power; 1–2 minutes after the required temperature is reached, the crystal pulling mechanism is switched on. The optimal pulling rate is 1–5 cm/hour. The diameter of the growing crystal depends on the heating power, and on the rate of pulling. If the pulling rate is kept at a constant value the diameter can be increased by a slight decrease of the power, while it can be decreased if the power is slightly increased. If a crystal of uniform cross-section is desired the heating power must be properly regulated, since the decrease of the mass of the melt changes the temperature distribution in the system continuously. The entire mass of the melt should be used up for the growth process because any melt remaining in the crucible may crack it on solidifying. When all the material has been pulled out, the pulling is stopped, and the heating power switched off. The flow of protecting gas is continued until the whole system has cooled down to room temperature. After the equipment is dismounted, the crystal can be removed with care from the seed holder.

II.3. CRYSTAL GROWTH FROM VAPOUR

The method of crystal growth from the vapour phase is mainly used to obtain thin single crystal platelets with relatively large surfaces, thin crystal layers and metal whiskers, and for the growth of certain organic crystals. An advantage of growth from the vapour is that in some cases extremely pure crystals with perfect surfaces are produced. The crystallographic orientation of the crystals can easily be influenced by a proper selection of the substrate onto which the material is condensed. A disadvantage of the method is that the material to be crystallized is present in relatively small concentrations, and it is difficult to keep the growth parameters (temperature, pressure) constant; therefore the volume of the crystals produced is generally not very large.

The main types of crystallization from the vapour phase are growth by thermal (condensation) and chemical transport processes.

Growth by condensation. In the simplest case the material to be crystallized is evaporated (sublimated) at a sufficiently high temperature, and the vapour is then led to a region of lower temperature where it crystallizes by condensation (Fig. II.3.1). In other cases (Frerich's method), the gaseous compound to be crystallized is produced under the required conditions (pressure, temperature, etc.) by the reaction of its gaseous components, and is crystallized by condensation either in the same place or in a region of lower temperature.

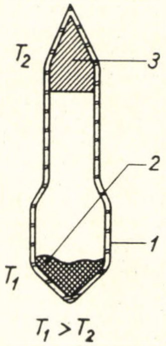


Fig. II.3.1 Simple case of growth by condensation
1 closed glass or quartz ampoule, *2* polycrystalline material, *3* single crystal

Chemical transport reaction method. The solid compound to be crystallized is transformed by a reversible reaction into one or more gaseous compounds and transported into some other zone where it crystallizes under the proper conditions by the reaction in the opposite direction (Fig. II.3.2). In simple cases the reaction is demonstrated by the reaction scheme

$$\alpha A + \beta B \rightleftharpoons \gamma C + \delta D$$

where A denotes the material to be crystallized, B, C and D denote the other materials participating in the reaction, and α, β, γ, and δ are stoichiometrical ratios. The zone of the system where the reaction takes place from left to right is called the source, whereas the zone where the reaction proceeds from right to left is called the zone of crystallization.

In every case of growth from the vapour, the vapourized material must be transported to the place of crystallization. A simple method of transport is diffusion of the vapourized materials. Since the rate of diffusion is usually not sufficient, either some neutral gas flow and temperature gradient are used to increase the rate of transport and the vapour concentration (open system), or only a temperature gradient is produced in the system (closed system), and the convection current carries the vapours with it. In this case the lower part of the crystallization vessel is kept at a higher, and the upper part at a lower temperature. In both cases it is difficult to keep the concentration at the proper value. This not only limits the size of the crystals grown, but also reduces the reproducibility. In order to avoid explosion in the closed system the pressure developing in the vessel must be carefully controlled; for instance in the case of iodine at 1000° C in a concentration of 0.5 mg cm^{-3} the pressure is 0.16 atmospheres, whereas in a concentration of 50 mg cm^{-3} at the same temperature it is 16 atmospheres.

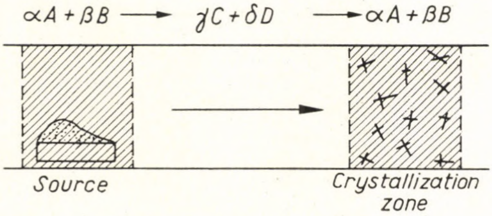


Fig. II.3.2 Growth by chemical transport reaction

II.3.1. Crystal Growth by Condensation

II.3.1.1. Growth of anthracene crystal plates

Polycrystalline anthracene is placed at the bottom of a closed vertical glass tube, and melted in a hydrogen atmosphere (melting point: 208° C). The anthracene vapour streams towards the upper, cooler part of the tube, and condenses there. The experimental assembly is shown in Fig. II.3.3.

A 70–80 cm long glass tube with a diameter of 6–7 cm, made of good heat-resistant glass is used for the growth. One end is spherical in shape, the other is closed with a tap. The length of the furnace is 30–40 cm, while its internal diameter should be only slightly larger than the growth tube, so that it can be easily moved in the furnace. In order to regulate the temperature distribution, a furnace constructed of several independent parts is advised. The furnace temperature for the growth process is set so that the temperature within the tube for a length of approximately 30 cm is 220 ± 5° C.

Experimental procedure. A funnel with a stem of about 2 cm in diameter reaching to the bottom of the tube is placed in the cleaned and dried growth tube; 20–30 g zone refined anthracene is poured through the funnel into the tube. (For the cleaning of the tube see experiment II.2.1.3; for the zone refining experiment II.2.2.1.) By using the long funnel it is possible to avoid the adherence of the anthracene to the wall of the growth tube which leads to unwanted nucleation. When full, the growth tube is evacuated to a pressure of 0.1 torr or even less and filled with hydrogen. (The purification of hydrogen is described in experiment II.2.1.3.) During this operation the manometer must also be connected and evacuated. The evacuation and filling with hydrogen must be repeated three times to remove all traces of oxygen. Finally the hydrogen pressure is set to 400 torr. Afterwards the heating of the furnace is begun. During heating the hydrogen pressure in the tube rises. When the temperature reaches the melting point of anthra-

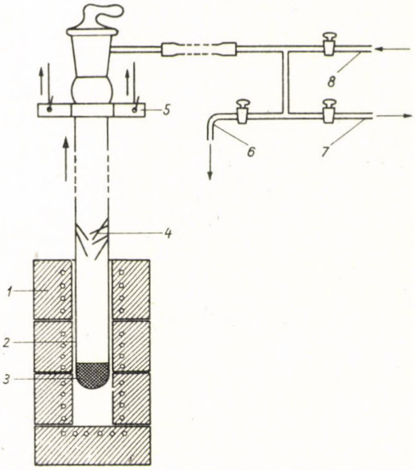


Fig. II.3.3 Assembly to grow anthracene plates

furnace consisting of several parts, *2* growth tube, *3* polycrystalline anthracene, *4* anthracene plates, *1* clamp to pull the growth tube, *6* tube connected to an open mercury manometer, *7* tube connected to a rotary pump, *8* hydrogen inlet

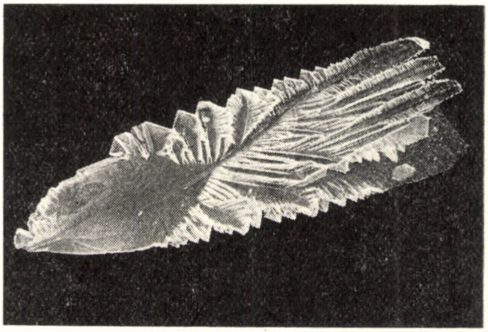


Fig. II.3.4 Anthracene crystal plate

cene the pressure in the tube is decreased to 350 torr, and the growth carried out at this reduced pressure. The rate of evaporation, the rate of nucleation, and also the rate of growth can be influenced by changing the pressure. During the heating period the higher pressure reduces the rate of evaporation, and during the period of growth the decrease of pressure increases the rate of evaporation. In order to obtain large crystal plates (and whiskers) the growth tube is pulled out from the furnace gradually. If the pressure in the tube is 350 torr the suggested rate of pulling is 1.2 mm/minute.

With the method described platelets 10–15 cm long, 3–5 cm wide and 0.1–0.3 mm thick grow in a few hours. The crystals are usually dendritic, though on many plates pure, uniform zones of various sizes can be found (Fig. II.3.4).

II.3.1.2. Growth of CdS (I)

CdS is a yellow compound insoluble in water, but dissolving well in acids. Its melting point is 1475° C. The crystals are hexagonal (wurtzite) in structure, and are used as photoconductors.

Pure cadmium is evaporated in a hydrogen atmosphere at about 650° C. The cadmium vapour is transported by a hydrogen stream into a zone at 900–1000° C, where it mixes with hydrogen sulphide. The hydrogen stream transports the vapour mixture into a zone of lower temperature, and at 700–800° C cadmium sulphide platelets are formed. The experimental assembly is demonstrated in Fig. II.3.5. The charge is cadmium distilled in a hydrogen stream of decreased pressure at approximately 650° C, or zone-purified cadmium, and hydrogen sulphide generated from reagent grade ferric sulphide and 20% reagent grade sulphuric acid. The hydrogen sulphide is rinsed by bubbling it through a pure sodium sulphide solution, and dried first in a trap cooled with a $-10°$ C mixture of sodium chloride and ice, and finally over anhydrous calcium chloride. The hydrogen gas is purified by the method described in experiment II.2.1.3. The shorter furnace is placed at the beginning of the experiment about 15 cm from the left end of the growth tube. The distance between the two furnaces is about 10 cm, and the boat containing 5–6 g cadmium is put into this space. The hydrogen sulphide is introduced into the system through a quartz tube the right end of which reaches into the centre of the longer furnace.

Experimental procedure. After mounting the assembly, the air is expelled from the gas generator and from the growth tube by hydrogen and hydrogen sulphide streams. When the hydrogen sulphide vapour is already free of air, the greater part of it is also expelled from the growth tube. The furnaces are switched on and the smaller furnace is heated up to 650° C, and the larger one to 900–1000° C. When these temperatures are attained the smaller furnace is pushed over the boat containing the cadmium (until it comes into contact with the other furnace), and the hydrogen sulphide flow is switched on.

The flow rate of the two gases is set empirically, and is checked at the wash liquor. If the conditions are favourable crystal platelets 1–3 mm wide and 1–2 cm long grow at about 700–800° C in the vicinity of the right end of the larger furnace (Fig. II.3.6). If the temperature of the cadmium is low or the flow of hydrogen transporting the cadmium vapour is too weak, a crust-like layer consisting of very small crystals is deposited on the wall of the quartz tube. If the concentration of cadmium vapour is greater, i.e. at higher temperature and in the case of a stronger hydrogen flow, cotton-like crystal masses develop. A further increase of the concentration of the cadmium vapour results in the larger crystals mentioned above. If the cadmium concentration is increased still more the crystals become even larger, their width reaching 1 cm, but due to the excess cadmium their quality deteriorates (the dark current becomes relatively high).

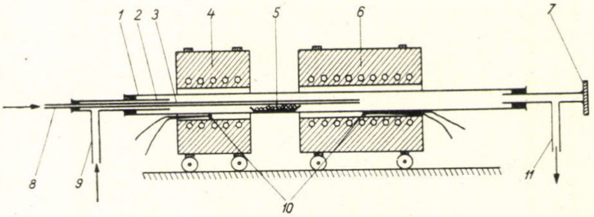


Fig. II.3.5 Assembly to grow CdS crystal plates

1 75–80 cm long quartz tube of 3.0–3.5 cm diameter (growth tube), *2* glass tube of 1.0–1.5 cm diameter, *3* 60 cm long quartz tube of 0.6 cm diameter, *4* approximately 15 cm long furnace heatable to 700° C, *5* 8–10 cm long porcelain boat, *6* 25 cm long furnace heatable to at least 1000° C, *7* glass window glued to the furnace with Araldite to observe the growth process, *8* hydrogen sulphide inlet, *9* hydrogen inlet, *10* Pt–PtRh thermocouples, *11* vapour exhaust (exhaust tbues lead either to the open air, or into an exhauster)

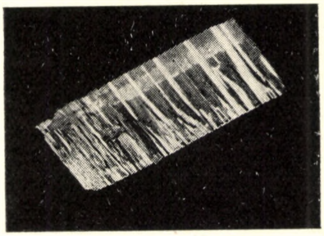


Fig. II.3.6 CdS crystal platelets

The hydrogen sulphide flow must always be regulated to ensure an excess of hydrogen sulphide. If hydrogen sulphide is not present in a sufficient quantity metallic cadmium is deposited in the form of a grey layer on the colder parts of the quartz tube. The result of a small deficiency of hydrogen sulphide is that the cadmium content of the crystal becomes greater than the stoichiometric ratio. When this happens the quality of the crystals deteriorates, and they become a darker yellow. It is recommended to terminate the crystal growth before the cadmium in the boat is completely used up. When the growth is terminated, the smaller furnace is pulled away from the boat and the heating of first the smaller, and then the larger furnace is switched off. When the temperature of the larger furnace has decreased to such an extent that, on looking through the observation window, the inside of the furnace is completely dark the hydrogen sulphide flow is switched off, and the furnace with the crystals in it is allowed to cool down in the hydrogen stream.

II.3.1.3. Growth of CdS (II)

Polycrystalline cadmium sulphide is put into a quartz ampoule which is then evacuated and heated up to 1 200° C (the melting point of CdS is 1475° C). When this temperature is attained the vertical ampoule is pulled up slowly, so that its conical tip gradually gets into a colder zone. The CdS vapour condenses in the tip, and if the circumstances are favourable one single nucleus is formed which grows further if pulling is continued.

The method is similar to the crystallization of other substances by simple condensation in vacuum. However, in this case it has to be considered that the CdS vapour dissociates strongly above 1000° C:

$$2\text{CdS} \rightleftharpoons 2\text{Cd} + \text{S}_2$$

In a closed system at a certain temperature an equilibrium is reached between the solid CdS and the vapour components. Both this equilibrium and the transport of material are extremely sensitive to the stoichiometric relations. A small excess of cadmium or sulphur in the starting material changes the equilibrium essentially and at the same time the growth conditions. Good quality crystals are obtained only from fairly non-stoichiometric starting materials. However, serious difficulties may arise in this respect. In most cases the starting material is microcrystalline CdS obtained in an aqueous medium from cadmium salts and H_2S. This material usually contains impurities incorporated from the mother liquor, and a few per cent moisture. Both must be removed before the growth of the crystal.

The majority of water and halides can be removed by heating in an inert gas, or in vacuum. In this case, however, the material also changes stoichiometrically, and consequently the material treated in this way is not suitable for crystal growth. Stoichiometrically suitable material is obtained if the microcrystalline cadmium sulphide is heated at approximately 960° C in a water-free and oxygen-free H_2S atmosphere. The growth equipment is shown in Fig. II.3.7.

The furnace must be heatable to at least 1200° C. The temperature distribution inside the furnace is nearly homogeneous along the total length of the ampoule. This homogeneous zone changes upwards (and downwards) into zones with temperature gradients of 3–6° C/cm. In order to decrease the radial temperature gradient the furnace is lined with a tube slightly larger in diameter than the ampoule. The ampoule is pulled up with a clock-work-driven horizontal spindle with the aid of a stranded KANTHAL or tungsten wire (made of 4–5 fibres each of 0.1 mm diameter). The wire is stretched with the aid of a counterweight of about 100 p. A quartz tube connected to the counterweight holds the ampoule in the furnace, the lower end of the tube being soldered to the tip of the ampoule.

Experimental procedure. The smooth-walled quartz ampoule (Fig. II.3.8) is washed in a hot 1 : 1.5 mixture of hydrochloric and nitric acids, then

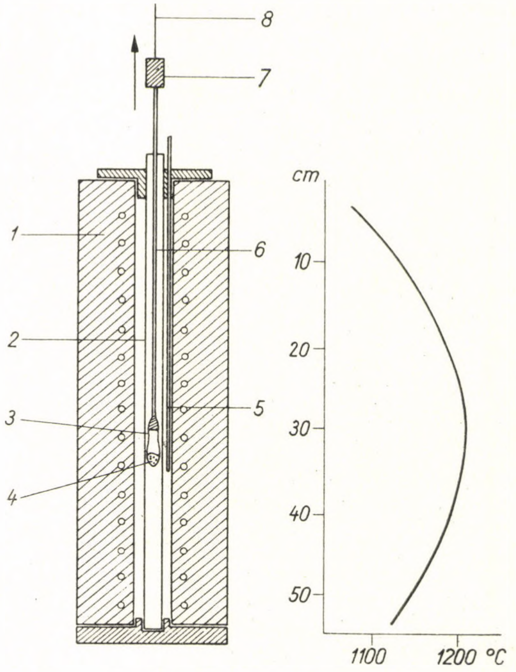


Fig. II.3.7 Assembly to grow CdS; on the right: temperature distribution along the longitudinal axis of the furnace

1 furnace, *2* quartz tube lining the furnace, *3* ampoule, *4* polycrystalline CdS, *5* Pt–PtRh thermocouple, *6* quartz tube suspending the ampoule, *7* counter-weight, *8* stranded KANTHAL or tungsten wire

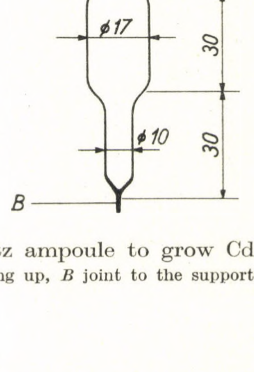


Fig. II.3.8 Quartz ampoule to grow CdS (sizes in mm)

A place of sealing up, *B* joint to the supporting quartz tube rinsed with distilled water. The boiling and rinsing are repeated several times and the tube is dried at 120° C. About 3 g of cadmium sulphide heated in hydrogen sulphide and previously dried for 24 hours at 110° C in a vacuum drying oven is put into the ampoule, its neck is narrowed, and it is sealed off at a pressure of about 10^{-5} torr. The ampoule is lowered into the furnace until its upper conical end reaches the lower end of the homogeneous heat zone of the furnace. Heating is switched on, and the furnace is heated at an arbitrary rate up to 1200° C (this temperature refers to the homogeneous zone). The ampoule is kept for about an hour in this position; during this period the cadmium sulphide powder which may have adhered to the upper tip evaporates. After an hour the temperature is stabilized very carefully, and the pulling up of the ampoule is started. The optimum pulling rate is 1.0–1.2 mm/hour if the ampoule diameter is 8 mm, and a temperature gradient of 3–6° C/cm is maintained. If the diameter or the temperature gradient is larger, a lower pulling rate is recommended. Under the circumstances described the growth lasts about 40 hours; during this time the total mass of the polycrystalline CdS is transported into the upper part of the ampoule. If the composition of the starting material differs from the stoichiometric ratio only grain growth takes place. This, however, may be so strong that from the bulk formed in 3–4 days at the lower end of the ampoule, single crystals measuring 100 mm^3 may be cut.

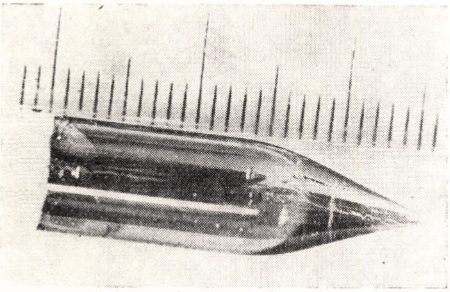


Fig. II.3.9 CdS crystal

The quality of crystals obtained depends much on the cooling which must therefore be carried out very carefully. If the rate of cooling is too high, stresses are formed in the grown crystal which may cause the crystal to shatter at room temperature. The recommended cooling rate is 20° C per hour. The orientation of the crystal is determined by that of the nucleus formed in the tip of the ampoule. In the formation of the nucleus in the cone tip, the hexagonal *c* axis is usually normal to the envelope of the cone. Figure II.3.9 shows a CdS crystal grown with the condensation method.

II.3.2. Crystal Growth by Chemical Transport Reactions

II.3.2.1. Production of germanium single crystal layer

The method is used to produce up-to-date semiconducting devices. The surface of the carefully selected substrate (e.g. Ge, GaAs, GaP) becomes covered with a thin, single crystal germanium layer. The orientation of the layer is determined by that of the substrate.

The layer is formed by growth from the vapour. Evaporation onto the substrate cannot be carried out directly, because the germanium evaporates sufficiently only at high temperatures at which the substrate becomes damaged or even ruined. To avoid this, germanium is transformed to some halide compound, usually to germanium iodide, which evaporates at a low temperature. The GeI_2 vapour is transported to the substrate, where it disproportionates, and a part of the germanium is deposited on the surface of the substrate in the form of a single crystal layer.

The chemical processes involved are shown by the following equations:

$$Ge + I_2 \xrightarrow{600^\circ\ C} GeI_2$$

$$2GeI_2 \xrightarrow{400^\circ\ C} Ge + GeI_4$$

The experimental assembly is shown in Fig. II.3.10.

The glass tube containing the iodine can be connected to a thermostat heated to approximately 70° C. The iodine vapour is transported to the polycrystalline germanium in an argon stream, and here the GeI_2 is formed. The GeI_2 vapour is transported in an argon stream to the right side of the reaction vessel where the substrates have previously been placed. The crystalline germanium is deposited here. Both parts of the reaction vessel must be surrounded with a furnace; the one surrounding the left part of the reaction vessel must be heatable to at least 600° C and the one surrounding the right part to at least 400° C.

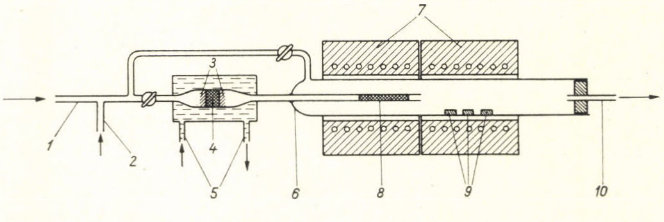


Fig. II.3.10 Assembly to grow epitaxial germanium layers (one fifth actual size)

1 argon inlet tube, *2* nitrogen inlet tube, *3* glass wool, *4* iodine, *5* connections to the thermostat, *6* quartz tube (reaction vessel), *7* furnaces, *8* germanium pieces, *9* substrate, *10* gas exhaust tube

Experimental procedure. First some loose glass wool is placed into the glass tube which will contain the iodine, then small iodine crystals, and finally more glass wool. The part of the tube reaching into the reaction space is filled with small pieces of germanium. The length of the tube filled with germanium must be approximately 5 cm. This part must be in the centre of the left furnace in a homogeneous heat zone. The substrates must be so oriented that the surfaces serving for deposition should be $\{100\}$, $\{110\}$, or $\{111\}$-type planes. The proper orientation can be checked either optically or by X-ray diffraction. On any of these surfaces the germanium grows epitaxially, i.e. the orientation of the germanium crystal formed corresponds to the orientation of the substrate surface. The proper preparation of the substrate surface is very important, because coherent layers grow only on extremely pure surfaces. The substrate surface is prepared either by cleaving or by mechanical processing (cutting, polishing). The surfaces obtained in this way are cleaned by chemical polishing. The best mixture for Ge, GaAs and GaP substrates consists of 68% HNO_3, 40% HF and H_2O in the volumetric ratio 3 : 1 : 2. The crystals are kept in this mixture for 1–2 minutes at room temperature and then thoroughly rinsed with distilled water, until completely acid-free. They are then dried at room temperature in some dust-free place, e.g. in an exsiccator.

After the substrates have been placed in the reaction vessel the whole assembly is flushed at room temperature with dry oxygen-free nitrogen for 15 minutes. The iodine saturator is disconnected, the argon flow is started at 50–70 liter/hour, and the heating currents of both furnaces are switched on. The temperatures are set to 600° C (and to 400° C). The heating rate should be as high as possible. The tube containing the iodine is immersed in the thermostat set previously to 70° C. If the experimental assembly is constructed so that the iodine container is constantly in the thermostat the heating is switched on and it is heated to 70° C. When this temperature has been attained, the argon stream is led through the iodine saturator into the system by opening or closing the appropriate taps. The gas leaving the system is led to an exhauster. At the beginning of the reaction an orange-coloured coating may be observed; this consists of germanium polyiodides. After half an hour an approximately 10 μm thick single crystal germanium layer has been formed on the substrate. The iodine source is disconnected, and the heating current switched off. The gas flow must be maintained until the system cools down completely to room temperature.

The germanium layer deposited on the substrate usually has a metallic reflecting surface. With a sufficiently high magnification growth forms characteristic of the orientation can be observed with an optical microscope. In the case of a $\{111\}$ orientation trigonal pyramids are visible, while in the case of $\{110\}$ or $\{100\}$ orientations rectangular pyramids can be seen.

II.3.2.2. Growth of epitaxial silicon layer

(1) For the production of epitaxial silicon layers silicon crystal plates are frequently used as substrate. The growth of the layer rigidly follows the structure of the substrate crystal and its orientation is identical with

that of the substrate, but some of its physical properties (e.g. the type of electrical conduction in it) may be different.

One of the most frequently used methods of producing epitaxial silicon layers is the hydrogenation of $SiCl_4$.* This is a heterogeneous reaction. There have been a number of assumptions as to the mechanism of the process. According to one of these the reaction takes place on the surface of the substrate crystal. In another assumption the gaseous $SiCl_4$ decomposes at a distance of a few microns from the surface. As a result of this process individual silicon atoms and groups of several atoms are formed, and carried to the surface by diffusion.

First we are dealing with a classical heterogeneous reaction consisting of the following steps: transport to the surface of the materials taking part in the reaction; adsorption of these materials on the surface; reaction or a chain of reactions on the surface; desorption and elimination of the reaction by-products; attachment of the formed atoms to the growth steps, viz. their incorporation into the steps. If one step takes place at a considerably slower rate than the others this determines the growth rate of the layer. At lower temperatures the growth rate is determined by the rate of the surface reaction, obviously depending on the adsorption rate of the silicon compound used. At higher temperatures the rate of transport of the reacting materials is the determining factor.

According to another assumption the silicon atoms are formed in the flowing gas layer at a certain distance from the substrate surface. The formed atoms move towards or away from the substrate by diffusion. The atoms which reach the substrate may migrate along the surface and produce oriented islands as in the previous model. It can easily happen that the distribution of silicon atoms in the gaseous phase above the silicon crystal is not homogeneous, and this may cause structural defects in the epitaxial layer; it may lead for example to the development of growth pyramids and polycrystalline regions.** One may conclude that the growth mechanism depends on the material transport process and on kinetic and thermodynamic factors, but it is affected by the geometry of the reaction chamber and other experimental parameters too.

When the apparent growth rate is to be determined, to a first approximation two reactions must be considered. One is the main process producing silicon from the $SiCl_4$ led into the reaction chamber:

$$SiCl_4 + 2H_2 \rightleftharpoons Si + 4HCl$$

The other reaction is a competing one:

$$Si + SiCl_4 \rightleftharpoons 2SiCl_2$$

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* E. G. Bylander (1962): *J. Electrochem. Soc. 109*, p. 1171.

** T. L. Chu, I. R. Gavaler (1963): *J. Electrochem. Soc. 110*, p. 388; T. L. Chu, I. W. Faust, H. F. John (1964): *A Survey of the Literature on Crystal Defects and their Effect on Device Reliability*. Westinghouse Res. Lab. Contract No. NAS 8–11432, Pittsburgh.

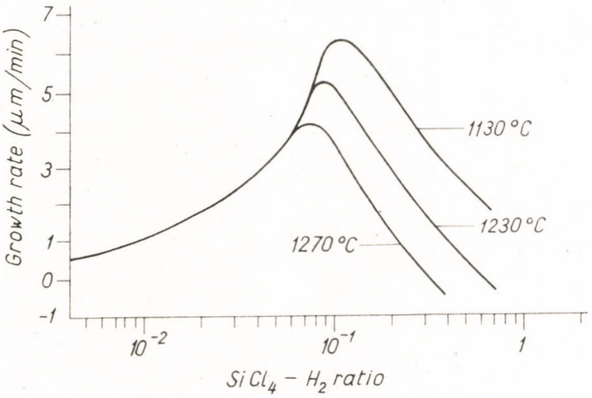

Fig. II.3.11 Growth rate of the Si layer as a function of the initial $SiCl_4$:H_2 molar ratio

Negative rates indicate vapour etching of the substrate Si plate

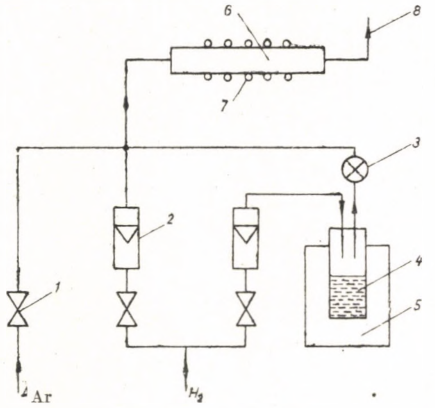

Fig. II.3.12 Growth apparatus

1 valves, *2* flowmeters, *3* key, *4* evaporation vessel, *5* thermostat, *6* reactor tube, *7* water-cooled radio-frequency coil, *8* exhaust

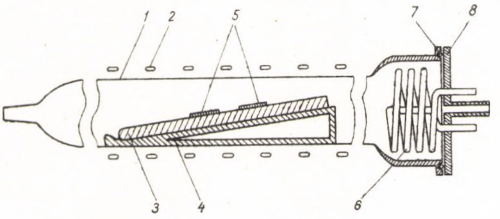

Fig. II.3.13 Reactor tube

1 reactor tube of 10×5 cm² rectangular cross-section of extremely pure silica, *2* water-cooled radio-frequency coil, *3* SiC-covered graphite support, *4* silica support inclined to about 5°, *5* Si substrate plates, *6* water-cooled glass-spiral to cool the reaction by-products, *7* teflon sealing ring, *8* metal lid

The investigation of the growth process as a resultant of the above two reactions gives the curve shown in Fig. II.3.11. In this case the flow rate of the gas was assumed to be so low that equilibrium could be attained. In practice this is not so in most cases, but the character of the curve remains the same. Consequently, the growth rate initially increases with increasing $SiCl_4$ concentration, reaches a maximum and afterwards gradually decreases.

The required value of the dopant concentration in the grown layer is set by the admixture of the dopant to the $SiCl_4$. In the case of *n*-type layers and *p*-type layers, phosphorus (in the form of phosphorus chloride) and boron (in the form of BCl_3 or diborane), respectively, are mostly used.

(2) For the production of an epitaxial silicon layer a growth apparatus with a horizontal reactor tube is advised (Fig. II.3.12). The apparatus is first rinsed with an argon flow, then hydrogen carefully purified from oxygen and water is introduced. One part of the hydrogen is led directly into the reactor tube, the other part into the evaporation vessel containing $SiCl_4$. The $SiCl_4$ content of the hydrogen, or more exactly the $SiCl_4:H_2$ molar ratio, can be varied by varying the quantity of hydrogen passing through the evaporation vessel and the temperature of the evaporation vessel. An important part of the apparatus is the reactor tube, which can be seen separately in Fig. II.3.13. The graphite support placed in the reactor tube is heated to the required temperature by a radio-frequency coil. It is advisable to use a radio-frequency generator of 10–20 kW output; the tube is surrounded by the coil along the whole length of the graphite support. The temperature should be measured with an optical pyrometer; the required temperature range is 1 000–1 300° C.

(3) Suggested experiments. (a) An epitaxial layer is grown at about 1200° C with a $SiCl_4/H_2$ ratio of $\sim 1/120$, and after about 20 minutes the thickness of the grown layer is measured. The flow rate of the H_2 passing through the reactor tube should be set to 50 l/min, and the temperature of the evaporation vessel to 20° C. (b) The experiment is carried out at other $SiCl_4/H_2$ ratios too, and the dependence of the growth rate on the concentration at the given temperature (e.g. at 1 200° C) is determined. (c) The experiment is repeated at a given concentration at different temperatures (in the range 1 050–1 250° C), and the temperature dependence of the growth rate is determined. The logarithm of the growth rate is plotted against the reciprocal of the absolute temperature. From the straight line part of the curve the (apparent) activation energy for the whole process is determined.

(4) Experimental procedure. The silicon crystal plates serving as substrate should be polished, and when clean (degreased surfaces) placed on the graphite support and the reactor tube closed. Afterwards the reactor tube is carefully rinsed with argon, and the hydrogen flow started. (The hydrogen should always be burned at the outlet of the reactor tube.) After the rinsing gas has been switched off, the hydrogen flow through the reactor tube is continued for about 10 minutes. The radio-frequency generator is switched on and the silicon plates are heated to the required temperature. The temperature is measured by a pyrometer. After the required temperature is

reached, suitable flow rates and the prescribed $SiCl_4$:H_2 ratio are set. It is advisable to calibrate the apparatus beforehand in order to ensure a quick and exact setting. (It should be noted that the quantity of evaporated $SiCl_4$ is determined by measuring the weight loss of the evaporation vessel.) The deposition of silicon is carried on for about 20 minutes, the radio-frequency heating is then switched off, and the reactor tube is rinsed with hydrogen until the graphite support cools down. Rinsing is continued afterwards with argon.

The thickness of the grown layer may be determined in several ways. The simplest method is to deduce the thickness of the layer from the size of the stacking faults (Fig. II.3.14). If the edge length of the largest tetrahedral defect to be found is measured (a), the thickness of the layer (w) can be calculated from the following expression:

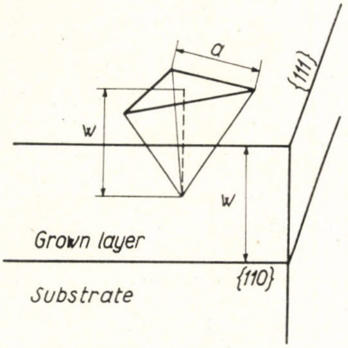

Fig. II.3.14 Drawing for the measurement of the thickness of the layer with the aid of stacking faults

$$w = a\sqrt{\frac{2}{3}}\,.$$

The measurement can be carried out with a metallurgical microscope after decoration with the aid of a suitable etchant. It is advisable to use the Sirtl etchant: 1 part by volume of a 33 weight % aqueous solution of CrO_3 and 2 parts by volume of a 48% HF solution.

The thickness of the epitaxial layer can also be determined by the interference of infrared rays. The rays reflected by the surface of the grown epitaxial layer interfere with those reflected by the layer–substrate interface, and from the interference pattern obtained the thickness of the layer can be deduced.

II.4. DEVICES FOR CRYSTAL GROWTH

A great variety of different accessories and devices are available commercially for the purposes of crystal growth. Detailed catalogues describe their use. To assist in the design and construction of laboratory-made equipment, in the following sections some general remarks are made concerning the devices used to grow single crystals from the melt or the vapour phase.

II.4.1. Crucible Material

General requirements. (a) The crucible must be thermally and mechanically stable even at temperatures high (at least 100° C) above the melting point of the material to be crystallized.

(b) The crucible must not contaminate the melt, and must not influence the desired properties of the grown crystal if this is to be of a prescribed quality. This requirement also refers to eventual impurities present in the crucible material.

(c) In order to avoid any possible contamination the protecting atmosphere used should also be considered when selecting the crucible material.

(d) The crystal should not adhere to the crucible wall if deformations, stresses or cracks, likely to occur during temperature changes, are to be avoided.

(e) The material of the crucible must be of suitable porosity to avoid any leak of the melt.

(f) With gradient methods the material of the crucible must be able to withstand the temperature changes involved, and at the same time it must be of poor heat conductivity to obtain large gradients.

The data relating to the more important crucible materials are given in Table II.II.

Because of its poor heat conductivity and good softening properties (softening occurs only at very high temperatures), *fused silica* is one of the most frequently used crucible materials. A further advantage of this material is that it withstands sudden temperature changes rather well. On the other hand, unfortunately, a great number of elements and compounds react so strongly with silica that their use requires some consideration. Such reacting materials are for example the alkali and alkaline earth metals, boron, titanium, tantalum, silicon, fluorine and at high temperatures tellurium, aluminium, rare earth metals, magnesium and manganese. Similarly, hydrofluoric acid, hydrolysing fluorides, melts of basic oxides, phosphoric acid, phosphates, tungstates, borates, hydroxides of the alkali and alkaline earth metals, and lead, tin and cadmium containing oxide impurities attack silica.

The fused silica made from natural quartz is transparent, whereas it is opaque if made from quartz sand. In order to satisfy special high purity requirements (e.g. for the purpose of growing semiconducting crystals), containers made of synthetic silica are now available. The metal impurity content of synthetic silica is less, but its OH content is greater than those of crucibles made from natural material. For this reason they are not suitable for the growth of alkali halides.

In the case of wetting materials, e.g. metals, a thin carbon (soft or hard) layer must be deposited on the silica surface. Metal melts do not adhere to carbon but the danger of carbide formation must be taken into account.

Loose, incoherent carbon layers are obtained by burning benzene or paraffin; the carbonization of acetone or alcohol at 600–1 000° C in an oxygen-free atmosphere gives a coherent, so-called hard carbon layer.

Silica containers are cleaned by boiling them for two hours in a 1 : 1 mixture of concentrated nitric and sulphuric acids; after rinsing with distilled water the containers are vacuum dried for 2–3 hours at 1 100° C. If an especially high degree of purity is needed the containers are treated with a 1 : 1 mixture of concentrated nitric acid and 40% hydrofluoric acid prior to the cleaning procedure, then rinsed with doubly distilled water, and after drying they are heated close to their softening point ($\sim$1 300° C) with an oxygen–hydrogen, or an oxygen–propane flame.

Porcelain may be used for acidic melts, metals, alloys and salts. Strongly alkaline melts, however, and hydrofluoric and phosphorous acids attack porcelain. The porosity is decreased by glazing. The enamels of various chemical composition may react with the melt at low temperature and contaminate it.

With regard to the various types of *glasses*, it should be remembered that the silicon content of hard glasses is relatively high, and therefore they withstand any changes of temperature quite well. In contrast to silica, glasses are not attacked by metal melts. Glass and glazed porcelain containers may be cleaned with a cold 33 : 5 : 2 : 60 solution of nitric acid, hydrofluoric acid, alkyl sulphonate and water. Traces of water adhering to the glass surface after rinsing may be removed by drying in vacuum.

The properties of *oxides* depend considerably upon the sintering procedure. Lithium and beryllium attack porcelain crucibles in a reducing atmosphere, chromium, manganese, and iron in an oxidizing one. Lead oxide can be melted only in magnesium oxide or zirconium oxide, while boron oxide in aluminium oxide crucibles. Fluorides cannot be melted in oxide crucibles.

Carbon and *graphite* crucibles may be used only in a reducing or neutral atmosphere. This type of crucible material can be used with good results to melt metals (with the exception of boron, aluminium and iron), but they must not be used for metal oxides or silicon. Since graphite is not very sensitive to changes of temperature it can be heated directly with an electric current or by induction. A further advantage is its high purity, though, on the other hand, its porosity may be disadvantageous. For special purposes vitreous carbon crucibles are available commercially.

Carbon and graphite crucibles are cleaned before use in boiling dilute hydrochloric acid and afterwards in water, and finally by heating in vacuum at 2 000° C.

The most frequently used *metal* crucible is made of platinum. It is resistant to oxides, carbonates, borates, etc. in an oxidizing atmosphere, but cannot be used to melt metals, phosphorus, arsenic, sulphur, selenium or halides. It cannot be used either in cases when, owing to the presence of reducing materials, the elements mentioned may be released in the course of heating. The rhodium–platinum alloys (less than 20% rhodium) may be used at higher temperatures and are harder than pure platinum crucibles. The platinum crucibles are cleaned in boiling concentrated nitric or sulphuric acid, or with a $KHSO_4$ melt.

TABLE II.II

Crucible materials

Group	Detailed indication	Commercial denomination	Melting point (° C)	Max. temperature of use (° C)	Gas sealing	Resistance to changes in temp.
Silica glass	Quartz sand Natural quartz crystal	Vitreosil Rotosil Homosil, etc.	1 725	1 400	Good	Very good
Aluminium silicates	Hard porcelain without enamel;		1 500 – 1 700	1 300	Good	Satisfactory
	with enamel		1 500 – 1 700	1 100	Very good	Satisfactory
	Porcelain-like pastes	Pyrolan	1 700	1 400	Very good	Good
		K paste	1 800	1 700	Very good	Good
		Pythagoras paste	1 820	1 700	Very good	Good
		Marquardt paste	1 820	1 700	Porous	Good
	Fireclay		1 750 – 1 850	1 500 – 1 700	Porous	Good
	Sillimanite	Ignodur	1 800 – 1 850	1 650 – 1 700	Porous	Good
	Mullite	Thermodur	1 830	1 700	Porous	Good
Magnesium silicates	Potstone Talcum	Steatite Calite	1 400	1 250	Good	Satisfactory
Zirconium silicates			2 430 – 2 550	1 750	Porous	Good
Glass		Vycor		1 050	Very good	Very good
		Supremax		720	Very good	Good
		Jena glass		570	Very good	Good
		Duran		540	Very good	Good
		Thüringen glass		510	Very good	Satisfactory
		Pyrex		500	Very good	Good
Sintered oxides	Al_2O_3	Degussite Al 23	2 050	1 850	Good	Good
		Alundum Alunite	2 000	1 800	Porous	Good
	MgO	Degussite MG 25	2 700	2 200	Porous	Satisfactory

	BeO		2 550	2 200	Good	Very good
	ZrO_2	Degussite ZR 23	2 700	2 500	Slightly porous	Small
	ThO_2		2 800	2 700	Good	Unsatisfactory
	$MgO \cdot Al_2O_3$ (spinel)	Degussite SP 23	2 100	1950	Good	Good
Carbons	Electrographite Carbon		>4 300 (subliming)	>3 000	Porous	Very good
Carbides	SiC	Silite Globar Crucilite, etc.	>2 500 (decomposing)	1 500	Slightly porous	Very good
	B_4C		2 350	2 000	Porous	Very good
Metals	Platinum		1 769	1 600	Very good	Very good
	Rhodium		1 966	1 800	Very good	Very good
	Gold		1 063	900	Very good	Very good
	Silver		960	800	Very good	Very good

II.4.2. Construction of Resistance Furnaces

The main parts of resistance furnaces are the heating element, the heating element support and the heat-insulating filler. The most frequently used materials are given in Tables II.III and II.IV; Figs II.4.1. and II.4.2 show schematically the various furnace types.

The resistances are metal wires or tapes wound on a cylindrical support made of some insulating material. Sometimes spiral-shaped notches are made in the cylinder. In some cases spirals are made of the wires, and these spirals are wound round the cylinder. It is advisable to develop the spiral so that its diameter is about six times larger than that of the wire. The coils are frequently fixed to the support by covering them with some heat resisting paste. Al_2O_3 and MgO pastes may be used up to 1500° C, ZrO_2 up to 1800° C. In the case of smooth supporting tubes, the heating wires

TABLE II.III

Electrical resistance materials

Name	Maximum working temperature (° C)	Atmosphere
Chromel D	760	Air
Cekas Chrome-nickel	1000–1050	Air
Alumel Chromel-C Nichrome Tophet-C	1000–1100	Air
Chromel-A Tophet-A Vichrome-V	1175	Air
Kanthal-D (1), (2)	1100	Air
Kanthal-A (1), (2)	1300	Air
Megapyr Permatherm	1330	Air
Platinum(3)	1400	Air
Platinum-rhodium(3)	1540	Air
Silicon carbide	1550	Air
Kanthal-super(4)	1600	Air
Molybdenum	1800	Vacuum Hydrogen
Tantalum	2000	Vacuum
Zirconium oxide (with cerium oxide)	2200	Air
Tungsten	2600 3200	Vacuum Helium
Graphite	3000	Inert gas

(1) Attacked by halides.
(2) Becomes brittle and fragile after the first heating.
(3) Must not be put on a silica support.
(4) Softens above about 1500° C; must be placed on a notched support embedded in aluminium oxide paste.

(filaments) or coils should be pulled through heat insulating beads made of Al_2O_3 or MgO. It is important that neither the support, nor the heat insulating beads and pastes contain any impurities which react with the filament. The pastes should be prepared with distilled water.

At very high temperatures chemical reactions between the heating element and the supporting materials can hardly be avoided. For this reason it is advantageous to use self-supporting heating elements. These can be made for example of thin plates (up to several tenths of a mm) of tungsten or molybdenum rolled into tubes. Another type of self-supporting system is made of graphite tubes (with a wall thickness of a few mm) with incisions at equal distances to lengthen the current path (Fig. II.4.3). The SiC heating elements are used in the form of rods; in order to avoid any bending the rods are placed horizontally. The specific electrical resistivities of some resistance materials are given in Fig. II.4.4.

Of all the filament supporting materials Al_2O_3 and MgO are the best as regards mechanical strength; BeO is less good. Amorphous quartz has the lowest heat expansion, but almost equally good are ZrO_2 and mullite; the heat expansion of MgO is relatively large. Of the materials listed in Table II.IV the heat expansion of Al_2O_3 has a medium value and is greater than those of tungsten or molybdenum. BeO has the largest thermal

TABLE II.IV

Some filament-supporting and heat-insulating materials (thread-like or granulated fillers)

Material	Maximum working temperature (° C)
Silica glass⁽¹⁾	1100
Ceramics containing corundum	1500
Mullite	1600
Corundum	1900
Beryllium oxide⁽²⁾	2300
Magnesium oxide⁽³⁾	2400
Stabilized zirconium oxide⁽⁴⁾	2400

(1) Must not come into direct contact with a platinum filament.
(2) Highly toxic.
(3) Stable in an oxidizing atmosphere.
(4) The structure of pure ZrO_2 transforms at about 1 100° C from monoclinic to cubic. The cubic modification can be stabilized throughout the whole temperature range by adding cerium oxide or magnesium oxide (stabilized zirconium oxide). Its specific electrical resistivity is 100 ohm cm at 1000° C and only a few ohm cm at 2400° C.

conductivity, followed by MgO and Al_2O_3, with ZrO_2 having the smallest value. Materials of low heat expansion and large heat conductivity are the most advantageous for the heating filament supports. The specific electrical resistivities of the materials in Table II.IV vary between 10^7 and 10^{18} ohm cm at room temperature, and between 10 and 10^{11} ohm cm at 1500° C. BeO has the largest specific resistivity, and ZrO_2 the smallest. Stabilized ZrO_2 may also be used as a heating resistance above 1000° C. It must be stressed that the above values are only approximate ones since the various properties of the materials depend a good deal upon their compactness. Although BeO is advantageous, care must be taken because of its high toxicity. The materials listed in Table II.IV may also be used as heat insulating fillers. For this purpose, however, these materials must not be applied in their compact form, but are used rather in thread-like or granulated form (e.g. quartz wool). If the use of heat insulating fillers is difficult with furnaces heated to very high temperatures, thin, polished metal plates are placed at certain distances around the heating elements; these decrease the heat loss by reflecting the radiating heat.

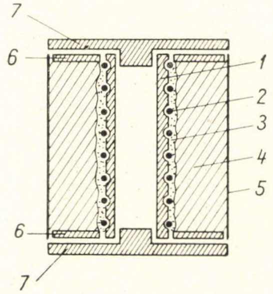

Fig. II.4.1 Simple cylindrical resistance furnace

cylindrical heating filament support, *2* heating filament wound on the support, *3* insulating paste fixing the filament, *4* heat insulating material, *5* metal jacket, *6* closing plates, *7* cover plates

A few additional remarks follow concerning the construction of the furnaces.

If a furnace is about five times longer than its diameter, and the heating filament is coiled up uniformly on a cylindrical support, a nearly constant temperature is attained in about two-thirds of the furnace length. In this case, however, the heating filament (spiral or tape) is wound onto the cylindrical support so that the distance between the coils is not more than twice the diameter of the filament or spiral, i.e. the width of the tape. In order to secure a uniform heat distribution a metal cylinder is sometimes placed into the inner wall of the supporting tube; this compensates for the temperature inhomogeneities caused by the coils. The range of constant temperature can be increased if the heat loss at the ends of the furnace is compensated by an increase in the number of turns of the heating coil, or by applying a supplementary heating coil on the ends of the supporting tube. The ends of the filament wire or tape are fixed to the supporting cylinder by clamps made of a suitable metal (e.g. iron or nickel). These clamps may also be used as electrical connections. In general, at the points of electrical contact the temperature must be considerably below incandescence. 'Cold' junctions may be made for example by thickening the ends of the heating filament (e.g. by twisting), or by applying the clamps already mentioned. In some cases the furnace is provided with a double wall covering or jacket in which water is circulated. In this way not only are the cold

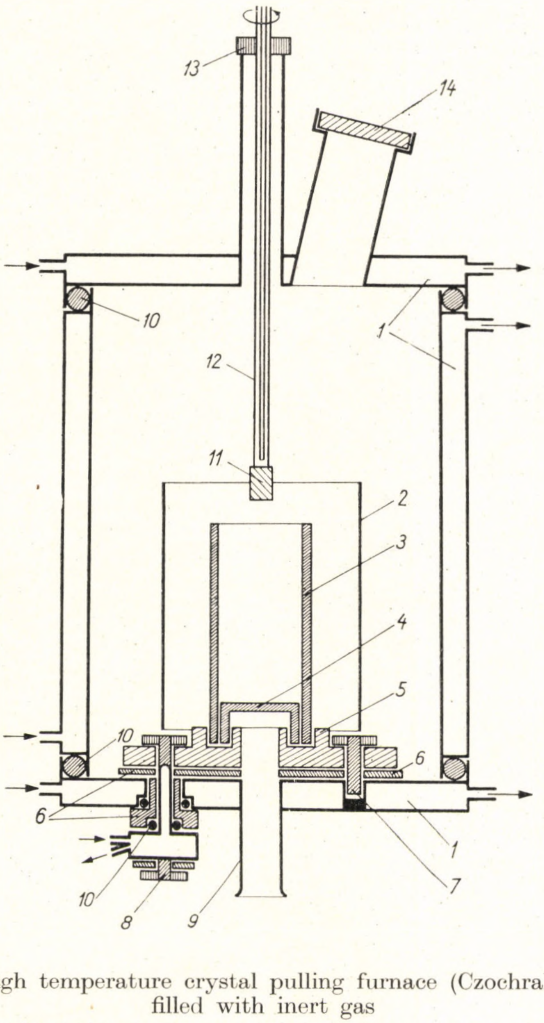

Fig. II.4.2 High temperature crystal pulling furnace (Czochralski method) filled with inert gas

1 double-walled water-filled jacket, *2* reflecting metal plate (e.g. polished molybdenum), *3* cut graphite heating tube, *4* cut graphite bottom heating, *5* graphite blocks supporting the heating element, *6* electrical insulators, *7* earthed terminal connected to jacket, *8* water-cooled electrical input, *9* junction to vacuum pump, *10* packing, *11* head to fasten the seed crystal, *12* rotating crystal puller, *13* packing box, *14* window. The furnace can also be used in the reverse position, when the crucible containing the melt should be fastened to *11*, and lowered with the rod (Bridgman method)

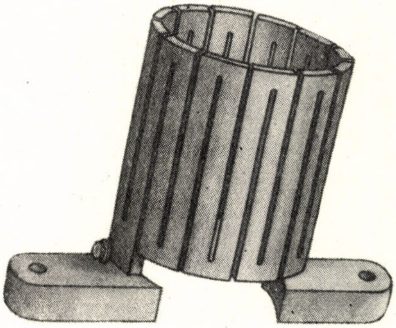

Fig. II.4.3 Cut cylindrical graphite heating element

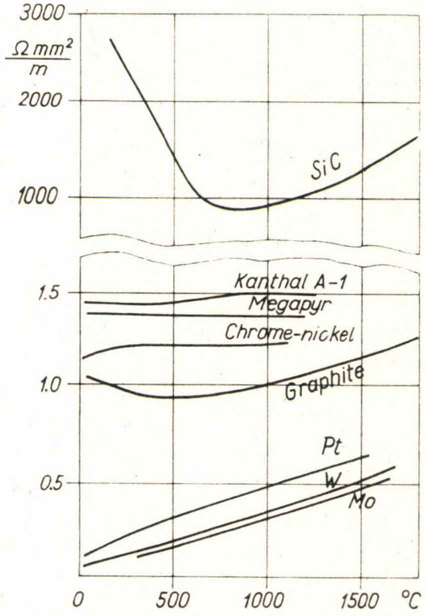

Fig. II.4.4 Variation of specific resistivities of some resistance materials with temperature

Since specific resistivity depends upon the composition and purity of the material used, the actual values may differ from the values given here

electrical connections secured, but the outer temperature of the furnace can be kept at a nearly constant value. As a result several technical needs can be better satisfied (e.g. sealing in the case of vacuum furnaces, or furnaces which are filled with some inert gas, or installation of a window to check the growth process, etc.). The furnaces are usually constructed as mains-operated devices, but it is advisable to use lower (stepped-down) voltages, because in this case the heating resistances can be made of thicker wires which have a longer life-time. Tube-shaped plate elements (e.g. graphite tubes, molybdenum cylinders) may be operated only at low voltages as a result of their low resistance.

In order to regulate the temperature gradient, furnaces consisting of two parts should be used. The two parts are heatable independently of each other. The gradient may be changed by placing heat insulating or metal baffles of various thicknesses and widths between the two parts.

It is advantageous to design furnaces with high electrical output and regulate the necessary working output with the aid of a variable transformer. The data regarding the heating filament of a vertical tube furnace may be estimated in the following way. For simplicity, it may be assumed that the heat loss at the ends of the tube is negligible compared with the loss on the cylinder jacket. This is the case for tube furnaces covered at both ends, and the heat loss due to heat conduction in unit time may be calculated according to the following formula

$$P = S\lambda(T_2 - T_1) \tag{II.4.1}$$

where P is the heat loss, T_1 the temperature of the outer and T_2 the temperature of the inner wall of the furnace, and λ is the average thermal conductivity of the heat insulating material between the walls. The geometrical factor S may be calculated for the above conditions from the length L and the outer and inner radii, R_1 and R_2, from the formula

$$S = \frac{2\pi L}{\ln \frac{R_1}{R_2}} \tag{II.4.2}$$

The electrical input under stationary conditions is also given by equation (II.4.1). The heat insulating materials used are either granulated or powders; consequently, because of their uncontrollable compactness their

TABLE II.V

The usual electrical loads of some resistance materials

Temperature (° C)	Chrome-nickel	KANTHAL-A1	Pt	SiC
	(W/cm^2)			
1100	3	4	10	120
1100	1	3	7	100
1200	—	2	5	80
1300	—	1	3	60
1400	—	—	2	40
1500	—	—	1	30
1600	—	—	—	10

exact thermal conductivities are not known. Nevertheless the value $\lambda \approx \approx 0.011\ \mathrm{W cm^{-1}\ degree^{-1}} \approx 0.0026\ \mathrm{cal\ s^{-1}\ cm^{-1}\ degree^{-1}}$ may be accepted as a good estimation. This value is about one order of magnitude smaller than the value given in the literature for Al_2O_3, MgO and BeO at 1000° C, and one order of magnitude larger than the thermal conductivity of air at atmospheric pressure and 1000° C.

In the selection of the diameter of the filament one must consider the expected surface load of the wire measured by the electrical output taken up by the wire on unit surface. With a larger surface load less wire should be coiled, but the wearing out of the filament is faster. The optimum economic conditions are characterized by the normal or permissible surface load τ (Table II.V). With the aid of equation (II.4.1) the diameter d of the filament in mm may be obtained from the output P measured in watts, the voltage U in volts, the normal surface load τ measured in watts/cm^2 and the specific resistance ϱ in ohm mm^2/m using the formula

$$d = \frac{1}{2.91} \sqrt[3]{\left(\frac{P}{U}\right)^2 \frac{\varrho}{\tau}} \tag{II.4.3}$$

The length of the wire l can be calculated from the equation

$$l = \frac{\pi}{4} \frac{U^2 d^2}{\varrho P} \tag{II.4.4}$$

II.4.3. High-Frequency Induction Furnaces

Materials with high electrical conductivities are heated up in a high frequency electrical field by the eddy currents induced in them. This type of power input may be applied in many cases with great advantage for melting the material to be crystallized. Heating by induction is mainly used to melt metals. By this method insulators can be melted only indirectly in a graphite or metal container. In some cases when the electrical conductivity of the material to be melted increases sufficiently with increasing temperature, the material may be preheated before high-frequency induction heating is applied (Fig. II.4.5). In most cases the high-frequency coil is made of a copper tube instead of solid copper and is cooled by circulating water. Great care must be taken of the correct electrical adjustment in the dimensioning, construction and positioning of the high-frequency coil. The detailed technical descriptions of commercially available high-frequency induction furnaces contain valuable information. Usually the crucible is moved, but the equipment can easily be constructed so that the coil travels along the material to be crystallized.

Heating by induction has many advantages. A considerable quantity of heat can be concentrated in a relatively small volume. This is highly advantageous in zone refining and crystallizing of metals, since, because of their large heat conductivities it is difficult to produce the necessary temperature gradient in metals with resistance furnaces. This also renders possible crucible-free zone melting. Further advantages may be summarized as follows: the heating rate may be relatively high; the magnetic field accompanying the electrical field stirs the melt thereby increasing its homogeneity; there are no current feed and contact problems which present difficulties in the case of resistance furnaces, and which quite frequently can be solved only elaborately and by distorting the heat distribution. Nevertheless there are also drawbacks such as the poor efficiency of transforming the network power to the high-frequency power; the difficulties in measuring and regulating the temperature; and the great space needed for the high-frequency generator. The stirring due to the magnetic field influences unfavourably the growth process.

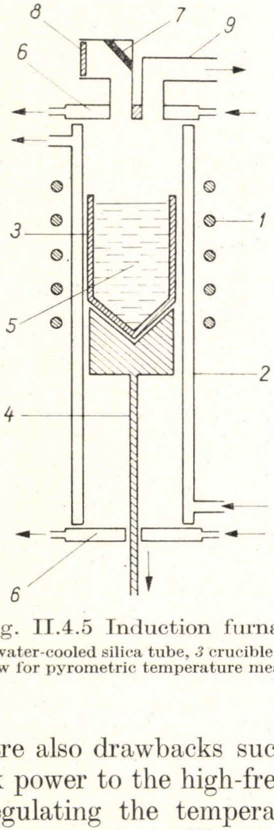

Fig. II.4.5 Induction furnace

1 high frequency coil, *2* double-walled, water-cooled silica tube, *3* crucible, *4* crucible lowering rod, *5* melt, *6* cooled closing plates, *7* metal mirror, *8* window for pyrometric temperature measurement, *9* junction to vacuum pump

II.4.4. Measurement and Regulation of Temperature

(1) The temperature is most conveniently measured with thermocouples made of two different metals or alloys (Table II.VI; Fig. II.4.6). They occupy little room, have small heat capacities and follow changes of the temperature quite rapidly.

If work of a high standard is required the following considerations must be kept in mind. There may be slight differences in the composition of given metals or alloys resulting in temperature values different from those given in Table II.VI. The error of measurement may attain a few per cent The thermoelectric power of a thermocouple may deteriorate during its use, and consequently it is recommended to calibrate each thermocouple before use (and also after prolonged use) with baths of known temperature (Table II.VII).

TABLE II.VI

Electromotive force of some thermocouples in mV
(reference temperature: 0° C)

Temperature (° C)	Copper–Constantan (1),(4)	Chrome-nickel-Constantan(4)	Iron–Constantan (2),(4)	Nickel–Chrome-nickel(4)	Platinum–Platinum-Rhodium(3) 10%	Tungsten–Tungsten-Rhenium(5),(6)
100	4.3	6.1	5.4	3.9	0.6	1.25
200	9.3	13.3	11.1	8.1	1.4	2.66
300	14.9	21.1	16.7	12.1	2.3	4.21
400	20.9	28.9	22.2	15.8	3.3	5.86
500	27.5	36.9	27.8	19.5	4.2	7.53
600	34.4	45.1	33.5	23.2	5.2	9.17
700		53.4	39.6	27.2	6.3	10.83
800		61.4	46.0	31.1	7.3	12.48
900			52.6	34.9	8.4	14.10
1000				38.7	9.6	15.66
1100				42.5	10.7	17.19
1200					11.9	18.66
1300					13.1	20.01
1400					14.3	21.37
1500					15.5	22.74
1600					16.6	24.09
1800						26.58
2000						28.98

(1) Copper oxidizes above 300° C.
(2) It is advisable to use a reducing atmosphere.
(3) Attacked by a reducing atmosphere.
(4) Constantan: 55 Cu + 45 Ni. Chrome-nickel: 85 Ni + 12 Cr + additives.
(5) Used in a reducing or inert atmosphere. Tungsten: 95 W + 5 Re; Tungsten-rhenium: 80 W + 20 Re; J. Neugebauer and L. Körtvélyessy (1966): *Mérés és Automatika 12*, p. 365.
(6) Used up to 2600° C; the folloving thermocouples are also used to measure high temperatures: Ir/50 Ir–50 Rh (up to 2000° C); Ir/90 Ir–10 Rh (up to 2300° C; W/75 W–25 Mo (up to 2600° C) .

The most reproducible values are given by the platinum–platinum-rhodium thermocouple. The lifetimes of thermocouples made of thicker wires are longer (e.g. the wire diameter of platinum–platinum-rhodium thermocouples should be at least 0.5 mm). If on the other hand the wires are thick and reach only a short distance into the heated space, owing to the dissipation of heat a temperature value lower than the real one is obtained.

TABLE II.VII

Reference temperatures
(at atmospheric pressure, °C)

Melting point of	
Mercury	−38.87
Ice	0.00
Tin	231.8
Cadmium	320.9
Zinc	419.5
Antimony	630.5
Silver	960.5
Gold	1063
Platinum	1770
Tungsten	3400
Boiling point of	
Water	100.00
Naphthalene	217.9

Consequently, it is recommended to carry out the calibration under circumstances identical to the actual measuring.

The resistivity of a metal increases nearly proportionally with temperature; the resistivity of a semiconductor on the other hand decreases exponentially. This phenomenon is used to make resistance thermometers.

Resistance thermometers are more sensitive than thermocouples but occupy more room. Of the various metals, platinum may be used up to 1000° C, nickel up to 300° C and copper not above 120° C. Thermometers made of semiconductors (thermistors) can be used up to 300–400° C. The platinum resistance thermometers are most reliable (Fig. II.4.7). Usually

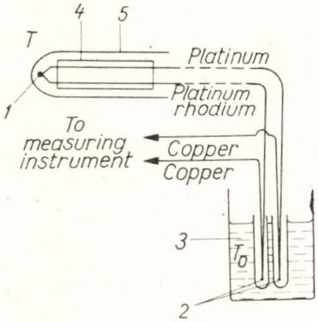

Fig. II.4.6 Platinum–platinum-rhodium thermocouple

1 hot junction, *2* cold junctions, *3* reference bath, *4* tube with double boring made of heat resistant electrically insulating material (e.g. porcelain or corundum, see also Table II.IV) or insulating beads to prevent any contact between the two metals, *5* thin-walled protecting box made of heat resistant electrically insulating material, T temperature to be measured, T_0 reference temperature a Wheatstone bridge circuit is used to measure the change of resistance. For platinum the temperature dependence of the relative change of resistance is expressed by the following equation:

$$\frac{R - R_0}{R_0} = At - Bt^2 \qquad \text{(II.4.5)}$$

where R_0 is the resistance at 0° C and R that at t° C, while

$$A = 3.978 \times 10^{-3}/\text{degree}, \quad B = 5.84 \times 10^{-7}/\text{degree}^2$$

The temperature of an incandescent body may also be determined from the radiation emitted; above 2 600° C this is the only method of measuring temperature. At not very high temperatures the approximate temperature value may be determined from the colour with the naked eye (Table II.VIII).

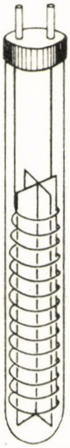

Fig. II.4.7 One possible assembly of resistance thermometers made of platinum
Diameter of the wire is a few tenths of a mm, its resistance 30–40 ohms. The wire is wound supported by a toothed porcelain cross placed in a thin-walled insulating box

Pyrometers are devices to determine the temperature by measuring the radiant energy. Figure II.4.8 depicts schematically the construction of one type of optical pyrometer. The beam of rays L, radiated by a body of unknown temperature (e.g. an incandescent part of the furnace, crucible) is focused by the objective lens O to have its image coincide with that of the incandescent filament of a tungsten lamp F; both images are observed through a red filter G (e.g. 650 nm) with an eyepiece E; the current flowing through the lamp is regulated until the image of the tungsten filament disappears in the image of the incandescent body. The current values which are read on an ammeter (A) may be calibrated to temperature directly since the light intensity of the incandescent lamp depends upon the heating current, and an increasing incandescence of the radiating body may be compensated by increasing the current heating the filament of the lamp.

TABLE II.VIII

Colour temperatures

Colour	Approximate temperature (° C)
Incipient red heat	500 – 550
Dark red heat	700
Bright red heat	900
Yellowish-red heat	1100
Incipient white heat	1300
White heat	1500

(2) Crystal growth is a process which lasts for hours and sometimes even for days. During this period the crystallization zone (the phase boundaries) must proceed in the melt at a low, uniform rate. This requirement is satisfied either by ensuring a constant temperature in the crystallization range as in the Stockbarger method, or by changing the temperature in the area of the crystallization according to a given programme as in the Stöber method. It occurs frequently that in the same equipment a constant temperature is maintained during a given period of the crystallization, whereas at some other period the temperature is slowly changed (e.g. in the Kyropoulos method). The temperature must also be changed if corrections have to be carried out during the growth, e.g. one part of the already grown crystal must be remelted as a result of defective growth.

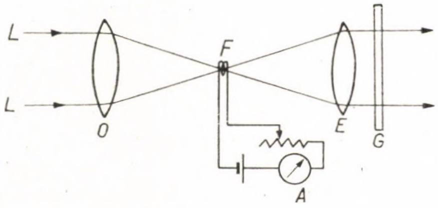

Fig. II.4.8 Function of a pyrometer

The ideal temperature conditions may be obtained in two ways. One possibility is to use a well-insulated furnace of large heat capacity, the heating current being either stabilized or changed at a given rate. Another method consists in regulating the temperature of a furnace of small heat capacity which is not well insulated. Voltage, current and temperature regulating devices are commercially available; their construction and use is described in detail in the various catalogues. Some features, however, are discussed below. A block diagram of temperature regulation is given in Fig. II.4.9; T_0 is the temperature that must be maintained in the range of investigation (e.g. near the heating element of a resistance furnace denoted in the Figure by *1*), and T is the actual temperature which can be best measured with a thermocouple *2*. The voltage U given by the thermocouple is compared with the voltage U_0 corresponding to the prescribed temperature T_0 for the same thermocouple. This comparison is made in the comparator unit *3*, by generating the voltage difference $\Delta U = U_0 - U$ in the form of an error signal. This signal *4* ($k\ \Delta U$), which is properly amplified, operates the heating unit *5* which in turn changes the heating current ΔI to decrease the error signal (negative feed-back). If for instance the temperature in the heating space is larger (i.e. $U > U_0$), the heating current and consequently the temperature decrease; if, on the other hand, the temperature is less than desired ($U < U_0$) the process is reversed. The device renders possible not only stabilization at a given temperature T_0 but also its change. This can be done by comparing the voltage of the thermocouple with a voltage changing according to a given programme.

The temperature regulating unit may be operated continuously or periodically. In the case of crystal growth, continuous operation is better; the thermocouple must be placed in close proximity to the heating element. This is important since materials of high heat capacity placed between the heating element and the temperature detector may result in phase shifts in the temperature regulation, causing a positive feed-back and a periodical change in the furnace temperature (hunting).

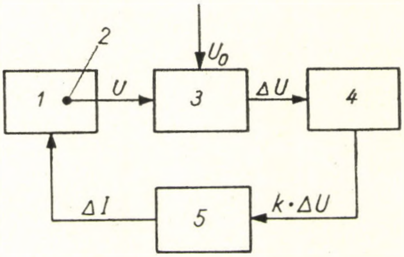

Fig. II.4.9 Block diagram of a temperature-regulating system

Any changes in the laboratory surroundings of the crystallization furnace may influence the temperature in the crystallization space to some extent. Undesired effects may be caused for example by turning the central heating system on or off, by the ventilation, or by sun-rays falling onto the equipment. The following rule of thumb may be kept in mind: the conditions for crystal growth are the more favourable the smaller the temperature changes and the less the undesired vibrations taking place in the surroundings of the crystallization equipment.

II.5. PROCESSING OF CRYSTALS

In some cases the shape, dimensions, crystallographic data, etc. of the growing crystals may be selected in such a way that the single crystal can be used directly as grown for scientific or practical purposes. In most cases, however, the desired samples are developed from the as-grown crystals by some special process. Frequently, pieces cut out from larger crystals are used as seeds; these are sometimes drilled through. In the following section a few practical ideas will be discussed concerning the cutting, grinding, polishing and drilling of crystals.

II.5.1. Cutting and Drilling

II.5.1.1. Cutting and drilling with a solvent

(1) The simplest way of cutting is to wet a thread with a suitable solvent (etching reagent), and draw it across the crystal surface. The advantage of this method is that the temperature of the crystal does not increase and it does not become mechanically deformed during cutting. The method is best applied to water-soluble ionic crystals (Fig. II.5.1). Cutting is done in case (a) with an 80–100 m long crochet yarn about 0.5 mm thick which, placed

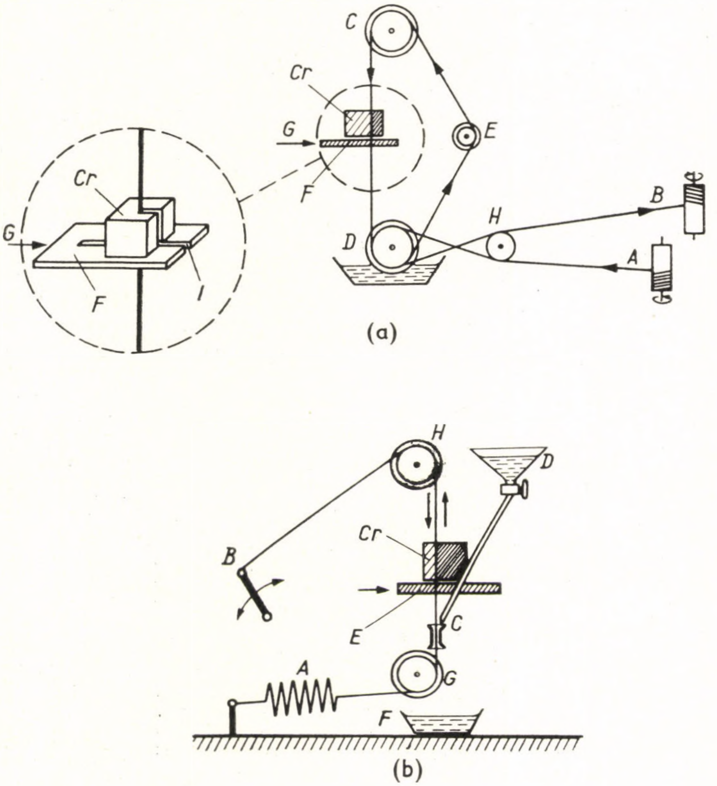

Fig. II.5.1 Crystal saws

on the grooved rims of the discs C and D, goes from the reel A to the motor-driven reel B. The diameter of the discs is about 4 cm, the distance between them about 20 cm, and the maximum speed of the yarn should not be more than 4–5 cm/s. The solvent is placed in a dish below the disc D. The excess solvent is removed from the yarn by a hard rubber roll E which rotates around its longitudinal axis. For this purpose a groove about 0.3 mm wide and 1 mm deep is cut into the roll and the yarn is placed into it. The roll turns only in so far as it is carried with the yarn running in the groove. The crystal Cr is put on a small table F moving on rails, and is fixed to it with for example adhesive tape. The table is moved forwards (in the direction of the arrow G) by a motor-driven screw. The speed of the motion can be regulated by cogwheel transmissions. The optimum speed is usually 0.5 mm per minute. A yarn of the given length is suitable for cutting 3–4 cm thick crystals. Care must be taken to guide the yarn accurately. The grooves on the rim of the discs and the slit I cut into the table serve this purpose. With this crystal saw several crystals of various thicknesses can be cut simultaneously. In this case, however, dises with several grooves and a table with several slits are necessary. It is advisable to construct the equipment so that the discs and also the table can be changed according to the number and thickness of the crystals to be cut. The glass cylinder (denoted by H in the Figure) also serves to guide the cutting yarn. The apparatus can be improved by a rotatable table, by an adjustably strained cutting yarn and by reels of reversible rotation direction, and so on.

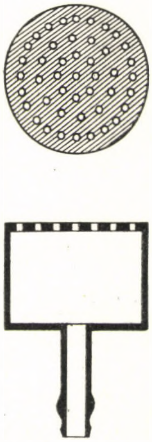

Fig. II.5.2 Tool to process crystal plates
Upper part is top-view of the porous cover plate

Another crystal saw is shown in (b) of the Figure; this is simpler but less suitable for high quality work. The silk yarn is strained by a spring A, and is moved saw-like by the joint B. The solvent dripping from the jar D wets the yarn in the desired way with the aid of the socket placed at C. The crystal is fixed on the table E, and moves together with it in the direction indicated by the arrow. The water dripping down is collected in the dish F. The grooved discs G and H serve to guide the yarn.

(2) Sometimes one needs samples of given sizes cut out of thin crystal plates. An example of this is the preparation of a circular crystal disc from anthracene plates with a thickness of a few tenths of a mm with the dimensions of the photomultiplier for scintillation purposes. A serious difficulty is the brittleness of the crystal plates. The problem can be solved as follows. A brass cylinder a few cm long is prepared with a diameter equal to that of the required crystal plate (Fig. II.5.2). The cylinder is closed at one end with a plate containing small holes. A brass tube is soldered to the centre of the plate closing the other end of the cylinder. The cylinder is fixed to a frame, the plate with holes being on top and the plate with the tube at the bottom. The tube is connected by a rubber pipe to a water gauge. A sufficiently large crystal plate, placed on the brass plate with holes, is held securely by the pressure difference without cracking. The overreaching parts of the crystal can be broken off with forceps so that only a 1–2 cm wide rim remains; this is solved off carefully with a piece of linen soaked in a solvent (in the case of anthracene in cyclohexane). The dissolution of the rim is continued until the desired diameter is obtained.

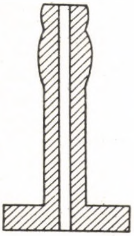

Fig. II.5.3 Tool to transport thin crystal plates

Thin, brittle plates should not be handled with a pair of forceps, but instead with a perforated disc of 1–2 cm diameter made of plexi or some other plastic material to which a suitable tube is fixed (Fig. II.5.3). A rubber hose is fitted onto this tube, and suction is applied to the other end of it. If the disc is close enough to the crystal plate the higher air pressure outside presses the sample to it. In this way the sample can be taken to the desired place, and put down by terminating the pressure difference.

(3) The drilling of crystals may also be carried out in various ways. A hole of the desired diameter can be made by first drilling a small hole (with a diameter of 1 mm), and then enlarging it to the desired dimensions with a yarn soaked in solvent. The drill is operated with a desk machine at a low rate, and rinsed from time to time with the solvent. The crystal is placed on some soft material, e.g. on several layers of paper filters. The drilling machine must be operated with very low pressures. In order to avoid any rupture (bursting) it is advisable to drill the other side of the plate

too before drilling through. This method is slow but reliable. If a drill of larger diameter (4–5 mm) is used the crystal is put into a liquid in which it is not soluble. The drill is operated in this case at a rate of 1 400 revolutions per minute. Although this method is fast the crystals frequently crack.

Good quality drilling can be carried out with the drill shown in Fig. II.5.4, which is based on the local solution of the crystal. The solvent is streamed in the inner tube *1* onto the crystal, and sucked away with the aid of a water gauge through the outlet of the outer tube *2*; the guide cone *3* ensures a uniform dissolution of the crystal along the whole cross-section of the outer tube. The paper filter *4* is used to blot up the leaking solvent.

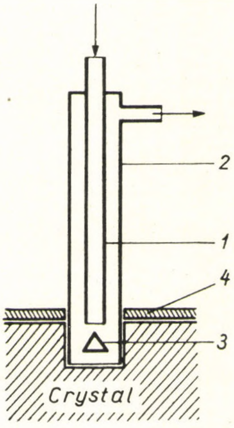

Fig. II.5.4 Crystal drill

II.5.1.2. Cutting by mechanical methods, ultrasound, spark machining

These methods are mainly used in the case of metal crystals, elementary and compound semiconductors, and generally for the processing of hard crystals. The mechanical methods include cutting with jeweller's saws, and with string and disc cutting machines. In practice these latter two machines are most often used. With *string machines* cutting is done with a 0.1–0.2 mm tungsten wire fixed to two cylinders. The backwards and forwards motion of the wire is also performed by these cylinders. An aqueous suspension of the polishing material (silicon carbide, boron carbide, aluminium oxide, etc.) is dripped onto the wires. Usually several stretched wires are used so that several slices can be cut off at the same time. In the case of *disc machines* fast motors capable of a large number of revolutions per minute are used with thin bronze or copper discs mounted onto the motor axes. Diamond or carborundum grains are pressed onto the rim of the disc (diamond or carborundum disc). In order to avoid warming up water is dripped on the surface.

The mechanical methods usually cause large mechanical deformations in the crystals. Processing with ultrasound or electrical erosion (spark machining), results in considerably smaller deformations. For the purposes of cutting with *ultrasound* magnetostriction ultrasound generators are generally used. A copper cutting tool is usually placed in the cutting head which oscillates with a small amplitude (Fig. II.5.5).

The shape and dimensions of the cutting tools are developed according to the sample to be cut out. For example, plane plates are selected for the purpose of slicing, whereas thin-walled tubes must be used to obtain disc-shaped samples. When ultrasound is applied the cutting itself is carried out by a suspension of a proper grinding material. In addition, the material transport accompanying an *electrical spark discharge* may be used for the purpose of cutting (spark erosion). The crystal to be processed is in this case the positive electrode, while the negative electrode is the cutting tool (Fig. II.5.6). The electrodes are placed in some insulating fluid (e.g. petroleum) Electrical impulses are generated on the electrodes by a periodical discharge of condensers. The discharges take place in a few microseconds in channels of very small cross-sections at a very large current intensity. Their frequency is 2–100 kHz. As a result of the thermal and dynamic effects of the sparks craters develop on the opposite electrode surfaces, and the electrode used as a tool becomes copied onto the sample.

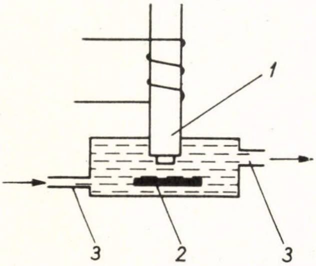

Fig. II. 5.5 Cutting with ultrasound
1 drill head, *2* crystal to be cut, *3* inlet and outlet for the suspension containing grinding powder

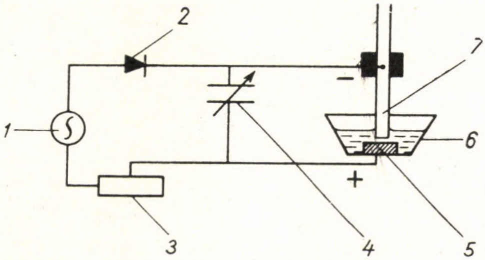

Fig. II.5.6 Cutting by electrical erosion
1 a.c. supply unit, *2* rectifier, *3* variable resistance, *4* variable condenser, *5* crystal to be cut, *6* insulating liquid, *7* cutting tool

II.5.2. Grinding and Polishing

The purposes of these operations may be manifold, e.g. the removal of strongly deformed layers resulting from cutting, or the production of plane or plane-parallel surfaces necessary for certain technological operations and indispensable for various physical and chemical investigations.

Grinding must always be carried out in several (usually 3–4) stages with suspensions of various grain distributions. The grains are usually quartz, carborundum or diamond with dimensions of 1/10 mm in the case of rough grinding. The grain size gradually decreases to a final value of a few times 10^{-3} mm. Any liquid not reacting chemically with the sample may be used as a suspending medium; in the case of crystals soluble in water the use of alcohol or petroleum may be quite satisfactory. Polishing is a multi-stage process similar to grinding. For this purpose, in addition to the materials already mentioned, ferric oxide, chromic oxide, etc. may also be used. The grain diameter of the polishing materials is a few tenths of a micron or even less. An essential difference between grinding and polishing is that while grinding is carried out on a hard support (e.g. a glass plate), polishing is always done on some soft material (e.g. on a glass or metal plate covered with beeswax, tar or some soft textile).

II.5.2.1. Grinding and polishing of germanium and silicon crystal plates

3 or 4 pieces of 2 mm thick crystal plates with surfaces of 3–4 cm^2 are cut off parallel to the {111} faces. (A diamond disc of a cutting machine is used with a tungsten wire.) The plates are first placed on a suitably polished steel disc and ground by hand using Al_2O_3 powder with an average grain diameter of 10 μ. Grinding must be carried out by pulling the plate always in the same direction on the disc wetted with the suspension, and pressing it slightly with a finger-tip to the disc. In this way a layer of about 80–100 μ is removed from the surface of the plate in about 10 minutes. The same is done with the other side of the plate. To continue the procedure the plates are glued at a distance of about 10–20 mm from each other onto a steel disc with a diameter of 60–70 mm (Fig. II.5.7). The steel disc contains 0.4–0.5 mm deep saw cuts in a mesh-like arrangement at a distance of 5 mm from each other. Gluing of the crystals onto the disc is carried out in the following way. A glue is prepared by mixing 50% resin, 45% beeswax and 5% Canada-balsam. This mixture is dripped onto the steel disc and is warmed up (e.g. by placing it on an electrical hot plate) until it spreads uniformly all over the surface filling the saw cuts. The samples are put on the surface, and the disc is placed on an asbestos plate, and left there until it cools down to room temperature. Before gluing, it is advisable to cover the crystal plates with silicone rubber, and to put lead weights (100 g/cm^2) on the rubber. After the disc has cooled down it is put into the grinding machine, and the crystal slices are ground at 600–700 revolutions per minute for a few minutes with an Al_2O_3 powder with a grain diameter of 15–20 μ until a surface layer of about 50 μ has been removed. After this the slices and the grinding disc are washed, and the grinding is continued for 1–2 minutes, this time using an Al_2O_3

powder with a grain diameter of 10 μ. This operation is followed by hand grinding which is carried out in the same way as previously, but this time for 1 hour, and the grain diameter of the Al_2O_3 should be first 10 μ, and then 5–7 μ. With this the grinding is finished, the crystal plates are solved off with the aid of petroleum-soaked cotton wool, and washed three times in a beaker containing 10 ml pure petrol.

Polishing is carried out with a standard polishing machine and emery paper. The diameter of the Al_2O_3 grains is 0.4–5.0 μ, the operation lasting 5–10 hours. (If grinding is not followed immediately by polishing the crystal plates are washed carefully in tepid distilled water before the polishing in order to remove any dust particles adhering to them.) For a second fine polishing some special polishing material is used (e.g. Linde A and B polishing powder) with an even smaller grain diameter (0.05–0.30 μ) than before.

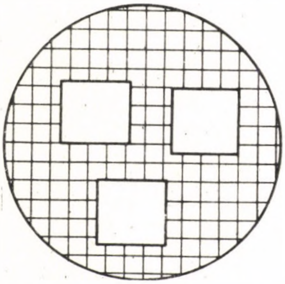

Fig. II.5.7 Metal disc with crystal plates
Thin lines represent saw cuts

If no proper polishing material is at hand MgO (with a grain diameter of 1–2 μ) suspended in alcohol may be used.

To investigate the quality of the polished surface microscopical methods are the most suitable. If a more exact surface qualification is required an interference microscope is used.

II.5.2.2. Grinding and polishing of semiconducting compounds

The crystals of semiconducting compounds (e.g. the $A^{II}B^{VI}$ compounds such as ZnS, or the $A^{III}B^{V}$ compounds such as GaP) cannot always be obtained with the same dimensions and quality as the single crystals of metals and elementary semiconductors. Frequently small whiskers or crystal plates of the dimensions of a few mm² must be processed. In such cases grinding and polishing are rather laborious.

It is advisable to embed the crystals in some not too brittle support, e.g. in plastic, even for the most simple hand grinding. If the crystals are used for further investigations they must be easy to remove from the embedding material after grinding is finished. Unfortunately most plastics do not satisfy this requirement, but sulphur for example does serve this purpose well. The procedure is as follows. The crystal is glued (by the surface to be ground) to a microscopic slide with the aid of a thin layer of a well-soluble glue. A 20–30 mm high glass cylinder with a diameter of 30–40 mm is then placed over the crystal, and molten sulphur is poured into it. (Care must be taken that the sulphur melt is not overheated, since in that case a strongly viscous modification of the sulphur is formed which is very difficult to handle. This is indicated by the darkening of the light yellow melt.) When the sulphur has completely solidified the slide is removed, and the sulphur column is pushed out together with the embedded crystal from the glass cylinder. It is advisable to wash the free surface of the crystal and also the sulphur surrounding it carefully with an appropriate solvent in order to eliminate all traces of the glue.

The grinding of the embedded crystal is carried out with increasingly finer emery papers, and should be finished with the finest grade (600). The crystal must always be pulled along the grinding paper in the same direction to avoid scratches caused by grinding grains breaking away from the paper. Polishing is also carried out by hand using a suitable material (cloth, or silk) which must be stretched over a glass or metal plate. The material is wetted with distilled water, a small amount of Al_2O_3 powder of grain diameter 10 μ is smeared onto it, and the crystal is moved on it in a circle or in a figure eight. After intensive polishing for about 15 minutes the sample is washed in distilled water, and the polishing is continued using a second, and then a third piece of material for about 15 and 30 minutes, respectively. The grain diameter of the Al_2O_3 should be 5 μ in the second stage, and 1–2 μ in the third stage. The surface obtained by this method is not usually perfect, since the edges of the crystals become rounded off in the grinding. The reason for this is that sulphur is rather soft. Good quality crystals can be obtained, however, if the crystals are glued onto a metal disc, as described in II.5.2.1. In this case plates with large surfaces which are harder than the crystals are glued between the samples. Although the polishing process is slower, the entire crystal surface becomes uniformly polished.

After polishing is finished the crystals are taken out from the sulphur block with warmed forceps or a knife blade. The sulphur adhering to the crystal surface can easily be removed by placing the crystal on an analytical filter paper which is then put on a metal plate preheated to about 150° C. The hot filter paper absorbs the molten sulphur almost completely. If all traces of sulphur are to be removed the crystals must be shaken in carbon disulphide or acetone. (Care should be taken with carbon disulphide because it is inflammable, explosive and highly toxic.)

II.5.2.3. Processing of some alkali halide crystals

Alkali halides are easy to process, and therefore are most suitable for obtaining experience in the field of processing crystals as described in the previous section. In this section only crystals suitable for γ-ray detection: NaI(Tl), KI(Tl) and CsI(Tl) will be dealt with. Some special procedures will be discussed too.

From the roughly cylindrical NaI(Tl) crystals grown as described in II.2.1.2 a piece of suitable length is cut out with a fret-saw. Since sodium iodide dissolves well in water a cutting rate of 3 mm/minute can be obtained with a wet thread. The cut surfaces are ground on a fairly wet linen cloth stretched over a glass plate until they become plane-parallel (the use of grinding powder is unnecessary). These operations are carried out in an exhaust chamber with rubber gloves because the thallous iodide used as activator is toxic and is even absorbed through the skin. The desired diameter of the crystal is obtained by proper turning and surfacing. It is not advisable to fix the crystal directly in the holder of the turn-bench, since it may crack under this pressure. With the method outlined in Fig. II.5.8, however, the crystals can be turned without difficulty. A metal support of 30 mm diameter is placed in the holder, and the crystal is placed into it by

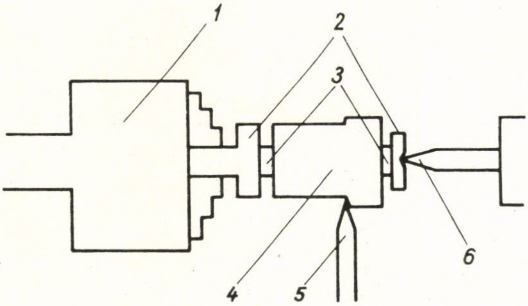

Fig. II.5.8 Turning and surfacing of crystals
1 clamping grip, *2* metal supports, *3* rubber discs, *4* crystal, *5* knife, *6* fixing mandrel

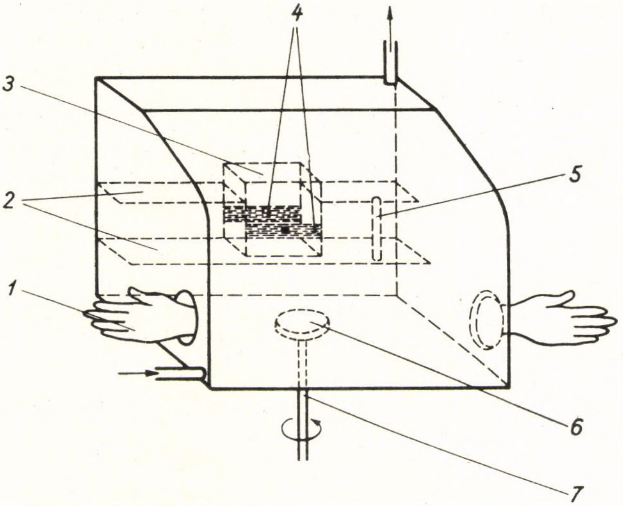

Fig. II.5.9 Dry chamber
1 rubber gloves, *2* shelves, *3* lock chamber, *4* plates to open or close the lock chamber, *5* hygrometer, *6* rotating discs, *7* flexible shaft

inserting a 5 mm thick rubber disc between the crystal and the support. Another metal disc is connected to the other crystal surface via a rubber disc. This metal disc is supported in its centre by a fixing mandrel. The turning knife is sharpened to an acute angle, and fixed so that its edge is nearly vertical. The turning speed and the rate of feed must be set at a minimum. The feed is first 0.5–1.0 mm but this is later decreased continually. In order to avoid any temperature increase the supporting mandrel must be cooled with oil. When the desired dimensions have been attained the crystal surfaces are pulled once or twice over a wet cloth stretched on a glass plate. Afterwards the crystal is put in a dry chamber. The polishing of the rather hygroscopic crystal is carried out here on a piece of satin or chamois leather stretched over a rotating disc. The satin or chamois is either dry or moistened slightly with a piece of cotton-wool soaked in *n*- butanol.

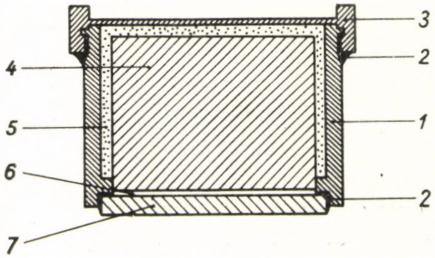

Fig. II.5.10 Crystal in socket

1 cylindrical socket made of 'fredal', *2* seal, *3* threaded cover, *4* crystal, *5* magnesium oxide powder, *6* silicone oil, *7* glass plate

An airtight plexi box of about 50×30×30 cm is quite satisfactory as a dry chamber (Fig. II.5.9). The various operations in the chamber can be carried out with rubber gloves sealed hermetically into the side walls of the box. The processing tools, materials and also the crystal are placed into the box through a lock chamber. A water-free inert gas (e.g. nitrogen) atmosphere is maintained in the box. Humidity is checked with a hygrometer.

When mounting γ-detecting NaI(Tl) crystals, the crystals may be encased in various ways; Fig. II.5.10 shows only one possibility. The operations must be carried out in dry surroundings, and thus it is advisable to put the tools and materials into the dry chamber about 5 or 6 hours before mounting. (The air-lock is used only when necessary.)

In addition to the materials and tools shown in Fig. II.5.10, and to those necessary for polishing the following things are also put into the dry chamber: a cork stopper on which the crystal is put for cooling during and after polishing; a 4–5 cm diameter plexi disc with a handle to smooth the magnesium powder in the socket; a small aluminium shovel about 0.8 mm thick to pack the magnesium oxide around the crystal; a glass rod to drop silicone oil onto the crystal; a sheet of paper to cover the polishing disc during the operations with the magnesium powder, thus protecting it against any contamination;

some glue (adhesive) (e.g. resinous beeswax dissolved in benzene) to seal the socket hermetically.

Only that surface of the crystal is polished very carefully through which the luminescent light emerges. The quality of the silicone oil is important. An oil is used with a viscosity of about 2×20^4P, and with a refractive index which falls between the refractive indices of the glass cover and the crystal, and which transmits the luminescent light (380–440 nm) emerging from the NaI(Tl) crystal.

The water-free nitrogen streaming through the dry chamber may be obtained from liquid nitrogen. The humidity of the dry chamber can be kept below 1% simply and at low cost by the following method. The air is first expelled from the chamber with a nitrogen stream. The nitrogen stream obtained directly from the gas-cylinder is led first through a tube about 1 m long with a diameter of about 5 cm filled loosely with phosphorus pentoxide, then into the chamber. When the chamber is filled with nitrogen the latter is circulated in a closed circuit with the aid of a pump (Fig. II.5.11).

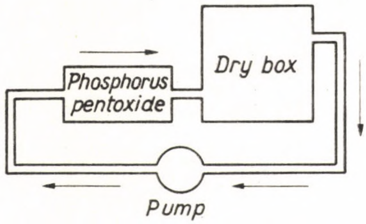

Fig. II.5.11 Circuit of drying nitrogen

The processing of KI(Tl) is similar to that of NaI(Tl) but grinding and polishing are carried out with *n*-butanol instead of water. Grinding powder is also used in this case since KI dissolves less readily in *n*-butanol. The advantage of CsI(Tl) crystals is that they do not crack, but become somewhat smeared during their turning. The final polishing is carried out with chromic oxide and glycerine.

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