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LSF EFFECTS IN AL - 3D-TRANSITION METAL ALLOYS: LOW TEMPERATURE dHvA EXPERIMENTS AND THE TEMPERATURE DEPENDENCE OF THE CHARGE PERTURBATION AROUND THE IMPURITIES

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3d-transition metal impurities - originally believed to be non-magnetic in aluminium - are good examples of localized spin fluctuations /LSF/. Our aim in this paper is to show that:

1./ the low-temperature macroscopic properties /resistivity, susceptibility, specific heat, dHvA effect/ can be described quantitatively by the renormalized random-phase approximation of the LSF, and that

2./ at higher temperatures the situation occurring in Al - 3d-transition metal alloys bears a close similarity to the situation occurring in noble metal hosts where the impurities are magnetic. This suggests that Mn in aluminium appears to become magnetic at high temperatures.

To begin with we shall summarize the different types of experiments /both macroscopic and microscopic/ that have been performed on Al - 3d-transition metal alloys. After this short review, the low-temperature de Haas van Alphen /dHvA/ experiments and the NMR measurements of the charge perturbation around the impurities are discussed.

Residual resistance measurements at low temperatures /BOATO 1966, AOKI 1967/ display a "one-peaked" distribution of $\Delta R/c$ as one goes through the 3d-series, with the peak between Mn and Cr. In terms of the Friedel-Anderson model this indicates that the impurities are non-magnetic in aluminium, i.e. the virtual bound state is spin-degenerate. In the Friedel-Anderson partial wave analysis neglecting nonresonant phase shifts, the residual resistivity can be written as

$$\Delta R/c \sim \sin^2 \eta_2 \qquad \eta_2 = \frac{N}{10} \qquad /1/$$

where N is the number of d-electrons in the unfilled d-level of the impurity. Going through the 3d-series $\sin \eta_2$ rises and then falls, according to the filling of the d-level. /This behaviour should be contrasted to the situation occurring in noble metal hosts, where a "double-peaked" curve in $\Delta R/C$ indicates a spin splitting of the ubs./

The low-temperature susceptibility /AOKI 1968/ shows a large enhancement in the case of Mn and a somewhat smaller enhancement in the case of Cr, indicating that at least these impurities are near to the

magnetic-nonmagnetic limit. There is a large enhancement of the electronic specific heat in the case of Mn and Cr /AOKI 1969/ and an anomaly in the superconducting transition temperature /BOATO 1963, AOKI 1968/.

A temperature-dependent impurity resistivity between 1 and 4°K of the form

$$\Delta R(T) = \Delta R(O) \left[1 - (T/\theta)^2\right] , \qquad /2/$$

with $\theta = 530^{\circ}K$ for Mn and $1200^{\circ}K$ for Cr impurities has been observed by CAPLIN and RIZUTTO /1968/. This behaviour, together with the susceptibility enhancement, has led to the LSF concept, worked out theoretically by RIVIER, ZUCKERMANN and SUNJUC /1969/ in analogy to the spin fluctuations occuring in the nearly magnetic metals Pd and Pt /LEDERER, MILLS 1967/. It has since been shown that both the specific heat enhancement /HARGITAI, CORRADI 1969, CAROLI et al. 1969/ as well as the superconducting transition temperature /ZUCKERMANN 1970/ and the temperature dependence of the impurity susceptibility /HEDGCOCK, LE 1970/ can be analysed within the LSF picture.

Among the "microscopic" methods only nuclear magnetic resonance /NMR/ has been used to investigate the Al - 3d-transition metal alloys. By this means the Knight shift, a parameter related to the susceptibility, has been measured. The advantage of the NMR method lies in the fact that one can measure the local distribution of the electronic polarization. In principle, one can perform three types of measurements:

1. by measuring the impurity Knight shift the susceptibility localized on the impurity site can be obtained

2. by measuring distinct satellites near to the central resonance of the matrix nuclei the perturbation at a certain distance from the impurities can be investigated

3. by analyzing the central resonance of the matrix nuclei one can obtain the average polarization outside the impurity cell.

The first type of measurement has been performed by NARATH and WEAVER /1969/ on AlMn, AlCr and AlV alloys, and by LAUNOIS and ALLOUL /1969/ on AlMn. These measurements show that the susceptibility is localized on the impurity site and is enhanced in a similar

way as the total susceptibility. ALLOUL et al. /1971/ have measured the temperature dependence of the Knight shift at the first neighbours of the Mn impurities, and they have observed a temperature dependence of the form $\Delta K_1 (T) = \Delta K_1 (0) [1 - \text{const.}T]$, which is clearly in disagreement with the temperature dependence of the macroscopic susceptibility measured by HEDGCOCK and LI /1970[x]/. The central ^{27}Al resonance has been investigated by LAUNOIS /1969/ and GRÜNER et al. /1971/. The magnetic field dependence could be well described by assuming the existence of exchange enhancement on the impurity site. Moreover, the negative definite spin polarization around the Mn impurity /as implied by the Kondo scattering/ was not observed. The various experimental facts are summarized in Table 1.

In summary, the experimental results of both macroscopic and microscopic experiments have led to the qualitative picture that the impurities are "nonmagnetic" at low temperature in aluminium, and there is a large exchange enhancement in the case of Mn and a somewhat lesser enhancement in the case of Cr impurities.

In order to investigate the magnetic behaviour of manganese in aluminium /which shows the most pronounced anomalies/ it is necessary to estimate the parameters which describe the magnetic state. These parameters are as follows:

- Δ – half width of the vbs
- U – effective Coulomb exchange between pairs of electrons with opposite spins on the impurity site
- $U/\pi\Delta$ – defines the magnetic state within the HF limit, with
  - $U/\pi\Delta \lesssim 1$ nonmagnetic limit
  - $U/\pi\Delta \sim 1$ local spin fluctuations
  - $U/\pi\Delta > 1$ magnetic limit
- ε_d – position of the d-state measured relative to the Fermi energy
- $N_d(0)$ – density of states /spin at the Fermi level, where

$$N_d(\varepsilon) = \frac{2\ell+1}{\pi} \frac{\Delta}{(\varepsilon-\varepsilon_d)^2 + \Delta^2} \qquad /3/$$

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x/ It should be mentioned that there is a large diamagnetic contribution due to the impurities in Al-based alloys, which has to be taken into account, and on the other hand the K_1 value ΔK_1 should not be directly proportional to the susceptibility.

$\tau_s = \frac{\hbar}{\Gamma_s}$ - the lifetime of the LSF which can be expressed in terms of U and Δ within the renormalized random-phase approximation /PATON, ZUCKERMAN 1971/ as

$$\Gamma_s^{-1} = \left(\frac{Z_1}{\Delta}\right) \frac{U/\pi\Delta}{Z_1 - U/\pi\Delta} \qquad /4/$$

Z_1 - mass renormalization of the LSF , which has a value of 1 when the impurity is nonmagnetic and increases as $U/\pi\Delta$ increases (see Fig. 1). This parameter can be given within the framework of the RRPA theory /HARGITAI, CORRADI 1969/.

The dHvA effect has been used to estimate these parameters in dilute single crystal alloys of AlMn, /PATON 1971/. The advantage of this type of experiment is that in one experiment one can determine four variables which are sensitive to the impurity scattering. These are:

1./ dHvA frequency /samples the normal Coulomb scattering/
2./ scattering term /samples the normal and resonance scattering/
3./ effective mass /samples the many-body effects; electron-phonon interaction and LSF/
4./ conduction electron g-factor /samples the many-body effects/

The values for the parameters described above, as obtained from the dHvA experiments, are shown in Table 2 together with the values determined from other types of experiments. The internal consistency of these parameters suggests that the low-temperature properties of AlMn alloys can be described qualitatively by a renormalized RPA, even though this alloy system is rather close to the magnetic-nonmagnetic limit /i.e. $U/\pi\Delta \sim 0.9$/

The measurement of the macroscopic parameters is restricted to the low-temperature regime, because at higher temperatures the change of the matrix parameters and the phonon term hamper the determination of the temperature dependence in a broad range. In order to get some insight into the high-temperature behaviour, we have measured the temperature dependence of the charge perturbation around the impurities in aluminium. Far from the impurity this perturbation has the form /FRIEDEL 1958/

$$\Delta\rho_{tot}(r) = \frac{\alpha}{2\pi^2} \frac{\cos(2k_F r + \varphi)}{r^3} \qquad /5/$$

where the oscillation amplitude α and phase factor φ are determined by the phase shifts of the scattered electrons. If the resonant phase shift η_2 dominates, we get

$$\alpha = 5 \sin\eta_2 \qquad \varphi = \eta_2 \qquad /6/$$

It should be emphasized that α samples the same matrix element as the impurity resistivity. By measuring the oscillation amplitude one gets essentially the same information as from the impurity measurements /i.e. one expects the same distribution going through the 3d-series as in the case of residual resistivity/.

The charge perturbation around the impurities yields a field gradient distribution /KOHN, VOSKO 1960/ of the form

$$\Delta q(r) = \frac{8\pi}{3} \mu \, \delta\rho_{tot}(r) \qquad /7/$$

where the antishielding factor μ resembles the matrix properties and for Al $\mu \simeq 22$ /FUKAI 1970/.

If $q = Q$, the nuclear Zeeman levels are displaced by an equal amount from each other and one resonance broadened by the interaction between the nuclei is obtained. In the case of a field gradient q_o, the interaction between this field gradient and the nuclear quadrupole moment yields a perturbation which in first order shifts the satellite transitions by ν_Q. The latter is proportional to q_o and depends on the orientation between the main component of the field gradient tensor and the external magnetic field, while the central /1/2 → -1/2/ transition remains unchanged. Hence we get the characteristic pattern of Fig. 2b. In polycrystalline samples the average over Θ has to be taken and we get the pattern of Fig. 2c. There are two observable effects for one fixed q_o value: the reduction on the main line intensity, and satellites beside the central resonance displaced by $\nu_Q = \text{const.}\ q_o$ and $2\nu_Q$ /DRAIN 1968; JÁNOSSY and GRÜNER 1971/. With a distribution of q values according to eq. 7 the patterns of Fig. 2c must be summed up for the different q values in order to obtain the whole spectrum. We get:

1./ Intensity reduction of the main line, which on statistical considerations can be given as

$$D = D_o \, (1 - c)^n \qquad /8/$$

/ROWLAND 1965/, where D and D_o are the signal intensities of the alloy and pure metal, and c is the concentration. The first-order wipe-out number, n, is proportional to α, and does not depend

on φ /TOMPA et al. 1969/. By measuring the wipe-out number we can measure the oscillation amplitude.

2./ Under optimal circumstances we can observe weak satellites corresponding to certain neighbour shells around the impurities where the field gradient depends on α and φ. From the intensity of these satellites we can determine the neighbour configuration.

As there is no perturbation in pure metals, no correction is necassary, and we can perform the measurements in a broad temperature range. A further advantage of the latter type of measurements is that they are free from impurity-impurity interactions.

The room-temperature signal intensity measurements and wipe-out numbers are shown in Fig. 3 for normal metal /Si, Zn, Cu/ and transition metal impurities /Fe, Mn, Cr/. The inset shows the wipe-out numbers obtained by measurement and by a calculation that assumes that η_2 dominates. As can be seen from Fig. 3, there is a discrepancy between the measured and calculated η values in the case of Mn and Cr impurities. The temperature dependence has been determined by measuring the signal intensities at different temperatures. No temperature dependence was found in the case of Si and Cr impurities, and for Mn and Cr impurities we get a T^2 law up to rather high temperatures /see Fig. 4/. The characteristic Θ values are somewhat larger than those obtained from the resistivity measurements. This difference will be explained later.

A satellite structure /second type of measurements/ has been observed in AlCr alloys, as shown in Fig. 5, which has a characteristic first-order quadrupole pattern /Fig. 2c/. The q value can be determined from the shifting of the satellites /JÁNOSSY, GRÜNER 1971/ but what is more important in the present analysis is that it has a T-dependence

$$q(T) = q(o)\left[1 - (T/\Theta)^2\right], \Theta = 860 \pm 30^{\circ}K \qquad /9/$$

as can be seen from Fig. 6. Comparison with the value determined by the oscillation amplitude measurements indicates that the phase of the charge oscillation does not change very much in this temperature range.

It can be shown /GRÜNER, HARGITAI 1971/ that effects like the reduction of the mean free path are not important here, and that the temperature dependence of n and q are connected with the

LSF effects. We are now going to analyse the connection between the impurity resistivity and the charge perturbation. As regards the temperature dependence, the main difference between the two parameters lies in the fact that the resistivity is a real "Fermi surface effect". From the relaxation time

$$\tau^{-1}(\varepsilon) = \left|V_{k\alpha}\right|^2 n_d(\varepsilon) \qquad /10/$$

we get the conductivity

$$\sigma \sim \int \tau(\varepsilon) \frac{\partial f}{\partial \varepsilon} d\varepsilon = \tau(o) + \frac{\pi^2 k^2 T^2}{6} \frac{\partial^2 \tau(\varepsilon)}{\partial \varepsilon^2}\bigg|_{\varepsilon=o} + \ldots \qquad /11/$$

There are two contributions to the temperature dependence, one coming from the energy dependence of the density of d-states, which is enhanced by the LSF effects, and one coming from the temperature dependence of $n_d(0)$. The temperature dependence in principle could be explained by the second term in eq. 12 only, without involving a temperature dependence in the density of states /CAPLIN, RIZUTTO 1968/.

The oscillation amplitude, on the other hand, can be written in the case of impurities with ubs at the Fermi level as

$$\Delta\rho_{tot}(r) \sim \frac{\left|V_{kd}\right|^2}{r^3} n_d(o) \sin 2k_F r \qquad /12/$$

which is not a Fermi surface effect like the resistivity /because we have to sum up from the bottom of the band to get the total charge perturbation/ and <u>the temperature dependence of the oscillation amplitude means a temperature-dependent density of states,</u> too. In the framework of the LSF theory we get /GRÜNER, HARGITAI 1971/

$$\alpha(T) = \alpha(o)\left[1 - \frac{\pi^2 k^2 T^2}{2\Gamma_s^2}\right] \qquad /13/$$

and only the key parameter of the LSF, namely Γ_s, comes into the temperature dependence. With $\Theta = 750^{\circ}K$ we obtain $\Gamma_s = 0.15$ eV for <u>Al</u>Mn, which agrees rather well with the value determined from the low-temperature macroscopic parameters /see Table 2/. Fig. 7 shows the oscillation amplitudes extrapolated to T = 0 and meas-

ured at "high" temperature /T = 450°K/. At low temperatures the resistivity curve measured in Al - 3d-transition metal alloys is a single-peaked distribution, while at high temperatures this curve is "double-peaked". This resembles the situation occuring in noble metal hosts and indicates a magnetic-like behaviour in the HF limit. This indicates that both Al- and noble-metal-based alloy systems behave similarly, the difference showing up only in the temperature scale. On the basis of the dHvA and NMR observations it appears that these alloy systems are nonmagnetic at T = 0 but appear to become magnetic at high temperatures.

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FIGURE CAPTIONS

Fig. 1. Mass renormalization parameter Z_1 vs $U/\pi\Delta$

Fig. 2. First-order quadrupole pattern for ^{27}Al nuclei.

Fig. 3. First-order wipe-out numbers at T = 300 ^{o}K

Fig. 4. Temperature dependence of n in AlMn and AlCr

Fig. 5. First-order quadrupole structure in AlCr

Fig. 6. Temperature dependence of q in AlCr

Fig. 7. First-order wipe-out numbers at $T \to 0$ and T = 450 ^{o}K

TABLE CAPTIONS

Table 1. Experiments on Al- 3d-transition metal alloys

Table 2. The experimentally determined parameters for the AlMn system

Table 1.

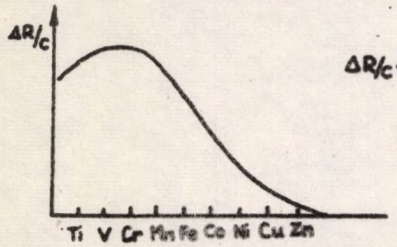
Macroscopic	Microscopic
1. Impurity resistivity $\Delta R/c$  $\Delta R/c \sim \sin^2 \eta_2$ $\eta_2 = \frac{N\pi}{\Delta}$	
1a. T-dependent resistivity CAPLIN 1968 $\Delta R(T) = \Delta R(o) \left[1 - (T/\theta)^2\right]$	
2. Susceptibility AOKI 1969 x enhancement in the case of Mn, Cr	1. Impurity Knight shift NARATH /1969/ local susceptibility enhancement /Mn, Cr/
2a. T-dependent susceptibility, HEDGCOCK 1970 $\chi(T) = \chi(o) \left[1 - (T/\theta)^2\right]$	2. Knight shift at first neighbours ALLOUL et al /1971/ $K_1(T) = K,(0)x$ [1 - const.T]
3. Specific heat AOKI 1969, γ enhancement in the case of Mn, Cr	3. Spin perturbation in the matrix LAUNOIS /1969/ GRÜNER /1971/
4. Superconducting transition temperature T_c anomaly in the case of Mn, Cr	

Table 2.

Parameter	dHvA	Other properties[x]			
ε_d(eV)	0			0_{Tc}	
Δ(eV)	0,24	$0,33_{\gamma}$	$0,13_{(0)}$	$0,29_{x(T)}$	$0,55_{\rho(0)}$
$U/\pi\Delta$	0,90	$0,96_{\gamma}$	$0,93_{Tc}$		
z_1	1,85	$1,95_{\gamma}$	$1,90_{Tc}$		
Γ_s(eV)	0,16	$0,16_{\rho(T)}$			
$N_d(o)(eV^{-1})$	6,1	$4,8_{\gamma}$	$5,6_{Tc}$		

[x] for details see B.E. PATON, M.J. ZUCKERMANN J.Phys.F. 1, 125 /1971/

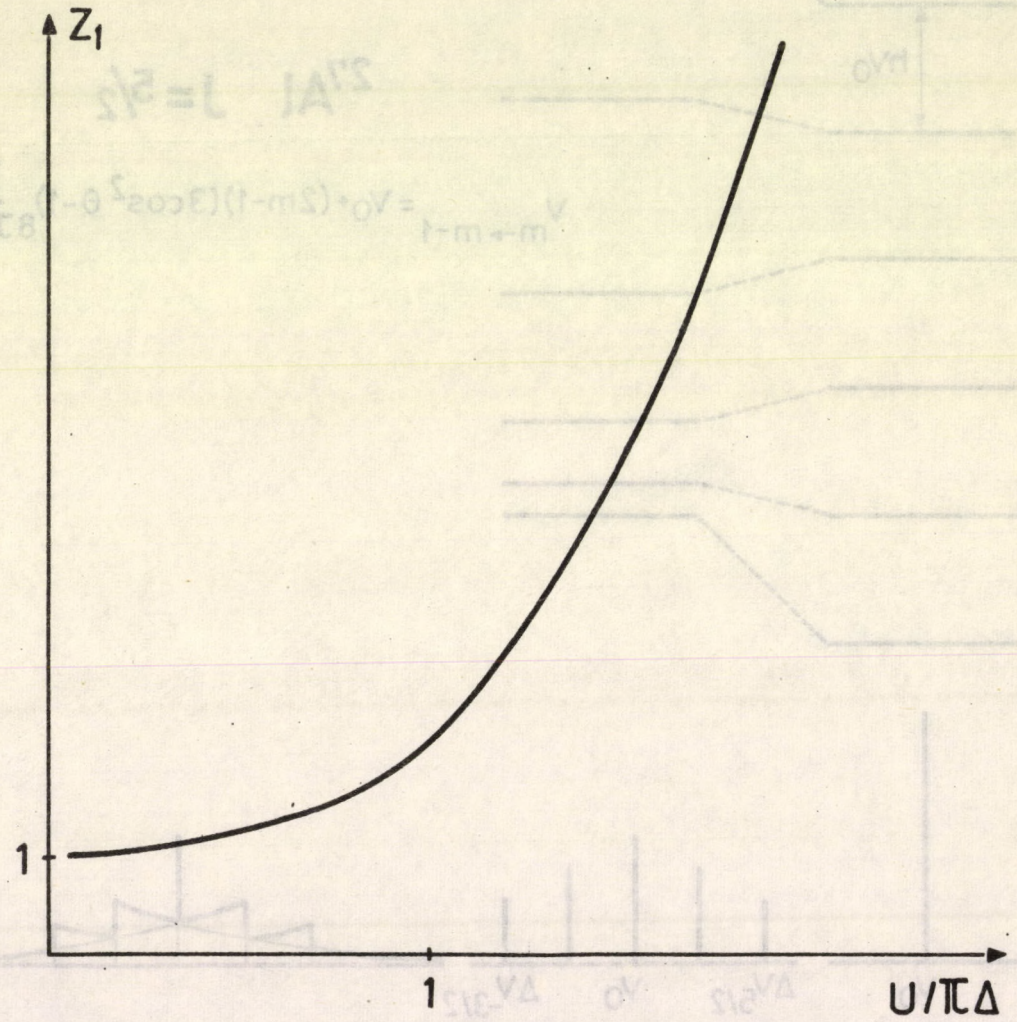


Fig. 1

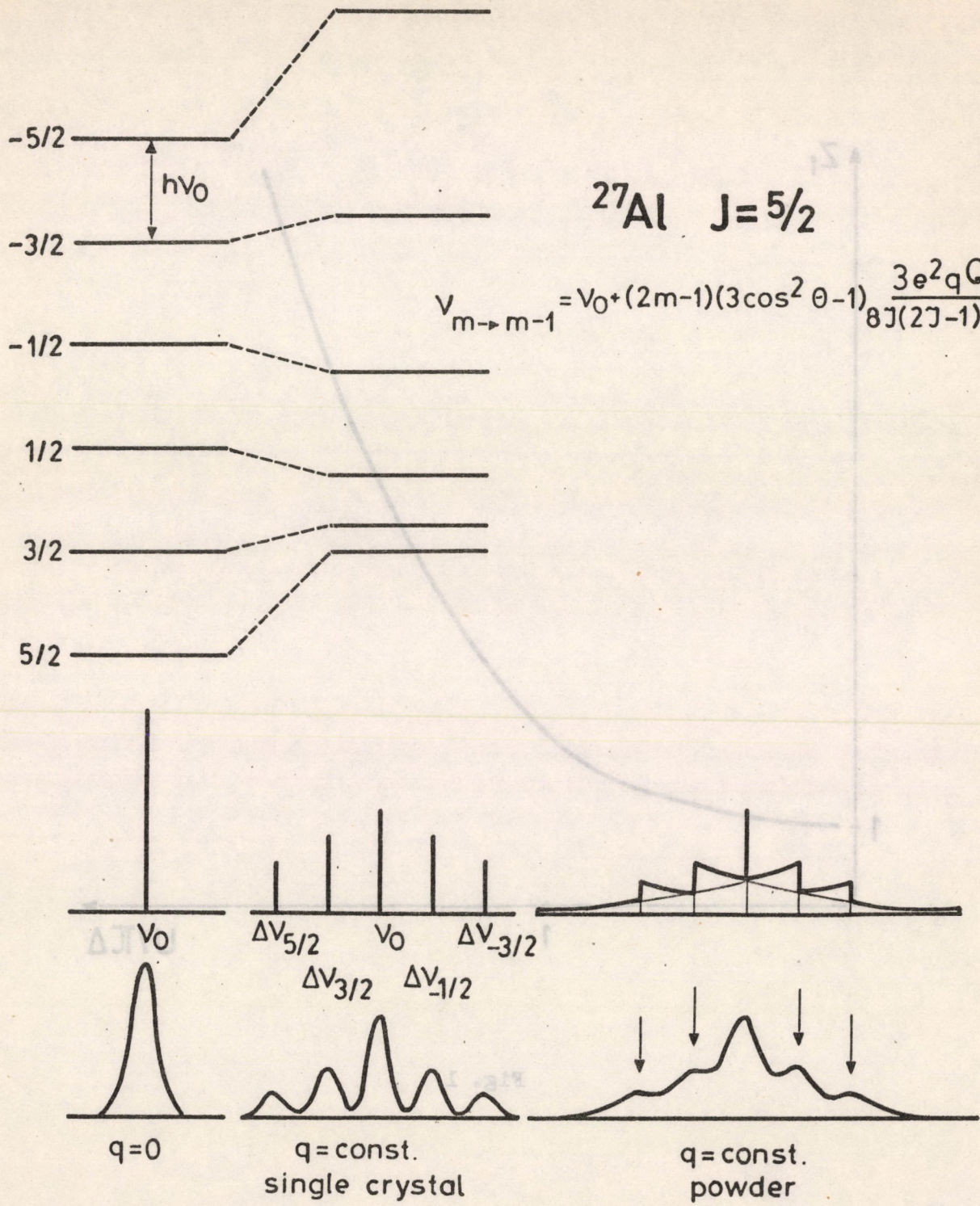

-5/2
hν0
-3/2
-1/2
1/2
3/2
5/2
27Al J=5/2
Vm→m-1 = V0 + (2m-1)(3cos2 θ-1) 3e2qQ / 8J(2J-1)h
ν0
Δν5/2
ν0
Δν-3/2
Δν3/2
Δν-1/2
q=0
q=const.
single crystal
q=const.
powder

Fig. 2

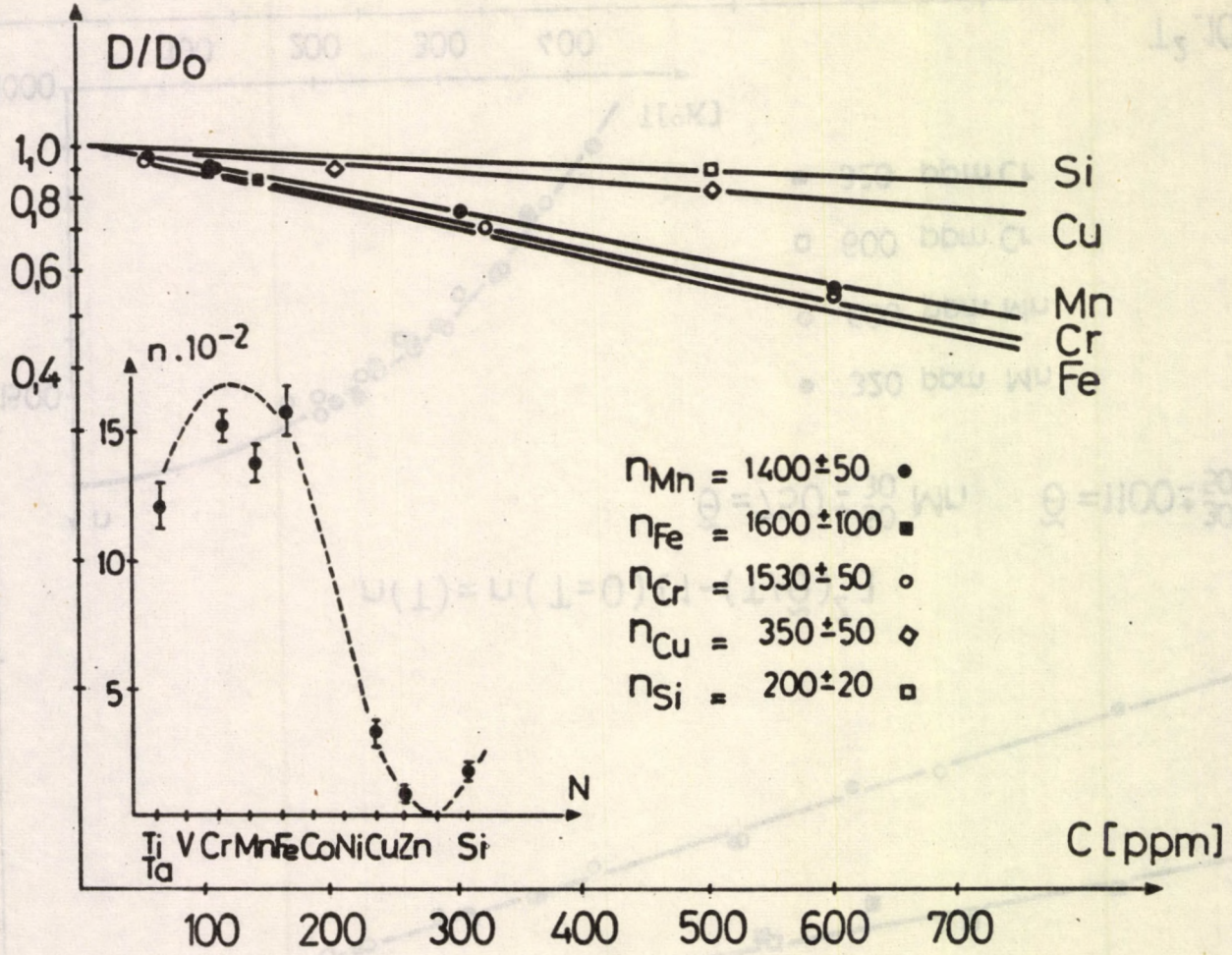

D/D$_o$
1,0
0,8
0,6
0,4
Si
Cu
Mn
Cr
Fe
n .10^{-2}
15
10
5
N
Ti
Ta
V
Cr
Mn
Fe
Co
Ni
Cu
Zn
Si
n_{Mn} = 1400±50 ●
n_{Fe} = 1600±100 ■
n_{Cr} = 1530±50 ○
n_{Cu} = 350±50 ◇
n_{Si} = 200±20 □
C [ppm]
100
200
300
400
500
600
700

Fig. 3

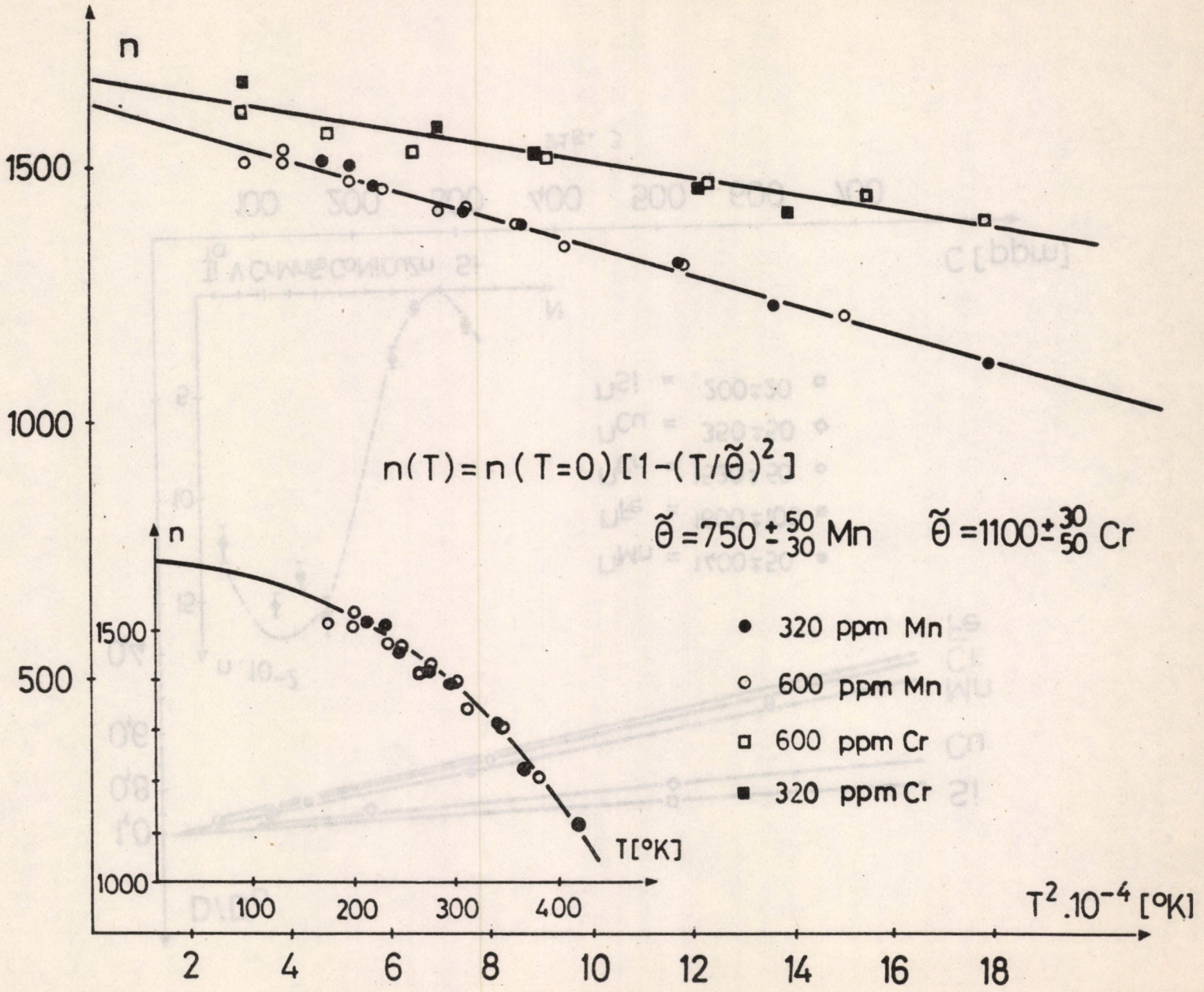

n
1500
1000
500
$n(T) = n(T=0)[1-(T/\tilde{\Theta})^2]$
$\tilde{\Theta} = 750 \pm \frac{50}{30}$ Mn
$\tilde{\Theta} = 1100 \pm \frac{30}{50}$ Cr
• 320 ppm Mn
○ 600 ppm Mn
□ 600 ppm Cr
■ 320 ppm Cr
n
1500
1000
T[°K]
100
200
300
400
$T^2 .10^{-4}$ [°K]
2
4
6
8
10
12
14
16
18

Fig. 4

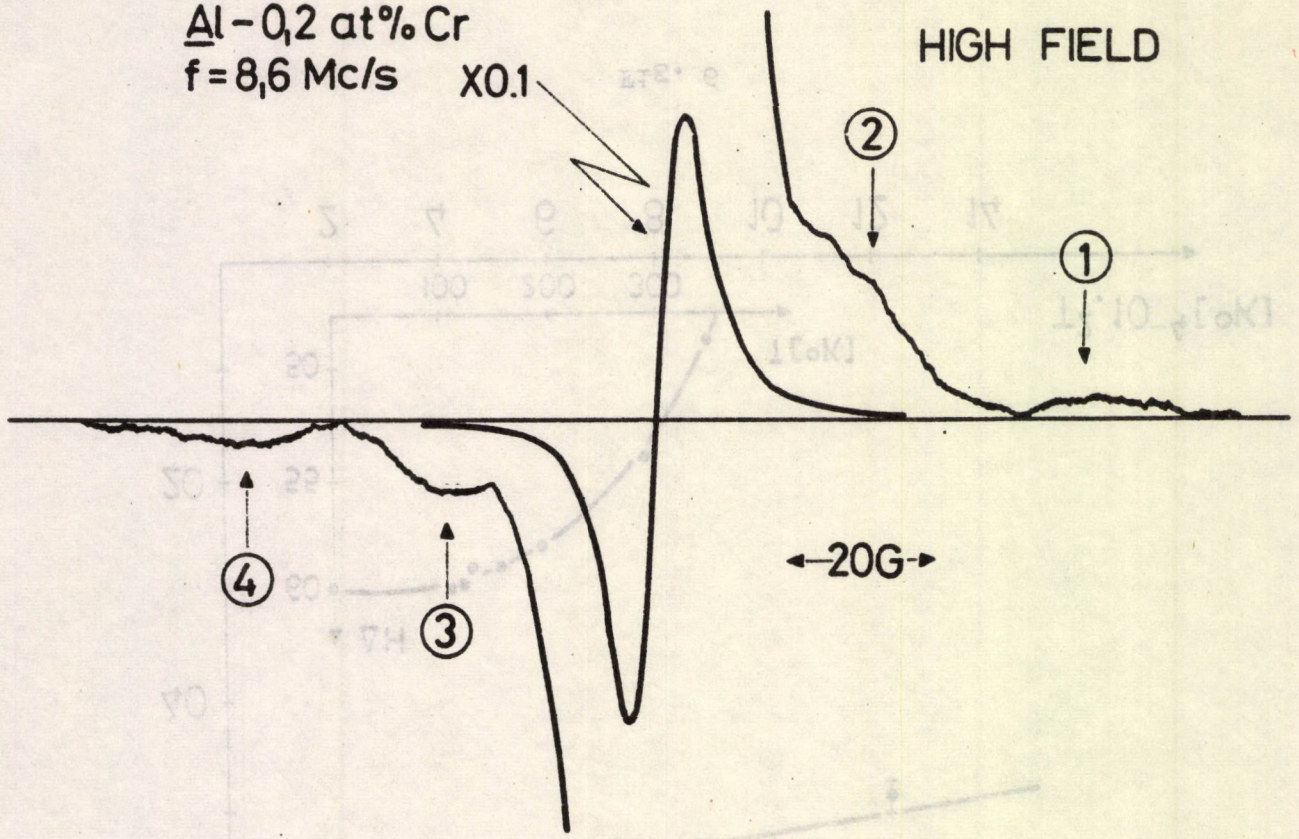


Fig. 5

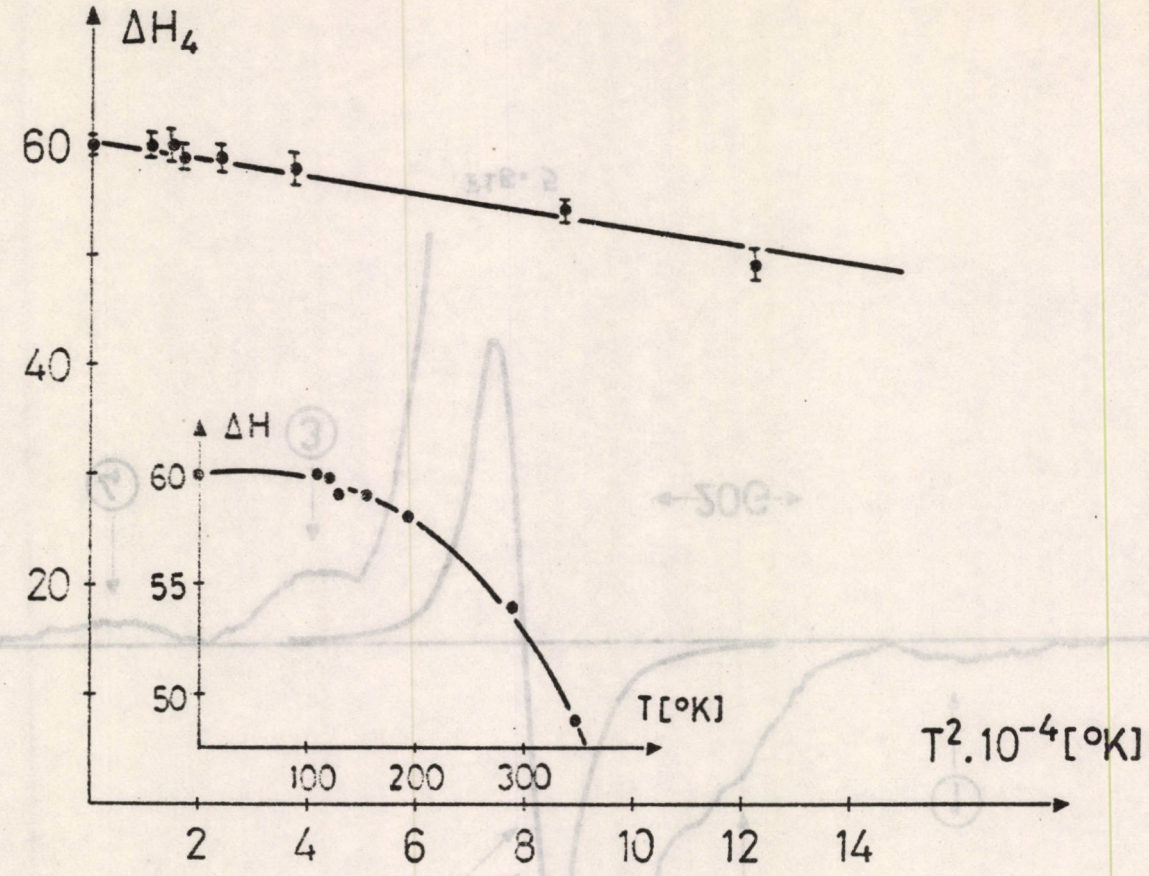


Fig. 6

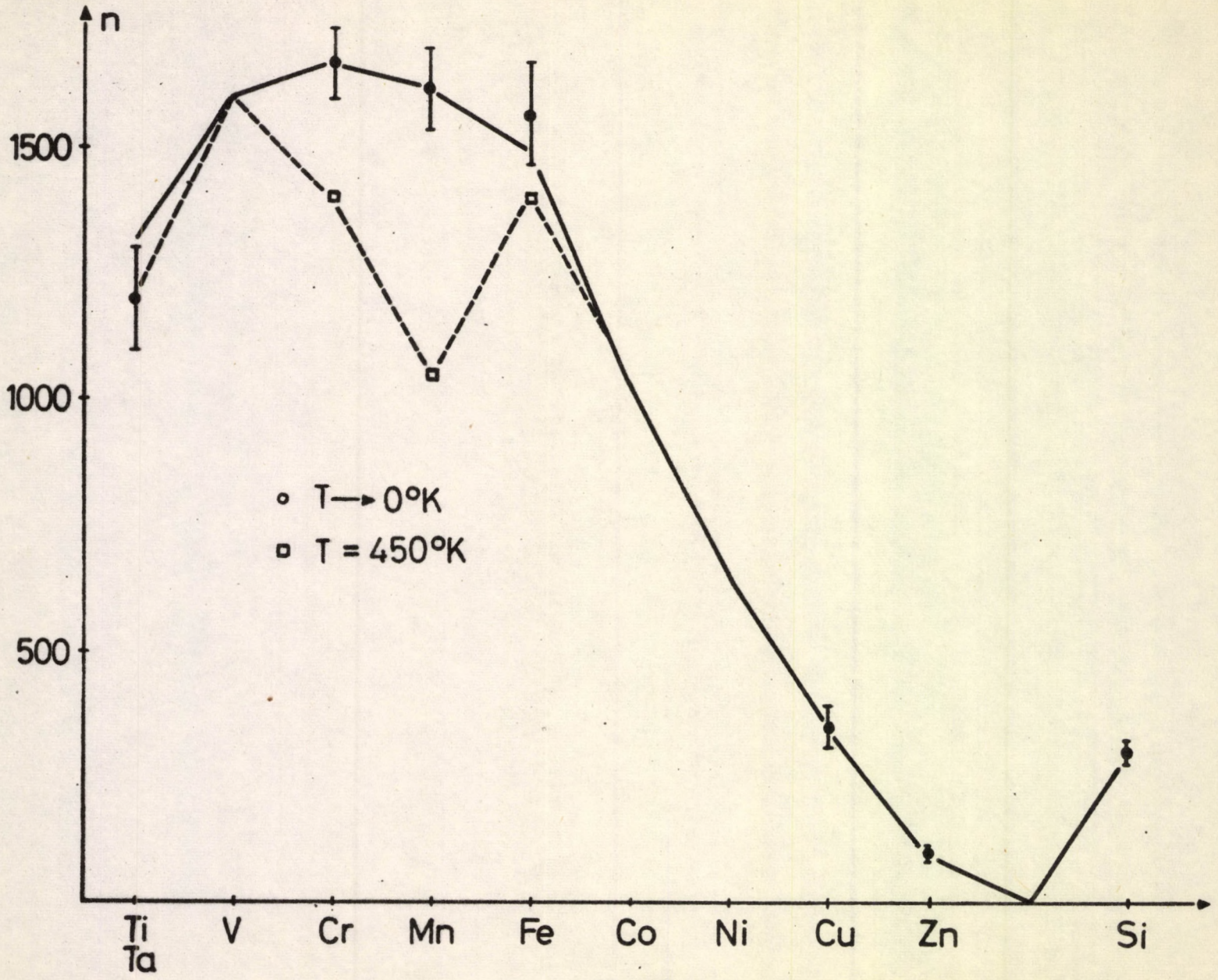
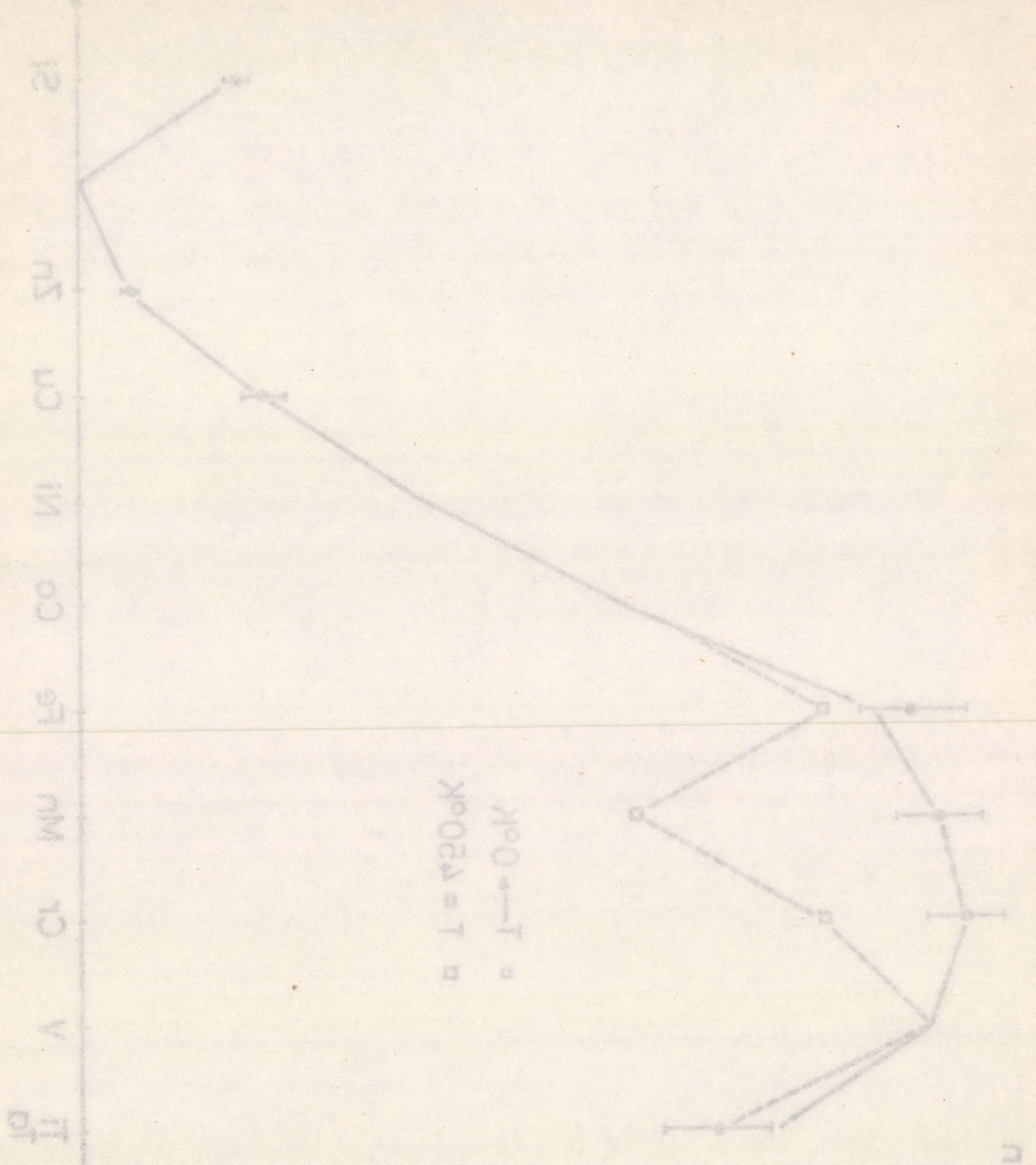


Fig. 7



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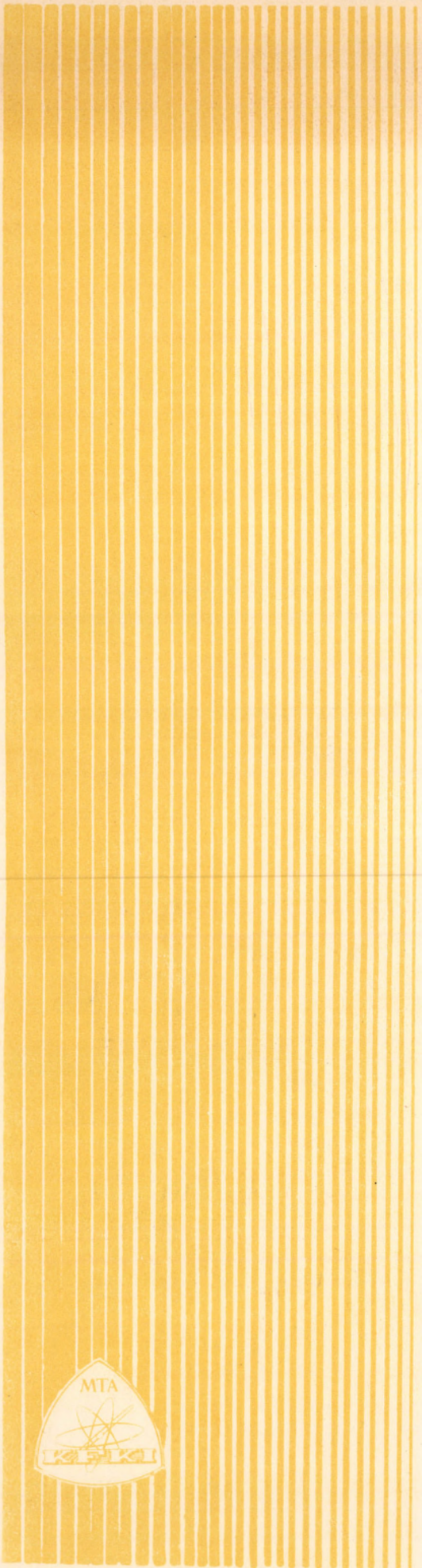

Kiadja a Központi Fizikai Kutató Intézet
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