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MÖSSBAUER STUDIES IN DEVELOPING COUNTRIES

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## MÖSSBAUER STUDIES IN DEVELOPING COUNTRIES

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### 1. INTRODUCTION

The subject of this paper may seem at first sight a little out of place beside the lectures given by the other participants in this panel. Whereas these give a scientifically exact and comprehensive account of the present status of applications of the Mössbauer effect in various fields and suggest new fields in which the effect promises to find use in the future, I have acted on a proposal of the IAEA to make an evaluation of Mössbauer studies being carried out in the developing countries and in small laboratories /the two terms, are not, of course, exclusive/.

This is an interesting and important topic, because, as I hope to show, even where only modest resources are available, valuable contributions have been and still can be made by the laboratories of developing countries to the applications of the Mössbauer effect. It is my aim, to evaluate the present status of Mössbauer studies in developing countries and to stress the benefits that such studies in these places can be expected to bring in the future.

Another proposal from the Agency was that I spend some time in describing the growth of our laboratory in Budapest in



order to illustrate the sort of approach that might be followed in the development of smaller laboratories.

To this end I shall deal first with some characteristic results of Mössbauer work being done in developing countries. This must inevitably be a selective view as there is no time to mention all of the many noteworthy points that could have been included. I should remark that I have given myself a considerable freedom of choice of examples.

I shall then proceed by giving an analysis of the examples I have listed in the first section. In the next section there will be a brief survey of the Mössbauer studies made in our laboratory in Budapest. In the fourth section I shall analyse the educational aspects of Mössbauer studies, with particular regard to the benefit that can be derived from them in university teaching. Lastly I would like to make some proposals in connection with the sort of aid programme I would like to see being extended to promote Mössbauer research in developing countries.

Here I must admit that I have never had the chance to visit a laboratory referred to here under the laboratories of developing countries and so I have no first-hand knowledge of the problems that are faced in this field by such a country. The information I have used in this paper is taken entirely from published material and from personal contact with workers from such countries.

## 2. MÖSSBAUER RESULTS IN THE LABORATORIES OF DEVELOPING COUNTRIES

The importance of studies on the Mössbauer effect was realized in the laboratories of the developing countries within only a few years after its discovery and though the first papers on the effect were aimed at introducing the application technique to physicists and chemists, original results were reported at a relatively early period.



S.JHA and his coworkers of the Tata Institute of Fundamental Research, Bombay, India reported in 1961 the observation of the recoilless emission and resonance absorption of the 26 keV gamma rays emitted in the  $\beta$ -decay of  $^{161}\text{Tb}$  [1]. A paper on the resonance scattering of low energy gamma rays was published in 1962 by B. Sood [2] of the Punjab University.

A report from the Centro Brasileiro de Pesquisas Fisicas in Brazil analysing the Mössbauer parameters of high and low spin ferrous and ferric ions in terms of the ligand field theory [3], shows that this country's first efforts in the field can be dated back to 1961 or 1962.

In Roumania, Poland and Hungary studies using the Mössbauer effect began at about the same period. A. Gelberg [4] from the Roumanian Institute of Atomic Physics published a paper on the polarization of recoil-free emitted gamma rays. Bara and coworkers [5] from the Jagellonian University, Cracow, Poland described a constant velocity spectrometer in 1962. In the same year I. Dézsi and L. Keszthelyi [6] from the Central Research Institute for Physics, Budapest were the first to observe the Mössbauer effect for the 59 keV gamma rays from  $^{159}\text{Tb}$ .

The activities which started in the above mentioned laboratories in the early sixties have been continued ever since and quite a number of publications has already appeared reporting further results.

In Brazil the Mössbauer studies at the Centro Brasileiro de Pesquisas Fisicas have covered two main fields; namely, properties of different alloys and the electronic structure of organic and inorganic compounds. These studies have led to very important results concerning the structure of these materials. I do not intend to specify these results because they are generally known and they have already been discussed in earlier Mössbauer panel meetings.



In India I. Baijal [7] from the University of New Delhi reported the results of an attempt to calculate the exponent of the Debye-Waller factor in terms of the Born-Karman model for lattice vibration.

C.R. Kanekar, K.R.P.M. Rao and V.V.S Rao [8] from the Tata Institute Fundamental Research, Bombay measured the isomer shift and quadrupole splitting in Sn-Pt alloys and estimated the number of 5s-electrons at the tin sites from the Mössbauer parameters.

In 1964 a thorough work was started on Co-doped  $\text{BaTiO}_3$  by Bhide, Shenoy and Multani at the Institute of Sciences, Bombay. In their paper on the ionic character of  $\text{Fe}^{3+}$  in  $\text{BaTiO}_3$  [9] they estimated from the measured isomer shift that the ionic contribution is  $50 \pm 20 \%$ . The particular aim of these workers was to utilize the Mössbauer effect for the study of ferroelectric transitions. The first attempt was made on the ferroelectric-antiferromagnetic transition in  $\text{BiFeO}_3$ . The transition was apparent from the spectra measured at different temperatures and the Néel temperature  $/T_N/$  could be determined from the experimental data. The quadrupole splitting spectrum indicated an asymmetrical distribution of  $\text{Fe}^{3+}$  ions in the oxygen octahedra.

The investigations of Co-doped  $\text{BaTiO}_3$  yielded some very interesting information. The Mössbauer study of ferroelectric materials at temperatures around the Curie point is of particular interest from the point of view of lattice dynamics. Cochran [10] and Anderson [11] have shown that the frequency of the homogeneous transverse -optical modes /wave vector  $\vec{k} = 0/$  progressively decreases as the Curie temperature is approached from the high temperature side. This change in the optical modes is expected to be manifested by a variation of the Debye-Waller factor in the vicinity of  $T_C$ . In  $^{57}\text{Co}$ -doped  $\text{BaTiO}_3$  Bhide and Multani [12] observed a change in the total area of the Mössbauer line proportional to the Debye-Waller factor /Fig. 1/. In the vicinity of the transformation temperature a



change, attributable to a structural transformation in  $\text{BaTiO}_3$ , was observed in the quadrupole splitting and in the central shift.

Bhide and Bhasin from the National Physical Laboratory, New Delhi published papers on the study of  $\text{SrTiO}_3/^{57}\text{Co}/$  and  $\text{SrTiO}_3/^{57}\text{Fe}/$  systems in 1967 [13] and in 1968 [14]. The  $\text{SrTiO}_3/\text{Fe}/$  system had been investigated earlier by other methods, but two problems still remained for further study:

- the valence state of Fe in  $\text{SrTiO}_3$ , and
- the dynamics of the incompletely understood phase transformation at  $110^\circ\text{K}$ .

The results of Bhide and Bhasin's Mössbauer studies can be summarized as follows: Low spin  $/d_e^5/$  and high spin  $/d_e^3 d_y^2/$  ferric states were shown to coexist in  $\text{SrTiO}_3/^{57}\text{Co}/$ . The relative intensities of these states were found to be temperature dependent. A cubic-tetragonal phase transition at  $110^\circ\text{K}$  was detected from the temperature variation of the isomer shift of the high spin ferric state. The studies on  $\text{SrTiO}_3/^{57}\text{Fe}/$  used as an absorber showed that iron in the high-spin ferric state enters the  $\text{SrTiO}_3$  lattice at the  $\text{Ti}^{4+}$  site, in agreement with the EPR evidence. The quadrupole splitting of the spectra indicated that there is a lower than octahedral symmetry around the  $\text{Fe}^{3+}$  ion. The valence state of the iron was found to change in oxidized and reduced samples. The formation of colloidal iron was observed in hydrogen-reduced samples. These samples showed Zeeman splittings and the isomer shift had the value characteristic of metallic iron. In air firing the clusters dispersed and the spectra consisted of simple quadrupole-split doublets.

In 1966 Bhide and Shenoy studied the iron states in  $\text{NiO}/^{57}\text{Co}/$  and  $\text{CoO}/^{57}\text{Co}/$  sources after the EC decay of  $^{57}\text{Co}$ . They found the intensity of ferrous and ferric states to be strongly temperature dependent in these oxides as inferred from the temperature dependence of the cross-section of the ferric ions.



Bhide, Date, Shenoy and Umadikar [17] were the first to investigate polynuclear organoferric complexes by Mössbauer effect. Such polynuclear complexes are of particular interest because there is an exchange interaction between the metallic ions within the molecule but the intermolecular interactions between the ions are extremely weak. The ferric citrate, benzoate and malate complexes studied by these authors showed hyperfine splitting in the spectra.

In 1966 intense work was started at the Physics Department of Roorkee University, Roorkee, India. The first publications dealt with structural investigations of ferro- and ferricyanide complexes and the study of  $\text{Fe/M/}_2/\text{SO}_4/2 \cdot 6\text{H}_2\text{O}$  salts  $/\text{M} = \text{NH}_4^+, \text{K}^+, \text{Rb}^+, \text{or } \text{Cs}^+ /$  [18], [19]. Later Mössbauer effects in  $^{40}\text{K}$ ,  $^{182}\text{W}$  and  $^{18}\text{W}$  were studied. For the last two isotopes the recoilless fractions were calculated over a wide range of temperature  $/4^\circ - 300^\circ\text{K}/$  from the experimentally determined phonon frequency distribution function /Chen and Brockhouse/ as compared with that predicted from the Krebs' model. A reasonable agreement was obtained between the experimental and theoretical results [20]. Further results of this group have been reported in more than 10 papers.

Garg and Goel [21] from the India Institute of Technology, Kanpur observed the Mössbauer effect in ferricyanide acid and attributed the quadrupole splitting of  $^{57}\text{Fe}$  to hydrogen bonding between the cyanide ligands. The existence of this type of bonding had been already suggested by IR, crystallographic and refractometric data.

In 1964 Wang, Lu and Tseng [22] Taiwan were the first to suggest the application of the Mössbauer effect to the study of the structure of iron ions in cation exchange resins. A detailed paper on these investigations was written by Huang, Weng and Tseng [23] from the Cheng Kung University, Taiwan. These workers studied the effect of the organic solvent on the diffusion of ferric ions in Dowex 50W-x8 resin. By reference to Gainer and Metzner's equation of binary diffusion they were able



to conclude that the self-diffusion of cations in resin is a binary process, i.e., the solute diffuses through the medium of the solvent. Some other dynamic effects connected with the diffusion of the cation in the resin were also discussed.

Mössbauer studies were started recently in Argentina, at the University of Buenos Aires. The first publication, which appeared in 1969, concerned the nitrosyl iron/II/ bis-dithiocarbamates [24]. The Mössbauer effect revealed slight changes in the chemical bonding of these complexes originating from differences in the inductive effects of the ligands. The authors compared the results of Mössbauer, optical, ultraviolet and infrared spectroscopy and ESR measurements.

New Mössbauer groups have been formed lately in Brazil. One of them from the University of Brazil reported results on frozen solutions of some Fe/III/EDTA compounds [25]. A strong pH dependence of the Mössbauer spectra of these frozen solutions was observed.

### 3. A BRIEF SURVEY OF THE MÖSSBAUER STUDIES IN THE CENTRAL RESEARCH INSTITUTE FOR PHYSICS, BUDAPEST, HUNGARY

Mössbauer studies started at this Institute in 1961. The first measuring apparatus, built for the investigation of the Mössbauer effect in  $^{159}\text{Tb}$ , was very simple, a modified lathe being used to move the radioactive source.

The systematic work begun in 1963 when a hydraulic, constant-velocity spectrometer was built for studying frozen aqueous solutions. On this equipment the velocity could be varied with high precision. This spectrometer was later replaced by a conventional Mössbauer spectrometer with multichannel analysers to get rid of the tedious mechanical regulation of the velocity.

Aqueous solutions were chosen for the investigations because anomalous effects had been found in these systems and the states of the solute ions in rapidly frozen solutions were suf-



ficiently known. It was also hoped to get information about the transformation of the various ice modifications.

The Mössbauer spectra of different ferrous salt solutions showed interesting features [26]. The close values of the isomer shift and the quadrupole splitting observed at liquid nitrogen temperature after freezing suggested identical symmetries around the ferrous ions, thus symmetries which are independent of the anions in the solute salts. The temperature dependence of the recoilless fraction, line width and quadrupole splitting exhibited a remarkable change at certain temperatures /Fig. 2/. Equivalent changes were not observed in the spectra of pure crystalline hydrates of dissolved ferrous salts. The changes in the Mössbauer parameters are an indication of different structural transformations (meltings, recrystallizations) involving violent movements of the solute ions.

After the observations of these effects extensive investigations were started in different Mössbauer laboratories and both the results of these groups and our further studies on frozen solutions permitted some of these effects to be explained. Other experimental methods, such as differential thermal analysis, nuclear magnetic resonance, perturbed gamma angular correlation, were also employed. The explanations which have been suggested up to present can be summarized as follows. After the rapid freezing of the liquid sample the solute ions separate from the bulk ice and get into a state which is the same or nearly the same as a glassy state. On heating the system, the fraction containing the solute ions gradually melts and the solute salts crystallize out in the form of hydrates which are stable at the temperature of recrystallization. These hydrates are probably included in the solid eutectic formed with the ice crystals. The eutectic melts as the temperature further increases, as indicated by the disappearance of the Mössbauer effect. Other interesting transformations have been observed in these systems, but to mention all of them would be beyond the scope of this review.



The investigations have been extended to the study of other features in solutions:

- paramagnetic relaxation in dilute systems,
- observation of different ionic species in solutions
- measurement of electronic exchange in solutions
- measurement of the phase diagram of solvent-solute salt systems.

The investigations of these phenomena are still going on.

The Mössbauer parameters of the crystalline ferrous salt hydrates  $\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Fe/ClO}_4/2 \cdot 6\text{H}_2\text{O}$  were studied in order to utilize them for the identification of the spectra observed in frozen solutions. In addition to the phenomena observed in the frozen solutions, the crystalline hydrates exhibited transformations which had not yet been studied by Mössbauer effect or which in some cases were completely new. In  $\text{Fe/ClO}_4/2 \cdot 6\text{H}_2\text{O}$  the ground state of the d-electrons of the ferrous ions was observed to transform from a singlet state at low temperature to a doublet state at higher temperatures [27]. The different electron distributions in the two states mean that the field gradient can differ in sign and its magnitude may change by a factor of 2 /Fig. 3/\* . X-ray structural analysis of this salt has not been made. Further analysis is necessary to clarify whether we are dealing with a polymorphous transformation or with a structural change confined to the octahedron surrounding the ferrous ion.

We have investigated the exchange interaction between the nearest neighbours in  $\text{Zn}_x\text{Mn}_{1-x}\text{Fe}_2\text{O}_4$  ferrites [28]. The complicated spectra could be analyzed in terms of the numbers of Zn neighbours of  $\text{Fe}^{3+}$  ions in the sublattices.

In cooperation with the Solid State Physics Department an intense study has been made of FeAl alloys [29].

\* This work has been carried out with the collaboration of Dr. M.D. Coey /University of Manitoba, Winnipeg, Canada./



The different modifications of  $\text{FeOOH}$  /  $\alpha, \beta, \gamma, \delta$  / have also been investigated. Although the compositions of these modifications are the same, their magnetic structures are different. The effect of superparamagnetism on the Mössbauer spectra could be studied in these samples. The investigations of the ferric oxihydroxides led to the study of the corrosion products of iron, which are different types of  $\text{Fe}_2\text{O}_3$ ,  $\text{FeOOH}$  and  $\text{Fe}_3\text{O}_4$ . A knowledge of the structure and composition of these products is important since certain modifications are capable of slowing down the progress of corrosion. Modifications of the oxihydroxides could be identified from the Mössbauer spectra of the corrosion products of various materials [31] /Fig. 4/. This work can be regarded as a preliminary study; further experimental investigations are needed before suitable methods can be made available for useful practical applications in this field.

We have studied some organo-metallic complexes of iron- /II/, such as  $\text{Fe/II/}$  - phthalocyanine and  $\text{Fe[phenanthroline]}_2$ .  $[\text{SCN}]_2$  and  $\text{Fe[bipyridyl]}_2[\text{SCN}]_2$ . The latter two show a high spin - low spin transformation of ferrous ions [33]. The coexistence of the two phases as shown in Fig. 5 was observed.

It is apparent from our results that we have been engaged mainly in the application of the Mössbauer effect in solid state physics and chemistry. These applications do not require very expensive experimental facilities, and in addition we have the advantage of possessing a well equipped radiochemical and chemical laboratory which can properly prepare the sources and absorber material for the experiments.

At the beginning only two researchers worked with the Mössbauer effect in the Nuclear Physics Department. Since 1967 three other workers from the Solid State Physics Laboratory have joined the Mössbauer "group". In addition, every year two graduate students have been working here on their diploma work. The occasional cooperation with the other departments of the Institute has proved to be very useful. This can be said also about the cooperation with the Mössbauer group of the Eötvös Loránd University, Budapest.



Fruitful international partnerships have been established by our group with scientists working on Mössbauer studies at the Joint Institute of Nuclear Research, Dubna, USSR, at the Institute of Nuclear Physics, Poland. I personally have had the opportunity to conduct research at the University of Louisville, Louisville, Ky U.S.A.

#### 4. SOME CONCLUSIONS CONCERNING THE MÖSSBAUER STUDIES IN DEVELOPING COUNTRIES

As regards the results cited in section 2., it can be stated that they are all original and in no way do they reproduce Mössbauer data obtained in laboratories of more developed countries.

Because of the modest instrumental facilities, these efforts have been directed to the special problems of solid state physics and structural chemistry. These are up-to-date problems and in many cases their study can be considered to have pioneered similar work in other more advanced laboratories.

To support this statement let me choose two problems of special interest:

- the study of ferroelectric transitions, particularly in perovskites
- the problems of intramolecular exchange interactions.

It was first suggested by Muzihar and his coworkers [33] that the anomalous behaviour of the frequency of the optical mode  $|\omega_T|$  in ferroelectrics must lead to a minimum in the recoilless fraction  $|f|$ .  $f$  can be expressed as a sum over the normal modes of the crystal lattice [34], as

$$f \sim \exp \left[ \sum_s \left[ - (2n_s + 1) \left| \frac{(\hbar K)^2}{2M\hbar\omega_s} \right| a_s^2 \right] \right] \quad /1/$$

where  $n_s$  is the occupation number for the mode,  $K$  is the wave



vector of the gamma ray,  $M$  is the nuclear mass and  $a_s^2$  is a coefficient in the expansion of  $K$  in terms of the normal coordinates of the lattice.

If we assume that the removal of one term from the sum in Eq./1/ does not materially affect the sum as a whole, then we can remove the anomalous mode /e.g.  $s = a/$  and treat the remainder of the sum using the Debye model of a solid, thus

$$f = f_D(T) \exp \left\{ -(2n+1) \left[ \frac{\hbar K^2}{2M\hbar\omega_a} \right] a_a^2 \right\}$$

$f_D/T/$  is the normal Debye model temperature dependence of  $f$ . /For a more detailed description of this expression, see ref. [35]./  $\omega_T^2 = G/T - T_0$ . Using Bose - Einstein statistics for  $n_a$  to give  $\omega_a$ , we have

$$f(T) = f_D(T) \exp \left\{ - \left( \frac{2}{e^y - 1} + 1 \right) \left[ \frac{(\hbar K)^2}{2M\hbar} a_a^2 \right] \frac{\hbar}{k_B T_y} \right\}$$

$$y = \left( \hbar/k_B T \right) \left[ G(T - T_0) \right]^{1/2}$$

For a second order transition  $T_0 = T_C$  and  $T = T_C$ ,  $y = 0$  and  $f/T = T_C/0 = \infty$ , while for a first order transition  $T_0 \neq T_C$ . Thus  $y$  never equals zero, but it has a minimum and therefore  $f/T$  has a minimum at  $T = T_C$ .

Later Hazony and his coworkers [36] suggested that it is possible for the  $k = 0$  optical mode in the Mössbauer active sublattice to exhibit an anomaly in the opposite sense, that is  $\omega_T' \rightarrow \infty$  at  $T_C$ . Such an anomaly would lead to a maximum in  $f$ . Although this maximum would require a rather anomalous frequency distribution in the lattice, the possibility of this maximum cannot be completely excluded.

Another problem arises if the ferroelectric transition is a displacement transition and the Bravais lattice bearing the Mössbauer nuclei does not participate in the  $\omega_T \rightarrow 0$  lattice mode, or if an order-disorder transition takes place. In both cases no anomaly is expected to be apparent in  $f$  at  $T_C$ .



For this reason the Mössbauer study of the ferroelectric transition is particularly important in the phenomenological investigation of the behaviour of  $f$  at  $T_C$  and in the determination of the structure of ferroelectric material.

The work of Bhide and his co-workers was the first step in the experimental study of  $f$  in the most investigated ferroelectric material  $\text{BaTiO}_3$ . Since the publication of their study many efforts have been devoted to Mössbauer experiments on ferroelectric samples.

Because of the complex nature of these transformations the results are often contradictory or inconsistent. For instance, Hazony et al. [36] observed a significant anomaly of  $f$  around  $T_C$  in  $\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$  yet this effect was not found by Gleason and Walker [35] or Clauser [37]. Recently Montano and his coworkers [38] have established an increase in the area of the Mössbauer effect at  $T_C$  for gamma beams directed along an axis near the ferroelectric  $[10\bar{1}]$  axis of a single crystal of this compound. Chekin and his coworkers [39] measured a considerable change of  $f$  in the ferroelectric  $\text{SnTe-10\%GeTe}$  alloy at  $T_C$ , but Knauer [40] obtained a negative result. It seems that the ferroelectric transition needs further investigations by Mössbauer effect.

Another model material,  $\text{SrTiO}_3$ , has been used for the study of the lattice dynamical effect of this type of phase transition. This perovskite is now under extensive study by other experimental methods.

The investigation of polynuclear complexes of transition metals has lately become of renewed and rapidly growing interest to both experimentalists and theoreticians. Although very little Mössbauer work has been done on polynuclear complexes with  $\text{Fe}^{3+}$  cations, the data that is available has yielded interesting new information. The quadrupole splitting lines appearing in most of these complexes indicate the presence of the same type of iron. The asymmetry of the line width and/or of the area confined by the lines observed in some of these complexes



[41, 42] can be attributed either to Goldanskii-Karyagin or to spin relaxation effect, or to both. For the unequivocal explanation of the observed asymmetries further work seems to be necessary. The application of the Mössbauer effect combined with other experimental techniques /e.g. magnetic susceptibility, NMR measurements/ is expected to yield useful information on the polynuclear complexes while the Mössbauer effect is particularly suitable for the determination of the order of the exchange coupling constant.

Recent studies of frozen solutions have revealed two important fields of application of Mössbauer spectroscopy. One of them is the investigation of glass transitions, the other is the study of the phase diagrams of solute-solvent systems [43], [44]. The latter is important in the analysis of the pH dependence of the Mössbauer parameters.

As has been already pointed out, Mössbauer studies in developing countries have hitherto been restricted to problems in solid state physics and chemistry. Geological or biological applications are very scarce or non-existent. This is surprising seeing that the application of the Mössbauer effect in geological research does not require greater financial efforts than its use in pure chemistry. Moreover, geological samples worthy of study are in many cases readily available in a natural form suitable for investigation.

Most Mössbauer studies have been concerned with basic problems in physics and chemistry; less attention has been paid to applied research and technical applications. As is usual with new discoveries, it takes some time to adapt the results and the technique for use in applied science. This holds for the Mössbauer effect as well. Now, it would seem to be important to find ways in which fundamental results can be utilized in technology in order to raise the technological level in developing countries. Technical applications have been already devised for use in metallurgy, and ore analysis, and it is expected that similar uses will be found also in other fields.



## 5. EDUCATIONAL ASPECTS OF THE MÖSSBAUER EFFECT

The Mössbauer effect is a complex phenomenon. An adequate knowledge of nuclear physics, solid state physics and chemistry is necessary in order to understand resonance absorption and hyperfine interactions in matter.

The curriculum devised for university students of physics and chemistry provides sufficient knowledge for the understanding of the theoretical and experimental foundations of the Mössbauer effect. In a number of universities the students of graduate classes perform routine measurements with Mössbauer spectrometers. This practice develops the ability of the students to interrelate the facts and different aspects of the various disciplines /nuclear physics, solid state physics, etc./ A simple Mössbauer spectrometer for educational purposes does not necessitate great investments. A mechanical set-up with suitable scalars is sufficient for training purposes. A simple cryostat and furnace permit the temperature dependence of the parameters to be readily measured. It would seem useful, therefore, to introduce the Mössbauer effect as a curriculum topic in the universities in developing countries. Students, according to my experience, usually participate enthusiastically in measurements by this method.

To other scientists than physicists and chemists it is in some cases difficult to explain the essence and the advantages of the application of the Mössbauer effect because of the complexity of nuclear resonance absorption. Incidentally, the same applies to many of the advanced physical methods. It is thought therefore that it would be useful if in the universities of the developing countries, or indeed of any country, more attention could be paid to the Mössbauer method in the biological, medical, geological and engineering faculties.



## 6. SUGGESTIONS CONCERNING THE INTRODUCTION AND PROMOTION OF THE MÖSSBAUER STUDIES IN DEVELOPING COUNTRIES

The introduction of the application of the Mössbauer effect presents the following advantages:

a/ The experimental work does not require too expensive equipment and high level research can be done at a relatively low cost.

b/ The studies can be extended over various fields: basic research, applied research, technical applications. The cooperation of scientists working in different fields promotes the establishment of a powerful, active scientific community.

c/ Numerous students from the developing countries working on an exchange basis in the Mössbauer laboratories of developed countries can get a high level training and practice which they can profitably utilize in their own countries.

Support needed by the laboratories of developing countries:

Internal support:

a/ Laboratories for the preparation of special materials. In many cases the acquisition of special sources and absorbers is very difficult, or even impossible, in a developing country. Therefore the installation of a preparative laboratory seems to be very important.

b/ Provision of computer facilities.

c/ Help in organizing the cooperation of the scientists and engineers who are interested in Mössbauer studies.

d/ Strong encouragement of the extension of studies to technical problems.



International aid:

- a/ Financial support of laboratories by international organizations; such support could be utilized for the purchase of Mössbauer spectrometers, cryostats, furnaces and special equipments and materials.
- b/ Collaboration between IAEA and different laboratories for the investigation of special scientific problems by Mössbauer effect.
- c/ Establishment of a laboratory by IAEA in which special standards and other materials would be produced for use in Mössbauer studies. An alternative approach could be a contract with one or more of the developed laboratories to produce these materials.
- d/ IAEA fellowships for scientists of the developing countries for training in developed Mössbauer laboratories.
- e/ Financial support of experts in the application of Mössbauer effect who would aid efforts in the laboratories of developing countries.
- f/ Formation of a permanent subcommittee of the IAEA for the coordination of grants to the Mössbauer laboratories of developing countries.



## FIGURE CAPTIONS

Fig. 1 Temperature dependence of the total area of  $^{57}\text{mFe-BaTiO}_3$  source spectrum showing the change in the vicinity of  $T_c$  [12]

Fig. 2 Variations with temperature of the intensity of Mössbauer effect, line width and quadrupole splitting in the spectra measured on the frozen solutions  $\text{Fe/ClO}_4/2:(\bullet)$  and  $\text{FeCl}_2:(\circ)$ .

Fig. 3 Mössbauer spectra of  $\text{Fe/ClO}_4/2 \cdot 6\text{H}_2\text{O}$  in external magnetic field.

Fig. 4 Mössbauer spectra at room temperature measured on corrosion products of iron in different corrosive media.

a/ rust produced in the presence of saturated water vapour

b/ rust produced in  $\text{CaCl}_2$  solution [31]

Fig. 5 Temperature dependence of the Mössbauer spectra of  $\text{Fe/phenanthroline/2[SCN]}_2$  complex. [32]



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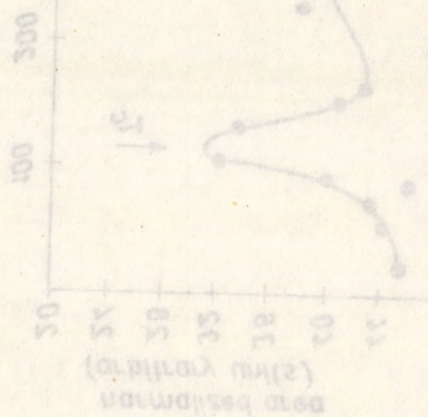
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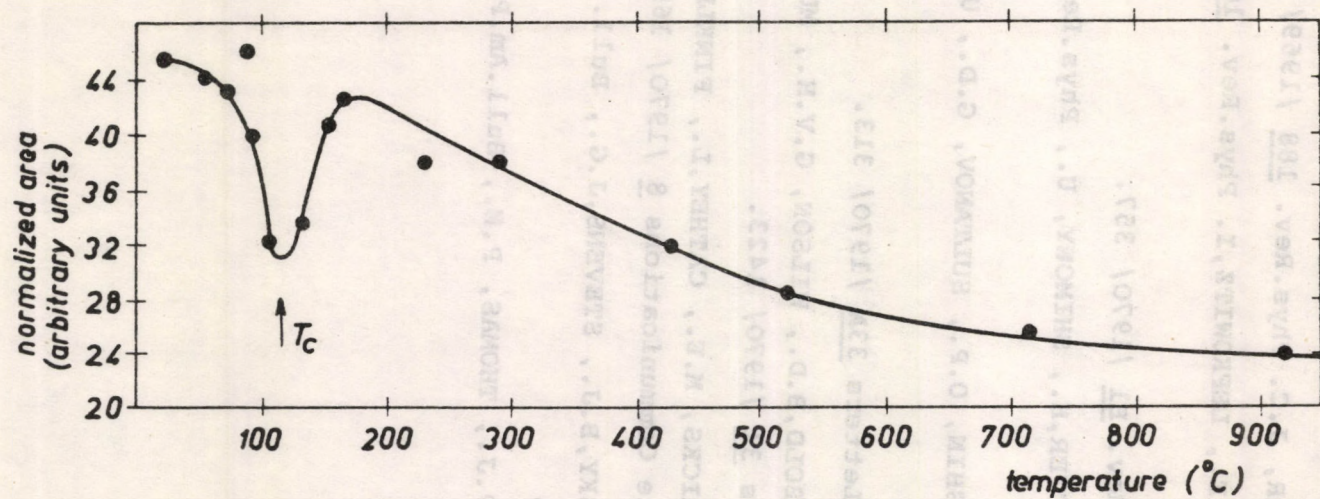


Fig. 1

Temperature dependence of the total area of  $^{57m}\text{Fe}$ -BaTiO<sub>3</sub> source spectrum showing the change in the vicinity of  $T_c$  [12]



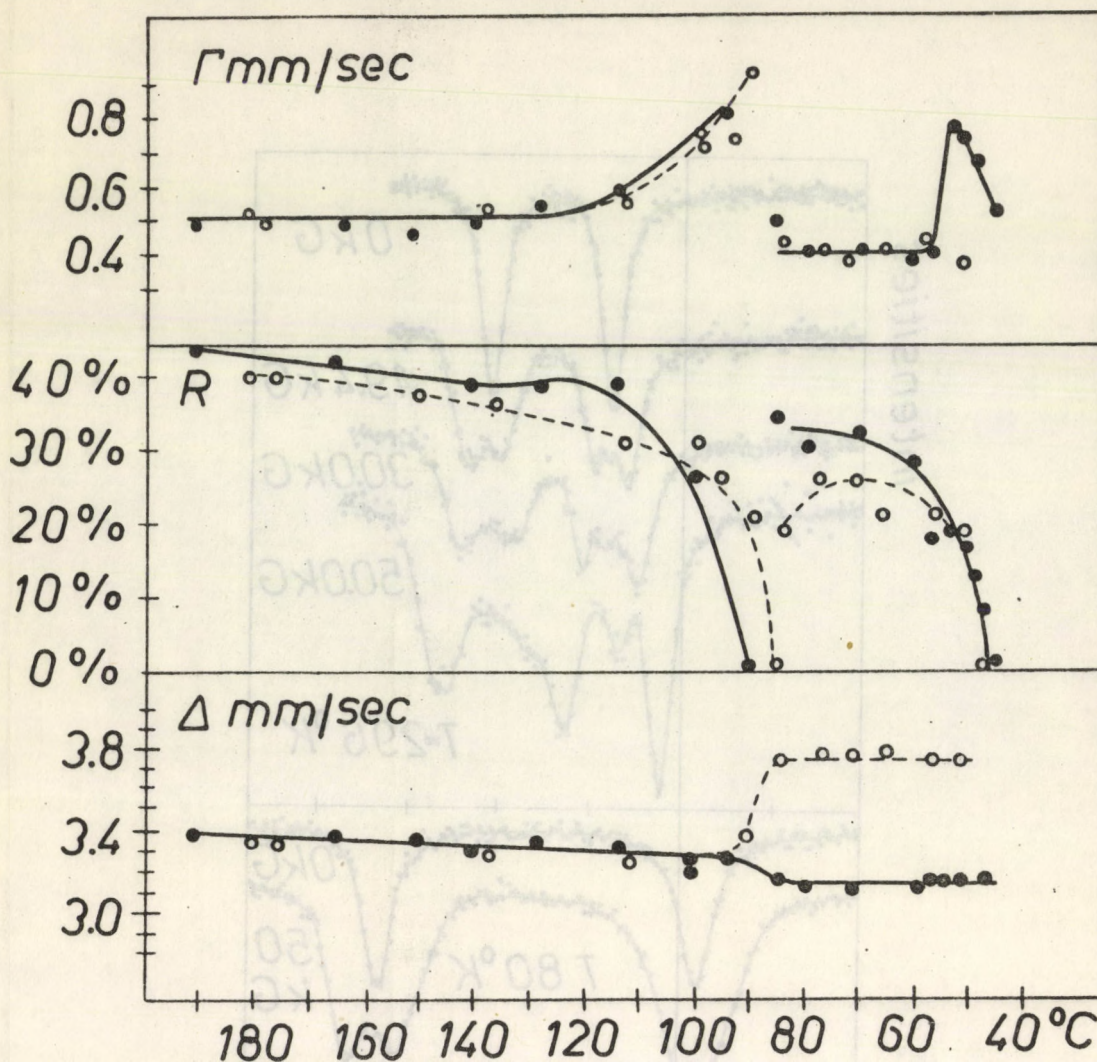


Fig. 2  
Variations with temperature of the intensity of Mössbauer effect, line width and quadrupole splitting in the spectra measured on the frozen solutions  $\text{Fe/ClO}_4/2$  (•) and  $\text{FeCl}_2$  (o).



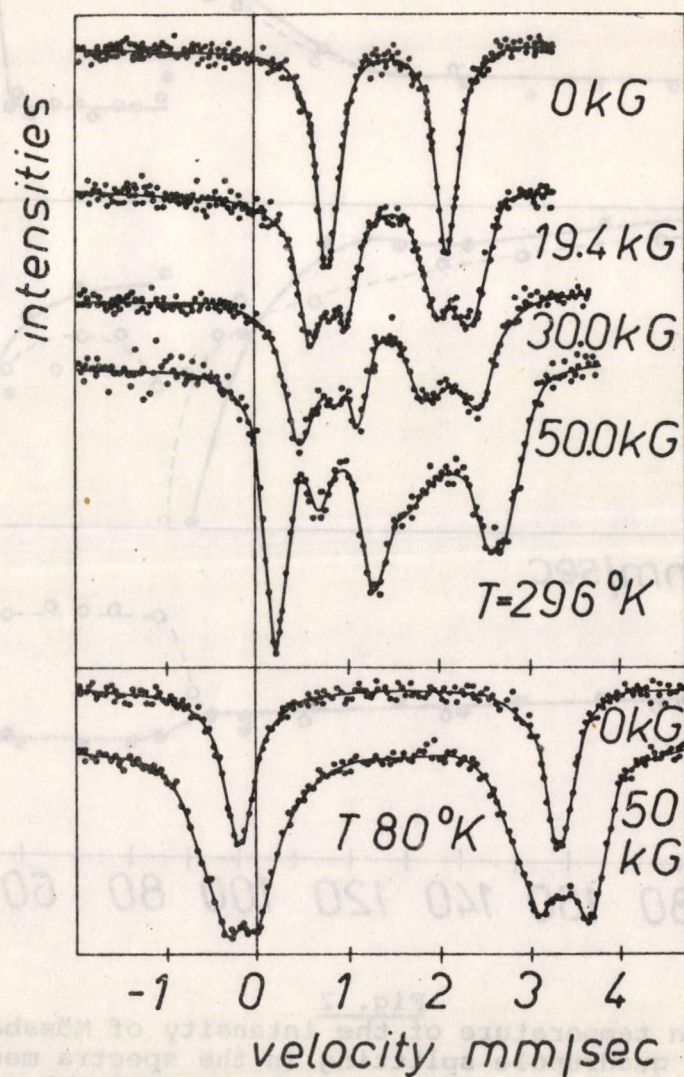
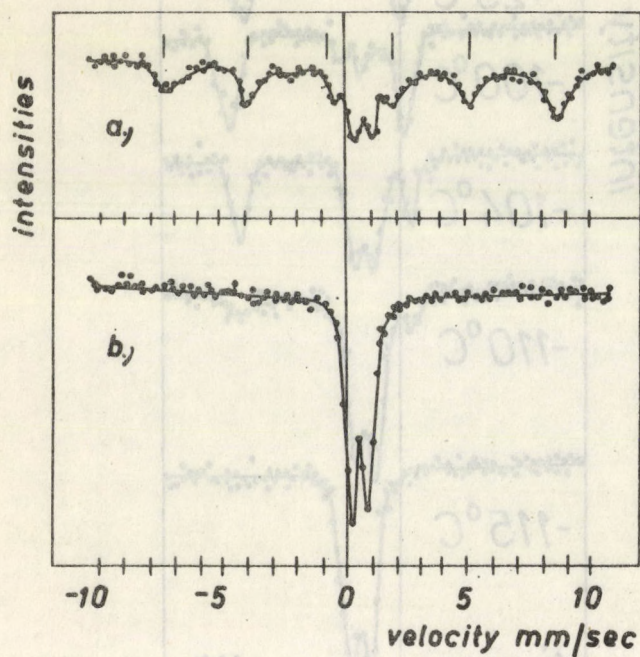


Fig. 3  
Mössbauer spectra of  $\text{Fe/ClO}_4/2.6\text{H}_2\text{O}$  in external magnetic field





**Fig. 4**

Mössbauer spectra at room temperature  
measured on corrosion products of iron  
in different corrosive media

- a/ rust produced in the presence of  
saturated water vapour
- b/ rust produced in  $\text{CaCl}_2$  solution [31]



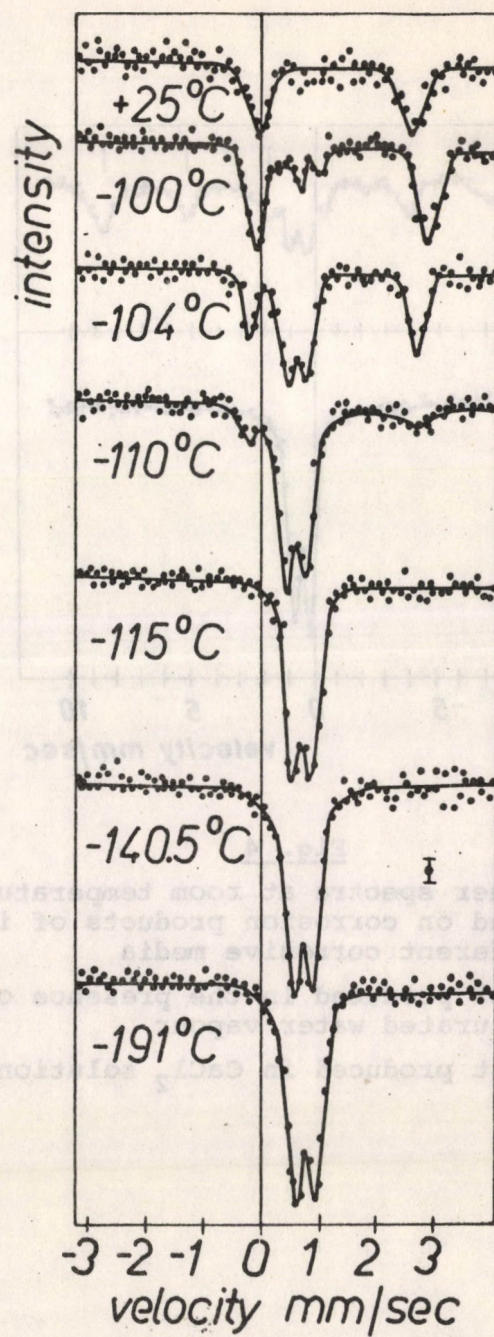


Fig. 5

Temperature dependence of the Mössbauer spectra of Fe/phenanthroline/<sub>2</sub>[SCN]<sub>2</sub> complex [32].

















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