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PROCEEDINGS OF THE [illegible] MÖSSBAUER [illegible]

8 – 10 October [illegible]

[illegible]

D. S. KULGAWCZUK, K. [illegible]

druk na prawach rękopisu

PROCEEDINGS
OF THE POLISH MÖSSBAUER COMMUNITY MEETING

8 - 10 October 1986, Cracow

25 years of Mössbauer Spectroscopy in Poland

Editors: D.S. Kulgawczuk, K. Ruebenbauer

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EDITORIAL

The camera-ready manuscripts of the papers presented during the Polish Mössbauer Community Meeting held at the Institute of Nuclear Physics in Cracow from Oct. 8th till Oct. 10th, 1986 are reproduced here directly from the best available copy. The manuscripts received before Dec. 31st, 1986 have been included.

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INTRODUCTION

K.Ruebenbauer
Institute of Nuclear Physics
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Polish Mössbauer Community Meetings were organized by the Institute of Nuclear Physics in Cracow since early seventies mostly due to the efforts of Dr. D.S.Kulgawczuk. They were aimed at gathering of the majority of domestic workers in the field in order to exchange information about the latest scientific and technological achievements and to establish informal ties between different groups scattered across this country. The previous Meeting has been held at Mogilany near Cracow in October 1981.

This Meeting was held in the Institute of Nuclear Physics from Oct. 8th till Oct. 10th, 1986. It was a somewhat particular Meeting as it coincided with the 25-th anniversary of the application of Mössbauer spectroscopy in Poland. Therefore,, a special session reviewing achievements and development of the major groups has been organized. The Meeting gathered about 80 participants from 23 scientific establishments. It has to be noted, that at present about 10 groups are pursuing active experimental investigations by means of Mössbauer spectroscopy in this country.

A Steering Domestic Committee of the Polish Mössbauer Community has been formed during this Meeting. Its main aims are as follows:

to pursue some kind of lobbying and advicing mostly concerned with the design of new equipment offered by domestic commercial companies, to advice and help newly formed groups, to coordinate expensive and sophisticated experiments, to exchange information between groups /mostly software/ and last but not least to be a domestic representative of our Community to the ICAME. The Committee is open to all individuals interested in the mentioned above activity and especially invites group leaders to cooperate with. The following people are the members of the Committee at present:

Dr. L.Dobrzyński /Białystok/, Prof. K.Krop /Cracow/, Dr. T.Panek /Katowice - industrial relationships/, Dr. K.Ruebenbauer /Cracow - software development and exchange, chairman/, Dr. J.Suwalski /Warsaw - Mössbauer sources, especially short-living/, Mr. J.Szlanta /Radom - high temperature equipment/, Dr. M.Szuszkiewicz /Wrocław - cryogenic equipment/, Dr. W.Zych /Warsaw - spectrometers/. The Committee asks to contact members responsible for particular topics in all matters concerned with a given topic. As far as the software is concerned we want to make a complete list of available items and therefore all people interested in exchange are kindly requested to send a short, but comprehensive description to Dr. K.Ruebenbauer /Institute of Nuclear Physics, Cracow/. Those interested in MOSSLIB implementation should make a contact as mentioned above.

Next Meeting is to be organized by Dr. W.Zych at Warsaw Technical University in Sept. 1988 in cooperation with the whole Warsaw Mösbauer Community.

Finally, I would like to thank all the people and establishments who contributed to the organization of the Meeting, i.e. the Board of Directors of the Institute of Nuclear Physics for a financial assistance and continous interest, Mr. W.Nowicki and his staff for their technical help, Dr. K.Ptak, Mr. W.Bednarz and their staff for printing all the necessary materials, Mrs. C.Szklarz for her secretarial work and last but not least my colleagues from the Organizing Committee, i.e. Dr. D.S.Kulgawczuk who did most of the organizational work, Ms. B.Miczko and Mr. B.Sepiol.

Cracow, Jan. 5th, 1987.

K. Ruebenbauer

BEGINNINGS OF THE MÖSSBAUER INVESTIGATION IN POLAND - MÖSSBAUER SPECTROSCOPY IN THE INSTITUTE OF NUCLEAR PHYSICS IN CRACOW

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In memory of Prof. H. Niewodniczański - first Director of the Institute of Nuclear Physics and Mr D. Keller - first head of mechanical work-shop staff of that Institute.

It was 25 years ago. In the middle of 1961, three physicists, dr A.Z. Hrynkiewicz /from the Institute of Nuclear Physics and the Institute of Physics of Jagiellonian University/, D.S. Kulgawczuk /from INP/ and H. Lizurej /from IFJU/ had an idea to construct an apparatus for the investigation of nuclear fluorescence of gamma rays, the new phenomenon discovered by R.L. Mössbauer in 1959. For this /known at that time as the Mössbauer effect/ he was awarded the Nobel Prize at the end of that year.

Our plans were interesting but we really did not know how to start. The Mössbauer literature at that time was very scarce, mostly short papers in Phys. Letters.

Our main problem was how to prepare the source with monoenergetic line of 14.41 keV of ^{57}Fe and how to move this source relative to the absorber or vice versa.

One of us /D.S.K./ proposed a special cam easy to make on a turnig-lathe. It consisted of two halves of left and right screw twirl. Such a cam as well as the rest of the mechanical skeleton of this apparatus was made by mechanical work-shop staff in our Institute /Fig.1/.

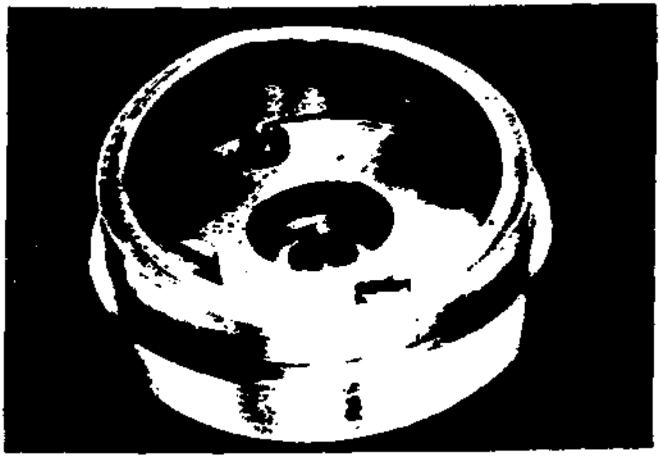


Fig. 1. The cam for changing the rotative movement on two-directions linear movement /from [1]/.

The first Mössbauer source by direct activation of stainless thin foil was made in cyclotron of INP in Cracow. From the activation by deuterons with about 7 MeV energy and after nuclear reaction,

$$^{56}\mathrm{Fe}(d,n)\,^{57m}\mathrm{Co} \xrightarrow[270d]{E.c.} {}^{57}\mathrm{Fe}.$$

we received radioactive ^{57m}Co, but unfortunately in a magnetic matrix. /Six line Mössbauer pattern with stainless steel absorber/. Demagnetization of such a source was achieved by heating /in quartz tube/ and next by rapidly cooling it. After that a single monoenergetic of 14.41 keV line of ^{57}Fe was seen. Ours was not a very good source, but at that time in Poland it was a success. At that time a young student J. Bara joined our small group and he calibrated the apparatus as his diploma work.

The scheme of this new mechanical apparatus can be seen in Fig. 2.

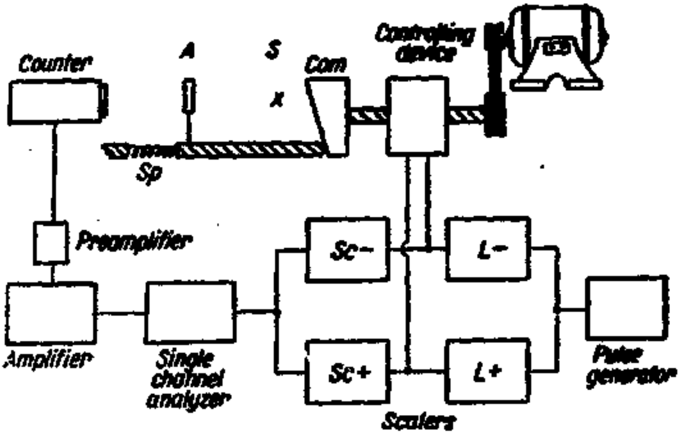
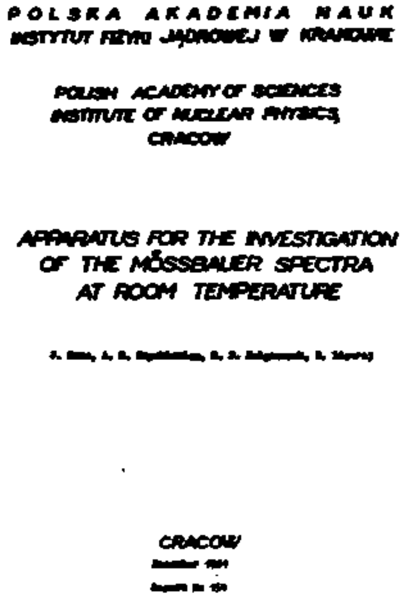


Fig. 2. The schematic view of the new apparatus /from [1]/.

Generally, the operation of this apparatus was the following. Gamma rays from the source S passed the absorber A and then were detected by scintillation counter (with 1 mm thick NaJ Tl) crystal. Pulses from the detector due to gamma Mössbauer line after preamplifier and amplifier were selected by a single channel analyzer and registred by scalers S_+ and S_-. At the same time a second pair of scalers /L_+ and L_-/ counted the standard pulses /from pulse generator/ for the pulse time calibrator. All scalers were operated by a controlling device for positive and negative relative velocities of the source-absorber. I should like to add now that later we used three pairs of scalers-third pair for long time measurements as a normalization.

In the years 1961-1968 /in 1968 INP bought modern M.S. with 400- multichannel Intertechnique analyzer/ we had only that Mössbauer apparatus to use.

It is worth noting that the first Report referring to our new apparatus appeared in December 1961 [1], see Fig. 3.



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APPARATUS FOR THE INVESTIGATION
OF THE MÖSSBAUER SPECTRA
AT ROOM TEMPERATURE

CRACOW

Fig. 3. The first report /from [1]/.

The first lecture on the Mössbauer investigation by A.Z. Hrynkiewicz and D.S. Kulgawczuk was given by myself at Dubna Mössbauer Conf. /1962/. The paper presented preliminary results of Mössbauer measurements in siderite /$FeCO_3$/, lepidocrocite /γ-FeOOH/, goethite /α-FeOOH/, and two others iron compounds [2].

Just after the conference D.S.K. made a new and more modern Mössbauer source $^{57}Co/Pt/$ by direct current-heating of thin platinum foil with a drop of ^{57}CoCl solution. This pioneering method /at that time/ for Mössbauer source preparation is illustrated in Fig. 4.

That new and much better source made serious Mössbauer investigations possible. /Monoenergetic gamma line of 14.41 keV of ^{57}Fe with "f" about 30% and $2\Gamma = 0.54$ mm/s was published by J. Bara, A.Z. Hrynkiewicz and J. Stroński [3]/.

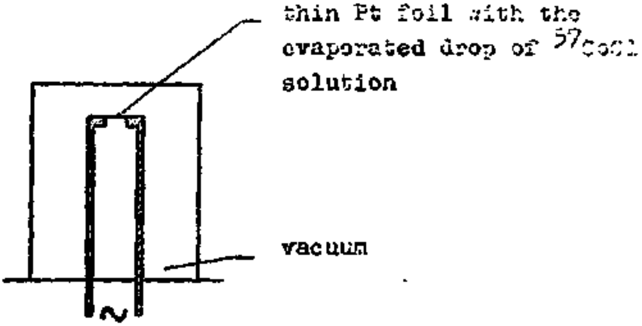

Fig. 4. Current heating for the Mössbauer source preparation

Then D.S.K. could more accurately repeat Mössbauer's study in lepidocrocite and goethite at room temperature. Unfortunately at that time we could calculate the Mössbauer spectra by a "by hand" method only. The time needed for those calculations was much longer as compared with modern computer techniques just now.

In lepidocrocite only a doublet of quadrupole interaction appeared but in goethite(so complicated that at first my coworkers said it had to be a mistake)—a double Zeeman Splitting was found.

All the same these measurements were published as Report INP /May 1963/ and Acta Phys. Polon. /1963/ [4], see Fig. 5. Today we know that in some samples of goethite /as well in ours from Poland/ a continuum of internal magnetic fields exists.* But at that time and with that method it could not have been calculated.

In 1963 in cooperation with Dr J. Kubisz from the Academy of Mining and Metallurgy in Cracow the Mössbauer measurements at room temperature were performed in iron sulphates of the jarosite group /six samples/ and published [5]. Also in 1963 in cooperation with Dr J. Dézsi from Central Research Institute for Physics in Budapest /Hungary/ the Mössbauer spectra measured at room temperature were performed in $CoFe_2O_4$, [6].

The measurements of the Mössbauer spectra made at room temperature only were not sufficient, so I decided to measure the Mössbauer spectra in goethite vs. temperature. To this aim /D.S.K/

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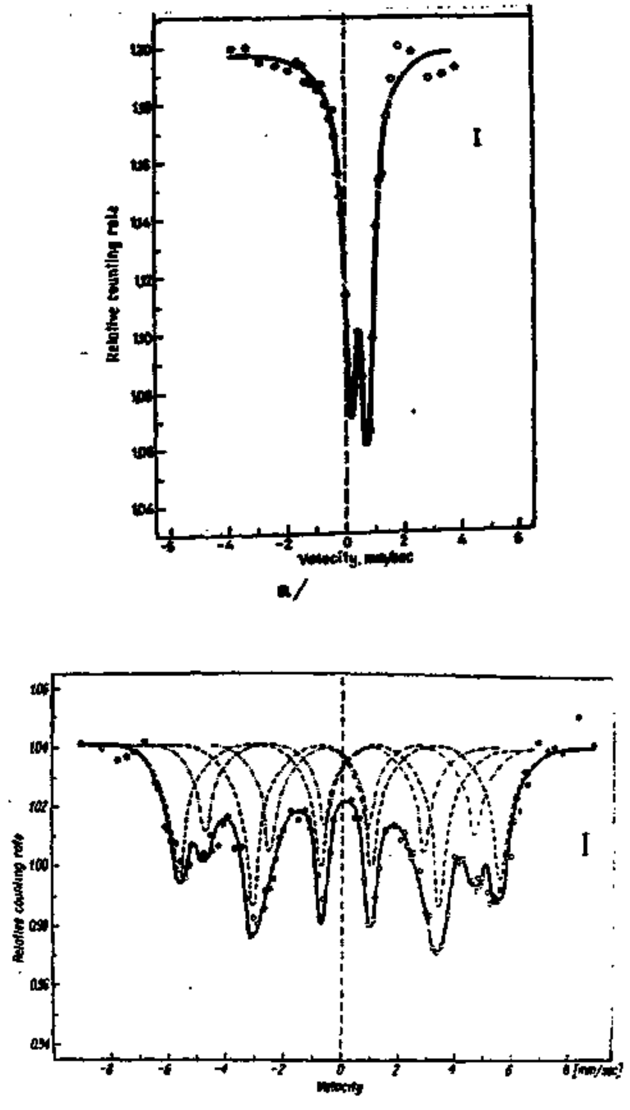
* Between H_{max} and H_{min}



a/

b/

Fig. 5. Mössbauer spectra in lepidocrocite /a/ and in goethite /b/ taken at room temperature /from [4]/.

a simple dewar /for LN_2 temperature/ and also a simple furnace /without vacuum/ were made, see Fig. 6.

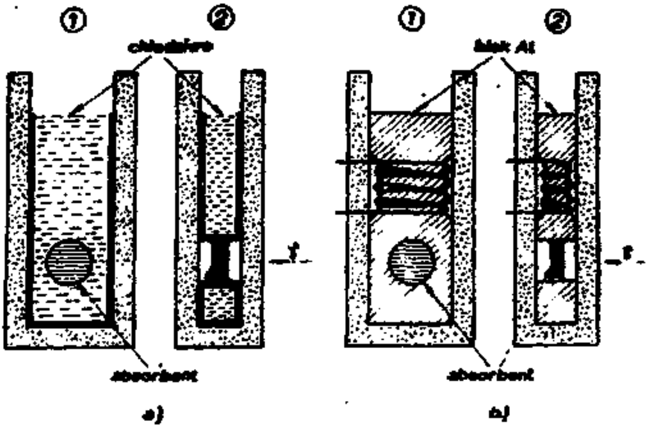


Fig. 6. A simple dewar for LN_2 temperature measurements /left/ and a simple furnace with mercury contact thermometer operated in flip-flop mode /right/, /from [10]/.

This additional equipment simple and easy to operate has worked up to now /temperature measurements with accuracy ± 0.5 deg./.

The Mössbauer measurements vs. temperature of hpf structure in natural goethite /from Poland/ from LN_2 up to about 500 K have been performed. Those measurements were murderous, because twelve spectra /about 48 h of nonstop for each one/ were needed, which involved practically no sleep for all that time, and I still remember it.

After the measurements I began the calculations by the same method as before. After elaboration the results /Fig. 7 and Fig. 8/ were published in the Report INP /May 1965/ and /a little change of the text/ in Phys. Letters 1965 [7].

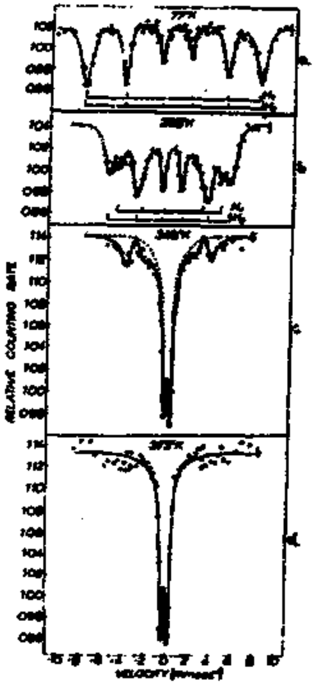


Fig. 7. Some of the Mössbauer spectra in goethite taken at different temperatures /from [7] and [10]/.

In spite of bad resolution /at that time I had no other possibility/ of our spectra it certainly was the first discovery of antiferromagnetism of goethite /below their T_N temperature/in controversy to earlier monographs /Selwood 1956/ [8] which treated goethite as a paramagnetic compound.
In our paper in Phys. Letters [7] there was a problem as to the existence of four antiferromagnetic sublattices in elementary cell of α-FeOOH according to a hypotheses of Naish and Turov [9]. The authors of this hypotheses have proposed a "cross structure" for D_{2h}^{16} space group /goethite structure belongs to that one/ but it was not confirmed in later papers.

In 1965 D.S.K. was the first to receive a PhD in the Mössbauer Spectroscopy in Poland, for a thesis entitled "Temperature

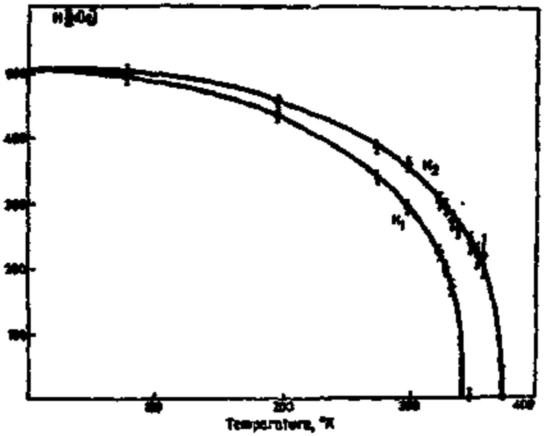


Fig. 8. Temperature dependence of the effective internal magnetic fields in goethite /from [7] and [10]/.

dependence of internal magnetic fields in goethite investigated by means of Mössbauer method effect*. This thesis also presents the results of the temperature dependence of isomer shift and quadrupole splitting from which the angle between the magnetic and electric field gradient direction in goethite was calculated [10].

Almost at the same time in our library two papers important for that problem appeared. Phys. Letters with our paper [7] and J. Phys. Soc. Japan with a short /one page/ notice by Takada et al. [11] about Mössbauer goethite measurements. The Japanese Mössbauer group observed only one internal magnetic field in their goethite sample, see Fig. 9.

Since that time a considerable problem has appeared: why had different results been obtained in the same mineral compound known up to that time in mineralogical tables as goethite? The end to different speculations and comments /very unpleasant for me/ was put by a Hungarian Mössbauer group [12].

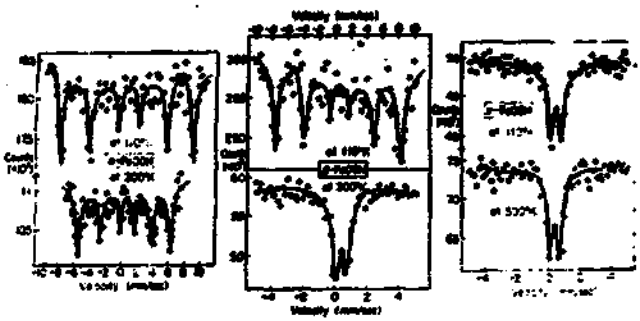


Fig. 9. Japanese Mössbauer group measurements in goethite at 110 K and room temperature /from [11]/.

Dezsi and Fodor /1966/ from Central Research Institute for Physics in Budapest in their laboratory, on their Mössbauer apparatus measured both Polish and Japanese samples and their results confirmed both previously obtained results, those by both the Polish and those Japanese group.

Moreover, Dezsi and Fodor made additional measurements by DTA method [12]. In our goethite sample the authors of [12] found crystallization water but in the Japanese sample no water was found. It became clear that at least two different minerals of goethite exist, not to be differentiated by a rentgenographic method.

In the same year /1966/ the "Mössbauer Effect in α-FeOOH" paper appeared [13]. Van der Woude and Dekker in their elegant work on the temperature dependence measurements of hpf structure in goethite /from Losewithiel/ also observed one internal magnetic field. Their conclusion drawn from the Mössbauer and other methods was that there is a whole range of goethites that can be divided into two classes: A - goethite showing two internal magnetic fields and two peaks in DTA, B - goethites showing one internal magnetic field and one peak in DTA method.

Comparison of the most important /at that time as well as modern/ measurements data by Mössbauer Spectroscopy method can be seen in Table 1.

Authors, refs and years	H_{eff} (kOe)			$2\varepsilon(T<T_N)$ (mm/s)	T_N (K)
	$T \rightarrow 0K$	90K	300K		
D S.K. et al. [6] /1963 - 1965/	505 ± 5	H_1=500 ± 5 H_2=495 ± 5	H_1=342 ± 7 H_2=282 ± 5	0,24 ± 0.05	370 340
T.Takada et al. [10] . /1964/	-	520 ± 15	360 ± 15	0,00 ± 0,10	400
F.V.d.Woude et al. [12] . /1966/	510	500 ± 3	389 ± 2	0,26 ± 0.02	393,3
S.Morup et al. [13] /1983/	506 ± 1	501,4 ± 0,5	381,1 ±0,5	0,28 ± 0.01	393,5±05

Table 1. Data of the Mössbauer Spectroscopy measurements by different authors in goethites; H - internal magnetic fields, 2ε- the quadrupole splitting, T_N - Néel temperature

It is interesting that the internal magnetic fields in the natural as well as in synthetic samples of goethites reach almost the same value for T→0 (K) [14].

The Mössbauer group started by us grew very quickly and it was gammated according to the rule of evolution. Later other young Mössbauer groups were formed. Those groups generated around J. Bara /the first Mössbauer diploma work/, around J. Sawicki /the second one/ and K. Tomala /the third one/.

After D.S.K. had defended his thesis, he spent one year /1967-1968/ at the Central Research Institute for Physics /Budapest/. There, together with a Hungarian Mössbauer group, they carried out the Mössbauer temperature dependence measurements of hpf structure in β - FeOOH and δ -FeOOH [15], see Fig. 10 and Fig. 11.

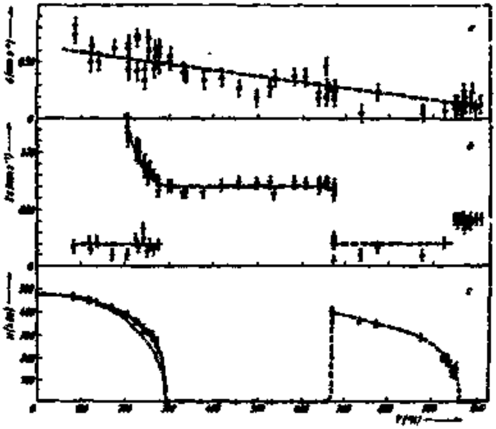


Fig. 10. Variations of the isomer shift δ, the quadrupole splitting 2ε and internal magnetic field H as a function of temperature in β-FeOOH, /from [15] /.

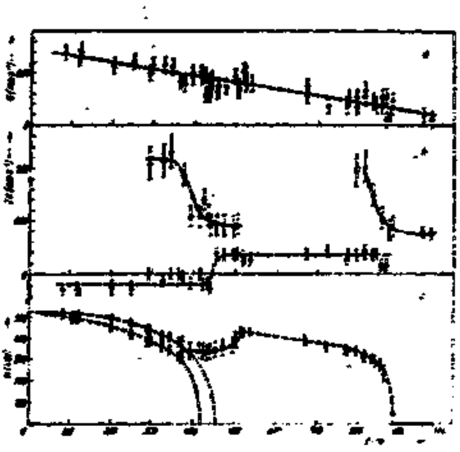


Fig.11. Variations of δ, 2ε and H vs. temperature in δ-FeOOH /from [5] /.

Therein, the Mössbauer measurements for a group of $Mn_{1-x}\ n_x Fe_2O_4$ type ferrites with $0 \leq x \leq 0.80$ were performed [16].

Later, in 1969 we studied iron chelate complexes/eleven samples/ by the Mössbauer effect method [17].

In cooperation with the Institute of Iron Metallurgy of the Academy of Mining and Metallurgy - Cracow, there was performed and elaborated a very interesting work /at room temperature/ of hpf structure for a group of nonstoichiometric iron oxides of the $Fe_{1-x}O$ type /eleven samples/ with $0.002 \leq x \leq 0.250$ [18], see Fig.12.

In the same collaboration the Mössbauer measurements in calcium iron olivines $(Fe_{1-x}Ca_x)SiO_4$ with $0 \leq x \leq 0.65$ were performed at room temperature and [illegible]00K [19]. Also from that collaboration resulted yet another work on the Mössbauer study of calcium magnetites of $Ca_xFe_{3-x}O_4$ type with $0 \leq x \leq 0.55$ /nineteen samples -

- spectra taken at room and LN$_2$ temperatures/ [20].

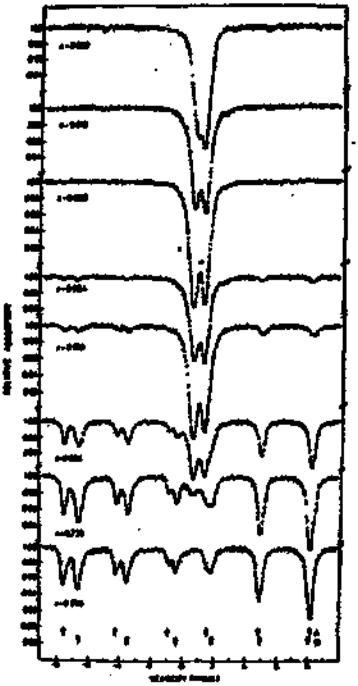


Fig.12. Some of the Mössbauer spectra for Fe$_{1-x}$ O samples taken at room temperature, /from [18]/.

In 1974, in cooperation with a Mössbauer group of the J.V. Kurchatov Institute of Atomic Energy, Moscow, the Mössbauer measurements in three samples of jarosite group /from L.H. up to LN$_2$ temperature [21] were performed, at low temperature.

In addition to the problems mentioned above, D.S.K. was interested in molecular biology. Some collaboration with respective groups from the Chemical Department of the Wroclaw University and the Medical Academy in Cracow was started: with a group of Prof.B.Jeżowska-Trzebiatowska /to ChDWU/, the synthesis of nucleic acid fragments /adenina, guanine/ with iron Fe was studied [22]. Also with a group of Dr H.Przywarska-Boniecka /to

ChDWU/ catalase model complexes /biological enzyme/ [23]as well as the synthesis of homoglobine /synthetic hem + natural globine/ were investigated.

With a group of dr.J.Frendo /to MA Cracow/ we started the investigation by Mössbauer Spectroscopy of a sulfhomoglobine /hemoglobine connected with sulfur/.

In 1976 /in collaboration with the Institute of Geology and Mineral Deposits of the Academy of Mining and Metallurgy, Cracow/ research was performed on the problem of the nature of iron compounds in well-encrasting sediments [24]. Also in collaboration with the Chemical Department of the Jagiellonian University the Mössbauer measurements of the reduction of iron catalysts for amonia synthesis [25] were performed.

Last but not least D.S.K's paper entitled "Problem of magnetic dilution and particle superparamagnetion in iron oxides investigated by the Mössbauer Spectroscopy" [26] appeared in the Report of INP, No 1324/PL /August 1986/.

Nowadays the Mössbauer Spectroscopy in the Institute of Nuclear Physics in Cracow belongs to the Applied Nuclear Spectroscopy Labaoratory as a part of the Nuclear Spectroscopy Division. The Mössbauer Spectroscopy staff in our Institute have investigated after different problems, Among them /Mr.R.Kmieć and Mr.J.Kraczka/ rare-earth with 3d, 4d and 5d /elements/ alloys were studied. This group also performed the investigation of diluted alloys impurities like Sn in copper and silver matrices alloyed with some d-elements, and carried out a research of natural minerals. This group cooperates with a Mössbauer group of Nuclear Radiospectroscopy Division of the Institute of Physics at the Jagiellonian University as well as with CNR-Strasbourg /France/ and with Kernforschungszentrum - Karlsruhe /FRG/.

The second problem in which Dr.K.Ruebenbauer, Mr.B.Sepiol from INP and Mr.B.Miczko from ChDJU are interested is the high temperature diffusion and the lattice dynamics via the Mössbauer Spectroscopy. The group works in close cooperation with both the domestic and international centers /domestic - The Department of Chemistry of the Jagiellonian University, the Department of Physics of the Technical University in Radom, the Institute for Materials Science of the Academy of Mining and Metallurgy, Cracow; international - McMaster University, ILL - Concordia University/.

The group is especially concerned with the development of high temperature equipment, single-crystal sources and at last but not least with the development of highly sophisticated Mössbauer software.

The third issue D.S.K. has lately been interested in is the Mössbauer studies of drugs. In the middle of 1985 /the starting date/ and in this year in cooperation with Dr K.Ruebenbauer and Mr.B.Sepiol from INP the measurements of temperature dependence of hpf structure in commercial drugs containing iron were performed. The detailed studies of ferrous gluconate - main component of anemia drugs /at LN_2 temperature up to about 400K/ were also carried out. After the elaboration of the obtained results, the paper was written and sent to the Hyperfine Interaction Conference /Bangalore, India 1986/ [27].

Apart from that D.S.K. has almost finished his habilitation thesis.

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MOSSBAUER SPECTROSCOPY IN AGH

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Mössbauer Spectroscopy (MS) in AGH exists in the Department of Solid State Physics of the Institute of Metallurgy. The beginning of this activity dates back to the term 1969/70 when one of us (K. K.) as a Leverhulme Fellow at Physics Department of Sheffield University was intensively working in this field. After coming back home MS was being initiated in the Group of Bulk Magnetic Materials in the above mentioned Solid State Physics Department.

1. Laboratory - past, present and future.

Our laboratory was started with NOKIA-Electronics (Finland) Mossbauer spectrometer based on multichannel analyzer with 800 channels. It was only in 1972 that the first Mossbauer spectra were measured. Shortly after our Mössbauer laboratory was equiped with continuous flow cryostat and a cryostat with superconducting magnet (3T) of Oxford Instruments Company to initiate measurements at liquid helium temperatures. At this time the activity of Mossbauer Group was mostly directed to enlarge our measuring possibilities and to collect computer programs to fit (interpret) the measured spectra. So then, vacuum Mössbauer furnace was constructed to measure spectra at elevated temperatures (above RT up to Curie point of iron (1050K)) and vibrator to measure spectra in the moving-absorber geometry was also constructed. Computer programme to fit static and dynamic (relaxation dependent) Mössbauer spectra was brought into operation.

To collect gasous helium from the operating cryostats Leybold's helium recovery system was installed.

The actual measuring possibilities allow to measure transmission Mössbauer spectra on Fe, Sn and Eu nuclei at temperatures 1.7K -4.2K (pumped cryostat), 20K - 300K (continuous flow cryostat), 4.2K - 300K (top loading cryostat) and 300K - 1100K (Mössbauer furnace).

The spectrometers are connected on line with NEPTUN minicomputer which is afterwards connected with IBM-AT one. This enables to fit every measured spectrum.

The nearest future of our MS is to introduce "in situ" CEMS in UHV on oligoatomic Fe films, and additionaly measurements on some rare-earth nuclei with the possibility of simultaneous cooling of the source and absorber.

2. Projects

The first subject of Mössbauer investigations (still in Physics Department, University of Sheffield) was an ensemble of β-Co particles in Cu-1%Co alloy. The scope of this studies was to determine the spin-lattice correlation time of magnetic moments of β-Co particles, including the range where cobalt particles exhibited superparamagnetism. Thermal excitation analysis of very small Co particles which sizes did not exceed 100 atoms per Co particle, was also the subject of investigation in the newly opened MS laboratory.

One of the first studied subjects were also magnetic properties of disordered Fe-X (X :Cr, Si, Sn) alloys for which the influence of X-element on hyperfine field, spin and charge transfer were studied.

In the second half of the seventies our Mossbauer laboratory started new problem i.e. magnetic properties of intermetallic compounds of rare earth - 3d transition metal. This subject is studied with good results untill now and hydrides of these intermetallics were also included.

Our laboratory made also some contribution to the knowledge on physics of amorphous Fe-B and Fe-Zr alloys.

The MS Group got recently valuable results on magnetic properties of oligoatomic and monoatomic iron films (untill now in the cooperation with Technical University, Clausthal-Zellerfeld).

There are several problems which were tackled by our group due to contacts with people and other laboratories that willingly cooperated with us:

- cation distribution in titanomagnetites (subject brought by the post doctoral fellow from Australia),
- phase analysis of tin oxide thin films (also doped with indium and antimony) in cooperation with the Group of Thin Semiconducting Films, IM AGH, Kraków,
- lattice dynamics of europium-tungsten bronzes (in cooperation with the Laboratory of Magnetochemistry, Warsaw University),
- phase analysis of minerals (in cooperation with the Institute of Geology and Mineral Resources, AGH, Kraków).

In the frame of listed subject 73 papers were published; two habilitations (another two very advanced), seven Ph.D. thesis and twelve diploma works were completed.

3. Staff and international contacts

At present the HS Group counts ten people including three staying actually abroad. The Group cooperates with following foreign and domestic laboratories:

1. Physics Department, University of Sheffield, England,
2. Mining Academy, Freiberg, DDR,
3. University of Saarbrücken, FRG,
4. KFKI, Julich, FRG,
5. Technical University, Wien, Austria,
6. Freie Universität, Berlin West,
7. Technical University, Clausthal-Zellerfeld, FRG,
8. Institute of Nuclear Physics, Swierk, Poland,
9. Institute of Solid State Physics, University of Lodz, Poland.

MÖSSBAUER SPECTROSCOPY LABORATORY AT SWIERK

by J.Suwalski *

I. Introduction and general description.

Twenty years have already passed since the creation of the Mössbauer Spectroscopy Laboratory in Swierk. If one takes into account that the discovery of Mössbauer effect took place 28 years ago and the Nobel prize was granted to R.Mössbauer only 25 years ago, the anniversary of our laboratory seems quite impressive.

In early stages of the development of our laboratory the activity was directed towards the construction of Mössbauer spectrometers for our own needs and to fulfill the increasing demand for this type of equipment from research and university institutions. Few simplified spectrometers were constructed also for industrial use. In the same time cryogenic techniques and cryostat constructions were developed.

Initially the measurements of ^{57}Fe resonance were carried out but other resonant nuclei were consecutively introduced, namely ^{119}Sn, ^{125}Te, ^{151}Eu, ^{121}Sb, ^{61}Ni and ^{161}Dy. The studies of the latter two were made possible due to existence of accelerators and reactors suitable for the irradiation of short-life isotopes.

The research carried out in our laboratory combined the construction of spectrometers, the methodology of Mössbauer effect studies as well as basic research concerning magnetic and related properties of ferrites, iron based metals and more recently synthetic metals. The application studies on the demand of industry or other research centers were also carried out.

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The laboratory staff have published more than 100 scientific papers from which ca 40% were published in the most prestigeous international journals, the rest being published in international conference proceedings or in technical and popular science journals. Several non published technical reports and expert's reports for industry were also performed.

Four MSc theses, four PhD theses and two habilitation theses were completed in our laboratory. Several researchers from Poland and abroad finished Mössbauer spectroscopy courses and trainings which lasted from 1 month to 1 year.

II. Present staff:

Five employees including two highly qualified technicians, two senior assistents completing their PhD and one associate professor. Beside the permanent staff the laboratory employs also MSc candidates and traineers on the temporary basis. The number of permanent staff has been reduced, as compared to the to the level at early stages of the laboratory, from 8-9 to 5 positions.

III. Equipment.

Home-made constructions:

a/ Mössbauer spectrometer SM-4 working in the velocity range +25mm/s. It is used to the studies of the following isotopes: iron, tin, telurium and nickel isotopes.

b/ Mössbauer spectrometer SM-6 working in the velocity range +600mm/s. It is applied to the studies of rare earths isotopes.

c/ Gammaresometer ie spectrometer of v-constant with automatic registration in two arbitrary applied velocities.

d/ Austenitmeter ie spectrometr for quick determination of the retained austenite content in construction steels.

The same spectrometers were built for Silesian University (a), Wroclaw University (a) and University of Leipzig (b). Gammaresometers (c) were applied in several coal mines, namely:

KWK Wujek in Katowice, KWK Brzeszcze in Oświęcim, OBR-EMAG in Katowice and in heating power plant Siekierki and Bełchatów as meters for the determination of the content of sulphur in coal.

Other important equipment:

e/Superconducting solenoid combined with a cryostat in vertical geometry. Magnetic field up to 6T.
f/Microcomputer IBM-PC-XT

It must be stressed that we are fortunate to have in Swierk a unique opportunity to carry out the research requiring the existence of nuclear reactors, accelerators of particles, high speed computers, cryogenic systems and radiological protective service. This fact greatly facilitates the undertaking of difficult and non-typical experiments.

IV. Research interests and major scientific achievements.

In the early stages of the Mössbauer laboratory the research interests were focused mainly on the construction of scientific equipment and the initiation of Mössbauer Effect (ME) measurements involving various resonant nuclei. In addition to ME studies, neutron and X-ray spectroscopic and diffraction techniques were applied in order to obtain complementary results. In particular spinel type ferrites, garnets and iron-uranium, iron-telurium intermetallic systems were studied.

A series of theoretical papers were also published at that time. The papers were devoted to the calculation of hyperfine structure parameters from Mössbauer spectra in the presence of magnetic and electric field influencing simultaneously the resonant nucleus. Interestingly these papers remain, till now, frequently quoted in the literature.

The results of the studies concerning magnetically ordered state and spin microstructure in diluted ferrimagnetic oxides turned out to be extremely interesting. Spin canting and spin flipping predicted by theory were observed. A method of distinction between different spin alignment processes in external magnetic field was developed. $3d^5$ shell deformation of Fe^{3+} ions in some spinel ferrites were determined. The distribution of iron cations between octahedral and tetrahedral positions was measured. The substitution of magnetic cations by the nonmagnetic ones (^{121}Sb, ^{119}Sn) in spinels enabled us to calculate the supertransfered hyperfine field at these nominally diamagnetic ions. The results of the above studies created significant interest in industry and as a result large portion of this research was financed by POLFER.

Another important part of our research was devoted to the investigations of atomic order and disorder in alloys. It was shown that ME is a suitable method for such studies. For example in alsifer alloys which are routinely used for the manufacturing of magnetovisual heads perfect ordering and a preferential occupation of alloing elements were discovered. Alloys exhibiting large segregation of components and amorphous alloys were also investigated. Spinodal decomposition occurring in alnico alloys due to thermomagnetic treatment was traced. In the materials used for the fabrication of permanent magnets a texture was observed as a result of column crystallization. Early stages of crystallization in amorphous alloys were investigated as well as their magnetic anisotropy transverse to layer plane. A simple method of the determination of retained austenite content in steel was elaborated. High temperature corrosion studies in electricity power plants (Konin, Turoszów) and atmospheric corrosion of the body cars were carried out.

In the seventies several investigations concerning the methodology of ME studies in rare earth were undertaken. For this purpose a special spectrometer was constructed (see section 3.5). An original technology of preparation of short-life ^{161}Dy isotope in reactor was developed. It must be stressed that despite a large interest in rare earth chemistry and physics the ME studies of material containing RE elements are extremely rare.

The research interests were focused on RE-TM intermetallic compounds due to their interesting magnetic properties and their potential application. This part of work was carried out in collaboration with Solid State Physics Laboratory of AGH and Institute of Physics of UJ. A series of experiments involving intermetalic compounds of Dy, Sm, Y, with Fe, Co, Pd and Al or B were performed. This part of research resulted in several papers published in regular journals and conference proceedings.

In early eighties in collaboration with the Department of Chemistry PW our laboratory initiated the application of ME spectroscopy to the studies of synthetic metal ie organic compounds exhibiting metallic conductivity. It must be stressed that the first ME studies of conducting polymers was carried out in Swierk. The discovery that ME can be applied with success to the characterization of organic conducting materials containing Mössbauer nuclei stimulated a large research interest all over the world. Very quickly several research groups from MIT, Tsukuba University, Max Planck Stuttgart, Free University Berlin, GTE, and University of Strassburg followed the route initiated by Swierk. However till now the Warsaw-Swierk research group still holds the largest contribution to the field.

The ME technique enabled us to determine the chemical nature of the intercalated species and the charge transfer between the host matrix and the intercalate. From the temperature dependence of the recoil free absorption Debye-Waller-Mössbauer lattice temperatures of several intercalates were calculated. Finally, careful ME studies enabled us to differentiate between the "true intercalates" and degradation and/or contamination products which helped to resolve several controversies existing in the literature.

V. Domestic and international collaboration.

As it has been already stated important scientific achievements were accomplished through collaboration with several research institutions. Similarly some industrial applications were made possible through the cooperation with research and development centers of the industry. The limited space of this activity review does not allow to mention all institutions with which we collaborated over twenty years. For each of them important and sometimes crucial Mössbauer studies were made.

Acknowledgment

The author and his collaborators wish to acknowledge the enormous contribution of the former staff members, namely: Doc.Dr Hab.J.Piekoszewski head of the laboratory from 1966 to 1977, Dr L.Dábrowski, Doc.Dr Hab.S.Ligenza, R.Mundkowski (MSc), K.Cieloch, W.Kulesz, Z.Rolke and especially Mrs K.Kisyńska (MSc) whose untimely death deprived us a valued friend and colleague. Without their enthusiasm, creativity and hard work many of the presented research achievement could not be accomplished.

Our Contribution to the Mössbauer Spectroscopy

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A short review of our 26-years scientific activity in a field of Mössbauer spectroscopy, based on selected publications, is given.

My adventure with the Mössbauer spectroscopy began in 1960 when at the Jagellonian University I started to prepare my masters thesis „Apparatus for the Investigation of the Mössbauer Effect at Room Temperature" /1,2/. This, fully automatized /3/, constant velocity Mössbauer spectrometer is being used till now for special purposes /4,8b,8d/. In the second half of the first decade a constant acceleration Mössbauer spectrometer was bought and located in the cryogenic building of the Institute of Nuclear Physics. This creates low temperature fascilities for the Mössbauer effect group. In the middle of the second decade two new departments were established at the Institute of Physics of the Jagellonian University. As the result of this the Mössbauer effect group was split into three independent groups. Soon after two new Mössbauer laboratories were organized. Our laboratory, organized in 1976 at the Science Teaching and Methodology of Physics Department, is equiped with two constant acceleration Mössbauer spectrometers of the Polon type.

In the first decade of our Mössbauer effect research we studied microdynamical properties of Co-57 impurity atoms. It was found that the force constants for impurity atoms are almost the same as for host atoms /5-7,11a/.

In our new Mössbauer laboratory two scientific research programs, mainly methodological ones, have been developed. The first one, which became our speciality, is concerned with unconventional aspects of the nuclear resonance scattering of γ-rays. It was started with detailed analysis of Mössbauer scattering spectra recorded in a single scattering geometry /8a/. This analysis was then extended for spectra recorded in double and multiple scattering geometries. The nuclear resonance, Rayleigh and Compton scattering processes were taken into consideration. First of all the integral and analytical expressions were derived for a shape of a background corrected single resonance scattering line /8a/, Mössbauer filtration /8b/ and Mössbauer dispersion /8c/ spectra, time independent selective excitation double resonance spectra /8d/, as well as double /8e/ and multiple /8f/ scattering spectra. The integral expressions were then used in numerical evaluation of the spectra parameters. Samples of various thicknesses and having various abundances in resonant isotope were analysed. The influence of an excitation energy setting on the shape of the Mössbauer filtration and time independent selective excitation double resonance spectra was also studied.

The conclusions derived from theoretical considerations were experimentally verified. It was found that the magnitude of Mössbauer effect derived from the single resonance scattering line has its highest value for very thin samples for which the linewidth is the smallest one /7c/. The use of carefully designed the low noise scattering geometry gave the high magnitude of Mössbauer effect both for enriched and non-enriched samples.

The double resonance Mössbauer experiments are much more sophisticated than the ones performed in the transmission or scattering geometries. However, some of them enable one to utilize in one experiment all unique properties of Mössbauer spectroscopy such as high energy resolution, short observation time as well as large value of the nuclear resonance cross section.

The high energy resolution is the most widely utilized property. In order to improve it a Mössbauer line narrowing has to be achieved. The narrowing of on-resonance filtration and on-resonance time independent selective excitation double resonance lines as well as the narrowing of double and multiple resonance scattering lines was theoretically predicted. Reduction in linewidth to the value of nearly one gamma may be obtained by application of the source and scatterer filtering method /8f/. Using a specially designed transmissional-scattering geometry narrowing of Mössbauer line and amplification of its amplitude were observed /8b/ for on-resonance excitation. Moreover, dispersion phenomena were observed /8c/ in Mössbauer spectra recorded in similar geometry by detecting scattered γ-rays, conversion X-rays or conversion electrons. Very small difference in resonance energies of absorber and scatterer were indicated by the spectra.

Due to sufficiently large recoilless fraction of scattered γ-rays and very low noise geometry used, selective excitation double resonance spectra were successfully recorded /8d/ both for the enriched metallic iron foil and for the non-enriched magnetite scatterer of a natural origin. The results of these experiments are in good qualitative agreement with the interpretation of time independent selective excitation spectra.

An attempt was made to observe a double resonance scattering process. The double resonance scattering spectrum was recorded /8e/ by detecting conversion X-rays following resonance absorption in enriched hematite of γ-rays which were previously recoilless-recoillessly scattered by enriched metallic iron foil.

A more detailed analysis of scattering and transmission geometries have resulted in new interesting findings /9,10,12,13/.

The experimental conditions suitable for observing a line inversion in Mössbauer scattering spectra were predicted by the numerical analysis of the Rayleigh and Compton contributions to Mössbauer scattering spectra. The line inversion was observed /9c/ for beryllium scatterers with small iron impurities.

The performance of the X-ray-e^- coincidence technique for recording depth selective Fe-57 CEMS spectra was investigated /10a,b,d/. The technique proved useful for selection of the Fe-57 K-shell conversion electrons from a beam of back scattered electrons. This makes it possible to observe depth sensitivity of CEMS spectra recorded with an He/CH_4 proportional counter.

The compensation conditions were utilized for observing interference effects in Mössbauer scattering spectra recorded for the enriched hematite scatterer placed in front of beryllium plates of properly chosen thicknesses /11e/. The method for absolute calibration of the intensity scale of Mössbauer spectra was proposed /11e/, a distorsion of Mössbauer spectra caused by geometric effects was studied /13a/ and a comparison of spectra simultaneously recorded in transmission and scattering geometries was performed /13b/. It was found that in some cases the scattering method predominates the transmission one as far as line quality parameters and linewidths are concerned.

In some scattering experiments already described a pulse shape discriminator composed of commercially available electronic blocks was used /14/. It efficiently reduces a detector background, produced in proportional counters by high energy γ-rays, and a time interval of storing Mössbauer spectra.

Our second research program is concerned with studies of ferrites /9b,10c,15/, intermetallic compounds /16/, amorphous materials /17/ and vanadium oxide bronzes /12,18/. Papers published in that field by our coworkers during their stay abroad were not included in this report.

The results of our investigations were presented at the International Conferences on Application of Mösbauer Effect: Varna-1967 /6b/, Tihany-1969 /11a/, Dresden-1971 /11b/, Cracow-1975 /11c/, Bucharest-1977 /11d/, Portorož-1979 /9a,b/, Jaipur-1981 /11e/, Alma-Ata-1983 /12/ and Leuven-1985 /10b,c/.

One habilitation report /19/, three doctor's thesis /20-22/ and 30 master's thesis were prepared in our Mössbauer laboratory.

A few review papers on application of the Mössbauer spectroscopy have been published /11a,23-25/.

We were actively engaged in organization of ICAME-Cracow-1975 /11c/ and of the Winter School on Physics-Zakopane-1985 /26/.

Let us hope to have a prosperous future.

The author acknowledges the long term cooperation with all cooworkers.

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MÖSSBAUER LABORATORY AT THE FACULTY OF PHYSICS, WARSAW UNIVERSITY

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The Laboratory of the Mössbauer Effect was founded in 1966 as a part of newly organized Chair of Nuclear Methods of Solid State Physics in the Institute of Experimental Physics at the Faculty of Physics in Warsaw University. Hence, we have now double occassion for celebration: 25 years of Mössbauer spectroscopy in Poland and 20 years of our lab. I joined this laboratory in 1967. In 1981 our lab was attached to the Department of Solid State Physics where it belongs till now.

The begining twenty years ago was similar to that in other laboratories. We had primitive home-made mechanical v-const. spectrometer with the velocity range up to ±3 mm/s, and LN cryostat. Using this equipment we studied phase transitions in KNO_3 and published in 1968 the first paper fully made in our lab /1/. In 1968 we received spectrometer purchased in DDR - v-const. Carl Zeiss Jena MS-10K. This spectrometer, which from the begining was obsolete and unreliable had a velocity range up to ±12 mm/s, so we could study magnetic interactions in iron compounds. The situation improved very much in 1973 when we obtained new spectrometer of European standard - Nokia (Finland). The spectrometer, later developed in our lab, is our main tool till now. In the same time we constructed another spectrometer based on Polish CAMAC units (γ-spectrometer) and 400 channels analyser developed at Technical University in Warsaw. In 1975 we bought modern flow cryostat CF-100 from Oxford Instruments (England). Unfortunalety due to permanent shortage of liquid helium we use this cryostat for the temperature range 70 - 300 K. In that time we constructed new spectrometer working with Nokia-Polon analyser, which parameters are similar to the original Nokia spectrometer. So, today we have two good, but rather old, spectrometers using which the measurements for 6 different samples can be carried out simultaneously. We deal almost exclusively with ^{57}Fe Mössbauer spectroscopy. In addition since 1979 we have in our lab Polish made minicomputer Mera 400.

In this twenty years our scientific effort was concentrated on three main topics: proton irradiation effects induced in iron compounds, study of atmospheric aerosols, and investigations of the influence of the radio frequency (rf) fields on the properties of ferromagnetic crystalline and amorphous materials.

In 1968 we started investigations of effects induced in iron compounds by energetic protons. Using the Mössbauer effect it was possible to study radiation damage and chemical decomposition of the materials caused by protons of energies varying from 0.3 to 2 MeV. We investigated dielectric iron compounds such as: $FeSO_4.7H_2O$, $K_4Fe(CN)_6.3H_2O$, $K_3Fe(CN)_6$, $NH_4Fe(SO_4)_2.12H_2O$, $(NH_4)_2Fe(SO_4)_2.6H_2O$, $FeCl_2.4H_2O$, $Fe(C_5H_5)_2$. It was found that as a result of local chemical decomposition due to proton irradiation new chemical compounds appear and that the final products of decomposition are magnetic compounds such as Fe_2O_3, Fe_3O_4, Fe_3C and metallic iron. In several cases, depending on the proton energy and dose, magnetic compounds were formed in the form of ultrafine particles exhibiting superparamagnetic behaviour. Using the "thermal spike" model it was possible to estimate the size of regions containing magnetic fractions formed by proton irradiation. The agreement of the experimental data with such simple model was good. We published 14 papers on this subject (see e.g./2-7/ and refs. therein). In 1977 we extended this subject to other materials and studied proton irradiation effects in Fe-Ni metallic alloys /8/.

In 1969 we employed the Mössbauer spectroscopy to study atmospheric aerosols. This was the first and unique application of the Mössbauer spectroscopy in atmospheric physics. Mössbauer effect proved to be a powerfull tool in the investigations of the properties of iron containing particles in atmosphere. We could estimate the chemical form in which iron appears in the atmospheric aerosol, concentration of iron, and the size of iron containing particles /9/. The method is accurate enough to follow the seasonal variations of the concentration of iron in the air /10/. These results threw some light on the origin of iron in the atmosphere. It was possible to study the relation of iron concentration in the atmosphere with the radioactivity of the air /11/, and the process of washing-out of the pollution from the atmosphere by rain /12/. The influence of industrial pollution on the properties and total concentration of iron containing aerosol was investigated /13/. The Mössbauer data were found to be sensitive to the circulation process in the atmosphere. 8 papers were published on this subject. This study is performed in collaboration with the Institute of Geophysics, Polish Academy of Sciences.

Since 1973 we study the effects induced in ferromagnetic materials by an external magnetic radio frequency fields. Our scientific effecrt is concentrated on this subject till now. The rf power generators constructed in our lab allow us to study two kinds of effects: (1) the modulation of the Mössbauer gamma radiation due to vibrations of Mössbauer nuclei induced by the rf field via magnetostriction as a result of which the sideband lines appear in the spectra ("rf sidebands" effect), and (2) the effect of the fast magnetization reversal forced by the rf fields in soft ferromagnets which is manifested as a collapse of magnetic hyperfine splitting to a single line or quadrupole doublet ("rf collapse" effect). In order to observe the "rf sidebands" effect the material must be magnetostrictive. We studied this effect in detail for metallic iron /14/ and as an accompanying effect to the " rf collapse" in various iron containing alloys /14-18/. The "rf collapse" effect occurs when the frequency of the rf field is larger than Larmor precession frequency and when the intensity of the rf field is larger than the anisotropy field, so that the switching time is comparable to the period of the rf field applied. The first paper from our lab related to the "rf collapse" effect was presented on the International Mössbauer Conference in Krakow, 1975, and published in 1976 /15/. A detailed study of the "rf collapse" effect in Fe-Ni alloys was performed /16/. It was hown that since the collapse and sideband effects can be separated their origin is different: sidebands are of magneto-acoustic origin and collapse is a purely magnetic effect of relaxation origin /17/. The influence of the spin pinning on the "rf collapse" effect was demonstrated /18/.

In 1979 the investigations of the rf induced effects were extended to include ferromagnetic amorphous alloys. It was found that the rf field causes irreversible and reversible changes in the materials studied. The application of the rf field to amorphous alloys of high magnetostriction (e.g. $Fe_{40}Ni_{40}B_{20}$) induces the irreversible effect – the crystallization of the amorphous system at temperatures much lower than normally observed crystallization temperatures. This new effect was studied as a function of the frequency, intensity, exposure time to the rf field for various amorphous materials of different magnetostriction constants. The results show that magnetostrictively induced vibrations ("rf sidebands" effect) destabilize the amorphous structure and cause the crystallization /19-21/.

For many amorphous alloys it is possible to observe the "rf collapse" effect, which, because of averaging to zero the magnetic hyperfine field experienced by Mössbauer nuclei, allows to separate the magnetic dipole and electric quadrupole interactions in the ferromagnetic state of amorphous alloys. Hence the quadrupole splitting distributions and isomer shifts can be studied directly. This unique method, first introduced in /22/, makes possible to follow changes of the short range order (SRO) in amorphous metals, which are inaccessible by other methods. SRO in $Fe_{90-x}Si_xB_{10}$, $Fe_{84-x}Si_xB_{16}$, $Fe_xNi_{75-x}Si_{10}B_{15}$, $Fe_{75}Si_xB_{25-x}$ and other FeNiB and FeB amorphous alloys was studied /23-26/. The results obtained were in good agreement with the structural model for FeSiB alloys (see also M.Kopcewicz, this conference).

Application of the stress to amorphous alloys showed that stress induced magnetic anisotropy strongly influences the "rf collapse" effect. If the stress induced anisotropy field is larger than the applied rf field, the "rf collapse" effect disappears. This effect is similar to the influence of the static field on the "rf collapse" effect and clearly proves the purely magnetic origin of the "rf collapse" effect /27/.

The study of rf induced effects in amorphous metals were performed in collaboration with the University in Saarbrücken (Fachbereich Angewandte Physik), F.R.Germany.

We published 30 papers related to the rf studies.

More conventional studies of amorphous metals were also carried out /28/.

Moreover, the "rf sidebands" effect was studied for Ni samples implanted with ^{57}Fe. The composition of the surface layer formed due to implantation and the range of ^{57}Fe ions implanted was determined.

The effect of the Mössbauer magnetoacoustic echo was observed in Fe-Ni alloys using pulsed rf fields /29/.

In collaboration with the University in West Berlin the investigations of relaxation processes in milikelvin temperature range were performed.

The results of our studies were presented on many international Mössbauer, Hyperfine Interactions and Amorphous Conferences.

During all that 20 years besides scientific activity we were involved in teaching. About 20 M.Sc. thesis were done in our lab and a large number of students became aquainted with the Mössbauer spectroscopy during the course of IIIPhysical Laboratory and seminars.

Scientific degrees were obtained by the members of our group:
M.Kopcewicz - Ph.D. in 1973, and habilitation in 1981,
A.Kotlicki - Ph.D. in 1974, and habilitaion in process,
B.Kopcewicz - Ph.D. in 1974.

In conclusion I think that despite rather limited and difficult conditions we marked our presence in the international Mössbauer society. We hope that next 20 years will not be worse.

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The BEGINNING of MÖSSBAUER SPECTROSCOPY at the INSTITUTE of PHYSICS of the WARSAW TECHNICAL UNIVERSITY

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The history of Mössbauer spectroscopy at the Warsaw Technical University began in the year 1982 after we bought the Mössbauer Spectrometer from Hungarian Institute KFKI equipped with minicomputer TPA-70. Our interest in the Mössbauer Spectroscopy was rather natural, because of scientific profile of our Institute, where Solid State Physics plays main role and there is also a group of physicists working on nuclear physics. Mössbauer Spectrometer was important for us from few points of view. Firstly, we could extend the subject of research devoted to solid state physics. Secondly, the work concerning substances based on iron enables us to collaborate with our theoretical group working on magnetic properties of solids. It was also important, that Mössbauer Spectroscopy is very useful thema of diploma and doctor -works, what after organisation of the Faculty of Applied Physics and Mathematics at our University, has essential meanning.

Our main subject of interest are measurements of Mössbauer spectra of amorphous alloys based on Fe. This is connected with a more wide research of magnetic and structural properties of amorphous metallic alloys of the composition: $Fe_{80-x}TM_xB_{20}$, where TM - transition metal : Ti,V,Mn,Cr,Co,Ni and x - atom % of metalloid, B - boron.

Temperature range of measurements is from 4.2 K to about 1000 K. The Mössbauer effect studies are performed in the transmission geometry by constant acceleration technique. The source ^{57}Co (Cr) of activity about 100 mCi was used in all experiments. The spectra are calibrated at room temperature by iron ARMCO spectrum. The numerical analysis of the obtained data is carried out by the magnetic field distribution method developed by Window, and computer program based on Hesse and Rubartsch method.

Let us now describe our spectrometer and his main features. The equipment is mainly used in constant acceleration mode, but in the single-channel Mössbauer spectrometer assembly it also works in constant speed operation mode. The spectrometer is suitable for the simultaneous control of 2 analysers of different types and two independent measurements can be simultaneously carried out under the same movement conditions. One of its advantages is the direct coupling to TPA/70 computer produced by KFKI. The electronic units are build of integrated circuits and Si-transistors, thus ensuring long lifetime and reliable operation. Mechanical construction bases on module units in CAMAC system. Corresponding to the kind of the samples tested, the plane of the measurement is horizontal or vertical. The samples can be investigated over the temperature range from liquid N_2 to 1000°C. The evacuated and heated ovens can be slid into rack, while the sample reaches the required temperature enabling other measurements to be carried out in its place. The construction of the rack and the special vacuum oven, facilitates the investigation of the sample in a magnetic field. The ND-220 Scintillation Detector is capable of detecting low-energy gamma rays, thus it is suitable for Mössbauer spectroscopy measurements. Velocity is adjustable by a switch between the values 0.1 - 0.5 - 2.5 and by a helipot in the 2 - 12 cm/sec. The Velocity Control Driver controls the multichannel and single channel analysers and drives the velocity transducer. The functional error of the actual velocity indicated by automatic error indicator is less than 2‰.

The data stored in the memory are transferred to the tape perforator or other peripheral device connected with DATAWAY through the peripheral drive unit. The result stored on punched tape is printed by the Teletype in a convenient form for evaluation. The X-Y recorder also records the data belonging to one point of the Mössbauer spectrum. Since 1986 year we have "INTELLIGENT MÖSSBAUER ANALYSER". The Intelligent Mössbauer Analyser is a microcomputer based data processing system wchich is capable of displaying the data stored in the spectrum memory, recording them on different data carriers, and of performing operations with them. It is built of a programmable microcomputer coupled to a measurement-, data collecting- and control system. The advantage of this construction is that the computer peripherals serve not only for the input and output of digital data but they also control the measurements and fulfil spectial tasks. In contrast with ordinary Mössbauer analysers which are usually universal multichannel analysers, the Intelligent Mössbauer Analyser , while operating only in externally controlled multiscaler and simple amplitude analysis modes, can be programmed to carry out complicated operations for spectrum evaluation. Rather then simply displaying the spectra it also displays results of computations, programs and alphanumeric information essential for the user. The Intelligent Mössbauer Analyser is produced by KFKI-Budapest. It is a pleasure to thank on this place to Dr.T.Pawlak for his very essential contribution in organisation of Mössbauer Laboratory at the Institute of Physics -Warsaw Technical University as also to Ing. Swinarski.

Development and Achievements of the Mössbauer Spectroscopy Laboratory in the Institute of Experimental Physics of Wrocław University.

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The paper contains a short history and review of achievements of the Mössbauer Spectroscopy Laboratory in the Instytitute of Experimental Physics of Wrocław University.

The Mössbauer Spectroscopy Laboratory (MSL) in the Institute of Experimental Physics of Wrocław University initiated by prof. S.Rozenfeld was established in the mid seventies. The management was commited to assistent professor M.Szuszkiewicz. Two scientific workers dr. J.Chojcan and mgr. A.Ostrasz are the members of his group now.

In the beginning the MSL had at its disposal the Mössbauer spectrometer SM-4 produced by the Experimental Establishment for Non-Serial Equipment of the Institute of Nuclear Research at Świerk (Poland). For three years the device base has been enriched by the Mössbauer spectrometer of POLON production and by the Hungarian electronic device for registration and elaboration of the experimental data.

The subject matter of the investigation carried out by MSL is subordinated to the long-term plans of the Nuclear Physics Applications Department of the Institute of Experimental Physics of Wrocław University, which the Laboratory belongs to. The attention of the MSL workers was initially concentrated on the investigation of the electronic structure of binary alloys of 3d-transition metals containing Fe [1-6]. The range of investigations has been next (since 1980) extended to the hydrogenated alloys of iron and vanadium [7,0]. Experiments were also performed for some tin compounds [9,10].

Basing on the results of the first experiments it was noticed that the simultaneous investigation of a substance by means of positron annihilation and the Mössbauer effect can supply additional information on the electronic structure of the substance under investigation. In particular, for binary 3d-transition metal alloys containing Fe one is able to estimate the distribution of valence electrons. This idea has been used for the estimation of the electron distribution in some V-Fe, Cr-Fe and Fe-Co alloys as well as hydrogenated V-Fe alloys. It was done by using angular correlation data from positron annihilation experiments and isomer shift data from Mössbauer effect measurements. The obtained results for Fe-Co system have appeared to be at variance with the neutron diffraction data concerning the magnetic moments of Fe atoms in those alloys. Moreover, for paramagnetic V-Fe, Cr-Fe and hydrogenated V-Fe alloys the obtained results seem to be in contradiction with information on their magnetic properties resulting from magnetic susceptibility measurements. Finally, for most of the examined specimens the obtained results differ essentially from those expected on the basis of the cellular atomic model of alloys by Miedema. First of all for concentrated alloys the determined direction of electron transfer between different atoms is opposite to the one predicted by Miedema's model.T This is surprising in view of the fact that the model is semiempirical one and its predictions remain in agreement with a large class of experimental data concerning particularly the binary alloy formation heats.

Considering the above, the possibility was assumed that there is an essential inaccuracy in the interpretation of the analysed parameters of positron annihilation and/or nuclear gamma resonanse absorption. In particular the attention was paid to the relationship between the Mössbauer isomer shift (IS) of ^{57}Fe and the electron surroundings of ^{57}Fe nuclei in iron alloys. Basing on the results of positron annihilation, nuclear gamma resonance absorption and neutron diffraction investigation for Fe-Co alloys it was shown that in the first approximation IS is proportional to the total number of electrons transfered between Fe and Co atoms due to alloying, independently of the character of the electrons. The experimental result is at variance with generally accepted interpretation of IS based on theoretical estimations and many scientists doubt its correctness. The latter is somewhat surprising if it is noticed that other experimental data are in agreement with the result. Watson and Bennett, for instanee, showed that for dilute binary alloys with iron as a solute the Mössbauer isomer shift is proportional to the matrix electronegativity parameter or to the total electron flow on/off iron atoms. Moreover in the Miedema's and Van der Wonde's model for the isomer shift in binary alloys, it is assumed that the IS is proportional to the total electron transfer between different atoms. It is interesting that the model is widely used by many authors and the assumption is not criticized at all. Eventually, application of the assumption for determining the valence electron distributions in V-Fe, Cr-Fe and hydrogenated V-Fe alloys on the basis of positron annihilation and Mössbauer effect data yields results which are in agreement with magnetic properties of the alloys and Miedema's model predictions.

Along with the studies of the problems mentioned above the V-Fe-H system was examined to explain the role of H in the creation of permanent magnetic moments at Fe atoms in the alloys. It was noticed that dependences of Mössbauer parameters on H concentration change their slopes when concentration of electrons in the alloy reaches so-called "critical" concentration at which local magnetic moments at Fe atoms occur. For instance width of the Mössbauer spectrum increases essentially on passing the concentration. It was shown by low-temperature measurements (at 5 K) that the effect is not due to magnetic splitting of the spectrum but thanks to the quadrupole interaction. The result was supported by X-ray measurements which have revealed tetragonal deformation of the crystal lattice of V-Fe-H alloys with electron concentration greater than the critical one.

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SURFACE MAGNETISM OF *Fe*(110)-FILMS STUDIED BY IN SITU CONVERSION ELECTRON MOESSBAUER SPECTROSCOPY

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ABSTRACT

The magnetic properties of epitaxial atomically flat Fe(110) films were studied using in situ Conversion Moessbauer Electron Spectroscopy. The submonolayer detection limit of the method was applied to follow the local structure of the magnetic hyperfine field. The Friedel-type oscillations of B_{HF} were detected near the free Fe(110) surface. The temperature dependence of the film magnetization, probed by B_{HF} is discussed.

1. INTRODUCTION

First applications of the Moessbauer spectroscopy (MS) to the magnetism of ultra thin films come from early sixtieth[1]. The applied γ-transmission geometry set a serious limitation of the minimum absorber thickness used in Moessbauer experiment. Informations about properties of films consisting of few atomic layers were available only from measurements of sandwich probes of total thickness above 10 nm, in which magnetic layers of ^{57}Fe or its alloys were separated with nonmagnetic ones[1-3]. This technique (which originally was a mean compensating imperfections of the experimental method and later developed in advanced form to the "Multilayered Films with Artificial Superstructure" - problem[4]) led inevitable to ill-defined films. Intrinsic magnetic properties of films, surfaces and interfaces were dissembled with complicated, impossible to define real structure, affected by island forming or alloying. The near ideal films are obtainable in process of epitaxial growth, especially for some chosen systems preferring layer-by-layer growth mode[5]. This type of sample preparation for Moessbauer measurements was applied for the first time by Duncan et al.[6], who measured in transmission mode the system of Ag(111)-Fe(110)-Ag deposited on mica substrate. To increase the thickness of the absorber, avoiding the "sandwich-procedure" the samples were cut into pieces and stacked together. Although the authors claimed the flat growth mode of Fe(110) on Ag(111), it is known from the paper of Snyman and Olsen[7] that iron grows tree-dimentionally forming small, uniformly oriented microcrystals, which size distribution depends on preparation temperature. The observed linear, instead of $T^{3/2}$ - dependence of the magnetic hyperfine field B_{HF} on temperature (T < 300 K) already for films thinner than 7 nm is probably due to film discontinuities.

The described above some pioneer thin film application of MS as well as the conclusion of Bayreuther in his review paper[8] show clear the main experimental difficulties:

a. - achieving the monolayer detection limit of MS in the wide temperature range in reasonable time of measurement (acquisition time of few hours)
b. - using of atomically flat single crystal thin films with the well defined structure.

Only fulfillment of these two conditions allows to use probably the most attractive feature of MS : its local character of analysis. Already applying of scattering geometry with detection of conversion electrons (conversion electron Moessbauer spectroscopy - CEMS) profited with considerable improvement of detection limit by using of efficient H/CH_4 detectors and offered some depth selection. The small penetration depth of electrons in matter (about 100 nm for 7.3 KeV conversion electrons from ^{57}Fe) gives the possibility of local analysis useful for corrosion studies or for non destructive surface analysis in material science. It is of course insufficient for probing of surface magnetic properties, where the disturbance connected with lack of translational symmetry ranges few atomic layers only. The depth selectivity can be considerably increased performing the analysis of the conversion electron energy, as their energy loss is related to the depth at which they were originated. This type depth selective CEMS (DS-CEMS) applies different types of electron spectrometers[9-13]. High or ultra high vacuum is combined with this technique (which is necessary to perform the electron spectrometry) and gives then possibilities for the sample preparation, structural and chemical analysis and the Moessbauer experiment in situ. Unfortunately, this solution is used only occasionally[11,12]. The applicability of the DS-CEMS system in the surface studies is limited by the long time of measurements resulting from the low transmission of the high resolution electron spectrometers. The Moessbauer spectra have to be deconvoluted, considering the distribution of the possible escape depth for electrons of the given measured energy.

The local Moessbauer analysis can be realized also in a simpler way[14,15]. In a thin film, prepared of non-Moessbauer ^{56}Fe isotope, at the certain distance from the surface a probe layer (few atomic layers) of ^{57}Fe is placed. Varying the position of the probe layer leads to the depth profiling of the hyperfine parameters. This type of measurements performed in Walker's group[14] suffer of the insufficient sensitivity of the Moessbauer analysis and separation of technological and measuring procedure.

Recently[16], the literally local analysis of the hyperfine parameters with the monolayer ^{57}Fe probe in epitaxial Fe(110) films on W(110) was achieved using in situ *CEMS* combined with *UHV* molecular beam epitaxy and standard methods of surface characterization (LEED, AES). In the present paper the application of this method for studies of magnetic phenomena in oligoatomic (consisting of few atomic layers) iron films is presented. Section 2 describes the apparatus and its possibilities. Section 3 contains the details of the sample preparation and some methodological aspects of the experiment. In sections 4 and 5 the depth profiling of the B_{HF} near the surface and interface and thermal excitation of magnetization are discussed.

2. APPARATUS

The leading line by the construction of the experimental system was the possibility to combine the molecular beam epitaxy in UHV, providing structurally well defined single crystal iron films with the in situ CEMS, offering the submonolayer detection resolution. W(110) chosen as the substrate for a good epitaxy of iron (see the next Section) introduces in the CEMS experiment a very high non-resonant background due to photo-, Compton and Auger electrons. To minimize crucial signal-to-noise problems, they have to be separated from 7.3 keV conversion electrons using some energy filter. Its transmission and resolution should be optimize to give the shortest acquisition time of the Moessbauer spectrum with the sufficient signal-to-noise ratio.

The experimental system is shown in Fig.1[17]. The UHV chamber was evacuated by the turbomolecular pump Turbovac 560 M and the titanium sublimation pump with the cold trap. The base pressure better then 3×10^{-9} Pa was easily achieved after baking out. The chamber is equipped with the standard techniques of surface analysis: four grid LEED optics and cylindrical mirror Auger electron spectrometers. The sample (1) is mounted on the 10 cm long arm on the VG manipulator.

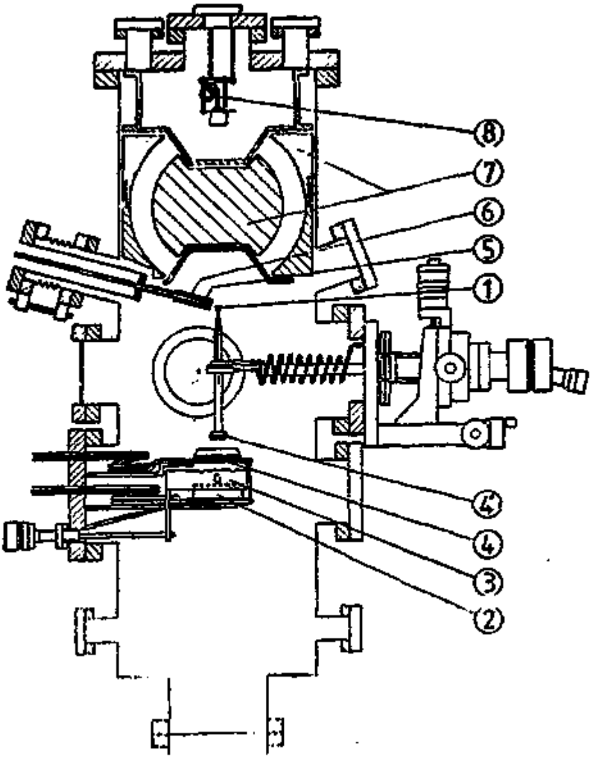

Fig. 1. Schematic of experimental setup[17)]

For the CEMS experiment (this situation is shown in Fig.1) the specimen is transferred in front of the small area, high activity ^{57}Co/Rh Moessbauer source (5), vibrating outside the vacuum. γ-rays, collimated with the tungsten shield (6), irradiate the sample through the beryllium window at a grazing angle of 15°, what increases the sample effective thickness by factor 1/cos15°. As the mentioned energy filter the 106°-spherical condenser[18)] (7) is used. Because of its axial symmetry, the nice geometry for sample manipulation in almost field free space is provided. The condenser (mean radius 11.75 cm and the gap spacing 3.5 cm) is made of Al-Cu alloy. The dimensions and geometry of the condenser yield the value .609 V/eV for the ratio of the focusing potential to the electron energy, what results in about 4.5 kV for the

7.3 keV electrons. The combination of Al_2O_3 balls, used as centering elements and mica spacers provides the electrical insulation for about 12 kV, what means that the spectrometer can be used also for ^{119}Sn CEMS. After passing the condenser, electrons are detected with the channeltron (6), which detection efficiency and the effective entrance radius is increased by placing in front of them a stainless steel tube, coated with MgO. The parameters of the spectrometer were optimized using a thin ^{57}Co source, simulating the Moessbauer scatterer. Transmission of 7% of 4π at the energy resolution of 4% for the pass energy 7.3 keV was achieved. Due to a very low non-resonant background of electrons originated by the 122 keV rays the resulting Moessbauer spectra show the total resonance effect of 30% per one monolayer of ^{57}Fe in a film evaporated on the Al substrate. Replacing Al by tungsten reduces this value to 12%, but nevertheless, with a 100 mC source the spectrum of one monolayer of ^{57}Fe in a film consisting otherwise of ^{56}Fe of the total thickness of about 4 nm can be recorded in 15 hours with the signal-to-noise ratio of 20 for the most intense lines of a Zeeman pattern. Table 1. reproduced from the paper of Toriyama et al.[13)] and completed with the data of the system presented in this paper (referred as Clausthal Technical University) gives the comparison of the several electrostatic electron spectrometers, constructed for CEMS. The quite acceptable parameters of the electron optics, combined with the high signal-to-noise ratio and the unique combination with the advanced molecular beam epitaxy (MBE) system (see below), make the Clausthal apparatus the powerful tool of the surface Moessbauer analysis.

The W(110) single crystal, 0.3 mm thick, 10 mm in diameter is mounted as the substrate (1). It can be operated at temperatures between 90 K and 2500 K using a standard VG cooling module or combination of thermal irradiation and an electron bombardment. The temperature is controlled with a W/W-Rh thermocouple spot welded to the crystal.

The MBE system consists of six BeO crucibles heated by tungsten spirals, surrounded by Ta radiation shields and placed in the water cooled cooper housing (2). With the shutter (3) a one single evaporator or certain combinations of two (for alloying) can be chosen. The deposit thickness is controlled during the preparation independently for each evaporator with the six water cooled quartz crystal oscillators (4). The seventh one (4') can be moved exactly to the sample position, giving the geometrical calibration factor for the other oscillators. With this arrangement the film thickness can be reproduced within ±0.1 monolayer (ML) and measured with the absolute accuracy of ±5%. For a typical evaporation range of a few A/min. the pressure during the deposition of ^{56}Fe, ^{57}Fe and Ag, which were used in the

TABLE 1

Comparison of electron spectrometers for Moessbauer Spectroscopy

Institute	Type	Energy resolution at 7.3 KeV [%]	Detection efficiency [%]	Sample dimension	Signal-to-noise ratio for enriched ^{57}Fe absorber
Stockholm University[9)	cylindrical mirror	2.5	6	5 mm ϕ	1
Rutgers University[10)	spherical condenser	2.0	13	10 mm ϕ	8
Duisburg University[11)	150° spherical sector	2.0	0.27	10 mm×4 mm	3
Freie Universitaet Berlin[12)	ellipsoidal mirror retarding grid	9	35	5 mm ϕ	1
Tokyo Inst. of Technology[13)	spherical retarding grid	2	5.5	4 mm ϕ	3
TU Clausthal (present)	105° spherical condenser	4.5	7	10 mm ϕ	7

experiment, remains below $1{*}10^{-8}$ Pa.

The tungsten substrate was cleaned by heating it in oxygen at the partial pressure $1{*}10^{-5}$ Pa.The contamination level of C and O below 1% of a monolayer was achieved, as checked with AES. Similarly, fast atomically clean iron surface was obtained for freshly deposited films of ^{57}Fe or ^{56}Fe. This was achieved by a careful thermal treatment of the initial materials and the perfect UHV conditions. The extreme difficulties to get a free from impurities bulk iron surface were eliminated by using the thin film technique.

3. SAMPLE PREPARATION AND METHODOLOGY OF MEASUREMENTS

Atomically flat ferromagnetic single crystals prepared in the epitaxial growth can realize fast ideal structure, used for theoretical approaches. The epitaxy of Fe(110) on W(110), studied extensively by Gradmann and Waller[5], gives to some extent this type of the model structure. Some doubts exist only for the thinnest films (up to four atomic layers), which grow probably as pseudomorphic double layer islands at 500 K and in layer-by-layer mode at room temperature. The two first atomic layers remain pseudomorphic, then the periodic lattice distortions, due to interaction with the misfitting W(110) substrate, appear. At about 10 ML the distortions fade out and the visual inspection of the LEED pattern reveals the features of the undistorted Fe(110) face. The monoatomic steps separated less than 20 nm can be excluded. The optimum temperature of the epitaxial growth for films thicker than 10 ML was established as 570 K.

For the purposes of the local Moessbauer analysis the monolayer probe of ^{57}Fe should be placed at the defined distance from the surface of the film consisting otherwise of ^{56}Fe. This must be done in a way excluding ^{57}Fe-^{56}Fe interdiffusion[16], which could occur during the time period needed for the preparation at elevated temperature. The bulk and the surface self diffusion data yield 520 K and 420 K respectively as a high temperature limit for these processes. The samples for CEMS experiment were prepared following this hint. First, the base layer of D_1 ML of ^{56}Fe was deposited at optimum temperature 570 K. The following probe layer of D_2 ML of ^{57}Fe (usually 1 ML) and the uppermost layer of D_3 ML of ^{56}Fe were prepared at 420 K. The iron film was coated with about 5 nm of Ag, resulting in the sample denoted as "D_1-D_2-D_3/Ag".

Examples of the room temperature CEMS spectra for films of the total thickness of 21 ML, with the probe layer in the center of the film ("8-5-8/Ag"), in the second and in the

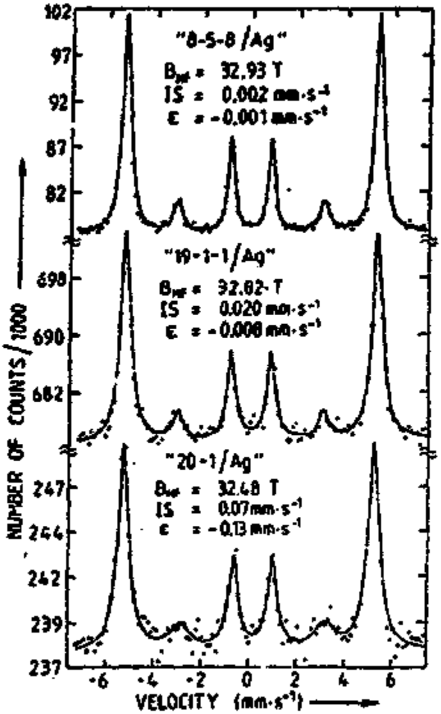

Fig. 2. Conversion electron Moessbauer spectra of Ag-coated Fe(110) films on W(110) with the ^{57}Fe probe layer. Hyperfine interaction parameters as given in the figure. [ε: $(eQV_{zz}/8)(3\cos^2\beta - 1)$].

first monolayer counted from the top of the iron film ("19-1-1/Ag" and "20-1/Ag" respectively) are shown in Fig. 2. For all spectra, revealing the magnetic hyperfine splitting, the ratio of the line intensities for the Zeeman pattern is closed to 3 : 0.14 : 1, indicating that the magnetization lies in the film plane in [110] direction (which is also the γ-irradiation azimuth). In contrast to the bulk, where the easy axis is of a [100]-type, for the films thinner than about 10 nm, the magnetization switches to [110]. The reason is the in-plane surface magnetic anisotropy, as discussed elsewhere[19]. The fitted values of the hyperfine interaction parameters: magnetic hyperfine field B_{HF}, isomer shift IS and quadrupole splitting are given also in Fig. 2. For the center of the film and even for the second layer they are close to the bulk values. The unique feature of the top most layer is the non vanishing quadrupole interaction, which disappears in bulk iron because of cubic symmetry. Its existence at the surface and interface of cubic crystals is the natural consequence of the broken translational symmetry. The rapid screening of electrical fields in metals causes, that ε vanishes already for the second monolayer, in accordance with the PAC measurements for In surface[20]. This observation provides the excellent proof, that interlayer diffusion does not take place under the proper preparation mode. The variation of the preparation and annealing temperature gives the 450 K as the temperature at which interdiffusion starts, as shown in Fig. 3.

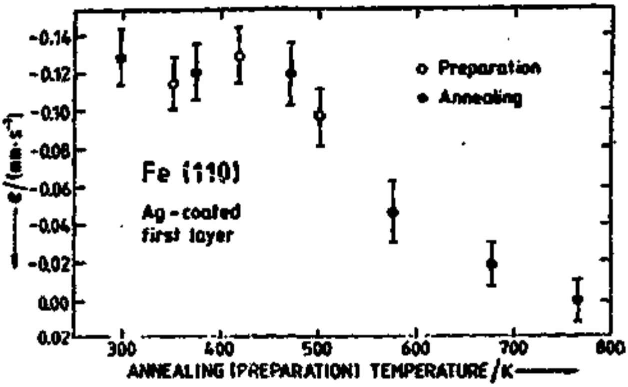

Fig. 3. Interdiffusion between the first and the second Fe ML in a "PO-1/Ag" sample, analyzed by a thermally induced changes of the quadrupole splitting . First, one series of samples (open circles) was prepared at preparation temperatures as indicated. Secondly, one sample, prepared at 420 K, was annealed at temperatures given (filled circles) for a period of about 40 h. Obviously, interdiffusion starts only above 450 K[16].

The essential limitation of the Moessbauer measurements for the free surface is the long acquisition time and consequently, the contamination of the sample surface from the residual gas atmosphere. Although it was possible to get a reasonable CEMS spectrum for one monolayer in few hours, the adsorption of residual gases could not be avoided. 0.1 monolayer of C and O could be detected with AES on the iron film surface one day after preparation. The same amount of hydrogen can be supposed, taking into account the composition of the residual gas atmosphere and the sticking coefficient of hydrogen. Consequently, the increase of B_{HF} in time during which the subsequent spectra were measured for the "20-1" film (as shown in Fig. 4.) should be interpreted

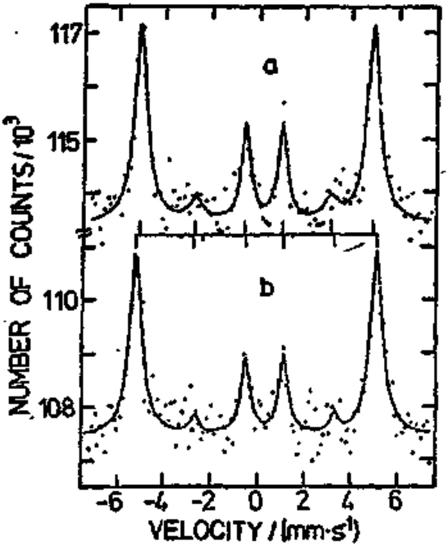

Fig. 4. Moessbauer spectra of 1 ML ^{57}Fe on the top of a 20-layer $^{56}Fe(110)$ film on W(110) recorded in 8 hours immediately after preparation (a) and 16 hours later (b)[17].

in terms of contaminations. To get data for the clean surface, the CEMS spectra for the uncoated films were recorded for a sequence of time periods, and the hyperfine interaction parameters were determined by interpolation of slowly varying values to the time immediately after the preparation. As the lowering of the sample temperature favors gas adsorption, this type of measurements were performed only at room temperature.

4. SPATIAL DISTRIBUTION OF THE MAGNETIC HYPERFINE FIELD

In contrast to bulk ferromagnets, some inhomogeneities of the local magnetization are expected in thin films and near the surface and interface. According to the band calculations[21,22], the spin densities are modified by the surface, leading to the enhancement of the ground state magnetic moments in the outermost layers of iron and nickel. From the other side, the existing phenomenological approaches of thermal excitations (spin-wave theory[23], Monte-Carlo calculations[24] or Green - function calculations[25]) predict the thermally induced monotonous decrease of the magnetization toward the surface. Experimentally, the situation is more complicated. Different methods, which are able to probe the local magnetic structure involve different physical parameters (spin polarization, magnetic moment, magnetic hyperfine field) and have the different spatial resolution. Any comparisons between them and with theories must be very careful.

Tyson et al.[26] reported as the first the depth profiles of B_{HF} for epitaxial Ag-coated Fe(110) films on Ag(111). They detected an increase of the ground state B_{HF} at the Fe(110)/Ag interface. Applying the usual interpretation for a bulk solid, that the B_{HF} is proportional to the local magnetization, they claimed the surface enhanced magnetic moments, as predicted by Wang and Freeman[22] for the Fe(100) surface. This interpretation had to be verified, when Ohnishi, Freeman and Weinert[27] showed, that the contribution to B_{HF} may be significantly different at the surface and in the bulk. They discuss only the Fermi contact term, being the largest contribution to the hyperfine field for 3-d metals. In the bulk ferromagnets like Fe and Ni it results from the large negative polarization of the core s-electrons (proportional to the local magnetic moment) and from the polarization of the conduction electrons, which is also negative. At the surface, the conduction electron term, depending on the local environment, can become even positive. The total B_{HF} is reduced in magnitude as compared with the bulk. Additionally, Bayreuther[8] pointed out that at the boundary of a cubic ferromagnet the dipolar fields, vanishing inside a spherical sample, can contribute considerably to the total B_{HF}.

Using the experimental procedure described in the previous sections the detailed analysis of the spatial distribution of hyperfine magnetic field in 21-layer Fe(110) films on W(110) were carried out[28]. The temperature dependence of the B_{HF} was measured for a series of Ag-coated films, with the ^{57}Fe probe layer placed at the different depth, varied from the iron film surface to the center of the film. The results for the two chosen films are shown in Fig.5. The plot reflects the described above aspects of spatial inhomogeneities of B_{HF}: thermally induced reduction of B_{HF} (pronounced at the magnetic surface) and an increase of the ground state magnetic hyperfine field for the Fe(110)/Ag interface. While the first effect could be analyzed in agreement with the spin wave theory[23], the second one, al-

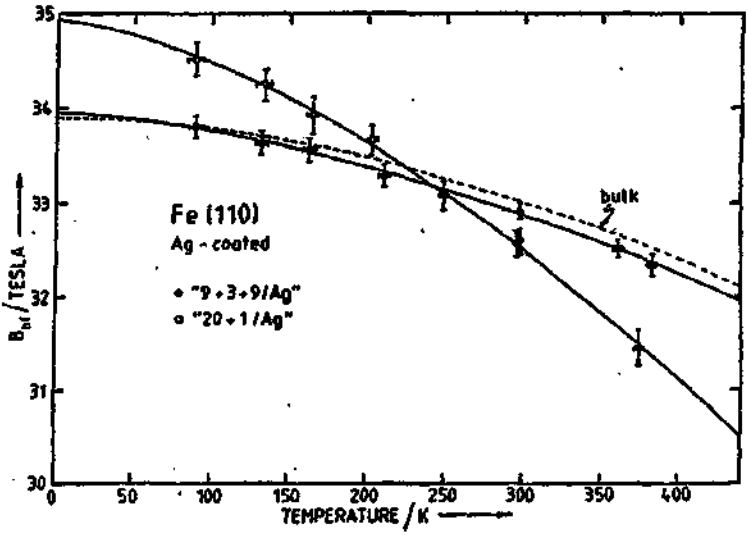

Fig. 5. Temperature dependence of B_{HF} in Fe(110) films coated by Ag, for the topmost layer below Ag ("20+1/Ag") and for the centre of the film ("9+3+9/Ag"). Bulk dependence is given for comparison. All data are fitted by $B_{HF}(T) = B_{HF}(0)(1-b*T^{3/2})$ (from[28]).

ready reported by Tyson et al.$^{28)}$, contradicts with only available calculations of Ohnishi, Weinert and Freeman$^{29)}$ for the Fe(100)/Ag interface. However, beside of the different orientation used in the calculations, the essential role in this disagreement can play also the omitted in the theory dipolar fields and the thickness of the Ag overlayer taken for calculation (only 1 ML). Probably, the free iron surface is more convinient for comparison between theory and experiment. Instead of a monotonous behaviour, the calculations$^{29)}$ predict huge "Friedel-type" oscillations of B_{HF} for the Fe(100) surface. The oscilations, amounting 14 T for Fe(110) surface and "reduced" recently$^{30)}$ for the Fe(110) surface to 7 T, are localized in the three outermost layers. Indeed, the room temperature measurements of the B_{HF} spatial distribution in uncoted 21-layer Fe(110) films on W(110) confirm experimentally the non monotonous character of the surface structure, as shown in Fig. 6. To verify the reliability of the experiment, the measurements for two series of samples, with slightly different preparation mode

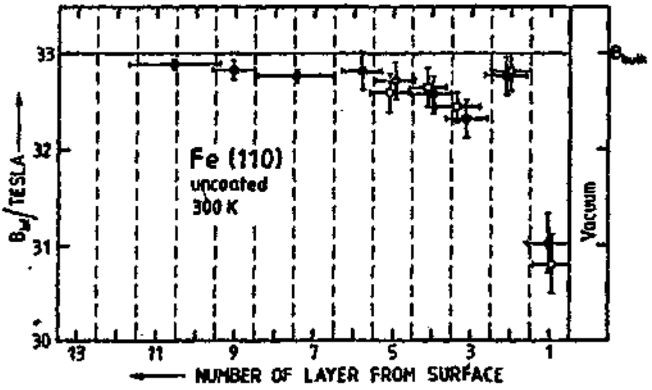

Fig. 6. B_{HF} near a free Fe(110) surface at 300 K, taken from two series (●, ○) of Fe(110) films on W(110), consisting of 21 layers. Epitaxial growth started at 570 K for both series; the temperature was lowered to 420 K for the probe layer and all following layers (●) or for the 11. layer and all following layers (○)[28].

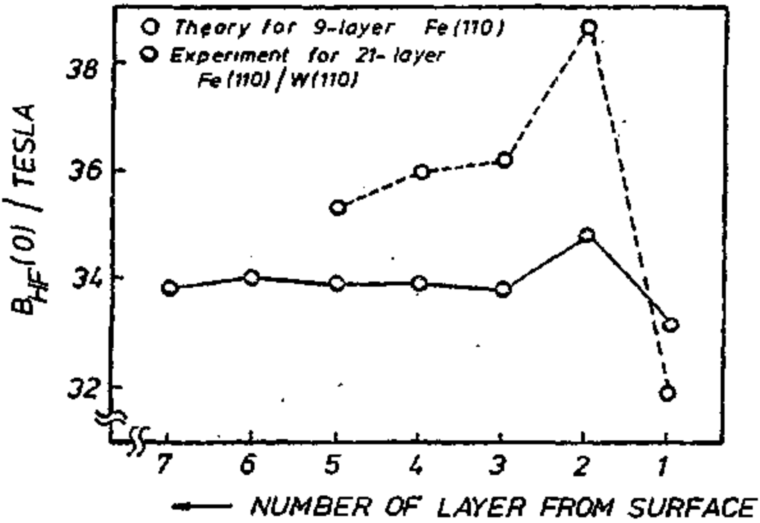

Fig. 7. Ground state B_{HF} calculated for 9-layer Fe(110) film[30] (○) and compared with the experimental values, obtained near the surface of the 21-layer Fe(110) film on W(110) (●).

were done. The ground state properties are obviously overlapped with the thermally induced decrease of magnetization, which should be of the same order as for the Ag-coted films. The results for the free Fe(110) surface,extrapolated with this assumption to 0 K, are compared schematically in Fig. 7 with the band calculations[30]. The qualitatively similar character of the experiment and theory should stimulate the farther activity in this field.

Up to now the magnetic structures near the free and Ag-coated Fe(110) surface were discussed.. Intensive CEMS studies of the W(110)/Fe(110) interface were also carried out[31]. The room temperature CEMS spectra for the 21-layer Fe(110) films on W(110), with the ^{57}Fe monolayer probe deposited just on tungsten are shown in Fig.8. The top spectrum was taken for the sample prepared at room temperature, but the similar were obtained also for the standard preparation mode. They could be decomposed in a two six line Zeeman patterns: the more intense one,with the B_{HF} similar to the bulk value, and the second one, yielding much smaller B_{HF} of about 22 T. Obviously, the deposited amount of ^{57}Fe does not remain in the first layer (counted from the tungsten side) but mixes with following ^{56}Fe. When the preparation temperature was lowered to 90 K, which should depress thermally activated mixing process and "freeze" the ^{57}Fe atoms in the first monolayer,the drastic reversal of the intensities ratios of the two Zeeman components was observed (compare the bottom spectrum in Fig.8). Additionally, a change of the magnetization direction, as indicated by the ratio of the line intensities, took place. This originates, probably, from the changed film structure, which is degraded by the low preparation temperature.

Obviously, the Zeeman component with the small B_{HF} accounts for the W(110)/Fe(110) interface. Whereas at the Fe(110)/Ag interface and for the free Fe(110) surface only minor inhomogeneities were detected (maximum about 1.5 T), for the W(110)/Fe(110) interface the reduction of the B_{HF} by over 10 T is observed. Possibly, the tungsten 5d electrons are responsible for this phenomenon, similar to that, observed by Hosoito et al.[4] for iron at the interface with another d-metal - vanadium. Some role can play also the structural factor - pseudomorphie of iron with tungsten in the first atomic layer causes a slightly modified lattice spacing.

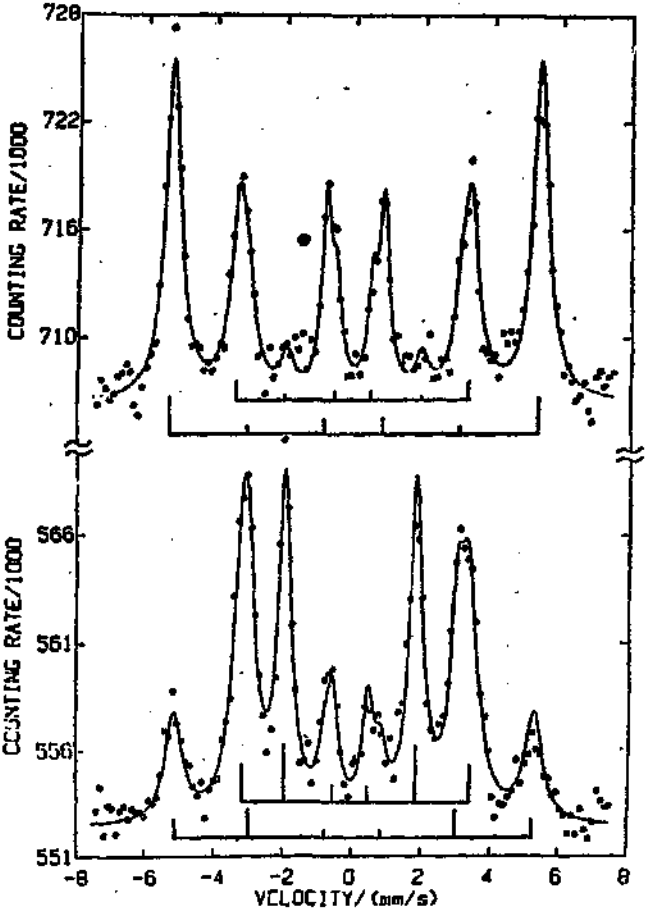

Fig. 6. The room temperature CEMS spectra for the 21-layer Fe(110) films on W(110), with the ^{57}Fe monolayer probe deposited just on tungsten. The preparation temperature was 300 K and 90 K for films corresponding to the top and bottom spectrum, respectively[31].

5. TEMPERATURE DEPENDENCE OF THE SPONTANEOUS MAGNETIZATION, PROBED BY HF-MAGNETIC FIELD

What type of temperature dependence does follow the magnetization of the ultra thin film? Is it linear, as predicted by the spin wave theory[32] for the film consisting of few atomic layers or deviates from linearity even for the thinnest films as suggested by Bayreuther in his review paper[8]. Different types of behaviour were found experimentally. The magnetic measurements of Gradmann and Mueller[33,34], which in contrast to the previous experiments concern flat, monocrystalline films, suggest for the Co(111) and 48Ni/52Fe(111) films nearly perfect agreement with the spin wave theory[32]. This results in the strong decrease of the spontaneous magnetization M_S with the decreasing film thickness. Simultaneously, for the thinnest films (below 2 ML), the change of the magnetization direction to the film plane occurs. It is accompanied by the change in the character of the magnetization temperature dependence from non-linear to linear one. It is plausible, that for the thinnest films an additional anisotropy (surface anisotropy) causing the magnetization reversal, is involved also in the $M_S(T)$ dependence, as indicated by the theoretical calculations of Levy and Motchane[35]. The argument of decreased effective anisotropy (for example by the island like film structure) can explain the linear $M_S(T)$ dependence even for thicker films[26]. The Fe(110) films on W(110) form a suitable system for the Moessbauer analysis of the mentioned problems. They are free from structural imperfections and homogeneously magnetized even for thinnest films. The average hyperfine magnetic field measured as the function of temperature can be used as the probe of the total film magnetization[36]. The normalized to $B_{HF}(0)$ values of the hyperfine magnetic field for Ag-coated ^{57}Fe films of thicknesses ranging between 3 and 20 ML are shown in Fig.9. For all films the data could be fitted by $B_{HF}(T) = B_{HF}(0)*(1-b*T^{3/2})$ with the b values ranging from $7.7*10^{-6}$ $K^{-3/2}$ for the 20-layer film to $2.2*10^{-5}$ $K^{-3/2}$ for the thinnest consisting of about 3 atomic layers (compare with $b_{bulk} = 5.6*10^{-6}$ $K^{-3/2}$). Whereas the 20-layer film shows nearly bulk behaviour, for the thinnest one the B_{HF} dependence on temperature is much stronger but definitely non-linear. The results of theoretical calculations of Jellito[32] (spin-wave theory - SW) and Haubenreisser et al.[37] (Green function calculations - GF) for some chosen film thickness are shown also in Fig.9 as the dotted and dashed lines, respectively. The calculations were done for model systems to some extent different than that used in the experiment: GF results concern the bcc lattice but with (100) orientation, SW theory used the spin of 1/2. However, the surprisingly good agreement with the theoretical GF curves is to be noticed in the wide temperature range.

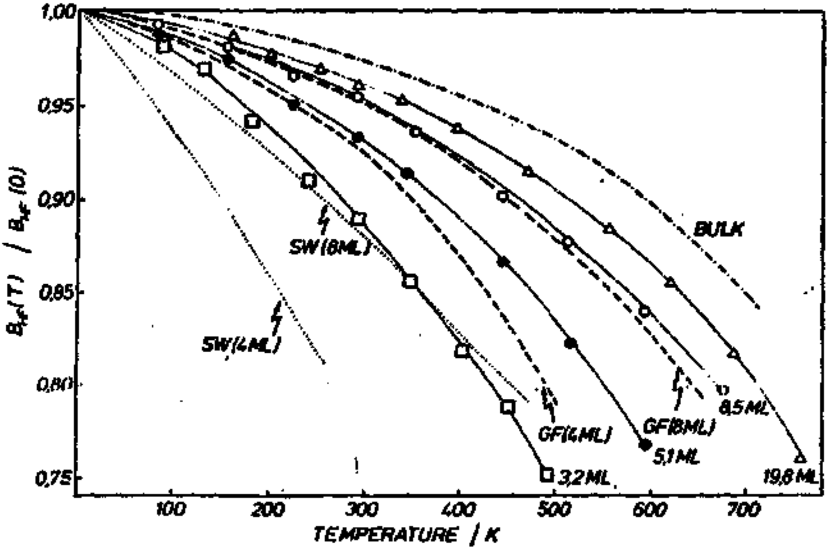

Fig. 9. The temperature dependence of the average B_{HF}, normalized to $B_{HF}(0)$, for the ^{57}Fe(110) films on W(110) (□, ●, o, Δ for 3.2 ML, 5.1 ML, 8.5 ML and 19 ML films, respectively). The solid lines are the best fits to $B_{HF}(T)/B_{HF}(0)=1-b*T^{3/2}$. The dotted and dashed lines are the results of the SW GF calculations, resp.

The aim of this paper was to demonstrate the applicability of the developed experimental method to problems of magnetic surfaces and ultra thin films. The capabilities of the Moessbauer experiment have reached the level enabling the reliable comparison with the developing "an initio" calculations and the common interplay of theory and experiment.

6. ACKNOWLEDGMENTS

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STUDIES OF Fe$_{3-x}$Al$_x$Si ALLOYS BY NEUTRON AND MOSSBAUER TECHNIQUES

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Studies of Fe-Al and Fe-Si alloys have a long history [1-3]. In recent years considerable attention has been paid to Fe$_3$Al and Fe$_3$Si alloys with the DO$_3$-type of structure. The particular interest in studying the DO$_3$-type ordered Fe$_3$Si-based alloys stems from the preferential site occupancy exhibited by 3d impurities in these alloys [4]. This effect can be explained qualitatively basing on the band structure of Fe$_3$Si [5]. Surprisingly, the site preference which, according to band structure calculations, should be the same in Fe$_3$Al, is by no means so clear in this alloy [6]. Moreover, the unusual properties of Fe-Al alloys of the composition Fe$_{0.7}$Al$_{0.3}$ which can be explained qualitatively using competing interaction model, are to the best of our knowledge-not observed in similar Fe-Si alloys. This fact is most probably connected with a strong dependence of effective exchange interaction on the distance between iron atoms [7].

The samples have been prepared from 99.8% pure iron and 99.999% pure aluminium and silicon. The metals have been melted in an induction furnace, homogenized and annealled so to ensure the DO$_3$-type of order. The sample compositions are shown in Table 1.

Table 1.
Composition of the samples

sample No	At % Al	At % Si
1	2.9	23.5
2	5.8	23.4
3	7.2	23.4

The distribution of atoms among different crystallographic sites has been studied by means of neutron diffraction. The intensities of neutrons scattered from powder samples non-magnetised and magnetised along the scattering vector have been measured. From these two intensities the magnetic and nuclear parts of the scattering have been obtained.

The conclusion from the studies of the nuclear part of the neutron scattering is that the excess non-ferrous atoms locate preferentially at the B-site. In accordance with statistical errors of measurements, the possible content of these atoms in A(C) sites should not be larger than 1 at. %. However, we have not found any systematic trend in the distribution of aluminium atoms among B and D sites.

Somehow independent confirmation of such an atomic distribution comes from the magnetic part of neutron scattering. It is well-known that iron moments are very sensitive to their environments. From the results of measurements on $Fe_{3-x}T_xSi$ [3] , where T denotes vanadium or manganese, one knows that the substitution of one iron atom at the A-site by an impurity atom causes a decrease of the magnetic moment of the B-site by 0.105 Bohr magnetons (BM). On the contrary, if iron atom at the B-site is substituted by another atom, the moment at the

A-site decreases by as much as 0.34 BM. In addition, Burch et al. [9] found no essential difference between the behaviour of magnetisation distribution in $Fe_{3-x}V_xSi$ and $Fe_{1-x}Si_x$ alloys. The magnetic moments determined from the magnetic neutron scattering fit well to this picture if the atomic distribution determined from the nuclear part of scattering is taken into acount.

The Mössbauer spectra were recorded in transmission geometry with a standard constant acceleration spectrometer. The source was ^{57}Co in a chromium matrix.

The spectra have been found to consists of two parts: a linear combination of four Zeeman sextets of the Lorentzian lines abbreviated by Fe(8), Fe(8'), Fe(4) and Fe(3) and a low-field central part. The Fe(n) denotes the iron site surrounded by n iron neighbours. The sextet Fe(8') is due to iron at B-site surrounded by 8 Fe atoms in the first coordination sphere but with 11Fe+1(Al,Si) atoms in the third coordination sphere.

Fig. 1 shows the Mössbauer spectra for various compositions measured at room temperature. The solid line is a fitted curve resulting from a combination of 4 Zeeman sextets and a low field part of the spectra. The difference between the experimental points and fitted 4 Zeeman sextets is also displayed. Note, that in the case of sample No. 1 (the least aluminium) this low field part is very small.

The most important experimental observations are the following:

1) The Mössbauer spectra of the ordered ternary $Fe_{3-x}Al_xSi$ alloys exhibit a low (below 90 kOe) magnetic field components for $x > 0.1$. The absorption area of this part of the spectrum depends on the Al content and for $x \approx 0.3$ amounts to about 30% of the total absorption.

2) Magnetic fields corresponding to four Zeeman sextets increase almost linearly with decreasing temperature. Within accuracy of our results the magnetic field associated with the low-field central part of the

spectra remains unchanged.

3) The linewidths of the Zeeman sextets increase drastically with aluminium content from 0.37 mm/s (sample No.1) to 0.70 mm/s (sample No.3). Assuming that distributions of hyperfine magnetic fields have the Lorentzian shape, the widths fitted by the Zeeman sextets are within acuracy of about 20%, equal to 6, 12 and 16 kOe for samples 1, 2, and 3, respectively. The temperature dependence of the broadening measured for the sample No. 3 is weak, if any, in the temperature range of 80-300 K.

4) In the temperature range of 80-300 K the relative intensities of the subspectra of the sample richest in aluminium ($x=0.3$) do not depend on temperature.

For the concentration of Fe atoms in the B-sublattice, C_B, close to 1, the relative intensities I(i) for sextets Fe(i) can be as easily calculated assuming statistical distribution of impurities among B-sites. For example, in the case of sample No.1 the best agreement with experiment is obtained for $C_B = 0.97$ which is consistent with neutron diffraction results. Contribution from Fe atoms with environments different from those considered above is negligible (less than 2%). One can also show that the weak fields observed in Mössbauer spectra cannot result from the interaction between Fe atoms and their nearest neighbours (nn) having 2, 1 or 0 iron atoms, even when a strong short-range order at B-sites is assumed.

An aluminium or silicon atom when substituted for Fe in Fe_3Si weakens ferromagnetic interaction by breaking one ferromagnetic bond. Because of competing interactions known to exist in Fe-Al system [10 and references therein] the concentration fluctuations can produce a distribution of magnetic moments decoupled or weakly coupled with the basic ferromagnetic lattice. The total volume of such regions, which can exhibit low hyperfine magnetic fields, should increase with increasing Al concentration, resulting in the increase of the intensity of the central part of the spectra. The magnetic fields fitted by sextets increase with decreasing temperature while the mean values of the central part is practically temperature independent. This indicates that the low-field regions can be only weakly coupled to ferromagnetic lattice.

Ling et al. [11] who studied $Fe_3Al_xSi_{1-x}$ alloys argued that an excess Al atom deforms the unit cell and the appearing quadrupole interaction leads to the line broadening, because several different orientations of the effective field with respect to the gradient of the electric field are possible. For much the same reason as above, in such a case, however, we would expect to observe broadening of Fe(3) sextet only. As our data show, the broadening, is observed for all the sextets. Therefore we find this explanation unlikely.

The low field regions affect ferromagnetic ones and the resulting magnetic hyperfine structure depends on the "contact area" between these two kinds of regions. The inhomogeneity of the distribution of low-field regions should in turn lead to the line broadening of the Zeeman sextets. The total volume of such regions and inhomogeneity should increase with increasing Al content and lead to the increase of both the relative intensity of the central part of the spectra and the line broadening. This picture is fully consistent with our observations.

ACKNOWLEDGEMENTS

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The full account of the studies is submitted for publication to Physica Status Solidi.

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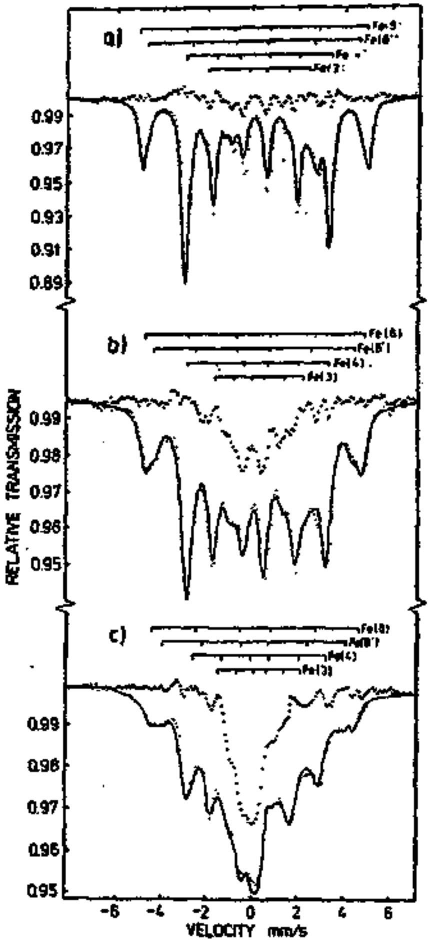

Fig. 1 The Mössbauer spectra at room temperature. The solid line is the result of the least-square fitting. Difference between experimental points and four Zeeman sextets is also shown.

THE CORRELATION BETWEEN THE RESULTS OF MAGNETIC CRYSTAL STUDIES DONE BY THE MÖSSBAUER EFFECT AND BY THE NEUTRON DIFFRACTION METHODS

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The results of studies of the properties of the magnetic crystals by means of the Mössbauer effect and the neutron diffraction performed in Cracow and Warsow centers of physics are discused. The special attention is given to the completion of both methods.

Magnetic properties of the matter can be studied by various experimental methods. Different techniques provide complementary information. The present paper is on the comparison of the neutron diffraction and the Mössbauer spectroscopy methods to the investigation of the following subjects:

1. α-FeOOH /Goethite/, is one of the polymorphic modifications of the hydrated ferric oxide /FeOOH/. The antiferromagnetism of goethite was established quite recently when A. Hrynkiewicz and D. Kulgawczuk /1/ discovered the zeeman splitting of its Mössbauer spectrum. Goethite has two internal magnetic fields and two critical points $T_N^{/1/} = 340$ K and $T_N^{/2/} = 370$ K. The neutron diffraction data for α-FeOOH /2/ indicate that existence of antiferromagnetic collinear spin ordering below the Néel point $T_N = 362 \pm 5$ K. The spins of iron ions are aligned parallely to the b-axis. The results of neutron diffraction data do not agree with the Mössbauer effect data. The collinear antiferromagnetic structure excludes two values of magnetic fields and two critical points.
2. Heusler alloys are the metallic compounds crystallizing in a characteristic structure /$L2_1$ type/. The orginal Heusler alloys are ferromagnetic and based on the composition X_2MnZ, where X is a 3d metals, Z is a B sub-group metal such as Al, Sb, Sn, Ga or In. The neutron diffraction studies of X_2MnZ compounds

indicate that the Heusler alloys are ferromagnetics with high values of the Curie temperatures /3/. The magnetic moment per Mn atom is near 4 μ_B. In the case of the Co_2MnZ alloys the saturation of the magnetization reaches 5 μ_B/atom. It suggests that the magnetic moment is localized on both Mn and Co atoms. The compounds Co_2YZ, where Y is Ti, Zr, Hf or Nb are also ferromagnetic with the magnetic moment localized only on the Co atoms /~1 μ_B/ /4/.

The experimental values of the hyperfine field at the non-magnetic sites in Heusler alloys /Sn, Sb, In, Cd/ and magnetic site Mn were measured for different authors /5/. The obtained results have been compared with the prediction of Caroli-Blandin, Campbell-Blandin and RKKY models /6/. The plain dependence of the magnetic field value on the magnitude of the magnetic moment localized on the Mn or Co atoms was not observed. Till now, there is no satisfying explanation of the mechanism of the magnetic moment interaction. The majority of the authors that the interaction is of the long-range character /7/, while the experimental results obtained for the diluted Heusler alloys /$Ni_2Mn_{1-x}T_xSn$, T=Ti, V/ suggest the short-range interaction /8/.

3. FeSn is an intermetallic compound of the hexagonal B55 type structure. It is an antiferromagnet with Néel temperature at 365 K. The combined Mössbauer Effect and neutron diffraction studies on powder FeSn sample /in the temperature range between 4.2 K and 400 K/ indicate the spin-flip effect at temperatures about 70 K. The observed phase transition is due to the change of spin direction, the magnetic moment is set along [100] direction for $T < 70$ K whereas at $70 \text{ K} < T < T_N$ it is directed along [210] /9/.

4. Ferrites. It is the group compounds with the cubic crystal structure of spinel described generaly by the following formula $M^{2+}M_2^{3+}X_4^{2-}$ /M^{2+} is a divalent metal, for example Zn^{2+}, Fe^{2+}, M^{3+} - trivalent ion, for example Fe^{3+}, Al^{3+}, X - O, S, Se, Te/. The mixed spinels Zn-Ni, Zn-Li-Ti have been investigated using Mössbauer Effect and neutron diffraction method. For $Zn_{0.8}Mn_{0.2}Fe_2O_4$ compound the neutron diffraction method indicate the magnetic ordering at 293 K, while the Mössbauer test measurements

at 80 and 293 K indicate only a quadrupole doublet characteristic for the paramagnetic state /10/. Similar effect is observed in the case of $Zn_xLi_{1-0.5x}TiFe_{1-0.5x}O_4$ compounds. The results of experiments indicate the different value of Curie point with Mössbauer effect and neutron diffraction methods. For $x=0$ $T_c^{ME}=342\pm10$ K, $T_c^{ND}=430\pm5$ K, $x=0.3$ $T_c^{ME}=335\pm10$ K, $T_c^{ND}=480\pm5$ K. On the other hand in the case of $/Zn_{0.8}Ni_{0.1}Fe_{0.1}/Fe_2O_4$ compound neutron diffraction method does not indicate the magnetic ordering up to 4.2 K, while Mössbauer effect method give $T_c^{ME}=55$ K. The obtained results indicate that in the case of $T_c^{ND} < T_c^{ME}$ the sample is composed of the claster of small dimension /~100 Å/ and it shows a large magnetocrystalline anisotropy, while in the case $T_c^{ND} > T_c^{ME}$ the clasters are of large dimensions /~1000 Å/ and a small magnetocrystalline anisotropy is observed.

5. MM'Ge Germanides /M, M' – transition 3d metals crystallize in the hexagonal crystal structure of the Ni_2In type. The 3d metal atoms are distributed in two sites. The Mössbauer effect and neutron diffraction combined experiment allows to determine the magnetic structure and the distribution of atoms. The pyramidal sites are preferred by Mn and Fe atoms, while Co and Ni atoms tend to occupy tetrahedral sites /11/.

6. RET_2X_2 compounds /RE is either lantanide or actinide metal, T is a "nd" transition element, X stands for Si or Ge/ crystallize in the tetragonal $ThCr_2Si_2$ type /space group I4/mmm/, with RE atoms in the 2/a/, T atoms in 4/d/ and X atoms in 4/e/ sites, respectively. In these compounds from amongst T elements only Mn atom has the magnetic moment. The rare earths moments order usually antiferromagnetically or ferromagnetically at low temperatures /12/.

The Mössbauer effect measurements showed that Fe and Ni atoms never have magnetic moments in these materials /13/. The Mössbauer studies of ^{151}Eu, ^{155}Gd and ^{161}Dy have the magnetic ordering at low temperatures. /14/ In the case of EuT_2X_2 and GdT_2X_2 compounds the orientation of the magnetic moments relative to the local fourfold axis /c-axis/ also was determined. It turns out that in the Eu compounds the easy axis of magnetization is close to the c-axis, while in Gd compounds it is in the basal plane.

Orientation of the magnetic moments in the unit cell is connected with signs of B_2^0 coefficients. The crystal field hamiltonian for a rare earth ion situated in the site with the point symmetry 4/mmm is

$$H_{CF} = B_2^0 O_2^0 + B_4^0 O_4^0 + B_4^4 O_4^4 + B_6^0 O_6^0 + B_6^4 O_6^4$$

where the c-axis of the tetragonal cell has been chosen as a quantization axis. The operators O_n^m and the coefficients B_n^m are like defined by Hutchings /15/.

According to Greedan and Rao /16/ the positive value of the B_2^0 coefficient indicates that the magnetic moment lies in basal plane or makes ϕ angle with the c-axis, while the negative value of B_2^0 coefficient indicates that the magnetic moment is parallel to c-axis.

The results of Mössbauer effect and neutron diffraction studies suggest that increase in the number of 4f and nd electron leads to change of the B_2^0 value /see Table 1/.

The comparison of the effective hyperfine magnetic fields /H_{eff}/ in DyT_2X_2 compounds and of the respective magnitudes of the ordered magnetic moment /μ/ observed in the neutron diffraction gives the relation H_{eff}/kOe/$\sim$600 μ /μ_B/. This result is an evidence for a localization of 4f electrons.

Table 1. The values of B_2^0 coefficients and the direction of the magnetic moment for RET_2X_2 compounds.

RE/T	Mn	Fe	Co	Ni	Cu
Ce					-0.3
Pr	-0.07	-0.63, 0°	0°		0°
Nd					
Eu			29°	44°	52°
Gd	82°	84°	84°	31.5°	90°
Tb	0°	-0.3,	0°	0°	90°
Dy	-4,35	-1.8, 28°	-1.0, 0°	+0.17, 90°	+0.6, 90°
Ho		-0.61, 28°	0°	90°	90°
Er		+0.67, 90°	90°		0°
Tm		+2.54	90°		+0.12

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MAGNETIC and STRUCTURAL STUDIES of AMORPHOUS METALLIC ALLOYS with the HELP of MÖSSBAUER SPECTROSCOPY

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Summary

Mössbauer Spectroscopy is used to study the magnetic and structural properties of amorphous substancea, whose composition was of the type $Fe_{80-x}TM_xB_{20}$, where TM- transition metal. The spectra were taken at temperatures from 4.2 - to about 800K. The results were analysed using Window's method. The coefficients B in the Bloch's law were avalusted from the data. The influence of TM subatitution and temperature dependence are discussed.

1. Introduction

Mössbauer Spectroscopy is a very useful tool for the study of noncrystalline magnetic solids, because it is microscopic measurement, and therefore became important method for investigation of the magnetic and structural properties of the amorphous iron alloys (1,2,3,4). In ferromagnetic amorphous iron alloys, the magnetic moments of iron atoms are affected by nearby atoms, and therefore the internal magnetic field distribution obtained from Mösbauer spectrum can be used to examine the atomic arrangements in the amorphous structure. Especially, magnetic dipole interaction leading to the nuclear Zeeman effect is a measure of the internal hyperfine magnetic field. We have studied magnetic properties of the amorphous foils of the type $Fe_{80-x}TM_xB_{20}$, where TM -transition metal : Mn,Cr,Co,Ni and x was 6, 10, 20 at %, B - boron. Great interest in the metal-metalloid ferromagnetic glasses based on Fe, may be attributed to their various magnetic applications, but also to the interesting theoretical aspects. The iron-rich alloys have very good soft magnetic properties combined with good mechanical strength and hardness. A number of studies concerning the magnetic properties of Fe-based glasses have been reported , but there is still a need for a more systematical research. We want to clarify the effect of transition metal substitution on the physical properties of the Fe-based amorphous alloys with constant value of metalloid (in our case - B_{20}). This report constitutes part of a broader research devoted to $Fe_{80-x}TM_xB_{20}$ (x=6, 10, 20) amorphous alloys, where TM = Ti,V,Cr,Mn,Co,Ni and $Fe_{80}B_{20}$ is reference substance (5,6).

2. Experimental

The amorphous substances investigated here were in a form of long ribbons with a nominal width of 5 mm and thickness of 35 µm. The non-crystalline nature of the samples were checked by X-rays. All the spectra were recorded in the standard transmission geometry with a ^{57}Co source in Cr matrix. The measurements above room temperature were performed using a vacuum cryostat with temperature stability of about ± 0.2 K. Room temperature Mössbauer spectrum of thin Armco foil was used as a standard to calibrate the spectrometer. The results concerning measurements at 4.2 K were taken from our earlier publication (5). An appriopriate way to characterise Mössbauer effect data of the Fe-based ferromagnetics is through their hyperfine field distribution and this will be the main point of our analysis. Information concerning the magnetic hyperfine field distribution were obtained by fitting the spectra using the Window's method (7).

3. Results and discussion

All alloys show rather structureless P(H) curves consisting of a single peak with dispersion ΔH . The spectral linewidth, number of Fourier coefficients N, and the intensity ratio 3 : b : 1 were varied to find the optimum fit, as measured by the chisquared criterion. In some cases larger width obtained is assumed to reflect the distribution of isomer shift and quadrupole splitting that have been neglected in present analysis as the values of the second order. The influence of composition, particullary transition metals Mn,Cr,Co,Ni and temperature on hyperfine magnetic field and dispersion of this field is the subject of the report. Our experiment clearly indicates that ferromagnetism may exist in a wide range of composition, where Fe-atoms are substituted by TM-atoms. As an example, the Mössbauer spectra and the corresponding hyperfine field distribution P(H) at selected temperatures for amorphous $Fe_{74}Mn_6B_{20}$ are shown in Fig.1. It is clear from the overlaping broad line widths, that measured spectra do not represent a unique hyperfine magnetic field, because of noncrystalline nature of sample. The larger linewidths arise from the superposition of several subspectra due to a distribution of internal hyperfine magnetic fields as a consequence of randomly distributed atomic environment around the Mössbauer absorber atoms of ^{57}Fe. Because of the prolonged heating at temperatures near T_c, the Mössbauer measurements are not adequate for determination of the Curies temperatures T_c for amorphous alloys. Amorphous state does not show a rapid transformation into crystalline state, but the changes take place in some temperature interval depending on TM and composition. As we can see, the value of the hyperfine magnetic field distribution shows a slight decrease as the temperature increases, and it was also observed in (9). Fig.2. show~~e~~s the dependence of the hyperfine magnetic field versus atomic number Z (or 3d + 4s electrons) of various transition metals that were substituted for Fe-atoms. The measurements were performed for three values of x and three different temperatures. The value of hyperfine

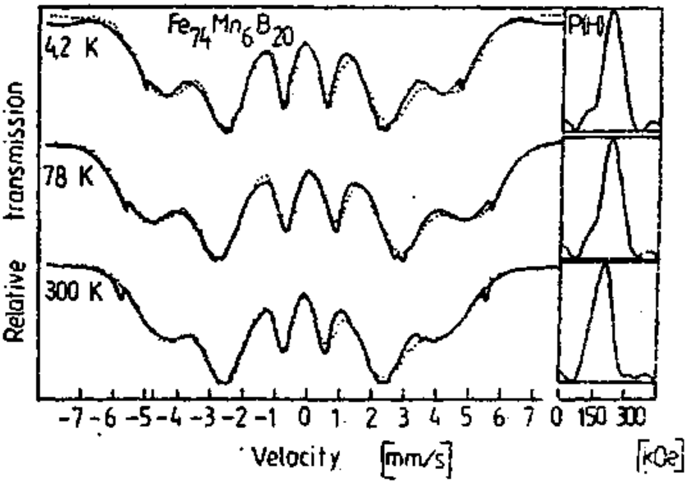
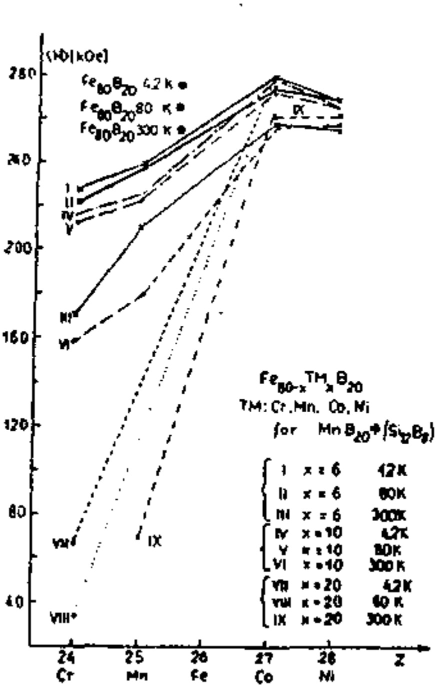


Fig.1. The Mössbauer spectra and the corresponding hyperfine field distribution P(H).



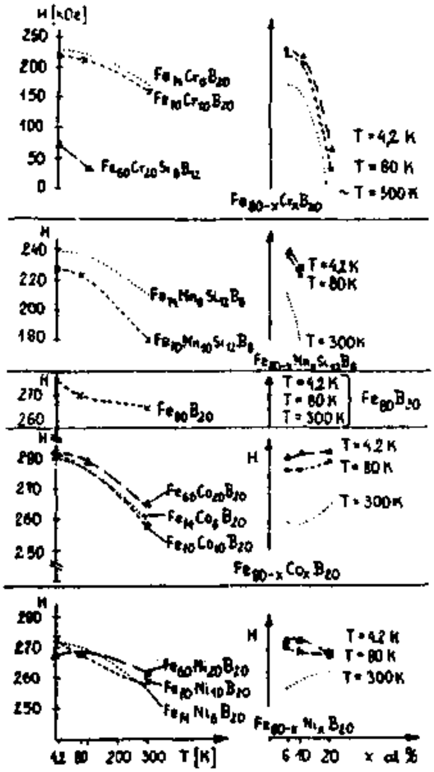


Fig.2. Dependence of hyperfine magnetic field versus Z of transition metal

Fig.3. The dependence of hyperfine magnetic field on T and x

field H is increasing with number of Z (3d +4s electrons) reaching a maximum for Co and has lower value for Ni. This can be a direct evidence that magnetisation of the Fe-based glasses is determined by the charge transfer between the constituents. Essential changes in the case of Mn and Cr - could result from drastic changes in the local structural order proving the tendency towards antiferromagnetic behavior. From Fig.2. we can see, that the highest values of the hyperfine field are observed for x = 6, T = 4.2 K /I/ and also for x =6, T = 80 K /II/. There is not great difference between the curves / I and II/ and /IV and V/. On the other hand much greater differences in the value of H are found for the set of curves taken at room temperature for x = 6 and 10 /T=300K, III and VI . The values of H for x=20 that correspond to Cr and Mn are significantly lower. The alloys with Cr=20 at% is nearly paramagnetic at room temperature. By reducing the Fe-content by Cr and Mn substitution , the hyperfine magnetic field rapidly decreases. In general , H field versus Z , i.e. transition metal content is seen to exhibit a maximum , which is contrary to the dependence of dispersion of hyperfine magnetic field distribution H as a function of Z. It is already known, that the hyperfine field depends on composition and temperature. To observe this trend more closely, H-value is plotted against TM-concentration and temperature. The data points follow a consistent gradual fall with exception for samples containing Co and Ni , at room temperature. As we can see from Fig 3, H varies almost linearly with composition. Only the curve for Co content sample shows a minimum at T=300K for x = 10. The values of reduced hyperfine magnetic field calculated from our measurements (10) confirm the same temperature dependence as that of the reduced magnetisation. Also higher values of $B_{3/2}$ coefficients in Bloch's law for our samples than for crystalline , were obtained. Fig. 4 illustrates the correlation between hyperfine magnetic field and the mean magnetic moment per Fe-atom (6) as the

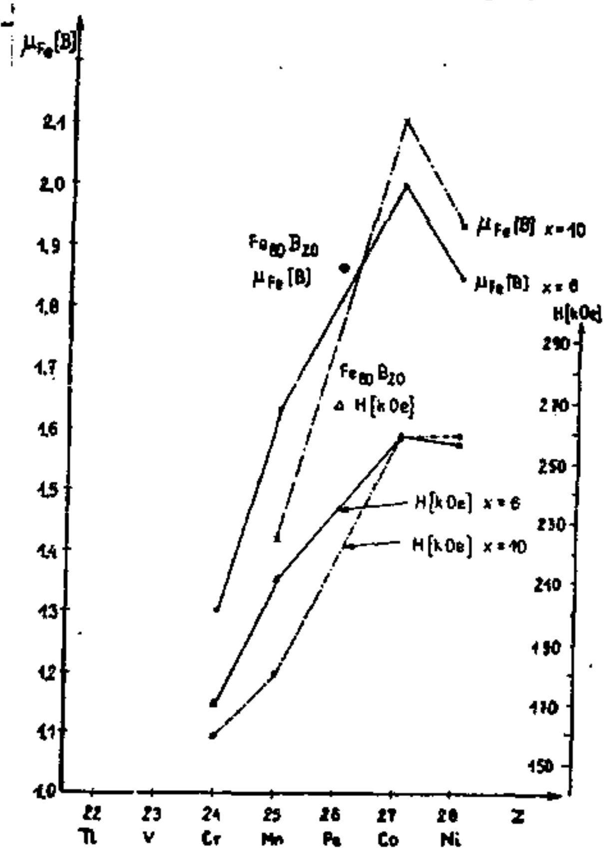


Fig.4. The correlation between hyperfine magnetic field and magnetic moment per Fe-Atom

function of Z of the transition metals substituted for Fe-atoms. The influence of TM-addition on properties of amorphous alloy appears to be very interesting problem for theoretical consideration and practical applications. The local short-range atomic ordering as well as the temperature of the glasses may contribute to the strength of magnetic interaction as it is seen from our results. But further systematical experiments are desirable to clear up various viewpoints. The author would like to thank Doc.Dr.J.Suwalski and Dr.M.Łukasiak for very helpful collaboration. The amorphous ribbons were produced in Institute of Material Science of the Warsaw Technical University. This work was sponsored by the Polish Academy of Sciences in the frame of the Scientific Program MR I.4.II. and CPBP 01.04.II.

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MÖSSBAUER STUDIES OF ISOTROPIC FERROMAGNETS IN CRITICAL REGION.

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Mossbauer experiments measuring the statical critical exponent β and the dynamical exponent ω in the isotropic ferromagnets are reviewed. The results of our experimental studies on the critical behaviour of Fe are presented and compared to that obtained by Kobeissi.

1. Introduction.

In the last few years the statics and the dynamics of isotropic ferromagnets: Co, Fe, Ni, EuO, EuS, and nominally isotropic one Gd, around T_c has been of considerable experimental and theoretical interest. The critical behaviour even in such simple systems, which may be good examples of theoretical models, is still an object of controversy. To obtaine a unique picture all experimental techniques, especially Mössbauer spectroscopy, are important because measurements are performed over different critical regions and give direct information about various critical exponents.

The Mössbauer effect was used to test the predictions of magnetic critical phenomena, both in the area of statics and dynamics, under the following not trivial assumptions [1] .

- The hyperfine field H_{hf} is proportional to the magnetization .

$$H_{hf}(T) = const.\, M(T) \qquad /1/$$

- The line shape is a Lorentzian and the line broadening $\Delta\Gamma$ is proportional to the spin autocorrelation time τ

$$\Delta\Gamma(T) = const.\, \tau(T) \qquad /2/$$

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Careful measurements of the statical critical exponent β and a determination of the dynamical critical exponent z have been made using the scaling relations [2]

$$M(t) = A_0 t^{\beta}, \qquad \tau(t) = \tau_0 t^{-\omega}, \qquad \omega = \nu(z+2-d-\eta) \quad /3/$$

where t is the reduced temperature, d -dimension, ν and η -the statical critical exponents.

Table 1

Mössbauer nuclei useful for critical studies.

Isotope	Transition Energy /keV/	Parent half-life /days/	Natural linewidth /mm/s/	Excited State I_e	Excited State μ_e	Ground State I_g	Ground State μ_g
^{181}Ta	6.2	140	0.0065	9/2	5.14	7/2	2.35
^{57}Fe	14.4	270	0.19	3/2	-0.15	1/2	0.09
^{161}Dy	25.6	7	0.37	7/2	0.59	5/2	-0.47
^{119}Sn	23.8	250	0.63	3/2	0.67	1/2	-1.04
^{151}Eu	21.6	120	1.44	7/2	2.58	5/2	3.46
^{149}Sm	22.5	106	1.60	5/2	-0.62	7/2	-0.66

Mössbauer spectroscopy has a number of significant advantages over competing techniques [1, 3]. This method offers the ability to:

- work in zero applied field below and above T_c,
- observe the effects of critical fluctuations below and above T_c
- utilize samples of very small size, so that problems from temperature and compositional homogeneity are minimized.

But there are the disadvantages of this method too:

- limitation to local magnetization effects, with no direct ability to probe the size of correlated regions,
- limitation to the wave number q- averaged correlation times, so that the exponent ω, not the critical exponent z, is directly measured,
- limitation to a few radioactive probe atoms, listed in Table 1. [1].

2. Review of critical behaviour in isotropic ferromagnets

The first Mössbauer studies of magnetic critical phenomena were done in Fe by Preston, Hanna and Heberle [4]. However experimental determination of critical exponents in ferromagnets requires precise measurements very close to T_c with good resolution of Mössbauer lines. From all Mössbauer experiments presented in Table 2., only recent experiments in Fe and Ni were disigned with sufficient attention to sample and temperature homogeneity to permit decisive tests of model predictions

Table 2.

The critical exponents β and z for isotropic ferromagnets.

$T<T_c$	Material	Range in t	β		Reference
	$Fe^{57}Fe$	$10^{-4}-10^{-2}$	0.37 /2/		[illegible]
	$Fe^{57}Fe$	$10^{-3}-10^{-2}$	0.345 /1/		5
	$Fe^{57}Fe$	$10^{-4}-10^{-2}$	[illegible] /9/		6
	$Fe^{57}Fe$	$10^{-3}-10^{-2}$	[illegible] /4/		5
	$Fe^{57}Fe$	$10^{-3}-2\ 10^{-2}$	[illegible]		7
	$Ni^{57}Fe$	$10^{-4}-10^{-1}$	0.379 /[illegible]/		8
	$EuO^{151}Eu$	$10^{-2}-10^{-1}$	0.34 /1/		9
	$Ni^{121}Sn$		0.625		10
	Theory: $d=3$ Heisenberg system		0.365		11
$T>T_c$	Material	Range in t			Reference
	$Fe^{57}Fe$	$10^{-4}-5\cdot10^{-2}$	0.62 /13/	1.93 /18/	6
	$Fe^{57}Fe$	$5\cdot10^{-4}-5\cdot10^{-3}$	0.82 /20/	2.17 /27/	12
	$Ni^{57}Fe$	$5\cdot10^{-4}-5\cdot10^{-3}$	1.0 /1/	2.50 /15/	13
	$Ni^{57}Fe$	$10^{-4}-5\cdot10^{-2}$	0.71 /24/	2.06 /30/	14
	Theory: $d=3$ Heisenberg system			2.5	2
	spin nonconserved system			2.0	2

The dynamical crossover of the exponents ω or z was not observed, contrary to other techniqes.

3. Static and dynamic critical behaviour in Fe.

Our Mössbauer data on Fe [7,12] illustrating determination of the statical and dynamical exponents, and the correction to scaling form below T_c

$$M(t) = A\,t^{\beta}(1 + a\,t^{\Delta})$$

are shown in Fig.1. and Fig.2.

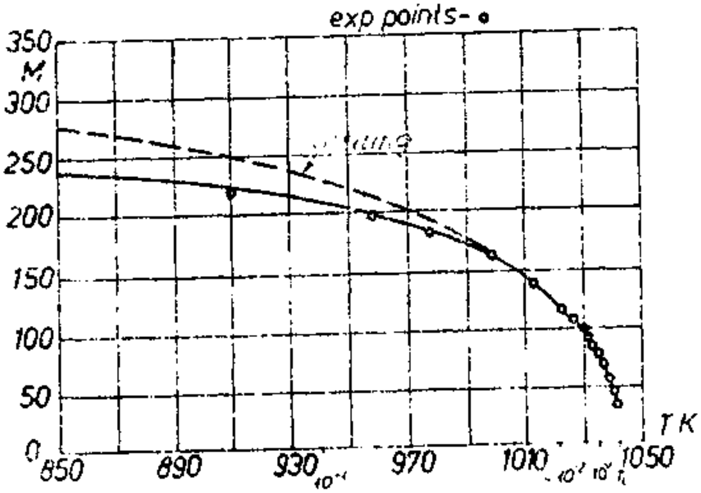

Fig.1. Scaling and correction to scaling below T_c for Fe.

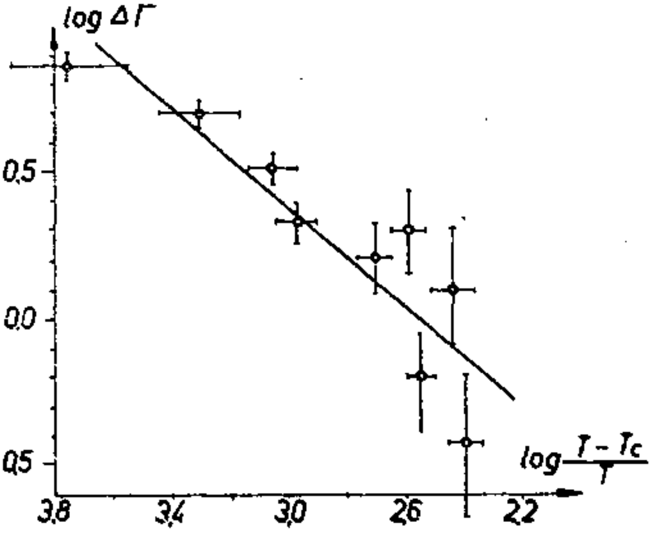

Fig.2. Determination of the exponent ω above T_c for Fe.

In contrast to Kobeissi, we used the second term in /4/ as a correction term to the asymptotic critical behaviour/3/. The comparison of both results is shown in Table 3.

Table 3.

Correction to scaling below T_c for Fe.

Reference	T_c	β	A	a	Δ
6	1043.05	0.367	552	-0.458	0.55_{fixed}
7	1043.25	0.365_{fixed}	547	-0.38	0.52

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MÖSSBAUER STUDIES OF STATIC CRITICAL PHENOMENA IN AMORPHOUS FERROMAGNETS.

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Mössbauer experiments measuring the magnetization exponent β in the amorphous ferromagnets are reviewed and our experimental studies on the static critical behaviour of $Fe_{40}Ni_{40}Si_{13}B_7$ are presented.

1. Introduction.

The nature of the ferromagnetic-paramagnetic transition in amorphous ferromagnets has fascinated both theorists and experimentalists for more than a decade now. In the recent *review papers [1,2] the present experimental data have been* re-analysed by Kaul and compered with those previously reported on crystalline ferromagnets and with the predictions of the existing theories. We focus our attention on the Mössbauer studies of static critical behaviour of amorphous ferromagnets.

^{57}Fe Mössbauer spectroscopy has been extensively used to understand ferromagnetism in amorphous structure [3]. The first Mössbauer measuremente [4] on amorphous Fe-P-C alloys, indicated a sharp transition at the Curie temperature T_c, were reported in 1968. However only in the few works [5-10] a quantitative analysis of the critical behaviour was carried out to data. There ere many difficulties, especially the undesirobly large uncertainly in T_c and the poor spectral resolution caused by a progressive smearing of the already broad inherent linewidths due to the increasing width of the hyperfine field distribution $P(H)$ as $T \rightarrow T_c$ [1]. The true asymptotic values of the critical exponents can be determined when the experimental data are fitted to the scaling relations in the asymptotic range of the reduced temperature $t = \frac{T_c - T}{T_c} < 2 \cdot 10^{-2}$.

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2. Magnetization exponent β of amorphous ferromagnets from Mössbauer measurements.

The Mössbauer effect technique is one of the direct and accurate methods of determining the static critical exponent β characterising the deviations of the spontaneous magnetization M from its value at T_c via the scaling relation

$$M(t) = M_o t^{\beta} \qquad /1/$$

A linear relationship between the hyperfine field $H(T)$ and the magnetization $M(T)$ as $T \to T_c$ is used to deduce $M(T)$ from the measured $H(T)$. All β values determined from Mössbauer measurements using the relation /1/ are presented in Table 1 [1].

Table 1.

The critical exponent β for amorphous ferromagnets.

Material	Range in t	β	Reference
[illegible]$B_{14.5}Si_{3.5}C_2$	$8\cdot10^{-2}-9\cdot10^{-1}$	0.31 /2/	5
[illegible]$_{76}$[illegible]$_{15}$[illegible]$_9$	$9\cdot10^{-2}-3\cdot10^{-1}$	0.34 /2/	6
$Fe_{75}P_{15}C_{10}$	$3\cdot10^{-2}-6\cdot10^{-1}$	0.33 /5/	7
$Fe_{0.65}Mn_{0.3575}Gd_{25}$	$1\cdot10^{-2}-5\cdot10^{-1}$	0.42 /14/	8
$Fe_{40}Ni_{40}P_{14}B_6$	$3\cdot10^{-2}-6\cdot10^{-1}$	0.32 /5/	7,9
$Fe_{32}Ni_{36}Cr_{14}P_{12}B_6$	$4\cdot10^{-3}-7\cdot10^{-1}$	0.40 /3/	10
Theory:			
d=3 Heisenberg order system		0.365	11
extreme disorder limit		0.50	12

Kaul has concluded [illegible] that:

- width of the asymptotic critical region in 3d amorphous transition metal-metalloid alloys is of similar magnitude in both crystalline and amorphous ferromagnets;
- the values of β in such alloys tends to be slightly higher than the values in crystalline ferromagnets or Heisenberg model.

3. Static critical behaviour in amorphous ferromagnet $Fe_{40}Ni_{40}Si_{13}B_7$.

A series of Mössbauer measurements was performed, in the temperature range 300-700 K, on the amorphous $Fe_{40}Ni_{40}Si_{13}B_7$ /VITROVAC 4/ in the form of continuous ribbon 10 mm wide and about 25 μm thickness [13]. The sharp transition from ferromagnetic to paramagnetic phase is observed near T_c=509.6 K. The cristallisation process begins a long distance of T_c above T=690 K. This property ensures that metastable amorphous state is not disturbed while studying the critical behaviour near T_c [2].

Mössbauer spectra of $Fe_{40}Ni_{40}Si_{13}B_7$ at temperatures below T_c exhibit well-defined but broadened six-line patterns. As a first attempt, we have fitted the spectra to six Lorentzian peaks, characterized by a mean hyperfine field $H_{eff}/T/$, with a Lorentzian field distribution P/H/ [14]

$$P(H) = \frac{1}{1 + 4\left(\frac{H - H_{eff}}{\Delta}\right)^2} \qquad /2/$$

It seems that the formula /2/ adequatly describes P/H/ in amorphous transition metal-metalloid alloys as $T \to T_c$. The values of $H_{eff}/T/$ obtained from the Lorentzian peak fit and the values of the ratios $\Delta / H_{eff}(T)$ are shown in Fig.1.

The scaling relation

$$H_{eff}(t) = H_0 t^{\beta}$$

was used to deduce the exponent β from the measured $H_{eff}/t/$. The values of the Curie temperature T_c = 509.6 ± 0.3K and the critical exponent $\beta = 0.55 \pm 0.03$ have been derived from a three parameter least-square fit to a simple power law /3/ in the asymptotic range $t = 3 \cdot 10^{-3}$ to $2 \cdot 10^{-1}$. As was shown in Fig.2. the width of the asymptotic critical region for the exponent β is much wider than that in the cristalline Fe [15], in agreement with the theoretical prediction [16]. The obtained value of the critical exponent $\beta = 0.55$ is rather unexpected.

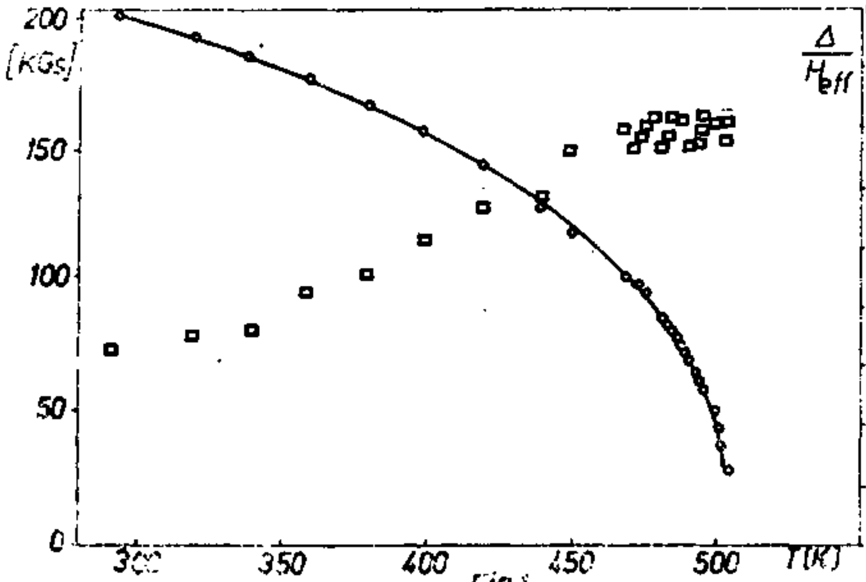
200
[KGs]
150
100
50
0
300
350
400
450
500
T(K)
$\frac{\Delta}{H_{eff}}$
0,9
0,8
0,7
0,6
0,5
0,4
0,3
0,2
0,1
0

Fig.1.

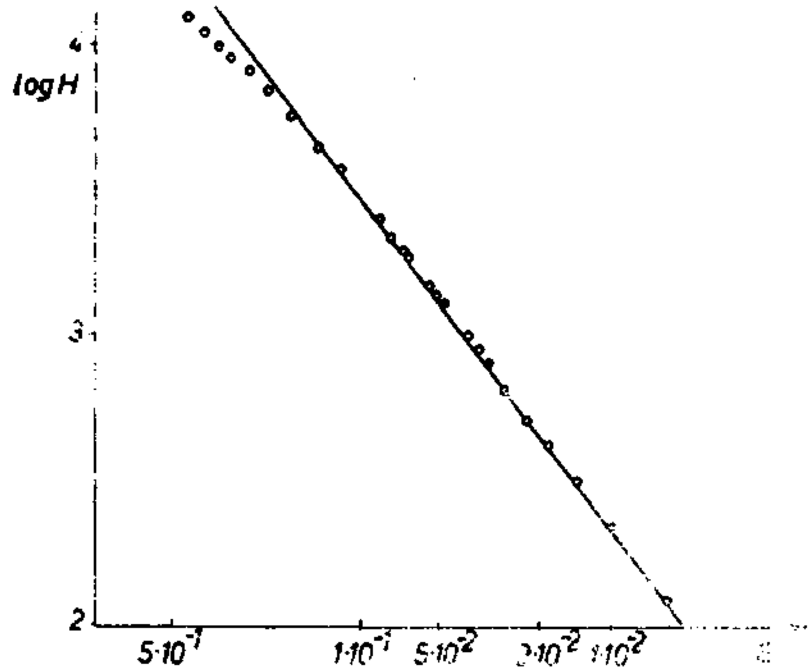
log H
4
3
2
$5\cdot10^{-1}$
$1\cdot10^{-1}$
$5\cdot10^{-2}$
$2\cdot10^{-2}$
$1\cdot10^{-2}$
ε

Fig.2.

Acnowledgments.

The authors would like to thank Dr M. Kopcewicz for kindly supplying the $Fe_{40}Ni_{40}Si_{13}B_7$ samples.

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Investigations of Crystal and Magnetic Properties of the $(Fe_xV_{1-x})_3Al$ Alloys

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The new series of cold-worked alloys $(Fe_xV_{1-x})_3Al$ were synthesized and investigated by the X-ray diffraction, magnetometric and Mössbauer effect methods. It was found that increase in iron concentration causes continuous transition from atomically disordered A2 type crystal structure /x=0, 0.17 and 0.33/ to ordered B2 type structure /x=0.67/ and then back to A2 type structure /x=1.0/. The x=0, 0.17 and 0.33 alloys are Pauli paramagnets above 4.2 K, while the iron-rich compositions /x=0.83 and 1.0/ are ferromagnets with Curie temperature 502 K and 808 K, respectively. Broad line Mössbauer absorption patterns and distributions of hyperfine interaction parameters are consistent with crystal disorder within sublattices.

1. Introduction

The Fe-Al alloys, depending on the aluminium concentration and thermal treatment, may crystallize into three types of crystal structure: A2, B2 and DO_3 /1/. Each of these structures exhibit cubic symmetry but differs from each other in the degree of atomic ordering of the crystal lattice.

The V-Al alloys prepared by arc melting from a solid solutions of A2 type crystal structure /2/.

Up to now, apart from the Fe_2VAl composition /3/, no investigations on Fe-V-Al alloys have been reported. Presented here are the results of investigations of the polycrystalline $(Fe_xV_{1-x})_3Al$ alloys performed by the X-ray, magnetometric and Mössbauer effect methods.

2. Experimental details

Polycrystalline $(Fe_xV_{1-x})_3Al$ alloys with $/0 \leq x \leq 1/$ were prepared by arc melting from stoichiometric quantities of the starting metals in argon atmosphere. They were quenched from liquid state onto water cooled copper plate. Investigations of crystal structure were performed at room temperature on powdered samples by the Debye-Scherrer method. Magnetic measurements were carried out at temperatures from 80 K to 1100 K in a magnetic field up to 1.2 T using the Faraday method.

^{57}Fe Mössbauer absorption spectra were recorded both at room and liquid nitrogen temperature using ^{57}Co/Cr/ source and a constant acceleration Mössbauer spectrometer. A high purity metallic iron foil was used for velicity calibration of the Mössbauer spectrometer. The least squares computer programmes were used to derive from Mössbauer absorption spectra discrete values or distributions of hyperfine interaction parameters.

3. Results

The X-ray phase analysis have shown that all samples were single phases of body centered cubic structure but differs from each other in the degree of atomic ordering of the crystal lattice. Fig.1 shows how many percentages of Fe /V, Al/ atoms occupy the B-sites in the crystal structure. The x=0.67 composition is nearly completely ordered. The lattice constant of the investigated alloys decreases nonlinearly with increase in Fe concentration, reaching a minimum at about x=0.67.

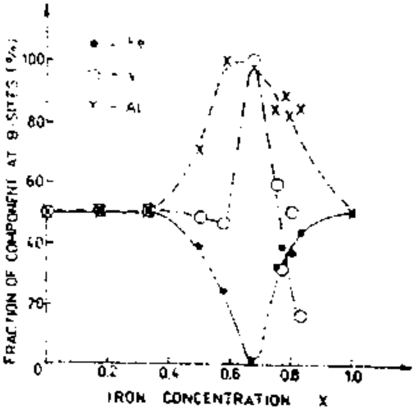

Fig.1. Fraction of the Fe V, Al component at the B-sites versus iron concentration x. The lines are drawn by hand in order to gide the eye. The unit cell of the B2 type bcc structure is inserted.

Magnetic investigations showed that in the measured temperature range magnetic susceptibility of alloys with x=0, 0.17 and 0.33 is independent on temperature. This sugests that they are Pauli paramagnets. At temperatures above 80 K magnetic susceptibility of the alloys with x=0.5, 0.58 and 0.67 decreases with increasing temperature, thus indicating the apparence of iron magnetic moment, but does not obey the Curie-Weiss law. At temperatures above 80 K the x=0.75 alloy does not exibit a long range magnetic order but shows a strong field dependence of the magnetization, characteristic for superparamagnetic alloys. The alloys with x=0.83 and 1.0 are ferromagnets with Curie temperature T_c=502 K and 808 K, respectively.

Some selected ^{57}Fe Mössbauer absorption spectra recorded for $(Fe_xV_{1-x})_3$Al alloys at room and liquid nitrogen temperatures are shown in Fig. 2. Fig. 3 shows variations with composition of isomer shift and quadrupole splitting.

4. Discussion of the results

Structural investigations of cold worked $(Fe_xV_{1-x})_3$Al alloys have shown that increase in iron concentration causes the continuous transition from atomically disordered structure of the A2 type /x=0, 0.17, 0.33/ to ordered structure of the B2 type /x=0.67/ and then back to the A2 type structure /x=1.0/. This concentration dependent transition may be a result of competition among the Fe-V, Al-V, Fe-Al, Fe-Fe, Al-Al and V-V bounds.

Analysis of the results of magnetic investigations shows that local enviroment of iron atoms has great influence on magnetic properties of $(Fe_xV_{1-x})_3$Al alloys. For low iron concentrations the iron atoms do not possess magnetic moments since number of magnetic nearest neighbours at a given iron site is very small. The appearence of magnetic moment on iron atom is associated with its at least six iron nearest neighbours. This is fully realized in alloys of highest iron concentrations. The presence of both nonmagnetic and magnetic iron atoms in the crystal lattice of intermediate compositions results in Curie-Weiss and band contributions to magnetic susceptibility.

The broad line Mössbauer absorption patterns /Fig.2/ and the distributions of hyperfine interactions parameters are consistent with crystal disorder within sublattices. The line broadening is due to the fact that at a given concentration of iron the values of isomer shift, quadrupole splitting and hyperfine magnetic field for a particular ^{57}Fe atoms depend on the number of Fe, Al and V atoms that occupy the nearest-neighbours sites. The ^{57}Fe Mössbauer effect investigations confirm the magnetometric data according to which all compositions but x=0.83 and 1.0 are paramagnets at room temperature. At 78 K the hyperfine magnetic field was found for x ≥ 0.75 compositions.

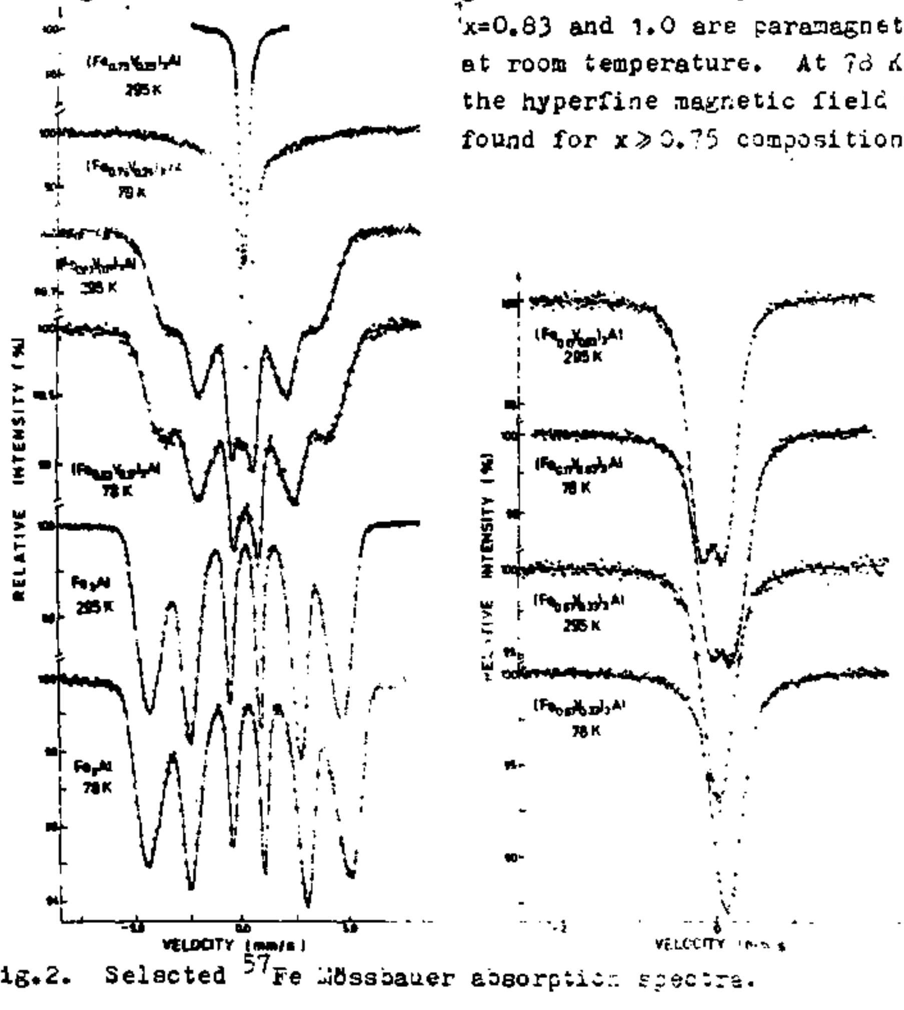

Fig.2. Selected ^{57}Fe Mössbauer absorption spectra.

The Mössbauer absorption patterns recorded at 295 K for $x \leqslant 0.75$ compositions can be well described by quadrupole doublets. Variations with composition of room temperature isomer shift and quadrupole splitting values are smooth and very small /Fig.3/. The quadrupole interaction is observed in spite of the fact that the crystal lattice of $(Fe_xV_{1-x})_3Al$ alloys is nominally cubic. This is because random distributions of Fe, Al and V atoms at the lattice sites cause departures from exact cubic symmetry about the Fe atoms. It should be noticed, however, that both isomer shift and quadrupole splitting values are not much influenced by the degree of crystal disorder.

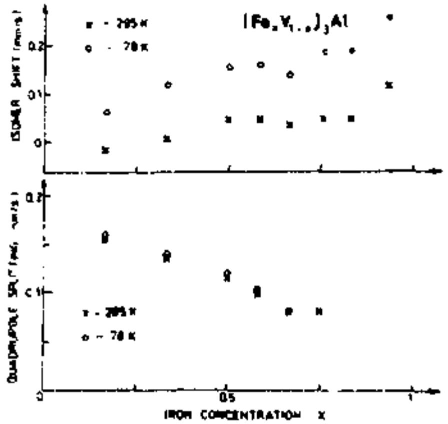

Fig.3. Variations with composition of isomer shift and quadrupole splitting.

The behaviour of Mössbauer absorption patterns as function of iron concentration gives some information on magnetic ordering of $(Fe_xV_{1-x})_3Al$ alloys. At 78 K magnetic ordering seems to start in x=0.75 composition and is fully evident in x=0.83 and 1.0 ones.

Further investigations are in progress.

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MÖSSBAUER OBSERVATIONS OF THE MAGNETOACOUSTIC ECHO SIGNAL

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An experiment to observe magnetoacoustic echo signals by the Mössbauer technique is described. The absolute value of the atomic vibration amplitude corresponding to the echo signal is measured. The simple model of magnetoacoustic echo effect is reported.

This paper describes the first Mössbauer observation of an echo signal [1]. It has been reported [2-4] that in some cases the echo signal is due to the magnetostrictive excitation of elastic waves in the material, the response of which is nonlinear. The object of the experiment was the confirmation of this suggestion and the measurement of the absolute value of amplitude of nuclear vibrations associated with the echo signal. An electronic system was designed to store the γ-ray counts detected in a preset time interval after the exciting r.f. pulses in the quarters of the memory of a multichannel analyzer (fig.1). The counts corresponding to the time Δt_1 were stored in the first quarter of the analyzer memory, the ones corresponding to Δt_2 in the second quarter, etc. The Mössbauer drive was synchronized with the analyzer in the conventional way so that each quarter of the memory contained the full Mössbauer spectrum corresponding to the state of the sample in the chosen time interval after the exciting r.f. pulses.

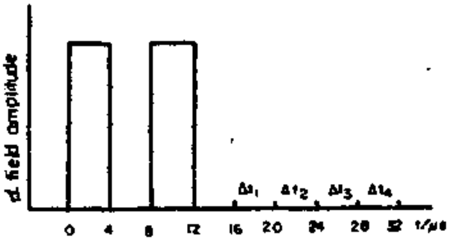
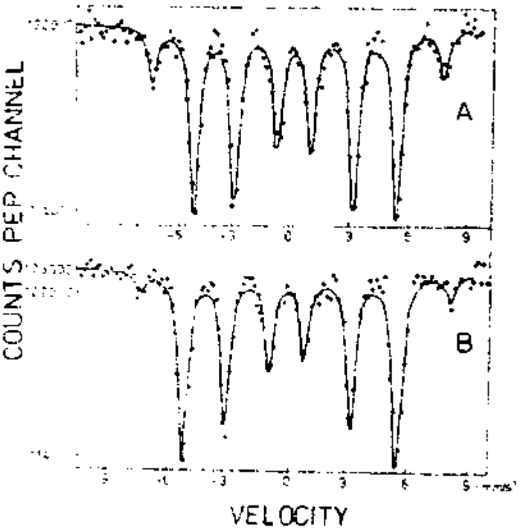


Fig.1. Timing of r.f. pulses and time intervals corresponding to stored Mössbauer spectra.

It has been shown by many workers (see e.g. [5,6]) that the Mössbauer spectrum of a sample in which acoustic vibrations in the 20-200 MHz range were excited contains sidebands or satellite lines separated from the main lines by an energy $\hbar\omega$, where ω is the frequency of vibrations. The intensity of these sidebands is well described by a modulation index $m = x_0/\lambda$, where λ is the wavelength of the γ radiation over 2π and has the value of 0.137 Å, and x_0 is the average amplitude of the nuclear displacement due to magnetoacoustic vibrations.

The natural iron foil samples were cut from a sheet of natural iron rolled to a thickness of 15 μm and annealed at 1200 K in hydrogen. These samples were used as the stationary absorbers and were placed in a helical coil which constituted a part of the resonant circuit of the generator. The r.f. field was applied in the plane of the sample. The measurements were made with a conventional constant acceleration Mössbauer spectrometer, which utilized [illegible] electronic multiscaler analyzer in the multiscaler mode and a source of 50 mCi of ^{57}Co in Cr. Lorentzian line shapes were fitted to the experimental points and the line intensities were used to obtain the value of the modulation index[4].



[illegible] spectra [illegible] in the intervals (A) [illegible] μs, [illegible] 4 μs r.f. pulses [illegible]

In the run which the strongest echo signal was observed, 4 μs r.f. pulses separated by 4 μs intervals were applied. The time intervals corresponding to the first I, second II, third III and fourth IV quarters of the analyzer memory are marked in fig.1. Three separate runs were performed for each pulse length and separation: one with both exciting pulses, one with only the first pulse, and one with only the second pulse. Such a sequence of runs allowed the r.f. sideband effects originating from the acoustic vibration decay following each pulse to be distinguished from the real echo effect.

Fig. 2A shows the Mössbauer spectrum obtained in the time region 16-20 μs after the application of two 4 μs r.f. pulses starting at 0 μs and 8 μs. The r.f. sideband modulation index for this spectrum is 0.74 ± 0.05, as compared with 0.00 ± 0.05 and 0.54 ± 0.05 for the spectra obtained with the first and second pulse only. Fig.2B shows the Mössbauer spectrum obtained in the time region 20-24 μs. The r.f. sideband modulation index for this spectrum is 0.24 ± 0.05, as compared with 0.00 ± 0.05 and 0.25 ± 0.05 for the spectra obtained with the first and second pulse only.

It is clear that the spectrum observed in the time interval corresponding to the echo reflects the actual increase of the amplitude of the atomic vibrations in the direction perpendicular to the sample. This amplitude of vibrations was measured to be about 4 times smaller than that observed while the r.f. pulses were applied. This is consistent with the values observed using conventional NMR techniques in lithium ferrite[3].

From the point of view of future applications of this effect it is interesting to describe the formalism given by J.Mycielski, one can utilize in treating the problem[6]. Let us consider the system in which one can excite the vibrations in the broad frequency range. We excite in this system vibrations the amplitudes of which are given by the normal distribution.

$$f(\omega) = \frac{\beta}{\sqrt{\pi}} \exp\left[-\beta^2(\Delta\omega)^2\right]$$

where $\beta > 0$, $\beta \gg \frac{1}{\omega}$ and $\int_{-\infty}^{\infty} f(\omega)\, d\omega = 1.$

In the case of experiment described above ω is the frequency of the pulsed r.f. field and β is of the order of pulse length. After the two exciting pulse applied at times $t=0$ and $t=\tau$ the amplitude of the atom corresponding to frequency $\omega + \Delta\omega$ is given by

$$x = E\cos\left[(\omega + \Delta\omega)t\right] + E\left\{1 - \alpha\cos\left[(\omega + \Delta\omega)\tau\right]\right\}\cos\left[(\omega + \Delta\omega)(t - \tau)\right]$$

ε is describing the interaction of r.f. field with acoustic vibration and α is related to the nonlinearity of the system and measures how the amplitude of vibrations excited with second pulse depends on the amplitude of vibrations existing in the system. The damping of vibrations was left out in the first approximation.

From the experimental point of view we are interested in the average value of the vibrations amplitude corresponding to all excited frequencies

$$\langle x \rangle = \int x \, f(|\Delta\omega|) \, d\,\Delta\omega$$

The integration gives

$$\langle x \rangle = \varepsilon\left(1 - \frac{\alpha}{2}\right)\exp\left[-\frac{t^2}{4\beta^2}\right]\cos\omega t + \varepsilon\exp\left[\frac{-(t-\tau)^2}{4\beta^2}\right]\cos\left[\omega\left(t - 2\tau\right)\right] - \frac{\alpha}{2}\exp\left[-\frac{(t-2\tau)^2}{4\beta^2}\right]\cos\left[\omega\left(t - 2\tau\right)\right]$$

The last term describes the echo - the increase of the amplitude vibrations at time $t = 2\tau$.

This relatively simple model indicates that the echo measurements may give some interesting information about the nonlinearity of the system and consequently of the interactions between the acoustic modes.

The further improvement of the model particularly including the damping of the vibrations might be necessary.

The author is indebted to Mr.S.Fijałkowski for the assembly of the electronic system and for technical assistance. This work was supported by program MR.I.5.

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SHORT RANGE ORDER IN AMORPHOUS METALS STUDIED USING THE RF COLLAPSE EFFECT

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The fast magnetization reversal induced by the magnetic radiofrequency field causes the collapse of the magnetic hyperfine splitting and leads to the paramagnetic-like spectra in the ferromagnetic state. In order to observe fully collapsed spectra the frequency of the rf field must be higher than the Larmor frequency and the intensity of the *rf field* should be large enough to overcome magnetic anisotropy field, so that the switching time of magnetization reversal will be comparable to the period of the rf field. Than the magnetic hyperfine field experienced by the Mössbauer nuclei is averaged to zero /1-3/. This effect, called the "rf collapse", allows to separate magnetic dipole and electric quadrupole hyperfine interactions and makes possible to observe directly the quadrupole splitting doublet (QS) in the ferromagnetic state /4, 5/. Since the quadrupole interaction provides more direct information about local structure than magnetic interaction or isomer shift, QS is a useful probe for the short range order in amorphous metals.

The rf collapse effect was employed to study QS distributions in iron based amorphous alloys such as: $Fe_{90-x}Si_xB_{10}$, $Fe_{84-x}Si_xB_{16}$, $Fe_xNi_{75-x}Si_{10}B_{15}$, $Fe_{75}Si_xB_{25-x}$ and various FeB, FeNiB and FeNiSiB /6-9/. The rf collapsed spectra were obtained with 62 MHz, 20 Oe rf field. They consist of an asymmetric broadened QS doublet. The distributions of QS were determined using the constrained Hesse-Rübartsch method as described in /10/. To account for the observed asymmetry of QS doublet the linear correlation between isomer shift and quadrupole splitting was introduced. The average values of $\overline{QS}$ and $\overline{IS}$ were extracted from the distributions of QS.

For the series of samples investigated the following general trends were observed: (1) $\overline{QS}$ decreases with increasing Fe content, (2) isomer shift $\overline{IS}$ initially decreases with increasing Fe concentration than begins to increase again for iron concentration above about 80%, (3) for fixed metal concentration $\overline{IS}$ decreases with increasing boron concentration, (4) $\overline{QS}$ decreases initially when boron is replaced by silicon in $Fe_{75}Si_xB_{25-x}$, (5) asymmetry of the QS doublet increases with increasing Fe concentration. Furthermore $\overline{QS}$ shows clearchanges of slope as a function of composition for FeSiB series (Fig. 1).

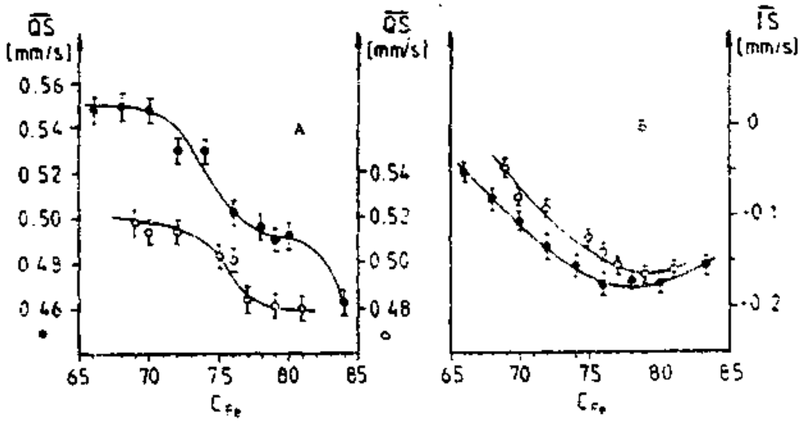

Fig. 1. Variation of average quadrupole splitting $\overline{QS}$ (A), and average isomer shift $\overline{IS}$ (B) with iron concentration (● - $Fe_{84-x}Si_xB_{16}$, o - $Fe_{90-x}Si_xB_{10}$)

For $Fe_{84-x}Si_xB_{10}$ there are "steps" at 73% and 81% of Fe, and for $Fe_{90-x}Si_xB_{10}$ - at 76% of Fe /7,8/. Such changes of QS are predicted by the structural model and reflect the changes of short range order in this alloys /11/. When Si is introduced to FeSiB it takes Fe positions with no boron nearest neighbours. When all such places are filled than the structure changes to create new Fe sites without boron as nearest neighbour. This leads to different local symmetries and hence to different QS. When Si concentration is further increased the next structural change occurs, observed in the experiment as a second step in $\overline{QS}$ vs. Fe concentration plot.

In the case of amorphous $Fe_xNi_{75-x}Si_{10}B_{15}$ alloys $\overline{QS}$ decreases continuously with increasing iron content (Fig. 2.). This suggests the gradual change of short range order from Ni-rich to Fe-rich compositions related to stronger chemical interaction between Ni and B than between Fe and B.

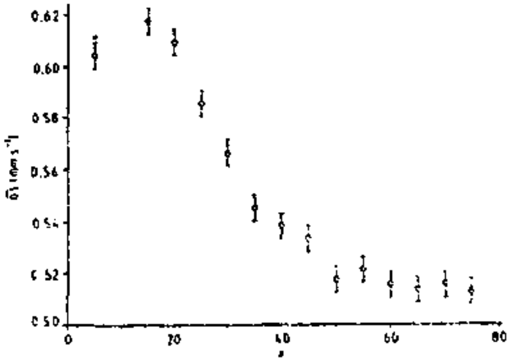

Fig. 2. Average quadrupole splitting $\overline{QS}$ against Fe concetration for $Fe_xNi_{75-x}Si_{10}B_{15}$ (o - determined from rf collapsed spectra, x - from paramagnetic spectra at room temperature)..

The results obtained show that by using the rf collapse effect reliable information about quadrupole splitting in ferromagnetic amorphous alloys can be obtained and provide valuable data about short range order. QS distributions are very sensitive to even small changes of the local structure which can not be seen in diffraction experiments. It is therefore important to use the QS data from Mössbauer experiments when testing the structural models.

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Comparison of X-ray - e^- Coincidence and Noncoincidence Conversion Electron Mössbauer Spectra

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The performance of the X-e^- coincidence technique for recording depth sensitive ^{57}Fe CEMS spectra was investigated.

1. Introduction

Conversion Electron Mössbauer Spectroscopy /CEMS/ is increasingly being used, as a nondestructive depth integrated or depth sensitive tool, for the analysis of the surface layers. The depth integrated technique is suitable for the identification of the chemical compounds comprising surface layers. In this technique almost all back scattered electrons are detected by an He/CH_4 flow proportional counter. For the ^{57}Fe isotope, these are the L-shell /13.6 keV/ and K-shell /7.3 keV/ conversion electrons as well as the K-LL /5.6 keV/ and L-MM /0.53 keV/ Auger electrons. The intensity ratios and the energy distributions of these originally monoenergetic beams of electrons are changed during the electron interaction in the scatterer. The contribution of each surface layer to the depth integrated CEMS spectrum originates from a few electron beams of different energies and thus of different penetration depth. This complicate interpretation of the depth integrated CEMS spectrum.

In a more detailed surface analysis the depth sensitive technique is used. It is based on knowledge of an electron energy distribution as a function of depth in the scatterer. The K-shell conversion electron line is usually selected by application of an electron spectrometer and the correlation between electron energy loss and the electron depth of the origin is utilized in depth profiling Mössbauer studies. The depth sensitive technique is time consuming due to very low transmission of an electron spectrometer. This limits wide applications of that technique.

The use of the He/CH$_4$ flow proportional counter and the X-e$^-$ coincidence technique in CEMS studies offers some sort of compromise between the depth resolution and the spectra storage time. The purpose of this paper is to investigate the performance of the He/CH$_4$ flow proportional counter and the X-e$^-$ coincidence technique for recording depth sensitive ^{57}Fe CEMS spectra.

Experimental technique

The He/CH$_4$ proportional counter has widely been used in depth integrated CEMS investigations. This is mainly due to its high counting efficiency and 2π geometry for scattered electrons. Up to now the energy resolution of the He/CH$_4$ proportional counter was thought to be very poor and therefore it was not taken into account in depth integrated CEMS investigations. However, the energy resolution of the He/CH$_4$ flow proportional counter is about 17.7% for the 6.36 keV electrons /1/. This allows selecting at least four nonoverlaping energy intervals within the 0 to 7.3 keV energy range and studying depth sensitivity of the CEMS spectra /2/. Iven if depth sensitivity of the counter is not sufficiently good for depth profiling CEMS investigations one should know how the experimental conditions, such as setting of discrimination levels or instability of gas stream, effect the results.

In order to improve depth sensitivity of the He/CH$_4$ flow proportional counter one should eliminate all contributions but the K-shell conversion-electron one to the CEMS spectra. This can be done, without a large decrease in the counting rate, by application of the X-e$^-$ coincidence technique. Our experiments were performed at room temperature using a ^{57}Co/Cr/ source and a constant acceleration Mössbauer spectrometer. Two Mössbauer absorbers were used in the experiments: a 90.7% ^{57}Fe enriched stainless steel foil and 90.6% ^{57}Fe enriched hematite and magnetite layers on an iron substrate. A duplex layer of hematite and magnetite was produced by oxidizing an iron foil at 623 K in 1013 hPa of air for 3.[illegible] hours. Hematite was the top layer, magnetite was the second layer and the iron substrate was the third layer of the investigated scatterer. The iron foil was neither polished no annealed prior to oxidizing. An one-wire He/CH_4 flow proportional counter was used for detection of electrons emerging from a scatterer surface. Conversion X-rays /6.47 keV/, produced inside the scatterer simultaneously with the K-shell conversion electrons /7.3 keV/, were registered by an Ar/CH_4 proportional counter which was placed just behind the resonant scatterer. The X-ray pulses were used for coincidence purposes /1, 2/.

. Results and discussion

In order to show the performance of the X-e^- coincidence technique for CEMS investigations the nuclear resonance contribution to the electron pulse-height spectrum /of the stainless steel scatterer/ was determined /Fig. 1/ with application /A/ and without application /B/ of the coincidence technique. The coincidence spectrum /A/ originates only from the K-shell conversion electrons. The intensity of the K-shell electron beam increases with the increase in electron energy /decrease in depth/ what should be expected. Apart from the K-shell conversion electrons, the L-shell conversion electrons and the K-LL Auger electrons are seen in the noncoincidence spectrum B.

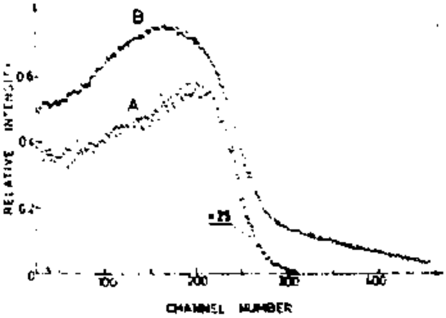

Fig. 1. The nuclear resonance contribution to the beam of back scattered electrons determined for the ^{57}Fe enriched stainless steel scatterer with /A/ and without /B/ application of the X-e^- coincidence technique.

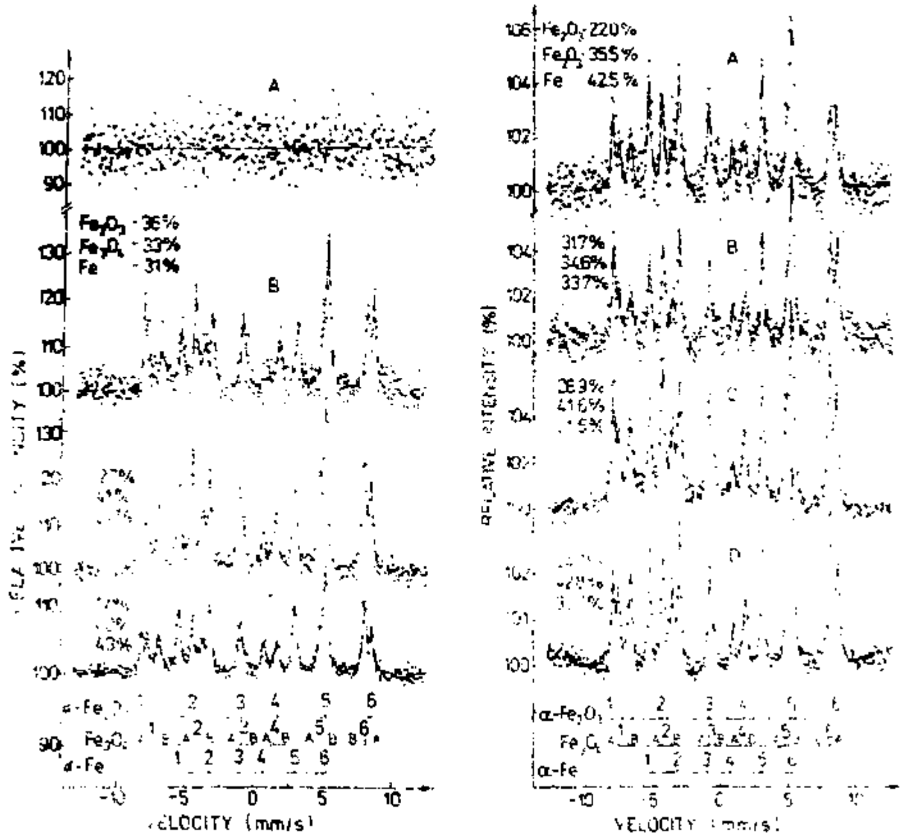

Fig.2. The coincidence /left/ and non-coincidence /right/ CEMS spectra simultaneously recorded for the upper /A/, two intermediate /B and C/ and lower /D/ energy intervals of electrons emerging from the duplex layer of hematite and magnetite on the iron substrate.

In study of the depth sensitivity of the coincidence and noncoincidence CEMS spectra we used the resonant scatterer composed of the duplex layer of hematite and magnetite on an iron substrate. Eight /four coincidence and the corresponding four non-coincidence/ CEMS spectra were simultaneously recorded /Fig. 2/ for four energy intervals of the electron pulse-height spectrum. The A spectra were recorded for electrons of highest energy while the D ones for electrons of lowest energy. Each CEMS spectrum can be decomposed into four Zeeman sextets. The outer sextet corresponds to the hematite layer /top layer/, the inner one to the iron substrate /third layer/ and the remaining two sextets are due to the A and B sublattices of the magnetite layer /second layer/. The positions of the peaks arising from various phases present and percentages of the total spectrum area contributed by each phase are indicated in Fig. 2. From their comparison the depth sensitivity of both coincidence and non-coincidence CEMS spectra is evident. The depth sensitivity is also vizualized by changes of line amplitude ratios of various phases. The top hematite phase is most pronounced in the B coincidence spectrum while the deepest iron phase in the D one what should be expected. The L-shell conversion electrons and the K-LL Auger electrons noticeably influence the non-coincidence CEMS spectra. The iron contribution to the non-coincidence spectrum A is the largest one while the hematite contribution is the smallest one. This CEMS spectrum originates mainly from the L-shell conversion electrons. There is no corresponding one recorded by the coincidence technique.

In conclusion, both the X-e^- coincidence and non-coincidence CEMS spectra recorded with the He/CH_4 flow proportional counter are depth sensitive. This property should be taken into account in the depth integrated investigations or may be utilized in the preliminary depth sensitive surface studies. The X-e^- coincidence technique improves depth sensitivity of CEMS spectra recorded with the He/CH_4 flow proportional counter.

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High Pressure Mössbauer Study of ^{197}Au in $Cs_2Au_2Cl_6$ and CsAu

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Abstract

Mössbauer spectra of ^{197}Au in $Cs_2Au_2Cl_6$, $Cs_2AuAgCl_6$, AuI and CsAu were studied up to 68 kbar. The pressure-induced changes in the isomer shift, δ, and the quadrupole splittings, Δ, of $Cs_2Au_2Cl_6$, $Cs_2AuAgCl_6$ and AuI suggest a positive sign of the electric field gradient at the Au^+ nuclei and a negative sign at the Au^{3+} nuclei. On this basis, the chemical bonds in the gold halides are concluded to be primarily ionic. The Mössbauer spectra shown that the Au^+ and Au^{3+} ions are distinguishable up to 45 K in the high pressure state of $Cs_2Au_2Cl_6$. Thus, the averaging of the Au valence states observed at 52 kbar with x-ray diffraction is a dynamical process with a relatively long relaxation time due to the corner sharing topology of coordination octahedra. The spectra of CsAu suggest a phase transition from the CsCl-type structure to a structure of lower symmetry, at a pressure somewhat below 27 kbar. The transition is indicated by an increase of Debye temperature, a decrease of the isomer shift, and the occurence of a quadrupole splitting in the high-pressure phase.

Introduction

The structure of $Cs_2Au_2Cl_6$ is related to perovskite $CaTiO_3$ with [illegible], and Cl atoms corresponding to the positions of Ca, Ti, and O. According to the most recent single crystal x-ray diffraction data /1/, it consists of chains of distorted, corner-sharing $AuCl_6$ octahedra. The Au^+ and Au^{3+} ions are ordered and occupy the crystallographically nonequivalent positions 2a and 2b of space group I4/mmm, with typical square and linear elongations of the coordination octahedra as shown in Fig. 1.

Cesium gold chloride shows interesting phenomena under high pressure. With increasing pressure the Cl atoms shift gradually towards an apparently symmetrical position between the gold atoms that is attained at 52 kbar /1/. As a result the gold atoms assume geometrically pseudoequivalent positions. They become indistinguishable from a crystallographic point of view, possessing a nominal valence state of +2. This structural change is associated with a strong continuous increase in the electrical conductivity by nearly nine orders of magnitude from ambient pressure to 60 kbar /2/.

The Mössbauer measurements beyond pressures at which critical changes in structural geometry and electric conductivity occur, should provide a microscopic insight into the electronic state of Au in $Cs_2Au_2Cl_6$ at high pressures. Moreover, results of $Cs_2AuAgCl_6$ and [illegible] are also presented. The crystal structure of $Cs_2AuAgCl_6$ is [illegible] the same as that of $Cs_2Au_2Cl_6$, with Ag^+ replacing Au^+. Its behaviour at high pressures is expected to be similar to $Cs_2Au_2Cl_6$. AuI is assumed to be the most stable aureus halide. Its crystal structure (space group $P4_2/ncm$) consists of long zigzag polymer chains of Au-I /3/. A comparison of Mössbauer data of $Cs_2Au_2Cl_6$, $Cs_2AuAgCl_6$ and AuI will provide some new information about chemical bonding of gold halides and allows a discussion of $Cs_2Au_2Cl_6$ results on a related basis.

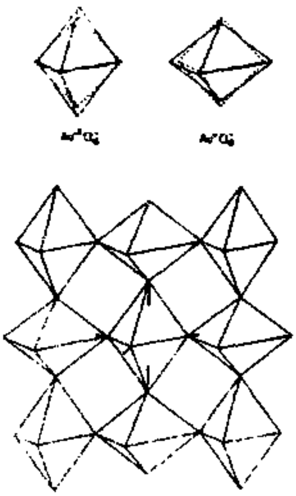

Fig.1. Crystal structure of $Cs_2Au_2Cl_6$ at [illegible] bar. Arrows show the direction and relative amplitudes of Cl^- ions shifts when pressure is applied.

The intermetallic compound CsAu crystallizes in the CsCl-type (B2) structure. Its band gap has been measured /4,5/ as 2.[illegible] eV at room temperature. The lattice constant is reported to be 4.263 Å /6,7/. The semiconducting compound melts at 59[illegible] °C to a liquid with predominantly ionic conduction /7/. The photo-emission valence-band data /8,9/ [illegible] with the relativistic Korringa-Kohn-Rostoker (KKR) band-structure calculation /10,11/. [illegible] this calculation a significant charge transfer from the cesium to the gold site is [illegible]. The latter is consistent with measurements of the Mössbauer isomer shifts /12/.

A recent total-energy calculation /13/ for CsAu predicts a pressure-induced phase transition from the B2 to the B32 NaTl structure at pressure of about 45 kbar; in the framework of this theory where only these two structures are compared. The present study was undertaken in order to extend the earlier zero-pressure Mössbauer measurements /12/ to higher pressures and in particular to explore the suggested pressure-induced phase transition /13/.

Experimental

a/ Mössbauer spectroscopy of [illegible] Au.

The methods and results of Mössbauer spectroscopy [illegible] reviewed, e.g. in /14/. [illegible] a few relevant details [illegible]. Due to the relatively high energy of the Mössbauer transition [illegible] ^{197}Au (77.4 keV) the measurements were carried out at [illegible] temperature. A source of 200 mCi [illegible] with a half-life [illegible] obtained in a nuclear reactor from the [illegible](n,γ)[illegible]. The nuclear spins of ^{197}Au in excited and ground state are [illegible], respectively. Since the radius of the [illegible] Au nucleus in the [illegible] state is greater than in the ground state δ of [illegible] Au is [illegible] proportional to the electron density at the nucleus. The half-life time of the 77.4 keV nuclear level is 1.89 ns which corresponds to a natural linewidth of 1.882 mm/s, i.e. several times smaller than observed differences in δ and Δ of different valence states of Au.

b/ High pressure apparatus.

The apparatus for high pressure Mössbauer studies was similar to the one described, e.g. in /15/. The absorber pellet / 4 mm in diameter/ was placed between two B_4C anvils. For CsAu case the pelet was formed and sealed into thin plastic bag under argon atmosphere. Pressure was applied at room temperature and maintained using a copper-berylium clamp while the system was cooled to liquid He temperature. The effective pressure on the sample at room temperature was determined with a bismuth-wire calibrant. At 4.2 K a lead manometer was used for pressure calibration.

Results

a/ Gold halides /16,17/.

^{197}Au spectra of $Cs_2Au_2Cl_6$ were taken at 1 bar /4.2 and 25 K/ and at 68 kbar /2.1, 4.2, 25 and 45 K/. Some spectra are shown in Fig. 2.

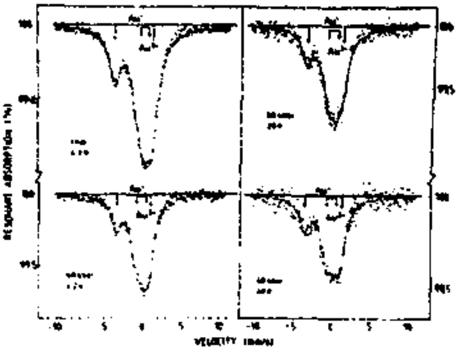

Fig. 2. ^{197}Au spectra of $Cs_2Au_2Cl_6$ taken at different pressures and temperatures.

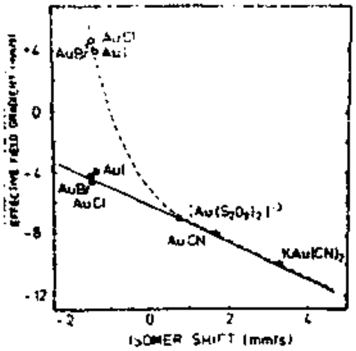

Fig. 3. The isomer shift - electric field gradient relationship for Au^+ compounds. Solid line, cf. Ref/18/, broken line, cf. this work.

In each case the spectrum consists of two lines of different intensities. The stronger line is a sum of the unresolved Au^{3+} quadrupole doublet and the low-energy line of the Au^+ doublet, the weaker line being the high-energy line of the latter. Because $Au^{3+}/Au^+ = 1$ in stoichiometric $Cs_2Au_2Cl_6$ the intensity ratio of the two apparent lines should be in a first approximation 3:1. In fact, the experimental ratio is about 5:1. This discrepancy was explained by the determined difference in recoil-free fractions of Au^+ /0.039/ and Au^{3+} /0.080/ at 4.2 K.

In $Cs_2Au_2Cl_6$ [illegible] of δ_{Au^+}, $\delta_{Au^{3+}}$ and $\Delta_{Au^{3+}}$ is induced. No pressure dependence of Δ_{Au^+} was found beyond the limit of experimental error. For $Cs_2AuAgCl_6$ a decrease of δ_{Au^+} and an increase of Δ_{Au^+} could be established. In AuI an increase of δ and a decrease of Δ with increasing pressure were found.

For the electronic state of Au^+ two alternatives are considered: /i/ $5d^{10}(6s6p)^N$ configuration, where N is a varying degree of covalency. The electric field gradient, V_{zz} is negative. /ii/ $5d^{10-x}6s^x$ state. In this case two anionic ligands "press" $5d_{z^2}$ electron density into 6s orbital. The $5d_{z^2}$ "hole" in the otherwise fully occupied $5d^{10}$ shell produces a possitive V_{zz}.

Square-planar Au^{3+} complexes are usually interpreted in terms of $5d^8(5d6s6p^2)^N$ orbital configuration. The two electron holes in the $5d_{x^2-y^2}$ orbital produce a negative contribution to the electric field gradient, while the partly filled $5d6s6p^2$ hybrid yields a positive one.

The pressure induced change in the crystal structure of $Cs_2Au_2Cl_6$, and most probably of $Cs_2AuAgCl_6$, is rather unusual. The Au-Cl distances in the $(Au^+Cl_2)^-$ and the $(Au^{3+}Cl_4)^-$ complexes of the coordination polyhedra increase gradually up to 52 kbar. So, the decrease of δ in $Cs_2Au_2Cl_6$ and $Cs_2AuAgCl_6$, and its increase in AuI with increasing pressure are indicative of a strengthening and weakening of σ bonds due to decrease and increase of overlap integrals, respectively.

The pressure induced decrease of Δ_{Au^+} can be well interpreted using both models of bonding for the $(Au^+Cl_2)^-$ complex. Considering the 6s6p hybridization the increase of Au-Cl distances causes a decrease of $6p_z$ population and a decrease of the absolute value of the negative electric field gradient. In the frame of $5d_{z^2}6s$ hybridization transformation to the octahedral coordination lead to refilling of the hole in the $5d_{z^2}$ orbital and to a decrease of the positive EFG. Because both models appear adequate, a high pressure Mössbauer experiment was carried on AuI.

The nearest Au-I distances in AuI are expected to decrease with increasing pressure, which is consistent with increase of δ, yielding an increase of $6p_z$ population, i.e., an increase of the negative contribution to the total EFG. Experimentally, a decrease of Δ was observed. Thus, it is concluded that the positive contribution dominates. Previously, a negative sign was assumed for EFG in the univalent gold compounds /18,19/ based on 6s6p bonding. However, the sign was determined only for $KAu(CN)_2$ /20/. It is believed, that it may be well reversed in AuCl, AuBr, AuI and $Cs_2Au_2Cl_6$ due to 5d6s rather than 6s6p bonding.

The conclusion of a positive sign for Δ in these compounds is not inconsistent with the general δ-Δ relation for Au^+ compounds /Fig. 3/. A positive Δ, with increasing magnitude in the sequence AuCl, AuBr, and AuI would yield a more proper relationship in terms of a decreasing degree of ionicity.

For Au^{3+} the increase of the Au-Cl distances within xy plane should, with increasing pressure, decrease the positive contribution. An increase of Δ was observed unexpectedly in $Cs_2AuAgCl_6$, showing that initially the EFG was negative. So far a negative EFG in Au^{3+} compounds has been predicted only in the case of AuF_3.

In the view of the geometrical pseudoequivalency of the two Au positions in $Cs_2Au_2Cl_6$ a zero energy difference between the filled Au^+ electronic state and the empty Au^{3+} state can be assumed. As result fast electronic exchange between Au^+ and Au^{3+} producing an apparent average Au^{2+} state might be expected. However, the Mössbauer spectra show that this is not the case up to pressure of 48 kbar and temperature of 45 K. Fast electron hopping in this case is primarily excluded because of the topology of $Cs_2Au_2Cl_6$ structure, in which the coordination octahedra share corners and Au^+ and Au^{3+} orbitals do not overlap directly /cf. Fig. 1/.

b/ Phase transition in CsAu /21/

Samples of CsAu were synthesized by melting the stoichiometric amounts of Cs and Au in a vacuum-tight molybdenum crucible at 5[illegible] °C. Two samples (Ia) and (Ib) were cooled to room temperature within minutes, while a third sample (II) was cooled down over a few hours. Further examination revealed that sample (II) contained many more additional phases than samples (Ia) and (Ib). All three samples were dark brown with a tiny yellow glitter. In open air they changed to yellow color.

The 4.2 K Mössbauer spectra of CsAu were taken at 1 bar, 27, [illegible], and 40 kbar. The spectra of sample Ib, covered with a metallic gold foil, are shown in Fig. 4.

At 27 kbar a substantial decrease of δ occurs in CsAu (δ(1 bar) - δ(27 kbar) = 0.2 mm/s). This change of δ is significant. It is greater than the difference in δ between RbAu and CsAu, both compounds being semiconductors, but it is smaller than the difference between Au in Li /metal/ and CsAu /semiconductor/. Thus, the obtained results supply no hint whether the postulated high-pressure phase is still semiconductor or metal.

There are several possible contribution to the change in δ of ^{197}Au at high pressure. Just a depopulation of 5d shell would lead to an increase of δ. This is inconsistent with the experiment. Contribution from some population of 6p orbitals is negligible. Thus, the observed decrease of δ must be caused primarily by a direct depopulation of 6s.

Probably the most striking evidence of the structural and chemical transformation of CsAu at high pressure is the pressure-induced Δ observed above 27 kbar. The crystal structure of the high-pressure phase is not known. The observed Δ suggests, however, that it cannot be due to the NaTl (B32)-type structure /13/ phase which requires cubic point symmetries for both atomic positions. A more likely structure for the high-pressure CsAu phase is a simple distortion of the CsCl type along one of the four [111] directions.

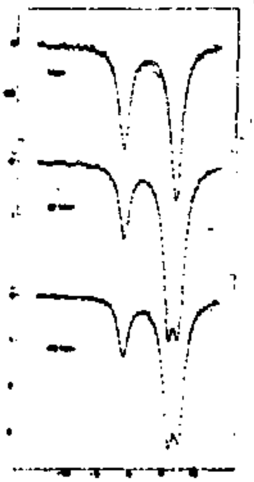

Fig. 4. Mössbauer spectra of CsAu covered with metallic gold foil.

The observed Δ indicates that the spherical symmetry of the $5d^{10}6s^2$ shell of Au^- is no longer maintained. In ionic Au^+ compounds, gold is linearly coordinated due to 6s6p hybridization. Assuming the same linear configuration, 6s6p hybridization can be also assumed for Au^-. In other words, the fundamental indirect energy gap between the 6s valence band the conduction 6p band at X point of the Brilloun zone closes at high pressure. Such tendency is clearly visible from the results of band-structure calculation in the series of CsAu, RbAu, and KAu /11/. It should be noted that mercury, being isoelectronic to Au^- strongly favors the linear coordination, also due to 6s6p hybridization.

From the spectra of CsAu which was superimposed by a foil of metallic gold it was possible to estimate the ratios of the recoil-free fractions. Next, using the known pressure dependence of the Debye temperature, Θ_D, of metallic gold, it was possible to determine the variation of the Debye temperatur of CsAu with pressure. It turned out, that Θ_D(CsAu) = 72 K at 1 bar increases to 96 K and 99 K at 27 and 40 kbar, respectively.

The observed strong and probably abrupt increase in Debye temperature, the pressure induced quadrupole splitting, Δ, and the jump in isomer shift, δ, are evidences for a pressure induced change in crystal structure and in chemical bonding of Au in CsAu.

Acknowledgments

The author wishes to thank Professor S.S. Hafner from the Institute of Mineralogy, University of Marburg, for suggesting the subject of this studies, his permanent interest and stimulating discussions. The samples of $Cs_2Au_2Cl_6$ and $Cs_2AuAgCl_6$ were kindly provided by Professor H. Schulz from the Max Planck Institute, Stuttgart. The samples of CsAu were prepared by N. Nicoloso and M. Gerlach. The sources of ^{197}Pt were activated at the Kernforschunsanlage Jülich and at Kernforschungszentrum Karlsruhe. The experiments were supported by the Deutsche Forschungsgemeinschaft, Grant SFB 127, and by the Alexander von Humboldt Foundation.

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SELF-CORRELATION FUNCTIONS FOR IMPURITY DIFFUSION IN HEXAGONAL LATTICES

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If one considers monoatomic hcp-like lattices containing a dilute impurity in the lattice sites and diffusing within the encounter model [1] via the lattice sites and due to the monovacancy mechanism the situation becomes much more complex as compared to the situation encountered in the corresponding cubic lattices [2]. The macroscopic symmetry is no longer spherical but rather cylindrical and therefore coordinate shells [2, 3] have to be indexed by two independent indices. Even and odd layers have to be distinguished, too /see Fig. 1/. A five-frequency model [4] has to be generalized to a 16-frequency model, what leads to 13 normalized frequencies in contrast to the situation encountered in the fcc-lattice /3 normalized frequencies/ and bcc or sc-lattices /2 normalized frequencies/. A diagram [2] becomes thus quite complicated /see Fig. 1/.

A natural simplification occurs for two distinct cases, i.e. for a hcp lattice /3 normalized frequencies/ or for a self-diffusion /1 normalized frequency u_o/. The latter case has been studied more detaily and some relevant results are summarized in Figs. 2 and 3.

A detailed report of this study is to be published elsewhere.

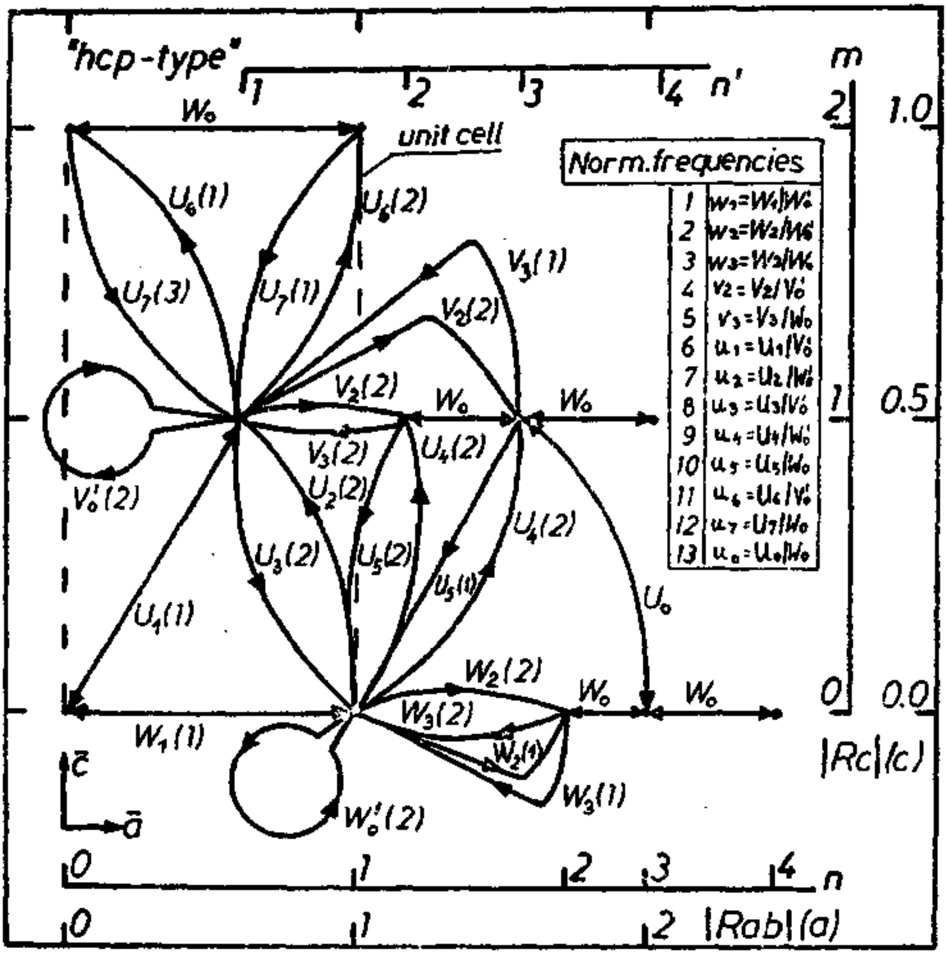

Fig. 1. A diagram for a hcp-like lattice. This diagram is a generalization of diagrams for cubic lattices [2]. Only few W_o and U_o routes are shown.

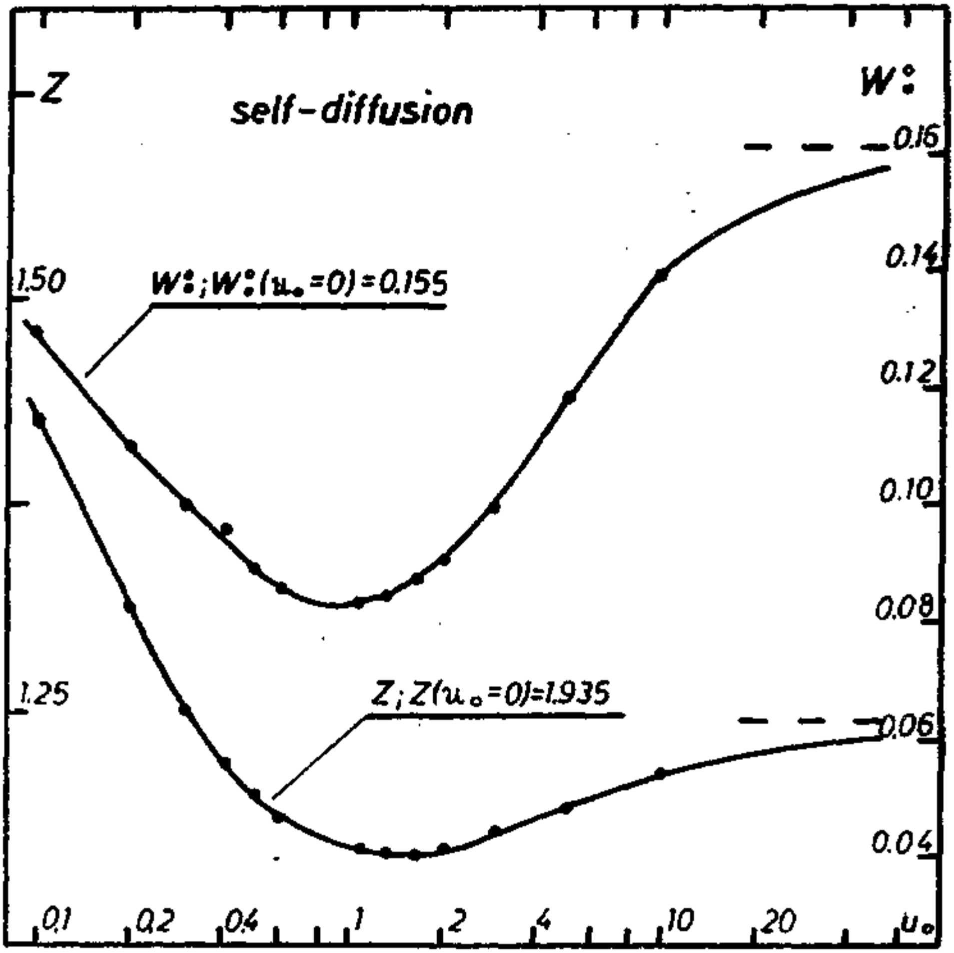

Fig. 2. W_o^o /probability to come back to the origin during an encounter/ and Z /average number of impurity jumps per encounter/ plotted versus normalized frequency u_o.

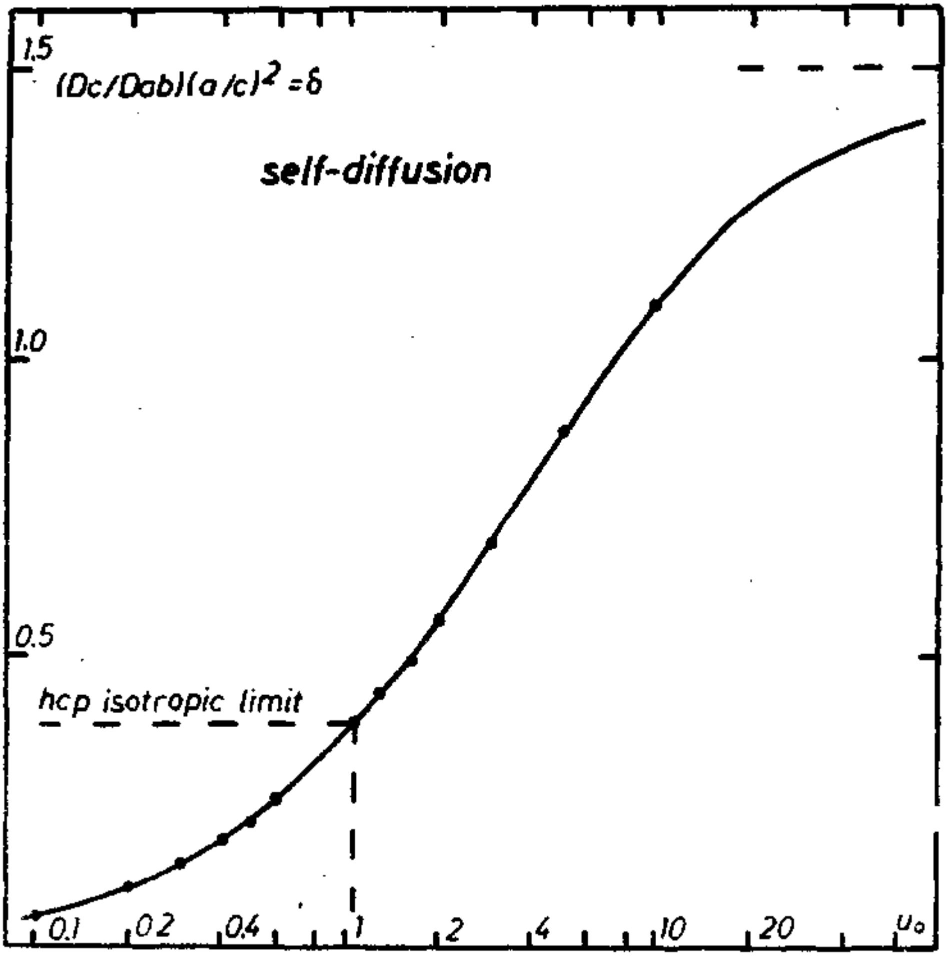

Fig. 3. δ /reduced anisotropy of the diffusion coefficient/ plotted versus u_o. Note, that for u_o=1 in the hcp lattice diffusion is slightly anisotropic due to the higher order loops in the diagram. For such a case a naive "empty lattice" approximation gives a completely isotropic diffusion coefficient.

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GOLDANSKII-KARYAGIN EFFECT AND EXTERNAL MAGNETIC FIELD METHOD AS TOOLS TO MEASURE ANISOTROPY OF THE RECOILLESS FRACTION IN AMORPHOUS MATERIALS

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Diffraction of X-rays or neutrons can not be used to obtain details about the atomic vibrational anisotropy in the case of amorphous materials due to the lack of well-defined Bragg reflections. Mössbauer spectroscopy can yield some model independent information in such cases, either via the Goldanskii-Karyagin effect /GKE/ or by applying a magnetic field, preferably along the beam axis. The latter method /EMFM/ can be applied to the preferably diamagnetic samples exhibiting an electric quadrupole interaction /preferably significantly non-axial/ and the magnetic field should be chosen in such a way as to produce significant off-diagonal elements in the hyperfine hamiltonian. The external magnetic field method /EMFM/ is capable of yielding much more information than the Goldanskii-Karyagin effect in most cases, provided sufficiently strong magnetic fields are available. Both methods require high nuclear spins and relatively high transition energies for general applications, but the external magnetic field method /EMFM/ does not rely upon high mixing ratios required in the application of the Goldanskii-Karyagin effect /GKE/.

A detailed theory of both methods and some results of EMFM simulations performed for a ^{129}I /27.77 keV/ Mössbauer transition have been published previously [1].

Here, we would like to present a short summary of some recent EMFM simulations performed for a ^{127}I /57.60 keV/ Mössbauer transition. The spectra have been calculated for the following set of parameters /for a detailed explanation of symbols see [1]/:
$I_e = 7/2$, $I_g = 5/2$, $L_0 = 1$; $N = 259$, $M = 6$; $B_0 = 10^7$ /counts/, $f_s/\lambda = 0.1$, $t = 2.0$, $\Gamma_s = \Gamma_a = 1.245$ /mm/s/, $p = 0$, $a_2^1 = 0$, $g_e/g_g = 0.6463$, $(Q_e/Q_g)\{[I_g(2I_g-1)]/[I_e(2I_e-1)]\} = -0.4265$, $\delta_0 = 0$, $a_0 = 3.0513$ /mm/s/ for the ground state /equivalent to $H' = 7.92$ /T/ and $H = 8$ /T//, $A_0 = 1.2282$ /mm/s/ for the ground state /equivalent to the NQR frequency of 1100 MHz/, $\eta = 0.2$, $S = 0$ /mm/s/, $\alpha_0 = \beta_0 = \gamma_0 = 0$ and variable A and B. It has been assumed, that: $\vec{H} \times \vec{k} = 0$ and the grid 20 x 20 over the full sphere was used. The velocity span taken into account was ± 26.7675 /mm/s/. The spectrum calculated for $A = B = 0$ has been compared with the spectra calculated for A and B satisfying a relationship $g_{11}^1 = 1$, i.e. along the track Z for $g_{11}^1 = 1$ of Fig. 4 of reference [1]. The resulting χ^2 is summarized in Table 1 and plotted versus Z in Fig. 1. It has to be noted, that $q_{127}^2 = 4.3018\ q_{129}^2$ and therefore a lower resolution of ^{127}I spectra is compensated to some extent by the increased transition energy as compared to the ^{129}I spectroscopy.

Finally, we would like to comment, that the software being able to process spectra obtained within both methods is readily available from the MOSSLIB library [1 - 4].

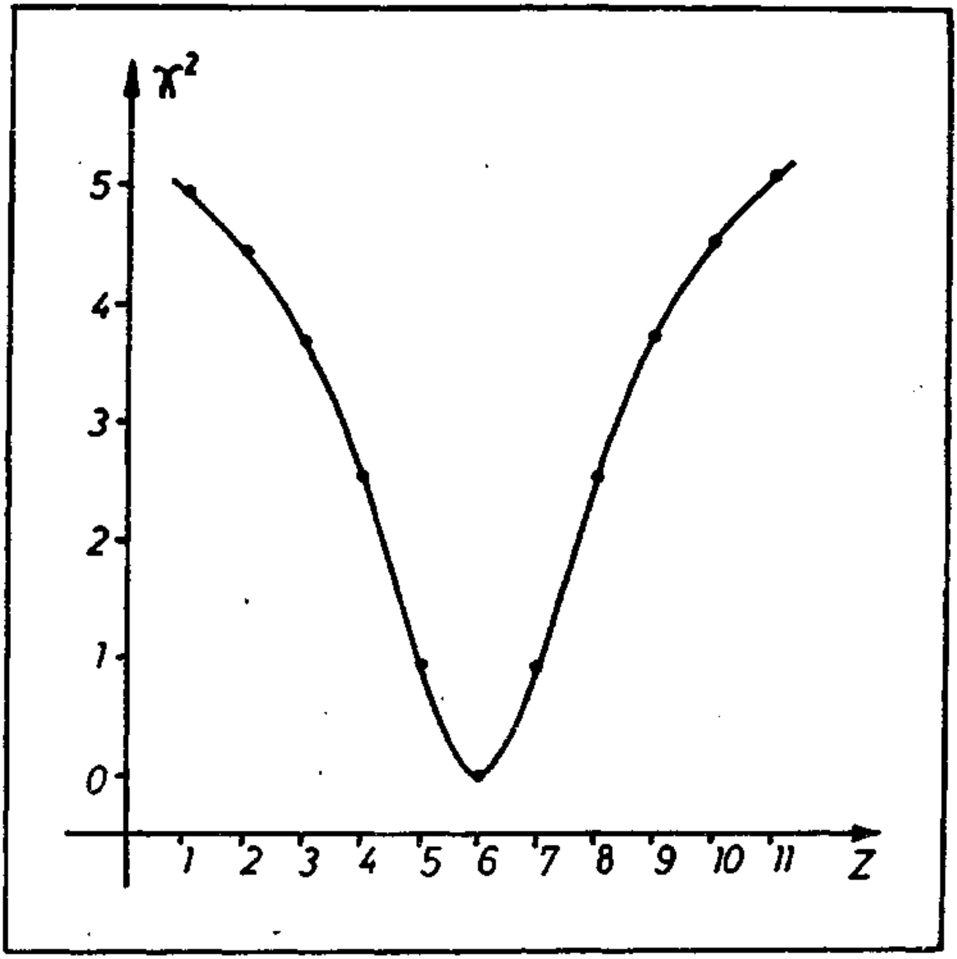

Fig. 1. χ^2 plotted versus Z.

Table 1

Results of simulations.

A	B	Z	χ^2
-8.6966	-10.0	1	4.93
-6.7328	-8.0	2	4.43
-4.7993	-6.0	3	3.68
-2.9402	-4.0	4	2.52
-1.2697	-2.0	5	0.93
0.0	0.0	6	0.00
0.7303	2.0	7	0.93
1.0599	4.0	8	2.53
1.2007	6.0	9	3.73
1.2672	8.0	10	4.52
1.3034	10.0	11	5.05

Prof. T.Birchall, Dept. of Chemistry, McMaster University, Hamilton, Ontario, Canada is deeply appreciated for pressing us strongly to perform ^{127}I simulations, the latter being necessary in planning future experiments.

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MÖSSBAUER STUDY OF FERROUS GLUCONATE

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Ferrous gluconate $Fe/C_6H_{11}O_7/_2 \cdot 2H_2O$ was investigated by means of ^{57}Fe /14.4 keV/ - Mössbauer spectroscopy and thermogravimetry. Mössbauer study was performed in the temperature range 77-423 K. It has been found, that Fe^{2+} occupies two distinct Mössbauer sites in the hydrated phase. One of these sites having larger isomer shift and quadrupole splitting disappears upon dehydration. This "water coordinated" site is five times more abundant then the other site in the fully hydrated phase. All the samples have been found to be contaminated by some amount of Fe^{3+}. A significant oxidation occurs at the dehydration temperature /about 378 K/ at least for the samples exposed to the air. No Goldanski-Karyagin effect has been detected in contrast to the previous claim [1]. It has to be noted, that the crystal structure of the ferrous gluconate is unknown.

A detailed report of this study is to be published elsewhere.

Ms. J. Inasińska, Dept. of Chemistry, Jagiellonian University, Cracow, Poland is warmly thanked for performing thermogravimetric measurements. Dr E. Wenda, Dept. of Chemistry, Jagiellonian University, Cracow, Poland is acknowledged for preparation of one of the samples and for performing iodometric analyses.

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DOUBLE ELECTRON EXCHANGE IN $Fe_{1-x}O$: A MoßBAUER STUDY

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INTRODUCTION

The lowest iron oxide, wustite, exists as a stable phase only above 570°C. Wustite has a sodium chloride structure but at atmospheric pressure is always nonstoichiometric, and can be represented by $Fe_{1-x}O$, where x varies between 0.05 and 0.15. The lack of Fe^{2+} ions results in existence of cation vacancies in octahedral sites, and in order to impose electrical neutrality Fe^{3+} ions must be present.

The occupation of interstitial (tetrahedral) sites by some Fe^{3+} ions and the defect aggregation in wustites is now very well established. The presence of Fe^{2+} and Fe^{3+} ions, both of them in various surroundings because of defect structure, results in extensive studies of hyperfine interactions in wustites by means of Mößbauer spectroscopy.

The Mößbauer effect studies were reviewed by Gohy *et al.* [1] in general and by Gavarri *et al.* [2] from the structural point of view. All the spectra of nonstoichiometric wustites recorded by different authors have a similar overall shape of an asymmetric doublet but they have been analyzed in different ways. These different analyses have been related to different interpretations. Two problems should be pointed out when considering the literature data i.e. electron exchange between Fe^{2+} and Fe^{3+} ions and poor agreement between the Fe^{3+} concentration deduced from the Mößbauer data and the chemical analysis results. The localization of Fe^{3+} ions and their behaviour in wustites was the aim of our studies.

EXPERIMENTAL

Five samples of different composition ($0.05<x<0.094$) were prepared by heating the mixture of appropriate amounts of metallic iron and α-Fe_2O_3 in evacuated silica tubes at about 930-950°C for 20 hours. The samples were quenched by rapid extraction from the furnace. The stoichiometry of wustites was determined by thermogravimetric oxidation to Fe_2O_3. The samples of following composition were obtained: $Fe_{0.9[illegible]}O$, $Fe_{0.920}O$, $Fe_{0.9[illegible]}O$, $Fe_{0.9[illegible]}O$ and $Fe_{0.906}O$.

The Mößbauer measurements were performed at room temperature using a conventional spectrometer. A ^{57}Co (Cr) source was used and γ-rays were detected by means of a Kr-filled proportional counter. The velocity scale was calibrated thanks to spectra of a natural isotopic abundance α-Fe foil. Spectra were analyzed within the transmission integral approximation using a CYBER computer and the most recent version of GMFP5S program [3].

RESULTS & DISCUSSION

The Mößbauer spectra recorded at room temperature are shown in FIGURE 1. They have similar shape from, a well-resolved asymmetric doublet for the sample of the lowest stoichiometry ($Fe_{0.906}O$) to a weakly-resolved doublet for the sample of the highest stoichiometry ($Fe_{0.950}O$).

Spectra were analyzed using the following model: two doublets were assigned to the iron ions in octahedral sites and one singlet was assigned to the Fe^{3+} ions in tetrahedral sites. The results of data fitting are summarised in TABLE 1.

The dependences of quadrupole splitting Δ and of isomer shift δ on the wustite composition for both doublets are shown in FIGURE 2 and FIGURE 3 respectively.

It is worth noticing that both the maxima on plots of quadrupole splitting and the slope changes on plots of isomer shifts occur near the same composition of $x \sim 0.08$. In this region a transition semiconductor-"*metal*" was recently found [4].

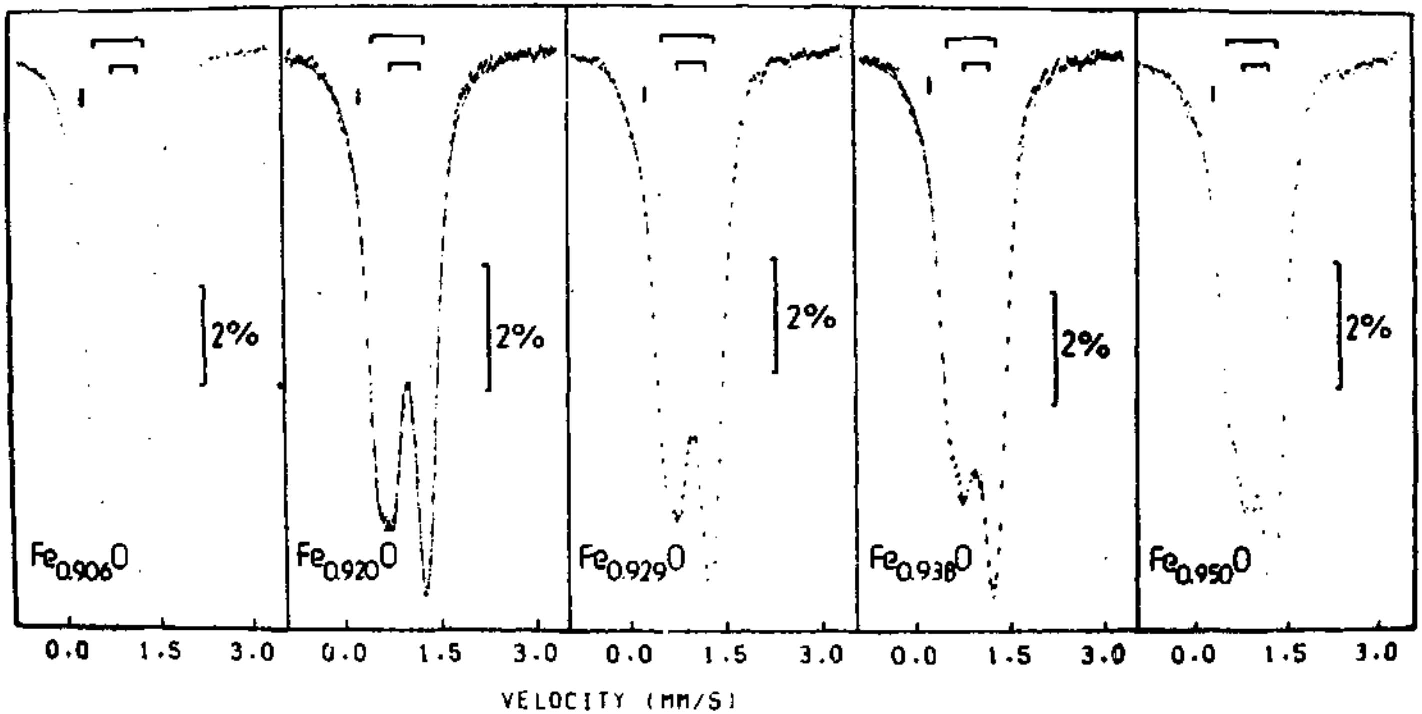
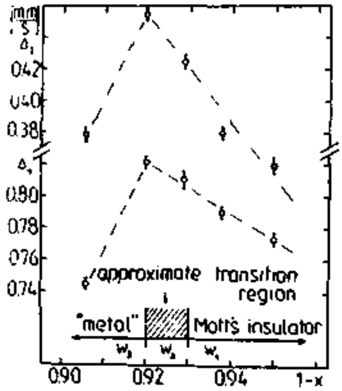


FIGURE 1   Mößbauer spectra of wustites recorded at room temperature.

TABLE 1 Mößbauer resonance parameters for Fe$_{1-x}$O

1-x	Doublet No 1			Doublet no 2			Singlet		
	Δ_1	δ_1	A_1	Δ_2	δ_2	A_2	δ_3	A_3	A*
	(mm/s)		(%)	(mm/s)		(%)	(mm/s)	(%)	(%)
0.906	0.745 ±0.002	0.902 ±0.009	60.4 ±0.9	0.379 ±0.004	0.968 ±0.009	35.3 ±0.9	0.272 ±0.011	4.3 ±0.2	20.8
0.920	0.822 ±0.004	0.925 ±0.009	43.5 ±1.4	0.455 ±0.005	0.972 ±0.009	52.0 ±1.4	0.270 ---	4.5 ±0.3	17.4
0.929	0.811 ±0.004	0.926 ±0.009	42.3 ±1.3	0.424 ±0.004	0.983 ±0.009	55.6 ±1.3	0.230 ---	2.1 ±0.2	15.3
0.938	0.791 ±0.004	0.921 ±0.009	41.8 ±1.3	0.379 ±0.004	0.998 ±0.009	57.8 ±1.3	0.200 ---	0.4 ±0.2	13.2
0.950	0.773 ±0.005	0.933 ±0.009	38.9 ±1.7	0.359 ±0.004	1.023 ±0.009	59.9 ±1.7	0.200 ---	1.2 ±0.4	10.5

(*) Amount of Fe^{3+} ions according to thermogravimetric data



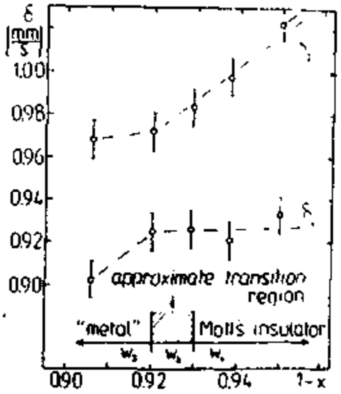


FIGURE 2 Dependence of quadrupole splitting Δ on the composition of wustites for both doublets.

FIGURE 3 Dependence of isomer shift δ on the composition of wustites for both doublets.

One can easily see from TABLE 1 that the content of Fe^{3+} ions deduced from Mößbauer data is much lower than that expected from the thermogravimetric oxidation. Also the isomer shifts of both doublets are lower than that for Fe^{2+} ions in octahedral sites. It means that Fe^{3+} ions must contribute to both doublets. Under some assumptions the contributions of Fe^{3+} ions to doublet No 1 (y) and to doublet No 2 (z) were calculated from the following relations:

$$\delta_1 = y\,\delta_{Fe^{3+}} + (A_1 - y)\,\delta_{Fe^{2+}}$$
$$\delta_2 = z\,\delta_{Fe^{3+}} + (A_2 - z)\,\delta_{Fe^{2+}}$$

The results of calculations are shown in FIGURE 4 where also the total amount of Fe^{3+} ions from the Mößbauer data in comparison to the thermogravimetrically determined Fe^{3+} ions content is drawn. An agreement between those two methods of determination of Fe^{3+} ions content was quite good.

The above presented results confirm the hypothesis that the defect structure in wustite is very complicated and that it changes depending on the stoichiometry. Two doublets result probably from two kinds of clusters, which are more or less stable in the range of pseudophase (see FIGURE 4).

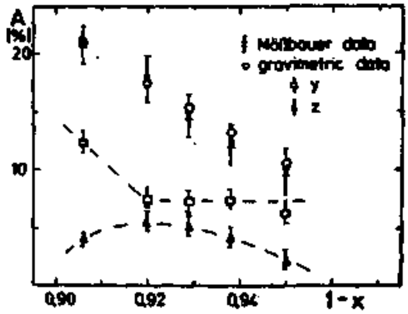


FIGURE 4 Content of Fe^{3+} ions deduced from Mößbauer data and from chemical analysis.

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THE MößBAUER STUDIES OF THE MODEL IRON CATALYSTS FOR AMMONIA SYNTHESIS

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INTRODUCTION

Ammonia, one of the most important products and half-finished products in the inorganic chemical industry is obtained in the catalytic synthesis from nitrogen and hydrogen (in a determined conditions of temperature and pressure). This synthesis is carried out on the iron catalyst. The iron catalyst for ammonia synthesis is produced in two steps. First, iron oxides (magnetite ore) are fused with the unreducible promoters (the appropriate oxides of mono-, di- or trivalent metals) at high temperatures. The obtained spinel-type structure is then reduced giving the active catalyst. In the active form of the catalyst the important role play such promoters as Al_2O_3, which improves the texture of the contact and K_2O which is called the *chemical promoter* because it influences the catalytic activity. The quality of the active catalyst depends on the composition of the catalyst in unreduced form as well as on reduction process. In unreduced form the catalysts contain magnetite, wustite and promoters. Because of the presence of iron in different phases in the catalyst, the Mößbauer spectroscopy is a good tool for a characterization of the catalysts [1-4].

EXPERIMENTAL

The investigated samples were of the same type as the industrial iron catalysts for ammonia synthesis containing magnetite, wustite and promoters.

Eight model catalysts e.g. unpromoted, singly promoted (with alumina or potassium oxide) and doubly promoted (with alumina and potassium oxide) each of them containing large (about 30 wt %) or small (about 9 wt %) amount of wustite have been studied by Mößbauer spectroscopy. The composition of the samples is given in TABLE 1.

TABLE 1 Variation in Composition of Samples

	Sample	Content of FeO (wt%)	Content of Al_2O_3 (wt%)	Content of K_2O (wt%)
V	unpromoted	traces	0.36	-
W		32.88	0.26	-
AlV	promoted with Al_2O_3	traces	3.90	-
AlW		21.15	4.28	-
KV	promoted with K_2O	traces	0.32	0.67
KW		21.71	0.27	2.26
KAlV	promoted with Al_2O_3 & K_2O	9.09	3.71	1.49
KAlW		28.43	3.06	1.78

Symbol **V** denotes a small amount of wustite
Symbol **W** denotes a large amount of wustite

The Mößbauer measurements were performed at room temperature using a conventional spectrometer. Spectra were analyzed within the transmission integral approximation. A model of two sextets attributed to magnetite and of one doublet and one singlet attributed to wustite was used for calculations.

RESULTS & DISCUSSION

Some examples of Mößbauer spectra of the model catalysts are shown in FIGURE 1.

In view of the results of the analysis of all spectra the following conclusions may be drawn:

- Isomer shifts of both sites in magnetite *do not depend* on the promoter content.
- Addition of potassium oxide to the catalysts *does not change* the magnetic field in both sites of magnetite.
- Addition of alumina to the catalysts *decreases* the magnitude of magnetic field in both sites of magnetite - approximately there is a linear correlation between the magnetic field and alumina content (see FIGURE 2)
- The Mößbauer parameters of wustite phase *do not depend* on the presence of alumina and potassium oxide.

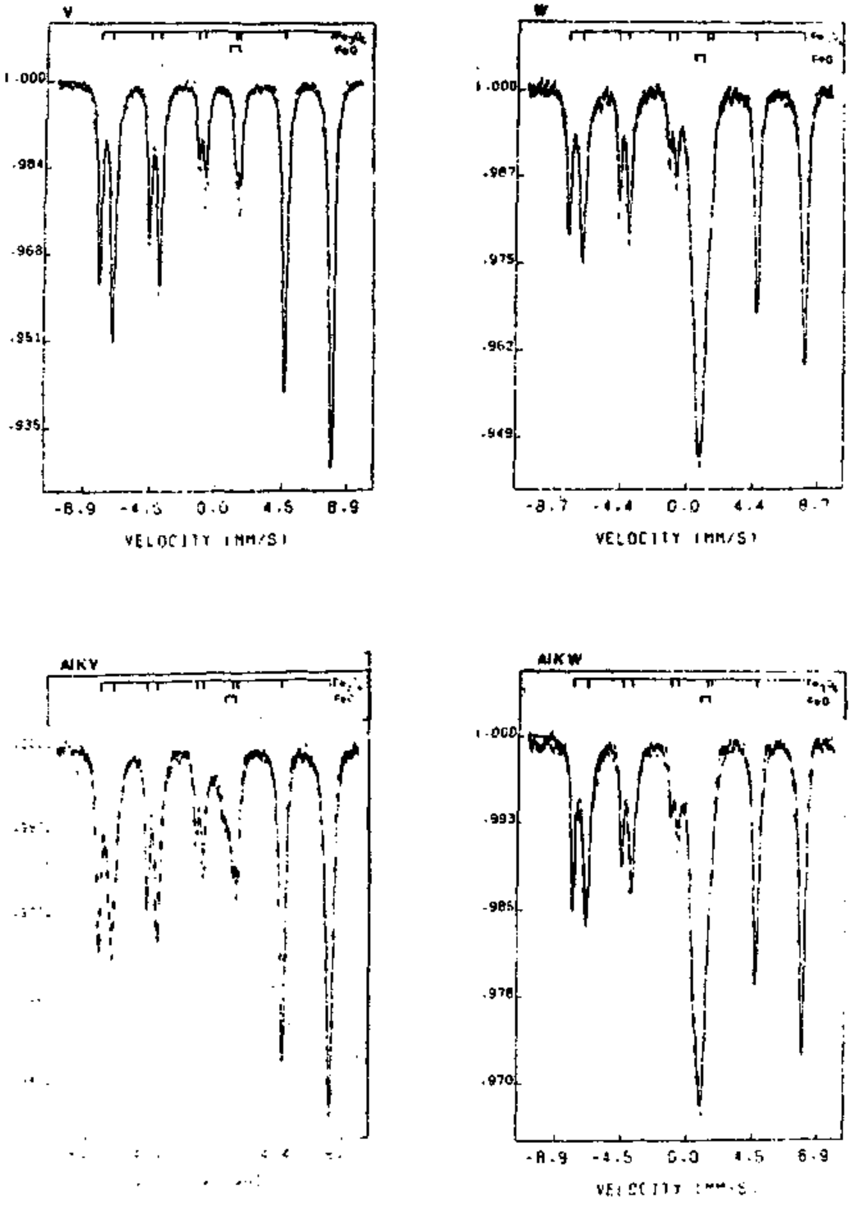

FIGURE 1 Mößbauer spectra of model catalysts recorded at room temperature

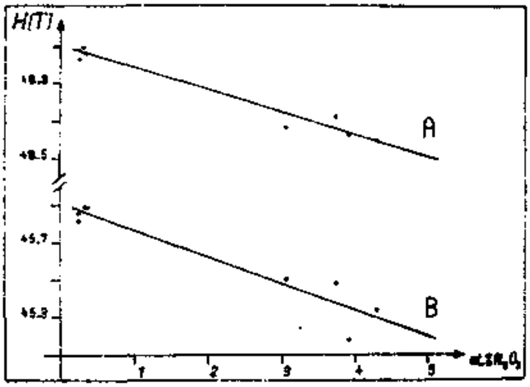

FIGURE 2 Dependence of magnetic field on alumina content for A and B sites subspectra in magnetite.

In order to determine the percent content of wustite and magnetite phases in the catalyst their stoichiometry must be first calculated.

For wustite $Fe_{1-x}O$, parameter x was calculated according to the expression:

$$x = \frac{S/D}{2 + 3\, S/D}$$

where S and D are the Mößbauer spectral areas of singlet and doublet respectively.

For magnetite $Fe_{3-z}O_4$, parameter z was calculated according to the expression [5]:

$$z = \frac{2 - B/A}{5\, B/A + 6}$$

where A and B are the areas of the A site and B site subspectra respectively.

If the stoichiometry of both iron phases is known the percent content of two iron oxides may be calculated from the equation:

$$g_k = \frac{A_k\, S_k}{\sum_i A_i\, S_i\ \epsilon 1}$$

where g_k determines the weight concentration of a component k in a mixture of i components containing Mößbauer nuclei. The A_i are the areas of the different Mößbauer subspectra, S_i are the stoichiometric factors of the components and ε_i^k are the relative f-factors. The ratios of Debye-Waller factors, $\varepsilon_i^k = f_k/f_i$ where determined in [3], and the same values were used for calculations in the present paper.

The knowledge of phase composition of the catalysts makes possible the calculations of Fe^{2+} and Fe^{3+} ions content deduced from Mößbauer spectra and comparison of those values with the results of chemical analysis. Results of such comparison obtained for three catalysts are shown in TABLE 2.

TABLE 2 Comparison of the iron and oxygen content deduced from the Mößbauer spectra and obtained from the chemical analysis

Sample	Content of total iron		Content of Fe^{2+}		Content of oxygen	
	spectrum	chemical analysis	spectrum	chemical analysis	spectrum	chemical analysis
W	72.35	72.62	35.77	34.80	25.97	25.70
AlW	68.83	69.75	31.66	32.98	25.31	24.48
KAlW	69.23	69.37	34.97	34.72	24.74	24.60

In view of the above presented results one may see that the Mößbauer spectroscopy can be used, among the other techniques, as a tool for characterization of the phase composition of iron catalyst for ammonia synthesis.

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PRESENTATION OF THE MÖSSBAUER EFFECT SPECTROMETERS GENERATION DEVELOPED IN THE INSTITUTE OF RADIOELECTRONICS OF THE WARSAW UNIVERSITY OF TECHNOLOGY.

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SUMMARY

The CAMAC based Mössbauer spectrometers systems generation is described. Principal technical characteristics, types of CAMAC modules and block diagram of the system is presented.

The first Mössbauer effect spectrometer system was developed in Nuclear and Medical Electronics Division of the Institute of Radioelectronics in 1974. The origins of this spectrometer were strictly connected with the beginning of applications of the CAMAC system in Poland.
The basic assumption was to build a multiaccesible Mössbauer effect spectrometer system, based on CAMAC system, that would be able to collect the spectra simultaneously from four detectors, placed on both sides of two electrodynamics vibrators.
The first version of the spectrometer included two vibrators, four analog signal tracks, multiscaler adaptor module, waveform generator, drive systems for vibrator, display driver and crate controller. Spectrometer worked in constant acceleration mode. There was only one type of detectors used in this version of the spectrometer: xenon filled type PXXeBe proportional counters. As a display unit worked usual oscilloscope with external X input. Oscilloscope was very helpful to adjust the proper parameters of the analog tracks /gain and shape of the pulses/ and than it was used as a display unit to observe the collected spectra.
The first version of the Mössbauer effect spectrometer was

controlled by the very simple 8 bit, 8k byte RAM, type MERA 300 polish microcomputer with the help of the type 105 crate controller module. Microcomputer collected the spectra in the real time mode.

Elaborated software enabled:

1. four spectra collecting, every in 512 or 256 channels, maximum number of pulses in every channel was $2^{24} - 1$,
2. displaying of spectra,
3. printing of spectra,
4. every spectrum drawing on the line printer,
5. adding, moving and reversing of spectra.

The exchange of the data collected during the experiment by the MERA 300 microcomputer and some bigger computers to process the spectra was able only by the paper tape.

Several Mössbauer effect spectrometers in the above configuration work successfully in Poland due to the reliability of the CAMAC modules and MERA 300 microcomputers.

Futher developments of the spectrometer system concerned with three main subjects:

1. to enlarge the variety of the possible physical experiments by developing new types of detectors and new types of CAMAC modules,
2. to automize the data acquisition within the CAMAC system, to make possible off-line computer controll during the spectra collection,
3. to enlarge the variety of computers controlling the spectrometer system.

In the first of above subjects were developed two new types of detectors eg.:

- type WLP-2-gas flow, very fast-up to 10^6pulses/sec, multiwire proportional counter,
- type LEK-2-gas flow, conversion electrons detector.

The description of the above detectors can be found in the paper /1/. To collect the spectra from WLP-2 counter, the fast analog amplifier module type 1101A and fast single channel analyser module type 1202 were designed.

Due to the interest of the Mössbauer spectrometer system users, the constant velocity generator module type 1406 was build.
In the second of above subjects- two CAMAC modules were designed: autonomous crate controller type 163, described in paper /2/ and autonomous display driver module accompanied with display unit presented in paper /3/.
Any computer connected to the autonomous spectrometer system can be used to other tasks during the data acquisition and data displaying.
Mössbauer effect spectrometer system can be generally controlled by computers from PDP-11-compatible family eg.: SM-3, SM-4, SM-1300 and MERA-60. Existing software operates under RSX-11 and RT-11 operating systems and is written in FORTRAN.
After designing the crate controller module type 111 the autonomous version of Mössbauer system effect spectrometer system could be also controlled by IBM PC compatible computers under MS-DOS operating system.
Block diagram of the system is presented on fog.1.

LITERATURE:

/1/ W.Cudny et all - "Detectors for Mössbauer effect spectroscopy designed at the Institute of Radioelectronics of the Warsaw University of Technology", this proceedings.

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/3/ W.Cudny et all - "Data visualisation system for autonomous Mössbauer effect spectrometer in CAMAC system", this proceedings.

Editor's Note:
References /1/ and /3/ have been not received in due time.

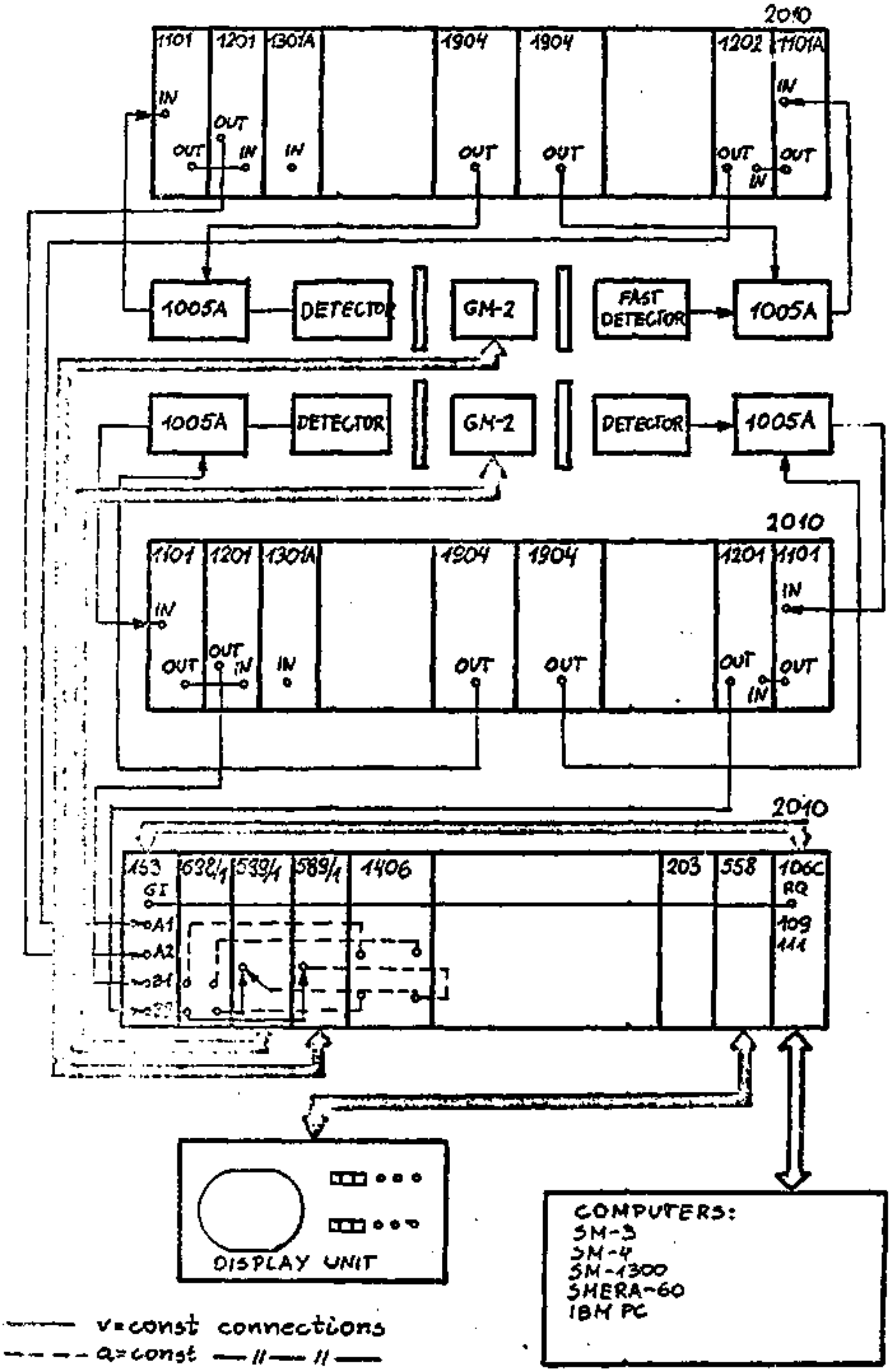

Fig. 1. BLOCK DIAGRAM OF THE MÖSSBAUER EFFECT SPECTROMETER SYSTEM.

PRINCIPAL TECHNICAL CHARACTERISTICS:

Modes of operation	constant velocity or constant acceleration
Velocity ranges	0 - 200 mm/sec for a=const 0 - 100 mm/sec for v=const
Velocity nonlinearity	less than 0,1%
Number of measurement traks	up to 4
Number of multiscaler channels	256 or 512
Maximum frequency on the multiscaler input	0,5 x 10^6 pulses/sec
Types of detectors:	
Proportional counter type PXXeBe	
- supply voltage	1200V - 2000V
- gas	xenon
- FWHM	gamma energy 6,5 keV 18% 17,5 keV 13%
Conversion electrons detector type LEK 2	
- supply voltage	approx. 1200V
- gas mixture	95%He+5%CH_4
- type of detector	gas flow counter
- beryllium window diameter	35 mm
Multiwire proportional counter type WLP-2	
- supply voltage	1800V - 2500V
- type of detector	gas flow counter
- gas mixture	P10
- FWHM /14,4keV, 500000 pulses/sec/	less than 12%
- window dimensions	input Ø 50 mm output 80 x 50 mm
- maximum frequency	10^6 pulses/sec

THE SYSTEM INCLUDES:

Type	Module	Quantity
2010	CAMAC crate	3
1904	High voltage supply	4
1101	Spectrometer amplifier	3
1101A	Fast spectrometer amplifier	1
1201	Single channel analyser	3
1202	Fast single channel analyser	1
1301A	Linear integrator	1
589/1	Drive system	2 /C/
689/1	Waveform generator	1 /C/
1406	Constant velocity generator	1 /C/
163	Autonomous crate controller	1 /C/
	Display driver	1 /C/
	Display unit	1
106,109,111	Crate controller	1 /C/
1005A	Charge preamplifier	4
PXXeBe	Proportional counter	3
LEK 2	Conversion electrons detector	1
WLP-2	Multiwire proportional counter	1
GM - 2	Electrodynamic vibrator	2
L-1	Manipulation table for vibrators, detectors and samples	2

The modules indicated by the letter /C/ should be placed in digital crate, together with the main crate controller.

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AUTONOMOUS CONTROL OF DATA ACQUISITION in MOSSBAUER EFFECT SPECTROMETER

SUMMARY.

The CAMAC module type 163 is described in this paper. This module is used to control data acqusition process in MOSSBAUER EFFECT SPECTROMETER in full autonomical way.

In the earlier versions of MOSSBAUER EFFECT SPECTROMETER (MES) all data processing, including data acqusition, were controlled by the main microcomputer. In the MES produced by POLON it was SM-4 (PDP 11/40). This processor, during data acqusition, could not do anything else. It would be very useful to transfer control of data acqusition to the other processor, using the main one for analyse of data collected earlier. This is the origin of designing an AUTONOMUOS CAMAC CONTROLLER for this purpose.

This controller was designed in NUCLEAR & MEDICAL ELECTRONICS DIVISION in WARSAW UNIVERSITY of TECHNOLOGY. The earlier versions of apparature for MOSSBAUER SPECTROSCOPY were constructed in the same place.

The CAMAC type 163 module is a kind of processor, collecting data from MES and storeing it in an external memory (CAMAC 203 module 2048*24 bits RAM). The block diagram of this module is presented on figure 1. The central control unit sends signals to internal counters, internal CAMAC address generator, CAMAC NAF generator and the internal adder. The CCU is controlled by the CAMAC NAF decoder, which can turn on and off data acqusition process, and is synchronised by the start, stop and channel advance signals from module 669 (the triangle voltage generator to control vibrators). The CCU realises a microprogram which flow-diagram is shown on fig.2.

```
   C A M A C   D A T A W A Y lines F,A,N,X,Q and ACB lines
  -------------------------------------------------------
     !      / \    !                        / \
     ! N,A,F ! X,Q  !                   F,A   ! N,RQ,GI
     v       !     ! START                   ! for ACB
  -------------    ! STOP              -------------
  ! CAMAC NAF !    ! CHANNEL ADVANCE   ! CAMAC NAF !
  !  DECODER  !    ! signals from      ! GENERATOR !
  -------------    ! CAMAC 698 module  -------------
        !          !                       / \
        V          V                        !
    -------------------                     !
    ! CENTRAL CONTROL !----------->---------
    !      UNIT       !                     !
    -------------------                     !
         !   !                              !
         !   !      R1 - R24 CAMAC lines    !
         !   !      --------------------    !
         !   ----->-----   !                !
         V             !   V                V
     ------------     ----------     ----------------
     !          !     !        !     !              !
A1 ->! INTERNAL !     ! 24 BIT !     ! CAMAC MEMORY !
     !          !     !        !     !              !
A2 ->! COUNTERS !     ! ADDER  !     !   ADDRESS    !
     !          !--->-!        !                    !
B1 ->!          !     !        !       GENERATOR    !
     !          !     !        !                    !
B2 ->!          !     !        !       --------------
     !          !     !        !            !
     ------------     ----------            !
                          !                 !
                          !                 !
                          V                 V
            --------------------  --------------------
            W1 - W24 CAMAC lines  W1 - W12 CAMAC lines
```

fig.1.

```
                    -------------
                    !   START   !
                    -------------
                          !  Start collecting data in areas A1,B1
        -----------------------------------
        ! CLEAR INTERNAL ADDRESS REGISTER !
        -----------------------------------
                          !
        -----------------------------------
->------! WAIT FOR CHANNEL ADVANCE SIGNAL !
!       -----------------------------------
!         -------------------------------
!         ! SET ADDRESS IN CAMAC MEMORY !
!         -------------------------------
!         -------------------------------
!         ! READ DATA FROM CAMAC MEMORY !
!         -------------------------------
!       -----------------------------------
!       ! ADD DATA FROM INTERNAL COUNTERS !
!       -----------------------------------
!         ------------------------------
!         ! WRITE DATA TO CAMAC MEMORY !
!         ------------------------------
!                         !
!            ---------------------------
!            ! CLEAR INTERNAL COUNTERS !
!            ---------------------------
!            --------------------------
!            ! COUNT FOR NEXT CHANNEL !
!            --------------------------
!                         !
!     ---------------------------------------
!     ! INCREMENT INTERNAL ADDRESS REGISTER !
!     ---------------------------------------
!                         !
!              NO    ----------
-------------<-------! STOP ? !
                     ----------
                         ! YES
                         ! Start collecting data in areas A2,B2
                         V
         ------------------------------------
         ! CHANGE INTERNAL ADDRESS REGISTER !
         ------------------------------------
                         !
                         .
                    -----------
                    ! START ? !                  fig.2
                    -----------
```

Signal START sets the internal address register for data area in CAMAC memory consisting collected data for tracks A1 and B1. The input counters are initialized and started to count signals from detectors. The channel advance signal stopes one pair of counters and starts to send input signals to the second one. Next, the CCU generates 3 (6 for colecting data in areas A and B) CAMAC cycles. The first one is CAMAC function F(17)A(0) which set an address in CAMAC memory. The second one is F(0)A(0) - read data from CAMAC memory to an internal register. In this register data are added to data counted in the last channel and send back to a CAMAC memory by function F(16)A(0). This procedure is the same for the next channel advance signals.
Receiving the stop signal CCU changes address register for data area A2 and B2. The procedure is then the same as it was written above.

•

The CAMAC module 163 has the following possibilities:

1. Data collection in four areas called A1,A2,B1,B2.
2. Data are collected in 256 or 512 channels depending on module 689.
3. Data collection in normal mode (multiscaler mode) or with " inversive summation " (A1+A2),(B1+B2)

List of CAMAC commands accepted by this block is as follows:

1. F-26 A-1 - collect data in areas A1 and A2
2. F-26 A-2 - collect data in areas B1 and B2
3. F-26 A-0 - collect data in both areas
4. F-24 A-1 - stop data acqusition in areas A
5. F-24 A-2 - stop data acqusition in areas B
6. F-24 A-0 - stop data acqusition in both areas

The design of the autonomous controller for MES in CAMAC system was the simplest way to give the new possibilities of data analysis for all MOSSBAUER SPECTROMETER users. Data collection always needs a long time, so using the main processor to do it is a waste of its possibilities. Using CAMAC 163 module, the main processor serves only to start data acqusition, to stop it and to analyse collected data. This system connected with the autonomous display module (which is described in the next paper) gives a very useful, for physicists, spectrometer with a wide possibilities of data processing and analysing.

REMOTE MÖSSBAUER DATA TRANSMISSION TO THE COMPUTER SYSTEM ODRA-1305 /ICL-1900/; IMPLEMENTATION OF THE MOSSLIB LIBRARY UNDER THE GEORGE-3 SYSTEM

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1. Introduction

A remote Mössbauer data transfer to the powerful mainframe computer being operated on the around the clock basis still offers some adventages as compared to the data evaluation by means of some local microcomputer of the PC family at least as long as the sophisticated software of the MOSSLIB class is required [1]. On the other hand, multichannel analysers are best suited for accumulation of the Mössbauer data due to their flexible dwell times, well designed memory buffers and last but not least high quality and fast converters being indispensable in the background measurements. Unfortunately, many otherwise high quality analysers like our NTA-1024 do not have serial data outputs of the RS-232C standard and many mainframes like ODRA-1305 /ICL-1900/ are poorely designed as far as the remote communication is considered.

Here we describe a remote data link we have designed and put in operation in our laboratory between the NTA-1024 analyser and ODRA-1305 computer, a mainframe in the Institute of Nuclear Physics.

2. Hardware

A basic hardware configuration is shown in Fig. 1. The Mössbauer spectrometer has been purchased from POLON /except detectors/, while NTA-1024 analyser, X-Y recorder, printer and compact cassette unit with the cassette tape recorder were delivered by EMG. A remote terminal IMP-8502M equipped with the keypad and monitor has been purchased from IMPOL-II. A dot printer DZM-180 is a product of MERA. A Computer Centre equipped our mainframe /ODRA-1305, product of ELWRO/ with the MPXSCAN scanner being able to operate at the moment up to 16 remote stations. The protocols being able to operate IMP-8502M terminal and a remote printer DZM-180 have been purchased from MICOMP /producer of MPXSCAN scanners/. A printer is operated at the moment in the synchroneous mode with the synchroneous protocol /4 wires required/, while IMP-8502M can be operated either asynchroneously /it has to be equipped with the special clock for this purpose/ or synchroneously. We have found the synchronous mode much more reliable and at the moment IMP-8502M is operated synchroneously /also 4 wires required/. It has to be noted, that in order to operate a synchroneous mode, a clock has to be installed in the appropriate MPXSCAN channel. A DZM-180 printer has to be equipped with the serial/parallel interface designed for either synchroneous or asynchroneous work. Such interfaces could be purchased from MICOMP and/or made by any electronic workshop. The printer can be also operated as a hard-copy of the terminal /all necessary connectors can be purchased from IMPOL-II/, but this mode is very inconvenient in printing FORTRAN outputs. Summarizing, at the moment our Computer Centre is able to operate up to 8 stations similar to the one described above provided they are closer than 600 m from the mainframe site.

The main problem was to interface a compact cassette unit with the terminal IMP-8502M. The interface No 2 has been made by IMPOL-II on special request and extensively modified by us, while the interface No 1 has been entirely made by us. The data are transmitted in blocks having the following format 127(I6, ':'), I6 using a terminal screen memory as a buffer. The file structure is a simulation of a punched tape input and could be read by FORTRAN programs operated under the GEORGE-3 system due to the exceptionally long internal record of the ICL-1900 systems. Transmitted files are stored in the mass-storage of the system.

A transmission of 1024 channels (7 characters/channel) takes about 90 s. For a remote link to the mainframe we have applied existing phone lines /except for short non-existent previously parts/, however they were rewired to make them non-commutable.

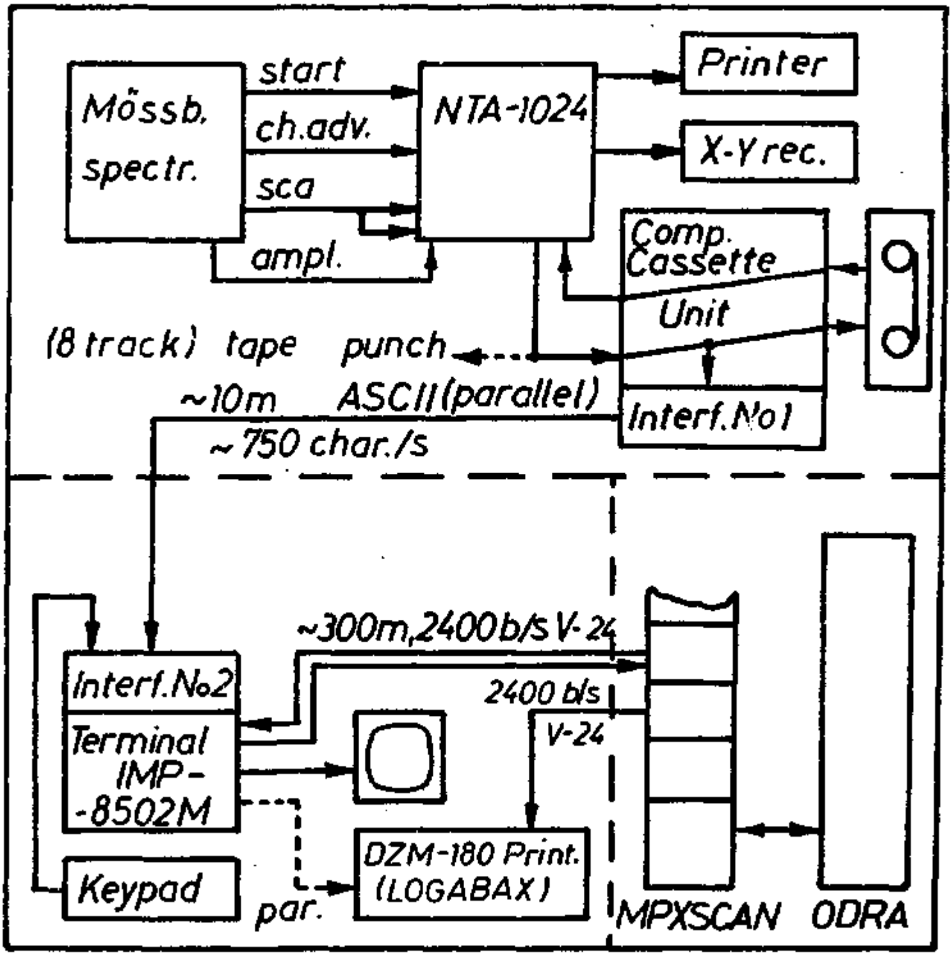

Fig. 1. Basic hardware configuration.

3. Software

A MOSSLIB software [1] is being continously adopted to be operable under the GEORGE-3 system. Some modifications, especially in string variables were essential due to the peculiarites of either operational system or FORTRAN compiler. Some formats have to be modified due to the limitations in existing hardware. At the moment GMFP5S [1] is fully operable as well as ODRA-CALFIT-an interactive and somewhat simplified version of CALFIT, similar in design to LCALF [1]. Free formats are extensively introduced for either batch or interactive processing. The main drawback is a complete absence of a graphic library and therefore MPLOT can not be transferred. At the moment data for plots can be transferred to CYBER-72 only by means of non-standard magnetic tapes. However, the staff of our Computer Centre develops a direct link between the two systems by means of a microcomputer.

The basic flow of data within the implemented MOSSLIB library is shown in Fig. 2.

The execution time for ODRA-CALFIT is about 150 s as compared to 20 s on CYBER-72. The turn-around time is usually less than 10 min. GMFP5S execution takes typically 1000 s /150 s on CYBER-72/ and turn-around time should not exceed 3h in the worst case.
It has to be noted, that GMFP5S requires about 240 kbytes of the central memory (8 bits/byte), while ODRA-CALFIT is significantly shorter. The total system operational memory is at present 768 kbytes. We have found no need to use a double precision despite the fact, that ODRA operates on 48 bit reals, while CYBER-72 has 60 bit reals. It seems, that the arithmetic of complex variables is much slower under the ICL FORTRAN as compared to the CDC-FTN.

A detailed list of the MOSSLIB library content can be obtained upon request as well as copies of the programs. Nine versions of the fitting program, three versions of the calibrating program and two versions of the plotting program are available at present.

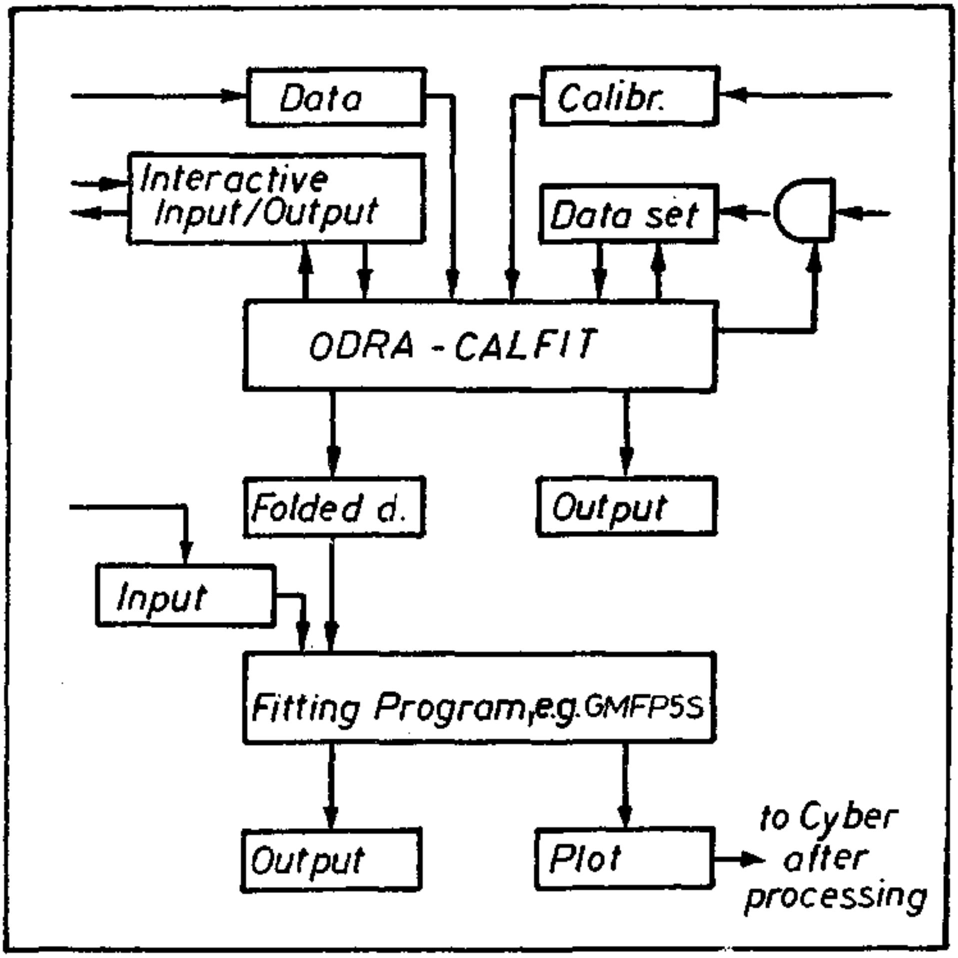

Fig. 2. Flow of data within the implemented MOSSLIB library. Data set is used to store some frequently used input parameters. ODRA-CALFIT is an interactive program, i.e. it occupies a terminal link until the execution is terminated. However, all the questions to the operator are bunched at the beginning of execution.

Acknowledgements

Mr A. Cyz, Computer Centre-Head as well as his staff are warmly thanked for their indispensable help and enthusiasm during the hard days of interfacing our laboratory to the mainframe computer. Mrs B. Ostrowicz, Chief Programmer is deeply appreciated for explaining to us many intricacies of the operational system and compilers. Last but not least, we would like to thank the IMPOL-II Company for their assistance in interfacing KTA-1024 to the terminal IMP-8502M.

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THE ORDER IN ALLOYS STUDIED BY THE MÖSSBAUER EFFECT

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ABSTRACT

Some applications of the Mössbauer spectroscopy in investigations of iron-based alloys are presented. In particular we discuss: determination of order parameters and ordering process in Fe_3Al alloys.

1. Introduction

The atomic ordering in substitutional solid solutions of metals is an example of collective phenomena. The distribution of atoms in ordered A_xB_{1-x} alloys is described by function $w_{AA}(\underline{x}_k)$, which gives fraction of A atoms in the k-th shell of an arbitrary A atom. While the classical methods of studying ordering are in principle capable of determining the average values $\bar{x}_k$, the Mössbauer effect based on the measurement of hyperfine interactions /hf/ is sensitive to the $w(\underline{x}_k)$ itself. In contrast, hf interactions at nuclei s are determined mainly by its first /i/ and second /j/ neighbour atoms. It restricts the Mössbauer spectroscopy to the study of the $w(i,j)$ function.

Many attempts is made to determine the order parameters of alloys from Mössbauer spectra. In ferromagnetic alloys the influence of ordering is first of all visible on the outer lines of the Mössbauer spectrum. It is sometimes possible measure the $w(i,j)$ for a limited set of (i,j) configurations [1-3] . In the second step from these $w(i,j)$ values the order parameters can be calculated by using the computer simulation technique [4] .

Mössbauer spectra of ordered and disordered alloys often differ primarilly in the line width of the outer lines. The interpretation of the line broadening is consequence of the existence of a distribution of atomic environments for the iron atoms which forms a distribution of hyperfine fields. In this case use of the correct formula for the $w(i,j)$ is important for determination of the order parameters [5-7] .

In this paper we present some chosen applications of the Mössbauer spectroscopy in the study of order in Fe-based alloys. In the section 2 we describe a method of determining the long-range order parameter S from hyperfine fields distribution P(H) . In the section 3 the results of Mössbauer measurements on ordered Fe_3Al alloys are presented.

2. Determination of the long-range order parameter from hyperfine fields distribution P(H) .

Following many works, mainly on iron alloys with dilute impurities, we can assume that in binary A_xB_{1-x} alloys, where A atoms are Fe atoms, the isotropic and additive magnetic contributions of only the nearest and succesive neighbours are important. In this interpretation, the hyperfine field H_{hf} is a well-defined quantity for a given atomic configuration. It was shown [7] that basing on the procedure for constructing the w(i,j) function [8] , the mean value $\bar{H}$ and variance D_H of hyperfine fields distribution P(H) in alloys with $L1_2$ and $L2_0$ superstructures can be written in the form of

$$\bar{H} = \bar{H}_d - K\cdot S^2$$
$$D_H = D_d + A\cdot S^2 + B\cdot S^3 - K^2 S^4 \qquad /1/$$

where:

$\bar{H}_d$ is the mean value of hyperfine magnetic field in the disordered alloy,

D_d is the variance of magnetic fields distribution in the disordered alloy,

$K = \Delta H_1(z_1 - 3z_2\alpha)/(16c)$ for $L1_2$ structure,

$K = \Delta H_1(z_1 - z_2\alpha)/(4c)$ for $L2_0$ structure,

ΔH_1 and ΔH_2 are the changes of the hyperfine field at the central Fe atom due to nn and nnn iron atoms,

$\alpha = \Delta H_2/\Delta H_1$, c is concentration of Fe atoms in the alloy,

z_1 and z_2 are the numbers of nn and nnn sites respectively.

The parameters A and B are square functions of the parameter [7]. We have seen from /1/ that the mean value of hyperfine fields distribution in ordered alloys is a linear function of the parameter S^2. This linear dependence has been observed in Ni_3Fe and FeCo alloys [7] . In Fig. 1 the relation between $\bar{H}$ and the value of S^2 for Ni_3Fe and FeCo alloys investigated in [7] is shown.

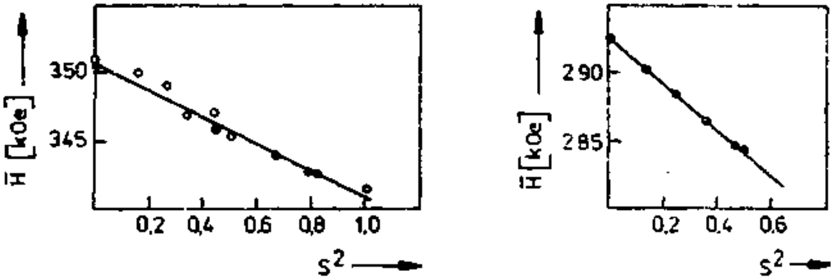

Fig. 1. The mean hyperfine field $\bar{H}$ as a function of the parameter S^2 for Ni_3Fe and FeCo alloys.

The straight line calculated from /1/ satisfactorily described the experimental relation.

The value of parameter S can be determined directly from /1/ if the values of parameters K or ΔH_1 and ΔH_2 are known. On the other hand, if ΔH_1 are unknown they can be determined by the elimination of parameter S from /1/.

In Fig. 2 the dependence of $\bar{H}$ and D_H for disordered and ordered Fe-Co alloys as the function of Co concentration is shown.

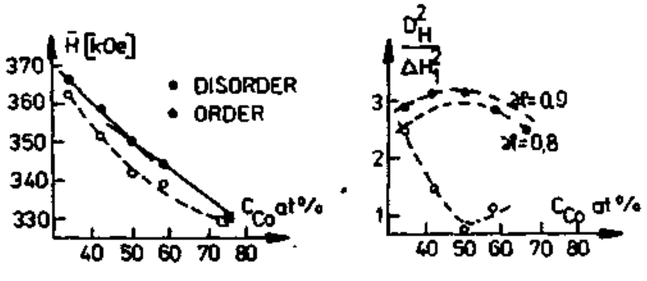

Fig. 2. $\bar{H}$ and D_H parameters vs cobalt concentration for Fe-Co alloys [9].

In the paper [9], the value of parameter ϰ was calculated using relations /1/. For the c_{Co} range /34-50/at% the obtained value ϰ equals 0.9 while for c_{Co} $\in$/50-75/at% it is 0.8. The theoretical lines /dotted lines in Fig. 2/ well fitted experimental points.

1. Determination of order parameters of Fe_3Al alloys.

Binary Fe-Al alloys in the range /22.4-25.2/ at% Al were investigated with use of Mössbauer spectroscopy and X-ray diffraction technique. The specimens were prepared by vacuum induction melting using electrolytic Fe and Al. A chemical analysis gave 25.2, 24.3 and 22.7 at% Al. The ingots were filed into powder finer than 40 µm. The powder specimens were annealed in vacuum at 950 C for 6 h and then slowly cooled. In the second step the powder was crushed by an agate mortar. The particle sizes were less than 10 µm. The filed and crushed specimens were used for the ^{57}Fe Mössbauer and X-ray diffraction measurements.

A standard Mössbauer spectrometer operating in the constant acceleration mode was used. The Mössbauer spectra were computer analysed by a least-squares fitting program assuming Lorentzian lines. The magnetic fields distribution P(H) was also determined by the Hesse-Rübartsch method /10/. In this calculation the linear relation between hyperfine fields H_{hf} and isomer shift IS was assumed.

The Mössbauer spectra of ordered Fe-25.2, 24.3 and 22.7 at% Al alloys as well as corresponding P(H) distributions are shown in Fig. 3.

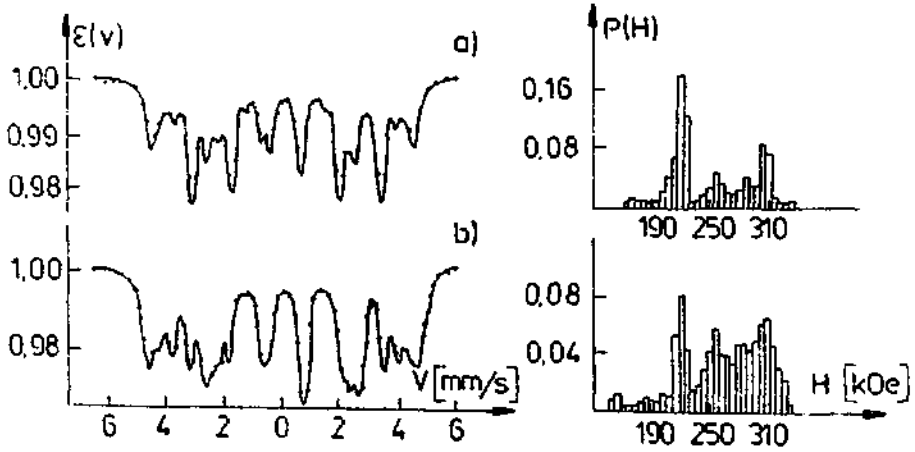

Fig. 3. Mössbauer spectra of ordered a/ $Fe_{74.8}Al_{25.2}$ and b/ $Fe_{77.6}Al_{22.4}$ alloys and corresponding P(H) curves.

As we can see from Fig. 3. the peak distributions, characteristic for H(8), H(7,6), H(5), H(4) and H(3) iron enviroments are visible. In this way, the corresponding fractions w(i) can be determined as well as the average number N_1 of Fe atoms within the first shell.

For comparison results of Mössbauer and X-ray investigations we introduce according to [11] an order parameter

$$\Omega = (N_0 - N_1)/(N_0 - 5.33)$$

where N_0 is the average number of Fe atoms within the nn volume for random distribution. The $N(DO_3) = 5.33$ is the average number of Fe atoms in the first shell for ordered Fe_3Al alloy.
The order parameters Ω_M calculated from Mössbauer spectra and Ω_X parameters calculated from X-ray diffraction results [12] are collected in Table I.

Table I.

Order parameter	Annealed	sample		Cruched		
	25.2	24.3	22.7	25.2	24.3	22.7
Ω_M	0.99	0.96	0.16	0.35	0.60	0.12
Ω_X	0.90	0.63	0.15	0.58	0.41	0.05

As we can see the order parameters Ω_M for annealed samples are higher then Ω_X parameters. This results suggest once more that the Mössbauer effect is sensitive to the order within domains while X-ray diffraction averages over the crystal. For the crushed alloys the plastic deformations create large numbers of antiphase boundaries across which increase the number of Fe-Fe pairs.

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THE FIFTEEN YEARS OF MÖSSBAUER SPECTROSCOPY IN KATOWICE

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1. INTRODUCTION

The main purpose of this paper is a short presentation of results of Mössbauer effect applications to study the structure and properties of alloys. These applications were done in the Institute of Physics and Chemistry of Metals by a group of physicists (now 6 scientific workers are working in this area). The obtained results are our small contribution to the celebration of 25 years of Mössbauer spectroscopy in Poland.

In 1971 we started with constructing a spectrometer with constant acceleration of source (T.Panek, B.Jankowski, J.Frackowiak). The electronic part of this spectrometer based on three electronic elements: tubes, semiconductors and integrated circuits [1, 39]. Next we bought two other spectrometers produced by Institute of Nuclear Research in Świerk and by POLON firm. In these spectrometers the ^{57}Co/Cr/ and Ba^{119}SnO$_3$ sources produced by USSR are held.

The interest focused on three subjects :

a/ Methodology of the Mössbauer effect
b/ Phase transformations in alloys, particularly the atomic order-disorder transition and the precipitation process in the supersaturated solid solutions.
c/ The application of the Mössbauer effect to the fast quantitative analysis of iron content in coal and other mining materials.

It can be mentioned that in Katowice there are two other smaller groups which applied Mössbauer spectroscopy to study the magnetic materials (Drs E.Popiel, W.Zarek in Institute of Physics Silesian University) or to study medicines (Prof.T.Wilczok, Institute of Pharmacy, Medical Academy Katowice).

2a. CONTRIBUTIONS TO THE MÖSSBAUER EFFECT METHODOLOGY

In the Mössbauer effect spectroscopy (ME) the complex spectra as a result of the overlap of many near positioned individual lines are often observed. In this case the method of calculation of the transmission integral $\varepsilon(y)$ for an arbitrary number of the ME spectrum lines has been proposed [6, 7, 42]. The final formula on the $\varepsilon(y)$ is given in the form of equations which are very convenient in numerical calculations:

$$\varepsilon(y) \cong \alpha f \sum_{p=1}^{N} (-1)^{p-1} \sum_{k_1,\ldots k_p} A'_p(k_1,\ldots k_p)$$

where y is gamma quantum energy in the excited level width units, f- emission recoilless fraction; α - constant; N - number of lines; A'_p is given by recursive relations [7, 42].

It is known that both the sample with the non-homogeneity of thickness and the dead-time of spectrometer influences on the determining of the Debye-Waller factor. For the low activity of the source the first reason plays an important role and to obtain the correct theoretical transmission spectrum it is necessary to take into consideration the electronic absorption coefficient (μ_e) and the term proportional to the second derivative of the transmission integral $\epsilon(y)$ which should be added to $\epsilon(y)$ [22, 27, 42] :

$$\epsilon(y) = \epsilon(t', y) + \frac{1}{2}\langle t\rangle d \, \frac{\partial^2 \epsilon(t', y)}{\partial t'^2}$$

where $\langle t\rangle d=\sigma^2$ is the dispersion of the grain size distribution in sample and $t'=\langle t\rangle\ (1-\frac{\mu_e}{\sigma_0}d)$.
This relation on $\epsilon(y)$ introduced to the analysis of ME spectra for pyrite the Debye temperature and the anisotrophy of the Fe atoms thermal vibrations allowed to obtain [23, 28, 42] Furthermore the computer programs in FORTRAN IV were done for analysis of simple spectra by the least square fitting procedure of single loretzian shape lines, dublets or Zeeman patterns to the measured spectra [2, 4, 39]. The program for obtaining the magnetic hyperfine field distribution by Hesse-Rübartch method [13, 15, 16]. The program for modelling the structure of ordered crystallite by the use of the Monte-Carlo method [8, 40].

2b.c THE STUDY OF PHASE TRANSFORMATIONS IN ALLOYS

The atomic pair interaction model gives the possibility of a unique theoretical description the atomic ordering or clustering in alloys. Assuming the near neighbours interaction in the binary AB alloy the configuration energy of system is equal $E=\frac{1}{2}wN_{AB}$. N_{AB} is the number of AB atom pairs and $w=2E_{AB}-E_{AA}-E_{BB}$
E pairs interaction energy.
But this experimental evidence is not enough to confirm this theory. Therefore, we have investigated by means of ^{57}Fe Mossbauer spectroscopy the binary and ternary alloys that show atomic ordering ($w>0$) or clustering phenomenon ($w<0$).
The method of obtaining the long-range order parameter (S) from the experimentally determined mean value of the magnetic hyperfine field and the variance D_H of hyperfine field distribution P(H) was developed [20, 33]. This method was applied to the investigation of atomic ordering in Ni_3Fe, Ni-Fe and Fe-Co alloys [3, 8, 24, 29, 30, 32, 40]. Using the ^{119}Sn Mössbauer spectroscopy the study of influence of ageing effects on the structure of CuZnSn shape memory alloy was also performed [25, 34].
The Cu base Fe alloys were taken as good model alloys for study of atomic clustering [19, 31]. The influence of Sn and Be on Fe precipitation kinetics and the dispersive hardening of alloy were carefully analysed [11, 12, 21]. Also the precipitation was studied in more complicated materials as for example in steel [5, 13, 14, 16, 18]. The correlation between isomer shift and a positron annihilation parameter S has been observed in Ni-Fe alloys [9, 41].

One of the practical applications of the Mössbauer effect involves the quantitative analysis of iron in coal and some ores. The basic description of this method and proposal of analyser was reported in [17, 36, 37,38].

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