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Mössbauer Effect in the $Fe_{2-x}Ge$ Intermetallic Compounds.

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Summary. — Resonance absorption of ^{57}Fe 14.4 keV γ-rays by $Fe_{2-x}Ge$ compounds is investigated. These compounds are ferromagnetic, and contain two kinds of iron atoms, at whose nuclei induction is different. The separation of multiplets and the probability of Mössbauer effect result to be dependent on the iron content of the compound and are measured for x in the range $0.5 \div 0.3$. The results are discussed and compared with evidence from X-ray diffraction, polarized-neutron diffraction, and magnetic measurements.

1. – Introduction.

The structural and magnetic properties of the $Fe_{2-x}Ge$ binary compound have been recently investigated by a number of authors [1-7] with the help of X-ray and polarized neutron diffraction and with measurements of magnetic susceptibility and saturation magnetization. Some basic properties of the compound have been well established, like the fact that its structure is hexagonal, $B8_2$ type, with some distortion [6], the $2(a)$ lattice positions being occupied by

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(1) K. YASUKOCHI, K. KANEMATSU and T. OHOYAMA: *Journ. Phys. Soc. Japan*, **16**, 429 (1961).

(2) G. AIROLDI and R.-PAUTHENET: *Compt. Rend.*, **268**, 3994 (1964).

(3) H. KATSURAKI: *Journ. Phys. Soc. Japan*, **19**, 863 (1964).

(4) K. KANEMATSU: *Journ. Phys. Soc. Japan*, **20**, 36 (1965).

(5) J. J. BECKER and E. M. SYMES: *Journ. Appl. Phys.*, **36**, 1000 (1965).

(6) J. B. FORSYTH and P. J. BROWN: *Proceed. Intern. Conf. on Magnetism* (Nottingham, 1964), p. 524.

(7) K. KANEMATSU and T. OHOYAMA: *Proceed. Intern. Conf. on Magnetism* (Nottingham, 1964), p. 512.

iron atoms and the 2(*c*) and 2(*d*) lattice positions being mainly occupied by germanium and iron atoms, respectively. The existence of ferromagnetic order has also been established in a wide range of x values ($0.1 \leqslant x \leqslant 0.7$).

However, evidence was found of several complicated structural features ([1,4,6]), which so far prevented a complete description of the properties of the compound. The above-mentioned structure (β phase) seems to exist only in the range of compositions corresponding to the extreme formulas $Fe_{1.5}Ge$ and $Fe_{1.7}Ge$ ([4]), a different hexagonal structure having been individuated for $0{,}5 < x < 0{,}7$ through measurements of saturation magnetization and X-ray diffraction, and two phases appearing to coexist for larger iron concentrations.

Apart from the complexity of the state diagram of the system, it was concluded ([2]) that, whenever the iron concentration is large, specimens containing iron precipitates are always obtained, so that compounds approximating closely the formula Fe_2Ge cannot be prepared. Precipitates are absent in the β phase ($Fe_{1.5}Ge$ - $Fe_{1.7}Ge$), and in this case the structure seems to be characterized by the presence of lattice vacancies in the 2(*d*) lattice positions. The existence of vacant lattice sites within the compound, together with the fact that two types of iron atoms exist, with different nearest neighbours, determines a not simple situation, as far as the magnetic moments of iron atoms are concerned. The existence of two different magnetic moments was demonstrated ([3,6]) with the help of the diffraction of polarized neutrons, but no information is available as far as the dependence of the magnetic moments on the composition is concerned, as the investigations with polarized neutrons were restricted to the compounds $Fe_{1.76}Ge$ ([3]) and $Fe_{1.67}Ge$ ([6]). Moreover the results reported in the quoted papers are somewhat contradictory, the magnetic moments at the iron atoms being 1.56 μ_B for the atoms at the 2(*a*) lattice points and 0.53 μ_B for the atoms at the 2(*d*) lattice points according to KATSURAKI ([3]), while more recently FORSYTH and BROWN ([6]) found that the magnetic moments are equal to 1.4 μ_B and 1.9 μ_B respectively. The difference between the compositions of the two investigated specimens does not look to account for such a big difference in the results.

As also the magnetic properties of the $Fe_{2-x}Ge$ compounds do not seem completely established, it was considered worthwhile to perform an investigation with the help of the Mössbauer effect, with the main purpose of measuring the induction at the iron nuclei as a function of the iron content.

2. – Experimental procedure.

The specimens used had the following compositions: $Fe_{1.50}Ge$, $Fe_{1.58}Ge$, $Fe_{1.65}Ge$ and $Fe_{1.68}Ge$. We restricted ourselves to the range of iron content corresponding to x between 0.5 and 0.3 because only in this range the unper-

turbed β phase seems to exist certainly, as it is shown by the absence of iron precipitates and by the smooth dependence of both Curie temperature and saturation magnetization on the iron content ([4]).

Specimens were prepared by heating them ixed high-purity iron and germanium powders at 800 °C and successively melting the mixtures in an induction furnace in vacuo. The absence of precipitates was checked with the help of an X-ray diffractometer.

The resonance absorption measurements were performed at room temperature, the 14.4 keV γ-ray emitter being a source of ^{57}Co diffused in copper, and the mentioned compounds being used as absorbers. They were in shape of layers about 35 mg/cm^2 thick.

A preliminary investigation of the shapes of the absorption spectra was carried out with the help of an already described ([8]) constant acceleration electromagnetic transducer, used in connection with a multichannel pulse analyser. Thus the most convenient lines for the purpose of a detailed analysis could be rapidly individuated; successively the investigation was restricted to a few absorption lines, as it will be discussed later, and was performed with the help of a mechanical velocity selector. This apparatus allowed a velocity resolution which was adequate for the purpose of examining a complex absorption spectrum, which was characterized by several, partially overlapping lines.

The γ-ray detector was a proportional counter filled with $Xe + CH_4$ at atmospheric pressure.

3. – Experimental results.

Figure 1 shows a typical absorption spectrum, as obtained with the above-mentioned electromagnetic transducer: what is evident is the existence of a double system of absorption lines, corresponding to the multiplets which are associated with the two values of the induction at the iron nuclei. It is also apparent that in this case the velocity resolution of the apparatus is not sufficient to clearly separate the majority of the lines. However such preliminary measurements allowed the classification of some lines, as far as their attribution to the above-mentioned multiplets was concerned: these lines are labelled with either A or B in Fig. 1. Successively the mechanical velocity selector was used and an accurate analysis of the extreme regions of the spectrum was performed: two A type and two B type lines were included in these regions and could be satisfactorily resolved, thereby allowing measurements of the inductions at the iron nuclei.

([8]) G. FABRI, E. GERMAGNOLI, M. MUSCI and V. SVELTO: *Phys. Rev.*, **138**, A 178 (1965).

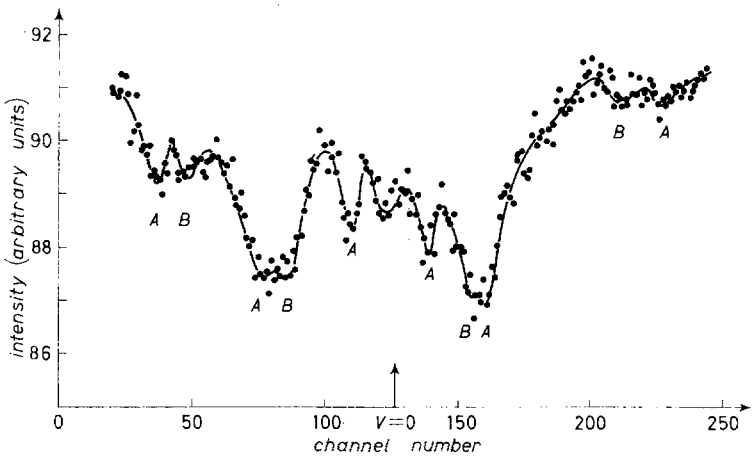

Fig. 1. – Typical Mössbauer spectrum ($Fe_{1.68}Ge$). 1 channel = 0.0472 mm/s.

The two absorption lines (one of either type) corresponding to the extreme negative velocities are given in Fig. 2; quite similar results were obtained from the measurements performed with positive velocities. It is immediately noticed that the shown absorption lines display a regular dependence on the iron content of the specimens, as far as the areas below the lines and the positions of the lines are concerned. The pertinent data are reported in Table I, in which the results concerning positive and negative velocities are averaged. The inductions at the iron nuclei were obtained after calibration with the above-mentioned emitter and a metallic iron absorber, 91.2% enriched in the isotope ^{57}Fe: the induction was taken equal to 333 kG for iron metal.

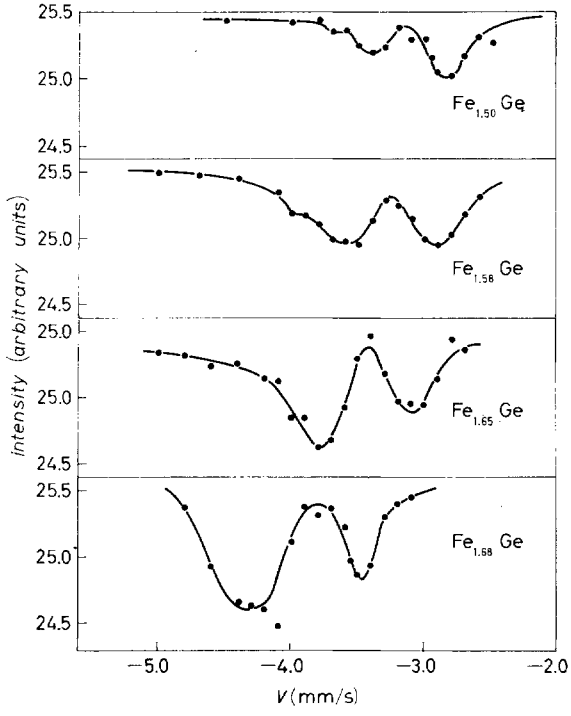

Fig. 2. – Mössbauer spectra for all investigated compounds. Large negative velocities.

TABLE I. – *Summary of experimental data.*

Specimen	*A* lines		*B* lines	
	Area (arb. units)	Induction (kG)	Area (arb. units)	Induction (kG)
$Fe_{1.50}Ge$	4.3	233 ± 5	9.2	168 ± 5
$Fe_{1.58}Ge$	11.3	236 ± 5	10.7	184 ± 5
$Fe_{1.65}Ge$	20.7	241 ± 5	10.8	195 ± 5
$Fe_{1.68}Ge$	26.5	257 ± 15	10.1	207 ± 10

It seems convenient to conclude the present paragraph by briefly summarizing the general features of the experimental results collected in Table I. According to one of the main conclusions which were recalled in the introduction, if the composition of the considered compound is varied by adding more and more iron atoms, initially vacant lattice sites at the $2(d)$ positions become gradually occupied by iron atoms. The whole explored range of composition corresponds to a 36 % increase of iron concentration in the sublattice to which the $2(d)$ sites belong: an increase of the probability of resonance absorption of this order of magnitude would be expected to a first approximation, as self-absorption effects are not important with the adopted thin specimens and according to the fact that nonenriched iron was used. The effect observed is much larger than expected, as far as *A* type lines are concerned, the areas under the absorption peaks increasing by a factor 6 or thereabout if the iron content of the specimens is increased as indicated; on the contrary, pratically no effect was observed on the *B* type lines.

Such a striking difference between the two types of lines was not observed as far as the values of induction at the iron nuclei is concerned; according to the data given in Table I both values increase similarly if the iron content is increased, the B/A ratio being 0.72 ± 0.03 for the $Fe_{1.50}Ge$ specimen and $0.81 \pm 0{,}05$ for the $Fe_{1.68}Ge$ specimen. It can be concluded that such ratio is either constant within experimental errors or slowly and regularly increasing with increasing iron content.

From an inspection of both complete and partial Mössbauer spectra which were obtained, it is concluded that they are nearly symmetrical with respect to the zero velocity. The isomeric shifts, relative to iron metal, were measured and found small and positive for both multiplets: they are about 0.10 mm/s for the *A* lines and about 0.15 mm/s for the *B* lines.

4. – Conclusions.

As mentioned in the Introduction, the magnetic moments were determined and attributed to the iron atoms belonging to the two sublattices with the help of diffraction measurements with polarized neutrons. The conclusions of the

authors quoted ([3,6]) were not in agreement: KATSURAKI ([3]) found that the magnetic moment on the iron atoms at the 2(*a*) lattice sites (Fe_I) was equal to 1.56 μ_B while the magnetic moment on the iron atoms at the 2(*d*) sites (Fe_{II}) was only 0.53 μ_B. Conversely, the magnetic moments were 1.4 μ_B (Fe_I) and 1.9 μ_B (Fe_{II}) according to FORSYTH and BROWN ([6]). The present results do not indicate the big difference between the two magnetic moments which was found by KATSURAKI and suggest furthermoret hat the Mössbauer multiplet previously labelled with *A* should be attributed to the Fe_{II} sublattice, and that the *B* multiplet should be attributed to the Fe_I sublattice.

The bases for such attributions are essentially the following:

a) The ratio between the values of the magnetic moments on the iron atoms is 1.36 ± 0.12 according to FORSYTH and BROWN, which is consistent within experimental errors with the ratio between the induction values resulting from the present paper for the $Fe_{1.68}Ge$ compound (the measurements by FORSYTH and BROWN were carried out with a $Fe_{1.67}Ge$ crystal). Actually:

$$\frac{A}{B} = \frac{257 \pm 15}{207 \pm 10} = 1.24 \pm 0.10 .$$

For this comparison proportionality is assumed, at least to a first approximation, between induction at the iron nuclei and magnetic moments on the iron atoms. The same ratio as before is found if the data concerning the $Fe_{1.65}Ge$ compound are used.

b) The areas below the *B* lines are little dependent on the iron content, which is consistent with the fact that the Fe_I sublattice is completely occupied by iron atoms at any iron concentration in the investigated range.

The *A* lines corresponding to the extreme velocity intervals, like those shown in Fig. 2, look markedly asymmetrical and suggest some splitting. Though this effect was not investigated in any detail, it is worth-while to point out that a similar fact was noticed by STEARN ([9]) in the case of iron-rich FeSi, FeAl, FeMn, FeV alloys. A detailed interpretation was given by the quoted author in terms of indirect interaction energy via the 4*s* conduction electrons of the iron atoms: this fact was evident in the diluted Fe alloys in which the solute atoms behave in a localized manner and do not alter the atomic structure of the matrix. The occurrence of a similar situation for the $Fe_{2-x}Ge$ compound would imply that the number of 3*d*-electrons is in the present case nearly unchanged with respect to the case of metallic iron. This is consistent with the fact that the observed isomeric shift is very near to the one measured with metallic iron and is an argument in favour of a relevantly metallic character of the bonds involved in the Fe_{II} sublattice.

([9]) M. B. STEARNS: *Journ. Appl. Phys.*, **36**, 913 (1965).

A partial covalency of such bonds, as concluded by KANEMATSU ([10]), cannot be however excluded, mainly due to the fact that the ratio between the induction at the iron nuclei and the magnetic moment on the iron atoms is for the Fe_{II} sublattice somewhat lower than the one found for metallic iron, while no departure from the linear dependence given by KOCHER and BROWN ([11]) is noticed in the case of the Fe_I sublattice, for which Fe-Fe bonds display certainly a metallic character.

The dependence of the induction on the iron content we just found is in good agreement with the findings by KANEMATSU ([4]) from measurements of saturation magnetization. In the interval of compositions explored in the present paper, the relative increase of saturation magnetization is about 16 % which is intermediate between the relative increases of the induction at the iron nuclei for the Fe_I (23 %) and for the Fe_{II} (11 %) sublattices. The essential proportionality between the inductions at the Fe_I and Fe_{II} nuclei would seem to be an argument in favour of a nonnegligible superexchange interaction between the two sublattices. Such Fe-Fe interaction via the germanium atoms was considered by YASUKOCHI *et al.* ([1]).

Concerning the observed dependence on iron content of the probability of Mössbauer effect in the Fe_{II} sublattice, no precise comment can be made at the present time. A rather obvious argument is that the addition of iron atoms into vacant lattice sites results in an effective stiffening of the atomic bonds, thereby increasing the « Mössbauer temperature », but it looks impossible to develop any quantitative consideration on this point.

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([10]) K. KANEMATSU: *Journ. Phys. Soc. Japan*, **17**, 85 (1962).
([11]) C. W. KOCHER and P. J. BROWN: *Journ. Appl. Phys.*, **33**, 1091 (1962).

RIASSUNTO

Vengono esaminate le caratteristiche dello spettro di assorbimento in risonanza per i γ da 14.4 keV del ^{57}Fe da parte di composti del tipo $Fe_{2-x}Ge$, con x compreso nell'intervallo tra 0.3 e 0.5. Detti composti sono ferromagnetici e sono caratterizzati da due tipi di atomi di ferro, per i quali l'induzione al nucleo è differente. La separazione dei multipletti e la probabilità dell'effetto Mössbauer risultano dipendenti dal contenuto in ferro del composto. I risultati sono discussi e confrontati con quelli ricavati mediante diffrazione dei raggi X, diffrazione neutronica e misure di magnetizzazione.