MAGNETISM FROM MÖSSBAUER SPECTROSCOPY

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Résumé. - *Ce travail discute l'effet des atomes voisins magnétique hyperfin à* ^{57}*Fe dans des isolateurs demi-conducteurs, alliages cristallins et amorphes, qui sont ordonnées magnétiquement. Le valeur, et la dependance de la température des champs magnétiques hyperfins donnent information complémentaire sur les interactions locales et non locales.*

Abstract. - *The effect of neighbours on the hyperfine field will be discussed in magnetically ordered, mostly iron based insulators, semiconductors, alloys and metallic glasses. It will be shown that the value and the temperature dependence of the hyperfine field offer complementary information on the local and nonlocal magnetic interactions.*

1. Introduction. - In this short review we will discuss contributions of Mössbauer spectroscopy in the field of magnetism. This title might cover almost the whole Mössbauer literature. Since this is an impossible task for authors to compose this encyclopedia and for readers to digest it, we have to make a choice. Our main problem in this paper is the use of MES in a study of local vs. nonlocal effects. The best parameter for this is the magnetic hyperfine field at the γ-ray emitting or absorbing nucleus which means that mostly magnetically ordered systems will be discussed. In the first part crystalline systems in the categories insulators, semiconductors and metals are treated and observations in these systems are then used for the investigation of metallic glasses.

2. Iron oxides. - The magnetic hyperfine fields as measured with ME spectroscopy in ionic compounds as ferrites [1], $(Rh_2O_3)_{1-x}$ $(Fe_2O_3)_x$ [2] and orthoferrites [3,4,5] have been explained in great detail. With the LCAO method describing the valence electron wavefunctions, and the Schmidt procedure assuring orthogonality of the core wavefunctions, expressions for the supertransferred hyperfine field can be obtained. The orthoferrites $RFeO_3$ with R going from R = La to Lu are of interest for two reasons. The bond angle dependence of the supertransferred hyperfine field can be studied [4] and by substituting a nearest Fe^{3+} neighbour by a nonmagnetic one also the supertransfer per magnetic neighbour [5].

In order to discuss the magnetic hyperfine field at the central iron atom we write

$$H_{hf} = H_{free} + H_{cov} + H_{STHF}, \qquad (1)$$

H_{free} is the free iron contribution of approximately -630 kOe; H_{cov} contains two covalent contributions: (i) a reduction of the free ion contribution due to electron transfer in the empty 3d orbitals of the central iron, and (ii) the covalent contribution from the differences in overlap and transfer effects of the iron spin up and dows s orbitals; H_{STHF}, the supertransfer contribution is caused by the overlap distortion of the central s orbital by the oxygen p orbitals, which are spin polarized by transfer into the empty 3d orbitals of the neighbouring Fe ions. For the calculation of the STHF only the central s-wavefunctions and the relevant wavefunctions which can mix with these are taken into account in a cluster of a central Fe^{3+} ion, octahedrally surrounded by 6 O^{2-} anions and 6 Fe^{3+} cations and an antiferromagnetic order is assumed [4]. The result is

$$H_{STHF} = c \{ (A_\sigma^2 - A_\pi^2) \cos^2\theta + A_\pi^2 \}, \qquad (2)$$

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where c is a constant mainly determined by the overlap between s and p wavefunctions. A_σ^2 and A_π^2 are the amounts of unpaired spin in the O^{2-} 2p shell due to transfer of 2p electrons to the 3d orbitals for the σ and π symmetries, respectively. The existence of the $\cos^2\theta$ dependence of H_{STHF} has been found experimentally in a study of the rare earth orthoferrites and is shown in Fig. 1.

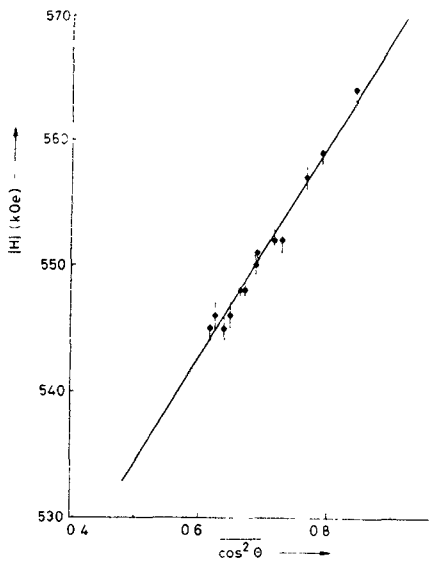

Fig. 1. - Measured hyperfine fields vs. $\overline{\cos^2\theta}$ for the series of orthoferrites from $LaFeO_3$ to $LuFeO_3$ [4].

A second way for studying H_{STHF} is by means of substituting impurities for the iron ion. For (6 - n) diamagnetic impurities as Ga^{3+} ions and n iron nearest neighbours giving a supertransfer contribution of h_{st}, we can rewrite eq. (2):

$$H_{STHF} = \frac{1}{6}\, nc\, \{ (A_\sigma^2 - A_\pi^2) \cos^2\theta + A_\pi^2 \} = nh_{st}. \qquad (3)$$

From Mössbauer data of Ga doped $LaFeO_3$ at 4.2 K an average supertransfer contribution per iron ion, $h_{st} \approx 10$ kOe has been found [5]. This value is in reasonable agreement with the "theoretical" value of about 15 kOe deduced from the angle dependent study in the series of orthoferrites [4].

3. Temperature dependence of the hyperfine field. - The temperature dependence of the magnetic hyperfine field $H_n(T)$ at a Fe^{3+}-ion with n iron ions and 6 - n diamagnetic impurities as nearest cations is shown in Fig. 2a for the case of $(Fe_{0.64}Rh_{0.36})_2O_3$ [2]. As can be seen from the figure $H_n(T)$ drops more rapidly as n increases. This behaviour can be described by local molecular field theory. For the molecular field acting on the Fe^{3+} ion we write

$$H_n = \frac{2nJ < \bar{S}_z >}{g\mu_B},$$

$$< S_z^n > = S\, B_S \left(\frac{g\, \mu_B\, H_n}{kT}\right). \qquad (4)$$

For the Fe^{3+} ion S = 5/2; $< S_z^n >$ is the average spin of an iron with n iron ions as nearest atoms; $< \bar{S}_z >$ is the spin of an iron ion, averaged over all the different environments; J is the superexchange parameter, which is related to T_N. For iron ions the magnetic hyperfine field is approximately proportional to the sublattice magnetization.

The same analysis has been done successfully for substituted ferrites and orthoferrites. In general it can be stated that in highly ionic compounds like oxides the temperature dependence of the sublattice magnetization can be described by only taking into account the first shell of cations. The same conclusion has been drawn earlier for the size of the magnetic hyperfine field.

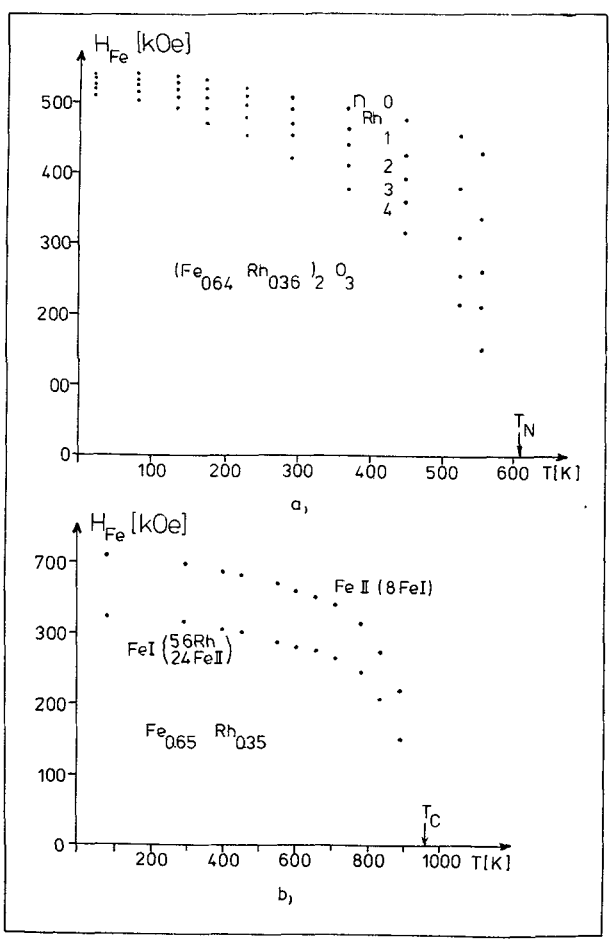

Fig. 2. - Temperature dependence of the iron hyperfine fields in an insulator (a) [2] and in a metal (b) [14].

3. Semiconductors. - The local picture of superexchange and supertransfer in a cluster of a central ion plus its nearest neighbours will break down in more covalently bound compounds. In sulfides, selenides and tellurides the anion-anion interactions become so large that a band approach becomes more appropriate resulting in long range exchange interactions and transferred hyperfine fields [6,7].

The Mössbauer study of the transferred hyperfine fields at the ^{151}Eu nuclei in the $Eu_{1-x}Sr_xS$ series shows this behaviour quite well [8]. These materials have the NaCl structure and the Eu^{2+} is a S-state ion with a magnetic moment of 7 μ_B. The magnetic hyperfine field increases from 280 kOe to 330 kOe between $x \lesssim 1$ and $x = 0$. Assuming that this increase is all due to a supertransfer and arises from the Eu ions in the first and second neighbouring shell, a considerable line broadening should be expected. In fact no additional broadening beside the linear increase from $x = 0$ to $x = 1$ has been observed and it is shown [8] that when more than 6 cation shells in EuS are transferring to the central Eu^{2+} ion, the linewidth at $Eu_{0.5}Sr_{0.5}S$ can be explained. These results can rather well be described by a model with broad valence bands in which an indirect polarization mechanism gives rise to long range magnetic interaction.

4. Iron alloys. - The situation concerning H_{hf} in iron is more complicated due to the contribution of conduction electrons. The various contributions to H_{hf} are the following:

$$H_{hf} = H_C + H_{con} + H_{nl} + H_L + H_{dip}, \qquad (5)$$

where H_C is the Fermi contact hyperfine field caused by the spin polarized 1s, 2s and 3s electrons: estimates and calculations give results between -220 and -400 kOe. H_{con} represents the spin polarized contribution of the 4s electrons. This term contains a contribution of the local parent magnetic moment $H_{con,l} \approx 180$ kOe and one from the nonlocal neighbouring moments $H_{con,nl} \approx -200$ kOe. H_{nl} is the nonlocal field produced by neighbouring atoms: (i) dipole fields from localized moments and (ii) transfer fields via overlap distortion of the core s orbitals. This last contribution is of the order of 10 kOe and much smaller than the supertransfer in oxidic compounds. The orbital contribution H_L is estimated to be 50 kOe and the dipolar magnetic field H_{dip} of the parent atom is zero in pure iron and small (< 10 kOe) in alloys.

The contributions H_c and H_{con} to H_{hf} are of the same magnitude which already indicates the absence of a simple relation between the magnetic moment and the magnetic hyperfine field in iron alloys. This is nicely demonstrated in Fig. 3 where the average

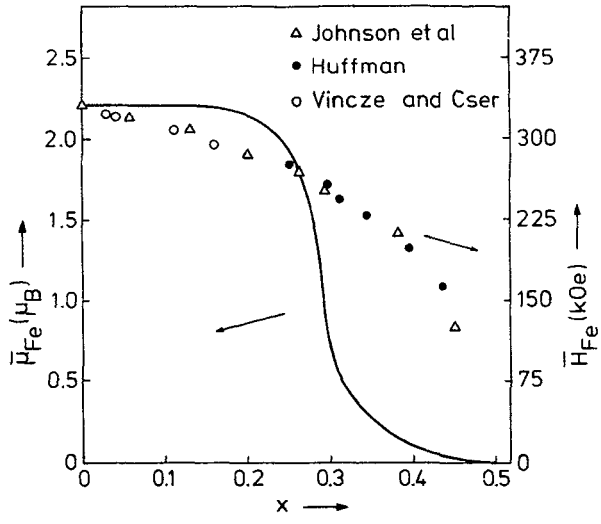

Fig. 3. - Average iron magnetic moment $\bar{\mu}_{Fe}$ and average iron hyperfine field $\bar{H}_{Fe}$ in bcc $Fe_{1-x}Al_x$ alloys. The solid line represents μ_{Fe} taken from Refs. [9], the hyperfine field data were taken from Refs. [10].

iron magnetic moment and average iron hyperfine field in bcc Fe-Al alloys has been plotted. On the iron side the Al is a simple diluent, the magnetic moment of iron is not perturbed by the substitution. However, $\bar{H}_{Fe}$ decreases because by removing a Fe moment also the spin polarization of the conduction electrons around the spinless impurity is taken away. The rapid decrease in $\bar{\mu}_{Fe}$ at about 30 at.% Al has been explained [11] by the fact that at least 4 neighbouring iron atoms are necessary for the formation of a magnetic moment. At iron contents somewhat more than equiatomic ($x \lesssim 0.5$) only the iron atoms having 8 Fe nearest neighbours are magnetic. Their magnetic moment is ≈ 2.2 μ_B according to magnetization measurements [11] and their hyperfine field is about 145 kOe [12]. In this case we measure directly the core polarization contribution to the hyperfine field because the rest of the iron atoms has no magnetic moment and thus the conduction electron polarization is absent. A core polarization constant of $a = 65$ kOe/μ_B can be deduced this way which agrees well with the value obtained for dilute iron based alloys [13].

The itinerant character of the exchange interactions in iron alloys as observed via the temperature dependence of magnetic hyperfine fields can

also be seen in Fig. 2.b. In $Fe_{0.65}Rh_{0.35}$ the temperature dependence of the sublattice magnetizations are very similar suggesting that it is determined by long-range correlations. This is in great contrast with similar curves in $(Fe_{0.64}Rh_{0.34})_2O_3$ where only direct near neighbour exchange is present.

Intermetallic compounds and metallic glasses. - We have seen that the value of the hyperfine field and its temperature dependence is influenced quite differently in insulators and alloys. The contribution of nearest neighbours to the value of the hyperfine field is relatively small ($\lesssim$ 10%) in insulators but the temperature dependence of magnetization is dominated by the first neighbour exchange interactions. On the other hand, in alloys about half of the hyperfine field originates from nonlocal contributions and the temperature dependence of magnetization is quite insensitive for the local neighbourhood. Both the value and the temperature dependence of the hyperfine fields of intermetallic compounds are insensitive for the transition metal neighbours. Fig. 4 shows that the value of the hyperfine field follows quite well the trends observed for the magnetic moments which are determined mostly by the metalloid neighbourhood. The proportionality constant, however, is different from that observed for alloy systems: a_r = 130 kOe/μ_B and it is near to the value characteristic for oxidic insulators. At the same time the temperature dependence of magnetization is similar to that of alloys and it is determined by long-range correlations. Similar trends were observed for metallic glasses [17]. These data indicate a fundamental rearrangement of the conduction electron band in intermetallic compounds and metallic glasses. The temperature dependence of the hyperfine field in agreement with resistivity measurements shows the presence of extended electron states.

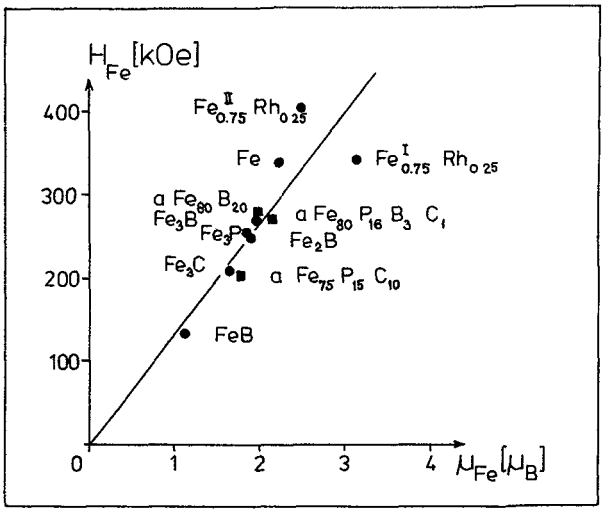

Fig. 4. - Iron hyperfine field and magnetic moment in intermetallic compounds and metallic glasses. Data are taken from Refs. [15] and [16].

The symmetry of these electron states is different, however, from that in the alloys. This is indicated by the small neighbour contribution to the hyperfine field ($\lesssim$ 10%) and by the absence of the local conduction electron contribution, $H_{con,1}$, which results in the two times larger core polarization constant. With considerable oversimplification we may say that the symmetry of conduction electrons in these systems is dominated by p-type of electrons, while the outer electrons of iron are rearranged and have mostly d-symmetry (there is no detectable amount of 4s electron).

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