Distribution of electron spin density in intermetallic yttrium-iron compounds

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The spectra of nuclear magnetic resonance in the intermetallic compounds YFe_2, YFe_3, and Y_2Fe_{17} are measured. The results are discussed together with the published values of the magnetic moments of the iron atoms. A model of formation of the magnetic moment of iron, with account taken of the polarization of the yttrium valence electrons, is proposed.

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INTRODUCTION

An important question in the development of the theory of transition 3*d* metals and their alloys is that of the state of the "magnetic" electrons. There exist now many theoretical models based on assumption of some degree of localization (or collectivization) of these electrons, but none explains consistently the host of observed magnetic and electric properties of these substances. The interest of physicists in the results of experimental investigations of the distributions of the spin and charge densities of the electrons in magnets is therefore understandable. The most direct method of obtaining this information is assumed to be neutron and x-ray diffraction. Unfortunately, we encounter here the circumstance that an insufficiently thorough reduction of the initial experimental data leads frequently to contradictions in the information. This, naturally, hinders objective interpretation of the data.

Whereas in pure 3*d* metals it is impossible at the present stage to explain the basic magnetic properties within the framework of a single model, the problem may turn out to be more manageable for intermetallic compounds of these metals. This is made possible by the presence of a large number of intermetallides with close crystal structure, and a comprehensive analysis of their magnetic properties reveals certain regularities.

In the present paper the object of such an analysis will be intermetallic compounds of yttrium with iron, having a general chemical formula Y_xFe_y. Even though the magnetic properties of these compounds have been sufficiently well studied, the character of the change of these properties on going from one compound to another has not yet found a satisfactory explanation. Special attention will be paid here to a discussion of the possible mechanisms that induce local fields at the nuclei of the nonmagnetic yttrium ions. The results of this discussion will permit an estimate of the influence of the spin density of the yttrium valence electrons on the magnetic moments of iron atoms.

EXPERIMENT

We investigated the nuclear magnetic resonance (NMR) of Y^{89} nuclei in the compound YFe_2, YFe_3, and Y_2Fe_{17}, as well as the NMR of Fe^{57} nuclei in YFe_2. The NMR spectra were obtained with a spin-echo spectrometer and recorded at 4.2 K. The durations of the first and second pulses, as well as the delay between them, were chosen to obtain a maximum signal amplitude. The investigated samples were fused in an arc furnace on a water-cooled copper bottom. Metallographic analysis and the NMR spectra showed that some samples contained small amounts of impurity phases. In such cases the ingots were remelted and annealed again.

With respect to magnetism, all the investigated compounds are ferromagnets whose magnetic moment is due to the iron sublattice.[1–3] The crystal structure of these compounds is described in detail in the specialized literature.[2,4,6] In contrast to YFe_2, the yttrium ions in YFe_3 occupy two nonequivalent sites in the crystal lattice, while the iron atoms occupy three. The compound Y_2Fe_{17} can have either a hexagonal structure (of the Th_2Ni_7 type) or a rhombohedral (Th_2Zn_{17}) one.[2] In the latter, all the yttrium positions are equivalent, whereas the hexagonal structure is characterized by the presence of two crystallographic sites for the yttrium ions. Notwithstanding the difference between the coordination characteristics, the structures of the investigated compounds are related. They can be obtained from a hexagonal lattice of the $CaCu_5$ type by simple atom rearrangements accompanied by layer shifts.[5]

In YFe_2 we observed two NMR signals at 28.8 and 45.9 MHz. Measurements performed with participation of an external magnetic field indicate that the high-frequency signal is due to the Y^{89} nuclei, and the low-frequency one to Fe^{57}. YFe_2 reveals five resonance lines at 29.0, 31.7, 34.3, 38.4, and 48.1 MHz. Comparison with the results of Ref. 7 gives grounds for assuming that the 38.4- and 48.1-MHz signals are due to resonance of the yttrium ions in two nonequivalent postions 3(*a*) and 6(*c*), respectively, while the 29-, 31.7-, and 34.3-MHz signals are due to resonance of Fe^{57}. For the Y_2Fe_{17} sample we observed one Y^{89} NMR signal at 42.6 MHz, attesting to the rhombohedral structure of the compound.

Table I lists the values of the local fields H^Y at the yttrium nuclei in the Y_xFe_y compounds. The average value of the field H^Y for YFe_2 was found with account taken of the quantitative difference between the yttrium ions at the sites (*a*) and (*c*).

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TABLE I. Values of local fields for different crystallographic positions of the yttrium in Y_2Fe_3.

Compound	Average magn. moment μ^{Fe}/μ_B	Position of Y	Number of nearest Fe neighbors	H^Y_{exp}, kOe	H^Y_{av}, kOe	H^Y_{calc}, kOe
YFe_2	1.45	8(*a*)	12	−219,6	−219.6	−210.6
YFe_3	1,63	3(*a*)	18	−183,7	−214	−183.7
		6(*c*)	12	−230		−230
Y_2Fe_{17}	1.9	6(*c*)	19	−204	−204	−212,1

*In the calculation of H^Y_{calc} with the aid of Eq. (7), the starting point was the value of the field at the yttrium nuclei in site (*a*) of the YFe_3 compound. The lattice parameters for Y_2Fe_{17} were taken to be $a = 8.51$ Å and $c = 12.43$ Å (Ref. 2).

DISCUSSION

a. Analysis of the results on the basis of the mean values of the local fields and of the magnetic moments of the iron

Investigations of the magnetic properties of the intermetallic yttrium-iron compounds indicate that the yttrium ions in these substances have no magnetic moment.[1–3] The local fields at their nuclei should therefore be due entirely to the influence of the neighboring magnetic atoms. The magnetic moment μ^{Fe} of iron in Y_xFe_y compounds increases from $1.45\mu_B$ in YFe_2 (Ref. 8) to $1.9\mu_B$ in Y_2Fe_{17} (Ref. 9). It would therefore be natural to expect a similar increase of the induced local field at the yttrium nuclei. Our measurement results however, show that such notions concerning the mechanism whereby the magnetic fields are induced are greatly oversimplified. It can be seen from Table I that with increasing moment of the iron on going from compound to compound, the mean values of the induced local fields H^Y remain practically unchanged.

To make clear the relation between the fields at the yttrium nuclei and the magnetic moments of the iron atoms we use the results of Ref. 10. It was shown there that:

a) the iron moment in Y_xFe_y depends linearly on the number $(3x/y)$ of the yttrium valence electrons per iron atom,

$$\mu^{Fe}=\mu^0-\mu^1=\mu^0-K(3x/y)\,\mu_B, \tag{1}$$

where K is the degree of polarization of these electrons:

b) the local fields at the Y^{89} nuclei in YFe_2 are due to the polarized collectivized electrons of yttrium.

In accord with item b), the magnetic fields at the Y^{89} nuclei should depend on the number n of the yttrium valence electrons and on the degree of their polarization:

$$H^Y\approx KnA^Y\mu_B. \tag{2}$$

Here A^Y is the parameter of the hyperfine interaction of the polarized yttrium electrons with the nucleus. Since the number of valence electrons and the degree of their polarization are constants for YFe_2, YFe_3, and Y_2Fe_{17}, the local fields at the yttrium nuclei in these compounds should also be equal, as is indeed confirmed by experiment. As for the correlation between μ^{Fe} and the field at the Y^{89} nuclei, however, this correlation exists only between μ^{Fe} and the field H^Y/m per iron atom,

$$H^Y/m=A^Y(nx/y)\,\mu_B, \tag{3}$$

where $m = y/x$ is the number of iron atoms per yttrium atom. The physical meaning of this field is that it is due to the influence of that part of the polarized yttrium electrons which contributes to the magnetic moment per iron atom.

From a comparison of (1) and (3) it can be seen that the reduced local fields H^Y/m are directly proportional not to the total moment μ^{Fe} but only to its component μ^1.

The model (1) of the formation of the magnetic moment of the iron and the proposed mechanism whereby the fields are induced at the yttrium nuclei permit a quantitative calculation of μ^0. Regarding the parameter A^Y as constant, we write for two arbitrary compounds (A) and (B) the equations

$$\frac{H_A^Y}{m_A}\Big/\frac{H_B^Y}{m_B}=\frac{\mu_A^1}{\mu_B^1}, \tag{4}$$

$$\mu_A^{Fe}=\mu^0-\mu_A^1,\quad \mu_B^{Fe}=\mu^0-\mu_B^1. \tag{5}$$

Equations of (4) and (5) for μ^0 leads to the expression

$$\mu^0=\frac{H_A^Y m_B\mu_B^{Fe}-H_B^Y m_A\mu_A^{Fe}}{m_BH_A^Y-m_AH_B^Y}. \tag{6}$$

Using the experimental values of μ^{Fe} and H^Y/m for the three possible combinations of compound pairs ($YFe_2 - YFe_3$, $YFe_3 - Y_2Fe_{17}$, $YFe_2 - Y_2Fe_{17}$) we obtain for μ^0 the respective values $1.96\mu_B$, $2.03\mu_B$, and $2.02\mu_B$.

We have so far left out of the exposition an essential detail of the field-induction mechanism, namely the source of the spin polarization of the collectivized electrons. Since the yttrium ions have no magnetic moment, this source, or more accurately the polarizing spin moment, should be related to the iron atoms. The constancy of the degree of polarization K in the Y_xFe_y sequence indicates that this moment is localized. It is therefore reasonable to assume that the constant magnetic contribution μ^0 in (1) is the aforementioned local moment responsible for the polarization of the collectivized electrons.

b. Allowance for the local surroundings

Of course, the foregoing analysis give only a general idea of the mechanism that induces the fields H^Y and of the participation of the yttrium electrons in the formation of the iron moment. The use of averaged values of the local fields H^Y, of the magnetic moments of the iron atoms, and of the total number of magnetic atoms obscures the details of this mechanism. We shall show below that allowance for the local surroundings permits further elaboration of the mechanism without changing the basic quantitative results obtained above.

The experimental results offer evidence that the local fields at the yttrium nuclei in YFe_3 depend on the crystallographic position of the Y atom. It can be seen from Table I that the field at the nuclei of the yttrium ions, which have 18 iron atoms in their nearest surrounding, is much weaker than the field at the yttrium nuclei, which are surrounded by 12 nearest Fe neighbors. In the case of Y_2Fe_{17}, where yttrium has 19 nearest Fe atoms, the field H^Y is close in value to that of H^Y in YFe_2 and YFe_3 for yttrium ions with 12 iron neighbors. It is thus obvious that the number of nearest magnetic atoms can by itself not serve as a criterion for the estimate of the induced field. We have attempted to determine the field H^Y for YFe_3 by using the expression

$$H^Y \sim \sum_i N_i/r_i^\alpha,$$

where N is the number of iron atoms in the ith coordination sphere of radius r_i. The necessary ratio of the values of H^Y in different positions is reached at $\alpha = 12$. However, so strong a dependence of the local field at the yttrium nuclei on the distance between ions is not confirmed by experiment.[6]

The values of the fields H^Y at nonequivalent yttrium ion sites can be explained by using the premise that these fields are due to the intrinsic polarized electrons of yttrium. The polarization ρ should in this case be proportional to the number N of the iron atoms responsible for the polarization, and to the number $(3/N)$ of the yttrium valence electrons per such iron atom. Taking into account the dependence of the polarization on the distance between ions, we obtain

$$H^Y = A_0{}^Y \rho \sim A_0{}^Y \frac{3}{N} \sum_i \frac{N_i \langle S \rangle}{r_i^\alpha}. \tag{7}$$

It can be seen that (7) is a modified form of (2), with the degree of polarization K replaced by the factor

$$\frac{\langle S \rangle}{N} \sum_i \frac{N_i}{r_i^\alpha},$$

that reflects the dependence of the polarization on the distance to the polarizing spin $\langle S \rangle$.

At first glance, expression (7) for H^Y differs little from the preceding ones. However, the use of the number $3/N$ allows us to recognize that the yttrium electrons from different sites (I and II in YFe_3) are polarized by different numbers of iron atoms. Indeed, considering the local surroundings of the ions YI and YII by iron atoms, and of the iron atoms FeI, FeII, and FeIII by yttrium ions, we can find that the number of Fe atoms is 4.4 for YI as against only 2.3 for YII. Let us demonstrate this with site YI as the example. As seen from Table II, this yttrium site has in its nearest surrounding 6 FeII atoms and 12 FeIII atoms. From the local surrounding of the FeII and FeIII atoms we obtain their weight fractions relative to one nearest yttrium ion, namely $\frac{1}{3}$ and $\frac{1}{5}$. Consequently we get $(\frac{1}{3}) \times 6 = 2$ FeII atoms and $(\frac{1}{5}) \times 12 = 2.4$ FeIII atoms per YI ion. We determine similarly the magnetic surrounding for the YII ions, namely 0.5 and 1.8 FeI and FeIII atoms. It is easily shown that this analysis of the local magnetic surrounding of the yttrium ions takes into account also the stoichiometry of the YFe_3 compound. Since the number of YII ions is double that of YI, we get for the three yttrium ions (YI + 2YII) a total of $4.4 + 2 \times 2.3 = 9$ Fe atoms.

Table II. Coordination characteristics of the structures of YFe_2 and YFe_3.

Compound	Atom	Neighbors	Number of neighbors	Distance, Å
YFe_2	Y	Fe	12	3,05
	Fe	Y	6	3.05
YFe_3	Y I	Fe II	6	2.98
		Fe III	12	3,31
	Y II	Fe III	3	3,10
		Fe III	6	2,93
		Fe I	3	3.03
	F• I	Y II	6	3.03
	Fe II	Y I	3	2.98
	Fe III	Y I	2	3,31
		Y II	1	3,10
		Y II	2	2,93

The number N in (7) is thus the sum ΣN_i and is equal to 4.4 or 2.3 (depending on the yttrium site), while N_i takes on values 2, 2.4, 0.5, and 1.8. Substituting the values of N, N_i, and r_{Y-Fe} in (7) we find that the best agreement with experiment is reached at $\alpha = 5$. The condition in this case was the ratio of the observed local fields at the nuclei of the YI and YII ions, namely $H^{YI}/H^{YII} = 0.8$.

A similar calculation was made also for the compounds YFe_2 and Y_2Fe_{17}. Assuming that the polarizing spin (which determines the local part μ^0 of the magnetic moment of iron) and the hyperfine interaction parameter A_0^Y are the same for the compounds YFe_3, YFe_2, and Y_2Fe_{17}, we find that for the last two H^Y equals 210.6 and 212.1 kOe, respectively. The insignificant deviation from the experimental value (see Table I) may be due to a certain error in the estimate of the distance r between the ions, since the lattice parameters of the investigated compounds were determined at room temperature, but the NMR spectrum is usually investigated at $T < 77$ K.

An earlier study 7 of NMR in the intermetallic compounds $Gd_xY_{1-x}F3_3$ has revealed an anisotropic distribution of the electron spin density in the rare-earth sublattice, A feature of the mechanism proposed in the present paper for inducing the fields H^Y is likewise an anisotropic distribution of the charge and spin densities of the yttrium-atom valence electrons in nonequivalent crystallographic positions. Neutron-diffraction investigations[11] of $HoFe_3$ have shown that the magnetic moments of iron in different crystallographic sites differ noticeably. The presence of several values of the magnetic moment for iron atoms in different yttrium-ion surroundings confirms the existence of the indicated anisotropy in YFe_3.

We consider now the contribution of the polarized yttrium electrons to the magnetic moment of iron atoms for the sites FeI, FeII, and FeIII. According to the scheme (1) of the formation of the moment for the iron atoms in YFe_2, we write

$$\mu^{FeI} = \mu^0 - \mu_I{}^1 = \mu^0 - C \frac{3}{2,3} \frac{2N_1}{r^5{}_{2-1}} \mu_B, \tag{8}$$

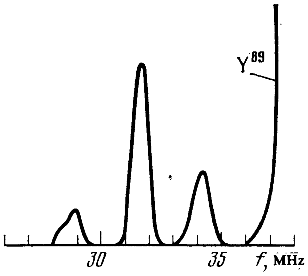

FIG. 1. NMR spectra of Fe^{57} in the compound YFe_3.

$$\mu^{FeII}=\mu^0-\mu_{II}{}^1=\mu^0-\frac{1}{2}C\frac{3}{4.4}\frac{N_2}{r^5_{1-2}}\mu_B, \tag{9}$$

$$\mu^{FeIII}=\mu^0-\mu^1_{III}=\mu^0-\frac{1}{6}C\left[\frac{3}{4.4}\frac{N_3}{r^5_{1-3}}+\frac{3}{2,3}\frac{2N_4}{r^5_{2-3}}\right]\mu_B. \tag{10}$$

Since the average moment of the iron in YFe_3 is $1.63\mu_B$ (Ref. 12), we have

$$\bar{\mu}^{Fe}=\mu^0-\bar{\mu}^1=1{,}63\mu_B. \tag{11}$$

We have similarly for the moment of iron in YFe_2

$$\mu^{Fe}=\mu^0-C\frac{3}{2}\frac{1}{r^5_{Y-Fe}}\mu_B=1.45\mu_B. \tag{12}$$

In Eqs. (8)–(12), $N_1 = 0.5$ and $N_3 = 2.4$ are the numbers of the FeII and FeIII atoms per YI ion: $N_2 = 2$ and $N_4 = 1.8$ are the numbers of FeI and FeIII atoms per YII ion; C is a normalization factor. The first subscript of r is the number of the site occupied by the yttrium ion, and the second is the number of the iron site.

The numbers of the iron atoms in sites I, II, and III are in a ratio 1:2:6. Taking this into account, the solution of Eqs. (8)–(12) for μ^{FeI}, μ^{FeII}, μ^{FeIII}, C and μ^0 yields the following values: $\mu^{FeI} = 1.50\mu_B$; $\mu^{FeII} = 1.73\mu_B$; $\mu^{FeIII} = 1.62\mu_B$; $C = 10^2$ Å^5; $\mu^0 = 2.02\mu_B$.

The published data on the magnetic distribution in the iron lattices of compounds of the RFe_3 type are very skimpy and ambiguous. Neutron-diffraction results for $HoFe_3$ show that at 77 K the largest moment is possessed by the iron atoms in the first position, and at $T = 297$ K by those in the third.[11] The use of these results for other compounds, particularly for YFe_3, can be justified only in the case of almost complete localization of the iron magnetic moments. At the same time the change of the local fields at the Fe^{57} nuclei, as well as the change of the moment of the iron in the pseudobinary compounds $Gd_xY_{1-x}Fe_2$ and $Gd_xY_{1-x}Fe_3$, takes place quite smoothly,[7,8] a situation difficult to describe in the framework of the theory of localized states.

For an experimental estimate of the value of μ^{Fe} of iron atoms in different crystallographic positions we have studied the NMR of Fe^{57} in YFe_3. It can be seen from Fig 1, which shows the NMR spectra of Fe^{57}, that according to the statistical weight of the number of iron atoms in the different positions, the NMR signals at 29.0, 34.3, and 31.7 MHz should be ascribed to the nuclei of the atoms FeI, FeII, and FeIII. A similar magnetic distribution in the iron sublattice is reported also in Ref. 13 on the basis of data on the Mössbauer effect in YFe_3. With allowance for the constant ratio of the hyperfine field and the magnetic moment of iron, we determined the values of μ^{Fe} that follow from the resonance measurements. Calculations made under the assumption that $H^{Fe}/\mu^{Fe} = 145$ kOe/μ_B (Ref. 14) are in satisfactory agreement with the results obtained by solving Eqs. (8)–(12) (see Table III).

It was shown above that allowance for the local surrounding leads to the same value of the localized part μ^0 of the magnetic moment of iron as was obtained by us above using an approach with the average local field H^Y and the total number of the iron atoms. From a comparison of (2) and (7) it can be seen that this agreement between the results is due to the approximate equality of the mean values of the distance r_{Y-Fe} between the ions for the sequence YFe_2, YFe_3, Y_2Fe_{17}.

CONCLUSION

Concepts concerning the mechanism that induces local fields at the nuclei of the nonmagnetic yttrium nuclei and concerning the effect of their electron structure on the magnetic moment of iron were advanced previously[10] on the basis of experimental data on the influence of hydrostatic pressure on the local fields in YFe_2. In the present study we have succeeded in extending the region of applicability of these concepts to include other compounds that are close in structure, and gained at the same time a deeper insight into the physics of the phenomena involved. We have proposed a model for the formation of the magnetic moment of the iron in Y_xFe_y compounds, an essential detail of the model being a superposition of a collectivized and a localized component of the moment.

We believe that our results can be useful for the interpretation of the magnetic properties of yttrium compounds with cobalt, where a similar distribution of the local fields at the yttrium nuclei is observed.[15]

TABLE III. Values of local fields and of magnetic moments of iron for different crystallogrphic positions of Fe in YFe_3.

Compound	Position	Values of μ^{Fe}/μ_B, calculated from (8)–(12)	H^{Fe}_{exp}, kOe	μ^{Fe}/μ_B, from Fe^{57} NMR data
YFe_3	Fe I	1.50	−211,7	1,46
	Fe II	1.73	−250,3	1,72
	Fe III	1,62	−231,4	1,59

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