NMR study of effect of hydrostatic pressure on local magnetic fields in Y_6Fe_{23}

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The local magnetic fields at Y^{89} and Fe^{57} nuclei and the pressure-induced shifts of these fields in the intermetallic compound Y_6Fe_{23} have been determined by an NMR method. The results are discussed in a model in which the magnetic moment of the iron atoms includes a moment of polarized collectivized electrons, which create the chemical bond of the yttrium with the iron. A reduction of the yttrium concentration in $Y_x Fe_y$ compounds is accompanied by a delocalization of the "magnetic" electrons of the iron.

INTRODUCTION

Experiments and calculations on the electronic structure of intermetallic compounds of yttrium and iron show that the electron system of yttrium plays an important role in shaping the magnetic moment of the iron atoms.[1-3] According to Ref. 1, the average size of this moment in the compounds YFe_2, YFe_3, Y_2Fe_{17} can be described in a first approximation by the formula

$$\bar{\mu}_{Fe}=\mu_0-\mu_1, \qquad (1)$$

where μ_0 is a magnetic moment which does not depend on the stoichiometry of the compound, and μ_1 is the moment of collectivized electrons. The latter is directly proportional to the yttrium concentration in these compounds. Aspects of the distribution of the electron spin density in the compounds listed above were brought out in Refs. 4 and 5 on the basis of formula (1). In discussions of how the magnetic moment of iron varies with the stoichiometry of $Y_x Fe_y$ compounds, however, it has not yet been found possible to obtain information concerning the nature of the component μ_0 of the magnetic moment. The size of this component is close to the magnetic moment of Fe atoms in metallic iron. On the other hand, the very possibility that this component can be distinguished as a constant component of the iron moment in $Y_x Fe_y$ compounds provides a basis for the assumption that the moment μ_0 is related to localized $3d$ electrons. In other words, there is the problem of choosing a model for describing the state of the "magnetic" electrons for iron-based intermetallic compounds.

This problem can be solved by combining the high-pressure technique with precise resonance methods for detecting changes in the magnetic properties of a substance during hydrostatic compression. Collectivized electrons, being outer atomic electrons, constitute a system which is more sensitive than localized electrons to the application of a pressure. For this reason, experimental results obtained during the hydrostatic compression of a sample might provide information about the state of the electrons of the magnetic atom.

In this paper we are reporting a study of the NMR of Y^{89} and Fe^{57} in the compound Y_6Fe_{23} and of the effect of hydrostatic pressure on the local magnetic fields at these nuclei. A discussion of the experimental data reveals details of the distribution of the electron spin density in Y_6Fe_{23} and of the formation of the magnetic moment of the iron atoms in the $Y_x Fe_y$ series of compounds.

EXPERIMENTAL PROCEDURE

The intermetallic compound Y_6Fe_{23} crystallizes in a cubic structure of the Th_6Mn_{23} type (space group $Fm3m$).[6] It has one crystallographic position for yttrium atoms and four nonequivalent positions for iron atoms. A study of the magnetic properties of this compound has shown[7] that it is a ferromagnet whose magnetic moment is associated with the iron sublattice. For the present experiments we used a sample prepared by arc smelting of the components (the Y was 99.9% pure, and the Fe 99.99%), followed by a homogenizing annealing at 1250 K for 70 h. According to metallurgical and x-ray diffraction analysis, the content of foreign structural phases was less than 1%.

A high hydrostatic pressure (up to $7\cdot10^8$ Pa at a temperature of 4.2 K) was produced with the help of a beryllium bronze chamber. The pressure-transmission medium was a mixture of transformer oil and kerosene. The pressure produced in the chamber was measured by the method described in Ref. 1.

The NMR spectra were recorded with the help of a spin-echo spectrometer at a temperature of 4.2 K. The lengths of the first and second pulses and the delay between them was selected by striking a compromise between a minimum width and a width sufficient for measuring the signal intensities.

For the compound Y_6Fe_{23} we found five spectral lines, at frequencies of 34.1, 37.6, 39.3, 42.2, and 49.3 MHz. Figure 1 shows the shape of the NMR spectra. Measurements carried out in an external magnetic field showed that the most intense signal, at 39.3 MHz, corresponds to Y^{89}, while the signals at 34.1, 42.2, and 49.3 MHz correspond to Fe^{57} nuclei. When an external field is imposed, the resonant frequencies of the echo signals shift downward, indicating that the local fields at the nuclei have a negative sign. The broadening of the Y^{89} line in the NMR spectrum in an external field prevented us from determining the shift of the signal at 37.6 MHz. However, a comparison with the results of Ref. 8 suggests that it is a consequence of a resonance of Fe^{57} nuclei.

A hydrostatic pressure p reduces the NMR frequencies of Y^{89} and Fe^{57}. For the Fe^{57} nuclei, the frequency change $\partial f/f\partial p$ was found to be the same, $(-1.9\pm0.3)\cdot10^{-11}\text{Pa}^{-1}$, while that of the Y^{89} nuclei was found to be $\partial f/f\partial p=(-1.7\pm0.1)\cdot10^{-11}\,\text{Pa}^{-1}$.

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DISCUSSION OF RESULTS

The four lines of Fe^{57} in the NMR spectrum of Y_6Fe_{23} are logically associated with the corresponding number of crystallographic positions of Fe atoms, and the intensities of these lines with the statistical weight of each crystallographic position for the given structure. According to x-ray structural studies,[6] the numbers of iron atoms in the various positions have ratios 1:6:8:8 (for the b, d, f_1, and f_2 positions, respectively). On this basis we find the local fields at the iron nuclei in these positions to be $-28.5\cdot 10^6$, $-21.7\cdot 10^6$, $-24.4\cdot 10^6$, and $-19.7\cdot 10^6$ A/m, respectively. A similar distribution of local magnetic fields in the iron sublattice was reported in Ref. 8, on the basis of a Mössbauer-effect study of Y_6Fe_{23}. Working from a constant ratio of the local field to the magnetic moment of the iron, μ_{Fe}, we calculated the values of μ_{Fe} which would result from measurements. The results of these calculations, which were carried out under the assumption $H^{Fe}/\mu_{Fe} = -11.5\cdot 10^6$ A/m (Ref. 8), are shown in Table I. The average calculated value, $\bar{\mu}_{Fe} = 1.93\mu_B$, agrees satisfactorily with results of measurements of the saturation magnetization of the compound Y_6Fe_{23}: $\bar{\mu}_{Fe} = 1.91\mu_B$ (Ref. 7).

It can be seen from Fig. 1 that the Y^{89} line in the NMR spectrum undergoes an inhomogeneous broadening in the low-frequency direction. This broadening can be explained easily, as a consequence of an anisotropy of the dipole fields on the side of the nearest iron atoms. A calculation of these fields for various directions of the easy axis reveals an agreement with experiment when the easy axis is along the [100] direction. In this case the spectrum is a superposition of two symmetric lines, which are separated from each other by 0.9 MHz and which have an intensity ratio 2:1.

To discuss the results of this study of the Y^{89} NMR, it is convenient to make use of the data in Table II, which lists coordination and magnetic characteristics of Y_xFe_y compounds with various stoichiometries. It can be seen from this table that the average induced local fields at the yttrium nuclei in the various compounds with iron do not exhibit a direct relationship with the number of nearest Fe atoms or their magnetic moment: The changes in the fields $\bar{H}^Y$ from compound to compound are insignificant. This fact indicates that the mechanism by which the electron system of yttrium interacts with the iron atoms is unusual (for metal alloys).

To reach an understanding of this mechanism, it is useful to go back to Ref. 4, where it was pointed out that there is a correlation between the reduced field $x\bar{H}^Y/y$ at the yttrium nuclei, i.e., between the field per iron atom, and the component μ_l of the magnetic moment of this atom [see expression (1)]. An increase or decrease in the reduced field (as we go from one compound to another) is accompanied by the same relative change in μ_l. Characteristically, a proportionality $x\bar{H}^Y/y \sim \mu_l$ has made it possible to explain the opposite changes in the field $\bar{H}^Y$ and the moment μ_{Fe} in YFe_2 which have been observed during the absorption of hydrogen by this compound.[9]

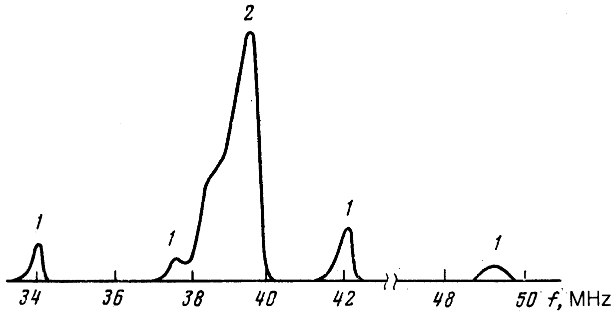

FIG. 1. Nuclear-magnetic-resonance spectra of the compound Y_6Fe_{23} at a temperature of 4.2 K. 1—Fe^{57} nuclei; 2—Y^{89} nuclei.

The essence of this correlation is the existence of a system of polarized collectivized electrons, which make the contribution μ_l to the magnetic moment of the iron and at the same time give rise to the local field $x\hat{H}^Y/y$. The twofold role played by the collectivized electrons suggests that the chemical bond between the yttrium and the iron is predominantly covalent and that the moment μ_l is associated with a covalent magnetism in intermetallic compounds.[10] If we take this approach, we find an explanation for the "constancy" of the average fields $\bar{H}^Y$ in Y_xFe_y. Specifically, since we have $x\bar{H}^Y/y \propto \mu$ and $\mu_l \propto x/y$, we find that $\bar{H}^Y$ does not depend on the parameter x/y, i.e., on the stoichiometry of the compound. A previous study[5] of Y_xFe_y compounds other than Y_6Fe_{23} and also of Y_xCo_y compounds has shown that the field $\bar{H}^Y$ exhibits a dependence on only the interion distance r_{Y-3d} and the "type" of 3d atom.

It is interesting to compare these arguments with calculations[2,3] of the band structure of Laves phases of AFe_2, where A = Y, Lu, Zr, Hf, Sc. According to these calculations, 3d states of iron hybridize with 4d (or 5d) states of the second component of the alloy in AFe_2 compounds. Hybridization effects are accompanied by a decrease in the moment μ_{Fe} and the appearance near the nominally nonmagnetic A atoms of a magnetic moment μ_A, directed antiparallel to μ_{Fe}. The extent of this interband mixing depends on the distance r_{A-3d} and also on the ratio of atomic potentials (the number of valence electrons) of the components of the compound. Opinion in the literature is divided regarding the mechanism for the appearance of a magnetic moment μ_A. According to certain sources,[11,12] this moment may be a consequence of an exchange splitting of a hard paramagnetic band. According to other sources,[2,10] the magnetic moment

TABLE I. Values of the local magnetic field at Fe^{57} nuclei and values of the magnetic moments of iron atoms in the compound Y_6Fe_{23} at T = 4.2 K.

Fe position	Value of H^{Fe}, in units of 10^6 A/m	μ_{Fe}/μ_B according to data on Fe^{57} NMR	Fe position	Value of H^{Fe}, in units of 10^6 A/m	μ_{Fe}/μ_B according to data on Fe^{57} NMR
32f_2	−19.7	1.71	32f_1	−24.4	2.11
24d	−21.7	1.88	4b	−28.5	2.47

TABLE II. Average local magnetic fields $\bar{H}^Y$ at Y^{89} nuclei, number of nearest neighbors of Fe atoms, and average magnetic moment $\bar{\mu}_{Fe}$ of iron atoms in Y_xFe_y compounds. Coordination and magnetic characteristics of the compounds YFe_2, YFe_3, and Y_2Fe_{17} from Ref. 4.

Compound	Average magnetic moment μ_{Fe}/μ_B	Number of nearest neighbors of Fe	Average value of $\bar{H}^Y$, in units of 10^6 A/m
YFe_2	1.45	12	−17,5
YFe_3	1,63	18,12	−17,0
Y_6Fe_{23}	1,91	13	−15,0
Y_2Fe_{17}	1,90	19	−16,2

μ_A is primarily a result of a covalent interaction of atoms of species of A with iron atoms in the course of which band "softens," and the density of states at the Fermi level has a indefinite value.

A comparison of the calculations of the electronic structure of Laves phases with our own results leads to the conclusion that this hybridization of states reduces the moment of the iron atoms by an amount $\mu_0 - \mu_{Fe} = \mu_1$ and gives rise to a magnetic moment $\mu_Y \sim y\mu_1/x$ near the yttrium atoms. The value of μ_Y and the related field H^Y are essentially independent of the stoichiometry of the compound.

Our ideas regarding the nature of the chemical bond between the yttrium and the iron and the role played by the electron system of yttrium in forming the magnetic moment of iron in Y_xFe_y are thus generally consistent with the results of the band calculations.

We mentioned above that the magnetic field at the yttrium nuclei in Y_xFe_y is related to the magnetic-moment component μ_1. As in Ref. 13, we can thus assume that the change caused in the field H^Y by the hydrostatic compression of the Y_6Fe_{23} sample is determined by a change in the moment μ_1. We then conclude that the magnetic component μ_1, like the field H^Y, is reduced by the application of pressure: $\partial \ln \mu_1/\partial p \approx \partial \ln H^Y/\partial p = (-1.7 \pm 0.1) \cdot 10^{-11}\,\mathrm{Pa}^{-1}$. Corresponding previous studies[13] of the compound YFe_2 have revealed a pressure-induced increase in H^Y and μ_1. The difference in the signs of the changes in the local fields at the Y^{89} nuclei in YFe_2 and Y_6Fe_{23} indicates that, despite the overall intensification of hybridization effects during the compression, the value of $\partial \ln \mu_1/\partial p$ and its sign depend on the nature of the change in the density of d states for the subbands with ↑ and ↓ spins. According to Ref. 3, an expansion (or compression) of the crystal lattice of an intermetallic compound is accompanied by not only a change in the density of states at the Fermi level but also a restructuring of the entire band. The presence of an "unhard" band of this sort is characteristic of a covalent-magnetism model.[10]

To discuss the results on the effect of pressure on the local fields at Fe^{57} nuclei, we use expression (1), according to which we have

$$\frac{\partial \ln \mu_{Fe}}{\partial p} = \frac{\mu_0}{\mu_{Fe}}\frac{\partial \ln \mu_0}{\partial p} - \frac{\mu_1}{\mu_{Fe}}\frac{\partial \ln \mu_1}{\partial p}. \qquad (2)$$

Experimental and theoretical studies[14,15] show that the fields at the iron nuclei in intermetallic compounds with nonmagnetic elements are directly proportional to the size of the magnetic moment of the Fe atoms. For the compound Y_6Fe_{23}, the relation $\partial \ln \mu_{Fe}/\partial p = \partial \ln H^{Fe}/\partial p = (-1.9 \pm 0.3) \cdot 10^{-11}\,\mathrm{Pa}^{-1}$ thus holds.

Previous studies have revealed that pressure induces changes in the fields H^Y and H^{Fe} in opposite directions in the compound YFe_2. A study of the baric properties on the basis of the expression (2) has revealed $\partial \ln \mu_0/\partial p \approx 0$. In other words, the pressure-induced change in the moment μ_0 in YFe_2 is either zero or very small. In the compound Y_6Fe_{23}, in contrast, the pressure dependence of μ_{Fe} can not be linked with a change in the component μ_1 alone. In this case the values of $\partial \ln \mu_{Fe}/\partial p$ and $\partial \ln \mu_1/\partial p$ are negative, so we find $\partial \ln \mu_0/\partial P < 0$ from (2). In other words, the magnetic moment of the Fe atoms in Y_6Fe_{23} changes (decreases) upon a compression of the crystal if we ignore the Y–Fe covalent interactions. This result shows that in compounds with a small yttrium content, in contrast with YFe_2, the assumption that the moment μ_0 is localized becomes a rather crude one. Consequently, the transition from YFe_2 to Y_6Fe_{23} is accompanied by a delocalization of iron electrons. This change in the degree of localization is logically linked with a decrease in the distances between iron atoms and an increase in the number of Fe–Fe bonds. The same conclusion can be drawn from a comparative analysis of the band structures of Y_2Fe_{17}, Y_6Fe_{23}, and YFe_3 (Ref. 12). For Y_2Fe_{17} the average local density of states at Fe atoms is described by a uniform, slightly modulated curve. With increasing yttrium content and thus with increasing $r_{Fe\text{-}Fe}$ distances, however, the local density of states is instead described by a curve with clearly expressed peaks.

CONCLUSION

While calculations of the electronic structure of metallic systems are undoubtedly important, a substantial component of the research on these systems is represented by experimental methods which make it possible to compare objective information with some model or other. Our studies show that the magnetic properties of yttrium-iron compounds correspond to an intermediate case which cannot be described on the basis of the model of localized moments or ideas involving a weak band magnetism. As the yttrium content varies in these compounds, however, one can follow the evolution of $3d$ states. In YFe_2, for example, the magnetic moment of iron is described fairly well by a superposition of a localized moment and a moment of collectivized electrons, the latter being responsible for the chemical bond between the iron and the yttrium atoms. When we move on to the compound Y_6Fe_{23}, in which the distances between Fe atoms are smaller than those in YFe_2, we observe a delocalization of $3d$ electrons, which is evidence of a shift of this intermediate case in the direction of band magnetism. Confirmation of a sort for this conclusion comes from the results of a study of the effect of pressure on the Curie temperature T_C of the compounds YFe_2, YFe_3, Y_6Fe_{23}, and Y_2Fe_{17} (Ref. 16): For YFe_2, T_C increases with the pressure, while for Y_6Fe_{23} and

Y_2Fe_{17} it decreases. According to theoretical studies by Edwards and Bartel,[17] a decrease in the Curie temperature is characteristic of weak band-magnetism substances.

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