Effect of pressure on the effective magnetic fields at Fe^{57} nuclei in the dielectric magnetic substances $Y_3Fe_5O_{12}$ and FeF_3

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The dependences of effective magnetic field strength H_n at Fe^{57} nuclei on pressure (up to 14 kbar) are measured on basis of the Mössbauer effect in the dielectric magnetic substances $Y_3Fe_5O_{12}$ and FeF_3. It is found that for both substances the equality $\partial H_n/H_n\partial p = \partial\sigma/\sigma\, dp$ holds, where σ is the magnetization. The reason for this fact may be that owing to the absence of a conduction band in $Y_3Fe_5O_{12}$ and FeF_3 and owing to the pure spin nature of the Fe atomic magnetic moments, the main contribution to H_n is from the field H_c due to the electrons of the ionic core. The relation established between H_c and σ is extended to the case of metallic iron. From this point of view the pressure dependence of H_n at Fe^{57} nuclei is analyzed and the following estimates of the contributions to H_n from the polarized electrons of the ionic core and the conduction band are obtained: $H_c \approx -280$ kG and $H_{ce} \approx -100$ kG. It is also shown that for metallic magnetic substances the pressure dependence of the coefficient A in the familiar relation $H_n(T) = A\sigma(T)$ is due to the greater compression of conduction electrons as compared to the compression of the inner-shell electrons in Fe.

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INTRODUCTION

The effective magnetic fields at the nuclei (H_n) have been measured for a large number of magnets. Interest in these fields has not decreased, because the understanding of their nature is equivalent to the understanding of the nature of magnetic ordering at the microscopic level. The fields H_n are brought about by the spin polarization of the electron shells, and the mechanisms of this polarization are quite varied, in accordance with the variety in the types of magnets. There is at present no satisfactory theory of the effective magnetic fields at the nuclei. The nub of the problem is the known difficulties of determining the wave functions of the electrons responsible for the magnetic ordering. An analysis of the experimental data yields so far only some general ideas on the mechanisms of the fields H_n, according to which we have, in the absence of an external field,

$$H_n = H_c + H_{ce} + H_L + H_D. \qquad (1)$$

Here H_C is the contact Fermi field from the s electrons of the ion core of the atom, H_{ce} is the Fermi contact field from the conduction electrons, H_L is the field from the unquenched orbital momentum of the unfilled shells, and H_D is the dipole field from the neighboring atoms and is the result of the anisotropy in the spin-density distribution. $H_D = 0$ in crystals with cubic symmetry. For transition elements of the iron group, H_L is relatively small ($\sim 10^4$ G), and can therefore always be neglected in comparison with the other contributions. Even in these cases, however, the question of the nature of H_n remains complicated: Whereas the field H_C has been sufficiently accurately determined for a number of substances,[1] there are no reliable data for the field H_{ce}. Moreover, even the sign of H_{ce} is not known as a rule.

In this situation, progress in the understanding of the nature of the field H_n can be expected only through a study of magnets in which, by virtue of peculiarities of the chemical bond and the simplicity of the crystal structure, H_n is determined by a minimal number of contributions. Examples of such substances are ferrites with cubic structure and with a pure spin character of the atomic magnetic moments.

In most experiments on effective fields, studies were made of the effects produced on these fields by the temperature, the atomic composition, the chemical bond, etc. At present, in view of the progress made in high-pressure techniques, it has become possible to study the influence of one more parameter—the interatomic distance. The most convenient methods for this purpose turned out to be those of NMR and the Mössbauer effect. We report here an investigation of the influence of hydrostatic pressure on the effective magnetic fields at the Fe^{57} nuclei in two magnets: yttrium iron garnet ($Y_3Fe_5O_{12}$) and antiferromagnetic FeF_3. These substances have no conduction bands, and the field H_n is determined mainly by the polarization of the electrons of the ion core. An attempt was also made to generalize the correlation, observed for these substances, between the changes of the field H_C and the magnetization σ under pressure, to include the case of metallic iron, so as to determine the different contributions made to H_n. The choice of these substances was governed also by the relatively large probability of the Mössbauer effect, which ensured to a considerable degree the reliability of the precision measurements of the Mössbauer spectrum parameters under high-pressure conditions.

EXPERIMENT

The effective magnetic fields at the Fe^{57} nuclei were measured with the aid of the Mössbauer effect using absorbers in powdered form. In the synthesis of the FeF_3, a small amount of the phase FeF_2 was produced and its presence did not seem to influence significantly the magnetic properties of the investigated phase FeF_3, since the Néel temperature and the value of the field H_n of our samples coincided with those known from the literature.[2] The resonance spectra were measured with a spectrometer at constant velocity, and the γ source was Co^{57} in chromium, with an activity 50 mCi.

The hydrostatic pressure was produced on the ab-

sorbers by a steel cell of the cylinder-piston type, with beryllium windows for the passage of the γ rays. The construction of a similar chamber is described in[3]. As the pressure transmitting medium we used a mixture of kerosene and transformer oil. The pressure in the cell was measured with calibrated manganin resistance pickups with accuracy ±0.1 kbar. During the temperature measurements, the high-pressure chamber was placed in a thermostat, in which the temperature could be varied from room temperature to ~100°C accurate to ±0.1°.

To interpret the results on the influence of the pressure on H_n in the case of FeF_3, we needed to know the pressure dependence of the Néel temperature (T_N). We measured T_N of the same samples at various pressures by the method of temperature scanning of the Mössbauer effect.[4] The value of the field was determined from the distance between the outermost peaks of the six-line hyperfine-splitting spectra, and the spectra were reduced by least squares. The time to measure one spectrum at a fixed pressure was 12—16 hours.

MEASUREMENT RESULTS AND DISCUSSION

A. $Y_3Fe_5O_{12}$

The Mössbauer spectra of Fe^{57} in $Y_3Fe_5O_{12}$ were superpositions of two sextets corresponding to two nonequivalent positions of the Fe atoms in the crystal lattice: octahedral (A) and tetrahedral (B) sites. Figure 1 shows the outermost peaks of the two sextets under normal conditions (spectrum 1) and at 14 kbar pressure (spectrum 2). The parameters of spectrum 1 are the following: H_{n1} = 393.7 kG, ϵ_1 = 0.262 mm/sec and H_{n2} = 490.0 kG, ϵ_2 = 0.490 mm/sec for sites A and B (here ϵ is the isomeric shift proportional to the s-electron density at the Fe^{57} nuclei). The lines of the sextet B are somewhat broadened because of the superposition of the two sextets from the nonequivalent positions of the Fe atoms in the sublattice B in[5]. Since the field difference for the B and B′ sites is small (~6 kG), we were able to trace only the variation of the average field H_n in the sublattice B. For the same reason, we neglected in the reduction of the results the possible changes, under pressure of the small quadrupole splittings for the sites B and B′.

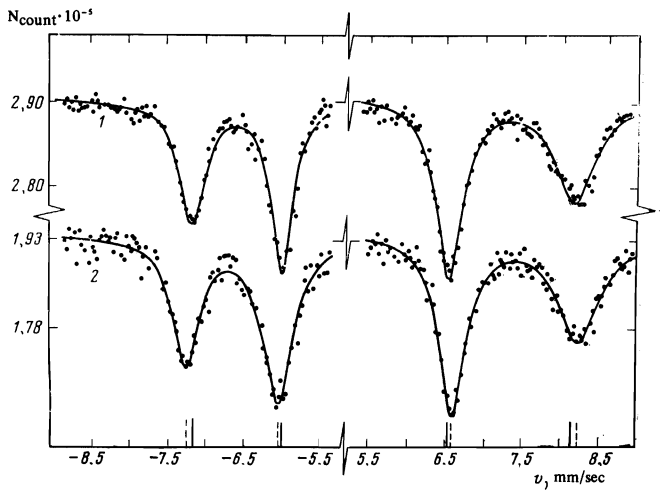

FIG. 1. Mössbauer spectra of Fe^{57} nuclei in $Y_3Fe_5O_{19}$ (outer peaks of two sextets): 1) P = 1 atm, 2) P = 14 kbar, N_{count}—number of counts.

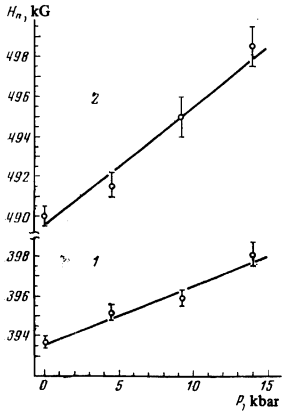

FIG. 2

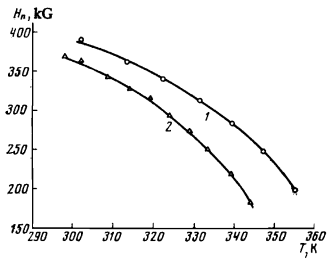

FIG. 3

FIG. 2. Plots of the effective magnetic fields at the nuclei Fe^{57} in $Y_3Fe_5O_{12}$ against pressure: 1—Fe atoms in octahedral sites, 2—Fe atoms in tetrahedral sites.

FIG. 3. Dependence of the effective field at the Fe^{57} nuclei in FeF_3 on temperature: 1) P = 1 atm, 2) P = 7 kbar.

Figure 2 shows plots of H_{n1} and H_{n2} against pressure. As seen from the figure, the fields increase linearly with coefficients $\partial H_{n1}/H_{n1}\partial P = (0.8 \pm 0.1)\cdot10^{-3}$ kbar^{-1} and $\partial H_{n2}/H_{n2}\partial P = (1.0 \pm 0.1)\cdot10^{-3}$ kbar^{-1}. Since the macroscopic magnetic moment of the sample is made up in this case of pure spin angular momenta of the 3d shells,[6] which are the main cause of the field H_n, it is of interest to establish the connection between H_n and the magnetization σ, which is proportional to the average magnetic moment $\bar{\mu}$ of the iron ions. According to the data of[7], obtained from measurements of the magnetization under pressure at room temperature, $\partial\bar{\mu}/\bar{\mu}\mu P = (0.96 \pm 0.06)\times10^{-3}$ kbar^{-1}. Taking into account a 3 :2 ratio of distribution of the Fe atoms among the sites A and B, we find that the relative changes of the magnetic moments and of the effective fields produced by them are equal to each other within the limit of errors. It must be emphasized to so far investigations of metals and alloys have shown these quantities to be unequal.[8,9] These facts can be explained as follows:

It is known that the internal shells of the atoms are less compressed under pressure than the external ones.[10] Since the change of μ is due mainly to the "internal" electrons, say the 3d electrons, and the change of H_n is due to both "internal" and "external" ones, say 3d and 4s electrons, it follows that the presure should lead in the general case to large relative changes of H_n in comparison with μ. The degree of inequality of the relative changes of H_n and σ should depend on the number of "external" s electrons per Fe atom. This number is of the order of unity in metallic magnets, whereas for $Y_3Fe_5O_{12}$ it is practically equal to zero (the electron configurations of the Fe^{+3} ion in the tetrahedral and octahedral sites, determined from the calibration curve of the isomeric shifts,[11] are of the form $3d^54s^{0,1}$ and $3d^5$). The variation of H_n therefore follows the variation of σ.

As shown by Wajne et al.,[7] the increase of σ in $Y_3Fe_5O_{12}$ under pressure (at room temperature) can be attributed fully to the dependence of the Curie temperature on the pressure. This means that the magnetic moments of the ions Fe^{+3} at T = 0 are practically not altered by the pressure, and the change of the macroscopic moment, which is proportional to μ at T = 300°K,

is due to the increase of the energies of the exchange interactions. From this point of view, the equality of the relative changes of the magnetization and of the effective fields becomes all the more obvious.

We disregarded in the preceding discussion the covalent effects, which were used in a number of cases to explain the difference between the fields H_{n1} and H_{n2}.[13] In a qualitative treatment, the covalent effects can apparently be neglected. For a quantitative analysis of the $H_n(P)$ dependences it is necessary to know the actual form of the electronic wave functions and of their overlap integrals.

B. FeF_3

To check on the general character of the regularities observed for yttrium iron garnet, we carried out analogous investigations on the antiferromagnet FeF_3. This substance has weak ferromagnetism because of the canting of the antiferromagnetic sublattices.[13] At T = 0 the field at the nuclei Fe^{57} in FeF_3 equals 620 kG, i.e., exactly the value calculated in[1] for the Fe^{+3} ion. Since the quadrupole splitting of the Fe^{57} levels is very small, the large deviation from cubic symmetry in the FeF_3 structure can apparently be neglected, and it can consequently be assumed that $H_D = 0$. In addition, the magnetic moments of the Fe^{+3} ions have a spin character,[14] i.e., $H_L = 0$. Thus, FeF_3 is a unique magnet in which all the contributions except H_c (see formula (1)) are equal to zero, and the $H_c(P)$ dependence can be traced in pure form. The relatively low Néel temperature (T_N = 91°C) makes it also possible to investigate $H_n(T)$ under hydrostatic-pressure conditions. These experiments are of interest in connection with the question whether the known relation

$$H_n(T)=A\sigma(T), \tag{2}$$

where A is a constant, is satisfied under pressure. The point is that relation (2) is valid for a large number of magnets at atmospheric pressure, but does not hold when the pressure is increased, at any rate in the case of metals and alloys. The reason for this was not clear. The experiments mentioned above allow us to establish a correlation between $H_n(T)$ and $\sigma(T)$ under pressure and by the same token evaluate the role of the conduction electrons.

We measured $H_n(T)$ (Fig. 3) near T_N at 1 atm (curve 1) and at a pressure of 7 kbar (curve 2). Comparison of these curves shows clearly the influence of the pressure on T_N. We consider these data from the point of view of the known temperature dependence of the reduced field $h = H_n(T)/H_n(0)$[15]:

$$h=D(1-T/T_N)^{\beta}, \tag{3}$$

where D and β are constant coefficients. We note that

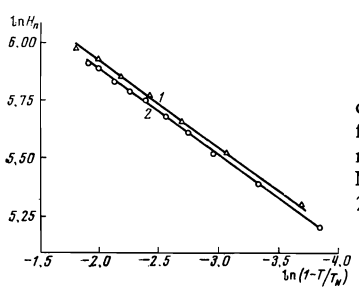

FIG. 4. Dependence of ln H_n on ln (1 − T/T_N). H_n is the effective magnetic field at the Fe^{57} nuclei in FeF_3, and T_N is the Néel temperature. 1) P = 1 atm, 2) P = 7 kbar.

calculations by the Green's function method yield D = 1.20 and β = 0.36, which coincide with the experimental values.[16] It was shown earlier that relation (3) is satisfied also for the relative magnetization $\sigma(T)/\sigma(0)$, i.e., the coefficient A is a constant at atmospheric pressure.[17]

Figure 4 shows plots of ln H_n on ln(1 − T/T_N), and curve 1 corresponds to P = 1 atm. A reduction of curve 1 yields D = 1.20 ± 0.02 and β = 0.36 ± 0.01, in agreement with the published data. To ascertain whether relation (3) remains valid under pressure, it is necessary to take into account the pressure dependence of T_N. We measured $T_N(P)$ by the aforementioned method of temperature scanning the Mössbauer effect and obtained $\partial T_N/\partial P = -(1.7 \pm 0.1)$ deg/kbar. With this coefficient taken into account, we plotted curve 2 of Fig. 4, from which we obtained D = 1.18 ± 0.02 and β = 0.36 ± 0.01. Some disagreement between curves 1 and 2 may indicate a tendency of D to decrease, but within the limits of the errors in the measurements and the data reduction the parameters D and β should be regarded as independent of the pressure. Thus, the coefficient A in (2) does not depend on the pressure.

Figure 5 shows the Mössbauer spectra of the nuclei Fe^{57} and FeF_3 (two outside lines each of the sextet at positive and negative velocities of the γ-ray source) at pressures 1 atm (spectrum 1), 5 kbar (spectrum 2), 10 kbar (spectrum 3). The reduction of these spectra yielded the $H_n(P)$ plot of Fig. 6, on which the points indicate the experimental data and the solid curve is a plot of the function (3) with allowance for the $T_N(P)$ dependence. As expected, the agreement is satisfactory.

We turn now to a discussion of relation (2) for metallic magnets. The dependence of A on the pressure is the consequence of the inequality of the relative changes of H_n and σ, which is apparently the result of the pressure dependence of H_{ce} (see formula (1)). The expression for H_{ce} is

$$H_{ce}=\frac{8\pi}{3}\mu_B\langle|\psi(0)|^2\rangle_F n\rho, \tag{4}$$

where $\langle|\psi(0)|^2\rangle_F$ is the probability density of the s-like conduction electrons at the nuclei, averaged over the states on the Fermi surface, n is their number per unit cell, ρ is the degree of polarization, and μ_B is the Bohr magneton. Since ρ is proportional to σ, formula (4) can be written in the form

$$H_{ce}=\text{const}\,\langle|\psi(0)|^2\rangle_F\sigma.$$

It is easily seen that the relative changes of H_{ce} and σ

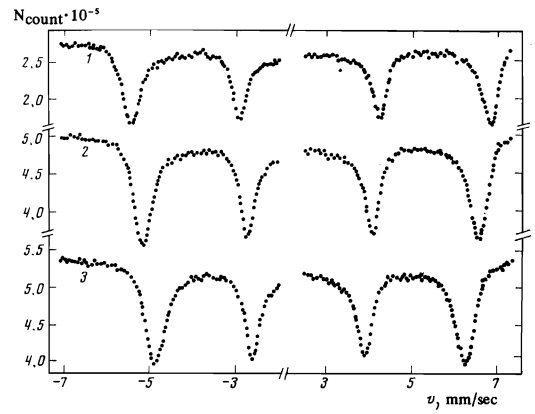

FIG. 5. Mössbauer spectra of Fe^{57} nuclei in FeF_3: 1) P = 1 atm, 2) P = 5 kbar, 3) P = 10 kbar.

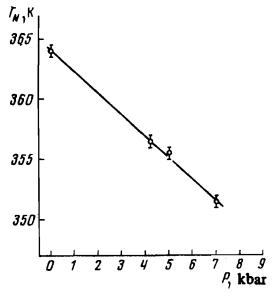

FIG. 6. Pressure dependence of the effective magnetic field at the Fe^{57} nuclei in FeF_3.

under pressure are not the same, owing to the pressure dependence of $\langle|\psi(0)|^2\rangle_F$, which manifests itself in the experiments in the form of a change of the isomeric shift of the Mössbauer spectrum. The field H_{ce} is an appreciable component of H_n, and therefore

$$\partial H_n/H_n\partial P \neq \partial\sigma/\sigma\partial p,$$

and consequently $A \neq$ const. Thus, the pressure dependence of A in metallic magnets is connected with the conduction band.

We note in conclusion that for $Y_3Fe_5O_{12}$ and FeF_3 we observed no changes in the isomeric shifts under pressures. This is apparently the consequence of the small number of external s electrons in the Fe ions.

C. Metallic Iron

Using the results of the investigations of the effective magnetic fields in the dielectric magnets $Y_3Fe_5O_{12}$ and FeF_3, we shall attempt to estimate, on the basis of the data of[8] on the pressure dependences of the isomeric shift ϵ and of the field H_n in metallic iron, the values of the contributions made to H_n in this more complicated case.

For metallic iron, the contributions H_{ce} and H_L (see formula (1)) are quite important. Of these two fields, H_{ce} is the least determined. For the field H_L, the following approximate estimates are given in[18,19]: +50 kG and +70 kG. As already noted, in cubic crystals $H_D = 0$. Then the change of the field H_n in iron under the influence of pressure can be expressed in the form

$$\Delta H_n = \Delta H_c + \Delta H_{ce} + \Delta H_L. \quad (5)$$

This expression becomes simpler if the following assumptions are made: According to[8], the change of the isomeric shift under pressure is proportional to the relative decrease of the volume V of the unit cell:

$$\Delta\varepsilon = 1.4\Delta V/V\ [\text{mm/sec}]. \quad (6)$$

On the other hand, it follows from the calibration of the isomeric shifts[11] that increasing the number of 4s electron by unity corresponds to a decrease of ϵ by 1.4 mm/sec. Since the proportionality coefficient in (6) is equal to 1.4 mm/sec, and the electronic configuration of the Fe atom in iron is $3d^74s^1$, this ratio can be regarded as a confirmation of the perfectly natural assumption that in the region of relatively low pressure there occurs in the main a "compression" of only the wave functions of the conduction electrons. This gives grounds, in turn, for regarding the radius of the 3d shell of the Fe atom as constant, i.e., $\Delta H_L = 0$.

As the basis for further estimates we assume that the correlation $\partial H_C/H_C\partial P = \partial\sigma/\sigma\partial P$ obtained for dielectric magnets is value also in the case of metallic iron. This assumption seems reasonable to us, since the source of polarization of the ion core of the Fe atom is the magnetic moment of the localized 3d electrons, which amounts, according to neutron-diffraction investigations,[20] to at least ~0.9 of the resultant magnetic moment of the Fe atom. Then, for a certain fixed pressure we have $\Delta H_C = H_C\Delta\sigma/\sigma$. Further, differentiating formula (4) and dividing by H_{ce}, we obtain

$$\frac{\partial H_{ce}}{H_{ce}\partial P} = \frac{\partial\langle|\psi(0)|^2\rangle_F}{\langle|\psi(0)|^2\rangle_F\partial P} + \frac{\partial n}{n\partial P} + \frac{\partial\rho}{\rho\partial P}.$$

In the range of pressures up to 50 kbar, the number of conduction electrons in the band can apparently be regarded as constant,[8] i.e., $\partial n/n\partial P = 0$. Since ρ is proportional to σ, it follows that $\partial\rho/\rho\partial P = \partial\sigma/\sigma\partial P$. From the linear dependence of ϵ on the pressure and from the assumption of the predominant compression of the conduction electrons, we obtain

$$\frac{\partial\langle|\psi(0)|^2\rangle_F}{\langle|\psi(0)|^2\rangle_F\partial P} = \frac{|\Delta V|}{V\partial P} = K$$

(K is the compressibility of the iron). Then

$$\Delta H_{ce} = H_{ce}(|\Delta V|/V + \Delta\sigma/\sigma),$$

and expression (5) takes the form

$$\Delta H_n = H_c\frac{\Delta\sigma}{\sigma} + H_{ce}\left(\frac{|\Delta V|}{V} + \frac{\Delta\sigma}{\sigma}\right). \quad (7)$$

We substitute in (7) the quantities $\Delta\sigma/\sigma = -2.9 \times 10^{-3}$,[21] $\Delta V/V = 5.9 \times 10^{-3}$, and $\Delta H_n/H_n = 1.7 \times 10^{-3}$,[8] which correspond, to be specific, to a pressure of 10 kbar. Then, solving the system of equations (1) and (7) at $H_D = 0$, $H_L = +50$ kG, $H_n = -330$ kG, and $\Delta H_L = 0$, we obtain $H_c \approx -280$ kG and $H_{ce} \approx -100$ kG.

Favoring the likelihood of these estimates are the following facts: A negative sign of the field due to the conduction electrons in iron was also obtained recently[22]. In addition, from the value of the field H_{ce} and from the estimates of the contribution made to H_n by one unpaired 4s electron[1] we can obtain $\rho = 6\%$, which coincides with the estimates of other workers. In particular, recent experiments on the precession of μ^+ mesons in iron yield $\rho = 6.5\%$.[23] In turn, the value of H_c is close to that calculated in[1]. However, the values of H_c and H_{ce} obtained by us must be regarded as very approximate, and they can be used only as a working hypothesis in subsequent investigations.

Thus, our experiments have established that in the case of dielectric magnets under pressure the relative changes of the effective magnetic fields at the Fe nuclei, as well as the corresponding magnetizations, are all equal. The reason for the previously observed inequality of these quantities in the case of metallic magnets lie in the presence of a conduction band and in the difference in the action of the pressure on the internal and external electron shells of the atoms. To determine the individual contributions to the effective field it is necessary to investigate a larger group of magnets, in which one of the contributions or another predominates.

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