Magnetic hyperfine field at the nuclei of nonmagnetic iron ions in ferromagnetic $Co_{0.97}Fe_{0.03}S_2$

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By the method of the Mössbauer effect it is found that the direction of the hyperfine field indirectly induced at the nuclei of the nonmagnetic Fe^{2+} ions and the direction of the magnetization of the Co^{2+} ions inducing the field are opposite. The mechanism, previously only assumed, in which the field is induced via spin-density transfer from the e_g subband of Co^{2+} to the unoccupied e_g band of the nonmagnetic iron is thereby displayed experimentally. The electric-field gradient V_{zz} is shown to be positive. In addition, the experimental results confirm the assumptions about the angular structure of the Co^{2+} moments. The measurements were carried out in external magnetic fields up to 60 kOe at $T = 4.2$ K.

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1. INTRODUCTION

Compounds with the pyrites structure MX_2, where M = Fe, Co, Ni, ... and X = S, Se, have been the subject of a number of investigations in recent years [1-3]. These compounds possess well-known peculiarities in the conjunction of their magnetic and electrical properties, and it is of interest to investigate these. For example, FeS_2, because of the low-spin configuration of the Fe^{2+} ions, is a nonmagnetic semiconductor with weak temperature-independent van Vleck paramagnetism. At the same time, CoS_2, which is isostructural with it, is a ferromagnet (T_C = 120 K) with metallic conduction [1].

It was shown recently [4] that a magnetic hyperfine field is induced at the nuclei of nonmagnetic iron ions Fe^{2+} substituted in CoS_2 at a temperature below T_C. However, a rigorous theoretical analysis of the Mössbauer spectrum of Fe^{57} in $Co_{0.98}Fe_{0.02}S_2$ at 91 K obtained by Woodhams et al. [4] was found to be impossible because of the mixing of the magnetic-dipole and electric-quadrupole interactions, which are comparable in magnitude. Analytical modeling gave two equally likely sets of hyperfine (HF) interaction parameters, depending on the sign of the electric-quadrupole direction. The sign of the magnetic HF field was undetermined in both cases.

It is pertinent to recall that as long ago as 1965 Kamimura [5] gave a theoretical treatment of the so-called temperature-dependent shift of the NMR frequency at the nucleus of the low-spin diamagnetic ion Co^{3+} in the compound Co_3O_4. It was shown that this shift is due to the appearance at the nucleus of the Co^{3+} ion of a HF field indirectly induced by the magnetic Co^{2+} ions. Since the Co^{3+} ion in Co_3O_4 is isoelectronic with the Fe^{2+} ion in FeS_2, and is also analogous to it in its spin state and in the presence in both cases of constant temperature-independent van Vleck paramagnetism, it was of interest to compare the mechanisms of the indirect HF interactions in Co_3O_4 and $(CoS_2)_{0.97}(FeS_2)_{0.03}$. A direct experimental determination of the sign of this field is of decisive significance for the correct analysis of these interactions. Moreover, in the papers [1,4] postulates about the angular spin structure of the Co^{2+} ions in CoS_2 were put forward.

The aim of this work is to elucidate these questions by means of an investigation of the HF interactions at the Fe^{57} nuclei in $(CoS_2)_{0.97}(FeS_2)_{0.03}$ in external magnetic fields up to 60 kOe and in the temperature range 4.2–135 K.

2. PREPARATION OF THE SAMPLES AND THE MEASUREMENT TECHNIQUE

The synthesis of the Fe^{57}-enriched compound $(CoS_2)_{0.97}(FeS_2)_{0.93}$ was carried out in steps. First the monosulfides of Co and Fe were obtained from metallic Co and Fe [of grade OSCh (of extreme purity)], previously reduced in a stream of hydrogen at 500°C, and elemental sulfur (OSCh) in evacuated quartz ampoules at 800°C. A mixture of the monosulfides with excess S, previously thoroughly ground under acetone, was maintained at 600°C in evacuated quartz ampoules for 14 days. The ampoule was then opened, and the contents were ground and again maintained at 600°C for 30 days. After the excess sulfur had been removed by benzene, the substance was checked for homogeneity by the x-ray method.

The measurements at 4.2 K were performed on a standard Mössbauer spectrometer, additionally equipped with a liquid-helium cryostat and a superconducting magnet.

The source was Co^{57}(Cu) at liquid-helium temperature. The absorber was magnetized along the direction of propagation of the γ-rays. The stray fields at the source did not exceed 5% of the fields at the absorber.

3. THE MÖSSBAUER SPECTRA

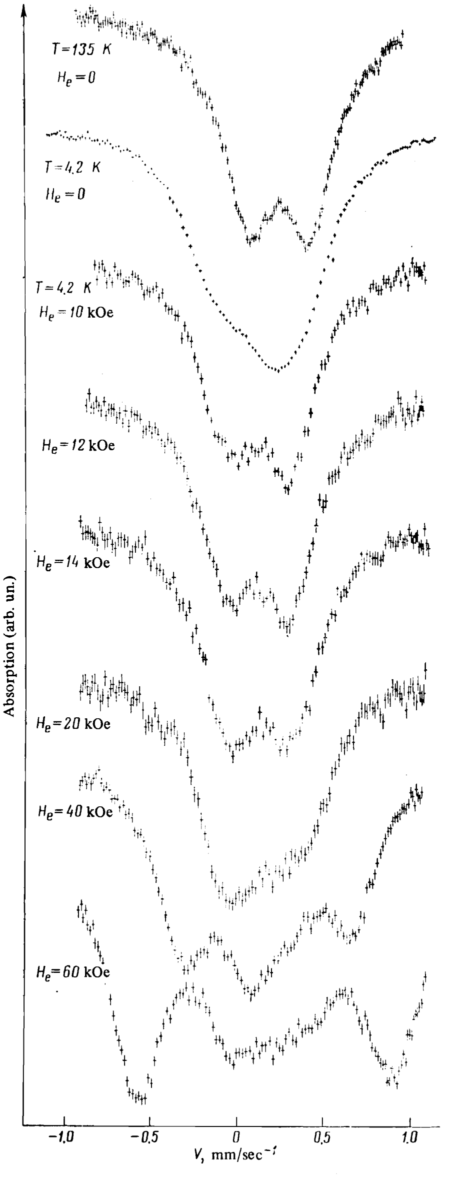
The figure shows the spectra of $(CoS_2)_{0.97}(FeS_2)_{0.03}$ at 135 K and at temperature 4.2 K—in different external magnetic fields. The spectrum at 135 K is characterized by quadrupolar splitting with ΔE_q = 0.31(1) mm/sec, which is in agreement with the values reported in [4,6]. Below the Curie temperature (~ 130 K [1]) the spectra have an asymmetric shape because of the imposition of the small additional HF field. The spectrum at 77 K (which is not given here) and the spectrum at 4.2 K (H = 0) are similar to the spectrum at 91 K in [4].

In the figure one can trace the effect of external magnetic fields of 10, 12, 14, 20, 40 and 60 kOe on the magnetic HF structure. It can be seen that the asymmetry in the shape of the spectrum with no external field decreases when fields up to 14 kOe are applied.

The spectrum for H_e = 20 kOe looks like the mirror reflection of the spectrum with H_e = 0. In fields of 40 and 60 kOe a partially resolved magnetic splitting, distorted by the quadrupolar interaction, is observed. The splitting of the outer lines corresponds to the internal magnetic field, which is approximately 10—14 kOe smaller than the applied external field.

The spectra plotted in external fields of 20, 40 and 60 kOe at T = 4.2 K were processed on a computer, with approximation to a Lorentzian lineshape and with the assumption of complete polarization of the Co^{2+} ions, i.e., complete collinearity of the HF field at the Fe^{57} nuclei with the direction of the γ-ray beam. In this case nuclear transitions with $\Delta m = 0$ are forbidden and the Mössbauer spectra consist of four lines.

The results of the processing are given in the table, where the average half-width $\Gamma/2$ of the line, the isomer shift δ relative to Co^{57}(Cu), the total magnetic field H at the nucleus and the quadrupolar shift ΔE_q are given. Fitting of the spectrum plotted at temperature T = 78 K with no external magnetic fields applied gave the value $H_i = 6 \pm 1$ kOe for the field induced at the Fe^{57} nuclei. The width of the line was taken to be equal to its width at T = 135 K, i.e., still in the paramagnetic region but close to T_C.



Parameters of the Mössbauer spectra of pyrites $(CoS_2)_{0.97}(FeS_2)_{0.03}$ in external magnetic fields at 4.2 K.

H_e, kOe	$\Gamma/2$, mm/sec	δ, mm/sec	H		ΔE_q, mm/sec
			mm/sec	kOe	
20	0.189 (8)	0.112 (4)	0.466 (13)	14.5	0.056 (9)
40	0.209 (3)	0.135 (2)	0.936 (4)	29.1	0.041 (2)
60	0.238 (3)	0.146 (2)	1.432 (4)	45.0	0.016 (3)

4. DISCUSSION

A rigorous analysis of the Mössbauer spectra we have obtained requires the development of special fitting programs for mixed HF interactions. The spectrum in the magnetically-ordered region without application of an external field can be described in the framework of an analysis of the interaction for a definite fixed orientation of the axes of the electric-field gradient (EFG) with respect to the induced HF field. Further, when an external field is applied the resultant magnetic moment of the polycrystalline sample is aligned along the field direction even at values $H_e \approx 2$ kOe; the magnetization of the sample remains constant in fields up to 10 kOe[2]. The Hamiltonian of the HF interaction in this case includes the total magnetic field (external + induced) and the electric-field gradient, the axes of which are oriented randomly with respect to the external field. A fitting procedure that takes into account all the above features has not yet been applied. However, the principal physical deductions can already be made on the basis of a direct analysis of the experimental data or by the aforementioned simpler method of processing the data.

1. Sign of the Induced Field, and Its Nature

Apparently, the first clear experimental proof of the existence of an indirect HF interaction between magnetic and nonmagnetic ions of metals in salts of the transition elements is the work of Laurance et al.[7]. Here, by means of the electron-nuclear double resonance method, the authors investigated the HF fields induced at the Al^{27} nuclei by Cr^{3+} ions introduced as an impurity into Al_2O_3.

Transfer of spin density from magnetically-ordered atoms to neighboring anions and cations has also been observed in other cases. We note the observations of the magnetic fields, and their temperature dependence, at Sn^{119} nuclei in tin-substituted yttrium garnet[8], in nickel ferrite-spinel[9], and in orthoferrites[10]. The principal mechanism inducing the hyperfine field here is the transfer of a polarized d-electron from a nearest-neighbor magnetic atom to the empty 5s orbital of the Sn atom. This transfer can be either direct (magnetic cation—Sn), like, e.g., the contribution of the BB interaction in the spinels[9], or indirect (metal-ligand-Sn)[8]. The HF field at the nucleus then arises from the usual Fermi contact interaction. A contribution to the HF field from this type of mechanism is also observed at the nuclei of the magnetic ions as an increase in the interaction of the nucleus of the ion with its own electrons[11].

In all these cases, the direction of the field induced at the nucleus of the diamagnetic atom, or the direction of the additional HF field from this mechanism at the nucleus of the magnetic atom, coincides with the direction of the moment of the cation inducing the field. The sign of the induced HF field is conventionally assumed to be positive.

In our case, however, the opposite picture obtains. The indirectly induced field observed at the nucleus of the nonmagnetic low-spin Fe^{2+} ion in $Co_{0.97}Fe_{0.03}S_2$ has a direction opposite to the magnetization of the Co sublattice inducing the field. This follows, e.g., from a comparison of any of the spectra taken in external fields of 10, 12 or 14 kOe with the spectrum taken with no applied external field (see the Figure). It can be seen that the application of an external field leads to a decrease of the resultant magnetic field at the Fe^{57} nucleus, and this is manifested in a noticeable narrowing of the components of the spectrum. The value of the magnetic field at T = 4.2 K is −10(4) kOe, and at 77 K is −6(1) kOe.

In the paper[5] already mentioned above, it was postulated that, besides transfer of spin polarization from the magnetic atom directly to the unoccupied s-orbitals of another ion, transfer of spin density to the unoccupied 3d-orbitals of the nonmagnetic ion can also occur. In the framework of a model of localized electrons and nearest-neighbor interaction, this leads to the appearance of a local field that is now negative.

Applying this model specifically to the compound $Co_{0.97}Fe_{0.03}S_2$, we must consider several possible mechanisms inducing a HF field at the nucleus of the nonmagnetic Fe^{2+} ion. One of these might be associated with direct Co → Fe spin-density transfer as a result of the direct overlap of the e_g orbital of Co^{2+} with the unoccupied e_g or 4s orbitals of Fe^{2+}. However, in the CoS_2 structure the metal-metal nearest-neighbor distance is 3.9 Å[2]. Since the Fe^{2+} ions in the pyrites structure replace Co^{2+} ions, because of the large Co-Fe interatomic distance we can evidently neglect this direct transfer.

A more likely mechanism here could be indirect transfer of unpaired spin density along chains of the type Co-S-Fe or Co-S-S-Fe. The first case is the more favorable, since the transfer is effected from 12 Co ions via one anion. Here the Co-S-Fe bond angle is 115°. In the second case the transfer is effected via the disulfide link S-S from 6 Co^{2+} cations along the [100] crystal directions.

Accepting this analysis, we can represent the indirectly induced field in a simplified way in the form of two terms:

$$H_i = f_{4s}H_{4s} + f_{3d}H_{3d}, \tag{1}$$

where f_{4s} and f_{3d} are the spin densities in the 4s and 3d orbitals, respectively, of the Fe^{2+} ion, and H_{4s} and H_{3d} are the fields induced by a pure unpaired 4s or 3d electron. The first term describes the field that arises as a result of the Fermi contact interaction of the 4s electron with the Fe^{57} nucleus, while the second also describes a Fermi interaction—that which now arises from the polarization of the inner s shells of the Fe^{2+} core as a result of the exchange interaction with its e_g spin density. The essential point is that, for either of these mechanisms or for both together, the contributions of $f_{4s}H_{4s}$ and $f_{3d}H_{3d}$ have, by definition, opposite signs. The existing experimental data give no grounds for preferring either one of these mechanisms. Starting only from the Kanamori-Goodenough rules for indirect exchange, it is impossible to predict beforehand the sign of the induced field in each individual case.

To elucidate this question it is useful to make use of the itinerant-electron model. This model corresponds to our actual case, since CoS_2 possesses metallic conduction as a result of the delocalization of the only unpaired e_g electron[1]. The HF field at the Fe^{2+} nucleus can then be regarded as being due to the partial overlap of the polarized e_g band of Co^{2+} with the unoccupied e_g or 4s levels of the impurity Fe^{2+} ion. Formula (1) for the induced HF field is also valid in the itinerant-electron model.

Adachi, Sato and Takeda[2] have measured the magnitude of the magnetic HF field at the nuclei of the Co^{2+} ions in CoS_2 by the NMR method. At 80 K this field amounted to 52 kOe. Since in our case the field at the Fe nucleus at the same temperature has magnitude 6 kOe and direction opposite to the magnetization of the Co sublattice, we can assume that about 11% of the spin density of the e_g band of Co^{2+} enters the low-lying unoccupied e_g states of the Fe^{2+} impurity ions.

2. Sign of the Electric-Field Gradient

The positions of the outer lines relative to the inner ones in an external field of 60 kOe are evidence that the electric-field gradient is positive in the region of the Fe^{2+} nucleus (cf. e.g., [12]). This means that the line on the positive-velocity side in the uppermost spectrum in the Figure is due to the transition $m_g = \pm 1/2 \rightarrow m_e = \pm 3/2$. This is in agreement with the sign of the EFG in the isostructural FeS_2[4,13], and also with the linear dependence on x of the quadrupolar splitting in the series $Co_{1-x}Fe_xS_2$[6]. A direct consequence of this is the fact that the angle θ between the axially symmetric EFG and the direction of the induced field should be greater than 54°44′ (for $H_e = 0$; see the figure). In[4], for a positive EFG, a calculated value $\theta = (75 \pm 15)°$ is given and this, evidently, must be taken as the most probable value.

3. Orientation of the Magnetic Moments of the Co^{2+} ions

As can be seen from the figure, the application of low-intensity external fields (10, 12, 14 kOe) does not lead to complete compensation of the resultant magnetic field at the Fe^{57} nucleus and to the appearance of a pure quadrupole doublet, as in the uppermost spectrum. The lines in the spectra are either asymmetric (H_e = 10, 12 kOe) or broadened (H_e = 14 kOe), which indicates the existence of a small (~2—4 kOe) magnetic splitting. In order to determine the values of H_e for which the magnetic splitting at the Fe nuclei is a minimum, the spectra obtained for H = 10, 12 and 14 kOe were analyzed with the aid of a program that provided for the resolution into two lines. At H_e = 10 kOe the right-hand line has its smallest width, while the left-hand line in this field is still significantly broadened. At H_e = 14 kOe the two lines are broadened to the same extent. Taking into account that, as already shown above, the EFG > 0, such changes in the linewidths can be explained if we assume only that the resultant magnetic field at the Fe^{2+} nucleus is perpendicular to the axis of the applied field of H_e = 10 kOe and oriented at an angle to this axis for H_e = 14 kOe. This is a further proof of the noncollinear magnetic structure of the Co^{2+} ions and, consequently, of the fields induced at the Fe^{2+}. For H_e = 10 kOe the external field exactly cancels the component antiparallel to the external field, and the picture observed in the Figure is due entirely to the component perpendicular to the external field. On increase of the applied field the resultant field is rotated in the direction of the external field. For H_e = 14 kOe the components are broadened to an equal extent, and for H_e = 20 kOe the external field leads to a further large broadening of the right-hand line.

The parameters obtained for the spectra of $Co_{0.97}Fe_{0.03}S_2$ in fields of 20, 40, 60 kOe at 4.2 K (the table) under the assumption of a collinear magnetic structure are only approximate. The most reliable parameter, however, is the magnitude of the resultant field H at the Fe^{57} nucleus. As can be seen from the data in the table, H is not simply the sum of the external and HF fields, even when the noncollinearity is taken into account. Although the basic magnetic structure of CoS_2 is not changed [2] in external fields up to 10 kOe, it is not ruled out that in fields above 20 kOe the angle of noncollinearity of the local cobalt moments decreases (cf., e.g., [14]), and the saturation moment correspondingly increases. This will lead to an increase in the magnitude of the induced field H_i at the Fe^{57} nucleus.

Spiral ordering of the Co^{2+} moments in CoS_2 was postulated in the paper [1] by Jarret et al. If, as postulated in [1], we assume a value of 25° for the angle between the moments, this could explain the deviation of the saturation moment per Co^{2+} ion, equal to 0.84 μ_B [1, 2], from the value 1 μ_B expected theoretically in the case of a collinear structure. In the framework of the itinerant-electron model, the angular spin structure is explained by the decrease in the observed moment as a result of the partial overlap of the magnetic sub-bands of itinerant d-electrons with spin up and spin down.

Preliminary calculations on a computer (with a fixed angle) indicate a strong correlation between the experimental linewidth and the magnitude of the magnetic HF field. Obviously, an analysis of spectra with inseparable magnetic-dipole and electric-quadrupole interactions should also include the effect of the thickness of the absorber. The study of these questions is continuing.

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