# Chalcogenides of the Transition Elements. IX. Transferred Hyperfine Field at $^{57}$Fe in the Pyrite Co$_{0.98}$Fe$_{0.02}$S$_2$*

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A supertransferred hyperfine magnetic field has been observed at $S = 0$ $^{57}$Fe atoms in the pyrite Co$_{0.98}$Fe$_{0.02}$S$_2$ using the Mössbauer effect. The spectrum obtained at 91°K is consistent with a canted spin arrangement of the Co atoms.

Magnetic measurements show that the pyrite FeS$_2$ is essentially diamagnetic (1–3). This behavior corresponds to a low-spin ($S = 0$) $t_{2g}^6$ configuration of the Fe atoms. A Mössbauer spectrum taken at 10°K in an external magnetic field of 45 kOe parallel to the $\gamma$-ray direction shows four lines, the $\Delta m = 0$ transitions having zero intensity. The effective magnetic field at the $^{57}$Fe nucleus as calculated from the splittings of the four-line spectrum equals the applied field, which confirms the $S = 0$ configuration, and the quadrupole splitting is positive, i.e., $e^2qQ > 0$. If the spin of the Fe atoms were greater than zero a hyperfine magnetic field of between $-200$ and $-500$ kOe would be expected for such large values of $H/T$.

The isostructural CoS$_2$ is unique among the pyrites in that it orders ferromagnetically. The Curie temperature has been reported variously as 110 (2, 4, 5), 116 (6), 118 (2), 122 (7, 8), 124 (9), and 130°K (3). Above the Curie temperature the susceptibility exhibits a Curie–Weiss behavior with an effective magnetic moment of 1.80–1.85 $\mu_B$ (3–5); a value of 2.17 $\mu_B$ has also been reported (6). This moment corresponds to one unpaired electron per Co atom, i.e., to a $t_{2g}^6 e_g^{1}$* configuration. Below the Curie temperature the saturation magnetization corresponds to a value of 0.84 $\mu_B$ per Co atom (9), which is slightly smaller than the theoretical value of $1\mu_B$ that would be expected for a completely spin-polarized localized

electron model. Jarrett et al. (10) have suggested that the reduced moment observed is consistent either with a canted arrangement of the Co spins, each making an angle of 25° with a crystallographic axis, or, more likely, with an itinerant electron model in which the splitting between the spin-up and spin-down bands is smaller than the band width. Neutron powder diffraction measurements at 4.2°K (11) confirm the ferromagnetic order but leave undetermined the direction of the moments within the (pseudo) cubic unit cell.

Mössbauer spectra of a series of solid solutions Co$_{1-x}$Fe$_x$S$_2$ ($x = 0.01$, 0.25, 0.5, 0.75) at temperatures well below the respective Curie temperatures have been reported by Gallagher, MacChesney, and Sherwood (12). These spectra are presented as single quadrupole doublets; they contain no visible evidence of any six-line spectra that would be expected for Fe atoms with $S > 0$, thus giving assurance that the Fe atom remains in a low-spin configuration. However, for $x = 0.01$ and 0.25 the spectra at 100°K shown in Fig. 3 of Ref. (12) appear asymmetric, with the possibility of some line broadening, although no values were quoted for line widths.

In the course of a study of the Mössbauer effect in pyrites we have taken spectra of Co$_{0.98}$Fe$_{0.02}$S$_2$ at room temperature and at 91°K. The homogeneous sample enriched in $^{57}$Fe was prepared by direct synthesis from high-purity elements. Weighed quantities of the freshly reduced metal powders were dissolved in nitric acid and the solution was evaporated to

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dryness. The mixed oxide obtained by calcining the nitrate residue was reduced to metal in $H_2$. Requisite amounts of this alloy powder and sulfur were introduced without loss into a degassed quartz tube which was then carefully evacuated and sealed. After reaction the sample was ground, resealed, and homogenized. This was repeated till the X ray powder pattern of the product was completely sharp and identical with that of pure $CoS_2$. No evidence of foreign lines could be detected even in overexposed powder photographs. As a check, powder patterns of the absorber were also obtained after the Mössbauer experiments. The Mössbauer spectrometer and computer fitting technique have been described previously (13).

The symmetric quadrupole doublet observed at room temperature (Fig. 1a) has an isomer shift of $0.374 \pm 0.002$ mm/sec relative to metallic iron and a quadrupole splitting of $0.315 \pm 0.004$ mm/sec in good agreement with the values quoted for $x = 0.01$ in Ref. (12). The 91°K spectrum (Fig. 1b), however, is noticeably asymmetric and very similar in appearance to the spectrum for
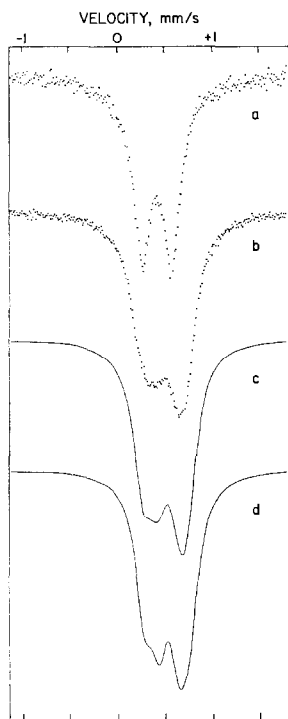


FIG. 1. Mössbauer $^{57}$Fe spectra of the pyrite $Co_{0.98}Fe_{0.02}S_2$. (a) Room temperature; (b) 91°K; (c) simulated spectrum A; (d) simulated spectrum B (see text). The zero of velocity refers to the centre of $^{57}$Fe calibration spectrum.

$x = 0.01$ at 100°K of Gallagher, MacChesney and Sherwood (12). This asymmetry is unlikely to arise from Gol'danskii-Karyagin, relaxation or preferred orientation effects, since a two-line fit with no constraints gave an unacceptable $\chi^2$ value of 688; the acceptable range of $\chi^2$ values for this fit is 198 to 302. An asymmetric spectrum of this type is, however, expected if, in addition to the electric field gradient (EFG) at the $^{57}$Fe nucleus, there is also a small static magnetic field.

Mössbauer spectra for the case of mixed electric quadrupole/magnetic dipole interaction were simulated using the LVSPHS program of Gabriel and Ruby (14). The program is appropriate for a powder absorber, i.e., for a situation where there is a fixed orientation between the magnetic field and the axes of the EFG, but all orientations between the crystallographic axes and the $\gamma$-ray direction are equally probable. The shape of the resonance lines was assumed to be Lorentzian. In the pyrite structure (space group $Pa3$) the four metal atoms in the unit cell are in equipoint $4(a)$, which has site symmetry $\bar{3}$. In the absence of unpaired electrons the EFGs of these atoms thus have axial symmetry ($\eta = 0$), the principal axis $V_{zz}$ of each being parallel to one of the four body diagonals of the unit cell. The relative orientation of the magnetic field and the EFG at a metal atom is defined by the angle $\theta$ between the field and the $V_{zz}$; $\theta$ and a second angle $\phi$ specify the orientation of the field with respect to the crystallographic axes. If it is assumed that the ferromagnetic spin alignment is collinear, there will in general be four distinct values of $\theta$. These four values are related by the symmetry operations of the space group. The expected Mössbauer spectrum will then be the sum of four spectra, each of the four metal atoms giving rise to one spectrum. Only when the magnetic field is parallel to one of the crystallographic axes are the four $\theta$ values identical ($\theta = 54°44'$) and a single spectrum results [case (i)].

Mössbauer spectra were simulated to cover the complete range of $\theta$ and $\phi$ combinations in steps of 15°. They included the special cases of the magnetic field parallel to a face diagonal [case (ii)] and to a body diagonal [case (iii)] of the unit cell. Contrary to expectation, all of these composite simulated spectra, as well as the single spectrum for case (i), were nearly *symmetric* doublets, quite unlike the observed asymmetric spectrum. Consequently the spin arrangement in $CoS_2$ cannot be a collinear one.

A helical arrangement may be considered in which the magnetic field $H$ at each atom makes a constant angle $\theta$ with the $V_{zz}$. A series of spectra were simulated for $\theta$ between 0 and 90°. The spectra for angles $\theta$ other than 54°44′ were asymmetric doublets [54°44′ corresponds to the collinear case (i)]. When $e^2qQ$ is negative, the low-velocity peak is less intense, for $\theta < 55°$, than the high-velocity peak, while for $\theta > 55°$ the opposite is true. The asymmetry is reversed when the sign of $e^2qQ$ is reversed. Good fits are obtained to a single spectrum with the following parameter values: either (A) $H = 7 \pm 1$ kOe, $QS = \frac{1}{2}e^2qQ = +0.33 \pm 0.03$ mm/sec, $\theta = 75 \pm 15°$ (Fig. 1c), or (B) $H = 6 \pm 1$ kOe, $QS = -0.34 \pm 0.03$ mm/sec, $\theta = 30 \pm 15°$ (Fig. 1d). The line width was taken as 0.24 mm/sec, the value obtained from the room-temperature spectrum. Variations smaller than the uncertainties quoted did not produce visible changes in the simulated spectra. The two fits were equally acceptable. It is not possible to choose between them unless the sign of $e^2qQ$ is known. Thus it would appear that the spins in ferromagnetic $CoS_2$ are arranged, not in a collinear fashion, but on a helix, each spin making an angle of about 30°, or about 75°, with the $V_{zz}$. Such an arrangement would account for the reduced saturation magnetization as mentioned by Jarrett et al. (10). It is interesting to note that a similar spin arrangement has been inferred in antiferromagnetic $MnTe_2$ from a $^{125}Te$ Mössbauer study (15).

The origin of the observed magnetic field is undoubtedly a supertransferred field (STHF) from the magnetically ordered Co atoms via a super-exchange mechanism (16–18). STHFs have previously been observed in a large number of cases including $^{119}Sn$ nuclei in tin-substituted nickel ferrites (19), the spinel $Mn_{1.1}Fe_{1.8}Sn_{0.1}O_4$ (20), and yttrium iron garnet matrices. Recently the STHF at $^{119}Sn$ in yttrium iron garnet has been shown to be of very short range, originating mainly on the first nearest-neighbor metal atoms (21). One of the origins of STHFs is thought to be due to the transfer of a $d$ electron from a nearest-neighbor metal atom to the first empty $s$ orbital of the Sn atom, $5s$ (22). This transfer may be either direct (metal → Sn) or indirect (metal → ligand → Sn). The hyperfine field then arises from the usual Fermi contact interaction. STHFs at diamagnetic atoms have also been observed by NMR [e.g., Ref. (23)]. In $Co_{0.98}Fe_{0.02}S_2$ the dominant interaction is probably

due to spin polarization of the $s$ cores of the Fe atom via overlap with a polarized ligand $\sigma$ orbital. The ligand polarization arises from a transfer of a ligand $\sigma$ electron into a $3d\ e_g$ orbital of the Co atom. Huang et al. (22) have calculated the STHF on going from magnetically dilute $LaAlO_3 : Fe^{3+}$ to "concentrated" $LaFeO_3$ to be about 25 kOe. The much smaller STHF observed in $Co_{0.98}Fe_{0.02}S_2$ is due probably to the much smaller overlap between the $3d\ e_g$ metal orbital with the intervening $4p$ orbital of the sulfur ligand. The M–S–M bond angle is 115° compared with optimum 180° in $LaFeO_3$.

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