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Mössbauer study of $Co_{0.995}{}^{57}Fe_{0.005}S_2$ in external magnetic fields: Magnetic structure of CoS_2 and the quadrupole splitting of the FeS_2-CoS_2-NiS_2 system

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The Mössbauer effect of ^{57}Fe-doped ferromagnetic CoS_2 was measured at 4.2 K in external magnetic fields up to 40 kOe. Ferromagnetic powder spectra were analyzed by taking into account the effect of the ferromagnetic moment. The hyperfine field induced by the ferromagnetic moment is -16 kOe when the moment lies along the principal axis of the electric field gradient and -7 kOe when the moment is perpendicular to it. The sign of the electric field gradient is negative at the ^{57}Fe nucleus. Using these results, we conclude that the spectrum at zero external field is explicable from the collinear magnetic structure with a [111] easy direction of Co spins. The quadrupole splitting is negative in the FeS_2-CoS_2-NiS_2 system. The quadrupole splitting changes around the metal-semiconductor phase boundary because of a delocalization of e_g electrons in the metallic region. The absolute value in the low-resistivity region is smaller than that in high-resistivity regions by about 0.1 mm/sec.

I. INTRODUCTION

Cobalt disulfide CoS_2 is a ferromagnetic metal with pyrite structure. The magnetic and electrical properties of this substance have been studied by many workers.[1-5] The Curie temperature is 124 K, and the saturation moment is $0.84\mu_B$/Co at 0 K.[2] The easy direction of the Co spin is along the [111] axis.[4]

The Mössbauer effect of ^{57}Fe-doped CoS_2 was first reported by Gallagher *et al.*[6] Since the Mössbauer spectrum does not exhibit magnetic hyperfine splitting down to 5 K, they concluded that divalent iron ions remain in the low-spin state and that 3*d* electrons are localized on the cobalt ions. After that, Shinjo and Takada[7] determined the value of the supertransferred hyperfine field at ^{57}Fe nucleus to be -8 ± 5 kOe at 4.2 K from Mössbauer experiment in an external magnetic field. As for the magnetic structure, a noncollinear spin arrangement of Co atoms was suggested by Woodhams *et al.*[8] from analysis of the supertransferred hyperfine field. That is, each Co spin makes an angle θ with the principal axis of the electric field gradient (efg), which is parallel to one of the four-body diagonals of unit cell. Wortmann *et al.*[9] reported that Mössbauer spectra in external magnetic fields lead to the positive efg at Fe nucleus and that the most probable value of θ is $(75 \pm 15)^\circ$. Recently, McCann and Ward[10] have also shown that the best fit of the Mössbauer spectrum of $Co_{0.99}Fe_{0.01}S_2$ at 100 K gives a positive sign for the efg and a θ of $(74 \pm 2)^\circ$. In NiS_2 the noncollinear antiferromagnetic structure was determined from results of the Mössbauer effect[11-13] and neutron diffraction.[14] However, in CoS_2 the noncollinear magnetic structure reported from the Mössbauer experiment conflicts with results of magnetic torque and nuclear-magnetic-resonance measurements.[4] The sign of efg for Fe is negative in FeS_2 (Ref. 15) and NiS_2.[11] Only the sign of CoS_2 is reported to be positive in the pyrite-type MS_2 system.

We have measured the Mössbauer effect of ^{57}Fe in CoS_2 and FeS_2 in external magnetic fields and made a careful analysis of the spectra to clarify the relation between the Mössbauer spectrum and the magnetic structure of CoS_2 and to examine the reason why the sign of efg of CoS_2 is different from other sulfides. We find that the sign of efg is not positive as reported but negative. This paper reports the detail of analysis, an effect of magnetization to the Mössbauer spectrum in external magnetic fields, and discussions about the magnetic structure of CoS_2 and the quadrupole splitting of FeS_2-CoS_2-NiS_2 system.

II. EXPERIMENTAL PROCEDURE

Samples were polycrystals of CoS_2 doped with ^{57}Fe and FeS_2 prepared by a sintering method. The quadrupole splitting and isomer shift of these samples at room temperature are given in Ref. 16.

In the measurement of Mössbauer spectrum under magnetic field, a superconducting magnet with a compensation coil was used to eliminate fields at a γ-ray source. The magnet was set vertically at the bottom of a cryostat. A transducer was set at the top of the cryostat and motion was transmitted to the source through a stainless-steel rod. The source was 10-mCi ^{57}Co diffused into Cu and was placed 9 cm up from the center of the magnet. The field strength at the source was less than 0.5 kOe. The temperature of absorbers was 4.2 K and the source was nearly 5 K. The velocity scale was calibrated with a spectrum of metallic iron at room temperature.

III. EXPERIMENTAL RESULTS AND ANALYSIS

A. Mössbauer spectra in external magnetic fields

Figure 1 shows Mössbauer spectra of FeS_2 in external magnetic fields at 4.2 K. The spectrum broadens with increasing magnetic field. A slight asymmetry appears above 20 kOe. Since the iron in FeS_2 has no magnetic moment, we can fit the observed spectra to the computed powder spectra by setting internal magnetic fields equal to the applied fields. Solid curves show the computed powder spectra. Fitting parameters are the quadrupole splitting, isomer shift, and linewidth of a Lorentzian. We get an excellent fit when the sign of efg is negative. The result is in agreement with that reported by Montano and Seehra.[15] The absolute value of quadrupole splitting slightly increases with increasing applied field, as shown in Fig. 2.

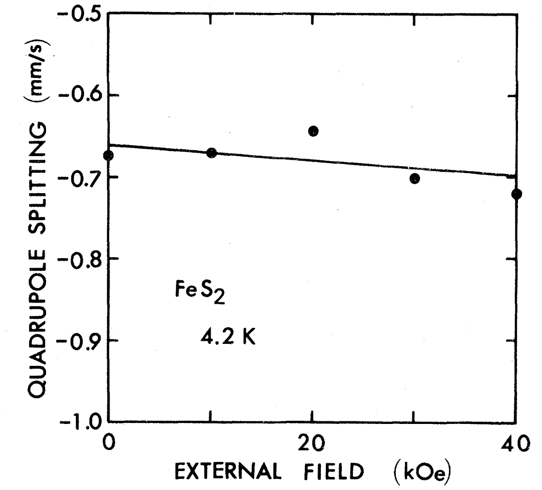

FIG. 2. Quadrupole splitting $\frac{1}{2}e^2qQ$ of FeS_2 vs external magnetic fields.

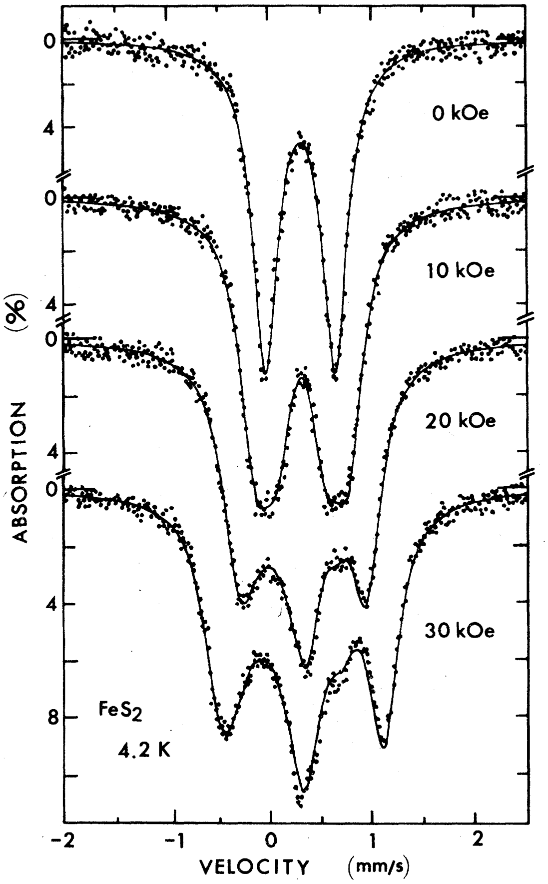

FIG. 1. Mössbauer spectra of FeS_2 in external magnetic field at 4.2 K.

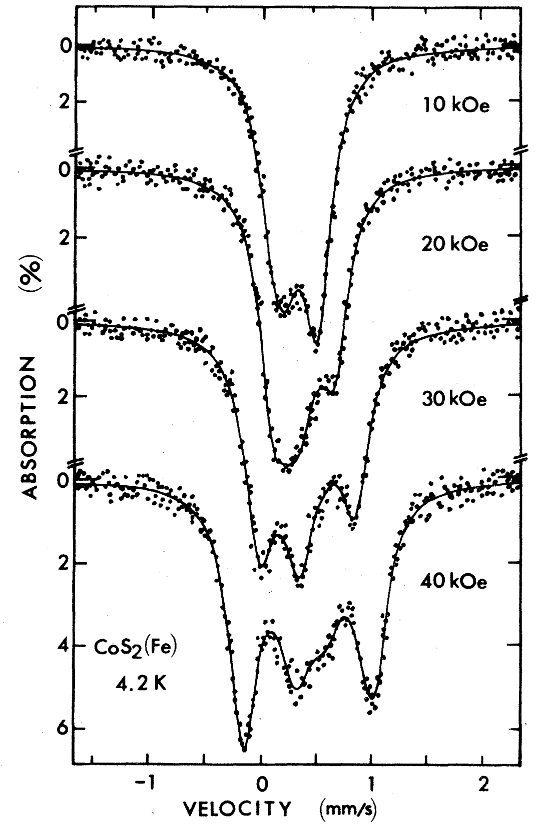

FIG. 3. Mössbauer spectra of $Co_{0.995}{}^{57}Fe_{0.005}S_2$ in external magnetic field at 4.2 K.

Figure 3 shows Mössbauer spectra of ^{57}Fe-doped CoS_2 in external magnetic fields. The width of the spectrum becomes sharp around 10 kOe. Thus, we find that the internal field for ^{57}Fe is antiparallel to the magnetic moment of Co. From similar spectra, Wortmann *et al.*[9] determined that the hyperfine magnetic field for ^{57}Fe in CoS_2 is -10 ± 4 kOe at 4.2 K. In general, the internal magnetic field H_{int} acting on ^{57}Fe is written

$$H_{\text{int}} = H_{\text{hyp}} + H_{\text{appl}} \quad , \tag{1}$$

where H_{hyp} is the hyperfine field produced by the magnetic moment and H_{appl} is the external magnetic field. Therefore, when H_{hyp} is about -10 kOe and H_{appl} is 40 kOe, it is expected that the internal field for ^{57}Fe in CoS_2 is nearly equal to that in FeS_2 at $H_{\text{appl}} = 30$ kOe. However, the observed spectrum of CoS_2 at 40 kOe is remarkably different from that of FeS_2 at 30 kOe, as seen in Figs. 1 and 3. The spectrum of CoS_2 is fairly asymmetric and the absorption near the center of the spectrum is weaker than that of FeS_2. These differences cannot be understood only from a difference in the quadrupole splitting. An effect of the ferromagnetic moment probably results in the asymmetric spectrum of CoS_2. Therefore, it is indispensable to study the magnetization effect on Mössbauer spectra under magnetic fields for the analysis of the spectra of CoS_2.

B. Effect of magnetization on Mössbauer spectra in external magnetic fields

The field dependence of magnetization for polycrystalline CoS_2 at 4.2 K was reported by Adachi *et al.*[2] Their result shows that the ferromagnetic moment of CoS_2 lies along the external field direction above ~2 kOe. That is, the magnetocrystalline anisotropy energy of CoS_2 is small. Therefore, in this section we assume that the magnetic moment of the sample is along the applied magnetic field direction.

When the applied field and the magnetic hyperfine field produced by the magnetic moment are in the same direction, one expects the Mössbauer spectra of CoS_2 to be essentially similar to the spectra of FeS_2. However, as discussed in Sec. III A the spectrum of CoS_2 is fairly asymmetric compared with that of FeS_2. Thus, it is suggested that the hyperfine coupling constant of Fe in CoS_2 is anisotropic, as Co is in CoS_2.[4,5] In this case, the internal field varies according to the direction of applied field and the Mössbauer spectrum becomes asymmetric.

For most iron-group ions with a quenched-orbital momentum the hyperfine magnetic field is given by

$$\vec{H}_{\text{hyp}} = \underline{\tilde{A}} \cdot \vec{S} \quad , \tag{2}$$

where $\underline{\tilde{A}}$ is a hyperfine tensor and $\vec{S}$ is an effective spin. Under the external magnetic field, the effective internal field $\vec{H}_{\text{eff}}$ at ^{57}Fe is expressed as

$$\vec{H}_{\text{eff}} = \vec{H}_{\text{appl}} + \underline{\tilde{A}} \cdot \vec{S} \quad . \tag{3}$$

Here, we denote principal components of $\underline{\tilde{A}} \cdot \vec{S}$ as A^x, A^y, and A^z. Then the x, y, and z components of the effective field are written

$$\begin{aligned} H_{\text{eff}}^x &= (H_{\text{appl}} + A^x) \sin\theta \cos\phi \quad , \\ H_{\text{eff}}^y &= (H_{\text{appl}} + A^y) \sin\theta \sin\phi \quad , \\ H_{\text{eff}}^z &= (H_{\text{appl}} + A^z) \cos\theta \quad , \end{aligned} \tag{4}$$

where θ and ϕ are polar angles of $\vec{H}_{\text{appl}}$ with respect to the x, y, and z axes. When the local symmetry is trigonal, as for the iron site in the pyrite structure,[17] we can assume that $\underline{\tilde{A}}$ has the same principal axes as the electric field gradient. Using the above effective fields and assuming that the γ ray is parallel to the applied magnetic field, we can get powder Mössbauer spectra in magnetic fields. The summation is carried out over random orientations of the efg axes. In CoS_2 the efg at the metal site is axial symmetric.[17] Then, we take $A^x = A^y$, $\phi = 0$, and the asymmetry parameter of efg $\eta = 0$. Solid curves in Fig. 3 are obtained by the least-squares fittings. By the fittings, we have determined the hyperfine fields A^z and A^x, the quadrupole splitting $\frac{1}{2}e^2qQ$, the isomer shift, and the linewidth of Lorentzians. The observed asymmetry in the spectra of CoS_2 is explicable from the effect of the anisotropic hyperfine interaction. As far as we know, this is the first application of the rigorous analysis of Mössbauer spectra to ferromagnetic powder patterns in magnetic fields.

C. Sign of electric field gradient

Figure 4 shows the Mössbauer spectrum of $Co_{0.995}{}^{57}Fe_{0.005}S_2$ in external field of 40 kOe at 4.2 K. To determine the sign of efg, we made computer fittings of the spectrum by fixing the sign of efg. Solid curves in the figure are computed spectra. The fitting with the positive efg leads to the values of $\frac{1}{2}e^2qQ = 0.35$ mm/sec, $A^z = -3.8$ kOe, and $A^x = -8.4$ kOe. But the structure at the inner part of the spectrum cannot be fitted to the spectrum with the positive efg. The best fit is obtained when the efg is negative ($\frac{1}{2}e^2qQ = -0.37$ mm/sec), $A^z = -14.1$ kOe, and $A^x = -4.7$ kOe. Thus, it is concluded that the sign of efg is negative for ^{57}Fe in CoS_2. The spectra in Fig. 3 are analyzed by assuming the negative sign of efg. Figure 5 shows the external field dependence of quadrupole splitting. The absolute value slightly in-

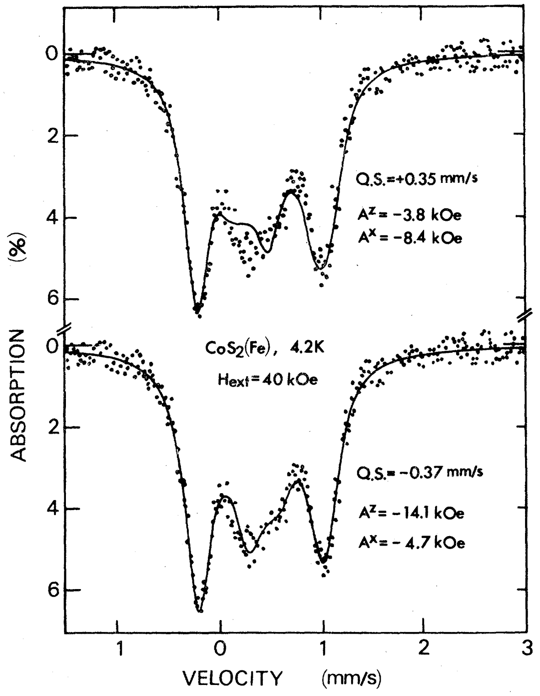

FIG. 4. Computer fittings of the Mössbauer spectrum of $Co_{0.995}{}^{57}Fe_{0.005}S_2$ in external field 40 kOe at 4.2 K. The upper curve shows the result of the fitting with the positive efg and the lower one with the negative efg.

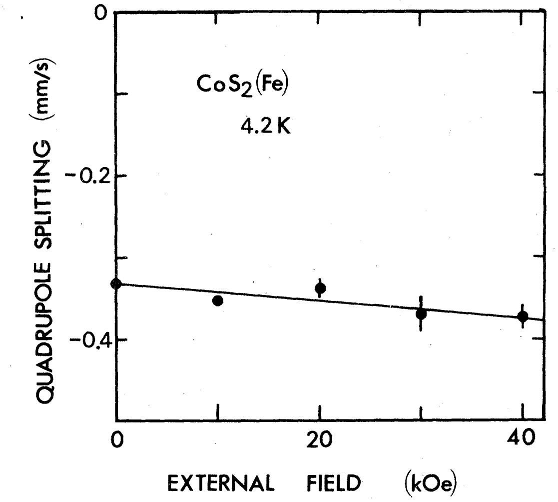

FIG. 5. Quadrupole splitting $\frac{1}{2}e^2qQ$ of ^{57}Fe in CoS_2 vs external magnetic fields.

creases with increasing applied field, as in FeS_2. The isomer shift of these spectra is 0.372 ± 0.008 mm/sec relative to metallic iron. The linewidth of the Lorentzian is 0.302 ± 0.017 mm/sec.

Wortmann *et al.*[9] determined that the sign of efg at ^{57}Fe in CoS_2 is positive from an analysis of the Mössbauer spectrum of $Co_{0.97}{}^{57}Fe_{0.03}S_2$ in external fields. They fitted the spectrum with four Lorentzian lines and derived the quadrupole splitting from relative positions of the four lines. That is, they assumed a symmetric hyperfine coupling constant of ^{57}Fe and neglected the influence of random orientations of efg axes with respect to the external field direction. However, as seen from our rigorous analysis, this simple analysis of the Mössbauer spectrum cannot be used in the case of ferromagnetic powder spectrum in magnetic field.

The sign of efg for ^{57}Fe has been reported to be positive[8, 10, 16] in pyrite-type disulfides except for NiS_2. However, accurate analyses made by Montano and Seehra,[15] and us lead to the conclusion that the efg is negative in FeS_2 and CoS_2. Thus, the efg is negative in all the pyrite-type disulfides. The quadrupole splittings of ^{57}Fe in FeS_2, CoS_2, and NiS_2 are listed in Table I.

TABLE I. Quadrupole splittings of ^{57}Fe in FeS_2, CoS_2, and NiS_2.

	$\frac{1}{2}e^2qQ$ (mm/s) 4.2 K	Room temperature	Ref.
FeS_2	−0.66 ± 0.01	−0.62 ± 0.01	15
	−0.674 ± 0.002	−0.621 ± 0.002	This paper
CoS_2	−0.328 ± 0.013	−0.305 ± 0.003	This paper
NiS_2	−0.221 ± 0.011	−0.273 ± 0.002	11

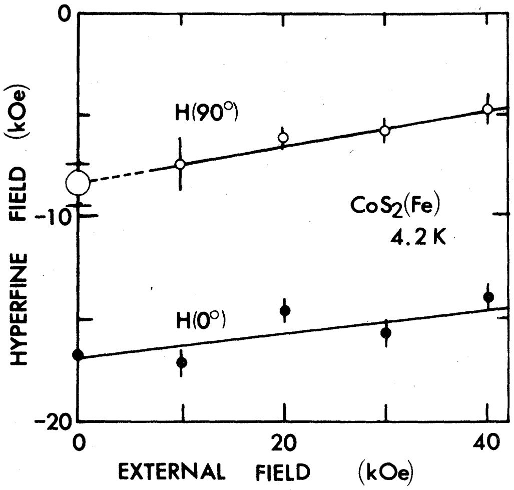

FIG. 6. External field dependence of the hyperfine field at ^{57}Fe induced by the ferromagnetic moment of CoS_2. Solid circles $H(0°)$ show the hyperfine fields when the moment is parallel to the principal axis of efg and open ones $H(90°)$ perpendicular to it. The open circle at zero external field is the value of $H(70.5°)$.

D. Anisotropic hyperfine field

We have determined the hyperfine field induced by the ferromagnetic moment for iron, assuming that the hyperfine field for ^{57}Fe has the same principal axes as the electric field gradient. The results are shown in Fig. 6. Values at zero external field were determined by assuming a collinear magnetic structure of CoS_2, which will be discussed in Sec. IV. The hyperfine field induced by the ferromagnetic moment is −17 kOe [$A^z = H(0°)$] when the iron moment lies along the principal axis z of efg and −8 kOe [$A^x = H(90°)$] when the moment is perpendicular to the z axis at zero external field. The sign of the hyperfine field is negative. The hyperfine field increases with increasing applied field. The increasing rate $\Delta H_{\text{hyp}}/H_{\text{appl}}$ is about 0.075.

Yasuoka[5] made the measurement of ^{59}Co nuclear magnetic resonance in CoS_2. The hyperfine field for the Co nucleus is $H(0°) = -70$ kOe and $H(90°) = -54$ kOe. The anisotropy for Fe is larger than that for Co. $H(0°)/H(90°)$ is about 2.3 for Fe and 1.3 for Co in zero external field.

IV. DISCUSSION

A. Hyperfine field at ^{57}Fe

The $3d$ transition-metal dichalcogenides with pyrite structure are $3d$ e_g-electron system having a narrow energy band. Magnetic and electrical properties are explained by the e_g band model.[1,3] The metallic conduction of CoS_2 results from a delocalization of unpaired electrons on Co atoms. Therefore, it seems that the hyperfine field for ^{57}Fe is produced by a partial transfer of the polarized e_g electrons of Co to unoccupied e_g levels of Fe. In this case, since the hyperfine field is induced by polarizations of the inner s shells of Fe core through the exchange interaction with e_g spin density, the sign of the hyperfine field for ^{57}Fe becomes negative. The experimental result is consistent with this expectation.

In NiS_2 the hyperfine field at ^{57}Fe is $|H(0°)| \simeq 20$ kOe.[11] This field is produced by four Ni spins with $\sim 1\mu_B$ contributing to the first kind ordering of fcc. Then, the hyperfine field per spin is ~5 kOe. In CoS_2, on the other hand, the field $|H(0°)| = 16.6$ kOe is produced by the 12 nearest-neighbor Co spins with $0.8\mu_B$. The hyperfine field per spin is ~1.7 kOe. The result may suggest that the e_g level of the impurity iron has a smaller transfer from the e_g band of CoS_2 than that of NiS_2.

The anisotropic hyperfine field at ^{57}Fe has been reported also on $ZrFe_2$ (Ref. 18) and Fe_3Ga.[19] However, in these materials the anisotropy is very small, that is $H(0°)/H(90°) \simeq 0.9$. In CoS_2 metal atoms form fcc lattice. Thus, the dipole field arising from the magnetic moments of neighboring atoms has no anisotropy. The large anisotropy [$H(0°)/H(90°) = 2.3$] of CoS_2 may result from a spatial distribution of e_g electrons depending on the direction of local magnetization. The temperature dependence of the hyperfine field and the direction of it for ^{57}Fe in $NiS_{1.6}Se_{0.4}$ also suggest the presence of the anisotropic hyperfine interaction of iron.[13]

B. Magnetic structure of CoS_2

The magnetocrystalline anisotropy of single crystal of CoS_2 was measured by torque method.[2] The anisotropy constants were determined as $K_1 < 0$ and $K_2 \simeq 0$ with the easy axis of [111]. The ^{59}Co nuclear-magnetic-resonance spectrum was explained from a powder pattern assuming the collinear magnetic structure and the anisotropic hyperfine interaction.[2,5]

On the other hand, the Mössbauer spectrum in zero external field was analyzed by Woodhams *et al.*[8] They interpreted the spectrum in terms of a noncollinear spin arrangement in which the magnetic field at each atom makes a constant angle with the principal axis of efg. The Mössbauer effect in external magnetic fields was measured by Wortmann *et al.*[9] The application of external field does not lead to complete compensation of the resultant magnetic field at the ^{57}Fe nucleus. Thus, they pointed out that this is a proof of the noncollinear magnetic structure of CoS_2. However, as shown in Fig. 3, the incomplete compensation of the hyperfine field for ^{57}Fe is fairly well accounted for by the effect of anisotropic hyperfine interaction. Thus, we have to take into account the effect of anisotropic hyperfine interaction in the analysis of the Mössbauer spectrum also at zero external field. McCann and Ward[10] reported that the spectrum at 19 K cannot be fitted to a simple noncollinear model.

Figure 7 shows the Mössbauer spectrum of $Co_{0.995}{}^{57}Fe_{0.005}S_2$ at 4.2 K in zero external field. Two solid curves in the figure were obtained by least-squares fitting assuming the noncollinear and collinear spin structure. The curve drawn together with the observed spectrum is the spectrum corresponding to the collinear magnetic structure with the easy axis of [111]. In this case, the number of ^{57}Fe atoms with the hyperfine field $H(0°)$ along the principal axis of efg is one-third of that with $H(70.5°)$ making an angle of 70.5° with efg. Fitting parameters are the isomer shift, quadrupole splitting, linewidth, and hyperfine field. From the fitting, the hyperfine field $H(0°)=-16.6\pm0.5$ kOe, $H(70.5°)=-8.3\pm1.0$ kOe, the quadrupole splitting $\frac{1}{2}e^2qQ=-0.328\pm0.013$ mm/sec, and the isomer shift 0.373 ± 0.003 mm/sec relative to metallic iron were obtained. In Figs. 5 and 6 these values are plotted at zero external field. The values are in good agreement with those determined from the spectra in magnetic field. The linewidths are 0.234 ± 0.023 mm/sec for the spectrum of $H(0°)$ and 0.347 ± 0.026 mm/sec for $H(70.5°)$. Since the magnetic anisotropy of CoS_2 is sensitive to the shape of the sample,[4] one of reasons of the line broadening would be a distribution of the angle between the hyperfine field and efg.

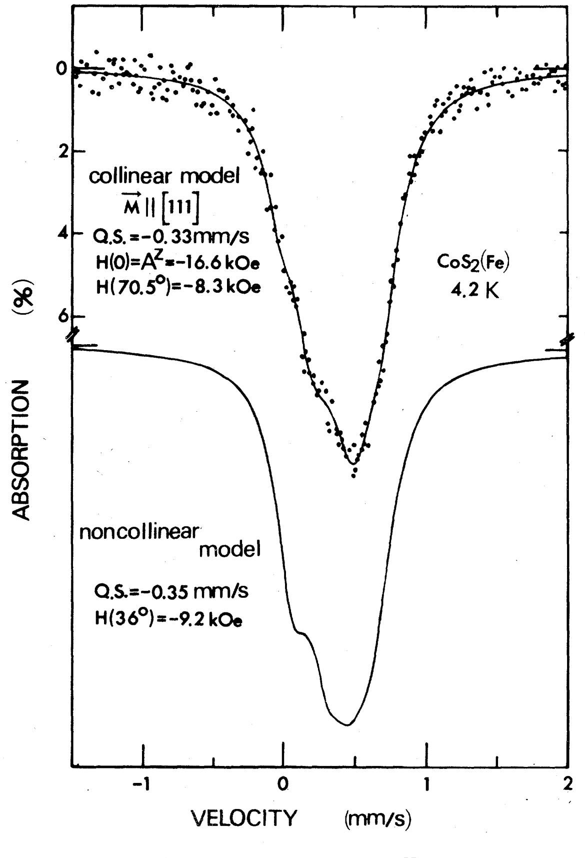

FIG. 7. Mössbauer spectrum of $Co_{0.995}{}^{57}Fe_{0.005}S_2$ in zero external field at 4.2 K. Solid curves are computed spectra corresponding to the collinear (upper curve) and noncollinear (lower curve) magnetic structure of CoS_2.

The curve drawn below the observed spectrum shows the spectrum corresponding to the noncollinear magnetic structure. The negative sign of efg was assumed in the calculation. The fitting to the observed spectrum is not satisfactory, as pointed out by McCann and Ward.[10] Therefore it is concluded that the collinear model is better than the noncollinear model for the magnetic structure of CoS_2.

C. Quadrupole splitting of the pyrite-type disulfides

Figure 8 shows the quadrupole splitting of ^{57}Fe in the system of FeS_2-CoS_2-NiS_2 at room temperature. Roughly speaking, the absolute value of quadrupole splitting decreases with increasing the atomic number of metals. The electric field gradient results from aspherical distributions of electrons in the valence orbitals (electronic part) and charges on distant atoms surrounding the Mössbauer atom in noncubic symmetry (lattice part).[20] In this system divalent irons are in the low-spin state.[16] Thus, the lattice part of efg has the most important contribution to the quadrupole splitting. The lattice constant of solid solu-

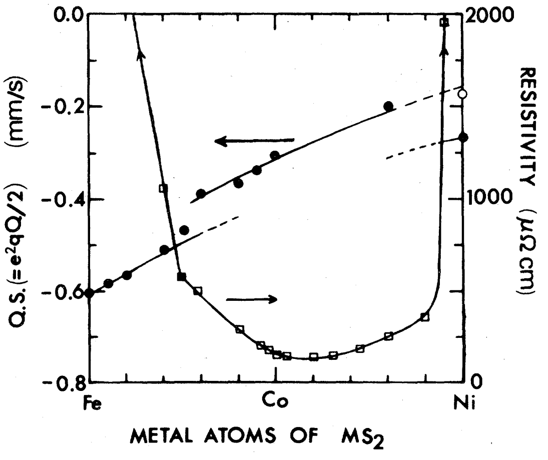

FIG. 8. Quadrupole splitting and the electrical resistivity (Ref. 3) of FeS_2-CoS_2-NiS_2 system at room temperature. The open circle at NiS_2 shows the quadrupole splitting at the metallic phase estimated from Ref. 16.

tions FeS_2-CoS_2-NiS_2 increases with increasing atomic number of metals.[3] Since a lattice part of efg decreases generally as an atomic distance increases, the gross feature of the concentration dependence of quadrupole splitting is explicable from the change in the lattice part of efg by the lattice expansion.

FeS_2-CoS_2-NiS_2 is a $3d$ e_g electron system.[1,3] FeS_2 is a semiconductor with a filled t_{2g} band, CoS_2 is a metallic ferromagnet with $\frac{1}{4}$-filled e_g band and NiS_2 is a Mott-Hubbard insulator with a half-filled e_g band. The electrical resistivity[3] at 300 K of this system is shown in Fig. 8. A metallic phase spreads over both sides of CoS_2. The quadrupole splitting of NiS_2 at the metallic phase can be estimated from the concentration dependence of quadrupole splitting in $NiS_{2-x}Se_x$,[16] which shows a metal-insulator transition near $x = 0.5$. The open circle in the figure shows the estimated value. The absolute value of quadrupole splitting changes by about 0.1 mm/sec around the low-to-high resistivity boundaries. As mentioned above, the lattice part of efg has a large contribution to the quadrupole splitting of ^{57}Fe in the pyrite-type compounds. Thus, when e_g electrons are delocalized, positive ions are effectively shielded and the quadrupole splitting becomes small. It is concluded, therefore, that the decrease in the quadrupole splitting by about 0.1 mm/sec at the low-resistivity region is caused by delocalization of e_g electrons at metallic region.

V. SUMMARY

The ferromagnetic moment of CoS_2 gives a large influence on the powder Mössbauer spectrum through the anisotropic hyperfine interaction. The spectra in external magnetic fields at 4.2 K are interpreted in terms of the effect of the ferromagnetic moment. The hyperfine field induced by the ferromagnetic moment is -16 kOe when the moment lies along the principal axis of efg and -7 kOe when the moment is perpendicular to it. The sign of efg is negative at ^{57}Fe nucleus. Hitherto, it has been reported that the Mössbauer spectrum of CoS_2 at zero external field is explicable from a noncollinear magnetic structure of CoS_2. However, by taking into account the anisotropy of the hyperfine field, it is concluded that a collinear model is better for the magnetic structure of CoS_2. The quadrupole splitting is negative in the FeS_2-CoS_2-NiS_2 system. The absolute value at the low resistivity region is smaller than the value at high resistivity regions by about 0.1 mm/sec. The concentration dependence of quadrupole splitting is explained by effects of lattice expansion and delocalization of e_g electrons.

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