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Effects of sulfur vacancies on the crystallographic and spin-rotation transitions of iron sulfide

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Sulfur-deficient iron sulfide, $Fe_{1.04}S$, has been studied in comparison with FeS by Mössbauer spectroscopy at various temperatures ranging from 82 to 600 K. It is found that the 4 at. % sulfur vacancy makes the crystallographic α transition from the (NiAs,MnP) structure to a superstructure take place abruptly within 5 K with the superstructure stable up to 410 K. The spin-rotation transition of $Fe_{1.04}S$ takes place at 455 K, which is higher by 63 K than that of FeS. The Néel temperature is not affected appreciably by the sulfur vacancy concentration.

I. INTRODUCTION

Iron sulfide exhibits interesting magnetic and crystallographic phase transitions. Bertaut[1] has shown that FeS exists with a NiAs structure above $T_\alpha \cong 400$ K and transforms to a superstructure below this temperature. The volume of the supercell[2] is six times as large as that of the unit cell of the NiAs structure. Since the length of the c axis of the supercell is twice that of the high-temperature phase, we will call the phase with the hexagonal superstructure the $2c$ phase.

Through Mössbauer measurements Thiel and van den Berg[3] verified that both $1c$ (NiAs) and $2c$ structures coexist between T_α and about 200 K with a larger hyperfine field corresponding to the $2c$ structure. Recently, King and Prewitt[4] reported that the iron sulfide transforms into the orthorhombic MnP structure at T_α, which in turn transforms into the NiAs structure at about 580 K.

The volume of the unit cell of the MnP structure is twice that of the NiAs structure. Since one of the three lattice parameters of the MnP structure has the same length as the c value of the NiAs structure, we will call both phases the $1c$ phase. In fact, as far as Mössbauer measurements are concerned, there seems to be no appreciable difference between the two phases because no discontinuity whatsoever in the Mössbauer parameters has been observed above T_α.[3,5]

Magnetic-susceptibility and neutron-diffraction measurements[6,7] show that the iron sulfide is antiferromagnetic with a Néel temperature of about 600 K and that the spin direction changes from a perpendicular to the c axis above $T_M \cong 400$ K to parallel with the c axis below T_M. T_M is also found to be independent[3,7] of T_α and very sensitive to the kind and amount of impurity atoms.[5]

The purpose of this paper is to report Mössbauer measurements for FeS and $Fe_{1.04}S$ obtained in an effort to determine the effects of sulfur vacancies on the α and spin-flip transitions of iron sulfide.

II. EXPERIMENT

FeS and $Fe_{1.04}S$ samples were prepared from sulfur and iron of 99.999% and 99.995% purity, respectively, by heating accurately weighed quantities in an evacuated quartz tube. The sealed tube was heated slowly to 450 °C, kept at this temperature for one day, heated further to 650 °C for another day, and then heated finally to 950 °C for three days. After cooling to room temperature the sample was ground, pressed into a pellet, and annealed at 950 °C for a second time in an evacuated and sealed quartz ampoule for three days.

Extra precaution has been exercised to prevent sulfur vapors from escaping from the initial mix during the sealing process, as shown in Fig. 1. The quartz tube having two narrow necks was filled first with the desired amount of sulfur that was subsequently covered by iron, thereby blocking any light from the torch reaching the sulfur. Furthermore, both light and heat from the torch were prevented from reaching the sulfur by immersing the quartz tube in black ink during sealing. One may argue that sulfur vapors may diffuse into the quartz tube during the heating process. However, sulfur vapors in the sealed quartz ampoule combined with iron to form solid material during the initial heating at 450 °C, at which temperature diffusion is negligible.

X-ray-diffraction patterns of the samples at room temperature were obtained using a Rigaku diffractometer with Cu $K\alpha$ radiation. An analysis of the diffraction peaks showed that each sample crystallized with a hexag-

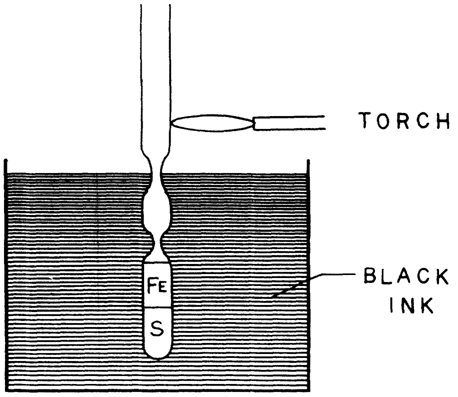

FIG. 1. Sealing technique.

onal superstructure[2] with the following lattice parameters:

$a_0 = 5.972 \pm 0.005$ Å

and $c_0 = 11.72 \pm 0.05$ Å for FeS ,

and

$a_0 = 5.952 \pm 0.005$ Å

and $c_0 = 11.76 \pm 0.05$ Å for $Fe_{1.04}S$.

Mössbauer measurements were made on a spectrometer of the electromechanical type manufactured by Austin Science Associates used in the constant-acceleration mode. A ^{57}Co source in a rhodium matrix was used at room temperature. The measurement and control of the absorber temperature was carried out with an accuracy of 0.5 K using copper-constantan and chromel-alumel thermocouples in conjunction with a heater.

III. RESULTS AND DISCUSSION

Figures 2 and 3 illustrate the temperature variation of the Mössbauer spectra from the FeS and $Fe_{1.04}S$ samples, respectively. At both the high and low temperatures the Mössbauer spectra consist of single sets of hyperfine patterns, while for the intermediate temperatures, they consist of a mixture of the two sets of hyperfine patterns, which indicate a coexistence[3] of the 1*c* and 2*c* phases.

All the Mössbauer spectra have been analyzed by a least-squares fitting to 2, 6, or 12 Lorentzian lines. Figure 4 shows some representative residual plots for the data displayed in Fig. 2. It seems to be evident in Fig. 4 that no other lines exist. Linewidths for the FeS spectra in Fig. 2 are about 10% broader than those for the $Fe_{1.04}S$ spectra in Fig. 3, because the FeS absorber contained more ^{57}Fe per unit area than the $Fe_{1.04}S$ absorber. Quadrupole slittings just above the Néel temperatures are found to be 0.28 ± 0.01 mm/s for both FeS and $Fe_{1.04}S$.

Figure 5 shows the temperature dependence of the magnetic hyperfine field H_{hf} and the quadrupole shift ΔE_Q for FeS. ΔE_Q was calculated from the positions of the Mössbauer absorption lines using the expression

$$\Delta E_Q = (V_1 - V_2 - V_5 + V_6)/4 ,$$

where V_i represents the position of the *i*th absorption line in mm/s in order of descending value. When the quadrupole interaction is much weaker than the magnetic hyperfine interaction, ΔE_Q can be written as[8]

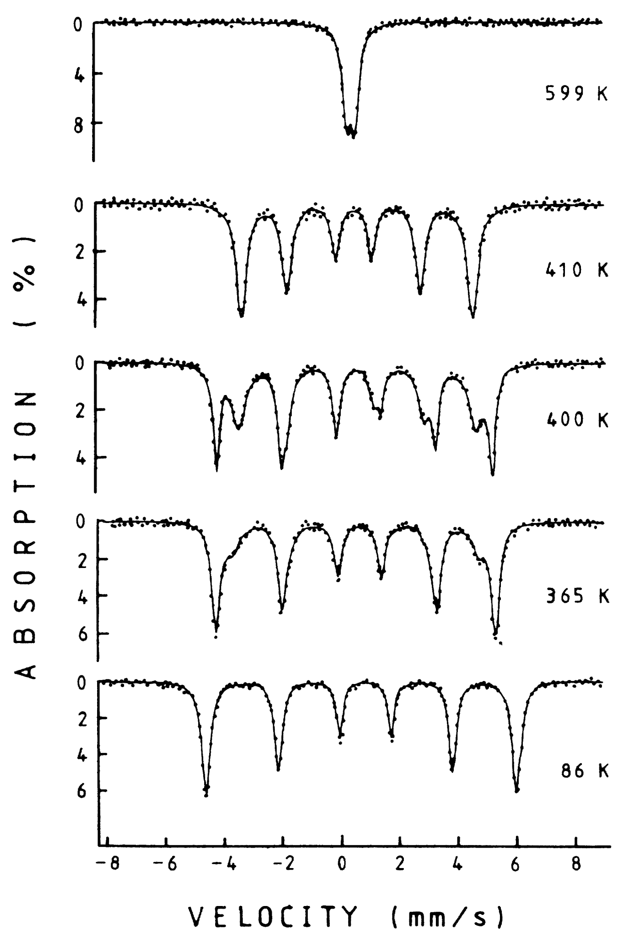

FIG. 2. Mössbauer spectra of FeS.

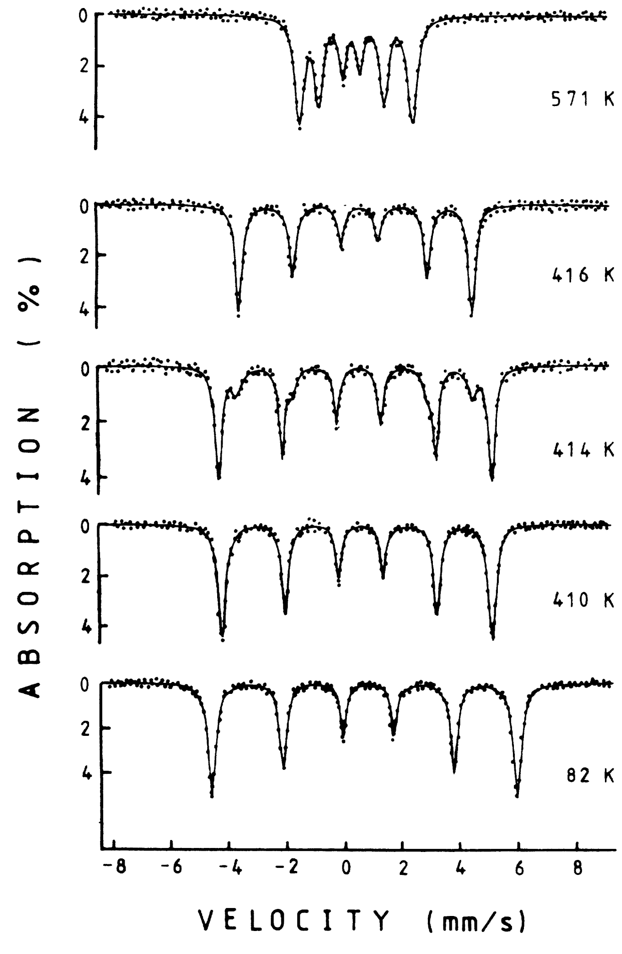

FIG. 3. Mössbauer spectra of $Fe_{1.04}S$.

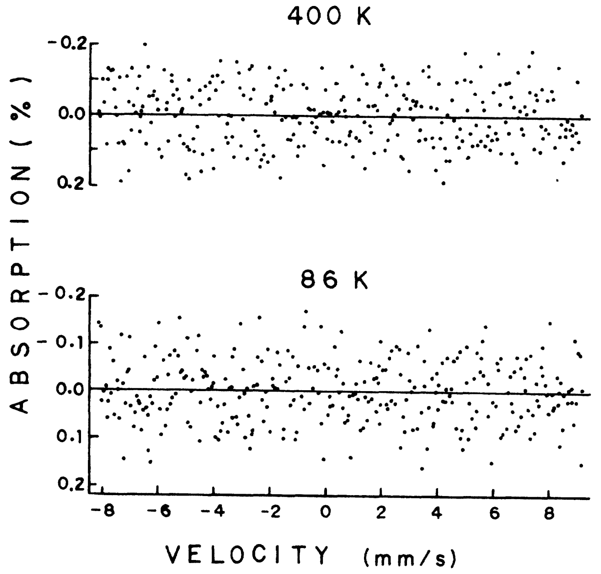

FIG. 4. Residual plots for the Mössbauer spectra of FeS at 86 and 400 K displayed in Fig. 2.

$$\Delta E_Q=(\tfrac{1}{8}e^2qQ)[3\cos^2\theta-1+\eta\sin^2\theta\cos(2\phi)]\ ,$$

where θ and ϕ are the angles, in polar coordinates, between the magnetic hyperfine field vector and the principal axes of the electric-field-gradient tensor. It is evident from Fig. 5 that only the 1c phase exhibits a spin-rotation transition at about $T_M=392$ K, which is lower by 15 K than $T_\alpha=407$ K, the α-transition temperature marking the upper end of the coexistence region. The results for FeS shown in Fig. 5 are very similar to those[3] for $Fe_{0.995}S$

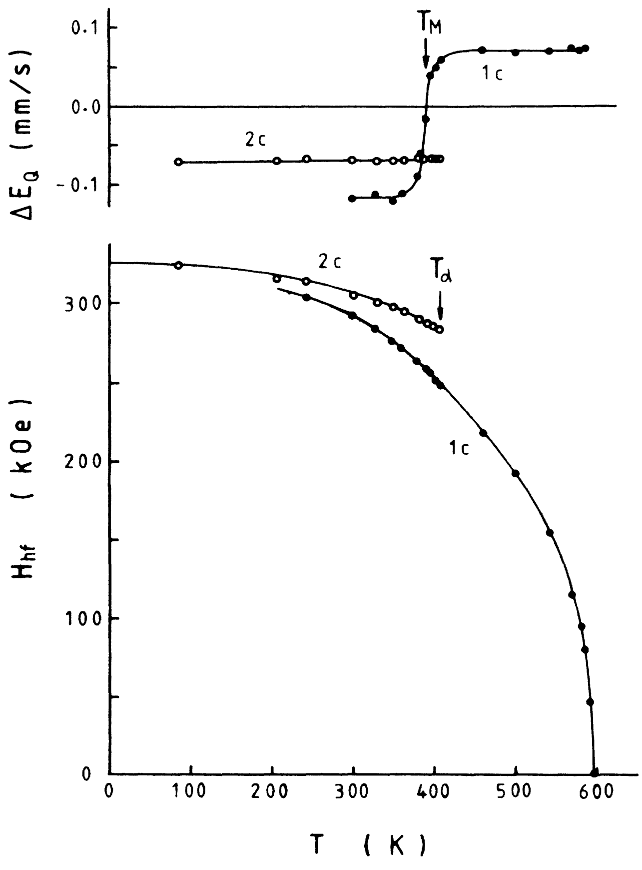

FIG. 5. Temperature dependence of the magnetic hyperfine field H_{hf} and the quadrupole shift ΔE_Q for FeS.

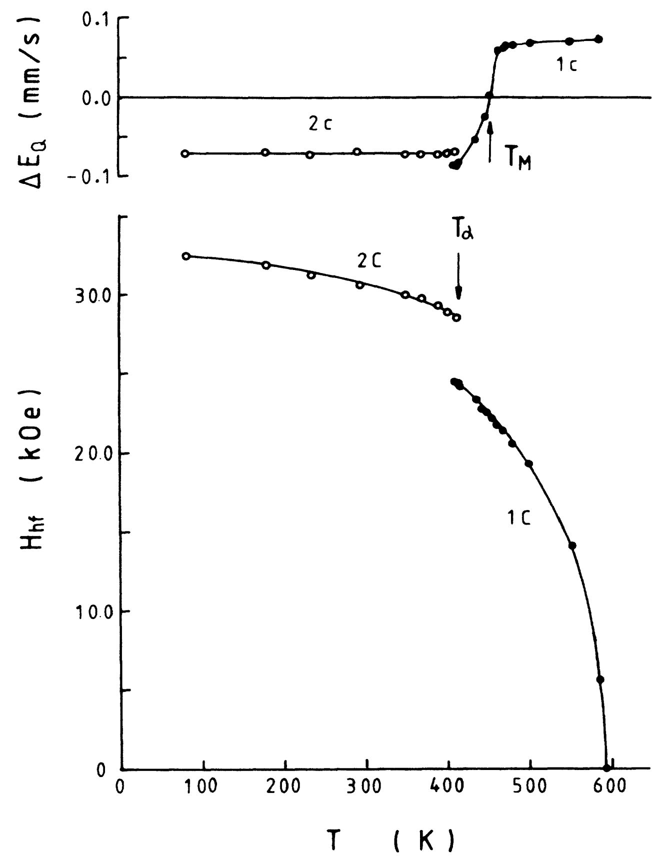

FIG. 6. Temperature dependence of the magnetic hyperfine field H_{hf} and the quadrupole shift ΔE_Q for $Fe_{1.04}S$.

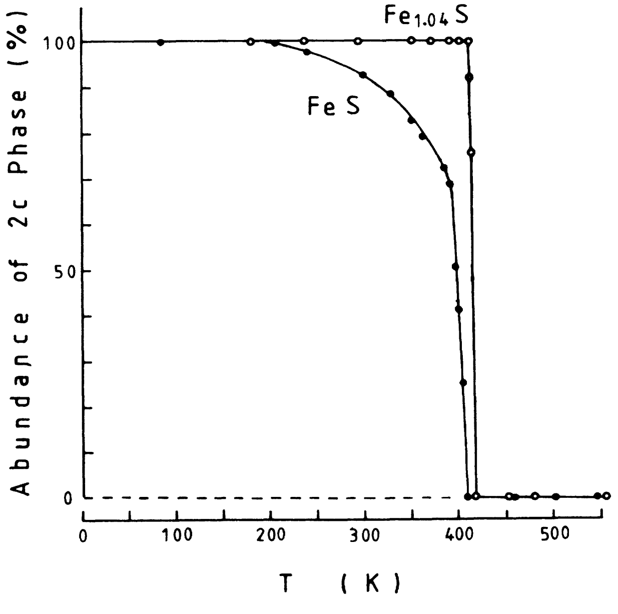

FIG. 7. Abundance of the 2c phase as a function of temperature for (a) FeS and (b) $Fe_{1.04}S$.

in all respects, particularly in that the 1*c* and 2*c* phases coexist over a wide temperature range of about 200 K. Figure 6 shows the temperature dependence of the magnetic hyperfine field and quadrupole shift for $Fe_{1.04}S$. It is noted in this figure that the spin-rotation transition takes place at about 455 K, which is higher by 63 K than that for FeS. The α-transition temperature of 415 K for $Fe_{1.04}S$ is also higher than that for FeS, suggesting that sulphur vacancies tend to stabilize the superstructure. This point can be seen more clearly in Fig. 7, which shows the abundance of the 2*c* phase as a function of temperature for FeS and $Fe_{1.04}S$, calculated from the relative ratios of the Mössbauer absorption areas corresponding to the 1*c* and 2*c* phases. It is evident in this figure that the upper limit of the temperature up to which the 2*c* phase solely exists without any 1*c* phase is 410 K for $Fe_{1.04}S$, whereas that for FeS is about 200 K. Furthermore, the crystallographic α transition in $Fe_{1.04}S$ takes place abruptly; the coexistence region for the two phases is only 5 K in marked contrast to about 200 K for FeS. One may argue that the wide coexistence region for FeS is possibly due to sample inhomogeneities; in other words, our FeS sample is extremely inhomogeneous, while the $Fe_{1.04}S$ sample is homogeneous. In order to check this point, we ground and heated the FeS sample repeatedly only to find the same Mössbauer spectra, thereby proving that the wide coexistence region had nothing to do with sample inhomogeneities. It should also be mentioned that our results are reproducible for different samples of the same composition.

The Néel temperatures of FeS and $Fe_{1.04}S$ were determined to be 597±2 K, and 595±2 K, respectively, implying that the 4 at. % sulfur vacancy does not affect the superexchange interactions in the 1*c* phase appreciably.

ACKNOWLEDGMENTS

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