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Effects of vanadium impurities on the crystallographic and spin-rotation transitions of iron sulfide

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It is found by Mössbauer measurements on $V_xFe_{1-x}S$ that the vanadium impurities profoundly affect both the crystallographic and spin-rotation transitions of iron sulfide. When the vanadium concentration is increased to 2.5% of the metal atoms, the crystallographic α transition proceeds an order of magnitude more rapidly than for iron sulfide, and the separation between the spin rotation and the α-transition temperatures increases by as much as 114 K compared with that for iron sulfide. The Morin transition temperature for $V_{0.025}Fe_{0.975}S$ was measured as 486 K, which is 86 K higher than the α-transition temperature. It was also found that the α transition for $V_{0.025}Fe_{0.975}S$ has a hysteresis width of 4 K.

Iron sulfide FeS exhibits interesting magnetic and crystallographic phase transitions. In the neighborhood of $T_\alpha \simeq 400$ K, a crystallographic phase transition appears, usually called the α transition. Bertaut[1] has shown that FeS exists with a NiAs structure above T_α and transforms to a superstructure below this temperature. However, Mössbauer measurements[2] indicate that both structures coexist between the α transition and about 200 K. 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 NiAs structure the 1c phase, and that with the hexagonal superstructure the 2c phase.

Magnetic-susceptibility and neutron-diffraction measurements[3,4] show that the FeS is antiferromagnetic with a Néel temperature of about 600 K and that the spin direction changes from perpendicular to the c axis above the α transition to parallel with the c axis below this temperature. However, Sparks, Mead, and Komoto[5] demonstrated through more accurate neutron-diffraction measurements that for $Fe_{0.996}S$ the spin-rotation transition (the Morin transition) takes place at a temperature T_M higher by 31 K than T_α. Similar independence of the Morin and α transitions was reported by Thiel and van den Berg[2] using Mössbauer measurements for $Fe_{0.995}S$, though they found that T_M was lower by 28 K than T_α in contrast to the former result.[5]

The purpose of this paper is to report Mössbauer measurements for the mixed system $V_xFe_{1-x}S$ in an effort to determine the effects of V ions on the Morin and α transitions of iron sulfide.

$V_xFe_{1-x}S$ samples were prepared by direct reaction[6] of Fe, V and S powders of 99.995, 99.9, and 99.999% purity, respectively, in evacuated and sealed quartz tubes at 980 °C for seven days followed by a quench. All the samples were ^{57}Fe enriched to 5 at.% of the metal atoms for Mössbauer measurements. Examination of the samples by x-ray diffraction at room temperature showed that each sample crystallized in a single phase with a hexagonal structure. Mössbauer spectra were recorded using a conventional Mössbauer spectrometer of the electromechanical type with a ^{57}Co source in a rhodium matrix. To produce a uniform thickness over the area of the Mössbauer absorber, each sample was mixed with boron nitride powder and clamped between two thin boron nitride plates. The measurements above room temperature were made in a furnace with a temperature stability of 0.25 K. Those below room temperature were obtained in a cryostat with a stability of 0.20 K.

Figures 1 and 2 illustrate the temperature variation of the Mössbauer spectra for the $V_{0.01}Fe_{0.99}S$ and $V_{0.025}Fe_{0.975}S$ samples. The Mössbauer absorption lines are six in number and sharp at both the high and low temperatures shown while they are 12 in number for the intermediate temperatures, suggesting coexistence[2] of the 1c and 2c phases. All the Mössbauer spectra have been analyzed by a least-squares fitting to 6 or 12 Lorentzian lines with the help of an UNIVAC computer. Figure 3 shows the temperature dependence of the magnetic hyperfine field H_{hf} and the quadrupole splitting E_Q' for $V_{0.01}Fe_{0.99}S$. E_Q' was calculated

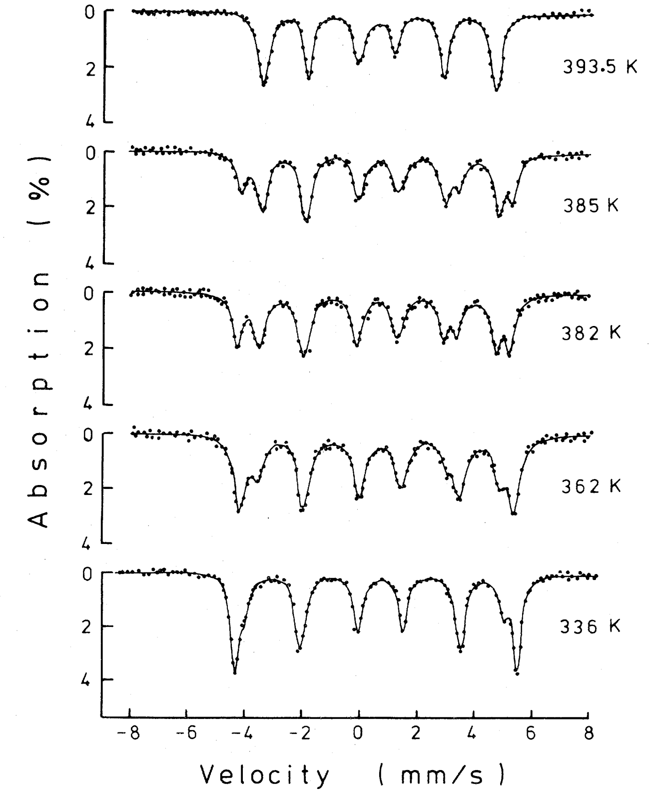

FIG. 1. Mössbauer spectra of $V_{0.01}Fe_{0.99}S$.

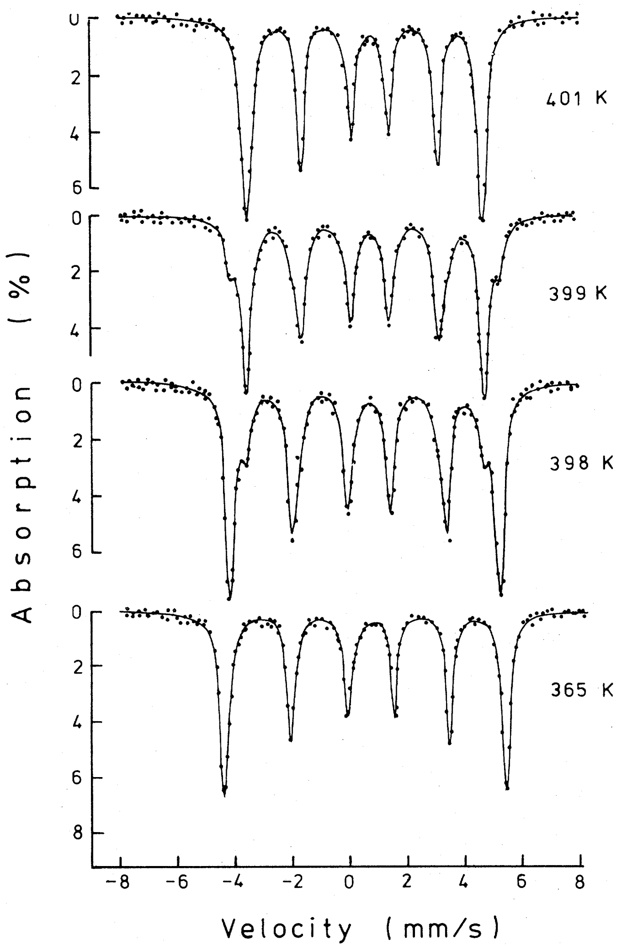

FIG. 2. Mössbauer spectra of $V_{0.025}Fe_{0.975}S$.

from the positions of the Mössbauer absorption lines using the expression

$$E'_Q = \tfrac{1}{4}(V_6 - V_5 + V_1 - V_2) \ , \qquad (1)$$

where V_i represents the position of the ith absorption line in mm/s. When the quadrupole interaction is much weaker than the magnetic hyperfine interaction, the quadrupole splitting can be described by[7]

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

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. Thus, it can be expected from Eq. (2) that E'_Q should change considerably at the Morin transition. It is evident from Fig. 3 that only the 1c phase exhibits a Morin transition and T_M is lower by 24 K than T_α, the α-transition temperature marking the upper end of the coexistence region. The results for $V_{0.01}Fe_{0.99}S$ are very similar to those[2] for $Fe_{0.995}S$. However, when the vanadium concentration was increased to 2.5% of the metal atoms, all these properties changed drastically.

Figure 4 shows the temperature dependence of the magnetic hyperfine field and quadrupole splitting for $V_{0.025}Fe_{0.975}S$. It is noteworthy that the Morin transition takes place at about 486 K which is higher by 86 K than T_α;

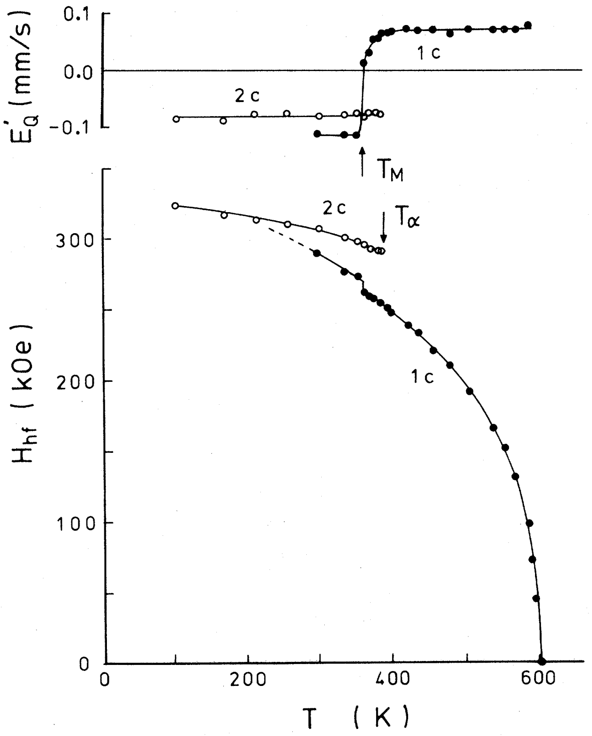

FIG. 3. Temperature dependence of the magnetic hyperfine field H_{hf} and the quadrupdole splitting E'_Q for $V_{0.01}Fe_{0.99}S$.

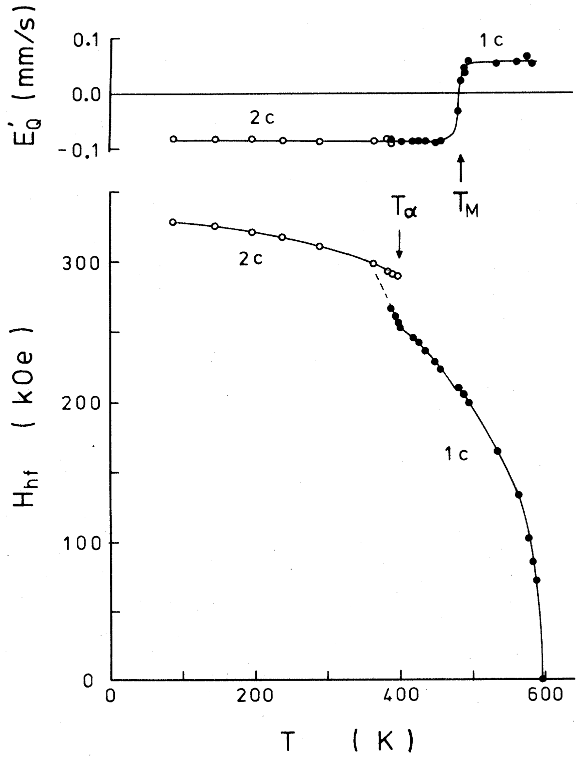

FIG. 4. Temperature dependence of the magnetic hyperfine field H_{hf} and the quadrupole splitting E'_Q for $V_{0.025}Fe_{0.975}S$.

in other words, an additional increase of only 1.5% in the vanadium concentration increased $(T_M - T_\alpha)$ by as much as 110 K. Furthermore, the coexistence region of the two phases for $V_{0.025}Fe_{0.975}S$ is very much narrower than for $V_{0.01}Fe_{0.99}S$ or $Fe_{0.995}S$ (Ref. 2) as can be seen in Figs. 1–4. Figure 5 indicates the abundance of the two phases as a function of temperature for $V_{0.01}Fe_{0.99}S$ and $V_{0.025}Fe_{0.975}S$, calculated from the relative ratios of the Mössbauer absorption areas corresponding to the two phases. It is noted in this figure that the crystallographic phase transition for $V_{0.025}Fe_{0.975}S$ takes place an order of magnitude more rapidly than that for $V_{0.01}Fe_{0.99}S$ or $Fe_{0.995}S$; furthermore, the α transition for $V_{0.025}Fe_{0.975}S$ has a hysteresis width of 4 K, whereas no hysteresis[2] was observed for FeS. A change in the sublattice magnetization is to be expected at the Morin transition.[8] Such changes seem to be present at T_M (Figs. 3 and 4), although they are not much greater than the error limits.

In conclusion, a vanadium impurity of 2.5% of the metal atoms in the iron sulfide makes the crystallographic transition take place rapidly in a narrow temperature region of about 15 K, while the α transition in FeS takes place over a wide temperature range[2] of about 200 K; and it raises the spin-rotation temperature by 86 K above T_α while T_M for the iron sulfide is 24 K below T_α. The increase in the Morin transition temperature seems to saturate at a vanadium concentration of about 2.5%; the value of T_M for $V_{0.075}Fe_{0.925}S$ is 490 K, which is higher by only 4 K than that for $V_{0.025}Fe_{0.975}S$. In a hexagonal crystal like $V_xFe_{1-x}S$, the spin direction is determined by the relative magnitudes and signs of the anisotropy constants $K_1, K_2, \ldots$. Thus, it is somewhat surprising that the abrupt change in anisotropy constants for $V_{0.025}Fe_{0.975}S$ takes place at a temperature separated by 86 K from the crystallographic transition temperature. Furthermore, the sharpening of the crystallographic transition due to the vanadium impurities is in marked contrast to the broadening of the coexistence region by Co or Cr impurities as observed in $Co_{0.025}Fe_{0.975}S$ (Ref. 9) and $Cr_{0.025}Fe_{0.975}S$ (Ref. 10).

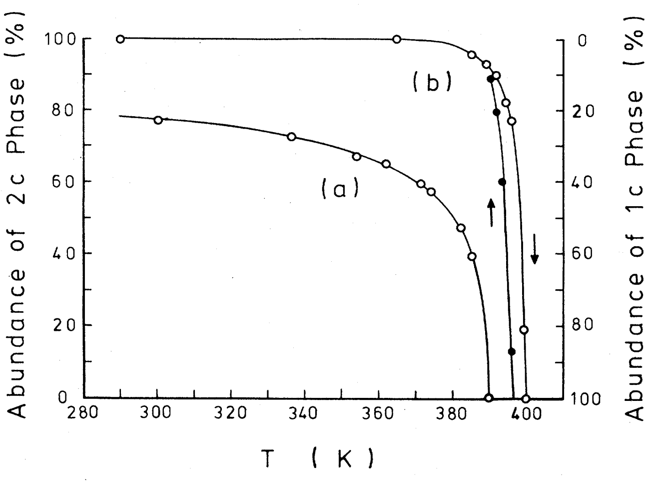

FIG. 5. Relative abundance for the 1c and 2c phases as a function of temperature for (a) $V_{0.01}Fe_{0.99}S$ and (b) $V_{0.025}Fe_{0.975}S$.

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[1] F. Bertaut, Bull. Soc. Fr. Mineral. Cristallogr. **79**, 276 (1956).

[2] R. C. Thiel and C. B. van den Berg, Phys. Status Solidi **29**, 837 (1968).

[3] E. Hirahara and M. Murakami, J. Phys. Chem. Solids **7**, 281 (1958).

[4] J. T. Sparks, W. Mead, A. J. Kirschbaum, and W. Marshall, J. Appl. Phys. **31**, 356S (1960).

[5] J. T. Sparks, W. Mead, and T. Komoto, J. Phys. Soc. Jpn. **17**, Suppl. B1, 249 (1962).

[6] H. N. Ok, Y. Chung, and J. G. Kim, Phys. Rev. B **20**, 4550 (1979).

[7] H. N. Ok and J. G. Mullen, Phys. Rev. **168**, 563 (1968).

[8] F. van der Woude, Phys. Status Solidi **17**, 417 (1966).

[9] K. S. Baek, J. Y. Park, and H. N. Ok, J. Korean Phys. Soc. **17**, 91 (1984).

[10] H. N. Ok, K. S. Baek, and C. S. Kim, Phys. Rev. B **26**, 5223 (1982).