

Magnetic Susceptibility of Single-Crystal Fe_{1-x}S

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Stoichiometric FeS is characterized by three phase transitions, one structural at T_z and the others magnetic at T_s and T_N . We have obtained magnetic susceptibility data, in the temperature range 80 to 600°K, on single crystals of several compositions of Fe_{1-x}S for $0 \leq x \leq 0.07$.

The magnetic susceptibilities of very nearly stoichiometric FeS show the two transitions well separated [$T_z \doteq 420^\circ\text{K}$, $T_s \doteq 445^\circ\text{K}$]. In the region of T_s , the spins do not rotate gradually with temperature, but flip locally due to a small spread in composition. By comparing the data with that of NiS we infer that FeS is a localized spin antiferromagnet, in contrast to NiS which is generally considered to be an itinerant antiferromagnet.

$T_s(x)$ decreases linearly with increasing metal deficiency. This dependence can be partly accounted for by a decrease in the spin-orbit coupling energy arising from increasing covalency; however, we conclude that a concomitant increase in magnetocrystalline anisotropy energy also occurs in this range.

1. Introduction

In Fe_{1-x}S , phase transitions and their related magnetic and electrical properties have been a source of much interest and controversy (1); many of the existing discrepancies have resulted from materials that were either insufficiently well prepared, annealed, or characterized.

A study is made in the present work of the phase transitions and magnetic properties in a number of single crystals of Fe_{1-x}S (with $0 < x \leq 0.07$) which were grown by the Bridgman technique and carefully annealed.

Stoichiometric iron sulfide is antiferromagnetic and is characterized by three phase transitions:

(1) The α -transition, occurring at about 420°K (T_z), is a transition from an NiAs type structure at high temperature to a closely related superstructure at low temperature (2). The axes of this superstructure are related to those of the small NiAs type cell by $a = a_0\sqrt{3}$ and $c = 2c_0$; the iron atoms are displaced from

the NiAs positions by small distances in directions perpendicular to c to form triangular clusters in the c plane (3). On decreasing the temperature through T_z there is an abrupt increase ($\sim 1\%$) in the magnitude of c and a corresponding decrease in conductivity; the conductivity appeared to be metallic (4, 5); however, this seems incorrect, as discussed later.

(2) Neutron diffraction on powdered nearly stoichiometric FeS shows that, on heating, the spins rotate from $\parallel c$ to $\perp c$ at a temperature T_s higher than T_z ($T_s = 453^\circ\text{K}$) (6, 7). T_s is very sensitive to composition (7), and earlier magnetic studies on single crystals of nominally stoichiometric FeS indicated that T_z and T_s coincided (5); we will show below that this does occur for $x = 0.012$.

(3) The third transition occurs at the Néel temperature at about 600°K; this transition appears to be insensitive to composition.

A first-order rotation of the spins can occur at $T_s(x)$ when the trigonal field and spin-orbit

coupling interactions are of comparable magnitude (8, 9). On the other hand, the driving mechanism of transitions such as the α -transition in FeS is not generally understood at present.

In order to aid further in the understanding of the nature of the transitions at T_x and T_s in Fe_{1-x}S , results are reported here for magnetic susceptibility in single crystals of composition in the range $0 \leq x \leq 0.07$ at temperatures between 80 and 650°K. In addition, some thermoelectric power and DTA results are also reported. Mössbauer results are described in (10). For each particular composition, these various measurements were made on crystals cut from the same boule.

The properties of stoichiometric FeS are compared and contrasted with those of NiS, in which there is a first-order phase transition that is currently a subject of much controversy (11-13).

2. Experimental Procedure

Crystals of Fe_{1-x}S ($0 \leq x \leq 0.07$) were grown by the Bridgman method in sealed evacuated silica capsules. The Fe_{1-x}S charges were initially synthesized from the elements in sealed evacuated silica glass capsules at 800°C. Each charge was then transferred to a prepared silica capsule with a pointed lower end. The capsule was evacuated, sealed, and placed in a vertical tube furnace that was heated and then controlled to give a peak temperature close to 1200°C. The charge was lowered slowly (6 mm/hr) from the hot zone of the furnace. After completion of the crystal growth, the boule was cooled to room temperature in the furnace, re-encapsulated, and annealed as indicated in Table I in order to promote homogeneity.

The Fe/S atomic ratios of the crystals were determined by powder X-ray diffraction using a Guinier focussing camera with $\text{CoK}\alpha$ radiation and KCl as internal standard. The compositions were found from the 102 interplanar spacings of the NiAs-type cell (114 interplanar spacings of the troilite cell) using the data of Arnold (14) and Toulmin and Barton (15) relating the 102 interplanar spacing to the atomic percentage Fe. The

TABLE I
COMPOSITION AND HEAT TREATMENT
OF CRYSTALS

Fe/S atomic ratio	Annealing
0.996	850°C for 10 days
0.988	900°C for 14 days
0.662 ^a	900°C for 10 days
0.929	600°C for 8 days

^a Samples annealed at 80°C disproportionated into two phases with Fe/S = 1.00₂ and 0.93₆.

results are listed in Table I; the uncertainty in the Fe/S ratios is estimated to be ± 0.004 .

The material that was prepared as nominally stoichiometric FeS showed an apparent Fe/S ratio of 0.996. To verify that this material had the maximum Fe/S ratio, a portion was sealed in a capsule and equilibrated at 850°C for 2 weeks with iron powder, in the presence of H_2 as a transporting agent for sulfur. Matted iron whiskers grew on the surface of the iron sulfide. X-ray diffraction indicated an Fe/S ratio of 0.997, with a trace amount of Fe metal present. A sample of this material was used for magnetic measurements. The values of T_s and T_x in this material were not appreciably different from those in nominally stoichiometric FeS; to within experimental error, the original boule appeared to have the maximum Fe/S ratio attainable at 850°C.

Each crystal was oriented using a precession camera and plates were cut with the c -axis either perpendicular to the plane of the plate or in the plane of the plate. Polished faces of the plates were examined under a polarizing microscope in order to detect any misorientation. For magnetic measurements, oriented pieces of each composition were cut from the plates and sealed into small evacuated silica capsules; samples were prepared either with the c -axis vertical (along the axis of the capsule) or with the c -axis horizontal (perpendicular to the axis of the capsule) for each composition. Magnetic susceptibilities were determined at temperatures between 78 and 650°K using

the Faraday method in fields up to 8.5 kOe. Thermoelectric power measurements were made with a temperature difference of 5°K , the value of dV/dT was simultaneously derived by an analog computer, and the results plotted directly on an X - Y recorder.

3. Results and Discussion

3.1. Composition dependence of T_α and T_s

The range of composition over which the 2C structure exists at room temperature is believed to be narrow, and there is a miscibility gap at room temperature (16, 17) between this structure and another hexagonal phase at about $\text{Fe}_{0.93}\text{S}$.

T_α , as determined from DTA and magnetic susceptibility, is not strongly dependent on composition, up to about $\text{Fe}_{0.975}\text{S}$. The transformation at T_α is a true polymorphic transition, however, only for the stoichiometric composition FeS; for compositions between FeS and about $\text{Fe}_{0.93}\text{S}$, as indicated in Fig. 1, a phase separation takes place on cooling from the single-phase high-temperature region to the two-phase region at lower temperature.

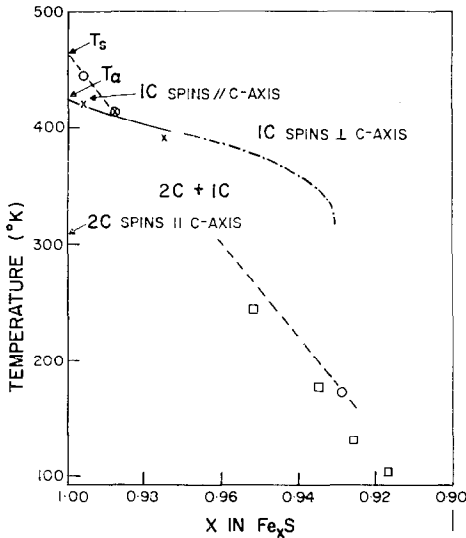


FIG. 1. Composition dependence of T_α (boundary of two-phase region)-x and T_s ---○ (our measurements); T_s ---□--- (18),--- boundary of two-phase region (17).

The slight decrease of T_α with increasing metal deficiency (Fig. 1) is accompanied by a decrease in the c/a ratio and by a decrease in both the contraction in c and the latent heat at T_α (4).

In the case of Ni_{1-x}S , the temperature of the first-order phase transition decreases also (from 260°K in NiS) with increasing metal deficiency and decreasing c/a ratio. The lower T_c in NiS relative to FeS parallels its lower value of the c/a ratio (at 300°K in NiS $c/a = 1.556$ and in FeS $c/a = 1.706$).

$T_s(x)$ on the other hand, based on results from this work and those from (18) for Fe_{1-x}S , is observed to decrease rapidly with increasing metal deficiency. This may be understood by extending Adachi's calculation of the magnetocrystalline anisotropy energy (8, 9). The anisotropy energy for the case when the spins lie at an angle θ to c was found to be

$$F(\theta) = -C_1 kT \ln \left\{ \cosh \left(\frac{\lambda l_z S \cos \theta}{kT} \right) \right\} + C_2 K_1 \cos^2 \theta + C_4 K_4 \cos^4 \theta \quad (1)$$

(Eq. (1) is slightly modified from that given in (8), which was for monoclinic symmetry) where λ is the spin-orbit coupling constant, l_z is the z component of the orbital angular momentum in the orbital doublet ground state, under the trigonal field, K_1 and K_4 are the first- and fourth-order anisotropy constants, respectively, and C_1 , C_2 , and C_4 are numerical constants which are determined by the population of Fe^{2+} ions on the crystal lattice site. The first term is the energy due to the ground doublet state in which the spin aligns preferentially along the c -axis; the second term contains contributions from the second-order mixing of the excited orbital singlet state into the ground state, and from the magnetic dipole interaction; this term aligns preferentially in the c plane; the last term comes from the fourth-order perturbation.

If we now introduce the condition for a first-order rotation of the spins at T_s , namely: $F(0) - F(\pi/2) = 0$, and solve for T , we obtain

$$kT_s = \frac{[K_1(C_2/C_1) + K_4(C_4/C_1)]}{\ln \{ \cosh(\lambda l_z S)/(kT_s) \}}$$

or

$$K = kT_s \ln \left\{ \cosh \left(\frac{\lambda I_z S}{kT_s} \right) \right\}, \quad (2)$$

where we have grouped the anisotropy terms into

$$K = K_1(C_2/C_1) + K_4(C_4/C_1).$$

We can rewrite (2) as the universal relation

$$\psi = \phi_s^{-1} \ln(\cosh \phi_s) \quad (3)$$

where

$$\psi = K/(\lambda I_z S), \quad \text{and} \quad \phi_s = \frac{\lambda I_z S}{kT_s}.$$

Experimentally kT_s decreases linearly from 400°K in FeS to 100°K in Fe_{0.92}S (Fig. 1). From Eq. (2) it is evident that the variation in kT_s may result from variation in the magnitude of $\lambda I_z S$ and/or K .

From Eq. (3) we find

$$\frac{\partial kT_s}{\partial K} = \frac{\phi_s^{-1}}{\psi - \tanh \phi_s}$$

and

$$\frac{\partial kT_s}{\partial \lambda I_z S} = \frac{\tanh \phi_s \cdot \phi_s^{-1}}{\tanh \phi_s - \psi}, \quad \therefore \frac{\partial kT_s}{\partial \lambda I_z S} = -\tanh \phi_s \cdot \frac{\partial kT_s}{\partial K}.$$

Substitution of reasonable values for the parameters in the above shows that kT_s may decrease for decreasing $\lambda I_z S$ and/or increasing K .

From the steady decrease of the Mössbauer isomer shift with increasing metal deficiency (10), shown in Table I, we deduce that the degree of covalency steadily increases from FeS to Fe₇S₈. The gradual increase in covalency would tend to produce a steady fall in $\lambda I_z S$ providing us therefore with one likely mechanism for the experimental fall in $T_s(x)$.

From the experimental values of $T_s(x)$, by making a reasonable estimate of $\lambda I_z S$ we may calculate K using the universal curve Eq. (3). Thus, in FeS for $\lambda I_z S = 50 \text{ cm}^{-1}$ (the value suggested in (9) for Fe₇S₈) we find $K = 7 \text{ cm}^{-1}$. If K were constant with composition, $\lambda I_z S$ would have to decrease by 45% for $T_s(x)$ to fall from 400°K in FeS to 100°K in Fe_{0.92}S. This would appear unreasonable;

we might expect less than a 15% reduction in $\lambda I_z S$ for increasing covalency. If instead we allow K to vary with composition, then for a fall in magnitude in $\lambda I_z S$ of the above order (15%) we find that K must increase to 14 cm^{-1} in Fe_{0.92}S. The conclusion that K must be approximately doubled for a 15% reduction in $\lambda I_z S$ does not appear to depend on the initial estimate of $\lambda I_z S$: similar results are obtained for $\lambda I_z S = 100$ or 200 cm^{-1} .

We may conclude, therefore, that within the context of Eq. (1) while a decrease in the spin orbit energy with increasing metal deficiency from FeS to Fe_{0.92}S contributes to the experimental fall in $T_s(x)$, a concomitant appreciable increase in magnetocrystalline anisotropy energy is required in order to keep the former change within conceptually acceptable bounds.

Much remains, however, to be learned of the nature of the transition at T_s ; there is no knowledge of the lattice dynamics at temperatures close to T_s , nor have X-ray measurements been made in this temperature range on crystals of the homogeneity required to resolve T_x and T_s .

In what follows detailed results for three compositions, nearly stoichiometric iron sulfide, Fe_{0.93}S, and Fe_{0.96}S are discussed.

3.2. Magnetic and electrical properties of stoichiometric FeS

The magnetic susceptibilities measured with field parallel and perpendicular to the c -axis in Fe_{0.996}S are shown in Fig. 2. The α -transi-

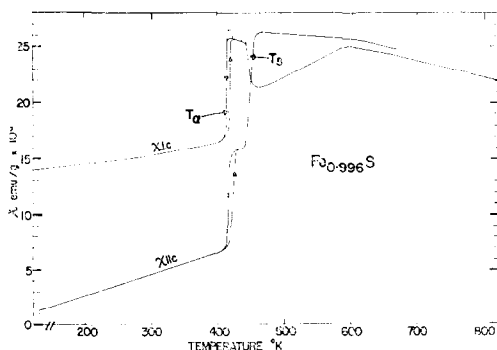


FIG. 2. Magnetic susceptibility of single crystal Fe_{0.996}S.

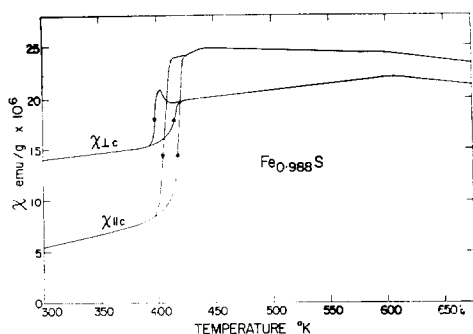


FIG. 3. Magnetic susceptibility of single crystal $\text{Fe}_{0.988}\text{S}$.

tion at 420°K coincides with the endothermic peak observed on heating in our DTA curves, and is well separated from the spin rotation at $T_s \sim 445^\circ\text{K}$. However, with a small increase in metal deficiency, e.g., in $\text{Fe}_{0.988}\text{S}$, the two transitions appear to be superimposed; see Fig. 3. Some earlier measurements (5) were made on material that was not sufficiently stoichiometric and the distinction between T_s and T_x was not clear; this led to the erroneous conclusion that the spin rotation was triggered by the abrupt change in c/a at T_x (19). During the course of this work, Takahashi (20) has reported magnetic susceptibility data on nearly stoichiometric FeS, that are broadly in agreement with those reported here for $\text{Fe}_{0.996}\text{S}$.

The abrupt increase in χ_{\perp} on heating through T_x , Fig. 2, reflects a decrease in the exchange energy. From the expression

$$\chi_{\perp} = \frac{-g^2 \mu \beta^2}{2ZS(S+1)J_3},$$

where Z is taken as 2 and J_3 is the intersub-lattice magnetic exchange interaction in the c direction, we obtain $J_3 = -3.9$ meV below T_x , and -2.4 meV above T_x , giving a decrease in $|J_3|$ at T_x of 1.6 meV. These values are considerably smaller than those estimated for NiS ($J_3 = 0.1$ eV).

The change in magnetic entropy at T_x is expected to be very small since the material is near saturation above and below T_x . From the enthalpy change at T_x , 550 cal/mole, we obtain an entropy change of 5.5

J/mole/°K; as at present there is no knowledge of the free electron concentrations nor of the nature of the lattice dynamics above and below T_x , we are unable to estimate the relative contribution of electronic and lattice effects to this quantity.

By orienting the c -axis in the horizontal plane and rotating the magnetic field in the same plane, the anisotropy in χ was followed as a function of temperature above 80°K. The results lead to the conclusion that there is no slow rotation of the spin moment below T_s ; just below T_s , the minimum in χ obtained with $H \parallel c$ flattens with increasing temperature and goes over, without change of azimuth, to a maximum above T_s (Fig. 4). This indicates that the spins do not rotate gradually with increasing temperature, as suggested earlier (6), but rather that, owing to a spread in composition in the crystal, spins in slightly different environments rotate, from $\parallel c$ to $\perp c$, at different transition temperatures close to T_s . Therefore, from the width of the transition ($\sim 16^\circ\text{K}$) and the fact that $dT_s/dx = -40^\circ\text{K}$ per 1% metal deficiency we estimate a spread in composition of $dx = \pm 0.002$ in Fe_{1-x}S .

If the temperature is raised above the Néel temperature at about 598°K, we observe a residual anisotropy, thereby confirming an earlier observation (5); this appears to be due to short-range order. Above T_N the susceptibilities follow the Curie-Weiss law, $\chi = c/(T - \theta_p)$, with $C = 3.74$, i.e., an effective moment of 5.5 $\mu\beta$ compatible with Fe(II) with an orbital contribution in the ground state, and $\theta_p = 1160^\circ\text{K}$.

At temperatures above T_s , χ was found to be isotropic in the c plane, confirming earlier work (5), and the isotropy persisted even when the applied field was reduced from several thousand to a few hundred oersted. This suggests that, above T_s , the spins lie in domains directed symmetrically in the c plane. [The sharp peaks in the cooling curve of χ_{\perp} , shown by a dotted line in Fig. 2, depend on the heating cycle above T_s ; they are intensified if the material is heated to just below T_s and immediately cooled, and may be extinguished by holding the temperature above 450°K for a few minutes before cooling.

The peaks are field-independent, and therefore, are not due to ferrimagnetism, but rather (since they occur only in χ_{\perp}) result from an increase in anisotropy that depends on the annealing cycle, and is probably related to the diffusion of iron vacancies in the crystal. One may conjecture that annealing above 450°K distributes the vacancies evenly in the crystal, whereas in material that is not annealed, there may possibly be, for example, clusters of vacancies or vacancies at the surface.]

A localized moment is suggested for Fe in FeS both by the Curie-Weiss behavior above T_N and because the experimental parameters are fitted quite well by the molecular field theory: the value of T_N calculated from χ_{\perp} by molecular field theory or spin wave theory using a Heisenberg model is of the same order as the experimental value. Thus, using molecular field theory, from $\chi_{\perp} = 1/A$, we find $A = 424$ mole/emu for $T > T_x$ and $A = 735$ mole/emu for $T < T_x$. Substituting the value of A for $T > T_x$ and the experimental value of T_N , 598°K, in $T_N = (C/2)(A - \Gamma)$, we obtain $\Gamma = 105$ mole/emu where Γ is the ferromagnetic coupling constant $\perp c$. The relative values of A and Γ are entirely reasonable. Substitution in $\theta p = (C/2)(A + \Gamma)$ gives $\theta p = 1008^{\circ}\text{K}$, close to the experimental value of 1160°K.

Our attempts at fitting the FeS data to a simple (molecular field) model (21) of an itinerant antiferromagnet were unsuccessful, the susceptibility being too high (an order of magnitude greater than that of NiS). In the case of NiS, the magnetic susceptibility (11) cannot be fitted to localized molecular field theory, nor is there Curie-Weiss behavior above the critical temperature. On the other hand, its magnetization and susceptibility may be fitted to the simple model of itinerant antiferromagnetism (21, 22), and the moment in NiS is generally considered to be delocalized (22, 23). The comparison of FeS data with those of NiS further supports our conclusion that FeS is a localized spin antiferromagnet; this contrasts with a recent model (12) for FeS as an itinerant antiferromagnet.

Our thermoelectric power (θ) measurements are broadly in agreement with previous

work (4). Below T_x $\theta \sim 125 \mu\text{V}/^{\circ}\text{K}$ and above T_x $\theta = -10 \mu\text{V}/^{\circ}\text{K}$, which indicates a possible p -type semiconducting behavior below T_x and metallic conductivity above T_x . Somewhat similar behavior is found in NiS $\theta \sim 50 \mu\text{V}/^{\circ}\text{K}$ below T_c and $\theta \sim 10 \mu\text{V}/^{\circ}\text{K}$ above T_c ; since there is still some controversy on the question of NiS being semimetallic or semiconducting below T_c , no firm conclusions should be made for FeS from this evidence alone. It has been reported that FeS is ferroelectric below T_x (24); a qualitative model has been discussed (25).

Some indication of the band structure in FeS comes from the fact that above T_x the magnetic exchange energy falls but does not go to zero, whereas in NiS the magnetic order disappears above the first-order phase transition. The latter has been ascribed to the fact that the Ni 3*d* band is superimposed on the top of the S 3*p* band and that increased hybridization between Ni 3*d* and S 3*p* at the critical temperature broadens the 3*d* band, causing a first-order loss of moment (12). In this context, it is tempting to speculate that the Fe 3*d* band lies just above the S 3*p* band and that hybridization between metal 3*d* and sulfur 3*p* is thereby diminished. Such a shift in the 3*d* band might be expected for decreasing atomic number in transition metal compounds (26).

Conductivity measurements in Fe_{1-x}S suggests metallic properties (4, 5, 27) implying, since the moment is localized, that conductivity does not occur in the *d* bands, but, rather, in the adjacent sulfur 3*p* band. However, Goodenough (19, 28) has proposed an intermediate model in which five *d* electrons are localized and the sixth *d* electron is delocalized. This would not be inconsistent with our value of the effective moment, $5.5 \mu\beta$, which would then correspond to an effective Fe(III) with some reduction of the moment due to band overlap or covalency. Goodenough (19) predicted localization of the sixth *d* electron through bonding below T_x , although metallic conductivity appeared to persist to low temperature; he ascribed this to the presence of metal vacancies. It is therefore important that the electrical properties of stoichiometric FeS be determined; preliminary measure-

ments by Gosselin in this laboratory indicate that $Fe_{0.996}S$ is in fact semiconducting in the c plane below T_s .

3.3. Magnetic susceptibility in $Fe_{0.93}S$

It is evident from the susceptibility curve of $Fe_{0.93}S$ (Fig. 5) that the spins rotate from $\parallel c$ to $\perp c$ at a $T_s(x)$ of 170°K. The sharpness of the transition indicates that crystals of $Fe_{0.93}S$, the congruent melting point composition, are very homogeneous; from the width of the transition, $\sim 6^\circ K$, and the fact that (in $Fe_{1-x}S$) $dT_s/dx \simeq -40^\circ K$ per 1% metal deficiency,

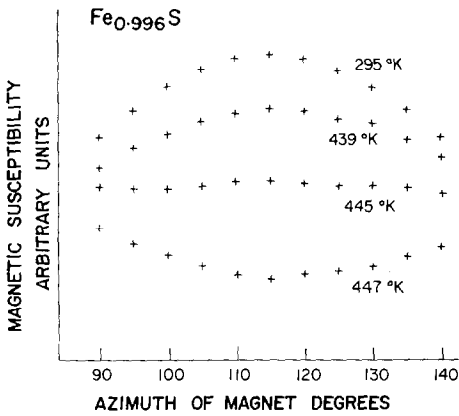


FIG. 4. Anisotropy of susceptibility in $Fe_{0.996}S$, c -axis is horizontal at 25° , and points are shown around a direction, 115° , at 90° to c . Points at different temperatures are displaced from each other.

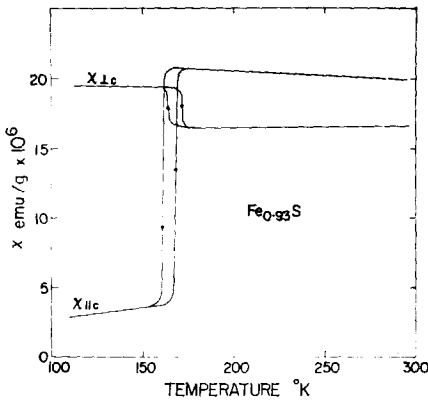


FIG. 5. Magnetic susceptibility of single crystals $Fe_{0.93}S$.

we estimate a spread in composition $dx \simeq \pm 0.0007$ for this sample.

3.4. Two-phase region, $Fe_{0.96}S$

If material of composition between $0.01 < x < 0.065$ in $Fe_{1-x}S$ is quenched from $900^\circ C$ to room temperature, a single metastable phase is obtained. T_s for a particular composition is predicted by the straight dashed curve in Fig. 1; however, if at temperatures lower than the predicted T_s , the rate of iron vacancy diffusion becomes appreciable the two phases separate before the spins can rotate. The separation of the metastable phase into two phases is marked by an exothermic peak on heating in our DTA curves.

The susceptibility curves of $Fe_{0.96}S$ show a broad hysteresis (Fig. 6). If the material is cooled rapidly down to room temperature at $60^\circ K/hr$, the subsequent separation into two phases is sufficiently slow to be followed magnetically. χ_{\parallel} returns very slowly (24 hr) to its equilibrium value, as shown by the vertical dotted line at $300^\circ K$ in Fig. 6. This suggests a potentially useful method for studying the kinetics of solid-state reactions in the two-phase region.

Andresen and Torbo (7) using neutron diffraction have investigated the magnetic transitions in a range of compositions of powdered $Fe_{1-x}S$ by monitoring the intensity of the (001) magnetic reflection which is zero when the spins are $\parallel c$. They found a sharp transition corresponding to the spin rotation in nominally stoichiometric FeS at T_s ($\simeq 458^\circ K$), and in $Fe_{0.93}S$ at

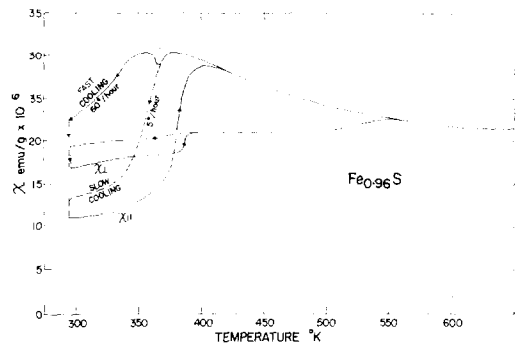


FIG. 6. Magnetic susceptibility of single crystals $Fe_{0.96}S$.

$T_s = 50^\circ\text{K}$. However, for intermediate compositions, they found two transitions, one at high temperature and the other at low temperature. Their interpretation of the latter results does not appear to take proper account of the miscibility gap. We believe that in their $\text{Fe}_{0.95}\text{S}$ and $\text{Fe}_{0.98}\text{S}$ compositions, their high-temperature transition represents the separation of the high-temperature 1C phase with spins $\perp c$ into two components on cooling through the phase boundary of the miscibility gap. One component has the 1C structure with spins $\perp c$ and the other component has the 2C structure with spins $\parallel c$; this separation of the 2C structure with spins $\parallel c$ below the phase boundary, accounts for the fall in intensity of the (001) reflection on cooling. Their low-temperature transition then results from a rotation of the spins from \perp to $\parallel c$ in the 1C component on further cooling.

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