SEMICONDUCTOR TO METAL TRANSITION IN FeS

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Résumé. — Nous donnons ici les résultats d'un travail de recherche sur des monocristaux de Fe_{0.99}S, comprenant des analyses de susceptibilité magnétique, de spectrométrie Mössbauer, de conductivité électrique, de puissance thermoelectrique et de DTA. La conductivité électrique montre à T (≈ 420 K) une augmentation d'un facteur de ~ 10^3 dans les deux directions étudiées soit parallèle et perpendiculaire à l'axe c. A basse température le déplacement isomérique correspond à celui d'une substance non métallique mais sa variation en fonction de la température semble anormale. La séparation quadrupolaire donne une indication sur la structure de bande dans la phase 2C (basse température). Les données Mössbauer concernant le champ magnétique interne en plus des résultats de susceptibilité magnétique suggèrent que le moment magnétique ne change pas agréablement à T. La température de Debye, calculée à partir des fractions Mössbauer, tombant de façon importante à la transition, indique une contribution du réseau à l'entropie de transition.

En conclusion, le FeS est un semiconducteur antiferromagnétique à spin localisé et à bande interdite étroite sous T, et un métal antiferromagnétique à spin localisé non typique au-dessus de T. Si l'augmentation de la conductivité à T est due à la délocalisation du 6^e électron à spin P, l'électron itinérant semble conserver un moment.

Abstract. — Summarised here are the conclusions of an investigation by differential thermal analysis, magnetic susceptibility, Mössbauer spectroscopy, electrical conductivity and thermoelectric power on single crystal Fe_{0.99}S. There is an increase in conductivity both parallel and perpendicular to the c-axis by a factor ~ 10^3 at T (≈ 420 K). At low temperature the I. S. is characteristic of a non-metal but its temperature dependence appears to be anomalous. Quadrupole hyperfine parameters give some indication of the band structure in the low-temperature (2C) phase. Mössbauer magnetic-hyperfine field data together with the susceptibility results suggest that the magnetic moment does not change significantly at T. The Debye temperature, calculated from the Mössbauer fractions, drops significantly at the transition, indicating a lattice contribution to the entropy of transition.

We conclude that FeS is a localised-spin antiferromagnet and narrow-band-gap semiconductor below T, and a localized-spin antiferromagnet and a not-well-behaved metal above T, If the increase in conductivity at T arises from delocalization of the 6th P-spin electron, the itinerant electron appears to retain a moment.

1. Introduction. — From a systematic investigation of synthetic single crystal Fe_{0.99}S by Mössbauer spectroscopy, magnetic susceptibility, conductivity, DTA and thermoelectric power it has been concluded that FeS is a localized-spin antiferromagnet above and below the phase transition at T (≈ 420 K), but changes from a narrow-band-gap semiconductor below T, to a not-well-behaved metal above T [1, 2, 3, 4].

This contrasts with earlier conclusions that FeS is a metallic antiferromagnet [5, 6], and allows for an interesting comparison with NiS and CoS which have a similar structure (NiAs). NiS is believed to be an itinerant antiferromagnet and semimetal below T = 260 K [7, 8], and a Pauli-paramagnetic metal above T [9], while Co_{0.92}S is a Pauli-paramagnetic metal [10].

Independently, neutron inelastic scattering measurements by the Harwell group suggest probably a more critical differentiation between NiS and FeS as mainly itinerant- and localized-spin antiferromagnets, respectively [7, 11].

Earlier work showed FeS to be a source of much interest and controversy [12, 13, 14]; some of this controversy arose from the use of material that was either insufficiently well-prepared annealed or characterized. In the present study crystals were prepared with particular care; large single crystals of Fe_{0.99}S were grown by the Bridgman technique, annealed at 850 °C for ten days, and cut into oriented slices.

FeS is characterized by two phase transitions, at T, and at T:

(1) The a-transition, observed at about 420 K (T), is a transition from an NiAs type structure (1C) at high temperature to a closely related superstructure (2C) at low temperature. The axes of this superstructure are related to those of the small NiAs type cell a = a_0 \sqrt{3} and c = 2 c_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 [15]. On increasing the temperature through T, the c/a ratio decreases abruptly by ~ 1 % and the...
volume of the unit cell increases by \( \approx 0.7\% \) [16]; simultaneously, there is a sharp increase in the conductivity both parallel and perpendicular to the c-axis [4].

(2) Below 598 K \((T_N)\) FeS is antiferromagnetic with spins \( \perp c \). At \( T_a (= 445 \text{ K}) \) the spins rotate from \( \perp c \) to \( \parallel c \) [2, 3]. Adachi [17] explained this spin-rotation by assuming a \( E(d^5) \) ground state and considering two competing interactions, the spin-orbit coupling and the dipole-dipole energies.

Bertaut [15] first remarked that a supplementary negative charge appeared to be situated in the centre of the contracted triangles in the c-plane in the 2C phase. Goodenough [6, 18] developed this idea and proposed that the 6th \( \delta \) electron was localized in a spin 3/2 molecular orbital below \( T_a \) and delocalized in an itinerant band above \( T_a \). He was handicapped in his treatment of the \( \alpha \)-transition [6], because owing to the use of non-stoichiometric material some experiments at that time suggested that \( T_a \) and \( T_S \) coincident and that FeS was a metallic antiferromagnet.

It has been claimed that FeS is ferroelectric in the 2C phase with polarization along the c-axis [19]. However, the crystal class 6 \( m \) 2 is not one of the 10 polar classes that allow pyroelectricity, nor is the magnetic class 6 \( m \) 2, among those in which pyroelectricity is permitted. On the other hand, tertiary pyroelectricity could occur, if the crystal were strained unevenly by non-uniform heating, but symmetry would require the piezoelectric polarization to lie in the c-plane and not along the c-axis as in the effect claimed [4]. A pyroelectric current [19] and an anomalous voltage [20] at \( T_a \) appear to be the result of a sharp discontinuity in the thermoelectric power at \( T_a \) [4].

In the present work we introduce further results and analysis from Mössbauer spectra and make some suggestions concerning the \( \alpha \)-transition; an explanation for the discontinuity in the thermoelectric power at \( T_a \) is proposed.

2. Results and discussion. — 2.1 Magnetic properties. — Above \( T_N \) (598 K) the susceptibilities, figure 1, follow, \( \chi = C/(T + \theta) \) with \( C = 3.74 \), i.e.

\[
\chi = \frac{g^2 \mu_B^2}{2 |J|} T + \theta
\]

where \( z \) is taken as 2 and \( J_3 \) is the intersublattice magnetic exchange interaction in the c-direction, we obtain \( J_3 = -11.7 \text{ meV} \) below \( T_a \) and \( -2.2 \text{ meV} \) above \( T_a \) giving a decrease in \( |J_3| \) at \( T_a \) of 4.8 meV. In NiS \( J_3 \sim 0.1 \text{ eV} \), and the magnetic susceptibility [9] cannot be fitted to localized molecular field theory, nor is there Curie-Weiss behaviour above the critical temperature. On the other hand, Coey et al. [8] have shown that magnetization and susceptibility of NiS may be approximately fitted to the Stoner-Lidiard model of itinerant antiferromagnetism [8], and its moment is generally considered to be delocalized [7, 8]. The comparison of FeS data with those of NiS supports our conclusion that FeS is a localized-spin antiferromagnet.

Evidence in favour of our earlier assumption that the increase in \( \chi \perp c \) at \( T_a \) results primarily from a decrease in exchange interaction rather than from an increase in moment is provided by the temperature dependent magnetic hyperfine splitting derived from Mössbauer spectra, figure 2. We have fitted the hyperfine fields below \( T_a \) to a Brillouin function, allowing the value of the spin-parameter \( S \) to float; the fit converges to the value of \( S = 2.0 \). Above \( T_a \) as there is insufficient data to allow the same procedure, we have fitted our data together with the experimentally known \( T_N \) (598 K) to

![Fig. 1. — Magnetic susceptibility of single crystal FeO.996S.](image1)

![Fig. 2. — Magnetic hyperfine field in the 2C • and 1C ○ phases in FeO.99S; owing to a coexistence of 2 phases we have some 1C points below \( T_a \); 2C data fitted to a Brillouin function allowing \( S \) to float, \( S \) converges to 2.0; 1C data fitted to Brillouin with \( S = 2.0 \).](image2)
a Brillouin function with a fixed value of $S = 2$. Extrapolation of both curves to 0 K shows them to coincide at a value of 323 kOe, figure 2. Varying the value of $S$ in the fit to the 1C data does not significantly affect the estimated 0 K value. The coincidence at 0 K suggests that the value of the moment does not change significantly at $T_s$. We infer that, if the 6th $\beta$-spin electron is indeed delocalized, it is likely to be in a spin-polarized band, for otherwise we would have a d$^5$ spin core and might expect a hyperfine field ~ 370 kOe as for FeIII in CuFeS$_2$ [22]. The relative exchange energies ($\rho$) in the 2C and 1C phases may be estimated from $T_N$ calculated for the 2C phase (807 K) and $T_N$ experimental for the 1C phase (598 K) giving $\rho = 1.33$; this compares with that calculated from $\chi_{\perp}$ ($\rho = 3.9/2.4 = 1.6$), in reasonable agreement considering the fact that we take no account of anisotropy energies in our treatment.

Powder neutron diffraction data from only a few reflections suggest the moment is greater in the 2C phase [23]. In this connection, Goodenough [24] proposed that the orbital angular momentum should be greater in the 2C phase due to the formation of a spin 3/2 molecular orbital. We don’t think this would be the case: in this model the E atomic function on each Fe atom would split into bonding and antibonding functions below $T_N$, and thus the orbital angular momentum should be quenched in going from 1C to 2C. Evidently, a direct determination of the moments near $T_s$ by neutron diffraction would be useful.

### 2.2 ELECTRIC PROPERTIES.

The positive sign of the thermoelectric power, figure 3, indicates p-type conduction although the low values suggest conduction in more than one band. At low temperatures, between 80 K and 120 K, the activation energies for conduction parallel and perpendicular to the c-axis, figure 4, are + 0.009 and + 0.006 eV, respectively; these values together with the broad peak in the thermoelectric power at 280 K suggest a low-lying impurity band. At higher temperatures, between 200 K and 300 K, the activation energies derived from the conductivities parallel and perpendicular to the c-axis are + 0.022 eV and + 0.020 eV, respectively, suggesting a band-gap of + 0.04 eV.

Above $T_s$, the conductivities are high (~ 10$^{5}$) like that of a metal but are still increasing with temperature; this may be due to disorder in the crystal. Earlier results of Hirahara and Murakami [12] on less-stoichiometric material indicated much higher values of conductivity and an appreciable discontinuity at $T_s$ only for conduction parallel to the c-axis; this led to the initial assumption of metallic behaviour. The appreciably higher conductivity in their slightly less-stoichiometric material may possibly result from broadening of the impurity band with increasing metal deficiency. Of interest is their data above 600 K ($T_N$), where the conductivity begins to drop as in a normal metal [12].

The thermoelectric power ($\theta_p$) shows a small sharp increase at $T_s$, and at higher temperatures it is not typical of that of a metal, figure 3; for example, metallic NiS [9] and Co$_{0.97}$S [10] have low negative thermoelectric powers growing negatively with temperature. Available data over a more extended temperature range indicates that $\theta_p$ is more characteristic of a metal above 520 K [25].

We tentatively attempt to account for the increase in $\theta_p$ at $T_s$ by a two-band model. We assume the $\beta$-spin electron is in an E ground state that is split below $T_s$; a qualitative scheme is shown in figure 5. Then

$$\theta_p = -\frac{k}{e} \times \left( n\mu_1 \left( 2 - \frac{\epsilon}{kT} \right) - p\mu_2 \left( 2 - \frac{\eta}{kT} \right) \right) / (n\mu_1 + p\mu_2)$$

(i)

where the first term on the right is due to electrons in the conduction band and the second term from hole conduction in an impurity band or the sulphur 3p band. At $T_s$, the splitting of the E state reduces to zero giving a large increase in density of states, accounting for the increase in conductivity. The absolute magnitude of the first term on the right in (i) decreases, as
the large negative semiconductor value changes to a small negative metallic value; this result in an increase in \( \theta_e \), providing the positive contribution due to the hole condensation is preserved through the transition. As another possibility, excitation of \( \alpha \)-spin electrons might be important above and below \( T_c \).

Hall effect measurements on less-stoichiometric material suggested that the discontinuity in conductivity at \( T_c \) resulted from a discontinuity in carrier mobility [26]. Such conclusions should be treated with caution since these measurements give only the algebraic sum of carriers in a multi-band system and, therefore, may not be sufficiently diagnostic.

2.3 Mössbauer QUADRUPOLE AND ISOMER SHIFTS. — The five Mössbauer parameters \( \Delta H, e^2 Q, \theta, \phi \) and \( \eta \) (magnetic hyperfine field splitting, quadrupole splitting polar and azimuthal angles of \( H \) in the e. f. g. frame, and asymmetry parameter, respectively) cannot be obtained from the hyperfine splittings alone, there being only four experimental parameters for \( Fe^{57} \). Thus \( \eta \) is usually equated to zero in order to reach a solution, as in [27] for FeS. However, this is questionable for the 2C structure since here the point group site symmetry for Fe is \( C_1 \). A further complication is that a pair of consistent solutions exist for \( e^2 Q \) and \( \theta \); these two solutions in \( e^2 Q \) straddle \( \theta_e = \arccos(1/\sqrt{3}) = 54.7^\circ \) for \( \eta = 0 \) and carry opposite signs. In addition one must not overlook the fact that the quadrupole tensor is the sum of two contributions: A lattice term, and an electronic term from the 6th \( \beta \)-spin electron in Fe(II).

In spite of these complications some useful information can be derived from the quadrupole data in \( Fe_{0.90}S \). Thiel [14] has calculated the lattice terms in the 2C and 1C phases and finds their relative magnitude to be \( \sim 20:1 \). Since the experimental quadrupole splittings appear to be much closer in these two phases we believe that the electronic contribution is probably dominant. We shall assume in the following that this is the case.

We have used an analytical method originally proposed by Brown and Parker [28] to obtain a relation between the five hyperfine parameters. Our results indicate that \( | e^2 Q | \) is temperature independent and is approximately equal to 1.5 mm/s below \( T_c \). A non-zero electronic contribution means that the bandwidths are sufficiently narrow (\( < 0.2 \text{ eV} \)) to allow resolution of the trigonal field splitting of the ground \( T_2 \) state into \( A_1 \) and \( E \). Whilst we cannot evaluate \( \eta \), from a statistical analysis of all our results below \( T_c \), we have found that \( \eta \neq 0 \) is favoured. We cannot exclude the possibility that \( e^2 Q \) arises from the electronic term and \( \eta \) from the lattice contribution; this is unfortunate because a non-zero electronic \( \eta \) would imply a ground \( E \) state split by the orthorhombic distortion, which is our model for the transition, figure 5. However, such a ground state is the only possible one that can account for a temperature independent \( e^2 Q \). In the ionic limit the electric field gradient equals \( +4/7 < r^{-3} > \) for the \( A_1 \) state and \(-2/7 < r^{-3} > \) for each of the two components of \( E \). If in the ground state the \( E \) band were split by \( A \) then the efg would be given by:

\[
e. f. g. = \frac{e^{-4/7} \kappa T}{1 + e^{-4/7} \kappa T}
\]

\[
e. f. g. = \frac{e^{-4/7} \kappa T}{2 + e^{-4/7} \kappa T}
\]

i.e. it would be temperature independent. If, on the other hand, the ground state were \( E \) and the excited state \( A_1 \) we have:

\[
e. f. g. = \frac{e^{-4/7} \kappa T}{2 + e^{-4/7} \kappa T}
\]

\[
e. f. g. = \frac{e^{-4/7} \kappa T}{2 + e^{-4/7} \kappa T}
\]

and for \( A = 0.04 \text{ eV} \) the quadrupole splitting should decrease markedly between 4 K and 400 K. Similarly, an appreciable decrease would be expected for an \( A_1 \) ground state and an \( E \) excited state.

In figure 6, the isomer shift is plotted as a function of temperature and compared to the classical high-temperature limit of the second-order Doppler effect. At 80 K the value (0.78 mm/s wrt Fe) is typical of covalent Fe(II) and is higher than the value expected.
for a metal: in the octahedral site of metallic (Fe, Ni)\textsubscript{2}S\textsubscript{4}, I. S. = 0.6 [29]. Note that, the I. S. falls off much more rapidly between 200 K and \( T_s \) than predicted classically. There appears to be no ready explanation for this behaviour. We attempted to fit the steep drop in I. S. by using a relation of similar form to that used for \( e^2 qQ \) assuming that the 6th \( \beta \)-spin electron was being excited from an essentially localized valence band to a delocalized conduction band. However, no reasonable combination of band splitting and I. S. in the excited state appeared to fit the data.

The slight increase in I. S. at \( T_s \) is unexpected (but confirms an earlier measurement [16]) and may possibly reflect the volume increase at the transition. We should note that the conductivity in the just below \( T_s \) starts to climb steeply figure 3, and we have tentatively suggested that this results from a small spread in composition [4]. Such an explanation does not suffice for the anomalous temperature dependence of the isomer shift.

2.4 LATTICE DYNAMICS. — The volume increases by 0.7\% at \( T_s \) with increasing temperature, and the transition temperature is lowered by pressure [16, 30]. Ozawa and Anzai [31] claimed to have related these changes via the Clausius-Clapeyron equation,

\[
\frac{dT}{dP} = T \frac{\Delta V}{\Delta H},
\]

but in fact they overlooked the discrepancy in sign (\( \Delta H \) is positive). It has been shown that this discrepancy arises because of the formation of a new superlattice under pressure, a high-pressure polymorph [30].

We have fitted specific heat data in the literature [32] to the relation

\[
\frac{C_p}{T} = \gamma + \beta T^2
\]

and from the value of \( \beta \) we calculate a Debye temperature \( \theta_D = 234 \text{ K} \). As the data only goes down to 10 K we are unable to comment on the value of \( \gamma \) (which should be zero for a semiconductor).

We have also calculated \( \theta_D \) from the Mössbauer fractions. Figure 7 shows a fit of the experimental points to a theoretical function:

\[
f(T) = \exp \left\{ -\frac{3}{2} \frac{R}{\theta_D} \left[ 1 + 4 \left( \frac{T}{\theta_D} \right)^2 \int_0^{\theta_D} \frac{x}{(e^x - 1)^2} \, dx \right] \right\}.
\]

We find \( \theta_D = 260 \text{ K} \) below \( T_s \) and 230 K above \( T_s \).

These values are slightly higher than those calculated by Thiel [14]. The fall in \( \theta_0 \) at \( T_s \) is too large to be explained by the small volume increase, and must reflect a softening of the lattice phonons, and a gain in the lattice entropy, in the 1C phase. (We calculate \( \Delta S = 2.4 \text{ joules/mole K} \) compared to the experimental 5.5 joules/mole K the difference being mainly from the electronic and the magnetic contribution.) Coey et al. [33] find a drop in \( \theta_0 \) at \( T_s \) in NiS, and taking into account the volume decrease at \( T_s \) they proposed that screening of the phonon interaction by the conduction electrons is important. In FeS where the volume increases at \( T_s \) such an effect is less likely.

Clearly, neutron inelastic scattering experiments to investigate possible freezing of soft phonon modes at \( T_s \) and \( T_5 \) would be of interest.

3. Conclusions. — Our experiments indicate that FeS is a localized-spin antiferromagnet and that the \( z \)-transition is probably a semiconductor-to-metal transition. There is a gain in entropy in the 1C phase both from lattice magnetic and electronic contributions. The structural distortion below \( T_s \) indicates that electron-lattice interactions are probably more important than pure electron correlation effects. Models such as that of Adler and Brooks [34] might be relevant here and this would mean that the band splitting at 0 K could be greater than that measured just below \( T_s \). In a bonding model [24], the transition would be driven by progressive excitation of electrons from a bonding to an antibonding molecular orbital. In the 1C phase the delocalization of the 6th \( \beta \)-spin electron must screen out any cooperative Jahn-Teller effect; though given the nature of the ground state, the distortion below \( T_s \) might itself appear to be a related phenomenon.

References