JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN VOL. 17, SUPPLEMENT B-I, 1962
PROCEEDINGS OF INTERNATIONAL CONFERENCE ON MAGNETISM AND CRYSTALLOGRAPHY, 1961, VOL. I

Neutron Diffraction Investigation of the Magnetic and Structural Properties of Near-Stoichiometric Iron Sulfide*

JOSEPH T. SPARKS, WARREN MEAD, AND TED KOMOTO
Lawrence Radiation Laboratory, University of California
Livermore, California

The temperature dependent magnetic behavior and lattice changes in $Fe_{0.996}S$ have been investigated simultaneously in the vicinity of the α-transition ($T_\alpha=142$°C) by means of powder neutron diffraction. The accurate determination of the shifts in the (100) and (102) nuclear peak positions with decreasing temperature shows that the C-axis lattice parameter abruptly increases by 1% and that the A-axis parameter abruptly decreases by 0.5% at T_α. The superlattice is also observed to form at this temperature and, in addition, the powder susceptibility exhibits an anomalous decrease of about 50% here. The behavior of the magnetic reflections shows that a rotation of the magnetic moments out of the basal plane begins at 185°C and ceases at 160°C, having rotated to within approximately 20° of the C-axis. At T_α, the g-factor abruptly increases about 25% as a result of the lattice distortion and then, with decreasing temperature, the moments resume their rotation toward the C-axis.

Near-stoichiometric iron sulfide, Fe_xS, shows interesting magnetic, structural, and electrical properties which have been the subject of numerous investigations. At temperatures above the so-called α-transition ($T_\alpha \simeq 140$°C), the crystal structure is of the NiAs type ($B8_1$) in which the sulfur atoms form a close-packed hexagonal lattice with the octahedral sites occupied by the iron atoms. The structure thus consists of alternating iron and sulfur planes normal to the c-axis of the crystal. At T_α a distortion occurs which can be described by a superlattice cell[1] derived from the undistorted NiAs cell by lengthening the c- and a-axes ($C=2c$, $A=a\sqrt{3}$) and by rotating the a-axis 90° in the basal plane. Bertaut[2] has worked out the distorted structure in detail.

In addition to the appearance of the superstructure, other changes have been reported to occur on cooling through T_α. The powder susceptibility[3], which exhibits the general characteristics of an antiferromagnetic material ($T_N=320$°C), shows an abrupt decrease of almost 50% at T_α. Perhaps even more striking is the decrease in the electrical conductivity along the c-axis by several orders of magnitude, while the conductivity in the basal plane decreases by only a small amount[4),5)]. Haraldsen[3] has reported an abrupt increase of about 1% in the c-axis lattice parameter, but only a change in slope in the a-axis parameter at T_α. Our data, however, show abrupt changes in both lattice parameters. A rather broad λ-type anomaly in the specific heat in the vicinity of T_α has also been observed[6].

The single-crystal susceptibility investigation of Hirahara, *et al.*,[4] indicated that above T_α the magnetic moments are arranged in ferromagnetic sheets perpendicular to the c-axis with antiferromagnetic coupling between adjacent sheets. The data below T_α were interpreted on the basis of a 90° rotation of the magnetic moments at T_α, the moments on adjacent iron sheets remaining antiparallel but directed along the c-axis. Neutron diffraction powder studies of iron sulfide[7),8)] confirmed both the high and low temperature antiferromagnetic arrangements suggested by the single-crystal susceptibility measurements. However, the question concerning the temperature at which the rotation of the moments occurs remained obscure. Andresen[7] observed such a rotation over a rather broad temperature range (177°–117°C) and interpreted this result as a confirmation of the suggestion that the susceptibility anomaly at T_α was due to a 90° rotation of the magnetic moments. Our neutron diffraction results[8] indicate, on the other hand, that for near-stoichiometric compositions the rotation occurs at temperatures well above T_α and is unrelated to the prominent susceptibility

---

* Work performed under the auspices of the U. S. Atomic Energy Commission.

anomaly.

Our earlier work in the near-stoichiometric region indicated that the spin rotation temperature, T_s, is very sensitive to the composition-much more so than T_α-and also sensitive to contaminants that apparently originated in the preparation of the material. To resolve the question concerning the simultaneity of T_α and T_s and to determine the intrinsic behavior of iron sulfide uncomplicated by phase segregation[9] and contaminants, samples were carefully prepared for which X=1.000, 0.998, 0.996 and 0.994. The method of preparation consisted of carefully weighing out the proper amounts of high purity iron and sulfur to give the desired composition and then reacting these components very slowly at 600°C in an evacuated quartz tube with subsequent homogenizations at 980°C. Considerable care must be taken in carrying out the reaction to avoid the occurrence of excessive local temperatures due to the evolution of the heat of reaction. The local temperatures can easily become high enough to cause local fusing and reaction with the quartz container. The accuracy of the iron-to-sulfur ratios is about 0.05% determined from the weighing. Indications of the degree of homogeneity can be obtained by observing, for example, the sharpness of the x-ray pattern and the abruptness of the susceptibility anomaly at T_α. X-ray analysis and magnetic measurements show that the X=0.996 and 0.994 compositions are single phase at room temperature, but that X=0.998 and 1.000 possess two phases, one of which is magnetic.

We have examined the X=0.996 preparation in detail by means of neutron diffraction. In order to accurately locate the spin rotation transition, T_s, with respect to the abrupt lattice changes, the heights and angular positions of certain diffraction peaks were measured during a single cooling run. The magnetic behavior was determined by observing the temperature dependence of the intensities of the (001) magnetic reflection and the (101) mixed nuclear and magnetic reflection. Simultaneously, the lattice changes were determined by observing the (211) superstructure reflection and by the accurate measurement of the shifts with temperature in the (100) and (102) nuclear peak positions. The measured shifts in the peak positions indicate the behavior of the A- and C-axis lattice parameters with temperature. This procedure avoids difficulties in correlation and interpretation that can arise when the lattice parameter data are obtained separately by x-ray methods. The magnetic susceptibility was determined by the Gouy method using the same sample investigated in the neutron diffraction measurements.

The results from a typical cooling run are shown over a limited temperature interval in Fig. 1. Both the magnetic (001) reflection and the magnetic part of the (101) reflection begin to depart from Brillouin-like behavior at about 185°C. The behavior of both peaks down to about 142°C is consistent with a rotation of the magnetic moments out of the basal plane. The superlattice is seen to form abruptly at 142°C, as shown by the appearance of the (211) superlattice peak. Both lattice

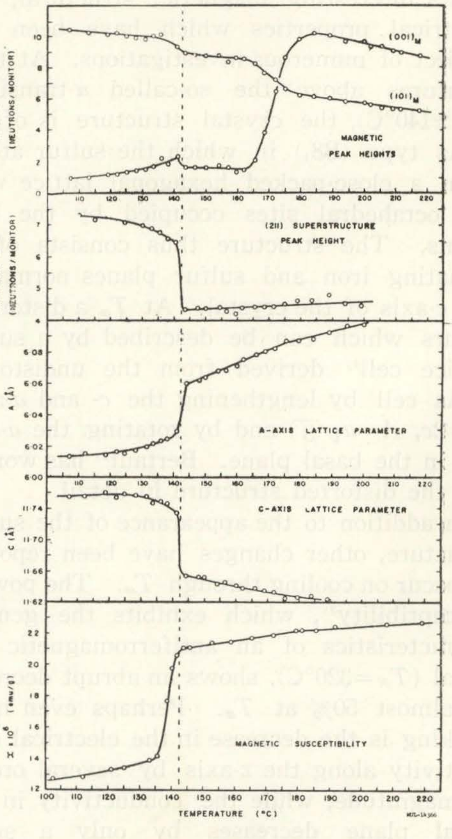

Fig. 1. Temperature dependent behavior of the magnetic peak intensities, a superlattice peak, the lattice parameters, and the magnetic susceptibility of $Fe_{0.996}S$ on cooling in the vicinity of T_α.

parameters exhibit abrupt changes at 142°C resulting in a sudden decrease in cell volume. The increase in the *C*-axis parameter is in agreement with Haraldsen's[3] results; the abrupt decrease in the *A*-axis parameter, however, is not. The lattice parameters and the susceptibility show little change in the temperature interval where the magnetic moments are rotating as compared to the changes occurring at the α-transition. These data clearly show that the magnetic moment rotation is distinct from the α-transition and from the large susceptibility anomaly. It seems plausible that the abrupt decrease in the susceptibility is due to a sudden increase in the anisotropy energy (or possibly the exchange energy) brought about by the distortion of the lattice in forming the superstructure.

The (001) peak behavior shows that the rotation of the moments begins at 185°C and ceases at 160°C. The (001) intensity at 185°C is consistent with the moments lying in the basal plane perpendicular to the *C*-axis, while the intensity at 160°C indicates the moments have not rotated sufficiently to point exactly along the *C*-axis but instead make an angle about 20° with it. No further changes occur in the orientation of the moments between 160°C and the α-transition. The (101) behavior from 185°C to the α-transition is consistent with this description to within the accuracy of the data. The width of the rotation transition (185°-160°C) can be interpreted as a gradual rotation of the magnetic moments out of the basal plane. Integrated peak intensity measurements of the (001) and (101) reflections are in agreement with this interpretation. Such a gradual rotation can be qualitatively described by the expression $\sin^2\theta = -K_1/2K_2$ derived from the well-known phenomenological expression for the anisotropy energy of a hexagonal crystal. K_1 and K_2 are the first and second anisotropy parameters which are allowed to vary with temperature or lattice spacing, and θ is the angle between the direction of the magnetic moments and the *C*-axis of the crystal. Inhomogeneities of composition, strain, temperature, etc., could be the cause of the transition breadth, rather than a gradual rotation of the moments, but in these cases broadening of the (001) peak and an increase in the background would be expected, neither of which is observed within our experimental accuracy.

The situation at and below the α-transition is somewhat more complicated. The abrupt increase in the intensity of both the (001) and (101) peaks at T_α cannot be explained merely on the basis of the change in structure factor due to the appearance of the superlattice, nor as a result of the completion of the rotation of the moments to the *C*-axis. Also, no new magnetic reflections are observed to appear, which indicates the antiferromagnetic ordering has not changed. To account for the observed behavior of the (001) and (101) reflections at T_α and below, we conclude that the *g*-factor increases abruptly at T_α as a result of the distortion and then, as the temperature is lowered, the moments resume their gradual rotation toward the *C*-axis. A 20 to 25% increase in g at T_α would account for the observed behavior at that temperature. A more complete account of this investigation will be published elsewhere.

We are indebted to Dr. W. Marshall for originally suggesting the iron sulfide investigation and for many discussions on various aspects of the problem. Thanks are also due Dr. R. J. Elliott for several helpful discussions and to Dr. A. J. Kirschbaum for his continued encouragement.

References

1 G. Hägg, I. Sucksdorff: Z. Phys. Chem. **B22** (1933) 444.
2 F. Bertaut: Bull. Soc. franc. mineral et crist. **79** (1956) 276.
3 H. Haraldsen: Z. anorg. u. allgem. Chem. **231** (1937) 78; **246** (1941) 169; and **246** (1941) 195.
4 E. Hirahara, M. Murakami: J. Phys. Chem. Solids **7** (1958) 281.
5 T. Kamigaichi, T. Hihara, M. Tazaki, E. Hirahara: J. Phys. Soc. Japan **11** (1956) 606.
6 T. Hirone, S. Maeda, N. Tsuya: J. Phys. Soc. Japan **9** (1954) 503.
7 A. F. Andresen: Bull. Am. Phys. Soc. Ser. II **5** (1960) 456; Acta Chem. Scand. **14** (1960) 919.
8 J. T. Sparks, W. Mead, A. J. Kirschbaum, W. Marshall: J. Appl. Phys. **31** (1960) 356S; Bull. Am. Phys. Soc. Ser. II **5** (1960) 457.
9 F. Gronvold, H. Haraldsen: Acta Chem. Scand. **6** (1952) 1452.

DISCUSSION

E. HIRAHARA: The α-transition temperature of your samples is rather higher than our value, 138°C, on stoichiometric samples. I am afraid your samples might be deficient in sulphur. In our measurements, the α-transition temperatures of sulphur-deficient samples are rather higher than that of a stoichiometric one. The strong change of (001) reflection at 180°C may also be due to the deficit of sulphur.

J. T. Sparks: I feel quite certain that our samples which show an α-transition greater than 138°C are not deficient in sulphur. As stated in the preprint the accuracy of X is about 0.05%.

T. Hihara: I have measured the magnetic susceptibility of iron sulphide single crystals and found that the spin rotation and the α-transition occur at slightly different temperatures on cooling, but they occur at nearly the same temperature on warming. I think that the complicated patterns which you obtained on warming may be due to the simultaneous occurence of both transitions. So far as the magnetic structure is concerned, it may be simpler to work with specimens which contain excess of sulphur, because in such specimens the α-transition completely disappears and only the spin rotation occurs.

J. B. Goodenough: Does your data indicate an increase or a decrease in the Fe^{2+} atomic moment below T_α?

J. T. Sparks: At the α-transition we cannot explain the increase in the (101) reflection by either the completion of the rotation of the moments to the c-axis nor due to the change in structure factor. Also we see no new magnetic peaks appearing so that the antiferromagnetic ordering apparently does not change. Thus we conclude that the moment has increased.

K. Adachi: The experimental evidence that the α-transition temperature does not coincide with the transition temperature for the spin direction may be explained as follows. The lowest three energy levels of a ferrous ion, which are degenerate under the cubic crystalline field and the exchange field, can be expressed in terms of the trigonal crystalline field and the spin-orbit coupling in an appropriate approximation as

$$E_\pm = -(1/3)a\varepsilon \pm 2\lambda \cos\theta \text{ and } E_0 = (2/3)a\varepsilon + K\cos^2\theta\ ,$$

where $a\varepsilon$ is the level splitting due to the trigonal lattice distortion ε in this crystal, λ the spin-orbit coupling constant, K the uniaxial magnetic anisotropy energy for the singlet E_0 and θ the angle made by the spin direction and the c axis. The expression for the free energy can be obtained from these energy levels with the addition of the elastic energy term which is proportional to ε^2. By minimizing the free energy with respect to ε and θ, the temperature dependence of ε and θ can be obtained. Below the α-point the spins have to point in the c direction, since the ground state is doublet. However, the spin can point in the c direction even above the α-point because of the free energy gain due to the thermal population for these three energy levels. Also it can easily be shown from the present consideration that the α-transition is of the first order while the transition of the spin direction is of the second order. This theory might have some possibility to explain the experimental data by Sparks et al.

J. B. Goodenough: I would like to call attention to the fact that I have submitted a paper to the Phoenix Magnetism Conference, to be held in the USA this November, in which I have interpreted the phenomena reported for FeS along similar lines. I would like to call attention to the fact that complete ordering of the "extra" d electron on Fe^{2+} into the basal plane below T_α permits the cation-anion-cation and cation-cation exchange interactions to add, rather than subtract as above T_α, so that $\chi_\perp \propto 1/n$ (where n is the exchange parameter for total coupling between antiferromagnetic sublattices) decreases abruptly on cooling through T_α. Further, the formation of three-cation clusters in the basal planes below T_α indicates the formation of molecular cation-cation orbitals within these clusters which are three-halves filled. They are therefore compatible with ferromagnetic coupling and a total spin contribution to the atomic moment that remains constant through the bond-forming transition. However, the orbital angular momentum associated with a triangular ring may indeed be large, to give rise to the change in g factor that is observed below T_α.