ACTA CHEMICA SCANDINAVICA 14 (1960) 919–926

Magnetic Phase Transitions in Stoichiometric FeS Studied by Means of Neutron Diffraction *

ARNE F. ANDRESEN

Institutt for Atomenergi, Kjeller, Norway

Stoichiometric FeS has been examined by means of neutron diffraction in order to study the phase transitions and the orientation of the magnetic moments in the two antiferromagnetic phases. The magnetic moments are found to point along the c-axis below T_α and perpendicular to the c-axis above T_α. The superstructure derived by Bertaut for the low temperature antiferromagnetic phase has been confirmed only with a larger displacement of the Fe atoms.

According to susceptibility measurements by Haraldsen [1] two phase transitions are taking place in stoichiometric FeS. The α-transition occurring at $T_\alpha \approx 140°C$ is a transition between two antiferromagnetic phases, while the β-transition at $T_N = 325°C$ is a transition between an antiferromagnetic and a paramagnetic phase. Despite continuous efforts the nature of the first transition is not yet fully understood. However, several significant contributions have been made.

X-Ray investigations by Hägg and Sucksdorff [2] revealed slight structural changes at the transition. Above T_α the structure is of the regular NiAs-type with a hexagonal unit cell of dimensions $a_o = 3.44$ Å and $c_o = 5.88$ Å. Below this temperature weak superstructure reflections appear indicating a larger unit cell. Bertaut [3] succeeded in deriving an atomic arrangement to account for this superstructure. However, the small atomic displacements derived by him can not explain the large anomaly in the specific heat, 550 cal/mole, observed by Hirone *et al.*[4]

Recently electrical and magnetic measurements on single crystals of FeS by Kamigaichi *et al.*[5] and Hirahara *et al.*[6] showed a marked anisotropy in the electrical and magnetic properties with abrupt changes at the transition temperature. They interpret their results as indicating a change in the spin direction at the transition. Below T_α the spin is assumed to be parallel to and above T_α perpendicular to the c-axis. In the last case their data are consistent

* Sponsored jointly by *Reactor Centrum Nederland* and *Institutt for Atomenergi*.

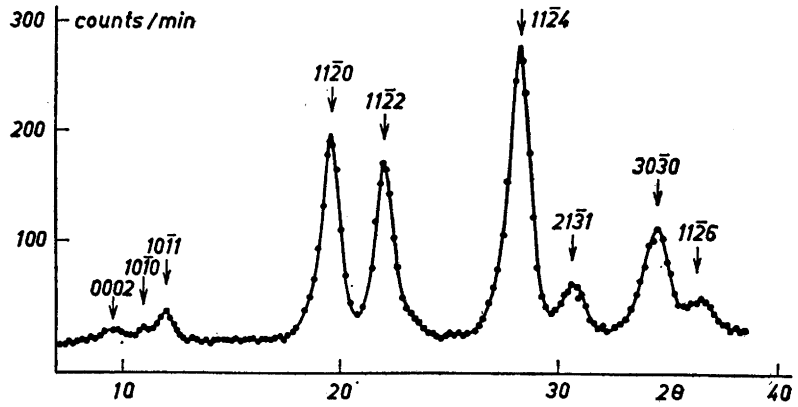

Fig. 1. Room temperature neutron diffraction diagram of $FeS_{1.0}$, instrumental background subtracted (λ = 1.03 Å).

with a model in which the moments take up two or more fixed directions in the *c*-plane.

By neutron diffraction it is possible to determine directly the orientation of the magnetic moments on the individual lattice sites. This was utilized by Sidhu [7] in determining the direction of the magnetic moments in pyrrhotite (FeS_{1+x}). He found here the magnetic moments to be perpendicular to the *c*-axis. Being unaware of the work of Kamigaichi *et al.* and Hirahara *et al.*, but anticipating some change in the spin system at the α-transition of the stoichiometric compound, we undertook a neutron powder diffraction investigation of $FeS_{1.0}$.

Low Temperature Antiferromagnetic Phase

A room temperature diffraction diagram of FeS obtained with the automatic diffractometer at the Kjeller reactor JEEP is shown in Fig. 1. The peaks observed can be well accounted for on the basis of the hexagonal super cell derived by Hägg and Sucksdorff [2]. The axes of this cell are related to those of the small NiAs-type cell mentioned above by $a = a_0\sqrt{3} = 5.97$ Å and $c = 2c_0 = 11.74$ Å.

In Fig. 2 is given the *c*-axis projection of this unit cell, the dotted lines indicating a NiAs-type cell. To account for the observed superstructure Bertaut [3] has suggested small displacements of the atoms from the NiAs positions. The directions of the displacements of the Fe atoms are indicated by the small arrows in the figure. The Fe atoms are displaced only in the *x* and *y* directions while the sulphur atoms are displaced along the *c*-axis. One can visualize the Fe atoms forming triangles of which some are contracted and some dilated. The sulphur atoms situated above or below the center of these triangles are displaced away from contracted triangles and in towards dilated triangles. The atomic positions are given in Table 1.

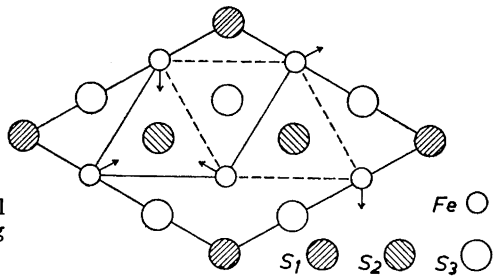

Fig. 2. c-Axis projection of the super cell derived by Bertaut; dotted lines indicating the NiAs-type unit.

From this model nuclear intensities were calculated using the coherent nuclear scattering amplitudes $b_{Fe} = 0.96 \times 10^{-12}$ cm and $b_S = 0.31 \times 10^{-12}$ cm taken from the compilation by Shull and Wollan [8]. By normalizing the observed intensities to the calculated ones for the outer reflections where the magnetic contribution is negligible due to the form factor fall-off, the amount of the inner reflections due to magnetic scattering could be estimated.

The only strong magnetic contribution was found for the reflection $(11\bar{2}2)$ corresponding to the $(10\bar{1}1)$ reflection from the NiAs-type cell (Table 2). This is compatible with an antiferromagnetic alignment of the magnetic moments in which the moments are parallel within each (0001) plane and antiparallel in neighbouring planes, provided the moments point along the c-axis.

Table 1. Atomic positions. Space group: $D_{3h}^4 - P\,\bar{6}2c$.

2 S_1 in	2 *a*:	(0,0,0); (0,0,1/2)
4 S_2 in	4 *f*:	$\pm$ (1/3, 2/3, *z*); $\pm$ (1/3, 2/3, 1/2−*z*); with $z = 0.016$
6 S_3 in	6 *h*:	(*x*, *y*, 1/4); ($\bar{y}$, *x*−*y*, 1/4); (*y*−*x*, $\bar{x}$, *z*); (*y*, *x*, 3/4); ($\bar{x}$, *y*−*x*, 3/4); (*x*−*y*, $\bar{y}$, 3/4); with $x = 2/3$; $y = 0$
12 Fe in	12 *i*:	(*x*, *y*, *z*); ($\bar{y}$, *x*−*y*, *z*); (*y*−*x*, $\bar{x}$, *z*); (*x*, *y*, 1/2−*z*); ($\bar{y}$, *x*−*y*, 1/2−*z*); (*y*−*x*, $\bar{x}$, 1/2−*z*); (*y*, *x*, 1/2+*z*); ($\bar{x}$, *y*−*x*, 1/2+*z*); (*x*−*y*, $\bar{y}$, 1/2+*z*); (*y*, *x*, $\bar{z}$); ($\bar{x}$, *y*−*x*, $\bar{z}$); (*x*−*y*, $\bar{y}$, $\bar{z}$); with $x = 1/3 + \varepsilon$; $y = \varepsilon$; $z = 1/8$; Betaut's value: $\varepsilon = 0.035$ Author's value: $\varepsilon = 0.050 \pm 0.005$

The magnetic intensities were calculated from the expression

$$I_{magn} = v\ Lp^2\ |F|^2\ B_S^2\ q^2 \qquad (1)$$

where v is the multiplicity of the reflection (not necessarily equal to the multiplicity of the corresponding nuclear reflection). L is the Lorentz factor.

$$p = \frac{e^2 \gamma}{m c^2} S f \qquad (2)$$

Table 2.

hkil NiAs-type	*hkil* super cell	Calculated intensities I_{nucl} $\times 10^{-2}$	I_{magn} $\times 10^{-2}$	I_{tot} $\times 10^{-2}$		Obs. intensities I_{obs} norm.	Δ
	0001	0	0	0			
0001	0002	0	0	0		3.74	
	$10\bar{1}0$	3.84	0	3.84		2.57	1.27
	$10\bar{1}1$	8.06	5.94	14.0		9.34	4.66
	0003	0	0	0			
	$10\bar{1}2$	0	1.57	1.57			
	$10\bar{1}3$	2.43	0.81	3.24			
$10\bar{1}0$	$11\bar{2}0$	71.40	0	71.40	94.44	96.02	1.58
0002	0004	19.80	0	19.80			
	$11\bar{2}1$	0	0	0			
$10\bar{1}1$	$11\bar{2}2$	15.87	57.77	73.64			
	$20\bar{2}0$	1.84	0	1.84			
	$10\bar{1}4$	1.99	0	1.99	85.50	85.97	0.47
	$20\bar{2}1$	5.98	2.05	8.03			
	$11\bar{2}3$	0	0	0			
	$20\bar{2}2$	0	0.91	0.91			
	0005	0	0	0			
	$20\bar{2}3$	5.18	0.79	5.97			
	$10\bar{1}5$	3.57	0.09	3.66	149.52	149.06	0.46
$10\bar{1}2$	$11\bar{2}4$	139.89	0	139.89			
0003	0006	0.06	0	0.06			
	$21\bar{3}0$	6.68	0	6.68			
	$20\bar{2}4$	1.90	0	1.90	32.67	32.24	0.43
	$21\bar{3}1$	19.94	4.09	24.03			
	$21\bar{3}2$	0	2.04	2.04			
	$11\bar{2}5$	0	0	0			
	$10\bar{1}6$	0	0.03	0.03			
	$21\bar{3}3$	16.98	1.99	18.97	65.79	68.69	2.90
	$20\bar{2}5$	1.32	0.17	1.49			
$11\bar{2}0$	$30\bar{3}0$	45.30	0	45.30			
	$30\bar{3}1$	0	0	0			
	0007	0	0	0			
$11\bar{2}1$	$30\bar{3}2$	0	0	0			
$10\bar{1}3$	$11\bar{2}6$	5.16	2.22	7.38			
	$21\bar{3}4$	8.99	0	8.99	18.90	20.79	1.89
	$10\bar{1}7$	2.52	0.01	2.53			

where γ is the neutron magnetic moment, $S = 2$ the spin of the iron atoms and f the magnetic form factor. As this we have used the values from the curve for Mn^{2+} derived by Corliss *et al.*[9] F is the geometric structure factor, B_S the Brillouin function for spin S, and $q = \sin a$ where a is the angle between the scattering vector and the direction of the magnetic moment. A Debye-Waller temperature factor with $B = 0.7$ Å^2 was applied. This value was obtained assuming a Debye temperature of approximately $\Theta \approx 344$°K derived from the specific heat measurements of Grønvold *et al.*[10]

Using the parameters given by Bertaut the calculated intensities of the superstructure reflections came out much too low indicating larger displacements. The best fit was obtained with a displacement of the iron atoms of

magnitude $\varepsilon = 0.050 \pm 0.005$ compared to Bertaut's value $\varepsilon = 0.035$. As for the sulphur atoms, their contribution was too small to decide anything about their displacements.

The calculated intensities are given in Table 2 together with the normalized observed values. The fit is seen to be very good leading to a percentage mean error in the integrated peaks of 2.9 %. The (0001) reflection has been omitted. It is calculated zero, but a small peak still exists. This is possibly due to slight impurities or incomplete transition from the high temperature phase. The size of the peak varied from sample to sample and also completely vanished.

High Temperature Investigation

For high temperature runs the sample was placed in an evacuated quartz tube surrounded by a heating coil. A thermocouple protruding from the bottom of the cylinder had its junction near the center just below the irradiated part. A diagram obtained at 177°C, well above the α-transition, is shown in Fig. 3, instrumental background subtracted. Here no superstructure peak is visible and all the reflections can be indexed on the small NiAs-type cell previously described.

The most striking difference from the room temperature diagram is the appearance of a strong (0001) reflection. This must be of magnetic origin since the nuclear reflection is extinguished. However, with an antiferromagnetic alignment of the moments along the c-axis, a magnetic contribution may still occur. At room temperature it was negligible due to the q factor which is zero when the moments point along the scattering vector. Since the reflection now appears, the magnetic moments must have turned away from the c-direction. According to formula (1) the intensity of this reflection varies as $\sin^2\alpha$ with the angle α which the moments make with the c-direction.

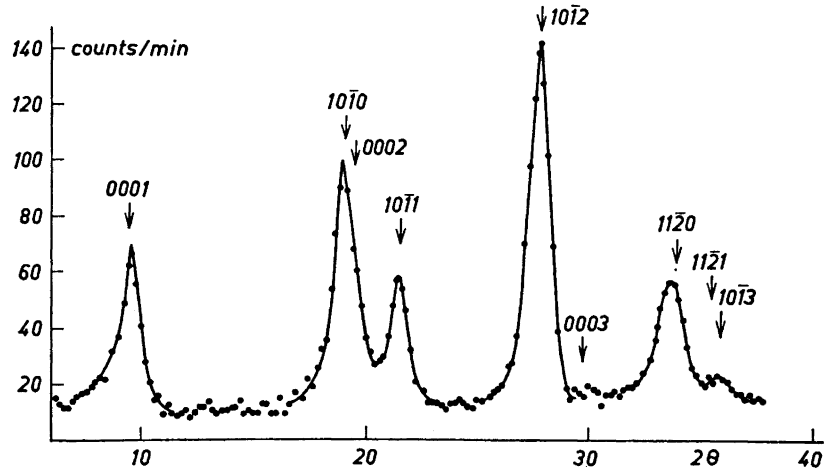

Fig. 3. Neutron diffraction diagram of $FeS_{1.0}$ at 177°C, instrumental background subtracted ($\lambda = 1.03$ Å).

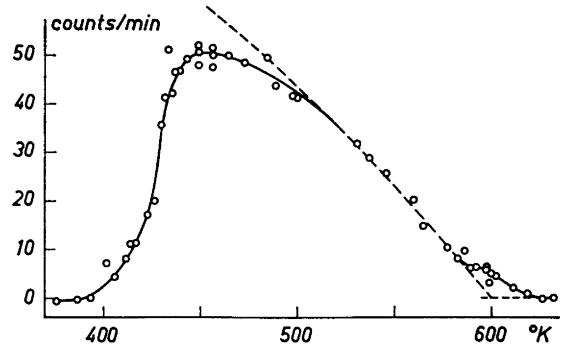

Fig. 4. Peak height of the (0001) reflection as a function of temperature. Dotted line derived from Brillouin function with $S = 2$.

As the (0001) reflection is also completely magnetic, it lends itself remarkably well to a study of the magnetic phase transitions. We have therefore recorded the intensity of this reflection as a function of temperature from room temperature up to 632°K. A close examination of the peaks did not reveal any change in their width with temperature which could be detected with our experimental conditions. We therefore take the peak value as representative of the intensity and this is plotted in Fig. 4 as a function of temperature.

We see that the α-transition starts already at 390°K (117°C) and a maximum is reached at 450°K (177°C). From here on the intensity starts to fall due to the temperature motion of the atoms and reaches zero at 627°K (354°C). Assuming a Néel temperature of $T_N = 600$°K (327°C) the larger part of the slope can be fitted to the Brillouin function with $S = 2$ (dotted line in the figure). The heel on the curve can be ascribed to the critical magnetic scattering which peaks at the Néel point as demonstrated by McReynolds and Riste [11]. Here some broadening of the peaks is expected, but this was not detected due to the low intensity compared to the background scattering.

High Temperature Antiferromagnetic Phase

The diagram shown in Fig. 3 was obtained at the temperature (450°K) corresponding to the maximum of the transition curve (Fig. 4). Still the magnetic intensity has clearly not reached its full value, but is reduced because of the broadness of the α-transition and its close proximity to the Néel point. Extrapolating back from the Brillouin curve, the magnetic intensities at 450°K were found to be reduced by the factor 0.41.

Utilizing this factor and assuming the antiferromagnetically aligned moments to point perpendicular to the c-axis, we find the calculated intensities given in Table 3. A Debye-Waller temperature factor with $B = 1.0$ Å^2 deduced from the Debye temperature $\Theta \approx 344$°K has been applied. The fit to the normalized observed values is seen to be good leading to a percentage

mean error in the integrated peaks of 8 %. The direction of the moments within the c plane can as pointed out by Shirane [12] not be determined from neutron powder diffraction data alone.

Table 3.

	$FeS_{1.0}$ Calculated intensities			Obs. intensities	
hkil	I_{nucl}	I_{magn}	I_{tot}	I_{obs} norm.	Δ
0001	0	198.0	198.0	197.9	0.1
$10\bar{1}0$	251.0				
0002	52.6		303.6	339.0	35.4
$10\bar{1}1$	44.0	74.0	118.0	137.6	19.6
$10\bar{1}2$	451.4		451.4	418.0	33.4
0003	0	5.3	5.3	—	
$11\bar{2}0$	192.8		192.8	180.0	12.8
$11\bar{2}1$	0	6.8			
$10\bar{1}3$	15.4	10.2	32.4	28.9	3.5

DISCUSSION

The results of this investigation is largely in agreement with those derived by other methods. At the α-transition the direction of the magnetic moments change from pointing along the c-axis to pointing perpendicular to it. In the low temperature phase the superstructure is well explained by the arrangement proposed by Bertaut if the displacements of the iron atoms are made somewhat larger. While the β-transition at 327°C is rather well defined and corresponds well with the temperature given by Haraldsen, 325°C, the α-transition is rather broad and varies somewhat from sample to sample both with respect to sharpness and position. This might be due to slight variations in the composition and differences in preparation.

It is interesting to note the close similarity between FeS and α-Fe_2O_3. In the last case there is a transition between two antiferromagnetic states at approximately −20°C, and also here the magnetic moments are found to point along the trigonal axis below the transition and perpendicular to it above the transition (Shull *et al.*[13]). The iron atoms are in both cases surrounded by nearly regular octahedra of sulphur and oxygen atoms, respectively. No attempt will be made here to correlate the slight structural changes observed with the change in the orientation of the magnetic moments.*

Acknowledgements. The author would like to acknowledge the kind cooperation of F. Grønvold and P. Thurmann Moe of the University of Oslo in supplying the samples and much valuable information. He is also indebted to J. A. Goedkoop and T. Riste for illuminating discussions.

* After this investigation was completed the author has become aware of a more extensive investigation of the FeS_{1+x} system by neutron diffraction being carried out at Lawrence Radiatoin Laboratory, University of California, by J. T. Sparks, W. Mead, A. J. Kirschbaum and W. Marshall.

REFERENCES

1. Haraldsen, H. *Z. anorg. allgem. Chem.* **231** (1937) 78.
2. Hägg, G. and Sucksdorff, I. *Z. physik. Chem.* **B 22** (1933) 444.
3. Bertaut, E. F. *J. Bull. Soc. franc. Minér. Crist.* **79** (1956) 276.
4. Hirone, T. Maida, S. and Tsuya, N. *J. Phys. Soc. Japan* **9** (1954) 503.
5. Kamigaichi, T., Hihara, T., Tazaki, M. and Hirahara, E. *J. Phys. Soc. Japan* **11** (1956) 606.
6. Hirahara, E. and Murakami, M. *J. Phys. Chem. Solids* **7** (1958) 281.
7. Sidhu, S. S. Pittsburgh, Diffraction Conference (1954).
8. Shull, C. G. and Wollan, E. O. *Solid State Physics* **2** (1956) 137.
9. Corliss, L. M., Elliott, N. and Hastings, J. M. *Phys. Rev.* **104** (1956) 924.
10. Grønvold, F., Westrum, E. F., Jr. and Chien Chou. *J. Chem. Phys.* **30** (1959) 528.
11. McReynolds, A. W. and Riste, T. *J. phys. radium* **20** (1959) 175.
12. Shirane, G. *Acta Cryst.* **12** (1958) 282.
13. Shull, C. G., Strauser, W. A. and Wollan, E. O. *Phys. Rev.* **83** (1951) 333.

Received December 23, 1959.