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Phase Transitions in Fe_xS (x = 0.90 — 1.00) Studied by Neutron Diffraction

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Annealing at 300°C of samples in the composition region Fe_xS ($x = 0.90-1.00$) brings about a sharpening of the magnetic and crystallographic transitions showing them to be separated and strongly composition dependent. On deviation from stoichiometry two magnetic spin-flip transitions appear separated by a composition dependent temperature interval. This is attributed to the presence of two phases, the β_1- and the β_2-phase appearing below 330°C.

The α-transition at 140°C [1] in stoichiometric FeS is a transition from an NiAs-type structure at high temperature to a closely related superstructure.[2] In the same temperature range there is a spin flip transition in which the moments turn by 90° from lying in the basal plane above the transition to point along the *c*-axis below.[3] The magnetic structure is antiferromagnetic with the moments oriented parallel within each basal plane layer and antiparallel between neighbouring layers (antiferromagnetic ordering of first kind).[4,5] In a previous neutron diffraction study by one of us [5] a rather broad transition was observed between 117°C and 177°C and it was not possible to separate the crystallographic and magnetic transitions.

Sparks *et al.*[6] found, however, the two transitions to be separated, the spin flip transition occurring at a higher temperature, T_s, than the crystallographic transition, T_α. Both transitions, and in particular the magnetic, were found to be strongly composition dependent. For a sample of composition $Fe_{0.996}S$ the crystallographic transition occurred at 142°C, whereas the turning of the moments started at 185°C and ceased at 160°C. Using as evidence for the rotation the intensity change of the (0001) reflection they found that the moments had not turned completely by 90° at this temperature, but had stopped in an intermediate position 20° off the *c*-axis. On further cooling below 142°C the moments would resume their gradual rotation towards the *c*-axis.

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Another possible explanation for this observation would be to assume the presence of two phases with different transition temperatures. In their studies on the phase relations of synthetic and natural pyrrhotites Grønvold and Haraldsen [7] actually found that a β_1-phase exhibiting superstructure did only exist at stoichiometric composition. With decreasing iron content a two phase region between the β_1- and β_2-phase appeared. The β_2-phase with an NiAs-type structure had a homogeneity range between $Fe_{0.935}S$ and $Fe_{0.900}S$.

In our earlier work we had noticed the rather pronounced effect of both preparation procedure and composition on the sharpness and position of these transitions. To study this more closely we have now carried out neutron diffraction measurements on a series of well annealed samples in the composition range $Fe_{1.000}S$ to $Fe_{0.900}S$. In the course of these investigations it has been possible to throw further light also on the nature of the γ-transition [1] occurring in these compounds between 150° and 210°C.

PREPARATION AND EXPERIMENTAL TECHNIQUE

The samples were prepared from distilled sulphur (Merck AG, purified for isotope production) and iron wire 99.999 % pure (Johnson, Matthey & Co.) by heating accurately weighed quantities in evacuated quartz tubes. The tubes were heated slowly to 600°C to prevent reaction with the quartz, kept at this temperature for 3 days and then heated further to 980°C for one day. After cooling slowly to room temperature the samples were ground and annealed for various lengths of time at 300°C. To check whether any significant amount of sulphur had been lost during preparation the composition of a few of the samples was checked by chemical analysis. It was found that the final compound did not deviate by more than $x = \pm 0.002$ from the weighed in composition.

The crystallographic transition in FeS was studied by measuring the appearance and disappearance of the strongest super-lattice reflection $(21\bar{3}1)$ of the low temperature modification, while the magnetic transitions were studied by measuring the temperature dependence of the (0001) reflection of the NiAs-type structure. For a regular NiAs-type structure without ordered vacancies this is a purely magnetic reflection, and its intensity depends upon the factor $q^2 = \sin^2\alpha$, where α is the angle between the magnetic moment and the scattering vector. Therefore, if the moments point along the hexagonal axis, this reflection is zero, but when they lie in the basal plane it has a maximum.

For the high temperature runs the samples were sealed in thin-walled quartz tubes with a thermocouple inserted in the center. The tubes were placed in a furnace with aluminium walls. Care was taken to reduce as much as possible the temperature gradient over the sample. Using two heating coils, one fed through a transistor-operated temperature regulator,[8] the total temperature differences over the sample during a measurement could be kept within $\pm$ 2°.

Below room temperature a liquid nitrogen cryostat was used. This was supplied with a heating coil between the sample and the nitrogen reservoir. A resistance wire in thermal contact with the sample holder near to the heating coil served for temperature control. A thermocouple was inserted in the other end of the holder. No particular measurements were in this case carried out to determine the temperature gradients over the sample, but from the sharpness of some of the transitions measured we assume the temperature variation to be within the limits quoted above.

Neutrons of wavelength 1.147 Å were obtained from the JEEP I reactor.

EFFECTS OF ANNEALING

The effects of annealing at 300°C on the magnetic and crystallographic transition are shown in Fig. 1 for a sample of composition $Fe_{0.996}S$. To the left is given the temperature dependence of the $(21\bar{3}1)$ nuclear super-reflection

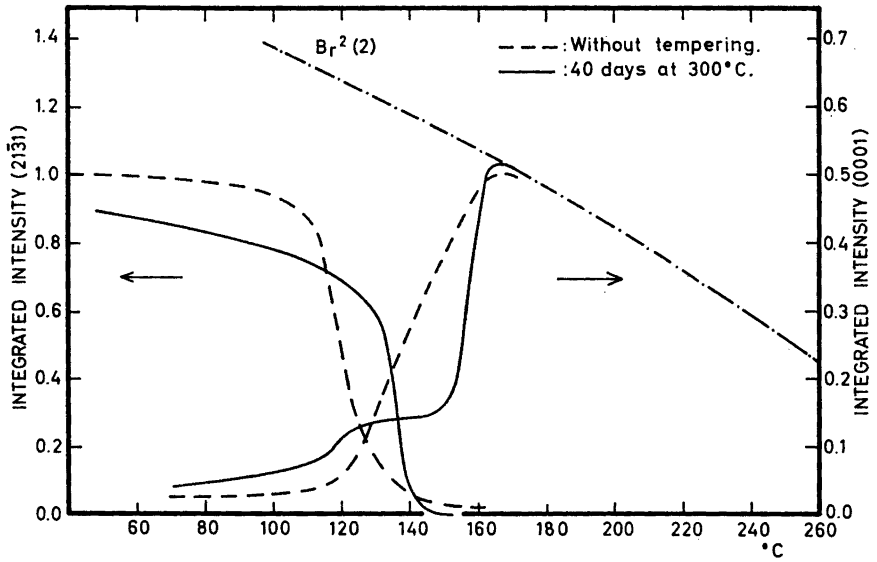

Fig. 1. The effect of annealing on a sample of composition $Fe_{0.996}S$. The curves to the left show the integrated intensity of the (21$\bar{3}$1) superreflection, the curves to the right the integrated intensity of the (0001) reflection.

appearing below the crystallographic transition point and to the right the intensity of the magnetic (0001) reflection. For clarity the experimental points are omitted. The dashed curves were obtained before annealing and the fully drawn curves after annealing for 40 days at 300°C. The dash-dot curve represents the calculated values of the square of the Brillouin function for $S = 2$ which is fitted to the experimental points above 180°C and normalized to unity at absolute zero.

As seen from Fig. 1 annealing brings about a pronounced sharpening of both transitions. At the same time both transitions move towards their higher limits. In the magnetic transition a knee develops. With increasing annealing time an ever increasing sharpening of the transitions could be obtained, and their widths could apparently be brought below our experimental uncertainty. For some samples annealing at 300°C had little or no effect. In these cases a reheating to 900°C followed by further annealing at 300°C brought improvement. This shows that a certain degree of homogeneity will have to be obtained at high temperature before low temperature annealing has any effect.

THE MAGNETIC TRANSITIONS

In Fig. 1 both the crystallographic and magnetic transition occur at slightly lower temperatures than observed by Sparks *et al.*[6] for this composition, but the magnetic transition shows the same knee as observed by them. To find out whether this knee should be ascribed to a gradual turning of the moments,

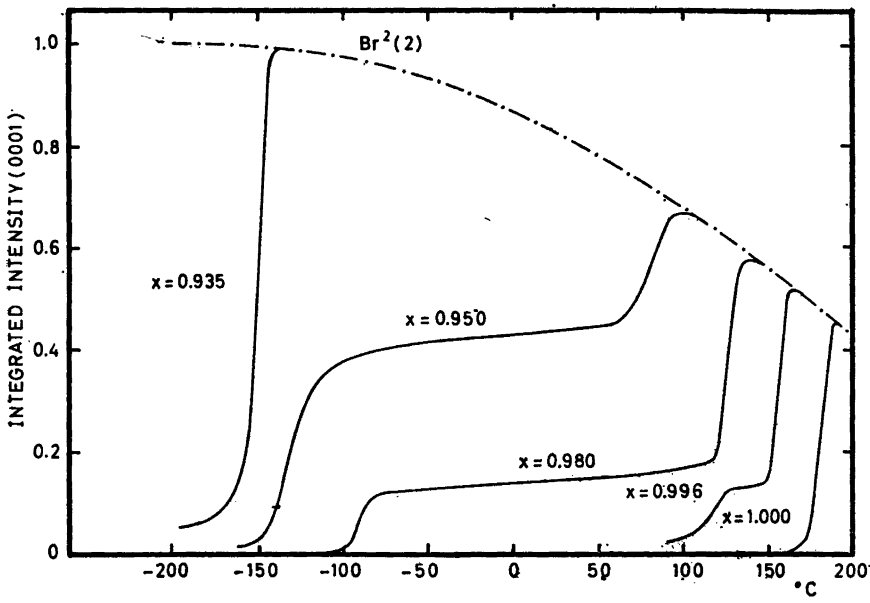

Fig. 2. The integrated intensity of the (0001) reflection as a function of temperature for compositions between $Fe_{0.935}S$ and $Fe_{1.000}S$.

or whether it can be attributed to the presence of two phases, the temperature dependence of the (0001) reflection was measured for a series of well annealed samples in the composition range $Fe_{1.000}S$ to $Fe_{0.935}S$. The results are shown in Fig. 2. All curves have been fitted to the square of the Brillouin function at high temperature by normalizing to 1.0 at saturation.

In the stoichiometric compound there is only one sharp transition at 185°C. With only a small reduction in iron content the transition moves rapidly to lower temperatures and a knee develops. Thus the position of this transition is very strongly dependent on composition, and to check if 185°C is really its upper limit, we also prepared a sample with an excess of iron. This excess remained unreacted and the transition corresponded with that of the stoichiometric compound.

With a further decrease in iron content two transitions separated by a rather large temperature interval appears. With decreasing iron content both transitions move to lower temperatures until at $F_{0.935}S$ only the lower transition remains. This is according to Grønvold and Haraldsen [7] the composition limit of the β_2-phase. It is then reasonable to assume that the splitting of the magnetic transition in the intervening region is due to the presence of the two phases, the β_1- and the β_2-phase. The upper transition should then be interpreted as a transition in the β_1-phase and the lower transition in the β_2-phase. Due to the low resolution in the neutron diagrams the (0001) reflection of the two phases could not be separated. However, with X-rays the presence of the two phases was confirmed.

In the phase diagram of Grønvold and Haraldsen [7] a two-phase region is only indicated below the α-transition. In our case, however, a separation in two phases has evidently taken place already at 300°C. We therefore assume the two phase region to extend all the way up to the β-transition at 330°C. The reason why this was not observed with X-rays must be attributed to a close similarity between the unit cells which makes the separation visible only below T_α where the β_1-phase develops its superstructure. Weak additional lines were, however, also observed by Grønvold [7] above the α-transition.

The fact that the transition temperature in the β_1-phase decreases from its value in $Fe_{1.000}S$ and that the transition temperature in the β_2-phase increases beyond that of $Fe_{0.935}S$ shows that these are not the composition limits of the two phases at 300°C. However, the deviation from these limits may be small as the transition temperatures seem to be strongly dependent upon composition in particular for the β_1-phase. Possible reasons for this will be discussed in the last chapter.

The knee observed in the magnetic transition on slight deviations from stoichiometry ($Fe_{0.996}S$) can, however, hardly be ascribed to the presence of a small amount of β_2-phase. The transition temperature is too far removed from that of the β_2-phase and the amount of this phase would be too small to give measurable intensities. The knee is most likely due to a lack of equilibrium in the sample. During annealing the vacancies will start migrating out of the β_1-phase leading to a difference in vacancy concentration in the inner and outer part of the grains. The outer part with the larger vacancy concentration will then have a lower transition temperature than the inner part.

THE γ-TRANSITION

In his early work Haraldsen [1] discovered another transition, the γ-transition, which appeared as a kink in the susceptibility curve at 150°C for $Fe_{0.94}S$ and developed into a strong susceptibility maximum at 210°C for $Fe_{0.90}S$. This has been attributed to an ordering of the vacancies in one sublattice leading to ferrimagnetism.[9] However, at lower temperatures the compound turned antiferromagnetic again suggesting a disordering of the vacancies upon further cooling.

This was explained by Lotgering [10] as resulting from a competition between the spin ordering and vacancy ordering. Since the spin ordering is a second order transition and the vacancy ordering is a first order transition, Lotgering argued that it was possible for the free energy of a magnetically ordered vacancy-disordered phase to be less than that of the magnetically ordered vacancy-ordered phase at some temperature below the Curie point. For the whole composition range spin ordering occurs at about 330°C. Considering a compound of composition $Fe_{0.900}S$ Lotgering assumed that at 300°C where the vacancies order the spins disorder. At 265°C where the spins again order ferrimagnetism appears. Finally at 210°C, the socalled Haraldsen or anti Curie point, disordering of the vacancies again leads to antiferromagnetism.

In order to check these assumptions we have measured the temperature dependence of the (0001) reflection also for $Fe_{0.900}S$. The result is shown in

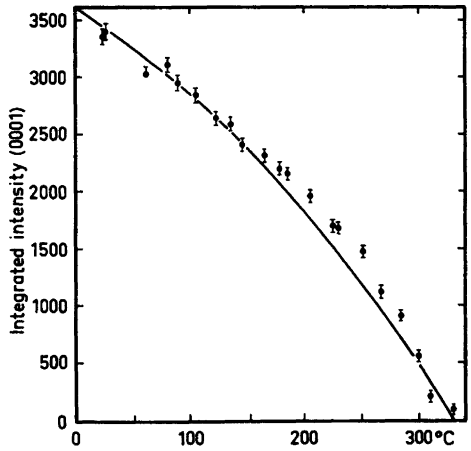

Fig. 3. The integrated intensity of the (0001) reflection of $Fe_{0.900}S$ showing deviation from Brillouin type dependence.

Fig. 3. It is seen that the intensity of this mainly magnetic reflection decreases regularly with temperature up to the Néel point at 330°C. There is thus no disordering of the spins taking place below this temperature. This is also in agreement with the results of Hihara [11] who measured a nearly constant susceptibility along the *c*-axis below the Néel point.

However, the observed intensities do show a deviation from normal Brillouin type dependence. In Fig. 3 the fully drawn curve represents the square of the Brillouin function for $S = 2$ fitted to the observed points at low temperatures and to a Néel point of 330°C. Between 180° and 300°C all the experimental points lie above this curve. This can be attributed to an added nuclear contribution due to the ordering of the vacancies on every second metal layer. The added intensity is of the correct order of magnitude for this. The upper limit of this region corresponds with the ordering temperature given by Lotgering, but the lower limit falls below his anti Curie point. Lotgering assumes a disordering of the vacancies below this point. However, what our data and the disappearance of ferrimagnetism show is that there is an even distribution of the vacancies over all metal layers. This could also be achieved by another type of ordering as suggested by Hirone and Maeda.[12]

DISCUSSION

Both the crystallographic transition and the change in spin direction have been found to be strongly dependent on composition. This must be connected with changes in the interatomic distances and with the amount of vacancies present. The direction of the spins depends through the magnetic anisotropy energy mainly on two effects, the dipole-dipole interaction and the spin-orbit coupling. Calculations on these effects for the NiAs-type structure have been carried out by Adachi.[13] He finds for an antiferromagnetic ordering of

first kind that the dipole-dipole interaction always tends to keep the spins in the c-plane when the axial ratio $c/a = 1.2—1.8$. For the spin-orbit coupling, however, he finds a critical value, $(c/a)_0$, below which the spins tend to lie in the c-plane and above which they should align themselves parallel to the c-axis. The critical value ranges from 1.67 to 1.73 depending on the shape of the $3d$-wave function.

In the β_1-phase the axial ratio changes from 1.66 to 1.71 on cooling from 190°C to 20°C.[7] This change is mainly due to an abrupt increase in the c-axis on passing through the α-transition. Well above the transition we may therefore assume the axial ratio to be below the critical value and both the spin-orbit coupling and the dipole-dipole interaction will keep the spins in the c-plane. However, as the temperature is lowered the axial ratio will increase and may pass the critical value. Then the spin-orbit coupling will tend to align the spins along the c-axis, and as the importance of the dipole-dipole interaction is expected to decrease with increasing c-axis, the spin-orbit coupling will finally dominate. In the same way it is now possible to explain the decrease in the spin-flip temperature with iron content. According to Grønvold and Haraldsen [7] a deficiency in iron content leads to a decrease in the axial ratio. This means that a further cooling is required in order to reach the critical value.

The α-transition is also accompanied by a change in the charge distribution, which is reflected in an abrupt decrease in the c-axis conductivity.[11] The Fe^{2+}-ion has 6 electrons in the $3d$-shell. Assuming the validity of Hund's rule 5 of these will each occupy one of the available orbitals, the three t_{2g} and the two e_g orbitals. In the octahedral environment of the NiAs-type structure the 6th extra electron is expected to occupy one of the lowest lying t_{2g} orbitals. Above T_α the trigonal field component of the ligand field will probably favour the t_{2g} orbital pointing along the c-axis. With these orbitals fully occupied the direct exchange interaction along the c-axis is according to Goodenough [14] ferromagnetic and will counteract the antiferromagnetic superexchange interaction through the intervening S^{2-}-ions. However, below T_α the extra electron charge will be transferred to the basal plane, and with half-filled orbitals along the c-axis also the direct exchange interaction will be antiferromagnetic. The presence of the extra electron charge in the basal plane will increase the orbital moment and thereby the spin-orbit coupling.

A characteristic difference between the β_1 and the β_2 phase is the appearance of a superstructure in the β_1-phase. This is connected with the formation of triangular clusters of iron atoms in the basal plane.[15] Within these clusters the distance between the iron atoms is 3.00 Å whereas it is 3.73 Å between the clusters. According to Goodenough [14] this short distance is compatible with the formation of collective electron orbitals within the clusters. The presence of such orbitals will increase the orbital moment below T_α and thereby strengthen the spin-orbit coupling. This effect will help to explain the large difference in the spin-flip temperature between the β_1 and the β_2-phase.

The cluster formation can also contribute to the understanding of the strong composition dependence of the spin-flip temperature. The formation of triangular clusters is a cooperative effect and removal of a few of the iron atoms will certainly have a pronounced effect on the ability of the lattice for cluster formation.

In several investigations, notably on magnetic susceptibility, a different behaviour has been observed on cooling and heating. In our measurements on well-annealed samples we have observed no such effect.

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