The Magnetic Structure of Fe_3Se_4

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In order to resolve a discrepancy between the results of two previous neutron diffraction investigations of the magnetic structure of Fe_3Se_4, a new investigation has been performed on the basis of high resolution powder diagrams. The moments have been found to point along the b-axis.

Iron selenide with composition Fe_3Se_4 crystallizes in a pseudo NiAs type structure with ordered vacancies. Its space group is monoclinic, with $a \approx a_H \sqrt{3}$, $b \approx a_H$, and $c \approx 2c_H$, a_H and c_H being the edges the NiAs sub-cell.

In a previous investigation one of the authors[1] found that the magnetic ordering leads to no enlargement of the unit cell. The ferrimagnetic structure consists of ferromagnetic layers perpendicular to the c-axis, neighbouring layers being oppositely aligned. The observed ferrimagnetic moment[2] is due to the ordering of the vacancies on every second metal layer. It was stated that the available data did not allow an unambiguous determination of the spin direction. However, it was assumed that the spins were lying in the c-plane and a best fit seemed to be obtained with the spins pointing along the face diagonal.

In some later measurements Lambert-Andron and Berodias[3] were able to separate the (101) and (10$\bar{1}$) peaks using long-wavelength neutrons, $\lambda = 2.026$ Å. They arrived at the same spin structure as described above, but the spin axis was concluded to be perpendicular to the (101) plane. This conclusion was based on the fact that no magnetic contribution to the (101) reflection was observed. However, because this reflection has a rather small magnetic structure factor, it will be weak irrespective of the moment orientation. This means that a determination of the spin direction based on this observation is unreliable.

As it was expected that a high resolution powder diagram could resolve the discrepancy between the above mentioned results a new investigation has been undertaken.

EXPERIMENTAL

The investigation was carried out on the same material as was used in Ref.[1]

Neutron diffraction diagrams were obtained at 372°K and 4.2°K on the powder diffractometer at the H.F.R. in Petten, using a wavelength of (2.582 ± 0.001) Å. To remove higher order wavelength neutrons a pyrolytic graphite filter was employed.

Two Soller slits with angular divergences of 15' were placed between reactor and monochromator and in front of the BF_3 counter. The sample was contained in a cylindrical sample holder of vanadium, 20 mm in diameter.

RESULTS

Both at 372°K and 4.2°K least-squares parameters were fitted to the neutron data by means of the profile refinement programme described by Rietveld,[4] which makes it possible to utilize all the available information in the diagram. Fig. 1 shows the fit obtained between observed and calculated powder patterns. Final parameters are given in Tables 1 and 2.
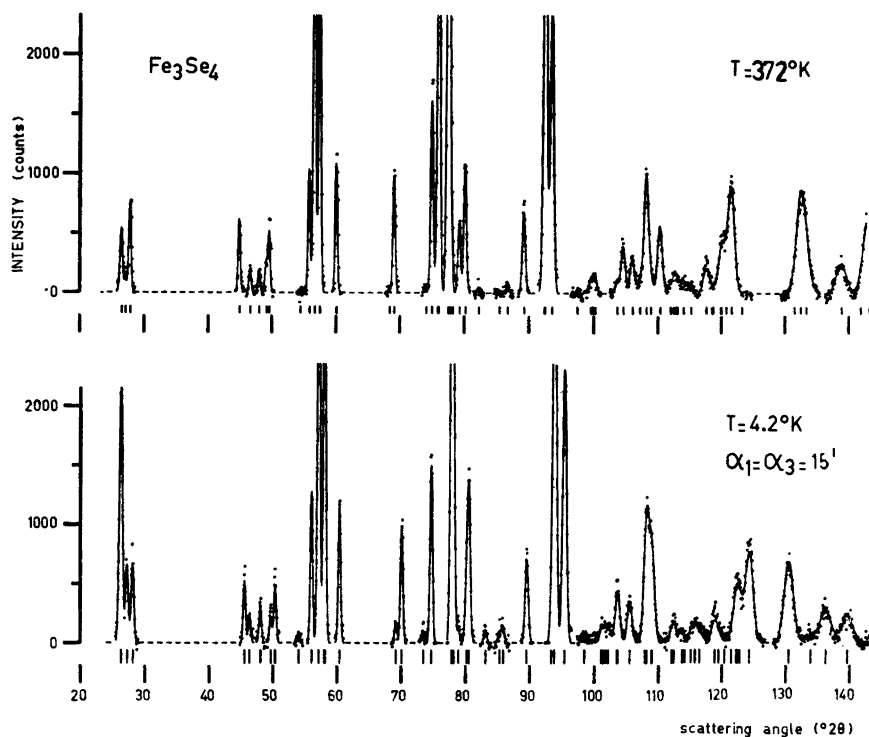

Fig. 1. Observed and calculated neutron powder diffraction patterns at 372°K and 4.2°K. Dots: observed data, corrected for background. Full curve: calculated pattern.

Table 1. Cell dimensions of Fe$_3$Se$_4$.

	372°K	293°K	4.2°K
a	(6.208 ± 0.002) Å	(6.187 ± 0.002) Å	(6.159 ± 0.003) Å
b	(3.541 ± 0.001)	(3.525 ± 0.001)	(3.493 ± 0.001)
c	(11.281 ± 0.003)	(11.290 ± 0.005)	(11.385 ± 0.003)
β	$(91.807 \pm 0.004)°$	$(91.98 \pm 0.02)°$	$(92.202 \pm 0.003)°$

Table 2. Atomic positions and moment values in Fe$_3$Se$_4$. Space group $I\ 2/m - C_{2h}^3$.

$(0,0,0; \frac{1}{2},\frac{1}{2},\frac{1}{2})+$

	372°K	4.2°K
2F$_I$ in (2c) : 0,0,$\frac{1}{2}$		
4Fe$_{II}$ in (4i): $\pm(x,0,z)$	$x = 0.0431 \pm 0.0006$	0.0455 ± 0.0006
	$z = 0.2429 \pm 0.0004$	0.2402 ± 0.0004
4Se$_I$ in (4i) : $\pm(x,0,z)$	$x = 0.3370 \pm 0.0009$	0.3358 ± 0.0008
	$z = 0.8623 \pm 0.0004$	0.8616 ± 0.0005
4Se$_{II}$ in (4i) : $\pm(x,0,z)$	$x = 0.3366 \pm 0.0008$	0.3371 ± 0.0008
	$z = 0.3889 \pm 0.0004$	0.3890 ± 0.0005
μ_{Fe_I}		$(2.89 \pm 0.12)\ \mu_B$
$\mu_{Fe_{II}}$		$(2.27 \pm 0.08)\ \mu_B$
$\mu_{average}$		$(2.48 \pm 0.09)\ \mu_B$

In the refinement the following scattering lengths were employed $b_{Fe} = 0.96 \times 10^{-12}$ cm and $b_{Se} = 0.86 \times 10^{-12}$ cm. The last value is that determined by Andresen[1] from his previous data on this compound. In view of the large discrepancy in the earlier published values for this scattering length another refinement was also made in which b_{Se} was varied in addition to the structural parameters. Using the data obtained at 372°K a value of $b_{Se} = (0.82 \pm 0.01) \times 10^{-12}$ cm was deduced. The other parameters were not significantly affected. In both cases the final values for the temperature factors were between 0.5 and 1 Å^2. As form factor, the one calculated by Watson and Freeman[8] for Fe^{2+} was, arbitrarily, chosen.

The neutron diagram at 4.2°K confirmed the conclusion from the former investigations[1,3] that the periodicities of the magnetic and nuclear structures are the same. The magnetic contributions indicated a magnetic ordering of the type previously given. To determine which moment orientation would give the best fit, refinements were carried out for four different spin orientations, namely along $\vec{a}$, $\vec{b}$, $\vec{a} + \vec{b}$ and normal to the (101) planes. The obtained fit in each case for the first three reflections is shown in Fig. 2. The best fit is clearly obtained with the moments pointing along the b-axis. This orientation was used in the calculations leading to the moment values in Table 2, and gave an excellent fit for the whole diagram as shown in Fig. 1.
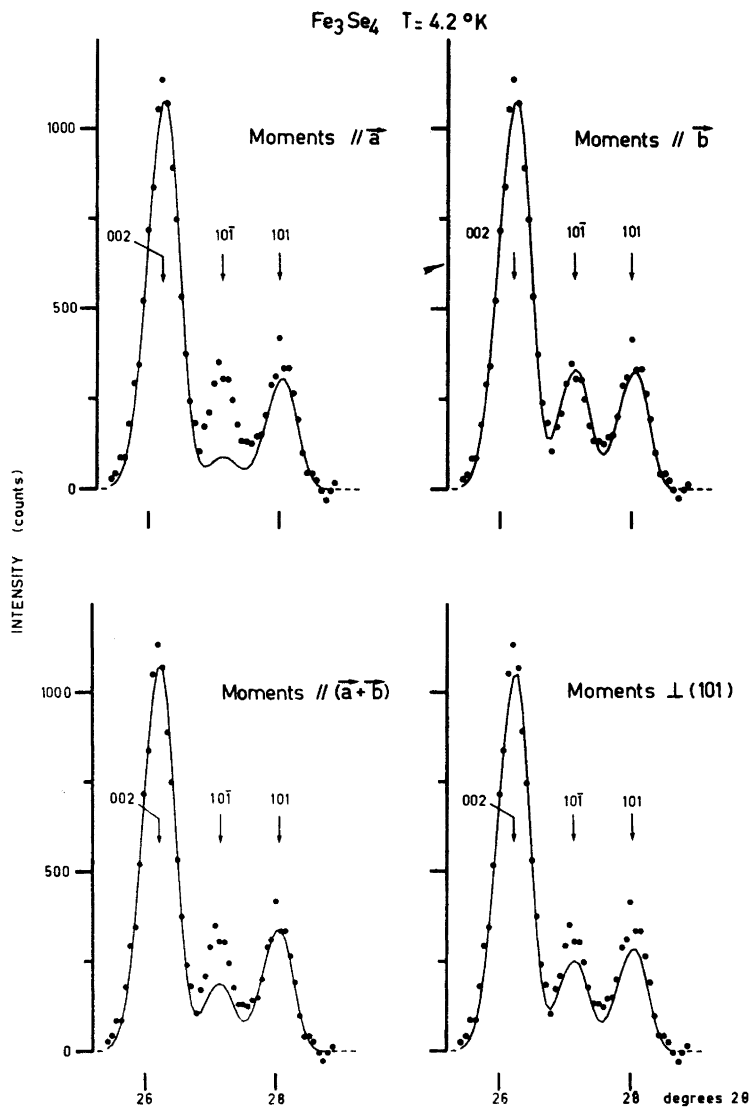
Fig. 2. First three peaks of observed neutron powder diffraction diagram at 4.2°K (dots) and pattern calculated on the basis of four models for the spin arrangement as indicated (full curve).

DISCUSSION

As the results presented in Fig. 1 are hardly influenced by the choice of the form factor the conclusion that the spin axis is along the *b*-axis seems to be well founded.

Thus the assumption made by Andresen[1] that the spins point perpendicular to the c-axis is substantiated. However, neither the spin direction proposed by him, along $(\vec{a}+\vec{b})$, nor the direction proposed by Lambert-Andron et al.[3] perpendicular to the (101) plane, leads to a satisfactory agreement.

The atomic positions derived are rather close to those in the previous papers. The largest discrepancies are found in the x-parameters of the Se-atoms which are now close to the values they would have in the undistorted NiAs-type structure. The displacements in the c-direction are much larger.

Also the values for the magnetic moments deduced from our results are not much influenced by the choice of the form factor, as the peaks with the most important magnetic contribution, (002) and $(10\bar{1})$ appear at a $\sin\theta/\lambda$ values as low as 0.09. Our moment values are not too far from those derived by Lambert-Andron et al., who found 3.25 μ_B and 1.94 μ_B for Fe_I and Fe_{II}, respectively. They are, however, considerably reduced from the values expected for the Fe^{2+} and Fe^{3+} ions and also from the values observed in Fe_7Se_8 [5] which are 4.50 μ_B and 3.60 μ_B. This is most likely due to the delocalization of the $3d$-electrons which is connected with the short metal to metal distance along the c-axis. This distance decreases from 2.94 Å to 2.79 Å in going from Fe_7Se_8 to Fe_3Se_4. One should then also expect an increase in the electrical conductivity. Recent conductivity measurements by Serre et al.[6] have shown, however, that both compounds show metallic conductivity and that the resistivity at room temperature and above is larger for Fe_3Se_4 than for Fe_7Se_9. The decisive factor here is probably the presence of vacancies. In the ordered Fe_7Se_8 "4c" structure the metal-metal chains along the c-axis are interrupted at every 8th metal layer whereas in Fe_3Se_4 the same occurs at every 4th layer.

With the moment values deduced the overall moment per atom is:

$$\mu_{tot} = 0.333 \, (\mu_{Fe_I} - 2 \, \mu_{Fe_{II}}) = (-0.55 \pm 0.04) \, \mu_B$$

This is somewhat larger than the experimental values, 0.23 μ_B as given by Adachi[7] and 0.30 μ_B as measured by Lambert-Andron et al.[3]

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