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A Neutron Diffraction Investigation of Fe_3Se_4

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Fe_3Se_4 is isostructural with the compounds Cr_3X_4 (X = S, Se, Te). However, in contrast to these compounds the magnetic unit cell is found to be of the same size as the chemical unit cell. The magnetic structure is collinear with the moments in each *c*-plane ferromagnetically aligned and the moments in neighbouring planes antiferromagnetically aligned. The moment direction is in the *c*-plane and probably along the face diagonal. Spin values of 1.08 for the ions in the vacancy layers and 0.71 for the ions in the fully occupied layers are deduced.

Iron selenides with an excess of selenium in the composition range 53.1 to 57.5 at.% Se crystallize below 350°C with structures derivable from a simple NiAs type unit cell.[1,2] The deviation from stoichiometry is connected with the formation of iron vacancies and ordering of these leads to the formation of superstructures. Okazaki and Hirakawa [3] found two types of superstructure in this composition region, one connected with the composition Fe_7Se_8 and another with Fe_3Se_4. The first one has previously been studied extensively by neutron diffraction [4,5] and this paper is concerned with a neutron investigation of the latter.

With X-rays Okazaki and Hirakawa [3] derived for Fe_3Se_4 a monoclinic unit cell (Fig. 1) of dimensions A = 6.167 Å, B = 3.537 Å, C = 11.17 Å and $\beta = 92.0°$. This can be related to a small NiAs-type cell with cell edges a_H and c_H putting $A = \sqrt{3}a_H$, $B = a_H$ and $C = 2c_H$. Like in Fe_7Se_8 the vacancies order on every second metal layer and in accordance with the requirement that the vacancies should be distributed as far apart as possible,[6] a bodycentered arrangement is formed.

In Fe_7Se_8 the magnetic structure was found to be ferrimagnetic [4] with the moments in each *c*-plane ferromagnetically aligned and the moments in neighbouring planes antiferromagnetically aligned. With the vacancies ordered on every second metal layer an excess of atoms with the moments in one direction will occur.

Using an ionic picture each vacancy introduced leads to the formation of 2 Fe^{3+} ions. If these are concentrated in the vacancy layers a moment of 0.29 μ_B per metal ion is expected [7] in good agreement with the observed moment

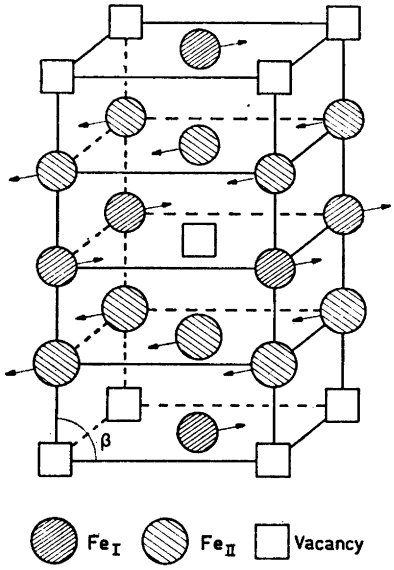

Fig. 1. The unit cell of Fe_3Se_4 showing the orientation of the magnetic moments.

value of 0.20 μ_B.[2] For Fe_3Se_4 similar assumptions would predict a moment value of 1.33 μ_B per atom whereas the observed value is only 0.23 μ_B.[8] Putting also Fe^{2+} ions in the vacancy layers only leads to higher moments.

For the isostructural compounds Cr_3X_4 (X = S, Se, Te) Bertaut *et al.*[9] deduced rather complicated magnetic structures requiring an enlargement of the unit cell in two directions. The main objects of the present investigation was to see whether a similar structure was also present in Fe_3Se_4 and to find possible reasons for the low observed moment.

EXPERIMENTAL

The samples were prepared from hydrogen reduced iron filings obtained from 99.999 % pure iron rods (Johnson, Matthey & Co.) and selenium shots spectrographically standardized (Johnson, Matthey & Co.). Accurately weighed quantities were sealed in double walled evacuated silica tubes fired at 1050°C for 4 h and then kept at 800°C for 3 days. After cooling to room temperature the samples were crushed, again sealed in evacuated tubes and homogenized at 350°C for one week.

X-Ray powder photographs could be indexed on the monoclinic unit cell of Okazaki and Hirakawa (Fig. 1) and showed no extra lines. Only reflections with $h + k + l = 2n$ were observed confirming the bodycentered arrangement. The presence of an (002) reflection indicated ordering of the vacancies on every second metal layer.

In order to resolve as well as possible the composite neutron peaks caused by the monoclinic symmetry, high resolution neutron diffraction diagrams were required. These were obtained through the courtesy of Dr. B. O. Loopstra at the H.F.R. reactor in Petten, The Netherlands, using neutrons of wavelength $\lambda = 1.253$ Å. Two diagrams were run, respectively, at 81°K and 371°K on either side of the Curie point ~313°K.[2] These were obtained under identical conditions using a liquid nitrogen cryostat. For the

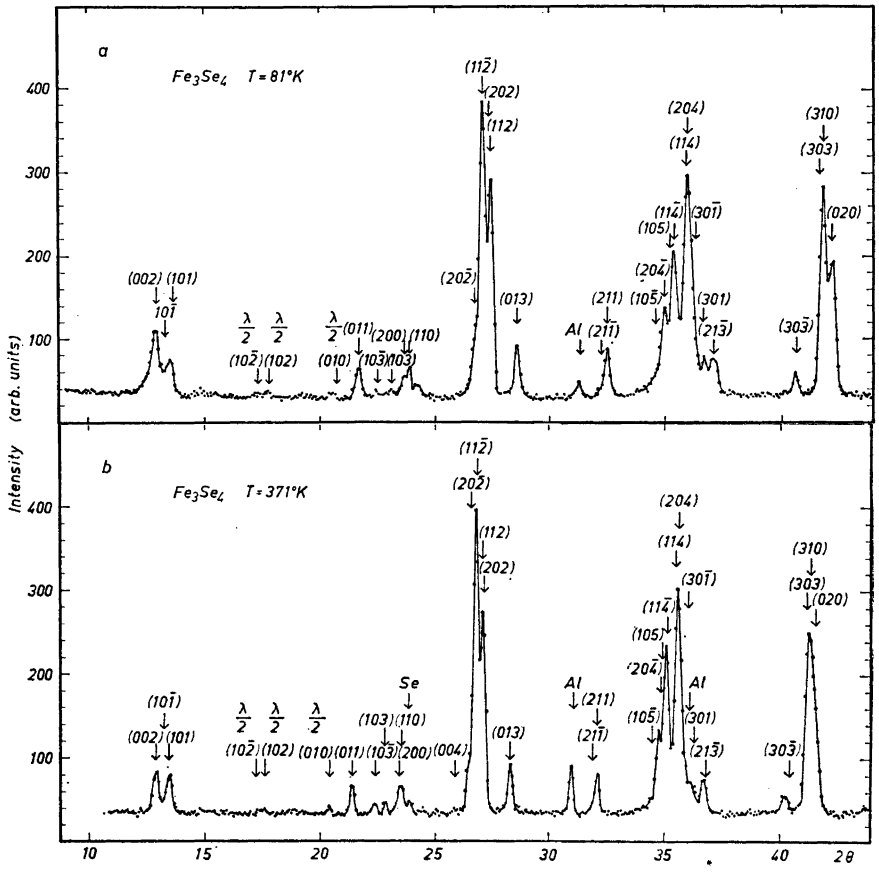

Fig. 2. Neutron diffraction diagram of Fe_3Se_4 at a) 81°K and b) 371°K. $\lambda = 1.253$ Å.

low temperature run the cryostat was filled with liquid nitrogen, and for the high temperature run with water brought to its boiling point by immersing an electrical heater.

A diagram run later at 4.2°K but with lower resolution was similar to that at 81°K and showed no added peaks.

NEUTRON DIFFRACTION

The two neutron diffraction diagrams obtained respectively at 81°K and 371°K are shown in Figs. 2a and b. The diagrams look very similar except for small intensity changes and slight shifts in the peak positions. Except for a few very weak peaks, which can be ascribed to the $\lambda/2$ contamination of the monochromatized beam, and two impurity peaks due, respectively, to some unreacted selenium and the aluminium of the cryostat, all peaks can be indexed on the unit cell of Okazaki and Hirakawa. Basing ourselves on only

well resolved reflections and assigning weight factors of 1 to 10 to the peak positions, the lattice parameters at the two temperatures could be calculated using a least squares refinement. The result is given in Table 1. The errors

Table 1.

	Temp.	a	b	c	β
Okazaki and Hirakawa	room temp.	6.16,	3.53,	11.1,	92.0
This work	371°K	6.172 ± 0.008	3.534 ± 0.002	11.195 ± 0.012	91.51 ± 0.14
—»—	81°K	6.113 ± 0.006	3.486 ± 0.002	11.139 ± 0.006	91.66 ± 0.08

quoted are two times the calculated standard deviations. Also included are the lattice parameters at room temperature determined by Okazaki and Hirakawa.

The diagrams look very similar to those obtained by Bertaut *et al.*[9] for Cr_3X_4 (X = S, Se, Te) in particular for Cr_3Te_4. However, in our case the magnetic ordering requires no enlargement of the unit cell. All the extra peaks observed are present both above and below the Curie point. The weak peaks appearing at the positions of the $(10\bar{2})$, (102) and (010) reflections can be accounted for as $\lambda/2$ reflections corresponding to the composite peaks at $2\theta \sim 35°$ and 41°. The observed intensities are about 1.5 % of the intensities of these peaks which is of the expected order of magnitude for the $\lambda/2$ contamination at this wavelength at H.F.R.[11] Also the shape of corresponding peaks is very similar. Indeed at 371°K, where the splitting of the peak at 41° disappears, a pronounced sharpening also of the corresponding $\lambda/2$ peak is observed. The $\lambda/2$ peak corresponding to the strongest observed peak at $2\theta \sim 27°$ is overlapped by the (101) peak. In a diagram obtained using neutrons of the shorter wavelength 1.09 Å these small peaks were not observed. Another weak peak appearing at the edge of the (110) reflection can not be ascribed to the $\lambda/2$ contamination. This falls, however, at the position of the strongest Se-peak, and can be attributed to the presence of a small amount of unreacted selenium.

The observed intensities at 371°K were used to calculate atomic positions using the ORFLS least squares programme of W. R. Busing, K. O. Martin and H. A. Levy. As preliminary calculations had shown the parameters of Bertaut *et al.*[9] for Ce_3Se_4 to give a reasonably good fit, these parameters (see Table 2) were used as starting parameters. The refinement was based on 14

Table 2. Atomic positions. Spacegroup $I2/m-C_{2h}^3$. $(0,0,0;\frac{1}{2},\frac{1}{2},\frac{1}{2})+$

	Fe_3Se_4	Cr_3Se_4
2 Fe_I or 2 Cr_I in *c*:	$0,0,\frac{1}{2}$	$0,0,\frac{1}{2}$
4 Fe_{II} or 4 Cr_{II} in *i*: $\pm(x,0,z)$	$x = 0.035 \pm 0.005$	$x = 0.028$
	$z = 0.243 \pm 0.003$	$z = 0.240 \pm 0.003$
4 Se_I in *i*: $\pm(x,0,z)$	$x = 0.329 \pm 0.006$	$x = 0.336 \pm 0.01$
	$z = 0.861 \pm 0.004$	$z = 0.866 \pm 0.003$
4 Se_{II} in *i*: $\pm(x,0,z)$	$x = 0.341 \pm 0.005$	$x = 0.329 \pm 0.01$
	$z = 0.386 \pm 0.003$	$z = 0.379 \pm 0.003$

resolved reflections putting unobserved reflections at half the lowest observable value. Since the anions form an approximately closepacked hexagonal lattice the largest displacements could be expected in the x and z parameters of the Fe_{II} ions, and the first refinement concerned these parameters and the scale factor. Later all six position parameters were included. The result is given in Table 2.

In the temperature factor was used $B_{Fe} = 2.03$ Å^2 and $B_{Se} = 1.44$ Å^2 calculated from the same Debye temperature 194°K as used for Fe_7Se_8.[4] A Debye temperature of 250°K calculated from specific heat data[12] was found to give too low values.

As scattering amplitudes were first employed $b_{Fe} = 0.96 \times 10^{-12}$ cm and $b_{Se} = 0.89 \times 10^{-12}$ cm in accordance with the *International Tables*.[13] Lately the last value has been disputed and Colominas[14] derived from her data on $CuCr_2Se_4$ a value of $b_{Se} = (0.779 \pm 0.014) \times 10^{-12}$ cm. Using this value, however, the parameters were still found to lie within the errors quoted in

Table 3. Observed and calculated intensities for Fe_3Se_4.

	371°K				81°K				
hkl	I_{nucl}		I_{obs}	$\lvert\Delta\rvert$	I_{nucl}	I_{magn}	I_{tot}	I_{obs}	$\lvert\Delta\rvert$
002	0.84		0.92	0.08	0.85	1.19	2.04	2.01	0.03
10$\bar{1}$	0.18	0.75	0.82	0.07	0.18	0.16	0.98	0.87	0.11
101	0.57				0.59	0.05			
011	0.63		0.54	0.09	0.65	0.11	0.76	0.64	0.12
10$\bar{3}$	0.21		0.22	0.01	0.22	0.01	0.23	0.16	0.07
103	0.27		0.17	0.10	0.28	0.05	0.33	0.23	0.10
200	0.23	0.72	0.73	0.01	0.25	0	0.78	0.86	0.08
110	0.49				0.53	0			
004	0.04		—		0.04	0	0.04	—	
20$\bar{2}$	0.98				1.02	0.06			
11$\bar{2}$	4.86	9.56	9.58	0.02	5.13	0.24	10.68	10.88	0.20
202	2.34				2.47	0.07			
112	1.38				1.44	0.25			
013	0.95		0.98	0.03	1.02	0.04	1.06	0.97	0.09
21$\bar{1}$	0		—		0	0.05	0.05	—	
211	0.76		0.75	0.01	0.84	0.01	0.85	0.93	0.08
10$\bar{5}$	0		—		0	0.03	0.03	—	
20$\bar{4}$	1.51				1.68	0			
105	0.54				0.60	0.01			
11$\bar{4}$	3.88				4.31	0			
114	3.49	11.79	11.99	0.20	3.90	0	13.16	13.15	0.01
204	1.81				2.02	0			
30$\bar{1}$	0.01				0.01	0.01			
301	0.55				0.62	0			
21$\bar{3}$	0.79		0.76	0.03	0.89	0	0.89	0.84	0.05
213	0.08		—		0.09	0.03	0.12	—	
015	0.04		—		0.04	0.03	0.07	—	
006	0.03		—		0.04	0.05	0.09	—	
30$\bar{3}$	0.46		0.46	0	0.53	0	0.53	0.51	0.02
303	0.05				0.05	0.01			
310	4.56	7.20	7.06	0.14	5.23	0	8.27	8.15	0.12
020	2.59				2.98	0			
			$R = 2.3$ %					$R = 2.7$ %	

Table 2. Now keeping the position parameters fixed and refining only the selenium scattering amplitude and the scale factor the value $b_{Se} = 0.86 \times 10^{-12}$ cm was obtained. This value was used in calculating the full list of intensities given in Table 3. The agreement with the observed intensities is seen to be good also for the composite peaks which were not used in the refinement. Defining a discrepancy factor

$$R = \sum|I_{obs}-I_{calc}|/\sum I_{obs}$$

and including only observable reflections we obtain $R = 2.3$ %.

THE MAGNETIC STRUCTURE

The magnetic contribution to the intensity for a collinear spin arrangement with only one type of atoms can be calculated from the following expression:

$$I_n = 0.291\ \nu f^2 q^2 |F_M|^2 e^{-2w} B^2 L \quad (1)$$

Here ν is the multiplicity, f the magnetic form factor, F_M the magnetic structure factor, e^{-2w} the Debye Waller factor, B the Brillouin function, and L the Lorentz factor. q^2 is given by

$$q^2 = 1-\langle\cos^2\eta\rangle \quad (2)$$

where for $\langle\cos^2\eta\rangle$ we have used the expression valid for orthorhombic symmetry [15]

$$\langle\cos^2\eta\rangle = (h^2a^{*2}\cos^2\varphi_a + k^2b^{*2}\cos^2\varphi_b + l^2c^{*2}\cos^2\varphi_c)d^2 \quad (3)$$

neglecting the small monoclinic deformation. Here a^*, b^* and c^* are the reciprocal lattice vectors and φ_a, φ_b, and φ_c the angles between the spin direction and the a, b, and c axes, respectively. d is the interplanar distance.

The magnetic structure factor can be calculated from

$$F_M = \sum_j \pm S_j \exp\ 2\pi i\ (hx_j + ky_j + lz_j) \quad (4)$$

where S_j is the absolute spin value of the ion at position (x_j,y_j,z_j). From Table 2 and Fig. 1 it appears that there are two kinds of iron ions, the 2 Fe_I ions situated in the vacancy layers and the 4 Fe_{II} ions filling the fully occupied layers. Since these have different surroundings it is reasonable to assume different spin values. Let us call the spin of the Fe_I ions S_I and the spin of the Fe_{II} ions S_{II}. Assuming a collinear spin arrangement similar to that in Fe_7Se_8,[4] and disregarding the small displacements of the Fe_{II} ions, the magnetic structure factor falls into three different groups:

a) $F_M = S_I + 2S_{II}$ when $h + k = 2n$, $l = 4n + 2$
b) $F_M = S_I - 2S_{II}$ when $h + k = 2n$, $l = 4n$
c) $F_M = -S_I$ when $h + k = 2n + 1$, $l = 2n + 1$

The only peaks for which a significant added contribution at 81°K is observed are the (002) peak and the composite peak consisting of the reflections $(20\bar{2})$, $(11\bar{2})$, (202) and (112). All these reflections belong to group a)

above. On the other hand reflections like (200), (110) and (004) belonging to group b) show no extra contributions. This confirms the above model and calls for a low value of $S_I - 2\ S_{II}$. Also the overall moment which depends on this expression is found to be low, 0.23 μ_B per atom.[8] If we assume a spin only moment this observed value can be used to give us one relation between S_I and S_{II} provided the sign $S_I - 2\ S_{II}$ is known. This can be determined by observing that no reflections with $h + k = 2n + 1$ and $l = 2n + 1$ have significant magnetic contributions. According to case c) above this means that S_I must be small, and considering the other diffraction data certainly smaller than 2 S_{II}. We thus obtain:

$$S_I - 2\ S_{II} = -0.34 \tag{5}$$

Another relation is provided by the absolute value of the magnetic contribution to the (002) reflection. The observed intensities can be brought on an absolute scale by normalizing the purely nuclear reflections. Since (002) seems to be the strongest magnetic reflection we assume $q^2 = 1$ for this reflection implying a moment alignment perpendicular to the c-axis. Now, taking into account also the other factors of expression (1) and the displacements of the Fe_{II} ions, which are all known, we arrive at the relation:

$$S_I + 1.99\ S_{II} = 2.48 \tag{6}$$

Solving (5) and (6) the following effective spin values at 81°K can be deduced: $S_I = 1.08$, $S_{II} = 0.71$.

It is not easy on the basis of the observed data to say in which direction within the c-plane the spins may point. However, the best fit seems to be obtained with the spins pointing along the face diagonal. This has been assumed in calculating the magnetic intensities given in Table 3. As magnetic form factor was used the form factor for Fe^{3+} derived by Nathans *et al.*[16] and for temperature factor $B_{Fe} = 1.0$ and $B_{Se} = 0.7$. The agreement with the normalized observed intensities is seen to be good leading to $R = 2.7$ %.

DISCUSSION

The chemical unit cell of Fe_3Se_4 is very similar to that of Cr_3X_4 (X = S, Se, Te) but unlike in these compounds the magnetic ordering leads to no enlargement of the unit cell. The magnetic ordering is similar to that in Fe_7Se_8 with the moments ferromagnetically aligned within each c-plane and antiferromagnetically aligned in neighbouring planes. The moment direction is in the c-plane and probably along the face diagonal.

The observed magnetic intensities in combination with the small resultant moment require low spin values, $S_I = 1.08$ for the ions in the vacancy layers and $S_{II} = 0.71$ for the ions in the fully occupied layers. These values are considerably reduced from the spin values found in Fe_7Se_8,[4] which are 2.25 and 1.8. The structural changes in going from Fe_7Se_8 to Fe_3Se_4 are rather small. Aside from a slight monoclinic deformation the main difference is in the number of vacancies and their distribution within the vacancy layers.

Of most significance for the spin value is probably the large contraction of the lattice in particular along the *c*-axis. The Fe—Fe distance in this direction decreases from 2.94 Å to 2.79 Å. According to Goodenough [17] one may then expect at least for Fe_3Se_4 a delocalization of some of the *d*-electrons. This should show up as an increase in the electrical conductivity. However, reliable conductivity measurements have to our knowledge not yet been carried out on these compounds.

If we employ an ionic picture, one formula unit of Fe_3Se_4 can be written $Fe^{2+}Fe_2^{3+}LSe_4^{2-}$ where L denotes a vacancy. As the positions of the Fe_I ions are 2-fold whereas the positions of the Fe_{II} ions are 4-fold it seems reasonable to assume the ferrous ions to occupy the Fe_I positions and the ferric ions the Fe_{II} positions. That the divalent ions in similar compounds actually occupy the vacancy layers has been shown by measurements on $FeCr_2Se_4$ [18] and $NiCr_2S_4$.[19] In analogy one may assume this to hold also for Fe_7Se_8. Previous arguments for putting the ferric ions in these layers [2,7] was based on the observed low overall moment which required the highest moment on the ions in the vacancy layers. Assuming a spin only moment this is 5 μ_B for the Fe^{3+} ions with 5 *d*-electrons but only 4 μ_B for the Fe^{2+} ions with 6 *d*-electrons due to pairing. However, as electrons are lost either due to delocalization of *d*-electrons or the covalency effect [20] the moment of the previous Fe^{2+} ion may finally exceed that of the previous Fe^{3+} ion.

The observed moment values in Fe_7Se_8 can thus be explained from a covalency effect of about 25 % for both kind of ions. In Fe_3Se_4 the further reduction of the moments can probably be ascribed to an increased covalency effect due to the contraction of the lattice but also to a delocalization of some of the *d*-electrons brought about by the short metal to metal distance along the *c*-axis. The possibility of a low spin state for the ions can be ruled out. With all the *d*-electrons present this would lead to a moment value of 1 μ_B for the Fe^{3+} ions and no moment on the Fe^{2+} ions. As electrons are lost the moments would increase, but the moments on the ions in the Fe_{II} positions would most likely remain larger than the moments in the Fe_I positions in contrast to the experimental result.

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