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A Neutron Diffraction Study of Magnetic Ordering in Iron Telluride

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The alignment of magnetic spins in iron telluride $Fe_{1.11}Te$ below and above a lambda transition point occurring at 63°K has been investigated by neutron diffraction. $Fe_{1.11}Te$ is ferrimagnetic at liquid helium temperature with magnetic spins pointing in a direction perpendicular to the crystallographic unique axis. At room temperature $Fe_{1.11}Te$ is ferromagnetic with spins aligned along this axis. The magnetic moment derived from neutron measurements is 1.8 Bohr magnetons at 4°K. The 0.22 additional iron atoms per unit cell are distributed at random in the octahedral holes of the tellurium lattice.

The beta phase in the iron-tellurium system exhibits certain physical properties which it seemed of interest to examine by neutron diffraction:

1. At 63°K a peak on the specific heat *vs.* temperature curve was found by Westrum *et al.*[1] indicating a lambda type transition. A corresponding peak on the magnetic susceptibility *vs.* temperature curve was discovered at the same temperature by Tsubokawa and Chiba.[2] It would be of interest to examine the nature of this transition, whether it is connected with the change of magnetic ordering or a structural order-disorder process.

2. Naya *et al.*[3] found the Curie point at 479°K. The determination of the magnetic spin alignment below this temperature is of interest in connection with the transition at 63°K.

3. At 533°K an anomaly on the electrical conductivity curve was observed by Naya *et al.*[3]

Beta iron telluride is stable within the homogeneity range $Fe_{1.18}Te$ and $Fe_{1.05}Te$. The crystal structure of $Fe_{1.11}Te$ was determined by Grønvold, Haraldsen and Vihovde[4] to be of the PbO type (B10 according to the *Strukturbericht* notation). The space group is D_{4h}^7 — $P4/nmm$. The atomic positions are:

2 Fe at 2(*a*): 3/4, 1/4, 0; 1/4, 3/4, 0.
2 Te at 2(*c*): 1/4, 1/4, z_{Te}: 3/4, 3/4, $\bar{z}_{Te}$; with $z_{Te} = 0.285$.

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The density measurements as carried out by Grønvold *et al.*[4] supported the idea that the excessive iron atoms are accommodated interstitially in a random way leading to the formula Fe_9Te_8. Consequently the excessive iron atoms were placed at the (*c*)-sites with $z_{Fe} = 0.70$. The magnetic moment of this compound was determined by Tsubokawa and Chiba [2] to be 2.44 Bohr magnetons at room temperature.

X-RAY MEASUREMENTS

A sample of composition $Fe_{1.11}Te$ was obtained in the following way: iron and tellurium filings of spectroscopic purity were weighed in required proportion and sealed in an evacuated silica tube and heated to 500°C for one week. After cooling and grinding in an agate mortar a pellet was prepared in a hydraulic press. The pellet was homogenized for one week at 400°C. An X-ray powder diagram taken with a Philips diffractometer revealed only one phase present, that of iron telluride with the unit cell dimensions reported earlier by Grønvold *et al.*[4] No indication of a superstructure or of a foreign phase was found. The intensities of the X-ray peaks appearing up to $2\Theta = 60°$ were measured and the free parameters of tellurium and excess iron atoms were checked by trial and error. The integrated intensities were obtained by measuring the areas under the peaks. For the following parameters:

$$z_{Te} = 0.285 \pm 0.002 \text{ and } z_{Fe} = 0.692 \pm 0.002$$

the discrepancy factor defined as

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

was found to have a minimum, $R = 0.12$.

A list of observed and calculated intensities (Cu$K\alpha$ radiation) is shown in Table 1. The lattice constants for the composition $Fe_{1.11}Te$ were determined from a film taken in a standard Ø 114 mm camera with a Straumanis film

Table 1. Observed and calculated X-ray intensities for iron telluride.

h k l	jF^2_{obs}		jF^2_{calc}
0 0 1	14		12.55
1 0 1	503		539.76
0 0 2	50		34.54
1 1 0	97		98.80
1 1 1	235		259.92
1 0 2	75		83.12
0 0 3	181		147.22
1 1 2	795		922.08
2 0 0	520		520.76
1 0 3	341	275.04	248.00
2 0 1			27.04
2 1 1	662	676.47	672.64
1 1 3			3.83
2 0 2	98		95.60
0 0 4	179		117.42

arrangement. The data were subsequently refined by a least squares procedure using a programme written for the Ferranti Mercury computer by E. Wait [6]:

$$a = 3.829 \pm 0.002 \text{ Å}$$
$$c = 6.288 \pm 0.004 \qquad c/a = 1.642$$

NEUTRON DIFFRACTION MEASUREMENTS

Powder neutron diffraction patterns were obtained at liquid helium temperature, room temperature and 500°K. By seeving, the maximum grain size was made 50 μ. Neutron diffraction data at liquid helium temperature were collected using a Hoffman research dewar. Neutrons of wavelength 0.972 Å were obtained by reflection from the (111) plane of a Cu crystal. The neutron source was the reactor JEEP I operating at a power of 550 kW. Only reflections in the angular range up to $2\Theta = 38°$ were recorded, since only in this range the resolution was satisfactory. The instrumental background was measured separately.

The measurements at 500°K were carried out in a glass sample holder sealed under vacuum and surrounded by a heating coil. The temperature was controlled by a chromel-alumel thermocouple inserted inside the sample holder. Data were also collected at 633°K.

All reflections appearing in the neutron diagrams could be indexed on a tetragonal unit cell with lattice constants as quoted above. No additional reflections were found either at liquid helium or room temperature which would indicate a magnetic superstructure. Also diagrams obtained at 500°K and 633°K revealed no extra reflections.

In order to determine the magnetic moment from the difference in the intensities of peaks obtained at different temperatures, the Debye temperature was calculated using the specific heat data of Westrum *et al.*[1] The Debye temperature was found to be 208°K. Assuming this to be constant, a temperature factor was derived for the different temperatures. They are listed in Table 2. The temperature factors were taken isotropic and the same for Fe and Te atoms. For calculating the intensities the following data were used:

1. The free parameters for tellurium and the excess iron atoms obtained from X-ray measurements

$$z_{Te} = 0.285 \qquad z_{Fe} = 0.692$$

2. Neutron scattering lengths (in 10^{-12} cm):

$$b_{Te} = 0.56 \pm 0.02$$
$$b_{Fe} = 0.950 \pm 0.002$$

Table 2. The Debye-Waller factors for iron telluride.

T°K	B (in Å²)
293	1.17
500	2.72
633	4.19

The Debye temperature: $\Theta = 208°K$.

Table 3. Observed and calculated neutron intensities for iron telluride at liquid helium temperature. The intensities in columns III and IV are calculated for a ferro- and ferrimagnetic configuration, respectively.

I	II	III	IV
$h\ k\ l$	jF^2_{obs}	jF^2_{calc}	jF^2_{calc}
0 0 1	6.7	6.41	6.74
1 0 1 0 0 2	8.9	8.59	8.99
1 1 0	1.6	1.30	1.30
1 1 1 1 0 2	42.5	43.12	42.72
0 0 3 1 1 2	90	91.44	91.24
2 0 0	42.1	41.70	41.70
2 0 1 1 0 3	22.5	24.46	24.46
2 1 1 1 1 3 2 0 2	2.68	25.76	25.76
0 0 4	11.1	13.90	13.90

3. The magnetic form factor for iron reported by Nathans *et al.*[6] At the initial stage the magnetic spin quantum number $S = 0.82$ as reported by Tsubokawa and Chiba [2] was adopted.

The observed integrated intensities at room temperature normalized to the calculated ones are given in Table 2. In Table 3 a comparison of the observed and calculated intensities obtained at liquid helium temperature is presented. A striking feature of the liquid helium run as compared to that of room temperature is the increase in intensity of the (001) peak whereas other peaks have changed very little or not at all. Consequently the magnetic intensities at 4°K were calculated assuming the magnetic moments aligned perpendicular to the crystallographic unique axis. The intensities were calculated for a ferri- and a ferromagnetic ordering of moments. The magnetic spin quantum number

Table 4. Observed and calculated neutron intensities at room temperature.

$h\ k\ l$	jF^2_{obs}	jF^2_{calc}
0 0 1	4.2	4.94
1 0 1 0 0 2	7.2	7.49
1 1 0	1.7	2.68
1 1 1 1 0 2	41.5	42.33
0 0 3 1 1 2	90.0	91.16
2 0 0	43.0	43.05
2 0 1 1 0 3	31.0	26.14
2 1 1 1 1 3 2 0 2	27.0	25.76
0 0 4	10.5	13.90

Table 5. Observed and calculated neutron intensities at 500°K.

$h\,k\,l$	jF^2_{obs}	jF^2_{calc}
0 0 1	4.8	4.94
1 0 1, 0 0 2	6.5	7.49
1 1 0	0	1.30
1 1 1, 1 0 2	39.2	40.62
0 0 3, 1 1 2	95.3	90.76
2 0 0	41.1	41.70
2 0 1, 1 0 3	23.6	24.46

$S = 0.9$ was found at liquid helium temperature by trial and error. The discrepancy factors are, respectively: 3.18 % and 3.54 %.

The observed and calculated intensities at room temperature are shown in Table 4. The intensity of the (001) peak remained unchanged except for a temperature variation when the temperature was increased to 500°K indicating that the moments in the ferromagnetic state are directed parallel to the crystallographic unique axis.

In the neutron diagram taken at 633°K no additional peaks or changes in intensities were observed indicating no atomic rearrangement which could be the cause of the anomaly in the electrical conductivity.

The observed and calculated intensities for the 500°K run are compared in Table 5.

DISCUSSION

The result of neutron diffraction measurements shows that at the room temperature $Fe_{1.11}Te$ is ferromagnetic with moments aligned along the fourfold axis. At 63°K a magnetic transition occurs, the moments being now aligned perpendicular to this axis. This process is responsible for the peaks in the specific heat and the susceptibility curves. The point of interest is whether there is a ferro- or ferrimagnetic ordering at liquid helium temperature. The neutron intensity data suggest the latter. However, the differences in the observed and calculated intensities for both cases are rather small. It is impossible on the basis of powder data alone to determine uniquely the directions of moments for the case when they are perpendicular to the crystallographic unique axis (Shirane [7]). The magnetic moment calculated from the neutron intensities of the (001) and (002) peaks measured at liquid helium temperature is $\mu = 1.8$ Bohr magnetons as compared to $\mu = 2.44\ \mu_B$ found by Tsubokawa and Chiba [2] from magnetic susceptibility data.

The crystal structure of $Fe_{1.11}Te$ as reported by Grønvold *et al.*[4] has been confirmed by neutron diffraction. The composition $Fe_{1.11}Te$ corresponds to Fe_9Te_8, *i.e.* to one excess iron atom per four unit cells. No indication was found of any ordering of those atoms, even at 4°K. The random distribution of the excess iron atoms is confirmed by the good agreement between observed and calculated intensities.

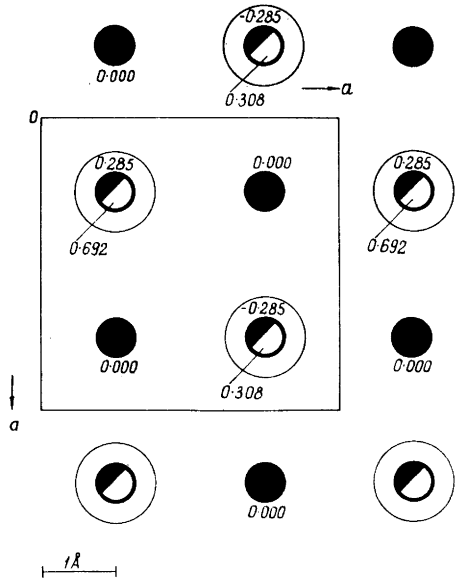

Fig. 1. Projection of the unit cell of $Fe_{1.11}Te$ along *c*-axis.

The crystal structure of iron monotelluride can be derived from a close packed cubic lattice built of tellurium atoms:

$$a_{\text{cubic}} = \sqrt{2}\, a_{\text{tetr.}}$$
$$c/a = 1.414 \qquad z_{\text{cubic}} = 0.25$$

The iron atoms occupy in an ordered manner 1/2 of the tetrahedral holes, the excess 0.22 iron atoms – the octahedral holes at random. The actual tellurium parameter $z_{\text{Te}} = 0.285$ indicates that the distance Fe—Te is slightly longer than in the ideal cubic lattice. $Fe_{1.11}Te$ has a typical layer structure: the iron atoms are grouped at the bottom and at the top of the tetragonal unit cell (see Fig. 1). Each tellurium atom is linked to four irons at a distance of 2.62 ± 0.01 Å. This distance is close to the sum of atomic radii of both elements. The coordination polyhedron is a regular tetragonal pyramid. Each tellurium atom utilizes four valence electrons for bonding leaving one pair inert which is directed towards the empty space between the layers. Pauling and Moore [8] suggested such an electronic configuration in the crystal structure of tetragonal PbO. Each iron atom coordinates tetrahedrally four tellurium atoms. The observed iron moment is 1.8 Bohr magnetons which is less than that expected for Fe^{3+} as well as for Fe^{2+} ions. This indicates that the bonding scheme is rather complex. Qualitatively this may be explained by postulating the participation of $3d$ electrons in the covalent bonds which would decrease the iron moment. The perfect tetrahedral environment of each iron atom suggests that d^3s hybrid orbitals are used for bonding. The strongest magnetic exchange interaction takes place between the iron atoms in the same layer, where each Fe atom has four iron neighbours at a distance of 2.70 Å situated

at the corners of a square. The magnetic coupling within the layer remains ferromagnetic below and above the lambda transition temperature.

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