A Neutron Diffraction Investigation of Cr_2Te_3 and Cr_5Te_6

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Neutron diffraction diagrams of Cr_2Te_3 and Cr_5Te_6 have been run above and below the Curie points to investigate the magnetic ordering process. In both compounds the magnetic moments are found to order ferromagnetically with their direction along the hexagonal axis. On cooling Cr_2Te_3 shows a contraction of the unit cell along the c-axis, but no atomic displacements. In Cr_5Te_6 no contraction is visible, but the tellurium atoms are slightly displaced in the c-axis direction. The monoclinic splitting in Cr_5Te_6 decreases at low temperatures. The average magnetic moments deduced are 2.70 μ_B for Cr_2Te_3 and 2.10 μ_B for Cr_5Te_6. Possible reasons for the low magnetic moments are discussed.

In many of the transition metal chalkogenides two composition regions of hexagonal structure are found to be separated by a region of monoclinically deformed structures. Thus in the system chromium-tellurium Haraldsen and Neuber[1] found the two compounds CrTe and Cr_2Te_3 of respectively 50 and 60 atom % Te to crystallize in nickel-arsenide type structures and to be separated by a monoclinically deformed region. Galperin and Perekalina[2] found a solid solubility range from 50—70 atom % Te with Cr vacancies in the Te rich alloys. These compounds are of particular interest because of their magnetic behaviour. At low temperatures they all become ferromagnetic, but the Curie point changes drastically with composition[1]. Staying close to 70—80°C in the region 50—58 atom % Te, it suddenly drops to —80°C at 60 % Te.

For CrTe there is a decrease in the magnetic moment on magnetic ordering and this led Guillaud[3] to propose a ferrimagnetic arrangement. However, later measurements by Gaidukov *et al.*[4] of the spontaneous magnetization in the vicinity of the Curie point have confirmed the ferromagnetic ordering. Goodenough[5] has proposed the low moment to be due to interstitial ions or a ferromagnetic spiral.

Recent specific heat measurements by Grønvold *et al.*[6] indicate the para- to ferromagnetic transition in particular for the monoclinically deformed compounds to be drawn out and to be associated with a rather small entropy change. Careful X-ray investigations by Berg[7] have revealed that CrTe does not exist at low temperatures. Annealing at 600°C or slow cooling from higher temperatures leads to disproportionation of CrTe into free chromium and a

compound of approximate composition Cr_5Te_6. This has a slightly monoclinically deformed structure.

To shed further light on the mechanism of ordering in these compounds and to investigate further some of the related phenomena, a neutron diffraction investigation of the two compounds Cr_2Te_3 and Cr_5Te_6 was undertaken. These compounds were chosen since they crystallize in a small NiAs-type unit cell whose reflections can be approximately resolved in a low resolution neutron diagram. For Cr_5Te_6 a slight monoclinic deformation is observed, but in this work we will only consider the hexagonal pseudocell.

PREPARATION OF SAMPLES AND X-RAY EXAMINATION

Calculated amounts of chromium 99.97 % pure and tellurium 99.999 % were heated to 1000°C for two days in evacuated and sealed quartz tubes. After cooling they were crushed and annealed at 800°C for two days. After again cooling and crushing finely, they were annealed at 800°C for one week and then at 600°C for another week.

X-Ray examination showed Cr_2Te_3 to be well crystallized having a hexagonal unit cell of dimensions $a = 3.92$ Å and $c = 6.04$ Å. Cr_5Te_6 was less well crystallized and showed a slight monoclinic deformation. To see whether this would change on further heat treatment, prolonged heating at 800°C followed by annealing at 600°C was undertaken, but no significant changes were observed. The dimensions of the hexagonal pseudocell were $a = 3.96$ Å, $c = 6.18$ Å.

For Cr_2Te_3 X-ray intensities obtained by planimeter reading of a diffraction diagram (Cu-$K\alpha$ radiation) are given in Table 1. The appearance of a (0001) reflection indicated ordering of the Cr vacancies on every second Cr layer, and as seen in Table 1, good agreement was obtained assuming every second layer 1/3 filled in a NiAs-type structure.

As the compound crystallizes in platelets perpendicular to the crystallographic c-axis, great care had to be exercised to avoid preferred orientation. Some degree of orientation is still apparent from the strong (0002) reflection. For Cr_5Te_6 a similar ordering of the Cr vacancies was apparent and the relative intensities of the (0001) and (0002) reflections indicated a 2/3 filling of every second Cr layer.

NEUTRON DIFFRACTION INVESTIGATION OF Cr_2Te_3

Neutron diffraction diagrams obtained on the diffractometer described by Goedkoop [8] at the Kjeller reactor JEEP I using neutrons of wavelength 0.972 Å are shown in Fig. 1. The sample was placed in a cylindrical 10 mm diameter thin-walled Al-cylinder in a Hoffman liquid helium research dewar, and neutron diffraction diagrams were obtained at room temperature, liquid air and liquid helium temperatures. The diagrams shown were obtained at

Table 1. X-Ray diffractometer data for Cr_2Te_3.

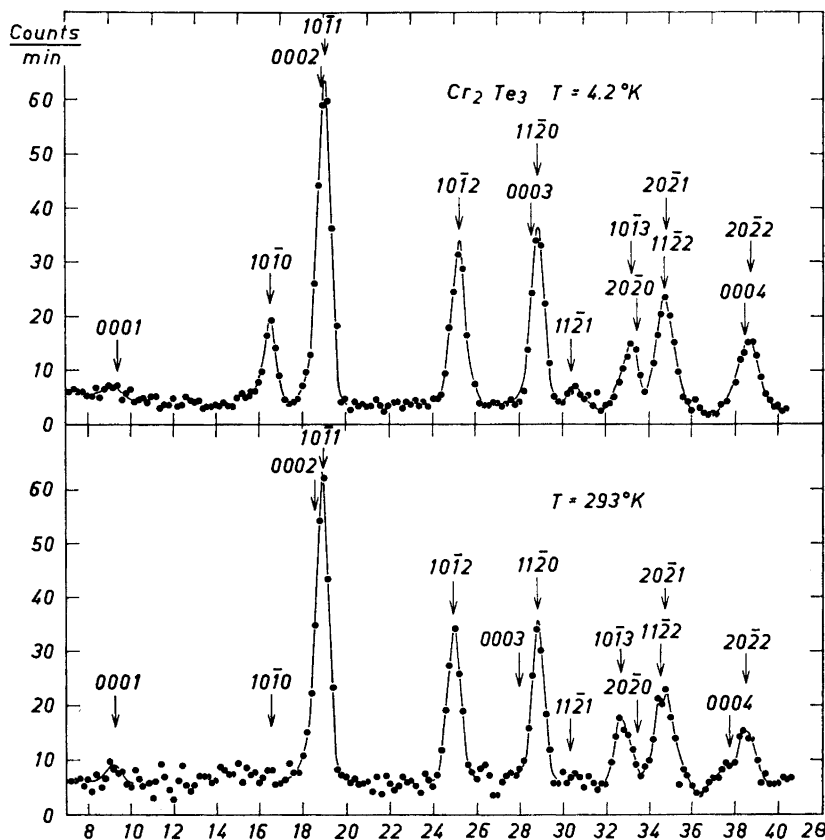| $hkil$	I_{calc}	I_{obs}
0001	19	23
10$\bar{1}$0	62	57
0002	133	215
10$\bar{1}$1	978	878
10$\bar{1}$2	313	363
0003	1	0
11$\bar{2}$0	286	240
11$\bar{2}$1	4	0
10$\bar{1}$3	192	211

Fig. 1. Neutron diffraction diagrams of Cr_2Te_3 at 4.2°K and 293°K, instrumental background subtracted ($\lambda = 0.972$ Å).

293°K and 4.2°K. They only include angles up to $2\Theta = 40°$, since at higher angles there is a severe overlap of the peaks. Due to the magnetic form factor, all significant magnetic contributions are included in this range.

It is immediately apparent that a contraction of the unit cell along the c-axis has taken place at liquid helium temperature. To the attainable accuracy no change in the a-axis could be observed. The length of the c-axis at 4.2°K is estimated to $c = 5.91 \pm 0.02$ Å.

In Table 2 the observed intensities are compared with the calculated ones. For the room temperature data good agreement is obtained for a NiAs-type structure assuming ordering of the Cr vacancies on every second Cr layer. As scattering amplitudes were used $b_{Cr} = 0.35 \times 10^{-12}$ cm and $b_{Te} = 0.56 \times 10^{-12}$ cm,[9] and as temperature factor $B = 0.7$ Å^2, derived from the specific heat data of Grønvold *et al.*[6] A discrepancy factor for the intensities of $R = 5.7$ % was obtained.

Table 2.

hkil	293°K				4.2°K				
	I_{calc} nucl. $B = 0.7$	I_{obs}		Δ	I_{calc} nucl. $B = 0$	I_{calc} magn.	I_{calc} total	I_{obs}	Δ
0001	7.8	—		—	7.8	0	7.8	—	—
10$\bar{1}$0	1.5	—		—	1.5	76.9	78.4	75.0	3.4
0002	15.8⎫	230.7	231.9	1.2	16.4	0 ⎫	259.3	274.5	15.2
10$\bar{1}$1	214.9⎭				223.9	19.0⎭			
10$\bar{1}$2	129.7		118.2	11.5	139.5	16.5	156.0	132.5	23.5
0003	0.8		—	—	0.9	0	0.9	—	—
11$\bar{2}$0	114.8		121.8	7.0	126.2	10.4	136.6	143.6	7.0
1121	4.1		—	—	4.5	3.7	8.2	14.4	6.2
10$\bar{1}$3	70.2⎫	70.5	62.1	8.4	78.9	0.7⎫	84.9	78.3	6.6
20$\bar{2}$0	0.3⎭				0.4	4.9⎭			
11$\bar{2}$2	26.4⎫	88.3	98.4	10.1	30.0	5.5⎫	107.7	115.5	7.8
20$\bar{2}$1	61.9⎭				70.4	1.8⎭			
0004	22.0⎫	74.6	72.6	2.0	25.6	0 ⎫	90.3	87.8	2.5
20$\bar{2}$2	52.6⎭				61.9	2.8⎭			
				$R = 5.7\%$					$R = 7.8\%$

At liquid helium temperature the appearance of a strong (10$\bar{1}$0) reflection indicates a ferromagnetic ordering of the magnetic moments, the moments pointing along the c-axis. Magnetic intensities calculated using the formula:

$$I_{magn} = \nu \; L \; |F|^2 \; P^2 q^2$$

are given in column 6 of Table 2. ν is the multiplicity of the reflection, L the Lorentz factor and F the geometric structure factor. p is the magnetic scattering amplitude:

$$p = 0.539 \times 10^{-12} \; Sf$$

where S is the electron spin quantum number assuming a spin only momentum. A value of $S = 1.35$ was derived from the purely magnetic (10$\bar{1}$0) reflection. As magnetic form factor f, the form factor for Mn^{2+} given by Corliss and Hastings [10] was used. q is an angular factor depending on the angle η between the direction of the magnetic moments and the scattering vector:

$$q^2 = 1 - \langle \cos^2 \; \eta \rangle$$

For the hexagonal system

$$\langle \cos^2 \; \eta \rangle = \left[\tfrac{1}{2}(h^2 + k^2 + hk)a^{*2}\sin^2\varphi + l^2 c^{*2}\cos^2\varphi \right]d^2$$

when averaged over the equivalent reflections (hkl) [11]. a^* and c^* are the reciprocal lattice vectors and φ the angle that the magnetic moments make with the hexagonal axis. d is the spacing of the planes.

The calculated nuclear intensities are the same as those for room temperature, but the temperature factor has been omitted since only low angle reflections are considered. Comparing the total added intensities at 4.2°K with the normalized observed ones we find a disagreement factor of $R = 7.8 \%$.
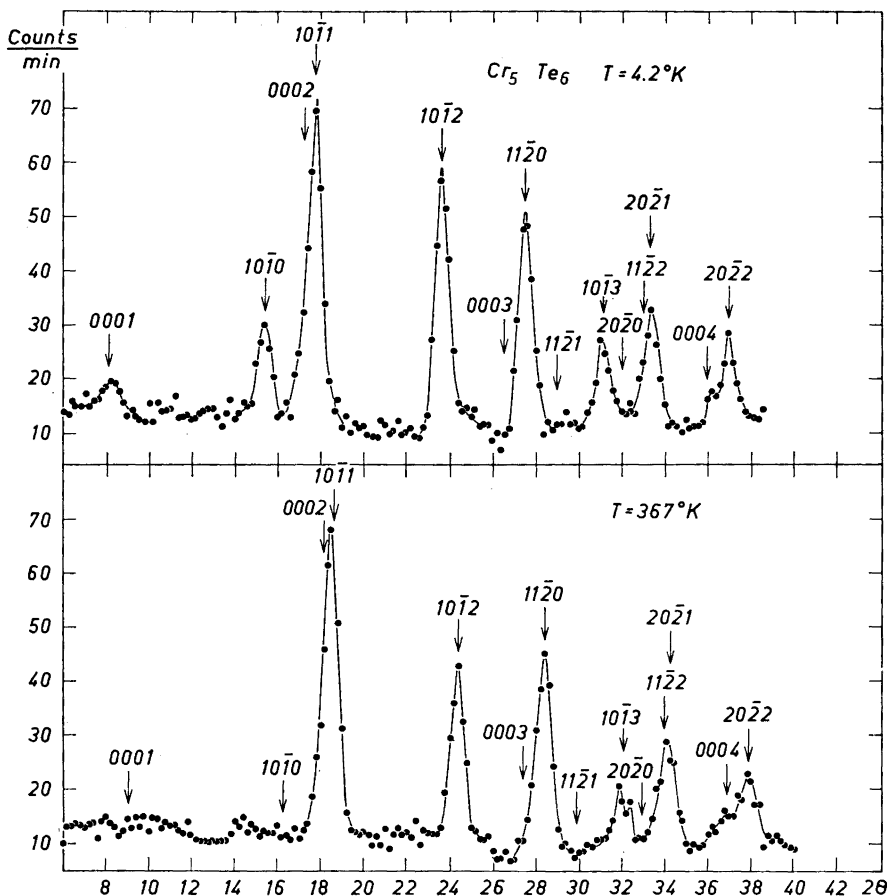
Fig. 2. Neutron diffraction diagrams of Cr_5Te_6 at 4.2 °K and 367°K, instrumental background subtracted ($\lambda = 0.972$ Å).

Some degree of preferred orientation was also noted in the neutron diffraction diagrams. Apparently when packing the cylindrical container the crystal platelets had a tendency to orient themselves perpendicular to the cylinder axis, increasing the reflections with $l = 0$ and decreasing those with high l indices. To avoid this the cylinder was filled in a horizontal position and packed loosely.

NEUTRON DIFFRACTION INVESTIGATION OF Cr_5Te_6

For Cr_5Te_6 neutron diffraction diagrams were run at 367°K, 293°K, 100°K, and 4.2°K. The low temperature diagrams were obtained in the liquid helium research dewar and the high temperature ones in a quartz cylinder surrounded by a heating coil. The diagrams obtained at 367°K and 4.2°K are given in Fig. 2.

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Table 3. Atomic positions in Cr_5Te_6. Space group: $D_{3d}^3 - P\bar{3}m1$.

        1 Cr in 1 a : (0,0,0)
    2/3 Cr in 1 b : (0,0,1/2) stat. dist.
        2 Te in 2 d : (1/3, 2/3,z) ; (2/3,1/3,z) with $z = 0.215$

No change in the lattice constants could be observed in this case, however, a pronounced sharpening of some of the peaks in the liquid helium diagram indicates a decrease or disappearance of the monoclinic splitting at this temperature. To which extent this is the case can not be decided from our low resolution diagrams.

In Table 4 the observed intensities are compared with calculated values assuming a NiAs-type structure with every second Cr layer 2/3 occupied. For the high temperature data a disagreement factor for the intensities of 7.4 % was obtained.

Again the appearance of a strong $(10\bar{1}0)$ peak below the Curie point indicates a ferromagnetic alignment with the magnetic moments pointing along the c-axis. A striking difference from the Cr_2Te_3 diagram is the appearance of a pronounced (0001) peak at low temperature. This peak can not, for a ferromagnetic alignment, be due to the chromium atoms alone, since this would require a number of vacancies in the depleted chromium layer larger than the number in Cr_2Te_3. The peak can, however, be ascribed to a slight displacement of the tellurium atoms in the direction of the fully occupied chromium layers.

The space group of the hexagonal pseudo-cell is then $P\bar{3}m1$, with positions as given in Table 3. The value of the parameter $z = 0.215$ is based on the intensity of the (0001) reflection. Intensities calculated for these positions are given in column 5 of Table 4. In the next column are found the calculated

Table 4.

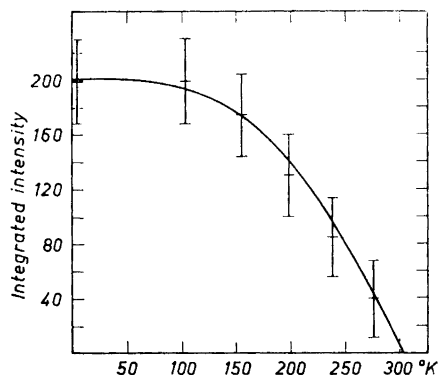| $hkil$	367°K			4.2°K				
	I_{calc} nucl. $z = 0.25$	I_{obs}	$\varDelta$	I_{calc} nucl. $z = 0.215$	I_{calc} magn.	I_{calc} total	I_{obs}	$\varDelta$
0001	1.7	—	—	21.7	0	21.7	25.0	3.3
$10\bar{1}0$	0	—	—	0	74.3	74.3	72.0	2.3
0002	11.4 ⎫	224.1	17.4	7.3	0 ⎫	217.9	250.8	32.9
$10\bar{1}1$	212.7 ⎭	241.5		207.7	2.9 ⎭			
$10\bar{1}2$	164.9	151.9	13.0	182.7	16.3	199.0	183.5	15.5
0003	0.2	—	—	5.9	0	5.9	—	—
$11\bar{2}0$	134.9	125.3	9.6	148.2	10.1	158.3	141.9	16.4
$11\bar{2}1$	0.9	—	—	12.2	0.5	12.7	—	—
$10\bar{1}3$	69.7 ⎫	69.7	3.8	65.3	0.1 ⎫	70.1	70.4	0.3
$20\bar{2}0$	0 ⎭	65.9		0	4.7 ⎭			
$11\bar{2}2$	18.8 ⎫	80.3	12.1	14.7	5.3 ⎫	85.8	93.2	7.4
$20\bar{2}1$	61.5 ⎭	92.4		65.5	0.3 ⎭			
0004	26.6 ⎫	94.8	1.3	17.6	0 ⎫	101.8	92.1	9.7
$20\bar{2}2$	68.2 ⎭	93.5		81.4	2.8 ⎭			
	$R = 7.4$ %					$R = 9.5$ %		

Fig. 3. The integrated intensity of the $(10\bar{1}0)$ peak from Cr_5Te_6 as a function of temperature. Curve representing Brillouin function for $S = 1$.

magnetic contributions assuming a ferromagnetic alignment, the moments pointing along the c-axis. The value used for the spin quantum number was $S = 1.05$ which was deduced from the purely magnetic reflection $(10\bar{1}0)$. This value corresponds to a magnetic moment of 2.10 μ_B which is somewhat lower than the values 2.39 [3] and 2.45 μ_B [12] which have been found by susceptibility measurements. In column 7 and 8 of Table 4 the total calculated intensities are compared with the normalized observed ones. The disagreement factor is 9.5 %.

Since the specific heat measurements of Grønvold *et al.*[6] indicated the ferromagnetic ordering transition to be spread out over a considerable temperature range, the ordering process was investigated by measuring the intensity of the $(10\bar{1}0)$ reflection as a function of temperature from 4.2°K to 367°K. In Fig. 3 the integrated intensity is plotted as a function of temperature, the vertical bars representing the estimated probable error. The curve fitted to the experimental points represents the square of the Brillouin function for $S = 1$. It is seen that the fit is quite good when assuming a Curie temperature of 30°C (303°K). Thus there is no sign of an unusually large transition region. The Curie point is lower than the value 70°C found by Haraldsen and Neuber,[1] but agrees well with the value 35°C found by Tsubokawa [13].

DISCUSSION

A striking difference between Cr_2Te_3 and Cr_5Te_6 is the contraction of the Cr_2Te_3 unit cell along the c-axis at low temperatures. In Cr_5Te_6 where no contraction is apparent there is a displacement of the tellurium atoms in the c-axis direction.

The contraction of Cr_2Te_3 is probably related to the strong superexchange interactions between adjacent Cr layers [12]. In Cr_5Te_6 the asymmetric displacements of the Te layers can probably be ascribed to the substitution of Cr^{3+} ions by Cr^{2+} ions and the ordering of these on the fully occupied Cr layers.

The decrease in the magnetic moment in going from Cr_2Te_3 to Cr_5Te_6 in spite of the increase in the number of d-electrons on replacing Cr^{3+} by Cr^{2+} has been interpreted by Gaidukov *et al.*[4] as due to some d-electrons taking part in bond formation, or the giving up of some d-electrons to a d-conduction band. Grønvold [6] has proposed that the low magnetic moment may be due to

the splitting of the d-orbitals in an octahedral environment into a lower triplet and a higher duplet. If all the four d-electrons in Cr^{2+} go into the lower spin states, there will be two unpaired electrons left corresponding to a magnetic moment of 2 μ_B. For Cr^{3+} the moment is 3 μ_B. In Cr_5Te_6 with 40 % Cr^{3+} and 60 % Cr^{2+} this leads to an overall magnetic moment of 2.40 μ_B.

Goodenough [5] has pointed out that in a NiAs-type structure with large anions and small cations tetrahedral interstitials will readily form. As these will be antiferromagnetically aligned, they may cause a low magnetic moment. Neither in our X-ray data nor in the neutron diagrams have we found any evidence for a large amount of interstitials, however, the accuracy of our data can not exclude the possibility of a concentration of interstitials less than 10 %. The fact that it seems impossible in this system to prepare compounds with an excess of metal [2,3] should preclude the possibility of a large number of interstitial metal ions.

We have here not discussed the possibility suggested by Goodenough [5] of a spiral spin arrangement, as our data show no evidence for such an arrangement. The possibility that the (0001) peak in Cr_5Te_6 could be due to a tilting of the spins away from the c-axis can be immediately ruled out since the geometric structure factor for this reflection is too small. To make it large enough would require, even with a 45° tilt, a number of vacancies in the depleted layer larger than that in Cr_2Te_3. Besides it is highly unlikely that these ions, which are presumable Cr^{3+} ions, could be accommodated interstitially in tetrahedral holes [5].

For Cr_2Te_3 we have found a magnetic moment 2.70 μ_B which is smaller than that corresponding to the 3 unpaired electrons in Cr^{3+}, and for Cr_5Te_6 the moment deduced is also smaller than that obtained by susceptibility measurements. Our values are based on the intensity of the purely magnetic $(10\bar{1}0)$ reflection by assuming the magnetic moments to point along the c-axis. If the moments are tilted with respect to this axis, higher moments are possible. Antiferromagnetically aligned tetrahedral interstitials will not explain the low intensities of this reflection, since they would actually enhance the reflection.

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