

The Magnetic Structure of Cr_2Te_3 , Cr_3Te_4 , and Cr_5Te_6

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The magnetic structure of slowly cooled compounds of composition Cr_2Te_3 , Cr_3Te_4 , and Cr_5Te_6 have been reinvestigated by neutron diffraction in order to determine with precision the size and orientation of the magnetic moments. For Cr_2Te_3 the moments in the fully occupied layers are $2.56 \mu_B$ and point along the trigonal axis. The moments in the vacancy layers have a negligible ferromagnetic component. For Cr_3Te_4 the moment values are, respectively, $3.36 \mu_B$ and $3.00 \mu_B$. A ferromagnetic component is pointing along the a -axis whereas an antiferromagnetic component is pointing along the $(b+c)$ direction. For Cr_5Te_6 the moment values are, respectively, $4.24 \mu_B$ and $2.24 \mu_B$. Also in this case the ferromagnetic component is pointing along the a -axis, but the antiferromagnetic component is along the b -axis. The average ferromagnetic moment per atom is $2.40 \mu_B$.

It has been found by several authors^{1,2} that stoichiometric CrTe does not exist in equilibrium at room temperature. However, with less chromium, metal vacancies are formed, and several superstructures derivable from the NiAs-type structure appear. In a previous neutron diffraction investigation by this author³ on compounds of composition Cr_2Te_3 and Cr_5Te_6 these were treated as crystallizing with an NiAs-type unit cell. The vacancies were found to be randomly distributed over every second metal layer. As for the magnetic moments these were found to order ferromagnetically with their direction along the hexagonal c -axis.

Later measurements on Cr_2Te_3 by Chevreton⁴ have, however, shown that on slow cooling the vacancies also order within the layers giving rise to a superstructure. Suchet⁵ has suggested that this slowly cooled compound may have a ferri- or antiferromagnetic ordering of the moments.

For Cr_5Te_6 the presence of a strong (0001) peak at liquid helium temperature led this author to assume a displacement of the Te-atoms in the c -direction. However, X-ray diagrams at room temperature and at liquid helium temperature (kindly performed for us at Brookhaven National Laboratory, U.S.A., by Dr. D. E. Cox) failed to show any change in the X-ray intensity of this peak, thus ruling out the possibility of atomic displacements in this direction.

For the composition Cr_3Te_4 on the other hand, Bertaut *et al.*⁶ found that below 80°K additional superreflections appeared due to the formation of a weak antiferromagnetic component superimposed on the ferromagnetic one. One of the additional peaks appeared close to the (0001) peak of the NiAs-type cell. As the phase with the Cr_3Te_4 type structure is stated to have a large range of homogeneity² one may assume Cr_5Te_6 to have the same structure and to give the same antiferromagnetic reflections at low temperature. The antiferromagnetic peak overlapping the (0001) peak could then explain the large observed intensity of this peak.

With the increased intensity and resolution now available it was found of interest to make a restudy of Cr_2Te_3 and Cr_5Te_6 on well annealed and slowly cooled samples. One could then hope to get a more detailed picture of the magnetic ordering in these compounds and possibly find a better explanation for the moment values which have been obtained by susceptibility and magnetization measurements. It was also decided to include Cr_3Te_4 in this investigation since the previously published data⁶ were insufficient to give a detailed picture of the moment distribution in this compound.

PREPARATION AND EXPERIMENTAL TECHNIQUE

The samples were prepared from the elements as described in the previous paper.³ However, after the last annealing which took place at 900°C the samples were slowly cooled in steps of 20° to 300°C in the course of one week.

Neutron diffraction diagrams were obtained at the JEEP II reactor using neutrons of wavelength 1.864 ± 0.002 Å obtained from the (111) planes of a pressed Ge-crystal. This has the advantage of giving a low $\lambda/2$ contamination since the (222) reflection is extinguished. The $\lambda/2$ contamination still present is due to multiple scattering. Corrections were made for this contribution which amounted to 0.3 % of the primary beam intensity and for the $\lambda/3$ contribution amounting to 0.07 %. Two soller slits were used, one of 10' opening angle in front of the monochromator crystal and one of 20' opening angle in front of the BF_3 -counter.

For liquid helium runs a Hofman Research Dewar without temperature control was used, and for the other low temperature runs a liquid nitrogen variable temperature cryostat of our own design. In this the temperature could be controlled to $\pm 1^\circ\text{K}$. For the liquid helium runs no accurate temperature measurement could be done. The sample container of Al was in direct contact with the liquid helium reservoir, and the temperature was assumed to be close to 4.2°K.

Great care had to be taken in order to avoid preferred orientation. This was in particular the case for Cr_2Te_3 which crystallizes in platelets perpendicular to the trigonal axis. The powder was finely ground, sieved and loosely packed in cylindrical containers. Several runs were made on the same sample under different conditions to check whether any preferred orientation was present.

For Cr_5Te_6 runs were made at 4.2°K with a magnetic field along the scattering vector in order to determine which reflections had a ferromagnetic contribution. The maximum field strength was 6 kOe. To prevent the particles from turning in the magnetic field the powder was pressed into cylindrical discs of diameter 0.5". These runs were kindly made for us at Brookhaven National Laboratory by Dr. D. E. Cox.

NEUTRON DIFFRACTION INVESTIGATION OF Cr_2Te_3

Chevreton⁴ has found that slowly cooled Cr_2Te_3 is isomorphous with the trigonal form of Cr_2S_3 described by Jellinek.⁷ Its hexagonal unit cell (Fig. 1) is related to the small NiAs-type cell by $a \approx \sqrt{3} a_0$ and $c \approx 2 c_0$. In our neutron

diffraction diagrams obtained at room temperature (293°K) and liquid helium temperature (4.2°K) all the peaks, except for a few very weak ones, can be indexed on this cell. The weak peaks can be ascribed to the $\lambda/2$ and $\lambda/3$ contamination of the monochromatized beam and a slight amount of Cr₂O₃.

The dimensions of the unit cell derived by a least squares analysis from the positions of the resolved reflections are given in Table 1. Our room tempera-

Table 1. Lattice parameters of Cr₂Te₃.

	Temp.	<i>a</i>	<i>c</i>
Chevreton	Room temp.	6.812 ± 0.002 Å	12.070 ± 0.004 Å
This work	293°K	6.814 ± 0.006 Å	12.073 ± 0.012 Å
»	4.2°K	6.829 ± 0.006 Å	11.922 ± 0.012 Å

ture values are seen to agree closely with those given by Chevreton.⁴ On cooling to 4.2°K we observe, however, a considerable contraction along the *c*-axis and a small elongation of the *a*-axis. At this temperature an added contribution to some of the reflections could be ascribed to a ferromagnetic ordering. This contribution followed closely a Brillouin type temperature dependence and disappeared at $T_c = 182 \pm 2^\circ\text{K}$.

In neither X-ray nor in neutron diffraction diagrams were reflections of the type $(h, h, 2\bar{h}, l)$ with $l = 2n + 1$ observed, thus confirming the space group $P\bar{3}1c$ derived by Chevreton. The atomic positions in this space group for an NiAs-type lattice are given in Table 2. Chevreton assumed a complete ordering of the Cr-vacancies on the (*a*) and (*d*) positions, an assumption which seemed to agree well with our data.

Table 2. Atomic positions for Cr₂Te₃. Space group $P\bar{3}1c - D_{3d}^2$.

2 □	in <i>a</i> : ±(0, 0, $\frac{1}{2}$)
2 □	in <i>d</i> : ±($\frac{2}{3}, \frac{1}{3}, \frac{1}{2}$)
2 Cr _I	in <i>c</i> : ±($\frac{1}{3}, \frac{2}{3}, \frac{1}{2}$)
2 Cr _{II}	in <i>b</i> : (0, 0, 0) (0, 0, $\frac{1}{2}$)
4 Cr _{II}	in <i>f</i> : ±($\frac{1}{3}, \frac{2}{3}, z$; $\frac{2}{3}, \frac{1}{3}, \frac{1}{2}-z$)
12 Te	in <i>i</i> : ±(<i>x</i> , <i>y</i> , <i>z</i> ; \bar{y} , <i>x</i> - <i>y</i> , <i>z</i> ; <i>y</i> - <i>x</i> , \bar{x} , <i>z</i> ; <i>y</i> , <i>x</i> , $\frac{1}{2}+z$; \bar{x} , <i>y</i> - <i>x</i> , $\frac{1}{2}+z$; <i>x</i> - <i>y</i> , \bar{y} , $\frac{1}{2}+z$)

There are four position parameters to be determined, *z* for Cr_{II} in (*f*) and *x*, *y*, *z* for Te in (*i*). An attempt was first made to determine these using the ORFLS least squares programme of W.R. Busing, K.O. Martin and H. A. Levy (ORNL-TM-305). With this programme only resolved reflections could be used, which excluded most of the strong reflections. Nevertheless, a refinement on the four position parameters and the scale factor could be carried out using the room temperature data. With the scale factor from this refinement the magnetic intensities at 4.2°K could be put on an absolute scale and approximate values for the magnetic moments deduced. For the atoms in the fully occupied layers, Cr_{II}, an average ferromagnetic moment of 2.82 μ_B was derived, the moments pointing approximately parallel to the *c*-axis. However, the atoms

in the vacancy layers, Cr_v, seemed to contribute very little to the ferromagnetic scattering and no other coherent magnetic contribution could be found.

This unexpected result needed further confirmation, and this became possible when the profile refinement programme written by Rietveld* became available. This programme utilizes all the available information in a powder diagram by performing a least squares analysis based on each individual observation. A simultaneous refinement is possible both on the nuclear and magnetic structure. The peaks are assumed to have a Gaussian shape, which has been found to be closely true for the peaks in our diagrams, and the angular dependence of the half-width is expressed as

$$H_K^2 = U \tan^2 \theta_K + V \tan \theta_K + W$$

Here H_K is the half-width of the reflection with wave vector K and U , V , W are constants which can be determined using a separate least squares programme.

As mentioned in the previous chapter a serious problem was posed by the presence of preferred orientation due to the tendency of Cr₂Te₃ to crystallize in platelets perpendicular to the trigonal axis. In the present programme this could be taken account of by applying a correction factor of the type:

$$I_{\text{corr}} = I_{\text{obs}} \times \exp(-G\alpha^2)$$

Here α is the acute angle between the scattering vector and the normal to the platelets. G can be considered as a preferred orientation parameter, and included in the refinement.

The other parameters to be refined were: the four atomic position parameters, the isotropic temperature parameters for Cr and Te, the unit cell dimensions, the scale factor and at 4.2°K the components of the magnetic moments. With the Rietveld programme a refinement could also be carried out on the occupation numbers defined as the fraction of the positions occupied by an atom. In the first refinement all the atomic positions given in Table 2 were included. It soon appeared, however, that the occupation numbers for the (*a*) and (*d*) positions turned out small and negative. This indicated a complete ordering of the vacancies, and these positions were omitted.

As for the moments, refinements were first carried out with components both in the basal plane and along the trigonal axis. However, the components in the basal plane did not converge and showed large standard deviations. Omitting these components the refinement of the other parameters converged more rapidly and resulted in lower R -factors. In the last refinements therefore, only the z -axis components were included.

For the room temperature data an R -factor for the intensities of 7.9 % was obtained, whereas for the 4.2°K data the best refinement gave $R = 3.2$ % as a total value for the nuclear and magnetic intensities combined. The obtained agreement between the observed and calculated intensities at 4.2°K is shown in Table 3. In the calculations the following scattering amplitudes

* The programme which is written in Algol by H. M. Rietveld, R.C.N., The Netherlands and published as RCN-report 104 has been adapted to the CDC-3600 computer by J. E. Engebretsen.

Table 3. Observed and calculated intensities for Cr₂Te₃ at 4.2°K.

<i>hkl</i>	$I_{\text{nucl}} \times 10^{-2}$	$I_{\text{magn}} \times 10^{-2}$	I_{tot}	I_{obs}	Δ
00.2	8.55	0	8.55	8.89	+0.34
10.0	2.71	1.00	3.71	4.26	+0.55
10.1	5.92	0	5.92	4.92	-1.0
10.2	1.32	0.12	1.44	0.94	-0.50
11.0	2.20	56.75	58.95	57.97	-0.98
10.3	3.56	0.22	3.78	3.66	-0.12
00.4	13.34	0	13.34	13.32	-0.02
11. $\bar{2}$	63.98	18.83	82.81	82.48	-0.33
11.2	148.83	18.83	167.66	166.99	-0.67
20.0	0.15	0.15	0.30	0.29	-0.01
20.1	1.74	0	1.74	2.40	+0.66
10.4	0.26	0.02	0.28	0.72	+0.44
20.2	0.58	0.06	0.64	0.06	-0.58
20.3	1.98	0.16	2.14	5.02	+2.88 (Al-cont.)
11.4	46.93	3.71	50.64	51.70	+1.06
11.4	62.49	3.71	66.20	67.60	+1.40
21.0	0.38	0.10	0.48	0.54	+0.06
10.5	0.26	0.02	0.28	0.50	+0.22
12. $\bar{1}$	1.04	0	1.04	2.44	+1.40
12.1	0.96	0	0.96	2.26	+1.30
20.4	0.56	0.02	0.58	1.28	+0.70
12. $\bar{2}$	0.84	0.02	0.86	1.00	+0.14
12.2	0.06	0.02	0.08	0.10	+0.02
30.0	155.34	7.29	160.64	157.86	-2.78
21. $\bar{3}$	1.34	0.08	1.42	1.20	-0.22
21.3	1.26	0.08	1.34	1.16	-0.18
30.1	0	0	0	0	0
10.6	0.24	0	0.24	0.94	+0.70
30.2	5.94	7.76	13.70	14.18	+0.48
20.5	0.18	0.04	0.22	0.22	0
21.4	0.22	0	0.22	0.66	+0.44
21.4	0.26	0	0.26	0.76	+0.50
30.3	0	0	0	0	0
11. $\bar{6}$	47.99	0.51	48.50	45.52	-2.98
11.6	16.26	0.51	16.77	15.74	-1.03
22.0	1.21	3.51	4.72	4.51	-0.21
20.6	0.16	0	0.16	0.70	+0.54
30.4	35.76	2.86	38.62	38.96	+0.34
22. $\bar{2}$	51.72	2.01	53.73	54.22	+0.49
22.2	24.63	2.01	26.64	26.88	+0.24
13.0	0.58	0.02	0.60	0.60	0
10.7	1.14	0.02	1.16	1.16	0
12. $\bar{5}$	0.12	0.04	0.16	0.14	-0.02
12.5	0.14	0.02	0.16	0.16	0
31. $\bar{1}$	0.50	0	0.50	0.46	-0.04
31.1	0.54	0	0.54	0.48	-0.06

were used:⁸ $B_{\text{Cr}} = 0.352 \times 10^{-12}$ cm and $b_{\text{Te}} = 0.56 \times 10^{-12}$ cm, and as magnetic form factor the one for Cr³⁺ calculated by Watson and Freeman.⁹

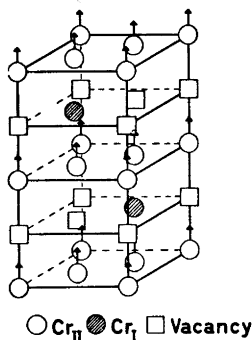
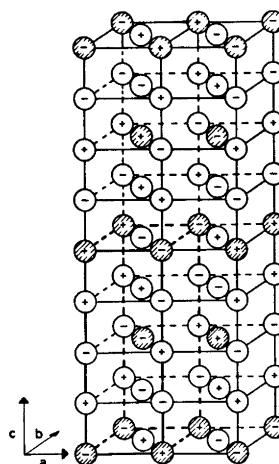
In Table 4 are given the final values of the refined parameters together with their standard deviations. The atomic positions deviate slightly from the ideal NiAs-type positions, and the preferred orientation parameter is closely the same in both refinements. The temperature parameters at 4.2°K are unreasonably high in particular for Cr. This may be partly due to the use of an

Table 4. Result of least squares profile refinement on Cr_2Te_3 .

		293°K	4.2°K
Cr_{II} in (f)	$z =$	0.000 ± 0.002	-0.007 ± 0.002
Te in (g)	$x =$	0.340 ± 0.002	0.337 ± 0.003
	$y =$	0.003 ± 0.002	0.000 ± 0.002
	$z =$	0.372 ± 0.001	0.379 ± 0.002
Isotropic	$B_{\text{Cr}} =$	$(1.42 \pm 0.23) \text{ \AA}^2$	$(2.71 \pm 0.52) \text{ \AA}^2$
	$B_{\text{Te}} =$	$(0.82 \pm 0.13) \text{ \AA}^2$	$(0.76 \pm 0.18) \text{ \AA}^2$
	$G =$	0.21 ± 0.01	0.20 ± 0.01
Cr_1 in (c)	$\mu_x =$		$(0.20 \pm 0.18) \mu_{\text{B}}$
Cr_{II} in (b)	$\mu_x =$		$(2.49 \pm 0.29) \mu_{\text{B}}$
Cr_{II} in (f)	$\mu_x =$		$(2.61 \pm 0.23) \mu_{\text{B}}$
	$R_{\text{nucl}} =$	7.9 %	3.4 %
	$R_{\text{magn}} =$		2.0 %

inappropriate magnetic form factor. However, the amount of magnetic data was in this case not sufficient to warrant any adjustment of the form factor. Putting $B = 0.2$ for both Cr and Te the R -factor increased, but the other parameters remained the same.

The average magnetic moment in the fully occupied layers is $2.56 \mu_{\text{B}}$, whereas the atoms in the vacancy layers have a negligible ferromagnetic moment. An antiferromagnetic alignment of the moments in the vacancy layers was also attempted, but led to the same result. This is in agreement with what had previously been found. As a complete disorder of these moments down to 4.2°K seemed highly unlikely other type of arrangements like a spiral structure was also considered. No satellite peaks were found, but the possibility still exists that these could not be resolved due to a long periodicity of the spiral. Using good collimation a thorough search was made for a $(000)^{\pm}$ satellite, but none was found down to $2\theta = 2^\circ$.

Fig. 1. Unit cell of Cr_2Te_3 . Te atoms omitted.Fig. 2. Unit cell of Cr_2Te_6 . Positions with shaded atoms $1/3$ occupied.

NEUTRON DIFFRACTION INVESTIGATION OF Cr₅Te₆

Neutron diffraction diagrams of Cr₅Te₆ were obtained at 293°K, 80°K, and 4.2°K. The diagram at 293°K could be indexed on the monoclinic unit cell indicated with heavy lines in Fig. 2 having the dimensions given by Grønvold and Westrum¹⁰ (Table 5). At 80°K and 4.2°K a series of additional

Table 5. Lattice constants of Cr₅Te₆.

	Temp.	<i>a</i>	<i>b</i>	<i>c</i>	<i>β</i>
Grønvold & Westrum	Room temp.	6.913	3.970	12.44	90.68°
This work	4.2°K	6.857	3.954	12.272	91.17°

lines appeared, which required a doubling of the unit cell in the *a* and *c* direction as shown in Fig. 2. In the diagram obtained at 4.2°K (Fig. 3) these superreflections are indicated with half indices. Whereas in the room temperature diagram the number of resolved reflections was not sufficient to allow a reliable estimate of the lattice constants, the presence of the superreflections at 4.2°K increased the amount of data so that a least squares analysis could be performed. The lattice constants derived for this temperature are given in Table 5.

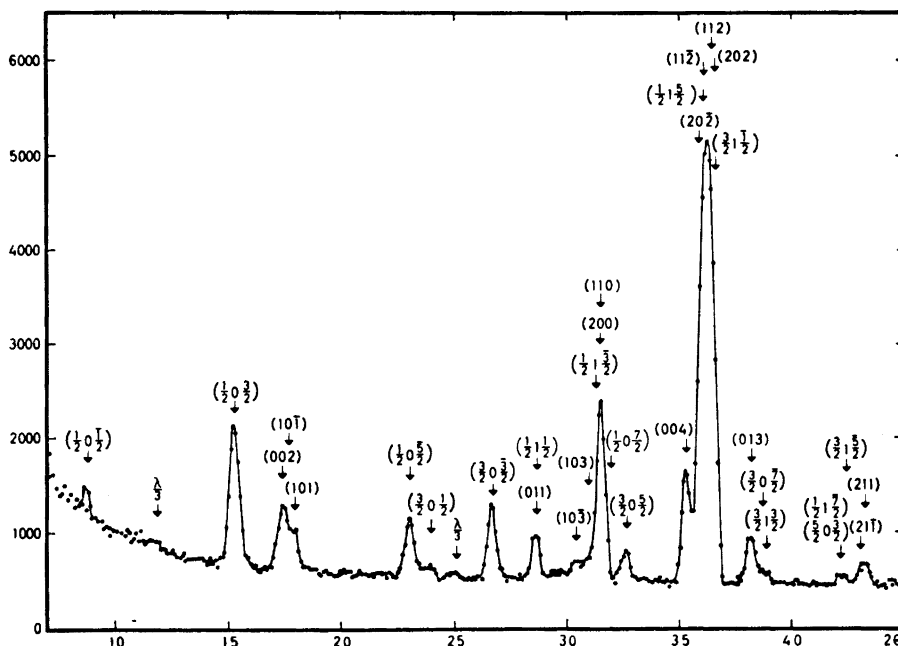


Fig. 3. Neutron diffraction diagram of Cr₅Te₆ at 4.2°K. $\lambda = 1.864 \text{ \AA}$.

Applying a magnetic field along the scattering vector at 4.2°K the intensity of the peaks at 17.5°, 28.5°, and 31.5° (Fig. 3) were reduced. These peaks, which thus have a significant ferromagnetic contribution, are all indexable on the small unit cell. From the change in the intensity of the (110) peak with the field strength it was apparent that saturation had not been achieved at the maximum attainable field, 6 kOe. The superreflections were all unaffected by the magnetic field, and should be ascribed to an antiferromagnetic component.

The situation is very similar to that observed for Cr_3Te_4 by Bertaut *et al.* However, whereas in that compound the Néel point was stated to be 80°K, the antiferromagnetic reflections in Cr_5Te_6 are only slightly reduced at this temperature. On further heating the intensity decreases only slowly until the temperature approaches 100°K where an abrupt change is taking place. From these measurements the Néel temperature is estimated to $102 \pm 2^\circ\text{K}$. The Curie point was determined by extrapolating the (110) reflection to zero. The intensity showed a Brillouin type dependence corresponding to a Curie point of $327 \pm 2^\circ\text{K}$.

Due to the increased amount of Cr the vacant positions, a , in Cr_3Te_4 are now being occupied each by 1/3 Cr-atom. It was considered whether in this case the vacancies were distributed also over the other positions in the vacancy layers. However, from the observed intensities, in particular the strong (011) reflection, this possibility could be ruled out. In the following calculations a complete ordering was assumed with the atomic positions as given in Table 6. The parameters are the same as those derived for Cr_3Te_4 by

Table 6. Atomic positions in Cr_5Te_6 . Space group $I2/m - C_{2h}^2$.

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

$\frac{3}{4}$ Cr _I	in a :	(0,0,0)
2 Cr _I	in c :	(0,0, $\frac{1}{2}$)
4 Cr _{II}	in i :	$\pm(x,0,z)$ $x=0.022$ $z=0.240$
4 Te	in i :	$\pm(x,0,z)$ $x=0.336$ $z=0.866$
4 Te	in i :	$\pm(x,0,z)$ $x=0.329$ $z=0.379$

Bertaut *et al.*⁶ from single crystal X-ray data. Due to the severe overlapping of the reflections, in particular at high angles, no attempt was made at deriving separate parameters for Cr_5Te_6 . For the same reason only the lower part of the diagram out to $\sin \theta/\lambda = 0.20$ was used.

The observed ferromagnetic intensities are in agreement with an alignment of the ferromagnetic component along the a -axis. This is also what Bertaut *et al.*⁶ deduced for Cr_3Te_4 by determining the orientation of a small single crystal in a magnetic field. The antiferromagnetic component is thus confined to the bc -plane.

As for the type of antiferromagnetic order Bertaut *et al.*⁶ derived from symmetry considerations four possible arrangements which they termed A, B, C, and D. Cr_3Te_4 was found to have a C-type of ordering. This is characterized by a propagation vector $\frac{1}{2}0\frac{1}{2}$, and an ordering in which each plane parallel to (101) contains atoms, not only of one kind, but of one particular

spin orientation. Since Cr_5Te_6 gives the same antiferromagnetic reflections as Cr_3Te_4 with approximately the same relative intensities we assume the same type of ordering. The distribution of the sign of the antiferromagnetic spin components is shown in Fig. 2.

If we assume two different spin values, S_I for the atoms in the vacancy layers and S_{II} for the atoms in the fully occupied layers we have four spin components to determine, the ferromagnetic components S_{If} , S_{IIf} and the

Table 7. Observed and calculated intensities for Cr_5Te_6 at 4.2°K.

hkl	I_{nucl}	I_{antif}	I_{ferro}	I_{tot}	I_{obs}
$\frac{1}{2}0\frac{1}{2}$		1.01		1.01	0.59
$\frac{1}{2}0\frac{3}{2}$		6.03		6.03	5.41
002	0.39		2.11	3.66	3.51
101	0.06		0.32		
101	0.25		0.53		
$\frac{1}{2}0\frac{5}{2}$		1.55		1.55	1.91
$\frac{3}{2}0\frac{1}{2}$		0.33		0.33	0.41
$\frac{3}{2}0\frac{3}{2}$		1.98		1.98	1.99
011	0.23		0.94	1.20	1.54
$\frac{1}{2}1\frac{1}{2}$		0.03			
103	0.03		0.59	0.62	0.68
103	0.17		0.37		
$\frac{1}{2}1\frac{3}{2}$		0.53		6.58	6.59
200	0		0		
110	0.01		5.50		
$\frac{3}{2}0\frac{5}{2}$		0.86		0.86	0.88
004	1.26		2.52	3.78	3.69
$\frac{1}{2}1\frac{5}{2}$		0.44		26.00	25.91
202	3.46		0.08		
112	9.72		0.48		
112	6.52		0.44		
202	4.78		0.07		
$\frac{3}{2}1\frac{1}{2}$		0.01		1.67	1.80
013	0.57		0.59		
$\frac{3}{2}0\frac{7}{2}$		0.12			
$\frac{3}{2}1\frac{3}{2}$		0.39		0.42	0.45
$\frac{5}{2}0\frac{1}{2}$		0			
$\frac{1}{2}0\frac{7}{2}$		0			
$\frac{3}{2}0\frac{5}{2}$		0.12			
$\frac{1}{2}1\frac{7}{2}$		0.09			
$\frac{3}{2}1\frac{5}{2}$		0.21		0.54	0.92
211	0.05		0.06		
211	0.24		0.19		

antiferromagnetic components S_{Ia} , S_{IIa} . Since most of the ferromagnetic peaks have overlapping reflections whereas there are six resolved antiferromagnetic peaks, we first determine the antiferromagnetic components.

The structure factor for the antiferromagnetic reflections is

$$F_{a'}(h', k', l') = \alpha(h', k', l') \cdot R(h', k', l')$$

where

$$\alpha(h', k', l') = 1/3 S_{Ia} + S_{Ia} \exp(\pi i l' / 2) - 2i S_{IIa} \sin 2\pi(h'x + l'z)$$

$$R(h', k', l') = [1 - \exp(\pi i h')] [1 - \exp(\pi i l')] [(1 + \exp(\pi i k')) \exp(\pi i / 2)(h' + l')]$$

Dashed indices refer to the supercell.

From the expression for $R(h', k', l')$ we see that all antiferromagnetic reflections must have h' and l' odd. Further, if $k' = 0$, only reflections with $h' + l' = 4n$ can occur. If $k' = 1$ the condition is $h' + l' = 4n + 2$. Within the angular range we consider these to be the only possible values of k' .

Using the almost purely nuclear peak consisting mainly of the reflections $(20\bar{2})$, $(11\bar{2})$, (112) , and (202) , and adjusting later for small magnetic contributions, the observed intensities could be put on an absolute scale (Table 7).

As mentioned above, the ferromagnetic contributions indicated the ferromagnetic component to be along the a -axis. From the relative intensities of the antiferromagnetic reflections we deduce that these components are parallel to the b -axis. With this orientation the observed intensities of the six resolved antiferromagnetic peaks give the following relations:

$$\begin{aligned} (1'01') \quad S_{Ia} - 1.27S_{IIa} &= -0.35 \\ (1'03') \quad S_{Ia} + 1.45S_{IIa} &= 1.89 \\ (1'0\bar{5}') \quad S_{Ia} + 1.06S_{IIa} &= 1.83 \\ (3'01') \quad S_{Ia} - 1.64S_{IIa} &= -0.89 \\ (3'0\bar{3}') \quad S_{Ia} + 1.77S_{IIa} &= 2.29 \\ (3'05') \quad S_{Ia} + 1.48S_{IIa} &= 2.04 \end{aligned}$$

From these equations the antiferromagnetic components could be derived using a least squares refinement procedure: $S_{Ia} = 0.70 \pm 0.06$; $S_{IIa} = 0.90 \pm 0.04$.

Subtracting now the nuclear and antiferromagnetic contributions, the ferromagnetic intensities were obtained. Due to overlapping reflections, sufficient data for a least squares analysis were not available. However, assuming the ferromagnetic components to point along the a -axis, the following average values could be deduced: $S_{If} = 2.0$; $S_{IIf} = 0.66$.

These values, together with those above, led to a very satisfactory agreement between the observed and calculated intensities as shown in Table 7. The total spin values are:

$$S_I = 2.12; \quad S_{II} = 1.12.$$

Both S_I and S_{II} lie in the ab -plane, S_I making an angle of 19° and S_{II} an angle of 54° with the a -axis.

The average ferromagnetic moment per atom, assuming $g = 2$, is $2.40 \mu_B$ in excellent agreement with the values $2.39 \mu_B$ obtained by Guillaud¹¹ and $2.45 \mu_B$ measured by Lotgering and Gorter.¹² These values were obtained by magnetization measurements on CrTe. However, as previously mentioned, stoichiometric CrTe does not exist at room temperature and the composition has probably been close to Cr_5Te_6 . The paramagnetic moment value, based on the average spin, is $3.92 \mu_B$ per atom also in excellent agreement with the value $3.99 \mu_B$ measured by Lotgering and Gorter.¹²

NEUTRON DIFFRACTION INVESTIGATION OF Cr₃Te₄

In their previous investigation of Cr₃Te₄ Bertaut *et al.*⁶ were not able to determine with precision the values of all the spin components. Due to low resolution and overlapping $\lambda/2$ -reflections from the brass of the cryostat, only one antiferromagnetic reflection was measured. They assumed the total spins to be $S_I=2$ and $S_{II}=1.5$ and deduced that nearly the whole of S_I was engaged in the ferromagnetic spin system, whereas S_{II} participated about equally in the ferromagnetic and the antiferromagnetic spin system.

A neutron diffraction diagram of Cr₃Te₄ obtained at 4.2°K is shown in Fig. 4. This is very similar to that of Cr₅Te₆ except for some characteristic

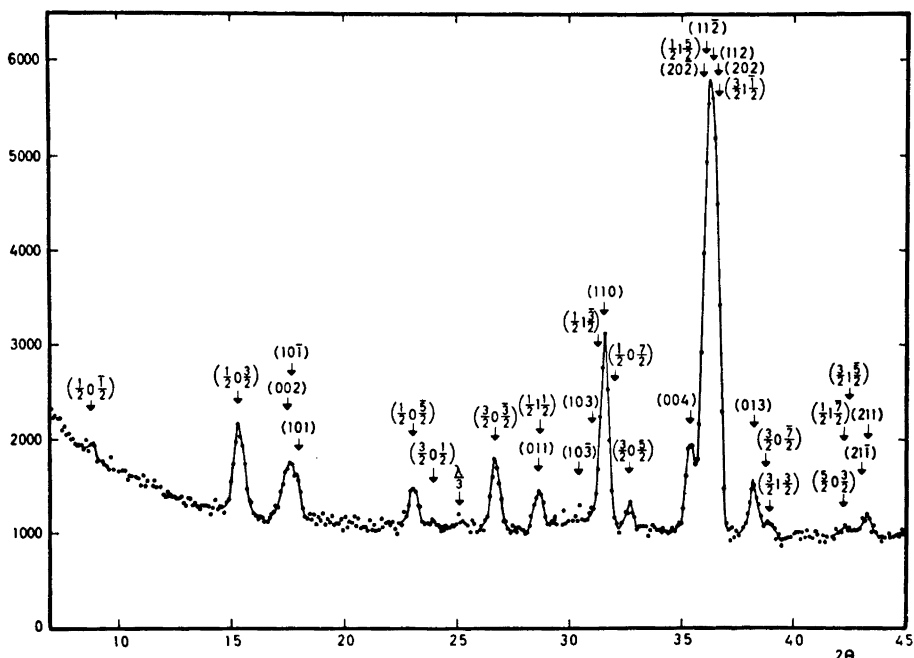


Fig. 4. Neutron diffraction diagram of Cr₃Te₄ at 4.2°K. $\lambda=1.864$ Å.

intensity changes. The ferromagnetic contributions are also here in agreement with an alignment of the ferromagnetic components along the a -axis. However, for the antiferromagnetic reflections one observes changes in the intensity ratios which cannot be ascribed to changes in the magnitudes of the antiferromagnetic spin components alone. They can, however, be explained from a turning of these components in the bc -plane. In fact, the observed changes in going from Cr₅Te₆ to Cr₃Te₄ correspond to a turning of the antiferromagnetic components from pointing along the b -axis to point in the $(\vec{b} + \vec{c})$ direction.

Under this assumption the six resolved antiferromagnetic peaks give the following relations:

$$\begin{aligned}
 (1'0\bar{1}') \quad S_{Ia} - 1.27S_{IIa} &= -0.31 \\
 (1'03') \quad S_{Ia} + 1.45S_{IIa} &= 1.95 \\
 (1'0\bar{5}') \quad S_{Ia} + 1.06S_{IIa} &= 1.92 \\
 (3'01') \quad S_{Ia} - 1.64S_{IIa} &= -0.69 \\
 (3'0\bar{3}') \quad S_{Ia} + 1.77S_{IIa} &= 2.41 \\
 (3'05') \quad S_{Ia} + 1.48S_{IIa} &= 2.38
 \end{aligned}$$

From these a least squares refinement gives the following antiferromagnetic components: $S_{Ia} = 0.84 \pm 0.07$; $S_{IIa} = 0.92 \pm 0.05$.

For the ferromagnetic components the following average values were deduced assuming their orientation to be along the a -axis: $S_{If} = 1.45$; $S_{IIf} = 1.18$. The obtained agreement between the observed and the calculated intensities is shown in Table 8. The total spin values of the two types of ions are:

$$S_I = 1.68; \quad S_{II} = 1.50.$$

Table 8. Observed and calculated intensities for Cr_2Te_4 at 4.2°K.

hkl	I_{nucl}	I_{antif}	I_{ferro}	I_{tot}	I_{obs}
$\frac{1}{2}0\frac{1}{2}$		0.44		0.44	0.39
$\frac{1}{2}0\frac{3}{2}$		4.48		4.48	3.94
002	0.77		0.88	3.38	2.97
10 $\bar{1}$	0.25		0.25		
101	0.53		0.70		
$\frac{1}{2}0\frac{1}{2}$		1.03		1.03	1.16
$\frac{1}{2}0\frac{3}{2}$		0.22		0.22	0.24
$\frac{3}{2}0\frac{1}{2}$		2.01		2.01	1.90
011	0.47		1.01	1.57	1.55
$\frac{1}{2}1\frac{1}{2}$		0.09			
10 $\bar{3}$	0.11		0.95	1.06	—
103	0.30		0.45		
$\frac{1}{2}1\frac{3}{2}$		1.36		7.11	7.04
200	0.02		0		
110	0.01		4.97		
$\frac{1}{2}0\frac{7}{2}$		0.07		0.07	—
$\frac{3}{2}0\frac{1}{2}$		0.78		0.78	0.91
004	1.56		2.26	3.82	3.48
$\frac{1}{2}1\frac{1}{2}$		0.64		25.92	25.85
20 $\bar{2}$	3.01		0.02		
11 $\bar{2}$	10.83		0.18		
112	5.37		0.19		
202	5.62		0.03		
$\frac{3}{2}1\frac{1}{2}$		0.03		1.78	1.73
013	0.89		0.89		
$\frac{3}{2}0\frac{7}{2}$		0.06		0.69	0.57
$\frac{3}{2}1\frac{3}{2}$		0.63			
$\frac{3}{2}0\frac{1}{2}$		0			—
$\frac{1}{2}0\frac{9}{2}$		0			—
$\frac{3}{2}0\frac{3}{2}$		0.26		0.60	0.51
$\frac{1}{2}1\frac{7}{2}$		0.05			
$\frac{3}{2}1\frac{1}{2}$		0.29			
211	0.01		0.03	0.71	0.87
211	0.40		0.27		

The spins are nearly parallel forming angles of, respectively, 30° and 38° with the a -axis.

The average ferromagnetic moment per atom is $2.54 \mu_B$, assuming $g=2$.

The spin components of the Cr_{II} ions are very close to the values deduced by Bertaut *et al.*, $S_{IIa}=0.99$ and $S_{IIb}=1.13$. However, their assumption that nearly the whole of S_I is taking part in the ferromagnetic spin system cannot be sustained.

The antiferromagnetic peaks were found to disappear at $85 \pm 2^\circ\text{K}$, whereas Bertaut *et al.* gave a Néel point of 80°K . This discrepancy can be due to a slight difference in composition. From the disappearance of the (110) reflection the Curie point was estimated to $325 \pm 2^\circ\text{K}$.

DISCUSSION AND CONCLUSIONS

In slowly cooled Cr₂Te₃ we have observed an ordered superstructure of the type described by Chevreton⁴ involving an ordering of the vacancies on every second metal layer. In the fully occupied layers the moments are ferromagnetically aligned with an average moment value of $2.56 \mu_B$. The moments in the vacancy layers seem to give a negligible ferro- or ferrimagnetic contribution. As it seems highly unlikely that the spins on these ions are very small, an antiferromagnetic or spiral arrangement could be expected. No peaks corresponding to arrangements like these have been found, but it cannot be excluded that they are too weak to be detected. In case of a spiral structure the period may be so large that the satellite peaks could not be separated. Making a careful search for a (000)[±] satellite no peak was observed down to $2\theta = 2^\circ$.

From the following arguments the forces tending to align these moments along the trigonal axis can in fact be expected to be weak. First of all we observe that the ordering of the vacancies within the vacancy layers have removed all the nearest neighbour metal atoms, so that the closest metal-metal distance in this direction is 6.83 Å. Thus within these layers only long range superexchange forces can be expected to be operative. Along the c -axis the nearest neighbour metal-metal distance is only 2.98 Å, and one should expect strong interactions. However, for the similar compounds Cr₃X₄ (X=S,Se,Te) Bertaut *et al.*⁶ have found that the resultant interaction along the c -axis is strongly negative for Cr₃S₄, weakly negative or close to zero for Cr₃Se₄ and positive for Cr₃Te₄. The interatomic distances are respectively 2.82 Å, 2.94 Å and 3.09 Å. We thus observe that the c -axis metal-metal distance in Cr₂Te₃ is exactly in the range where Bertaut *et al.* observed a transition from a negative to a positive exchange. Thus it appears possible that neither the exchange interactions within the vacancy layers, nor the exchange interactions to the neighbouring layers will be able to align these moments.

It was originally observed by Haraldsen and Neuber¹⁴ that the paramagnetic Curie point after remaining approximately constant at 343° to 353°K up to 57 % Te showed a rapid drop between 57 % and 60 % Te to 193°K . Correspondingly we find that the ferromagnetic Curie point which is $327 \pm 2^\circ\text{K}$ for Cr₅Te₆ (54.5 % Te) and $325 \pm 2^\circ\text{K}$ for Cr₃Te₄ (57.1 % Te) drops to $182 \pm 2^\circ\text{K}$ for Cr₂Te₃ (60 % Te). It seems reasonable to associate this with the ordering

of the vacancies and the weak exchange taking place within and through the vacancy layers when the composition approaches 60 % Te. From electrical resistivity and magnetization measurements Gaidukov *et al.*¹⁵ deduced a Curie point of 330°K for all compositions below 56 % Te. Bertaut *et al.*⁶ found for Cr₃Te₄ 329°K.

For Cr₃Te₄ the Néel point was observed at 85 ± 2°K, whereas Bertaut *et al.*⁶ found 80°K. This discrepancy can be attributed to a slight difference in composition, as the Néel point, in contrast to the Curie point, depends strongly on composition. In going from Cr₃Te₄ to Cr₅Te₆ the Néel point was found to increase from 85°K to 102°K. This is undoubtedly due to the stronger exchange forces connected with the filling up of the vacancies.

In Cr₂Te₃ the ferromagnetic moments are found to be aligned along the *c*-axis as previously assumed.³ However, in Cr₃Te₄ and Cr₅Te₆ the ferromagnetic component is along the *a*-axis. The antiferromagnetic component is pointing along the *b*-axis in Cr₅Te₆ and close to the ($\vec{b} + \vec{c}$) direction in Cr₃Te₄.

Bertaut *et al.*⁶ assumed for Cr₃Te₄ that nearly the whole spin of the Cr_I ion takes part in the ferromagnetic spin system. We have found this to be the case for Cr₅Te₆ but not for Cr₃Te₄. In Cr₅Te₆ the spins of the Cr_I ions make an angle of approximately 19° with the *a*-axis whereas the spins of the Cr_{II} ions make an angle of 54°. In Cr₃Te₄ the spins are nearly parallel forming angles of approximately 30° and 38° with this axis.

In Cr₃Te₄ the observed moment values are 3.36 μ_B for the Cr_I ions and 3.00 μ_B for the Cr_{II} ions. Considering this as an ionic compound one would expect the Cr_I ions to have the valency Cr²⁺ and the Cr_{II} ions the valency Cr³⁺. The observed moment of the Cr_I ions is then lower than the 4.00 μ_B we should expect for a Cr²⁺ ion, but the moment for the Cr_{II} ion is exactly that expected for a Cr³⁺ ion. Bertaut *et al.* assumed the two type of ions to have the moments 4 μ_B and 3 μ_B , respectively, and this is partly the reason why their components of the Cr_{II} ions agree so closely with those derived here.

The difference in the observed moment above and below the Curie point can now be explained from the tilting of the moments. The average ferromagnetic moment per atom for Cr₅Te₆ deduced from the observed ferromagnetic components is 2.40 μ_B , whereas from magnetization measurements Guillaud and Barbezat¹¹ found 2.39 μ_B and Lotgering and Gorter¹² 2.45 μ_B . The observed total spin would give an average paramagnetic moment value of 3.92 μ_B per atom in excellent agreement with the value 3.99 μ_B observed by Lotgering and Gorter.

From magnetization measurements Bertaut *et al.*⁶ deduced for Cr₃Te₄ a moment value at saturation of 7.05 μ_B per formulae unit. The ferromagnetic components derived here give a value of 7.62 μ_B .

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