Neutron diffraction studies of chromium telluride at high pressures

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The first results are reported of neutron diffraction studies of the magnetic P, T phase diagram of chromium telluride in the interval 7–300 K and pressures up to 35 kbar. It is established that the magnetic contribution to the nuclear reflection disappears at high pressures. At low temperatures at small scattering angles there is a weak antiferromagnetic peak which is stable over the entire pressure range investigated. The results confirm the existence of a magnetic phase transition at high pressures, as established earlier in chromium telluride by means of electron paramagnetic resonance.

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INTRODUCTION

The magnetic properties of chromium telluride are very sensitive to change of the interatomic distances[1] and to the smallest distortion of the crystal structure.[2-4] Investigations have shown[2-4] that quenched, disordered Cr-Te alloys (in the concentration range from 50 to 54 at.% Te) have a hexagonal crystal structure of the NiAs type (space group $P6_3/mmc$) and a Curie temperature T_c =340 K. Under the influence of high pressure the Curie point is greatly depressed, $dT_c/dP = -6$ deg/kbar,[1] and at pressures 25–30 kbar and $T = 100$ K ferromagnetism disappears in chromium telluride, as indicated by experiments on electron magnetic resonance.[5]

The nature of the magnetic transition arising in chromium telluride at high pressures is not clear. It may be a first-order magnetic phase transition, from the ferromagnetic to the paramagnetic state (F/P) or a transition due to a change of the magnetic structure from the ferromagnetic to the antiferromagnetic state (F/AF). According to the thermodynamic theory of Bean and Rodbell,[6,7] the cause of such magnetic transformations is a strong dependence of the exchange integral on the interatomic distances. However, there are also good reasons to suppose that part of the $3d$ electrons of chromium telluride are in a collectivized state, since CrTe is a semimetal, and in this case a magnetic transformation in the region 25–30 kbar may be due to modification of the band ferromagnetism.[8]

Consequently it is of interest to carry out studies of the P, T phase diagram of chromium telluride by means of neutron diffraction, in order to determine the magnetic structure of CrTe at high pressures and low temperatures. In the present work we report the first results of such studies, which were carried out at the Laue-Langevin Institute and the Institute of Strong Fields at Grenoble.

PREPARATION OF ALLOYS AND METHOD OF MEASUREMENT

All measurements were made in powdered polycrystalline samples of the alloy CrTe (50 at.% Te) prepared in the following manner: finely ground, well mixed powders of the initial chemically pure elements Cr and Te were pressed in the form of blocks $6 \times 5 \times 30$ mm and heated to 1000° C in evacuated double quartz ampoules. The temperature was raised slowly for a period of 29 hours, held at 1000° C for 29 hours, and the sample then quenched in water. The alloy obtained was powdered, again carefully mixed, pressed, and subjected to homogenizing annealing (24 hours) in vacuum at 1000° C with subsequent quenching in water. X-ray diffraction and microstructure phase analyses showed that in addition to the main CrTe phase there is also Cr in very small quanities. All diffraction lines in the diffraction patterns taken at room temperature were indexed on the basis of a hexagonal lattice of the NiAs type with the unit cell parameters $a = 4.000 \pm 0.005$ Å and $c = 6.240 \pm 0.007$ Å.

To carry out neutron-diffraction studies at high pressures we used a portable apparatus (weight 4.5 kg and outer diameter 68 mm) which has been described by Bloch et al.[9] The high-pressure cell is made of high-strength aluminum oxide, a material rather transparent for thermal neutrons. Its inner diameter was 5 mm, outer diameter 20 mm, and height 26 mm. The pressure inside the cell was determined by measurement of the lattice parameters of sodium chloride, which simultaneously served as the medium transmitting the pressure to the sample under study. For this purpose the CrTe sample in the form of a powder was placed between the two lightly pressed disks of sodium chloride. In order to avoid extrusion of the sample through the cracks which are formed in the high-pressure cell in the compression process, the sample and the NaCl were

placed inside a thin-walled tube of high-strength aluminum alloy. A piston of tungsten carbide entered the cell through a channel with a small gap. Extrusion of the sample into the gap was avoided by two ring gaskets with cadmium covering.

To carry out the experiments at low temperatures, the high-pressure chamber was placed in a cryostat with inner diameter 70 mm. The temperature in the cryostat was controlled by a flow of gaseous helium and monitored by means of a GaAs diode placed in thermal contact with one cell.

Neutron diffraction patterns were taken with a D2 diffraction camera at the Laue-Langevin Institute in Grenoble, France. The number of monitor readings was 2×10^5. A copper monochromator with reflection from the (111) plane was used, with a neutron wavelength 1.22 Å.

RESULTS AND DISCUSSION

Neutron diffraction patterns were obtained at pressures of 1, 15, and 35 kbar and temperatures 7–9, 75, and 298 K for each of the pressures. A typical diffraction pattern for $P = 35$ kbar and $T = 9$ K is shown in Fig. 1, where reflections arising from the chamber material (Al_2O_3), from NaCl, and from the CrTe sample studied are visible.

The weak intensities of the reflections from chromium telluride, resulting from the small size of the sample, of weight 1 gram, and also the partial superposition of the spectra of the chamber material and CrTe, did not permit determination of the magnetic moments of chromium telluride at high pressures. Accordingly, to obtain a diffraction pattern only of the CrTe sample (without the chamber) we took neutron diffraction patterns at atmospheric pressure at the Grenoble Nuclear Center (C.E.N.–G) with use of large amounts of chromium telluride powder of weight up to 10 grams. Here the neutron wavelength was $\lambda = 1.15$ Å.

In Fig. 2 we have shown the chromium telluride neutron diffraction patterns obtained at atmospheric pressure and temperatures $T = 298$ and 4.2 K, where in addition to the (100), (002), and (011) reflections, which were indexed on the basis of a hexagonal lattice of the
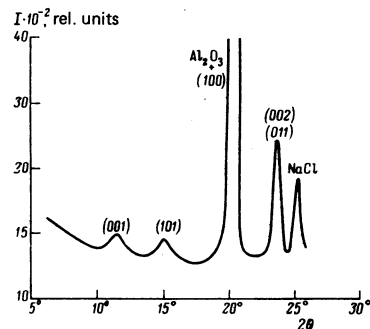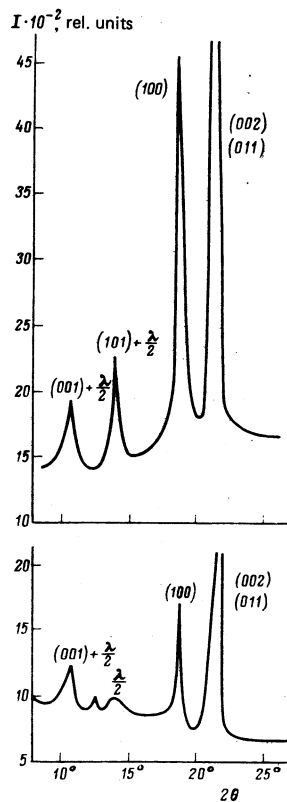

FIG. 2. Neutron diffraction patterns of chromium telluride obtained at atmospheric pressure and $T = 298$ K (below) and 4.2 K (above), $\lambda = 1.15$ Å. The indexing of the nuclear reflections (100), (002), and (011) is given in the hexagonal indices; the antiferromagnetic reflection (101) is given in the orthorhombic indices with the parameters $a' = 3^{1/2} a$; $b' = b$, $c' = c$.

NiAs type, at $T = 4.2$ K we can observe an antiferromagnetic reflection which can be indexed in the orthorhombic indices (101) with unit cell parameters $a' = 3^{1/2} a$, $b' = b$, and $c' = c$. In addition, at small angles $2\theta = 11.5°$ a weak (001) line is observed. This reflection is forbidden for a hexagonal structure of the NiAs type and may be due to a superstructure of ordered vacancies, as has already been noted elsewhere.[2,3]

Comparison of the neutron diffraction patterns obtained at $T = 298$ and 4.2 K indicates a large ferromagnetic contribution to the intensity of the (100) reflection. Thus, at atmospheric pressure and low temperatures there appears a coexistence of ferromagnetism and a weak antiferromagnetic mode (101).

Separation of the ferromagnetic contribution to the (100) reflection at high pressures was carried out by comparison of diffraction patterns obtained at room temperature and at low temperatures. These data are given in the Table. The difference in intensities, due to thermal factors in the temperature interval 7–300 K, is 550 relative units. Thus, the magnetic contribution I_{mag} to the intensity of the (100) reflection at 15 kbar amounts to 7200 relative units, and at 35 kbar this contribution in zero (within the error of our experiments), which enables us to conclude that ferromagnetism disappears at high pressures. The intensity of the (101) reflection at low temperatures does not change with in-

FIG. 1. Neutron diffraction pattern of chromium telluride taken at $P = 35$ kbar and $T = 9$ K, $\lambda = 1.22$ Å. The (100) reflection from CrTe is superimposed on the spectrum of the high-pressure cell (Al_2O_3). The (101) reflection is given in the indices of the antiferromagnetic unit cell.

TABLE I. Integrated intensity of the (100) reflection from CrTe and from Al_2O_3 at various temperatures and $P = 15$ and 35 kbar.

P, k bar	T, K	2θ, deg	Intensity I, rel. units	Error ΔI
15	298	20.2	13 156	400
	7	20.4	20 903	500
35	298	20.2	14 817	400
	75	20.2	15 849	400
	9	20.3	17 000	630

creasing pressure and in the interval 15–35 kbar it is $I_{(101)} = 1350 \pm 500$ relative units.

It should be noted that the presence of the antiferromagnetic (101) component in neutron diffraction patterns of chromium telluride at $T = 4.2$ K and atmospheric pressure was first observed by Cox, Chirane, and Takei,[10] who associated it with the noncollinear canted magnetic structure predicted theoretically by de Gennes on the basis of a double exchange mechanism.[11] Cox *et al.*[10] noted that at $T_s = 150$ K the (101) reflection disappears as a result of conversion of the noncollinear structure into a ferromagnetic structure. This transition is easily observed in Cr–Te alloys with a distorted crystal structure of the NiAs type on the basis of curves of the temperature dependence of the magnetization, which have a maximum at the point T_s. It was shown earlier[12] that T_s increases considerably with increase of pressure: $dT_s/dP = 6.2 \pm 0.2$ deg/kbar, which indicates an increase of the energy of antiferromagnetic exchange with decrease of the interatomic distances.

Our results indicate that at low temperature the antiferromagnetic component is almost independent of pressure. Thus, the two magnetic modes behave differently: the ferromagnetic component drops off at high pressure, and the antiferromagnetic component does not depend on pressure within the error of our experiments. These data, it appears to us, deserve attention, since the stability of noncollinear magnetic structures in the framework of the de Gennes double-exchange model is at the present time under discussion. For example, it has been shown[13,14] that in alloys with a narrow 3d band and a sufficient concentration of electrical current carriers, noncollinear magnetic structures are unstable, and instead of them an inhomogeneous ferromagnetic and antiferromagnetic state of the crystal is realized.

CONCLUSION

On the basis of the experimental results we can conclude that in chromium telluride at pressures above 30 kbar a magnetic phase transition occurs, in agreement with data on electron magnetic resonance. This transition involves disappearance of ferromagnetism without appearance of any new antiferromagnetic structure. Such a new phase could be expected according to the model of Bean and Rodbell. However, for a final conclusion regarding the magnetic structure of CrTe at high pressures and low temperatures, further neutron diffraction studies in single crystals are necessary. The present experiments do not permit us to determine accurately the value of the magnetic moment. However, the large magnetic contribution to the (100) reflection at $P < 30$ kbar indicates the existence of a localized moment (approximately ~1.5 μ_B). This indicates that in chromium telluride there are both localized and collectivized 3d states.

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