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X-RAY DIFFRACTION STUDY OF THE THERMAL EXPANSION OF ANTIFERROMAGNETIC MnTe

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The variation of the critical lattice parameters of manganese telluride in the vicinity of the antiferromagnetic transition point was investigated by x-ray diffraction. A hypothesis concerning the magnetic structure of MnTe is advanced on the basis of the data obtained. The Néel point $T_N = 310°K$ was determined from the anomalous variation of the thermal expansion coefficient, and the dependence of T_N on hydrostatic pressure was determined.

An x-ray diffraction investigation of the thermal expansion coefficient of the antiferromagnetic compound MnTe is of interest for two reasons. A detailed study of the anomalous expansion or compression of the crystal along its principal crystallographic axes in the temperature region of the antiferromagnetic transition (T_N) leads to a hypothesis regarding the magnetic structure of this antiferromagnetic substance. X-ray diffraction studies of the antiferromagnetic oxides MnO, FeO, and NiO[1-3] have shown that the transition from the paramagnetic to the antiparamagnetic state of these compounds is accompanied by reduced symmetry of their lattices, which are of the cubic NaCl type. The definite magnetic structure of these compounds that was inferred from this result was confirmed by neutron-diffraction experiments.[4] Very few such investigations have thus far been made of substances with hexagonal lattices. A study of the antiferromagnetic compounds CrSb[5,6] and MnTe,[7] which possess a hexagonal lattice of the NiAs type, has shown that the change in the crystal lattice near the Néel temperature of these compounds consists only in a change of their axial dimensions without a transition to another symmetry class. It should be noted that the data for MnTe need verification, since the Néel temperature which was determined by Greenwald[7] from the anomalous variation of the thermal expansion coefficient ($T_N = +50°C$) differs markedly from the value of 35°C given by the same author in another article.[5]

Investigation of the anomalous thermal expansion around the Néel temperature makes it possible through the use of thermodynamical calculations to determine the variation of the antiferromagnetic transition temperature of manganese telluride under changing hydrostatic pressure. This is of interest for its own sake and for verification of the Néel-temperature shift under hydrostatic pressure which was measured by Grazhdankina.[8]

PREPARATION OF SAMPLE AND METHOD OF MEASUREMENT

Manganese telluride samples were prepared by fusing carefully mixed fine powders of manganese and tellurium in sealed evacuated quartz ampoules at $t = 800°C$. The raw material was electrolytic manganese of the following composition: 99.8% Mn, 0.07% S, 0.07% C, and 0.03% P. The manganese was remelted under a high vacuum for degassing. Chemical analysis of the tellurium showed the following: Te > 99.999%, 0.0001% Cu, 0.0002% Ag, Bi < 0.0001%, 0.0001% Sb, and As. Samples in the form of discs of 9 mm diameter and 1 mm thickness were prepared by pressing finely powdered manganese telluride in a special mold. This was followed by annealing at a low temperature. X-ray phase analysis showed the presence of traces of $MnTe_2$ in addition to the principal MnTe phase.

The thermal expansion coefficient of manganese telluride was determined by the x-ray diffraction method that was developed by Kosolapov and Trapeznikov,[9] which differs from the ordinary back-reflection method mainly by the possibility it affords of obtaining aluminum lines as a standard and lines of the test material on the same film. Errors due to film shrinkage during development can thus be avoided and the accuracy of the measurements is considerably enhanced. Using the aluminum lattice constant a (20°C) = 4.040 A and the linear thermal expansion coefficient $\alpha_{Al} = 25.5 \times 10^{-6}\ deg^{-1}$, we calculated the effective

Lattice constants and volume (V) of MnTe unit cell

T, °K	a, A	c, A	c/a	V, A[³]	T, °K	a, A	c, A	c/a	V, A[³]
253	4.083	6.696	1.639	96.66	320	4.091	6.716	1.642	97.34
286	4.086	6.700	1.639	96.90	334	4.093	6.719	1.642	97.46
293	4.087	6.701	1.639	96.93	347	4.093	6.723	1.642	97.52
306	4.088	6.708	1.640	97.08	358	4.094	6.724	1.642	97.59
313	4.089	6.716	1.642	97.24					

distance A between the sample and the film, which differed for different lines of the x-ray diffraction pattern. From a knowledge of A for the two extreme lines we could determine A for any intermediate line of MnTe (taking into account the thickness of the aluminum standard foil which was cemented to the surface of the sample). The constants of the MnTe lattice were calculated from the lines (135) α_1, (306) α_1 and (135) α_2, (306) α_2. The error in the constants a and c, defined as the mean deviation of individual values of a and c from the average of five values, amounted to 0.026%.

The photographs were taken with a KROS-1 camera using the x-ray lines $K\alpha_1 = 1.537$ A and $K\alpha_2 = 1.541$ A from a tube with a copper anticathode. The sample and cemented-on aluminum foil were clamped to a heater by means of a special band consisting of a hollow brass cylinder through which water flowed from a Hoeppler thermostatic bath thus maintaining the temperature of the sample constant to within 0.1°. For the production of low temperatures the thermostatic-bath liquid was ethylene glycol with dry ice as the refrigerant. Temperatures were measured by a potentiometer with the aid of a copper-constantan thermcouple clamped tightly to the sample.

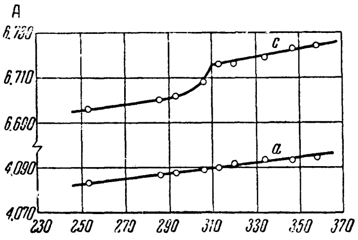

FIG. 1

RESULTS AND DISCUSSION

Thermal expansion of the manganese telluride lattice was investigated in the temperature range from 250 to 370°K. At room temperature (+20°C) the constants a and c had the following values: a = 4.087 ± 0.001 A and c = 6.701 ± 0.002 A. These differ somewhat from the values given by Oftedal[10] (a = 4.132, c = 6.711), Greenwald[3] (a = 4.142, c = 6.703) and Furberg[11] (a = 4.146, c = 6.709). The parameters of the MnTe lattice at different temperatures are shown in the table and in Fig. 1.

The given temperature range includes the antiferromagnetic transition temperature $T_N = 310$°K, at which point our measurements show a kink in the temperature dependence curves of electrical resistance and magnetic susceptibility. Figure 1 shows a kink located at the same point on the temperature dependence curve of the thermal expansion of c, although there is no change of the linearity of the temperature dependence of a in the same range. The ratio c/a increases from 1.639 at room temperature to 1.642 at 350°K. This represents an increase of unit cell volume by 0.27% during the transition from the antiferromagnetic to the paramagnetic state. A calculation of the linear thermal expansion coefficients along the a and c axes of the crystal gave the following results: $\alpha_a = 2.79 \times 10^{-5}$ deg^{-1}, α_c $(T > T_N) = 2.68 \times 10^{-5}$ deg^{-1} and α_c $(T < T_N) = 1.90 \times 10^{-5}$ deg^{-1}. At the Néel temperature the jump of the linear expansion coefficient along the c axis is $\Delta\alpha_c = 12 \times 10^{-5}$ deg^{-1} (Fig. 2). The volume thermal expansion coefficient of manganese telluride at T = 300°K is 7.48×10^{-5} deg^{-1}, which is close to the value of α_V for aluminum.

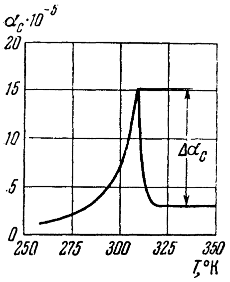

FIG. 2

As we compare our data with those of Greenwald[3] we must first note their qualitative agreement. In both instances we find that when manganese telluride is heated above T_N the anomalous expansion of the crystal occurs only along the c axis. The type of crystal structure was not observed to change within the investigated temperature range. However the temperature $T_N = 329$°K given by Greenwald and the anomalous change of the thermal expansion coefficient at the Néel temperature, $\Delta\alpha_c = 6 \times 10^{-5}$, are distinctly different from our results. We attribute this discrepancy to the fact that in the vicinity of T_N Greenwald measured the lattice parameters at large temperature intervals (20 to 30°), as a result of which it became very difficult to determine the exact position of T_N from a kink in the curve of c(T). The absolute values of c at different temperatures are in good agreement with our results.

The structure of the magnetic sublattices of the antiferromagnetic compound MnTe is unknown because no neutron-diffraction studies have been made up to the present time. However, by using the relation which Smart and Greenwald[3] established between the magnetic structure of antiferromagnetics and variations of the lattice parameter around T_N, as well as experimental results of the neutron-diffraction and x-ray diffraction studies of CrSb,[5,6] which has the same crystal structure as MnTe, we can draw some inferences regarding the magnetic structure of manganese telluride. The sharp change of crystal dimension along the c axis, while the constant a varies linearly, around T_N supplies evidence that the magnetic moments of the Mn atoms are parallel to the c axis, that is, perpendicular to the (001) plane, with all moments in any single (001) plane lined up parallel but with opposite orientations in neighboring (001) planes. Thus the nearest neighbors of Mn atoms have antiparallel magnetic moments, whereas next nearest neighbors have parallel moments.* In such a structure of the magnetic lattice the manganese atoms must interact mainly directly without participation of the tellurium atoms. The established anisotropic change of the lattice indicates that in the present case, unlike that of ferromagnets, magnetic forces rather than exchange forces are important at the magnetic transition temperature. From the foregoing we infer the invalidity for manganese telluride of Li's[13] ideas regarding the dominant role of a superexchange interaction in anisotropic changes of antiferromagnetic lattices upon passing through the Néel temperature.

In conclusion we shall calculate the shift of the Néel point of manganese telluride under hydrostatic pressure. Our value for the jump of the thermal expansion coefficient, $\Delta\alpha = 12 \times 10^{-5}$ deg^{-1}: and Kelley's value[12] for the anomalous change of the specific heat, $\Delta C_p = 5$ cal/deg-mol, at $T_N = 310°K$ are inserted into Ehrenfest's equation for a second order phase transition, $dT_n/dp = VT_N \times \Delta\alpha/\Delta C_p$. In calculating the molar volume V the density of manganese telluride was taken from x-ray data to be 12.48 g/cm^3. Our result is $dT_N/dp = 2.6 \times 10^{-3}$ deg/kg/cm^2, which agrees within the limits of experimental error with the value for dT_N/dp obtained through an investigation of the variation of electrical properties in the same compound under hydrostatic pressure.[8]

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*In a lattice of the NiAs type the nearest neighbors of a given magnetic atom are located along the c axis at the distance c/2.

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