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Magnetic and Electrical Properties of Manganese Telluride

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The temperature dependence of the susceptibility of the antiferromagnetic compound MnTe was measured over a range of temperature between liquid nitrogen temperature and 720°C. An abrupt change in slope and a maximum of the susceptibility curve were found at 37°C and at 55°C respectively. These results are compared with the observed Néel temperatures previously reported by Squire and by Serre. A thermal hysteresis was also found above the Néel temperature, relating to the heat history of the specimen. It is shown that the susceptibility of $MnTe_{1+x}$ ($0 \leq x \leq 1$), where x is the excess content of tellurium, is explicable in terms of two phases, MnTe and $MnTe_2$ which possess different susceptibilities. The electrical properties, i.e., the resistivity, the thermo-emf and the Hall emf, were measured as functions of temperature. Evidence was found of anomalous behaviours at the Néel temperature for them. A large thermal hysteresis of the resistivity is also found above the Néel temperature, which suggests a change of the crystal structure at about 130°C.

§ 1. Introduction

According to the previously published data[1], the crystal structure of the compound MnTe is the NiAs type with lattice spacings $a_0=4.12$ A and $c_0=6.70$A. The magnetic susceptibility has been investigated by Squire[2] and by Serre[3]. They found that the susceptibility showed the behaviour of an antiferromagnetic compound, the Néel temperature being reported as 37°C by Squire or 55.6°C by Serre. The heat capacity measurements of Kelley[4] have shown that MnTe exhibits a hump of the heat capacity with its maximum at 34°C (307° K). Antiferromagnetic resonance absorption measurements for MnTe have been made by Maxwell and McGuire[5], who reported the g values to be 2.00. Squire[6] has also studied the electrical resistivity of this compound and found that it shows an anomalous behaviour with a maximum at about the Néel temperature (30°C).

As mentioned above, the Néel temperature reported by Squire differs so much from that by Serre that the difference seems to be too large as an error of measurements. The present experiment is concerned with the confirmation of the Néel temperature. From the fact that the resistivity dependence on temperature shows a maximum at about the Néel temperature, it is expected that the

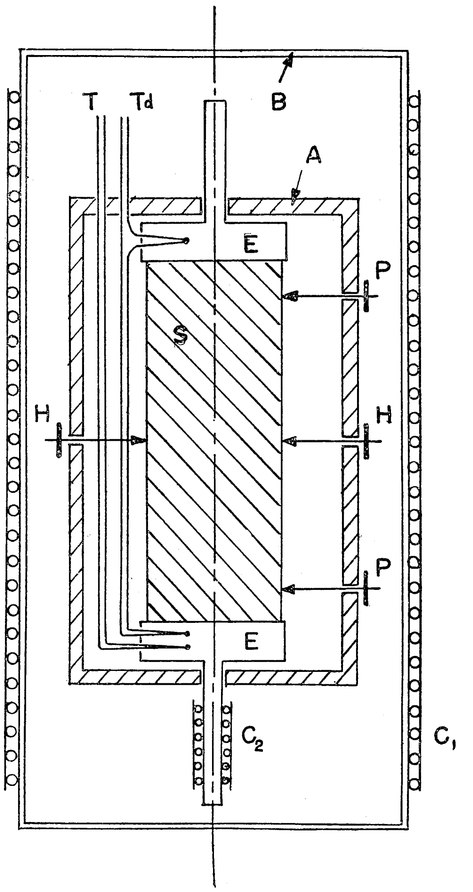

Fig. 1. Schematic representation of sample holder for electrical measurements.
A: micalex case; S: sample; E: current electrodes; P: probes for measuring potential; H: probes for measuring Hall emf; T: thermocouple (Cu-constantan); T_d: differential thermocouple; C_1: heating coil; C_2: heating coil for measurements of thermo-emf; B: brass case.

other electrical properties, i.e., the thermo-emf and the Hall emf, behave anomalously at the same temperature. The present experiment is also concerned with the investigations of the electrical properties in order to seek for possible evidence of the correlation of the electrical properties with the magnetic properties of this compound.

§ 2. Experimental

The procedure of the preparation of the compound $MnTe_{1+x}$ is as follows: Mixed powder of manganese (99.4 percent pure) and tellurium (99.9 percent pure) with a desired proportion was sealed in an evacuated silica tube (10^{-6} mm Hg), and this was heated in a furnace at 725°C for 20 hours and slowly cooled after that. The product was a solid material with a grayish appearance. The X-ray Debye-Scherrer diffraction pattern of a sample of stoichiometric composition was compatible with the NiAs structure.

The susceptibility was measured with the same technique and the same magnetic balance as those described in previous papers[7),8)].

The electrical properties i.e., the resistivity, the thermo-emf and the Hall emf were measured by the usual methods. The specimens used for the present electrical measurements were prepared by moulding the powder sample to a shape of 7 mm in length, 4 mm in diameter (for the resistivity and the thermo-emf measurements) or a shape of 5 mm × 7 mm × 2 mm (for the Hall effect measurements) in a press tool, and by subsequent heat treatment of the material at 725°C to convert it to the crystalline modification. The sample holder is shown in Fig. 1. After it had been held in a brass case which was serviceable to homogenize the temperature of the sample, the measurements were carried out in vacuum (10^{-2} mm Hg).

§ 3. Results

a) *Magnetic measurements*

Fig. 2 shows the molal susceptibility of $MnTe_{1+x}$ as a function of temperature. All curves in this figure are obtained in heating runs for various compositions except the one which represents the cooling curve for the stoichiometric composition. In all cases the heating curve is found reversible up to about 100°C but it ceases to be so beyond that temperature. The cooling curve, from a higher temperature than 100°C, appears to be influenced in some way by the previous temperature history of the sample. The side curves in Fig. 2 represent a typical set of the details of the heating and cooling curves in the vicinity of the Néel point. Similar curves are obtained with different specimens, when measurements are made with special regard to the question of the Néel temperature. The heating curve indicates an abrupt change in slope at 37°C (310°K) and a maximum value of the susceptibility is obtained at 55°C (328°K), while a little lower values of the susceptibility occur with a broadening of the maximum in the cooling run. We can see, in the data of reciprocal susceptibility against temperature obtained by Serre for MnTe, a point which might possibly correspond to the abrupt change in slope in question; an observed point at about 37°C in Serre's case, in fact, deviates slightly from the curve, although the deviation is found so small that it cannot be noticed without special attention to this point.

It is to be noted here that all the susceptibility curves of $MnTe_{1+x}$ in Fig. 2 can be understood as representing the sum of the molal susceptibilities of MnTe and $MnTe_2$, with the ratio of $(1-x)$: x, at corresponding temperature. Accordingly, the molal susceptibility of $MnTe_{1+x}$ is found to be a linear function of x as shown in Fig. 3. This certainly indicates that $MnTe_{1+x}$ is constituted of two phases, MnTe and $MnTe_2$.

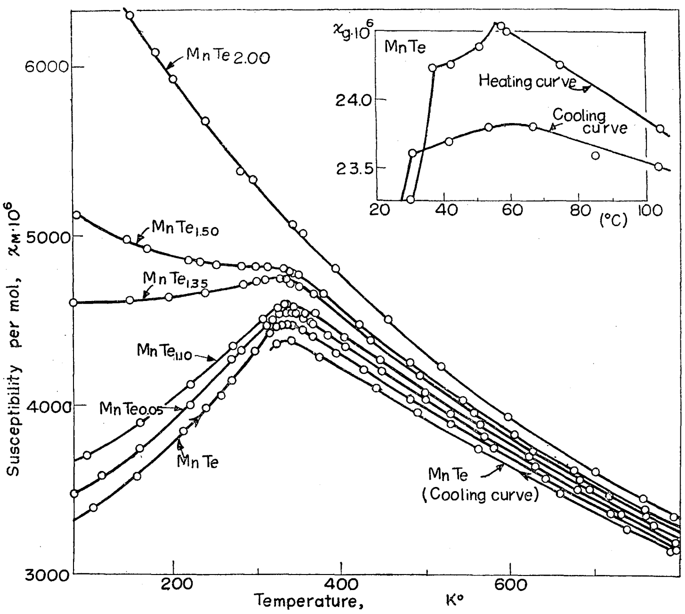

Fig. 2. Graph of molal susceptibility vs temperature for $MnTe_{1+x}$.

The reciprocals of the susceptibility for MnTe and $MnTe_2$ are plotted against absolute temperature in Fig. 4. As can be seen in this figure, plots for MnTe lie along a smooth curve, showing an upward concavity, which is in agreement to that previously observed by Serre. However, in the present case, the plots lie, above about 200°C, almost on a straight line, the extrapolation of this straight line crossing the temperature axis at −650°K. The molal susceptibility in the temperature range of this straight line can be written

$$\chi_M = C/(T+\theta)$$

with values of the Curie constant C, the characteristic temperature θ and the effective Bohr magneton numbers p for a manganese atom given by

$$C=3.24, \quad \theta=650°K, \quad p=5.10\mu_B$$

These values of C, θ and p are found to be a little smaller than those obtained by Serre.

From the linear relation of the reciprocal susceptibility against temperature of $MnTe_2$ (Fig. 4), the values of C, θ and p for $MnTe_2$ are also estimated as follows:

$$C=4.00, \quad \theta=430°K, \quad p=5.68\,\mu_B$$

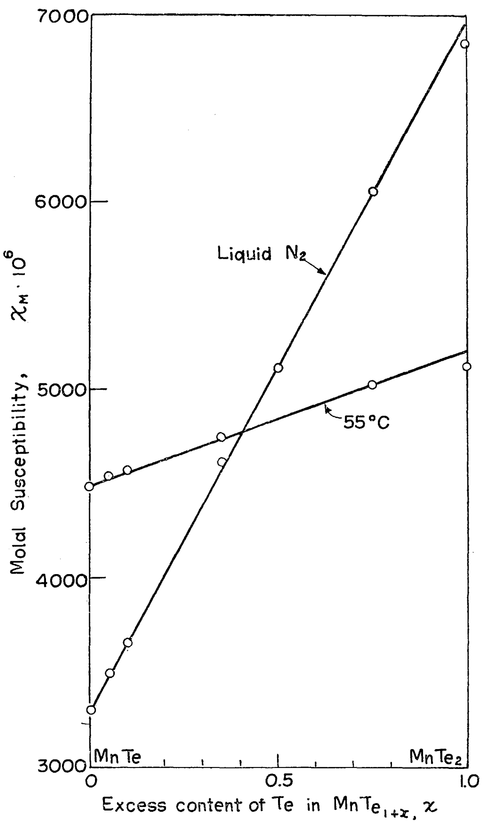

Fig. 3. Graph of molal susceptibility vs excess content of tellurium for $MnTe_{1+x}$.

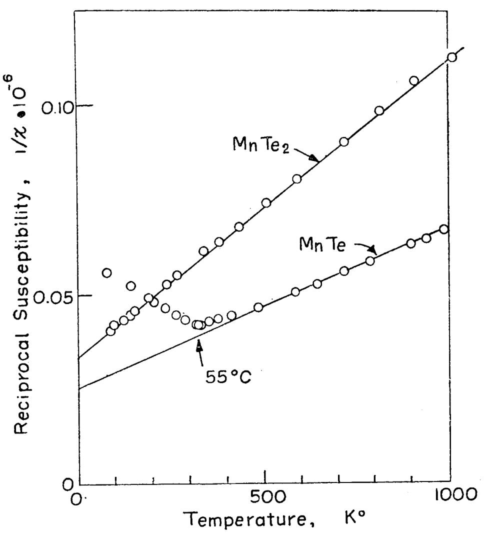

Fig. 4. Graph of reciprocal susceptibility vs temperature for MnTe and $MnTe_2$.

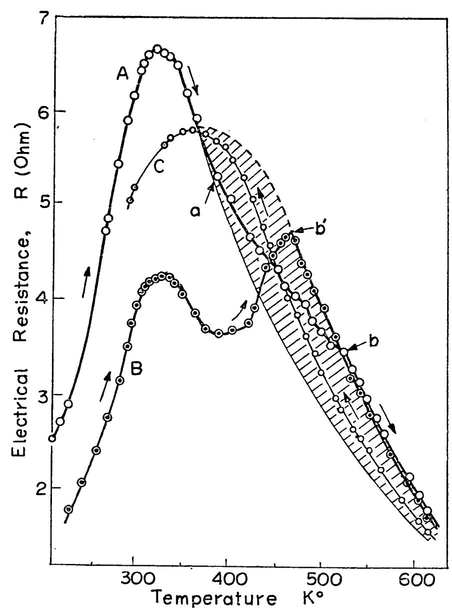

Fig. 5. Graph of electrical resistance vs temperature for MnTe.
Curve A: after 725°C heat treatment and subsequent slow cooling.
Curve B: after 725°C heat treatment and subsequent rapid cooling.
Curve C: after the runs for Curve A and for Curve B.

The fact that the paramagnetic Curie point of $MnTe_2$ is found in the negative region of temperature indicates an antiferromagnetic character of this compound, although no Néel point was yet found in the temperature range of the present experiment. It is to be noted that similar phenomena can be found in other intermetallic compounds, such as Mn_5N_2, FeTe or NiTe; each of them shows no evidence of the Néel point in the temperature range down to about 80°K and yet shows an antiferromagnetic character in its $1/\chi - T$ relation.

b) *Electrical properties*

The electrical properties of MnTe i.e., the resistivity, the thermo-emf and the Hall constant, are determined from liquid nitrogen temperature up to 400°C in order to see the correlation between the electrical and the magnetic properties of this compound.

The graph in Fig. 5 represents a set of typical runs in the measurements of resistivity. The data plotted on Curve A in this figure were obtained with the sample which has previously been subjected to a heat treatment at 725°C and to a subsequent slow cooling, by first cooling it to the liquid nitrogen temperature and then allowing it to warm up to the highest temperature of the measurements, usually at a rate of 2°/min. Up to the point ' a ' on the curve at some ten degrees above the Néel point, Curve A shows a noticeable resemblance to the magnetic susceptibility behaviour, with a maximum at about 50°C (323°K). But, beyond this temperature, the observation generally shows a long relaxation time for the resistivity to approach its final value which is shown by the broken curve in this figure. However, after it has once reached the broken curve at the point ' b,' in the case of Curve A, this relaxation is experienced no more in the successive heating run. Curve C represents the subsequent cooling run to Curve A with a cooling rate of 2°/min. In all cases the cooling curve is a function of the interval of time during which the sample is held at the highest temperature of the run, the highest temperature itself and also the cooling rate. The hatched area in Fig. 5 represents the region in which all the cooling curves subject to different cooling conditions fall.

For the data plotted on Curve B, the heating run was started with the sample used for Curve A, which this time has previously been subjected to a heat treatment at 725°C for 20 hours and then to a rapid cooling from that temperature. The heating rate in this run is 2°/min, same as in the case of Curve

A. Compared with the case of Curve A, the lower values of the resistivity occurred up to about 100°C (373°K) and the relaxation time for the resistivity to approach to the broken line appeared to be shorter; consequently the point 'b′' on this curve, which corresponds to 'b' on Curve A, was found at a lower temperature than the latter. It is to be noted that in either cases of the run for Curve A and that for Curve B, the curve is found to be reversible up to about 100°C and it ceases to be reversible beyond, a similar phenomenon being also found in the magnetic susceptibility measurements. The hysteresis effect of the temperature dependence of resistivity above the Néel point is a good evidence of a certain change of the crystal structure at about 130°C.

The specific resistivity value of MnTe at room temperature is usually found to be of the order of 1 ohm cm. This is a very high conductivity compared with those of other antiferromagnetic manganese compounds such as MnSe, MnS or MnO.

Fig. 6 gives a typical result of the temperature dependence of the thermo-emf developed by the present specimens. For this data, a constant temperature difference of 40° is held across the specimen at every temperature of the measurements. It is found that the thermo-electric power lies between the values 0.3∼0.6 mV/deg and shows a tendency to increase slowly with increasing temperature. The thermo-electric potential is always positive at the lower temperature side of the specimen, which indicates a predominanting hole conduction in MnTe.

Every plot in Fig. 7 represents the mean value of the data of ten repeated observations of the Hall voltage with a carrying current of 30 mA. The values of the Hall constant obtained by taking the slopes of the curves in this figure are plotted against temperature in Fig. 8. The sign of the Hall emf is found to be positive at all temperatures, which is consistent to the results of the thermo-emf measurements.

It is to be noted that both the thermo-emf and the Hall voltage behave anomalously at a temperature close to the Néel point (50°C), as in the resistivity; a maximum for the thermo-emf curve (Fig. 6) and a point of inflection for the Hall constant curve (Fig. 8) are found.

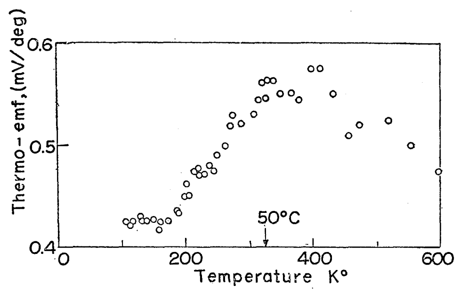

Fig. 6. Graph of thermo-electric power vs temperature for MnTe.

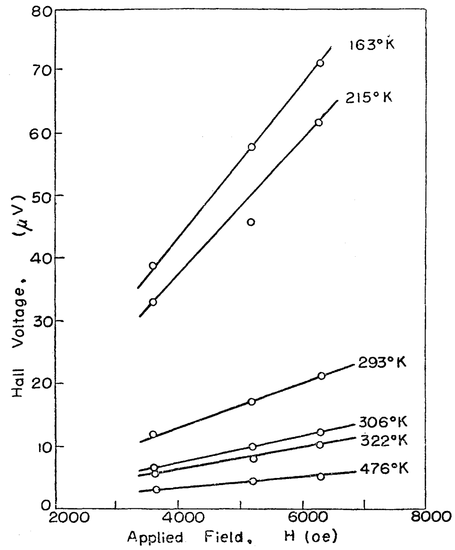

Fig. 7. Graph of Hall voltage vs applied field for MnTe.

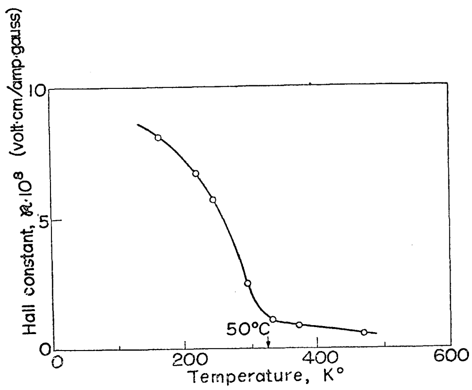

Fig. 8. Graph of Hall constants vs temperature for MnTe.

§ 4. Discussions

The results of the magnetic measurements showed the details of the behaviour of the susceptibility of MnTe in the vicinity of the

Néel point, i.e., we found a characteristic deviation from a simple λ-shape antiferromagnetic transition. Although this deviation is very small, we believe that the abrupt change in slope of the susceptibility curve at 37°C (310°K) correspond to the Néel temperature reported by Squire, and the maximum point at 55°C (328°K) to that reported by Serre. As mentioned in the preceeding section, the maximum at 55°C in fact broadens according to a heat history of the specimen. This broadening might have happened in the case of Squire. The anomalies in the resistivity and other electrical properties found at about 50°C (323°K) may be correlated with the maximum of the susceptibility curve at 55°C rather than to the abrupt change at 37°C. However, further experimental evidences (in particular of the specific heat or of the crystalline structure around the Néel point) may be necessary for the decision of the Néel point.

It should be mentioned that the temperature dependence of the electrical resistivity is very similar to that of the magnetic susceptibility, especially in the lower temperature region below 100°C. This is similar to the results reported by Squire. As shown in Fig. 5, conduction in MnTe changes its character in passing the Néel point from high to lower temperature, from a semi-conductor like conduction to a metallic one. We consider that this is an evidence of the influence of the magnetic properties of this compound on the conduction process at the Néel temperature. The decrease in conductivity with increasing temperature below the Néel point and the corresponding increases in thermo-emf and in Hall constant are qualitatively interpretable by supposing that the conduction in MnTe is contributed predominantly by holes above Néel temperature, while below the Néel temperature the part played by electrons increases with decreasing temperature.

§ 5. Conclusion

Results which are partly consistent to those of the previous works of Squire[2] and Serre[3] were obtained for MnTe in this experiment. It was also established that $MnTe_{1+x}$ is constituted of two phases involving MnTe and $MnTe_2$ in the range $0<x<1$.

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