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Fictitious Transitions of the Crystallographic Structure in Manganese Telluride at High Temperatures

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It has been shown by many workers[1)–4)] that magnetic properties of manganese telluride show antiferromagnetic behaviors with the Néel temperature at about 50°C. Furthermore, Uchida, Kondoh and Fukuoka[3)] have suggested a transformation of the crystallographic structure at 130°C from the observed anomaly of electrical resistivity. During the course of neutron diffraction study, it was desirable to determine the crystal structure at higher temperatures in order to estimate the magnetic scattering. The structure analysis by means of X-ray diffraction at high temperatures has revealed that the transition proposed by them is a fictitious one only observed in oxidizing atmosphere.

Equiatomic proportions of manganese (99.9%) and tellurium (99.99%) were heated in the evacuated doubly sealed silica tubes at 750°C for two days and cooled slowly down to room temperature in 18 hours. The yielded substance was crashed into powder and the heat-treatment above mentioned was repeated until any traces of $MnTe_2$ and metallic tellurium disappeared in X-ray diffraction patterns.

In order to determine the high temperature phase proposed by Uchida et al., diffraction patterns of X-ray were observed at high temperatures. The characteristic lines for MnTe decrease and those for $MnTe_2$ increase from 130°C in the samples placed in low vacuum (approximately 10^{-2} mmHg in pressure). This transition seems to correspond to the crystallographic transition proposed by Uchida et al., since the transition temperature agrees with each other. In Fig. 1, the most representative lines for MnTe and $MnTe_2$ are shown as a function of temperature. Surprisingly, the intensity from $MnTe_2$ vanishes at 720°C and that from MnTe recovers again at the same temperature. This kind of phase transformation is difficult to understand from a simple thermodynamic considerations but can explain the observed results of electrical resistivity.

However, the experiments made in high vacuum (approximately 10^{-4} mmHg in pressure) have shown that there is no change of structures from room temperature up to 750°C. Therefore, it is feasible to understand $\alpha \to \beta \to \alpha$ type transformation shown in Fig. 1 as fictitious transitions only appeared in oxidizing atmosphere. The first step of transformation should be accompanied by oxidation being expressed by a chemical reaction formula

$$2MnTe + \frac{1}{2}O_2 \to MnTe_2 + MnO.$$

This process is supported by the fact that lines characteristic for MnO have been observed at high temperatures in spite of its very low scattering amplitude. The high temperature transformation is interpreted as an evaporation of tellurium because the vapor pressure of tellurium becomes extremely high at that temperature. The reaction formula for the transformation is

$$MnTe_2 \to MnTe + Te.$$

This process is also confirmed by the observed deposition of tellurium metals on X-ray camera after the experiment.

The magnetic susceptibility is also different for two experimental conditions. The observed susceptibility is not reproducible in the experiments made in low vacuum. In high vacuum experiments, the Néel temperature is determined as 50°C, $\theta_p = -692$°K and $P_{eff} = 5.97$, which are in good agreement with Serres[2)] and Banewicz et al.[5)].

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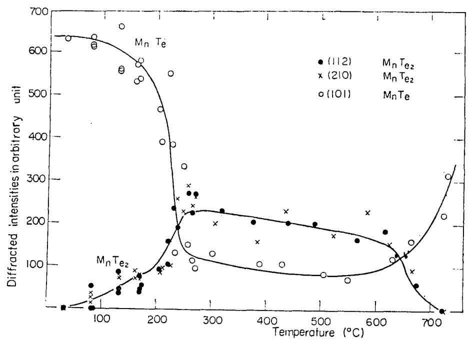

Fig. 1. Change of the diffracted intensities with increasing temperature in low vacuum.

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