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The Antiferromagnetic Structure Deformations in CoO and MnTe

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CoO and MnTe have been studied above and below their antiferromagnetic Curie temperatures with a symmetrical back-reflection camera. CoO exhibits a sharp change in lattice constants between 284° K. and 278° K., and thereafter a more gradual change in its transition from cubic to tetragonal symmetry. MnTe does not show a structure transition but only a sharp contraction of the hexagonal c axis below the Curie temperature.

Introduction

The first structure distortions observed for the transition element monoxides were those in MnO (Ruhemann, 1935) at approximately 80° K. and in NiO (Hedvall, 1922) at room temperature. Rooksby (1943, 1948) investigated NiO in more detail and showed that it was cubic above 250° C. and rhombohedral at room temperature. Later, Tombs & Rooksby (1950) observed similar rhombohedral distortions from the cubic in MnO and FeO at liquid-nitrogen temperature. At that time, they also investigated CoO at room temperature and at $-70°$ C. and $-120°$ C. A tetragonal distortion from the cubic room-temperature form was apparent at $-70°$ C. As the temperature was lowered the tetragonality increased. They found that the tetragonal a axes increased in length whereas the c axis shortened. Greenwald & Smart (1950) also reported that CoO became tetragonal in the neighborhood of its antiferromagnetic Curie point and that rhombohedral Cr_2O_3 showed a sudden contraction in the [111] direction at its Curie temperature. They suggested that the distortions observed by Tombs & Rooksby for the monoxides were associated with transitions from the paramagnetic to antiferromagnetic state.

Serres (1947) showed by magnetic susceptibility measurements that MnTe is antiferromagnetic with a Curie point at 323° K. Oftedal (1927) assigned the NiAs ($C6mc$) structure to MnTe.

This paper gives a more detailed study of the changes in CoO and in addition the results of an investigation of MnTe above and below its transition temperature.

Experimental method

A 10 cm. diameter symmetrical back-reflection camera which combines two useful features, (1) high resolution and (2) short exposure times, was adapted so that the sample temperature could be varied from 125° K. to 363° K. The powdered sample with a thermocouple embedded in one corner of it was mounted on a copper block machined to the same radius of curvature as the film holder. The temperature of the sample was increased by means of a small heating coil inserted in a hole in the copper block. A copper container, insulated with $\frac{3}{4}$ in. styrofoam and filled with various coolants, was used for lowering the temperature. By using a combination of these two arrangements, intermediate temperatures could be maintained. No precautions were taken to prevent the formation of ice crystals on the sample, and therefore a few ice lines were observed in some of the MnTe and CoO films with the longer exposures.

Filtered Fe radiation was used. Exposure times varied from one to three hours. The data were treated by Cohen's (1935) analytical method of extrapolation to eliminate systematic errors. Since the temperature was held constant only to 1° K. it was considered unnecessary to use Hess's (1951) more precise method, with its more involved and detailed calculation.

Results

CoO

A broadening of the 331 and 400 reflections first becomes apparent at 284±1° K. Ten degrees below this temperature, the lines are resolved into the 331 and 313, and 400 and 004 reflections, respectively. Eighteen degrees below the transition temperature there is complete resolution. My results confirm Tombs & Rooksby's conclusions that in the tetragonal form of CoO the c axis shortens as the temperature is lowered whereas the a axes increase. In addition, there is a very rapid change in the region of the transition temperature and thereafter a more gradual change, as shown in Fig. 1. Fig. 1 also demonstrates the fact that the volume decreases almost linearly with temperature. For convenience the cube root of the volume is plotted.

MnTe*

Back-reflection measurements on MnTe at 293° K. give

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* The chemical analysis of the sample used in the present study is: MnTe, 99·7%; Mn and MnO, 0·3%.

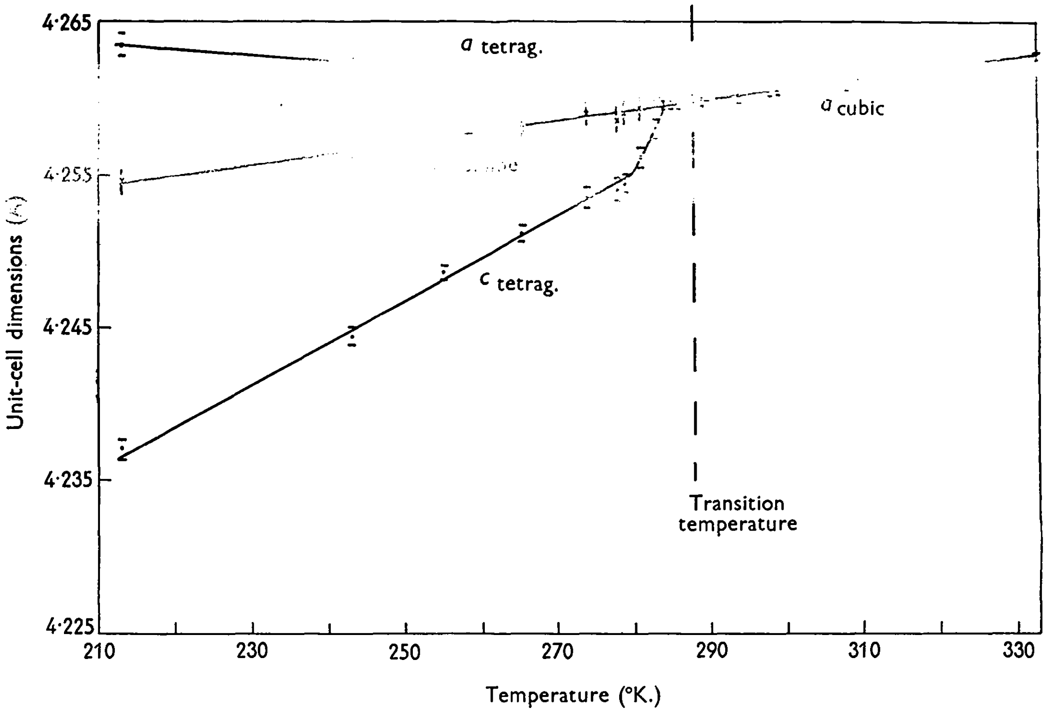

Fig. 1. Unit-cell dimensions of CoO above and below the transition temperature. The transition temperature as determined by magnetic susceptibility measurements is shown by the dashed vertical line.

$$c = 6{\cdot}703_1 \pm 0{\cdot}0005 \text{ and } a = 4{\cdot}142_9 \pm 0{\cdot}0005 \text{ Å}.$$

Measurements with a Norelco wide-range spectrometer goniometer confirm this within the experimental limits and also show no trace of free Mn or MnO. If Oftedal's (1927) measurements, which are based on Siegbahn's values for the wave length of copper, are corrected, then Oftedal's results are:

$$c = 6{\cdot}711 \pm 0{\cdot}005 \text{ and } a = 4{\cdot}132 \pm 0{\cdot}004 \text{ Å}.$$

From the X-ray data given in Fig. 2 the Curie temperature appears to be about 329° K. This is a slightly higher temperature than that obtained from magnetic susceptibility measurements on this sample. Back-reflection X-ray exposures taken above and below the Curie temperature show that the 311 and 116 reflections, which are superimposed above the Curie temperature, move apart and that there is a sudden change in unit-cell dimensions as the compound becomes antiferromagnetic. There is no change in symmetry as there is for the compounds which have the cubic NaCl structure above their Curie temperatures, but there is a sharp decrease in the length of the *c* axis. As shown in Fig. 2, this sharp decrease in *c* is unaccompanied by any significant change in the *a* axes. There is little evidence of a discontinuity in *c* and, therefore, little indication of a volume discontinuity at the transition temperature. A continuous volume *v*. temperature curve with a rapidly varying slope is in conformity with the idea that the antiferromagnetic transitions are second-order transitions.

A similar effect is observed in Cr_2O_3 (Greenwald, 1951), which has the rhombohedral corundum structure. For comparison, if a transformation to a hexagonal set of axes is carried out, then it can be shown that there is, at the Curie temperature, a sudden contraction along the *c* axis in Cr_2O_3 and no corresponding noticeable change in the *a* directions.

Discussion

A correlation between the magnetic structures observed by neutron diffraction and the small deformations and changes in symmetry observed by X-ray diffraction methods has been discussed by Smart & Greenwald (1951). For all the magnetic structures so far observed which produce distortions in the crystal structure, there are unique sets of planes—one set of (111) planes for the monoxides and the (0001) planes for Cr_2O_3—in which all atoms in a given plane have parallel spins while all atoms in neighboring planes have antiparallel spins. If we assume that there is an interaction between atoms with unlike spins there will be either a contraction or expansion perpendicular to these planes. This is borne out for all the monoxides, with the exception of CoO which becomes tetragonal instead of rhombohedral as would be expected. At present there is no explanation for the anomalous behavior. The magnetic structure of MnTe is not known but, judging from the fact that the *c* dimension of the unit cell contracts sharply at the Curie temperature whereas the

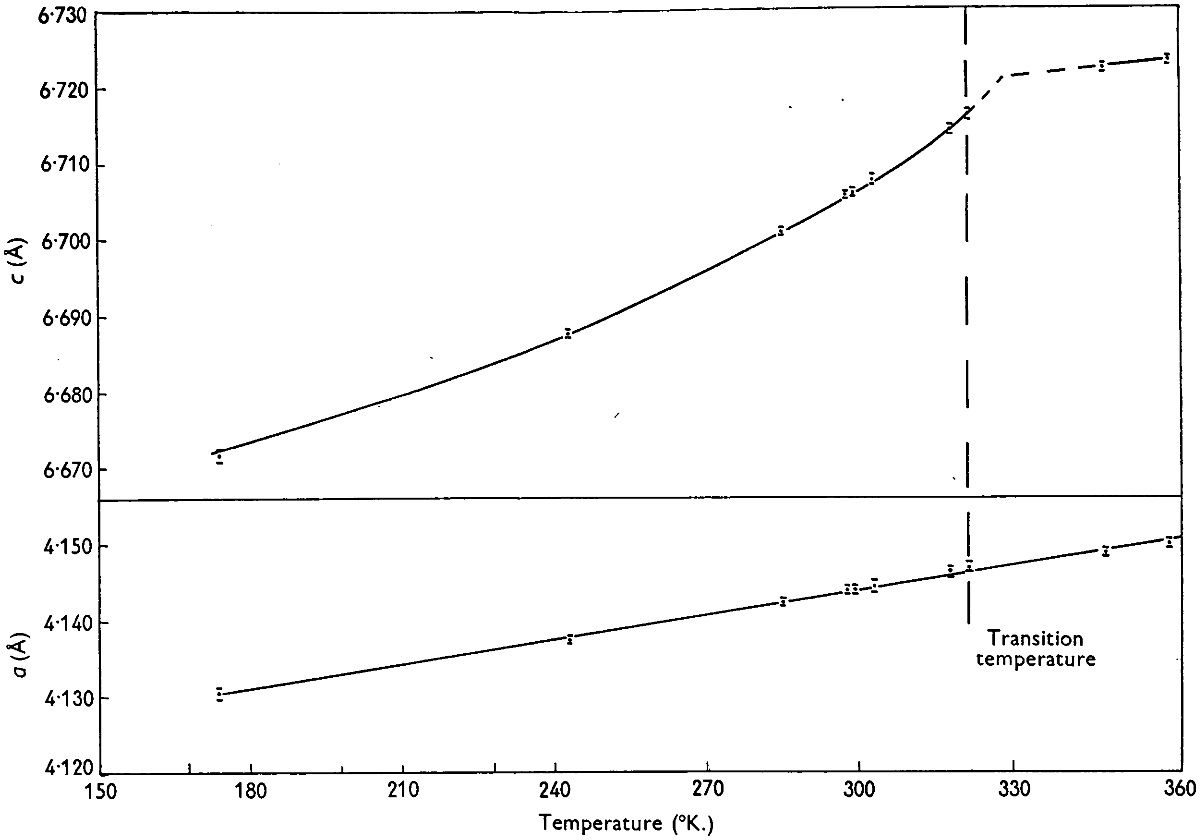

Fig. 2. Unit-cell dimensions of MnTe above and below the transition temperature. The transition temperature as determined by magnetic susceptibility measurements is shown by the dashed vertical line.

a dimensions decrease linearly, the magnetic ordering should be such that there are (0001) layers with alternating spins. This ordering would be especially favorable for nearest and third-nearest neighbor antiferromagnetic interactions. Snow (1952) has found by neutron diffraction this type of magnetic ordering in CrSb, which has the same crystal structure as MnTe.

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