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Crystal structure and antiferromagnetism of CrSb.*

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Introduction

Previous work (Rooksby, 1948; Rooksby & Tombs, 1951) on the crystal structures of the antiferromagnetic oxides MnO, FeO, CoO and NiO has shown that small lattice changes, involving a slight departure from cubic symmetry, take place in these compounds when they are cooled through their antiferromagnetic transition points. The bulk of the remaining known antiferromagnetic compounds have crystal structures, above their transition points, which do not belong to one of the cubic space groups. Nevertheless, it appears from recent studies on chromium sesquioxide (Greenwald, 1951) and α-ferric oxide (Willis & Rooksby, 1952) that non-cubic antiferromagnetic compounds also undergo lattice changes in the neighbourhood of their transition points. These changes are closely analogous to those displayed by the cubic oxides in that they comprise an anomalous expansion or contraction along a principal crystal axis. The changes in cubic crystals are inevitably accompanied by lowering of symmetry, whereas in hexagonal and rhombohedral crystals they can occur simply by an alteration of axial ratio without modification of symmetry.

The present investigation is concerned with the behaviour of the structure cell of the antiferromagnetic compound CrSb. Like MnTe, the subject of a recent study by Greenwald (see below), this crystallizes in the hexagonal system, and possesses the NiAs-type of crystal structure. The investigation has shown that the changes in the structure cell of CrSb in the neighbourhood of its transition point are those to be expected from the general picture outlined above.

Experimental

The compound was prepared by mixing chromium and antimony in the atomic ratio 0·45 Cr to 0·55 Sb, and heating in an evacuated quartz tube for 4 hr. at 650° C. One end of the quartz tube was then opened and attached to a diffusion pump, and the excess antimony was distilled off at 500° C. Homogenization of the product was achieved by reheating *in vacuo* for several hours at 550° C.

An X-ray powder photograph revealed only the presence of CrSb, with the NiAs-type structure. The room-temperature lattice parameters were:

$$a = 4{\cdot}108,\ c = 5{\cdot}440\ \text{Å},\ (\text{Cu}\ K\alpha_1 = 1{\cdot}54050\ \text{Å})\ .$$

These values are to be compared with those given by Wyckoff (1951):

$$a = 4{\cdot}115,\ c = 5{\cdot}479\ \text{Å}\ ,$$

and by Snow (1952):

$$a = 4{\cdot}127,\ c = 5{\cdot}451\ \text{Å}\ .$$

Chemical analysis showed the preparation to contain 33·6% Cr and 66·3% Sb, compared with the theoretical 29·9% Cr and 70·1% Sb for stoichiometric CrSb.

A small quantity of the powder was sealed in an evacuated quartz capillary tube of 0·3 mm. bore, and X-ray powder photographs were taken at various temperatures between room temperature and 650° C., using a 19 cm. high-temperature camera of the Owen (1943) type. An X-ray photograph at $-180°$ C. was also obtained, using the method described by Tombs (1952). Cu $K\alpha$ radiation was used throughout, no serious difficulties being encountered because of secondary fluorescence from the chromium in the specimen.

The above temperature range included the antiferromagnetic transition temperature, which is in the neighbourhood of 400° C. (Foëx & Graaf, 1939). The lattice parameters were calculated for each photograph to an accuracy of $\pm 0{\cdot}001$ Å. The results are given in Fig. 1, in which c and a are plotted against the temperature T. Another sample of CrSb was prepared using a similar technique to that described above, and the lattice parameter measurements for this sample are also included in Fig. 1.

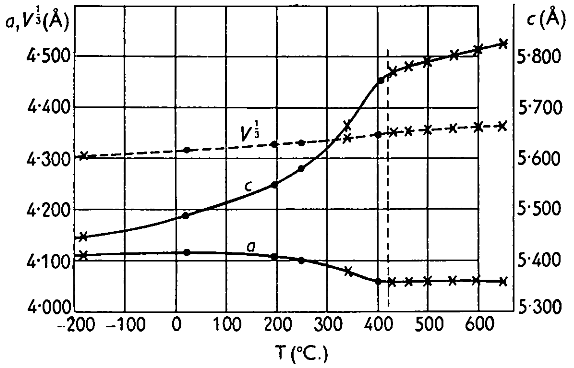

Fig. 1. Curves showing temperature variation of c, a and $V^{\frac{1}{3}}$ for structure cell of CrSb. The vertical broken line represents the magnetic transition temperature T_λ.

Both (c, T) and (a, T) curves possess a point of inflexion in the neighbourhood of 400° C. Thus the curves are divided into two portions on either side of the antiferromagnetic transition temperature T_λ. Between $-180°$ C. and T_λ, c and dc/dT increase steadily with temperature; above T_λ, c increases less rapidly with temperature and dc/dT is constant.

The value of the axial ratio c/a increases from 1·335 at room temperature to 1·422 at 420° C. Further, the linear expansion coefficient (α_c) along the c axis is exceptionally large between these two temperatures. Its value just below T_λ is approximately 3×10^4 per deg. C. It is remarkable that, whereas α_c is large and positive over the whole temperature range of $-180°$ C. to 650° C., α_a is zero above T_λ and negative for several hundred deg. C. below T_λ.

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In Fig. 1 the broken line represents the variation with temperature of $V^{\frac{1}{3}}$, where V ($= 0{\cdot}866\ ca^2$) is the structure cell volume. The slope of this curve is approximately uniform and the curve passes smoothly through the transition region in the neighbourhood of 400° C.

Discussion

In CrSb the magnetic atoms (Cr) are arranged in plane sheets perpendicular to [0001]. The results just described indicate that the distance between these sheets decreases anomalously as the temperature is lowered through the transition point. This effect takes place without any sudden change of structure cell volume or change of crystal symmetry. According to Snow (1952) the magnetic moments of the chromium atoms in a given (0001) plane are all parallel, but moments in neighbouring planes are antiparallel. Thus the antiferromagnetic exchange forces are directed predominantly along the [0001] direction, an interpretation which is strongly supported by the present work.

It is interesting to note that MnTe, which is also an antiferromagnetic compound with the NiAs-type structure, undergoes a similar decrease of c/a (Greenwald, 1952) on being cooled through the transition temperature near 35° C. The magnitude of the change for MnTe is, however, considerably smaller than in CrSb.

The transition temperature of CrSb has been variously reported as 400° C. (Foëx & Graaf, 1939) and 450° C. (Snow, 1952). It is not possible to obtain a more precise value from the shape of the magnetic susceptibility–temperature curve, as the maximum in this curve is exceptionally broad. If we assume that the lattice changes in CrSb appear as soon as the temperature falls below T_λ, we can determine the value of T_λ from Fig. 1 as $420 \pm 10°$ C.

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Enumeration of physical constants of crystals.

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Bhagavantam & Suryanarayana (1949) have given a method by which the number of constants necessary to specify different physical properties of crystals can be directly obtained by using a group theoretical formula which gives the number of times a certain irreducible representation of a group appears in a given representation; these authors have considered all the 32 crystal classes. An alternative method for the same purpose has been given by Jahn (1949) whose results confirm in every case those of Bhagavantam & Suryanarayana; in addition Jahn has also considered the case of a body with complete axial symmetry, his group R_∞, and one with complete axial symmetry together with an inversion, his group R^i_∞. The result for these two cases are given by Jahn in his Table 1 (where the heading for the fifth column has been misprinted: it should be R_∞ instead of R^i_∞). Jahn has further considered the groups C_∞, $C_{\infty v}$, D_∞ etc.

For the sake of completeness, an effort has been made to extend the method of Bhagavantam & Suryanarayana to give the number of constants where the symmetry group is no longer finite, making it necessary to use group integration instead of a finite summation in the formula mentioned above.

In the following we shall consider the groups which in the notation of Jahn are R_∞, R^i_∞, C_∞, $C_{\infty v}$, C^h_∞, D_∞ and D^h_∞. For the first two we need integration over the group of all orthogonal transformations in three dimensions for which the 'volume element' is $\sin^2 \frac{1}{2}\varphi d\varphi$, $0 \leqslant \varphi \leqslant \pi$, while for the rest the integration is essentially over a group of orthogonal transformations in two dimensions for which the 'volume element' is simply $d\varphi$, $0 \leqslant \varphi \leqslant 2\pi$. Let $\chi(\varphi)$ denote the character of a rotation φ about an axis and $\psi(\varphi)$ that of a rotation–reflexion φ. These are given in Table 1 of Bhagavantam & Suryanarayana; we need not specify the direction of the axis of rotation because the characters of the representations we are concerned with depend only on φ.

The required numbers are then obtained from the following formulae:

$$(1) \quad R_\infty,\ n = \int_0^\pi \chi(\varphi) \sin^2 \tfrac{1}{2}\varphi d\varphi \Big/ \int_0^\pi \sin^2 \tfrac{1}{2}\varphi d\varphi\ ,$$

$$(2) \quad R^i_\infty,\ n = \int_0^\pi [\chi(\varphi) \pm \psi(\pi-\varphi)] \sin^2 \tfrac{1}{2}\varphi d\varphi \Big/ 2 \int_0^\pi \sin^2 \tfrac{1}{2}\varphi d\varphi\ ,$$

$$(3) \quad C_\infty,\ n = \int_0^{2\pi} \chi(\varphi) d\varphi \Big/ \int_0^{2\pi} d\varphi\ ,$$

$$(4) \quad C_{\infty v},\ n = \int_0^{2\pi} [\chi(\varphi) \pm \psi(0)] d\varphi \Big/ 2 \int_0^{2\pi} d\varphi\ ,$$

$$(5) \quad C^h_\infty,\ n = \int_0^{2\pi} [\chi(\varphi) \pm \psi(\varphi)] d\varphi \Big/ 2 \int_0^{2\pi} d\varphi\ ,$$

$$(6) \quad D_\infty,\ n = \int_0^{2\pi} [\chi(\varphi) + \chi(\pi)] d\varphi \Big/ 2 \int_0^{2\pi} d\varphi\ ,$$

$$(7) \quad D^h_\infty,\ n = \int_0^{2\pi} [\chi(\varphi) \pm \psi(\varphi) + \chi(\pi) \pm \psi(0)] \Big/ 4 \int_0^{2\pi} d\varphi\ ,$$