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Crystal and Magnetic Structure of Copper Chromite

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Copper chromite, $CuCr_2O_4$, is a tetragonally distorted normal spinel with a c/a ratio, as referred to a face-centered unit cell, of about 0·91. A structure which is physically reasonable, belonging to the space group D_{2d}^{12}–$I\bar{4}2d$, is based on an environment for the copper ions which is distorted from a tetrahedron toward a square, and also slightly rotated about the c axis. The chromium ions are slightly displaced from their ideal positions. The magnetic neutron diffraction pattern, below a Curie point at about 135° K., indicates a triangular arrangement of moments such as one of those proposed by Yafet & Kittel.

Introduction

Bertaut & Delorme (1954) have reported that the crystal structure of copper chromite, $CuCr_2O_4$, is one which can be derived from the spinel structure by a compression along one of the cube axes, so the resulting unit cell is tetragonal. They find that the cation distribution is normal, that is, the divalent copper ions are in the '*A*' sites, with four oxygen neighbors at the corners of a distorted tetrahedron, and the trivalent chromium ions are in the '*B*' sites, with six oxygen neighbors at the corners of a distorted octahedron. On the other hand, magnetic measurements (McGuire, Howard & Smart, 1952; McGuire, 1956) show that this compound has a magnetic moment, below a Curie temperature at about 135° K., of 0·4–0·8 Bohr magnetons per molecule.

Most of the ferromagnetic spinels of which the magnetic structures have been determined previously (see Hastings & Corliss, 1956) have exhibited a structure the existence of which was predicted by Néel (1948). This structure, which exists when the *A*–*B* magnetic interaction, between ions on different kinds of site, predominates over the *A*–*A* and *B*–*B* interactions, among ions on the same kind of site, has all of the moments on the same kind of site coupled parallel, while the moments on the two different kinds of site are antiparallel to each other. This arrangement would result, in the case of copper chromite, in a moment of $5\mu_B$/molecule, in sharp contrast with the observed moment of about $0{\cdot}5\mu_B$/molecule. Yafet & Kittel (1952) have suggested that, in cases where the *A*–*A* or *B*–*B* interactions are comparable with the *A*–*B* interaction, the structure should be a triangular one in which the ions on one kind of site are divided into two sets with spins directed at an angle to each other, and with the spins of the ions on the other kind of site directed antiparallel to the resultant. Such structures have been suggested in several cases in which the simpler model could not account for the observed moment (Gorter, 1954), but none of these has previously been confirmed by any direct method. Because neutron diffraction data could give more accurate information on the cation distribution and crystal structure than X-ray diffraction could give, and because this seemed to be a promising substance in which to look for the triangular arrangement of moments, a neutron diffraction study was undertaken.

Crystal structure

A sample of copper chromite suitable for neutron diffraction analysis was prepared by heating a stoichiometric mixture of $CuCO_3$ and Cr_2O_3 to a temperature of 1200° C. in oxygen. All of the lines in an X-ray powder pattern could be indexed assuming a face-centered tetragonal unit cell with

$$a_0 = 8{\cdot}55,\ \ c_0 = 7{\cdot}78\ \text{Å},\ \ c/a = 0{\cdot}91\ ,$$

in good agreement with the previous report (Bertaut & Delorme, 1954). To follow crystallographic convention, we shall henceforth refer the structure to a body-centered tetragonal cell with

$$a_0 = 6{\cdot}04,\ \ c_0 = 7{\cdot}78\ \text{Å},\ \ c/a = 1{\cdot}29\ .$$

Neutron diffraction powder patterns ($\lambda = 1{\cdot}00$ Å) were taken at room temperature and at liquid-nitrogen temperature from a polycrystalline cylinder about 2·5 cm. in diameter and 5 cm. high.

Inspection of the intensities of the room-temperature pattern, which, because the Curie temperature is below room temperature, contains only nuclear diffraction peaks, confirmed that the cation distribution is normal. It was first assumed the structure could belong to the most symmetric subgroup of the space group to which cubic spinels belong, namely D_{4h}^{19}–$I4_1/amd$. In this space group it is necessary to determine only two nuclear parameters, the x and z parameters for the oxygen. However, adjustment of these two parameters did not give satisfactory agree-

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ment between observed and calculated intensities. A systematic investigation of the space groups which are subgroups of D_{4h}^{19}–$I4_1/amd$ revealed a most probable structure belonging to the space group D_{2d}^{12}–$I\bar{4}2d$. In this space group three parameters are available to the oxygen ions and one to the chromium ions. The first step in determining the values of these parameters was to calculate a likely structure from the Goldschmidt radii of the Cr^{+++} and O^{--} ions. This structure gave much better agreement of observed and calculated intensities, and the agreement was further improved by trial-and-error refinement. Table 1 shows the final observed and calculated intensities, while Table 2 shows the room-temperature structure parameters.

Table 1. *Observed and calculated neutron diffraction intensities for* $CuCr_2O_4$

Plane	I_c	I_o	Plane	I_c	I_o
101	0	0	312	12·1	8·8
200	7·6	9·7	204 321 303	39·3	40·6
112	13·1	13·2	105 400	35·8	40·4
211	16·9	16·4	224 411 323	76·8	78·5
103 202	65·0	69·6			
220	25·9	25·9			
004 301 213	24·8	24·1			

Table 2. *Atomic parameters in* $CuCr_2O_4$

Space group D_{2d}^{12}–$I\bar{4}2d$

Atom	Position	x	y	z
Cu	4(*a*)	0	0	0
Cr	8(*d*)	0·525	$\frac{1}{4}$	$\frac{1}{8}$
O	16(*e*)	0·280	$0{\cdot}028_5$	0·120

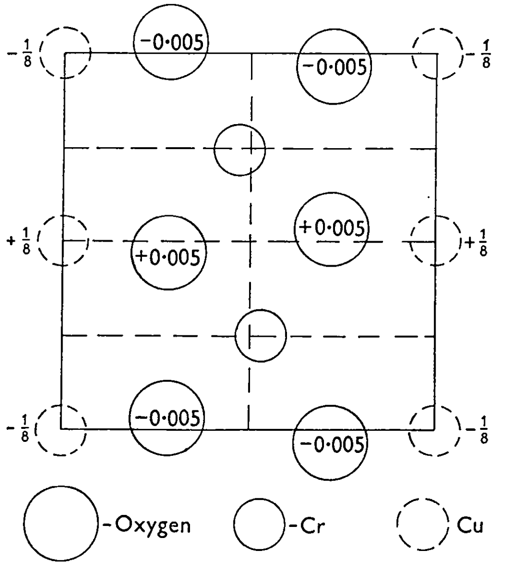

Fig. 1. Portion of $CuCr_2O_4$ structure projected on plane perpendicular to [001]; z parameters in fractions of c_0 from plane containing Cr.

Fig. 1 shows the portion of the unit cell from $z = 0$ to $z = \frac{1}{4}$ projected on a (001) plane. This plane contains the chromium ion sites, while the oxygen sites are displaced from it by $0{\cdot}005\,c_0$. The shortest O–O distance is 2·68 Å, and the Cu–O–Cu bond angle is about 103° in contrast to the tetrahedral angle of 109°, indicating a preference by the cupric ion for square coordination. This structure may be compared with the structure of copper ferrite (Prince & Treuting, 1956), which has the 'inverse' cation distribution, with the copper ions on *B* sites. Whereas the structure of copper chromite is distorted by a compression along one of the cube axes, the copper ferrite structure is extended along a cube axis. In each case, however, the distortion results in the coordination of the copper ion being more nearly square.

In cubic spinels the *B* sites lie at the corners of tetrahedra. Each tetrahedron shares one corner with each of four neighboring tetrahedra, so that a given *B* site is shared by two tetrahedra and has six nearest-neighbor *B* sites. In the copper chromite structure the tetrahedra are compressed along one of the cube axes and at the same time slightly twisted about that axis. If one tetrahedron twists clockwise, its four neighbors twist counterclockwise, all their neighbors twist clockwise, and so forth throughout the structure. The result of these displacements is that the environment of a *B* site is no longer centrosymmetric, and the neighboring *B* sites are not all equidistant. The sites in adjacent planes perpendicular to the *c* axis are closer together than those in the same plane. This has an important bearing on the magnetic structure.

Magnetic structure

Fig. 2 shows the low-angle portions of diffraction patterns taken at room temperature and at liquid-nitrogen temperature. The low-temperature pattern contains two purely magnetic peaks, (101) and (002), as well as significant magnetic contributions to several others. There is a magnetic contribution to (200), but not to (112), and no (110) appears. The magnetic moment of this sample, as measured in fields up to 9800 oersteds and extrapolated to infinite field, is $0{\cdot}45\mu_B$/molecule at 77° K. and $0{\cdot}51\mu_B$/molecule at 1·3° K. This is in good agreement with previously reported values (McGuire, 1956). There are no magnetic peaks which cannot be indexed on the same unit cell as the nuclear peaks, which means that the magnetic unit cell can be no larger than the nuclear unit cell. On the other hand, (002) is a space-group absence in the nuclear structure, because of the *d* glide operation. The appearance of the reflection with appreciable intensity can be produced only by non-parallel spins on chromium ions related by the glide operation. The absence of magnetic contributions to (110) and (112) implies that chromium ions in the same (001) sheet have parallel spins. Because there are only eight chromium ions in the unit cell, these two conditions, when combined with the body-centering operation, divide them uniquely into two sets of four having parallel spins, and rule out any possibility that there may be any more than two directions for the chromium spins. The neutron data are therefore consistent with a structure of the type proposed by Yafet & Kittel (1952) in which the spins of all chromium ions in any (001) sheet are parallel and those in adjacent sheets make angles with each other, while the moments of the copper ions are antiparallel to the resultant of the chromium ions. Fig. 3 shows schematically two ways in which two ions with moments of $3\mu_B$ can be combined with one ion with a moment of $1\mu_B$ to leave a net of $0{\cdot}5\mu_B$. Unfortunately the neutron data are insufficient to distinguish between these two arrangements, nor can they tell whether or not the moment directions are all perpendicular to the tetrad axis. It seems unlikely, therefore, that the arrangement of moments can be determined uniquely by powder data alone, but the evidence for the triangular arrangement is clear-cut. More definite information might be obtained from single-crystal neutron and X-ray diffraction experiments.

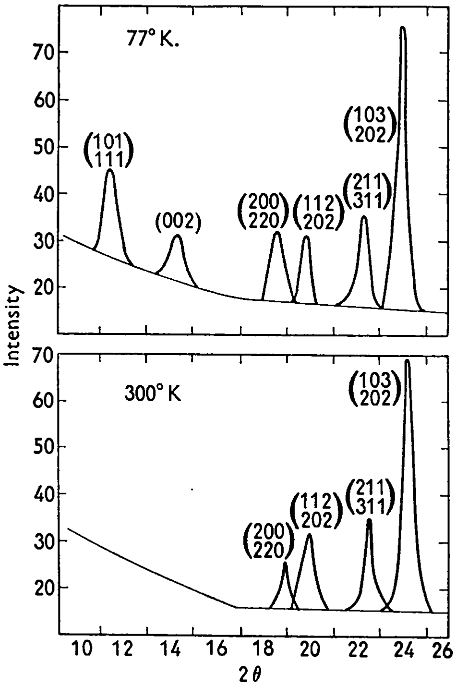

Fig. 2. Neutron diffraction patterns from $CuCr_2O_4$ at 300° K. and 77° K.

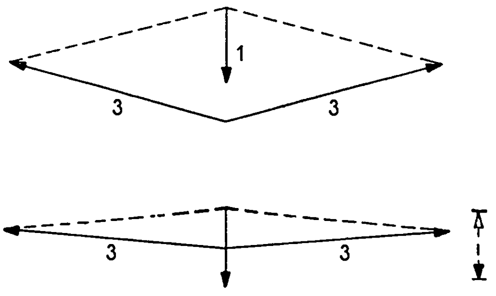

Fig. 3. Two possible ways of arranging ionic moments in $CuCr_2O_4$ to yield the observed moment of $0{\cdot}5\mu_B$/molecule.

Anderson (1956) has suggested that because of entropy considerations moments should be ordered according to the Yafet & Kittel scheme on a short-range basis only. His argument, however, depends on the fact that in cubic spinels all *B*–*B* distances and *B*–O–*B* angles are the same. In the structure of copper chromite the distortion removes this degeneracy, causing the ordered state to be more favorable than it otherwise would be.

Conclusion

The distorted structure of copper chromite is consistent with the view that it results from the tendency for the cupric ion to form square bonds. The magnetic structure contains a triangular arrangement of magnetic moments.

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