

Å. In the Tutton salt $\text{Mg}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ Margulis & Templeton (1962) also found 1.486 Å for the average S–O distance when it was corrected in the same way.

The average Mg–O distance is 2.06 Å without correction for thermal motion. Magnesium is also in water octahedra in $\text{Mg}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ with average Mg–O = 2.07 Å and in $\text{Ce}_2\text{Mg}_3(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$ (Templeton, Zalkin & Forrester, 1962) with average Mg–O = 2.06 Å. In all three crystals the average Mg–O distance is 2.07 Å with thermal correction assuming in-phase motion.

The hydrogen bond O–O distances average 2.82 Å, but scatter over a considerable range as is common in complicated hydrate structures. The accuracy of the hydrogen positions, about 0.2 Å, does not justify tabulation of the many bond distances and angles involving hydrogen atoms.

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Crystal Structure and Magnetic Properties of CoTiO_3 *

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The crystal structure of cobalt titanate, CoTiO_3 , has been refined by least-squares analysis of X-ray and neutron-diffraction data. Magnetic susceptibility measurements on polycrystalline samples gave a nearly ideal antiferromagnetic susceptibility curve with a Néel temperature of 38 °K. The ordered magnetic structure at low temperatures is identical with that of NiTiO_3 in which the spin direction is perpendicular to the rhombohedral [111] direction. Within each (111) plane the Co^{2+} moments are ferromagnetically coupled, but alternate layers are antiparallel.

Cobalt titanate, CoTiO_3 , is isomorphous with ilmenite (Barth & Posnjak, 1934) and antiferromagnetic at low temperatures (Ishikawa & Akimoto, 1958*b*). This paper reports a refinement of the crystal structure and the details of the magnetic transitions, including the low-temperature spin structure.

The lattice parameters of CoTiO_3 were determined from high-angle diffractometer data obtained with a polycrystalline specimen supplied by the National Lead Company.† Neutron-diffraction and magnetic-susceptibility measurements were carried out on the

same material. The rhombohedral unit-cell dimensions are $a = 5.4846 \pm 0.0007$ Å and $\alpha = 55^\circ 01' \pm 02'$, in substantial agreement with previous results (Ishikawa & Akimoto, 1958*a*). The space group of CoTiO_3 is $R\bar{3}$, with oxygen in general positions $\pm(x, y, z; z, x, y; y, z, x)$ and cobalt and titanium in special positions along the threefold symmetry axes at $\pm(u, u, u)$ and $\pm(v, v, v)$, respectively. Values of the atomic coordinates were obtained from Weissenberg intensity data with $\text{MoK}\alpha$ radiation and a small single crystal grown by the Verneuil process.‡ Intensities of 140 (*hkl*) reflections were estimated visually by comparison with a cal-

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ibrated scale; included among these data were 20 weak reflections with l odd, thus verifying the space group as $R\bar{3}$. Least-squares refinement (Busing, Martin & Levy, 1962) of the positional parameters and temperature factors gave an R index of 0.14 and the following results: $x=0.558$, $y=-0.044$, $z=0.221$, $u=0.354$, $v=0.146$, $B_{\text{Co}}=B_{\text{Ti}}=0.35 \text{ \AA}^2$ and $B_{\text{O}}=0.58 \text{ \AA}^2$. Tables of the observed and calculated structure factors are available upon request. A rough estimate of the accuracy can be obtained from the least-squares standard deviations, which are 0.005 for the oxygen coordinates, 0.0005 for the Co and Ti positions, and 0.2 \AA^2 for the temperature factors. These may be somewhat optimistic because the correlation matrix indicates sizeable interactions between several of the parameters.

Both titanium and cobalt are octahedrally coordinated in CoTiO_3 . Each Ti has three oxygen neighbors at 1.92 and three more at 2.06 \AA ; the corresponding Co-O distances are slightly longer, 2.08 and 2.16 \AA , respectively. Comparable data for the other ilmenites are given in the references by Shirane, Pickart, Nathans & Ishikawa (1959) and Shirane, Pickart & Ishikawa (1959). The mean interatomic distances of 1.99 for Ti-O and 2.12 for Co-O are not significantly different from the Goldschmidt ionic radii: $\text{Co}^{2+} 0.82$, $\text{Ti}^{4+} 0.64$, and $\text{O}^{2-} 1.32 \text{ \AA}$.

The magnetic susceptibility of polycrystalline CoTiO_3 was measured from 4 to 273 $^{\circ}\text{K}$ with a vibrating-sample magnetometer and fields as large as 12,000 gauss. The low-temperature behavior shown in Fig. 1 shows a maximum near $38 \pm 1 \text{ }^{\circ}\text{K}$, in good

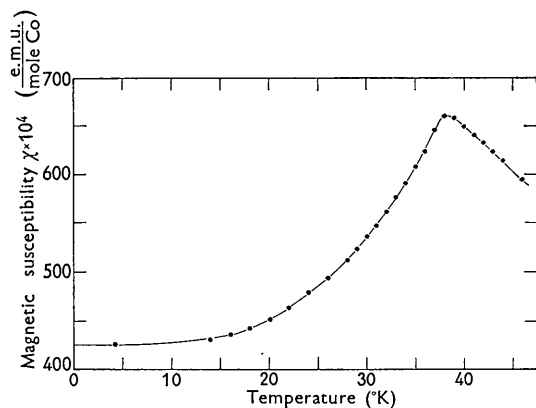


Fig. 1. Low-temperature magnetic susceptibility of polycrystalline CoTiO_3 .

agreement with independent measurements by Kern & Feldman (1962). Below the transition temperature, the susceptibility decreases and approaches two-thirds its peak value as T approaches 0 $^{\circ}\text{K}$, typical of a polycrystalline antiferromagnetic (Néel, 1948). In the paramagnetic region above 38 $^{\circ}\text{K}$, χ follows a Curie-Weiss law with $p_{\text{eff}}=5.3$ Bohr magnetons and

$\theta = -15 \text{ }^{\circ}\text{K}$. The susceptibility is independent of field over the entire temperature range.

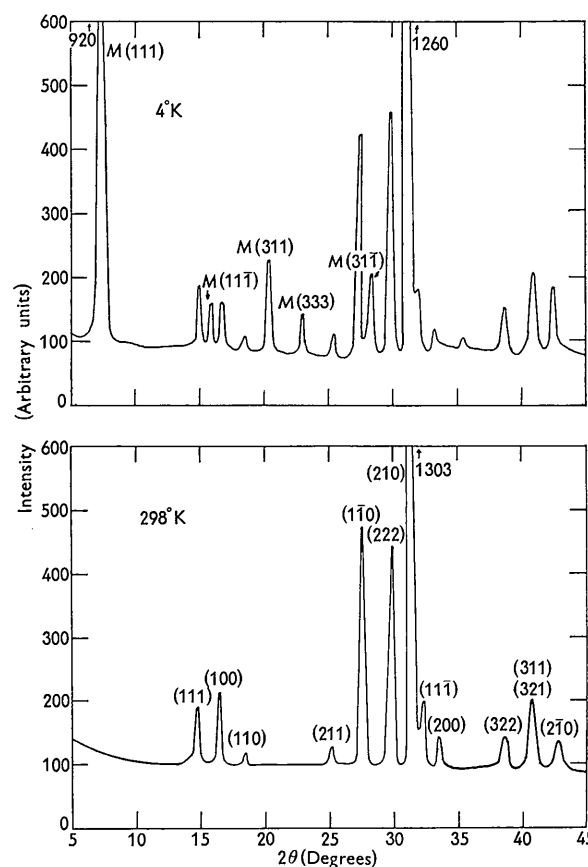


Fig. 2. Neutron-diffraction patterns of polycrystalline CoTiO_3 at 4 $^{\circ}\text{K}$ and at room temperature. The neutron wavelength is 1.20 \AA .

Neutron-diffraction patterns of polycrystalline CoTiO_3 taken at 4 and 298 $^{\circ}\text{K}$ are shown in Fig. 2. They were scanned in angular intervals of $3'$ in 2θ using a cylindrical aluminum specimen holder of 2 cm diameter and 6 cm height. Tables 1 and 2 list the observed nuclear and magnetic intensities. The former intensities are in good agreement with those calculated from the crystallographic parameters determined by X-ray diffraction. The following scattering lengths were used in the computation: Co 0.28, Ti -0.34 , O $0.58 \times 10^{-12} \text{ cm}$. No thermal-vibration corrections were applied. The difference between the scattering lengths of Co and Ti makes it possible to ascertain the degree of order of these two cations among the octahedral sites. Table 1 shows that the ordering is nearly complete since perfect order ($S=1.0$) is in closer accord with experiment than $S=0.9$.

A number of magnetic reflections appear in the low-temperature pattern; their intensities are listed in Table 2. They can be indexed on a rhombohedral

Table 1. Comparison of observed and calculated nuclear intensities for CoTiO_3

Angular corrections have been applied to the calculated values, which are scaled to an arbitrary observed scale

hkl	I_o		I_c	
	298 °K	4 °K	$S=1.00$	$S=0.90$
111	111	109	112	66
100	108	101	100	55
110	27	30	35	41
211	41	47	56	64
$\bar{1}\bar{1}0$	540	524	488	536
222	665*	670*	515	564
210	2136	2132	2060	2134
$11\bar{1}$	199	195	202	176
200	38	27	68	75
220	< 20	< 20	15	17
322	156	128	175	137
311, 321	334	292	320	350
$2\bar{1}0$	148	122	180	173

* Including Al(111).

Table 2. Observed and calculated magnetic intensities indexed on the rhombohedral superstructure

hkl	I_o (4 °K)	I_c ($S=1.00$)
111	1435	1386
$11\bar{1}$	94	90
311	227	230
333	87	104
331	< 20	1
$31\bar{1}$	220	290

cell with $a_{\text{mag}}=10.97 \text{ \AA}$ and $\alpha_{\text{mag}}=55^\circ 01'$. Magnetic intensities calculated with the NiTiO_3 spin structure (Shirane, Pickart & Ishikawa, 1959) and the Co^{2+} magnetic form factor given by Bacon (1955) compare satisfactorily with experiment, as shown in Table 2. The magnetic structure of antiferromagnetic CoTiO_3 is therefore isomorphous with that of NiTiO_3 which

consists of ferromagnetic sheets of Ni^{2+} moments orthogonal to the hexagonal c axis. Alternate nickel layers are oriented antiparallel and the spin direction is perpendicular to $[111]$; its orientation within the (111) plane cannot be determined from powder data alone (Shirane, 1959).

The direct and superexchange coupling interactions which give rise to the magnetic phenomena observed in the ilmenite family have been discussed by Goodenough (1960) and others.

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