

A Neutron Diffraction Study of α -Sb₂O₄

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Abstract. α -Sb₂O₄, orthorhombic, $Pna2_1$, $a = 5.456$ (1), $b = 4.814$ (1), $c = 11.787$ (2) Å. The structure has been examined by profile analysis of powder neutron diffraction data at 293 K. The atomic positions are quite different from those of the isomorphous SbNbO₄.

Introduction. The structures of *B*-metal oxides have attracted considerable interest in recent years. This has encompassed oxides containing the *B*-metal cation in both its group (*N*), and its (*N* – 2) oxidation state as well as oxides where both oxidation states are present (e.g. Andersson & Åstrom, 1972; Galy, 1972; Kafalas, 1972). When a lone pair of *s* electrons is present on a cation it is usually found to be stereochemically active. Also, the structure of a *B*-metal oxide containing a cation in its group oxidation state often differs markedly from that of the analogous *A*-metal oxide.

The structures of the two polymorphs α - and β -Sb₂O₄ have been investigated by X-ray diffraction (Dihlstrom, 1938; Rogers & Skapski, 1964; Skapski & Rogers, 1965). Dihlstrom first suggested $Pna2_1$ as the space group of α -Sb₂O₄ and reported $a = 5.435$, $b = 4.814$, $c = 11.78$ Å, confirmed by Swanson, Cook,

Evans & de Groot (1960). In a later study of SbNbO₄ (Skapski & Rogers, 1965), which Dihlstrom found to be isomorphous with α -Sb₂O₄, the structure was again found to be $Pna2_1$. However, Skapski & Rogers's accurate determination of the atomic positions in SbNbO₄ showed that Dihlstrom's O atom positional parameters, derived only from spatial considerations, were incorrect. Because of the difficulty of growing single crystals of α -Sb₂O₄, a complete structure determination by X-ray diffraction has not been possible.

Table 1. Atomic positional parameters of α -Sb₂O₄ at 293 K (space group $Pna2_1$)

Standard deviations are shown in parentheses.

		<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)
Sb(1)	4(<i>a</i>)	–0.032 (1)	0.036 (1)	0.009 (1)	–0.13 (6)
Sb(2)	4(<i>a</i>)	0.366 (1)	0.016 (2)	0.253 (1)	–0.13 (6)
O(1)	4(<i>a</i>)	0.340 (1)	0.177 (2)	0.0962 (6)	0.31 (5)
O(2)	4(<i>a</i>)	0.159 (1)	0.710 (1)	0.195 (1)	0.31 (5)
O(3)	4(<i>a</i>)	0.086 (1)	0.208 (1)	0.312 (1)	0.31 (5)
O(4)	4(<i>a</i>)	0.330	0.840	0.410	0.31 (5)

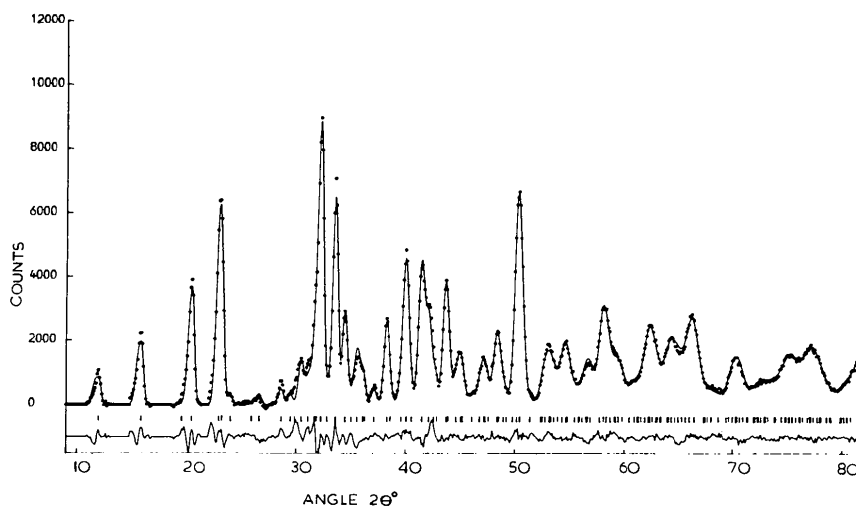


Fig. 1. Powder neutron diffraction profile for α -Sb₂O₄ at 293 K. Small circles are the experimental points, and the full curve passes through the calculated points. The small vertical lines mark the positions of the Bragg reflexions and the bottom trace is the difference profile.

Therefore, to determine the structural relationships present in α -Sb₂O₄, we have examined it by profile analysis of powder neutron diffraction data.

A 20 g polycrystalline sample was prepared by heating Sb₂O₃ ('Analar' grade, BDH Chemicals Ltd) at 750°C in air for 48 h with an intermediate regrind. Analysis of the Sb content by atomic absorption gave 79.8% compared with 79.3% estimated for ideal stoichiometry.

Powder neutron diffraction data were collected on the D2 diffractometer at the High-Flux Reactor, Institut Laue-Langevin, Grenoble. The sample was contained in a 16 mm diameter V can. A neutron wavelength of 1.2193 Å was obtained by reflexion from the (311) planes of a Ge monochromator. The wavelength was determined by Ni calibration. The data were collected with a 20 g sample, and recorded at 0.1° intervals in 2θ over the angular range 0° < 2θ < 100°. However, only data in the range 9° < 2θ < 82° were used in the structural refinement, since the counting statistics were too poor in the excluded regions.

The structural parameters for a model based on *Pna*2₁ were obtained by least-squares refinement of the diffraction profile (Rietveld, 1969). The scattering lengths were $b_{\text{Sb}} = 0.56$, $b_{\text{O}} = 0.58$ ($\times 10^{-12}$ cm) (Neutron Diffraction Commission, 1972). Absorption and extinction effects were considered to be small and no corrections were made. The refinement converged to give a profile *R* of 6.85% which may be compared with an expected *R* of 3.27%. Isotropic temperature factors were used, and the asymmetry parameter, lattice parameters, peak half-widths and counter zero point were also refined. All parameter shifts in the final refinement were less than 0.3 standard deviations. The results are presented in Table 1 and the observed, calculated and difference profiles are shown in Fig. 1. Lattice parameter *a* differs from that found by X-ray diffraction, probably because of a difference in the conditions of sample preparation. The negative temperature factor found for the Sb atoms almost certainly arises from an error in background estimation (Cheetham & Taylor, 1976).

Discussion. The coordinations of the Sb^{III} and Sb^V ions are broadly similar to those found for Sb^{III} and Nb^V in SbNbO₄. However, the bond distances are quite different in α -Sb₂O₄, as are the bond angles about Sb^{III} (Skapski & Rogers do not report the bond angles about Nb^V). The differences must arise from the relative proportion of *s*, *p* and *d* character in the bonding orbitals of the pentavalent ion, as well as their spatial extensions. The Sb^{III} and Sb^V polyhedra are shown in Figs. 2 and 3 respectively, with the bond lengths and angles in Table 2.

The coordination of Sb^{III} in α -Sb₂O₄ is similar to that in β -Sb₂O₄, the Sb—O bonds being 'one-sided', showing the presence of a stereochemically active lone pair.

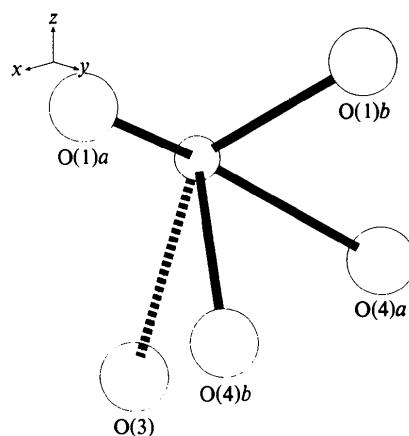


Fig. 2. The distorted pseudotrigonal-bipyramidal coordination of Sb^{III} in α -Sb₂O₄. The dashed line indicates that O(3) is not part of the Sb^{III} polyhedron.

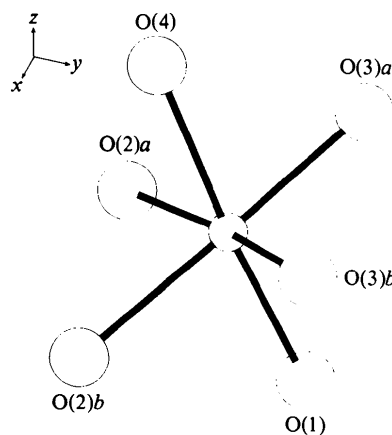


Fig. 3. The distorted octahedral coordination of Sb^V in α -Sb₂O₄.

Table 2. *Interatomic distances (Å) and angles (°) in α -Sb₂O₄ at 293 K*

Standard deviations are shown in parentheses.

Sb(1) (= Sb ^{III})		Sb(2) (= Sb ^V)	
Sb(1)—O(1) <i>a</i>	2.373 (2)	O(1)—Sb(1)—O(1)	82.5
Sb(1)—O(1) <i>b</i>	1.857 (2)	O(1) <i>a</i> —Sb(1)—O(4) <i>b</i>	66.8
Sb(1)—O(3)	2.619 (2)	O(1) <i>b</i> —Sb(1)—O(4) <i>b</i>	89.2
Sb(1)—O(4) <i>a</i>	2.088 (1)	O(1) <i>a</i> —Sb(1)—O(4) <i>a</i>	145.6
Sb(1)—O(4) <i>b</i>	2.172 (1)	O(1) <i>b</i> —Sb(1)—O(4) <i>a</i>	78.6
Sb(2)—O(1)	2.011 (3)	O(4)—Sb(2)—O(1)	170.3
Sb(2)—O(2) <i>a</i>	1.978 (3)	O(2) <i>a</i> —Sb(2)—O(3) <i>b</i>	175.6
Sb(2)—O(2) <i>b</i>	2.051 (3)	O(2) <i>b</i> —Sb(2)—O(3) <i>a</i>	176.6
Sb(2)—O(3) <i>a</i>	1.916 (3)	O(4)—Sb(2)—O(2) <i>a</i>	87.1
Sb(2)—O(3) <i>b</i>	1.921 (3)	Sb(2)—O(2)—Sb(2)	136.5
Sb(2)—O(4)	2.045 (2)	Sb(2)—O(3)—Sb(2)	134.5
		Sb(1)—O(1)—Sb(1)	107.2
		Sb(1)—O(1)—Sb(2)	110.3
		Sb(1)—O(1)—Sb(2)	140.2

There are two essential differences between the two polymorphs of Sb₂O₄. Firstly, the Sb^V octahedra are more distorted in the α form, and secondly, alternate chains of Sb^{III} polyhedra along *c* have an opposite tilt about *a*. Andersson & Åstrom (1972) have discussed the packing of oxides containing stereochemically active lone pairs, each lone pair being considered as a packing sphere. The hexagonal close packing apparent in β -Sb₂O₄ (Andersson & Åstrom, 1972) is also present in the α polymorph, although in a more distorted form.

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The Hydrogen Bonding of Hydromagnesite

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Abstract. Mg₅(CO₃)₄(OH)₂(H₂O)₄ (Dovez, Iran), monoclinic, *P*2₁/*c*, *a* = 10.105 (5), *b* = 8.954 (2), *c* = 8.378 (4) Å, β = 114.44 (5)°, *Z* = 2, *D_m* (flotation) = 2.25, *D_x* = 2.25 g cm⁻³. The H positions have been determined from three-dimensional X-ray data. The H atoms in the water molecules take part in a hydrogen-bond system, while those in the hydroxyl groups do not.

Introduction. Crystals of hydromagnesite were kindly provided by Professor P. Bariand, Laboratoire de Minéralogie et Cristallographie, Université de Paris VI. Although the crystals were strongly twinned on (100), a twin-free specimen of dimensions 0.23 × 0.07 × 0.07 mm could be isolated. Intensities were measured on a Philips four-circle diffractometer with Mo *K* α radiation, monochromated by a graphite plate, by the ω -2 θ scan technique with a scan speed of 4° min⁻¹ in ω . 2598 independent reflexion data were obtained for 2 θ ≤ 100°. Intensities were corrected for Lorentz and polarization factors but not for extinction. No correc-

tions were made for absorption, since μR of the crystal is less than 0.07 [$\mu(\text{Mo } K\alpha) = 5.3 \text{ cm}^{-1}$]. The systematic absences were *h*0*l* for *l* odd and 0*k*0 for *k* odd.

With the atomic coordinates given by Stephan (1974) and anisotropic thermal parameters the structure without H atoms was refined to an *R* value of 0.063. The positions of the H atoms were found from a difference Fourier synthesis. The structure was refined by the full-matrix least-squares program *LINUS* (Coppens & Hamilton, 1970) to a conventional *R* value of 0.052, with anisotropic thermal parameters for non-hydrogen atoms and isotropic for H. The weighting scheme employed was $w = 1/(A + B|F_o| + C|F_o|^2 + D|F_o|^3)$. The parameters *A*, *B*, *C* and *D* were varied so that $\langle w||F_o| - |F_c||^2 \rangle$ was independent of the magnitude of *F_o*. The values of *A*, *B*, *C* and *D* for the last cycles were 14.8, -1.31, 0.043, and -0.00029 respectively. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974) for the heavy atoms, and for H those of Stewart, Davidson & Simpson (1965) were used. Final atomic parameters are