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The Structure of Crystalline B_2O_3[*]

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The structure of crystalline B_2O_3 has been determined by electron diffraction from microscopic crystallites, the radial distribution function as determined from a Fourier transform of the X-ray intensity scattered by polycrystalline samples, and a random walk refinement procedure. The basic unit of the structure consists of oxygen atoms arranged in planar chains of equilateral triangles, each triangle being 2·40 Å on a side and containing a centered boron atom; the boron–oxygen bond distance is 1·38 Å, and the B–O–B bond angle is approximately 140°. Although the lattice is hexagonal, the molecular sub-units do not assume positions and orientations of high symmetry within each lattice cell. Measurement of the distribution function at 400°C in conjunction with that at 20°C shows a striking difference between the intra- and inter-molecular vibrations. The molecules appear to be in their zero-point vibratory states internally, while the lattice as a whole can be characterized by a Debye temperature of ~410°K.

Introduction

While it is clear that the most accurate determinations of crystal structure are accomplished with single-crystal specimens, in the absence of such specimens one must resort to polycrystalline samples. In either case, various Fourier transforms or sums of the measured intensities can be utilized. In fact, in the same issue of *Physical Review* in which Patterson proposed the use of the particular intensity sum which has come to bear his name, Warren & Gingrich (1934) proposed the use of the one-dimensional transform in deducing structures from polycrystalline data. Until recently, however, experimental and data analysis limitations have largely limited the use of the latter technique to non-crystalline materials. The complete one-dimensional transform, which yields a radial distribution function, is quite useful since it directly provides information about the near neighbor coordinations, and recent improvements allow its more general application.

The structure of crystalline B_2O_3, for which single crystals of significant size have not been available, has been a matter of controversy, in spite of a fairly recent proposal (Berger, 1953), based on polycrystalline Bragg-line intensities. The published results specify a C_3^2 space group, with a hexagonal unit cell ($a=4{\cdot}33$, $c=8{\cdot}392$ Å) containing 15 atoms. Because of a threefold screw axis, however, only 5 of the atom positions require unique specification; Berger's proposed positions are given in Table 1. We have utilized electron 'single-grain' diffraction, the complete one-dimensional transform of X-ray intensities, and a 'random-walk' refinement to obtain an improved description of the structure. Although the actual changes in atomic positions are seemingly minor, the new description differs in two fundamental respects: (*a*) the oxygen coordination about each boron atom is threefold triangular rather than fourfold tetrahedral, as Berger implied, and (*b*) the nearest neighbor bond distance (B–O) is a well defined quantity which exhibits none of the variation from pair to pair that has been previously proposed.

Experimental procedure

The diffracted intensity from crystalline boron oxide, prepared according to the method of McCulloch (1937), was measured with copper and molybdenum radiations with monochromators both before and after the sample. The use of double lithium fluoride monochromators effectively eliminated the Compton modified radiation with copper radiation and reduced the incoherent scattering to manageable proportions with molybdenum radiation (Strong & Kaplow, 1966).

The coherent X-ray intensity, in electron units per atom, is directly related to the partial density function, $\varrho_{ij}(r)$.

$$I=\sum_i X_i f_i^2+\sum_i\sum_j \frac{X_i f_i f_j}{k}\int_0^\infty 4\pi r\varrho_{ij}(r)\sin kr dr - \frac{[\Sigma X_i f_i]^2}{k}\int_0^\infty 4\pi r\varrho_0 \sin kr dr\,, \qquad (1)$$

where:

k $=4\pi\sin\theta/\lambda$
I = intensity in electron units per atom
X_i = atomic fraction of element i
f_i = atomic scattering factor of element i
r = radial distance
$\varrho_{ij}(r)$ = number of j-type atoms per unit volume at distance r from an i-type atom
ϱ_0 = average atomic density .

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It is convenient to define a reduced intensity function:

$$F(k)=k\left|\frac{I-\langle f^2\rangle}{\langle f\rangle^2}\right| \tag{2}$$

so that equation (1) becomes

$$F(k) = \sum_i \sum_j \frac{f_i f_j}{\langle f\rangle^2}\int_0^\infty 4\pi r\varrho_{ij}(r)\sin kr\,dr - \int_0^\infty 4\pi r\varrho_0 \sin kr dr\,. \tag{3}$$

If the sample is not monatomic, the assumption is made that the scattering factor for each of the elements present is adequately represented by

$$f_i = Z_i f_0$$

$$f_0 = \frac{\langle f^2\rangle^{1/2}}{\langle Z\rangle}\,, \tag{4}$$

leading to the conjugate relations

$$F(k) = \int_0^\infty 4\pi r(\varrho(r)-\varrho_0)\sin kr dr \tag{5}$$

$$G(r) = 4\pi r(\varrho(r)-\varrho_0) = \frac{2}{\pi}\int_0^\infty F(k)\sin kr dr\,, \tag{6}$$

where:

$$\varrho(r) = \sum_i \sum_j \frac{X_i Z_i Z_j}{\langle Z\rangle^2}\,\varrho_{ij}(r)\,. \tag{7}$$

The errors due to the use of an average form factor have been briefly discussed earlier (Kaplow, Strong & Averbach, 1965*a*), and will be treated more fully, for the particular case of B_2O_3, in a later paper concerning the structure of the non-crystalline phases. Although the effect is not entirely negligible, it can be ignored for the purposes of the present paper, except for one point which will be mentioned below.

The radial distribution function, $G(r)$, was obtained from the transform of the intensity function, corrected for multiple scattering (Strong & Kaplow, 1967). Previously described analysis methods were used, which eliminate most experimental errors and correct for errors in the scattering factors and for termination effects (Kaplow, Strong & Averbach, 1965*b*).

Analysis of results

The radial distribution function, $G(r)$, can be related to the crystallographic structure of the material that it represents, in two ways. First, the experimental radial distribution function for crystalline B_2O_3 at 20 °C (Fig. 1) shows directly the near neighbor pair distances. There is, for example, a nearest neighbor distance of 1·375 Å, represented by the first sharp peak. The first peak is well resolved, and it is safe to assume that it represents boron–oxygen pairs; its area ($\int 4\pi r^2\varrho(r)dr = 1{\cdot}98$) corresponds to 2·88 oxygen neighbors per boron atom. Similar data taken at 400 °C yielded 2·95 oxygen neighbors per boron atom. We believe, therefore, that there are, in fact, 3 nearest neighbor oxygen atoms per boron atom; the slightly lower value measured at room temperature, which deviation is probably beyond the experimental and analysis inaccuracies, may be indicative of residual defects remaining after the solid state transformation from the glass phase. In addition, there are clearly high multiplicity distances near 2·4, 3·0, and 3·7 Å, as well as at the expected unit-cell translation (Berger, 1953) of 4·33 Å. These oscillations in the distribution function, however, do not each necessarily correspond to a single type of pair. Moreover, it will be noted that beyond the immediate vicinity of the nearest neighbor distance the function never approaches $-4\pi r\varrho_0$, that is, there are some atom pairs at *every* distance, a circumstance which can be accounted for by the vibrations of the atoms. (The small peak at 1·95 Å is probably spurious. It appears to be caused by a data termination effect which is not properly corrected in the analysis.)

Secondly, it is evident that a proposed structure should lead to a calculated radial distribution function which agrees with the experimental $G(r)$ within experimental error over the entire range of r. To accomplish this comparison between a possible structure, represented by a space lattice and a set of fractional atomic coordinates u_i, v_i, w_i, associated with an atom of atomic number Z_i, a theoretical radial distribution function must be generated. The theoretical $G(r)$ is obtained by Gaussian broadening a set of multiplicities $C_j(R_j)$, where the R_j's are the interatomic distances between every atom in the lattice, and the C_j's are the electron weights of the pairs, given by

$$C_j = \frac{Z_k Z_m}{\left(\sum_1^N Z_i\right)^2/N} \tag{8}$$

where N is the number of atoms in the unit cell and the pair consists of atoms of atomic number Z_k and Z_m.

The Gaussian broadening function, which represents thermal vibrations of the atoms, is included in the sum over all pairs in equation (9), to yield the total pair distribution function:

$$G(r) = \sum_j \frac{C_j \exp\left[-(r-R_j)^2/2\gamma_j\sigma^2\right]}{R_j\sqrt{2\pi\sigma^2\gamma_j}} - 4\pi r\varrho_0\,. \tag{9}$$

ϱ_0 = average density in atoms.Å^{-3}
r = radial distance
σ = characteristic width due to average relative vibrations of distance pairs
γ_j = coupling factor to account for reduction in the amplitude of near neighbor relative vibrations (Kaplow, Strong & Averbach, 1964).

With all of the γ_j equal to 1·0, equation (9) represents independent, equal and isotropic vibrations of the atoms, with mean square displacements from equilibrium points $(\bar{u}_s^2)$ equal to $\sigma^2/2$; γ's less than 1·0 correspond to in-phase vibration or to vibrations which are smaller than average. In employing equation (2) to compare various structures with the experimental $G(r)$ it was found that at 20°C σ^2 should be 0·02 with $\gamma=0{\cdot}4$ for the first two peaks and $\gamma=0{\cdot}5$ for the peak at 3·0 Å. Beyond 3·0 Å, all the γ_j were set equal to 1·0.

The inadequacy of the previously proposed structure became evident when a radial distribution function, shown as the bottom curve in Fig. 1, was calculated from the reported atom positions. The most obvious discrepancy is in the shape of the nearest neighbor peak (B–O bonds); the experimental peak has a FWHM of only 0·2 Å, while the positions in the previously proposed structure predict a broad first peak because of a variety of B–O bond lengths. Also, the published structure was described as consisting of oxygen tetrahedra with the boron atoms in intermediate positions between the center and one face, which is inconsistent with the experimental results of three nearest neighbor oxygen atoms around each boron atom and the 0·576 ratio between the B–O and O–O bond lengths. For tetrahedra, this ratio would be 0·613, while for planar triangles the expected ratio is 0·577. Actually, it is unfortunate that Berger stressed the supposed fourfold coordination and tetrahedral configuration of his results; the fourth B–O bond, even with his atomic positions, is significantly longer than the three smaller ones.

Although it would seem that it should be fairly simple to place BO_3 triangles on a lattice with hexagonal symmetry, it soon became evident that the 4·33 Å lattice parameter and the 2·4 Å dimension of the triangles were not simply commensurate. The lattice symmetry therefore was of no help in finding the correct positions for the atoms in the unit cell. Since the symmetry of the BO_3 triangles could not be related to the symmetry of the lattice, it was considered desirable to check the unit-cell assignment. By dusting a small amount of powdered material on an electron microscope grid, it was possible to find small crystallites which yielded single-crystal electron diffraction patterns. These patterns were indexed, and verified that the unit cell assignment was correct.

Although the structure proposed by Berger is not correct, it can be seen from Fig. 1 that the general aspects of $G(r)$ derived from his structure are similar to those of the experimental $G(r)$. These similarities suggested that the true structure could be obtained by refinement. In considering what modifications were necessary in order to bring the structure specification into conformity with the actual near neighbor coordinations, the most obvious change required is that the borons must be moved to positions in the center of oxygen triangles. If one investigates the relative positions of the oxygen atoms in the published structure, it is found that there are three oxygen triangles with an oxygen–oxygen distance of approximately 2·4 Å for every two boron atoms in the structure. These three sites for the two boron atoms therefore yield three permutations to serve as initial trials for the refinement. In addition to the trial structures suggested by the published structure, several other structures consistent with fitting BO_3 triangles, as well as tetrahedra, into the unit cell were attempted.

The refinement of the various trial atomic distributions was accomplished by a random walk procedure. One of the five unique atoms in the cell was chosen at random and displaced a small distance in a random direction. The symmetry operations of the space group were then used to calculate all of the atomic positions, in 27 unit cells, and the C_j and R_j parameters were determined from these positions, to a maximum R_j of about 3·5 Å. If this near neighbor arrangement represented an improvement in the agreement between the calculated and experimental $G(r)$ the move was accepted, otherwise the move was rejected. This procedure was repeated until convergence was obtained. Each of the different starting structures that were used converged to a different final structure, indicating that the distribution function up to only 3·5 Å does not uniquely represent a single atomic arrangement, at least within our accepted convergence fit. However, one and only one of the sets of atom positions determined in this manner, a modification of one of the three permutations derived from Berger's initial proposal, was consistent with the experimental $G(r)$ over

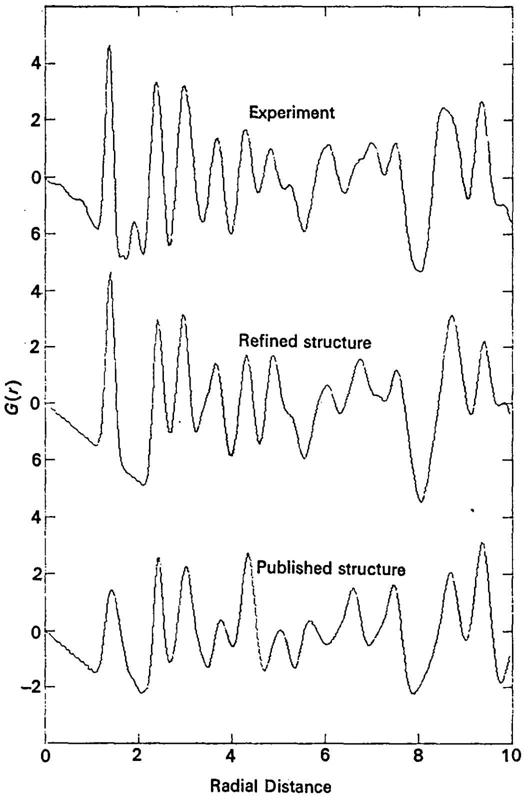

Fig. 1. Comparison of experimental radial distribution function with $G(r)$ derived from models for crystalline B_2O_3.

the entire range of distances. The fractional coordinates of the five unique atoms in the unit cell are shown in Table 1 for this refined structure and for the structure previously proposed by Berger. The calculated radial distribution function is shown as the middle curve in Fig. 1.

Table 1. *Atomic positions in crystalline* B_2O_3

	Refined structure			Berger		
	u	*v*	*w*	*u*	*v*	*w*
O(1)	0·173	0·082	0·0	0·20	0·15	0·0
O(2)	0·478	0·806	0·120	0·46	0·79	0·07
O(3)	0·497	0·245	0·577	0·51	0·23	0·56
B(1)	0·474	0·049	0·013	0·54	0·15	0·02
B(2)	0·677	0·785	0·245	0·59	0·77	0·26

A match comparable to that in Fig. 1 is found over the entire reduced intensity function, of course, since the two functions are Fourier transform related. Further confidence in the essential correctness of the derived positions was obtained by comparison of calculated Bragg diffraction cone integrated intensities with estimates from the data. No attempt was made to separate the diffuse scattering from the peaks, nor to planimeter individual areas. Since we have previously noted that peak widths are essentially constant on an intensity *versus* $k=4\pi \sin\theta/\lambda$ plot, relative 'Bragg areas' were estimated by multiplying the heights above background by k. Normalized values are presented in Table 2; $\Sigma\,|I_{\text{est}}-I_{\text{calc}}|/\,\Sigma\,I_{\text{est}}$ equals 0·15 for the refined positions, a factor of two improvement over the previous positions.

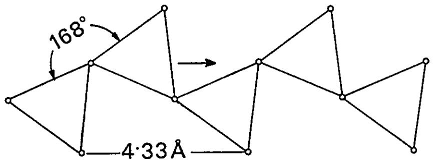

Fig. 2. B_2O_3 chain structure.

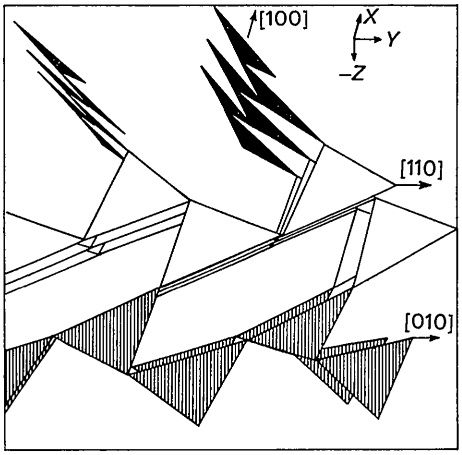

Fig. 3. Perspective view of B_2O_3 structure.

Table 2. *Estimated and calculated Bragg intensities for crystalline* B_2O_3

hkl	Measured	Berger	Refined
100	8	72	1
101	399	293	303
102 003	999	854	976
103	464	291	491
110	16	111	51
111	552	559	628
112	82	80	38
200	4	35	3
201 104	70	223	98
202 113	144	231	172
203	48	43	64
105	67	65	83
114	—	48	7
210	27	23	10
211 204	197	167	217
006	—	16	1
212	21	58	29
115	42	31	9
106	23	62	46
213	25	44	28
300 205	42	55	40
301	8	28	36
302	72	50	50
214 116	99	69	89
303 107	108	39	49
206	12	5	18
220 215	63	39	53

The radial distribution fit could be made even closer by additional 'random walking' with a finer step size, and/or by the introduction of additional vibrational coupling coefficients. Alternatively the fit to the relatively small number of peak intensity values could be improved, by a direct intensity fit of atom position and vibration parameters within constraints imposed by the radial distribution result (such as the nearest neighbor correlation). This has not been done, in part because such additional refinement might not be entirely meaningful in view of uncertainties in the data, in the analysis parameters and in structural imperfections in the sample. We believe, however, that the present description contains the essential elements of both the local configurations and the overall structure.

Description of the structure

Crystalline B_2O_3 has the trigonal space group $P3_1$ (no. 144) with unit-cell parameters $a=4{\cdot}33$, $c=8{\cdot}39$ Å, in agreement with Berger. Only five of the fifteen atoms in a unit cell (2 boron and 3 oxygen) require specification because of the threefold screw axis; refined values for those positions are given in Table 1.

The atomic arrangement can be characterized as consisting of intersecting chains of oxygen triangles

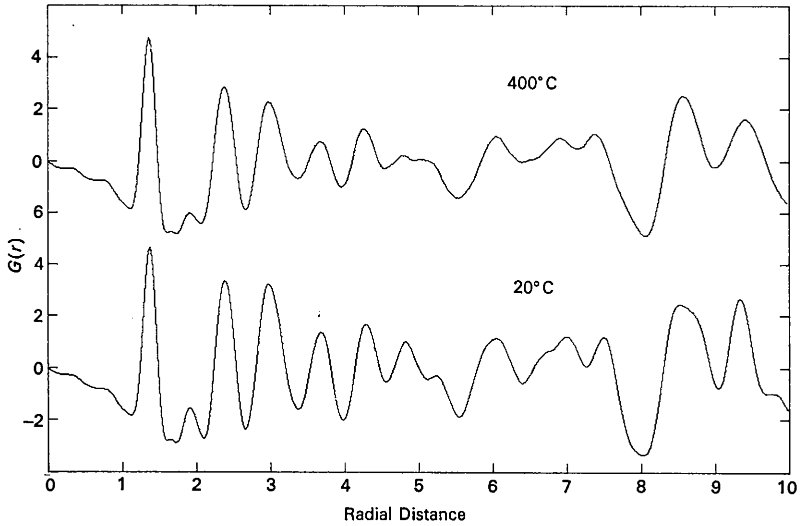

Fig. 4. Variation of the experimental radial distribution function with temperature.

triangles joined at their corners, with boron atoms centered in the triangles. The major bond lengths in the structure are: three oxygen atoms at 1·38 Å from each boron, four oxygen atoms at 2·4 Å from each oxygen atom, and six oxygen atoms near 3·0 Å from each oxygen atom. The B–O–B bond angle is approximately 140°.

The chain of oxygen triangles with sides of 2·39 Å and boron atoms at the center, which is the basic building block of the structure, is illustrated in Fig. 2. The chain is planar with the plane inclined at about 45° to the basal plane of the hexagonal unit cell. The arrow shown in Fig. 2 would be located in the basal plane and at $c/3$ and $2c/3$ and would be pointing in the [100], [010], and [110] directions respectively. A perspective view of the linkage between chains of triangles is shown in Fig. 3.

Thermal vibrations

In Fig. 4 the experimental distribution function, measured at 400°C, is compared with the previously discussed data for 20°C. Although the structure is unchanged, the effect of increased thermal vibrations is obvious in the lessened magnitudes of the oscillations beyond the second major peak. Fitting the results with equation (9), as previously discussed, yields the mean square amplitudes of vibrations for the individual bond distances, $\gamma_j\sigma^2$. In comparing these values for the two temperatures one finds a striking difference between the inter- and intra-molecular bonds. For the nearest neighbor B–O bond, there is no discernible temperature dependence of the peak width; $\gamma_1\sigma^2=0{\cdot}0072$ at 20° and 400°C. Beginning with the peak at 3·0 Å, which is the first totally inter-molecular correlation distance, the vibrations cause the expected classical thermal broadening; in terms of the Debye model, the σ^2's correspond to a characteristic temperature, $\theta_D \sim 410$°K. The peak at 2·4 Å is primarily due to the O–O bonds within the BO_3 triangles, but also has an unresolved contribution from an inter-molecular bond; it shows only a slight broadening which can be entirely accounted for by the classical vibration of the inter-molecular bond. We conclude, therefore, that the B–O and O–O intra-molecular bonds are in their zero-point vibrational states, at least regarding those modes which produce displacements along the bond directions. These observations qualitatively explain earlier specific heat measurements, which have been interpreted in terms of a Debye temperature ~ 325°K and several Einstein terms with $\theta_E > 1000$°K (Fajans & Barber, 1952).

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