motion, using a riding-model approximation. The shortest bromine---bromine contact within the group is 3·76 Å. All bond distances and angles are listed in Table 4 (see Fig. 1). Ring atoms of the 4-ethylpyridinium cation were fixed in the rigid-body refinement. The unusually short C(7)–C(8) distance obtained in the ethyl group is a result of the large thermal parameters associated with those atoms. Using the anisotropic thermal parameters obtained from the earlier refinement, this distance adjusts to 1·51 Å when a riding model is assumed. The high thermal motion of the cation can be attributed to the size of its cavity.

A unit-cell drawing of 4-ethylpyridinium tetrabromoferrate(III) is shown in Fig. 2. The $FeBr_4^-$ tetrahedra are nearly aligned with their threefold axes almost coincident in the **c** direction. The closest bromine---bromine distance in this direction is 4·00 Å, which is greater than the sum of the van der Waals radii of 3·90 Å. The shortest intermolecular bromine---bromine distance is 3·72 Å involving Br(1) across a center of symmetry. One significantly short hydrogen---bromine distance involving H(1) and Br(4) of 2·3 Å is present. The Fe–Br(4)---H(1) and Br(4)---H(1)–N(1) angles are 115 and 157°, respectively. The Fe–Br(4) bond distance is also slightly longer than the other Fe–Br distances. The N–H---Br(4) hydrogen bond may contribute to the slight ion deformation and the crystal stability of this compound.

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On the Crystal Structure of B_2O_3

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The crystal structure of B_2O_3 derived by Gurr, Montgomery, Knutson & Gorres is not essentially different from that reported earlier by Strong & Kaplow. Removal of an arbitrary transformation of axes shows the newer single-crystal results to be a refinement (associated with inequalities in the near-neighbor separation distances) which is verified by the original powder data and the atomic pair distribution fitting procedure.

Two of the present authors have previously published a description of the structure of crystalline B_2O_3 (Strong & Kaplow, 1968; hereafter referred to as SK). That description was based on analysis of the radial pair-distribution function, $4\pi r[\varrho(r)-\varrho_o]$, determined from the Fourier transform of the reduced X-ray intensities recorded from powder specimens. The reduced intensity is defined as:

$$k\{[I(k)-\langle f^2\rangle]/\langle f\rangle^2\}\,,$$

where: $k=4\pi\sin\theta/\lambda$
$I(k)$ = intensity, electron units
$\langle f\rangle=\sum x_i f_i(k)$
$f_i(k)$ = atomic scattering factor, ith element
x_i = atomic fraction, ith element
$4\pi r^2\varrho(r)\mathrm{d}(r)$ = number of atoms in a spherical shell of radius r and thickness dr about an average atom, each pair-type being weighted by its scattering power.
ϱ_o = mean number of atoms per unit volume.

The primary object of the previous work was to determine the local atomic arrangements and structural units for reference in the interpretation of the more common amorphous form and of the liquid. Also, the parameters of a previously reported unit cell (Berger, 1953) were confirmed, and atomic coordinates were derived which gave a long-range structure that seemed to fit the entire experimental pair-distribution function adequately.

More recently, Gurr *et al.* (1970; hereafter referred to as GMKG) obtained a pressure-grown single crystal of adequate size and redetermined the structure, using 130 Bragg-peak integrated intensities in a standard analysis. Although the GMKG description of the structure agrees with that previously reported (*i.e.*, three-dimensional connected ribbons of boron-centered, oxygen triangles), the newly derived atomic coordinates were represented as being an entirely different set. To clarify what appears to be an ambiguous situation, we wish to point out that the GMKG coordinates represent essentially the same structure reported earlier. A transformation of axes relates the two sets of coordinates within a maximum deviation of 0·05:

$$X_{\rm GMKG}=v_{\rm SK}-u_{\rm SK}+\tfrac{2}{3}$$
$$Y_{\rm GMKG}=v_{\rm SK}+\tfrac{1}{3}$$
$$Z_{\rm GMKG}=-w_{\rm SK}$$

The residual differences appear to be structurally dependent on the introduction of slightly greater irregularities and inequalities in the dimensions of the aforementioned oxygen triangles. This is consistent with the fact that the SK analysis was restricted by a weight being placed on minimizing the spread in the closest B–O and O–O equilibrium distances. The possibility that the slowly crystallized powder actually differs slightly from the pressure-grown crystal is dispelled by the fact that the single-crystal refinement does provide an improved solution to the pair-distribution analysis of the original powder data.

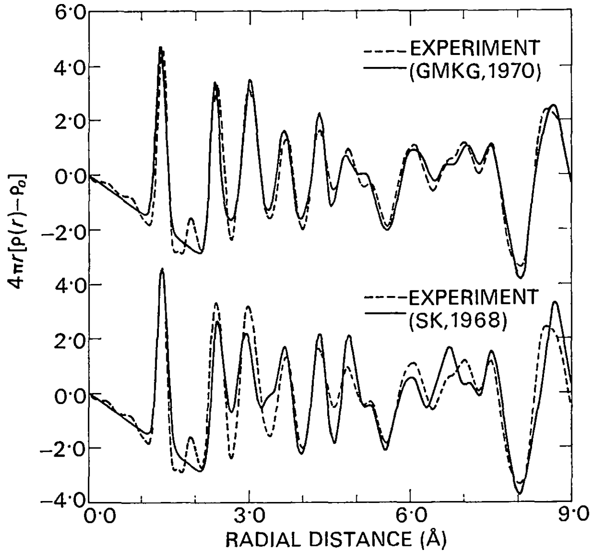

Fig. 1. Radial distribution functions for polycrystalline B_2O_3, showing the sensitivity of the powder analysis to the single-crystal refinement.

The comparison (Fig. 1) also clearly shows that the one-dimensional fitting procedure is sensitive enough to 'recognize' the refined structure, which it presumably would have achieved more closely without the ill-chosen restriction. Considered in the light of the relatively small variation in atomic coordinates, the comparison indicates that fairly high precision may be achieved. Note also that the slight modification of coordinates does not alter the thermal parameters derived from the match to the pair-distribution function. Particular values previously reported for the mean-square thermal deviation of the distance between atom pairs for nearest neighbors and distant neighbors, respectively, are

$$\sigma^2_{B-O}=0{\cdot}0072\ \text{Å}^2 \quad\text{and}\quad \sigma^2_\infty=0{\cdot}025\ \text{Å}^2\,.$$

The essential similarity of the reported structures was first noted through a consideration of the basic topology, which is most simply described as a 3-connected system of boron atoms joined through 2-connected oxygen atoms. Of particular interest to one of the present authors is the fact that a previously published tabulation of 3-connected nets (Wells, 1954) does not include the B_2O_3 net (which contains 6 points in the repeat unit and no circuits smaller than 10 gons).

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