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The crystal structure of KBF_4.*

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The crystal structure of KBF_4 is isostructural with that of $KClO_4$ and the B–F bond distances (1·378 to 1·391 Å) are almost identical to those published for $NaBF_4$.

Introduction

The crystal structure of the low temperature polymorph of KBF_4 is isostructural with that of $KClO_4$ and the lattice parameters $a_0 = 8{\cdot}6588 \pm 0{\cdot}0005$, $b_0 = 5{\cdot}4800 \pm 0{\cdot}0004$, $c_0 = 7{\cdot}0299 \pm 0{\cdot}0008$ Å at 24°C are in better agreement with the $KClO_4$ lattice parameters (Mani, 1957) than those previously published for KBF_4 by Ballanca & Sgarlata (1951) and Pesce (1930). The calculated density is 2·5067 g.cm^{-3} and $Z=4$.

The crystal structure of KBF_4 has been refined as part of the basic research on the properties of alkali metal fluoroborates, mixtures of which are being investigated as molten salt coolants for nuclear breeder reactors (ORNL, 1967).

Experimental

Euhedral crystals of KBF_4 were grown from a saturated solution of purified KBF_4 and HF in water. The crystals were prepared by L. O. Gilpatrick of the Reactor Chemistry Division and a chemical analysis of the crystals gave (in weight per cent): K, 30·9; B, 8·66; F, 60·3; H_2O, 0·20; theoretical: K, 31·06; B, 8·59; F, 50·38. The crystals contain 210 ppm of oxygen as measured by BrF_3 displacement. The oxygen is probably present as OH^-.

A small crystal 0·145 × 0·139 × 0·323 mm bounded by the forms {101} and {210} was mounted on a Picker four-circle goniostat, and the reflection intensities were measured with a scintillation-counter detector using unfiltered Cu$K\alpha$ radiation. Independent reflections out to $2\theta = 145°$ were measured by the 2θ scan technique (Busing, Ellison, Levy, King & Roseberry, 1968).

The conditions for reflection are: hkl, no conditions; $0kl$, $k+l=2n$; and $hk0$, $h=2n$; consistent with *Pnma* (No. 62) and $Pna2_1$ (No. 33). The lattice parameters were determined by least-squares adjustment from 31 Mo $K\alpha_1$ reflections (Mo $K\alpha_1 = 0{\cdot}709260$ Å).

The structure was refined by iterative least-squares with a modification of the Busing, Martin & Levy (1962) computer program. The starting parameters were the centrosymmetric set suggested by Wyckoff (1965) and the results

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Table 1. *Atomic parameters for* KBF_4

The number in parentheses is the standard error in terms of the last significant digit, as derived from the variance-covariance matrix.

	$x10^4$	$y10^4$	$z10^4$	$\beta_{11}10^4$*	$\beta_{22}10^4$	$\beta_{33}10^4$	$\beta_{12}10^4$	$\beta_{13}10^4$	$\beta_{23}10^4$
K	1844·9 (7)	2500	1611 (2)	37 (2)	183 (5)	116 (3)	0	−1·4 (8)	0
B	626 (4)	2500	6897 (7)	38 (5)	142 (12)	111 (9)	0	−9 (5)	0
F(1)	1789 (3)	2500	5560 (4)	110 (4)	287 (9)	153 (7)	0	50 (4)	0
F(2)	−814 (3)	2500	6049 (5)	75 (4)	385 (11)	245 (7)	0	−71 (4)	0
F(3)	774 (2)	440 (3)	8039 (3)	92 (3)	173 (6)	165 (5)	−1 (3)	8 (2)	42 (4)

* Coefficients in the temperature factor: $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$.

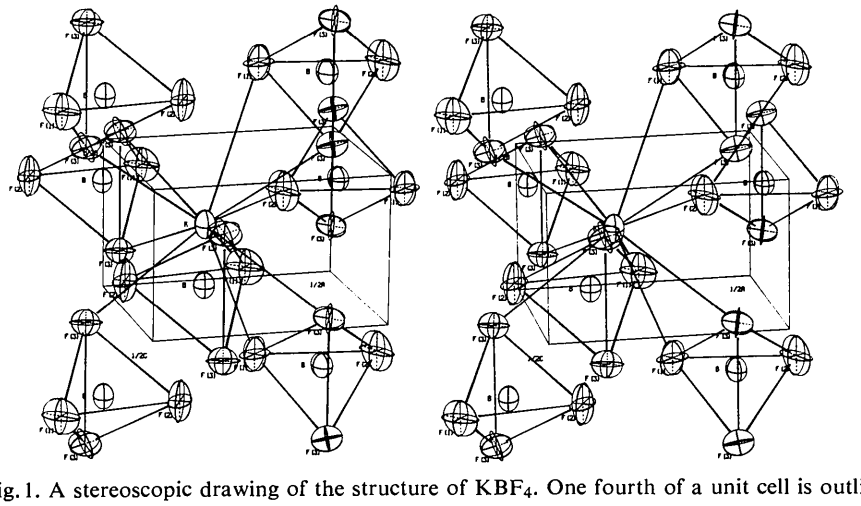


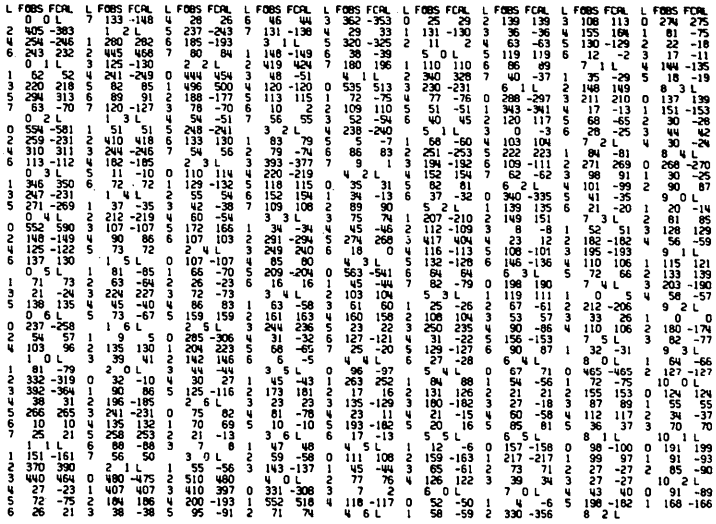
Fig. 1. A stereoscopic drawing of the structure of KBF_4. One fourth of a unit cell is outlined.

Table 2. *The interatomic distances and* F–B–F *angles for* KBF_4

The number in parentheses on the interatomic distances is $\sigma \times 10^4$ and on the angles $\sigma \times 10$.

K–F(2)	2·758 (3) Å	K–F(1)	2·776 (3) Å
2[K–F(3)]	2·793 (2)	2[K–F(3)]	2·803 (2)
2[K–F(3)]	2·905 (2)	2[K–F(1)]	3·075 (2)
B–F(1)	1·378 (5)	B–F(2)	1·382 (4)
2[B–F(3)]	1·391 (3)	2[F(1)–F(3)]	2·255 (3)
F(1)–F(2)	2·280 (4)	2[F(2)–F(3)]	2·263 (3)
F(1)–B–F(2)	111·4 (4)°	2[F(1)–B–F(3)]	109·0 (2)°
2[F(2)–B–F(3)]	109·4 (2)	F(3)–B–F(3)	108·5 (4)

Table 3. *Observed and calculated structure factors* $\times 10$ *for* KBF_4



are listed in Table 1. Scattering factors for K, B, and F were taken from Cromer & Waber (1965). The quantity minimized by the least-squares program was $\Sigma w||sF_o^2|-|F_c^2||^2$ with weights, w, equal to the reciprocals of the variances which were estimated from the empirical equation:

$$\sigma^2(F_o^2)=[T+B+(0{\cdot}05(T-B))^2]/[A(\mathrm{Lp})^2]$$

where T = total counts, B = background counts, A = absorption correction ($\mu = 15{\cdot}6$ cm^{-1} for Cu $K\alpha$), and Lp = Lorentz and polarization (Brown & Levy, 1964). Anisotropic temperature factors were calculated for all atoms. A stereoscopic drawing of one K atom and its BF_4 nearest neighbors is shown in Fig. 1.

The discrepancy indices are

$$R_1 \equiv \Sigma\,||F_o^2|-|F_c^2||/\,\Sigma\,|F_o^2| = 0{\cdot}0682$$

and $R_2 \equiv \Sigma\,||F_o|-|F_c||/\,\Sigma\,|F_o| = 0{\cdot}0384$, for 348 independent reflections. The standard deviation of an observation of unit weight, $[\Sigma\, w(F_o-F_c)^2/(n_o-n_v)]^{1/2}$, is 1·878 where n_o is the number of reflections and n_v the number of variables. The interatomic distances and F–B–F angles are listed in Table 2 and the observed and calculated structure factors are listed in Table 3. An extinction correction was made on F_c by the method suggested by Zachariasen (1967).

The K^+ ion is coordinated by $8F^-$ ions at distances less than 3·0 Å and by two more F^- ions at 3·075 Å. The K^+ polyhedron shares edges with three and corners with four $B–F_4$ tetrahedra. The $B–F_4$ tetrahedra are slightly irregular with tetrahedral angles of 108·5° to 111·4° and B–F distances 1·378 to 1·391 Å, Table 2. The B–F distances are almost equal to the B–F distances for $NaBF_4$ (1·386 and $1{\cdot}392 \pm 0{\cdot}002$ Å) found by Brunton (1968) from a refinement of the $NaBF_4$ structure proposed by Weiss & Zahner (1967). A calculated B–F single bond distance is 1·37 Å (Pauling, 1960).

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