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A note on the structure of $KBrF_4$.*

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Recently Siegel (1956) has investigated, by powder methods, the crystal structure of $KBrF_4$; he has proposed a structure based on the tetragonal space group D_{4h}^{18}–$I4/mcm$, with four molecules in a unit cell having the dimensions $a = 6{\cdot}174 \pm 0{\cdot}002$ Å and $c = 11{\cdot}103 \pm 0{\cdot}002$ Å.

A surprising feature of the structure derived by Siegel is the configuration of the BrF_4^- ion; he reported it to be tetrahedral, whereas structural theory would predict that the central bromine atom would form octahedral sp^3d^2 orbitals. If, as expected, two apical positions are occupied by unshared electron pairs, the resulting configuration of the BrF_4^- ion would be square.

A brief study of a three-dimensional model of the structure proposed by Siegel indicated that re-positioning the potassium and bromine atoms into different special positions of the space group and changing the z parameter of the fluorine atoms by $\frac{1}{4}$ would result in an approximately square configuration for the BrF_4^- ion; furthermore, this alternative arrangement would result in satisfactory interatomic distances and packing geometry. We have accordingly looked at this structure in some detail, and we believe that it should be accepted in preference to that proposed by Siegel.

The revised atomic positional parameters are

4 K in 4(*a*): $(0, 0, \frac{1}{4})$; $(0, 0, \frac{3}{4})$; $(\frac{1}{2}, \frac{1}{2}, \frac{3}{4})$; $(\frac{1}{2}, \frac{1}{2}, \frac{1}{4})$.
4 Br in 4(*d*): $(0, \frac{1}{2}, 0)$; $(\frac{1}{2}, 0, 0)$; $(\frac{1}{2}, 0, \frac{1}{2})$; $(0, \frac{1}{2}, \frac{1}{2})$.
16 F in 16(*l*): $(0, 0, 0;\ \frac{1}{2}, \frac{1}{2}, \frac{1}{2})+$
$(x, \frac{1}{2}+x, z)$; $(\bar{x}, \frac{1}{2}-x, z)$; $(\frac{1}{2}+x, \bar{x}, z)$; $(\frac{1}{2}-x, x, z)$;
$(x, \frac{1}{2}+x, \bar{z})$; $(\bar{x}, \frac{1}{2}-x, \bar{z})$; $(\frac{1}{2}+x, \bar{x}, \bar{z})$; $(\frac{1}{2}-x, x, \bar{z})$;

with $x = 0{\cdot}152$ and $z = 0{\cdot}880$.

The symmetry associated with the positions of the bromine atoms is mmm, rather than $\bar{4}2m$ for the positions proposed by Siegel. In addition to the change of $\frac{1}{4}$ in the z parameter of the fluorine atoms, as noted above, the x and z parameters have been changed slightly from those proposed by Siegel in order to improve the agreement between observed and calculated intensities and to give a more symmetric structure.

Although on theoretical grounds this revised structure is more reasonable than that derived by Siegel, the proof of its correctness must lie in the agreement between calculated and observed intensities. Unfortunately, the intensity data reported by Siegel hardly suffice, either in number or in quality, to distinguish between the two structures. Aside from the small changes in the parameters of the fluorine atoms, the differences between the two structures are manifested in only one class of reflections, those with l odd, which contain contributions from the fluorine atoms alone and of which only six are reported to be observed. Two of the six are obscured by impurity lines, two others are from a poorly resolved group of four reflections, and a fifth has been only approximately measured.

Intensity data for $KBrF_4$ are listed in Table 1; the observed and calculated $I^{\frac{1}{2}}$ values in the second and

Table 1. *Intensity data*

The brackets surrounding poorly resolved lines and the asterisks indicating interference by an impurity line are Siegel's. The reflections are in order of increasing sin (θ), as listed by Siegel

Columns (2) and (3): values given by Siegel
Column (4): values calculated by us from Siegel's parameters
Column (5): values calculated from our parameters

hkl (1)	$I_o^{\frac{1}{2}}$ (2)	$I_c^{\frac{1}{2}}$ (3)	$I_c^{\frac{1}{2}}$ (4)	$I_c^{\frac{1}{2}}$ (5)
002	65	94	95·6	68·1
110	97	111	101·0	108·2
112	203	219	217·7	210·0
200	93	91	89·2	98·0
004	32	34	33·5	26·6
202* ⎫	35	35	34·4	43·7
211* ⎭	70	58	60·3	73·6
114	22	22	19·2	12·5
213*	51	61	65·1	45·0
220*	73	77	79·7	76·2
204	110	110	111·9	109·6
222	34	33	31·7	29·2
310	0	4	0·9	0·4
006 ⎫	~ 0	3	3·9	8·1
312 ⎭	90	91	93·7	100·5
215*	< 33	3	3·8	33·0
224 ⎫	58	58	56·8	58·7
116 ⎭	57	54	54·3	59·5
321	0	3	2·9	9·5
314* ⎫	39	27	45·4	49·7
206* ⎭	26	35	27·9	20·1
323	0	4	3·6	6·6
400	23	23	22·9	19·7
402 ⎫	24	12	11·5	14·6
411 ⎭		9	14·3	13·4
330	27	27	27·4	26·3
†226 ⎫	19	35	11·0	13·7
†332 ⎭	43	45	46·0	41·5
413 ⎫	23	20	18·5	9·7
008 ⎪	27	23	24·2	29·6
420 ⎪	43	43	44·1	43·9
217 ⎭	19	20	21·7	12·0
325	0	2	0·3	5·8
404 ⎫	45	45	46·6	51·4
316 ⎬	50	60	61·5	53·8
422 ⎭	19	20	19·7	18·2
118	18	14	14·5	18·1
334	0	2	2·9	4·2
208	28	28	28·2	26·2
415	18	12	1·4	9·0
424	35	37	37·1	36·5
431	—	—	1·1	2·7
510	18	13	12·6	10·6
406 ⎫	18	16	15·8	11·8
512 ⎭	37	39	39·0	38·1
⎧ ‡433	—	—	1·4	2·0
⎩ ‡228	27	27	27·5	27·8
327	0	2	1·7	2·5

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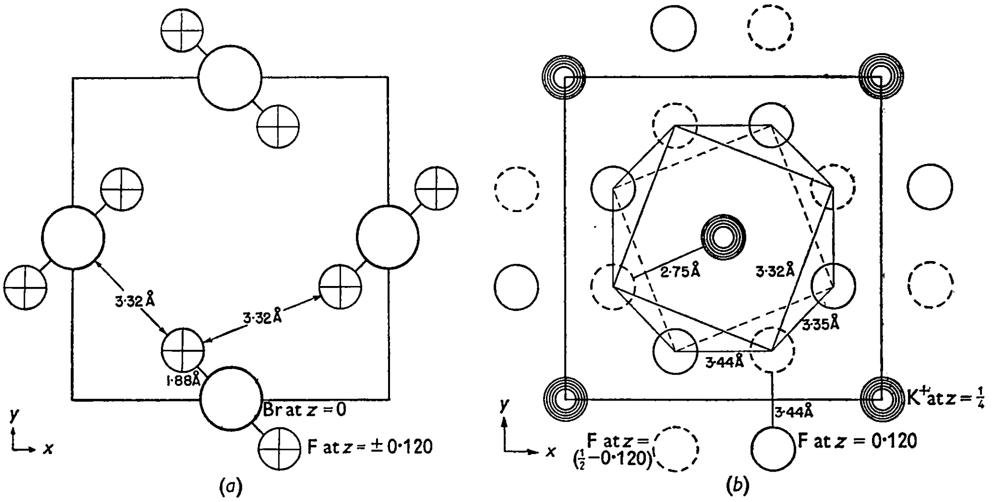

Fig. 1. (*a*) The projection on to (001) of the atoms between $z=-\frac{1}{4}$ and $z=\frac{1}{4}$. The potassium ions at $z=\pm\frac{1}{4}$ are omitted. (*b*) The projection on to (001) of the atoms between $z=0$ and $z=\frac{1}{2}$. The bromine atoms at $z=0$ and $z=\frac{1}{2}$ are omitted.

Table 1 (*cont.*)

hkl	$I_o^{\frac{1}{2}}$	$I_c^{\frac{1}{2}}$	$I_c^{\frac{1}{2}}$	$I_c^{\frac{1}{2}}$
(1)	(2)	(3)	(4)	(5)
336 }	20	17	16·1	23·0
521 }		12	8·8	11·9
318 }	12	9	8·4	3·3
219 }		5	5·6	11·3
0,0,10 }	17	10	9·8	6·0
514 }		10	9·5	11·4
426	13	9	8·7	11·1
523	~ 18	11	12·2	9·3
440 }	23	19	19·1	20·8
417 }	—	9	10·0	4·2
435	—	—	0·1	2·1
1,1,10	25	25	25·1	23·2
442	~ 12	9	9·0	8·3
530	~ 0	5	4·3	7·1
2,0,10	0	4	3·4	6·6
532	22	28	28·3	29·5
408	18	17	18·1	13·5

† We have calculated $\sin^2(\theta)$ for 226 to be 0·2982, while Siegel reports a value of 0·3004; accordingly, the order of listing of 226 and 332 has been inverted to agree with our calculations.

‡ From the calculated $\sin^2(\theta)$ values for 433 and 228, 0·4331 and 0·4332, respectively, it is very improbable that these two reflections could have been resolved and we have therefore added brackets.

third columns are reproduced from Siegel's publication* while the last two columns contain our calculated values for both structures. We have used Thomas–Fermi atomic form factors for neutral bromine (*Internationale Tabellen*, 1935) and Berghuis *et al.* (1955) form factors for K$^+$ and F, and have introduced a temperature factor with $B = 2$ Å^2, following Siegel; we have included the Lorentz and polarization and multiplicity factors in the calculated $I^{\frac{1}{2}}$ values and have introduced an empirical scale factor of $1/(10\sqrt{2})$. For a few reflections—notably, 314, 226, and 415—we have calculated, from the parameters given by Siegel, values significantly different from those reported by him. In addition we have included three reflections—431, 433, and 435—which were omitted by him.

Drawings of the revised structure of $KBrF_4$ are given in Fig. 1(*a*) and Fig. 1(*b*), which show the environments of the bromine atoms and potassium atoms, respectively. It should be noted that the fluorine atoms form a nearly regular square antiprism about the potassium ion, whereas in the structure proposed by Siegel the fluorine atoms form a somewhat distorted cube about the potassium ion. The interatomic distances shown in Fig. 1 may be compared with the predicted van der Waals distances of 3·30 Å for Br–F, 2·74 Å for K$^+$–F, and 2·70 Å for F–F.

Although on the basis of the intensity agreement reported in Table 1 there is little to choose between the two structures, we believe that, in view of the configuration of the BrF_4^- ion and the overall packing arrangement, the revised structure may be tentatively accepted as correct. Unambiguous proof must, of course, await the availability of more satisfactory intensity data.

References

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* It is not clear how Siegel was able to deduce individual values of $I_o^{\frac{1}{2}}$ from the observed intensities of poorly resolved lines; furthermore, the listing of $I_c^{\frac{1}{2}}$ values is unfortunate since the quantities are not additive for unresolved lines containing contributions from diffraction planes having different multiplicities.