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The Crystal Structures of Alkali Metal Bifluorides

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Potassium, rubidium and cesium bifluorides exist in cubic modifications at high temperatures and in a tetragonal modification at room temperature. Both sodium and lithium bifluoride decompose to hydrogen fluoride and normal salt upon heating. Crystal structures are proposed for five phases not previously studied.

Bifluoride ion has been subject to much study because of its importance in the theory of hydrogen bonding, and it is now well established that the ion is symmetrical. In their thermodynamic investigation of potassium bifluoride, Westrum and Pitzer[1] found that the crystal transition[2] at 196° is accompanied by an entropy change more than twice that of fusion. Moreover the transition to the soft, waxy β-phase results in a large density decrease.[3] Cesium bifluoride also exhibits a crystal transition.[4]

The present work was undertaken to find out what part the structural requirements of the bifluoride ion play in accounting for the interesting properties of β-KHF$_2$ and to determine whether the existence of more than one crystal modification is a general property of alkali metal bifluorides.

Experimental

Alkali metal bifluorides were prepared by adding a small excess of hydrofluoric acid to the appropriate carbonate. Crystallization was by slow evaporation. Recrystallization was effected by dissolving in water and adding ethyl alcohol to reduce solubility. Analysis by acidimetry showed that the desired compound, MHF$_2$, was formed in each case.

The crystals were examined with a polarizing microscope equipped with a Kofler hot-stage. Transition and melting points were determined in this way.

X-Ray diffraction data were obtained from powder specimens by means of a North American Philips Geiger spectrometer. An apparatus was provided to heat the specimens so that diffraction data could be obtained at high temperatures. Peak heights were taken as observed intensities, since they were found to be closely proportional to integrated values in the angular region considered. Copper Kα radiation was used.

Results and Discussion

Lithium Bifluoride.—Lithium bifluoride is optically anisotropic and rapidly decomposes in air at room temperature to give hydrogen fluoride and lithium fluoride. This was shown by the X-ray identification of a lithium fluoride residue. Diffraction data are consequently very difficult to obtain, although several attempts to obtain Laue photographs from bits of crystal showed hexagonal symmetry.

Sodium Bifluoride.—The structure of sodium bifluoride is known,[5,6] and the unit cell is rhombohedral. Sodium bifluoride decomposes to hydrogen fluoride and sodium fluoride upon heating.

α-**Potassium Bifluoride.**—The structure of α-KHF$_2$ has been redetermined by Helmholz and Rogers,[7] and the unit cell is tetragonal. The plane spacings determined in the present work (Fig. 1) show the thermal expansion similar to that observed dilatometrically by Fink and Westrum.[3]

α-**Rubidium Bifluoride.**—The powder data for the room temperature or α-phase may be indexed on a tetragonal unit cell. Cell dimensions are shown in Table I. In Table II structure factors calculated using the assumption that RbHF$_2$ is isostructural with KHF$_2$ are compared with those observed. A fluorine parameter was chosen that corresponds to the fluorine–fluorine distance in KHF$_2$. The over-all fractional deviation of calculated structure factors from those observed (R) is 0.12. Since most of the scattering is by rubidium atoms, the fluorine positions may be varied substantially without worsening the agreement. Thus, although RbHF$_2$ is not a suitable material for use in determination of accurate fluorine-fluorine distances, the agreement shown in Table II supports the proposition that RbHF$_2$ and KHF$_2$ have the same structure.

TABLE I

	KHF$_2$	RbHF$_2$	CsHF$_2$
Transition temp., °C.	196	176	61
M.p., °C.	238	188	170
Tetragonal α-phase			
a, Å.	5.67[a]	5.90[b]	6.14[c]
c, Å.	6.81	7.26	7.84
ρ (X-ray), g./cm.^{3}	2.36	3.27	3.86
Cubic β-phase			
a, Å.	6.36[d]	6.71[e]	4.21[f]
ρ (X-ray), g./cm.^{3}	2.02	2.73	3.81

[a] Ref. 7. [b] 25°. [c] 40°. [d] 200°. [e] 180°. [f] 80°.

TABLE II

AMPLITUDES FOR α-RbHF$_2$

(hkl)	F^a_{obsd}	F_{calcd}	(hkl)	F_{obsd}	F_{calcd}
110	26	25	222	28	−26
002	22	−15	004	50	36
200	28	28	213		7
112	40	−35	132	18	−19
211	10	10	114	25	21
202	32	−30	321	7	−5
310	27	20	204	23	24
220	23	27			

[a] Derived from maximum counting rate, I, according to $[I \cos^2\vartheta \sin\vartheta/(1 + \cos^2 2\vartheta)H]^{1/2}$ where H is the multiplicity.

α-**Cesium Bifluoride.**—The powder data for the room temperature phase may be indexed on a tetragonal unit cell. Cell dimensions are shown in Table I. In calculating intensities the cesium contribution virtually accounts completely for the

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[1] E. F. Westrum, Jr., and K. S. Pitzer, THIS JOURNAL, **71**, 1940 (1949).

[2] First noted by G. H. Cady, *ibid.*, **56**, 1431 (1934).

[3] R. W. Fink and E. F. Westrum, Jr., *J. Phys. Chem.*, **60**, 800 (1956).

[4] R. V. Winsor and G. H. Cady, THIS JOURNAL, **70**, 1500 (1948).

[5] F. Rinne, H. Hentschel and J. Leonhardt, *Z. Krist.*, **58**, 629 (1923).

[6] O. Hassel and C. C. Andersen, *Z. physik. Chem.*, **122**, 151 (1926).

[7] L. Helmholz and M. T. Rogers, THIS JOURNAL, **61**, 2590 (1939).

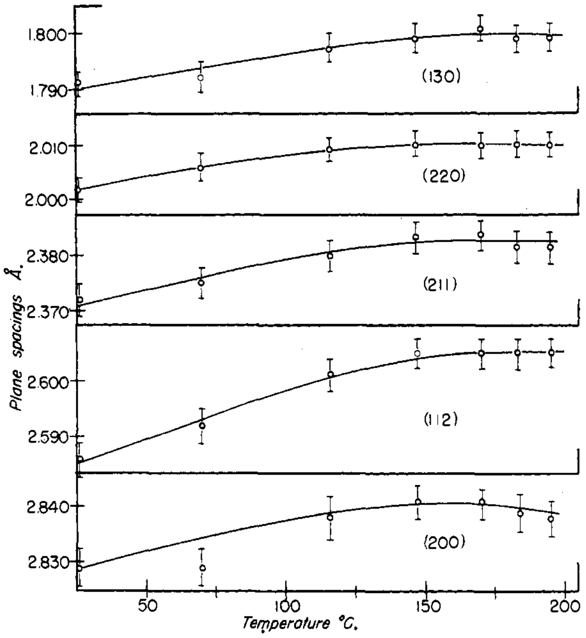

Fig. 1.—Interplanar spacings in α-KHF_2 at different temperatures. Figures in parentheses are Miller indices.

observed scattering. The similarity in intensities observed for $RbHF_2$ and $CsHF_2$ (Fig. 2) and the trend in unit cell dimensions suggest the KHF_2 structure for the latter, however.

β-Potassium Bifluoride.—On the Kofler hot-stage KHF_2 becomes isotropic above 196°. The transition is readily reversible although undercooling of 50–60° is possible upon rapid cooling.

In the X-ray experiments the diffraction pattern of the α-phase disappeared when the temperature was raised above 196°. Reflections from the waxy β-phase were somewhat irregular in intensity, but they could be indexed on a cubic unit with an identity period of 6.36 Å. The unmixed indices suggest a face-centered space lattice. Exploratory calculations show that in KHF_2 fluorine contributions alone would permit observation of reflections of mixed index if they existed. A careful search for such reflections was unsuccessful, and in what follows face-centering is assumed. This eliminates the pyrite structure as a possibility.

With the observed density,[3] 2.02 g./cm.^{3}, one finds 4 molecules per unit cell. There are accordingly only two possibilities for an ordered structure: (1) a fluorite-like structure with 4 K in $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ + F.C., 4 H in 000 + F.C., and 8 F in $\pm\,|\frac{1}{4}\frac{1}{4}\frac{1}{4}|$ + F.C.; and (2) with 4 K in $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ + F.C., 4 H in $\frac{1}{4}\frac{1}{4}\frac{1}{4}$ + F.C., and 4 F each in 000 + F.C. and $\frac{3}{4}\frac{3}{4}\frac{3}{4}$ + F.C.

In the first, one notes that along the body diagonal there is a regularly spaced sequence of ions F H F K F H F K. This arrangement, with a fluorine–fluorine distance of about 5.5 Å. in what might be expected to be a hydrogen bond, is considered unlikely. It gives, in addition, a vanishing (accidentally) structure factor for (200), the strongest reflection.

The second structure is even more unlikely in that it gives a sequence F F H K F F H K along the body diagonal.

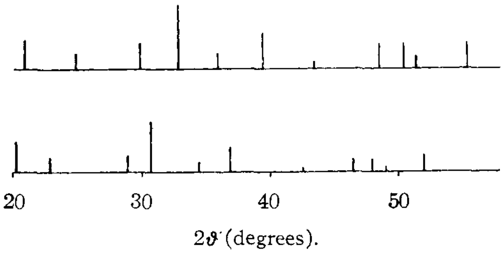

Fig. 2.—Intensities *versus* 2ϑ. The upper strip is for α-$RbHF_2$, and the lower one is for α-$CsHF_2$.

The only remaining possibilities involve positions of higher multiplicity, which therefore require random arrangements. These positions are of two types, namely, those in the vicinity of octahedral holes or tetrahedral holes among the potassium ions. In the following discussion use is made of the well-established[8–10] linear and symmetrical configuration of the bifluoride ion. Construction of a model shows that the tetrahedral holes are too small to accommodate the ion. On the other hand, a bifluoride ion fits into an octahedral hole, with the proton at 000, providing its axis is parallel to [111], *i.e.*, a body diagonal. Cubic symmetry gives four such equivalent orientations, so that it is proposed that bifluoride ions are arranged at random in the crystal along the four body diagonals. Crystallographically this places H at 000 + F.C., K at $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ + F.C., and one-quarter fluorine in $\pm\,|xxx, x\bar{x}\bar{x}, x\bar{x}x, xx\bar{x}|$ + F.C.

Free rotation, which had been suggested[4] to account for the high temperature modifications, is ruled out since alignment of the bifluoride parallel to a cube edge requires an unreasonably close contact between fluorine and potassium (6.36/2 − 2.26/2 = 2.05 Å. compared with 2.67 Å. in KF).

The arrangement proposed is similar to the one described above as the fluorite-like structure except that the sequence along the body diagonal is FHF K FHF K.

A comparison of calculated and observed intensities for β-KHF_2 is given in Table III. The observed intensities are averaged from several determinations, since the values obtained from the waxy phase lack good reproducibility. Although the intensity calculated for (311) using the proposed structure is not in good agreement with that observed, a lengthening of the fluorine–fluorine distance up to 4.0 Å. leads to still larger calculated values. In view of the properties of the high temperature phase it is difficult to tell whether the discrepancy is significant. It persists in spite of the application of a reasonable temperature correction. At any rate, the structure proposed above seems to us to be the only one consistent with symmetry and packing considerations, and with the known configuration of the bifluoride ion.

In addition the large entropy and volume increase accompanying the transition to the β-phase may well arise from the random occupation by each bifluoride of only one out of four possible positions.

(8) M. T. Rogers and L. Helmholz, THIS JOURNAL, 62, 1533 (1940).

(9) L. Pauling, *Z. Krist.*, **85A**, 380 (1933).

(10) S. W. Peterson and H. A. Levy, *J. Chem. Phys.*, **20**, 704 (1952).

TABLE III

INTENSITIES FOR β-KHF_2

	I_{obs}	I_{calcd}			
		a	b	c	d
(111)	20	18	21	20	19
(200)	80	70	68	0	74
(220)	27	28	29	28	28
(311)	15	45	47	8	43
(222)	5	8	8	0	3
(400)	2	2	1	3	3

[a] For random occupation by fluorine of $\pm\ |xx0,\ 0xx,\ x0x,\ x\bar{x}0,\ 0x\bar{x},\ \bar{x}0x|$ + F.C. [b] For random occupation by fluorine of $\pm\ |xxx,\ x\bar{x}x,\ \bar{x}xx,\ xx\bar{x}|$ + F.C. [c] For fluorite-like structure with fluorine in tetrahedral holes. [d] For spherically symmetrical rotation of bifluoride ion around 000 + F.C.

β-**Rubidium Bifluoride.**—Petrographic examination shows that the high temperature phase is cubic. X-Ray reflections have unmixed indices and correspond to a cubic unit cell with an edge of 6.71 Å. The previous discussion applies, and it is proposed that β-$RbHF_2$ is isostructural with β-KHF_2.

β-**Cesium Bifluoride.**—Petrographic examination shows that the high temperature phase is cubic. X-Ray reflections may be indexed on a cubic unit with an edge of 4.21 Å. It is interesting to compare the trend in cube edges for the instant compounds with those of the corresponding chloride and bromide. The sequence is 6.28, 6.54, 4.11 Å. for KCl, RbCl, and CsCl; and 6.59, 6.85, 4.29 Å. for KBr, RbBr, CsBr.[11] The edges for the high temperature forms of the bifluorides (Table I) are intermediate, and there is a strong suggestion that the structure of β-$CsHF_2$ bears some resemblance to that of CsCl. The fact that the structure proposed for α-$CsHF_2$ is a distorted CsCl-type structure (Fig. 3) makes such a relationship plausible.

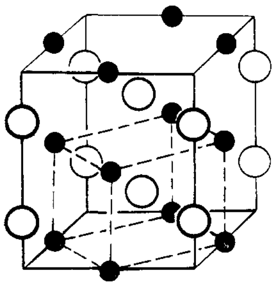

Fig. 3.—The unit cell of α-$CsHF_2$ is shown. Open circles are cesiums and shaded circles are hydrogens. Fluorines are omitted. The relationship between the α- and β-phase is shown by the dotted lines joining hydrogens. The unit outlined is 4.35 × 4.35 × 3.92 Å. and contains one $CsHF_2$. It is easily seen that a relatively small distortion will convert this to a cubic unit 4.21 Å. on an edge.

The only reasonable density for the size of unit cell found corresponds to one molecule per unit cell. Symmetry requirements demand either a random orientation or free rotation of the bifluoride ion. The latter is sterically prohibited. If one assigns cesium to $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ and places the bifluoride ion so that hydrogen is at 000 he finds that the available space only permits the bifluoride ion to lie parallel to [100], *i.e.*, the directions of the cell edges. It is proposed that this orientation is random in the crystal, so that we assign one-third fluorine to the positions $\pm\ |u00,\ 0u0,\ 00u|$. The value of u based on a fluorine–fluorine distance of 2.26 Å. is 0.27, and calculated and observed intensities (Table IV) are in good agreement, although this is not surprising in view of the relatively small contribution by fluorine to the structure factor. The cesium–fluorine distance is then 3.13 Å.

TABLE IV

INTENSITIES FOR β-$CsHF_2$

	I_{obsd}	I_{calcd}	
		a	b
(100)	12	12	19
(110)	18	18	15
(111)	6	6	6
(200)	4	4	3
(210)	5	8	8

[a] Random occupation by fluorine of $\pm\ |x00,\ 0x0,\ 00x|$. [b] Cesium contributions only.

As a result of the analysis of the several structures it is concluded that a randomly oriented bifluoride ion, rather than a freely rotating ion, typifies the β-phase. In each case the proposed direction of orientation is the one which yields the minimum electrostatic potential energy. It is interesting to note that $TlHF_2$ is cubic[12] at room temperature and does not undergo a transition to a structure of lower symmetry even down to liquid helium temperatures.[13] The structure proposed earlier[12] for this substance is a pyrite-like one wherein bifluoride ions lie along body diagonals between thallium ions. Based upon the shortest thallium–fluorine distance in TlF,[14] *viz.*, 2.59 Å., it is found that there is just enough room to fit the bifluoride between thallium ions. This is accomplished in practically the same space as available in β-$CsHF_2$—the thallium–thallium distance along the body diagonal is 7.43 Å., whereas the corresponding cesium–cesium distance is 7.30 Å. This is possible because of the smaller size of the thallium ion but the basis for the difference in structures is not clear. Failure to detect a low temperature phase is, however, not surprising since the cubic phase is most probably ordered.

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(11) R. W. G. Wyckoff, "Crystal Structure," Interscience Publishers, New York, N. Y., 1948, Section III.

(12) O. Hassel and W. Kringstad, *Z. anorg. allgem. Chem.*, **191**, 36 (1930).

(13) E. F. Westrum, Jr., private communication.

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