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The Crystal Structure of Lithium Fluoroantimonate(V)

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The crystal structure of $LiSbF_6$ has been determined by single-crystal counting techniques and least-squares refinement. The unit cell is rhombohedral, $R\bar{3}$, with $a = 5{\cdot}43$ Å, $\alpha = 56°\ 58'$ and contains one formula weight. The fluorine atoms form regular octahedra about the antimony and about the lithium atoms at distances of $1{\cdot}88 \pm 0{\cdot}02$ and $2{\cdot}03 \pm 0{\cdot}02$ Å, respectively. The structure may be described as a rhombohedral distortion of the cubic $NaSbF_6$ arrangement.

Introduction

The structures of compounds with the formula $RSbF_6$ have been reported for R^+ equal to Na^+ (Schrewelius, 1938); Ag^+ (Bode, 1951); K^+ (Bode & Voss, 1951); and Tl^+, Rb^+, NH_4^+ and Cs^+ (Schrewelius, 1942). The arrangement of R^+ and SbF_6^- ions in these crystals is of two types: NaCl and CsCl (distorted). Cox (1956) has pointed out that those fluoroantimonates(V) having R^+ within a certain size range all crystallize with the same structure. He attempted to extend the correlation by study of $LiSbF_6$, but only succeeded in showing that its powder pattern was not indexable as one of these structure types. In none of these investigations has an attempt been made to establish directly the fluorine parameters, except in the case of $KSbF_6$ (Bode & Voss, 1951) where the results are described as approximate and the limits of error not stated. The Sb–F distance in this compound was reported to be 1·77 Å and the SbF_6^- octahedron said to have a central angle of 97°.

The single-crystal study of $LiSbF_6$ to be described here was undertaken to establish the structure of this final member of the series of alkali-metal fluoroantimonates(V), with accurate distances and angles, in order that some generalization could be made about the structures of this group of compounds.

Experimental

Single crystals of $LiSbF_6$ were prepared by D. O. Campbell of this Laboratory through the addition of SbF_5 to a solution of LiF in anhydrous HF, followed by recrystallization from anhydrous HF solution. The crystals were sealed in glass capillaries to protect them from moisture. The unit-cell dimensions and space-group data were obtained from Weissenberg, Laue, and precession photographs, but the intensities were measured by counting techniques. For this purpose, a General Electric Goniostat was employed with a NaI scintillation counter equipped with pulse-height discrimination. Mo $K\alpha$ (Zr-filtered) radiation was used, and a 2θ scan was made for each reflection. The intensity of the X-ray source was monitored by frequent measurement of a standard reflection. The background intensity was taken as the average of that measured on each side of the Bragg peak.

After determination of the unit cell and space group, it seemed likely that a suitable trial structure could be postulated and a least-squares refinement carried out, so no attempt was made to collect complete intensity data. Instead, a more or less random sampling of reciprocal space within the range $2\theta < 70°$ was made; 111 reflections were measured, approximately one-third of those available in this region. The intensities were converted to F^2 by correction for Lorentz-polarization and scale factors, but no correction was made for absorption. The crystal specimen used for intensity measurements was an irregular polyhedron having maximum and minimum dimensions of 0·27 and 0·17 mm. A measurement of the variation in intensity with the orientation of the crystal as made; and for reflections at $\chi = 0°$, the total change was about 4%, and at $\chi = 90°$, about 10%. The majority of the reflections were, of course, measured at orientations intermediate to these extremes and were subject to less error. Since no correction was made for this systematic error, however, the accuracy of the parameters, obtained from the least squares analysis, may be somewhat less than indicated by the standard deviations. The experience of Cromer & Larson (1961) with a similar problem was that the application of an empirical absorption correction changed the final parameters by less than one standard deviation.

Unit cell and space group

The unit cell of $LiSbF_6$ is rhombohedral with

$$a = 5{\cdot}43 \pm 0{\cdot}02 \text{ Å} \quad \text{and} \quad \alpha = 56°\ 58 \pm 15'.$$

This corresponds to a hexagonal cell with

$$a = 5{\cdot}18 \pm 0{\cdot}02 \quad \text{and} \quad c = 13{\cdot}60 \pm 0{\cdot}02 \text{ Å}.$$

The Laue symmetry, obtained from Weissenberg and

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Laue photographs, is $\bar{3}$. Since there are no systematic absences with rhombohedral indexing, the possible space groups are $R3$ and $R\bar{3}$; the final structure agreed with the centrosymmetric choice. The calculated density with one formula weight per rhombohedral cell is 3·83 g.cm.$^{-3}$.

Trial structure and refinement of parameters

A trial structure based on $R\bar{3}$ was assumed, and the data were used to refine this model by least squares. The atoms were placed as follows in the hexagonal cell:

$$(0, 0, 0;\ 1/3, 2/3, 2/3;\ 2/3, 1/3, 1/3)+$$
$$\text{Sb}\ (a)\ 0, 0, 0;$$
$$\text{Li}\ (b)\ 0, 0, 1/2;$$
$$\text{F}\ (f)\ \pm(x, y, z;\ \bar{y}, x-y, z;\ y-x, \bar{x}, z).$$

Initial values of x, y, z were chosen so as to locate each F near a Sb · · · Li line at a distance of 1·96 Å from Sb. In addition to these coordinates, isotropic temperature factors for Sb and F and one overall scale factor were varied, making a total of 6 parameters. For Li a fixed value of $B=2·5$ Å^2 was used. The least-squares calculations were carried out on an IBM-7090 using the program of Busing & Levy (1959*a*), which they adapted for this machine. The refinement was based on F^2, and the observations were weighted as the inverse of the variance, $\sigma^2(F^2)$. An estimate of σ^2 was made from the relation

$$\sigma^2(F^2)=k(Lp)^{-2}\{T+B+[0·02(T-B)]^2\}$$

in which k = a scale factor, T = total count, B = background count, and the term in $(T-B)$ was added as an estimate of the error proportional to the net count, such as absorption and beam intensity variations. This expression is equivalent to that used by Busing & Levy (1957) and by Peterson & Levy (1957) in their neutron-diffraction studies but is also applicable to X-ray counting techniques.

Atomic scattering factors used in the structure factor calculations were those of Berghuis *et al.* (1955) for F$^-$; for Li$^+$ their value for Li^0 was used for

Table 1. *Final least-squares parameters and their σ's*

B(Sb) =	0·57 Å^2	σ = 0·02 Å^2
B(F) =	1·20	σ = 0·06
x(F) =	0·3186	σ = 0·0013
y(F) =	0·0540	σ = 0·0012
z(F) =	−0·0799	σ = 0·0004

Table 2. *Observed and calculated structure factors*

h	k	l	$\lvert F_o\rvert$	F_c	h	k	l	$\lvert F_o\rvert$	F_c	h	k	l	$\lvert F_o\rvert$	F_c
−6	0	0	47·7	48·2	−3	5	4	96·7	96·7	−4	1	10	89·0	81·0
−3	0	0	125·1	137·3	−2	6	4	43·4	43·4	−5	3	10	52·6	50·1
−5	1	0	57·6	58·3	−3	8	4	49·4	51·9	−2	3	10	90·1	85·7
−2	1	0	74·3	72·7	−6	1	5	57·2	59·6	0	5	10	32·9	31·9
−7	2	0	57·3	60·2	0	1	5	108·5	107·1	−5	6	10	52·8	52·8
−4	2	0	82·2	80·5	−2	2	5	102·4	97·6	0	1	11	83·7	78·3
−6	3	0	60·6	61·6	−1	3	5	72·1	65·9	−7	3	11	48·4	48·1
−8	4	0	35·0	36·9	0	4	5	61·6	62·0	−6	4	11	28·4	28·5
−5	4	0	65·9	66·7	−7	6	5	30·5	30·4	0	4	11	63·1	60·5
−7	5	0	52·2	52·7	−1	6	5	54·5	53·6	0	0	12	128·5	123·2
−2	0	1	95·6	103·1	0	7	5	32·8	35·7	−6	3	12	44·2	44·6
−4	1	1	51·5	51·2	−5	8	5	34·0	35·8	0	3	12	85·0	80·9
−1	1	1	119·4	132·3	−6	0	6	47·8	51·5	−5	4	12	49·0	48·3
0	5	1	58·4	60·5	0	0	6	13·2	14·4	0	6	12	41·2	36·3
−7	7	1	42·8	43·2	−2	1	6	149·0	147·2	−5	0	13	39·9	39·7
−1	7	1	55·5	58·6	−6	3	6	56·3	57·0	−1	1	13	77·7	72·7
−3	1	2	112·0	113·6	0	3	6	56·3	55·3	0	2	13	60·8	58·4
0	1	2	138·2	160·4	−7	5	6	40·7	42·2	0	1	14	76·8	74·1
−2	2	2	69·3	67·0	−6	6	6	50·5	50·0	−5	2	14	34·9	34·2
0	4	2	87·5	89·7	−5	0	7	59·6	58·7	−5	5	14	30·1	28·4
−8	5	2	27·9	28·8	−4	1	7	90·2	90·2	0	0	15	74·4	71·5
−2	5	2	61·7	60·0	−1	1	7	97·8	92·6	3	−3	15	61·7	57·5
−1	6	2	54·6	55·3	0	2	7	101·4	97·6	0	3	15	59·8	57·5
0	7	2	34·6	36·2	−3	5	7	64·7	65·0	0	2	16	69·6	66·0
3	0	3	87·1	86·7	−1	7	7	26·4	27·6	−5	3	16	46·6	47·0
0	0	3	131·7	134·1	0	1	8	91·7	85·9	−4	4	16	41·6	41·8
−5	1	3	63·9	64·9	−2	2	8	123·8	120·3	−1	4	16	46·0	44·2
−4	2	3	56·9	55·6	−7	3	8	37·4	37·3	0	1	17	54·7	53·5
6	−3	3	47·6	49·2	−1	3	8	87·4	84·1	0	4	17	41·4	39·5
3	−3	3	95·9	93·6	−3	4	8	63·8	60·4	0	0	18	34·6	32·0
−4	5	3	63·7	63·7	0	4	8	61·7	56·7	−4	2	18	42·1	41·5
0	6	3	52·6	55·1	−6	7	8	37·4	37·1	−1	1	19	46·5	44·0
−5	7	3	47·6	49·2	−3	0	9	65·0	64·4	−3	2	19	38·8	37·6
−5	0	4	85·5	88·0	0	0	9	80·7	77·7	0	2	19	50·9	48·4
−7	1	4	35·3	37·3	−4	2	9	86·3	83·7	−2	2	20	52·8	49·4
−1	1	4	105·2	102·6	−6	3	9	40·8	43·5	0	0	21	37·4	34·2
0	2	4	145·5	153·0	0	6	9	36·4	38·7	−1	2	21	53·9	51·5

$\sin\theta/\lambda > 0{\cdot}2$ and their curve extrapolated to Li^+ at $\sin\theta/\lambda = 0$. For antimony the curve of Thomas & Umeda (1957) for Sb^0 was used for $\sin\theta/\lambda > 0{\cdot}3$, and at smaller angles an extrapolation was made to Sb^{5+} at $\sin\theta/\lambda = 0$ by comparison with their curves for the various states of ionization. A dispersion correction of $-0{\cdot}6$ was applied to the antimony scattering factors (Dauben & Templeton, 1955).

The least-squares adjustment converged after four cycles, all shifts being within the standard deviations of the parameters. A fifth cycle was run and its results taken as the final parameters. Several additional cycles were calculated with the fluorines in acentric positions, but they returned to the centrosymmetric configuration. Table 1 shows the final parameters and their standard deviations, which were evaluated from the inverse matrix of the normal equations by the least-squares program. The properly-scaled structure factors, calculated from these parameters, and the values of $|F_o|$ are presented in Table 2. All of the calculated structure factors have a positive sign. The final value of $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ was 0·039.

Table 3. *Interatomic distances and angles and their σ's*

Sb–F	1·877 Å	$\sigma = 0{\cdot}006$ Å
Li–F	2·032	$\sigma = 0{\cdot}006$
F–F (in SbF_6 octahedron)	2·65	$\sigma = 0{\cdot}01$
F–F (in LiF_6 octahedron)	2·87	$\sigma = 0{\cdot}01$
F–Sb–F(¹)	89·9°	$\sigma = 0{\cdot}2°$
F–Sb–F(²)	90·1	$\sigma = 0{\cdot}2$
F–Li–F(¹)	89·7	$\sigma = 0{\cdot}2$
F–Li–F(²)	90·3	$\sigma = 0{\cdot}2$
Sb–F–Li	147·5	$\sigma = 0{\cdot}3$

(¹) Fluorines having same *z* value.
(²) Fluorines having different *z* values.

The interatomic distances and angles in $LiSbF_6$ and their σ's were calculated with the Busing–Levy (1959*b*) function-and-error program, which takes into account the σ's of the parameters and the estimated errors in the unit-cell dimensions. Some of these distances and angles are listed in Table 3, along with their σ's. It is seen that the SbF_6^- octahedron is regular within the experimental error; and although the octahedral arrangement about the Li^+ shows slight distortion, it is not significantly beyond experimental error.

Discussion of the structure

The lithium fluoroantimonate(V) structure, shown in Fig. 1, consists of regular octahedra of SbF_6^- which share all corners with Li^+ so that these ions are also octahedrally coordinated by fluorine. Although the true unit cell is a unimolecular rhombohedron, the structure can be viewed as a tetramolecular rhombohedron (dotted lines, Fig. 1) with $a = 7{\cdot}50$ Å, $\alpha = 92{\cdot}6°$ in which the Li^+ and SbF_6^- exhibit a slightly distorted NaCl arrangement. The SbF_6^- octahedron is oriented in such a way that the Sb–F bond makes an angle of 16·9° with the Sb · · · Li line.

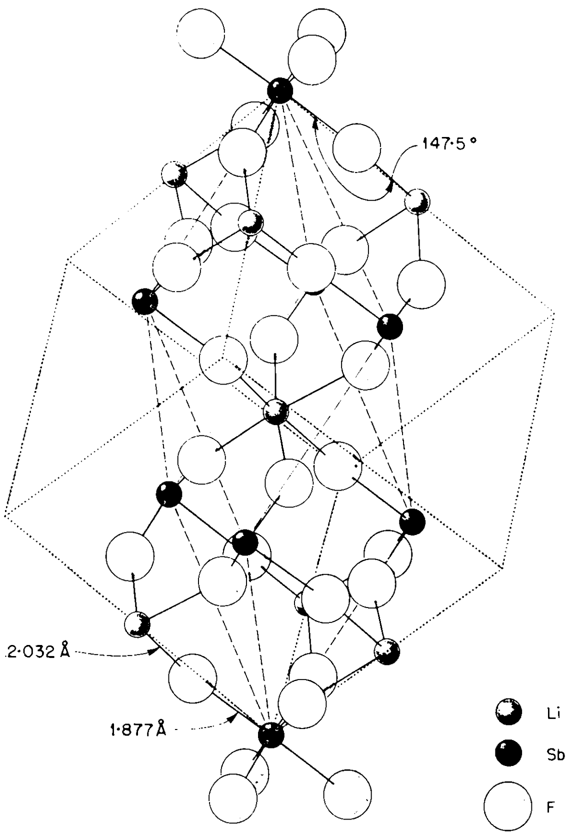

Fig. 1. Structure of $LiSbF_6$. Dashed lines show true unit cell. Dotted lines show tetramolecular rhombohedron.

With the elucidation of $LiSbF_6$ it is possible to generalize about the structures of the fluoroantimonates(V). All the reported structures can be classified as having either a NaCl or CsCl arrangement of the R^+ and SbF_6^- ions with various forms of distortion. In the NaCl category are $LiSbF_6$ and $NaSbF_6$ (Schrewelius, 1938). The latter is cubic, $a = 8{\cdot}18$ Å (greater than *a* for $LiSbF_6$ by approximately the difference in ionic diameters of Li^+ and Na^+) with the Sb–F bond inclined at 17·4° to the cube edge. The similarity between these two structures adds credibility to the F-positions in $NaSbF_6$, which were not claimed to be know accurately.

The fluoroantimonates(V) of Ag^+, K^+, Tl^+, Rb^+, NH_4^+ and Cs^+ may be described in terms of the CsCl structure. All but the first two of these compounds have the $BaSiF_6$ structure described by Hoard & Vincent (1941) i.e., the R^+ and SbF_6^- occupy a rhombohedrally distorted CsCl arrangement. This agrees with these authors' prediction that this structure will occur for RMF_6 when the radius ratio of *R* to F is approximately equal to, or greater than unity. Although $KSbF_6$ satisfies this criterion, it does not have this structure; instead, it is cubic (Bode & Voss, 1951) with adjacent SbF_6^- octahedra oriented differently and resulting in a superlattice of 8 CsCl-like cubes. Bode (1951) reported $AgSbF_6$ to be isostructural with this compound. Bode & Voss (1951) claim that the SbF^- octahedron is compressed along its 3-fold axis causing the F–Sb–F angle to be ~ 96°, and suggest that the rhombohedral fluoroantimonates(V) result from the periodic arrangement of these distorted octahedra. However, the SbF_6^- octahedron is regular in $LiSbF_6$, and the rhombohedral angle in the $BaSiF_6$ structure is a consequence of the regular 12-fold coordination of F^- about the Ba^{++} (the SiF_6^{--} shows little or no distortion). Thus, the proposal that there is an inherent distortion of SbF_6^- in these fluoroantimonates(V) is probably incorrect. In $KAsF_6$, described by Cox (1956) as having the $BaSiF_6$ structure, and for which the F positions were located by Roof (1955), the F–As–F angle is 88°, while the rhombohedral angle is ~ $97\frac{1}{2}$°.

There is little in the literature with which to compare the Sb(V)–F bond length of $1{\cdot}88 \pm 0{\cdot}02$ Å in $LiSbF_6$ (limits of error taken as 3σ). A determination of this interatomic distance in $KSbF_6$ (Bode & Voss, 1951) led to 1·77 Å, but the approximate nature of the work makes it unsuitable for comparison with the present results. The other fluoroantimonate structures described above were based on estimated Sb(V)–F distances of 1·95 to 1·97 Å and apparently need to be revised. In fact, the semi-empirical estimates of bond length using the methods of Pauling (1960) and Zachariasen (1931) are not very useful for this bond; the covalent single-bond radius is 1·96 Å and the sum of univalent radii, corrected for charge is 1·81 Å. Finally, the apparent bond length in $LiSbF_6$ may be too small because of the thermal motion of the atoms, but this correction is estimated to be less than 0·01 Å.

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Die Struktur der Hochtemperaturform des Bariumgermanates $BaGeO_3(h)$

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Crystals of the high-temperature form of $BaGeO_3$ are orthorhombic with lattice parameters

$$a = 4{\cdot}58,\ b = 5{\cdot}68,\ c = 12{\cdot}76 \text{ Å; space group } P2_12_12_1(D_2^4)\ .$$

There are 4 molecules $BaGeO_3$ in the unit cell. The structure has been determined with the aid of Buerger's minimum function for projections [010] and [100] and refined by Fourier-difference syntheses. The GeO_4 tetrahedra are linked to form infinite chains, with two tetrahedra per identity period.

Während im β-Wollastonit, der Tieftemperaturform des Calciumsilikates $CaSiO_3(t)$, nach Untersuchungen von Dornberger-Schiff, Liebau & Thilo (1955) und nach anderen Autoren Dreierketten als Anionen vorliegen, bilden in der Hochtemperaturform α-$CaSiO_3$ (Pseudowollastonit) nach Hilmer (1958, 1962) und