About SnF₂ Stannous Fluoride. I. Crystallochemistry of α-SnF₂

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The crystal structure of monoclinic stannous fluoride α-SnF₂ has been refined from single-crystal X-ray data. The unit cell contains four cyclic Sn_4F_8 tetramers. The structure contains two types of Sn atoms: Sn(1) is surrounded tetrahedrally by three fluorine atoms and a lone pair, E, and Sn(2) is surrounded octahedrally by five fluorine atoms and a lone pair. The structure is examined within the framework of Galy's and Brown's models. Topological relationships to rutile are presented.

Introduction

The results presented in this paper are from the first part of our investigation of the physical and chemical properties of SnF_2. Before our study, only the monoclinic phase α-SnF_2 was known (*1*). but we have discovered two new crystalline phases. We report here a crystallochemical investigation of α-SnF_2 which is needed to explain the observed physical properties and phase transitions. While this study was under way, the structure of α-SnF_2 was published by McDonald *et al.* (*2*); a good agreement is observed between both sets of results.

Experimental

1. Preparation of Crystals

SnF_2 used in this study was supplied by OSI. Single crystals were obtained by slow cooling (3°C/day) of aqueous solution from 30 to 20°C; crystallization was conducted in Teflon beakers under argon; SnF_2 solution was acidified with HF to prevent hydrolysis and kept in contact with a few pieces of tin metal to prevent formation of Sn^{4+}. Crystal shape was similar to that described by Acker *et al.* (*3*).

2. Space Group and Data Collection

Unit-cell parameters were determined on single crystals, then refined from powder data (Table I). Density was measured on single crystals. Weissenberg and precession photographs gave the following conditions:

$$(hkl), h + k = 2n; (h0l),$$

$$h = 2n \text{ and } l = 2n; (0kl), k = 2n,$$

indicating space group $C2/c$ or Cc. A negative second harmonic generation test supports the former group. Intensities were collected with a Nonius CAD-4 automatic diffractometer using $MoK\alpha_1$ radiation; one-quarter of the reciprocal space with $\Theta < 35°$ was used (1109 independent reflections).

3. Structure Refinement

The structure was solved and refined by using a system of crystallographic programs

TABLE I

CRYSTALLOGRAPHIC CONSTANTS OF α-SnF$_2$

	NBS (28)	Bergerhoff (7)	McDonald et al. (2)	This work
a (Å)	13.3520(10)	13.46	13.353(1)	13.3532(31)
b (Å)	4.9099(5)	4.92	4.9090(4)	4.9073(11)
c (Å)	13.7888(14)	13.86	13.787(1)	13.7860(33)
β (°)	109°102(008)	109°5	109°11(1)	109°29(18)
V (Å^3)	854.18(28)	865.2	853.93(71)	852.6(1.5)
ρ_{exp}		4.57	4.84(4)	4.84
ρ_{cal}	4.88	4.81	4.88	4.88
t(°C)	25		25	20
Z	16	16	16	16
Spacegroup	$C2/c$	$C2/c$	$C2/c$	$C2/c$

adapted by Le Marouille (4). Atomic scattering factors were taken from Moore (5) and the anomalous scattering corrections from Cromer (6). From a three-dimensional Patterson map, tin atoms were first localized in the $4b$, $4e$, and $8f$ positions of the $C2/c$ groups as previously observed by Bergerhoff (7). Further refinement of tin coordinates with a local version (8) of the SFLS-5 program using an Ibers (9, 10) weighting scheme led to $R = 23\%$, but we could not localize fluorine atoms on a Fourier map; changing from $C2/c$ to Cc did not improve the results. We consequently placed all tin atoms in the most general ($8f$) position of $C2/c$ by shifting the origin by a vector ($\frac{1}{8}$, 0, $\frac{3}{16}$) (Fig. 1).

Fluorine atoms were then localized on the Fourier difference map. Refinement of Sn and F coordinates led to $R = 14\%$. Further refinement of the anisotropic thermal parameters and secondary extinction led to $R = 4.5\%$ and $R_w = 5.2\%$. An absorption correction ($\mu R = 1.84$) did not improve the results and was then neglected. Atomic positions and thermal parameters are given in Tables II and III. Our results do not differ significantly from those of McDonald et al. (2). Our larger number of intensities (collected on a four-circle diffractometer) led to smaller standard deviations (by a factor of 3). The most significant improvement concerns the anisotropic thermal parameters.
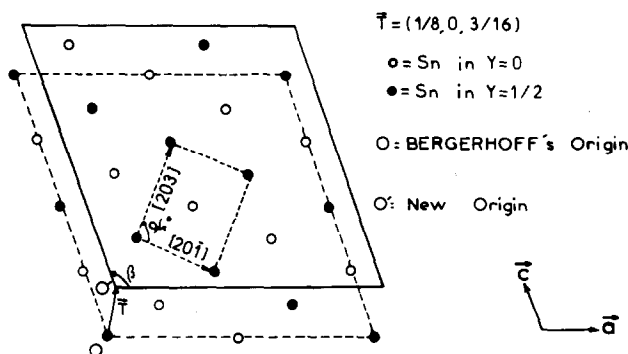

$\bar{T} = (1/8, 0, 3/16)$

o = Sn in Y = 0

● = Sn in Y = 1/2

O = BERGERHOFF's Origin

O' = New Origin

FIG. 1. The projection of the tin atoms on the (a, c) plane shows the body-centred sublattice of the cation.

TABLE II

α-SnF$_2$: FINAL ATOMIC COORDINATES

		This work			McDonald et al. (2)		
	Site	x	y	z	x	y	z
Sn(1)	(8f)	0.37217(4)	0.48913(13)	0.05704(4)	0.3724(1)	0.4900(4)	0.0574(1)
Sn(2)	(8f)	0.11801(4)	0.48152(12)	0.18683(4)	0.1183(1)	0.4825(3)	0.1867(1)
F(1)	(8f)	0.26096(26)	0.24363(96)	0.30802(35)	0.2606(10)	0.2376(30)	0.3077(12)
F(2)	(8f)	0.38390(38)	0.22108(115)	0.17918(35)	0.3852(11)	0.2195(31)	0.1787(11)
F(3)	(8f)	0.17401(39)	0.34331(110)	0.03828(37)	0.1749(11)	0.3391(30)	0.0406(10)
F(4)	(8f)	0.47045(35)	0.32856(107)	0.41529(36)	0.4717(11)	0.3259(32)	0.4157(12)

Discussion of the Structure

1. Sn$_4$F$_8$ Tetramers

The main feature of this structure is the existence of cyclic Sn$_4$F$_8$ tetramers previously identified by McDonald et al. (2) (Figs. 2 and 3). This unusual feature is in agreement with the strong molecular behavior of α-SnF$_2$. Existence of polymers (dimers and trimers) was also observed in gas phase (11). Distances and angles within a tetramer and between tetramers are given in Table IV.

The mean plane of each tetramer is parallel to the (a, c) plane at $y = \frac{1}{4}$ or $\frac{3}{4}$; there is a twofold axis parallel to b in the center of each tetramer. Each tetramer is surrounded by 10 other tetramers, 2 in the same plane and 8 translated from $\pm\frac{1}{2}$ b. This polymerization is quite common among oxides and fluorides of lone-pair cations and occurs, for instance, in senarmontite Sb$_2$O$_3$ (Sb$_4$O$_6$ tetramers) (12), in Sn$_2$F$_3$Cl (13, 14) and Sn$_3$BrF$_5$ (14–16) (tridimensional (Sn$_3$F$_5$)$_4^{4+}$ cation), and in NaSn$_2$F$_5$ (17) (infinite (Sn$_2$F$_5$)$_4^{4-}$ chains).

2. Stereochemistry of Sn^{2+}

The stereochemistry of lone-pair cations has been extensively studied in recent years and two different approaches have been used.

2.1. The Galy–Andersson Lone-Pair Model

The Galy–Andersson lone-pair model (18) is based on the Gillespie–Nyholm theory (19). The stereochemical activity of the lone pair can be shown by comparing the molecular volume per anion between Sn^{2+}- and Sn^{4+}-containing structures; such a

TABLE III

α-SnF$_2$: ANISOTROPIC THERMAL PARAMETERS β_{ij} AND ISOTROPIC EQUIVALENT PARAMETER B^a

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	B_{eq}
Sn(1)	0.00312(5)	0.01549(25)	0.00214(4)	0.00080(6)	0.00091(3)	0.00022(6)	1.674
Sn(2)	0.00223(5)	0.01697(25)	0.00197(4)	−0.00110(8)	0.00085(3)	−0.00055(7)	1.480
F(1)	0.00297(33)	0.02440(223)	0.00321(33)	0.00334(66)	0.00131(26)	0.00106(67)	2.181
F(2)	0.00517(45)	0.04290(326)	0.00277(35)	0.00150(91)	0.00190(32)	0.00585(81)	3.068
F(3)	0.00467(41)	0.03013(254)	0.00311(33)	−0.00227(78)	0.00178(29)	−0.00368(73)	2.672
F(4)	0.00269(34)	0.03230(252)	0.00338(33)	−0.00333(70)	0.00147(26)	−0.00337(72)	2.378

^{a} The β_{ij} factors are given as follows: $\exp\left|-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2\,hk\beta_{12}+2\,hl\beta_{13}+2\,kl\beta_{23})\right|$.
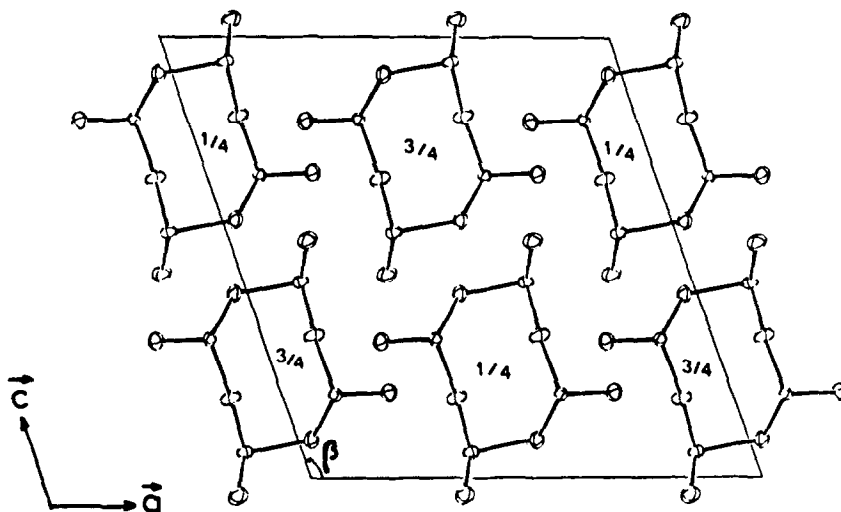
FIG. 2. Projection of the Sn_4F_8 tetramers on the (a, c) plane. The y coordinate of the mean plane of each tetramer is given.

comparison is presented in Table V for tin oxides, fluorides, and oxifluorides. It clearly demonstrates that the lone pair requires a volume comparable with that of an oxygen or fluoride anion.

A careful examination of the final Fourier difference map after refinement of atomic positions and anisotropic thermal parameters shows the existence of two electron density maxima (about $2e^-/Å^3$) in positions which are in reasonable agreement with the lone-pair positions calculated by Galy's method (18) (idealization of the anionic polyhedron around tin atoms) (Table VI). The $Sn(1)-E_1$ direction is parallel to the **b** axis while the $Sn(2)-E_2$ direction lies in the (**a**, **b**) plane (Fig. 4).
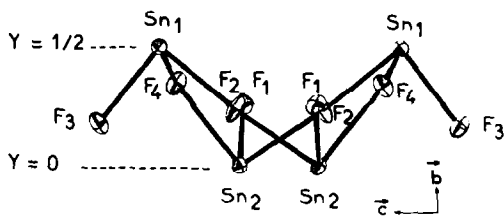

FIG. 3. Projection of a Sn_4F_8 tetramer on the (b, c) plane.

2.1.1. *Coordination of Sn(1)*. Sn(1) is tetrahedrally surrounded by three fluorine atoms (short bonds) and lone pair E_1. It presents an sp^3 hybridization. The geometrical characteristics of this tetrahedron are given in Table VII. The distance $Sn-E = 0.94$ Å is in good agreement with the mean value 0.95 Å (18); then the ratio of unshared pairs is 0.44 (mean value 0.43). the F–Sn–F angles are smaller than 109° (regular tetrahedron) because of strong F–E repulsions.

2.1.2. *Coordination of Sn(2)*. Sn(2) is octahedrally surrounded by five fluorine atoms and lone pair E_2; it then presents an sp^3d^2 hybridization. The very short Sn–F bond is the axial bond, the opposite vertex being occupied by the lone pair; the four Sn–F bonds with an intermediate length (2.20 to 2.50 Å) are equatorial bonds. the geometrical characteristics of the SnF_5E octahedron are given in Table VIII. α-SnF_2 is the first divalent tin fluoride compound exhibiting such a coordination, but such an MF_5E geometry has already been observed in tetravalent tellurium compounds (TeF_4 (23) and $KTeF_5$ (24)) and in trivalent

TABLE IV

α-SnF₂: Main Interatomic Distances and Angles[a]

A. Distances within tetramers

Sn_{11}–F_{36}	2.057(5)	Sn_{21}–F_{17}	2.048(5)
Sn_{11}–F_{21}	2.102(5)	Sn_{21}–F_{27}	2.197(5)
Sn_{11}–F_{43}	2.156(4)	Sn_{21}–F_{47}	2.276(4)
F_{36}–F_{21}	2.856(6)	F_{17}–F_{27}	2.790(8)
F_{36}–F_{43}	2.815(6)	F_{17}–F_{47}	2.730(6)
F_{21}–F_{43}	2.726(8)	F_{27}–F_{47}	3.118(6)

B. Distances between tetramers

Sn_{11}–F_{31}	2.671(5)	Sn_{21}–F_{11}	2.386(4)
Sn_{11}–F_{44}	2.834(5)	Sn_{21}–F_{31}	2.494(5)
Sn_{11}–F_{17}	3.221(5)	Sn_{21}–F_{25}	3.309(5)

C. Angles within tetramers

F_{21}–Sn_{11}–F_{36}	86°73(20)	F_{17}–Sn_{21}–F_{27}	82°10(19)
F_{21}–Sn_{11}–F_{43}	79°58(20)	F_{17}–Sn_{21}–F_{47}	78°12(19)
F_{36}–Sn_{11}–F_{43}	83°82(20)	F_{27}–Sn_{21}–F_{47}	88°38(19)
Sn_{11}–F_{21}–Sn_{27}	171°99(10)	Sn_{13}–F_{41}–Sn_{27}	131°23(09)

D. Angles between tetramers

F_{17}–Sn_{11}–F_{44}	138°21(13)	F_{11}–Sn_{21}–F_{31}	93°10(17)
F_{17}–Sn_{11}–F_{31}	56°00(14)	F_{11}–Sn_{21}–F_{25}	136°48(15)
F_{31}–Sn_{11}–F_{44}	133°46(15)	F_{25}–Sn_{21}–F_{31}	127°36(15)

[a] The i, j values of Sn_{ij} and F_{ij} are defined as follows: $i = 1, 2$ for Sn and 1, 4 for F; $j = 1, 8$. $j = 1$ (x, y, z); $j = 2$ $(\bar{x}, \bar{y}, \bar{z})$; $j = 3$ $(\bar{x}, y, \frac{1}{2} - z)$; $j = 4 (x, \bar{y}, \frac{1}{2} + z)$; $j = 5$ $(\frac{1}{2} + x, \frac{1}{2} + y, z)$; $j = 6$ $(\frac{1}{2} - x, \frac{1}{2} - y, \bar{z})$; $j = 7$ $(\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z)$; $j = 8$ $(\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z)$.

antimony compounds (KSbF₄ (25)); see Fig. 5. The Sn–E distance (1.17 Å) and the ratio of unshared pairs (0.51) are both larger than the mean values calculated for the tetrahedral and bipyramidal coordinations.

2.2. The Brown Bond Valence Model

Brown (26) has shown that the cation/anion ionic radii ratio for oxides and fluorides of Sn(II), Sb(III), Te(IV), I(V), and Xe(VI) is 0.5 to 0.7; therefore, this cation
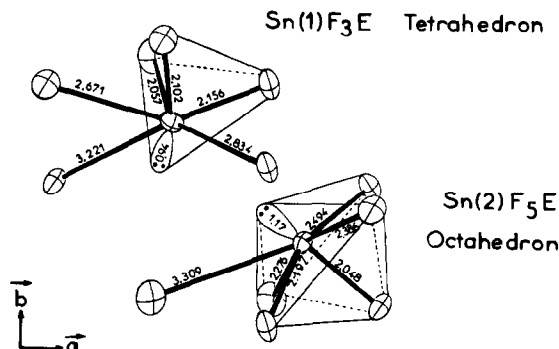

FIG. 4. Projection of the Sn(1)F_3E tetrahedron and Sn(2)F₅E octahedron on the (**a, b**) plane.

TABLE V

MOLECULAR VOLUME PER ANION (F^- OR O^{2-}) FOR Sn^{II}-AND Sn^{IV}-CONTAINING STRUCTURES[a]

Compounds	V_1 ($\AA^3$)	V_2 ($\AA^3$)	References
SnO_2	17.89	17.89	(29)
SnO (ortho)	39.75	19.88	(30)
SnO (tetra)	34.70	17.35	(31)
Sn_2O_3	27.74	16.64	(32)
Sn_3O_4	29.19	19.46	(33)
$SnOF_2$	19.52	19.52	(34)
Sn_4OF_6	26.85	17.09	(20, 21)[b]
Sn_2OF_2	31.44	18.87	(35)
SnF_4	16.95	16.95	(36)
SnF_4	16.24	16.24	(37)
$SnF_2\alpha$	26.65	17.77	This work
Sn_3F_8	21.65	17.32	(38)

[a] V_1 = molecular volume/number of anions in the molecule; V_2 = molecular volume/number of anions + number of lone pairs in the molecule.

[b] The orthorhombic phase of SnF_2 reported by Donaldson et al. (20, 21) is in fact the stannous oxifluoride Sn_4OF_6 (22).

should be octahedrally coordinated. However, the lone pair distorts this environment and decreases the coordination number. Brown has classified this distortions into five different arrangements ($\mathscr{A}$ to $\mathscr{E}$). In agreement with this model, one finds that:

—Sn(1) shows three strong Sn–F bonds and three weak ones (this is the usual $\mathscr{E}$ configuration); and

TABLE VI

COMPARISON OF THE POSITIONS OF THE LONE PAIRS OBSERVED ON THE FOURIER DIFFERENCE MAP AND CALCULATED BY J. GALY'S METHOD (18)

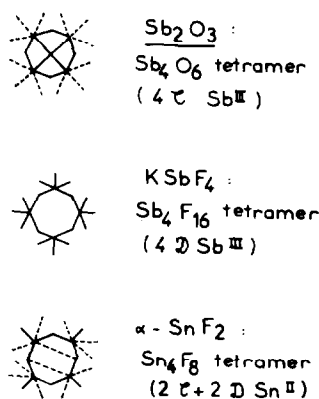|	Model E_1		Model E_2	
	Calc.	Fourier diff.	Calc.	Fourier diff.
x	0.36	0.35	0.05	0.08
y	0.68	0.59	0.32	0.40
z	0.05	0.02	0.18	0.15
d_{Sn-E} ($\AA$)	0.94	0.76	1.17	0.81

FIG. 5. Comparison of the tetramers observed in cubic Sb_2O_3 (12), $KSbF_4$ (25), and α-SnF_2.

—bridging fluorine gives a contribution of about 0.5 V.U.

However, Sn(2) occurs with a $\mathscr{D}$ configuration (one strong bond, four intermediate bonds, one weak bond) which was neither previously reported nor predicted by Brown.

Brown emphasized the easy formation of polymers in lone-pair compounds. Indeed tetramers have already been observed in many oxides and fluorides, for instance:

—in senarmontite Sb_2O_3 (13), the Sb_4O_6 tetramers are built up from four Sb(III) with $\mathscr{E}$ configuration; and

—in $KSbF_4$, the Sb_4F_{16} tetramers are built up from four Sb(III) with $\mathscr{D}$ configuration.

But α-SnF_2 is the first example of a tetramer (Sn_4F_8) made up from $2\mathscr{E} + 2\mathscr{D}$ configurations.

3. Stereochemistry of Fluorine

The four independent fluorine atoms may be divided into the categories:

—F(1) and F(3), which show only one very short bond to tin (terminal fluorine); and

—F(2) and F(4), which are nearly equidistant from two tin atoms (bridging fluorine).

Each fluorine is surrounded by three tin atoms forming an almost equilateral triangle (Fig. 6); fluorine atoms do not occupy the center of this triangle but are displaced

TABLE VII

GEOMETRICAL CHARACTERISTICS OF THE SnF_3E TETRAHEDRON
IN α-SnF_2

	Sn(1) (α-SnF₂)	NaSn₂F₅ (17)	Tetrahedral model
a (Å)	2.80(7)	2.86(4)	a = mean F–F distance
d (Å)	2.10(5)	2.16(2)	d = mean Sn(1)–F distance
$d(Sn_1-E_1)_{calc}$ (Å)	0.94	1.02	
γ (°)	83.4(2)	84.9(9)	γ = mean F–Sn(1)–F angles

toward a corner (terminal fluorine) or an edge (bridging fluorine).

4. Topological Relationship to Rutile Structure

4.1. Cationic Lattice

The pseudo-body-centered tetragonal arrangement of tin atoms in the structure of α-SnF₂ led us to suspect some relationship to rutile structure. Both unit cells are related in the following way:

Rutile axis	α-SnF₂ axis	Length (SnO₂)	Length (α-SnF₂)
|100|	|010|	4.74 Å	4.91 Å
|010|	|203|	4.74 Å	5.13 Å
|001|	|20$\bar{1}$|	3.19 Å	4.22 Å

The angle between the \|203\| and \|20$\bar{1}$\| directions is 94°. The mean periodicity along \|203\| and \|20$\bar{1}$\| is 5.02 Å; it results in a ratio c/a = 0.84, slightly higher than that of the rutile cell (0.62 to 0.71) (27). Figure 7 shows how the order between Sn(1) and Sn(2) along the \|203\| and \|20$\bar{1}$\| directions gives rise to a superstructure of rutile.

4.2. Rows of Octahedra

We indicated previously that the SnF_3E tetrahedron and the SnF_5E octahedron come from an octahedron which is strongly distorted by the lonepair. As in the rutile structure, one can observe rows of octahedra running along the c axis, but these octahedra are tilted in different directions and the linkage between rows is rather complex. In rutile, all the atoms are gathered in the (110) and (1$\bar{1}$0) planes; in the same way, all the

TABLE VIII

GEOMETRICAL CHARACTERISTICS OF THE SnF_5E OCTAHEDRON IN
α-SnF₂

	Sn(2) (α-SnF₂α)	Octahedral model
a_1 (Å)	3.25(7)	Mean F–F distance (equatorial plane)
a_2 (Å)	2.80(7)	Mean F–F distance (axial–equatorial)
d_1 (Å)	2.34(5)	Mean Sn(2)–F equatorial distance
d_2 (Å)	2.05(5)	Axial distance Sn(2)–F
$d(Sn_2-E_2)_{cal}$ (Å)	1.17	
Ψ(°)	79.1(2)	Mean F_{ax}–Sn–F_{eq} angles
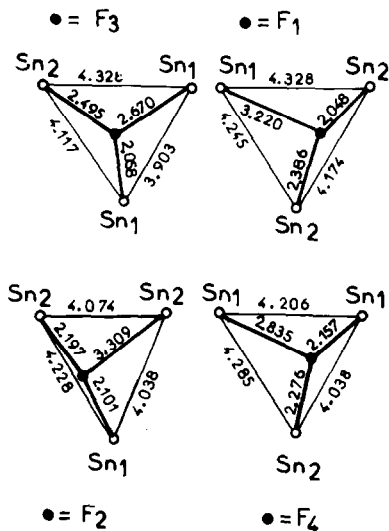
FIG. 6. Coordination polyhedra of fluorine atoms.

o : F⁻
E : LONE PAIR

FIG. 8. Hexagonal closest packing of the fluorine atoms and lone pairs in the anionic planes.

4.3. Anionic Lattice

In the rutile structure, the oxygen atoms form slightly distorted hexagonal close-packed planes parallel to (a, c). Each unit cell contains two such planes at $y = \frac{1}{4}$ and $\frac{3}{4}$; in SnO_2, the thickness of these layers is 0.52 Å. A similar feature is observed for α-SnF_2 if one includes the lone pairs in these planes: Figure 8 clearly shows this nearly hexagonal close packing of lone pairs and fluorine atoms in the structure. The order between lone pairs and fluorine in these planes is as follows:

—a direction: ... F–F–E–F–F–E ... ,

—c* direction: ... F–F–F–F–E–E–F–F–F–F–E–E ....

Figure 9 is a projection of these close-packed planes on the b, c*) plane.

The occupation of the cationic site is not the same in SnO_2 and α-SnF_2; in the rutile, all the tetrahedral sites between the anionic planes are empty while half of the octahedral ones are filled with Sn^{4+}; in α–SnF_2, Sn^{2+} are equally distributed between octahedral and tetrahedral sites.

• = F⁻
o = LONE PAIR
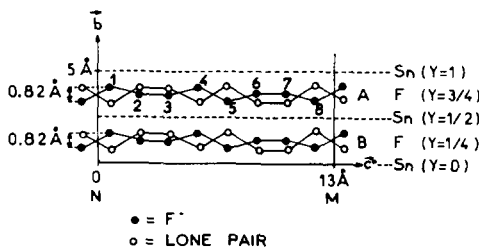
FIG. 9. Projection of the anionic planes on the (b, c*) plane.

1 = Sn(1)
2 = Sn (2)

FIG. 7. Projection of the tin atoms in coordinate $y \simeq 0$ on the (a, c) plane, showing the bidimensional superstructure from rutile in α-SnF_2.
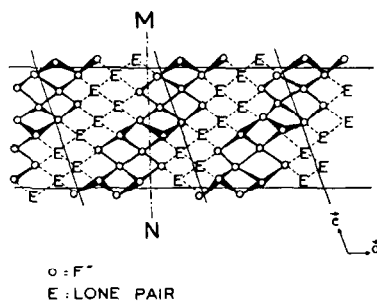
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