Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Fluorine Chemistry 124 (2003) 5–15
JOURNAL OF FLUORINE CHEMISTRY
www.elsevier.com/locate/jfluchem

Orientation disorder in ammonium elpasolites
Crystal structures of $(NH_4)_3AlF_6$, $(NH_4)_3TiOF_5$ and $(NH_4)_3FeF_6$

A.A. Udovenko, N.M. Laptash*, I.G. Maslennikova

Institute of Chemistry, Far Eastern Branch of RAS, Pr. Stoletiya 159, 690022 Vladivostok, Russia

Received 23 January 2003; received in revised form 28 May 2003; accepted 6 June 2003

Abstract

Crystal structures of the known $(NH_4)_3AlF_6$(I) and $(NH_4)_3FeF_6$(III) and new $(NH_4)_3TiOF_5$(II) elpasolites were refined by localizing anions (F^-, O^{2-}) in four acceptable positions of the cubic system *Fm*3*m* ($Z = 4$) with $a = 8.9401(3), 9.1104(3), 9.110(1)$ Å, respectively. According to the refinement data and a rather large entropy change due to fluorine (oxygen) octahedra disordering in the above compounds and in $(NH_4)_3WO_3F_3$(IV) elpasolite, it was found that fluorine (oxygen) atoms are randomly distributed in two ways, in general 192*l* position or in mixed 24*e* + 96*j* one. Statistics in fluorine (oxygen) distribution is, probably, the result of domain structure of the crystals.

Keywords: Ammonium fluoro-elpasolites; Crystal structure; Orientation disorder; Structural phase transitions; Entropy; Domains

1. Introduction

Rather large entropy changes at phase transitions [$\Delta S = (2.33-2.99)R$] from triclinic (low temperature) symmetry into cubic in ammonium elpasolites $(NH_4)_3M^{III}F_6$ (M^{III} = Al, Ga, Cr, V, Fe, Sc, In) are believed to be connected with orientation disorder both of $[MF_6]^{3-}$ octahedra and $[NH_4]^+$ tetrahedra in the cubic system *Fm*3*m* ($Z = 4$) [1,2]. Fluorine octahedra are assumed to be disordered with eight possible orientations in the general 192*l* position [3], and one of the ammonium ions at 4*b* sites is disordered in the cubic phase. The total entropy change connected with both octahedral and tetrahedral ordering could be given as $\Delta S = R\ln 8 + R\ln 2 = R\ln 16$. This value (23.05 J K^{-1} mol^{-1}) is in close agreement with the experimental value (24.8 ± 1.9 J K^{-1} mol^{-1}) for $(NH_4)_3FeF_6$ [3].

Nevertheless, there is no reliable structural investigation confirming this assumption. The crystal structure of ammonium hexafluoroferrate(III) has not been refined since the work of Pauling [4] and Minder [5]. The last description of the crystal structure of $(NH_4)_3AlF_6$ was given in 1953 [6]. All these structural data show that fluorine atoms are located in 24*e* position of the fcc lattice.

In this paper we have tried to check the above assumption using a series of ammonium fluoro-elpasolites $(NH_4)_3AlF_6$(I), $(NH_4)_3TiOF_5$(II), $(NH_4)_3FeF_6$(III) and $(NH_4)_3WO_3F_3$(IV) by refining their cubic structure with four different anionic positions.

2. Results and discussion

All the ammonium compounds investigated are isostructural and belong to the family of elpasolites. In accordance with our refinement in two acceptable space groups *F*43*m* (No. 216) and *Fm*3*m* (No. 225), the structures of I–IV should be related to *Fm*3*m* symmetry because the anionic (X = O, F) positions 96*i* and 48*h* in *F*43*m* give rather deformed octahedra MX_6 with short distances X–X = 2.40 Å, and 24*f* in 216 is identical with 24*e* in 225. It is possible that four variants of location of X atoms around the central one in *Fm*3*m* result in an acceptable octahedral geometry of MX_6 (Table 1):

1. 24*e*(1)
2. 96*k*(1/4)
3. 24*e*(1/3) + 96*j*(1/6)
4. 192*l*(1/8)

All these variants show X atoms to be located in the same electron density clouds but with some displacement of their centers from (0 0 *x*) site, and disordering of X atoms follows from the cases 2–4.

Refinement of the structure with X anions located on 24*e* site gives relatively high *R*-values, especially for I–III

---

[*] Corresponding author. Fax: +7-4232-311889.
E-mail address: laptash@ich.dvo.ru (N.M. Laptash).

0022-1139/$ – see front matter © 2003 Elsevier B.V. All rights reserved.
doi:10.1016/S0022-1139(03)00166-0

Table 1
Crystal structure refinement data of ammonium elpasolites

Parameter		Compound														
		$(NH_4)_3AlF_6$(I)				$(NH_4)_3TiOF_5$(II)				$(NH_4)_3FeF_6$(III)				$(NH_4)_3WO_3F_3$(IV)		
		Site														
		24*e*	96*k*	24*e* + 96*j*	192*l*	24*e*	96*k*	24*e* + 96*j*	192*l*	24*e*	96*k*	24*e* + 96*j*	192*l*	24*e*	96*k*	24*e* + 96*j*
X(1)	*x*	0	0.0224(1)	0	0.0202(2)	0	0.0240(2)	0	0.0181(2)	0	0.0301(1)	0	0.0233(2)	0	0.0262(2)	0
	y	0	0.0224(1)	0	0.0406(2)	0	0.0240(2)	0	0.0472(2)	0	0.0301(1)	0	0.0418(2)	0	0.0262(2)	0
	z	0.1966(2)	0.1947(1)	0.1969(2)	0.1942(1)	0.2025(2)	0.2009(1)	0.2025(2)	0.1999(1)	0.2062(2)	0.2035(1)	0.2082(3)	0.2031(1)	0.2025(3)	0.2005(2)	0.2025(3)
X(2)	*y*	–	–	0.0536(2)	–	–	–	0.0643(2)	–	–	–	0.0632(2)	–	–	–	0.0637(3)
	z	–	–	0.1923(1)	–	–	–	0.1975(2)	–	–	–	0.2005(2)	–	–	–	0.1985(2)
U_{iso}(X) (Å^2)		0.076(8)	0.038(3)	0.063(3) 0.042(2)	0.036(2)	0.130(9)	0.061(3)	0.054(3) 0.050(2)	0.056(2)	0.151(9)	0.068(3)	0.070(2) 0.052(2)	0.066(2) 0.054(2)	0.159(9)	0.064(5)	0.066(6) 0.055(4)
*R*1 (%)		5.79	2.91	2.40	2.36	5.27	3.64	2.55	2.63	4.04	1.89	1.68	1.58	1.73	1.31	1.17
N(Fo)		89	89	89	89	93	93	93	93	94	94	94	94	83	83	83
GooF		1.082	1.046	1.052	1.084	0.998	1.014	1.030	0.996	1.066	1.044	1.006	0.996	1.008	0.995	1.011
(M–X) (Å)		1.758(2)	1.764(1)	2 × 1.761(1) 4 × 1.785(1)	1.783(1)	1.845(1)	1.856(1)	2 × 1.845(2) 4 × 1.892(2)	1.878(1)	1.879(2)	1.894(1)	2 × 1.894(2) 4 × 1.914(2)	1.900(1)	1.854(2)	1.867(2)	2 × 1.854(3) 4 × 1.909(2)
$(X–X)_{min}$ (Å)		2.486(6)	6 × 2.478(3)	8 × 2.507(3)	2.420(3)	2.609(3)	6 × 2.606(3)	8 × 2.643(6)	2.497(3)	2.657(6)	6 × 2.650(3)	8 × 2.693(5)	2.601(3)	2.622(6)	6 × 2.618(6)	8 × 2.661(6)
$(X–X)_{max}$ (Å)		2.486(6)	6 × 2.510(3)	4 × 2.525(3)	2.619(3)	2.609(3)	6 × 2.643(3)	4 × 2.676(6)	2.806(3)	2.657(6)	6 × 2.707(3)	4 × 2.707(5)	2.773(3)	2.622(6)	6 × 2.661(6)	4 × 2.700(6)
XMX (^{o})		12 × 90	89.3–90.7(1)	12 × 90	85.5–94.5(1)	12 × 90	89.2–90.8(1)	12 × 90	83.3–96.7(1)	12 × 90	88.8–91.2(1)	12 × 90	86.3–93.7(1)	12 × 90	89.1–90.9(1)	12 × 90
n[a]		1	8	6	24	1	8	6	24	1	8	6	24	1	8	6

[a] Number of nongenerated equivalent orientations of MX_6 octahedra.

compounds and increased isotropic thermal parameters (0.130–0.159 Å^2) for II–IV. Polyhedra MX_6 are regular octahedra (Table 1).

In cases 2–4, isotropic thermal parameters and *R* are appreciably decreased. It should be noted that for compound IV, refinement of the X location on 192*l* leads to displacement of their coordinates to 96*j* or 96*k* positions, i.e. 192*l* site is not realized in this structure. Significant decrease of *R* from 24*e* to the other sites shows that X atoms are not located in 24*e*. Its relative decrease from I to IV is caused by the decrease of the X scattering contribution into the structure with increasing *Z*-value of a central atom.

Hydrogen atoms H(1) and H(2) of two ammonium groups in I–IV structures occupy the same positions with close coordinate values. Groups $N(1)H_4$ in the structures are fixed, 32 atoms H(1) occupy completely the 32*f* site. Groups $N(2)H_4$ are disordered, 16 hydrogen atoms H(2) are statistically distributed in this 32*f* site with population 1/2. During the refinement with hydrogen atoms addition, R decreased by 3.3, 2.3, 1.0 and 0.2% for I–IV, respectively.

As a result of refinement of structures I–IV, variants 3 and 4 of location X atoms are most acceptable due to the smallest *R* factors (Table 1). It should be noted that "split-atom" model (two X positions statistically occupied) has been proposed by Massa and others for ammonium peroxofluoro-elpasolites $(NH_4)_3Ti(O_2)F_5$ and $(NH_4)_3Zr(O_2)F_5$ [7,8]. This split model arose from the electron density profile of X atoms. We also used this procedure to determine the shape of electron density. Fig. 1 presents Fourier profiles passing through X(1) center in 24*e* site parallel (0 0 1) plane for all I–IV compounds. As is seen, a general view of electron density profiles and the orientation of their convexities relative to *x* and *y* axes in $(NH_4)_3AlF_6$ and $(NH_4)_3TiOF_5$ structures correspond to 96*j* or 24*e* + 96*j* positions (Fig. 1a and b). These profiles are very similar to that of $(NH_4)_3Ti(O_2)F_5$ first attributed to mixed 24*e* + 96*j* position of ligand distribution [7] but then refined with 96*j* + 96*k* position [8]. The electron density profile in the square form with insignificant convexities on its sides for $(NH_4)_3WO_3F_3$ (Fig. 1d) we cannot unambiguously interpret.

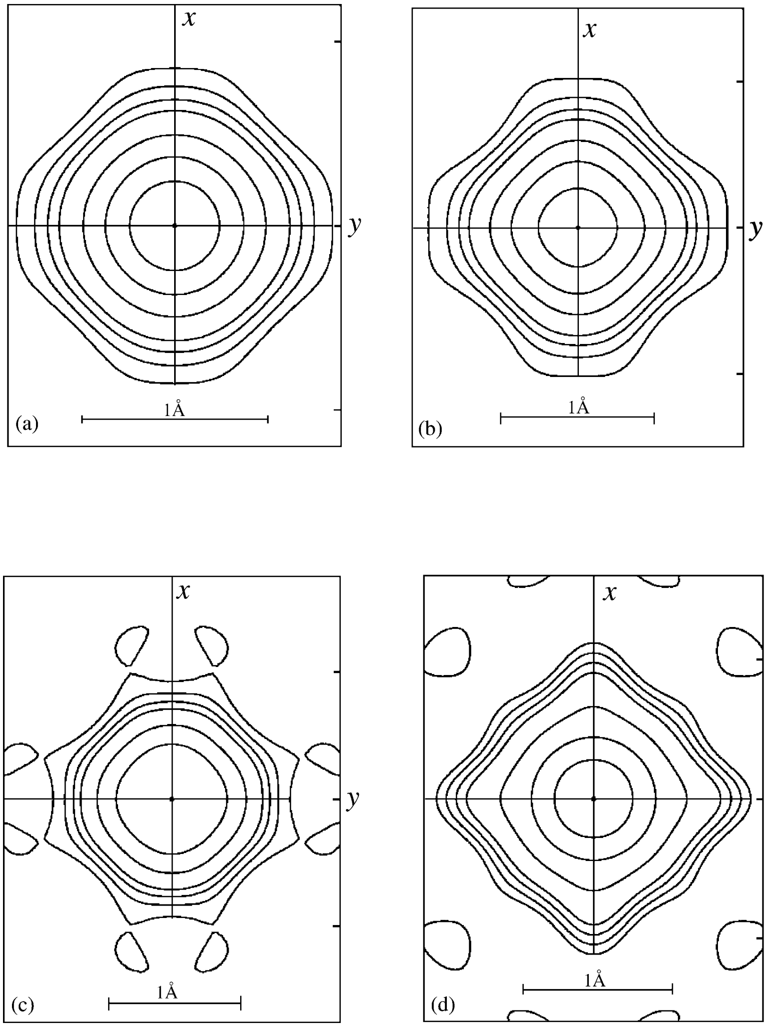

Fig. 1. Electron density profiles for structures of $(NH_4)_3AlF_6$ (a); $(NH_4)_3TiOF_5$ (b); $(NH_4)_3FeF_6$ (c); and $(NH_4)_3WO_3F_3$ (d). Fourier map isolines correspond to 0.8, 1.2, 1.6, 2.0, 3.0, 4.0 and 5.0 e/Å^3. Atom X(1) was not introduced under calculations.

Quite sharp corners on the profile oriented along *x* and *y* axes are responsible for the 96*j* position. The insignificant convexities on square sides are either the result of electron density superposition in 96*j* site or the result of X presence in 96*k* position. At the moment, we accept the first variant (but X atoms are located on 24*e* + 96*j* site) because the mixed 96*j* + 96*k* position gives 24 nongenerate equivalent states of octahedral orientations that does not account for the observed ΔS at the phase transition. Finally, eight convexities in electron density profile of $(NH_4)_3FeF_6$ (Fig. 1c) should be connected with general 192*l* position of X atoms.

In addition, to choose a real variant of ligand location in the structure, it is necessary to estimate (except *R*, thermal parameters and shape of electron density) geometries of all statistical polyhedra MX_6, which would correspond to crystal chemistry criteria. In particular, the minimum distance X–X in octahedron III on the 96*j* site is less then 2.40 Å, so this position without combination with 24*e* is forbidden.

Moreover, it is necessary to calculate the number of nondegenerate equivalent orientations of MX_6 octahedra to estimate the entropy change at the phase transitions.

Around atom M, 24 points of 96*k* position are placed, $4 + 4$ along each axis of the unit cell. Two equivalent position systems $(4X1' + 4X1'')$ (Fig. 2, shown for compound III, X = F) correspond to each pair of axial atoms X(1)–X(1). These systems form equatorial planes of two octahedra turned one against another around the axis by 12.4–16.6° for I–IV, respectively. Thus, axial atomic rotations along one axis of the unit cell result in eight orientations of octahedra. The other two axes give identical orientations. Hence, the 96*k* position gives eight nondegenerate equivalent orientations of octahedra with insignificant deformation of valence angles (from 0.7 to 1.2°) (Table 1).

In case 3, axial axes of two octahedra X(1)–X(1) are directed along each axis of the unit cell. These two octahedra are turned one against another by 29.7–35.7° for I–IV, respectively, atoms X(2) on 96*j* site are located in equatorial planes (Fig. 3, shown for compound I). This combination gives six nondegenerate equivalent orientations. Octahedra are slightly tetragonally distorted because of different bond lengths M–X(1) and M–X(2) ($0.020 \leq \Delta r \leq 0.055$ Å). All angles are 90°. Mixed 24*e* + 96*j* position is the result of MX_6 rotation around the axis 4, so two X atoms remain in 24*e* and four X atoms pass into 96*j* position.

Because $x \neq y \neq 0$ in the 192*l* position, 24 nondegenerate equivalent orientations of MX_6 octahedra with deformed angles are produced in the elpasolite structure (eight along each axis). Angle deformations are within the limit 3.7–6.7°, and minimal contacts X–X (2.420–2.601 Å) are the least compared with the other variants (Table 1).

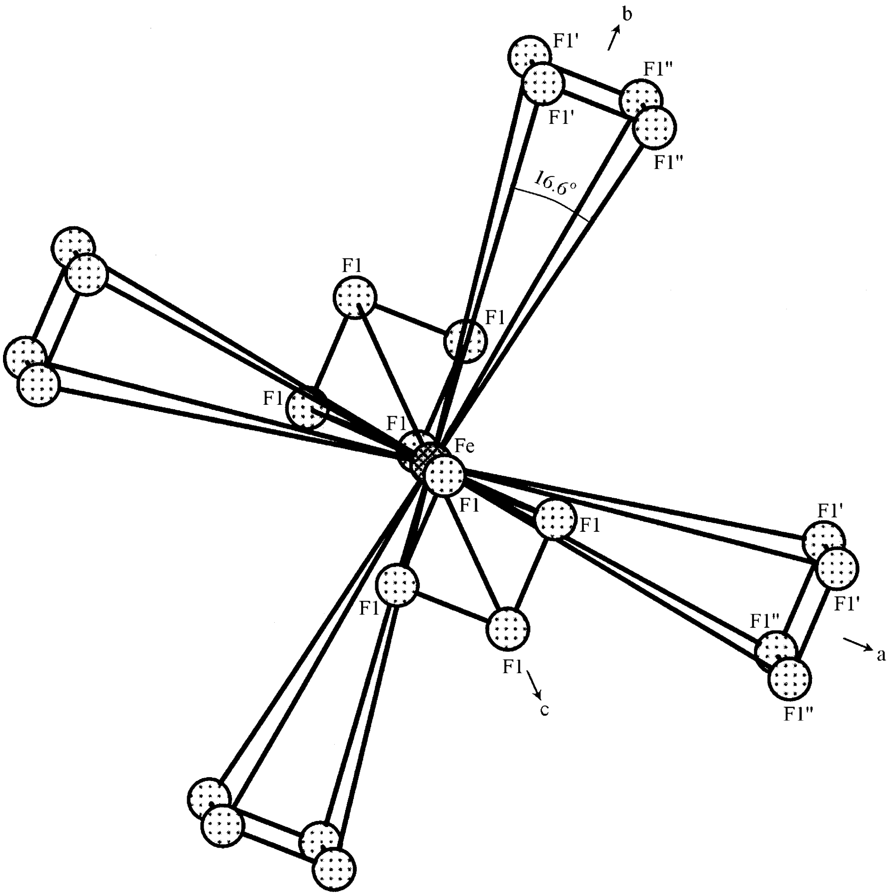

Fig. 2. Fragment of regular point system for 96*k* position in *Fm*3*m* symmetry for $(NH_4)_3FeF_6$.

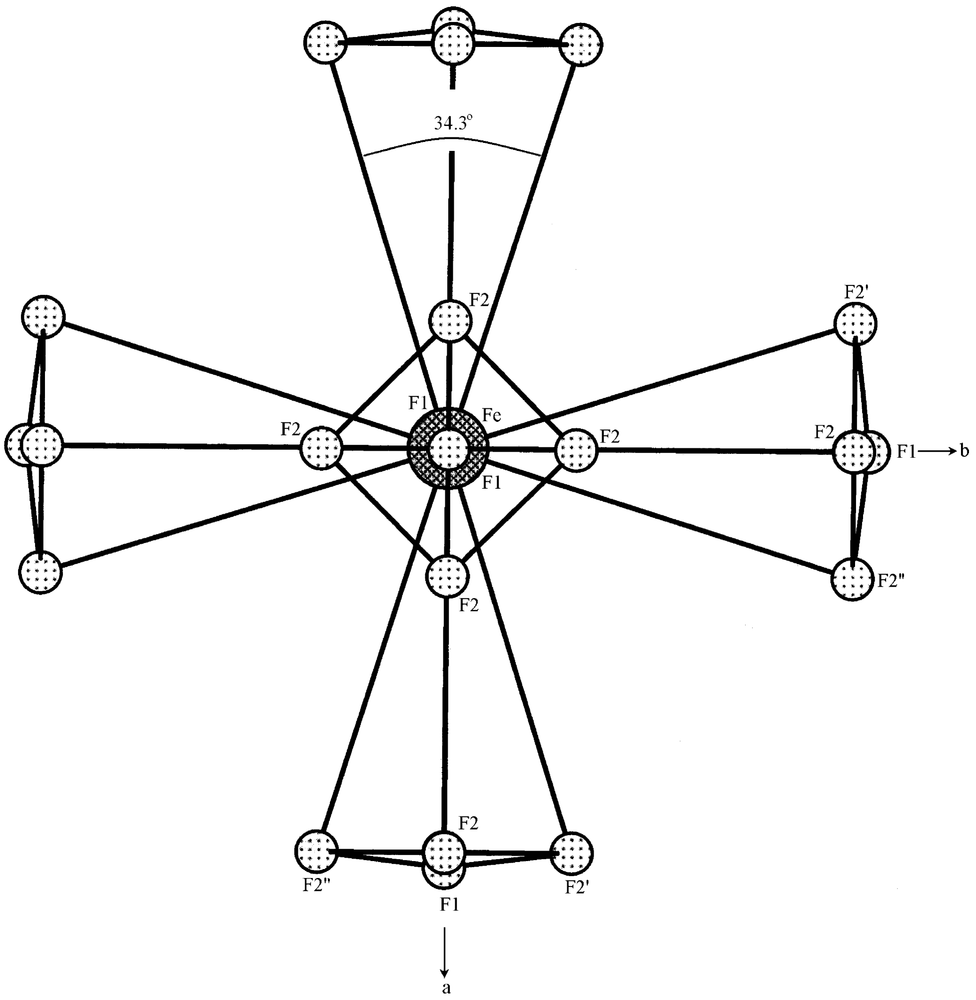

Fig. 3. Fragment of regular point system for 24*e* + 96*j* position in *Fm*3*m* symmetry for $(NH_4)_3AlF_6$.

Moriya et al. [3] deduced eight orientations of regular rigid octahedra for the 192*l* position in space group *Fm*3*m*. However, in accordance with our data, orthogonal bonds in this position are absent; equally they are not all orthogonal in the structure of $(NH_4)_3GaF_6$ with 24 F atoms at 192*l* ($x = 0.013$; $y = 0.052$; $z = 0.203$) [9].

Thus, 96*k* and 24*e* + 96*j* positions give rise to more regular octahedra than the 192*l* position, and the number of nondegenerate equivalent orientations are different for these variants.

The entropy change ΔS during the phase transitions in elpasolites (Table 2) is now considered. Flerov and others [1,2] reported rather large ΔS value at phase transition *Fm*3*m*–*P*1 for compounds $(NH_4)_3M^{III}F_6$ (M^{III} = Ga, Fe, V) as $\Delta S = R$ (ln 8 + ln 2), where ln 8 is associated with orientation disorder of MX_6 octahedra in the cubic phase

Table 2
Thermodynamic characteristics of phase transitions in elpasolites

Compound	Type of distorted structure	T_i (K)	ΔS (observed) ($J\ K^{-1}\ mol^{-1}$)	ΔS (calculated) ($J\ K^{-1}\ mol^{-1}$)
Rb_2KFeF_6	?	170	15.6 [1]	R ln 6 = 14.9
Rb_2KGaF_6	?	123	14.4 [1]	R ln 6
$(NH_4)_3FeF_6$	Tr	267	24.8 [1,3]	R (ln 2 + ln 8) = 23.1
$(NH_4)_3GaF_6$	Tr	250	23.0 [1]	R (ln 2 + ln 8)
$(NH_4)_3VF_6$	Tr	280	24.9 [1]	R (ln 2 + ln 8)
$(NH_4)_3AlF_6$	?	220	18.5 [1]	R (ln 2 + ln 6) = 20.7
$(NH_4)_3CrF_6$	Tr	270	19.4 [1]	R (ln 2 + ln 6)
$(NH_4)_3TiOF_5$	?	270	19.0 [12]	R (ln 2 + ln 6)
$(NH_4)_3WO_3F_3$	?	200	15.5 [12]	R ln 6

Tr: triclinic symmetry.

connected with eight possible orientations in the 192*l* site, and ln 2 is associated with orientation disorder of $N(2)H_4$ groups in 32*f* site. Entropy changes as *R* ln 6 for compounds $Rb_2KM^{III}F_6$ (M^{III} = Ga, Fe) were not clearly explained. According to the crystal structure data of Rb_2KFeF_6 [10], fluorine atoms occupy the 24*e* position that does not permit to explain the observed entropy change for this compound. This position (24*e*) was suggested not to be the best suited for fluorine atoms in $Rb_2KM^{III}F_6$ series, the preferable site seems to be 192*l* [11] which also does not give $\Delta S = R \ln 6$. This relative large value of ΔS characterizes orientation disorder of fluoride octahedra. Six orientations of octahedra in cubic phase arise from distribution of fluorine atoms on 24*e* + 96*j* positions (Table 1). For compounds $(NH_4)_3M^{III}F_6$ (M^{III} = Al, Cr) and $(NH_4)_3TiOF_5$ with ammonium groups instead of group I cations, ΔS is logically described as *R*(ln 2 + ln 6) in accordance with mixed 24*e* + 96*j* position.

Single crystals I, II and IV were measured at 173 K. However, structure determinations of low temperature phases were unsuccessful for the present since the crystals changed into polydomain states below the phase transition, and diffraction reflections had a mosaic structure. We conclude that I–IV also consist of micropolydomains above the phase transition and cubic *Fm*3*m* symmetry is averaged.

As a result of crystal chemistry analysis, it was found that orthorhombic domains of $P2_12_12_1$ symmetry (Fig. 4) correspond to cubic phase with 192*l* position for X atoms, and orthorhombic domains of *Aba*2 symmetry (Fig. 5) correspond to cubic phase with mixed 24*e* + 96*j* position of ligands. It should be emphasized that MX_6 octahedra in domains of $P2_12_12_1$ and *Aba*2 symmetry must be distorted as in low and middle symmetric structures of aluminum, titanium, iron and tungsten fluoride compounds. A general view of the elpasolite cubic structure for 24*e* + 96*j* position is given in Fig. 6. Based on cubic symmetry, *Fm*3*m*, we calculated atomic coordinates in orthorhombic unit cell for $(NH_4)_3FeF_6$ and $(NH_4)_3AlF_6$ (Tables 3 and 4, respectively). The parameters of orthorhombic and cubic cells are the same.

Differently oriented domains are linked via the face of (*h k* 0), (0 *k l*) and (*h* 0 *l*) type and connected one with an other by fourfold axes, which are symmetry elements of the average *Fm*3*m* phase. The maximum number of nongenerated orientations of domains is 24 and 12 for 192*l* position and for the mixed 24*e* + 96*j* one, respectively. Probably, rather large entropy changes at phase transitions in elpasolites can be explained on the basis of microdomain crystal structures. In accordance with the number of nongenerate orientations of domains, entropy change for $(NH_4)_3FeF_6$ must be $R \ln 24 = 26.4\ J\ K^{-1}\ mol^{-1}$ that is also quite consistent with the experimental data $24.8 \pm 1.9\ J\ K^{-1}\ mol^{-1}$ [3]. In the case of $(NH_4)_3AlF_6$ and $(NH_4)_3TiOF_5$ [12],

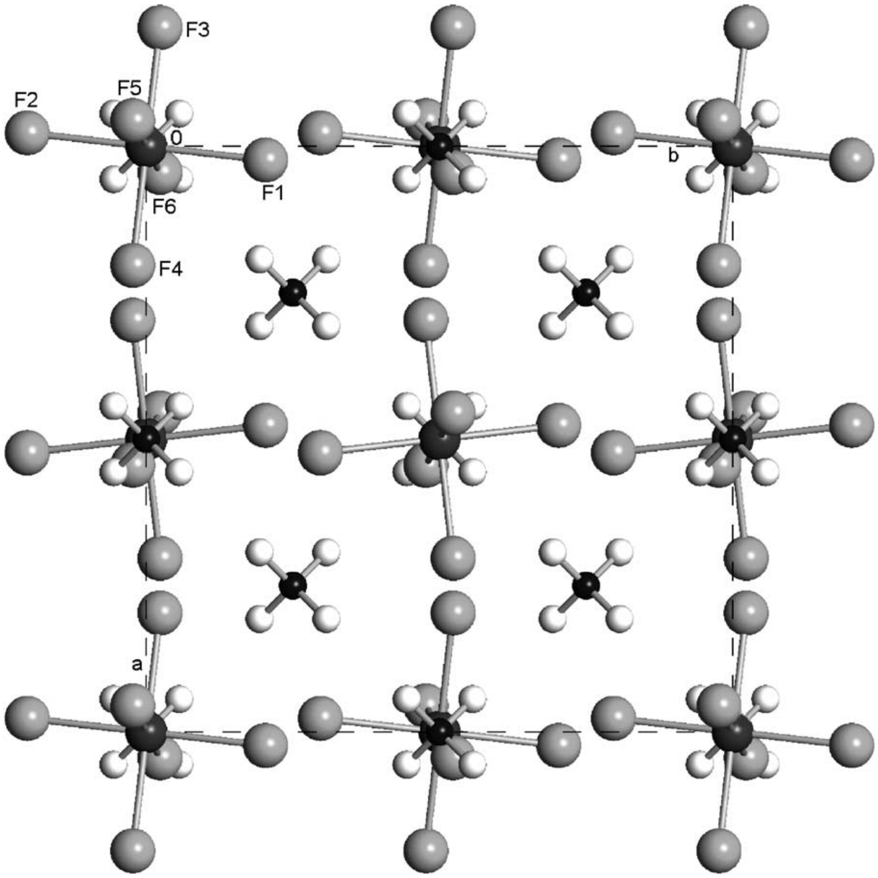

Fig. 4. Rhombic structure of elpasolite domain of $P2_12_12_1$ symmetry for $(NH_4)_3FeF_6$.

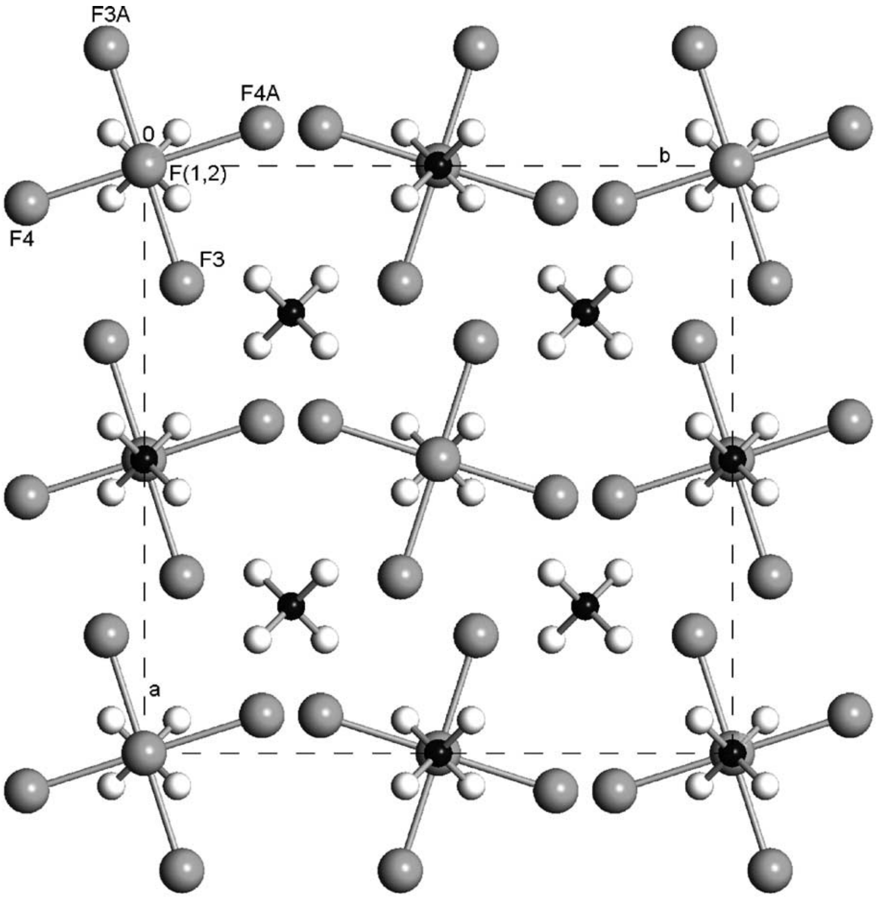

Fig. 5. Rhombic structure of elpasolite domain of *Aba*2 symmetry for $(NH_4)_3AlF_6$.

Table 3
Atomic coordinates and isotropic displacement parameters of rhombic domain with $P2_12_12_1$ symmetry for $(NH_4)_3FeF_6$

Atom	Site	Occupation	*x*	*y*	*z*	U_{iso} (Å^2)
Fe(1)	4*a*	1.0	0	0	0	0.02
N(11)	4*a*	1.0	1/4	1/4	1/4	0.05
N(12)	4*a*	1.0	1/4	1/4	3/4	0.05
N(2)	4*a*	1.0	1/2	1/2	1/2	0.05
F(1)	4*a*	1.0	0.023	0.203	0.042	0.06
F(2)	4*a*	1.0	−0.023	−0.203	−0.042	0.06
F(3)	4*a*	1.0	−0.203	0.023	0.042	0.06
F(4)	4*a*	1.0	0.203	−0.023	−0.042	0.06
F(5)	4*a*	1.0	0.023	−0.042	0.203	0.06
F(6)	4*a*	1.0	−0.023	0.042	−0.203	0.06
H(11)	4*a*	1.0	0.194	0.194	0.194	0.12
H(12)	4*a*	1.0	0.194	0.306	0.306	0.12
H(13)	4*a*	1.0	0.306	0.306	0.194	0.12
H(14)	4*a*	1.0	0.306	0.194	0.306	0.12
H(15)	4*a*	1.0	0.194	0.194	0.694	0.12
H(16)	4*a*	1.0	0.194	0.306	0.806	0.12
H(17)	4*a*	1.0	0.306	0.306	0.694	0.12
H(18)	4*a*	1.0	0.306	0.194	0.806	0.12
H(21)	4*a*	1.0	0.556	0.444	0.556	0.12
H(22)	4*a*	1.0	0.444	0.444	0.444	0.12
H(23)	4*a*	1.0	0.444	0.556	0.556	0.12
H(24)	4*a*	1.0	0.556	0.556	0.444	0.12

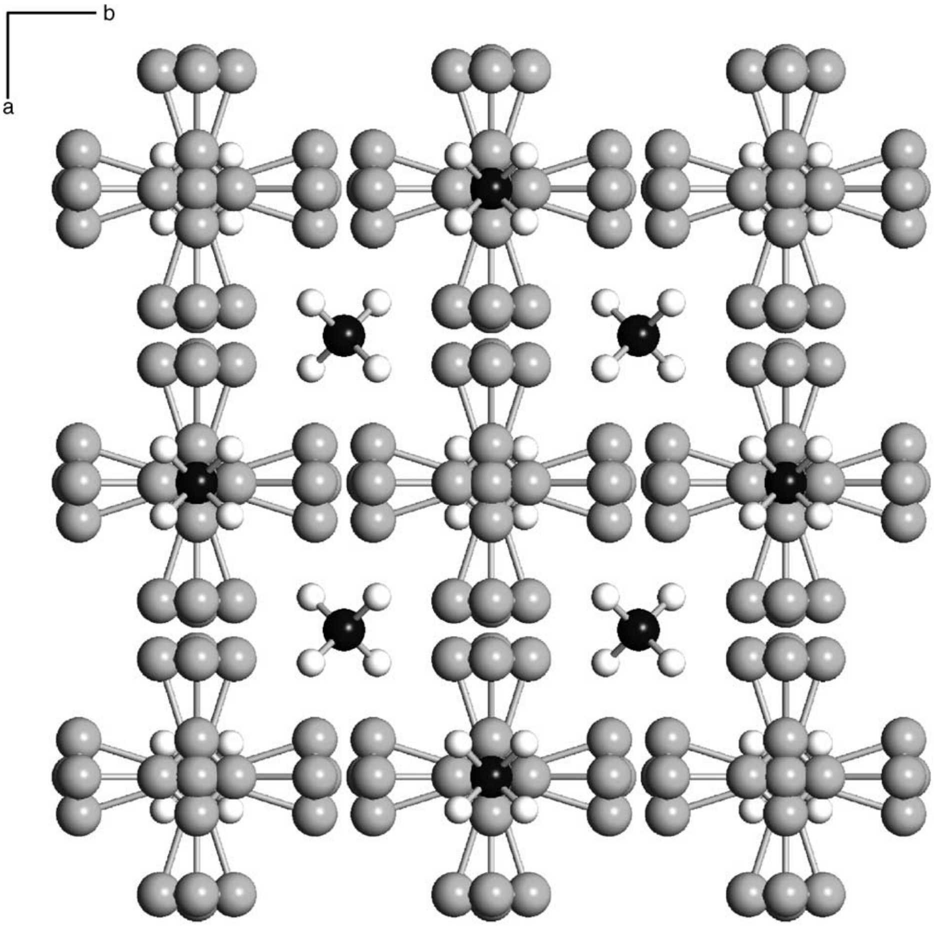

Fig. 6. General view of cubic elpasolite structure for mixed 24*e* + 96*j* position of ligands for $(NH_4)_3AlF_6$.

Table 4
Atomic coordinates and isotropic displacement parameters of rhombic domain with *Aba*2 symmetry for $(NH_4)_3AlF_6$

Atom	Site	Occupation	*x*	*y*	*z*	U_{iso} (Å^2)
Al(1)	4*a*	1.0	0	0	0	0.02
N(1)	8*b*	1.0	1/4	1/4	1/4	0.04
N(2)	4*a*	1.0	1/2	1/2	1/2	0.05
F(1)	4*a*	1.0	0	0	0.197	0.06
F(2)	4*a*	1.0	0	0	−0.197	0.06
F(3)	8*b*	1.0	0.192	0.054	0.000	0.07
F(4)	8*b*	1.0	0.054	−0.192	0.000	0.07
H(11)	8*b*	1.0	0.193	0.193	0.193	0.14
H(12)	8*b*	1.0	0.193	0.307	0.307	0.14
H(13)	8*b*	1.0	0.307	0.307	0.193	0.14
H(14)	8*b*	1.0	0.307	0.193	0.307	0.14
H(21)	8*b*	1.0	0.557	0.557	0.557	0.16
H(22)	8*b*	1.0	0.557	0.443	0.443	0.16

$\Delta S = R \ln 12$ which is in agreement with the observed values (Table 2). Entropy change for $(NH_4)_3WO_3F_3$ [12] is a unique case. It is close to $R \ln 6$ instead of $R \ln 12$ (as it should arise from the number of nongenerate equivalent orientations). Probably, this value ($R \ln 6$) is not final during the phase transitions in the observed temperature interval (120–300 K) due to strong fluorine-oxygen exchange so two nongenerate orientations exist below the detected phase transition. It is necessary to measure the heat capacity of $(NH_4)_3WO_3F_3$ at lower temperatures.

3. Concluding remarks

Taking in to account the crystal structure refinement of ammonium fluoro-elpasolite series and the entropy changes at phase transitions we can conclude that at least two groups of ammonium species are available. The first is like $(NH_4)_3FeF_6$ with disorder of X atoms in general 192*l* position causing the highest entropy change at the phase transition. The other one is connected with disordering of X atoms in mixed $24e + 96j$ position and a smaller entropy change at the phase transition as in the case of $(NH_4)_3AlF_6$ and $(NH_4)_3TiOF_5$. Ammonium oxofluorotungstate $(NH_4)_3WO_3F_3$ is a separate case which shows the necessity of low temperature structural determinations. Rather large values of entropy changes are associated with orientation order–disorder character of phase transitions in ammonium species. Probably, the model of regular rigid octahedra for entropy calculations is not quite correct. Our results show that MX_6 unites are distorted octahedra. Micropolydomain model of the elpasolite structure gives a better possibility for description of experimental values of entropy changes at phase transitions in the crystals under investigation.

4. Experimental

4.1. Synthesis

Transparent well shaped octahedral single crystals of the compounds were obtained from aqueous fluoride solutions. $(NH_4)_3AlF_6$ and $(NH_4)_3FeF_6$ were obtained by mixing MCl_3 solutions with the excess of NH_4F (40 wt.%), removing the fine powder and slowly evaporating the mother liquor. It should be noted that the real composition of the complexes was $(NH_4)_3Al(OH)_xF_{6-x}$ ($x = 0.2$) and $(NH_4)_xFe(OH)_{3-x}F_{2x}$ ($x = 2.85$). Anal. Calcd. for $(NH_4)_3Al(OH)_{0.2}F_{5.8}$: NH_4, 27.75; Al, 13.87; F, 56.63. Found: NH_4, 27.7; Al, 14.0; F, 56.8. Calcd. for $(NH_4)_{2.85}Fe(OH)_{0.15}F_{5.70}$: NH_4, 23.53; Fe, 25.62; F, 49.69. Found: NH_4, 23.6; Fe, 25.6; F, 49.8. Ammonia content was determined by the Kjeldahl method, fluorine and metal were analyzed by pyrohydrolysis from one sample. We used stoichiometric formulae of these compounds above because it seemed impossible to distinguish between OH^- and F^- (statistically distributed in the crystal lattice) by X-ray diffraction.

Single crystals of $(NH_4)_3TiOF_5$ and $(NH_4)_3WO_3F_3$ were synthesized from hot solutions of $(NH_4)_2TiF_6$ and $(NH_4)_2WO_2F_4$, respectively, with excess of NH_4F followed by addition of NH_4OH dilute (1:1) solution to pH 7–8. The details are given in [13].

4.2. X-ray studies

The crystal structures of the compounds I–III have been solved by X-ray diffraction using a SMART-1000 CCD diffractometer by a direct method and refined by least-squares method in anisotropic approximation of nonhydrogen atoms. Hydrogen atoms H(1) in I–III were localized

Table 5
Crystal and structure refinement data of compounds I–III with $24e + 96j$ (192*l*) of X locations

Parameter	Meaning (empirical formula)		
	$(NH_4)_3AlF_6$	$(NH_4)_3TiOF_5$	$(NH_4)_3FeF_6$
Formula weight	195.11	213.03	223.98
Temperature (K)	297(2)	297(2)	297(2)
Wavelength (Å)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
Crystal system, space group	Cubic, $Fm3m$	Cubic, $Fm3m$	Cubic, $Fm3m$
a (Å)	8.9401(3)	9.110(1)	9.1104(3)
V (Å^3); Z	714.54(4); 4	756.0(2); 4	756.16(4); 4
d_{calc} (g cm^{-3})	1.814	1.872	1.967
μ (mm^{-1})	0.338	1.173	2.045
F(0 0 0)	400	432	452
Crystal size	Octahedron (0.20 mm × 0.20 mm × 0.20 mm)	Octahedron (0.20 mm × 0.20 mm × 0.20 mm)	Octahedron (0.20 mm × 0.20 mm × 0.20 mm)
θ (°) range for data collection	3.95–31.83	3.87–31.46	3.87–31.56
Limiting indices	$-12 \leq h \leq 13$, $-13 \leq k \leq 12$, $-12 \leq l \leq 12$	$-13 \leq h \leq 11$, $-9 \leq k \leq 13$, $-13 \leq l \leq 10$	$-12 \leq h \leq 12$, $-8 \leq k \leq 12$, $-7 \leq l \leq 13$
Reflections collected	2353	1629	1439
Independent reflections	90 ($R_{int} = 0.0329$)	93 ($R_{int} = 0.0352$)	94 ($R_{int} = 0.0264$)
Reflections with I > 2σ(I)	89	93	94
Absorption correction	Sphere, $R = 0.09$ mm	Sphere, $R = 0.09$ mm	Sphere, $R = 0.09$ mm
Parameters	14 (14)	14 (14)	14 (14)
GooF	1.052 (1.084)	1.030 (0.996)	1.006 (0.996)
Final R indices [$F^2 > 2\sigma(F^2)$]	$R1 = 0.0240$ (0.0236), $wR2 = 0.0823$ (0.0810)	$R1 = 0.0255$ (0.0263), $wR2 = 0.0765$ (0.0795)	$R1 = 0.0168$ (0.0158), $wR2 = 0.0555$ (0.0504)
R indices (all data)	$R1 = 0.0246$ (0.0241), $wR2 = 0.0827$ (0.0813)	$R1 = 0.0255$ (0.0263), $wR2 = 0.0765$ (0.0795)	$R1 = 0.0168$ (0.0158), $wR2 = 0.0555$ (0.0504)
Extinction coefficient	0.015(1) (0.017)	0.002(1) (0.001)	0.037(1) (0.038)
$\Delta\rho_{(max)}$ and $\Delta\rho_{(min)}$ (e/A^3)	0.288/−0.309 (0.279/−0.353)	0.302/−0.232 (0.288/−0.289)	0.259/−0.211 (0.259/−0.197)

Table 6
Atomic coordinates and equivalent isotropic displacement parameters for I–III in 24*e* + 96*j* position

Atom	Site	Occupation	*x*	*y*	*z*	U_{eq} (Å^2)
Al(1)	*4a*	1.0	0	0	0	0.020(1)
N(1)	*8c*	1.0	1/4	1/4	1/4	0.042(1)
N(2)	*4b*	1.0	1/2	1/2	1/2	0.057(1)
F(1)	*24e*	1/3	0	0	0.1969(2)	0.071(1)
F(2)	*96j*	1/6	0	0.0536(2)	0.1923(1)	0.074(1)
H(1)	*32f*	1.0	0.307	0.307	0.193	0.14
H(2)	*32f*	1/2	0.557	0.557	0.557	0.16
Ti(1)	*4a*	1.0	0	0	0	0.038(1)
N(1)	*8c*	1.0	1/4	1/4	1/4	0.054(1)
N(2)	*4b*	1.0	1/2	1/2	1/2	0.068(1)
F(1)	*24e*	1/3	0	0	0.2025(2)	0.091(1)
F(2)	*96j*	1/6	0	0.0643(2)	0.1975(2)	0.091(1)
H(1)	*32f*	1.0	0.306	0.306	0.194	0.14
H(2)	*32f*	1/2	0.556	0.556	0.556	0.16
Fe(1)	*4a*	1.0	0	0	0	0.024(1)
N(1)	*8c*	1.0	1/4	1/4	1/4	0.050(1)
N(2)	*4b*	1.0	1/2	1/2	1/2	0.065(1)
F(1)	*24e*	1/3	0	0	0.2079(2)	0.099(1)
F(2)	*96j*	1/6	0	0.0632(2)	0.2005(2)	0.073(1)
H(1)	*32f*	1.0	0.306	0.306	0.194	0.12
H(2)	*32f*	1/2	0.556	0.556	0.556	0.16

from electron density difference map while atomic coordinates of H(2) were geometrically defined because of displaying only octahedra around N(2). Parameters of hydrogen atoms were fixed during refinement the structure. Data collection and redaction, refinement of the lattice parameters were performed using SMART and SAINT Plus programs [14]. Table 5 gathers the conditions of the diffraction experiment, crystallographic data and structure refinement for crystals I–III. All the calculations, polyhedra construction and analysis of their geometry were performed with SHELXTL/PC program [15]. Final atomic coordinates and thermal parameters are given in Tables 6 and 7.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Karlsruhe ICSD Centre as supplementary publications Nos. ICSD: 412981, 412982, 412983, 412984, 412985, 412986. Copies of the data can be obtained, free of charge, on application to ICSD, Hermann-von-Helmholtz-Platz 1, D-763444 Eggenstein-Leopoldschaften (e-mail: crysdata@fiz-karlsruhe.de).

Table 7
Atomic coordinates and equivalent isotropic displacement parameters for I–III in 192*l* position

Atom	Site	Occupation	*x*	*y*	*z*	U_{eq} (Å^2)
Al(1)	4*a*	1.0	0	0	0	0.020(1)
N(1)	8*c*	1.0	1/4	1/4	1/4	0.042(1)
N(2)	4*b*	1.0	1/2	1/2	1/2	0.058(1)
F(1)	192*l*	1/8	0.0202(2)	0.0406(2)	0.1942(1)	0.069(1)
H(1)	32*f*	1.0	0.307	0.307	0.193	0.14
H(2)	32*f*	1/2	0.557	0.557	0.557	0.16
Ti(1)	4*a*	1.0	0	0	0	0.038(1)
N(1)	8*c*	1.0	1/4	1/4	1/4	0.054(1)
N(2)	4*b*	1.0	1/2	1/2	1/2	0.069(1)
F(1)	192*l*	1/8	0.0181(2)	0.0472(2)	0.1999(1)	0.096(1)
H(1)	32*f*	1.0	0.306	0.306	0.194	0.14
H(2)	32*f*	1/2	0.556	0.556	0.556	0.16
Fe(1)	4*a*	1.0	0	0	0	0.024(1)
N(1)	8*c*	1.0	1/4	1/4	1/4	0.050(1)
N(2)	4*b*	1.0	1/2	1/2	1/2	0.065(1)
F(1)	192*l*	1/8	0.0233(2)	0.0418(2)	0.2030(1)	0.094(1)
H(1)	32*f*	1.0	0.306	0.306	0.194	0.12
H(2)	32*f*	1/2	0.556	0.556	0.556	0.16

Acknowledgements

We thank Prof. I.N. Flerov and Dr. A.D. Vasiliev for useful discussion and the Russian Foundation for Basic Research for financial support, grant No. 01-03-32719.

References

[1] I.N. Flerov, M.V. Gorev, Fiz. Tverd. Tela 43 (2001) 124–131.

[2] I.N. Flerov, M.V. Gorev, J. Grannec, A. Tressaud, J. Fluorine Chem. 116 (2002) 9–14.

[3] K. Moriya, T. Matsuo, H. Suga, S. Seki, Bull. Chem. Soc. Jpn. 50 (1977) 1920–1926.

[4] L. Pauling, J. Am. Chem. Soc. 46 (1924) 2738–2751.

[5] W. Minder, Z. Kristallogr. 96 (1937) 15–19.

[6] E.G. Steward, H.P. Rooksby, Acta Crystallogr. 6 (1953) 49–52.

[7] W. Massa, G. Pausewang, Mater. Res. Bull. 13 (1978) 361–368.

[8] R. Schmidt, G. Pausewang, W. Massa, Z. Anorg. Allg. Chem. 535 (1986) 135–142.

[9] S. Schwarzman, Z. Kristallogr. 120 (1964) 286–316.

[10] W. Massa, D. Babel, M. Epple, W. Rüdorff, Rev. Chim. Minér. 23 (1986) 508–519.

[11] I.N. Flerov, M.V. Gorev, K.S. Aleksandrov, A. Tressaud, J. Grannec, M. Couzi, Mater. Sci. Eng. R24 (1998) 81–151.

[12] I.N. Flerov, V.D. Fokina, A.F. Bovina, N.M. Laptash, Solid State Sci., submitted for publication.

[13] N.M. Laptash, I.G. Maslennikova, T.A. Kaidalova, J. Fluorine Chem. 99 (1999) 133–137.

[14] Bruker, SMART and SAINT-Plus, Versions 5.0, Data Collection and Processing Software for the Smart System, Bruker AXS Inc., Madison, WI, USA, 1998.

[15] G.M. Sheldrick, SHELXTL/PC, Versions 5.0, An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data, Bruker AXS Inc., Madison, WI, USA, 1998.