

## The Room-Temperature Structure of Potassium Tetrafluoroaluminate

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### Abstract

The crystal structure of  $\text{KAlF}_4$  at room temperature has been determined from single-crystal neutron diffraction data. The cell is tetragonal [ $a = 5.043$  (2),  $c = 6.164$  (6) Å; space group  $P4/mbm$ ,  $Z = 2$ ;  $R = 0.030$ ,  $R_w = 0.026$  for 152 independent observations]. This structure, deriving from the  $\text{TlAlF}_4$ -type ( $P4/mmm$ ), may be described as a sequence of  $[\text{AlF}_{4/2}\text{F}_2]_{\infty}^-$  layers of  $\text{AlF}_6$  octahedra sharing four corners in the (001) plane with  $\text{K}^+$  ions between the layers; the structural modification is due to correlated rotations ( $\varphi = 11^\circ$ ) of the  $\text{AlF}_6$  octahedra around the fourfold axis. This compound shows large anisotropic temperature factors for the  $\text{K}^+$  and shared  $\text{F}^-$  ions, the thermal motion being more important along  $c$ .

### Introduction

Perovskite layer compounds of the type  $AMF_4$  ( $A = \text{K}^+, \text{Rb}^+, \text{Tl}^+, \text{NH}_4^+$ ;  $M = \text{Al}^{3+}, \text{Fe}^{3+}$ ) have a special interest owing to their ferroelastic and/or magnetic properties (Abrahams & Bernstein, 1972; Heger, Geller & Babel, 1971) and to their two-dimensional structural phase transitions (Hidaka, Wood, Wanklyn & Garrard, 1979).

The tetragonal Al compounds have been described previously (Brosset, 1938). They are built up from  $[\text{AlF}_{4/2}\text{F}_2]_{\infty}^-$  layers of  $\text{AlF}_6$  octahedra sharing four corners in the (001) plane. The structural type is  $\text{TlAlF}_4$  [ $a_0 = 3.616$  (3),  $c_0 = 6.366$  (3) Å; space group  $P4/mmm$ ,  $Z = 1$ ]. During a reinvestigation of this series, we have recently shown (Fourquet, Plet, Courbion, Bulou & de Pape, 1979) that some of these

compounds ( $\text{KAlF}_4$ ,  $\text{RbAlF}_4$ ,  $\text{NH}_4\text{AlF}_4$ ) actually present small distortions from the aristotype  $\text{TlAlF}_4$ .

In the scope of structural phase transition investigations we report here the room-temperature structure of  $\text{KAlF}_4$ .

### Preparation and crystal growth

Single crystals were prepared by a modified horizontal Bridgman–Stockbarger technique. The compound melts incongruently: in view of the  $\text{KF–AlF}_3$  phase diagram (Phillips, Warshaw & Mockrin, 1966) a non-stoichiometric mixture ( $0.51\text{KF} + 0.49\text{AlF}_3$ ) was placed in a conically based Pt crucible. The crucible, not sealed, was enclosed in an alumina tube connected to a high-vacuum line and horizontally displaced through a temperature gradient of  $1 \text{ K mm}^{-1}$  under inert gas.

Large single crystals were obtained; they are colourless with a lamellar aspect. The plastic character of these soft crystals does not allow cutting without damage into small single crystals of high quality for X-ray experiments. Fortunately, large samples are suitable for neutron work.

### Crystallographic study and data collection

Laue photographs and visual observation under a polarizing microscope indicate that  $\text{KAlF}_4$  belongs to the Laue group  $4/mmm$ . The observed extinction condition ( $0kl$  with  $k \neq 2n$ ) leads to three possible space groups:  $P4/mbm$ ,  $P4b2$  and  $P4bm$ . The cell parameters were refined by least squares from X-ray

powder data giving  $a = 5.043(2)$ ,  $c = 6.164(6)$  Å. The density was measured by flotation:  $\rho_o = 3.01 \pm 0.01$  Mg m<sup>-3</sup>, which is consistent with  $Z = 2$  ( $\rho_c = 3.010$  Mg m<sup>-3</sup>).

Intensities were collected from a single crystal with boundary faces defined by planes (001), (110) and (1 $\bar{1}$ 0) with dimensions  $4 \times 5 \times 2$  mm and recorded on the D9 four-circle diffractometer (ILL, Grenoble) with a wavelength  $\lambda = 0.8410$  Å. With an  $\omega$ - $2\theta$  scanning technique, 532 reflections satisfying the conditions  $-7 < h, k < 7$  and  $0 < l < 9$  were explored. Profiles were reduced to  $F^2$  values by the method of Lehmann & Larsen (1974); the data were then averaged so that the final refinement was based on 152 independent observations with  $\sigma(I)/I < 0.333$ .

### Structure resolution

All calculations were performed with *SHELX* (Sheldrick, 1976). We first tried the most symmetrical group  $P4/mbm$ , the atoms being located according to our previous work on  $RbAlF_4$  (Fourquet, Plet, Courbion, Bulou & de Pape, 1979). In the isotropic-thermal-motion hypothesis the best fit gives a very poor value of  $R = 0.17$ . Atomic coordinates and anisotropic thermal parameters were then refined by full-matrix least squares to  $R = 0.030$  ( $R_w = 0.026$ ). Calculations in the two non-centrosymmetric groups gave no significant improvement; this is confirmed by the lack of a second-harmonic-generation signal. Final atomic and anisotropic thermal parameters are presented in Table 1.\* There are two kinds of F atoms: those shared between two Al are denoted as  $F_{eq}$ , the others lying along  $c$  as  $F_{ax}$ .

### Description of the structure

The structure is built up from  $[AlF_{4/2}F_2]_{\infty}^{-}$  planar layers of  $AlF_6$  octahedra sharing four corners in the (001) plane. Fig. 1 shows a projection of the structure on the (001) plane.  $K^+$  ions are located between the

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35665 (2 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Characteristic distances (Å) in  $A^IAlF_4$  compounds

Compound	Space group	Al-F <sub>ax</sub>	Al-F <sub>eq</sub>	A <sup>I</sup> -F <sub>ax</sub>
KAlF <sub>4</sub>	$P4/mbm$	1.752 (1)	1.817 (1)	2.848 (1)
RbAlF <sub>4</sub> *	$P4/mbm$	1.715 (8)	1.815 (10)	2.932 (8)
TlAlF <sub>4</sub> *	$P4/mmm$	1.846 (10)	1.808 (2)	2.885 (10)
NH <sub>4</sub> AlF <sub>4</sub> *	$I\bar{4}c2$	1.772 (2)	1.819 (2)	2.907 (1)

\* Fourquet, Plet, Courbion, Bulou & de Pape (1979).

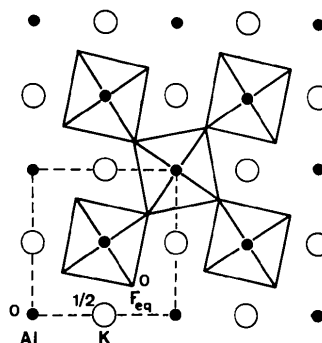


Fig. 1. Projection of the structure on the (001) plane.  $F_{ax}$  atoms are omitted for clarity; they are above the Al atoms at  $z = 0.2842$ .

layers at  $z = 0.5$ ; they have a regular F atom environment of eight  $F_{ax}$  neighbours. The structural modification with respect to the  $TlAlF_4$ -type ( $P4/mmm$ ) is due to correlated rotations of the  $AlF_6$  octahedra around the fourfold axis. The angle  $\varphi$  defining the new orientation of the octahedra with respect to its position in the aristotype  $TlAlF_4$  is  $11^\circ$ .

There is only one kind of  $AlF_6$  octahedron: in the (001) plane the Al-F<sub>eq</sub> distance is  $1.817(1)$  Å, in agreement with the sum of the ionic radii:  $1.820$  Å (Shannon, 1976); on the other hand, the Al-F<sub>ax</sub> distance of  $1.752(1)$  Å shows that the octahedra are compressed along the [001] direction. The K-F<sub>ax</sub> distance is  $2.848(1)$  Å, which is consistent with the sum of the ionic radii:  $2.81$  Å.

In Table 2 we report the characteristic distances in the  $A^IAlF_4$  Al compounds ( $A^I = K, Rb, Tl, NH_4$ ) which are built up from the same planar  $[AlF_{4/2}F_2]_{\infty}^{-}$  layers. The Al-F<sub>eq</sub> distances are very similar but the  $A^I$ -F<sub>ax</sub> distances fit the size of the  $A^I$  ion.

Table 1. Atomic coordinates and anisotropic thermal parameters ( $\times 10^4$ ) of  $KAlF_4$

	x	y	z	$u_{11}$	$u_{22}$	$u_{33}$	$u_{23}$	$u_{13}$	$u_{12}$
K	0	$\frac{1}{2}$	$\frac{1}{2}$	192 (7)	192 (7)	407 (13)	0	0	4 (9)
Al	0	0	0	59 (5)	59 (5)	137 (7)	0	0	0
$F_{eq}$	0.2989 (2)	-0.2011 (2)	0	76 (3)	76 (3)	550 (7)	0	0	18 (3)
$F_{ax}$	0	0	0.2842 (2)	347 (4)	347 (4)	123 (3)	0	0	0

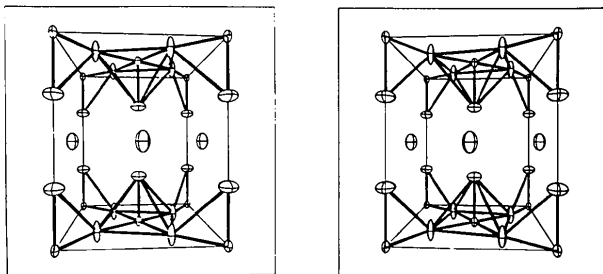


Fig. 2. Stereoscopic plot (ORTEP, Johnson, 1965) of the structure showing the thermal ellipsoids.

### Discussion

As we have already observed, the introduction of anisotropic thermal parameters is imperative to obtain the best fit. The main feature of the thermal motion is the large amplitude of the K atom motion in the [001] direction. Equally, we note that the motion of the octahedra is characterized by a large value of  $u_{33}$  for  $F_{eq}$  which is correlated with the large values for  $u_{11}$  and  $u_{22}$  of  $F_{ax}$ . Fig. 2 shows a plot of the thermal ellipsoids.

All these observations can be connected with the vicinity of the structural phase transition observed at

250 K. In order to study the lattice dynamics of this crystal a low-temperature structure determination is now in progress.

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## A Reinvestigation of the Structure of $\mu$ -Hyperoxo-bis(pentaamminecobalt) Tris(hydrogensulfate) Monosulfate at Room Temperature and at 17 K\*

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### Abstract

$[\text{Co}_2(\text{NH}_3)_{10}(\text{O}_2)](\text{HSO}_4)_3(\text{SO}_4)$ ,  $M_r = 707.44$ , is in space group  $P2_12_12_1$  [ $T = 293 \text{ K}$ :  $a = 16.360$  (1),  $b = 13.946$  (3),  $c = 9.978$  (1) Å;  $T = 17 \text{ K}$ :  $a = 16.198$  (4),  $b = 13.842$  (5),  $c = 9.963$  (3) Å], with  $Z = 4$ ,  $\rho_c = 2.064$ ,  $\rho_o = 2.060$  (5)  $\text{Mg m}^{-3}$  (293 K),  $F(000) = 1460$ ,  $\lambda(\text{Mo K}\alpha) = 0.71069$  Å. Final  $R$  values were 0.066 for both studies with 2377 and 2257 reflections respectively. The structure determined ear-

lier was confirmed in general. At room temperature the sulfate group has a twofold disorder. H atoms were located at both temperatures and a complete hydrogen-bonding pattern is presented.

### Introduction

Schaefer & Marsh (1966) have previously reported the structure of the title compound, determined from film data. H atoms were not located, although a plausible hydrogen-bonding pattern was worked out, and bond distances had e.s.d.'s of 0.02 or 0.03 Å. To locate the

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