K₂AlF₅ · H₂O: Location of Hydrogen Atoms by X-Ray Diffraction and Raman Spectroscopy Study

J. L. FOURQUET, B. BOULARD, AND F. PLET

Laboratoire des Fluorures, UA CNRS 449, Faculté des Sciences du Mans, Université du Maine, Route de Laval, 72017 Le Mans Cedex, France

The complete structural determination of $K_2AlF_5 \cdot H_2O$ is achieved by X-ray diffraction on a single crystal. As previously described, the cell is orthorhombic (*Cmcm*, $a = 9.200(3)$, $b = 8.119(4)$, $c = 7.486(3)$ Å, $Z = 4$). The structure is essentially characterized by very slightly kinked chains of AlF_6 octahedra, sharing opposite corners, running in the [001] direction. Hydrogen atoms are located by difference Fourier synthesis on 8f positions; their introduction in the structural model improved the final results significantly ($R = 0.0383$, $R_w = 0.0283$). The O–H . . . F hydrogen bonding system is discussed with the help of Raman spectroscopy. © 1989 Academic Press, Inc.

Introduction

In the general scope of the study of the crystallochemistry of the fluoroaluminates, we have revised the crystal structure of $K_2AlF_5 \cdot H_2O$ (*1*). The purpose is the location of the hydrogen atoms and the study of the interaction of the water molecules with the framework, constituted by chains of AlF_6 octahedra. The Raman spectroscopy study completes the static model from the X-ray determination.

Preparation

Single crystals of $K_2AlF_5 \cdot H_2O$ are grown by hydrothermal synthesis, at 350°C under 1800 bars, in aqueous HF 5 *M* solutions (*2*) from a stoichiometric mixture of KF and AlF_3. After 2 days of heating, the bomb cools naturally. Many colorless, parallelepipedic-shaped single crystals are isolated, rapidly washed with a dilute HF solution, and dried in air.

Crystallographic Study

The powder diffraction pattern is indexed on the basis of the orthorhombic cell claimed by Brosset (*1*): $a = 9.19$, $b = 8.11$, and $c = 7.45$ Å. Standard X-ray diffraction photographic techniques with a single crystal reveal the *mmm* Laue group and systematic absences for *hkl* with $h + k \neq 2n$ and *h0l* with $l \neq 2n$, thus leading to three possible space groups *Cmcm*, *C2cm*, and *Cmc2₁*. A single crystal, with boundary faces $\pm\langle 1\bar{1}0\rangle$, $\pm\langle 110\rangle$, and $\pm\langle 001\rangle$ (0.026 × 0.034 × 0.142 mm³), is chosen for the structural determination.

Table I gathers the experimental conditions of the data collection on an automated four-circle diffractometer.

Structural Refinement

All the calculations are performed with the SHELX 76 program (*3*). Atomic scattering factors and the values of $\Delta f'$ and $\Delta f''$

$K_2AlF_5 \cdot H_2O$. Molecular weight: 218.13
Space group: $Cmcm$
$a = 9.200(3)$ Å $V = 559.12$ Å^3, $Z = 4$
$b = 8.119(4)$ Å $\rho_{calc} = 2.59$ g cm^{-3}
$c = 7.486(3)$ Å
Radiation: Mo$K\alpha$ (graphite monochromatized)
μ(Mo$K\alpha$) = 18.63 cm^{-1}
$T = 20°C$
Scanning: $\omega/2\theta$; angular range: $5.44 < 2\theta < 90.0$
Region of reciprocal space explored: four independent sets
Absorption correction: by the Gauss method
Minimum and maximum transmission factors:
    0.9681, 0.9167
Extinction correction: none
Number of measured reflections: 4349
$R_{int} = 0.031$
Number of independent reflections with $\sigma(I)/I < 0.5$
    used in the refinement: 622

are taken from Ref. (4) for K^+, Al^{3+}, and F^-; the values for O and H come from SHELX 76.

The refinement is started in the space group $Cmcm$ with the model described by Brosset for the nonhydrogen atoms. It rapidly converges to $R = 0.0431$ and $R_w = 0.0344$ with atomic anisotropic thermal motion. At this stage, a difference Fourier map shows clearly peaks in 8f positions that are

attributed to the hydrogen atoms of the water molecule. The introduction of these atoms and the refinement of both their atomic coordinates and an isotropic temperature factor lead to $R = 0.0383$ and $R_w = 0.0283$,[1] the weighting scheme being $w = 7.6834/(\sigma^2(F) + 4 \times 10^{-6}F^2)$. The final difference Fourier map was featureless. The calculations performed in the noncentrosymmetric groups did not improve significantly the results of the preceding refinement. Table II shows the final set of atomic parameters.

Description of the Structure

Isotypic with $Rb_2AlF_5 \cdot H_2O$ (5) and $Rb_2MnF_5 \cdot H_2O$ (6), the structure is built from chains of AlF_6 octahedra sharing opposite corners. The chains extend with a very small kinking in the [001] direction. Figure 1 presents the projection on the (001) plane. Table III gathers characteristic interatomic distances. The AlF_6 octahedra are distorted and the longer Al–F distances are relative to the shared F3 fluorine atoms, the mean Al–F distance being very close to the sum of the ionic radii (7). Potassium atoms are 12 coordinated as shown in Fig. 2. The tilting of the octahedra around the a axis is very small: the value of the F3–Al–

[1] F_o and F_c values may be obtained by request to J. L. Fourquet.

TABLE II

STRUCTURAL PARAMETERS FOR $K_2AlF_5 \cdot H_2O$

Atoms	x^a	y	z	u_{11}	u_{22}	u_{33}	u_{23}	u_{13}	u_{12}	B_{eq} (Å^2)
K	2862(1)	2128(1)	2500	314(3)	251(2)	211(2)	0	0	60(2)	2.04(2)
Al	0	0	0	171(4)	125(4)	88(4)	−3(3)	0	0	1.01(3)
F1	1922(2)	0	0	199(7)	508(9)	253(8)	−133(7)	0	0	2.53(6)
F2	0	2189(2)	5(2)	619(10)	132(5)	214(7)	−16(7)	0	0	2.54(6)
F3	0	−12(3)	2500	411(12)	279(10)	86(8)	0	0	0	2.04(8)
O	0	4636(3)	2500	529(19)	225(14)	219(14)	0	0	0	2.56(12)
H	0	4030(34)	1566(33)	—	—	—	—	—	—	3.9(9)

^{a} All values are $\times 10^4$. The vibrational coefficients relate to the expression: $T = \exp[-2\pi^2(h^2a^{*2}u_{11} + k^2b^{*2}u_{22} + l^2c^{*2}u_{33} + 2klb^*c^*u_{23} + 2hla^*c^*u_{13} + 2hka^*b^*u_{12})]$.
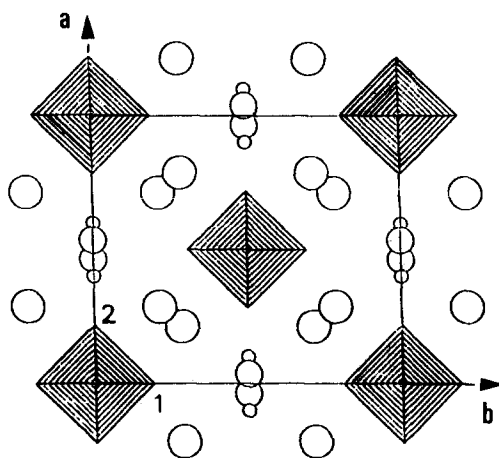
FIG. 1. K₂AlF₅ · H₂O. Projection on the (001) plane. The largest circles are for K atoms, the medium ones for O, and the smallest for H. The numbering refers to the unshared fluorine atoms.
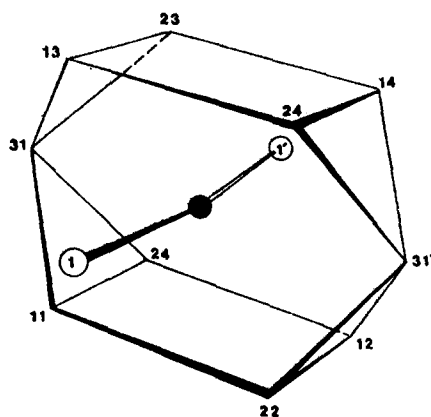

FIG. 2. K₂AlF₅ · H₂O. The coordination polyhedron for K⁺ (solid circle). The two indexes refer to the fluorine atoms as quoted in Table III. Water molecules are the large open circles.

F3 angle is 179.35°, larger than that found in Rb₂AlF₅ · H₂O: 175.21°.

As described previously in the case of Rb₂AlF₅ · H₂O, the water molecule is

linked by two hydrogen bonds O–H . . . F to two successive AlF₆ octahedra in the same chain; this association is responsible for the tilting of the octahedra as can be seen in Fig. 3. Table IV gathers distances and angles relative to the water molecule and to the hydrogen bonding system. The O–F2 distance (2.726(2) Å) is in the range 2.56–2.86 Å quoted by Simonov and

TABLE III

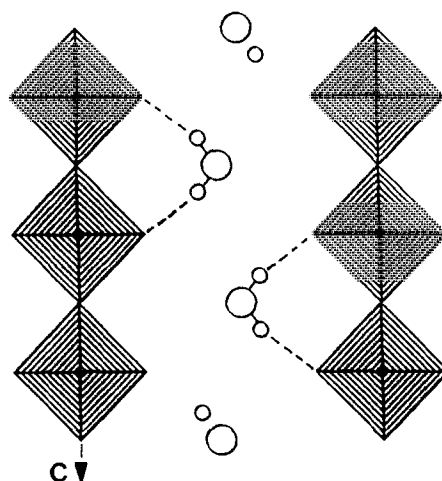### Characteristic Interatomic Distances (Å)

AlF₆ octahedra	Potassium environment[a]	
2 × Al–F1: 1.768(1)	K–F11 ⎫	
	K–F13 ⎬	2.690(1)
2 × Al–F2: 1.777(4)	K–F22 ⎫	
	K–F24 ⎬	2.774(1)
2 × Al–F3: 1.872(1)	K–O1	2.822(2)
$\overline{\text{Al–F}}$: 1.805		
	K–F12 ⎫	
	K–F14 ⎬	2.996(1)
	K–F31	3.043(2)
	K–F31'	3.145(1)
	K–F23 ⎫	
	K–F24 ⎬	3.228(1)
	K–O1'	3.328(2)

[a] The second index of the fluorine atoms relates to the rank of the position in the "International Tables"; for K and O, the same part is played by the unique index. The notation ' indicates that the position is affected by the (½ ½ 0) translation.

FIG. 3. The quasilinear chains of trans-linked (AlF₆) octahedra and the associated water molecules.

O–H	0.855(23)	O . . . F2	2.726(2)
H–H	1.399(50)	H . . . F2	1.897(24)
H–O–H	109.8(3.9)	O–H . . . F2	163.1(2.8)

Bukvetsky (8) and characteristic for O–H . . . F hydrogen bonding in metal fluoride hydrates; the distance H . . . F2 (1.90(2) Å) is close to the mean H . . . F distance, 1.85 Å, quoted by the same authors, indicating a rather strong interaction. Even in this favorable case for locating H atoms from X-ray data, neutron diffraction would be necessary to discuss further H-bonding geometry.

IR and Raman Spectroscopic Study

The group-theoretical analysis of normal vibration modes at $k = 0$, performed in the point group D_{2h} gives nine Raman active modes for O and H in the crystal

$$\Gamma_{O,H} = 3A_g + 2B_{1g}^* + 2B_{2g}^*, + 2B_{3g}^*$$

(* signifies the IR active modes).

The atomic displacements occurring in the normal vibrations, determined using the projection method (9), allow both symmetric stretching (ν_s) and bending (ν_b) of O–H bond of H_2O molecule (A_g symmetry): no antisymmetric stretching mode (ν_{ss}) is found in the D_{2h} group.

The Raman spectrum was recorded from 1000 to 4000 cm^{-1} under microscope (ULF ×50 objective) with a Dilor Z24 spectrometer using the 596.5-nm line of an argon-ion laser (COHERENT INNOVA 90) as the exciting line. The spectrum shown in Fig. 4 exhibits a strongly V–V polarized line at 3462 cm^{-1} assigned to the A_g (ν_s) mode: a shoulder is also observed at 3488 cm^{-1}. This line could be attributed to ν_{ss} although it generally appears more than 100 cm^{-1} higher than ν_s (see Table V).
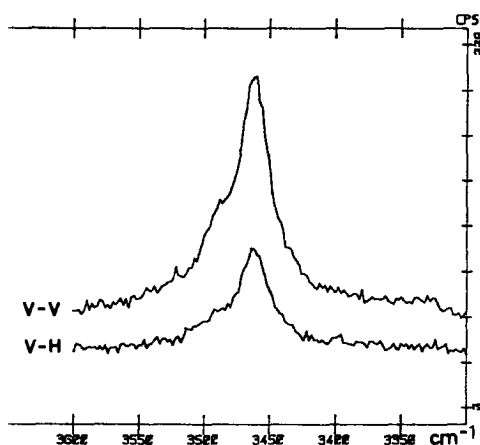

FIG. 4. V–V and V–H polarized Raman spectrum of $K_2AlF_5 \cdot H_2O$.

The IR absorption spectrum shows one very well-resolved line at 1680 cm^{-1}, characteristic of ν_b vibration mode. The comparison of frequencies observed in $K_2AlF_5 \cdot H_2O$ in solid, liquid and gaseous state (Table V) gives an idea of hydrogen bond strength. Indeed, studies of a large number of hydrogen bond systems X–H--Y (10) have shown that the value ν_s decreases in frequency and that ν_b shifts to higher frequency when a molecule H–X forms a hydrogen bond with Y. The 3462 and 1680 cm^{-1} lines are thus consistent with a strong hydrogen bond, actually found by the X-ray study (short H--F distance).

Conclusion

In the favorable case of $K_2AlF_5 \cdot H_2O$, the hydrogen atoms are located by X-ray

TABLE V

FREQUENCIES OBSERVED FOR H_2O MOLECULES (11)

Compound	ν_{ss} (cm^{-1})	ν_s (cm^{-1})	ν_b (cm^{-1})	O–H· · ·X distance (Å)
Ice	3250	3150	1640	2.76
H_2O liquid	3426	3190	1640	2.86
H_2O gas	3756	3652	1595	—
$K_2AlF_5 \cdot H_2O$	3488(?)	3462	1680	2.73

diffraction. The short O–F and H–F distances—2.73 and 1.90 Å, respectively—are consistent with a hydrogen bonding of the water molecules to the quasilinear chains of AlF_6 octahedra. This is well confirmed by the IR and Raman analysis showing values of ν_s and ν_b H_2O frequencies in agreement with a hydrogen bonding association.

References

1. C. BROSSET, Doctoral thesis, Stockholm (1942).
2. F. PLET, J. L. FOURQUET, G. COURBION, M. LEBLANC, AND R. DE PAPE, *J. Cryst. Growth* **47**, 699 (1979).
3. G. M. SHELDRICK, "SHELX 76, Program for Crystal Structure Determination," University of Cambridge (1976).
4. "International Tables for X-Ray Crystallography," Vol. IV, Kynoch Press, Birmingham (1974).
5. J. L. FOURQUET, F. PLET, AND R. DE PAPE, *Rev. Chim. Miner.* **18**, 19 (1981).
6. P. BUKOVEC AND V. KAUCIC, *Acta Crystallogr. Sect. B* **34**, 3339 (1978).
7. R. D. SHANNON, *Acta Crystallogr. Sect. A* **32**, 751 (1976).
8. V. I. SIMONOV AND B. V. BUKVETSKI, *Acta Crystallogr. Sect. B* **34**, 355 (1978).
9. F. COTTON, "Chemical Applications of Group Theory," Wiley, New York (1956).
10. G. C. PIMENTEL AND A. L. McCLELLAN, "The Hydrogen Bond," Freeman, San Francisco (1960).
11. E. WENDLING, "Problèmes de Chimie Minérale," p. 141, Dunod, Paris (1970).