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# Electron Diffraction Investigation of the Vapour Phase Molecular Structure of Potassium Tetrafluoro Aluminate

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The prevailing species above the heated equimolar mixture of potassium fluoride and aluminium fluoride is the 1:1 adduct from the two components [1]. The same composition was found also for other alkali–aluminium–halogen systems [2, 3]. Their structures have been characterized by halogen bridging bonds towards the alkali atom (see *e.g.* [4]). Concerning the molecular shape, however, controversies have appeared in the literature (*cf.* [1, 5], for a summary see [6]). Primarily molecular configurations shown in Fig. 1 have been considered. To extend the structural information on the tetrahalo aluminates we undertook this investigation at the suggestion of Prof. H. A. Øye (Trondheim). The results of a concurrent and extensive matrix isolation spectroscopic study [7] have eventually appeared and facilitated also our electron diffraction analysis.

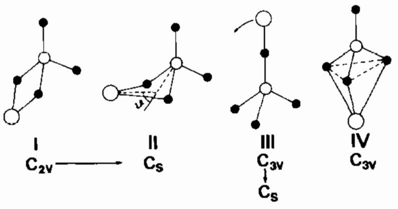

Fig. 1. Structural models for $KAlF_4$.

The sample used in the electron diffraction experiments was from the same source as that used in the spectroscopic study. A so-called radiation-type nozzle system [8] was heated to about 1000 K. According to mass spectrometric measurements, this temperature is favourable to achieving the maximum concentration of the adduct. The other experimental conditions were the same as described in Ref. 8 except that the photographic plates were not covered by Indian ink. The data reduction and structure analysis followed our usual procedure [9, 10]. The coherent and incoherent scattering factors were taken from Refs. 11 and 12, respectively. The molecular intensities and radial distributions are presented in Figs. 2 and 3, the results of the least squares refinements referring to model II of Fig. 1 are given in Table I.

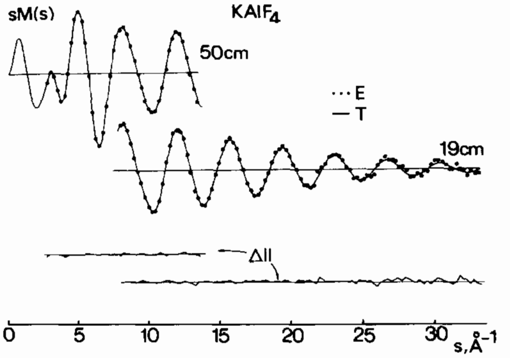

Fig. 2. Experimental (E) and theoretical (T) molecular intensities. The theoretical curves correspond to the parameters, model II, given in Table I.

TABLE I. Molecular Parameters of $KAlF_4$ Obtained in the Least-squares Refinement for a $C_s$ Model (II).

| Bond Lengths | $r_a$, Å | $l$, Å | $l$, Å$^a$ |
|---|---|---|---|
| $Al–F_b$ | 1.692(10) | 0.076 } (2)$^b$ | 0.072 |
| $Al–F_t$ | 1.692(8) | 0.064 | 0.060 |
| $K–F_b$ | 2.513(14) | 0.171(9) | 0.214 |
| $F_b..F_b$ | 2.647(13) | 0.145 } (12)$^b$ | 0.129 |
| $F_t...F_t$ | 2.897(13) | 0.141 | 0.125 |
| $F_t...F_b$ | 2.751(7) | 0.156 | 0.140 |
| K...Al | 3.119(14) | 0.238(25) | 0.207 |
| $K...F_t$ | 3.885(34) | 0.362(37) | 0.334 |
| $K...F_t$ | 4.528(14) | 0.222(20) | 0.229 |
| Bond Angles | $\angle$, ° | | |
| $F_bAlF_b$ | 102.9(11) | | |
| $F_tAlF_t$ | 117.7(8) | | |
| $F_bAlF_t$ | 108.8(5) | | |
| $F_bKF_b$ | 63.5(3) | | |
| $\theta$ | 25.9(25) | | |

[a] From spectroscopic calculations by Dr. Magdolna Hargittai.
[b] Bracketed amplitudes were coupled in the refinement.

The molecular parameters determined for $KAlF_4$ in general follow the observations made on other $MAlX_4$ structures [6].

The $K–F_b$ bonds are much longer than the bond in the KF molecule ($r_e(K–F) = 2.17144(5)$ Å [13]). This and the large vibrational amplitude for that bond indicate a rather weak alkali metal–fluorine bond, which is also supported by the low value of the bond stretching force constant (0.25 mdyne/Å [7]).

On the other hand, the $AlF_4$ fragment seens to be a rather rigid unit. This is indicated by the relatively little distorted tetrahedral coordination and by the equal or nearly equal $Al–F_b$ and $Al–F_t$ distances.

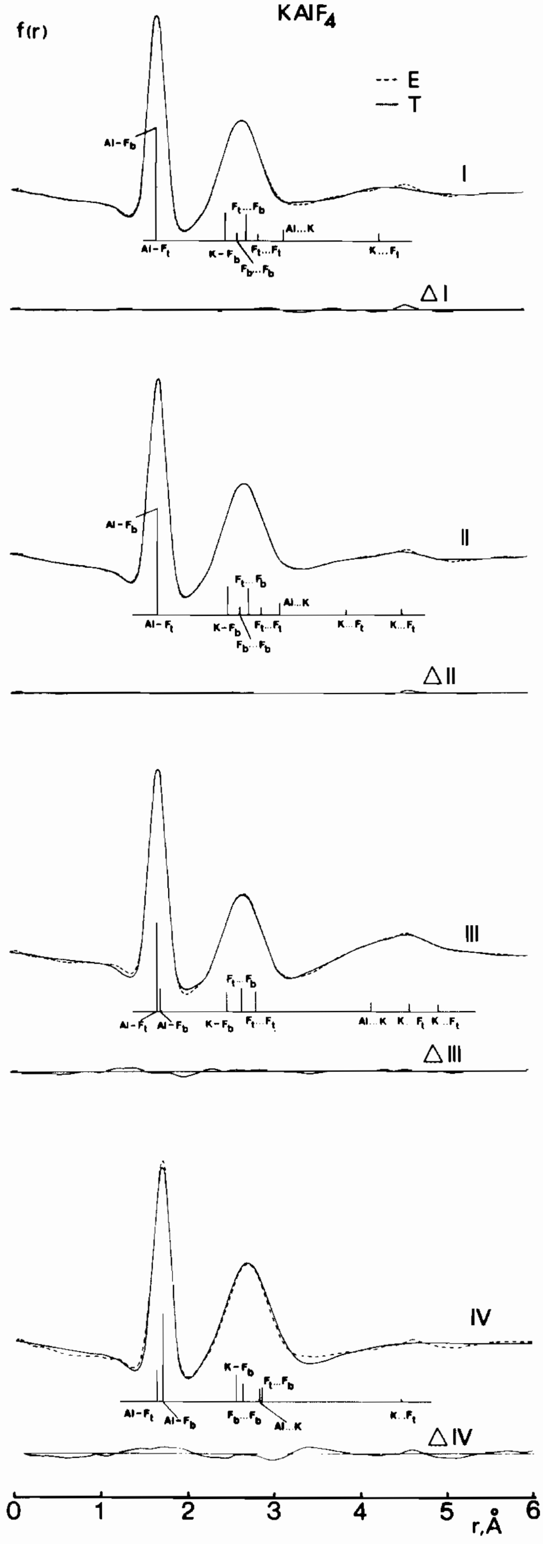

Fig. 3. Radial distributions (E, experimental; T, theoretical calculated for four models shown in Fig. 1). The difference curves (Δ = E – T) are also shown. The positions and relative weight of the interatomic distances are indicated by vertical bars.

The mean amplitudes of vibration refer to a weaker Al–$F_b$ than the Al–$F_t$ bond. The difference in bond strength of the terminal and bridge aluminium–fluorine bonds was also demonstrated by the respective stretching force constants for the whole alkali aluminium fluoride series [7].

In agreement with the earlier proposed structures (see *e.g.* [4, 6]) the experimental data could be best approximated by a geometry containing two bridging fluorine atoms and a puckered four-membered ring (Model II, Fig. 1). The vibrational amplitudes from electron diffraction data and those calculated on the basis of experimental infrared frequencies assuming a $C_s$ molecular symmetry are in good agreement (see Table I).

Nevertheless it is very difficult to determine the exact position of the potassium atom. A strict $C_{2v}$ molecular model led to a somewhat worse agreement between the experimental and theoretical data. Even a $C_{3v}$ geometry (*cf.* Model III, Fig. 1) allowing the K atom to rotate about the K–$F_b$ bond could not be excluded. This model, however, resembles the best fit one. The other possible $C_{3v}$ geometry (Model IV, Fig. 1) has the smallest probability of those considered, according to the electron diffraction data.

In conclusion we find the two halogen-bridged model with a puckered ring ($C_s$ symmetry) to be the best of the static models considered. At the same time the relative mobility of the potassium atom and the relative rigidity of the $AlF_4$ fragment indicate a dynamic structure for potassium tetrafluoro aluminate in agreement with proposed models for analogous systems [14, 15].

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