Raman Spectra of Molten Mixtures Containing Aluminum Fluoride. I. The LiF–Li$_3$AlF$_6$ Eutectic Mixture

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(Received January 10, 1974)

A diamond-windowed cell and a furnace for Raman spectroscopy of molten salts have been constructed. The apparatus can be used for fluorides up to 1100°. Two bands, one moderately strong at 556 cm^{-1} and one weak at 347 cm^{-1}, were observed for the molten LiF–Li$_3$AlF$_6$ eutectic mixture at 730°. The former frequency was assigned to $\nu_1(A_{1g})$ and the latter to $\nu_5(F_{2g})$ of the AlF$_6^{3-}$ ion. The half-width of the 556-cm^{-1} band, 140 cm^{-1}, suggests that the AlF$_6^{3-}$ octahedra are highly distorted. No dissociation into AlF$_4^-$, AlF$_3$, or other species was detected.

Introduction

Structural entities in molten mixtures containing aluminum fluoride have been of great interest for a long time, mainly in connection with the electrolyte in technical aluminum production. Till now, however, the main methods of investigating these systems have been calorimetry, density and viscosity measurements, and phase diagram investigations (see Holm[1] for further references).

Spectroscopy on the molten AlkF–AlF$_3$ systems would be a valuable supplement to these physicochemical measurements because the information given by spectroscopy is more closely related to the structure of the melt. Attempts to do this have only been made by Solomons, *et al.*[2] However, their dissociation degree of the AlF$_6^{3-}$ ion is far higher than those obtained by other methods. The present work can be regarded as an attempt to clarify the structural problems of AlkF–AlF$_3$ melts, starting with investigations of the lower melting systems.

Experimental Section

Apparatus for Raman spectroscopy on molten fluorides has previously been described in the literature.[2-4] This kind of apparatus should in general be designed to meet the following requirements. (i) It should be possible to heat the cell and furnace to a high temperature (1100° for alkali–aluminum fluorides). (ii) The corrosion problem should be taken into account. (iii) Evaporation of the melt should be kept to a minimum to prevent composition change of the sample and corrosion. (iv) The cell material should possess wetting properties which are suitable for molten fluorides. (v) The collection of the Raman light should be adequate. (vi) It should be easy to fill and empty the cell chamber. (vii) It should be easy to change samples.

Formerly two windowless cells have been constructed for Raman spectroscopy.[2,3] For absorption spectroscopy a cell with diamond windows has been reported.[5] The windowless Raman cells seem to cause great corrosion problems.[6] Solomons, *et al.*,[2] report that the sample, Na$_3$AlF$_6$(l), could be contained in the cell for approximately 30 min only, due to evaporation from the melt. Moreover, the wetting properties of a windowless cell are critical,[6] and the collection of the Raman light probably would not be as efficient as with a cell with diamond windows. Therefore, in spite of the high diamond costs, we decided to use a closed cell. Diamond may become somewhat opaque at 1100° because of intrinsic semiconductor properties.[7] However, the meniscus of molten cryolite could be observed visually at 1050° through the diamond window. With regard to the furnace, fulfilment of the above requirements is mainly a matter of choosing suitable materials. The apparatus described here has been tested with molten cryolite up to 1100°. The limiting temperature depends upon the lower annealing temperature of the quartz used in the furnace tube, which is about 1150°.[8]

Raman Cell. A graphite cell equipped with diamond windows and surrounded by a boron nitride sleeve was chosen to fulfil conditions i–vii. The cell is shown in Figure 1.

The cell body (D) was machined from a dense graphite, Graphitite-G (Carborundum Co.). In contrast to other graphite qualities this type is not wetted by the molten mixtures of LiF or NaF with AlF$_3$. Graphitite-G does not contain impurities corresponding to more than 0.04 wt % ashes. The cylindric sleeve (A) was made from boron nitride, Grade A (Carborundum Co.), in order to prevent corrosion of the quartz furnace tube. Experience showed that graphite in contact with the quartz increased the crystal growth in the glass, which then turned opaque.

A graphite ring (B) and a disk (F) together with the cylindric sleeve kept the windows (E) of diameter 6.35 mm, thickness 1.00 mm, in the correct positions. The side window rested against an edge in the cylindric hole while the bottom window rested on the graphite disk. Diamonds, Type IIA (D. Drukker & Zn., Amsterdam), were used as windows. However, it should be noted that Type I diamonds, which are less expensive, are also transparent in the visible region.

Excess vapor from the cell chamber escaped through a hole of diameter 0.8 mm in the upper part of the cell body
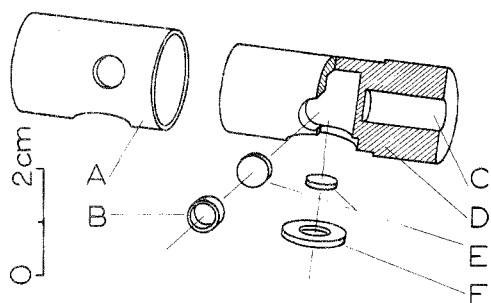
Figure 1. The Raman cell for molten fluorides: (A) boron nitride cyclindric sleeve, (B) graphite ring, (C) hole for thermocouple, (D) graphite cell body, (E) diamond windows, (F) graphite disk.
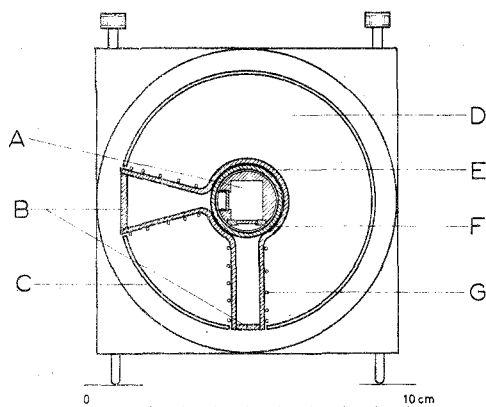

Figure 2. Cross-section diagram of the furnace and the cell: (A) cell chamber, (B) side tubes for beam passage, (C) copper furnace wall, (D) Kaowool insulation, (E) quartz furnace tube, (F) inner quartz tube, (G) Kanthal heating wire.

(not shown on Figure 1). This hole was necessary to allow thermal expansion of the gas in the cell.

In order to measure the temperature, a hole (C) was drilled in the graphite block as close to the cell chamber as the strength of the graphite would allow. The protecting tube of the thermocouple fitted tightly into this hole and had, at the same time, a supporting function for the cell, making it possible to regulate the cell position.

Furnace. The furnace was based on a Kanthal furnace described by Motzfeldt.[9] The model was reduced to a length of 20 cm and a width of 10 cm to fit the cell chamber of a Cary 82 spectrometer, and materials were chosen to suit our special purpose. Thus quartz was chosen as the furnace tube material instead of alundum because of its transparency. A cross-section diagram of the furnace is given in Figure 2.

The heating wire (G), Kanthal A, thickness 0.60 mm, was wound on the furnace tube (E) and on the side tubes (B). The side tubes were first covered with asbestos bands to reduce thermal radiation from the heating wire. The electrical circuits were adjusted with variable resistors which were connected to the furnace. In this way a temperature gradient less than $10°/cm$ was maintained in the cell region at $1000°$.

The side tubes permitted a 90° beam alignment. The laser beam was incident on the bottom of the cell. The intensity loss of the escaping Raman light was reduced by the conical form of the horizontal side tube. To protect the furnace from accidental corrosion, an inner quartz tube (F) could be used. This tube was examined after the experiment and changed if necessary. It has the disadvan-

tage of reducing the intensity of the scattered beam by 20%.

Kaowool was used as insulating material (D) because of its ease of handling. The furnace was cooled by water circulated through copper tubes on the outside of the wall (C). To reduce the oxidation of graphite, inert gas (Ar or N_2) was passed through the furnace tube. Oxidation of the diamond windows is prevented by the presence of graphite.

Chemicals. The chemicals used were LiF, pro analysi (Merck, Darmstadt), and AlF_3, pure (Riedel de Häen A.G., Seelze-Hannover). LiF was dried, melted under vacuum, and purified by crystallization. AlF_3 was sublimated twice in a vacuum furnace at 910°. In each case clear crystals were used.

Procedure. Appropriate amounts of LiF and AlF_3 were weighed and transferred to the cell chamber in a drybox. The windows, graphite ring and disk, and the boron nitride sleeve were mounted. The closed cell was transferred to the furnace and the sample premelted to ensure adequate mixing.

The spectra were recorded with a Cary 82 spectrometer equipped with a Coherent Radiation Model 52 B argon ion laser using the excitation at 4880 Å. All the standard lenses of the spectrometer could be used, and the only critical adjustment necessary was the position of the furnace. As aluminum fluoride is a weak Raman scatterer, there were problems with intensity. These can be overcome by using a third diamond window in order to allow multiple passes of the laser beam.[10] Recording spectra at temperatures higher than 800° require, in addition, a chopper system to remove the thermal background radiation. In contrast to the $AlkCl-AlCl_3$ systems,[11] noise due to microparticles in the melt was not severe.

Results

The Raman spectrum of the molten $LiF-Li_3AlF_6$ eutectic mixture at 730° is presented in Figure 3. Apart from the $1332-cm^{-1}$ diamond band,[12] the spectrum reveals two broad Raman bands, one moderately strong and one weak. From the two spectra of highest quality the background was subtracted and the following frequencies were found: 556 ± 5 and 347 ± 10 cm^{-1}. The band at 556 cm^{-1} is approximately symmetric, with a half-width as high as 140 cm^{-1}.

The temperature is estimated to be accurate to $\pm 10°$, the main error being the temperature gradient in the furnace. Because of the sharply rising background, which strongly increased with temperature, we did not test for any possible temperature dependence of the spectrum. The eutectic mixture of the $LiF-Li_3AlF_6$ system, 85.5 mol % LiF + 14.5 mol % AlF_3,[1] was investigated because it represents one of the lowest melting binary fluoride systems containing aluminum. The uncertainty of composition is estimated to be ± 0.3 mol %. Error due to evaporation of $LiAlF_4$ is less than 0.1 mol %.

Discussion

It is reasonable to assume that the Raman spectrum of the $LiF-Li_3AlF_6$ eutectic mixture can be interpreted in terms of more or less well-defined Al–F complexes.

The corresponding sodium system has been investigated by many authors (see Holm[1] for further references) and according to these, the most probable entities occurring in the cryolite melts are AlF_3, AlF_4^-, and AlF_6^{3-}. Before

TABLE I: AlF_4^- (T_d) Totally Symmetric Stretching Frequency

Substance or method of calculation	$\nu_1(A_1)$, cm^{-1}	Ref
Na₃AlF₆(l), 1030°	633	2
Force constants transferred from NaAlF₄[a]	696	
Force constants transferred from LiAlF₄	631	
Compliants transferred from LiAlF₄	612	
Isoelectronic series of MF₄[b]	≤665	2

[a] The force field of NaAlF₄ is less reliable than for LiAlF₄ (ref 18). [b] The less than or equal sign is introduced due to the anomalous behavior of AlCl₄⁻ compared to other tetrachlorides.

TABLE II: AlF_6^{3-} (O_h) Raman Frequencies ν_1 and ν_5

Substance or method of calculation	$\nu_1(A_{1g})$, cm^{-1}	$\nu_5(F_{2g})$, cm^{-1}	Ref
Na₃AlF₆(s)	554	335	2[a]
(NH₄)₃AlF₆(s)	544	318	b
Na₃AlF₆(l), 1030°	575		2
LiF–Li₃AlF₆ eutectic (l), 730°	556	347	
Isoelectronic series of MF₆	~540		2

[a] The 335-cm⁻¹ band has not been assigned by the authors. [b] K. Wieghardt and H. H. Eysel, *Z. Naturforsch. B*, **25**, 105 (1969).

going into details in the interpretation, it is therefore necessary to estimate the positions of the Raman active modes of these species. The positions of the totally symmetric stretching frequencies are especially important. They should follow the general rule that an increase in coordination number leads to a decrease in the stretching frequency.[13]

Estimation of AlF_n Frequencies. For AlF₃ a planar D_{3h} model with three Raman active frequencies, ν_1, ν_3, and ν_4 is assumed. The ν_2, ν_3, and ν_4 modes have been observed by ir spectroscopy of the gas at 950–1250°[14,15] and by matrix isolation.[16] Average values for the antisymmetric stretch ν_3 and the bend ν_4 are 950 and 265 cm⁻¹, respectively. Büchler, *et al.*,[15] calculate a value of 800 cm⁻¹ for ν_1. However, this is far higher than the observed totally symmetric Al–F frequencies for AlF₄⁻ and AlF₆³⁻ (Tables I and II). The value 650 cm⁻¹ as estimated in the JANAF tables[17] is much more reasonable.

Solomons, *et al.*,[2] report the totally symmetric stretching frequency ν_1 of a tetrahedral AlF₄⁻ in molten cryolite. A tetrahedral configuration is also found in matrix isolated LiAlF₄ and NaAlF₄ gas molecules.[18] The published force fields of the latter molecules make possible a calculation of ν_1 for AlF₄⁻ (T_d) by transferring force constants. Transference of the more physically meaningful concept of compliants has also been performed. Cyvin[18,19] should be consulted for notations. The terminal stretching valence compliants of LiAlF₄ are given by

$$n_d = \frac{1}{2}(F_{33}^{-1}(A_1) + F_{11}^{-1}(B_1))$$

$$n_{dd} = \frac{1}{2}(F_{33}^{-1}(A_1) - F_{11}^{-1}(B_1))$$

which yield

$$F^{-1}(A_1) = n_d + 3n_{dd} = 2F_{33}^{-1}(A_1) - F_{11}^{-1}(B_1)$$

when $F^{-1}(A_1)$ refers to AlF₄⁻. Literature data as well as the results of the calculations are summarized in Table I. From the table it is reasonable to assume a value of 630 ± 20 cm⁻¹ for ν_1.
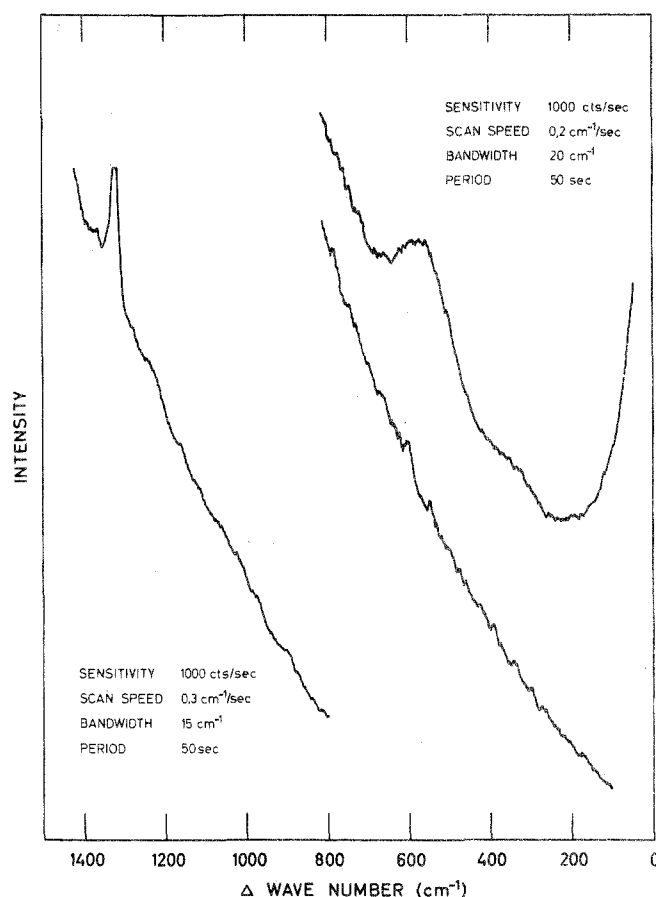

Figure 3. The Raman spectrum of the molten LiF–Li₃AlF₆ eutectic mixture at 730°. The lower right-hand curve shows the thermal background recorded at a speed of 0.6 cm⁻¹/sec and with a pen period of 20 sec.

The situation is easier for the octahedral AlF₆³⁻ since this ion exists as a discrete entity in the solid state. Table II gives the measured solid state Raman data, the previously assigned melt frequency[2] and the present data for the totally symmetric ν_1 mode and the bending mode ν_5. No value for the antisymmetric stretching vibration ν_2 has been reported.

Molten LiF–Li_3AlF_6 Eutectic Mixture. Although polarization data are not available there is little doubt that the observed frequency at 556 cm⁻¹ belongs to a totally symmetric Al–F stretching vibration. In Table II it should be noted that we assign this band to ν_1 of AlF₆³⁻. The correspondence with the frequency found for this ion in molten cryolite[2] is reasonably good, although it is a little surprising that this frequency, 575 cm⁻¹, is higher than the present one. This is contrary to the general rule for counterion effects.[20] However, the 575-cm⁻¹ band is reported "not to be really isolatable with any certainty from the intense and noisy background pattern." The occurrence of a weak band at 347 cm⁻¹ supports the interpretation of the LiF–Li₃AlF₆ eutectic mixture spectrum (Table II).

The very large half-width of the 556-cm⁻¹ band deserves a comment. A contribution from AlF₄⁻ to the high-frequency side, and from the antisymmetric stretching mode $\nu_2(E_g)$ and hot bands to the low-frequency side, cannot be rejected. However, due to the approximately symmetric shape of the band and no sign of shoulders, these contributions probably do not present the full explanation. Furthermore, it is not likely that broadening from

collisions resulting in short correlation times is essential. We may refer to the half-width of the totally symmetric stretching frequency of BF_4^- at 606° which was found[6] to be approximately 20 cm^{-1}. The ν_1 mode of an octahedral AlF_6^{3-} should be sensitive to environmental effects, but this could hardly give a broadening of the magnitude observed. It is more likely that the structure of the AlF_6^{3-} ions themselves is distorted, thus giving rise to a set of frequencies from differently perturbed octahedral species. Holm[21] proposed that some of the octahedra in the cryolite mixtures with mole fraction of $AlF_3 < 0.25$ should be distorted to a structure having an AlF_3 core and three additional fluorine ions at larger distances from aluminum. Such a complex would probably give a main symmetric stretching vibration at a higher frequency than the observed one. It should be mentioned that no conclusion regarding a quasilattice structure, ion-pair formation, or local charge fluctuations can be drawn at this stage.

From the two observed frequencies, the following symmetry and valence force constants may be calculated (see Cyvin[19] for notations)

$$F(A_{1g}) = f_r + 4f_{rr} + f_{rr}' = 3.46 \text{ mdyn/Å}$$

$$F(F_{2g}) = f_\alpha - 2f_{\alpha\alpha}' + f_{\alpha\alpha}''' = 0.34 \text{ mdyn/Å}$$

In accord with predictions, due to the greater number of ligands, the stretching force constant is somewhat lower than found in $LiAlF_4$.[18] The bending constant is in the same range as for the latter molecule. These statements are only qualitative since the influence of the interaction force constants is uncertain.

Dissociation Equilibria. The dissociation schemes

$$AlF_6^{3-} = AlF_3 + 3F^- \qquad (1)$$

$$AlF_6^{3-} = AlF_4 + 2F^- \qquad (2)$$
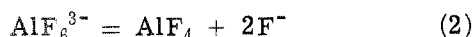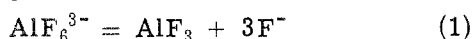
seem by now to be the most popular ones for the molten cryolite mixtures.[21] Vrebenska and Malinovsky[22] used the last equation and found by cryoscopic measurements a degree of dissociation α in pure lithium cryolite at 782° equal to 0.4. However, when the amount of AlF_3 in the system is decreased from 25.0 (at 782°) to 14.5 mol % (at 730°), the equilibrium will shift to the left and lower the value of α to approximately 0.2. This calculation is based on the assumption that the dissociation constant is independent of the temperature in the interval 730–782°, and that the activity coefficient term varies very little in the composition range 14.5–25.0 mol % AlF_3. The assumptions are justified by Holm[21] for the sodium system. Our investigation gives no sign of the species AlF_4^- (or AlF_3), but the thermodynamic value of $\alpha \sim 0.2$ cannot be rejected without further investigations.

For sodium cryolite Solomons, *et al.*, report, from the Raman spectrum, a degree of dissociation α as high as 0.8 for reaction scheme 2 at 1030°. With the same assumptions as above, this value will be reduced to 0.65 for a change in composition to 14.5 mol % AlF_3. When this result is compared to the present one, the difference in the temperature of the melts should be taken into consideration. A lower temperature should reduce the α value. On the other hand, the substitution of Na^+ with Li^+ should give a higher degree of dissociation. The counterion effect is found to be large for other molten salt equilibria.[11,23] The thermodynamic value $\alpha = 0.3$ (1030°) found for sodium cryolite[1] is in agreement with this effect when compared to $\alpha = 0.4$ (782°) for lithium cryolite.[22] The results found by Solomons, *et al.*, therefore seem to be at variance with ours. We hope to examine this problem further in the near future, using a Raman instrument fitted with a chopper to remove thermal radiation from the sample.

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