3682 *Inorg. Chem.* **2000,** *39,* 3682−3689

Raman Study of the Hexafluoroaluminate Ion in Solid and Molten FLINAK

Murray H. Brooker

Department of Chemistry, Memorial University of Newfoundland,
St. John's, Newfoundland, Canada A1B 3X7

Rolf W. Berg,* Jens H. von Barner, and Niels J. Bjerrum

Department of Chemistry, Building 207, Technical University of Denmark,
Kemitorvet, DK-2800 Lyngby, Denmark

Received March 7, 2000

Raman spectra have been obtained for matrix-isolated AlF_6^{3-} in an LiF/NaF/KF (FLINAK) eutectic mixture. Three Raman bands characteristic of the hexafluoroaluminate ion were identified in the solids formed from FLINAK melts which contained small amounts (5−11 mol %) of either AlF_3 or Na_3AlF_6. The three allowed Raman-active bands of the matrix-isolated octahedral complex ion, $\nu_1(A_{1g})$, $\nu_2(E_g)$, and $\nu_5(F_{2g})$, were observed at 560.5, 380, and 325 cm^{-1}, respectively, for the solid sample at 25 °C. Wavenumbers and relative intensities were similar to those of Na_3AlF_6 (cryolite), K_3AlF_6, and K_2NaAlF_6 (elpasolite) and other crystals known to contain discrete, octahedral AlF_6^{3-} ions. Peak positions, half-widths, and relative intensities for the bands were measured for samples at temperatures different from room temperature through the melting transition and into the molten state. The transition from high-temperature solid to molten salt at about 455 °C occurred gradually without perceptible change in the peak positions, half-widths, or relative intensities. For a sample in molten FLINAK at 455 °C, the $\nu_1(A_{1g})$, $\nu_2(E_g)$, and $\nu_5(F_{2g})$ modes of the AlF_6^{3-} ion were observed at 542, 365, and 324 cm^{-1}, respectively. Raman depolarization experiments were consistent with these assignments, and the low value of the depolarization ratio of the $\nu_1(A_{1g})$ mode at 542 cm^{-1} indicated that the sample was molten above 455 °C. Differential thermal analysis also indicated that the FLINAK samples melted at about 455 °C. Raman measurements were performed for samples at temperatures from 25 to 600 °C in a silver dish, on a hot stage, in an argon-filled atmosphere, under a microscope. Additional Raman experiments were performed on samples at temperatures from 25 to 750 °C in a conventional graphite windowless cell, in an argon-filled quartz tube, in a standard furnace. Over the concentration range 4.8−11 mol % AlF_3 (CR 23−8.0) in FLINAK, only bands due to the AlF_6^{3-} ion were detected. There was no evidence to support the presence of other aluminum complexes in these melts.

Introduction

Sodium aluminum fluoride, or cryolite, Na_3AlF_6, is an essential mineral for the Hall−Héroult process of aluminum production because the ionic liquid at about 1000 °C serves as a solvent for alumina, which is then reduced to aluminum metal. Considerable research has been performed in an attempt to understand the properties of the cryolite solvent and to determine the identity of the active species with the goal of improved efficiency. Thermodynamic activity data based on heats of mixing,[1,2] thermal analysis,[3] cryoscopy,[4,5] vapor pressure,[6] and potentiometric measurements[7] were used to develop a self-consistent model of liquid cryolite with AlF_6^{3-} as the major anionic species in equilibrium with about 20 mol % AlF_4^- and free F^- ions from partial dissociation.[8−10] Raman experiments[11,12] were consistent with this model. Peaks were detected for AlF_6^{3-} and AlF_4^- at about 555 and 620 cm^{-1} for molten cryolite at 1020 °C with relative intensities roughly proportional to the expected concentrations from the thermodynamic model. NMR studies by Stebbins[13] were also consistent with the thermodynamic model. Frequency shifts for aluminum-27 and fluorine-19 in solid and molten cryolite were interpreted on the basis of coordination number 6 for solid cryolite with an equilibrium between six- and four-coordinated aluminum in the melt. As the thermodynamic model was subjected to further tests by Dewing,[7] Kvande,[14] and Sterten[2,15] with new data from

---

* To whom inquiries may be addressed. E-mail: rwb@kemi.dtu.dk.

(1) Hong, K. C.; Kleppa, O. J. *J. Phys. Chem.* **1978**, *82*, 176.
(2) Sterten, Å.; Mæland, I. *Acta Chem. Scand.* **1985**, *A39*, 241.
(3) Holm, J. L.; Holm, B. J. *Thermochim. Acta* **1973**, *6*, 375.
(4) Førland, T.; Ratkje, S. K. *Acta Chem. Scand.* **1973**, *27*, 1883.
(5) Sterten, Å. *Electrochim. Acta* **1980**, *25*, 1673.
(6) Kvande, H. *Electrochim. Acta* **1980**, *25*, 237.
(7) Dewing, E. W. In *Proceedings of the 5th International Symposium on Molten Salts*; Saboungi, M. L., et al., Eds.; Electrochemical Society, Pennington, NJ, 1986; Vol. 86-1, p 262.
(8) Grjotheim, K. Contribution to the Theory of the Aluminium Electrolysis. *Skr.—K. Nor. Vidensk. Selsk.* **1956**, *No. 5*.
(9) Grjotheim, K.; Krohn, C.; Malinovsky, M.; Matiasovsky, K.; Thonstad, J. *Aluminum Electrolysis: Fundamentals of the Hall-Héroult Process*; Aluminum-Verlag: Dusseldorf, Germany, 1982.
(10) Frank, W. B.; Foster, L. M. *J. Phys. Chem.* **1960**, *64*, 95.
(11) Gilbert, B.; Mamantov, G.; Begun, G. M. *J. Chem. Phys.* **1975**, *62*, 950.
(12) Gilbert, B.; Mamantov, G.; Begun, G. M. *Inorg. Nucl. Chem. Lett.* **1976**, *12*, 415.
(13) Stebbins, J. F.; Farnan, I.; Dando, N.; Tzeng, S.-Y. *J. Am. Ceram. Soc.* **1992**, *75*, 3001.
(14) Kvande, H.; Xiang, F. N. *Acta Chem. Scand.* **1987**, *A41*, 146.
(15) Solheim, A.; Sterten, Å. Thermodynamic models for NaF-AlF3 melts. Paper presented at the Tenth Aluminium Symposium, Slovak-Norwegian Symposium, Stara Lesna-Ziar nad Hronom, Slovakia, Sept 21−23, 1999. Sterten, Å. Private communication.

10.1021/ic000260h CCC: $19.00

a wider range of cryolite ratios (CR is the NaF:AlF_3 molar ratio), it was suggested that a better fit to the activity data in the CR = 1−2 region could be achieved with the inclusion of the additional species $Al_2F_7^-$ and AlF_5^{2-}. In the model of liquid Na_3AlF_6 developed by Dewing,[7] AlF_5^{2-} was required only as an intermediate for a CR near 2. However, the same data treatment suggested that the Li_3AlF_6 system could be considered ideal without the need for the additional five-coordinated species.[7]

Raman spectra of liquid cryolite at 1020 °C exhibit two distinct features: a very broad band centered at about 555 cm^{-1} with a half-width of almost 100 cm^{-1} and a weak shoulder at 620 cm^{-1} with a half-width of about 30 cm^{-1}. Originally, Gilbert, Mamantov, and Begun[11,12] assigned these bands to AlF_6^{3-} and AlF_4^- for two reasons. The band at 555 cm^{-1} is of about the same wavenumber as that of a similar band for solid cryolite at room temperature, and cryolite is known to contain discrete AlF_6^{3-} ions, while pure molten $NaAlF_4$ has a strong band at 620 cm^{-1} and the spectrum typical of a tetrahedral molecule.[12] The two bands at 555 and 620 cm^{-1} varied in relative intensity as expected when the CR was altered.[11] Recently Gilbert and co-workers[16−20] published a series of papers in which the Raman data were reinterpreted in terms of a three-species equilibrium model with AlF_6^{3-}, AlF_5^{2-}, and AlF_4^-. The postulation of the existence of a discrete five-coordinated aluminum species as the major species in cryolite melts[16−20] is based on reassignment of the most intense Raman band at 555 cm^{-1} to AlF_5^{2-}. A new weak band identified at 510 cm^{-1} was assigned to AlF_6^{3-}. This reassignment was based primarily on curve analysis, since a peak at 510 cm^{-1} was not obvious to the eye in the spectra of the sodium cryolite melts. Although in one published spectrum (ref 20, Figure 2) a shoulder can be seen at about 510 cm^{-1} for a KF/AlF_3 melt at CR = 15, the origin of the shoulder is open to question. Mathematical methods[16−20] were employed to resolve three bands for NaF/AlF_3 and KF/AlF_3 in the 450−650 cm^{-1} region, at 510, 555, and 620 cm^{-1}, which were assigned to the discrete species AlF_6^{3-}, AlF_5^{2-}, and AlF_4^-, respectively. Relative intensities were converted to species concentrations. The thermodynamic model proposed by the authors required significant values for the activity coefficients to fit the thermodynamic activity data to the concentrations estimated from Raman intensities. In a recent paper,[20] it was claimed that Raman intensities indicated AlF_5^{2-} to be the principal species in molten cryolites even at CR's as high as 15 (see Table 1 in ref 20). If this interpretation is correct, it means that AlF_5^{2-} retains discrete five-coordination even in the presence of a 12 times excess of fluoride. New aluminum-27 NMR shift measurements of molten cryolites were also obtained and interpreted to support the three-species model.[21]

The new interpretation of the Raman spectra was not supported by Brooker,[22,23] who measured the Raman spectrum of cryolite as a function of temperature from liquid nitrogen temperature through the solid−solid phase transition temperatures of 560 °C to the liquid temperature of 1020 °C. Brooker measured the polarized (VV) and depolarized (VH) spectra for molten cryolite and constructed the normalized isotropic, R(ω), spectrum and found only the bands at 555 and 620 cm^{-1}. An additional band centered at 200 cm^{-1} in the isotropic spectrum was assigned to the interaction of the NaF ion pair.[22,23] The results of Brooker are consistent with the original interpretation of the Raman spectra of cryolite and did not require a third aluminum−fluoro species (i.e., AlF_5^{2-}).

There is also a clear conflict between the models of Dewing,[7] Kvande,[14] and Sterten[2,15] (based on thermodynamic data), which require six-coordinated AlF_6^{3-} species as the major species at CR > 3, and the new interpretation by Gilbert et al.[16−21] (based primarily on Raman spectra), which requires very little AlF_6^{3-} even at high CRs. The Dewing/Kvande/Sterten model requires fewer species and has activity coefficients close to unity (ideal), while the Gilbert model includes the extra AlF_5^{2-} species but still requires substantial activity coefficients to obtain a good fit to the thermodynamic data. Recently Solheim and Sterten[15] constructed six different thermodynamic structural models to describe the NaF−AlF_3 system based on formal activities for NaF(l) and AlF_3(s). It was shown that models based on NaF, Na_3AlF_6, $NaAlF_4$, and Na_2AlF_7 with small amounts of one other compound among the possible species Na_2AlF_5, $Na_4Al_2F_{10}$, $Na_5Al_3F_{14}$, and $Na_3Al_2F_9$ all behaved as nearly ideal solutions. The best models required AlF_6^{3-} as the principal species at CR ≈ 3.

The present study was initiated with the goal of establishing the identity of the aluminum fluoride species in FLINAK melts. The major advantage of FLINAK is its low melting point of about 455 °C. Furthermore, at this relatively low temperature, it has proven possible to perform experiments on very small samples under a microscope on a Raman microprobe. A 5 mol % solution of AlF_3 or Na_3AlF_6 in FLINAK corresponds to a CR of about 20, but the melt can be studied at 455 °C in contrast to solutions in pure NaF and KF, which require much higher temperatures. Finally, the solid formed from the FLINAK melt will contain the aluminum species in matrix isolation. The presence of any alumina (Al_2O_3) impurity, e.g., from reactions between aluminum fluoride vapors and glass containers, is not as serious a problem in molten FLINAK as it is with molten Na_3AlF_6 and K_3AlF_6 at temperatures close to 1000 °C. We expected that alumina would not be very soluble in FLINAK at the low temperatures used in this study. Beck[24] has shown that the solubility of alumina in a KF/LiF/NaF/AlF_3 eutectic melt at 750 °C with CR = 1.5 was only about 1 wt %, which is 1 order of magnitude smaller than that measured for the NaF/AlF_3 melt with CR = 1.5 at 980 °C. In the present study, it was possible to perform experiments on the same sample over several days because there was no actual contact of the glass with the melt and the glass windows of the container vessels were not attacked by fluoride vapors at the low temperatures.

The results of this study confirm the discrete, octahedral AlF_6^{3-} species as the major species in both solid and liquid FLINAK solutions up to the 750 °C limit of our temperature range for melts with cryolite ratios from 23 to 8. In a related

---

(16) Gilbert, B.; Robert, E.; Tixhon, E.; Olsen, J. E.; Østvold, T. *Inorg. Chem.* **1996**, *35*, 4198.

(17) Gilbert, B.; Materne, T. *Appl. Spectrosc.* **1990**, *44*, 299.

(18) Tixhon, E.; Robert, E.; Gilbert, B. *Appl. Spectrosc.* **1994**, *48*, 1477.

(19) Robert, E.; Olsen, J. E.; Danek, V.; Tixhon, E.; Østvold, T.; Gilbert, B. *J. Phys. Chem. B* **1997**, *101*, 9447.

(20) Robert, E.; Olsen, J. E.; Gilbert, B.; Østvold, T. *Acta Chem. Scand.* **1997**, *51*, 379. In this paper, the concentrations given in the caption to Figure 2B and the concentrations listed in Table 1 are inconsistent. Private communications with the authors confirm that Figure 2B (860 °C) corresponds to the data for $X_{AlF_3} = 0.063$ (CR = 15) at the same temperature is given in Table 1. The corrected figure caption for Figure 2B should read $X_{AlF_3} = 0.14$ (950 °C) and $X_{AlF_3} = 0.063$ (860 °C).

(21) Robert, E.; Lacassagne, V.; Bessada, C.; Massiot, D.; Gilbert, B.; Coutures, J.-P. *Inorg. Chem.* **1999**, *38*, 214.

(22) Brooker, M. H. In *International Harald A. Øye Symposium*; Soerlie, M., Østvold, T., Huglen, R., Eds.; Norwegian Institute of Technology: Trondheim, Norway, 1995; p 431.

(23) Brooker, M. H.; Johnson, J. J.; Shabana, A. A.; Wang, J. In *Proceedings of the 9th International Symposium on Molten Salts*; Hussey, C. L., Newman, D. S., Mamantov, G., Ito, Y., Eds.; Electrochemical Society: Pennington, NJ, 1994; Vol. 94-13, p 227.

(24) Beck, T. R.; *Light Met. Met. Ind.* **1994**, 417.

study, we have been able to convert AlF_6^{3-} to aluminum oxofluorides in both molten and solid FLINAK to which had been added Na_2O together with small amounts of AlF_3 or Na_3AlF_6.[25] The most intense band of the oxofluoro species was detected at about 500 cm^{-1} in molten FLINAK at 500 °C.[25]

Experimental Section

Chemicals were handled and weighed in a glovebox with a dry argon (99.99%, Hede Nielsen A/S) atmosphere (<5 ppm of H_2O). LiF, KF, NaF, and Na_2O were purified as described previously.[26] Anhydrous AlF_3 (Fluka) was dried and used as received, but for some experiments, samples were prepared from triply distilled AlF_3 stored under argon and supplied by SINTEF (Trondheim, Norway). Similar results were obtained with both AlF_3 samples, but the SINTEF sample was obviously purer and resulted in fewer particles in the melt. Al_2O_3 (99.8 mass % α-alumina, Aldrich), Na_3AlF_6 from Fluka and Aldrich, Na_3AlF_6 in the form of hand-picked Greenland cryolite, and K_3AlF_6 (Aldrich) were checked for purity by infrared and Raman spectroscopy and used without further preparation. K_2NaAlF_6 (elpasolite) was prepared from a chloride flux as the water-insoluble product of a fusion of Na_3AlF_6 in KCl.[27] For samples of the mixtures, the appropriate amount of each solid was weighed into a glassy carbon crucible (V25, Carbone-Lorraine), which was transferred to a closed furnace. Each sample was subjected to vacuum pressure at 200 °C for 2 h to remove traces of moisture, then equilibrated in the molten state for 20 h at 540−600 °C under an argon atmosphere, and finally slowly cooled to room temperature. The sample concentrations were calculated as moles of AlF_3 or moles of Na_3AlF_6 per mole of FLINAK. Samples in FLINAK were prepared for 4.8 mol % AlF_3 (CR = 23, Fluka), 11 mol % AlF_3 (CR = 8, SINTEF), 5 and 10 mol % Na_3AlF_6. The eutectic mixture, 46.5/11.5/42.0 mol % LiF/NaF/KF (FLINAK) melt, mp 455 °C, was prepared as previously described[28,29] from the appropriate amounts of the three dry salts, further dried under vacuum, mixed, melted, and kept at 700 °C for 20 h under an argon atmosphere, and finally cooled to room temperature. Clear pieces of the solid were selected for further use. The FLINAK mixtures with added cryolite or aluminum fluoride were prepared in a similar manner, slowly cooled in the furnace, and transferred to the glovebox for further manipulations and transfers of representative pieces to the Raman cells. Small lumps were loaded into a small cup-shaped indentation (2 mm i.d., 1 mm depth) of a silver disk and kept under argon in the sample chamber for studies up to 600 °C under a microscope with a Linkam temperature-controlled hot-stage (Linkam HFS91/TP93) as previously described.[28] Larger pieces of the samples were loaded into graphite windowless cells (hollow graphite blocks with holes small enough that the liquid will not run out) which were placed in quartz tubes under argon for studies up to 750 °C in a larger furnace previously described.[30] The macrofurnace temperature was measured with two thermocouples; it was uniform in space and time and believed to be correct within 3 °C. The temperatures for samples in the Linkam hot-stage were less precise because of temperature gradients, but calibrated temperatures are believed to be correct to 5 °C. Both furnaces were calibrated against the melting point of pure Zn metal (419.6 °C).

The solubility of cryolite in FLINAK does not appear to have been previously measured. Holm and Holm[3] reported an LiF/NaF/Na_3AlF_6 eutectic with a melting point of 628 °C for a composition of about 48 mol % LiF, 32 mol % NaF, and 20 mol % Na_3AlF_6. It would be expected that addition of KF would further reduce the liquidus. Kuvakin et al.[31] have shown that the addition of KF and LiF to Na_3AlF_6 reduces the melting point and gives clear eutectic melts (26 wt % KF at 740 °C and 27 wt % LiF at 665 °C). Visual inspection of the melting process under a microscope confirmed that the FLINAK sample with 4.8 mol % AlF_3 melted at about 455 °C, which is approximately the melting temperature of the FLINAK eutectic.[29] The FLINAK sample with 10 mol % Na_3AlF_6 was studied by differential thermal analysis and by thermogravimetric analysis. The DTA measurements indicated that the sample started to melt at 448 °C and was fully melted by 464 °C. The TGA analysis revealed that the sample started to lose mass at about 750 °C as the melt began to creep out of the platinum crucible.

Raman spectra were measured with a DILOR XY 800 mm focal length CCD spectrometer with both the macrofurnace and microscope paths leading to the entrance slit of the monochromator. Spectra were obtained for light scattered from the 514.5 nm line of an argon ion laser (Coherent Radiation). About 1 W laser power was employed for the macro method, and about 50 mW laser power was used for the micro method. The Rayleigh line was filtered with a Kaiser holographic SuperNotch-Plus filter (200 cm^{-1} cutoff approximately) or with a double premonochromator. Raman light was dispersed with a single 1800 line/mm grating onto the liquid-nitrogen-cooled CCD detector. The Raman spectral resolution was better than 5 cm^{-1}. A sheet polaroid analyzer, which permitted vertically (VV) or horizontally (VH) polarized light to pass, was used to obtain polarization data. Calibration of the wavenumber scale was achieved with neon lines superimposed on the spectrum, and reported wavenumbers were expected to be accurate to about 0.2 cm^{-1} for sharp peaks. Spectral files were collected as Labspec.tsf format files with the DILOR Labspec program and converted to Galatic.spc format files for use with the Grams32 suite of programs. All the spectra were curve-resolved with the Grams32 curve resolution program with mixed Gaussian−Lorentzian band shapes. Linear and nonlinear baselines gave essentially identical results. The data presented in our tables and figures are for the linear baseline.

Spectra of solid samples of Na_3AlF_6 (cryolite), K_3AlF_6, and K_2NaAlF_6 (elpasolite) were also obtained on a Renishaw Raman microprobe with the 514.5 nm line of an air-cooled argon ion laser at 25 mW power.

Results and Discussion

Aluminum coordination in solid state materials is almost exclusively dominated by six-coordinated aluminum with an octahedral geometry.[32] Although many compounds have aluminum with corner- and edge-shared octahedral coordination, there are a number of crystals with isolated or discrete AlF_6^{3-} ions, cryolite being the prototype.[32−38] A recent X-ray analysis of Na_3AlF_6 at different temperatures showed that the AlF_6^{3-} ion in the high-temperature phase (>650 °C) has almost perfect octahedral symmetry.[38] Compounds with Al^{3+}, Ga^{3+}, In^{3+}, Tl^{3+}, Sc^{3+}, and Fe^{3+} have similar structures and similar vibrational spectra.[34,39−44] The vibrational spectra of these crystals are primarily determined by the discrete octahedral ion with

---

(25) Brooker, M. H.; Berg, R. W.; von Barner, J. H.; Bjerrum, N. J. Accepted for publication in *Inorg. Chem.*

(26) von Barner, J. H.; Christensen, E.; Bjerrum, N. J.; Gilbert, B. *Inorg. Chem.* **1991**, *30*, 561.

(27) Brooker, M. H. Unpublished work.

(28) von Barner, J. H.; Andersen, K. B.; Berg, R. W. *J. Mol. Liq.* **1999**, *83*, 141.

(29) Janz, G. J.; Tomkins, R. P. T. *Natl. Stand. Ref. Data Ser. (U.S. Natl. Bur. Stand.)* **1981**, *NSRDS-NBS 61, Pt. IV.* Green, G. L.; Hunt, J. B.; Sutula, R. A. *Preparation and purification of FLINAK* ; U.S. National Technological Information Service AD Report No. 758001; GPO: Washington, DC, 1973.

(30) Berg, R. W.; von Winbush, S.; Bjerrum, N. J. *Inorg. Chem.* **1980**, *19*, 2688.

(31) Kuvakin, M. A.; Vol'khina, T. D.; Kuvakina, L. M. *Sov. J. Nonferrous Met.* (*N.Y.*) **1971**, *12*, 34.

(32) Wells, A. F. *Structural Inorganic Chemistry*, 4th ed.; Clarendon: Oxford, U.K., 1975.

(33) Steward, E. G.; Rooksby, H. P. *Acta Crystallogr.* **1953**, *6*, 49.

(34) Couzi, M.; Khairoun, S.; Tressaud, A. *Phys. Status Solidi A* **1986**, *98*, 423.

(35) Boulard, B.; Jacoboni, C.; Rousseau, M. *J. Solid State Chem.* **1989**, *80*, 17.

(36) Le Bail, A.; Ferey, G.; Mercier, A.-M.; De Kozak, A.; Samouel, M. *J. Solid State Chem.* **1990**, *89*, 282.

(37) Bulou, A.; Rousseau, M.; Nouet, J.; Loyzance, P. L.; Mokhlisse, R.; Couzi, M. *J. Phys. C: Solid State Phys.* **1983**, *16*, 4527.

(38) Yang, H.; Ghose, S.; Hatch, D. M. *Phys. Chem. Miner.* **1993**, *19*, 528.

(39) Nakamoto, K. *Infrared and Raman Spectroscopy of Inorganic and Coordination Compounds*; J. Wiley & Sons, Inc.: New York, 1997; Part A.

(40) Baran, E. J.; Lavat, A. E. *Z. Naturforsch.* **1981**, *36A*, 667.

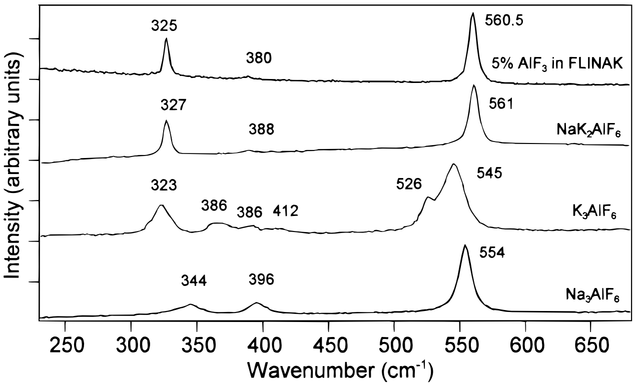

Figure 1. Raman spectra for solid samples of Na_3AlF_6 (cryolite), K_3AlF_6, and K_2NaAlF_6 (elpasolite) and for 4.8 mol % AlF_3 in FLINAK measured at room temperature.

Table 1. Vibrational Wavenumbers (cm^{-1}) and Assignments for the AlF_6^{3-} Ion in Na_3AlF_6 (Cryolite), K_3AlF_6, and K_2NaAlF_6 (Elpasolite) and for 5 mol % AlF_3 in Solid FLINAK Measured at Room Temperature[a]

mode	Na_3AlF_6	K_3AlF_6	K_2NaAlF_6	5 mol % AlF_3 in FLINAK
$\nu_1(A_{1g})$	554 s, p	545 s 526 w	561 s	560.5 s
$\nu_2(E_g)$	396 m	412 w 391 w 386 w	388 vw	380 vw
$\nu_5(F_{2g})$	344 m	323 m	327 m	325 m

[a] s = strong, m = medium, w = weak, vw = very weak, and p = polarized.

variations caused by different site and correlation field effects associated with the exact unit cell symmetry. A regular octahedron has point group O_h and six fundamental vibrational bands: ν_1 (A_{1g}, Raman active), ν_2 (E_g, Raman active), ν_5 (F_{2g}, Raman active), ν_3 and ν_4 (F_{1u}, infrared active), and ν_6, an inactive F_{2u} mode.

Raman spectra for solid Na_3AlF_6 (cryolite), K_3AlF_6, and K_2NaAlF_6 (elpasolite) and for AlF_6^{3-} in FLINAK are shown in Figure 1 to illustrate typical spectra for the AlF_6^{3-} ion in different crystal structures. The wavenumber values are given in Table 1. The spectrum of AlF_6^{3-} in solid FLINAK resembles that of K_2NaAlF_6, which might be expected since it is probably the first solid to be formed on cooling of the FLINAK melt.[31] The Raman bands for AlF_6^{3-} in the solid phase occur in three general regions, $\nu_1(A_{1g})$ at about 550 cm^{-1}, $\nu_2(E_g)$ at about 380 cm^{-1}, and $\nu_5(F_{2g})$ at about 330 cm^{-1}, but there can be a wide variation among different crystals. Furthermore, each region may have a number of components as a result of site and correlation field effects.[22,34] The peak maximum of the $\nu_1(A_{1g})$ mode of isolated AlF_6^{3-} can vary significantly as a result of crystal packing. It has been reported as low as 544 cm^{-1} for $(NH_4)_3AlF_6$,[43] at 564 cm^{-1} for $LiCaAlF_6$,[41] and as high as 606 cm^{-1} for Na_2MgAlF_7 (weberite).[44] For the K_3AlF_6 sample (Figure 1), a second component in the ν_1 region appeared as a shoulder at 530 cm^{-1} on the main band at 547 cm^{-1}. A similar splitting has been reported for an Rb_2KFeF_6 crystal,[34] and it may be a factor group component of the ν_1 mode. For Rb_2KFeF_6, a unit cell group analysis[34] also allowed for a Raman-active A_{1g} component of ν_3, which could gain intensity through Fermi resonance. The ν_3 mode occurs as a broad band centered at about 570 cm^{-1} in the infrared spectrum and is sufficiently close to the ν_1 mode for an interaction between these two modes to occur. The $\nu_2(E_g)$ mode is normally very weak for octahedral complexes, and for a number of crystals, this band has been too weak to be detected.[34,39,42] The relatively large intensity of the $\nu_2(E_g)$ mode at 396 cm^{-1} for Na_3AlF_6 is an anomaly. The intensities of the ν_2 band for K_3AlF_6, K_2NaAlF_6, and AlF_6^{3-} in FLINAK are weak and probably spread over several components. Site and correlation field effects allow for several components in the ν_2 and ν_5 regions for Na_3AlF_6, K_3AlF_6, and K_2NaAlF_6. Although the components for Na_3AlF_6 are unresolved at room temperature, some of them have been resolved at liquid nitrogen temperature.[22] However, the $\nu_5(F_{2g})$ mode is quite intense and well-defined for each of the samples (Figure 1). The value of 344 cm^{-1} for Na_3AlF_6 is much higher than the value for the other crystals, possibly due to the high potential field of the small sodium ion. There can be little doubt that the aluminum ion has octahedral coordination when matrix-isolated in the FLINAK solid.

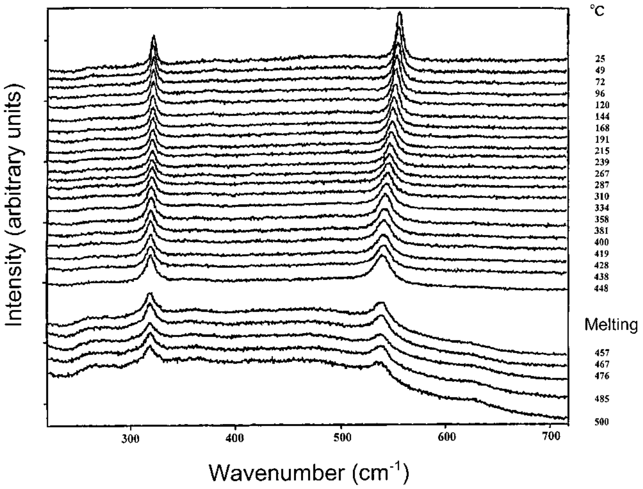

Figure 2. Raman spectra for 4.8 mol % AlF_3 in FLINAK at different temperatures from room temperature to 500 °C for samples studied under the microscope. The spectra up to about 450 °C correspond to AlF_6^{3-} isolated in the solid FLINAK matrix, while above this temperature the sample was molten.

The Raman spectra of AlF_6^{3-} in the 4.8 mol % AlF_3 in FLINAK medium were then recorded for different temperatures at small temperature intervals from 25 to 600 °C for a sample on a silver plate, under a microscope on the Linkam hot-stage. A selection of spectra for samples up to 500 °C are shown in Figure 2. Another set of experiments were performed with larger temperature intervals up to 750 °C for a 10 mol % Na_3AlF_6 in FLINAK sample in a graphite windowless cell in the macro-furnace. Spectra for samples at 400 °C (solid), 440 °C (solid), 480 °C (liquid), 520 °C (liquid), and 630 °C (liquid) are shown in Figure 3. These two sets of spectra illustrate the effect of temperature on the spectrum of AlF_6^{3-} in FLINAK at the melting point of FLINAK (455 °C). Each of the three spectral components of AlF_6^{3-} in FLINAK gradually decreased in wavenumber while the half-widths increased (Figures 2 and 3). Detection of the ν_2 band became more difficult as this weak band became broad. The shift of the peak maximum to lower wavenumbers was as expected and is caused by the gradual lattice expansion. Most remarkably, there was essentially no

---

(41) Daniel, P.; Gesland, J. Y.; Rousseau, M. *J. Raman Spectrosc.* **1992**, *23*, 197.
(42) Reisfeld, M. J. *Spectrochim. Acta* **1973**, *29A*, 1923.
(43) Wieghardt, K.; Eysel, H. H. *Z. Naturforsch.* **1970**, *25B*, 105.
(44) Brooker, M. H. In *Proceedings of the 11th International Conference on Molten Salts*; Trulove, P. C., DeLong, H. C., Stafford, G. R., Deki, S., Eds.; Electrochemical Society: Pennington, NJ, 1998; Vol. 98-11, pp 597−607.

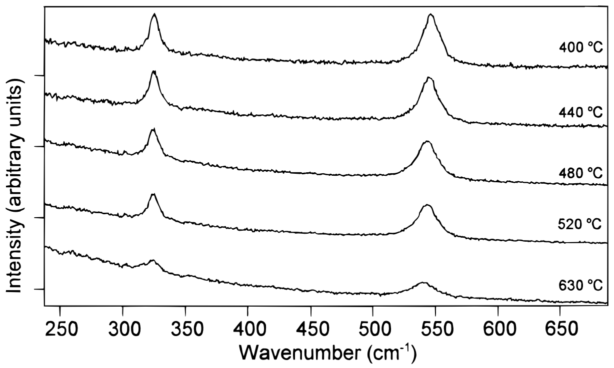

Figure 3. Raman spectra of 10 mol % Na_3AlF_6 (cryolite) in FLINAK at 400, 440, 480, 520, and 630 °C for samples studied in a graphite windowless cell. The sample melted between 440 and 480 °C.

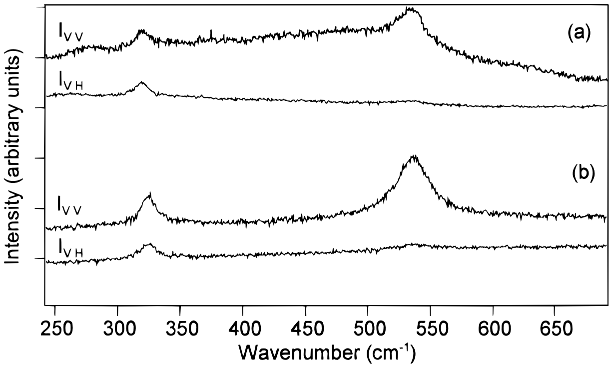

Figure 4. (a) Polarized Raman spectra (I_{VV} and I_{VH}) for 4.8 mol % AlF_3 (CR = 23) in a FLINAK melt at about 500 °C, measured under the microscope with a 180° backscattering geometry. (b) Polarized Raman spectra (I_{VV} and I_{VH}) for 11 mol % AlF_3 (sublimed) (CR = 8) in a FLINAK melt at 700 °C, measured in a graphite windowless cell. This is a 90° scattering experiment.

change in the spectrum as the sample converted from a high-temperature solid to a molten mixture at about 455 °C (Figures 2 and 3). The most obvious change that occurred was the change in the baseline at the melting point for the sample measured under the microscope (Figure 2), which occurred because the change in the sample from solid to liquid required an adjustment of the laser focus and scattering from the borosilicate cover glass was detected as a broad band at about 480 cm^{-1} and a weak feature near 630 cm^{-1}. To confirm that these were not bands due to dissolved oxide and to investigate the effect of concentration on the spectra, separate samples with 5 and 10 mol % Na_3AlF_6 and for 11 mol % AlF_3 in FLINAK medium were measured in the windowless graphite cell. Essentially identical results were obtained. Spectra of the solid as it passed through the phase transition into the melt were surprisingly similar. No bands other than those assigned to the AlF_6^{3-} ion were detected for CR = 23−8 and for temperatures up to 750 °C.

Depolarization measurements at 500 °C under the microscope revealed that the peak at 542 cm^{-1} was strongly polarized while the peak at 325 cm^{-1} was depolarized (Figure 4a). The depolarization experiments were repeated for the 11 mol % AlF_3 sublimed sample in the macroscopic windowless cell because the validity of the depolarization measurements obtained on a microprobe has not been well established. Spectra are shown in Figure 4b for the sample of 11 mol % AlF_3 in FLINAK (CR = 8) at 700 °C. The polarization measurements confirmed the assignments of the bands to the $\nu_1(A_{1g})$ and $\nu_5(F_{2g})$ modes of AlF_6^{3-}. The polarization properties of the $\nu_2(E_g)$ mode could not be established because of the weak intensity of the band at about 375 cm^{-1}.

Plots of peak position and half-width versus temperature (Figure 5) indicated only very small discontinuities at about 455 °C, the melting point of FLINAK. Identical results were obtained from both the microscopic and macroscopic studies. It should also be emphasized that peak positions, half-widths, and relative areas are the same for all the cryolite ratios from 23 to 8 for a given temperature. A plot of the ν_1 peak position versus temperature is shown in Figure 5a. It can be seen from the temperature dependence of the ν_1 mode that the change of wavenumber is considerable. It shifted from 560.5 cm^{-1} at room temperature to about 542 cm^{-1} at the melting point to 532 cm^{-1} at 750 °C. At higher temperatures, the spectra were too noisy for analysis and TGA results indicated that the sample had started to give off vapors. The half-width of the ν_1 mode, reported as the full width at half-height (FWHH), was also very sensitive to temperature (Figure 5b). From a value of 7 cm^{-1} at room temperature the FWHH increased to about 18 cm^{-1} at the melting point to 35 cm^{-1} at 750 °C. Areas were also measured for each peak by integration above an estimated baseline, but the values only have meaning in a relative sense and are not shown here. It is sufficient to state that the integrated intensity of the ν_1 mode remained constant relative to the integrated intensity of the ν_5 mode with a value of 2.8 ± 0.2 for $I(\nu_1)/I(\nu_5)$. In contrast to the large effect of temperature on the ν_1 mode position, the effect on the ν_5 mode position was rather small (Figure 5c). The wavenumber of the ν_5 mode shifted from 327 cm^{-1} at room temperature to about 324 cm^{-1} at the melting point and had a value close to 322 cm^{-1} at 750 °C (Figure 5c). The half-width of the ν_5 mode was also quite insensitive to the temperature in comparison to that of the ν_1 mode. From a value of 5 cm^{-1} at room temperature the FWHH increased to about 12 cm^{-1} at the melting point and had a value of only 17 cm^{-1} at 750 °C (Figure 5d). Values for the wavenumber of the ν_2 mode were subject to large uncertainties because of its weak intensity. However, it was possible to establish a shift to lower wavenumber position (Figure 5e) and an increase in the FWHH for the ν_2 mode (Figure 5f).

From a comparison of the spectra (Figures 1−4), the aluminum ion when matrix-isolated in FLINAK solid occurs as the octahedral AlF_6^{3-} ion. Furthermore, the aluminum ion must also be in the form of the octahedral AlF_6^{3-} ion in molten FLINAK for CR values of 8 or higher and at temperatures up to 750 °C because the spectra were essentially unchanged. The assignments are summarized and compared to literature values in Table 2.

No other bands were detected in these experiments. There was no evidence of a shoulder on the low-frequency side of the AlF_6^{3-} band as has been reported for molten potassium and sodium cryolite.[16−20] It must be stressed that the Raman measurements could be performed for FLINAK melts over a wide range of temperatures from 450 up to 750 °C. Even at 750 °C, the bands remained quite narrow and curve resolution gave excellent fits to the experimental spectra with single Gaussian−Lorentzian product functions although the baseline had started to deteriorate at 750 °C. A band due to a fluoroaluminate oxide complex has been reported[19] in the 500−520 cm^{-1} region for NaF/AlF_3 melts at 1030 °C, but our attempts to detect a band from aluminum oxofluoride complexes in this region due to possible oxide impurities in FLINAK were unsuccessful. The solubility of aluminum oxide in FLINAK is very low at 700 °C even with the presence of 5−10 mol % of AlF_3.[24] In fact, it was possible to visually detect solid particles

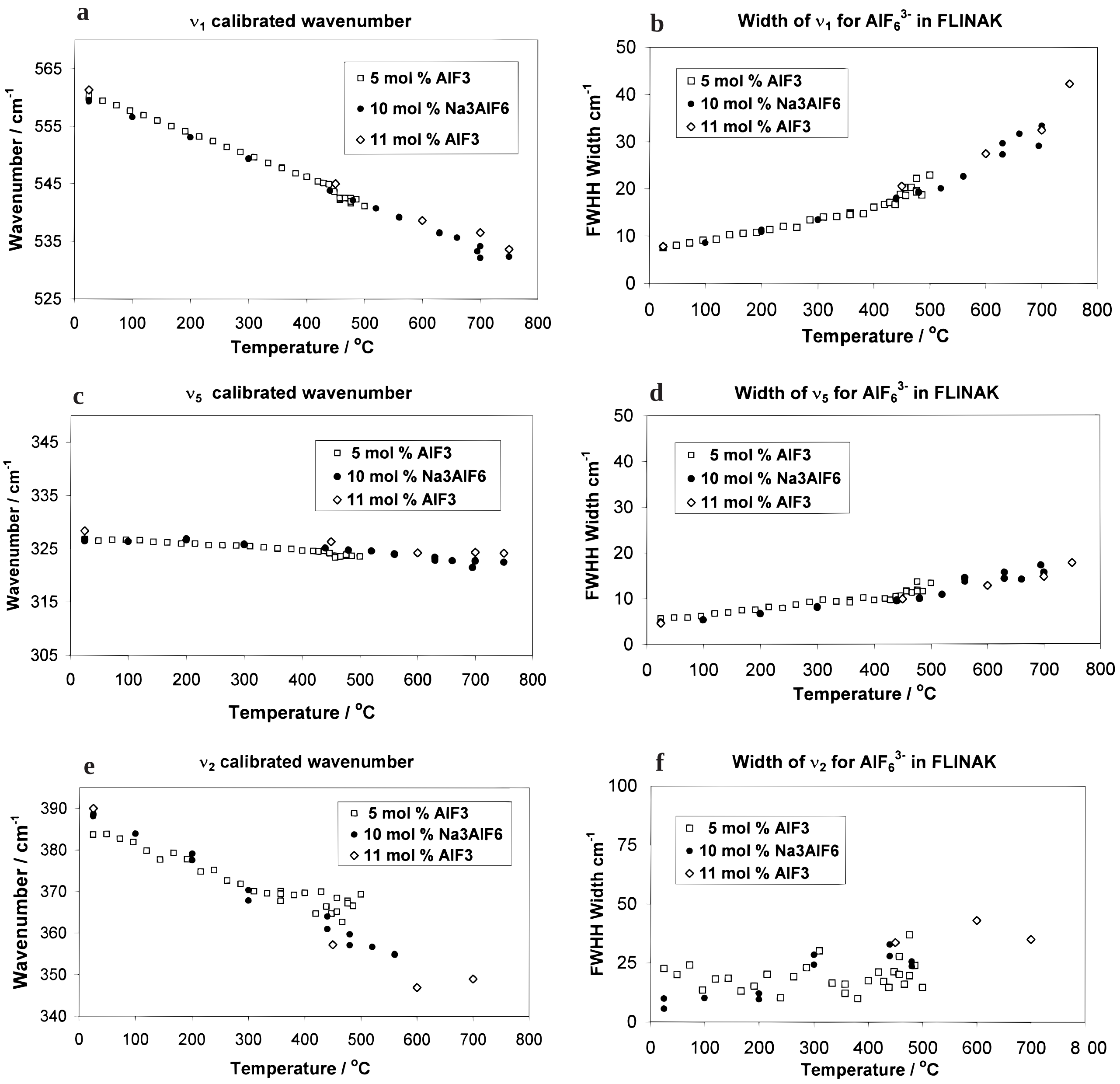

Figure 5. Plots of peak maxima and FWHH widths of the modes of the AlF_6^{3-} ion in FLINAK at temperatures from 25 to 750 °C. Squares represent measurements performed for 5 mol % AlF_3 under the microscope, closed circles are for measurements for 10 mol % Na_3AlF_6 in the graphite cell, and diamonds are for measurements for 11 mol % AlF_3 (sublimed) in the graphite cell. Plots: (a) $\nu_1(A_{1g})$ peak maximum versus temperature; (b) $\nu_1(A_{1g})$ FWHH versus temperature; (c) $\nu_5(F_{2g})$ peak maximum versus temperature; (d) $\nu_5(F_{2g})$ FWHH versus temperature; (e) $\nu_2(E_g)$ peak maximum versus temperature; (f) $\nu_2(E_g)$ FWHH versus temperature.

Table 2. Vibrational Wavenumbers (cm^{-1}) and Assignments for the AlF_6^{3-} Ion in Different media versus Temperature, Based on This Work and Literature References[a]

	FLINAK					
mode	25 °C, this work	455 °C, this work	750 °C, this work	solid salts, 25 °C, refs 39, 40,[c] 42	KF/AlF_3 melt, 860 °C, ref 20	cryolite melt, 1020 °C refs 11, 12
$\nu_1(A_{1g})$	560.5 s	542 s	532 s, p	~541	515[d] s, p	555 s, p
$\nu_2(E_g)$	380 w	365 vw	370 vw	(400)[c]		390 w, dp
$\nu_3(F_{1u})$	594 m[e] 622 w[e]			~568		
$\nu_4(F_{1u})$				~387		
$\nu_5(F_{2g})$	325 m	324 m	322 m, dp	~322	320[d] m, dp	345 m, dp
$\nu_6(F_{2u})$[b]				(~228)[b,c]		

[a] s = strong, w = weak, vw = very weak, p = polarized, and dp = depolarized. [b] Inactive. [c] Calculated by normal-coordinate analysis. [d] Assigned to AlF_6^{3-} by Gilbert et al.[20] Other bands at 555 (s, p) and 345 (m, dp) cm^{-1} were assigned to the AlF_5^{2-} ion. [e] See ref 25.

in a molten drop under the microscope, and the cloudy nature of some of the melts in the macroscopic furnace also suggested the presence of undissolved aluminum oxide. The sublimed sample of AlF_3 (11 mol % in FLINAK) gave a clear melt that was essentially free of solid particles, which accounts for the excellent depolarization measurements for this sample at 700 °C (Figure 4b). Attempts to dissolve aluminum oxide in the FLINAK melts were also not successful. However, in separate experiments, it was possible to dissolve **sodium oxide** in the 5% mol AlF_3 FLINAK melt. The most intense Raman band due to the oxyfluoaluminate species was detected at about 500 cm^{-1} in liquid FLINAK at 500 °C. These studies will be reported elsewhere.[25]

The results described above provide strong evidence that AlF_6^{3-} is the only species detectable by Raman spectroscopy in FLINAK melts for CR = 23−8 and temperatures up to 750 °C. Unfortunately, the unstable nature of the FLINAK melt precluded our attempts to extend the temperature range of our study up to the lower range of temperatures reported by Robert et al.[20] Nevertheless, on the basis of thermodynamic data[8,9,15,20] for cryolite dissociation with temperature, it seems difficult to accept that a temperature difference of 110 °C could cause the AlF_6^{3-} ion in FLINAK to dissociate substantially into AlF_5^{2-} and F^- ions. It is instructive to compare the Raman spectrum for AlF_3 in FLINAK at 700 °C and CR = 8 from the present study (Figure 4b) to the reported spectrum for AlF_3 in KF at 860 °C and CR = 15 (Figure 2B in ref 20; note that the caption for Figure 2B should read $X_{AlF_3} = 0.063$ for 860 °C). From the data in Table 1 of ref 20, it appears the fraction of AlF_6^{3-} never exceeds 30% of the total fluoroaluminate species even at CR's as high 15. For AlF_3 in FLINAK at 700 °C, there is a single band at about 535 cm^{-1} that has been assigned to the AlF_6^{3-} ion (Figures 1−4). For AlF_3 in KF at 860 °C and CR = 15 (Figure 2B in ref 20), there is an intense band at about 550 cm^{-1} with a shoulder at about 510 cm^{-1}. Gilbert et al.[16−20] assigned the shoulder at 510 cm^{-1} to AlF_6^{3-} and the main peak at about 550 cm^{-1} to the AlF_5^{2-} ion. The fact that there is twice the amount of excess fluoride in the FLINAK sample should be more than enough to compensate for the 110 °C temperature difference, but a single band due to AlF_6^{3-} is all that can be detected for the FLINAK sample up to 750 °C. These new results cast some doubt on the assignments of Gilbert et al.[16−21]

In a study similar to the present work, Brooker[22,23,44] followed the temperature dependence of the wavenumbers of Raman bands for solid and molten Na_3AlF_6 and presented polarization results for the Raman spectra of molten cryolite. The peak maximum for AlF_6^{3-} occurred at 556 cm^{-1} for solid cryolite at −196 °C. When the sample was heated, the peak maximum decreased slightly to a value of 549 cm^{-1} just before the phase transition at 650 °C. At the phase transition, the peak maximum actually increased by 2 cm^{-1}, but above the phase transition, the peak maximum continued to decrease until it reached a value of 541 cm^{-1} just before the melting point. When the sample had melted, the peak maximum increased to 555 cm^{-1}. Although a 14 cm^{-1} increase in wavenumber on melting is rather large, the values for the high-temperature solid and the melt are well within the range expected for octahedral AlF_6^{3-}.

The 14 cm^{-1} increase in the wavenumber of the strongest band on melting for Na_3AlF_6 is a fact, but is it due to a frequency shift of the octahedral AlF_6^{3-} ion or is it due to the formation of AlF_5^{2-} in the molten phase of cryolite? The range of frequencies for ν_1 of AlF_6^{3-} can be quite large, and a 14 cm^{-1} shift between those for the solid and the melt is within the range of observed values for ν_1, e.g., 554, 545, and 561 cm^{-1} for the different salts reported in Table 1. Furthermore, the increase in the wavenumber at the solid−solid phase transition at 650 °C can be explained by the **decrease** in the Al−F bond length and the **increase** in the average Na−F bond length at the phase transition that have been detected by high-temperature X-ray diffraction analysis.[38] A similar tightening of the Al−F bond can occur in the melt due to the high electrostatic repulsion of the Na^+ ions. In a classic neutron diffraction study, Levy et al.[45] were able to show that although most ionic liquids are less dense than the corresponding high-temperature solids, the melting process is usually accompanied by a decrease in the average first nearest neighbor bond distances and an increase in the average second nearest neighbor bond distances. This observation is consistent with "hole" theory and other fluidity models for molten salts. The effects of temperature on the wavenumbers of the ν_2 and ν_5 modes for AlF_6^{3-} in Na_3AlF_6 are also consistent with the presence of AlF_6^{3-} ions in molten cryolite. With increased temperature, the ν_2 band of AlF_6^{3-} (at about 395 cm^{-1} for solid cryolite at room temperature) was found to decrease in wavenumber and intensity and merge with the ν_5 band (at about 344 cm^{-1} for solid cryolite at room temperature).[23] At the phase transition temperature, the peak maximum of the ν_5 band was observed at about 338 cm^{-1}, while the intensity of the ν_2 band contributed a broad asymmetric shoulder at about 360 cm^{-1}. Well above the phase transition region, this region could be treated as a single, broad asymmetric Raman band centered at about 350 cm^{-1} that could be assigned primarily to the ν_5 mode of AlF_6^{3-} in the high-temperature phase of cryolite. The presence of a depolarized band at about 350 cm^{-1} for the high-temperature cryolite solid and the melt suggests a common origin. These assignments for cryolite are consistent with the literature values for AlF_6^{3-} listed in Tables 1 and 2.

Our present result for AlF_3 in FLINAK, that AlF_6^{3-} is the principal species in FLINAK at CR's down to 8 and at temperatures up to 750 °C, cannot disprove the possible presence of AlF_5^{2-} in NaF and KF melts at higher temperatures. However, these new results for FLINAK melts indicate that AlF_6^{3-} should probably also be the principal species in other cryolite melts. This would be in agreement with the thermodynamic models developed by Grjotheim and co-workers[8] and by Frank and Foster[10] and used successfully as the basis for analysis of activity measurements over the past 40 years. The Raman experiments described above leave little room for appreciable concentrations of five-coordinated aluminum in FLINAK. Given that both Dewing[7] and Kvande[6] have shown that the inclusion of an additional species such as AlF_5^{2-} provides an improved fit to the activity data in the CR = 2 region, it seems appropriate to speculate on the nature of the melt when both AlF_6^{3-} and AlF_4^- are present. There can be little doubt that the F^- ion undergoes rapid exchange. On the NMR time scale, only one signal is observed at all compositions.[13,21] However, Raman spectroscopy is a very fast process and chemical species that retain a fixed geometry for times on the order of a picosecond will give rise to a Raman spectrum consistent with that geometry. It would appear that both AlF_6^{3-} and AlF_4^- meet the time scale requirements. However, in melts with CR ≈ 2, there must be F^- ion exchange between AlF_6^{3-} and AlF_4^- and, on a time scale shorter than a picosecond, there will be species such as $Al_2F_{10}^{4-}$ or $(AlF_5^{2-})_2$. In thermodynamic terms, the AlF_6^{3-} and AlF_4^- ions are not ideal or noninteracting particles. The large FWHH for the symmetric stretching mode of AlF_6^{3-} in molten cryolite (about 90 cm^{-1} [11,23]) is an indication of considerable environmental broadening and a short lifetime for AlF_6^{3-}.

Recent theoretical studies are relevant. It has been shown in several reports that cations can stabilize both five- and six-

---

(45) Levy, H. A.; Agron, P. A.; Bredig, M. A.; Danford, M. D. *Ann. N.Y. Acad. Sci.* **1960**, *79*, 762.

coordinated fluoroaluminates.[46−48] Joubert and co-workers[48] have calculated the most stable configurations for the cluster of 3 Na + Al + 6 F (i.e., cryolite, Na_3AlF_6). These authors performed their calculations at a very high level using density functional theory (DFT) combined with topological analysis of the electron localization function (ELF) gradient field. The only stable configurations were found to be the 6-fold and 4-fold aluminum complexes. Other possible conformations either were unstable (imaginary frequencies) or had much higher energy. The 5-fold coordination was unstable, and the single imaginary frequency corresponds to a transition state.

One aspect of the present study is remarkable. The half-widths of the ν_1 and ν_5 modes of AlF_6^{3-} in FLINAK are very narrow, both in the solid phase and especially in the FLINAK melt. The presence of 40% LiF in the melt would be expected to result in a significant increase in the FWHH because for pure molten Li_3AlF_6 the Raman bands were found to be very broad.[11] The small Li^+ ion does not provide any impediment to the symmetric stretching movement of AlF_6^{3-}; thus the AlF_6^{3-} ion experiences a wide range of environments. Lithium ions tend to move with the Al−F stretching motions and a broad band results (environmental broadening). The features of the spectra for AlF_6^{3-} in FLINAK more resemble those of molten K_3AlF_6 and Cs_3AlF_6, where the larger, heavier cations restrict the range of environments and lead to narrow bands.[11,44] Possibly there is a local order on a very fast time scale that tends to result in a preference for the K^+ ion as the next nearest neighbor of the AlF_6^{3-} ion in FLINAK while the Li^+ ions remain with the excess F^- ions. Dewing has suggested a similar explanation to account for excess free energies of solution in the LiF/Na_3AlF_6 system.[49] He concluded that LiF existed in the LiF/Na_3AlF_6 melt as LiF, with the F^- ion more-or-less permanently attached to the Li^+ ion.

Conclusions

Raman spectra from matrix-isolated aluminum ions in the LiF/NaF/KF eutectic exhibit the characteristic pattern[39,40] of the discrete octahedral AlF_6^{3-} ion both in the matrix-isolated solid and in the melt. The octahedral AlF_6^{3-} ion is the only species in the melt over the CR range from 23 to 8 and up to 750 °C. These results suggest that the well-established thermodynamic model[8,9] based on the dissociation of octahedral AlF_6^{3-} into tetrahedral AlF_4^- and free F^- ions still should be considered for NaF/AlF_3 and KF/AlF_3 melts. Further studies are required to establish the origin of the shoulder at 510 cm^{-1} in the spectra of the high-temperature NaF and KF cryolite melts.

Acknowledgment. This work was sponsored by several Danish foundations that made possible the purchase of the DILOR Raman instrument and the Linkam accessories: the Danish Technical Science Foundation, Corrit Foundation, Tuborg Foundation, Danfoss A/S, Thomas B. Thrige Foundation, P. A. Fiskers Foundation, and Direktør Ib Henriksens Foundation. The work was also supported in part by the Natural Sciences and Engineering Research Council of Canada. M.H.B. is grateful to DTU for a travel grant. We wish to acknowledge Gerda Krarup for assistance with the DTA measurements and Åsmund Sterten, NTNU, for helpful discussions, and we are grateful to Geir-Martin Haarberg (SINTEF) for the gift of sublimed AlF_3 under argon.

IC000260H

---

(46) Akdeniz, Z.; Cicek, Z.; Tosi, M. P. *Chem. Phys. Lett.*, **1999**, *308*, 479.

(47) Bouyer, F.; Picard, G.; Legendre, J.-J. *Int. J. Quantum Chem*. **1997**, *61*, 507.

(48) Joubert, L.; Picard, G.; Silvi, B.; Fuster, F. *J. Electrochem. Soc.* **1999**, *146*, 2180.

(49) Dewing, E. W. *Light Met. Met. Ind.* **1985**, 737.