sheets composed of trigonal columns about (101). These planes are connected by sharing the remaining edges to constitute the three-dimensional structure and to give the large hexagonal channels (Figure 1). The connectivity of the trigonal prisms in Zr_5Sb_3-M is very different. The prisms do not share either the trigonal faces or the remaining third edge (Figure 6). Thus, a considerable rearrangement is required to convert the Y_5Bi_3-type into the Mn_5Si_3-type structure. This is likely not a concerted process, which could account for some of the apparently large kinetic barriers found for their interconversion.

The interstitial site at the center of the zirconium octahedra in Zr_5Sb_3-M has a counterpart in Zr_5Sb_3-Y; it is, however, a tetrahedral site with a distance of ~2.1 Å from the neighboring zirconium atoms. This position is much too small to accommodate any excess antimony without a very large distortion. Extra antimony atoms can be bonded much more easily in the interstitial site of Zr_5Sb_3-M and are likely to be the cause of the adoption of the Mn_5Si_3 structure for Zr_5Sb_{3+x} compositions. A small nonmetal (B, C, N) atom would be more likely physically to fit in the former tetrahedral site. However, investigations of these Zr_5Sb_3Z systems have shown that even such small nonmetal atoms prefer the octahedral hole in the Mn_5Si_3 modification, although tetrahedral site occupancy has been found in other examples of the Yb_5Sb_3 structure type.[3] Details will be forthcoming.

Acknowledgment. The crystallographic and computing facilities were graciously provided by R. A. Jacobson, while arc-melting equipment was kindly made available to us by H. F. Franzen.

Supplementary Material Available: Table of anisotropic thermal parameters for Zr_5Sb_3-Y and Zr_5Sb_3-M (1 page); listings of observed and calculated structure factors for the same compounds (3 pages). Ordering information is given on any current masthead page.

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Raman Spectroscopy of Fluoride-Containing Chloroaluminate Melts

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The effect of adding fluoride ions to chloroaluminate melts has been studied by Raman spectroscopy. In acidic (AlX_3/MX mole ratio greater than 1, where M^+ is an alkali-metal ion) melts at 200 °C, the fluoride ion acts as a dibase and the new species $Al_2Cl_6F^-$ is formed, as indicated by comparison of observed and calculated frequencies. The polarization of the Raman bands indicates that a fluoride replaces a terminal chloride. Measurements have also been made on several basic melts (AlX_3/MX mole ratio <1) at much higher temperatures (between 580 and 850 °C). The best results were obtained at 820 °C for mixtures of $NaAlCl_4$ with increasing amounts of NaF. It was found that fluoride replaces chloride progressively, depending on the molar ratio of NaF to $NaAlCl_4$. The new species $AlCl_3F^-$, $AlCl_2F_2^-$, and $AlClF_3^-$, together with the previously observed AlF_4^-, are clearly identified. Intensity measurements made on the characteristic bands allow a quantitative study of the distribution of each species as a function of melt composition. The calculated equilibrium constants follow the same trend as was found for similar chloro bromo species.

Introduction

Aluminum halide containing molten salt systems are of major importance to aluminum production; they are also of interest for high-energy batteries. Unusual redox and coordination chemistry has been observed in these melts.[1,2] The haloaluminate ions present in these melts are usually formed by the reaction between the alkali-metal halide and an aluminum halide, although lower melting point systems formed with organic halides have also been studied.[3] Mixed-halide melts have received some attention: for example, chlorobromoaluminate and chloroiodoaluminate systems have been studied by spectroscopic methods,[4-7] while electrochemical methods have been used to probe the behavior of F^- ion in acidic chloroaluminate melts.[8]

Tetrachloroaluminate ion has been shown to undergo fast exchange with a higher mass halogen (Br, I), in the liquid state (in CH_3CN solutions or in the molten state).[4-7] Vibrational spectroscopy and ^{27}Al NMR measurements provide evidence that when $AlCl_4^-$ is mixed with $AlBr_4^-$ or AlI_4^- the various mixed ions $AlCl_nX_{4-n}^-$ (X = Br, I) are formed, with n depending only on the mole ratio of the respective halides.[4-7]

Mixtures of $AlCl_4^-$ and fluoride ion should also exhibit similar behavior; however, no spectroscopic studies of such species have been reported, except for the Raman spectroscopic characterization of simple fluoro complexes, AlF_4^- and AlF_6^{3-}, in fluoride melts.[9,10]

In this paper we describe Raman spectroscopic studies of several new species formed by the exchange of fluoride for chloride in chloroaluminate melts.

Experimental Section

All chemicals were purified by the usual methods for chloroaluminate melt preparation.[11,12] The alkali-metal chlorides were melted in quartz tubes, treated with HCl and nitrogen, and crystallized from the melt. $AlCl_3$ (from Fluka) was distilled twice. NaF was melted in a nickel crucible and recrystallized twice by slow cooling. Clear crystals of each starting material were used to make the mixtures. Chemicals were handled in a drybox (water level <1 ppm) or under vacuum.

Because of the much lower viscosity of the present melts compared to that of pure fluoride melts, a windowless cell such as that used previously[13] was found to be impractical. With the size of the main holes

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about 3 mm, it was not possible to hold a drop of reasonable size (filling most of the sample compartment). Reducing the size of the hole to 1 mm allowed to drop to be stabilized occasionally, but the spectral intensities were frequently weak and not very reproducible. Fortunately, the acidic melts (those with $AlCl_3$ present in excess) could be studied in glass or quartz cells, since for these systems the fluoride ion was strongly complexed, and the temperature of the melt was quite low (near 200 °C).

In basic melts, reasonable solubility of the fluoride ion is achieved only at very high temperatures. Provided that the following sequence in the preparation of the solutions is followed, for the composition ranges studied here, quartz cells can still be used, and fluoride ion does not attack the cell. No changes in the Raman spectra were found even after repeated meltings at 820 °C for 3 h (the time period for the melt to reach its equilibrium temperature and for the recording of a spectrum).

The procedure used is as follows. The starting solvents LiCl/NaF (80/20 mol %) and NaCl/NaF (60/40 mol %) were first prepared by premelting the required amounts in a glassy-carbon crucible under an argon atmosphere. After the solids were melted, the liquids were frozen and the resulting pellet was broken into several chunks. A chunk of the required weight was then added to the quartz Raman cell (a simple round tube, 6 mm i.d.) together with the necessary amount of $NaAlCl_4$ (also previously prepared, but in glass ampules). The cell was sealed under vacuum and placed in the Raman furnace. When the mixture was heated, the $NaAlCl_4$ melted first and totally surrounded the still solid chunk containing the fluoride. When the temperature reached 400–600 °C, depending on the mixture, the $NaAlCl_4$ reacted rapidly with the fluoride-containing material. Using this procedure and keeping the F/Al molar ratio below 4 ensures that no free fluoride is present and no attack of the quartz cell occurs, even at 850 °C.

The furnace used is similar in design to the one previously described.[13] The only difference is that the inside of the main quartz tube contained a nickel block with the required openings for the laser and Raman light, to ensure a better temperature homogeneity in the sample.

A Ramanor HG2000 spectrometer (Jobin-Yvon) equipped with concave, aberration-corrected, holographic gratings was used to record the Raman spectra. A Coherent Radiation Model 52B Ar ion laser operating at 514.5 nm with power ranging from 40 to 200 mW was used as the excitation source. Spectra could be accumulated or subtracted through the use of an LSI 11/23 computer. For accurate measurements used in quantitative calculations, the slit length was kept much smaller than the projected mage of the laser beam, resulting in much better reproducibility of the intensities. The slit widths used were between 3 and 4 cm^{-1}, and the time constants were between 0.5 and 1 s, depending on the sample.

Results and Discussion

Because the results obtained depend on the modified Lewis acidity of the mixture, the results for basic and acidic melts will be presented and discussed separately.

Mixtures of Alkali-Metal Halides with $NaAlCl_4$. As explained in the Experimental Section, quartz cells were required for these samples; this fact severely restricts the type of mixture and composition range that could be studied. While it is possible that mixtures of $NaAlCl_4$ with Na_3AlF_6 where the amount of the latter is low may be relatively inert, they were not investigated.

Initial measurements were made with the lowest melting temperature alkali-metal chloride/alkali-metal fluoride mixtures in order to keep the attack on the container as low as possible. The first mixture chosen as solvent contained 80 mol % LiCl and 20 mol % NaF. This is a eutectic mixture that melts at 490 °C.[14] $NaAlCl_4$ is quite soluble in this mixture; Raman spectra of such solutions at 580 °C are shown in Figure 1. All of the observed bands, except the one at 490 cm^{-1}, are strongly polarized (the polarized spectra are not shown for the sake of clarity for this and several other figures). The spectrum at the top of the figure is that of a mixture containing an amount of $NaAlCl_4$ slightly lower than the amount of NaF. This spectrum shows a large background in the low-frequency region, which is characteristic of all LiCl-based melts and which precludes the observation of low-frequency bands. Despite this large background, an intense doublet located at 349 and 375 cm^{-1} and two weak bands at 416 and 490 cm^{-1} are observed. The 349-cm^{-1} band is the ν_1 band of $AlCl_4^-$ slightly shifted toward higher frequencies because of the presence of the Li cation.[15] The broad depolarized band at 490 cm^{-1} is the ν_3 band of $AlCl_4^-$. The other two bands are new and are believed to be due to the ν_1 mode of mixed chloro–fluoro aluminum tetrahalides, located between the ν_1 band of $AlCl_4^-$ at 349 cm^{-1} and the ν_1 band of AlF_4^- at 622 cm^{-1}.[9]

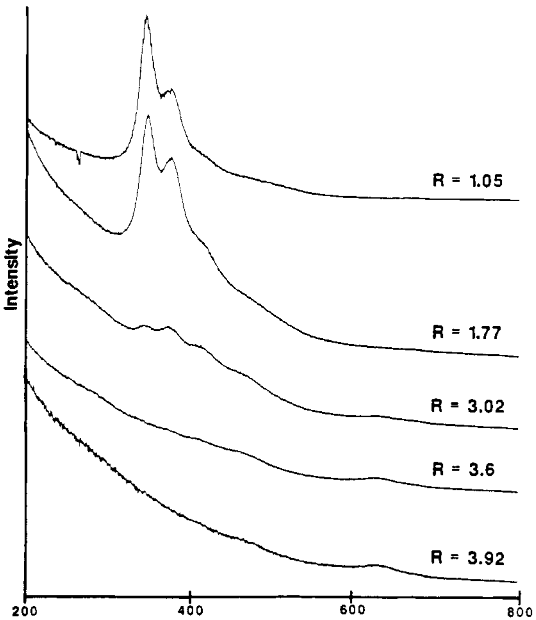

Figure 1. Raman spectra of several solutions of $NaAlCl_4$ in LiCl/NaF (80/20 mol %) mixtures (temperature 580 °C). The symbol *R* represents the formal ratio of NaF to $NaAlCl_4$.

If this is correct, the 375-cm^{-1} band should correspond to the species most likely to be present when the amounts of NaF and $NaAlCl_4$ are nearly equal, i.e. $AlCl_3F^-$, and the 416-cm^{-1} band to a species with more chloride exchanged for fluoride, i.e. $AlCl_2F_2^-$. In order to check this hypothesis, various mixtures were made by further diluting $NaAlCl_4$ with the solvent, thus increasing the ratio *R*. The resulting spectra, presented in Figure 1, exhibit other new, albeit very weak, bands found at 470 and 632 cm^{-1}. The 632-cm^{-1} band is almost certainly the ν_1 band of AlF_4^- (again shifted due to the effect of Li^+), and the 470-cm^{-1} band is probably due to the same vibration of the ion $AlClF_3^-$. The variation of the ν_1 band intensities as a function of *R* is consistent with a progressive replacement of Cl^- in $AlCl_4^-$ with F^- and a strong decrease in the molar scattering efficiency of each $AlCl_{4-n}F_n^-$ species as *n* increases.

Since the presence of Li^+ ion produces a large background and distorts the bandwidth and frequency of ν_1 bands,[16] solutions of $NaAlCl_4$ were made by using melts containing only Na^+ as the cation. For the system NaCl–NaF, a eutectic exists at 66 mole % of NaCl, which melts as 675 °C.[14] A solvent with the composition NaCl–NaF (60/40 mol %) was chosen for the following reasons. First, it allows a ratio $R = 1$ with a higher content of $NaAlCl_4$, thus increasing the intensity of the spectra. Second, the following exchange reaction is expected to produce a large amount of NaCl so that the resulting solution is far different from the initial solvent:

$$NaAlCl_4 + nNaF \rightleftharpoons NaAlCl_{4-n}F_n + nNaCl \qquad (1)$$

Despite the higher melting temperature of such solutions (820 °C, which is above the melting point of NaCl), much better spectra were obtained (Figure 2). The bands are sharper and are better defined; however, a similar variation of the band intensities as a function of the composition was observed as for mixtures with LiCl/NaF. Even better spectra were obtained by simply using mixtures of pure $NaAlCl_4$ with increasing amounts of NaF (Figure 3). In this case the spectra are more intense and the background in the low-frequency range is much lower, allowing the observation

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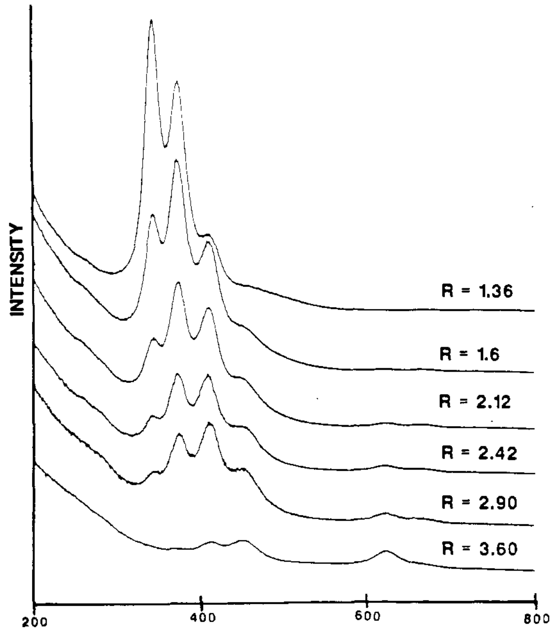

Figure 2. Raman spectra of several solutions of $NaAlCl_4$ in NaCl/NaF (60/40 mol %) mixtures (temperature 820 °C).

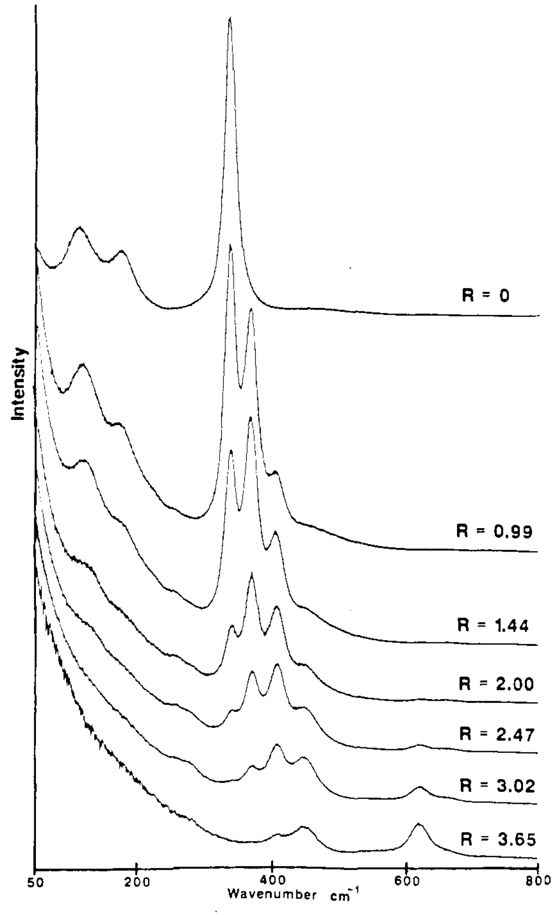

Figure 3. Raman spectra of several molten mixtures of $NaAlCl_4$ with NaF (temperature 820 °C). For the spectrum of pure $NaAlCl_4$ the laser power was 40 mW; for the other spectra the power was 200 mW. All other experimental conditions were kept identical.

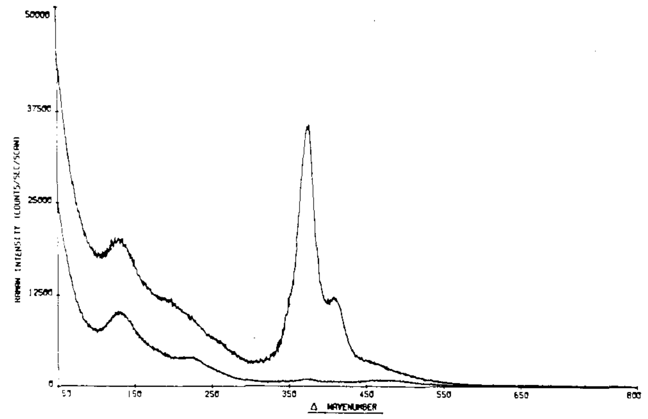

Figure 4. Raman spectra of the mixture of $NaAlCl_4$ with NaF (R = 0.99) from which the spectrum of $AlCl_4^-$ has been quantitatively subtracted: (upper curve) polarization parallel; (lower curve) polarization perpendicular.

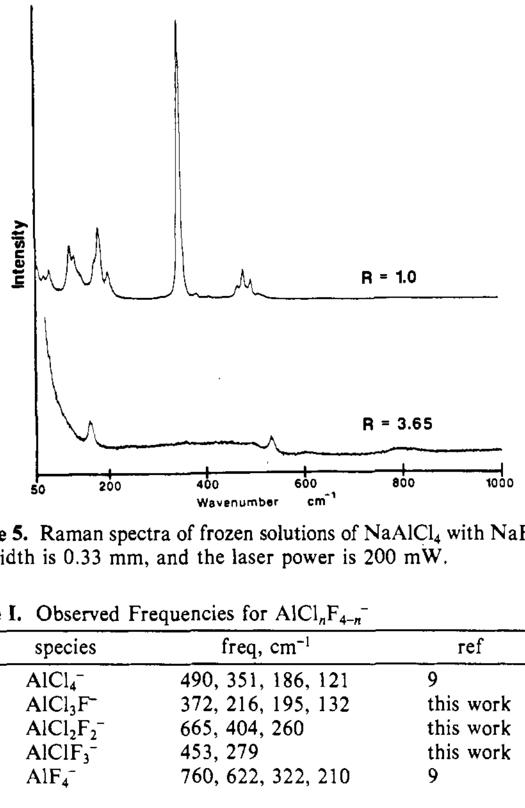

Figure 5. Raman spectra of frozen solutions of $NaAlCl_4$ with NaF. This slit width is 0.33 mm, and the laser power is 200 mW.

Table I. Observed Frequencies for $AlCl_nF_{4-n}^-$

species	freq, cm^{-1}	ref
$AlCl_4^-$	490, 351, 186, 121	9
$AlCl_3F^-$	372, 216, 195, 132	this work
$AlCl_2F_2^-$	665, 404, 260	this work
$AlClF_3^-$	453, 279	this work
AlF_4^-	760, 622, 322, 210	9

of several new low-frequency bands.

Digital subtraction of the Raman spectra was used to enhance the presentation of the spectra of the new species. The spectrum of pure $NaAlCl_4$ was recorded under conditions identical with those used for the spectra presented in Figure 3. This $NaAlCl_4$ reference spectrum was then scaled and subtracted from the spectra of Figure 3 in such a way that the ν_1 band of $AlCl_4^-$ vanished without any distortion of the background. This allowed several features in the spectra of the new species to be clearly observed. Figure 4 presents the results of such a subtraction where the major features of $AlCl_3F^-$ (with a small amount of $AlCl_2F_2^-$) can be identified. Table I presents all of the new frequencies found and their assignment to each of the species. This assignment was made by considering the variation of intensity with R and the results of the subtraction technique.

After spectra of the molten solutions were recorded, the solutions were cooled to room temperature and spectra of the frozen solutions were recorded. Examples of such spectra are shown in Figure 5. The sample whose spectrum is presented in the top of the figure contained equimolar amounts of NaF and $NaAlCl_4$, yet the spectrum corresponds very closely to the spectrum of $NaAlCl_4$ at room temperature obtained by Wallart et al.[17] When R is increased, the intensity of the spectrum of $NaAlCl_4$ decreases; it is replaced by two very weak bands at 156 and 531 cm^{-1}. These bands belong to AlF_6^{3-},[18] indicating that neither the mixed

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Table II. Calculated Mole Fractions for $AlCl_nF_{4-n}^-$

ratio	$X(AlCl_4^-)$	$X(AlCl_3F^-)$	$X(AlCl_2F_2^-)$	$X(AlClF_3^-)$	$X(AlF_4^-)$
0.99	0.3	0.4	0.3		
1.44	0.14	0.3	0.39	0.17	
2.0	0.05	0.18	0.39	0.32	0.06
2.5	0.02	0.1	0.36	0.44	0.08
3.0		0.04	0.23	0.5	0.22

chloro–fluoro species nor AlF_4^- exists in the solid state.

Halogen Distribution Equilibria. In order to compare the intensities of the spectra of the various mixed-tetrahalide species, the spectra of the whole series of $NaAlCl_4$ + NaF mixtures were recorded with all experimental conditions kept as constant as possible, pure $NaAlCl_4$ at 820 °C being used as a standard of intensity. A quantitative evaluation of the equilibria relating the various species was performed on the basis of the following two assumptions: (1) The fluoride exchanges with chloride in a fashion similar to the exchange of bromide and iodide with chloride. The general reaction scheme follows reaction 1. (2) In each reaction mixture no free fluoride is present, which implies that reaction 1 is essentially quantitative. This assumption is based on the fact that mixtures with R greater than 4 very quickly attack the quartz container, whereas mixtures with R less than 4 do not.

Under these conditions the equilibria among the tetrahaloaluminates can be written as three disproportionation reactions:[5]

$$2AlCl_{4-n}F_n^- \rightleftharpoons AlCl_{3-n}F_{n+1}^- + AlCl_{5-n}F_{n-1}^- \qquad (2)$$

For these reactions n = 1, 2, 3, and K_1, K_2, and K_3 are the corresponding equilibrium constants.

The analysis of these equilibria has been carried out in a stepwise fashion. Consideration of the first mixture of Figure 3 (R = 0.99) shows that there is apparently no $AlClF_3^-$ present. This implies that only the equilibrium where n = 1 should be considered for this mixture. From the relative intensity of the ν_1 band of $AlCl_4^-$ in the mixture, compared to that of pure $NaAlCl_4$, the mole fraction X of $AlCl_4^-$ in the mixture can be deduced, if the mole fractions are expressed in terms of 1 mol of total aluminum halide. Since there is apparently no $AlClF_3^-$, $X(AlCl_4^-) = X(AlCl_2F_2^-)$. Finally, $X(AlCl_3F^-)$ was deduced from mass balance. These calculations give the mole fractions of the species present in this mixture; these mole fractions, together with the intensities of the bands for the various species, were used to calculate the relative Raman scattering coefficients for the various species.[10] These relative scattering coefficients were then used to calculate the mole fractions of $AlCl_4^-$, $AlCl_3F^-$, and $AlCl_2F_2^-$ in the next mixture. A similar procedure was applied to the other mixtures, allowing the compositions of all the mixtures to be calculated. The results of this analysis are presented in Table II.

The averaged values for the equilibrium constants K_n were found to be $K_1 = 0.59 \pm 0.02$, $K_2 = 0.35 \pm 0.02$, and $K_3 = 0.19 \pm 0.04$. The relative scattering coefficients were found to be 135.4 (n = 0), 79.8 (n = 1), 25.8 (n = 2), 10 (n = 3), and 8 (n = 4).

It can be observed that the trend in the equilibrium constants observed here follows nearly the trend observed in the case of mixed chlorobromoaluminates. It does not correspond exactly to a purely random distribution, indicating stronger bonding between aluminum and fluoride. Fluoride ion exchanges very readily with chloride to form more stable fluoroaluminate complexes. Also, the trend observed in the scattering coefficients when n increases is expected, considering the much lower polarizability of an Al–F bond versus that of an Al–Cl bond.

As a general conclusion it is interesting to recall that the investigated mixtures do not attack quartz sample cells, provided that the ratio of total fluoride to aluminum does not exceed 4. This also means that the activity of the fluoride ion (which cannot be calculated from our Raman data) must be very low in these composition ranges and rises sharply when the ratio exceeds 4. In addition, by carefully choosing the composition range, it should be possible to study the behavior of various solutes in the presence of aluminum fluoride with much less experimental difficulty than with pure fluoride melts.

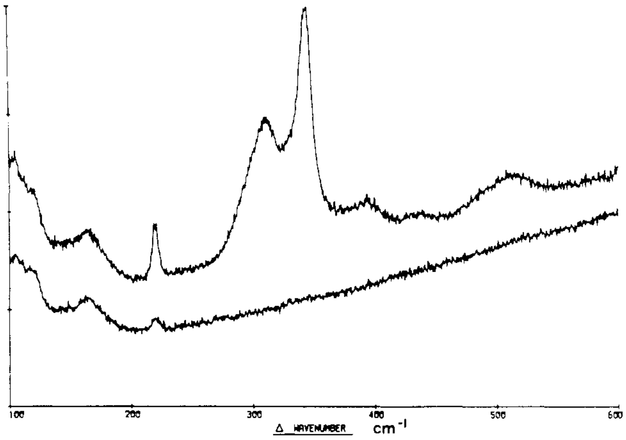

Figure 6. Raman spectra of molten Al_2Cl_6 saturated with NaF (temperature 205 °C): (upper curve) polarization parallel; (lower curve) polarization perpendicular.

Acidic Chloroaluminates. The influence of NaF on the Raman spectra of acidic chloroaluminates (that is, melts where the molar ratio of $AlCl_3/NaCl$ is greater than 1) has also been studied. Tremillon and Duchange[8] have shown from electrochemical measurements that F^- ion added to acidic chloroaluminate melts acts as a dibase. The proposed reaction is

$$2Al_2Cl_7^- + F^- \rightarrow Al_2Cl_6F^- + 2AlCl_4^- \qquad (3)$$

If indeed $Al_2Cl_6F^-$ is formed, it should exhibit a characteristic Raman spectrum that, in a favorable case, should show if the F atom is occupying a terminal or bridging position. Since the Raman spectrum of 63/37 mole % $AlCl_3/NaCl$ mixture is already quite complex (it contains bands due to $Al_2Cl_7^-$, $AlCl_4^-$, and Al_2Cl_6[19]), NaF was simply added to pure Al_2Cl_6. Figure 6 shows the Raman spectrum of a saturated solution of NaF in Al_2Cl_6 at 200 °C. In addition to Al_2Cl_6 bands at 102, 118, 166, 218, 341, and 512 cm⁻¹, four new bands are observed, at 312, 395, 437, and 489 cm⁻¹, all of which are totally polarized. These four new bands are located at frequencies nearly equal to several of the bands of $Al_2Cl_7^-$, but the respective intensities and bandwidths are not the same. For example, the 389-cm⁻¹ band of $Al_2Cl_7^-$ is clearly depolarized[20] whereas the 395-cm⁻¹ band shown here is polarized.

The nature of the products of the reaction between aluminum chloride and sodium fluoride that are responsible for these new bands will now be discussed. The two most likely candidates for the products are $Al_2Cl_6F^-$ or a mixture of $Al_2Cl_7^-$ and Al_2Cl_5F. These species could be formed by the reaction

$$Al_2Cl_6 + NaF \rightarrow Al_2Cl_6F^- + Na^+ \qquad (4)$$

or

$$Al_2Cl_6 + NaF \rightarrow Al_2Cl_5F + NaCl \qquad (5)$$

and

$$Al_2Cl_6 + NaCl \rightarrow Al_2Cl_7^- + Na^+ \qquad (6)$$

In the former case the product would be similar to $Al_2Cl_7^-$ with one of the chlorines replaced with a fluorine, while in the latter the product would be similar to Al_2Cl_6 with one of the chlorines replaced with a fluorine. While it is unlikely for a species like Al_2Cl_5F to exist in the presence of excess Cl^- (a basic melt), its possible existence in the acidic systems discussed here is not so easily dismissed. In either case it seems that the replacement occurs at a terminal chlorine, not a bridging one. There are two arguments in favor of this assumption: The spectrum of this mixture is very similar to that of acidic chloroaluminate melts,

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Table III. Force Field for $AlCl_nF_{4-n}^-$

force const	interpretation	value
F_1	Al–F str	3.393 mdyn/Å
F_2	Al–Cl str	1.658 mdyn/Å
F_3	Cl–Al–Cl bend	0.7081 mdyn Å/rad^2
F_4	Cl–Al–F bend	0.6124 mdyn Å/rad^2
F_5	F–Al–F bend	0.6784 mdyn Å/rad^2
F_6	Al–F:Al–F str–str	0.3437 mdyn/Å
F_7	Al–Cl:Al–Cl str–str	0.2912 mdyn/Å
F_8	Al–Cl:Al–F str–str	0.8076 mdyn/Å
F_9	X–Al–X:X–Al–X bend–bend[a]	–0.2311 mdyn Å/rad^2

[a] X = F or Cl.

indicating that the species present in the two melt systems must have similar structures; much larger differences would be expected for a bridged substitution. Also, it is important to note that *all* of the new bands are polarized; this implies a rather low symmetry for the reaction product. If the product were $Al_2Cl_6F^-$ with the fluorine as the bridge, the relatively small size of fluorine would favor a linear Al–F–Al structure, giving rise to D_{3h} or D_{3d} symmetry for the product.[21] It is unlikely that all of the observed bands would be polarized in such a case. A similar argument applies for the Al_2Cl_5F case: bridge substitution would give rise to a species with C_{2v} symmetry, and again it is unlikely that all of the observed bands would be polarized. For these reasons only F terminal species will be considered further. Hence, the question to be answered here is as follows: Is $Al_2Cl_6F^-$ or Al_2Cl_5F, both with terminal fluorines, present in the aluminum chloride/sodium fluoride mixtures?

Normal-coordinate calculations were made to determine approximate valence force fields for $Al_2Cl_7^-$ and Al_2Cl_6 with use of vibrational data from Manteghetti and Potier[22] and Tomita et al.[23] Similar calculations were carried out for $AlCl_4^-$, $AlCl_3F^-$, $AlCl_2F_2^-$, $AlClF_3^-$, and AlF_4^-, with use of data from this work and from Gilbert et al.[9] In addition to these calculations, a similar force field for AlF_3 was developed with use of the IR data of Snelson.[24] Appropriate valence force constants for Al–F and Cl–Al–F motions were then used together with the force fields for $Al_2Cl_7^-$ and Al_2Cl_6 to calculate frequencies for $Al_2Cl_6F^-$ and Al_2Cl_5F. The normal-coordinate calculations were carried out on an IBM XT personal computer, using a modified version[25] of the QCPE program No. 342. For the species whose structures were not known ($Al_2Cl_6F^-$ and Al_2Cl_5F), geometric parameters needed for the normal-coordinate calculations were obtained from semiempirical (MNDO Hamiltonian) molecular orbital calculations.[26] It should be emphasized that the results of the normal-coordinate calculations described should not be considered an accurate description of the potential energy of the species involved; they are quite approximate. The force field calculated for $Al_2Cl_7^-$ was able to reproduce 12 known frequencies with an rms error of 15.6 cm^{-1}; the calculation for Al_2Cl_6 was able to reproduce 16 known frequencies with an rms error of 9.1 cm^{-1}. Since the purpose of the calculations was to transfer force constants from the $AlCl_nF_{4-n}^-$ ions to either of the dialuminum species, the force fields used for the latter contained only bond-stretching and bond-angle-bending diagonal force constants, since these are the types calculated for the mononuclear ions. The force fields in ref 22 and 23 are more accurate since they include torsion and ring-puckering coordinates as well.

Table IV. Calculated Frequencies for Al_2Cl_xF

	$Al_2Cl_6F^-$		Al_2Cl_5F	
obsd	calcd	error	calcd	error
489	509.9	20.9	506.7	17.7
437	449.3	12.3	412.0	–25.0
393	364.4	–28.6	338.4	–54.9
311	290.8	–20.2	318.0	8.0
rms error		21.3		31.3, 31.9[a]

[a] The calculation giving this result used the Al–F stretching force constant derived from the fit of AlF_3 IR data.

A 9-parameter force field (5 diagonal and 4 interaction force constants) was developed that could fit the 17 known frequencies for the $AlCl_nF_{4-n}^-$ ions with an average rms error of 13.8 cm^{-1} for all five ions. Either of the two possible dialuminum species contains a single F atom; this implies that force constants from $AlCl_4^-$ and $AlCl_3F^-$ will be more important for this calculation than constants from other species. The force field for the tetrahaloaluminates gave less than 4 cm^{-1} error for $AlCl_4^-$ and $AlCl_3F^-$. The force constants are presented in Table III. In Table IV the results of transferring the appropriate force constants from Table III into the force fields for $Al_2Cl_7^-$ and Al_2Cl_6 to calculate the frequencies for $Al_2Cl_6F^-$ and Al_2Cl_5F are presented. It can be seen that the frequencies associated with the product of the reaction between Al_2Cl_6 and NaF are more closely matched with the frequencies calculated for $Al_2Cl_6F^-$. It may be argued that it is not appropriate to transfer force constants for an anion into the calculation of frequencies for a neutral species, such as Al_2Cl_5F. To address this point, the frequencies for Al_2Cl_5F were also calculated with use of the Al–F stretching force constant derived from the treatment of AlF_3; the error for this calculation is also presented in Table IV. Even when this possible source of error is included, it still seems that the predominant species is likely to be $Al_2Cl_6F^-$. While this does not constitute definite proof of the existence of $Al_2Cl_6F^-$ in this system, the vibrational data favor its existence.

This is also consistent with the chemistry observed for the chloroaluminate systems: the reaction to form $Al_2Cl_6F^-$ is an acid–base reaction very much like the one that results in the formation of $Al_2Cl_7^-$. The reaction that forms Al_2Cl_5F is a ligand-exchange reaction similar to the ones that result in the formation of $AlCl_nF_{4-n}^-$; such reactions are expected in these systems, but only at rather high temperatures. For these reasons it is the opinion of the authors that $Al_2Cl_6F^-$ ion is formed by the reaction between aluminum chloride and sodium fluoride in the 200 °C temperature range.

Conclusions

Quartz sample tubes may be used for Raman studies of fluoride-containing chloroaluminate melts, at temperatures up to 850 °C, provided that the molar ratio of fluorine to aluminum does not exceed 4. In basic melts of this type the new species $AlCl_3F^-$, $AlCl_2F_2^-$, and $AlClF_3^-$ were observed; halide ion distribution equilibrium constants indicate that aluminum–fluoride bonding is somewhat stronger than bonding between aluminum and other halogens. Acidic fluoride-containing chloroaluminate melts show spectroscopic evidence for the presence of the previously proposed species $Al_2Cl_6F^-$.

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