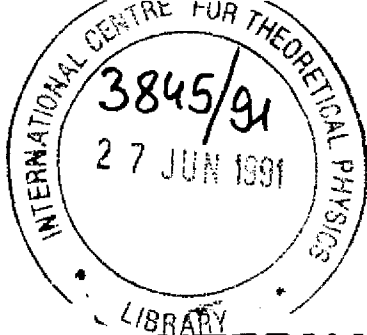


REFERENCE



**INTERNATIONAL CENTRE FOR  
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ALKALI HALIDE MELTS**

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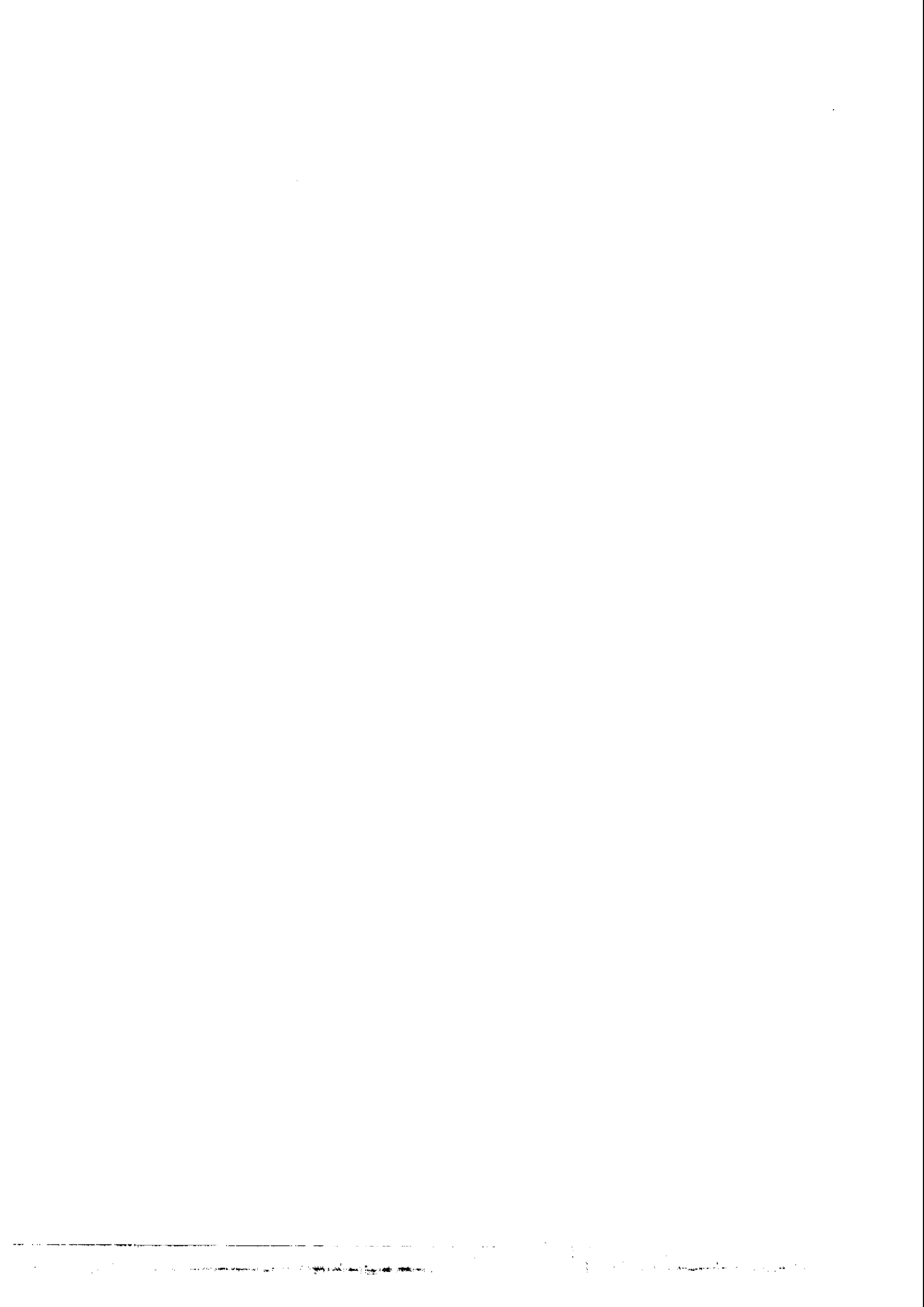


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INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS

**COMPLEXES IN POLYVALENT METAL – ALKALI HALIDE MELTS**

Z. Akdeniz

International Centre for Theoretical Physics, Trieste, Italy  
and  
Department of Physics, University of Istanbul, Istanbul, Turkey

and

M.P. Tosi

International Centre for Theoretical Physics, Trieste, Italy  
and  
Department of Theoretical Physics, University of Trieste, Italy.

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## ABSTRACT

Experimental evidence is available in the literature on the local coordination of divalent and trivalent metal ions by halogens in some 140 liquid mixtures of their halides with alkali halides. After brief reference to classification criteria for main types of local coordination, we focus on statistical mechanical models that we are developing for Al-alkali halide mixtures. Specifically, we discuss theoretically the equilibrium between  $(\text{AlF}_6)^{3-}$  and  $(\text{AlF}_4)^-$  complexes in mixtures of  $\text{AlF}_3$  and  $\text{NaF}$  as a function of composition in the  $\text{NaF}$ -rich region, the effect of the alkali counterion on this equilibrium, the possible role of  $(\text{AlF}_5)^{2-}$  as an intermediate species in molten cryolite, and the origin of the different complexing behaviours of Al-alkali fluorides and chlorides. We also present a theoretical scenario for processes of structure breaking and electron localization in molten cryolite under addition of sodium metal.

## 1. INTRODUCTION

Neutron diffraction studies of liquid structure have been carried out in recent years on a number of polyvalent metal halides and have in several cases shown the existence of intermediate range order appearing through a prepeak at wavenumber  $k \approx 1 \text{ \AA}^{-1}$  in the liquid structure factor. This type of order, which is also well known in other strongly structured liquids and in glassy materials [1], arises in the molten salt from the connectivity of well defined local coordinations of the polyvalent metal ions. We may mention as examples  $\text{ZnCl}_2$ , having a network-like structure from corner-sharing tetrahedral coordination in both the melt [2] and the glass [3], and molten  $\text{YCl}_3$ , which shows intermediate range order associated with edge-sharing octahedral-type coordination of the Y ions [4].

It is of interest to relate the structural evidence on pure molten salts of polyvalent metals with the ample evidence on their liquid mixtures with alkali halides. The alkali halide component acts as a halogen donor to break the connectivity leading to intermediate range order and to allow formation of

separate local coordination units for the polyvalent metal ions. Some 140 such liquid mixtures have been examined over the years by appropriate experimental probes, involving diffraction in a few systems but mostly Raman scattering, infrared absorption and emission, optical absorption from electronic transitions, and thermodynamic measurements [5].

The main alternative possibilities for the local coordination of polyvalent metal ions in halide mixtures are (i) long-lived fourfold "complexes" (e.g. for  $Zn^{2+}$  [6] and  $Mg^{2+}$  [7]), (ii) long-lived sixfold "complexes" (e.g. for  $Y^{3+}$  [8]), and (iii) loose fluctuating coordination (e.g. for  $Sr^{2+}$  and  $Ba^{2+}$  [9]). These types of coordination have been successfully classified [5] in terms of elemental properties of the mixture components, using a phenomenological chemical scale of the elements that had been earlier developed by Pettifor [10] for the purpose of sorting the crystal structures of binary stoichiometric compounds. The chemical scale orders the elements along a single axis  $\chi$  so that the Mendeleev-type features of the periodic table are preserved. Structural coordinates are constructed for each M-A(X) mixture from the elemental property  $\chi$  as  $X_{M-A(X)} = \chi_M - \chi_A$  and  $Y_{M-A(X)} = \chi_M + \chi_A - 2\chi_X$  (with M = polyvalent metal, A = alkali and X = halogen). It is then found that M-A(X) mixtures with similar coordination type group together in distinct regions of the (X, Y) plane.

Within the general frame provided by structure sorting, a number of liquid mixtures are of special interest and deserve microscopic evaluation. To convey the flavour of such theoretical work on a relatively simple problem, one may ask whether in the  $CaCl_2 \cdot 2KCl$  melt tetrahedral  $(CaCl_4)^{2-}$  complexes will form and persist over times at least as long as typical diffusional times (of order  $10^{-11}$  s). This question may be tackled theoretically by evaluating the reaction  $(CaCl_4)^{2-} \leftrightarrow Ca^{2+} + 4Cl^-$  in the dense liquid medium. The dissociation free energy (which selfconsistently depends on the concentration of complexes) is determined by a balance between the binding free energy of the complex and the change in interaction free energy of the components of the liquid on dissociation of a complex. We evaluate these two free energies [11] by the simplest possible theoretical means that we still believe are of semiquantitative usefulness. On the one side, we evaluate the binding free energy by treating the complex in vacuo by a polarizable-ion model, thus allowing both for the effects of ionic charges and sizes and, to some extent, for the effect of chemical bonding. On the other side, we treat the liquid by a statistical mechanical approach involving the mean spherical approximation (MSA) for a mixture of charged hard spheres [12]. While such methods cannot yield fully reliable answers to quantitative questions, they appear to be adequate for assessing trends and underlying physical factors.

In the problem at hand, insofar as the binding of  $(CaCl_4)^{2-}$  is mainly ionic and the effect of the liquid medium is primarily the screening of  $(CaCl_4)^{2-}$  complexes by free  $K^+$  ions, the balance between the above free energies is inversely equivalent to a balance between the cation-anion distance  $d$  within a complex and the screening length  $L$  of the liquid. Appeal to Mott's criterion for the stability of a bound state in a conducting fluid then suggests that complexes are stable if the ratio  $L/d$  is larger than some critical value [13]. The MSA calculation estimates  $L$  for various melts and indicates that the

Table 1. Range of  $L/d$  for polyvalent metal-alkali chloride mixtures on varying the alkali A from Li to Cs

	$AlCl_3 \cdot ACl$	$BeCl_2 \cdot 2ACl$	$MgCl_2 \cdot 2ACl$	$CaCl_2 \cdot 2ACl$	$SrCl_2 \cdot 2ACl$	$BaCl_2 \cdot 2ACl$
$L/d$	1.74+1.80	1.79+1.85	1.66+1.72	1.56+1.61	1.52+1.57	1.48+1.53

critical value of  $L/d$  is approximately 1.6 for molten salt mixtures. Table 1 shows that this critical ratio separates the alkaline earth - alkali chlorides into complex forming (Be and Mg) and non-forming (Sr and Ba), with fluctuations between fourfold and higher coordinations being expected in the systems close to it (Ca). The results of this stability sorting criterion are in agreement with the available Raman scattering evidence [9]. The Table includes also the Al-alkali chloride mixtures, in which the  $(AlCl_4)^-$  coordination is well known to be strongly stable [14-16].

## 2. ALUMINIUM-ALKALI FLUORIDE MIXTURES

As shown by Gilbert, Mamantov and Begun [17], the Raman scattering spectrum of molten  $(AlF_3)_c-(NaF)_{1-c}$  and other Al-alkali fluoride mixtures, in the composition range  $0.375 \leq c < 0.5$ , contains two distinct peaks with relative intensity varying with composition. These observations were interpreted as reflecting a gradual conversion of  $(AlF_4)^-$  into  $(AlF_6)^{3-}$  with decreasing  $c$ . It was further reported [17] that in molten cryolite ( $Na_3AlF_6$ , i.e.  $c = 0.25$ ) at  $T = 1288$  K the Raman spectrum contains a main peak, that was attributed to the  $(AlF_6)^{3-}$  species, with a high-frequency shoulder due to the  $(AlF_4)^-$  species in relative concentration of order 20+25%. Very recently Gilbert and Materne [18] have reported Raman scattering spectra from  $(AlF_3)_c-(NaF)_{1-c}$  in the composition range  $c \leq 0.25$ . They show that the distribution of intensity under the main peak undergoes shifts on decreasing  $c$  below  $c = 0.25$ . They attribute this observation to the presence of two bands under the main peak, that they separate by suitable fitting procedures, and propose as the most probable explanation for these two bands an ionic equilibrium between  $(AlF_6)^{3-}$  and  $(AlF_5)^{2-}$  species. They also show that the high-frequency shoulder attributed to the  $(AlF_4)^-$  species in molten  $Na_3AlF_6$  is no longer seen on replacing Na by Li and is resolved as a separate peak on replacing Na by K.

Let us consider first the dissociation equilibrium  $(AlF_6)^{3-} \leftrightarrow (AlF_4)^- + 2F^-$  in the  $(AlF_3)_c-(NaF)_{1-c}$  melt, without allowing for the possible presence of a long-lived  $(AlF_5)^{2-}$  intermediate species [19]. The equilibrium at temperature  $T$  and molar volume  $v$  is determined by the equation

$$\frac{x_6}{x_4 x_F^2} = \left( \frac{h^2}{2\pi k_B T v^{2/3}} \right)^3 \left[ \frac{m_{Al} + 6m_F}{(m_{Al} + 4m_F) m_F^2} \right]^{3/2} \exp \left[ - \frac{F_{64}(x_6)}{k_B T} \right] \quad (1)$$

where  $x_6$ ,  $x_4 = c - x_6$  and  $x_F = 1 - 2c - 2x_6$  are the molar fractions of  $(AlF_6)^{3-}$ ,  $(AlF_4)^-$  and free  $F^-$  ions, the  $m$ 's are the atomic masses and

$$F_{64}(x_6) = f_{64} + \left( \frac{\partial F_{ex}}{\partial x_6} \right)_{T,v,c} \quad (2)$$

The first term on the right-hand side of equation 2 is the difference in binding free energy of the two species in vacuo, while the second term arises from the excess free energy  $F_{ex}$  of the melt, due to the interactions between all its components, and is the change of  $F_{ex}$  on dissociation of an  $(AlF_6)^{3-}$  unit. This second contribution tends to stabilize the more highly charged species in the melt, whereas in vacuo these species are unstable against dissociation into the singly charged species and  $F^-$  ions.

The calculation thus starts with an estimate of the binding of isolated complexes (see Table 2). Screening in the melt suffices to stabilize  $(AlF_6)^{3-}$  relative to  $(AlF_4)^-$ , leading to only partial dissociation of the more highly charged species in substantial agreement with the data of Gilbert *et al.* [17].

Table 2. Estimated properties of isolated  $(\text{AlX}_4)^-$ ,  $(\text{AlX}_5)^{2-}$  and  $(\text{AlX}_6)^{3-}$  units

	$(\text{AlF}_4)^-$	$(\text{AlF}_5)^{2-}$	$(\text{AlF}_6)^{3-}$	$(\text{AlCl}_4)^-$	$(\text{AlCl}_6)^{3-}$
Assumed shape	tetrahedron	bipyramid	octahedron	tetrahedron	octahedron
Al-X bond length (Å)	1.71	1.78, 1.81(a)	1.90	2.15	2.39
Binding rel. to $(\text{AlX}_6)^{3-}$ (kcal/mol)	229.	173.	---	239.	---
Polariz. energy <sup>(b)</sup> (kcal/mol)	45.	19.	---	106.	---

(a) For  $\text{F}^-$  ions in the basal plane and at the apices of a trigonal bipyramid, respectively.

(b) Contribution to the binding from electronic polarization of the halogens, relative to  $(\text{AlX}_6)^{3-}$ .

Stabilization by screening increases with decreasing size of the alkali counterion [20], thus accounting for the observations of Gilbert and Materne [18] on the effects of replacing Na by Li or K in the molten fluoroaluminates. The halogen size effect, instead, largely cancels out from the combination of the two terms in equation 2. The origin of the different complexing behaviours of Al-alkali fluorides and chlorides is to be found in the large stabilization energy of  $(\text{AlCl}_4)^-$  from electronic polarization of the chlorines (see Table 2). As a consequence  $(\text{AlCl}_6)^{3-}$  remains completely unstable against dissociation in the melt [19].

Dissociation of an  $(\text{AlF}_6)^{3-}$  unit in the dense liquid medium may be visualized as a series of microscopic diffusion steps in which two  $\text{F}^-$  ions leave the first coordination shell of the  $\text{Al}^{3+}$  ion to join the excess alkali ions in the next coordination shell and to undergo further diffusional rearrangements. A long-lived intermediate  $(\text{AlF}_5)^{2-}$  species would imply a rather specific kinetics of the dissociation process, in which the two  $\text{F}^-$  ions are released over sufficiently different time scales for the intermediate state to attain equilibrium. Assuming that the kinetics is of the necessary type, the above calculations have recently been extended to examine the thermodynamic stability of an  $(\text{AlF}_5)^{2-}$  intermediate species in molten cryolite at 1288 K [20]. The calculations on isolated units (see Table 2) suggest a binding for  $(\text{AlF}_5)^{2-}$  which is closer to  $(\text{AlF}_4)^-$  than to  $(\text{AlF}_6)^{3-}$ , owing also to an appreciable stabilization from halogen polarization. However, stabilization by screening in the melt is also appreciably smaller than for  $(\text{AlF}_6)^{3-}$ . Although the balance of free energies is too delicate to draw firm conclusions on such a quantitative issue from our crude estimates, our best *a priori* estimates fail to provide theoretical support for the proposal of a long-lived  $(\text{AlF}_5)^{2-}$  species in the melt.

### 3. STRUCTURE BREAKING AND ELECTRON LOCALIZATION IN CRYOLITE-SODIUM METAL SOLUTIONS

Solutions of metals in molten salts are among the several classes of liquid systems which undergo a transformation from a nonmetallic to a metallic state on changing some thermodynamic variable. In alkali metal - alkali halide mixtures [21-23] the electrical conductivity above the consolute critical temperature increases gradually as the nature of the states for electronic carriers evolves with increasing metal concentration. At high metal dilution single electrons are trapped in localized states partaking of F-centre and polaron character, in the sense that localization occurs at favourable

fluctuations of potential via a substantial rearrangement of the local liquid structure. Such single-electron states are next rapidly replaced by spin-paired electron states, which further appear to evolve towards small fluctuating clusters of metal. The transition to a metallic state for the liquid as a whole is most strikingly signalled by a dielectric anomaly and appears to develop at metal concentrations appreciably below the critical concentration for demixing.

Much less attention has been given to electron localization in metal - molten salt solutions involving polyvalent metals. As a broad trend, and in correlation with the character of the liquid structure of the pure salt, one should expect that, as one proceeds through polyvalent metals along a path set by Pettifor's  $\chi$  scale, electron localization in the salt-rich region should occur by simultaneous reconstruction of local liquid structure and of chemical bonding. As an example one may mention the Hg-HgCl<sub>2</sub> system, which may be viewed as a nonmetallic mixture of HgCl<sub>2</sub> and Hg<sub>2</sub>Cl<sub>2</sub> in the composition range up to that of the 'subhalide' Hg<sub>2</sub>Cl<sub>2</sub> and as an Hg-Hg<sub>2</sub>Cl<sub>2</sub> solution at still higher metal concentration [21]. The appearance of such lower oxidation states for a polyvalent metal will shift the nonmetal-metal transition and the liquid-liquid miscibility gap towards the metal-rich side of the phase diagram.

A microscopic model for processes of structure breaking accompanied by the formation of reduced oxidation states has recently been evaluated in the specific case of solutions of sodium metal in molten cryolite [24]. In an effort to clarify the relative roles of Al and Na in the cathodic processes involved in the industrial production of Al metal from electrolytic baths containing cryolite, Grjotheim [25] exposed molten cryolite to sodium vapour and found that, after prolonged annealing followed by cooling, specks of Al metal were deposited in the frozen salt matrix. In thermodynamic calculations relating to this experiment, he suggested a role for monovalent Al. Grjotheim also enquired about the origin of the so-called "metal mist" and emission of gas bubbles that occur on adding various metals to molten cryolite. This experiment was later extended by Haupin [26], who reached the conclusion that on adding Al metal the "metal mist" forms in the presence of moisture and consists of hydrogen bubbles containing small partial pressures of AlF, NaAlF<sub>4</sub> and Na. These experiments indicate that the processes occurring on addition of sodium involve transfer of electrons from Na to Al in the melt, with formation of Al ions in a monovalent state and enhancement of the (AlF<sub>4</sub>)<sup>-</sup> structural units.

On assuming that the sodium metal enters molten cryolite in the form of Na<sup>+</sup> ions and electrons, our calculations [24] demonstrate how these added components break up the structure of the ionic melt to yield electron localization by the formation of Al ions in reduced valence states. The equilibrium state of the melt is equivalent to a set of dissociation reaction equilibria in the dense liquid matrix, restricted by the availability of valence electrons. The relevant reaction equilibria that we consider are (AlF<sub>6</sub>)<sup>3-</sup>  $\leftrightarrow$  (AlF<sub>4</sub>)<sup>-</sup> + 2 F<sup>-</sup>, (AlF<sub>4</sub>)<sup>-</sup> + e  $\leftrightarrow$  Al<sup>2+</sup> + 4 F<sup>-</sup> and (AlF<sub>4</sub>)<sup>-</sup> + 2 e  $\leftrightarrow$  Al<sup>+</sup> + 4 F<sup>-</sup>. Each of these reactions is described by its appropriate law of mass action, with an activation free energy which depends selfconsistently on the concentrations of the various species. It is found that with increasing Na metal content the equilibrium between (AlF<sub>6</sub>)<sup>3-</sup> and (AlF<sub>4</sub>)<sup>-</sup> shifts in favour of the latter, while at the same time Al<sup>3+</sup> ions are released into the melt and bind the available electrons to form Al<sup>2+</sup> and Al<sup>+</sup> ions. Eventually the latter oxidation state becomes the most stable one and the (AlF<sub>4</sub>)<sup>-</sup> complex is also destabilized. In fact, the enrichment of the melt in Na<sup>+</sup> ions suffices to shift the equilibrium between (AlF<sub>6</sub>)<sup>3-</sup> and (AlF<sub>4</sub>)<sup>-</sup> in favour of the latter. On the other hand, dissociation of (AlF<sub>4</sub>)<sup>-</sup> units, with a binding of order 1500 kcal/mol, can simultaneously occur only through the gain of free energy associated with electron localization on Al ions, which releases energies



corresponding to the third and second ionization potential of Al (644 kcal/mol and 405 kcal/mol, respectively). This scenario, which would be substantially unchanged by the inclusion of an  $(\text{AlF}_5)^{2-}$  species, is consistent with the forementioned macroscopic observations on the chemical products resulting from adding metals to molten cryolite [25, 26].

In summary, the processes that occur on addition of sodium metal to molten cryolite involve transfer of electrons from Na to Al in the melt, leading to Al ions in reduced valence states and to breaking of complexes. This specific system is illustrative of what one expects to be a rather general feature of electron localization in strongly structured molten salts: localization involving structure breaking should occur in such melts through reconstruction of chemical bonding.

#### 4. CONCLUDING REMARKS

We have illustrated in the foregoing the present state of the theory on rather complex molten salt systems and metal - molten salt solutions. The theory can provide classifications of the experimental evidence and crude semiquantitative scenarios for special systems, but is clearly not sufficiently developed to provide reliable quantitative help to the experimentalist. It should nevertheless be pointed out that the ideas that we have illustrated in our discussion can be further developed towards quantitative usefulness, through a combination of (i) quantum chemistry calculations on long-lived ionic species and metal clusters, and (ii) improved statistical mechanical theories, such as have been developed in the literature to treat simpler liquids.

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