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INTERNATIONAL CENTRE FOR
THEORETICAL PHYSICS

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AND ELECTRON LOCALIZATION
IN LIQUID CRYOLITE-SODIUM SOLUTIONS

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ABSTRACT

The continuous nonmetal-metal transition, which occurs on dissolving metals in molten salts, may be shifted to higher metal concentration in solutions involving polyvalent metal ions by the possibility that these metals go into lower oxidation states. We evaluate a microscopic model for these processes in the specific case of solutions of sodium metal in molten cryolite ($AlF_3 \cdot 3NaF$). The structure of the ionic melt is understood and calculable at the microscopic level in terms of a dominant sixfold-coordinated trivalent state of the Al ion (the $(AlF_6)^{3-}$ complex) with some admixture of a fourfold-coordinated trivalent state (the $(AlF_4)^-$ complex). The sodium metal is assumed to enter the ionic liquid in the form of monovalent ions and electrons. Our calculations demonstrate how these added components break up the structure of the ionic melt to yield localization by the formation of Al ions in reduced valence states, and provide order-of-magnitude estimates for the free energy changes involved in these processes. Specifically, we find that with increasing metal concentration the equilibrium between $(AlF_6)^{3-}$ and $(AlF_4)^-$ shifts in favour of the latter, while Al^{3+} ions are released in the melt and bind the available electrons to form Al^{2+} and Al^+ ions. The latter eventually become the most stable ones and also destabilize the $(AlF_4)^-$ complex. This scenario is consistent with available macroscopic observations. We also briefly discuss how the treatment could be extended to examine other events that may arise with increasing metal content, such as the formation of dimers or small metal clusters.

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. The equilibrium phase diagram of many of these systems and basic physical properties such as the electrical conductivity and the magnetic susceptibility as functions of composition were determined in early work summarized in the reviews of Bredig (1964) and Corbett (1964). These covered the alkali - alkali halide systems and a number of solutions of polyvalent (mainly alkaline earth, rare earth and post-transition) metals in their halides.

Considerable detail has since been added to the early data in the case of alkali - alkali halide solutions (Warren 1981 and 1985, Rovere and Tosi 1986, Freyland 1990). Most of these systems present a composition range of liquid-liquid immiscibility below a consolute critical temperature and are completely miscible on a macroscopic scale above it. Starting at such high temperature from the stoichiometric ionic salt, the electrical conductivity increases gradually as the nature of the localization state 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, a notable exception being the Bi - Bi halides (Warren 1985). A broad trend can already be recognized from the available data in Bredig's review. Starting from the alkaline earths as being immediately more chemically active than the alkalis, the observed behaviour of the electrical conductivity with metal concentration appears to correlate with the character of the liquid structures of pure alkaline earth chlorides, which have in the meantime been determined by neutron diffraction (McGreevy 1987). Thus, the conductivity in Ca - CaX_2 systems (X denoting a halogen) increases much more slowly than in Sr - SrX_2 and Ba - BaX_2 systems, while the liquid structure of $CaCl_2$ is intermediate in character between the loose ionic structures of $SrCl_2$ and $BaCl_2$ and those of network-forming liquids such as $ZnCl_2$. Naturally, electron localization should be stronger if it requires substantial local reconstruction of a molten salt structure with an appreciable connectivity of its own. Eventually, as one proceeds through polyvalent metals along a path set by a scale of chemical activity such as that proposed by Pettifor (1986), electron localization by reconstruction of chemical bonding will result. As an example we may mention the Hg - $HgCl_2$ system, which may be viewed as a nonmetallic mixture of $HgCl_2$ and Hg_2Cl_2 in the composition range up to the "subhalide" Hg_2Cl_2 and as a Hg - Hg_2Cl_2 solution at still higher metal concentration (Bredig 1964, Warren 1985). The stability of such lower oxidation states for a polyvalent metal broadens the nonmetallic range and shifts the liquid-liquid miscibility gap to the metal-rich side of the phase diagram.

We build in this paper a semiquantitative microscopic scenario for a further system in which electron localization by the formation of reduced valence states for polyvalent metal ions may be expected to occur. These are the Al ions in molten cryolite (Na_3AlF_6, or $AlF_3 \cdot 3NaF$) under addition of sodium metal in the assumed form of Na^+ ions and electrons. Our aim will be to illustrate in this specific system the interplay between the chemical localization of added electrons and the local breakage and reconstruction of a strongly connected molten salt structure.

A primary reason for our choice of system is the degree of understanding of the liquid structure of the ionic salt. Molten cryolite corresponds to a stoichiometric composition in a continuous range of liquid $(AlF_3)_c \cdot (NaF)_{1-c}$ mixtures. It is known from the Raman scattering spectra of these mixtures in the range $0.375 \leq c \leq 0.462$ at temperature $T \cong 1053K$ (Gilbert, Mamantov and Begun 1975) that they are structured into rather long-lived $(AlF_6)^{3-}$ octahedral units and $(AlF_4)^-$ tetrahedral units. The relative concentration of the former species is slightly below the ideal upper limit allowed by the available number of fluorines, which is $(1 - 2c)/2c$

for $1/4 \leq c \leq 1/2$. This fact indicates that each unit is essentially free in the liquid, rather than part of a fluorine-sharing network. The same experiments on molten cryolite at a somewhat higher temperature (T = 1288 K) show that the $(AlF_6)^{3-}$ units, which at this composition (c = 1/4) could ideally be the only ones present, have a degree of dissociation of 20÷25% into $(AlF_4)^-$ and F^- ions.

A quantitative account of all the above structural properties has recently been given within a simple ionic model (Akdeniz and Tosi 1990). The ionic equilibrium between long-lived $(AlF_6)^{3-}$ and $(AlF_4)^-$ units in the liquid is treated as resulting from a balance between the difference in binding free energy for the two species in vacuo and the change in the excess free energy of the liquid on dissociation of $(AlF_6)^{3-}$ into $(AlF_4)^-$ and two F^-. The former free energy is evaluated in an ionic model, whose validity is mainly tested through the Raman vibrational mode frequencies on the assumption that they are insensitive to the surroundings in such strongly bound units (Wang Li and Tosi 1988). The latter free energy is evaluated by a statistical mechanical theory of the liquid, involving a model of charged hard spheres treated in the mean spherical approximation (Waisman and Lebowitz 1972). Thus, having achieved a good theoretical description for the ionic structure of molten cryolite, we may feel some confidence that a suitable extension of the model will sensibly describe the effects of adding Na^+ ions and electrons.

In addition to the above, however, we should mention that our choice of system is also related to a specific set of macroscopic experiments. 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 (1953) exposed molten cryolite to sodium vapour and found that, after prolonged annealing and 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 (1960), 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, $NaAlF_4$ 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 $(AlF_4)^-$ structural units. As we shall see, our theoretical results are fully consistent with this interpretation.

The layout of the paper is briefly as follows. In § 2 we first describe the model that we adopt for liquid cryolite - sodium solutions. It allows for the presence of Al ions in the trivalent, divalent and monovalent states, but, by omitting the possibility of dimers or higher Al clusters, is restricted to the salt-rich region. The same section gives our statistical mechanical treatment of the model and specifies our choice of values for the model parameters. Section 3 reports the results of our calculations. We first consider separately the three possible valence states of Al ions, in order to elucidate the distinct roles that the added Na^+ ions and electrons play in structure breaking. These calculations exclude the presence of Al^{3+} ions in the melt and lead us to examine in the same section the possible coexistence of Al^{2+} and Al^+ ions as a function of metal concentration. Finally, § 4 gives a summary and a discussion of our results.

§ 2. THE MODEL AND ITS TREATMENT

As outlined above, the relevant questions are how the dilution of Na^+ ions and electrons in molten cryolite affects the relative and absolute stability of the $(AlF_6)^{3-}$ and $(AlF_4)^-$ structural units and what is the interplay between these units and the presumed chemical localization of electrons on Al^{3+} ions. In our model we shall allow the electrons to be either bound to Al^{3+} to form Al^{2+} or Al^+ ions (with a release of energy related to the third and second ionization potential of the Al atom as well as to changes in the excess free energy of interaction between the components of the solution) or frozen into a rigid neutralizing background. The latter schematization is known from work on alkali - alkali halide solutions (Chabrier, Senatore and Tosi 1982, Chabrier and Hansen 1983) to yield a reasonable description of the short-range

order and hence of the excess free energy of the liquid in the salt-rich region, where metallic screening is not yet operative.

With the above assumptions our present model is a direct extension of our earlier model for molten cryolite (Akdeniz and Tosi 1990). As will become clearer later, its applicability in the salt-rich region assumes that, whatever bound species (both in the nature of ionic complexes and of Al^{3+} - electron bound states) may be present in equilibrium in the liquid, they are so strongly bound that their internal structure is insensitive to their surroundings and their lifetimes are at least comparable with typical diffusion times. This is essentially correct for complexes in molten cryolite and in a host of other molten salt mixtures (Akdeniz and Tosi 1989 and references given therein), but is expected to become invalid for any given species when its relative equilibrium concentration is becoming very small.

We thus consider a liquid of composition $(AlF_3)_{(1-c)/4} \cdot (NaF)_{3(1-c)/4} \cdot Na_c$ at temperature T and model it for $c \ll 1$ as a fluid whose components are (i) $(AlF_6)^{3-}$ units in molar fraction $x_6(1 - c)$, (ii) $(AlF_4)^-$ units in molar fraction $x_4(1 - c)$, (iii)-(v) Al^{z+} ions in molar fractions $x_z(1 - c)$ with z = 1, 2 and 3, (vi) F^- ions in molar fraction $(3/2 - 4x_4 - 6x_6)(1 - c)$, and (vii) Na^+ ions in molar fraction $(3 + c)/4$. The fluid is embedded in a uniform neutralizing background of negative charge density n e, with

$$n = [c - (x_2 + 2x_1)(1 - c)] / v \qquad (1)$$

where v is the volume of the solution per formula unit. The inequality

$$x_2 + 2x_1 \le c / (1 - c) \qquad (2)$$

follows from the available number of electrons, while conservation of Al particles yields the further condition

$$x_1 + x_2 + x_3 + x_4 + x_6 = \frac{1}{4} \; . \qquad (3)$$

The equilibrium state is described by the values of the five variables x_i which, subject to the above restrictions, minimize the Helmholtz free energy F at constant T, v and c.

The Helmholz free energy of the liquid, aside from an irrelevant additive constant, is given by

$$F = F_t - TS_m + F_{int} + F_{ex} \qquad (4)$$

where F_t and S_m are the ideal translational free energy and the ideal entropy of mixing, while F_{int} is associated with the internal structure of the components and F_{ex} is the excess free energy arising from the interactions between all the components. We write

$$F_{int} = (1 - c) [x_6f_6 + x_4f_4 - x_2I_3 - x_1(I_2 + I_3)] \qquad (5)$$

where f_6 and f_4 are the binding free energies of $(AlF_6)^{3-}$ and $(AlF_4)^-$ units in vacuo, relative to the separated ions, while I_2 and I_3 are the second and third ionization potential of the Al atom. Clearly, our expression for F_{int} implies the limitations on the applicability of the model that we have already stressed earlier in this section.

It is useful at this point, before entering the statistical mechanical treatment of F_{ex}, to consider the explicit expression for the ideal entropy of mixing, which is

$$\begin{aligned} S_m = -k_B(1 - c) &\left\{ x_6\ln x_6 + x_4\ln x_4 + x_3\ln x_3 + x_2\ln x_2 + x_1\ln x_1 \right. \\ &\left. + (\frac{3}{2} - 4x_4 - 6x_6) \ln[(\frac{3}{2} - 4x_4 - 6x_6)(1 - c)] \right\} \\ &- \frac{1}{4} k_B \left[(1 - c)\ln(1 - c) + (3 + c) \ln[\frac{1}{4}(3 + c)] \right] \qquad (6) \end{aligned}$$

On insertion of eqn (6) in eqn (4) and minimization of F under the condition (3), it becomes apparent that the equilibrium state is equivalent to a set of dissociation reaction equilibria in the liquid, restricted by the availability of electrons in the background as expressed by the inequality (2). It is useful to view the equilibrium state as associated with the following four dissociation reactions:

$$(AlF_6)^{3-} \Leftrightarrow (AlF_4)^- + 2F^- \qquad (7)$$

$$(AlF_4)^- \Leftrightarrow Al^{3+} + 4F^- \qquad (8)$$

$$(AlF_4)^- + e \Leftrightarrow Al^{2+} + 4F^- \qquad (9)$$

and

$$(AlF_4)^- + 2e \Leftrightarrow Al^+ + 4F^- \; . \qquad (10)$$

Each of these reactions is described by its appropriate law of mass action, with an activation free energy which is determined by $F_{int} + F_{ex}$ and hence depends on all the x_i's through F_{ex}. The activation free energies for the processes (7) - (10) are derived in Appendix 1. We stress, however, that the schematization of the unbound electrons through a uniform background does not allow for their contribution to the entropy of mixing and hence the reaction bottleneck given by the inequality in eqn (2) is not accounted for when the reaction equilibria are expressed in the form of the mass action law. In actual practice, we have determined the equilibrium state by minimizing F numerically under the restriction imposed by eqn (2).

We turn now to the statistical mechanical treatment of the excess free energy F_{ex}. We schematize each component of the fluid through charged hard spheres having charges $z_i|e|$, that we have already indicated, and diameters σ_i. The mean spherical approximation yields analytic expressions for the liquid structure and the thermodynamic functions of such a fluid mixture of charged hard spheres on a neutralizing background (Parrinello and Tosi 1979). F_{ex} is the sum of a hard-core contribution and a Coulombic contribution,

$$F_{ex} = F_{hs} + F_C \ . \tag{11}$$

We take for F_{hs} the expression obtained by integration of the virial pressure in a fluid of neutral hard spheres,

$$F_{hs} = vk_BT \left[\frac{\pi \zeta_1 \zeta_2}{2\Delta} + \frac{\pi \zeta_2^3}{2\zeta_3\Delta} + \frac{3\zeta_2^3}{\zeta_3^2}\ln\Delta - \zeta_0\ln\Delta \right] \tag{12}$$

(Senatore, Parrinello and Tosi 1980). Here, $\Delta = 1 - \pi\zeta_3/6$ and $\zeta_n = \Sigma_i \rho_i\sigma_i^n$, ρ_i being the partial densities of the components ($\rho_i = c_i/v$ in terms of the molar fractions c_i). The Coulombic contribution F_C is given by

$$F_C = \frac{1}{3\pi} vk_BT\gamma^3 - e^2v\left(\gamma\sum_i \frac{\rho_i z_i^{*2}}{1+\gamma\sigma_i} + \frac{\pi}{2\Delta}\Omega P_n^2 + \frac{\pi}{2} n\phi_2 - \frac{\pi^2}{30} n^2\zeta_5\right) \ . \tag{13}$$

Here, $z_i^* = z_i - \pi n\sigma_i^3/6$ has the meaning of an effective valence, reduced from the bare valence z_i by the background charge contained inside the hard sphere, and the quantity 2γ has the

physical meaning of an inverse screening length in the dense ionic fluid, to be determined from the equation

$$2\gamma = \left\{ \frac{4\pi e^2}{k_BT} \sum_i \rho_i \left[\frac{z_i^* - (\pi/2\Delta)\sigma_i^2 P_n}{1+\gamma\sigma_i} \right]^2 \right\}^{1/2} \ . \tag{14}$$

The other quantities (P_n, Ω and ϕ_2) have simple expressions in terms of the model parameters, which can be found in the original work.

It remains for us to specify the model parameters, i. e. the free energies and ionization potentials in eqn (5) and the seven hard-sphere diameters σ_i. The values that we have adopted in the calculations to be reported in § 3 are collected in Table 1. The ionization potentials are from Fraga, Kaswowski and Saxena (1976). Many of the other parameters (f_4, f_6 and the diameters for $(AlF_6)^{3-}$, $(AlF_4)^-$, Na^+ and F^-) are taken over from our earlier work on molten AlF_3-NaF mixtures at $T = 1053$ K (Akdeniz and Tosi 1990). The diameters for Al ions in the three valence states are estimated from the requirements that (a) both $(AlF_6)^{3-}$ and $(AlF_4)^-$ should be stable in pure molten cryolite against dissociation into Al^{3+} and fluorines, and (b) the classical Coulomb energy of an electronic charge bound to Al^{3+} or to Al^{2+} should correspond to the ionization potentials I_3 and I_2, respectively. We remark that our choice for the diameter of Al^{3+} probably is an underestimate within the present model (e. g. from the equation of state of liquid AlF_3 we estimate a value of 2.33 Å for this diameter) and shall discuss in § 3 also the result of reasonable variations in all the three diameters of Al ions. Finally, the calculations refer to $T = 1053$ K and to a molar volume taken as the concentration-weighted average of those of cryolite and sodium. We anticipate that the pressure-volume product in our calculations was at most of the order of a few k_BT, i. e. small compared with the magnitude of the activation free energies in the dissociation equilibria (7) - (10).

§ 3. NUMERICAL RESULTS

It will be useful to examine first some special cases in order to bring to evidence the

various factors which determine the equilibrium state of our model fluid as a function of metal concentration c. Recalling that the model is applicable in the salt-rich region, we have arbitrarily chosen this thermodynamic variable to lie in the range $0 \leq c \leq 0.2$.

3.1. Absence of chemical localization ($x_2 = x_1 = 0$)

We first examine the reactions (7) and (8) in the absence of reactions (9) and (10). Figure 1 shows the results that we obtain in this case for x_6 and x_4 as functions of c. The values of x_3 are not shown, since they are zero throughout the concentration range. Two conclusions can be drawn:

(1) The excess of Na^+ ions is sufficient to drive the conversion of $(AlF_6)^{3-}$ units into $(AlF_4)^-$ units, with a release of fluorine ions in the melt. The corresponding activation free energy f_{64} (see eqns (A1.4) and (A1.5)) is estimated to vary from -64 kcal/mol at $c \approx 0$ to -25 kcal/mol at $c \approx 0.2$. As we shall see immediately below, such a destabilization of the $(AlF_6)^{3-}$ units in favour of the $(AlF_4)^-$ units is a general feature of our results, which persists when chemical localization of the electrons is allowed, although the dependence of f_{64} on c becomes progressively weaker.

(2) Conversely, the $(AlF_4)^-$ units are completely stable against dissociation in the absence of chemical localization. The reason behind this stability is the huge value of the binding free energy f_4 in Table 1. Indeed, the activation free energy f_{43} for the dissociation process in eqn (8) (see eqns (A1.6) and (A1.7)) is estimated in this case to be of order -160 kcal/mol, with a weak dependence on c. As already noticed, our choice for the hard-sphere diameter of the Al^{3+} ions in Table 1 probably is an underestimate, tending to favour the formation of these ions in the presence of added metal under the condition that the $(AlF_6)^{3-}$ and $(AlF_4)^-$ units are stable in pure molten cryolite. We shall consequently assume $x_3 = 0$ in all our subsequent calculations.

3.2. Formation of divalent Al ions only ($x_1 = 0$)

We consider next the reactions (7) and (9) in the absence of reactions (8) and (10). Our

results are reported in Figure 2 and show that chemical localization, with formation of Al^{2+} ions at the expense of $(AlF_4)^-$ units, is possible in the initial stages of the process of conversion of $(AlF_6)^{3-}$ into $(AlF_4)^-$, i. e. at low metal concentration. The activation free energy f_{42} for the reaction (9) (see eqns (A1.6) and (A1.8)) is estimated to be in this case of order -90 kcal/mol in the relevant concentration range. The energy gain associated with the ionization potential I_3 is clearly responsible for the partial stability of Al^{2+} ions and, relative to the case of Al^{3+} in § 3.1, overcomes the loss of excess free energy associated with the reduced valence and the increased diameter. The concentration range of stability of Al^{2+} is, however, rather sensitive to the choice of the hard sphere diameter for this ion: it expands (shrinks) appreciably on decreasing (increasing) this diameter by a few tenths of an Å.

3.3. Formation of monovalent Al ions only ($x_2 = 0$)

Figure 3 shows our results for the reactions (7) and (10) in the absence of reactions (8) and (9). The additional energy gain coming from the ionization potential I_2 stabilizes the monovalent Al^+ state in an amount which is equal to its maximum allowed value x_1^{max} at all metal concentrations, in spite of the loss in excess free energy relative to the case of Al^{2+} in § 3.2. Comparison with Figure 2 shows that the process of chemical localization by formation of Al^+ ions is occurring at the expense of the $(AlF_4)^-$ units: the rate of formation of these units by dissolution of $(AlF_6)^{3-}$ with increasing c is substantially slower in Figure 3, and eventually the relative molar fraction of $(AlF_4)^-$ unit decreases. These results are completely insensitive to the choice of hard sphere diameter for Al^+. The activation free energy f_{41} for the reaction (10) (see eqns (A1.6) and (A1.9)) is strongly positive at $c \approx 0$ (of order 130 kcal/mol) and decreases to a value of the order of a few kcal/mol at $c \approx 0.2$. This is consistent with the fact that this localization process, accompanied by the structure-breaking process of destabilization for $(AlF_6)^{3-}$ and $(AlF_4)^-$ units, is merely limited by the available number of electrons, as is evident from Figure 3.

3.4. Competition between divalent and monovalent states of Al

Our last calculations concern the study of the simultaneous reactions (7), (9) and (10)

under the assumption $x_3 = 0$. The results are shown in Figure 4. The main new point to be noticed is that the reaction bottleneck on the processes of chemical localization coming from the available number of electrons allows the presence of Al^{2+} ions in a limited range of metal concentration, for high dilution of metal. We have already remarked in § 3.2 that the width of this concentration range is sensitive to the choice of the hard sphere diameter for Al^{2+}. The activation free energies are of the same order as illustrated previously for the separate reactions. Their values at a few values of c over the range of interest are reported in Table 2.

§ 4. SUMMARY AND DISCUSSION

The scenario that emerges from our calculations for the microscopic processes that occur on addition of sodium metal to molten cryolite may be summarized as follows. Conversion of $(AlF_6)^{3-}$ into $(AlF_4)^-$ units and eventually dissolution of $(AlF_4)^-$ units occur while Al^{3+} ions are released in the melt and chemically bind the available electrons to form Al ions in reduced valence states. The divalent state may be the preferred one at low concentration of added metal, but eventually the monovalent state becomes dominant. These results are fully consistent with the macroscopic observations of Grjotheim (1953) and Haupin (1960), that we have summarized in § 1. Unfortunately, their experiments do not allow a quantitative test of the theory, which would require determination of the amounts of added metal and of reaction products.

We have already discussed in the preceding sections the essential limitations of our approach, related to the assumptions that (a) the bound species that may be present in the liquid at equilibrium are long-lived, and (b) no dimers or small metal clusters are formed. Within our method the second assumption could be transcended if one had knowledge of the binding energy and shape of such units in vacuo, as can be obtained from quantum chemistry calculations. The evaluation of the excess free energy associated with non-spherical bound units in the liquid could be handled by presently available techniques in liquid state theory.

However, since in practice the method involves taking differences between large amounts of free energy, it cannot be expected to yield more than a semiquantitative assessment of the equilibrium state of the liquid.

In conclusion, we wish to re-emphasize that the specific system that we have evaluated is illustrative of what one may expect to be a rather general feature of electron localization in strongly structured liquids. Localization involving structure breaking should occur in such liquids through the reconstruction of chemical bonding.

APPENDIX 1. DISSOCIATION EQUILIBRIA

As we have already noted in the main text, the equilibrium state of the model fluid that we consider is given by the minimum of the free energy F with respect to the five variables x_i (at constant T, v and c, as we implicitly assume below) and is equivalent to a set of dissociation equilibria on account of the expression for the ideal entropy of mixing in eqn (6). The condition in eqn (3) implies that only four such equilibria need to be considered, and these are conveniently chosen as those shown in eqns (7) - (10). The appropriate laws of mass action follow by differentiation of F using eqns (4), (5) and (6) together with the well known expression for the ideal translational free energy F_t. We omit for the moment consideration of the restrictions imposed on the reaction products by the inequality in eqn (2).

Let us consider for instance minimization with respect to x_6. This immediately gives the equilibrium condition

$$\frac{x_6}{[(\frac{3}{2} - 4x_4 - 6x_6)(1 - c)]^6} = A_6 \exp\left(-\frac{F_6}{k_B T}\right) \qquad (A1.1)$$

where

$$F_6 = f_6 + \frac{1}{1 - c}\left(\frac{\partial F_{ex}}{\partial x_6}\right)_{\bar{x}_6} \qquad (A1.2)$$

and

$$A_6 = \left(\frac{h^2}{2\pi k_B T v^{2/3}}\right)^{15/2} \left(\frac{m_{Al} + 6m_F}{m_F^6}\right)^{3/2} \exp\left[\frac{\mu}{(1 - c)k_B T} - 1\right] . \qquad (A1.3)$$

Here, $\bar{x}_6$ denotes all the variables other than x_6, the m's are the atomic masses and μ is a Lagrange multiplier arising from the condition in eqn (3). By similarly minimizing F with respect to x_4 and taking the ratio of the two equilibrium equations for x_6 and x_4, one obtains the law of mass action for the dissociation reaction in eqn (7) as

$$\frac{x_6}{x_4[(\frac{3}{2} - 4x_4 - 6x_6)(1 - c)]^2} = \left(\frac{h^2}{2\pi k_B T v^{2/3}}\right)^3 \left[\frac{m_{Al} + 6m_F}{(m_{Al} + 4m_F)m_F^2}\right]^{3/2} \exp\left(-\frac{f_{64}}{k_B T}\right) \qquad (A1.4)$$

where

$$f_{64} = f_6 - f_4 + \frac{1}{1 - c}\left[\left(\frac{\partial F_{ex}}{\partial x_6}\right)_{\bar{x}_6} - \left(\frac{\partial F_{ex}}{\partial x_4}\right)_{\bar{x}_4}\right] . \qquad (A1.5)$$

Equation (A1.5) shows that the activation free energy for dissociation of $(AlF_6)^{3-}$ into $(AlF_4)^-$ and two F^- in the liquid arises from the balance between (a) the free energy gain for dissociation in vacuo and (b) the loss of excess free energy associated with the change in the interactions between the components of the liquid. We should recall in this connection that F_{ex} depends on x_6 and x_4 both directly and through the dependence of the molar fraction of F^- ions on these variables.

Similar calculations lead to the equilibrium equations for the reactions in eqns (8)-(10). These are compactly given for z = 3, 2 and 1 by

$$\frac{x_4}{x_z[(\frac{3}{2} - 4x_4 - 6x_6)(1 - c)]^4} \propto \exp\left(-\frac{f_{4z}}{k_B T}\right) \qquad (A1.6)$$

where

$$f_{43} = f_4 + \frac{1}{1 - c}\left[\left(\frac{\partial F_{ex}}{\partial x_4}\right)_{\bar{x}_4} - \left(\frac{\partial F_{ex}}{\partial x_3}\right)_{\bar{x}_3}\right] , \qquad (A1.7)$$

$$f_{42} = f_4 + I_3 + \frac{1}{1 - c}\left[\left(\frac{\partial F_{ex}}{\partial x_4}\right)_{\bar{x}_4} - \left(\frac{\partial F_{ex}}{\partial x_2}\right)_{\bar{x}_2}\right] \qquad (A1.8)$$

and

$$f_{41} = f_4 + I_3 + I_2 + \frac{1}{1 - c}\left[\left(\frac{\partial F_{ex}}{\partial x_4}\right)_{\bar{x}_4} - \left(\frac{\partial F_{ex}}{\partial x_1}\right)_{\bar{x}_1}\right] . \qquad (A1.9).$$

Of course, F_{ex} depends on x_2 and x_1 also through the background density in eqn (1).

The equilibrium equations (A1.4) and (A1.6) do not take account of the fact that the inequality (2) should be satisfied by the reaction products. Such a reaction bottleneck, imposed

by the available number of electrons in the background, could be included in the equilibrium equations if a contribution to the entropy of mixing were attributed to such electrons, bringing factors of the form $(nv)^{3-z}$ in the numerator on the left-hand side of eqn (A1.6). Equations (A1.5) and (A1.7) - (A1.9) serve nevertheless to define the activation free energies for the reaction equilibria within our model. Their orders of magnitude are presented and discussed in § 3 in the main text.

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Table 1. Model parameters for liquid cryolite - sodium solutions

	$(AlF_6)^{3-}$	$(AlF_4)^-$	Al^{3+}	Al^{2+}	Al^+	F^-	Na^+
σ_i (Å)	4.96	5.06	2.22	3.0	3.3	2.27	2.24
Binding (kcal/mol)	$f_6 = -1300$	$f_4 = -1516$	--	$I_3 = 644$	$I_2 = 405$	--	--

Table 2. Activation free energies for the reactions (7) - (10) in the case treated in § 3.4. (kcal/mol)

c	f_{64}	f_{43}	f_{42}	f_{41}
0.01	- 65	- 170	- 87	123
0.11	- 67	- 161	- 124	43
0.20	- 65	- 157	- 145	- 5

Figure 1. Relative molar fractions of $(AlF_6)^{3-}$ units (x_6) and $(AlF_4)^-$ units (x_4) versus concentration c of added metal, from the dissociation equilibria (7) and (8) in the absence of the reactions (9) and (10).

Figure 2. Relative molar fractions of $(AlF_6)^{3-}$ units (x_6), $(AlF_4)^-$ units (x_4) and Al^{2+} ions (x_2) versus concentration c of added metal, from the dissociation equilibria (7) and (9) in the absence of the reactions (8) and (10). The curve marked x_2^{max} shows the maximum amount of Al^{2+} ions allowed by the available electrons.

Figure 3. Relative molar fractions of $(AlF_6)^{3-}$ units (x_6), $(AlF_4)^-$ units (x_4) and Al^+ ions (x_1) versus concentration c of added metal, from the dissociation equilibria (7) and (10) in the absence of the reactions (8) and (9).

Figure 4. Relative molar fractions of $(AlF_6)^{3-}$ units (x_6), $(AlF_4)^-$ units (x_4), Al^{2+} ions (x_2) and Al^+ ions (x_1) versus concentration c of added metal, from the dissociation equilibria (7), (9) and (10) at $x_3 = 0$. The curve marked $(2x_1 + x_2)^{max}$ shows the maximum amount of Al ions in reduced valence states, which are allowed by the available electrons.
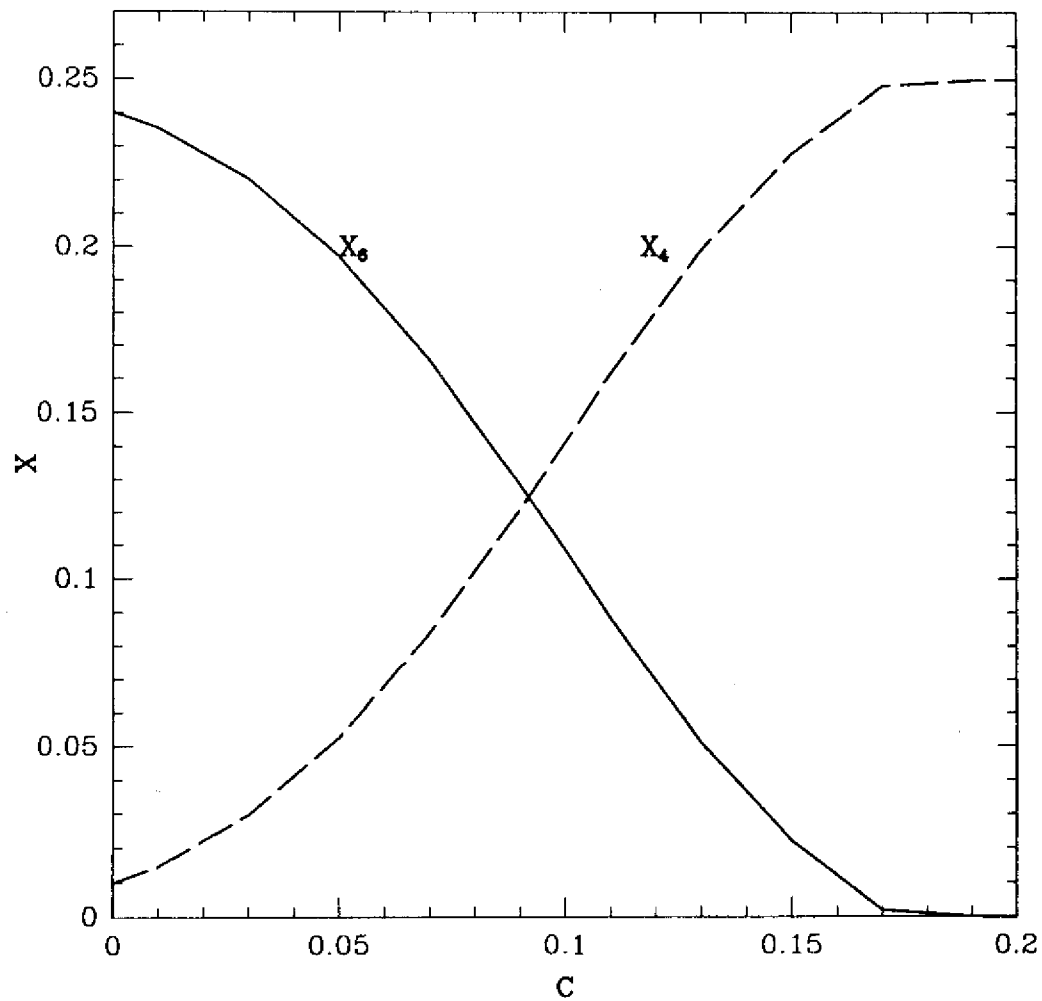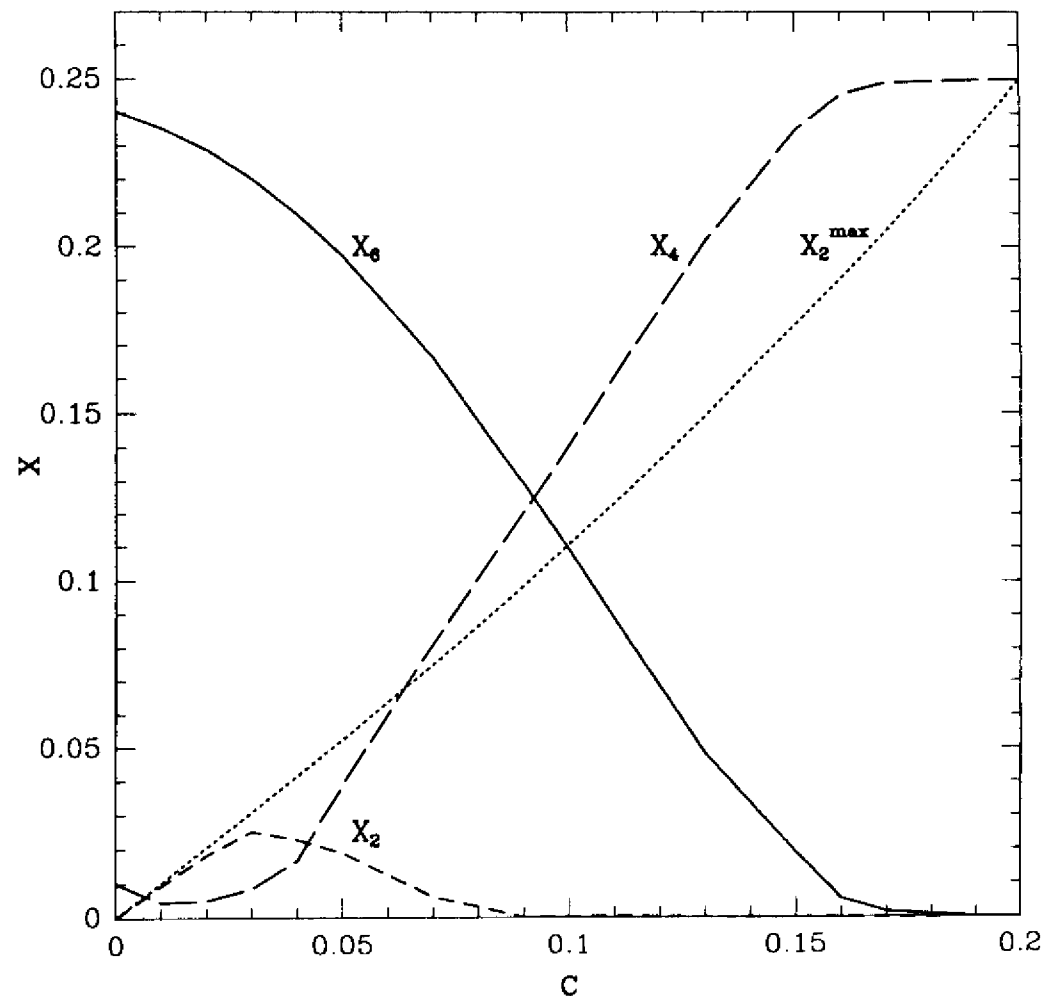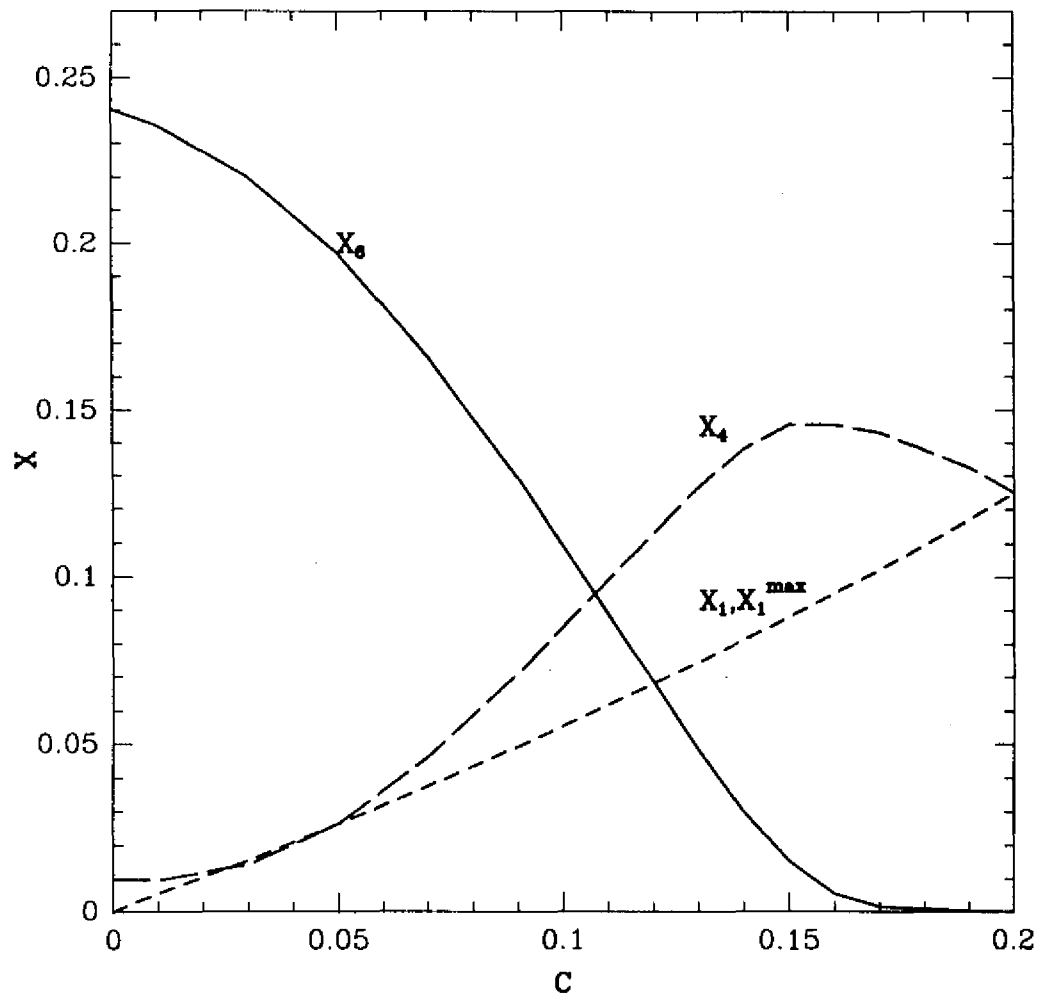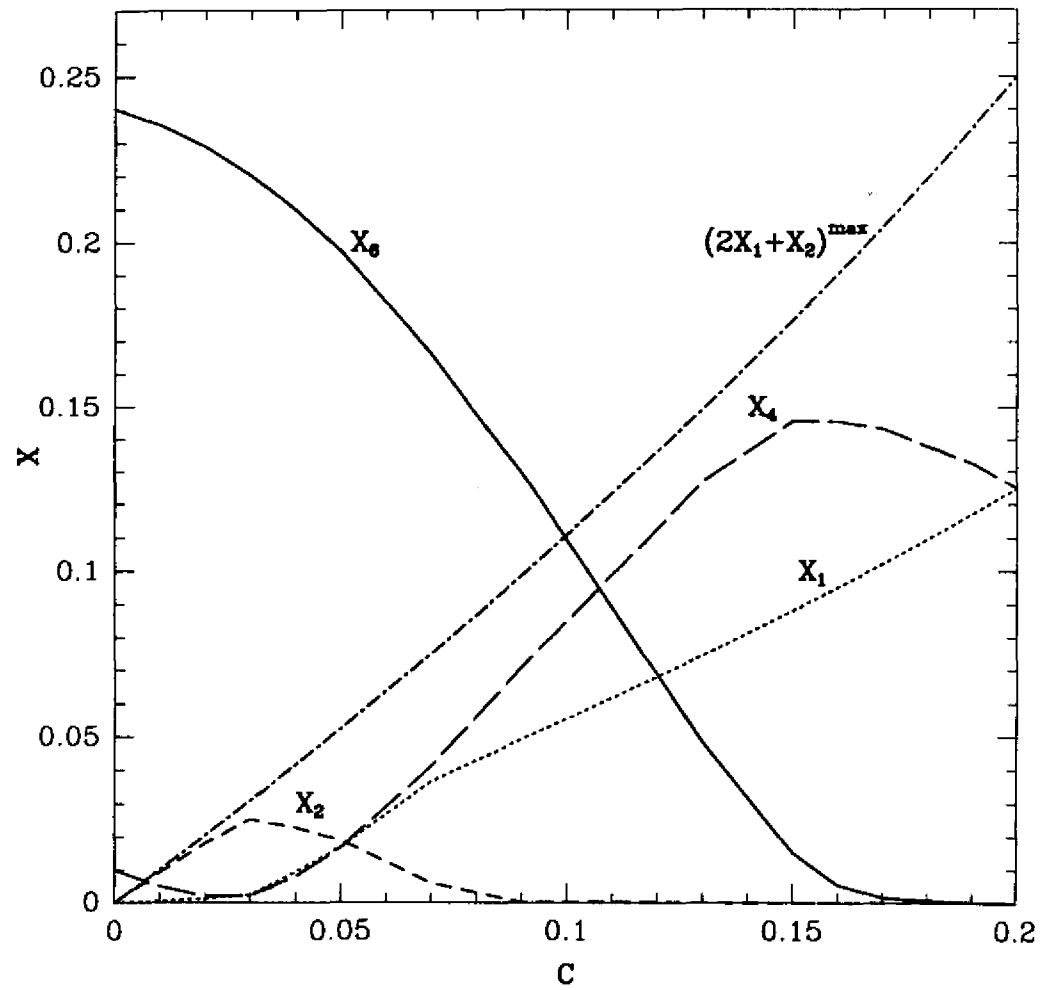
Fig.1

-20-

Fig.2

-21-

Fig.3

Fig.4