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HALIDE MELTS
A PROGRESS REPORT**

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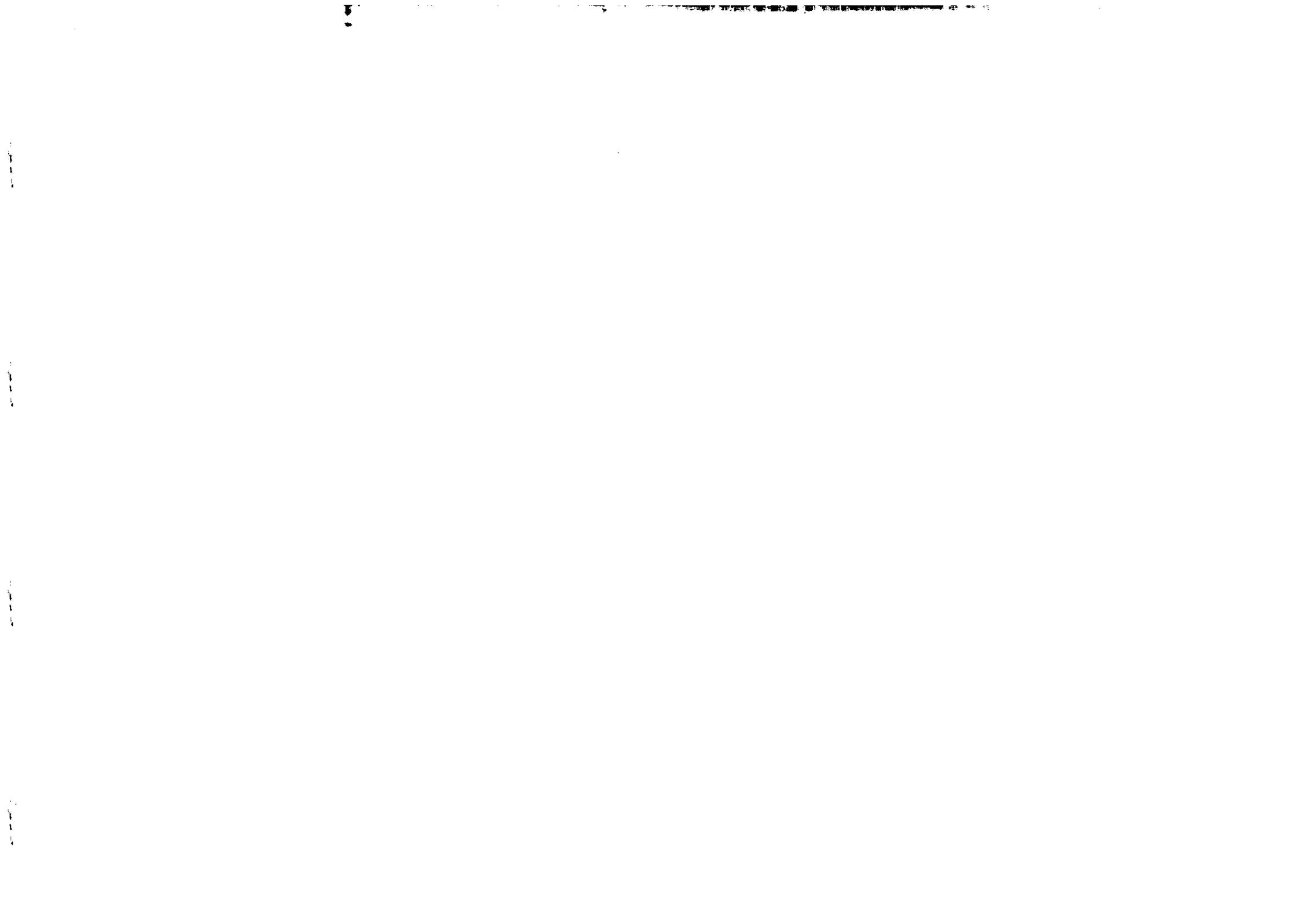


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STRUCTURE OF POLYVALENT METAL HALIDE MELTS

A PROGRESS REPORT *

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Abstract. - A short review is given of recent progress in determining and understanding the structure of molten halide salts involving polyvalent metal ions. It covers the following three main topics: (i) melting mechanisms and types of liquid structure for pure polyvalent-metal chlorides; (ii) geometry and stability of local coordination for polyvalent metal ions in molten mixtures of their halides with alkali halides; and (iii) structure breaking and electron localization on addition of metal to the melt.

1. Introduction

The liquid structure of alkali halides is well understood from neutron diffraction experiments by the isotope enrichment technique as well as from computer simulation and liquid structure theory based on pair potentials (for recent reviews see [1, 2]). A number of new and interesting structural behaviours are met when one turns to the melts of polyvalent metal halides. Several divalent metal halides have been examined by neutron diffraction [1 - 3] and the data show such diverse behaviours as a loose, cation-dominated liquid structure for SrCl_2 [4] and a tetrahedrally coordinated network-like liquid structure in the glass-former ZnCl_2 [5]. Among trivalent metal chlorides, neutron diffraction data that have recently become available for YCl_3 [6] show an octahedrally coordinated structure with network-like intermediate range order. It is remarkable that

YCl_3 in the crystalline phase has the same structure as AlCl_3 , which instead melts into a molecular liquid consisting primarily of Al_2Cl_6 units as demonstrated by X-ray studies [7]. We shall review these four systems in section 2, stressing that they may be taken as prototypes for different mechanisms of melting and pointing out the correlation that exists between melting behaviour and character of the chemical bond. For a measure of the latter we have recourse to the phenomenological chemical scale of the elements proposed by Pettifor [8], which orders all elements along a single axis χ so that the Mendeleev-type features of the periodic table are preserved. The scale has been used by him to classify crystal structures for a vast set of solid compounds.

The remarkable liquid structure of YCl_3 was earlier suggested from Raman scattering experiments on molten Y-alkali chloride mixtures, which showed persistence of the breathing mode associated with $(\text{YCl}_6)^{3-}$ octahedral units from alkali-rich mixtures up to the pure YCl_3 melt [9]. The alkali halide in such mixtures acts as a halogen donor to break the structure of the pure polyvalent metal halide melt: in particular, if the pure melt structure is network-like (involving halogen sharing at the corners of the network as in ZnCl_2 or along edges as in YCl_3), a suitable concentration of alkali halide breaks the network into separate molecular-ion units ('complexes'). Some 140 liquid mixtures of polyvalent metal halides and alkali halides have been examined over the years by appropriate experimental probes, involving diffraction experiments in a few systems but mostly Raman scattering, infrared emission and absorption, optical absorption from electronic transitions, and thermodynamic measurements. A critical discussion of the evidence with a full list of references has been given in [10]. The vast experimental evidence on such local structures formed around polyvalent metal ions allows meaningful statistics and a precise statistical correlation with the character of the chemical bond, as will be reviewed in section 3.

In section 4 we turn to the question of the stability of local structure against addition of metal in metal - molten salt solutions. Data on the phase diagram of many of these systems and on basic properties such as the electrical conductivity and the magnetic susceptibility as functions of metal content, which give information on the nonmetal-to-metal transition, were reviewed by Bredig [11] and Corbett [12]. Considerable detail has since been added to these data in the case of alkali - alkali halide solutions and in particular the mechanism of localization for the valence electrons of

the added metal in salt-rich solutions has drawn much attention [1, 13, 14]. On the other hand, a substantial local reconstruction of liquid structure and of chemical bonding may be expected for electron localization in polyvalent metal halides, when the molten salt has an appreciable connectivity of its own. Structure breaking may then be accompanied by the formation of lower oxidation states for the polyvalent metal ion, thus broadening the nonmetallic range and shifting the liquid miscibility gap to the metal-rich side of the phase diagram.

2. Melting and liquid structure in polyvalent metal chlorides

Table I compares some relevant physical properties of the four polyvalent metal halides that we have chosen to focus upon [6]. These are the crystal structure, the thermodynamic parameters of the melting process (melting temperature T_m , entropy change ΔS_m and relative difference $\Delta V/V$ in volumes between liquid at T_m and room-temperature solid) and transport coefficients of the melt (ionic conductivity σ and shear viscosity η). Comparison of these data in the four halides is already indicative of very different melting processes.

SrCl_2 crystallizes in the fluorite structure and before melting undergoes a continuous transition to a superionic state, across which a high dynamic concentration of anionic crystal defects is generated. The crystal in the superionic state may be viewed as a sublattice of Sr ions permeated by a 'lattice liquid' of Cl ions and the melting process is directly associated with the Sr sublattice [15]. The structure of the melt is still dominated by the short-range order in the system of Sr ions, while a poorer degree of order is observed in the system of Cl ions [4].

By contrast, the dominant structure factor in the ZnCl_2 melt is the Cl-Cl one [5]. The liquid structure of this material is similar to that of its glassy state [16] and both may be described as disordered networks of corner-sharing tetrahedra formed by a distorted close packing of Cl ions which provides tetrahedral holes for the Zn ions. As shown in the first two rows of table I, the very different melting mechanisms of SrCl_2 and ZnCl_2 are reflected in differences in T_m and, most strikingly, in the transport coefficients.

Turning to AlCl_3 and YCl_3 , although from a strict crystallographic viewpoint their AlCl_3 -type crystal structure is a monoclinic layer structure with a unit cell containing four formula

units, it can almost be viewed as a cubic close packing of Cl ions inside which the metal ions occupy some octahedral sites. A single layer in this idealized description (see Fig. 1) consists of two triangular lattices of Cl ions, with phase relationship as appropriate to adjacent (111) planes in the fcc lattice, which sandwich an hexagonal lattice of metal ions, each metal ion being at the centre of an octahedron of Cl ions and sharing three of the Cl-Cl edges with three other metal ions. Thus, 1/4 of the Cl-Cl coordination in the crystal arises from inter-sandwich Cl-Cl bonds and 1/3 of the intra-sandwich octahedral sites are empty.

The melting of AlCl_3 from this layer structure into a molecular liquid of Al_2Cl_6 units is accompanied by low T_m , very large values of ΔS_m and $\Delta V/V$, a very low value of σ in the melt and a rather low value of η (see table I). The melting process may be viewed as driven by a structural phase transition from the AlCl_3 -type to the AlBr_3 -type crystal structure, which is formed by chemically saturated molecular dimers weakly bound together by van der Waals forces and thus has low melting point. In an Al_2Cl_6 molecule each Al ion is surrounded by a tetrahedron of Cl ions and the molecule consists of two tetrahedra sharing a Cl-Cl edge. The idealized AlCl_3 layer in Fig. 1 can break into such units by a set of ionic displacements in which two of the three Cl-Cl edges shared by each Al ion with its Al neighbours are broken and the Al ion moves towards the third Cl-Cl edge and its third Al neighbour [17].

YCl_3 , though crystallizing in the same structure as AlCl_3 , shows very different values for its macroscopic properties (see table I). Neutron diffraction experiments have recently been made with the aim of providing a direct determination of the local structure and of its connectivity [6]. The main results of the diffraction measurements may be summarized as follows: (i) the measured structure factor $S(Q)$ exhibits a first sharp diffraction peak (FSDP) at $Q = 0.95 \text{ \AA}^{-1}$, which is characteristic of liquid structures with intermediate-range order [18] and has also been observed, in particular, in molten ZnCl_2 [5]; (ii) the coordination number for Cl about Y is 5.87, which confirms the Raman scattering finding [9] of rather long lived octahedral coordination for Y, though in detail the octahedra in the liquid are somewhat expanded and probably distorted relative to the crystal; and (iii) the second-neighbour Cl-Cl coordination is approximately 8.2, appreciably less than the value of 12 found in the solid.

The latter result, with reference to our earlier discussion of the AlCl_3 -type structure, can be interpreted as implying a substantial loss of the inter-sandwich correlations on melting as well as loss of long-range intra-sandwich order through distortions of the layer-forming octahedral network around the empty octahedral sites. Intermediate range order within the octahedral network persists in the liquid, as indicated by the FSDP in $S(Q)$. The network is relatively loose on a longer time scale than the Raman vibrational period, as indicated by the value of σ for molten YCl_3 in table I.

In summary, the melting mechanism of YCl_3 into a loose network of edge-sharing octahedra with intermediate-range order is alternative for trivalent metal chlorides to the mechanism of melting into a molecular liquid of dimers formed by two edge-sharing tetrahedra, exemplified by AlCl_3 . The difference in melting behaviours for AlCl_3 and YCl_3 is thus related to the question of the relative stability of tetrahedral and octahedral coordination and hence to a subtle difference in the balance between ionic and covalent components of the bonding. This difference is accounted for by the chemical scale of the elements proposed by Pettifor [8], which places YCl_3 in a region of relatively high ionicity and AlCl_3 in a region of stronger covalency, with Y lying in fact rather close to Sr in the chemical scale and Al close to Zn. The different character of the chemical bonding is reflected in the melting behaviour of the two trivalent metal chlorides, rather than in their crystal structure.

3. Local coordination of polyvalent metal ions in molten halide mixtures

The addition of alkali halide to the molten halide of a polyvalent metal may be viewed as donating (a) halogen ions that are available for coordination by the polyvalent metal ions, with breakage of the network or of the molecular units that may have been stable in the pure melt, and (b) free alkali ions, that may further act on the local structure through ionic-conductor screening. For definiteness we consider these mixtures at a 'stoichiometric' concentration c of alkali halide, defined as that which on mere consideration of the chemical formula maximizes the possibility of formation of fourfold coordination for the polyvalent metal ions. This is $c = 2/3$ for divalent ions and $c = 1/2$ for trivalent ions. An example of the evolution of local

structure with composition will be given in section 4 below, when we shall discuss the Al-Na fluoride mixtures.

The basic structural questions for a molten mixture are whether it contains 'complexes', i. e. molecular-ion units having a lifetime at least of the order of typical translational and rotational diffusion times, and what are the coordination and the geometry of these complexes. Our choice of 'stoichiometric' composition favours fourfold coordination, but this is not necessarily tetrahedral nor necessarily stable against sixfold octahedral coordination (as for instance in Y-alkali chloride mixtures). Alternatively, the polyvalent metal ions may fluctuate rapidly between different coordination states, with an average coordination number of order 5 or 6. As examples of the latter behaviour we may cite the case of $\text{CaCl}_2\cdot 2\text{KCl}$, where coexistence of loose tetrahedral-type and octahedral-type coordinations has been reported from Raman scattering data [19], and the Sr-alkali and Ba-alkali chlorides, where no structure is observed in the Raman spectrum.

General semiempirical approaches to such "structure sorting" problems are well known in solid state physics for the classification of crystal structures in broad families of compounds. In brief, these approaches lead to structural diagrams assembling compounds with similar structure in certain regions of a plane whose coordinates are constructed from parameters of the component elements. In the classification schemes developed by Zunger and Cohen [20] and by Andreoni *et al.* [21], the elemental parameters are radii associated with the valence electron orbitals, which are obtained from first-principles atomic calculations. These elemental parameters correlate to a considerable extent with classical ionic radii, although they carry information not only on geometric core sizes but also on chemical bonding properties. Pettifor's chemical scale is aimed at the same purposes in a more empirical viewpoint, though incorporating recent progress in understanding the cohesion of bulk solids from first-principles calculations [8].

The structure-sorting approaches have been successfully adapted to the liquid structure problem at hand [10]. As the best example we report in Fig. 2 the structural diagram obtained for molten mixtures of polyvalent metal halides and alkali halides on the basis of Pettifor's chemical scale. Successful structural coordinates are constructed for each M-A(X) liquid

mixture from the elemental property χ as

$$X_{M-A(X)} = \chi_M - \chi_A \quad , \quad Y_{M-A(X)} = \chi_M + \chi_A - 2\chi_X$$

(with M = polyvalent metal, A = alkali and X = halogen). Each mixture is represented in the diagram by an appropriate symbol distinguishing, on the basis of the available evidence, the stability of fourfold coordination as strong (dots), marginal (circles) or absent (lozenges). The marginal stability class includes cases of recognized coexistence between fourfold and more highly coordinated states, as well as systems for which the available evidence yields ambiguous indications. The plane in Fig. 2 can now be partitioned by lines into various regions, distinguishing (from top right to bottom left) (i) strong stability of fourfold coordination, (ii) strong stability of sixfold coordination, and (iii) loose fluctuating coordination. The separation lines between these classes of structural behaviour are set (i) by the Cr-alkali chloride systems, the Cr ion being known from electronic absorption spectra to be tetrahedrally coordinated in the divalent state and octahedrally coordinated in the trivalent state [22], and (ii) by the Y-alkali and Ca-alkali chloride systems, as discussed earlier in this review.

In supplement to the foregoing gross classification of types of structural behaviours for 'stoichiometric' liquid mixtures, a statistical mechanical treatment is possible for good ionic materials such as the alkaline earth - alkali halide mixtures [23]. It is found that the dissociation of a tetrahedral complex in the alkali-rich region is governed by a balance between the loss of its internal binding free energy and the gain in the excess free energy of the mixture due to interactions between all its components. This balance may be interpreted as equivalent to a Mott-type description of the stability of a bound state in a classical conductor. Indeed, the binding free energy of a complex in these materials is predominantly determined by Coulomb interactions and hence is measured by the cation-anion bond length within the complex. The excess free energy of the mixture, on the other hand, is measured by the screening length of the liquid. Since the screening length is itself a function of composition and of the number of complexes in the mixture, rapid dissociation of complexes can occur once the ratio between the screening length and the bond length with varying composition falls below a critical value.

A critical screening length to bond length ratio of about 1.6 has been estimated from model calculations [23]. Such a critical value is found to separate the alkaline earth - alkali chlorides into complex forming (Be and Mg) and non-forming (Sr and Ba), with rapid fluctuations between fourfold and higher coordinations being clearly expected in the systems close to the boundary [24]. This structure sorting criterion is in agreement with the available Raman scattering data [19].

In summary, ample experimental evidence is available in the literature on the geometry and the stability of local coordination for polyvalent metal ions in molten mixtures of their halides with alkali halides. Dissociation of tetrahedral halocomplexes in good ionic systems can be viewed as a classical Mott problem of bound-state stability in a conducting liquid matrix. More generally, established methods for crystal structure sorting can be adapted to construct structural coordinates for molten salt mixtures from properties of the component elements, which separate out systems with long-lived fourfold or sixfold coordination and distinguish between these.

4. Structure breaking and electron localization in metal - molten salt solutions

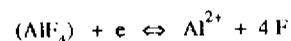
Solutions of metals in molten salts are among the several classes of liquid systems which undergo a transformation from a nonmetallic to a metallic state on changing some thermodynamic variable. In alkali - alkali halides above the consolute critical temperature, the electrical conductivity increases 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, a notable exception being the Bi - Bi halides [13]. A broad trend can already be recognized from the available data in the review by Bredig [11]. 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 structure of the pure alkaline earth chloride. Thus, the conductivity in Ca - CaX₂ systems (X denoting a halogen) increases much more slowly than in Sr - SrX₂ and Ba - BaX₂ systems, while the liquid structure of CaCl₂ is intermediate in character between the loose ionic structures of SrCl₂ and BaCl₂ and those of network-forming liquids such as ZnCl₂. Eventually, as one proceeds through polyvalent metals along a path set by Pettifor's χ scale, electron localization by reconstruction of local liquid structure and of chemical bonding will result. As an example one may mention the Hg - HgCl₂ system, which may be viewed as a nonmetallic mixture of HgCl₂ and Hg₂Cl₂ in the composition range up to that of the 'subhalide' Hg₂Cl₂ and as an Hg - Hg₂Cl₂ solution at still higher metal concentration [11, 13].

A microscopic model for processes of structure breaking accompanied by the formation of reduced oxidation states has recently been evaluated [25] in the specific case of solutions of sodium metal in molten cryolite (Na₃AlF₆, or AlF₃·3NaF). In AlF₃-NaF mixtures, a fourfold-coordinated trivalent state of the Al ion (the (AlF₄)⁻ complex) is stable at the 'stoichiometric' composition corresponding to AlF₃·NaF (see Fig. 2), but it is known from Raman scattering experiments [26] that it is gradually converted into a sixfold-coordinated trivalent state (the (AlF₆)³⁻ complex) as the NaF content is increased towards the composition of cryolite. In particular, the structure of molten cryolite is understood and calculable at the microscopic level [27] in terms of dominant (AlF₆)³⁻ complexes with some residual admixture of (AlF₄)⁻ complexes. The ionic equilibrium between long-lived (AlF₆)³⁻ and (AlF₄)⁻ units in the melt results from a balance between the difference in binding free energy for the two species in vacuo, which favours the (AlF₄)⁻ species, and the rise in the excess free energy of the liquid on dissociation of (AlF₆)³⁻ into (AlF₄)⁻ and two F⁻.

On assuming that the sodium metal enters molten cryolite in the form of Na⁺ ions and electrons, the calculations [25] 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 are



and



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 (see Fig. 3) that with increasing Na metal content the equilibrium between $(\text{AlF}_6)^{3-}$ and $(\text{AlF}_4)^-$ shifts in favour of the latter, while at the same time Al^{3+} ions are released into the melt and bind the available electrons to form Al^{2+} and Al^+ ions. Eventually the latter oxidation state becomes the most stable one and the $(\text{AlF}_4)^-$ complex is also destabilized. This scenario is consistent with macroscopic observations on the chemical products resulting from adding metals to molten cryolite [28]. These were aimed at experimentally clarifying the relative roles of Al and Na in the cathodic processes involved in the industrial production of Al metal from electrolytic baths containing cryolite.

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.

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Table I. - Physical properties of some divalent and trivalent metal chlorides

Salt	Crystal structure	T_m (K)	ΔS_m (e.u.)	$\Delta V/V^a$	σ ($\Omega^{-1}cm^{-1}$)	η (cp)
SrCl ₂	CaF ₂	1146	5.9 ^b	0.13	2.0	3.7
ZnCl ₂	ZnCl ₂	570	4.1	0.16	1.x10 ⁻³	4.x10 ³
AlCl ₃	AlCl ₃	466	18.1	0.88	5.x10 ⁻⁷	0.36
YCl ₃	AlCl ₃	994	7.6	0.0045	0.39	--

^a Relative difference between the volume of the liquid at T_m and that of the solid at room temperature, the volume of the solid at T_m being in some cases unknown.

^b Sum of the entropy change for the superionic transition and for melting.

Figure captions

Fig. 1. - Idealized structure of a layer in the $AlCl_3$ type crystal structure as seen along the c axis. The Cl ions are shown by gray spheres (top plane of the layer) and white spheres (bottom plane of the layer), while the black spheres show the metal ions in a plane sandwiched by the two Cl planes. For a structural illustration of the melting mechanisms of YCl_3 and $AlCl_3$, we also show (a) an octahedron centered on an Y ion and sharing three gray-to-white edges with the three neighbouring Y ions, and (b) the Al_2Cl_6 unit which deforms into two edge-sharing tetrahedra on melting of $AlCl_3$. From M.-L. Saboungi *et al.*, ref. [6].

Fig. 2. - Stability map for fourfold coordination in molten M-A(X) mixtures near 'stoichiometric' composition. The label (Cl) has been omitted for the chlorides. The break in the vertical scales refers to the fluoride systems. From Z. Akdeniz and M. P. Tosi, ref. [10].

Fig. 3. - Calculated 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 Na metal in molten cryolite. The curve marked $(2x_1 + x_2)^{max}$ gives the upper limit to the amounts of Al ions in reduced valence states from the number of available valence electrons. From Z. Akdeniz and M. P. Tosi, ref. [25].

