

REFERENCE

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LOCAL COORDINATION OF POLYVALENT METAL IONS IN MOLTEN HALIDE MIXTURES *

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ABSTRACT

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. Recent schemes for classifying this evidence are discussed. Dissociation of tetrahedral halocomplexes in good ionic systems can be viewed as a classical Mott problem of bound-state stability in a conducting matrix. More generally, structural coordinates can be constructed from properties of the component elements, to separate out systems with long-lived fourfold or sixfold coordination and to distinguish between these.

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1. INTRODUCTION

The liquid structure of alkali halides and of strongly ionic divalent metal halides such as SrCl_2 is now reasonably well understood¹. A number of new and interesting structural behaviours are met when one turns to the melts of other polyvalent metal halides. In particular, network-like liquid structures, with relatively long time scales for structural stability as indicated by Raman spectra and by transport data in the melt, are known for a number of such systems. We mention as examples (i) the glass-former ZnCl_2 , having a tetrahedrally coordinated network structure in the melt², and (ii) molten YCl_3 , which is expected to have a loose octahedrally coordinated network structure. The latter suggestion comes from Raman scattering experiments on molten Y-alkali chloride mixtures over a broad range of composition³, which show persistence of the breathing mode associated with $(\text{YCl}_6)^{3-}$ octahedral units from alkali-rich mixtures up to the pure YCl_3 melt. The alkali halide in such mixtures acts as a chlorine donor to break into separate units the network structure of the pure melt, which involves chlorine sharing between such units.

Some 140 such liquid mixtures 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, electronic transitions absorption, and thermodynamic measurements. A critical discussion of the evidence, with a full list of references, has been given in ref. 4. The basic structural questions being asked are (i) whether the molten mixture contains "complexes" (i. e. molecular-ion units with a lifetime which is at least of the order of typical translational and rotational diffusion times) and what are the (typically fourfold or sixfold) coordination and the geometry of these complexes, or (ii) whether the polyvalent metal ions fluctuate rapidly between different coordination states, with an average coordination number of order six. 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, and the Sr-alkali and Ba-alkali chlorides, where no structure is observed in the Raman spectrum⁵.

2. DISSOCIATION OF COMPLEXES AS A CLASSICAL MOTT TRANSITION

In good ionic materials such as the alkaline earth - alkali halide mixtures the dissociation of a complex in the alkali-rich region is determined 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 conductor⁶. 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 bond length and the screening length with varying composition exceeds a critical value.

The above qualitative argument has been substantiated by calculations on Ca-alkali chloride solutions, based on a charged-hard-spheres model in the mean spherical approximation of liquid structure theory. A critical bond length to screening length ratio of about 1.6 is thereby indicated for tetrahedral complexes in these systems. Such a critical value separates 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 it. This structure sorting criterion is in agreement with the available Raman scattering data⁵.

3. STABILITY DIAGRAMS FOR FOURFOLD AND SIXFOLD COORDINATION

In cases of strong stability of complexes, however, the structural evolution of the liquid mixture with decreasing concentration of alkali halide is towards halogen sharing among fourfold or sixfold-coordinated complexes, rather than towards dissociation of complexes (see the Introduction). 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 compounds⁷.

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 Cohen⁸ and by Andreoni et al⁹, 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 on chemical bonding properties as well as on geometric core sizes. In a semiempirical approach, instead, though incorporating recent progress in understanding the cohesion of bulk solids from first-principles calculations, Pettifor¹⁰ has proposed a chemical scale of the elements. This orders all elements along a single axis χ so that the Mendeleev-type features of the periodic table are preserved.

Such structure-sorting approaches have been successfully adapted to the liquid structure problem at hand⁴. As the best example we report in Figure 1 the structural diagram obtained for molten mixtures of polyvalent metal halides and alkali halides on the basis of Pettifor's phenomenological chemical scale. Successful structural coordinates are constructed for each M-A(X) liquid mixture from the elemental property χ as

$$X_{M-A(X)} = X_M - X_A \quad , \quad Y_{M-A(X)} = X_M + X_A - 2X_X$$

(with M = polyvalent metal, A = alkali and X = halogen). Each mixture has been indicated in the diagram with 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.

In addition, the plane in Figure 1 has been 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 coordination of the types already discussed in section 2 above. 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 state¹¹, and (ii) by the Y-alkali and Ca-alkali chloride systems, already discussed in the Introduction.

4. CONCLUDING REMARKS

In summary, we have seen that established concepts and methods for structure sorting in solid state physics find useful application in the specific problem of liquid structure that we have considered, where they allow a meaningful systematization of the very ample evidence. Of course, structural predictions are immediate for the systems that are not included in the map in Figure 1. The order of the various systems along the main diagonal in the map also shows interesting correlations with the liquid structure of pure polyvalent metal halides, in those cases where it has already been determined by neutron diffraction. These correlations have been discussed in ref. 4.

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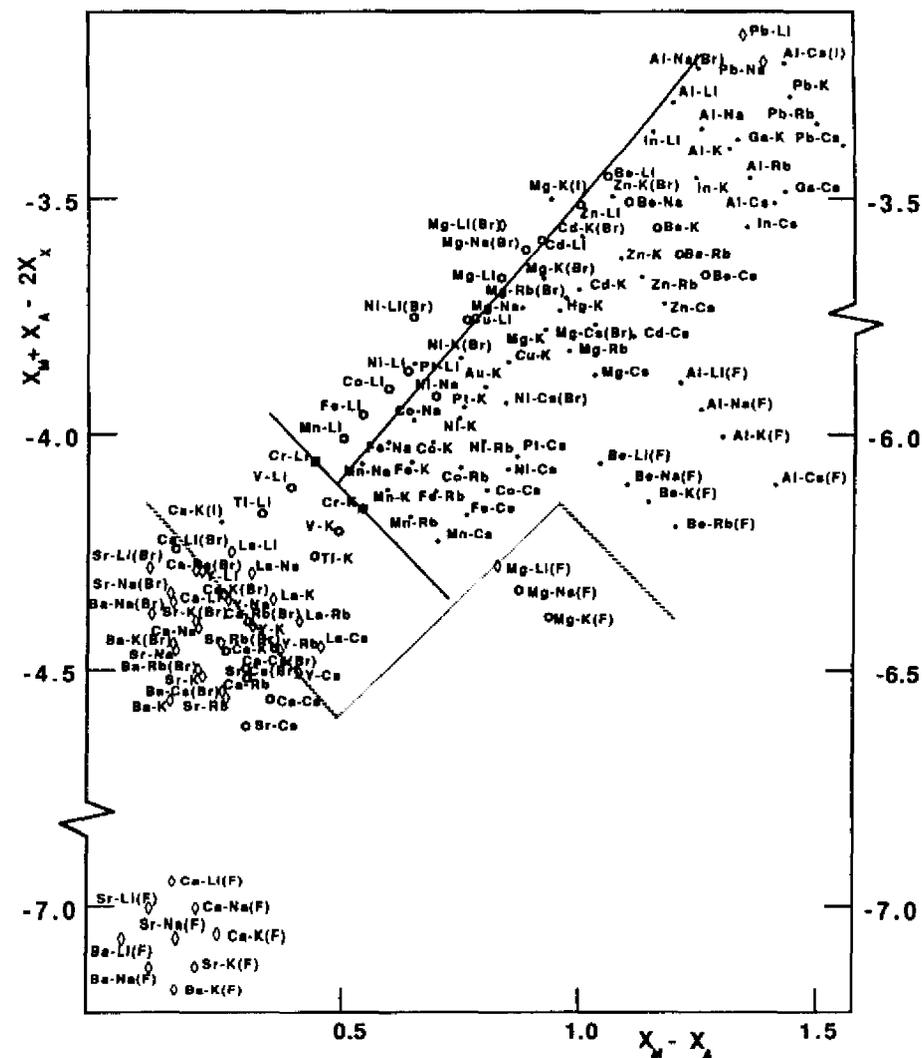


FIGURE 1

Stability map for fourfold coordination in molten M-A(X) mixtures at 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. 4.

