

**INTERNATIONAL CENTRE FOR
THEORETICAL PHYSICS**

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IN MOLTEN MIXTURES OF HALIDE SALTS

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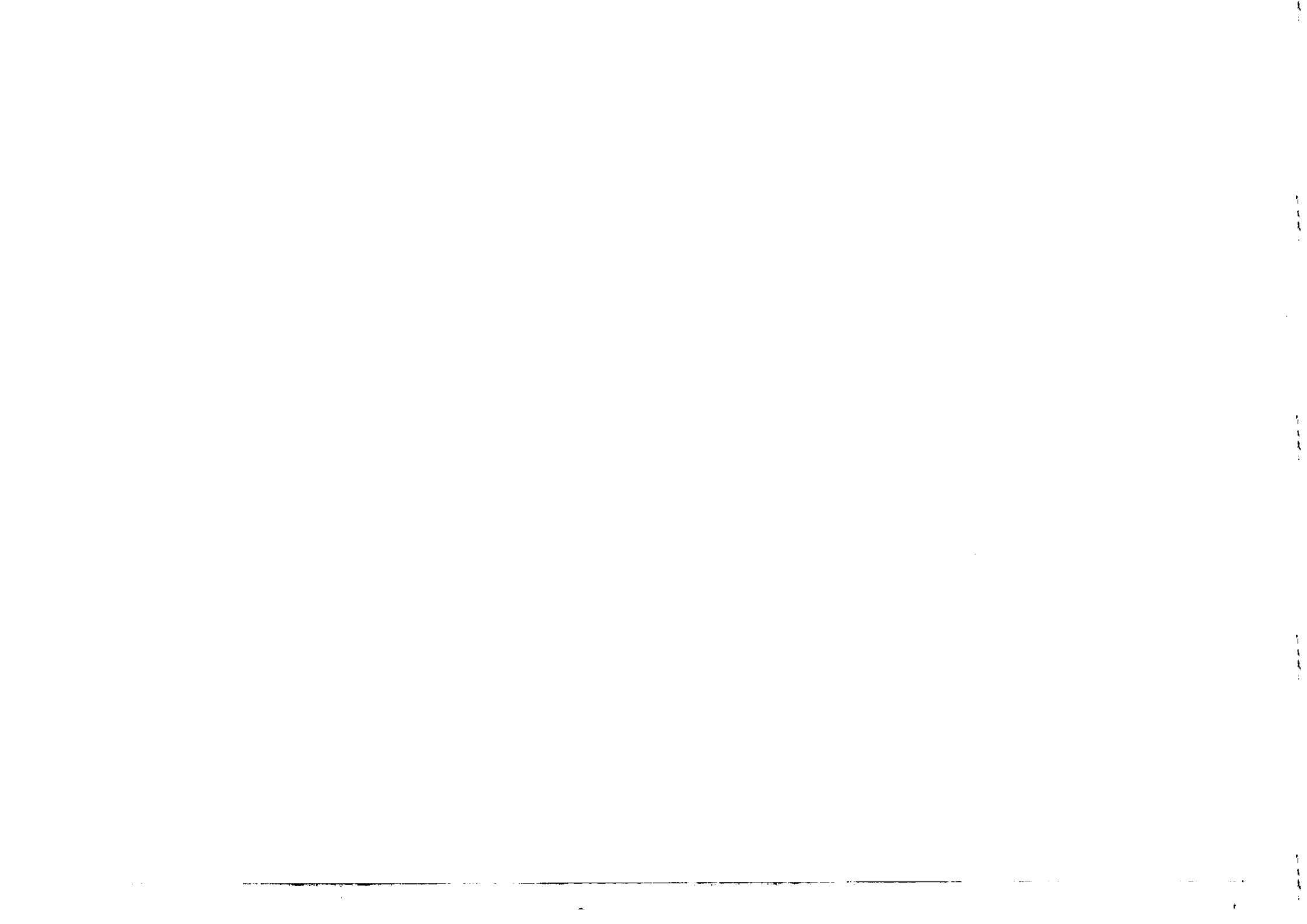
M.P. Tosi



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STABILITY DIAGRAMS FOR COMPLEXES IN MOLTEN MIXTURES OF HALIDE SALTS *

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ABSTRACT

The stability of local fourfold coordination for divalent and trivalent metal ions in liquid mixtures of polyvalent metal halides and alkali halides is classified by means of structural coordinates obtained from properties of the elements. In parallel with earlier classifications of compound crystal structures and molecular shapes, the elemental properties are taken from first-principles calculations of valence electron orbitals in atoms, in the form of (i) the nodal radii of Andreoni, Baldereschi and Guizzetti or (ii) the pseudo-potential radii of Zunger and Cohen. As a third alternative we also consider a classification based on Pettifor's phenomenological chemical scale of the elements. The alternative structural classification schemes that are developed from these elemental properties are very successful in distinguishing molten mixtures in which the available experimental evidence indicates stability of "complexes", i.e. long-lived fourfold coordination of polyvalent metal ions.

MIRAMARE - TRIESTE

October 1988

* Submitted for publication.

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1. Introduction

The prediction of the stable structure taken by an atomic aggregate in given thermodynamic conditions, starting from properties of its atomic constituents, has been a challenging problem for many years. As an alternative to full quantal calculations, a semi-empirical approach of "structure sorting" has been very popular for the structural classification of broad families of compounds. In the case of crystalline solids, this leads to structural maps for families of binary compounds, based on parameters of the elements (St John and Bloch 1974; Chelikowsky and Phillips 1978; Zunger and Cohen 1979; Andreoni, Baldereschi, Bièmont and Phillips 1979; Zunger 1980; Burdett, Price and Price 1981; Villars 1983, 1984, 1985; Andreoni 1985; Pettifor 1986; for a general review see Mooser 1986). The same approach has recently been adopted in the classification of the equilibrium shapes taken by small polyatomic molecules and atomic clusters (Andreoni, Galli and Tosi 1985; Andreoni and Galli 1987).

Extension of these methods to the classification of liquid structures can be expected to be at least as useful, but certainly more difficult. While a promising start has been made in the case of silicon to first-principles calculations of disordered structures (Car and Parrinello 1988), the theory of liquid structure still relies heavily on the use of pair (or more complex) interatomic potentials. On the other hand, it is hard to draw sharp distinctions between the liquid structures taken by different compounds of the same family, even if one compares them in somehow corresponding thermodynamic states -- for instance by referring to the liquid near freezing at atmospheric pressure. Nevertheless, correlations between crystal structure maps and liquid state diffraction data have already been noticed for MX_2 double-octet compounds (Rovere and Tosi 1986).

The structure sorting approach can be directly applied to at least one structural problem in liquid state physics, concerning the local coordination taken by polyvalent metal ions when they are supplied with an excess of halogen ions through mixing their halide salts with alkali halides in the molten state (Akdeniz,

Wang Li and Tosi 1988). There is ample evidence in the literature on this structural aspect of molten salt mixtures, although in most cases the evidence is not as direct as in a diffraction experiment. In many systems, the data indicate fourfold coordination of divalent or trivalent metal ions by halogens, of tetrahedral or distorted tetrahedral type. Such local coordination is usually, and somewhat loosely, referred to as a "complex". It is not, however, a general phenomenon occurring for all polyvalent metal ions. In a number of systems the data exclude the formation of complexes, in the sense that none of the characteristics that go with it (for instance, a typical behaviour of the heat of mixing versus concentration or structures in the Raman scattering spectrum) are observed. The polyvalent metal ions in such mixtures presumably have, and in some cases are observed to have, an "octahedral" coordination of order six.

A comprehensive classification of trends in complex stability with varying chemical species, i. e. in dependence of the polyvalent metal M, the halogen X and the alkali A, is the purpose of the present work. It extends our previous work under two main aspects, namely (i) a broad variety of divalent and trivalent metal ions, including transition metal ions, will be considered and (ii) various alternative schemes of structural sorting will be examined.

2. The evidence

The word "complex" has been used in the literature with somewhat different meanings by different authors. A strict viewpoint uses it to denote a kinetic entity persisting in the liquid over times appreciably longer than typical times for translational and rotational diffusion, i. e. longer than 10^{-11} s and possibly as long as 10^{-5} s. The same expression is still applied by some authors to systems in which polyvalent metal ions are fluctuating between fourfold - coordinated and more highly coordinated states over a time scale which is just sufficiently long for some

characteristic structure to be visible in a Raman scattering spectrum, the time scale of the experiment being then of order 10^{-13} s. As an example of a borderline case of the latter type we may quote the $\text{CaCl}_2\text{-2KCl}$ liquid mixture, as examined by Raman scattering and discussed in the work of Sakai, Nakamura, Umesaki and Iwamoto (1984). Data analysis in this mixture has led the authors to propose coexistence of tetrahedral-type and octahedral-type coordinations for the Ca ion.

Clearly, we are first of all interested in identifying systems of strong complex stability, in terms of observed characteristic behaviours that will be specified immediately below. In addition, however, we shall also try to recognize systems in which the stability of complexes may be described as marginal, since these naturally should lie at the boundaries of the stability region. The systems for which the available evidence excludes the presence of fourfold - coordinated states, except perhaps on a very fleeting and as yet unresolved time scale, should lie outside this region. We shall therefore classify the systems of present interest on the basis of the available experimental evidence into three classes, i. e. strong stability, marginal stability and instability of fourfold coordination.

The techniques of X-ray diffraction and neutron diffraction are, of course the most direct for the determination of local coordination in liquids. Such measurements are to our knowledge available only for the Be-Li(F) system (Vaslow and Narten 1973), the Al-Na(Cl) system (Takahashi, Maruoka, Koura and Ohno 1986) and the $\text{AlCl}_3\text{-LiCl}$ mixture (Takahashi, Muneta, Koura and Ohno 1985; Biggin, Cummings, Enderby and Blander 1985). In all cases the observed characteristics of the pair distribution functions show strong stability of $(\text{BeF}_4)^{2-}$ and $(\text{AlCl}_4)^-$ complexes. Fortunately, the same systems have also been studied by indirect techniques involving thermodynamic measurements (Holm and Kleppa 1969), Raman scattering (Quist, Bates and Boyd 1972) and infrared emission spectroscopy (Hvistendahl, Klaeboe, Rytter and Øye 1984). Further confidence is thus gained in conclusions based on these techniques for other systems.

Thermodynamic measurements carry evidence through the so-called interaction

parameter derived from the enthalpy of mixing as a function of concentration. It is commonly defined as the enthalpy of mixing divided by the concentrations of the two halide salts in the mixture and is itself a function of concentration. Data are available from the work of McCarty and Kleppa (1964), Kleppa and McCarty (1966), Holm and Kleppa (1969), Papatheodorou and Kleppa (1970, 1971a, 1971b), Østvold (1972) and Hong and Kleppa (1978). In cases of strong complex stability, mixing is strongly exothermic and the interaction parameter shows a marked minimum at or near a characteristic concentration of polyvalent metal halide, equal to $1/3$ for MX_2 and to $1/2$ for MX_3 . The need for measurements on a wide concentration range implies that the system is usually investigated by this technique at higher temperatures than in a Raman scattering or optical absorption experiment. While the identification of strong stability cases from these data appears to be unambiguous, one may not feel fully confident that negative evidence is probatory. We have taken the thermodynamic data as indicative of at least marginal stability, in the lack of other data, for systems where the interaction parameter is not flat as a function of concentration and is at least 10 kcal/mol in magnitude. We have tentatively inferred instability when the interaction parameter fails to satisfy both criteria.

A large number of Raman scattering experiments have been performed on M-A(X) systems. We have been able to find relevant data in the work of Bues (1955), Janz and James (1963), Ellis (1966), Clarke and Hester (1969), Begun, Boston, Torsi and Mamantov (1971), Maroni (1971), Maroni, Hathaway and Cairns (1971), Øye, Rytter, Klæboe and Cyvin (1971), Clarke, Hartley and Yuroda (1972), Quist *et al* (1972), Øye, Rytter and Klæboe (1974), Brooker (1975), Gilbert, Fung, Mamantov and Begun (1975), Gilbert, Mamantov and Begun (1975), Brooker and Huang (1980), Bues, Atapoor and Popperl (1983), Emons, Horlbech and Kiessling (1984) and Sakai *et al* (1984). The presence of stable complexes in the liquid mixture is revealed by fairly narrow bands superposed on a spectral background rising rapidly at low frequency. The band peak frequencies can be put in correspondence with Raman frequencies associated with the fourfold-coordinated ion in crystals or in aqueous solutions. Polarization studies give further information on the stable entity which is being

observed -- in particular, the band associated with the totally symmetric stretching mode of a tetrahedral complex is especially prominent and easily identified. In the absence of such prominent spectral features, a detailed analysis of the observed spectrum still allows identification of marginally stable complexes, as in the aforementioned work of Sakai *et al* (1984) on $CaCl_2 \cdot 2KCl$. We have also tentatively attributed marginal stability to complexes in mixtures where a well defined shoulder is seen in the Raman spectrum without further analysis of the data. Finally, we have interpreted the data of Prisyazhnyi, Baranov and Sunegin (1978) on molten $BeCl_2$ as indicative of at least marginal stability for $(BeCl_4)^{2-}$ complexes in Be - alkali chloride systems.

Infrared emission and absorption spectra are also available for a few systems and have been discussed by their authors in relation to the problem of complex stability (Wilmhurst 1963, Hvistendahl *et al* 1984). Of special interest among optical measurements are the absorption spectra in the near-visible and visible for transition metal ions in liquid chloride mixtures (Gruen and McBeth 1959 and 1963, Gruen 1964, Smith and Boston 1965). The coordination geometry of the ion is directly reflected in the spectrum through the splitting that it induces in the d-electron energy levels. For several divalent ions (Ni^{2+} , Cu^{2+} , Cr^{2+} , Fe^{2+} , Co^{2+} and Mn^{2+}) tetrahedral-type coordination is the only one observed, with an appreciable distortion from ideal tetrahedral symmetry for the three former ions. On the other hand, only octahedral-type coordination is observed for trivalent Cr^{3+} , while coexistence of octahedral and distorted tetrahedral configurations is reported for V^{2+} , V^{3+} and Ti^{3+} , at least at relatively high temperature.

With the benefit of the authors' discussion of their own data and following the criteria that we have briefly exposed in the foregoing discussion, we have achieved a classification of fourfold coordination for polyvalent ions into the three indicated classes, i. e. stable, marginally or possibly stable, and unstable. The results will be reported at a later stage, after we shall have presented the appropriate coordinates by which each system can be labelled. Needless to say, in some systems the available evidence is insufficient to allow more than a tentative assignment. We also met a

few cases where conflicting indications could be obtained from different measurements. We shall comment on such systems as appropriate in the final discussion.

3. Structural maps

We consider first the construction of structural parameters starting from the pseudopotential radii S_l ($l = 0, 1$) of Zunger and Cohen (1979) and from the nodal radii N_l ($l = 0, 1$) of Andreoni, Baldereschi and Guizzetti (unpublished). We recall that S_l is defined as the turning point of the l -component of the pseudopotential derived from atomic calculations in the local density approximation, while N_l is defined as the outermost node of the atomic valence electron orbital of angular momentum l from all-electron atomic calculations.

In the pseudopotential Zunger-Cohen (ZC) scheme one defines for each element E the elemental parameters

$$R_{\sigma}^E = S_0 + S_1 \quad (1)$$

and

$$R_{\pi}^E = |S_0 - S_1| \quad (2)$$

Compound parameters are then constructed for each binary compound of elements A and B as

$$Y_{AB}^{ZC} = |R_{\sigma}^A - R_{\sigma}^B| \quad (3)$$

and

$$X_{AB}^{ZC} = R_{\pi}^A + R_{\pi}^B \quad (4)$$

With specific reference to AB octet compounds and AB_2 double-octet (DO) compounds, Burdett *et al* (1981) have shown that successful sorting of crystal

structures is achieved in plots using the elemental parameters R_{σ}^A and R_{σ}^B as coordinates. The same choice of coordinates is successful in separating linear DO AB_2 molecules from bent ones (Andreoni *et al* 1985). On the other hand, use of the compound parameters defined in eqns (3) and (4) leads to very poor structure sorting for the DO AB_2 crystals (Burdett *et al* 1981). Evidently, we shall have to consider suitable combinations of elemental or compound parameters for each mixture in searching for two-dimensional structural plots for the systems of present interest.

In the nodal radii scheme proposed by Andreoni (1985), the elemental parameters are instead defined as

$$y_E = \frac{1}{4} (N_0^E + 3 N_1^E) \quad (5)$$

and

$$x_E = \frac{1}{4} (3 N_0^E - N_1^E) \quad (6)$$

The compound parameters are chosen as

$$Y_{AB} = y_B - y_A \quad (7)$$

and

$$X_{AB} = x_A + x_B \quad (8)$$

or (for AB_2 compounds)

$$X'_{AB} = 2 x_A + x_B \quad (9)$$

Use of Y_{AB} and X_{AB} (or X'_{AB}) as coordinates yields successful sorting of crystal structures (Andreoni 1985), whereas molecular shapes can be classified by adopting either the pair (X'_{AB}, Y_{AB}) of compound coordinates or the pair (y_A, y_B) of elemental coordinates (Andreoni *et al* 1985).

We may briefly comment at this point on the aims of structure sorting on the basis of the atomic parameters recalled above. Of course, structure sorting has a long history, during which various indices such as sets of ionic radii or Pauling's electronegativities have been used. The aim of the pseudopotential and nodal radii schemes is to avoid empirical parametrizations by translating such physical indices

into precisely defined parameters of the valence electron orbitals, which are evaluated from first-principles calculations on the atoms.

It has also proved possible, on the other hand, to translate the recent progress in understanding the cohesion of bulk solids from first-principles calculations into a phenomenological chemical scale of the elements (Pettifor 1984). This approach orders all the elements along a single axis χ so that the Mendeleev-type features of the periodic table are preserved. Such a one-dimensional ordering of the elements provides excellent sorting of crystal structures for a large variety of binary compounds with given stoichiometry A_mB_n in a plot using the pair (χ_A, χ_B) as coordinates (Pettifor 1986).

Let us now proceed to the selection of coordinates for two-dimensional structural maps of the liquid mixtures of present interest. The guidelines have already been described in relation to the nodal radii scheme (Akdeniz *et al* 1988). A broad feature of the available data for alkaline earth - alkali halide mixtures is that the stability of complexes decreases as the alkaline earth component is varied from Be to Ba and as the alkali component is varied from Cs to Li. This immediately suggests that the difference $X_{MX} - X_{AX} = x_M - x_A$ is a relevant structural coordinate. A more detailed examination of the evidence is necessary to identify a second coordinate. The dependence of the stability of complexes on the halogen species has not been so far studied experimentally in a fully systematic manner, and in particular very little evidence is available for iodides. Nevertheless the evidence indicates some tendency to increased stability from the fluoride to the bromide. Further hints come from comparisons of specific pairs of alkaline earth and alkali ions in their chloride mixtures, for instance the comparison of the Mg-Na(Cl) system, which is a strong stability case (Kleppa and McCarty 1966, Brooker and Huang 1980), with the Ca-K(Cl) system, which is a marginal stability case (Østvold 1972, Sakai *et al* 1984). All these features emerging from the body of available data can be incorporated into structure sorting by the choice of $Y_{MX} + Y_{AX} = 2y_X - y_M - y_A$ as the second structural coordinate in the nodal radii scheme.

The structural map obtained with the above choice of coordinates is shown in Figure 1. We have indicated with a dot those systems for which the evidence is strongly in favour of stable complexes. The other systems are marked with a lozenge when the available evidence tends to exclude the presence of fourfold coordination and with a circle in cases of marginal or possible complex stability. Each system is labelled by the notation M-A(X), except for the chlorides where the halogen label has been omitted for the sake of clarity.

The map in Figure 1 contains several more systems than our earlier simplified plot, but is still incomplete relative to the available evidence. It does not include transition metal ions nor heavy ions such as Pb and Au, in the lack of nodal radii for these elements. In view of its incompleteness we shall not comment in detail on it, but shall merely remark that a straight line through the marginal stability systems Ca-K(Cl) and Ca-Li(Br) achieves almost complete separation between stability and instability of complexes in the mixtures that are present in the plot. The only exceptions are Mg-Li(F) and Mg-Li(Br), on which we shall return later.

The guidelines that we have summarized above are again useful in identifying appropriate structural coordinates in the ZC pseudopotential scheme and in Pettifor's chemical scale scheme. In the former we find, with the definitions given earlier in eqns (3) and (4), that successful structural coordinates for each mixture can be obtained as

$$X_{M-A(X)} = X_{MX}^{ZC} - X_{AX}^{ZC} = R_{\pi}^M - R_{\pi}^A \quad (10)$$

and

$$Y_{M-A(X)} = Y_{MX}^{ZC} + Y_{AX}^{ZC} = |R_{\sigma}^M - R_{\sigma}^X| + |R_{\sigma}^A - R_{\sigma}^X| \quad (11)$$

The structural map obtained with the values of the pseudopotential radii reported by Zunger (1980) is shown in Figure 2. Finally, in the chemical scale scheme the appropriate coordinates for each mixture are found to be

$$X_{M-A(X)} = \chi_M - \chi_A \quad (12)$$

and

$$Y_{M-A(X)} = \chi_M + \chi_A - 2\chi_X \quad (13)$$

leading to the structural map shown in Figure 3. Here, the Y coordinate for the fluoride mixtures has been raised by 2 for compactness, as shown by the breaks in the vertical scales of the Figure.

It is immediately seen from Figures 2 and 3 that both maps yield very good separation between stability and instability of complexes. In Figure 2 straight lines drawn as shown through the marginal stability systems Ca-Li(Br), Ca-K(Cl) and Sr-Cs(Cl) achieve separation with some mixing in the boundary region. The plot in Figure 3 is even more successful, since a single straight line passing through the marginal stability systems Ca-Li(Br), Sr-Cs(Cl) and Mg-Na(F) achieves separation with a minimal amount of mixing in the boundary region. The relevant sources of the data are Emons *et al* (1984) for Ca-Li(Br), Østvold (1972) and Sakai *et al* (1984) for Ca-K(Cl) and Sr-Cs(Cl), and Hong and Kleppa (1978) for Mg-Na(F). More specific comments on the two structural plots will be given in the discussion immediately below.

4. Discussion

Having already noted that there is some more fuzziness in the boundary between stability and instability in the ZC map in Figure 2, we shall continue the discussion without distinguishing between the two structural plots except as necessary.

Firstly, three systems that we have classified as non-complexing, i.e. Pb-Li(Cl), Pb-Na(Cl) and Mg-Li(Br), are found to lie inside the strong stability region. We remark that only thermodynamic data are available for these systems (McCarty and Kleppa 1964, Østvold 1972). They would seem to be natural candidates for Raman scattering experiments. A similar comment applies to Mg-Li(F), which lies just outside the stability region in Figure 3 but inside it in Figures 1 and 2. We have

classified it as non-complexing on the basis of thermodynamic data by Hong and Kleppa (1978).

Secondly, the Be - alkali chloride data, that we have included in the intermediate class of marginal or possible complex stability in the lack of data except on the pure BeCl₂ melt (Prisyazhnyi *et al* 1978), are seen to lie well inside the strong stability region. Subject to experimental verification, we should infer that complexes are strongly stable in these mixtures.

Let us consider next a set of M-Li(Cl) systems, included by us in the intermediate class, which are seen to cluster in the bottom right-hand corner in Figure 2 and to lie at the upper edge of the strong stability strip in Figure 3. The optical absorption experiments show stable fourfold coordination for divalent Cu, Ni, Co, Fe and Mn ions in a solvent which is a molten mixture of LiCl and KCl near eutectic composition (Gruen 1964). Infrared absorption data in the case of Cu (Wilmhurst 1963) and thermodynamic data in the other cases (Papatheodorou and Kleppa 1970, 1971a) confirm stability of complexes in the KCl solvent but are against it in the LiCl solvent. There is clear conflict for Cd-Li(Cl) between thermodynamic data (Papatheodorou and Kleppa 1971b) and Raman scattering data (Clarke *et al* 1972), and for Zn-Li(Cl) between infrared absorption data (Wilmhurst 1963) and Raman scattering data (Ellis 1966). At least for the two latter systems, their location in our plots, and especially in Figure 3, would suggest an identification as strong complex stability cases. In the case of Zn-K(Cl) we have felt that the conflict between infrared absorption (Wilmhurst 1963) and Raman scattering (Bues 1955, Ellis 1966) ought to be resolved in favour of complex stability.

The Cr ion deserves special notice. As already pointed out in section 2, optical absorption experiments show that its coordination depends on its valence state, yielding stability for (CrCl₄)²⁻ complexes of distorted tetrahedral shape and instability for (CrCl₄)⁻ complexes. Our classification schemes make no provision for such dependence of complex stability on the number of valence electrons. The importance of this variable in structural stability problems has been stressed for

solids by Villars (1983, 1984, 1985) and is well known in relation to equilibrium molecular shapes (see for instance Andreoni *et al* 1985).

Finally, one may wish to ask how our structural plots fare on a less qualitative level in relation to the magnitude of the binding of a stable complex or to its specific shape, which may range from tetrahedral to distorted tetrahedral to square planar as in the case of $(\text{AuCl}_4)^-$ in Au-K(Cl) (Gilbert *et al* 1975). In this regard we can only remark that the prototype case of a strongly bound tetrahedral complex, i. e. $(\text{AlCl}_4)^-$, is found in all our plots to lie very far from the boundary between stability and instability.

Acknowledgments. This work was carried out during the 1988 Research Workshop in Condensed Matter, Atomic and Molecular Physics at the International Centre for Theoretical Physics in Trieste. One of the authors (Z. A.) wishes to thank Professor Abdus Salam, the International Atomic Energy Agency and UNESCO for hospitality at the Centre. The other author (M. P. T.) acknowledges sponsorship by the Ministero della Pubblica Istruzione and the Consiglio Nazionale delle Ricerche of Italy.

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Figure captions

Figure 1. Stability map for complexes from Andreoni's nodal radii. Dots, circles and lozenges denote systems of strong stability, marginal or possible stability, and instability. The line marks the approximate location of the boundary between stability and instability.

Figure 2. As in Figure 1, from the Zunger-Cohen pseudopotential radii. A special symbol has been used for the Cr ion, whose coordination depends on the valence state.

Figure 3. As in Figures 1 and 2, from Pettifor's chemical scale of the elements. The break in vertical scale refers to the fluoride systems. The same vertical break has been made in the boundary line between complex stability and instability.

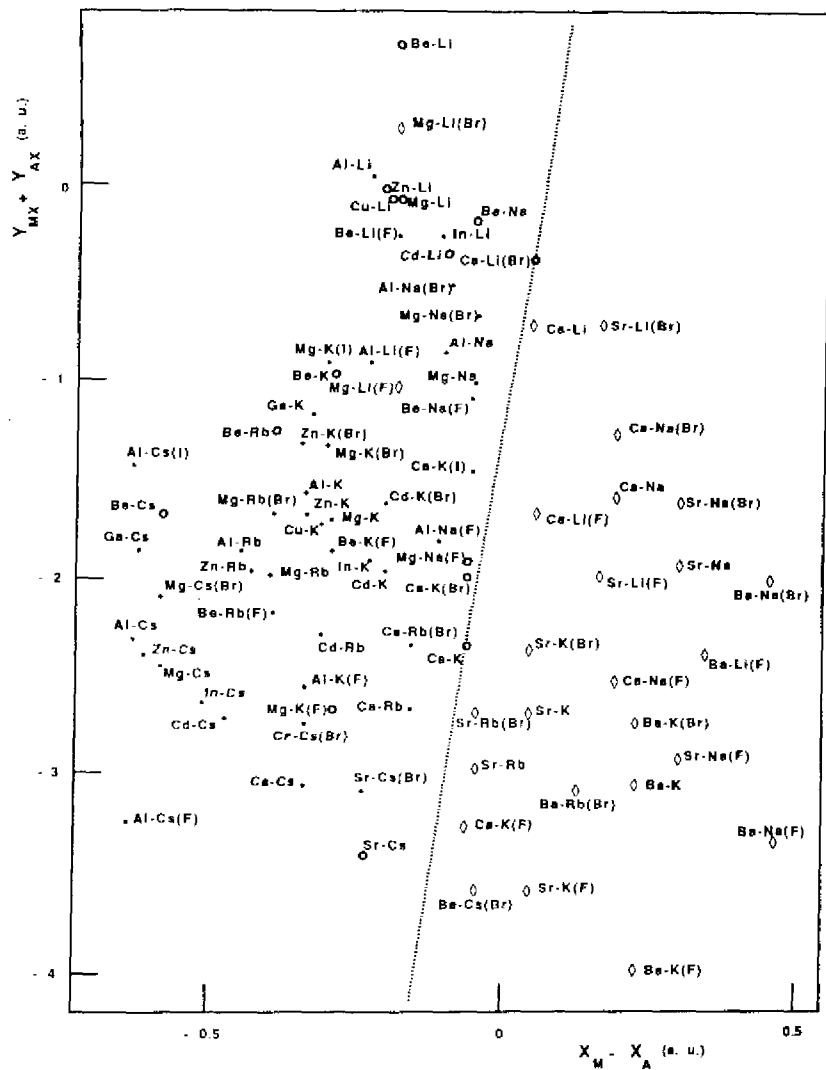


Fig.1

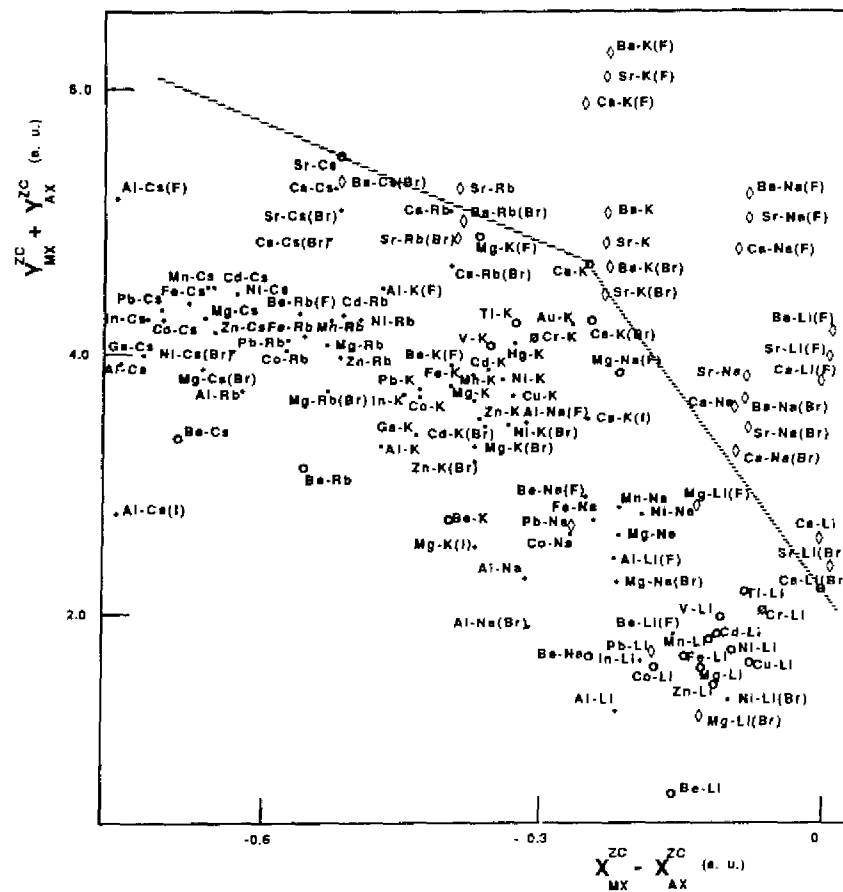


Fig.2

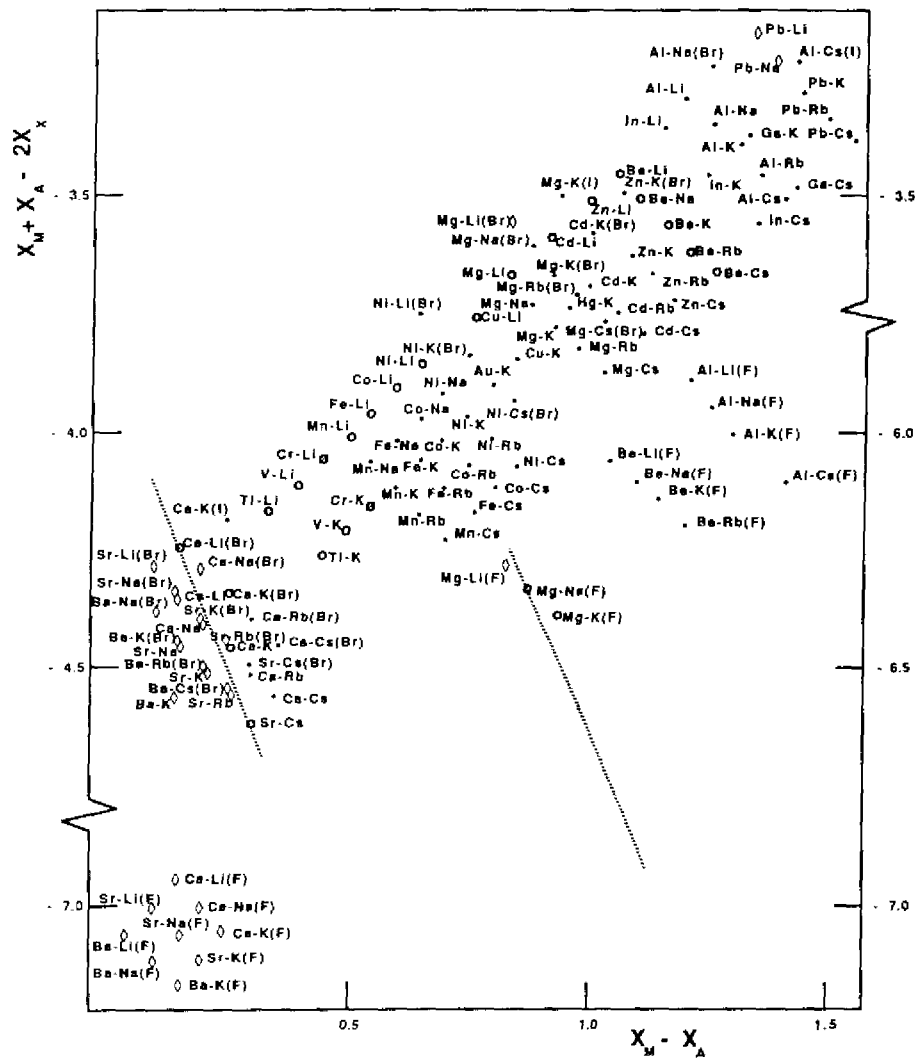


Fig.3

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