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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 pseudopotential radii of Zunger and Cohen. As a third alternative a classification based on Pettifor's phenomenological chemical scale of the elements is also considered. The alternative structural classification schemes that are developed from these elemental properties are generally successful in distinguishing molten mixtures in which the available experimental evidence indicates long-lived fourfold coordination of polyvalent metal ions. In addition, Pettifor's chemical scale scheme is useful in sorting out finer details of local coordination in the liquid state.

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 *et al* 1979a, Zunger 1980, Burdett *et al* 1981, Villars 1983, 1984a,b, 1985, Andreoni 1985, Pettifor 1986, for a general review see Mooser 1986). The same approach has been adopted in the classification of the equilibrium shapes taken by small polyatomic molecules and atomic clusters (Andreoni *et al* 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) inter-atomic 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 *et al* 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 that obtainable in a diffraction experiment. In order to embrace a large number of such mixtures, which may show different behaviours with varying concentration c of polyvalent metal halide, we shall refer as much as possible to a 'stoichiometric' composition given by $c = \frac{1}{3}$ for divalent ions and $c = \frac{1}{2}$ for trivalent ones. 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 may somewhat loosely be referred 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 enthalpy and entropy of mixing versus concentration or structures in the Raman scattering spectrum) are observed. The polyvalent metal ions in such mixtures presumably have a loose average coordination of order six. Formation of long-lived octahedral complexes has also been reported for several trivalent ions in molten salt mixtures, the 'stoichiometric' composition then being $c = \frac{1}{4}$.

The purpose of the present work is a comprehensive classification of trends in complex stability with varying chemical species, i.e. its dependence on the polyvalent metal M, the halogen X and the alkali A, in liquid mixtures of MX_2 or MX_3 with AX (abbreviated in the following as M–A(X)) at stoichiometric composition. It extends our previous work under two main aspects, namely (i) a broad variety of divalent and trivalent metal ions, including transition and rare-earth metal ions, will be considered and (ii) various alternative schemes of structural sorting will be adopted. The usefulness of each scheme will be taken as proven from its applications to crystal structure classifications and the various predictions will be examined for the insight that they may give into the present liquid structure problem.

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 timescale which is just sufficiently long for some characteristic structure to be visible in a Raman scattering spectrum, the timescale 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 $CaCl_2.2KCl$ mixture, as examined by Raman scattering and discussed in the work of Sakai *et al* (1984). Data

analysis has led the authors to propose coexistence of tetrahedral-type and octahedral-type coordinations for the Ca ion. One may expect in this case fairly rapid fluctuations for each Ca ion between these two preferred coordinations, given the good ionicity of the melt.

Clearly, we are first of all interested in identifying systems of strong stability for fourfold-coordinated states at stoichiometric composition, in terms of observed characteristic behaviours that will be specified immediately below. In addition, however, we shall also try to recognise systems in which the stability of such states may be described as marginal, since these naturally should tend to cluster in transitional regions. The systems for which the available evidence excludes the presence of fourfold-coordinated states, except perhaps on a very fleeting and as yet unresolved timescale, should in turn lie in separate regions of a structural map, with the possibility of further distinction between stable octahedral coordination and loose coordination due to rapid fluctuations. 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. We shall use the word 'complex' without further qualifications as an abbreviation for fourfold-coordinated state and shall include in the so-called marginal stability class cases of recognised coexistence between fourfold and more highly coordinated states as well as systems for which the evidence that we have found yields ambiguous indications.

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 $AlCl_3.LiCl$ mixture (Takahashi *et al* 1985, Biggin *et al* 1985), the Al–Na(Cl) system (Takahashi *et al* 1986) and the Al–K(Cl) system (Saboungi *et al* 1988). In all cases the observed characteristics of the pair distribution functions show strong stability of $(BeF_4)^{2-}$ and $(AlCl_4)^{-}$ complexes. Fortunately, the same systems have also been studied by indirect techniques involving thermodynamic measurements (Holm and Kleppa 1969), Raman scattering (Øye *et al* 1971, Quist *et al* 1972) and infrared emission spectroscopy (Hvistendahl *et al* 1984). Further confidence is thus gained in conclusions based on these techniques for other systems.

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) (Zn–K(Cl)), Janz and James (1963) (Hg–K(Cl)), Ellis (1966) (Zn–K(Br) and Zn–A(Cl) with A = Li, K, Rb, Cs), Clarke and Hester (1969) (In–A(Cl) with A = Li, K, Cs), Begun *et al* (1971) (Al–Na(Br) and Al–Cs(I)), Maroni (1971) and Maroni *et al* (1971) (Mg–K(X) with X = Cl, Br, I), Øye *et al* (1971) (Al–K(Cl)), Clarke *et al* (1972) (Cd–K(Br) and Cd–A(Cl) with A = Li, K, Cs), Quist *et al* (1972) (Be–A(F) with A = Li, Na), Øye *et al* (1974) (In–K(Cl)), Maroni *et al* (1974) (La–K(Cl)), Papatheodorou (1975) ($Cs_2NaLaCl_6$ and La–A(Cl) with A = K, Cs), Brooker (1975) (Mg–A(Cl) with A = K, Cs), Gilbert *et al* (1975a) (Au–K(Cl)), Gilbert *et al* (1975b) (Al–A(F) with A = Li, Na, K, Cs), Papatheodorou (1977) (Cs_2NaYCl_6 and Y–A(Cl) with A = Li, K, Cs), Brooker and Huang (1980) (Mg–A(Cl) with A = Li, Na, Rb, Cs), Bues *et al* (1983) (Ca–K(I)), Emons *et al* (1984) (Ca–A(Br) with A = Li, K, Rb) and Sakai *et al* (1984) (Ca–A(Cl), Sr–A(Cl) with A = K, Rb, Cs and Ba–K(Cl)). 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. Polarisation 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 permits identification of marginal stability, as in the aforementioned work of Sakai *et al* (1984) on $CaCl_2.2KCl$. 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 *et al* (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 from the work of Wilmhurst (1963) (M–A(Cl) with M = Zn, Cu and A = Li, K) and of Hvistendahl *et al* (1984) (Al–A(Cl)) and have been discussed by the authors in relation to the problem of complex stability. Of special interest among optical measurements are the electronic absorption spectra in the near-visible and visible regions for transition metal ions in liquid chloride mixtures. The coordination geometry of the ion is directly reflected in the spectrum through the splitting that it induces in the d electron energy levels. Reviews of the data have been given by Gruen and McBeth (1963) and Gruen (1964). Tetrahedral-type coordination is the only one observed for several divalent ions (Ni^{2+}, Cu^{2+}, Cr^{2+}, Fe^{2+}, Co^{2+} and Mn^{2+}) in a LiCl–KCl eutectic solvent, with an appreciable distortion from tetrahedral symmetry for the three former ions. Stability of $(NiCl_4)^{2-}$ in pure chloride solvents as well as of $(NiBr_4)^{2-}$ in pure bromide solvents is confirmed by the work of Smith and Boston (1965) (Ni–A(Cl) and Ni–A(Br) with A = Li, K, Cs), with the possible exceptions of the LiCl, NaCl and LiBr solvents. On the other hand, only octahedral coordination is observed for trivalent Cr^{3+} in the LiCl–KCl solvent, whereas for V^{2+}, V^{3+} and Ti^{3+} the spectra show a shift with increasing temperature from predominant octrahedral coordination to equilibrium between octahedral and distorted tetrahedral configurations. The shift can be strengthened by replacing the LiCl–KCl solvent with an appropriate different solvent (e.g. $CsGaCl_4$ in the case of $TiCl_3$). Finally, the $(PtCl_4)^{2-}$ complex in square planar configuration has been observed in Pt–A(Cl) systems with A = Li, K, Cs (Papatheodorou and Smith 1973).

Thermodynamic properties bearing on the problem at hand are the enthalpy of mixing from calorimetric measurements and the partial Gibbs free energies of mixing from EMF measurements in galvanic cells. Combination of the two experiments allows the evaluation of the entropy of mixing. Data are available from the work of McCarty and Kleppa (1964) (Pb–A(Cl)), Kleppa and McCarty (1966) (Mg–A(Cl)), Holm and Kleppa (1969) (Be–A(F) with A = Li, K, Rb), Ikeuchi and Krohn (1969) (Mg–A(Cl) with A = Na, K, Cs), Papatheodorou and Kleppa (1970 (Ni–A(Cl)), 1971a (M–A(Cl) with M = Mn, Fe, Co) and 1971b (Cd–A(Cl) with A = Li, Cs)), Østvold (1972a) (Mg–A(Br); Ca–A(X) with X = Cl, Br; Sr–A(Cl) with A = Na, K, Rb, Cs; Sr–A(Br); Ba–A(Br) with A = Na, K, Rb, Cs) and 1972b (Mn–A(Cl) with A = Li, Na, K, Rb), Dutt and Østvold (1972) (Co–A(Cl) with A = Li, Na, K, Rb), Papatheodorou and Kleppa (1974) (Ce–A(Cl)), Papatheodorou and Østvold (1974) (La–A(Cl)), Hong and Kleppa (1978) (M–A(F) with M = Mg, Ca, Sr, Ba and A = Li, Na, K) and Papatheodorou *et al* (1979) (Y–A(Cl)). The need for measurements on a wide concentration range implies that the system is usually at higher temperatures than in a Raman scattering or optical absorption experiment.

In the ideal case of infinitely strong complex stability, both the enthalpy and the entropy of mixing would show sharp minima at stoichiometric composition. However, calculations by Ikeuchi and Krohn (1969) show that the sharp minimum in the entropy

of mixing is already reduced to a small notch if the reaction constant for dissociation of $(MX_4)^{2-}$ becomes of order 10^{-2}, which at $c = \frac{1}{3}$ would still correspond to more than 80% of the divalent ions being on average bound in complexes. In practice most of the evidence concerns the enthalpy of mixing ΔH and is commonly interpreted by constructing the so-called interaction parameter $\lambda = \Delta H/c(1 - c)$ as a function of concentration. The presence of complexes is then inferred from the presence of a well defined minimum at or near stoichiometric composition. By comparison with the indications from other types of measurements it appears that this criterion is quite restrictive. For example in the Be–Li(F) system both ΔH and λ show only very broad minima in the region around $c \simeq 0.3$ (Holm and Kleppa 1969), although the stability of $(BeF_4)^{2-}$ complexes is demonstrated by x-ray diffraction (Vaslow and Narten 1973) and by Raman scattering (Quist *et al* 1972). We have therefore tended to give less weight to the thermodynamic evidence, but in the absence of other measurements we have tentatively accepted the conclusions drawn from the dependence of the interaction parameter on concentration and have inferred marginal stability of fourfold configurations at stoichiometric composition when λ is not flat and is at least 10 kcal mol^{-1} in magnitude. We have tentatively inferred instability when λ fails to satisfy both criteria.

With the benefit of the authors' discussion of their own data and following the criteria that we have exposed above, we have achieved a classification of fourfold coordination for polyvalent ions into the three classes indicated, i.e. stable, marginally or possibly stable, and unstable. The results will be reported at a later stage, after we have presented the coordinates by which each system may be labelled. We stress that in some systems the available evidence is insufficient to allow more than a tentative assignment and that we have 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 in § 4.

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 *et al* (1979b). We recall that S_l is defined as the classical 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

$$R_\sigma^E = S_0 + S_1 \tag{1}$$

and

$$R_\pi^E = |S_0 - S_1|. \tag{2}$$

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

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

and

$$X_{AB}^{ZC} = R_\pi^A + R_\pi^B. \tag{4}$$

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 (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

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

and

$$x_E = \tfrac{1}{4}(3N_0^E - N_1^E). \tag{6}$$

The compound parameters are chosen as

$$Y_{AB} = y_B - y_A \tag{7}$$

and

$$X_{AB} = x_A + x_B \tag{8}$$

or (for AB_2 compounds)

$$X'_{AB} = 2x_A + x_B. \tag{9}$$

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 parametrisations by translating such physical indices into precisely defined parameters of the valence electron orbitals, which are evaluated from first-principles calculations on the atoms. The elemental parameters in (1) and (2) or (5) and (6) correlate to a considerable extent with classical ionic radii (see e.g. Zunger 1980), although strictly they are properties of the valence electron orbitals rather than of ionic cores and carry information on chemical bonding properties in addition to geometric core size.

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 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 is varied from Cs to Li. This 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 so far not been studied experimentally in a fully systematic manner and, in particular, very little evidence is available for iodides. Nevertheless the evidence seems to indicate some tendency to increased stability from the fluoride to the chloride and bromide. Further hints come from comparisons of the behaviour of specific chlorides, for instance the comparison of the $BeCl_2$ melt and the Mg–Na(Cl) and Ca–K(Cl) systems, through which stability of fourfold coordination appears to progressively weaken. 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 in favour of good stability for fourfold coordination. The other systems are marked with an open diamond when the available evidence tends to exclude the presence of fourfold coordination and with an open circle in cases of marginal or possible 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 or rare-earth ions nor heavy ions such as Pb^{2+}, Hg^{2+} and Au^{3+}, in the absence 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 boundary through the marginal stability systems Ca–K(Cl) and Ca–Li(Br), as shown by the hatched line in figure 1, achieves almost complete separation of the non-complexing systems among the mixtures that are present in the plot. The only exceptions are Mg–Li(F) and Mg–Li(Br), to which we shall return later. It is also seen that the region of strong stability can be further delimited in the map, as shown by the full lines in figure 1.

The guidelines that we have summarised 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 (3) and (4), that successful structural coordinates for each mixture can be obtained as

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

and

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

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 appropriate coordinates for each mixture are found to be

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

and

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

leading to the structural map shown in figure 3. Here, the Y coordinate for the fluoride
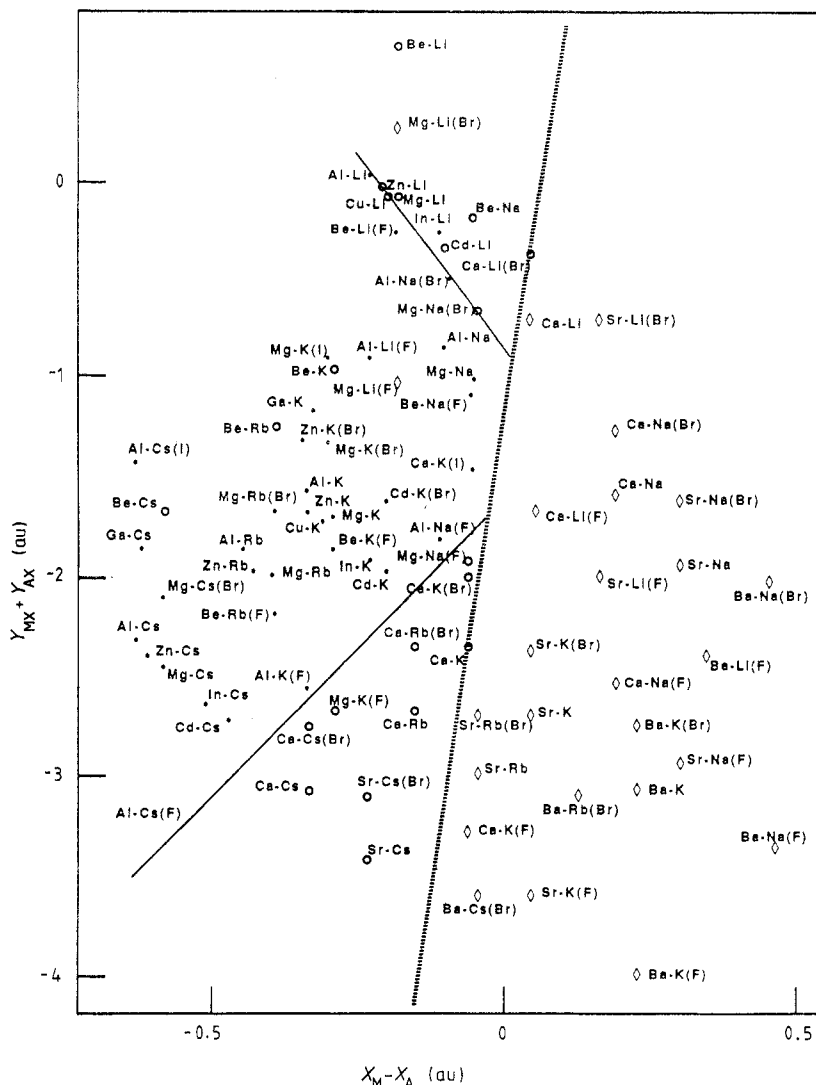
Figure 1. Stability map for fourfold coordination in molten M–A(X) mixtures at 'stoichiometric' composition, according to the nodal radii scheme. The label (Cl) has been omitted for the chlorides. Dots, open circles and open diamonds denote systems of strong stability, marginal or possible stability, and instability. The hatched line marks the approximate boundary of the region of instability, while the full lines approximately delimit the region of strong stability.

mixtures has been raised by 2 for compactness, as shown by the breaks in the vertical scales of the figure.

4. Discussion

It is immediately seen from figures 2 and 3 that both maps achieve very good separation between stability and instability of fourfold coordination. The strong stability cases are
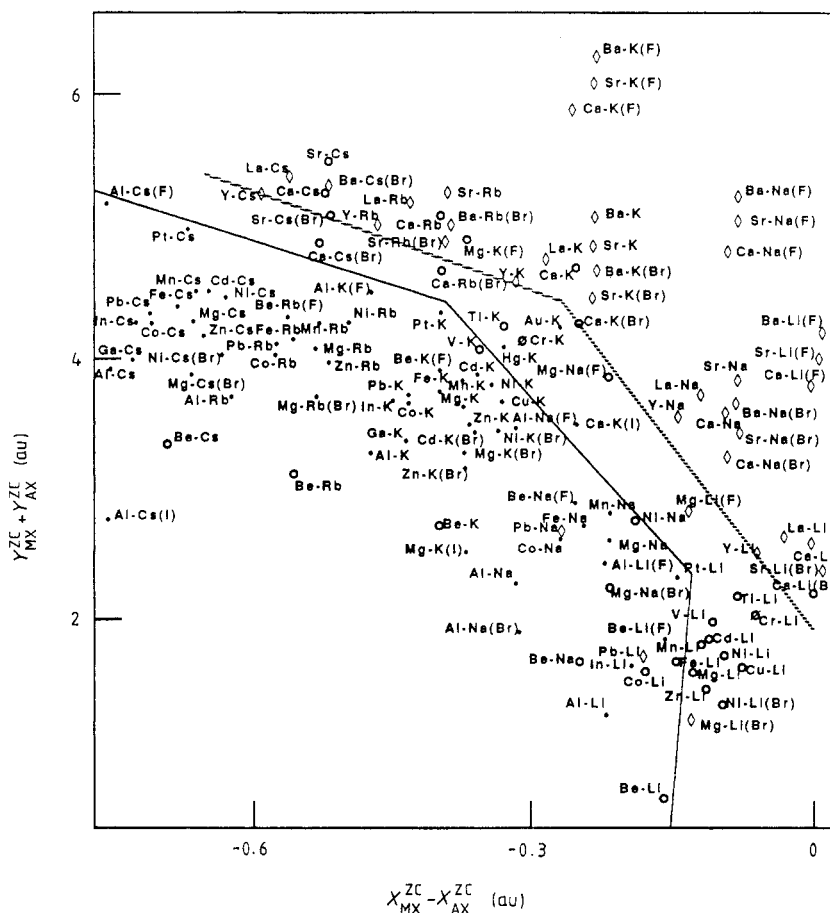
Figure 2. As in figure 1, from the Zunger–Cohen pseudopotential radii. A special symbol has been used for the Cr ion, whose coordination depends on the valence state.

clustered in the bottom left quadrant of figure 2 and in the upper right-hand part of the main diagonal in figure 3. The discussion of the two maps can be carried out in parallel to some extent.

We remark first of all that the Be–alkali-chloride systems, which we have included in the intermediate class of possible complex stability in the absence of data except for the pure $BeCl_2$ melt (Prisyazhnyi *et al* 1978), lie well inside the region of strong stability. Subject to experimental verification, we infer that $(BeCl_4)^{2-}$ complexes may be very stable in these mixtures.

We also note that two systems that we have classified as non-complexing, i.e. Pb–Li(Cl) and Pb–Na(Cl), appear to lie in a region of strong stability. We stress that our classification of these systems is solely based on enthalpy data (McCarty and Kleppa 1964) and suggest that they would be good candidates for Raman scattering experiments. Similar comments apply to Mg–Li(Br) and to Mg–Li(F), although the suggestions from our maps are clearly weaker in these cases. We have classified them as non-complexing on the basis of thermodynamic data by Hong and Kleppa (1978) and Østvold (1972a).

Having commented on those few systems that are clear exceptions to general patterns
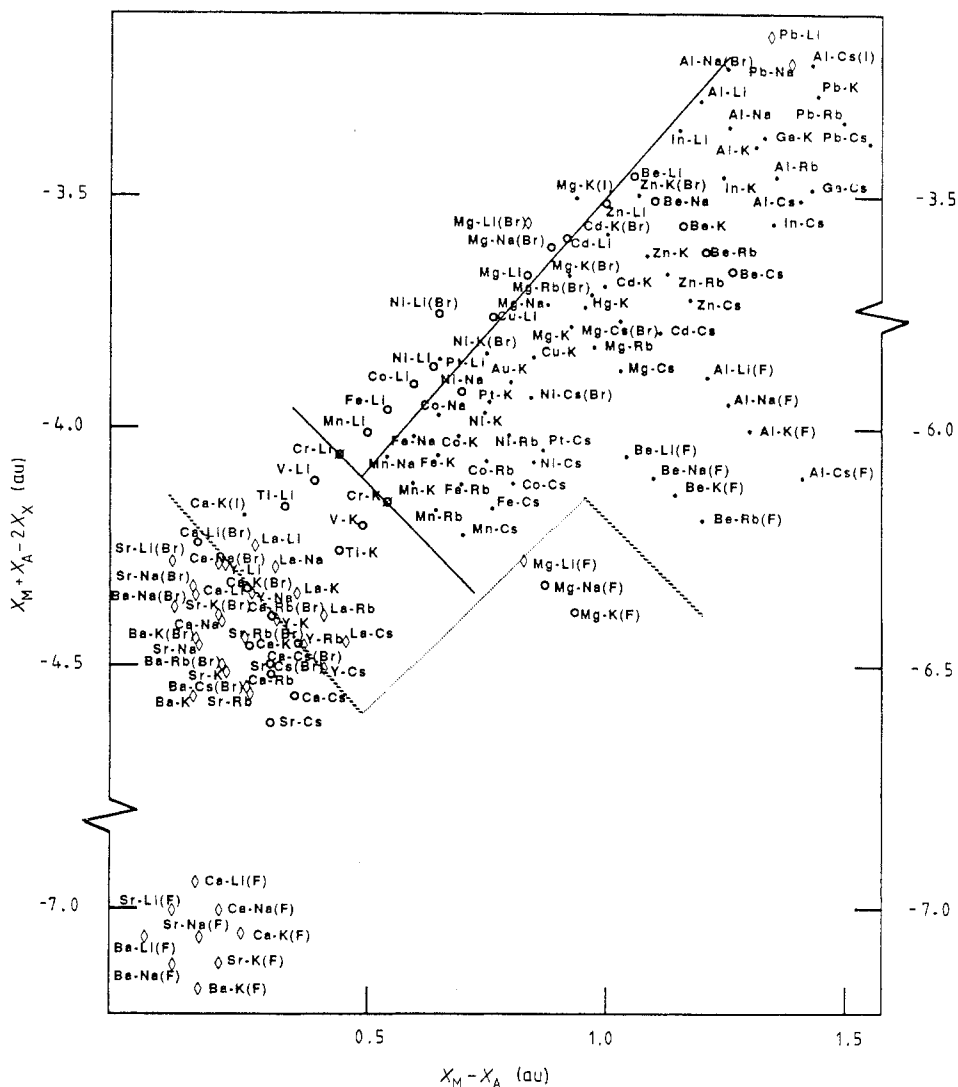
Figure 3. As in figures 1 and 2, from Pettifor's chemical scale of the elements. The break in the vertical scales refers to the fluoride systems. The open diamonds for the La–A(Cl) systems give also the locations and the behaviour of the Ce–A(Cl) systems. See the text for a detailed discussion of the various regions of the map.

in our structural maps, we may now try to make these patterns more evident by drawing approximate boundary lines inside the maps. We stress again that the nature of the evidence is not such as to ensure uniform reliability to our assignments and that gradual rather than sharp changes of behaviour should be expected in the liquid state. Our boundary lines should therefore be understood as only marking the approximate locations of transitional regions in structural behaviour.

Starting from the map in figure 2, it seems natural to focus first on the Y–A(Cl) systems for a possible boundary, since there is good evidence for stable $(YCl_6)^{3-}$ states

in these systems (Papatheodorou 1977, Papatheodorou *et al* 1979). Above this boundary, shown by hatched lines in figure 2, are found the vast majority of the systems in which fourfold coordination appears to be unstable, together with a few systems that we have assigned to the intermediate class. A second boundary, shown by the full lines, can be drawn to delimit the region of strong stability. We have drawn the latter boundary by referring to a few systems for which the evidence in favour of stable fourfold coordination is strong, i.e. Be–Li(F) (Vaslow and Narten 1973) and the Pt–A(Cl) systems (Papatheodorou and Smith 1973). The above approximate partition of the map in figure 2 into three regions of strong stability, marginal or possible stability and instability for fourfold-coordinated states appears to be the most use that can be made of it. However, we shall comment further below on the Li-based systems that are seen to cluster in the bottom right-hand corner of the map.

The map in figure 3 can be partitioned in a way which is considerably more significant. Again a hatched boundary line drawn through the Y–A(Cl) systems and continued as indicated through fluorides separates out in the bottom left-hand corner of the map most of the alkaline earth systems where fourfold coordination is unstable or marginally stable against loose higher coordinations. However, immediately above this boundary are found the La–A(Cl) and Ce–A(Cl) systems in which octahedral coordination appears to be almost as strongly stable as in Y–A(Cl), the La and Ce ions being practically indistinguishable in their structural parameters and coordination behaviour (Maroni *et al* 1974, Papatheodorou and Østvold 1974, Papatheodorou and Kleppa 1974, Papatheodorou 1977). Next to these are found the Ti-based and V-based chlorides, in which octahedral and distorted tetrahedral configurations are competitive in dependence on temperature (Gruen and McBeth 1963). A further region can thus be delimited to enclose the systems where well defined octahedral configurations are stable or dominant at low temperature. This is shown by the full line through the Cr-based chlorides, in which the coordination state depends on the valency of the Cr ion (Gruen and McBeth 1963). This line is part of the boundary delimiting the systems of strong stability for fourfold coordination, which can be completed as shown by the full line along the main diagonal in figure 3. In drawing this last boundary we have mostly relied on the evidence for Al–Li(Cl) (Takahashi *et al* 1985, Biggin *et al* 1985), Al–Na(Br) (Begun *et al* 1971), Pt–Li(Cl) (Papatheodorou and Smith 1973), Co–Na(Cl) (Papatheodorou and Kleppa 1971a, Dutt and Østvold 1972) and Mn–Na(Cl) (Papatheodorou and Kleppa 1971a, Østvold 1972b).

Two further points are worth noting with regard to the map in figure 3. Firstly, the systems that are known to form square planar complexes, i.e. Pt–A(Cl) (Papatheodorou and Smith 1973) and Au–K(Cl) (Gilbert *et al* 1975a), are seen to lie close to each other in the middle of the stability region. The Ni–A(Cl) and Cu–A(Cl) systems, for which appreciable distortions from tetrahedral symmetry have been reported (Gruen and McBeth 1963), also lie in the same neighbourhood. Secondly, the Al–A(F) systems are seen to lie in a separate region of the map. With decreasing concentration of AlF_3 below $c = \frac{1}{2}$, the $(AlF_4)^-$ tetrahedral complexes in these systems are gradually superseded by $(AlF_6)^{3-}$ octahedral complexes, the two types of complex being in coexistence in the range $\frac{1}{4} < c < \frac{1}{2}$ (Gilbert *et al* 1975b). This behaviour is quite different from that shown by the Y–A(Cl) systems, where $(YCl_6)^{3-}$ octahedral complexes are dominant at $c = \frac{1}{4}$ and persist with gradual distortions associated with edge sharing as c is increased up to $c = 1$ (Papatheodorou 1977).

It is also of interest to note the correlation between the order of the various systems along the main diagonal in the map in figure 3, which classifies the complexing behaviour

of mixtures at stoichiometric composition, and the known structural behaviours of pure polyvalent metal halide melts. Starting from the top right-hand end, we first meet $AlBr_3$, which melts from a molecular solid of Al_2Br_6 units into a molecular liquid, and $AlCl_3$, which melts from a mainly ionic layer structure into a molecular liquid of Al_2Cl_6 units (see for instance Ubbelohde 1978). The $ZnCl_2$ melt, according to the neutron diffraction data of Biggin and Enderby (1981a), has instead a tetrahedrally coordinated network-like structure, accompanied by very high viscosity and very low ionic conductivity. Among the systems that are next met along this path in figure 3, the liquid structure has also been determined by neutron diffraction for $MgCl_2$ (Biggin *et al* 1984), $NiCl_2$ (Newport *et al* 1985) and $NiBr_2$ (Wood and Howe 1988). Essentially fourfold coordination and traces of intermediate-range order, as reflected in a prepeak in the M–M partial structure factor at wavenumber $k \approx 1$ Å^{-1}, are present in these melts as in $ZnCl_2$. However, various other observed structural features and, in the case of $MgCl_2$, the measured values of transport coefficients, which are typical of non-associated molten salts, show that a fairly rigid ionic network is no longer present. Similar structural features are observed in molten NiI_2, accompanied by significant penetration of Ni^{2+} ions into the first coordination shell of Ni^{2+} (Wood *et al* 1988). The liquid structure of $MnCl_2$, though not fully known, closely resembles that of $MgCl_2$ in those features that have been determined by neutron diffraction (Biggin *et al* 1984). Finally, the liquid structure of molten $CaCl_2$ (Biggin and Enderby 1981b), with an average coordination number of 5.4 for the cation, appears to be of a transitional type towards the cation-dominated structures of the strongly ionic melts of $SrCl_2$ (McGreevy and Mitchell 1982) and $BaCl_2$ (Edwards *et al* 1978). The results of neutron diffraction experiments on pure melts inside the pocket of stable octahedral coordination bracketed by YCl_3 and $CrCl_3$ in figure 3, now being completed for lanthanide chlorides (Saboungi and Price 1988), will clearly be of great interest.

Let us now turn to the 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 just above the upper edge of the main 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 and McBeth 1963). Infrared absorption data in the case of Cu (Wilmhurst 1963) and thermodynamic data in the other cases (Papatheodorou and Kleppa 1970, 1971a, Dutt and Østvold 1972, Østvold 1972b) confirm stability of complexes in the KCl solvent but are against it in the LiCl solvent. Optical absorption data on Ni–Li(Cl) indicate marginal stability for $(NiCl_4)^{2-}$ in this system (Smith and Boston 1965). We also note the apparent conflicts between enthalpy data (Kleppa and McCarty 1966) and Raman scattering data (Brooker and Huang 1980) for Mg–Li(Cl), between enthalpy data (Papatheodorou and Kleppa 1971b) and Raman scattering data (Clarke *et al* 1972) for Cd–Li(Cl), and between infrared absorption data (Wilmhurst 1963) and Raman scattering data (Ellis 1966) for Zn–Li(Cl). The location of these three systems in figure 3 might suggest fairly strong complex stability. 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.

Finally, the Cr ion deserves special notice. As already pointed out, optical absorption spectra show that its coordination depends on its valence state, yielding stability for $(CrCl_4)^{2-}$ complexes of distorted tetrahedral shape and instability for $(CrCl_4)^{-}$ complexes. Our classifications 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, 1984a,b, 1985) and is well known in relation to equilibrium molecular shapes (see for instance Andreoni *et al* 1985).

In summary, we believe that we have demonstrated the usefulness of the established methods of structure sorting in relation to a specific problem in liquid state structure, for which the ample experimental evidence permits meaningful statistics. The most useful structural map that we have been able to obtain is that shown in figure 3, based on Pettifor's chemical scale approach. Of course, structural predictions are immediate for the systems not included in our maps, for which we have been unable to find relevant data.

Acknowledgments

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