

REF

IC/91/55

**INTERNATIONAL CENTRE FOR
THEORETICAL PHYSICS**

**LIQUID STRUCTURE
AND MELTING OF TRIVALENT METAL CHLORIDES**

M.P. Tosi

G. Pastore

M.-L. Sabounji

and

D.L. Price

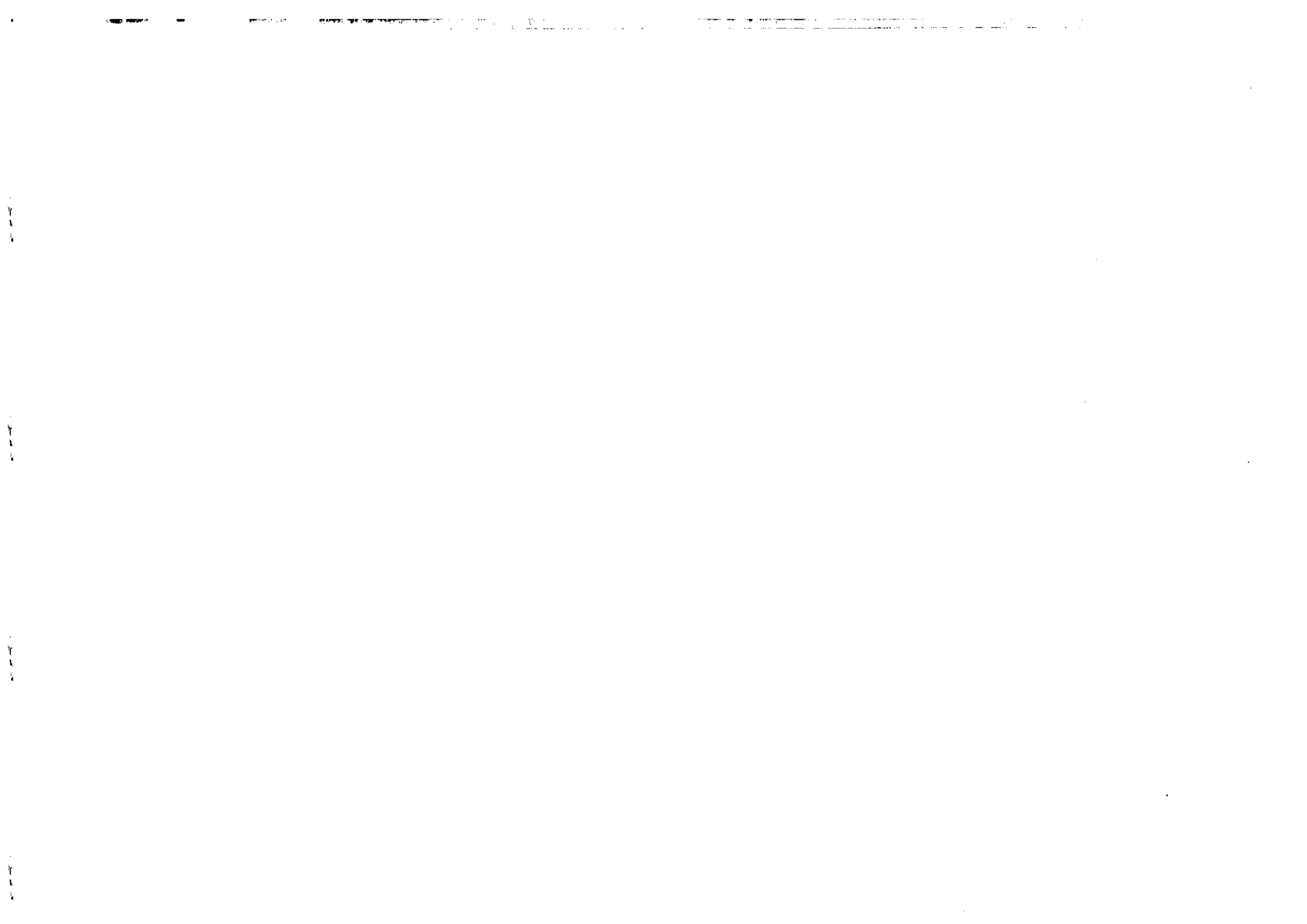


**INTERNATIONAL
ATOMIC ENERGY
AGENCY**



**UNITED NATIONS
EDUCATIONAL,
SCIENTIFIC
AND CULTURAL
ORGANIZATION**

1991 MIRAMARE - TRIESTE



International Atomic Energy Agency
and
United Nations Educational Scientific and Cultural Organization
INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS

LIQUID STRUCTURE AND MELTING OF TRIVALENT METAL CHLORIDES

M.P. Tosi, G. Pastore
International Centre for Theoretical Physics, Trieste, Italy
and
Department of Theoretical Physics, University of Trieste, Trieste, Italy

M.-L. Saboungi and D.L. Price
Argonne National Laboratory, Argonne, IL 60439, USA.

MIRAMARE – TRIESTE

March 1991

Abstract

Many divalent and trivalent metal ions in stoichiometric liquid mixtures of their halides with alkali halides are fourfold or sixfold coordinated by halogens into relatively long-lived "complexes". The stability of these local coordination states and the connectivity that arises between them in the approach to the pure polyvalent metal halide melt determines the character of its short-range and possible intermediate-range order. The available evidence on local coordination in some 140 mixtures has been successfully classified by a structure sorting method based on Pettifor's chemical scale of the elements. Within the general phenomenological frame provided by structure sorting, main attention is given in this work to the liquid structure and melting mechanisms of trivalent metal chlorides. The liquid structure of YCl_3 is first discussed on the basis of neutron diffraction measurements and of calculations within a simple ionic model, and the melting mechanisms of YCl_3 and $AlCl_3$, which are structurally isomorphous in the crystalline state, are contrasted. By appeal to macroscopic melting parameters and transport coefficients and to liquid structure data on $SbCl_3$, it is proposed that the melting mechanisms of these salts may be classified into three main types in correlation with the character of the chemical bond.

1. Introduction

The liquid structure of alkali halides is rather well understood from neutron diffraction experiments by the isotope enrichment technique as well as from computer simulations and liquid structure theories based on pair interactions (for recent reviews see [1-3]). A number of new and interesting structural behaviours are met when one turns to the melts of divalent or trivalent metal halides and their mixtures with alkali halides. A quantitative account of these melts through models for the interionic forces or more basic descriptions of the chemical bond remains largely a challenge. It is therefore appropriate at the present time for theory to pursue more limited aims within simpler and to some extent complementary approaches. These are (i) a systematization of the body of evidence within a general frame that stresses trends in structural behaviour and basic physical properties, as is afforded by the structure sorting methods in solid state physics, and (ii) the construction of semiquantitative scenarios for specific systems of special interest by means of primitive models which account for the role of Coulomb interactions.

In the structure sorting approach, a structural map for a given family of compounds assembles systems with the same local coordination or crystal structure in certain regions of a plane whose (X, Y) coordinates are constructed from parameters of the component elements (for a general review of crystal structure sorting, see [4]). In particular Pettifor [5] has proposed an essentially phenomenological chemical scale of the elements, which orders them along a single axis χ so that the Mendeleev-type features of the periodic table are preserved. He has shown that excellent structural separation of all binary compounds with a given stoichiometry M_mX_n is obtained within a (χ_M, χ_X) structure map.

The transferability of these methods to liquid structure problems requires, first of all, a test on a specific structural question on which the available evidence is sufficiently ample to permit meaningful statistics. This condition is met by the data on the local coordination of polyvalent metal ions in liquid mixtures of their halides with alkali halides [6]. Some 140 such mixtures have been examined by appropriate experimental probes, involving diffrac-

tion experiments in a few cases but mostly Raman scattering, infrared emission and absorption, absorption from electronic transitions and thermodynamic measurements. The basic structural question is whether such a mixture is structured into "complexes", i. e. molecular-ion units formed by the polyvalent metal ion coordinating halogens with a lifetime at least of order of typical diffusion times, and what are their coordination number and geometry. For example, tetrahedral coordination by chlorines is strongly stable for Al in Al-alkali chlorides [7] and for Zn in Zn-alkali chlorides [8], whereas octahedral coordination is strongly stable for Y in Y-alkali chlorides [9]. Alternatively, the polyvalent metal ions may fluctuate between different coordination states, as appears to be the case in molten $\text{CaCl}_2\text{-2KCl}$ where coexistence of loose tetrahedral-type and octahedral-type coordinations has been suggested from Raman scattering [10], as well as in Sr-alkali and Ba-alkali chlorides where no structure is observed in the Raman spectrum [10]. Compound coordinates constructed for each M-A(X) mixture from Pettifor's elemental coordinates as $X_{M-A(X)} = \chi_M - \chi_A$ and $Y_{M-A(X)} = \chi_M + \chi_A - 2\chi_X$ (with M = polyvalent metal, A = alkali and X = halogen) allow an excellent separation between the three structural behaviours corresponding to (i) strong stability of fourfold coordination, (ii) strong stability of sixfold coordination, and (iii) loose coordination [6].

The alkali halide in such mixtures acts primarily as a halogen donor to break the structure of the pure polyvalent metal halide melt. The above-mentioned structural classification of mixtures provides a general frame inside which one may locate the pure polyvalent metal halides and ask about correlations with the nature of their liquid structure. Correlations are indeed easily found for divalent metal halides, whose liquid structure is known in a number of cases from neutron diffraction experiments [11-16]. Thus, whereas a loose ionic structure is observed for the BaCl_2 [11] and SrCl_2 [14] melts, the stability of the $(\text{ZnCl}_4)^{2-}$ complex in mixtures correlates with the network-like liquid structure of corner sharing tetrahedra for pure ZnCl_2 [12].

Rather little is known as yet about the liquid structure of trivalent metal halides. In § 2, we shall contrast the results of recent neutron diffraction experiments on molten YCl_3

[17] with the structural behaviour of molten AlCl_3 [18]. These two compounds are structurally isomorphous in the crystalline state, but show entirely different melting mechanisms. Halogen sharing is achieved in the former melt by a loose network-like structure of edge-sharing sixfold coordination states, while in the latter molecular dimers composed of two edge-sharing tetrahedra are formed. We shall emphasize the correlation of these two melting behaviours with Pettifor's χ for the metal atom and with macroscopic melting parameters and transport coefficients in the melt. We shall also present a liquid structure calculation on a simple ionic model of YCl_3 , which provides some further insight on this essentially ionic melt [19].

A third possibility, i.e. a liquid structured in monomeric molecular units, is exemplified by SbCl_3 [20]. We shall try in § 3 to extend what is known about liquid structure and melting mechanism in YCl_3 , AlCl_3 and SbCl_3 to give a preliminary classification of other trivalent metal chlorides. The outcome of the discussion will be to suggest that one may classify the melting mechanisms of trichlorides as being of three main types in correlation with the character of the chemical bond, i.e. ionic-to-ionic, ionic-to-molecular and molecular-to-molecular. The discussion will also highlight compounds in this family that may be interesting for experimental liquid structure studies.

2. Melting and liquid structure of YCl_3 contrasted with AlCl_3

Table I reports some relevant physical properties of SrCl_2 , ZnCl_2 , HgCl_2 , YCl_3 , AlCl_3 and SbCl_3 [21]. These are Pettifor's χ_M , 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 (ionic conductivity σ and shear viscosity η) of the melt at freezing. Comparison of these data in these halides is already indicative of very different melting processes. The three divalent metal halides are included as prototypes of a strongly ionic liquid (SrCl_2), a network-structure liquid (ZnCl_2) and a system which is expected to melt from a molecular crystal into a molecular liquid (HgCl_2).

The AlCl_3 -type structure can almost be viewed as a cubic close packing of Cl ions inside which the metal ions occupy suitable octahedral sites. A single layer in this idealized description consists of two triangular lattices of Cl ions, with the phase relationship of 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 ionic 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, 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 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 [22].

YCl_3 , though crystallizing in the same structure as AlCl_3 , shows very different values for its melting and transport properties (see table I). A neutron diffraction experiment has recently been made on molten YCl_3 with the aim of providing a direct determination of the local structure and of its connectivity [17]. The main results of the experiment may be summarized as follows: (i) the measured Faber-Ziman 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 [23] and has also been observed, in particular, in molten ZnCl_2 [12]; (ii) the coordination number for Cl about Y is 5.9, 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 distorted; 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 persists in the liquid, as indicated by the FSDP in $S(Q)$. The network is relatively loose on a time scale longer than the period of the breathing mode of the octahedron ($\nu \sim 260 \text{ cm}^{-1}$ [9]), as indicated by the value of σ for YCl_3 in table I.

In summary, the melting mechanism of YCl_3 into a loose ionic 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 Pettifor [5], 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 (see table I). The different character of the chemical bonding is thus reflected in the melting behaviour of the two trivalent metal chlorides, rather than in their crystal structure.

2.1. Liquid structure calculation for YCl_3

The structure of an ionic model for molten YCl_3 has been calculated in the hypernetted chain approximation [19] using interionic pair potentials of the Busing type [24] with parameters for the Y^{3+} ion adjusted to the mean Y-Cl bond length in the crystal and to the breathing mode frequency of the $(\text{YCl}_6)^{3-}$ octahedron. Figure 1 shows a comparison with the neutron diffraction data of Saboungi *et al* [17] for the total correlation function $T(r)$,

$$T(r) = 4\pi\rho_0 r + (2/\pi) \int_0^{Q_{\max}} [S(Q) - 1] \sin(Qr) Q dQ, \quad (1)$$

ρ_0 being the total number density and $S(Q)$ the neutron structure factor, with cut-off at

$Q_{\max} = 8 \text{ \AA}^{-1}$ as in the Fourier transform of the $S(Q)$ data. The oscillations in $T(r)$ below 2 \AA are due to the finite cut-off. Considering the simplicity of the model and the finite resolution in the experiment, the agreement with the data is quite pleasing.

The additional information derived from the calculation concerns the partial Y-Cl, Cl-Cl and Y-Y correlations. The first peak in $T(r)$ is exclusively due to the Y-Cl correlations and it is evident from Fig. 1 that the Y-Cl bond length is somewhat expanded in the liquid relative to the crystal. We obtain a coordination number for Cl about Y of 5.89, against the value 5.9 deduced from the neutron data. In addition, we find that the first coordination shell of Cl about Y is quite stable, as judged from the height of the first minimum in the $g_{\text{YCl}}(r)$ distribution function, which is 0.10. The second peak in $T(r)$ is almost exclusively due to the Cl-Cl correlations, as was assumed by Saboungi *et al* [17] in the discussion of the neutron data. The calculated $g_{\text{ClCl}}(r)$ distribution function has the shape of a main peak followed by a shoulder, and by approximate separation of these two features we obtain a Cl-Cl near-neighbour coordination number of about 8, to be compared with the value 8.2 estimated from the second peak in the neutron data [17]. The shoulder in $g_{\text{ClCl}}(r)$ may be indicative of residual Cl-Cl interlayer correlations in the melt. Finally, the $g_{\text{YY}}(r)$ distribution peaks at about 5 \AA , where the data show a further broad peak in $T(r)$.

The most remarkable feature of the calculated Y-Y correlations is a strong FSDP in the partial $S_{\text{YY}}(Q)$ structure factor. This is indeed the dominant contribution to the FSDP in the calculated neutron structure factor, which contains only a small contribution from Y-Cl correlations and an essentially negligible one from Cl-Cl correlations. However, the calculated FSDP lies at a somewhat larger wave number than in the data (1.25 \AA^{-1} against 0.95 \AA^{-1}). We stress that the intermediate range order leading to the FSDP arises in the model purely from Coulomb interactions. Its incorrect location may be indicative of a subsidiary role of angle-dependent forces in determining the intermediate-range connectivity of the melt. Clearly, it would be interesting to examine the partial pair correlations in molten YCl_3 by neutron diffraction experiments using the isotope enrichment technique, especially in relation to the Y-Y correlations and to their resolution from the Cl-Cl correlations.

3. Classification of trivalent metal chlorides

3.1. Lanthanide metal chlorides

Table II reports the known crystal structure, melting parameters and transport coefficients of the melt at freezing for chlorides of trivalent metals that lie close to Y in Pettifor's chemical scale. Starting from the first five rows in the table, and also noticing a remark by Pettifor [5] to the effect that his crystal structure maps would be marginally improved by inserting Y between Ho and Dy, it seems reasonable to surmise [17] that ErCl_3 , HoCl_3 and DyCl_3 should show similar melting mechanism and liquid structure as YCl_3 . The FeCl_3 -type crystal structure taken by ScCl_3 , on the other hand, differs from the AlCl_3 -type structure primarily in the interlayer correlations, being based on an almost perfect hcp arrangement of Cl with each Fe at the centre of an almost perfect octahedron of Cl. The value for ΔS_m of ScCl_3 in table II suggests a role of interlayer correlations in the melting process, but again the liquid structure may be qualitatively similar to that of YCl_3 .

The rest of table II reports the available data for other trichlorides which crystallize in the UCl_3 -type and PuBr_3 -type structures. The latter appears to be of a transitional type between the AlCl_3 and UCl_3 types, as shown by the structural phase transitions undergone with increasing temperature by DyCl_3 (PuBr_3 -type to AlCl_3 -type) and by GdCl_3 (PuBr_3 -type to UCl_3 -type). The UCl_3 -type structure (also known as the Y(OH)_3 -type structure) is described as hexagonal, with each U surrounded by six Cl on the corners of a trigonal prism and further coordinated by three coplanar Cl at somewhat larger distance. A more transparent description would start by stacking into a chain UCl_3 units in the shape of trigonal pyramids with U at the apices, the three Cl in the base of each pyramid being shared between two U to yield the trigonal prism around each U, and would then pack such chains to give three interchain U-Cl bonds to each U. The PuBr_3 -type structure may be similarly described as a chain-like structure with different lengths for interchain bonds. In fact, the AlCl_3 -type structure may also be described as built from such pyramidal units, though arranged in layers rather than in chains.

As is seen from table II, melting from the UCl_3 -type or PuBr_3 -type structure involves

appreciably higher entropy and volume changes than from the AlCl_3 -type. The values of the ionic conductivity in the melt are approximately the same or only moderately higher. It appears that all the chlorides in table II may form good ionic liquids with essentially sixfold coordination of the metal ions by Cl and some amount of intermediate range order. Indeed, a neutron diffraction experiment from molten NdCl_3 has shown the presence of a FSDP in the total structure factor at approximately 1 \AA^{-1} [25]. We also recall Raman scattering experiments on La-alkali chlorides [26] and thermodynamic measurements on La-alkali and Ce-alkali chlorides [27, 28], indicating sixfold coordination of the trivalent metal ions in these liquid mixtures. Further studies aimed at ascertaining the connectivities of melts from UCl_3 -type and AlCl_3 -type crystals in a comparative way would be of interest.

3.2. Trichlorides of group IIIA and group VA metals

Table III reports the melting parameters and the transport coefficients of the melt at freezing for the trichlorides of In, Al, Ga, Bi, Sb and As, in order of increasing χ_M . It seems reasonable to surmise [17] that InCl_3 , crystallizing in the AlCl_3 -type structure and melting with an extremely large relative volume change, could have a melting mechanism similar to AlCl_3 , leading an essentially ionic layer crystal into a melt of dimeric molecular units. Indeed, the In_2Cl_6 dimer is known to be stable in the vapour phase [29]. However, the melting temperature of InCl_3 is sizably higher and the ionic conductivity of the melt is appreciable. This may indicate partial thermal breakage of molecular units in the melt.

The stable molecular units in the vapour phase for the other compounds in table III are the Ga_2Cl_6 dimer [29] and the BiCl_3 , SbCl_3 and AsCl_3 monomers [30, 31]. The liquid structure of SbCl_3 has been studied by Triolo and Narten [20] by both X-ray and neutron diffraction. The crystal structure of SbCl_3 is built from chains of separate SbCl_3 molecules in the shape of trigonal pyramids with Sb at the apices, forming the molecular-type counterpart of the essentially ionic UCl_3 -type structure as described earlier in § 3.1. The melt of SbCl_3 is found in the experiments of Triolo and Narten to consist of discrete SbCl_3 molecules with strong intermolecular correlations.

We notice from tables I and III a similarity in melting parameters and transport coefficients for HgCl_2 , SbCl_3 , GaCl_3 and AsCl_3 . In all these compounds the melting process may thus lead from a molecular-type crystal to an essentially molecular liquid. The melt of BiCl_3 in table III does not seem to conform with this pattern, since it combines an appreciable ionic conductivity with a rather large viscosity. The nature of order in these melts, and especially in molten BiCl_3 , appears to be worthy of further investigation.

4. Summary and concluding remarks

The foregoing discussion suggests that the melting mechanisms of trivalent metal chlorides may be classified as being of three main types, in correlation with the nature of the chemical bond as measured by Pettifor's chemical activity parameter χ_M for the metal element. YCl_3 and probably the lanthanide metal chlorides at low χ_M melt from essentially ionic crystal structures into essentially ionic liquids with intermediate range order, which should be reflected primarily in the metal-metal correlations. AlCl_3 and probably also InCl_3 , at rather high χ_M , melt from an essentially ionic layer structure into a liquid of molecular dimers. SbCl_3 and possibly also other trichlorides of group IIIA and group VA metals, at still higher χ_M , melt from molecular-type crystals into molecular liquids, in which appreciable intermolecular correlations may still be present.

Within this broad classification of melting and liquid structure types, there remain a number of interesting structural questions concerning both trends and specific systems of special interest. We may add that, while we have chosen to focus on trichlorides, a preliminary examination of similar data suggests that the above scheme may also be applicable to tribromides and iodides.

Acknowledgements

This work was performed under the auspices of the Ministero dell'Università e della Ricerca Scientifica e Tecnologica of Italy through the Consorzio Interuniversitario Nazionale di Fisica della Materia and of the U.S. Department of Energy, Office of Basic Energy Sciences, under Contract W-31-109-ENG-38. MPT wishes to thank the Materials Science Division of the Argonne National Laboratory for supporting his stay at Argonne during the initial stages of this work.

References

1. Rovere, M. and Tosi, M. P., *Repts. Progr. Phys.* **49**, 1001 (1986).
2. McGreevy, R. L., *Solid State Phys.* **40**, 247 (1987).
3. Enderby, J. E. and Barnes, A. C., *Repts. Progr. Phys.* **53**, 85 (1990).
4. Mooser, E., in *Crystalline Semiconducting Materials and Devices* (Edited by Butcher, P. N., March, N. M. and Tosi, M. P.), Plenum, New York (1986) p. 1.
5. Pettifor, D. G., *J. Phys. C* **19**, 285 (1986).
6. Akdeniz, Z. and Tosi, M. P., *J. Phys.: Cond. Matter* **1**, 2381 (1989).
7. Takahashi, S., Maruoka, K., Koura, N. and Ohno, H., *J. Chem. Phys.* **84**, 408 (1986).
8. Ellis, R. B., *J. Electrochem. Soc.* **113**, 485 (1966).
9. Papatheodorou, G. N., *J. Chem. Phys.* **66**, 2893 (1977).
10. Sakai, S., Nakamura, T., Umesaki, N. and Iwamoto, N., *Phys. Chem. Liquids* **14**, 67 (1984).
11. Edwards, F. G., Enderby, J. E., Howe, R. A. and Page, D. I., *J. Phys. C* **11**, 1053 (1978).
12. Biggin, S. and Enderby, J. E., *J. Phys. C* **14**, 3129 (1981).
13. Biggin, S. and Enderby, J. E., *J. Phys. C* **14**, 3577 (1981).
14. McGreevy, R. L. and Mitchell, E. W. J., *J. Phys. C* **15**, 5537 (1982).
15. Biggin, S., Gay, M. and Enderby, J. E., *J. Phys. C* **17**, 977 (1984).
16. Newport, R. J., Howe, R. A. and Wood, N. D., *J. Phys. C* **18**, 5249 (1985); Wood, N. D., Howe, R. A., Newport, R. J. and Faber, J. Jr., *J. Phys. C* **21**, 669 (1988); Wood N. D. and Howe R. A., *J. Phys. C* **21**, 3177 (1988).
17. Saboungi, M.-L., Price, D. L., Scamehorn, C. and Tosi, M. P., in course of publication.
18. Harris, R. L., Wood, R. E. and Ritter, H. L., *J. Am. Chem. Soc.* **73**, 3150 (1951).
19. Pastore, G., Akdeniz, Z. and Tosi, M. P., to be published.
20. Triolo, R. and Narten, A. H., *J. Chem. Phys.* **69**, 3159 (1978).
21. In constructing table I and the following tables II and III, we have used data for macroscopic physical properties from the following sources: Wyckoff, R. W. G., *Crystal Structures*, Wiley (1963) vol. 1 and 2; Landolt-Börnstein Tables, Springer, Berlin, vol. II/4 (1961) and NSIII/7a (1971); Pankratz, L. B., *Thermodynamic Properties of Halides*, Bull. U.S. Bureau of Mines, Washington, D.C. (1984); Dworkin, A. S. and Bredig, M. A., *High Temp. Sci.* **3**, 81 (1971); Igarashi, K. and Mochinaga, J., *Z. Naturforsch.* **42a**, 777 (1987); Janz, G. J., Dampier, F. W., Lakshminarayan, G. R., Lorenz, P. K. and Tompkins, R. P. T., *Natl. Bur. Stand. Ref. Data Ser.* **15**, 1 (1968); Janz, G. J., Tompkins, R. P. T., Allen, C. B., Downey, J. R., Gardner, G. L., Krebs, U. and Singer, S. K., *J. Phys. Chem. Ref. Data* **4**, 871 (1975); Janz, G. J., Tompkins, R. P. T., Allen, C. B., Downey, J. R. and Singer, S. K., *J. Phys. Chem. Ref. Data* **6**, 409 (1977); Torklep, K. and Øye, H., *J. Chem. Eng. Data* **27**, 387 (1982); Zuca, S. and Borcan, R., *Rev. Roum. Chim.* **19**, 553 (1974); Brockner, W., Torklep, K. and Øye, H., *Ber. Bunsenges. Phys. Chem.* **83**, 1 (1979); Iwadate, Y., Igarashi, K., Mochinaga, J. and Adachi, T., *J. Electrochem. Soc.* **133**, 1162 (1986); Greenwood, N. N. and Worrall, I. J., *J. Inorg. Nucl. Chem.* **3**, 357 (1957).
22. March, N. H. and Tosi, M. P., *Phys. Chem. Liquids* **10**, 39 (1980).
23. Moss, S. C. and Price, D. L., in *Physics of Disordered Materials* (Edited by Adler, D., Fritzsche, H. and Ovshinsky, S. R.), Plenum, New York (1985) p. 77.
24. Wang Li and Tosi, M. P., *N. Cimento D* **10**, 1497 (1988) and references given therein.
25. Lowe, M. A., Price, D. L. and Saboungi, M.-L., *Proc. Symp. Molten Salts, Electrochem. Soc., Montreal* (1990).
26. Papatheodorou, G. N., *Inorg. Nucl. Chem. Lett.* **11**, 483 (1975).
27. Papatheodorou, G. N. and Kleppa, O. J., *J. Phys. Chem.* **78**, 178 (1974).
28. Papatheodorou, G. N. and Østfold, T., *J. Phys. Chem.* **78**, 181 (1974).
29. Brode, H., *Ann. Phys.* **5**, 344 (1940).
30. Skinner, H. A. and Sutton, L. E., *Trans. Faraday Soc.* **36**, 681 (1940).
31. Allen, P. W. and Sutton, L. E., *Acta Cryst.* **3**, 46 (1950).

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

| Salt | χ_M | Crystal structure | T_m (K) | ΔS_m (e.u.) | $\Delta V/V^a$ | σ ($\Omega^{-1}\text{cm}^{-1}$) | η (cp) |
|-------------------|----------|-------------------|-----------|---------------------|----------------|------------------------------------------|--------------------|
| SrCl ₂ | 0.55 | CaF ₂ | 1146 | 5.9 ^b | 0.13 | 2.0 | 3.7 |
| ZnCl ₂ | 1.44 | ZnCl ₂ | 570 | 4.1 | 0.16 | 1.x10 ⁻³ | 4.x10 ³ |
| HgCl ₂ | 1.32 | HgCl ₂ | 550 | 4.4 | 0.25 | 3.x10 ⁻⁵ | 1.6 |
| YCl ₃ | 0.66 | AlCl ₃ | 994 | 7.6 | 0.0045 | 0.39 | -- |
| AlCl ₃ | 1.66 | AlCl ₃ | 466 | 18.1 | 0.88 | 5.x10 ⁻⁷ | 0.36 |
| SbCl ₃ | 2.08 | SbCl ₃ | 347 | 8.7 | 0.17 | 2.x10 ⁻⁴ | 2.4 |

^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.

Table II. - Physical properties of trivalent lanthanide metal chlorides

| Salt | χ_M | Crystal structure | T_m (K) | ΔS_m (e.u.) | $\Delta V/V^a$ | σ ($\Omega^{-1}\text{cm}^{-1}$) | η (cp) |
|-------------------|----------|--------------------------------|-----------|---------------------|----------------|------------------------------------------|-------------|
| YCl ₃ | 0.66 | AlCl ₃ | 994 | 7.6 | 0.0045 | 0.39 | -- |
| ScCl ₃ | 0.67 | FeCl ₃ | 1240 | 13.0 | -- | 0.56 | 1.7 |
| ErCl ₃ | 0.68 | AlCl ₃ | 1049 | 7.4 | -- | 0.43 | -- |
| HoCl ₃ | 0.6825 | AlCl ₃ | 993 | 7.3 | -- | 0.38 | -- |
| DyCl ₃ | 0.685 | AlCl ₃ ^b | 924 | 6.6 | 0.0032 | 0.44 | -- |
| TbCl ₃ | 0.6875 | PuBr ₃ | 855 | 9.7 ^c | -- | -- | 4.2 |
| GdCl ₃ | 0.69 | UCl ₃ ^b | 875 | 11.1 | 0.26 | 0.34 | -- |
| NdCl ₃ | 0.6975 | UCl ₃ | 1032 | 11.6 | 0.22 | 0.60 | 2.7 |
| PrCl ₃ | 0.70 | UCl ₃ | 1059 | 11.4 | 0.21 | 0.94 | 3.3 |
| CeCl ₃ | 0.7025 | UCl ₃ | 1090 | 11.7 | 0.21 | 1.1 | -- |
| LaCl ₃ | 0.705 | UCl ₃ | 1131 | 11.5 | 0.19 | 1.3 | 6.7 |
| PuCl ₃ | 0.73 | UCl ₃ | 1033 | 15. | -- | -- | -- |
| UCl ₃ | 0.735 | UCl ₃ | 1108 | -- | 0.12 | 1.1 | -- |

^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 High-temperature crystal structure; low-temperature crystal is PuBr₃-type.

^c Includes entropy change of phase transition in the crystal.

Table III. - Physical properties of trichlorides of group IIIA and group VA metals

| Salt | χ_M | T_m (K) | ΔS_m (e.u.) | $\Delta V/V^a$ | σ ($\Omega^{-1}\text{cm}^{-1}$) | η (cp) |
|-------------------|----------|-----------|---------------------|----------------|------------------------------------------|-------------|
| InCl ₃ | 1.60 | 859 | -- | 0.61 | 0.42 | -- |
| AlCl ₃ | 1.66 | 466 | 18.1 | 0.88 | 5×10^{-7} | 0.36 |
| GaCl ₃ | 1.68 | 351 | 7.4 | 0.17 | 2×10^{-6} | 1.8 |
| BiCl ₃ | 2.04 | 505 | 5.0 | 0.22 | 0.38 | 41. |
| SbCl ₃ | 2.08 | 347 | 8.7 | 0.17 | 2×10^{-4} | 2.4 |
| AsCl ₃ | 2.16 | 253 | 9.5 | -- | -- | -- |

^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.

Figure caption

Fig. 1. - The total correlation function $T(r)$ of molten YCl₃ at $T = 1020$ K from an ionic model solved in the hypernetted chain approximation [19] (full curve) and from neutron diffraction experiments of Saboungi *et al* [17] (dots).

