Structure of molten yttrium chloride in an ionic model

G Pastore†, Z Akdeniz‡§ and M P Tosi†‡

† Department of Theoretical Physics of the University of Trieste, I-34014 Trieste, Italy
‡ International Centre for Theoretical Physics, I-34014 Trieste, Italy
§ Department of Physics of the University of Istanbul, Istanbul, Turkey

Abstract. We report calculations of the liquid pair structure of YCl_3 as a prototype for strongly ionic melts of lanthanide metal trichlorides. The calculations adopt an ionic model involving a pair potential of the Busing type, with parameters for the Y^{3+} ion adjusted to the Y–Cl bond length in the YCl_3 crystal and to the breathing mode frequency of the $(YCl_6)^{3-}$ octahedral unit. The model is solved in the hypernetted chain approximation and the results are tested against neutron diffraction data on the Faber–Ziman structure factor and the total pair correlation function of molten YCl_3. The calculated partial structure factors and pair correlation functions provide insight into the origin and nature of the short-range and intermediate-range order in the melt.

1. Introduction

The melting mechanisms and liquid structure types of trivalent metal chlorides have recently been classified [1] on the basis of their measured melting parameters and transport coefficients in the melt, and with the help of Pettifor's chemical activity parameter χ_M for the metal [2] as an indicator of the character of the chemical bond in each compound. Three main types of melting mechanism have been proposed, as exemplified by YCl_3, $AlCl_3$ and $SbCl_3$ among the trichlorides that have been the object of liquid structure studies. YCl_3 [3] and probably the lanthanide metal chlorides at low χ_M melt from essentially ionic crystal structures into mainly ionic liquids with intermediate-range order. $AlCl_3$ ([4] and references therein) and probably also $InCl_3$, at high χ_M, melt from an essentially ionic layer structure into a liquid of molecular dimers. $SbCl_3$ [5] and possibly other trichlorides of group IIIA and VA metals, at still higher χ_M, melt from molecular-type crystals into molecular liquids with strong intermolecular correlations.

In this article we present liquid structure calculations for an ionic model of molten YCl_3. Our aim is to examine to what extent the main observed features of the total pair correlations can be ascribed to the Coulomb interactions between the components and to provide some insight into partial structure factors and partial pair correlation functions. A preliminary report of these results has already been given in [1]. We hope that our theoretical results will serve as a stimulus for further experimental studies of this melt and related molten trihalides.

It will be useful to recall at this point a number of facts that are known from experiments on molten YCl_3. The crystal structure of this compound is of the $AlCl_3$ type,

that is a layer structure which may be obtained by small distortions from an FCC packing of chlorines accommodating the trivalent metal ions at octahedral sites. Each layer in its idealized undistorted configuration comprises two triangular lattices of chlorines sandwiching the metal ions into edge-sharing $(YCl_6)^{3-}$ octahedra. The YCl_3 crystal melts at 994 K with a relatively moderate entropy change ($\Delta S_m = 7.6$ cal mol^{-1} K^{-1} [6]) and an essentially negligible volume change [7]. In an extensive Raman scattering study, Papatheodorou [8] observed the Raman modes of the $(YCl_6)^{3-}$ octahedron in stoichiometric mixed crystals of yttrium-alkali chlorides at room temperature and followed the Raman spectrum first with increasing temperature up to and across melting, and then with varying YCl_3 content up to the pure YCl_3 melt. Persistence of the breathing mode of the $(YCl_6)^{3-}$ unit at $\nu \simeq 260$ cm^{-1} through these vast spans of temperature and composition suggested strong stability for this coordination. On a longer time scale, however, the $(YCl_6)^{3-}$ coordination in the melt should be loose, since the ionic conductivity of the YCl_3 melt near freezing, though relatively modest, is still appreciable ($\sigma = 0.39$ Ω^{-1} cm^{-1} [9]). The neutron diffraction measurements of the Faber–Ziman structure factor of molten YCl_3 at 1020 K by Saboungi *et al* [3] have confirmed the essentially sixfold coordination of Y by Cl and have revealed a prominent first sharp diffraction peak (FSDP) at wavenumber $k = 0.95$ Å^{-1}. Such a feature in the total diffraction pattern is characteristic of strongly structured liquids and glasses with intermediate-range order [10]. It appears from all these data, including the type of crystal structure, that the structure of molten YCl_3 may resemble a loose ionic network of edge-sharing octahedra. The possible remnants of a layer-like structure and interlayer (mainly Cl–Cl) correlations in the melt are still obscure.

2. Model and results

Before introducing our model for inter-ionic forces in molten YCl_3, we should emphasize that the adoption of an ionic model for a polyvalent metal halide melt necessarily has more limited aims than for alkali halide melts. For the latter systems well tested procedures exist, since the work of Born and Mayer in the 1930s, to determine reliable pair interactions from crystalline state data on the whole family of compounds, thus allowing both theory and computer simulation to attain an almost fully quantitative account of the available liquid structure data [11]. In strongly ionic polyvalent metal halides, on the other hand, the nature of the bond is more complex—as is immediately evident from the fact that their real crystal structures often arise from small distortions of ideal simple crystal structures. This is the case for the AlCl$_3$-type structure, as already mentioned. A full determination of the effective interactions for a whole family of compounds requires a more complicated model which would include the ionic polarization effects leading to such distortions. A reduction to simple pair interactions thus implies that, after a sensible estimation of the interaction parameters, a statistical mechanical calculation of the liquid structure becomes practicable, but may only aim at giving a semi-quantitative scenario highlighting the role of the Coulomb interactions in structuring the liquid.

Yuen *et al* [12] have implemented the previously indicated approach to the determination of interaction parameters from crystalline data for alkaline earth halides, using the form of inter-ionic potentials earlier proposed by Busing [13]. Attention has subsequently been drawn [14] to the usefulness of their results in predicting the properties of both isolated alkaline earth halide molecules and tetrahedral molecular

ions formed by some of these metals with halogens in the liquid state. These properties are the molecular shape, the metal–halogen bond length and the vibrational frequencies. On this basis, the bond length and vibrational frequencies of tetrahedral molecular ions formed by Al^{3+} ions with chlorines have been used in the estimation of interaction parameters for Al halides [14]. The same approach is being implemented for octahedra-forming compounds [15]. In particular for YCl_3 we adopt Busing-type effective interactions, writing the pair potential $\Phi_{ij}(r)$ between ions of types i and j at separation r as the sum of their Coulomb interaction and a short-range overlap repulsion in the form

$$\Phi_{ij}(r) = Z_i Z_j \frac{e^2}{r} + f(\rho_i + \rho_j) \exp[(R_i + R_j - r)/(\rho_i + \rho_j)]. \tag{1}$$

Clearly, each ion is being described by a valence Z_i, an effective radius R_i and an effective hardness ρ_i. The overlap parameters in equation (1) are taken for the Cl^- ion from the work of Yuen *et al* [12] and are evaluated for the Y^{3+} ion by fitting the average Y–Cl bond length in the crystal ($r_{Y-Cl} = 2.63$ Å [16]) and the breathing mode frequency of the $(YCl_6)^{3-}$ octahedron ($\nu = 261$ cm^{-1} [8]), after supplementing the Busing interactions with ionic polarization effects treated in a deformation dipole model. The values of the interaction parameters that we have adopted for molten YCl_3 are reported in table 1. As a test of these results we find that the estimated frequencies of the other Raman-active modes of the $(YCl_6)^{3-}$ octahedron show the correct trends in comparison with their measured values [15].

Table 1. Interaction parameters for YCl_3.

Z_Y	Z_{Cl}	$f(e^2$ Å$^{-2})$	R_Y (Å)	R_{Cl} (Å)	ρ_Y (Å)	ρ_{Cl} (Å)
3	−1	0.05	1.12	1.71	0.007	0.238

With these model interactions we have evaluated the partial pair distribution functions $g_{ij}(r)$ and the corresponding partial structure factors $S_{ij}(k)$,

$$S_{ij}(k) = \delta_{ij} + n(x_i x_j)^{1/2} \int dr [g_{ij}(r) - 1] \exp(ik \cdot r) \tag{2}$$

at the temperature and density of molten YCl_3 in the experiments of Saboungi *et al* [3] ($T = 1020$ K, $\rho = 2.56$ g cm^{-3}). In equation (2) n is the number density of formula units and x_i is the number of ions of the type i in the formula unit. The calculation solves the Ornstein–Zernike equations for the partial direct correlation functions $c_{ij}(r)$,

$$h_{ij}(r) = c_{ij}(r) + n \sum_l x_l \int dr' h_{il}(r') c_{lj}(|r - r'|) \tag{3}$$

where $h_{ij}(r) = g_{ij}(r) - 1$, in combination with the hypernetted-chain closure,

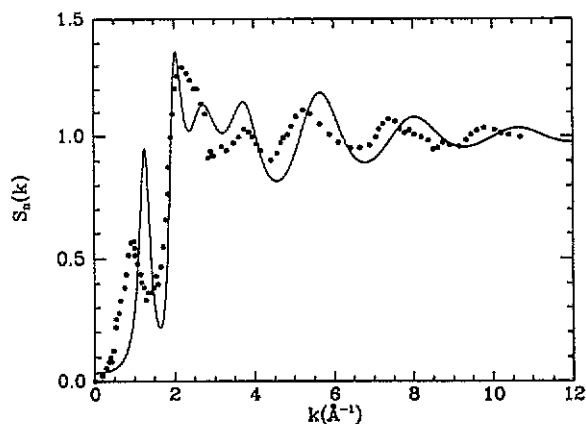$$g_{ij}(r) = \exp[-\Phi_{ij}(r)/(k_B T) + h_{ij}(r) - c_{ij}(r)]. \tag{4}$$

Figure 1. Calculated Faber–Ziman structure factor of molten YCl$_3$ (full curve), in comparison with the neutron diffraction data of Saboungi *et al* [3] (dots).
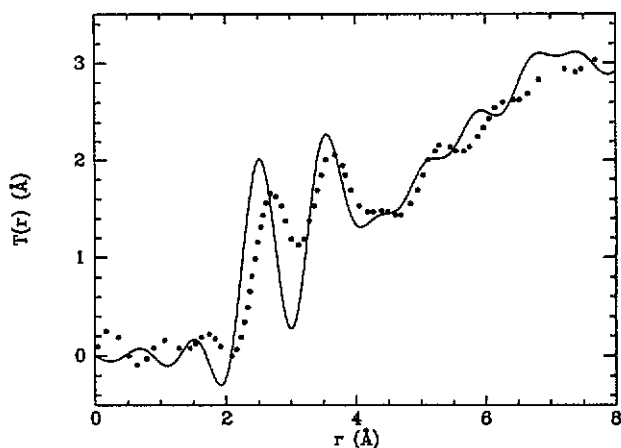

Figure 2. Calculated total pair correlation function of molten YCl$_3$ (full curve), in comparison with the neutron diffraction data of Saboungi *et al* [3] (dots).

These equations have been solved numerically on a grid of 513 points by means of the algorithm developed by Gillan [17, 18], with an r-spacing of 0.098 Å corresponding to a k-spacing of 0.063 Å^{-1}. The results are shown in figures 1 to 5.

Figures 1 and 2 report our results for the Faber–Ziman structure factor $S_n(k)$, defined as

$$S_n(k) = \left(\sum_i x_i b_i^2 \right)^{-1} \left[\sum_{ij} (x_i x_j)^{1/2} b_i b_j S_{ij}(k) \right] \tag{5}$$

where b_i is the neutron scattering length of ion i, and the total pair correlation function $T(r)$, defined as

$$T(r) = 4\pi n r + (2/\pi) \int_0^{k_{max}} [S_n(k) - 1] \sin(kr) k \, dk \tag{6}$$

in comparison with the data of Saboungi *et al* [3]. For the theoretical results we have adopted in the Fourier integral (6) the same upper cut-off $k_{max} = 8$ Å^{-1} as that used in the experimental work, to show that the oscillations in $T(r)$ below 2 Å are due to the finite cut-off. Figures 3 and 4 show our results for the partial pair distribution functions and for the partial structure factors, respectively. Finally, the running coordination numbers $N_{ij}(r)$, defined as

$$N_{ij}(r) = 4\pi n x_j \int_0^r g_{ij}(r')r'^2 \, dr' \qquad (7)$$

are shown in figure 5. The broken curve in this figure refers to the coordination of Y by Cl, which is three times as large as that of Cl by Y.
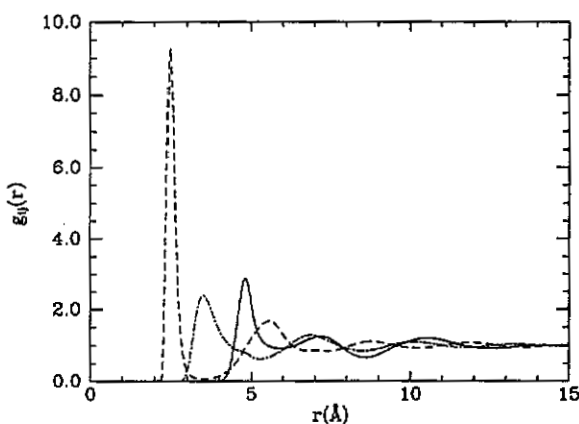

Figure 3. Partial pair distribution functions calculated for molten YCl$_3$: broken curve, $g_{YCl}(r)$; chain curve, $g_{ClCl}(r)$; full curve, $g_{YY}(r)$.
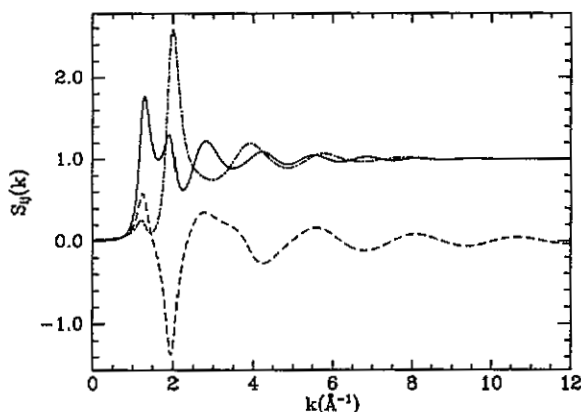

Figure 4. Partial structure factors calculated for molten YCl$_3$. Symbols as in figure 3.
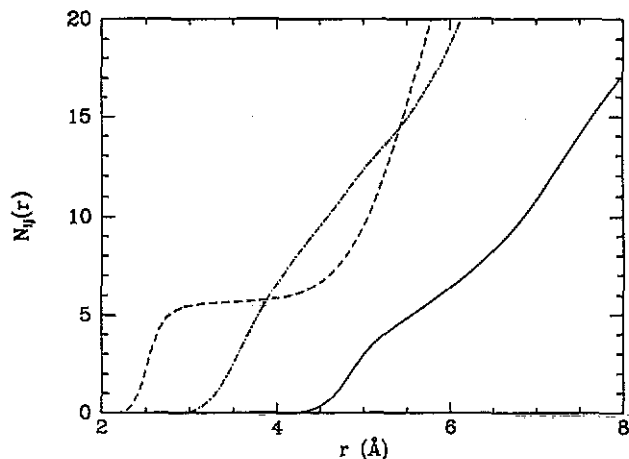
Figure 5. Running coordination numbers of Y by Cl (broken curve), Cl by Cl (chain curve) and Y by Y (full curve), calculated for molten YCl_3.

3. Discussion

It is immediately evident from figures 1 and 2 that our simple model does quite well in accounting for the short-range correlations in the liquid, including the first- and second-neighbour shells as seen in $T(r)$, but is much less successful in accounting for correlations at longer range. It is nevertheless very remarkable that such a simple model should yield an FSDP in $S_n(k)$, though at $k = 1.25$ Å^{-1} rather than at $k = 0.95$ Å^{-1} as in the measured structure factor. We conclude that the Coulomb interactions alone can lead to intermediate-range order in a 3:1 melt, and that the nature of the inter-ionic forces in the real trichloride melt is more complex and determines a different topology in the intermediate-range order. As a further detailed comment on figure 2 we should note that the discrepancies in the position of the first peak of $T(r)$ and in the valley following it could be easily mended by fitting the Y–Cl bond length in the liquid and by taking account of the finite resolution in the experiment. It appears from the comparison that the bond length is somewhat expanded in the liquid.

Bearing in mind the results of comparison with the neutron diffraction data, let us now discuss the calculated partial pair structure of the liquid. Figure 3 shows that the first peak in $T(r)$ is almost exclusively due to Y–Cl first-neighbour correlations and that these are long-lived, as can be seen from the very low value (0.07) attained by $g_{YCl}(r)$ at its main minimum. The running coordination number $N_{YCl}(r)$ in figure 5 attains a stable value of approximately 5.7 above 3 Å, which is to be compared with a Y–Cl coordination number of 5.9 obtained by fitting a Gaussian to the first peak in the measured $T(r)$. Furthermore, the ratio of the positions of the main peak in $g_{ClCl}(r)$ and $g_{YCl}(r)$ is very close to the value $\sqrt{2}$ that would be appropriate for octahedral coordination. Apparently, Coulomb interactions between trivalent cations and monovalent anions suffice to originate a stable coordination of octahedral type between them.

Figure 3 further shows that the second peak in the calculated $T(r)$ is almost exclusively due to Cl–Cl correlations. In figure 3 these have the shape of a main peak followed by a shoulder and further away by a minimum. $N_{ClCl}(r)$ in figure 5

does not show any special structure and attains the value 13.8 at the position of the minimum in $g_{ClCl}(r)$. However, the peak and the shoulder in $g_{ClCl}(r)$ become separated by a minimum if one plots the function $r^2 g_{ClCl}(r)$, and $N_{ClCl}(r)$ attains the value 9.6 at the position of this minimum. This value is to be compared with the Cl–Cl coordination number of 8.2 that was estimated by fitting a further Gaussian to the second peak in the measured $T(r)$, and with the intra-layer Cl–Cl coordination number of 9 in the idealized $AlCl_3$-type crystal structure. A further contribution of 3 to the first-neighbour Cl–Cl coordination number arises in the idealized crystal structure from inter-layer correlations. Thus, it appears that the inter-layer Cl–Cl correlations are substantially relaxed on melting and that their remnant may lie in the shoulder of $g_{ClCl}(r)$. In this viewpoint, the structure of the calculated $g_{ClCl}(r)$ of a main peak and a shoulder may reflect a residual layer-like character of the structure in the melt. We remark in this regard that our model, which lacks directional forces, should be expected to under-emphasize any such feature—which may on the other hand be important in determining the topology of the intermediate-range order at larger distances.

Turning next to the Y–Y correlations, $g_{YY}(r)$ is seen from figure 3 to have its main peak at almost 5 Å. This prediction is evidently the consequence of the strong Coulomb repulsions between Y^{3+} ions in the model, and its relevance to the real molten salt remains to be confirmed. We see from figure 4 that these correlations generate the largest FSDP in the partial structure factors. They therefore most directly reflect the topology of the intermediate-range order, which, as we have already stressed, is not correctly reproduced by our model. It would seem that one should invoke a complementary role of angle-dependent forces. If we assume that the structure of the real liquid should reflect more closely the crystal structure from which it came, we would expect some further structure in $g_{YY}(r)$ in the proximity of the main peak in $g_{ClCl}(r)$.

As a further comment on figure 4, we may explicitly point out the presence of a subsidiary peak in $S_{YY}(k)$, a main peak in $S_{ClCl}(k)$ and a deep trough in $S_{YCl}(k)$, all lying close to 2 Å^{-1}. These features are the well known markers of alternation of the components in a molten salt.

It may also be useful to contrast our views on the liquid structure on YCl_3 with what is known about molten dichlorides at the level of partial structure factors and pair distribution functions. Intermediate-range order is present in molten $ZnCl_2$ [19] and $MgCl_2$ [20, 21]. However, the prevailing fourfold coordination of the divalent metal ions in these two melts implies that both directionality of the inter-ionic forces and halogen polarization are much more important than in molten YCl_3 [22]. On the other hand, for molten $SrCl_2$ [23] and $BaCl_2$ [24] there is theoretical evidence for a role for halogen polarization, but none for directionality of the inter-ionic forces [25]. The structure of molten $CaCl_2$ [26] appears to be intermediate in character and the nature of the interactions in $CaCl_2$ and YCl_3 may be closely allied. The role of Coulomb interactions should be expected to be more evident in the latter system, thus allowing the primitive interpretation of its liquid strucure that we have presented in this work. All the foregoing observations correlate well with Pettifor's parameter for the metal elements under consideration: his chemical scale places them in the order Ba–Sr–Ca–Y–Mg–Zn with increasing χ_M, Y being close to Ca and very far from Mg [2].

In summary, evaluation of a simple model for a 3:1 ionic liquid adjusted to YCl_3 shows that the Coulomb interactions suffice to induce a long-lived, octahedral-type

coordination between first neighbours, developing further away into order at intermediate range. However, only the predicted type of short-range order is in essential agreement with what is known about molten YCl_3. Clearly, it would be of very relevant interest to determine experimentally and in more detail the structure of molten YCl_3 by measuring its partial structure factors. The detailed shape of the Cl–Cl correlations beyond their main peak and the whole of the Y–Y correlations should reflect the topology of the intermediate-range order in relation to remnants of layer-like ordering.

Acknowledgments

References

[1]   Tosi M P, Pastore G, Saboungi M-L and Price D L 1991 *Phys. Scr.* at press
[2]   Pettifor D G 1986 *J. Phys. C: Solid State Phys.* 19 285
[3]   Saboungi M-L, Price D L, Scamehorn C and Tosi M P 1991 *Europhys. Lett.* 15 283
[4]   March N H and Tosi M P 1980 *Phys. Chem. Liquids* 10 39
[5]   Triolo R and Narten A H 1978 *J. Chem. Phys.* 69 3159
[6]   Dworkin A S and Bredig M A 1971 *High Temp. Sci.* 3 81
[7]   Igarashi K and Mochinaga J 1987 *Z. Naturforsch. A* 42 777
[8]   Papatheodorou G N 1977 *J. Chem. Phys.* 66 2893
[9]   Janz G J, Dampier F W, Lakshminarayan G R, Lorenz P K and Tompkins R P T 1968 *Natl Bur. Stand. Ref. Data Ser.* 15 1
[10] Moss S C and Price D L 1985 *Physics of Disordered Materials* ed D Adler, H Fritzsche and S R Ovshinsky (New York: Plenum) p 77
[11] Rovere M and Tosi M P 1986 *Rep. Prog. Phys.* 49 1001
[12] Yuen P S, Murfitt R M and Collin R L 1974 *J. Chem. Phys.* 61 2383
[13] Busing R W 1970 *Trans. Am. Crystallogr. Ass.* 6 57
[14] Ferrante A, Wang Li and Tosi M P 1988 *Phil. Mag. A* 58 13
[15] Erbölükbas A, Akdeniz Z and Tosi M P unpublished
[16] Wyckoff R W G 1964 *Crystal Structures* vol 1 (New York: Interscience) p 57
[17] Gillan M J 1979 *Mol. Phys.* 38 1781
[18] Abernethy G M and Gillan M J 1980 *Mol. Phys.* 39 839
[19] Biggin S and Enderby J E 1981 *J. Phys. C: Solid State Phys.* 14 3129
[20] Biggin S, Gay M and Enderby J E 1984 *J. Phys. C: Solid State Phys.* 17 977
[21] Day S E and McGreevy R L 1985 *Phys. Chem. Liquids* 15 129
[22] Ballone P, Pastore G, Thakur J S and Tosi M P 1986 *Physica* B 142 294
[23] McGreevy R L and Mitchell E W J 1982 *J. Phys. C: Solid State Phys.* 15 5537
[24] Edwards F G, Enderby J E, Howe R A and Page D I 1978 *J. Phys. C: Solid State Phys.* 11 1053
[25] Pastore G, Ballone P and Tosi M P 1986 *J. Phys. C: Solid State Phys.* 19 487
[26] Biggin S and Enderby J E 1981 *J. Phys. C: Solid State Phys.* 14 3577