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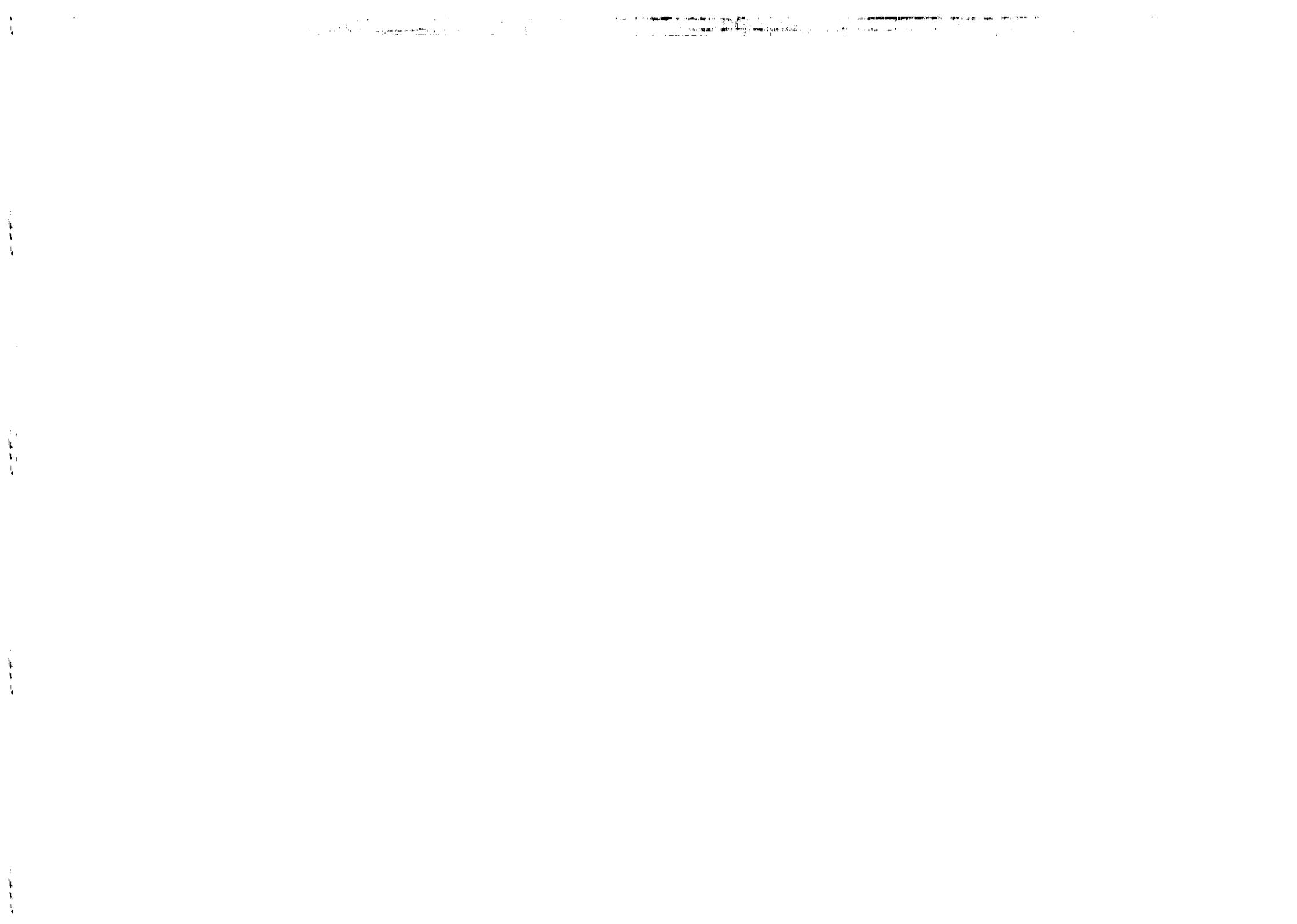


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MELTING IN TRIVALENT METAL CHLORIDES *

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ABSTRACT

We report a neutron diffraction study of the liquid structure of YCl_3 and combine the structural data with macroscopic melting and transport data to contrast the behaviour of this molten salt with those of $SrCl_2$, $ZnCl_2$ and $AlCl_3$ as prototypes of different melting mechanisms for ionic materials. A novel melting mechanism for trivalent metal chlorides, leading to a loose disordered network of edge-sharing octahedral units in the liquid phase, is thereby established. The various melting behaviours are related to bonding character with the help of Pettifor's phenomenological chemical scale.

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Over the last two decades, the liquid structure of a number of monovalent and divalent metal ion halides has been determined by neutron diffraction experiments and its gross character has been correlated with the nature of the chemical bond in these various materials (for recent reviews see [1-3]). We report in this letter for the first time a neutron diffraction study of the liquid structure of a trivalent metal chloride, that is YCl_3 , and discuss its character by contrast with the prototype structural behaviours shown by the melts of $SrCl_2$, $ZnCl_2$ and $AlCl_3$. Such a comparison identifies a novel type of melting mechanism for mainly ionic materials in relation to their bonding character.

We recall, first of all, that the structure of the highly ionic $SrCl_2$ melt is dominated by the short-range order in the subsystem of Sr cations (even though the Sr-Sr first neighbour distance is as large as 5 Å), while a noticeably poorer degree of short-range order is observed in the subsystem of Cl anions [4]. By contrast, the dominant structure factor in the partly covalent $ZnCl_2$ melt is the Cl-Cl one: the liquid structure of this material may be pictorially described as a network-like spatial arrangement of corner-sharing tetrahedra formed by a distorted close packing of Cl ions which provides tetrahedral holes for the Zn ions. A very similar description applies to the glassy state of $ZnCl_2$ [6]. As shown in the first two rows of table I, the very different structural behaviours of the $SrCl_2$ and $ZnCl_2$ melts are reflected in differences in macroscopic properties, in particular in the melting temperature T_m and, most strikingly, in transport coefficients such as the ionic conductivity σ and the shear viscosity η [7-14].

Turning to $AlCl_3$, this is known to melt from a mainly ionic layer structure into a molecular liquid consisting primarily of Al_2Cl_6 units, as demonstrated by X-ray studies [15]. As is shown in the third row in table I [7, 9, 10, 12, 16], the striking melting behaviour of $AlCl_3$ is accompanied by low T_m , very large values of the entropy change ΔS_m on melting and of the difference in specific volumes between liquid and solid, a very low value of σ in the melt and a rather low value of η . However, YCl_3 and some rare-earth trichlorides ($DyCl_3$, $HoCl_3$ and $ErCl_3$), though crystallizing in the same structure as $AlCl_3$, show very different values for the above macroscopic properties [9, 13, 17, 18] (see table I). In the case of YCl_3 an extensive

Raman scattering study by Papatheodorou [19] has suggested that the structure of the melt may be a network of distorted chlorine-sharing octahedra. This suggestion emerged from a comparison of the Raman spectra of pure liquid and solid YCl_3 as well as from a series of measurements on mixtures of YCl_3 and alkali chlorides, in which Raman modes of YCl_6 octahedra were observed in stoichiometric mixed crystals at room temperature and followed first up to and across melting and then as a function of YCl_3 content in the liquid mixture up to the pure YCl_3 melt. It thus appears that the melting behaviour of YCl_3 may differ in its characteristics from those already established for the prototypic SrCl_2 , ZnCl_2 and AlCl_3 systems. Our neutron diffraction measurements have the aim of providing a direct determination of the local structure and of its connectivity in this melt.

The diffraction measurements were carried out at the SEPD instrument at the Intense Pulsed Neutron Source (INPS). The YCl_3 sample, obtained from APL Engineered Materials, Urbana, IL, was encapsulated in a fused quartz tube of 3 mm I.D., 4 mm. O. D. The sample was heated to 1020 K with a vanadium resistive furnace. Runs were made with the YCl_3 sample, an equivalent empty quartz tube, the empty furnace as background, a 0.6 mm diameter vanadium standard rod, and a background for vanadium. Data collection and analysis was carried out with standard procedures for liquid and glass samples at INPS [20]. The parameters used in the analysis [19, 21] are shown in table II. Data from detector groups at angles of $\pm 60^\circ$, 30° and -14° were averaged with the flux-weighting technique and the resulting Faber-Ziman structure factor $S(Q)$ is shown in fig. 1. It exhibits a first sharp diffraction peak (FSDP) at $Q = 0.95 \text{ \AA}^{-1}$, which is characteristic of liquid structures with intermediate-range order [22]. The Fourier transform $D(r)$, obtained by transforming the data out to $Q = 8 \text{ \AA}^{-1}$, without the use of a modification function, is shown in fig. 2. The low- r part is in good agreement with the slope predicted from the measured density of the liquid.

The real space structure of the liquid can be analyzed by fitting Gaussian functions, broadened with a function representing the effect of truncation of the data at $Q_{\text{max}} = 8 \text{ \AA}^{-1}$, to the total correlation function $T(r)$. These Gaussians, with parameters given in table III, give an excellent fit to the data out to $r = 5.5 \text{ \AA}$, as shown in fig. 3. In the insert in fig. 3 the

interatomic distances for crystalline YCl_3 , derived from X-ray diffraction [23], are shown with the appropriate weighting. Comparing the crystal and liquid structures, it is reasonable to associate Peak 1 with Y-Cl bonds, leading to a coordination number for Cl about Y of 5.87. In the crystal, the Y-Cl coordination number is 6 and the mean bond distance and standard deviation are $\langle r \rangle = 2.636 \text{ \AA}$ and $\Delta r = 0.044 \text{ \AA}$. Comparing the values for the liquid from table III, we find that the Y ions in the liquid remain in octahedral-type coordination but the octahedra are somewhat expanded and probably distorted relative to the crystal. The other peaks in $T(r)$ are likely to arise from a combination of different types of bond, making it impossible to extract precise coordination numbers. However, if we associate the second peak in $T(r)$ with second-neighbour Cl-Cl coordination, neglecting the Y-Y coordination which in any case contributes with low weight, we derive a Cl-Cl coordination of approximately 8.2, appreciably less than the value of 12 found in the solid.

Although from a strict crystallographic viewpoint the AlCl_3 -type crystal structure of YCl_3 is described as a monoclinic layer structure with a unit cell containing four formula units, it can almost be viewed as built from a cubic close packing of Cl ions inside which the metal ions occupy suitable octahedral holes. A single layer in this idealized description of the crystal structure (see Fig. 4) consists of two triangular lattices of Cl ions, with phase relationship as appropriate to 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, we see that (a) 1/4 of the Cl-Cl coordination in the crystal arises from inter-sandwich Cl-Cl bonds, and (b) 1/3 of the intra-sandwich octahedral sites are empty. Our finding of a Cl-Cl coordination number of approximately 8.2 in molten YCl_3 can therefore 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 within the layer-like octahedral network seems nevertheless to persist in the liquid, as indicated by the FSDP in $S(Q)$ and by the values of the thermodynamic melting parameters in table I. From the dynamic point of view, it is evident from the Raman data of Papatheodorou

[19] that the YCl_6 coordination in the melt has a lifetime which is long compared with the inverse of the Raman breathing mode frequency at about 260 cm^{-1} . On the other hand, the value of the ionic conductivity σ for molten YCl_3 in table I shows, especially by comparison with $SrCl_2$ and $ZnCl_2$, that on a much longer time scale the network is relatively loose. We also note that the data for $DyCl_3$, $HoCl_3$ and $ErCl_3$ in table I suggest that these systems may have in the liquid phase a structural behaviour similar to that of YCl_3 .

It is next appropriate to ask why YCl_3 and $AlCl_3$, though crystallizing in the same $AlCl_3$ -type structure, have such different melting behaviours. As discussed earlier by March and Tosi [24], the melting process of $AlCl_3$ may be viewed as driven by a structural phase transition from the $AlCl_3$ -type to the $AlBr_3$ -type crystal structure, which is formed by chemically saturated molecular units weakly bound together by van der Waals forces and thus has low melting point. In an Al_2Cl_6 molecular unit each Al ion is surrounded by a tetrahedron of Cl ions and a unit consists of two of these tetrahedra sharing a Cl-Cl edge. The $AlCl_3$ -type layer structure that we have schematically discussed above can break down into such units by an appropriate 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.

The difference in melting behaviours for $AlCl_3$ and YCl_3 is therefore related to the question of the relative stability of tetrahedral and octahedral coordination under an increase of temperature and hence to a subtle difference in the balance between ionic and covalent components of the bonding. It is interesting to note that this difference is accounted for by the phenomenological chemical scale of the elements and classifications of crystal structures proposed by Pettifor [25]. In spite of the identity in crystal structure, this 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. 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.

Still within Pettifor's classification scheme, we note that $DyCl_3$, $HoCl_3$ and $ErCl_3$ lie

very close to YCl_3 , thus confirming our earlier suggestion of a similarity of structural behaviour for these systems in the liquid phase. On the other hand, among trivalent metal chlorides crystallizing in the same $AlCl_3$ -type structure, we have found that $InCl_3$ lies very close to $AlCl_3$ in Pettifor's classification. The available thermodynamic and transport data for $InCl_3$ are reported in the last row of table I [9, 10]. The volume change on melting is very large, similarly to $AlCl_3$, but the melting temperature is sizably higher and the electrical conductivity of the melt is appreciable. These data seem to suggest a melting mechanism for $InCl_3$ into a liquid of molecular units which are in part thermally ionized. Clearly a microscopic investigation of this melt would be quite interesting.

In summary, we have presented experimental data which have led us to propose the melting mechanism of YCl_3 as a breakage of the crystal structure into a loose octahedral network conserving layer-like order at intermediate range. This mechanism is alternative for trivalent metal chlorides to the mechanism of breaking of the structure into chemically saturated molecular units, as is known to occur in $AlCl_3$. By comparing the available thermodynamic and transport data for different trivalent metal chlorides having the same crystal structure and by noticing their respective locations within Pettifor's scheme of classification for bonding characters and crystal structures, we have been able to suggest other examples of the two alternative melting mechanisms for further investigation.

* * *

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

| Salt | Crystal structure | T_m (K) | ΔS_m (cal/mol K) | $(V_l^{T_m}/V_s^{RT} - 1)^a$ | σ ($\Omega^{-1}\text{cm}^{-1}$) | η (cp) |
|-------------------|-------------------|-----------|--------------------------|------------------------------|--|-------------------------|
| SrCl ₂ | CaF ₂ | 1146 [7] | 5.9 ^b | 0.13 [9,10] | 2.0 [9] | 3.7 [11] |
| ZnCl ₂ | ZnCl ₂ | 570 [7] | 4.1 [7] | 0.16 [12,10] | 1.x10 ⁻³ [13] | 4.x10 ³ [14] |
| AlCl ₃ | AlCl ₃ | 466 [7] | 18.1 [7] | 0.88 [12,10] | 5.x10 ⁻⁷ [9] | 0.36 [16] |
| YCl ₃ | AlCl ₃ | 994 [17] | 7.6 [17] | 0.0045 [18] | 0.39 [9] | -- |
| DyCl ₃ | AlCl ₃ | 924 [17] | 6.6 [17] | 0.0034 [18] | 0.44 [13] | 4.2 [13] |
| HoCl ₃ | AlCl ₃ | 993 [17] | 7.3 [17] | -- | 0.38 [9] | -- |
| ErCl ₃ | AlCl ₃ | 1047 [17] | 7.4 [17] | -- | 0.43 [9] | -- |
| InCl ₃ | AlCl ₃ | 859 [10] | -- | 0.61 [9,10] | 0.42 [9] | -- |

^a Relative difference between the volume of the liquid at T_m ($V_l^{T_m}$) and that of the solid at room temperature (V_s^{RT}), the volume of the solid at T_m being in most cases unknown. Except for YCl₃ and DyCl₃, the two indicated references refer to $V_l^{T_m}$ and to V_s^{RT} , respectively.

^b Sum of the entropy change for the superionic transition [8] and for melting [7].

TABLE II. - Parameters used in YCl₃ data analysis

| | Y | Cl | YCl ₃ |
|-----------------------------------|------|-------|------------------|
| density (g/cm ³) [19] | | | 2.56 |
| b (fm) [21] | 7.75 | 9.577 | |
| σ_i (b) [21] | 0.15 | 5.2 | |
| σ_a (b at 1.8 Å) [21] | 1.28 | 33.5 | |

TABLE III. - Parameters of gaussian fits to $T(r)$ for YCl₃

| Peak | $\langle r \rangle$ (Å) | σ (Å) | Area ^a |
|------|-------------------------|--------------|-------------------|
| 1 | 2.705 | 0.240 | 2.619 |
| 2 | 3.638 | 0.368 | 6.801 |
| 3 | 4.382 | 0.248 | 1.964 |

^a The relationship between the area and the coordination numbers $C_A(B)$ of B-type atoms around A-type atoms is $\text{Area} = \int_0^r T(r) dr = [b_Y^2 C_Y(Y) + 2b_Y b_{Cl} C_Y(Cl) + 3b_{Cl}^2 C_{Cl}(Cl)]/[4\langle b \rangle^2]$ where the b's are the scattering amplitudes in table II and $\langle b \rangle = (b_Y + 3b_{Cl})/4$.

FIGURE CAPTIONS

Fig. 1. - Structure factor $S(Q)$ of liquid YCl_3 .

Fig. 2. - Difference correlation function $D(r) = (2/\pi) \int_0^{Q_{\max}} [S(Q) - 1] \sin(Qr) Q dQ$ of liquid YCl_3 .

Fig. 3. - Total correlation function $T(r) = D(r) + 4\pi\rho_0 r$ of liquid YCl_3 , ρ_0 being the total number density. The dashed curve represents a four-gaussian fit. The interatomic distances in crystalline YCl_3 are shown with the appropriate weighting in the insert.

Fig. 4. - Structural illustration of melting in AlCl_3 -type trichlorides. A layer in the idealized crystal structure (top Cl plane in gray, bottom Cl plane in white and sandwiched metal plane in black) is a 2D network of edge-sharing octahedra, one of which is shown. Also shown is the Al_2Cl_6 unit which deforms into two edge-sharing tetrahedra on melting of AlCl_3 .

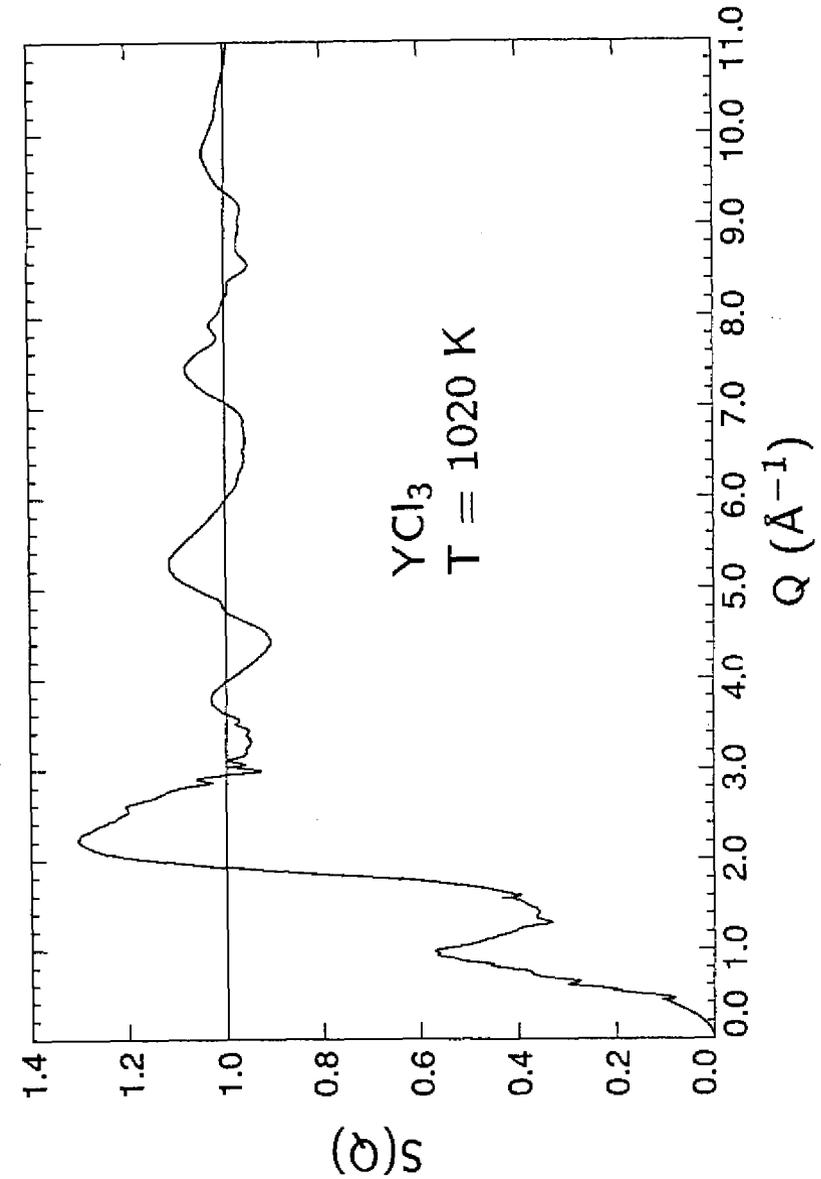


Fig. 1

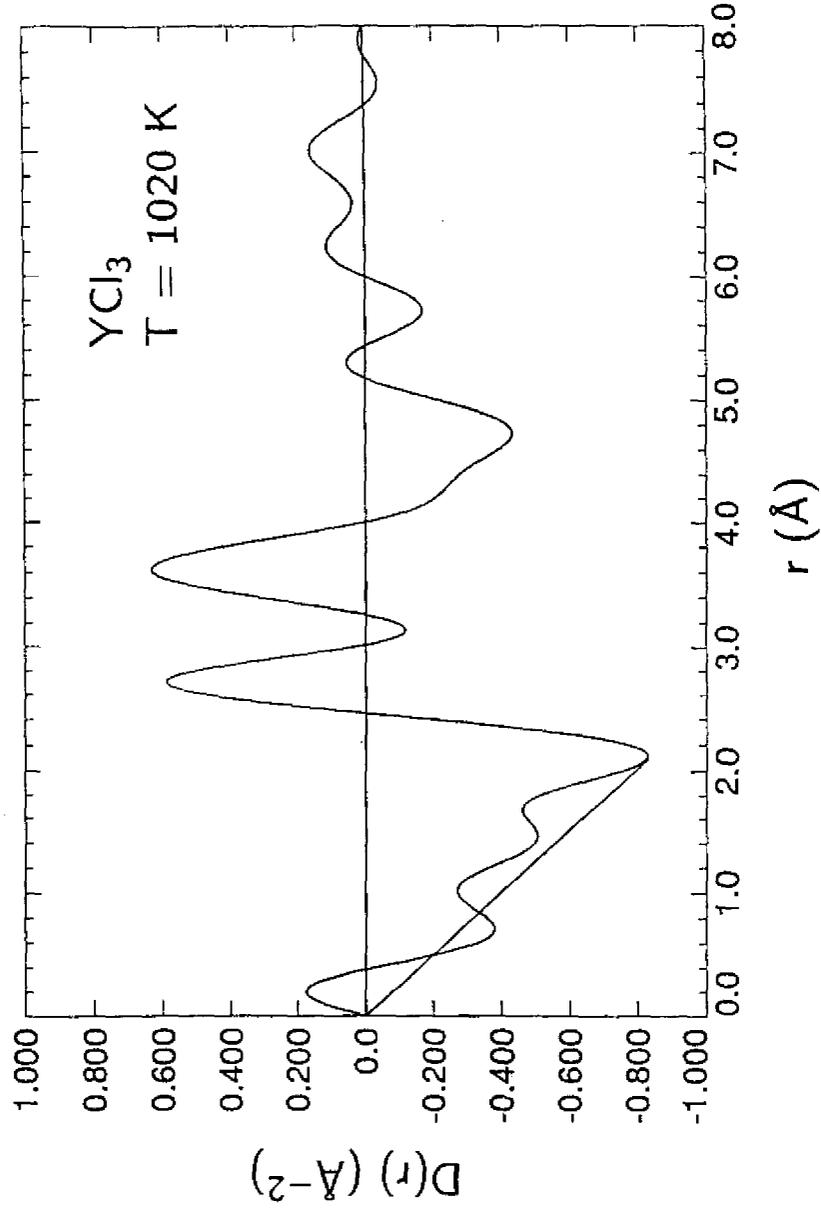


Fig. 2

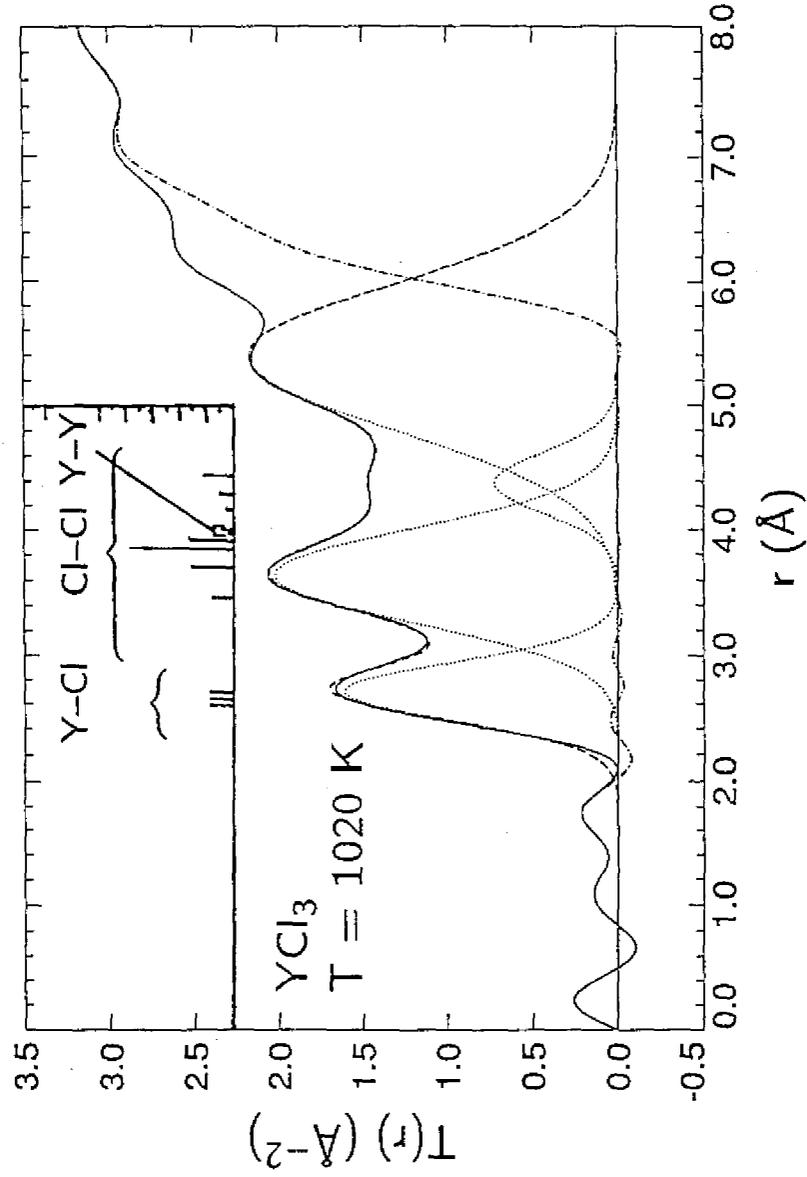


Fig. 3

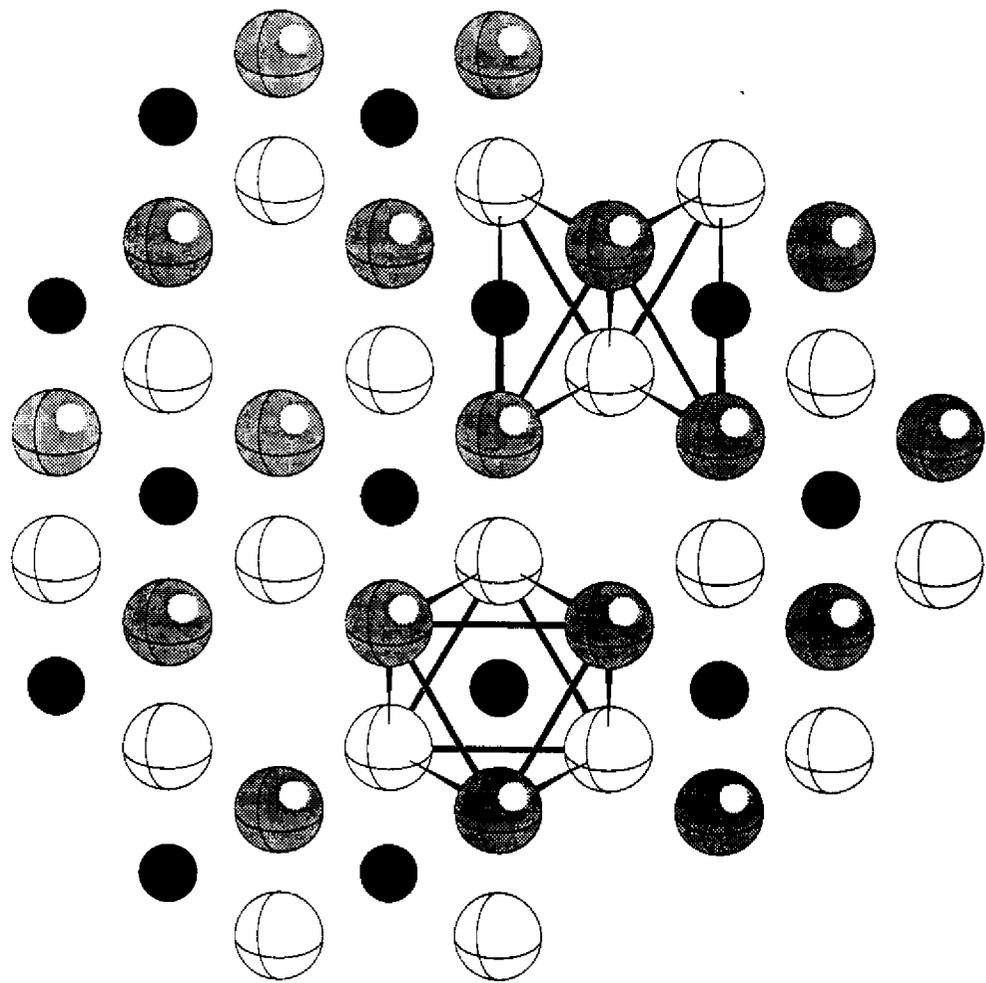


Fig.4



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