X-Ray Diffraction Study on the Local Structure of Molten $ErCl_3$

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The short range structure of molten $ErCl_3$ at 1053 K was investigated by X-ray diffraction. The nearest neighbour distance of $Er^{3+}-Cl^-$ and the coordination number of Cl^- around Er^{3+} were estimated to be 2.63 Å and 5.8 Å, respectively, and the $Er^{3+}-Er^{3+}$ and Cl^--Cl^- distances 4.05 Å and 3.75 Å, respectively. The ratio of the anion-anion pair distance to the cation-anion pair distance (r_{--}/r_{+-}) was, therefore, 1.43, being close to 1.41, characteristic of octahedral geometry. These results indicate that $ErCl_6^{3-}$ octahedra exist in molten $ErCl_3$. Probably $Er_2Cl_{10}^{4-}$ and a small amount of $Er_2Cl_{11}^{5-}$ ions are formed according to the geometrical calculations of bond lengths and bond angles.

1. Introduction

Pioneering high temperature Raman spectroscopic studies have been carried out in the 1970's on rare earth chloride systems in the liquid and solid state [1–3]. Structural analyses have been made by X-ray diffraction and Raman spectroscopy on pure lanthanide trichlorides [4, 5] with UCl_3-type crystal structure (hexagonal). Those results indicated that the nearest neighbour chloride coordination number of a lanthanide ion changed from 9 in the crystal to 6 in the melt, allowing for octahedral geometry around the lanthanide ions. Little is known about melts of lanthanide trichlorides with $AlCl_3$-type crystal structure (monoclinic), except for YCl_3 [6]. The melting behaviour of $ErCl_3$ might be similar to that of YCl_3, having the same crystal structure. Recently, structural correlations in molten trivalent metal chlorides have been estimated as functions of the metal ion size for $LaCl_3$ and $AlCl_3$-type lanthanide trichlorides, using a charged soft-sphere model and the hypernetted chain approximation [7]. Furthermore, Erbölükbas et al. [8] have analyzed the available data on bond lengths and Raman frequencies by treating an isolated octahedral complex ion within a model which adopts charged soft-sphere interionic potentials, supplemented by taking ionic polarization into account.

In the present work, the short range structure of molten $ErCl_3$ was studied by X-ray diffraction. Possible anionic pairs are discussed in view of interatomic distances and bond angles.

2. Experimental

$ErCl_3$ was prepared by heating a mixture of analytical grade Er_2O_3 and 2.5 times the theoretical amount of NH_4Cl at 623 K for 3 h. Excess NH_4Cl was removed by heating at 1173 K. The chlorination reaction is

$$Er_2O_3 + 6\,NH_4Cl \rightarrow 2\,ErCl_3 + 6\,NH_3 + 3\,H_2O\,.$$

$ErCl_3$ thus obtained was purified by $ErCl_3$ vapour deposition onto the surface of a quartz tube cooled with water under reduced pressure down to 10^{-2} Pa for 12 h. The vapour source was heated at 1253 K, so as to remove small amounts of water, oxychloride, unreacted NH_4Cl and oxide. The molar volumes were measured dilatometrically using a transparent thin goldfilm-coated furnace with a good thermal stability [9]. In the X-ray scattering measurements, the purified sample was sealed in a thin quartz tube cell.

The X-ray diffractometer, having a $\theta-\theta$ type reflection geometry (Rigaku Corporation, Tokyo, Japan), was employed with MoKα radiation, and the diffracted beam was monochromatized with curved graphite. The Q-range, $0.93 \leqq Q/\text{Å}^{-1} \leqq 12.5$, was explored with two pairs of slits [1/2°–1/2°] when $2.5° \leqq \theta \leqq 15°$, and [1°–1°] when $13° \leqq \theta \leqq 45°$ (2θ = scattering angle and $Q = 4\pi \sin\theta/\lambda$ with λ being the

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wavelength of the radiation). The scattered X-ray intensities so obtained were corrected for background, polarization, absorption and Compton scattering, and normalized to the coherent scattering intensity of the stoichiometric unit, in accordance with the usual procedure [10]. Atomic scattering factors and Compton scattering factors were taken from the literature [11, 12]. Thus experimental structure factors and radial distribution functions were obtained.

3. Results and Discussion

The radial distribution function $D(r)$, the pair correlation function $G(r)$ and the reduced intensity function $Q \cdot i(Q)$ are defined as follows:

$$Q \cdot i(Q) = Q \cdot \left[I_{\mathrm{eu}}^{\mathrm{coh}}(Q) - \sum_i f_i(Q)^2 \right] / \sum_i f_i(Q)^2 , \quad (1)$$

$$D(r) = 4\pi r^2 \left(\sum_i \bar{K}_i \right)^2 \varrho_0 + \sum_i (\bar{K}_i)^2 (2r/\pi) \int_0^{Q_{\max}} Q \cdot i(Q) \sin(Qr)\, \mathrm{d}Q , \quad (2)$$

$$G(r) = 1 + \left[\sum_i (\bar{K}_i)^2 / \left\{ 2\pi^2 r \left(\sum_i \bar{K}_i \right)^2 \varrho_0 \right\} \right] \cdot \int_0^{Q_{\max}} Q \cdot i(Q) \sin(Qr)\, \mathrm{d}Q , \quad (3)$$

where ϱ_0 is the number of stoichiometric units per unit volume, $\bar{K}_i$ the effective electron number in the atom i [13], $f_i(Q)$ the independent atomic scattering amplitude, $I_{\mathrm{eu}}^{\mathrm{coh}}(Q)$ the total coherent intensity function and $Q_{\max}$ the maximum value of Q reached in the experiments. Summation for i is made over the stoichiometric unit. These functions were calculated with the parameters listed in Table 1; details of the analytical procedure are described in [14].

3.1. Molar Volume and X-ray Diffraction Analyses

$ErCl_3$ forms a monoclinic crystal [15]. In order to study the volume change on melting, the molar volume, V, in the crystalline state was calculated by the equation

$$V = abc \sin\beta (N_A/Z) ,$$

where a, b, c, and β are the lattice constants. N_A and Z are Avogadro's number and the number of stoichiometric units contained in the unit cell, respectively. For the lanthanide trichlorides with hexagonal structure [16] the molar volume was calculated by

$$V = (\sqrt{3}/2)\, a^2 c (N_A/Z) .$$

Table 1. Numerical parameters in the radial disribution analysis.

System	$ErCl_3$
Temperature / K	1053
Density / g cm^{-3}	3.619
Number density / Å^{-3}	0.007965
Effective electron number	
$\bar{K}_{\mathrm{Er}}$	74.0714
$\bar{K}_{\mathrm{Cl}}$	14.9762
$Q_{\max}$ / Å^{-1}	12.5

Table 2. Molar volume changes on melting.

System	T_{mp}/K	V_s/cm^3 mol^{-1}	V_m/cm^3 mol^{-1}	$100 (V_m - V_s) V_s^{-1}$/%
$LaCl_3$	1150	63.90	76.30	19.1
$PrCl_3$	1059	61.40	74.30	21.0
$NdCl_3$	1029	60.47	73.65	21.8
$SmCl_3$	935	59.23	73.73	24.5
$GdCl_3$	875	58.03	73.34	26.4
$DyCl_3$	928	74.38	74.62	0.3
$HoCl_3$	993	73.02	74.00	1.3
$ErCl_3$	1046	72.11	75.65	4.9
YCl_3	987	74.83	75.17	0.5

T_{mp}, V_s, and V_m refer to the melting point, the molar volumes of solid and melt, respectively.

The molar volume of molten $ErCl_3$ was measured and expressed as a linear function of temperature as $V_m = 59.63 + 1.562 \times 10^{-2}\, T$ with V_m and T in cm^{3}mol^{-1} and K, respectively. The molar volumes of several lanthanide trichlorides are given in Table 2.

As can be seen from Table 2, the changes on melting of the molar volume of UCl_3-type lanthanide trichlorides are very large, those of $AlCl_3$-type lanthanide trichlorides being small. Therefore, the nearest neighbour ordering in molten $ErCl_3$ appears to be similar to that in the solid state.

The $G(r)$ and $D(r)$ curves of molten $ErCl_3$ are shown in Figs. 1 and 2, respectively.

The center of the first peak in $G(r)$ appeared in the range of 2.60 Å to 2.65 Å. Considering the sum of individual ionic radii given by Shannon [17] with Er^{3+} and Cl^- being 0.89 Å and 1.81 Å, respectively, the first peak was assigned to the nearest neighbour correlation, Er^{3+}–Cl^-; the other correlations hardly contributed to this peak. The coordination number of Cl^- ion around Er^{3+} ion was estimated at 5.8 ± 0.2 by inte-

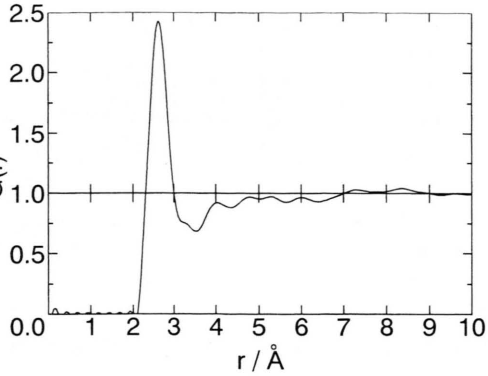

Fig. 1. Correlation function $G(r)$.

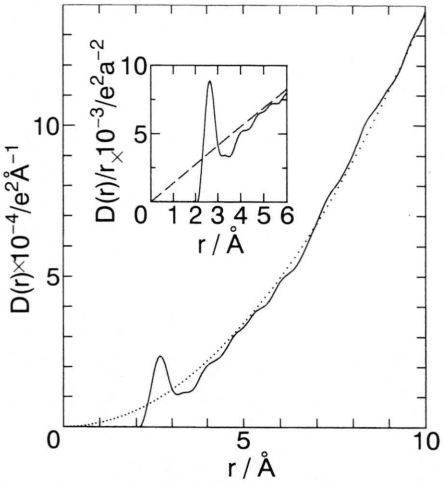

Fig. 2. Radial distribution function $D(r)$.

gration of the area under the peak of $D(r)$ shown in Figure 2. The second peak was found at 3.6–4.3 Å, being assignable to the Cl^-–Cl^- and Er^{3+}–Er^{3+} correlations. For example, the Er^{3+}–Er^{3+} distance in the solid $ErCl_3$ was estimated at 3.91 Å from crystallographical data [15] (see Table 1). Some model structure was taken into account, and the reduced intensity function, $Q \cdot i(Q)$, of the model was reversely computed from the equation

$$Q \cdot i(Q) = \left[\sum_i \sum_j n_{ij}\, f_i(Q)\, f_j(Q) \exp(-b_{ij} Q^2) \cdot \sin(Q r_{ij})/r_{ij} \right] \Big/ \sum_i f_i(Q)^2 , \quad (4)$$

where n_{ij}, r_{ij}, and b_{ij} are the coordination number, the interatomic distance, and the temperature factor for the i–j pair, respectively. The structural parameters obtained from $G(r)$ and $D(r)$ were used as the initial values of this process for their further refinement. Each parameter was optimized by a least squares calculation beyond $Q = 1.0$ Å^{-1}. The parameters of the most probable model in the $Q \cdot i(Q)$ fitting are given in Table 3. The observed and calculated $Q \cdot i(Q)$'s are shown in Figure 3. The R factor for the best fitted model, $R = \sum |Q \cdot i(Q)_{obs} - Q \cdot i(Q)_{calc}| / \sum |Q \cdot i(Q)_{obs}|$ at intervals of 0.05 Å^{-1} in the range of $1.0 \leqq Q/\text{Å}^{-1} \leqq 12.5$, converged to 0.24. From these results, the nearest neighbour distance was estimated at 2.63 Å and the coordination number of Cl^- around Er^{3+} was 5.8. Like-ion pair distances of Cl^-–Cl^- and Er^{3+}–Er^{3+} were calculated to be 3.75 Å and 4.05 Å, respectively. The ratio of r_{--}/r_{+-} was 1.43, being close to the value for octahedral geometry 1.41.

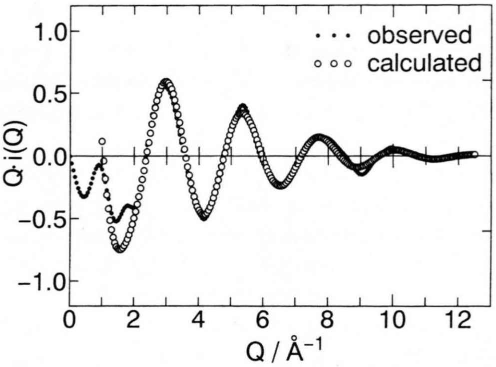

Fig. 3. Reduced intensity function $Q \cdot i(Q)$.

Table 3. Coordination number n_{ij}, interionic distance r_{ij} in crystal (averaged) [15] and melt, root mean square displacement $\langle \Delta r_{ij}^2 \rangle^{1/2}$, least squares fitted for molten $ErCl_3$, and temperature factor b_{ij} in (4).

i	j	n_{ij}	r_{ij}/Å		$\langle \Delta r_{ij}^2 \rangle^{1/2}$/Å	b_{ij}/Å^2
			Crystal	Melt		
Er^{3+}	Cl^-	5.8	2.58	2.63	0.23	0.03
Cl^-	Cl^-	8–9	3.36	3.75	0.72	0.26
Er^{3+}	Er^{3+}	1–2	3.91	4.05	0.89	0.39

3.2. Medium Range Structure

The interatomic structure, especially in the Er^{3+}–Er^{3+} correlation, was considered in terms of molar volume and obtained short range structural parameters. If Er^{3+} in $ErCl_3$ melt were distributed isotropically, the average $Er^{3+}-Er^{3+}$ pair-distance would be 5.01 Å. The corresponding distance obtained from the X-ray diffraction analyses was 4.05 Å. This indicates that, as to the $Er^{3+}-Er^{3+}$ pair, there is some specific configuration in the melt.

In order to discuss the medium range structure of the melt, the following models were taken into account: (i) edge-sharing octahedra, (ii) corner-sharing octahedra. When undistorted octahedral anions form an edge-sharing configuration, the $Er^{3+}-Er^{3+}$ pair-distance would be about 3.73 Å at most. This value is, however, smaller than that obtained by X-ray diffraction or molar volume analyses. The rigid octahedra edge-sharing model is thus not suitable for the medium range structure of molten $ErCl_3$, but a model assuming flexible octahedra with variable $Er^{3+}-Cl^-$ and Cl^--Cl^- bond lengths could be valid. This supports the suggestion by Saboungi et al. [6] that molten $ErCl_3$ may have a structure similar to YCl_3 (see Table 3). Next, a linear arrangement of octahedral ions was considered on the basis of corner-sharing. In this model, the $Er^{3+}-Er^{3+}$ pair-distance became 5.28 Å, a too large value. If the arrangement is not linear, i.e. $\angle Er^{3+}-Cl^--Er^{3+} \approx 100°$, and two octahedra were twisted with each other, this structure might exist. But corner-sharing is less probable than edge-sharing because of the steric hindrance between Cl^- ions, although corner-sharing has been expected from numerical calculations on Raman frequencies [8].

4. Conclusions

By X-ray diffraction, the existence of octahedral complex ions, $ErCl_6^{3-}$, in molten $ErCl_3$ is confirmed. Also expected is some clustering of distorted octahedra with edge-sharing.

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