X-Ray Diffraction Study on the Local Structure of Molten ErCl₃
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The short range structure of molten ErCl₃ at 1053 K was investigated by X-ray diffraction. The nearest neighbour distance of Er³⁺–Cl⁻ and the coordination number of Cl⁻ around Er³⁺ were estimated to be 2.63 Å and 5.8 Å, respectively, and the Er³⁺–Er³⁺ 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 ErCl₃⁻ octahedra exist in molten ErCl₃. Probably Er₂Cl₆⁻ and a small amount of Er₂Cl₁₀⁻ 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 UCl₃-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 AlCl₃-type crystal structure, except for YCl₃ [6]. The melting behaviour of ErCl₃ might be similar to that of YCl₃, having the same crystal structure. Recently, structural correlations in molten trivalent metal chlorides have been estimated as functions of the metal ion size for LaCl₃ and AlCl₃-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 ErCl₃ was studied by X-ray diffraction. Possible anionic pairs are discussed in view of interatomic distances and bond angles.

2. Experimental

ErCl₃ was prepared by heating a mixture of analytical grade Er₂O₃ and 2.5 times the theoretical amount of NH₄Cl at 623 K for 3 h. Excess NH₄Cl was removed by heating at 1173 K. The chlorination reaction is

Er₂O₃ + 6 NH₄Cl → 2 ErCl₃ + 6 NH₃ + 3 H₂O.

ErCl₃ thus obtained was purified by ErCl₃ 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 NH₄Cl 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 θ–θ 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 Å⁻¹ ≤ Q ≤ 12.5 Å⁻¹, was explored with two pairs of slits [1/2⁻–1/2⁺] when 2.5° ≤ θ ≤ 15°, and [1⁻–1⁺] when 13° ≤ θ ≤ 45° (2θ = scattering angle and Q = 4π sin θ/λ with λ being the...
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:

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

$$D(r) = 4\pi r^2 \left( \sum_i K_i \right)^2 q_0^2 + \sum_i K_i^2 (2r/\pi) \int_0^{q_{\text{max}}} Q \cdot i(Q) \sin(Qr) dQ, \quad (2)$$

$$G(r) = 1 + \left[ \frac{\sum_i K_i^2}{2\pi^2 r \left( \sum_i K_i \right)^2 q_0^2} \right] \int_0^{q_{\text{max}}} Q \cdot i(Q) \sin(Qr) dQ, \quad (3)$$

where $q_0$ is the number of stoichiometric units per unit volume, $K_i$ the effective electron number in the atom $i$ [13], $f_i(Q)$ the independent atomic scattering amplitude, $I_{\text{coh}}(Q)$ the total coherent intensity function and $q_{\text{max}}$ 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 $\beta$ are the lattice constants. $N_A$ and $Z$ are Avogadro's number and the number of stoichiometric units contained in the unit cell, respectively.

<table>
<thead>
<tr>
<th>System</th>
<th>$T_{\text{mp}}/K$</th>
<th>$V_m/\text{cm}^3\text{mol}^{-1}$</th>
<th>$V_s/\text{cm}^3\text{mol}^{-1}$</th>
<th>$100 (V_m - V_s)/V_s%$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaCl$_3$</td>
<td>1150</td>
<td>63.90</td>
<td>76.30</td>
<td>19.1</td>
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<tr>
<td>PrCl$_3$</td>
<td>1059</td>
<td>61.40</td>
<td>74.30</td>
<td>21.0</td>
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<tr>
<td>NdCl$_3$</td>
<td>1029</td>
<td>60.47</td>
<td>73.65</td>
<td>21.8</td>
</tr>
<tr>
<td>SmCl$_3$</td>
<td>935</td>
<td>59.23</td>
<td>73.73</td>
<td>24.5</td>
</tr>
<tr>
<td>GdCl$_3$</td>
<td>875</td>
<td>58.03</td>
<td>73.34</td>
<td>26.4</td>
</tr>
<tr>
<td>DyCl$_3$</td>
<td>928</td>
<td>74.38</td>
<td>74.62</td>
<td>0.3</td>
</tr>
<tr>
<td>HoCl$_3$</td>
<td>993</td>
<td>73.02</td>
<td>74.00</td>
<td>1.3</td>
</tr>
<tr>
<td>ErCl$_3$</td>
<td>1046</td>
<td>72.11</td>
<td>75.65</td>
<td>4.9</td>
</tr>
<tr>
<td>YCl$_3$</td>
<td>987</td>
<td>74.83</td>
<td>75.17</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Table 1. Numerical parameters in the radial distribution analysis.

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

For the lanthanide trichlorides with hexagonal structure [16] the molar volume was calculated by

$$V = (1/3/2) a^2 c (N_A/Z).$$

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 $D(r)$.

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).

<table>
<thead>
<tr>
<th>$i$</th>
<th>$j$</th>
<th>$n_{ij}$</th>
<th>$r_{ij}$/Å</th>
<th>$\langle \Delta r_{ij}^{2} \rangle^{1/2}$/Å</th>
<th>$b_{ij}$/Å$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Er$^{3+}$</td>
<td>Cl$^-$</td>
<td>5.8</td>
<td>2.58</td>
<td>2.63</td>
<td>0.23</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>Cl$^-$</td>
<td>8-9</td>
<td>3.36</td>
<td>3.75</td>
<td>0.72</td>
</tr>
<tr>
<td>Er$^{3+}$</td>
<td>Er$^{3+}$</td>
<td>1-2</td>
<td>3.91</td>
<td>4.05</td>
<td>0.89</td>
</tr>
</tbody>
</table>

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 ≤ $Q$/Å$^{-1}$ ≤ 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.

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 $\text{Er}^{3+} - \text{Er}^{3+}$ 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 $\text{Er}^{3+} - \text{Er}^{3+}$ 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 $\text{Er}^{3+} - \text{Er}^{3+}$ 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 $\text{Er}^{3+} - \text{Cl}^-$ and $\text{Cl}^- - \text{Cl}^-$ 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 $\text{Er}^{3+} - \text{Er}^{3+}$ pair-distance became 5.28 Å, a too large value. If the arrangement is not linear, i.e. $\angle \text{Er}^{3+} - \text{Cl}^- - \text{Er}^{3+} \approx 100^\circ$, 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$_6^{2-}$, in molten ErCl$_3$ is confirmed. Also expected is some clustering of distorted octahedra with edge-sharing.

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