X-ray Diffraction Analysis of $NdCl_3$ Melt

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The structure of molten $NdCl_3$ at 800 °C has been investigated by X-ray scattering and the correlation method. The nearest neighbor distance and coordination number of Nd–Cl are 2.77 Å and 5.5 Å, respectively. The Nd–Nd and Cl–Cl distances are 5.08 and 4.04 Å, respectively. The average nearest neighbor distance and coordination number decrease markedly on melting, and the resulting short range structure of the melt is approximately octahedral.

Introduction

The structure of many molten alkali and alkaline earth metal chlorides has been investigated by X-ray and neutron diffraction [1, 2] and by computer simulations [3–7], however, as to trivalent cations, only molten $AlCl_3$ [8] and InI_3 [9] have been analyzed by X-ray diffraction. They were found to be molecular liquids comprising A_2X_6 molecules. Recently Saboungi et al. [10] have carried out molecular dynamics simulations of molten AX_3. They reported a drastical change of the first coordination number on varying the diameter ratio of the ions.

Rare earth chlorides AX_3 form clear, low-viscosity liquids. We have already measured the physico-chemical properties of some rare earth chloride melts [11].

In the present study, we report the short range structure of molten $NdCl_3$ analyzed by X-ray diffraction.

Experimental

$NdCl_3$ was synthesized by heating at 350 °C a stoichiometric mixture of reagent grade Nd_2O_3 and NH_4Cl according to the reaction

$$Nd_2O_3 + 6\,NH_4Cl \rightarrow 2\,NdCl_3 + 6\,NH_3 + 3\,H_2O.$$

The $NdCl_3$ so obtained was purified by sublimation at about 950 °C under a reduced pressure for 8 hours. This procedure is very useful to remove impurities such as oxides, NH_4Cl, and water [12].

For X-ray scattering studies of melts, Takagi et al. [13, 14] sealed molten $CoCl_2$ and $CdCl_2$ in a fused silica tube to avoid oxidation of these hygroscopic salts when melted in air. Although the quartz tube lowers the intensity of both the incident and diffracted X-ray beam, it is very useful because a clean and stable melt surface is held. Since the $NdCl_3$ is also very hygroscopic, the same method was employed by us. The wall of the quartz cell was less than 1 mm in thickness, which decreased the intensity of the transmitted X-ray beam by about one tenth.

We used a $\theta-\theta$ X-ray diffractometer with a curved graphite plate mounted in the diffraction beam. Fixed counts were taken at every interval of 0.25°. The observable range of the scattering angle (θ) was $3° \leqq \theta \leqq 45°$, corresponding to the range

$$0.93 \leqq S \leqq 12.5\ \text{Å}^{-1} \qquad (S = 4\pi \sin\theta/\lambda,\ \lambda = 0.7107\ \text{Å})$$

for MoKα radiation. Silt systems of 1/2–1/2° and 1–1° types were employed in the low-angle ($3° \leqq \theta \leqq 15°$) and high-angle ($13° \leqq \theta \leqq 45°$) regions. The temperature of the melt was controlled to within 800 ± 10 °C throughout the experiments. The intensity data, corrected for background, polarization, absorption and Compton radiation, were normalized to the independent scattering factor for the stoichiometric unit according to the usual method [15].

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The radial distribution function $D(r)$, the correlation function $G(r)$, and the reduced intensity $S \cdot i(S)$ are given by the expressions

$$D(r) = 4\pi r^2 \sum_m \bar{K}_m g_m(r) \tag{1}$$

$$= 4\pi r^2 g_0 + \sum_m (\bar{K}_m)^2 \, 2r/\pi \int_0^{S_{\max}} S \cdot i(S) \sin(Sr) \, \mathrm{d}S,$$

$$G(r) = 1 + \sum_m (\bar{K}_m)^2/(2\pi^2 g_0 r) \int_0^{S_{\max}} S \cdot i(S) \sin(Sr) \, \mathrm{d}S, \tag{2}$$

$$S \cdot i(S) = S\left[I_{\mathrm{eu}}^{\mathrm{coh}}(S)/\sum_m f_m^2(S) - 1\right] \tag{3}$$

and

$$g_0 = \left(\sum_m \bar{K}_m\right)^2 \varrho_0, \tag{4}$$

where ϱ_0 is the number of stoichiometric units per unit volume, $\bar{K}_m$ the effective number of electrons in the atom m, g_m the effective electron density at a distance r, g_0 the average electron density, $f_m(S)$ the independent atomic scattering intensity, $I_{\mathrm{eu}}^{\mathrm{coh}}(S)$ the total coherent intensity function, and $S_{\max}$ the maximum value of S reached in the experiments. Summation is over the stoichiometric unit for m. The density was taken from [11 a]. The values of $\bar{K}_{\mathrm{Nd}}$ and $\bar{K}_{\mathrm{Cl}}$ used in the calculation of the r.d.f. were 61.4892 and 16.5036, respectively, the value of ϱ_0 being 0.00818 Å^{-3}.

Results and Discussion

Figures 1 and 2 show the observed total coherent intensity $I_{\mathrm{eu}}^{\mathrm{coh}}(S)$ and the reduced intensity $S \cdot i(S)$ curves of molten $NdCl_3$ at 800 °C, respectively. The r.d.f. $D(r)$ and function $D(r)/r$, and the correlation function $G(r)$ are shown in Figs. 3 and 4, respectively. The numerical values of $S \cdot i(S)$ and $G(r)$ can be obtained from Dr. Igarashi on request. Peaks in $G(r)$ curve are observed at $r = 2.75$, 4.95, and 8.20 Å and a shoulder is also observed at $r = 4.35-4.60$ Å. The first peak evidently corresponds to the nearest neighbor $Nd^{3+}-Cl^-$ interaction because the distance is almost the same as the sum, 2.793 Å, of ionic radii of Nd^{3+} (0.983 Å) and Cl^- (1.81 Å) [16]. The coordination number of chloride ions around a neodymium ion was calculated to be 5.6 from the function $D(r)/r$, assuming a Gaussian distribution. As seen in Fig. 4, the first peak in the $G(r)$ curve is sharp and the first minimum is relatively deep. In general, such a characteristic in $G(r)$ has been observed when the penetration of the second coordination shell into the first one is small [17].

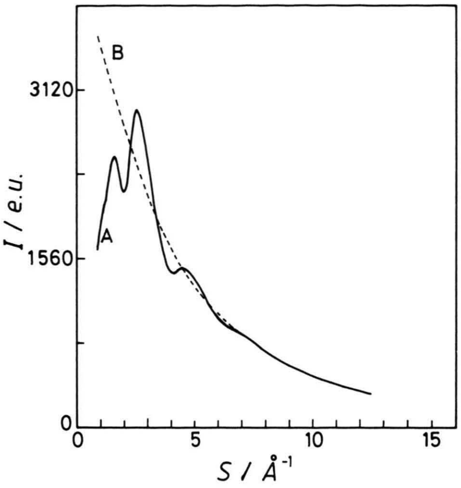

Fig. 1. Observed coherent intensity I_{eu} (A) and independent scattering (B) curves of molten $NdCl_3$ at 800 °C.

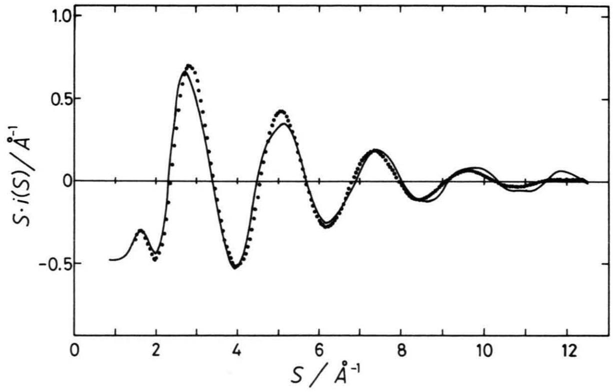

Fig. 2. Reduced intensity $S \cdot i(S)$ curve of molten $NdCl_3$. Solid line: observed, points: calculated.

It is difficult in the present study to determine the structure in further detail from the $D(r)$ and $G(r)$ curves. The strucutral analysis for near-neighbor interactions can be made by the correlation method. The reduced intensity function $S \cdot i(S)$ for near-neighbor interactions can be expressed by

$$S \cdot i(S) = \left[\sum_i^m \sum_j n_{ij} f_i(S) f_j(S) \exp(-b_{ij} S^2) \cdot \sin(S r_{ij})/r_{ij}\right] \Big/ \sum_i f_i^2(S), \tag{5}$$

where n_{ij}, r_{ij}, and b_{ij} are the average coordination number, average distance, and temperature factor, re-

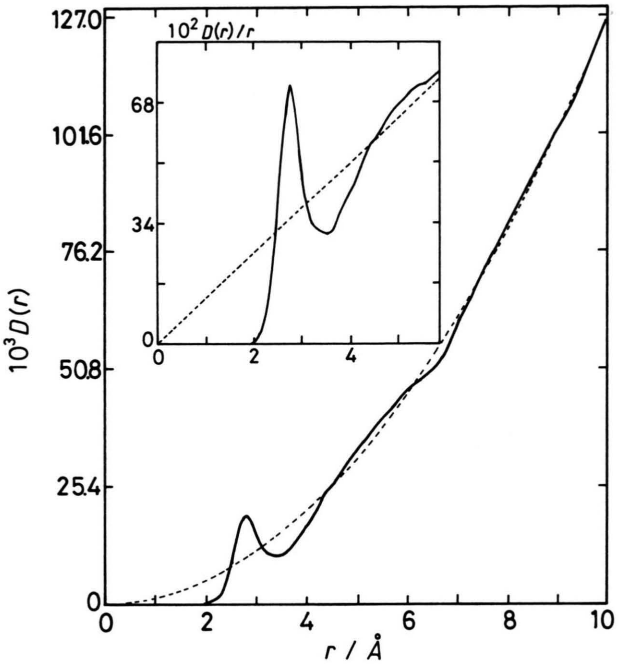

Fig. 3. Radial distribution function $D(r)$ and function $D(r)/r$ of molten $NdCl_3$.

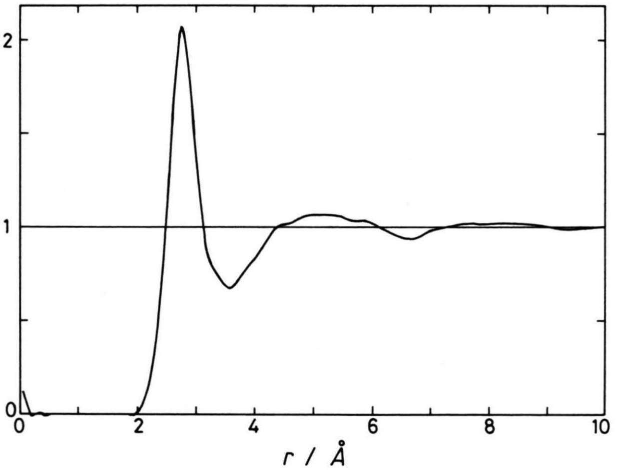

Fig. 4. Correlation function $G(r)$ of molten $NdCl_3$.

Table 1. Coordination numbers n_{ij}, nearest-neighbor distances r_{ij}, and mean square-root displacements $\langle \Delta r_{ij}^2 \rangle^{1/2}$ of molten $NdCl_3$ at 800 °C.

i	j	n_{ij}	$r_{ij}/\text{Å}$	$\langle \Delta r_{ij}^2 \rangle^{1/2}$
Nd	Cl	5.5	2.77	0.241
Cl	Cl	11.3	4.04	0.490
Nd	Nd	4.8	5.08	0.606

spectively. In this work, the three nearest-neighbor ion pairs Nd^{3+}–Cl^-, Nd^{3+}–Nd^{3+}, and Cl^-–Cl^- were assumed to be Gaussian distributed, centered at r_{ij} with a mean-square displacement $2b_{ij}$. The quantities n_{ij}, r_{ij}, and b_{ij} for these interactions can be obtained by a least-squares fitting of the variations in (5) against the observed intensity function $S \cdot i(S)$. In the first step, the values for the variations of the unlike-ion pair were determined using the observed $S \cdot i(S)$ values in the range 6.5 to 12.5 Å^{-1}, because the contributions from the like-ion pairs would tend to zero in this range. In the calculation, initial values for the variations of this pair were taken to be the same as those acquired in the analysis of the $D(r)$ and $G(r)$ curves. In the next step, the values obtained for the unlike-ion pair were fixed and the values of the variations for the like-ion pairs were calculated using the $S \cdot i(S)$ values in the range 2.0 to 6.5 Å^{-1}. For the initial values of like-ion pairs we made the following assumptions: Because in this compound the X-ray scattering intensity of the Nd atom is quite large compared to that of the Cl atom, the second peak position at 4.95 Å in the $G(r)$ curve may correspond to the distance of the Nd^{3+}–Nd^{3+} pair, and the distance of the Cl^-–Cl^- pair is 1.41 times that of Nd^{3+}–Cl^- pair because the first coordination number is about six. Finally, all parameters so obtained were refined again using the $S \cdot i(S)$ values beyond $S = 2.0\ \text{Å}^{-1}$. In order to check the goodness of the fit, the quantity

$$R = \sum |S \cdot i(S)_{\text{obs}} - S \cdot i(S)_{\text{calc}}| / \sum |S \cdot i(S)_{\text{obs}}| \quad (6)$$

was introduced. The parameters of the most probable arrangement in the molten $NdCl_3$ are listed in Table 1. The R value was 0.216 when the computation converged. The reduced intensity $S \cdot i(S)$ calculated using these parameters is also given in Fig. 2 by points.

As shown in Table 1, the Nd^{3+} ion is surrounded by 5.5 Cl^- ions centered at 2.77 Å, and the distance of Cl^-–Cl^- ion pair is 4.04 Å. The ratio of $r_{\text{Cl-Cl}}$ to $r_{\text{Nd-Cl}}$ is 1.46, which is close to 1.41, the value for an octahedral arrangement. Therefore, these results suggest that the short range structure of molten $NdCl_3$ is roughly octahedral.

The crystal structure of solid $NdCl_3$ is hexagonal dipyramidal and belongs to the space group $P6_3/m$ [18]. In this structure, the Nd^{3+} ion is surrounded by three chloride ions on the same plane as the metal ion at the distance 2.923 Å and by two sets of three chloride ions above and below the metal ion at the distance 2.886 Å, i.e., by nine chloride ions at an average distance of 2.898 Å. We have suggested in [11a] that, since for $NdCl_3$ the volume increase on melting is as large as 21.8%, the nearest ionic distances and the number of ions in the first coordination shell decreases significantly on fusion, similar to the alkali halides [19]. Evidently the present study confirms both decreases. On the other hand, the Nd^{3+}–Nd^{3+} distance was observed to increase slightly on melting.

The crystal structures of the rare earth chlorides from $LaCl_3$ to $GdCl_3$ are the same as that of $NdCl_3$ [20] and these chlorides also show the large volume increase on melting [11a]. Therefore the short range structure of these chlorides in the molten state is expected to be octahedral as that of $NdCl_3$.

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