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Short-range structure of molten $CeCl_3$ and $NdCl_3$ determined by XAFS

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Abstract

The local structures of molten $CeCl_3$ and $NdCl_3$ have been investigated by XAFS at SPring-8 with the K-absorption edges of Ce and Nd. The nearest-neighbour Ln^{3+}–Cl^- distances and coordination numbers, $\bar{n}_{Ln}^{Cl}$, are found to be 2.81 Å and 6.52 for $CeCl_3$, and 2.73 Å and 6.96 for $NdCl_3$, respectively. The coordination numbers are >6, implying thereby that the local structures around the lighter lanthanide ions are not exactly octahedral, but somewhat distorted. The XAFS technique using the 3rd generation X-ray sources is a powerful tool to elucidate the local structure around the lanthanide ions in the light rare earth compounds.

Keywords: Disordered systems; EXAFS; Cerium chloride; Neodymium chloride; Short-range structure

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1. Introduction

Rare earth elements have several specific physico-chemical properties, which are commercially useful in functional material synthesis, magnetic alloys, optical fibres, halogen lamps, etc. Among the rare earth compounds, the rare earth halides have been utilised for a variety of technical applications. However, their physico-chemical properties, especially, at high temperatures, have still not been explored systematically. Although there are heavy demands to carry out computer modeling for material synthesis and chemical engineering applications, no generic potential model of molten rare earth halides is yet available. This is mainly due to the lack of a physico-chemical properties database and relevant structural information.

The trivalent rare earth cations over the whole series of rare earth elements have been considered to be coordinated by six chlorides in the molten state, as was concluded by the earlier Raman spectroscopy [1,2] and X-ray diffraction studies [3]. Recently, some other approaches, such as neutron diffraction and molecular dynamics simulations, have been used to elucidate their structure. These studies, in contradiction to the earlier works, reveal that the lighter rare earth ions are coordinated by more than six chlorides [4–7]. To resolve these contradictions, we have performed extended X-ray absorption fine structure (EXAFS) experiments that allow us to investigate the local structure only around the X-ray absorption atom. This information is quite useful not only to refine the inter-ionic potentials used in molecular dynamics simulations [8], but also for practical applications, such as the pyrochemical treatment of spent nuclear fuels in the nuclear engineering field [9].

2. Experimental

Anhydrous chloride compounds (AAPL Japan, 4N) were sealed in specially designed funnel-shaped quartz cells, which were similar to those used in [10] under vacuum. The quartz-sealed samples were installed into a newly designed electric furnace (Rigaku Co.) with a thermal homogeneity

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and stability much better than those of the prototype used previously [11]. The temperature was elevated from room temperature (RT) to 1173 or 1123 K above the melting points of pure $CeCl_3$ and $NdCl_3$, respectively. The furnace was kept in the best orientation in order to obtain the highest possible resolution in the EXAFS oscillations.

Transmission extended X-ray absorption fine structure measurements on pure $CeCl_3$ and $NdCl_3$ were performed at BL01B1 and BL19B2 beamlines at SPring-8 (Japan), both in the molten state and at the room temperature by using Ln–K X-ray absorption edges, i.e., 40.45 keV Ce for and 43.57 keV for Nd. A white X-ray beam from a bending magnet source was monochromatised by Si(3 1 1) double crystals, and purified by two Rh-coated Si mirrors to avoid any interference from highly ordered reflection X-rays. The SPring-8 storage ring was operated at 8 GeV and 100 mA for the duration of all the measurements. This helped us to accumulate high resolution XAFS data even under high temperature conditions. The intensities of the incident (I_0) and transmitted (I) X-rays were detected by using ionisation chambers filled with Kr + Ar (1:3) and Kr, respectively. For energy calibration, Ln–K-edges of LnF_3 were used.

XAFS data were analysed by using the WinXAS Version 2.3 software [12]. Background subtraction and normalisation were performed by fitting the modified Victoreen equation to the pre-edge region and the linear polynomial to the post-edge region. Ln–K-absorption threshold was decided from the first root in the second derivative of the near-edge region. XAFS oscillation, $\chi(k)$, was obtained by removing the atomic background smoothly by using a cubic spline method. The radial structure function, $\mathrm{FT}|\chi(k)k^3|$, was obtained by Fourier transforming the k^3 weighted $\chi(k)$ function multiplied by a Bessel window function. The range of wave numbers used in the Fourier transformation was $2 < k$ (Å^{-1}) < 12 for the solids, and $2 < k$ (Å^{-1}) < 8 for the melts. The curve-fitting involved the nonlinear least-square fits on the predominant Ln^{3+}–Cl^- 1st neighbour correlation peak in R-space by using backscattering factors evaluated by FEFF 8.0 code [13]. At high temperatures, the 3rd and 4th cumulants were used as fitting parameters to include the anharmonic oscillations. The most reasonable coordination number of chloride ions around a lanthanum ion was chosen on the basis of the inter-ionic distance and the sum of effective ionic radii [14].

3. Results and discussions

The extracted XAFS oscillations and their Fourier transformed structure functions for pure $CeCl_3$ and $NdCl_3$ in both the solid and liquid phases are depicted in Figs. 1(a and b) and 2(a and b), respectively. As reported previously [10], the phase shifts in the EXAFS spectra on melting $LnCl_3$ were observed, and the predominant peaks corresponding to the first Ln–Cl coordination shell were shifted to shorter distances upon melting. Table 1 shows the structural parameters obtained from the curve-fitting procedure. Figs. 1(c) and 2(c) demonstrated the agreements between the experimental and fitted $\mathrm{FT}|\chi(k)k^3|$ curves in R-space.

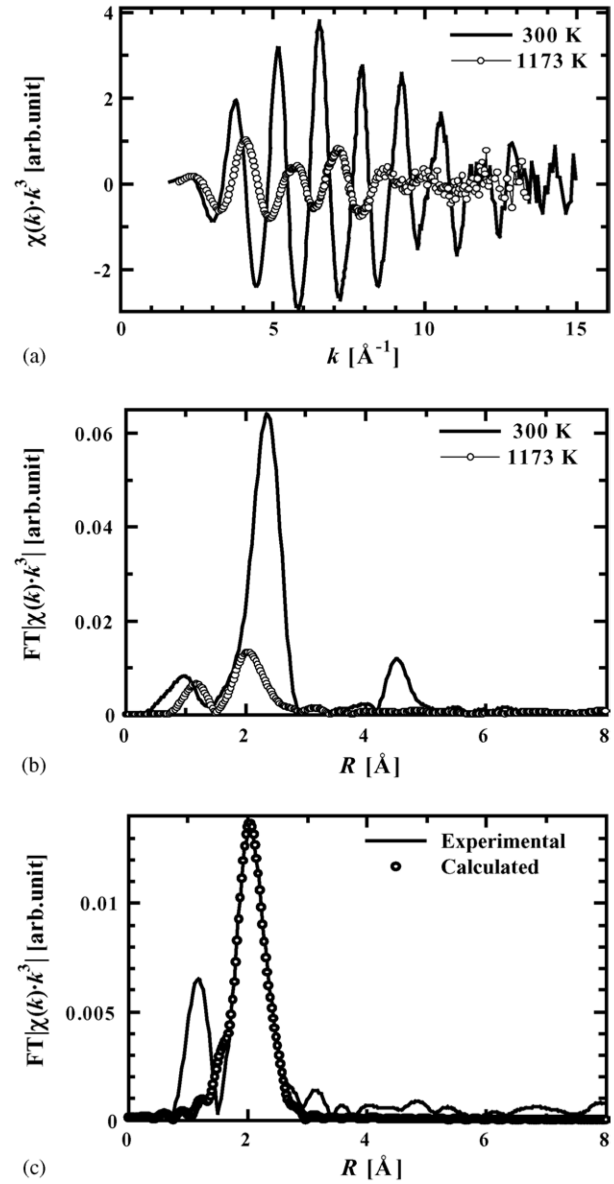

Fig. 1. (a) EXAFS oscillations $\chi(k)k^3$; (b) radial structure functions (RSFs) $\mathrm{FT}|\chi(k)k^3|$ at 300 and 1173 K; (c) experimental vs. fitted RSFs at 1173 K, for $CeCl_3$.

In the previous XAFS experiments on $LaCl_3$ [9], we mixed the salts with BN matrix powder to prepare pellets, which kept the molten salts in a homogeneous dispersed state. Although conscientious efforts were made to follow all the experimental procedures and useful information obtained for future studies, the inter-ionic distance in the liquid phase was rather underestimated in comparison with the value derived from diffraction techniques [3–5] and the other XAFS study [10]. In the present work, our newly designed quartz cells were well adapted to obtain highly resolved spectra. We, thus, believe that the structural parameters obtained here are

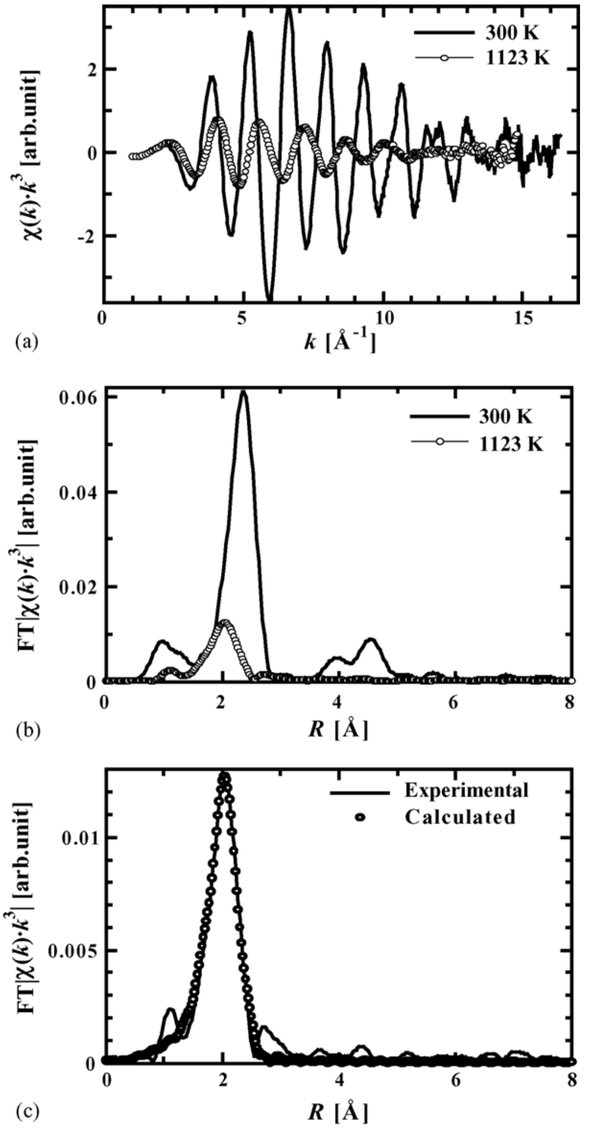

Fig. 2. (a) EXAFS oscillations $\chi(k)k^3$; (b) radial structure functions (RSFs) FT$|\chi(k)k^3|$ at 300 and 1123 K; (c) experimental vs. fitted RSFs at 1123 K, for $NdCl_3$.

much more reasonable. Additionally, the high energy X-rays derived from the 3rd generation synchrotron radiation sources made it possible to obtain the data over a wider k range using Ln–K-absorption edges, which had no short gap between L_{III} and L_{II} edge energies, and “ghost hump” arising from the multiple-electron excitations.

Table 1 also shows a typical tendency of decreasing inter-ionic (Ln^{3+}–Cl^-) distances and coordination numbers, $\overline{n}_{\mathrm{Ln}}^{\mathrm{Cl}}$, of chloride ions around a lanthanide cation upon melting, and this trend has already been known in diffraction studies [3]. As corrections for the phase shift and anharmonic oscillations in the high temperature spectra were incorporated in the data analyses, the above trend is thought to be a real feature in these compounds. The inter-ionic distances of Ce–Cl and Nd–Cl were consistent with that obtained for La–Cl (2.89 Å) [10]. With increasing in the atomic number of the lanthanide element, the inter-ionic distance Ln–Cl decreased in the molten state, reflecting probably the well-known “lanthanide contraction”.

The structural parameters listed in Table 1 might raise another argument on chlorine coordination numbers. The local structure of molten $CeCl_3$ and $NdCl_3$ obtained by X-ray diffraction [3] suggested that the 1st neighbour coordination numbers of chlorine around Ce and Nd are: 5.6 at 2.84 Å and 5.7 at 2.77 Å, respectively. Although our results on the inter-ionic distances are slightly underestimated, the coordination numbers are clearly larger than those obtained by X-ray diffraction. This is presumably because the spectra analysed by using stronger damping factors create larger uncertainties in the coordination numbers, while this procedure helps in smoothing the diffraction data. The light rare earth ions are surrounded by more than six chlorides in pure molten chlorides as suggested by the recent neutron diffraction isomorphic substitution experiments on molten $LaCl_3$ [4,5]. Also, the molecular dynamics simulations with polarisable ion model have been found recently to satisfactorily reproduce the experimental diffraction pattern obtained without using any damping factor; the results showing a coordination number >6 in the liquid phase [6,7]. Our results support these recent findings. Of course, only one technique is not sufficient to obtain authentic information on the structural parameters of a compound. It would be appropriate if all the experimentally extracted structural information were combined with molecular dynamics calculations. However, in the meantime, it is also essential that the experimental data were re-measured and/or re-analysed for complementary utilisation of experimental and modeling techniques.

Table 1
The nearest-neighbour Ln–Cl (Ln = Nd, Ce) structural parameters obtained by the curve-fitting procedure (intrinsic X-ray excitation probability, S_0^2, is fixed to 1.0)

T (K)	N_{CeCl}	R_{CeCl} (Å)	σ^2 (10^{-2} Å^2)	C_3 (10^{-3} Å^3)	C_4 (10^{-4} Å^4)	Residual (%)
$CeCl_3$ (beamline: BL01B1)						
300	9.34 ± 0.02	2.90 ± 0.00	0.98 ± 0.01	0.0 (fix)	0.0 (fix)	5.49
1173	6.52 ± 0.09	2.81 ± 0.01	2.98 ± 0.02	2.00 ± 0.01	2.99 ± 0.04	6.98

T (K)	N_{NdCl}	R_{NdCl} (Å)	σ^2 (10^{-2} Å^2)	C_3 (10^{-3} Å^3)	C_4 (10^{-4} Å^4)	Residual (%)
$NdCl_3$ (beamline: BL19B2)						
300	9.85 ± 0.01	2.87 ± 0.00	0.97 ± 0.03	0.0 (fix)	0.0 (fix)	5.00
1123	6.96 ± 0.23	2.73 ± 0.01	3.01 ± 0.02	1.10 ± 0.01	2.89 ± 0.04	7.45

4. Conclusions

The nearest-neighbour structural information on Ce–Cl and Nd–Cl correlations in molten $CeCl_3$ and $NdCl_3$ has been obtained by using the XAFS technique. The results suggest that both Ce and Nd are surrounded by more than six chlorides, a conclusion that is in close agreement with that obtained from recent neutron diffraction isomorphic substitution studies as well as from the molecular dynamics simulations with a polarisable ion model. In molten light rare earth chlorides, octahedral geometry appears to be somewhat distorted. Although, much improvement is still needed in the data analysis of XAFS spectra, this technique is a promising tool for elucidating the local structure around focused elements.

Acknowledgments

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