

## Phase transitions in rare earth chlorides observed by XAFS

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XAFS spectroscopy has increasingly been utilised to elucidate the nearest-neighbour structure in the condensed phases. In this paper, the XAFS spectra of NdCl<sub>3</sub> and DyCl<sub>3</sub> in both the solid and the liquid phases measured at the Nd and Dy LIII absorption edges on beam line BM29 of the European Synchrotron Radiation Facility (ESRF) are presented. The Fourier transformed radial structure functions,  $\phi(r)$  show that the prominent peaks corresponding to M-Cl (M: Nd or Dy) first shell contribution are shifted to shorter distances in the liquid melts as compared to those found in the corresponding solids. Similar behaviour has also been observed from other diffraction techniques in typical ionic melts such as NaCl. From the temperature dependence of the radial structure functions it is clear that the change in the M-Cl distance on melting is much larger in NdCl<sub>3</sub> than that in DyCl<sub>3</sub>.

Keywords: EXAFS; neodymium chloride; dysprosium chloride; phase transition; short-range order.

### 1. Introduction

The purpose of this study is to investigate the phase transitions in rare-earth chlorides (NdCl<sub>3</sub> and DyCl<sub>3</sub>) by using EXAFS analysis. It has been demonstrated in the past decade that the structure and properties of rare-earth trichlorides can be categorized into two groups. One of the groups contains La to Gd, the light rare-earth elements, and the other contains heavy rare-earth elements such as Dy to Lu and Y. The most striking difference between these two categories is in their crystal structures. The crystal structure of light rare-earth chlorides is UCl<sub>3</sub>-type in which one metallic element is surrounded by 3 chlorides triangularly and 6 chlorides at the corners of a hexagonal prism, resulting in a 9-fold coordination. The crystal structure of heavy rare-earth chlorides, by contrast, is AlCl<sub>3</sub> type in which one metallic element is coordinated by 6 chlorides octahedrally.

The table of the macroscopic properties compiled by Akdeniz and Tosi (1992) serves to strengthen the claim that there exist two categories even in molten rare-earth trichlorides. During the phase transition from solid to liquid, the molar volume of a typical light rare-earth chloride decreases by as much as 20% while that of a

heavy rare-earth chloride does not change so much ca. 0~5%. Also, the entropy change on melting of a light rare-earth chloride is larger than that of a heavy rare-earth chloride.

It has been suggested that the macroscopic behaviour during phase transition could be explained in terms of structural information obtained from experimental techniques such as X-ray diffraction (XRD), neutron diffraction (ND) and molecular dynamics (MD) simulations. Iwate et al. (1995) obtained the nearest-neighbour distances and coordination numbers of several ion pairs by a model fitting of the XRD structure factors. From these studies, they suggested that each rare-earth cation is coordinated to 6 chloride ions in the melt. They further suggested that the local octahedral units, MCl<sub>6</sub><sup>3-</sup> are linked to each other through apexes in light rare-earth chloride melts, while they share edges in heavy rare-earth chloride melts.

By ND experiments on isotopically enriched samples of DyCl<sub>3</sub>, Adya et al. (1998) extracted the three *partial structure factors*,  $S_{Dy-Cl}(Q)$ ,  $S_{Dy-Dy}(Q)$  and  $S_{Cl-Cl}(Q)$  for the first time in a trivalent metal halide melt. These experimental partial structure factors were compared with those obtained from the MD simulations performed by using both polarizable ion model (PIM) proposed by Wilson and Madden (1993) and rigid ion model (RIM) (Takagi et al., 1999). It was concluded that *i*) each Dy<sup>3+</sup> is surrounded by 6 chlorides octahedrally, *ii*) both edge- and apex-sharing octahedra exist in the melt, and *iii*) the Dy-Dy partial pair distribution function is well reproduced by the PIM rather than by the RIM. An isomorphic substitution technique on LaCl<sub>3</sub> and CeCl<sub>3</sub> samples was used in order to obtain some partial distribution functions (Wasse and Salmon, 1999). The total structure factors of several rare earth chlorides were calculated by using the PIM (Hutchinson et al., 1999). All these investigations revealed that while a light rare-earth cation (*e.g.*, La<sup>3+</sup>) is surrounded by more than 6 chlorides, each heavy rare-earth cation is coordinated to nearly 6 chlorides.

Contrasting observations have also been reported for the phase transitions occurring under the melting point for other halide compounds. For instance, the melting points of EuCl<sub>2</sub> reported so far by different workers differ by as much as 150 K. From the DSC measurements, Koyama et al. (1997) observed two phase transitions at 1123.9 K and 1016.8 K in EuCl<sub>2</sub>. Assisted by the signals from their Raman spectra, they conjectured the lower value to be the melting point of the compound. However, these results are still in dispute by other workers. Salmon and Adya et al. (2000) used the neutron powder diffraction technique to study the solid-solid phase transitions in ScCl<sub>3</sub> which were never observed before.

Although the diffraction techniques have the added advantage of revealing the long-range order, there seem to be conflicting conclusions on structural information obtained from X-rays and neutrons. To resolve these discrepancies, we feel that it is not enough to discuss the structure of rare-earth chlorides in terms of the results derived only from the diffraction techniques. Extended X-ray absorption fine structure (EXAFS) method can help resolve the above matters by providing useful additional information on the structure, especially the short-range order in rare-earth chlorides. This technique has been applied in the past to several halides, such as KBr (A. Di Cicco et al. 1996), RbBr and CuBr (A. Di Cicco et al. 1997).

## 2. Experimental

### 1) Sample preparation

NdCl<sub>3</sub> was synthesized by chlorination reaction from its oxide (Ohashi et al. 1999). DyCl<sub>3</sub> was used as reagent grade without any further treatment. The samples were ground inside a glove box into powder form with particle diameter less than several  $\mu\text{m}$ . The powdered samples were mixed homogeneously with matrix material such as boron nitride or graphite powder. The mixture ratio of the sample and the matrix (15 mg : 120 mg) was calculated by using X-ray absorption coefficient. The mixed powder was pressed into a pellet of thickness  $\sim 1$  mm. The pellet was broken into 2 half-moons to reduce the size to fit into the groove of a folded graphite sheet, which acted as a furnace element. A thermocouple was sandwiched between the two half-moons placed inside the graphite sheet. The furnace equipment has already been discussed in detail (Filipponi and Di Cicco 1994). The sample environment was evacuated during measurements by using a turbo molecular pump.

### 2) Data collection

The synchrotron radiation X-rays on beam line BM29 at the European Synchrotron Radiation Facility (ESRF) in Grenoble (France) were used to record the XAFS spectra. Since the LIII absorption edge energy of Nd and Dy are 6.214 keV and 7.793 keV, respectively, detuned Si(111) flat double monochromator system was chosen in order to remove parasitic reflection. The acquisition time per point was 1 second. The energy range of data collection for Nd and Dy samples were from 6.128 to 6.708 keV and from 7.71 to 8.54 keV, respectively. The temperature was controlled by changing the voltage applied between the ends of the graphite sheet. The temperature was increased step by step, and it was kept fixed and maintained for at least half an hour for attaining thermal equilibrium before data collection.

## 3. Results and Discussion

The EXAFS spectra of NdCl<sub>3</sub> at 293 K and 1073 K and those of DyCl<sub>3</sub> at 293 K and 1036 K were obtained by removing the background intensity estimated by using modified Victoreen equation, and normalized by McMaster coefficients. The EXAFS function,  $\chi(k)$  was extracted by the following procedure:  $\mu_0$  was estimated by divided cubic spline method. Absorption energy,  $E_0$  was determined from the point of inflection on the absorption jump.  $k^3$  weighted  $\chi(k)$  of NdCl<sub>3</sub> and DyCl<sub>3</sub> in both the solid and liquid phases are shown in Figs. 1 (a) and (b), respectively. As can be seen, the phase of the EXAFS function for both the salts in the molten state is clearly shifted as compared to that in the corresponding solid state.

The radial structure functions,  $\phi(r)$  were obtained by Fourier transformation of the  $k^3\chi(k)$  by using Hanning window function from  $\sim 5$  to  $15 \text{ \AA}^{-1}$ . The data were Fourier transformed without introducing any phase shifts.  $\phi(r)$  of NdCl<sub>3</sub> and DyCl<sub>3</sub> at several temperatures are shown in Figs. 2 (a) and (b), respectively.

Fig. 2(a) reveals that:

- 1) The prominent peak around 2.1-2.4  $\text{\AA}$  is related to Nd-Cl first-shell contribution. It is reasonable to assume that the peak position is very similar to the Nd-Cl distance (2.77  $\text{\AA}$ ) observed

by other techniques, e.g., X-ray diffraction (Ohno et al. 1994). In fact, if we introduce a phase shift by using MaKale's parameters to the main peaks in the solid and liquid phases, the peak positions change to 2.90  $\text{\AA}$  and 2.71  $\text{\AA}$ , respectively.

- 2) Above the melting point (1029 K), the principal peak in the spectra shifts to a shorter distance, ca. 2.1  $\text{\AA}$  as compared to 2.4  $\text{\AA}$  in the solid phase. Similar behaviour has also been observed in alkali metal halides. This decrease of the Nd-Cl distance in NdCl<sub>3</sub> suggests a structural change during phase transition (melting).
- 3) With increase in temperature, increased thermal vibrations result in a reduced structural ordering thereby, leading to a decrease in the height of the principal peak. Especially, below the melting point, a small shift in the Nd-Cl distance can be noticed between 633 K and 763 K. Although the peak shift suggests a possible phase transition, its origin due to the anharmonicity effect cannot be ruled out. A full analysis of the present XAFS data is in underway.

Fig. 2(b) shows that although the temperature dependence of the main peak position in DyCl<sub>3</sub> is broadly similar to that in NdCl<sub>3</sub>, there are inherent differences:

- 1) The shift in the main peak position of  $\phi(r)$  during melting in NdCl<sub>3</sub> is much larger than that in DyCl<sub>3</sub> indicating that the structural change of NdCl<sub>3</sub> during melting is much larger than that of DyCl<sub>3</sub>.
- 2) In DyCl<sub>3</sub>, the principal peak in the spectra shifts continuously with increasing temperature, indicating the absence of any phase transitions in its solid phase.

We expected to observe the metal-metal (M-M) first-shell contribution in the EXAFS spectra. However, by using relatively large range of  $\chi(k)$  data for Fourier transformation, the peaks obtained at larger distances ca.  $\sim 4 \text{ \AA}$  are so small that it is difficult to comment on the M-M correlations. In this paper, no information on coordination numbers is included since it requires some form of modeling to fit the  $\chi(k)$  curves, and the need to incorporate a variable of the Debye-Waller Factor (DWF) that cannot be evaluated *a priori* without a reference spectra. To reveal such structural details, further analysis of the EXAFS spectra by introducing some modeling is required. In the light of our own neutron diffraction and MD simulation results on molten DyCl<sub>3</sub> and NdCl<sub>3</sub>, this work is in progress and will be reported separately.

## 4. Conclusions

The analyses without introducing any phase shifts and without any modeling of the EXAFS spectra for NdCl<sub>3</sub> and DyCl<sub>3</sub> over a range of temperatures from solid to molten phases show structural changes on melting. In addition, NdCl<sub>3</sub> shows a solid-solid structural phase transition between 633 K and 763 K. Also, there is a clear indication that the type of phase transition on melting of the two compounds (NdCl<sub>3</sub> and DyCl<sub>3</sub>) is different. For calculation of precise distances and co-ordination numbers from EXAFS data, some form of modeling to fit the  $\chi(k)$  curves is required, and in the light of available neutron diffraction and MD simulation results on these melts, this work is in progress.

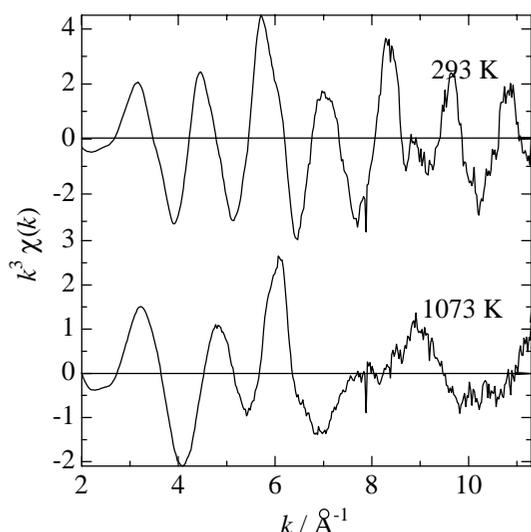


Fig. 1(a) The EXAFS signals of  $\text{NdCl}_3$  in the solid (293 K) and liquid (1073 K) phases.

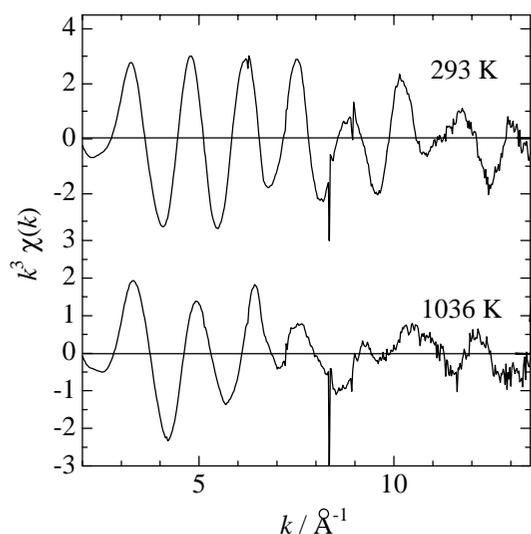


Fig. 1(b) The EXAFS signals of  $\text{DyCl}_3$  in the solid (293 K) and liquid (1036 K) phases.

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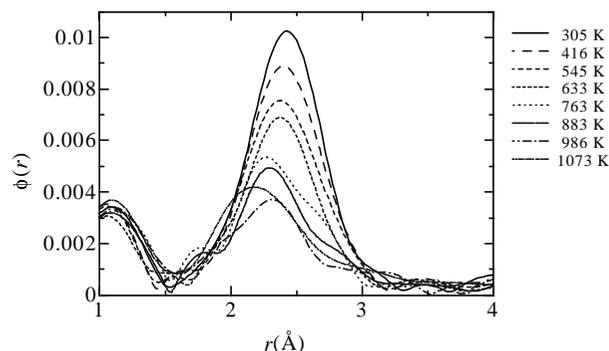


Fig. 2(a) The radial structure factors  $\phi(r)$  of  $\text{NdCl}_3$  at various temperatures.

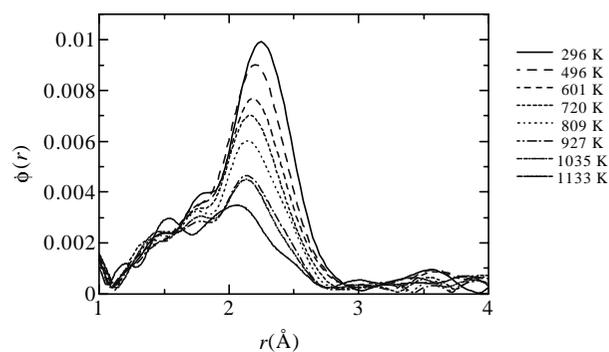


Fig. 2(b) The radial structure functions  $\phi(r)$  of  $\text{DyCl}_3$  at various temperatures.

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