ESRF	**Experiment title:** **EXAFS measurements on solid and liquid phases of MCl_3 and x MCl_3 + (1 - x) NaCl (M = Nd and Dy)**	**Experiment number**: CH648
Beamline: **BM29**	**Date of experiment**: from: **5 May 1999** to: **11 May 1999**	**Date of report**: 24 June 2002
Shifts:	**Local contact(s)**: **D. T. Bowron**	*Received at ESRF:*

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Report: The X-ray absorption fine structure (XAFS) spectra of neodymium ($NdCl_3$) and dysprosium chlorides ($DyCl_3$), and their mixtures with NaCl in both the solid and the liquid phases were measured over a range of temperatures at the Nd and Dy LIII absorption edges on beam line BM29. No problems were encountered in running the spectra on pure samples, however mixture samples were found to be problematic. In the initial runs, the pellets (~1 mm thick) were prepared by mixing homogeneously the powdered samples with BN powder matrix and pressing the mixture. It appears that one of the components of the mixture samples sublimed under high vacuum at high temperatures, thereby the composition of the mixture changed continuously during the mixture runs. The pellets for the mixture samples were then prepared in graphite powder matrix, which acted as a better binder and kept the mixture composition intact. Satisfactory data on mixture samples could then be finally collected. The mixture ratio of each sample and the matrix was calculated by using X-ray absorption coefficient.

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 keV to 6.708 keV and from 7.71 keV 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.

The EXAFS spectra of $NdCl_3$ at 293 K and 1073 K and those of $DyCl_3$ at 293 K and 1036 K, obtained after removing the background intensity estimated by using modified Victoreen equation, and normalized by McMaster coefficients, are shown in Fig. 1(a) and (b), respectively. As expected, the oscillations after the absorption edges in the molten state are more reduced than those in the respective solid phase. EXAFS function, $\chi(k)$, was extracted by the following procedure: μ_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 $NdCl_3$ and $DyCl_3$ in both the solid and liquid phases at the temperatures indicated earlier are shown in Figs. 2 (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 solid state.

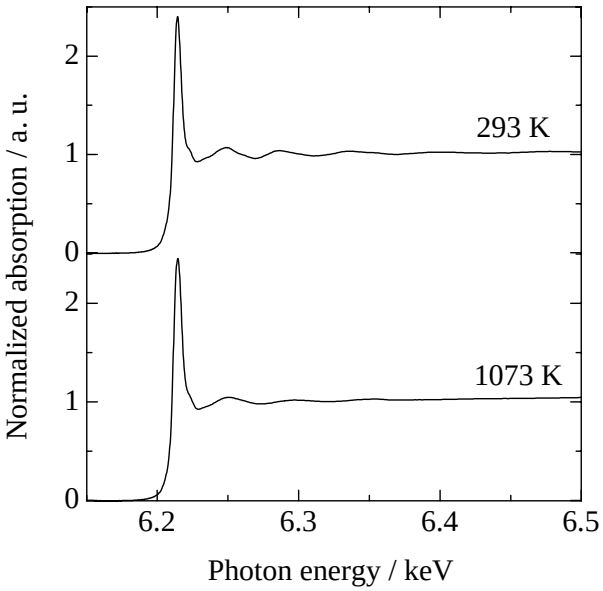

Fig. 1(a) The normalized absorptions of $NdCl_3$ in the solid (293 K) and liquid (1073 K) phases.

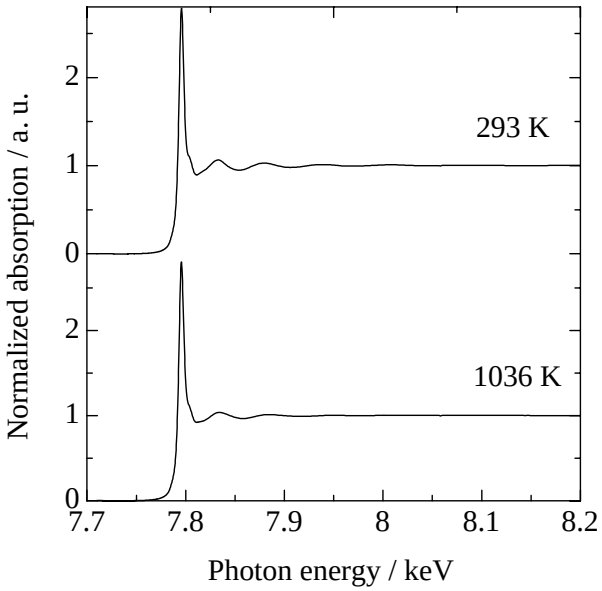

Fig. 1(b) The normalized absorptions of $DyCl_3$ in the solid (293 K) and liquid (1036 K) phases.

The radial structure functions, $\phi(r)$ were obtained by Fourier transformation of the $k^3\chi(k)$ by using Hanning window function from ~5 to 15 $Å^{-1}$. The data were Fourier transformed without introducing any phase shifts. $\phi(r)$ of $NdCl_3$ and $DyCl_3$ at several temperatures (not shown) reveal that the prominent peaks corresponding to the M–Cl (M: Nd or Dy) first-shell contribution are shifted to shorter distances in the liquid melts as compared to those in the solids. 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 $NdCl_3$ than in $DyCl_3$. Two papers from the above studies have already been published, and other work will be reported separately.

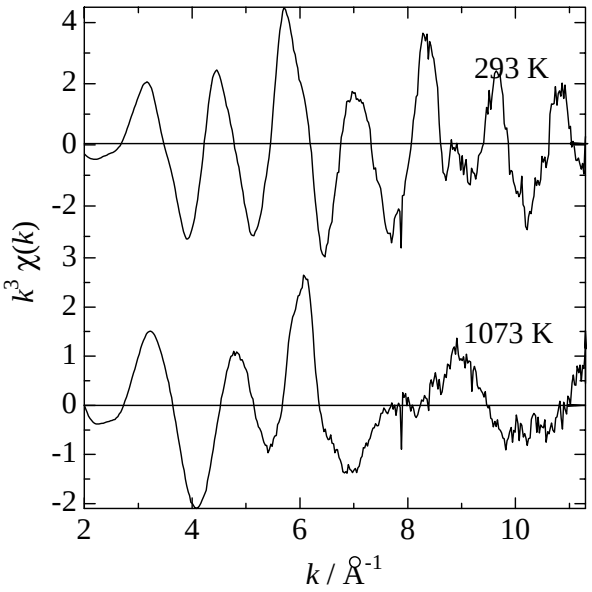

Fig. 2(a) The EXAFS signals of $NdCl_3$ in the solid (293 K) and liquid (1073 K) phases.

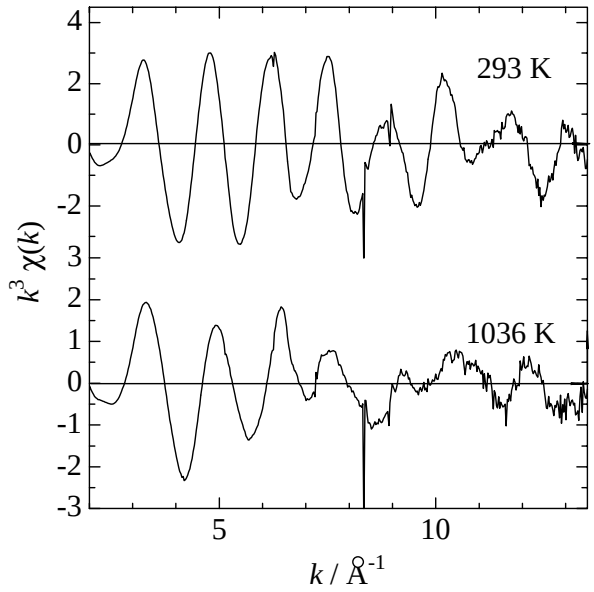

Fig. 2(b) The EXAFS signals of $DyCl_3$ in the solid (293 K) and liquid (1036 K) phases.

1. H. Matsuura, A.K. Adya, and D.T. Bowron, *J. Synchrotron Radiation*, 2001, **8**, 779.
2. H. Matsuura, A.K. Adya, & D.T. Bowron, "The Structure of rare earth chloride melts by XAFS analysis", *Progress in Molten Salt Chemistry 1*, eds. R.W. Berg and H.A. Hjuler, Elsevier Publishers, 2000, pp 335.