

## K- and L-edge XAFS determination of the local structure of aqueous Nd(III) and Eu(III)

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The short-range coordination of Nd(III) and Eu(III) ions in aqueous solutions has been investigated by means of K-edge x-ray absorption spectroscopy. Experimental data are presented which demonstrate that an accurate determination of the Nd(III) and Eu(III) hydration structural parameters can be obtained from the analysis of the K-edge spectra. It is shown that the large widths of the core hole states do not appreciably reduce the potential structural information of the K-edge EXAFS data. In addition the available k-range of the K-edge spectra is much wider compared to that of the L<sub>3</sub>-edge which is affected by the presence of double-electron excitations in a more severe fashion.

### 1. Introduction

A large amount of experimental work, as well as theoretical studies, has been devoted in order to elucidate the hydration structure of lanthanide(III) (Ln(III)) ions (Ohtaki *et al.*, 1993). Despite the large number of investigations carried out on this topic a conclusive description of the structural properties of these systems has still not been achieved. There appears to be a consent that the lighter lanthanide (III) ions from La(III) to Nd(III) are nonhydrated and the heavier ions after Tb(III) have eight water molecules in the first coordination sphere, while no conclusive results have been obtained for intermediate ions such as Sm(III) or Eu(III). The average bond distance for eight-coordinated ions is typically 2.41–2.51 Å, while being slighter longer for nine-coordinated ions.

In earlier studies it has been shown that the EXAFS technique is especially well suited for measurements of the structure of the local environment of ions in solution. There are many advantages of using EXAFS for solvation studies, firstly it isolates the pair distribution functions about the atom of interest and the first-neighbor environment can be obtained with high spatial resolution. Secondly, EXAFS measurements can be made at very low concentration where the ion-ion interactions are negligible, thus providing the simplest experimental conditions for determining the solvent-ion interactions. EXAFS investigations were previously carried out on Ln(III) aqueous solutions above the L<sub>3</sub>-edges (Yamaguchi *et al.*, 1988, Kodre *et al.*, 1995, Solera *et al.*, 1995, Benazeth *et al.*, 1998). However, the presence of the L<sub>2</sub>-edges, that typically occur a few hundred electron volts higher in energy, tends to restrict the range of the signal that may be used in the EXAFS analysis and consequently there is a reduction in the accessible information content when compared with K-edge data.

EXAFS has in general been confined to absorption edges below 30 keV due to the opinion that this technique is unable to provide significant structural information at K-edges of higher Z

atoms. For high atomic number elements the short lifetime of the excited atomic state causes a damping and broadening of the signal which in particular affects the high frequency components of the measured signal and consequently reduces the sensitivity of the technique to the longer range inter-atomic distances. Nevertheless, recent investigations have shown that in the case of Eu although the core hole width is five times larger at the K-edge than at the L<sub>3</sub> one, the corresponding loss in information is largely recovered by the large k-range which extends more than a factor of two over the L<sub>3</sub>-edge (Borowski *et al.*, 1999). In addition, in the case of disordered systems the structural information is intrinsically limited in the *r*-space and no high-frequency components are present in the spectra. The aim of the present work is to explore the Nd(III) and Eu(III) ion hydration using EXAFS spectroscopy at the K-edge of these elements.

### 2. Data analysis

Eu(III) and Nd(III) 0.1 M aqueous solutions have been prepared by dissolving the appropriate amount of Eu(NO<sub>3</sub>)<sub>3</sub> and Nd(NO<sub>3</sub>)<sub>3</sub> in freshly distilled water. The solutions were then acidified to about pH=2.5 by adding HNO<sub>3</sub>. The data were measured at the ESRF-BM29 spectrometer in transmission geometry. The spectra were collected using a Si(311) monochromator crystal with 50% and 30% detuning for the L and K edges, respectively. The optical paths were optimized for each sample and edge.

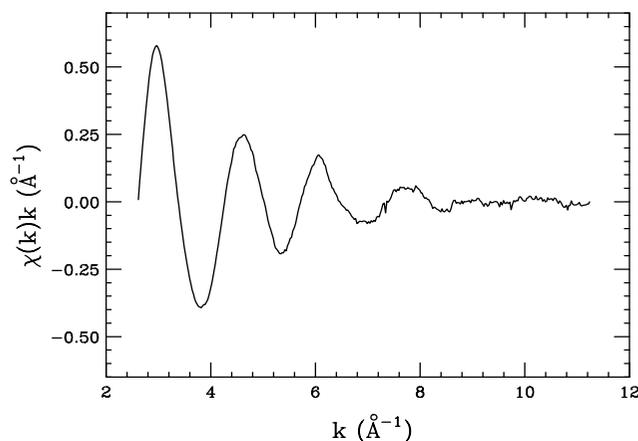
The K-edge EXAFS data analysis has been performed using the GNXAS program, which has proven to give reliable structural information in this high energy domain (Filippini *et al.*, 1995a, 1995b).

Several investigations on ionic aqueous solutions have shown that in many cases a correct description of the first hydration sphere has to account for asymmetry in the distribution of the ion-oxygen distances (D'Angelo *et al.*, 1994). In the present study the Ln(III)-oxygen first coordination shell has been modeled with a gamma-like function which depends on four parameters, namely the coordination number N, the average distance R, the distance mean-square variation  $\sigma^2$  and the skewness  $\beta$ . Note that  $\beta$  is related to the third cumulant C<sub>3</sub> through the relation C<sub>3</sub>= $\sigma^2\beta$ , and R is the first moment of the function  $4\pi \int g(r)r^2 dr$ . These parameters have been optimized by fitting the EXAFS theoretical signal to the experimental data.

### 3. Results

Previously, x-ray absorption spectroscopy at the L<sub>3</sub>-edges has been used for structural studies of hydrated rare earth ions (Benazeth *et al.*, 1998, Solera *et al.*, 1995). These investigations provided contradictory results both for coordination numbers and Ln(III)-O distances of the first hydration sphere. Difficulties in performing a reliable structural data analysis for these systems derive from two main reasons: the availability of a narrow k-range and the consequent reduction in the accessible information content, and the presence of strong double excitation effects.

Sharp multielectron resonances above the L<sub>3</sub>-edges of rare earth ions have been observed in previous investigations (Kodre *et al.*, 1995, Solera *et al.*, 1995). The presence of anomalous peaks, appearing in the range 5 to 7 Å<sup>-1</sup> and superimposed on the main oscillating signal, has been explained as being due to double-electron transitions 2p4d→5d<sup>2</sup>. It is well known that double-excitation contributions modify the fine structure beyond the absorption edge and introduce errors in the bond-length and coordination number determination, the effect being proportional to the magnitude of the double-excitation peak (D'Angelo *et al.*, 1996a).

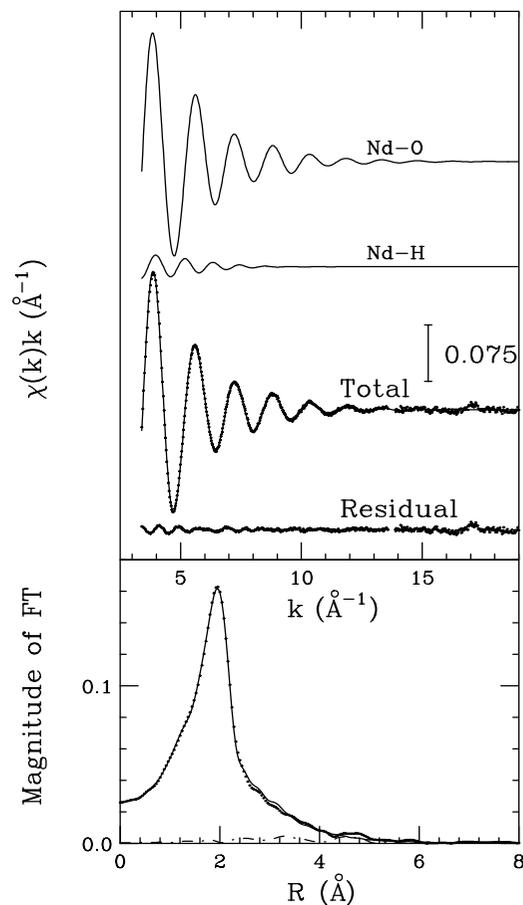


**Figure 1**  
EXAFS experimental structural signal of Nd(III) in water above the  $L_3$ -edge.

Fig. 1 shows the EXAFS signal at the  $L_3$ -edge of Nd(III) aqueous solution. An anomalous feature is clearly visible at about  $6 \text{ \AA}^{-1}$  which causes a distortion in the EXAFS structural oscillation. Recent data analysis methods account for the presence of double-excitation channels by properly modeling the atomic background used in the extraction of the  $\chi(k)$  signal. Step-shaped functions can be used to reproduce the background discontinuities and changes of slopes due to the presence of double-electron transitions. Nevertheless, when the features associated with the opening of multielectron thresholds are sharp and structured, they cannot be completely removed from the EXAFS structural oscillation. This hampers an accurate determination of the structural parameters, especially for disordered systems, where the presence of multielectron transitions is more evident due to the weakness of the structural contribution. Moreover, due to the presence of the  $L_2$ -edge, only four oscillations can be detected in the  $L_3$ -edge spectra of Ln(III) water solutions. The indeterminations on the structural parameters obtained from the  $L_3$ -edge EXAFS analysis stem both from the signal distortion due to double-excitation effects and from the low resolution caused by the limited  $k$ -range.

The presence of multi-electron excitation channels is detected also in the Nd(III) and Eu(III) aqueous solution K-edge spectra. Nevertheless, in this case they give rise to changes of slope and edges in the atomic background which can be properly reproduced by using appropriate model functions in the extraction of the EXAFS signal. The sharp features which are visible in the  $L_3$ -edge spectra are not present in the K-edge data due to the broadening effect caused by the short life time of the excited atomic state.

The results of the data analysis performed on the Nd(III) and Eu(III) aqueous solution EXAFS spectra at the K-edges are shown in Figs. 2 and 3, respectively. The first signals in the upper panel of Figs. 2 and 3 are associated with the Nd(III)-O and Eu(III)-O contributions, respectively, while the second curves represent the Nd(III)-H and Eu(III)-H contributions, respectively. It is evident that the EXAFS data are dominated by the Ln(III)-O contributions while the Ln(III)-H signals are weaker and mainly affect the low- $k$  region of the spectra. Nevertheless, the inclusion of these contributions is essential for a complete description of the structural signal. The importance of accounting for the hydrogen atoms in the EXAFS data analysis of water solutions has been pointed out in previous publications (D'Angelo *et al.*, 1996a, 1996b, 1996c).



**Figure 2**  
EXAFS experimental structural signal of Nd(III) in water above the K-edge (dots) compared to the  $\chi(k)$  theoretical signal and corresponding Fourier Transform spectra.

As previously mentioned an asymmetric distribution has been used to parametrise the first peak of the Ln(III)-O radial distribution function. As has been shown in previous papers the Gaussian approximation is not suitable for a correct description of the first neighbor coordination sphere of many ionic water solutions. A fitting procedure has been applied to the experimental data to extract structural parameters which are listed in Table 1.

The Nd(III)-O and Eu(III)-O first shell distances obtained from this analysis are slightly longer than those found by previous experimental determinations. This is due to the use of asymmetric shells. Note that in the present analysis  $R$  is the average distance and not the modal value of the distribution. The accuracy of the Nd phase shift calculations has been checked using crystalline  $[\text{Nd}(\text{OH}_2)_9](\text{CF}_3\text{SO}_3)_3$  (NdTFL) as reference compound.

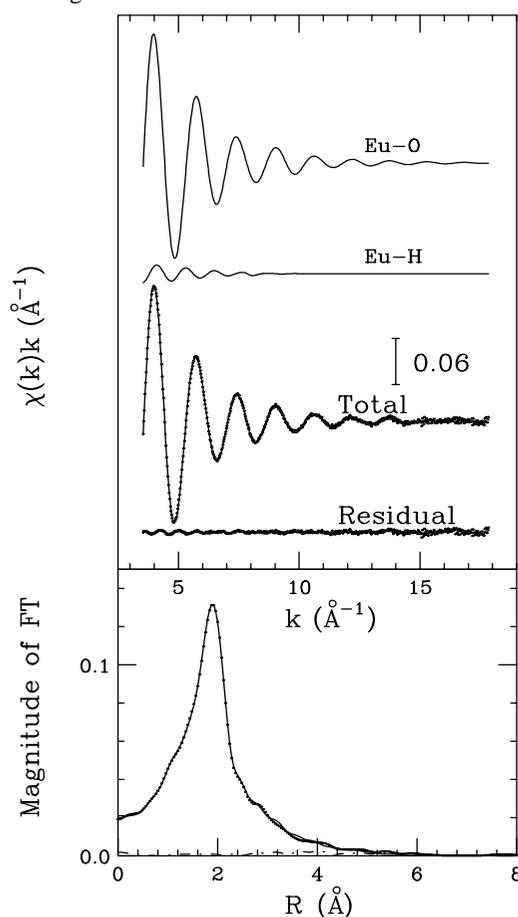
The coordination numbers are in good agreement with those reported in previous EXAFS investigations at the  $L_3$ -edges, while the

**Table 1**  
Structural parameters obtained from the fitting procedure for the K-edge spectra.  $N$  is the coordination number,  $R$  is the ion-oxygen first shell average distance,  $\sigma^2$  is the mean-square deviation and  $\beta$  is the skewness.

	$R(\text{\AA})$	$\sigma^2(\text{\AA}^2)$	$\beta$	$N$
Nd(III)-O	2.517(4)	0.0088(5)	0.33(7)	9.1(4)
Eu(III)-O	2.479(4)	0.0100(5)	0.71(8)	8.7(4)

Debye Waller factor values obtained from our analysis are slightly larger (Yamaguchi *et al.*, 1988, Solera *et al.*, 1995, Benazeth *et al.*, 1998). This is certainly the result of the use of asymmetric distributions. In NdTFL nine water molecules surround Nd in a tricapped trigonal prism with 6 and 3 Nd-O distances at 2.451 Å and at 2.568 Å, respectively. The presence of two different sets of distances increases the static disorder and hence the DW factor values when a single shell model is used. The amplitude reduction factors  $S_0^2$  were found to be 0.99 and 0.93 for Nd and Eu, respectively. The  $E_0$  energies were found to be  $1.5 \pm 0.2$  eV and  $4.2 \pm 0.3$  eV above the first inflection points of the spectra for Nd and Eu, respectively.

It is evident from Figs. 2 and 3 that there is a very good agreement between experimental and fitted data. Nevertheless, the residual curves show a primarily single high-frequency component which may be associated with multiple scattering contributions within the first hydration shell. This hypothesis will be subject of further investigation.



**Figure 3**  
EXAFS experimental structural signal of Eu(III) in water above the K-edge (dots) compared to the  $\chi(k)$  theoretical signal and corresponding Fourier Transform spectra.

#### 4. Conclusions

From the results of this preliminary investigation it is clear that K-edge spectra are suitable for a reliable determination of the hydration structure of Ln(III) ions in aqueous and non-aqueous solutions. There are many advantages of using the K-edge spectra for the structural investigation of these systems. Firstly, the resolution is higher due to the wideness of the k-range, as compared to the  $L_3$ -edge spectra. Secondly, double-electron excitations are not so pronounced and these features can be properly removed from the EXAFS data. Finally, in the case of solutions, the structural information is intrinsically limited in the r-space and no high-frequency components are present in the spectra which could be masked by the core-hole life time effect. Therefore, the K-edge analysis leads to an accurate determination of the coordination sphere structures of Ln(III) solutions.

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#### References

- Benazeth, S., Purans, J., Chalbot, M.-C., Kim Nguyen-van-Duong, M., Nicolas, L., Keller, F. & Gaudemer, A. (1998). *Inorg. Chem.* **37**, 3667–3674.
- Borowski, M., Bowron, D. T. & De Panfilis, S. (1999). *J. Synchrotron Rad.* **6**, 179–181.
- D'Angelo, P., Di Nola, A., Filipponi, A., Pavel, N. V. & Roccatano, D. (1994). *J. Chem. Phys.* **100**, 985–994.
- D'Angelo, P., Pavel, N. V., Roccatano, D. & Nolting, H.-F. (1996a). *Phys. Rev. B* **54**, 12129–12138.
- D'Angelo, P., Di Nola, A., Mangoni, M. & Pavel, N. V. (1996b). *J. Chem. Phys.* **104**, 1779–1790.
- D'Angelo, P., Nolting, H.-F. & Pavel, N. V. (1996c). *Phys. Rev. A* **53**, 798–805.
- Filipponi, A., Di Cicco, A., Natoli, C. R. (1995a). *Phys. Rev. B* **53**, 15122–15134.
- Filipponi, A., Di Cicco, A. (1995b). *Phys. Rev. B* **53**, 15135–15149.
- Kodre, A., Arcon, I., Hribar, M., Stuhec, M., Villain, F., Drube, W. & Troger, L. (1995). *Physica B* **208&209**, 379–380.
- Kowall, Th., Foglia, F., Helm, L. & Merbach, A. E. (1995). *J. Am. Chem. Soc.* **117**, 3790–3799.
- Ohtaki, H. & Radnai, T. (1993). *Chem. Rev.* **93**, 1157–1204.
- Solera, J. A., Garcia, J. & Proietti, M. G. (1995). *Phys. Rev. B* **51**, 2678–2686.
- Yamaguchi, T., Nomura, M., Wakita, H. & Ohtaki, H. (1988). *J. Chem. Phys.* **89**, 5153–5159.