	Experiment title: *XAFS Study with Picometer Accuracy of Eu(II), Eu(III) and Sr(II) Aqua Ions in Aqueous Solutions and Crystals*	**Experiment number**: CH-660
ESRF		
Beamline: BM29	**Date of experiment**: from: **April 17 1999** to: **April 20 1999**	**Date of report**: **June 15 1999**
Shifts: 9	**Local contact(s)**: **Michael Borowski**	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

L. Helm*,[1]
A. Kuzmin[2]
A. E. Merbach[1]
G. Moreau*,[1]
J. Purans*,[1,2]

[1] **Institut de chimie minérale et analytique, Université de Lausanne, BCH, CH-1015 LAUSANNE**
[2] **Institute of Solid State Physics, University of Latvia, LV-1063 RIGA**

Report:

We have performed XAFS measurements on Eu(II), Eu(III), Lu(III) and Sr(II) aqua ions in solutions and crystals. Eu(II) was one of the few cations for which the *hydration structure has not been established* in aqueous solution, neither for the first nor for second shell.

A multipurpose X-ray absorption cell (LURE) was used for in-situ XAFS measurements of sealed, oxygen free solutions in the transmission mode. The measurements were done at different optical lengths (1 to 2 mm for Eu; 1.5 mm for Lu and 4 mm for Sr) to estimate the saturation effect on the white line amplitude.

The XAFS spectra of the Eu L_3-edge (6976 eV; scan 6900- 7650 eV), Lu L_3-edge (9244 eV; scan 9150 - 10400 eV) and Sr K-edge (16105 eV; 16 000- 17 000 eV) have been measured for the aqueous solutions at RT and for the referenced crystals at different temperatures. The synchrotron radiation was monochromatized using the Si(111) double-crystal monochromator and harmonic rejection was achieved by slightly detuning the two crystals from the parallel alignment. Experimental spectra were recorded by two ionization chambers (He+N_2 mixture for Ln and He+Ar mixture for Sr measurements) with variable steps in the wave vector range 0.025 Å^{-1}, count rate 1 s per point. The energy resolution (FWHM) was 0.7 eV (Si(111)) at Eu L_3-edge.

The Eu(II) and Eu(III) L_3-edge XANES measurements (white line amplitudes) have clearly

demonstrated that sealed oxygen free samples of Eu(II) (0.1M) aqueous solutions are stable in the cell (LURE) from pH 1 to 5 for at least 10h. XANES spectra are very sensitive to small amounts of Eu(III) (~1%) as could be shown after slow oxydation of Eu(II) (addition of a small quantity of O_2, Figure 1). Therefore we are sure, that our EXAFS data was obtained for pure Eu(II) (0.1M, pH=1 and pH=5) aqueous solutions with Eu(III) concentration smaller than 1%.

The following XAFS measurements were performed on aqueous solutions:

1. In situ oxidation of Eu(II) to Eu(III) at pH 1 and 5 (Figure 1).
2. Eu(II) at pH 1 and 5. (Figure 2).
3. Eu(III) at pH 1 and 5 (Figure 2).
4. Lu(III) at pH 1.
5. Sr(II) at pH 1.

Two scan measurements on the crystalline reference compounds at different T:

1. Eu(III) at 20; 50; 100; 200; 300 K.
2. Lu(III) at 20; 50; 100; 200; 300 K.
3. Sr(II) at 20; 50; 100; 200; 300 K.

The experimental XAFS data were treated by software package 'EDA' (JP) in the new way similar to the one applied previously for high accuracy analysis of the thermal expansion of Ge [to be published in Phys. Rev. Letters 1999]. The EXAFS was interpreted using the cumulant approach by taking into account the experimental phases and amplitudes from the reference crystals measured at variable temperature.

The reference Sr(II) compound (mimic the local environment of Sr aqua ions with CN=8) is crystalline $[Sr(H_2O)_8](OH)_2$: the Sr(II) ions are surrounded by eight water oxygen atoms which form a slightly distorted antiprism. The reference Ln(III) compounds (mimic the local environment of Ln aqua ions with CN=9) are crystalline $[Eu(H_2O)_9](O_3SCF_3)_3$ and $[Lu(H_2O)_9](O_3SCF_3)_3$: the Ln(III) ions are surrounded by nine (6 + 3) water oxygen atoms which form a regular tricapped trigonal prism.

For the first time the hydration structure for the first shell of Eu(II) aqua ion has been established (Table 1). We have observed changes of RDF's when going from the triple charged Eu(III) to the double charged Eu(II) aqua ions (ion-water distances, coordination numbers, etc). High accuracy XAFS measurements and new XAFS data analysis software allowed us to reconstruct the RDF and to compare this RDF with results of MD simulations on Sr(II). The first coordination shell of Eu(II) aqua ions is composed of 7 ± 0.5 water molecules at the distance R(Eu-O)=2.58 ± 0.01Å with a MSRD 0.014 ± 0.002 Å^2, while that of Sr(II) aqua ions is composed of 7.5 ± 0.5 water molecules at the distance R(Sr-O)=2.595 ± 0.005 Å with a MSRD $\sigma^2 = 0.012 \pm 0.002$ Å^2. We confirm structural similarity between Eu(II) and Sr(II) in aqueous solution. The Eu-O_w-distance found by our investigation is 0.02 Å smaller than that of Sr(II). Therefore, it is in agreement with the known ionic radius difference between Eu(II) and Sr(II).

We have also observed for the *first time* the temperature dependence of structural and dynamic parameters for the studied aqua ions in the crystals. These data are important for a more careful analysis of structural and dynamic parameters for the studied aqua ions in the solutions and for analysis of kinetic data obtained by our NMR experiments.

Fig. 1 In situ XANES measurements of Eu-aqueous solution showing accelerated oxydation of Eu^{2+} after exposure to oxygen.

Fig. 2 EXAFS spectra of Eu^{2+} and Eu^{3+} in aqueous solution showing the destructive interference.

Table 1: First coordination shell structural data obtained by EDA program from the best-fit analysis of the Eu^{2+}, Eu^{3+} and Sr^{2+} aqua ions in the water solutions. N_1 is the number of atoms located in the first shell at the distance R from the metal, σ^2=C2 (here) is the DW factor, C3 and C4 cumulants characterizing the form of RDF; ε is the fitting error.

			Bonds $Eu-O_w$ and $Sr-O_w$				
State	**N_1,(S_0)**	**R_1(Å)**	**C2(Å^2)**	**C3 (10^{-4})**	**C4 (10^{-5})**	**Phases**	**ε_1 (10^{-2})**
			Eu^{2+} aqua ions in the solution				
Sol.	7.1±0.5	2.58±.01	0.014			Hyd 20	3.4
		Eu^{3+} aqua ions in the crystal $[Eu(H_2O)_9](O_3SCF_3)_3$					
Hyd 300	9.0*	2.444	0.0068			FEFF6	4.5
Hyd 300	9.0*	2.447	0.0096	1.6	0.0	Hyd 20	0.9
			Eu^{3+} aqua ions in the solution				
Sol.	9.0*	2.433	0.0936	0.5		Hyd 20	2.2
		Sr^{2+} aqua ions in the crystal $Sr(H_2O)_8(OH)_2$					
Hyd 20	8.0*	2.616	0.0056	0.0	0.0	FEFF6	5.0
Hyd 300	8.0*	2.619	0.0124	3.0	7.0	Hyd 20	1.1
			Sr^{2+} aqua ions in the solution				
Sol.	7.4	2.594	0.0115	0.0	0.1	Hyd 20	0.77
Sol.	7.5	2.594	0.0119	0.0	0.0	Hyd 300	0.80
Sol.	7.2	2.601	0.0118	4.9	3.3	Hyd 300	1.2