	Experiment title: Investigation of the short range ordering relaxation in the three component glass-forming melts of Al-Ni-REM (REM: La, Y, Ce) systems	Experiment number: MA-912
Beamline: ID26	Date of experiment: from: 17.09.2009 to: 22.09.2009	Date of report: 23-02-2010
Shifts: 15	Local contact(s): Dr. Kristina Kvashnina	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): J. Vegelius, S. Butorin , Uppsala University, Department of Physics, Box516, S75120, Uppsala, Sweden K. Kvashnina , European Synchrotron Radiation Facility (ESRF), BP22, 6 rue Jules Horowitz, 38043 Grenoble, France		

Report:

The aim of the experiment was to study the electronic structure of the rare earth (RE) oxides and metallic compounds using X-ray absorption near edge spectroscopy (XANES) in high-energy-resolution fluorescence detection (HERFD) mode at the *RE* L_3 edge.

The electronic and magnetic properties of lanthanides are defined by the electron configuration of the $4f$ shell. The f shell can be directly probed via dipole transitions from $3d$ core levels ($M_{4,5}$ absorption edge). The excitation energies of the $M_{4,5}$ edge lie in the soft X-ray range and the experiments therefore require UHV conditions. Hard X-ray studies are experimentally more favourable but transitions from the $2p$ and $2s$ shell to the f level are forbidden following the dipole selection rules. However, Carra and Altarelli [1] suggested that the intensity of quadrupole transitions between the $2p$ and $4f$ levels may be substantial. Following this theoretical prediction Hämäläinen and co-workers [2] measured the Dy L_3 XANES edge of $Dy(NO_3)_3$ by monitoring the Dy La_1 ($3d_{5/2} \rightarrow 2p$ transitions) fluorescence intensity using an analyzer crystal. They observed a spectral line narrowing below the natural core-hole lifetime width and clearly resolved transitions to the Dy $4f$ orbitals.

Various authors have used this technique since. The instrumentation has improved, and with higher data quality a deeper understanding of the electronic interactions becomes possible. We have studied the electronic structure of cerium and ytterbium in different oxidation states by means of HERFD. Experiment was performed at ID26 beamline in 16b mode. The incident energy was selected using the $\langle 311 \rangle$ reflection from a double Si crystal monochromator. Rejection of higher harmonics was achieved by two Si mirrors working under total reflection. The Ge $\langle 331 \rangle$ crystal analyzer was chosen as one of the suitable reflections in detection of the La_1 emission line of Ce (4839 eV) and Si $\langle 620 \rangle$ for Yb (7416 eV) systems. Sample, analyzer crystal and photon detector (avalanche photodiode) were arranged in a vertical Rowland geometry. A combined (incident convoluted with emitted) energy resolution of 0.8 eV was achieved for Ce systems, while for Yb compounds it was 1.2 eV. The difference in the energy resolution arises from the different Bragg angles of the crystal analyzer: Ge $\langle 331 \rangle$ at 87° for the Ce La_1 line and Si $\langle 620 \rangle$ at 67° for the Yb La_1

emission line. XANES spectra were simultaneously measured in total fluorescence yield (TFY) mode using a photodiode. The intensity was normalised to the incident flux.

Figure 1 show a comparison between HERFD and TFY curves of $\text{Ce}_2(\text{CO}_3)_3$, CeO_2 , CeFe_2 , $\text{Ce}(\text{PdFe})_3$, CeRhIn , CePO_4 and HERFD curves of Yb_2O_3 , YbF_3 , YbI_2 and $\text{Yb}_3\text{Fe}_5\text{O}_{12}$ compounds at the L_3 edge. Following the dipole selection rules at the Ce, Yb L_3 edge, electrons are excited from the $2p_{3/2}$ core level into unoccupied $5d_{5/2}$ states. The TFY curves of the Ce compounds are in agreement with previously reported data [3-4]. The HERFD spectra exhibit a better signal to noise ratio and show the sharpening of the absorption features compared to the TFY signal. The spectral features in the conventional XANES experiments are broadened by 3.5 eV at the Ce L_3 edge and 4.6 eV at Yb L_3 edge due to the $2p_{3/2}$ core hole lifetime. The spectral broadening of the XANES–HERFD spectrum is determined by the lifetime broadening of intermediate, final states and the instrumental resolution. We estimate the total spectral broadening of the Ce HERFD spectrum at the L_3 edge to be 1.7 eV and 2.4 eV for Yb HERFD spectra collected at $L\alpha_1$ emission line. The spectral sharpening in HERFD–XANES spectra reveals additional structures in the pre-edge excitations of some compounds, which will be discussed in details.

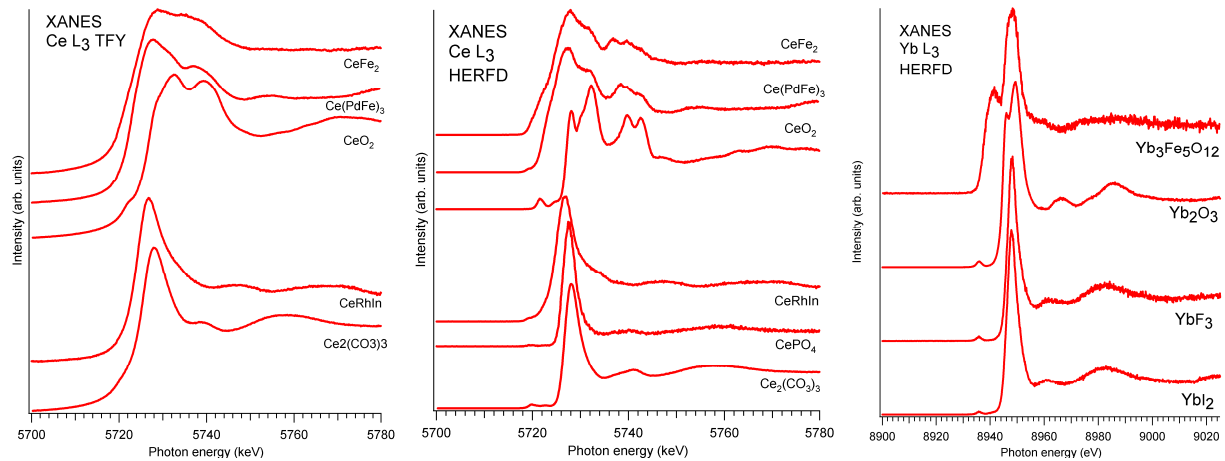


Figure1. XANES spectra at Ce, Yb L_3 edge of CeO_2 , $\text{Ce}_2(\text{CO}_3)_3$, CeFe_2 , $\text{Ce}(\text{PdFe})_3$, CeRhIn , CePO_4 , Yb_2O_3 , YbF_3 , YbI_2 and $\text{Yb}_3\text{Fe}_5\text{O}_{12}$ recorded in HERFD mode using X-ray emission spectrometer. High-energy resolution spectra (HERFD) of cerium systems are compared to TFY curves recorded using a photodiode.

Pre-edge excitations are observed in CeO_2 (formally Ce^{4+} system), CePO_4 and $\text{Ce}_2(\text{CO}_3)_3$ (formally Ce^{3+} systems), Yb_2O_3 and YbF_3 (formally Yb^{3+}) and YbI_2 (formally Yb^{2+} system). In general Yb^{2+} systems are rapidly oxidizing on the air. We believe that at the time of HERFD measurements YbI_2 compound was already oxidised to Yb^{3+} (energy position of the main white line and the pre-edge structure is similar to the Yb^{3+} system).

The experimental investigations showed that the shape of the pre-edge excitations of Ce^{3+} looks identical between different compounds in HERFD spectra. The same results are observed for Yb^{3+} system. For the simplification we will show only few examples of HERFD spectra measured experimentally and compared with theoretical calculations.

Figure 2 shows the Ce, Yb HERFD spectra over the pre-edge region of CeO_2 , $\text{Ce}_2(\text{CO}_3)_3$ and Yb_2O_3 compared with theoretical calculations of the $2p$ – $4f$ absorption process using atomic multiplet theory [5] for Ce^{3+} , Ce^{4+} and Yb^{3+} ions. A Ce^{4+} ion contains one $4f$ electron in the absorption final state and the CeO_2 spectrum shows a single peak at ~ 5722 eV in the pre-edge region. When the number of $4f$ electrons in the final state is increased to two

for a Ce^{3+} ion the spectral shape becomes broader. In that case the number of contributing states is increased to 46 due to electron-electron interactions in the $4f$ valence orbital. The Yb^{3+} ion with ground state $2p^6 4f^{13}$ shows a similar spectral shape as Ce^{4+} . It has only one hole in the $4f$ shell and shows a single peak profile at the pre-edge region of the Yb L_3 XANES spectrum.

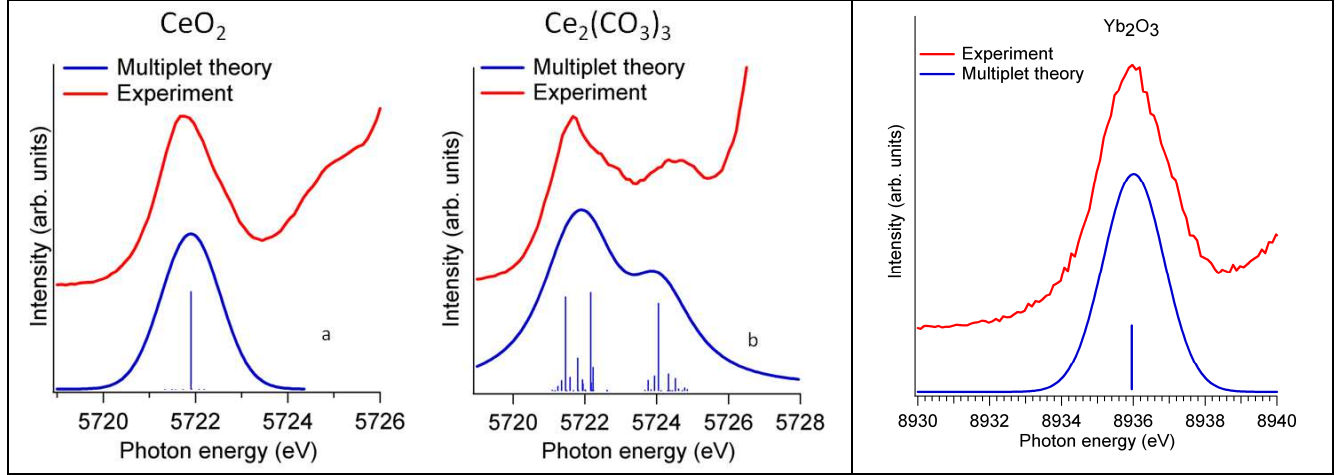


Figure 2. High resolution (HERFD) Ce, Yb L_3 absorption spectra over the pre-edge region of CeO_2 and $\text{Ce}_2(\text{CO}_3)_3$ and Yb_2O_3 compared with atomic multiplet calculations for Ce^{4+} , Ce^{3+} and Yb^{3+} ions.

An analysis of the spin-orbit couplings and electron-electron interactions shows that the splitting in the Ce^{3+} ($4f^1$) absorption spectral profile at the pre-edge is dominated by $4f$ - $4f$ interactions. This is nicely observed for the case of Ce^{4+} ($4f^0$) in CeO_2 where no $4f$ - $4f$ interactions are present. In case of Yb^{3+} ($4f^{13}$) no multiplet splitting is found in the final $2p^5 3d^{10} 4f^{14}$ state due to the filled $4f$ shell.

The present results show the effect of intra-atomic multiplet splitting at the L_3 XANES over the pre-edge region of Ce and Yb systems in different oxidation states with $4f^0$ and $4f^1$, $4f^{13}$ ground state configurations. The experimental method of detecting the high energy resolution XANES spectra using an X-ray emission spectrometer gives us an opportunity to resolve the shape of the pre-edge transitions. The observed excitations in Ce and Yb compounds are very well reproduced by atomic multiplet calculations. We demonstrate that pre-edge features involve electron-electron interactions and thus directly depend on the number of the available f electrons in the system.

References:

- [1] P. Carra and M. Altarelli, Phys Rev Lett **64**, 1286 (1990)
- [2] K. Hamalainen, D. P. Siddons, J. B. Hastings, and L. E. Berman, Phys Rev Lett **67**, 2850 (1991).
- [3] A. Bianconi, A. Marcelli, H. Dexpert, R. Karnatak, A. Kotani, T. Jo, and J. Petiau, Phys Rev B **35**, 806 (1987)
- [4] C. F. Hague, J. M. Mariot, R. Delaunay, J. J. Gallet, L. Journal, and J. P. Rueff, J Electron Spectrosc **136**, 179 (2004).
- [5] R. D. Cowan, University of California Press, Berkeley (1981).