ESRF	**Experiment title:** Resonant inelastic x-ray scattering (RIXS) applied to mixed-valent systems: $Ce_{\gamma} \rightarrow Ce_{\alpha}$ phase transition	**Experiment number**: HE-1454
Beamline: ID-12	**Date of experiment**: from: 21/06/2003 to: 28/06/2003	**Date of report**: 10/07/2003 *Received at ESRF:*
Shifts: 18	**Local contact(s)**: N. Jaouen	

Names and affiliations of applicants (* indicates experimentalists):

C.F. Hague *, J.P. Rueff *, L. Journel *, J.M Mariot

Laboratoire de Chimie Physique – Matière et Rayonnement, 11 rue Pierre et Marie Curie, 75231 Paris Cedex 05, France

J.P Kappler, G. Schmerber

IPCMS, 23, rue du Loess - BP 43 - 67034 Strasbourg Cedex, France

G. Krill

LURE, Centre Universitaire Paris-Sud, Bât. 209D, B.P. 34, F-91898 Orsay Cedex, France

Report:

It is now generally recognized that resonant inelastic x-ray scattering (RIXS) provides precise information about the electronic properties of rare-earth mixed valent systems [1-2]. By tuning the incident energy to salient features of the absorption edges, the various valence states can be resonantly enhanced. This enables an accurate determination of the spectral weight corresponding to each valent character, thus providing a precise estimate of the number of *f* electrons involved. Among the mixed valent systems, Ce is of particular interest because of the hybridization between the 4*f* and the conduction band, which is about one order of magnitude larger than that encountered in other mixed valent rare-earth compounds. In a previous experiment (see exp. Report HE-1127), we applied RIXS to follow the $\gamma \rightarrow \alpha$ transition in pure Ce under pressure. However, despite cautious sample handling, Ce oxidation could not be avoided in the pressure cell. This problem, related to the difficulty of protecting micrometer-sized samples from oxidation, was circumvented in the present experiment by using chemical pressure through doping of Ce. As reported in Ref. [3] for instance, the $\gamma \rightarrow \alpha$ transition can be mimicked in the Ce-Th alloys through temperature change. In this system, the $\gamma \rightarrow \alpha$ transition takes place at ≈100 K an easy temperature range to work with.

Here, we report on the investigation of the $\gamma \rightarrow \alpha$ transition by studying the temperature dependence of Ce *2p3d* RIXS signals in a variety of Sc and Th-doped Ce alloys, namely $Ce_{0.9}Th_{0.1}$, $Ce_{0.8}Th_{0.2}$ and $Ce_{0.93}Sc_{0.7}$ The experiment was carried out at ID-12. Polycrystalline samples were mounted on a cold head installed under vacuum in the UHV-compatible RIXS spectrometer after a thorough cleaning of their surface ex-situ. No oxidation of the samples was observed during the experiment. The RIXS spectra were obtained at the Ce-$L_{2,3}$ edge on our bent-crystal spectrometer fitted with a quartz (20-23) crystal. The overall resolving power at 4.8 keV was about 0.8 eV.

The evolution of the Ce *2p3d* RIXS spectra in $Ce_{0.93}Sc_{0.7}$ as a function of temperature, i.e., as the system goes through the magnetic transition, is shown in Fig. 1. The selected spectra were measured at fixed incident energy set in the Ce L_3 pre-edge region (see arrow in inset) where the largest changes upon temperature changes were observed. The RIXS spectra are normalized to the maximum of the main line intensity ($L\alpha_1$ at ~4833 eV). In addition to the main line which corresponds to 4f^1 component, a shoulder appears on the high emitted energy side; it can be attributed to the 4f^2 component, known to contain most of the information on the hybridization strength. The temperature-dependence of the shoulder intensity is presented in figure 2. A similar analysis was carried out in the Ce-Th alloys. In Ce$_{0.93}$Sc$_{0.7}$, the temperature cycle presents a large hysteresis, comparable to what is observed in the thermoelectric power and magnetization measurements. The width of the hysteresis loop is found to shrink as the concentration of alloyed component increases (going from left to right in figure 2).

This sensitivity of RIXS spectra to the *f* valence when the energy is tuned below the white line arises from the fact that the pre-edge region is usually ascribed to quadrupolar transitions (*2p* → *4f*) whereas the white line itself is predominantly of dipolar character (2p → *5d* transitions). It is valuable to note that the valence changes would have been barely visible in XAS because of the deep core-hole lifetime broadening effect. This effect is suppressed to a large extend in the RIXS process because it is characterized by a shallow core-hole in the final state. The spectra will be further analyzed in a first step within the phenomenological approach detailed in Ref. 2. Although oversimplified, this approach should provide important hints about the valence changes and the hybridization strength in doped systems and possibly unveil the mechanisms responsible for the $\gamma \rightarrow \alpha$ transition in Ce. Multiplet calculations are also envisaged in a near future.

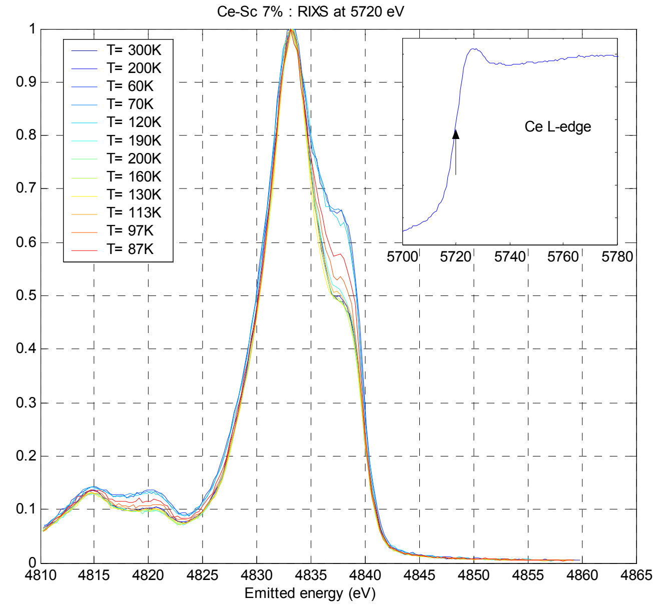
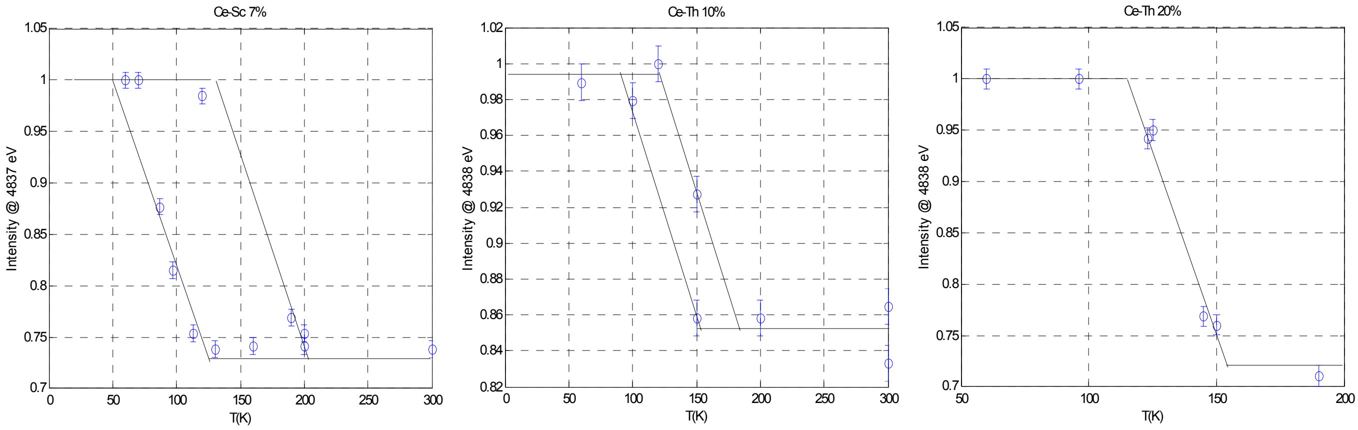


Figure 1 (left) : RIXS spectra taken in Ce-Sc 7% at 5720 eV in the pre-edge region of the Ce L-edge (see arrow in the inset) as function of temperature. The spectra were normalized to the maximum. The evolution of the high energy shoulder denotes the changes in population of the f^2 final state as the temperature is cycled through the magnetic transition.

Figure 2 (below) : Hysterisis loops derived from the intensity of the high energy shoulder in the RIXS spectra for Ce-Sc 7%, Ce-Th 10% and Ce-Th 20% as function of temperature. The left scale represents the relative changes with temperature of the f^2 component.



[1] C. Dallera et al., Phys Rev Lett. **88**,196403 (2002).
[2] L. Journel et al., Phys Rev B **66,** 045106 (2002).
[3] C. Fierz et al., J. Magn. Magn. Mater. **47-48**, 517 (1985)