



Experiment title: α - γ transition in Ce deposited on W:
Role of hybridization

Experiment number:
HE-1666

Beamline:
ID-12

Date of experiment:
from: 30/03/2004 to: 06/04/2004

Date of report:
20/04/2004

Shifts:
18

Local contact(s):
N. Jaouen

Received at ESRF:

Names and affiliations of applicants (* indicates experimentalists):

J.-P. Rueff*, **J.-M. Mariot***, **R. Delaunay***, **C. F. Hague**

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

J.-P. Itié*

Physique des Milieux Condensés, 140 rue de Lourmel 75015 Paris, France

J.-P. Kappler

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

Report:

We report here on the investigation of the γ - α transition in pure Ce by resonant inelastic x-ray scattering (RIXS). The initial experiment – looking at W-deposited Ce thin layers stabilized either in the γ or α phase – was ultimately replaced by a more ambitious plan: observing directly the phase transition under pressure. Our decision resulted from a delay in the preparation of the thin layer samples, which we feared might not be ready on time and recent advances in loading Ce in a pressure cell without risk of oxidation.

In our earlier attempt on Ce under pressure (see exp. report HE-1127), we had loaded Ce in a glove box under neutral atmosphere, but Ce oxidation could not be avoided despite cautious sample handling. In the present case, we started off with a chunk of Ce kept in silicon oil. A tiny piece cut off from the bulk and still embedded in oil was directly loaded in a diamond anvil cell (DAC) using a copper gasket with silicon oil as pressure medium. The L_3 absorption spectrum (XAS) in transmission mode obtained for the fresh-loaded sample (10 kbar) is presented Fig. 1 (magenta line). It shows none of the characteristic features of CeO_2 (red dashed line), namely a shift of white-line and an intense doublet in the near-edge region, giving us confidence that the sample was not (or only negligibly) oxidized. No further degradation of the sample quality was noticed upon pressure increase or release.

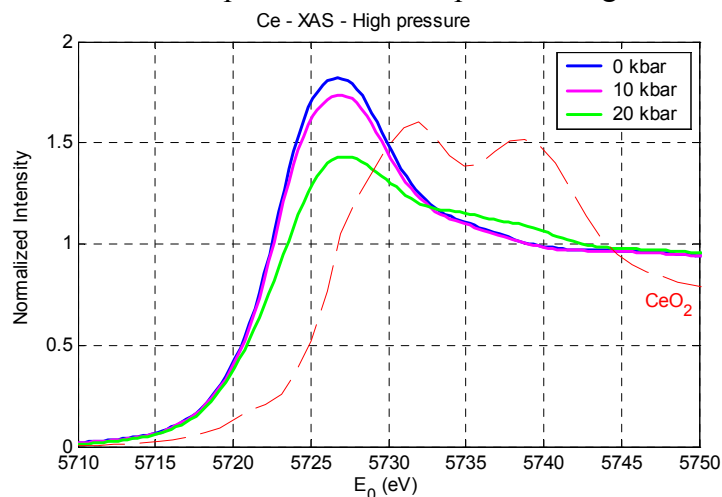


Figure 1 : Ce L_3 absorption spectra under pressure

The absorption spectra are characterized by an intense white line peaking at 5727 eV followed by a weak feature around 5735 eV. Those two structures well-known in Ce are characteristic of the f^1 and f^0 final states (in presence of a $2p$ core hole) [1]. As the pressure is increased, we note a collapse of the white line, while in contrast the f^0 structure gets stronger. In the intricate Ce puzzle though, a major piece is missing: the f^2 part of the Ce mixed-valent electronic configuration. As we demonstrated in a series of recent experiments on Ce-Sc and Ce-Th alloys (see exp. report HE-1454), the f^2 state plays a key role in the γ - α transition for it tightly relates to the f Kondo behavior [2]. The f^2 component is hidden in the XAS spectra but can be revealed by RIXS thanks to the resonant process, specific to this spectroscopic probe.

The RIXS experiment was carried out using our compact spectrometer equipped with a quartz analyzer and a proportional counter. The spectra were measured in transmission geometry, where both incident and emitted x-ray passes through the diamond anvils, at a scattering angle of $\sim 5^\circ$. To optimize transmission, we used a pair of perforated anvils capped with 500 μm -thick diamonds, resulting in a typical count-rate of about 1 cps in the resonant regime. We focus here on the $L_{\alpha 1}$ ($3d_{5/2} \rightarrow 2p_{3/2}$) RIXS spectra obtained by tuning the incident energy in the pre-edge region, where we observed the f^2 contribution in Ce-Sc and Ce-Th. Spectra taken 3.5 eV below the edge are shown on figure 2 on an energy transfer scale. The spectra consist of a clear-cut double structure, which we assign to the presence of the f^2 and f^1 final states. The f^1 / f^2 intensity ratio dramatically changes when Ce transforms from γ to α , ranging from 2.4 (0 kbar) to 1.2 (20 kbar). At high pressure, the two components appear closer by ~ 1 eV compared to the low-pressure phase.

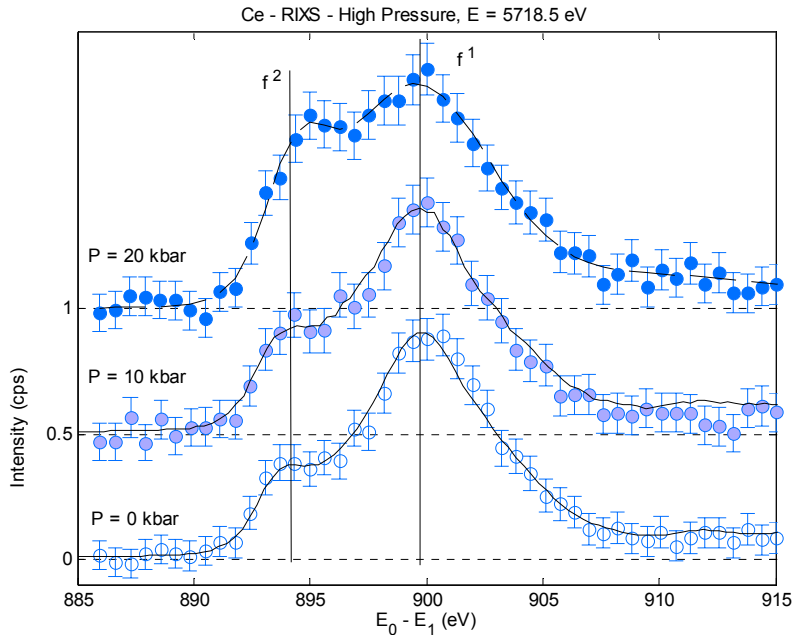


Figure 2 : $L_{\alpha 1}$ RIXS spectra measured in Ce under pressure (blue circles) at an incident energy tuned to the pre-edge region (5718.5 eV). Final state configurations f^2 and f^1 are indicated by vertical solid lines. Spectra showed with black lines are taken from earlier experiments on Ce-Sc alloys (Ref. 1) except for the top one, which results from a fit to the data. Both 0 and 10 kbar spectra refer to the Ce γ phase. The abrupt intensity increase of the f^2 shoulder at 20 kbar denotes the transition to the α phase.

The large change in the f^1 / f^2 intensity ratio ($\sim 50\%$) by far exceeds the mere 20% decrease of the “ f^1 ” white-line observed with pressure, demonstrating that the γ - α transition strongly affects the f^2 final states contribution as well. What is the exact role played by the f^2 electrons? How does this relate to the ground state properties? What do we learn about the mechanisms responsible for the γ - α transition? Here are the few questions that now need answering. Combining in-situ XAS and RIXS certainly provides the most complete picture obtained so far about the electronic properties of Ce under pressure.

[1] B. Lengeler et al., Phys. Rev. B **28**, 2276 (1983)

[2] J.P. Rueff et al, submitted to Phys. Rev. Lett.