ESRF EXPERIMENTAL REPORT
Proposal number: HE-2456
Title: HAXPES investigation of the bulk electronic structures of elemental Ce in its stable γ and α phases

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Beamline: ID16

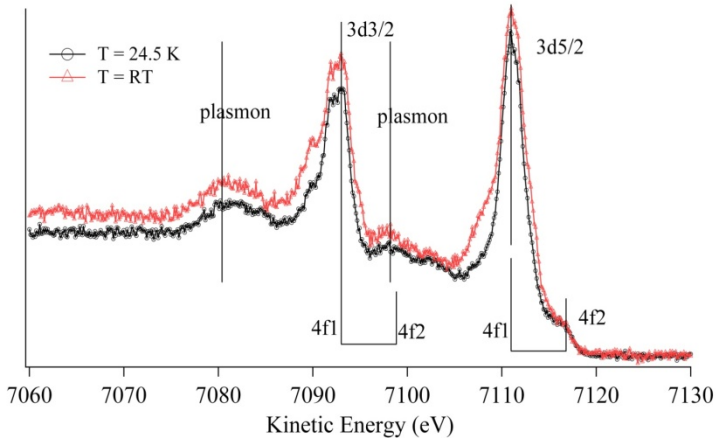
Required shifts: 18

The aim of this experiment was to investigate the bulk electronic structures of elemental Ce in its stable γ phase and α phase. The objective was to characterize the bulk electronic features associated to the f-electronic states by mean of core level and valence band photoemission measurements using Hard X-ray photoemission (HAXPES). Ce plays the role of a model system to investigate the effects of strong electronic correlations, including intermediate valence and unusual magnetic and transport properties. Elemental Ce is an intermediate valence compound which exhibits a reach p,T structural phase diagram, involving different crystalline structures. At ambient conditions the stable phase is a fcc crystalline structure (γ-phase). The isostructural α-phase could be obtained from the γ-phase by low temperature quenching. The transition from the γ to α phase is accompanied by a large volume reduction (about 15%) and a loss of magnetic moment which are the manifestation of subtle interactions between f-orbitals self-consistently embedded in a "sea" of delocalized electrons [Koskenmaki, Rueff]. Several basic questions about this are still being debated; 1- what is the interplay between the electronic structure and the unit cell volume in the γ to α phase transition? 2- what is the role of the hybridization between the strongly localized *f-bands* and the delocalized electrons near the Fermi surface and the γ to α phase transition? These fundamental questions continue to be the subject of experimental investigations [itie, Rueff]. Conventional band theory based on independent particles and extended wave-functions is not suitable to tackle this problem. Many theoretical hypotheses have been advanced to describe the electronic structure changes between the α and γ phases. Among them we may single-out the Mott transition scenario and the Kondo model. More recent theoretical approaches propose a hybrid behaviour in which both phases could be described by strongly correlated 4*f* electrons, but differ in their degree of localization: the occupation number n_f is almost equal to unity in the γ-phase and is reduced in the mixed-valent regime in the α-phase. Information about the transition and more particularly the effects of electron correlation in Ce, is contained not only in n_f , but also in the probability of double occupancy of the f sites [RTMs]. However, despite these theoretical efforts, a widely accepted model is still lacking. The electronic structure of Ce as a function of temperature has been widely studied by means of soft x-ray PES [softPES]. In fact, 4*f* states can be easily identified in photoemission (PE) spectra, due to the fact that the degeneracy of 4*f* electrons in the ground state is removed by different core-hole screening for the different states. This allows a direct estimation of the various *f* electron weights and helps to characterize their degree of hybridization. Unfortunately, the determination of the occupation number n_f and of the Ce valence is still matter of controversy. In fact, the surface sensitivity of EUV and soft x-ray photoemission affects these measurements meant to detect the bulk properties. For these and other reasons in these last years high resolution hard x-ray PES has received an increasing attention and today it has been demonstrated, for example, that with a 6 keV incident photon it is possible to obtain information from layers as depth as150-200 Å with a binding energy resolution of few tens of meV. [Sacchi].

To perform HAXPES measurements we obtained machine time (18 shifts) at the VOLPE end-station of the ID16 beamline at ESRF. We used all time shifts and we obtained high quality HAXPES spectra of the core levels of elemental cerium in its γ phase and α phase. The photon energy was 7912 eV, the energy resolution 200meV and the acquisition time for each spectra was 5 hours. The 4d and 3d core level spectra were taken on a polycrystalline sample of elemental metallic cerium 99.999% pure. The 4d and 3d core level spectra are reported in fig 1 and 2.

The most relevant result was obtained comparing the surface sensitive photoemission core level spectra [softPES] and the HAXPES. The $4f^0$ peak (binding energy 912 eV) results to be absent in the bulk sensitive spectra of the γ to α phase . This indicates that the $4f^0$ peak in the soft PES spectra has a complete surface character. The weight of the f^0 peak provides a semiquantitative measure of $(1-n_f)$.

We found that $n_f = 1$, thus the valence of Ce is 3^+ in the α-γ phases.



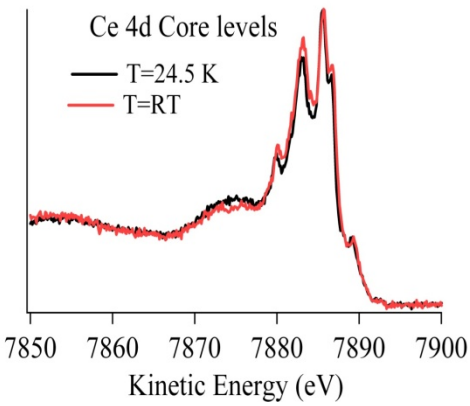


Fig. 1 and Fig. 2

References

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