



Experiment title: **3d level resonant photoemission in CeRh compounds**

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HE-15

Beamline:

BL13

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Shifts:

18

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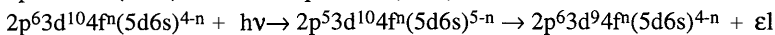
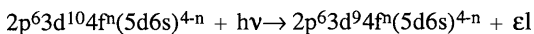
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Report: In many compounds, cerium exhibits unusual physical properties that are connected to its electronic structure: the partial delocalization of the 4f electrons which leads to an intermediate-valent ground state. High energy spectroscopic spectra (mainly XPS and XAS) measured on these compounds exhibit satellites that cannot be explained in a one electron picture. Core level (3d) photoemission results have been described assigning the satellite structures to the relaxation of the 4f electrons in the core hole potential. XPS could then become a technique giving specific information on valence fluctuation in cerium compounds. XAS at the L_3 edge has also been widely used to study intermediate valent materials, since it is less surface sensitive than XPS and does not need ultra high vacuum environment. However, from a theoretical point of view, it is more complicated because the interaction in the final state between the photoelectron and the system cannot be neglected. In order to progress in the understanding of both of these techniques, we have performed resonant 3d photoemission in three different CeRh compounds: Ce_7Rh_3 , where the Ce atoms are purely trivalent (with a $4f^1(5d6s)^3$ electronic configuration), and $CeRh_2$ and $CeRh_3$, where Ce has an intermediate ground state, consisting in a mixing of trivalent and tetravalent ($4f^0(5d6s)^4$) electronic configurations.

We have measured the 3d photoemission of Ce in the three different CeRh compounds with photon energies around the Ce L_3 absorption edge (5734 eV) (Figure 1a). The spectra presented here were obtained at the ESRF, on the ID32 beamline using a Si(111) double-crystal monochromator. The good energy resolution available on this beamline, even at this high energy (better than 1 eV at 5 keV), allowed us to isolate, in the $CeRh_3$ and $CeRh_2$ photoemission spectra, the peaks corresponding to mainly $4f^0$, $4f^1$ and $4f^2$ character of the final state. In Ce_7Rh_3 , the XPS spectrum shows a classical shape, with $3d_{3/2}$ and $3d_{5/2}$ peaks. In this photon energies range the mean free path of the photoelectrons is larger than 50 Å. The surface contribution can be therefore neglected, and it is an important advantage of this very high energy spectroscopy to procure a real probe of Ce bulk atoms.

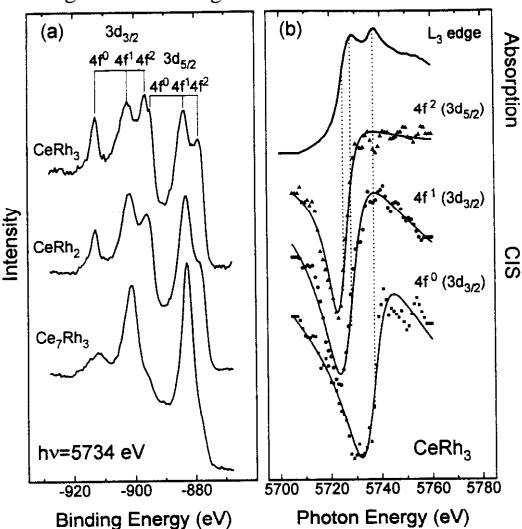
The experiment which we performed consisted in measuring the intensities of the Ce 3d photoemission peaks while sweeping the photon energy across the Ce L_3 absorption edge (CIS: Constant Initial State spectra). Around the L_3 edge, the direct photoemission process interferes with a resonant process (autoionization) which leads to the same final state. The two processes are:



These interferences were described by Fano [1], and can give rise to strong variations of the photoemission cross section for relatively localized electronic states. For Ce_7Rh_3 (where Ce is purely trivalent) the $3d_{3/2}$ and $3d_{5/2}$ CIS spectra display a typical Fano profile, and the two resonances occur at 5728 eV, at the maximum of the Ce absorption white line. For the CeRh_3 mixed valence compound, the CIS spectra were recorded for three lines of the XPS spectrum, due to final states of the Ce atoms with zero, one, or two 4f electrons (labeled $4f^0$, $4f^1$ and $4f^2$). They are reported in Figure 1b together with their fits with a Fano function. The results show different resonance energies for the contributions of the different final states: the photoemission line due to $4f^2$ final state resonates at 5725 eV, slightly before the first structure of the L_3 edge, the $4f^1$ contribution resonates at 5728 eV, on the first bump of the L_3 edge, whereas the $4f^0$ satellite resonates at 5737 eV, on the second bump of the L_3 edge. The results obtained on CeRh_2 , another intermediate valence compound, are similar. So, in the intermediate valent compounds, the position of the resonances allows to assign unambiguously the two main lines in the XAS profile to mainly $2p^5 4f^1$ and $2p^5 4f^0$ final states, and the break in the edge jump to a $2p^5 4f^2$ final state, as it was already suggested [2,3] but still discussed. In the same way, the understanding of the XMCD signal at the cerium L_3 edge is not yet completed. Some authors suggest that an atomiclike picture is most suited, with $4f^0 4f^1$ and $4f^2$ contributions at the same energy positions that we have observed [4].

This is the first observation of resonances for deep core levels, with those observed in other La and Ce compounds [5]. It is the evidence of the existence of coupling between core levels; it proves the interaction between the 3d and 5d6s levels of Ce in the presence of the 2p hole. The questions how this coupling influences the L edge profiles and how it should be taken into account for the theoretical calculations must be asked. The resonances are quite intense, of the order of 30%. These resonances are a probe that, in this energy range, the excitation and decay must be considered in a one step model, they are truly coherent processes.

In this work, high energy resonant photoemission has allowed a better understanding of the absorption edge lines of Ce in mixed-valent compounds. This kind of spectroscopy provides new elements for a global knowledge of the electronic structure in these strongly correlated systems.



We have also performed preliminar resonant Auger measurements on two samples with different valences of Ce : Ce_7Rh_3 and CeRh_3 . The study was done on the $L_3M_{4,5}N_{4,5}$ Ce Auger lines, and the spectra, obtained at different photon energies across the Ce L_3 edge are presented in our new proposal.

A complete paper presenting all these new results has been submitted to Physical Review Letters.

FIG.1 (a) Photoemission spectra recorded on Ce_7Rh_3 , CeRh_2 and CeRh_3 at a photon energy of 5734 eV. (b) Ce L_3 absorption edge (top part), and different CIS spectra of CeRh_3 for three photoemission lines: $3d_{5/2}, 4f^2$ configuration (triangles), $3d_{3/2}, 4f^1$ (circles) and $3d_{3/2}, 4f^0$ (squares). The solid lines are fits with the Fano function, and the vertical dotted lines show the positions of the resonance energies E_0 determined by the fits (respectively 5725 ± 1 eV, 5727 ± 1 eV and 5737 ± 1 eV).

References

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