EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

Experiment Report Form

ESRF	**Experiment title:** **Systematic study of intrinsic/extrinsic loss processes during photoemission**	**Experiment number**: 25-02-616
Beamline: BM25B	**Date of experiment**: from: 30-10-2007 to: 3-11-2007	**Date of report**: August 26, 2008
Shifts: 9	**Local contact(s)**: Juan Rubio-Zuazo	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

* Francisco Yubero (ICMSE, CSIC, Seville, Spain)

* F. Javier Ferrer (ICMSE, CSIC, Seville, Spain)

* M.Carmen López (ICMSE, CSIC, Seville, Spain)

* Germán Castro (ESRF, SpLine)

Report:

Introduction

Upon photoionization of a core electron in a solid, the sudden appearance of the photohole represents a strong perturbation leading to excitation of the weakly bound electrons. These excitations are referred to as *intrinsic* to distinguish them from those that take place during the escape from the surface of the created photoelectrons, that are refered as *extrinsic*.

Several theories have been put forward in the past [1-4] describing this phenomenon. They are either full quantum-mechanical treatments of the photoionization process, taking into account the band structure of the solid as well as the finite lifetime of the photohole [1-3] or semiclassical treatments that focus on the electrodynamic interaction of the photoelectron, the photohole and the medium where the interaction take place in terms of a dielectric response model [4]. The semiclassical models have the great advantage that they can be easily used to actually compare experimental results with theory for any material for which optical data are available.

The appearance of high energy photoemission (HE-PES) opens the possibility of study *intrinsic* and *extrinsic* effects in photoemission in a very wide energy range of photon excitation energies and kinetic energies of the photoelectrons. HE-PES expands the probing depth of photoemission from 3-5 nm when using conventional Mg or Al anodes to 20-30 nm when analysing photoelectron peaks of 10-15 keV kinetic energy.

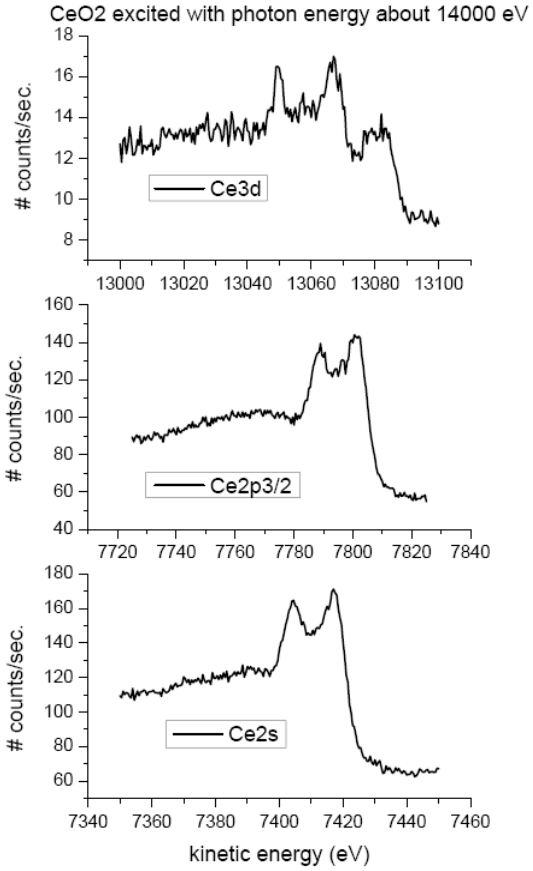
Previous investigations on Al [5], Si [6] and Ge [7] have showed some light on this topic, but they only refer to free-electron-like materials. With the present beamtime we wanted to start the this kind of study in transition metal oxides such us ZrO2, TiO2, CeO2 and Fe2O3. In this context, we planned to make

systematic measurements of several photoelectron peaks of these samples using exciting photon energies in the 6-15 keV and several angles of emission.

Experimental facts

During the first two days of allocated beamtime was possible to make some HE-PES preliminary measurements on a CeO2 thick sample (see figure) that allowed to identify the actual performance of the beamline/experimental station for the planned measurements. Note that there are several circunstances that make this experiment not a trivial task. First the photoionization cross sections of core levels excited with high energy photons (>7 keV) are not well known, that is particularly important for very deep core levels such us Ce2s or Ce2p (for the particular case of a thick CeO2 sample), which are not observed with standard XPS. Second, the experimental set up incorporates a novel CMA electron analyzer (HV-CSA300) implemented at the BM25B beamline, that had not been tested with these kind of samples. Despite these circumstances, we found a good compromise between sensitivity, energy resolution and time needed to adquire a satisfactory HE-PES spectum.to perform the planned experiments. Thus we needed about 24 hours counting time to adquire the three spectra shown in the figure.

In this figure is shown by first time the strong and complex shake up structure characteristic of Ce4+ in CeO2 that appears at the Ce3d, Ce2p and Ce2s emissions (excited with 15 keV photons) as a consequence of the strong hybridation of the Ce4f electrons with the O 2p of the valence band. Their interpretation, as a comparative study with the findings observed in standard XPS is under progress.



Several core levels of a thick CeO2 sample measured with about 14keV photons at the BM25B beamline

Unfortunatly the third day of the running experiment we had an accident during sample transfer to the analysis chamber. This accident forced to cancel the planned experiments, that had to be postponed for another beamtime allocation.

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