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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: 14-5-2008 to: 18-5-2008	**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)

* Pablo Romero (ICMSE, CSIC, Seville, Spain)

* Juan Rubio-Zuazo (ESRF, SpLine)

* 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

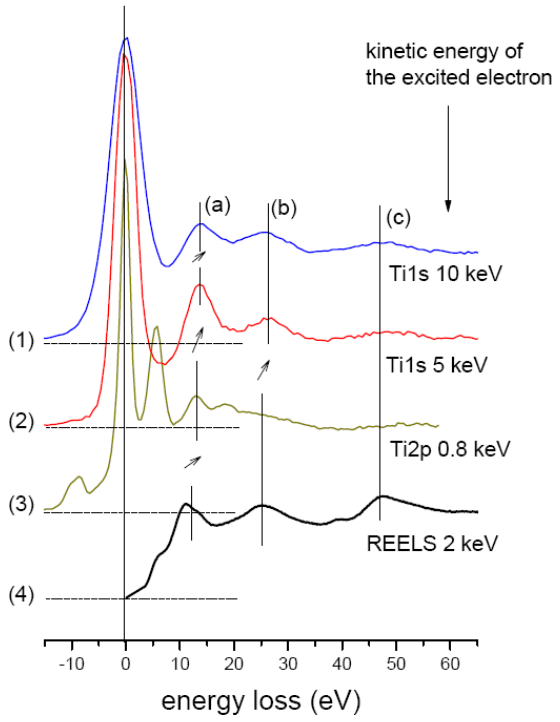
systematic measurements of several photoelectron peaks of these samples using exciting photon energies in the 6-15 keV.

Experimental facts

We have acquired several HE-PES spectra from transition metal oxides such us TiO2, Fe2O3, ZrO2, and CeO2. As an example of the measured spectra the figure shows a comparison of the Ti 1s photoemission line excited with 15 keV (1) and 10 keV (2) photons (adquired in TiO2) together with the Ti 2p line excited with an standard MgKa excitation source (3) and a REELS spectra acquired with 2 keV primary electrons (4) measured in the same material. The spectra have been shifted in order to compare the loss/shake up structure that appears in the low kinetic energy side of the main peak of the spectra

Although a more detailed interpretation of the results is under progress, we can advance the following findings:

- We observe a progresively positive energy shift of the loss features as the kinetic energy of the emitted electron increases. This effect is more pronounce at the bulk plasmon feature (a).
- We observe that the loss structure after the main PES peaks gets better defined as the kinetic energy of the photoelectron increases. This effect is more pronounced in features (b) and (c) that are related to transitions from the O2p and Ti 3p to the conduction band, respectively.



Several spectra acquired from a TiO2 sample: (1) HE-PES Ti 1s excited with 15 keV photons; (2) HE-PES Ti 1s excited with 10 keV photons; (3) standard PES Ti 2p excited with a MgKa source; (4) Loss structure acquired in a REELS experiment

It is also worth mentioning that in order to quantify the intrinsic/extrinsic contribution to each measured spectra, we have started to simulate HE-PES spectra according to the dielectric model described in ref.[4]. As a preliminary result it is found that the loss structure behind a photoelectron peak gets sharper when the kinetic energy of the photoelectrons is incresed (in agreement with the experimental findings). It is also found that about 15-20% of the photoemitted intensity is located out of the main peak (located at zero energy loss in the figure). This result may have consequences in terms of experimental evaluation of photoionization cross section and quantification of amount of material by this technique, with this type of samples.

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