EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

ESRF

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application:**

http://193.49.43.2:8080/smis/servlet/UserUtils?start

Reports supporting requests for additional beam time

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title: Valence Band Photoemisiion Spectroscopy in the 10 keV range on High Tc Superconductors**	**Experiment number**: HE1423
Beamline: ID32	**Date of experiment**: from: 25 June 2003 to: 1 July 2003	**Date of report**:
Shifts: 18	**Local contact(s)**: Bruce C.C. Cowie	*Received at ESRF:*

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Report:

Photoelectron spectroscopy (PES) employing synchrotron X-radiation is a newly emerging field at high brilliance third generation synchrotron X-ray sources. An early landmark experiment by I. Lindau, P. Pianetta, S. Doniach, and W. Spicer [Nature 250 (1974) 214] employing hard X-rays had not been followed up for many years because of insufficient X-ray intensity at first and second generation synchrotron radiation sources. Much of the recently published work in this field is related to core levels. However, we believe that valence band spectroscopy will be of even higher attractiveness in the future. First very encouraging results had been obtained up to 6 keV with commercial spectrometers by K. Kobayashi et al., [Appl. Phys Lett. 83 (2003) 1005] and Y. Takata et al. [Appl. Phys. Lett., in press]. In the present experiment we explored the energy region beyond, demonstrate the feasibility of such studies at third generation synchrotron radiation sources, and additionally determine the very first photoemission cross sections in the hard X-ray range.

In a pragmatic approach, we modified the standard, commercial multi-channel hemispherical electron analyzer at ID32 by adding an additional retarding lens. Using this new experimental set-up, we succeeded to measure the valence and conduction band of Au and graphite, as well as the valence band photoememission from $YBa_2Cu_3O_7$ (YBCO) crystals up to 14.5 keV. Furthermore, as a very useful byproduct we could determine the Au 6s, 5d, 5p, 4f and 5s cross sections between 5 and 14.5keV by referring them to the experimentally well established total cross section of carbon, since this is to 95% due to C1s excitations. With the necessary corrections for angular anisotropy effects our data are of an accuracy such that it will be possible to use the results for testing and improving theoretical models. The achieved count rates show that valence band investigations with high resolution are feasible in this energy range.

The supplementary retarding lens imaged photoelectrons from the sample onto the focal point of the Perkin Elmer PHI model 10-360 hemispherical analyzer equipped with a 16-channel detection system. The electrons emerging from the sample biased up to +10 kV relative to ground are handed over at ground potential to the PHI "Omega" lens (operational range of electron energies up to 4.8 keV). The supplementary retarding lens was mounted in a μ-metal shielding cylinder, which was attached to the PHI Omega lens as. The Synchrotron X-radiation entered through a hole in the lens and the shield, which was small enough to avoid field distortions. The manipulator head accommodated 10x10 mm sample holders, which could be transferred without breaking vacuum. The head was electrically insulated by a sapphire rod which could be connected to a liquid helium cryostat if desired. For better access to the sample, e.g. for transfer and cleaving, the whole analyzer arrangement could be retracted.

Experiments were carried out at the ID32 beam line at the ESRF, using unfocused radiation and a Si(111) monochromator ($\Delta E/E = 1.3\ 10^{-4}$). For some measurements at a photon energy of 8.0 keV additionally a Si(444) post-monochromator ($\Delta E = 40$ meV) was used. We performed a variety of measurements on Au, graphite, and $YBa_2Cu_3O_7$ (YBCO) up to 14.5 keV.

The Fermi edge of Au measured at 8 keV photon energy is shown in Fig. 1 and reveals a width of 241 meV. Thus, the natural width of the Fermi function at room temperature of 102 meV is broadened by 218 meV instrumental resolution. In principle, the instrumental resolution was determined by 40 meV X-ray energy bandwidth, a nominal resolution of the hemispherical analyzer of 85 meV, and not more than 80 meV by ripple and drift of the high voltage power supply for our retarding lens. This should have yielded an instrumental resolution of 123 eV. Most probable sources for the additional broadening are a non-nominal performance of the PHI analyzer and noise pick-up from the laboratory environment. However, given the inherent simplicity of the set-up, we consider the achieved energy resolution of $\Delta E/E = 2.7 \times 10^{-5}$, i.e., a resolving power of 37 000 already very satifactory.

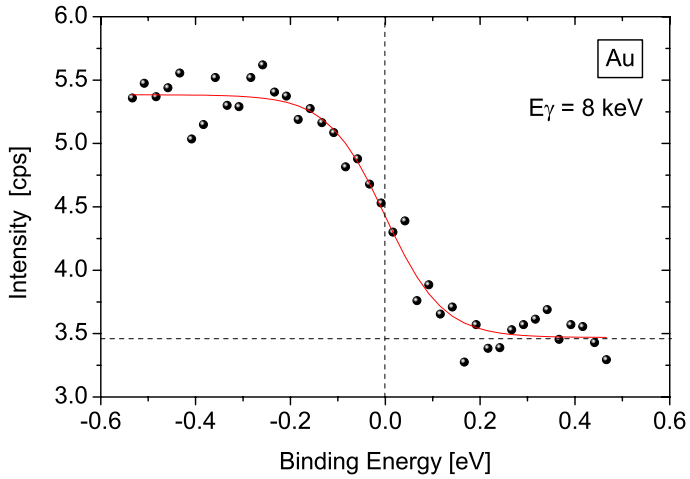

Fig. 1

The high temperature superconductor YBCO is a material of strong current interest, but it is well known for its reactive intrinsic surface being stable enough to allow PES or STM investigations, which are inherently very surface sensitive, under UHV conditions at temperatures below 40 K only. In our case, a single crystal was cleaved at ambient atmosphere immediately before it was introduced into the UHV chamber. The photon energy used was 13.5 keV with a bandpass of 1.8 eV and an electron analyzer resolution of nominally 700 meV. A survey spectrum of shallow core levels of YBCO is presented in Fig. 2a. In addition to the main O 1s peak at 528.3 eV binding energy, a smaller component at 531.2 eV can be distinguished in the O 1s spectrum shown in Fig 2b. This chemically shifted component is indicative of a chemically modified sample surface

over a depth of about 2 nm. This reveals that for such delicate samples, if prepared ex situ, despite of the mean free path of more than 10 nm for electrons at 13 keV, the modified surface, degraded over a depth of more than 2 nm contributes significantly to the spectrum. Still, at this high energy we can largly probe the underlying bulk. Howevr, this example shows also that employing hard X-ray spectroscopy will not necessarily exempt from conventionally preparing clean surfaces. In Fig. 2c., the valence band spectrum of YBCO is shown, recorded with the same instrumental parameters.

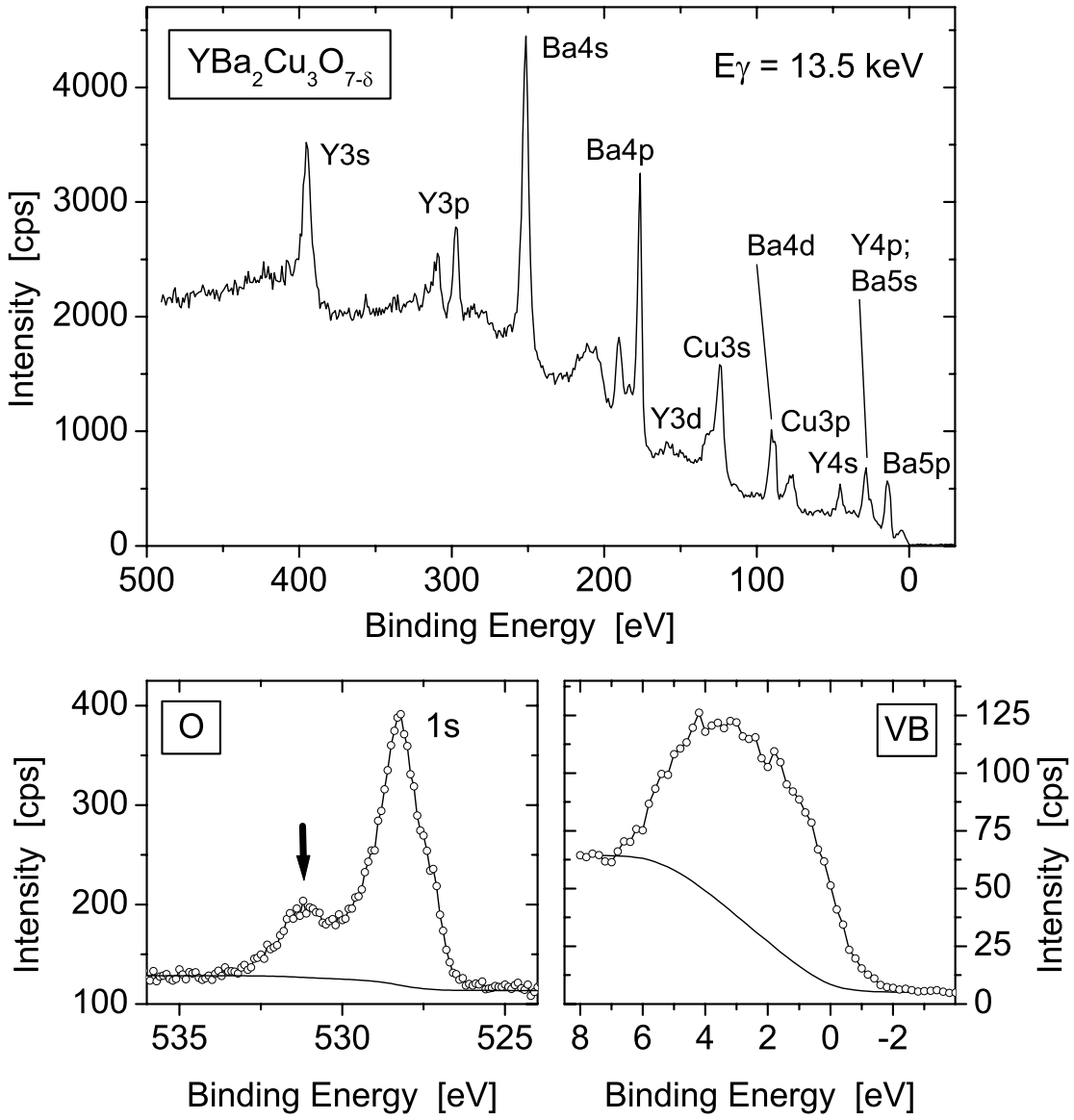

Fig. 2

In order to determine Au sub-shell cross sections accurately, we used the C 1s yield from a highly oriented pyrolitic graphite (HOPG) sample as a reference such that all geometrical factors cancel out. Cross sections for sub-shell excitations in Au were determined. We found that the cross section for valence states in Au is higher by approximately a factor of two than given by theoretical relativistic Hartree Slater central potential calculations. The 6s electrons, which form the conduction band, have a cross section which is almost one order of magnitude higher than the one calculated by atomic theory.