Available online at www.sciencedirect.com
SCIENCE DIRECT®
ELSEVIER
Nuclear Instruments and Methods in Physics Research A 547 (2005) 136–150
NUCLEAR INSTRUMENTS & METHODS IN PHYSICS RESEARCH Section A
www.elsevier.com/locate/nima

Bulk sensitive photoelectron spectroscopy with soft and hard X-rays: Soft X-ray ARPES toward high resolution HAXPES

A. Yamasaki[a,*], A. Sekiyama[a], S. Imada[a], M. Tsunekawa[a], A. Higashiya[b], A. Shigemoto[a], S. Suga[a]

[a]*Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan*
[b]*SPring-8 / RIKEN 1-1-1 Kouto, Mikazuki, Sayo, Hyogo 679-5148, Japan*

Available online 8 June 2005

Abstract

Soft and hard X-ray photoelectron spectroscopy (SX- and HAXPES) has been performed for strongly correlated transition-metal oxides and rare-earth compounds in order to reveal the bulk electronic structures and/or the bulk Fermi surfaces. The variation of the bulk V 3*d* spectrum for $Sr_{1-x}Ca_xVO_3$ depending on x and the feature of the Fermi surfaces for $Sr_{2-x}Ca_xRuO_4$ is consistent with other bulk-sensitive measurements and band structure calculations, respectively. It has been demonstrated for rare-earth compounds that the application of the HAXPES enables us to obtain more reliable information on the bulk electronic structures and valences.

PACS: 79.60.i; 71.20.Be; 71.20.Eh; 71.27.+a

Keywords: Photoelectron spectroscopy; Strongly correlated electron system; Soft X-ray; Hard X-ray; Bulk sensitive

1. Introduction

It has been demonstrated that high-resolution bulk-sensitive photoelectron spectroscopy with use of the soft X-ray (SXPES) can reveal bulk electronic states [1]. The bulk sensitivity arises from the long mean free paths of the high-energy photoelectrons. Bulk-sensitive measurements are crucial in the study of strongly correlated electron systems since the electron correlation effect is very important and essential to discuss their physics, and is often different between at the surface and in the bulk [1–3]. Angle-resolved photoelectron spectroscopy (ARPES) with high resolutions in energy and momentum, which has been realized at low-energy excitation ($h\nu = 15$–150 eV), has been extensively performed in order to investigate the electronic state, quasi-particle dispersions, and Fermi surfaces of strongly correlated electron systems in the last two decades [4–6]. However, it is known that low-energy

*Tel.: +81 66 850 6422; fax: +81 66 850 6421.
E-mail address: yamasaki@decima.mp.es.osaka-u.ac.jp (A. Yamasaki).

0168-9002/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.nima.2005.05.019

photoelectron spectroscopy is surface sensitive and often provides spectral shapes that are not consistent with bulk electronic structures in strongly correlated transition-metal and rare-earth compounds [1,6–8]. On the other hand, high-energy ($h\nu \geqslant 400$ eV) ARPES has been employed as a tool for studying photoelectron diffraction effects for a long time. In order to investigate the bulk quasi-particle dispersions as well as the Fermi surfaces of solids by using high-energy ARPES, high-resolution and high photon-flux soft X-ray light sources and a high-resolution (in both energy and angle) spectrometer are required [9,10]. Such works have been performed, being stimulated by pioneering high-energy ARPES studies [11,12].

Meanwhile, hard X-ray photoelectron spectroscopy (HAXPES) has recently attracted much attention for investigating the electronic structures of transition-metal and rare-earth compounds more bulk-sensitively [13–15]. The HAXPES has a longer probing depth than the SXPES due to the increase of the mean free path of photoelectrons, and has shown to be rather insensitive to surface contamination. However, HAXPES needs the high photon flux supplied by third generation synchrotrons and high performance electron analyzers to detect weak signals because the photoionization cross-sections drop rapidly at high photon energies (*hv*s) [16]. These severe conditions have hindered this technique until recently.

There are thousands of publications accumulated for studies of the electronic structure of strongly correlated electron systems with low-energy light sources. Most of them may not necessarily clarify the genuine bulk electronic structures because of the specific surface sensitivity. In this article, we report on high-resolution angle-integrated and/or angle-resolved PES for $Sr_{1-x}Ca_xVO_3$, $Sr_{2-x}Ca_xRuO_4$, $PrFe_4P_{12}$, and Sm_4As_3 performed with use of the soft and hard X-rays in order to investigate the *more bulk-sensitive* electronic structures.

2. Experimental

2.1. Transition metal oxides

The soft X-ray angle-integrated and angle-resolved photoelectron spectra were measured at the twin-helical undulator soft X-ray ($h\nu = 0.22$–2 keV) beamline BL25SU in SPring-8 [17] by using a GAMMADATA-SCIENTA SES-200 spectrometer. For the measurement of $Sr_{1-x}Ca_xVO_3$, single crystals of $SrVO_3$ and $Sr_{0.5}Ca_{0.5}VO_3$, and polycrystalline $CaVO_3$ were employed. The overall energy resolution for the angle-integrated spectra of $Sr_{1-x}Ca_xVO_3$ was set to about 140 and 80 meV at the excitation photon energies of $h\nu = 900$ and 275 eV, respectively. These results were compared with the low-energy PES spectra taken at $h\nu = 40.8$ and 21.2 eV by using a He discharge lamp, which were measured by using a VG CLAM4 spectrometer in Osaka University. The energy resolution was set to 50–80 meV. For the soft X-ray ARPES of $Sr_{2-x}Ca_xRuO_4$ measured at $h\nu = 700$ eV, single crystals of Sr_2RuO_4 ($x = 0$) and $Sr_{1.8}Ca_{0.2}RuO_4$ ($x = 0.2$) were used. The energy resolution was set to 120–200 meV for the measurements of $Sr_{2-x}Ca_xRuO_4$. The samples were cooled to 20 K for all the measurements. Clean surfaces were obtained by fracturing or cleaving the samples *in situ* at measuring temperatures and the surface cleanliness was confirmed before and after the measurements. The layered oxides $Sr_{2-x}Ca_xRuO_4$ were easily cleaved along the (0 0 1) plane. The base pressure was about 4×10^{-8} Pa.

2.2. Rare-earth compounds

For the SX-and HAXPES for Pr compounds, single crystals of $PrFe_4P_{12}$, $PrRu_4Sb_{12}$, $PrOs_4Sb_{12}$, and $PrSn_3$ in addition to a polycrystal of $PrRu_4P_{12}$ were fractured and a polycrystalline Pr metal was scraped in situ in ultra-high vacuum (UHV) for the resonant-PES (RPES) at the beamline BL25SU of SPring-8 and for Pr 3d core-level PES at the beamline ID32 of the European Synchrotron Radiation Facility (ESRF). The total energy resolutions (the full width at half maximum (FWHM, Γ)) of RPES and core-level PES were set to ~80 and ~500 meV, respectively.

Single crystals of Sm_4As_3 were fractured in situ in UHV ($\sim2\times10^{-8}$ Pa) for the SX and HAX valence band (VB) PESs at the BL25SU of SPring-8 ($h\nu = 220$–1750 eV) and at the HAX beamline ID32 of ESRF ($h\nu = 2445$ and 5445 eV). The total energy resolutions (ΔE) of the