Journal of Electron Spectroscopy and Related Phenomena 190 (2013) 242–248

Contents lists available at ScienceDirect

Journal of Electron Spectroscopy and Related Phenomena

journal homepage: www.elsevier.com/locate/elspec

Hard X-ray photoelectron spectroscopy: A few recent applications

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ARTICLE INFO

Article history:
Available online 23 January 2013

Keywords:
Recoil effect in photoelectrons
3D transition metal compounds
Cluster model calculation

ABSTRACT

In this report, we discuss a few recent applications of hard X-ray photoelectron spectroscopy (HAXPES) carried out at the RIKEN beamline BL29XU in SPring-8. We first provide a brief description of the salient features of the instrument in operation at BL29 XU in SPring-8. HAXPES studies on the recoil effect of photoelectrons in core levels and valence band states are presented. The experiments show remarkable consistency with theoretical results and indicate the role of phonon excitations in the recoil effect of photoelectrons. We then overview HAXPES applied to the study of a series of 3*d* transition metal (TM) compounds. The HAXPES experimental results often show an additional well-screened feature in bulk sensitive electronic structure of strongly correlated compounds compared to surface sensitive spectra. The extended cluster model developed by us for explaining this well-screened feature is validated for a series of TM compounds. These results show that HAXPES is a valuable tool for the study of doping and temperature dependent electronic structure of solids with tremendous potential for future activities.

1. Introduction

Hard X-ray photoelectron spectroscopy (HAXPES) has undergone a major revival in the last ten years. Early photoelectron spectroscopy (PES) studies were also actually hard X-ray based experiments using laboratory based Mo $K\alpha$ ($h\nu = 17.479$ keV), Cr $K\alpha$ ($h\nu = 5.417$ keV) or Cu $K\alpha$ ($h\nu = 8.047$ keV) X-ray sources [1–3]. While the incident photon flux as well as the detection efficiency did not allow valence band studies, pioneering core level studies could be carried out nicely. These studies played an important role in initiating the applications of PES such as atomic species identification and chemical valence state fingerprinting. Subsequently, the laboratory based HAXPES went out of vogue, mainly due to requirements of higher energy resolution which could be attained with lower energy soft X-ray (SX) laboratory sources such as the Mg $K\alpha$ ($h\nu = 1253.6$ eV) and Al $K\alpha$ ($h\nu = 1486.7$ eV) sources [4]. However, the improvements in resolution by reducing the incident energy also meant higher surface sensitivity of the technique. The HAXPES revival of the last ten years is mainly associated with a so-to-say, going back to the higher incident photon energies but with the important difference that laboratory sources were replaced with synchrotron radiation sources. This situation allowed us the energy resolution as well as the higher photon fluxes required to do core level and valence band studies with high-resolution and high-throughput. Today, several synchrotrons in the world have established HAXPES end-stations and this has already resulted in important results and directions [5–22] which could not have been possible in laboratory measurements.

In this report, we describe the salient features of the instrument developed by us at RIKEN beamline BL29XU in SPring-8. We then discuss typical examples of HAXPES applications carried out by us on: (i) the recoil effect of photoelectrons in solids, and (ii) the electronic structure of strongly correlated transition metal (TM) compounds from core level as well as valence band studies. The HAXPES experimental results often show an additional well-screened feature in the bulk sensitive core level states of strongly correlated compounds compared to surface sensitive measurements. We have developed an extended cluster model for explaining the well-screened feature and this model is validated for a series of TM compounds. HAXPES can today be considered to be a fairly standard and valuable tool for the study of the intrinsic electronic structure of solids.

2. Experimental

The HAXPES instrument development at BL 29XU in SPring-8 started in 2001. The main aim was to achieve high-energy resolution and throughput which would allow us to do valence band studies of solids at about 6–8 keV kinetic energy of the photoelectrons. One of the main features of the instrument was the use of a grazing incidence geometry [23], with the lens axis placed perpendicular to the incident X-ray beam with an incidence angle relative to the sample surface being set to typically 5°. The adopted configuration with a linearly polarized X-ray beam results in the lens

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[1] Passed away during this work on October 28, 2011. MT and AC wish to dedicate this article to his memory.

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http://dx.doi.org/10.1016/j.elspec.2013.01.005

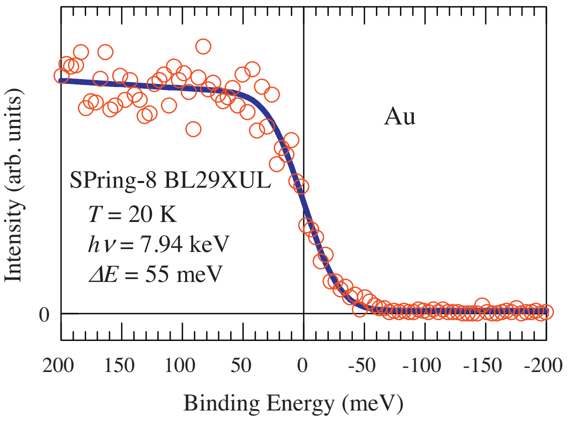

Fig. 1. The Fermi edge of gold measured at $T = 20$ K for determining the spectrometer resolution. Comparison with a fit to the Fermi-Dirac function convoluted with a Gaussian function gives an energy resolution of 55 meV FWHM.

axis being parallel to the polarization vector of the X-rays. This geometry helps us to gain photoelectron intensity, based on the assumption that the known behavior of angular distribution of photoelectrons from atoms is also valid for solids. It is well-known that the angular distribution of photoelectrons emitted from free atoms show a positive asymmetry parameter β with a maximum in the direction parallel to the polarization vector, which is expected to result in higher signal intensity of emitted photoelectrons in the experimental configuration used by us.

Based on the above considerations, we have developed a HAXPES apparatus at undulator beamline BL29XU in SPring-8 [23]. The available photon flux at the beamline is about 1×10^{11} photons/sec with a spot size of 55 (vertical) × 35 (horizontal) μm^2. The energy bandwidth of the incident X-rays at ~8 keV is nearly 40 meV (FWHM). The details of the X-ray optics has been described in an earlier study [24]. For the electron energy analyzer, we have used a modified SES R4000-10KV (VG-Scienta) analyzer. The system consists of a main chamber, a preparation chamber and a fast entry chamber. The base pressure of the main and preparation chambers is about 2×10^{-8} Pa. The sample preparation chamber is fitted with a cleaver for sample cleaving. The sample manipulator consists of a motorized XYZΘ stage with a closed cycle liquid helium cryostat which can cool the sample down to 20 K. As is usual, the resolution is obtained as the value of the Gaussain FWHM convoluted with the Fermi Dirac function at a specific temperature, which matches the measured Fermi edge spectrum of a reference metal. Fig. 1 shows the Fermi edge of gold measured at 20 K with the highest energy resolution of our spectrometer. The fit to the Fermi edge, shown as a line superimposed on the data, gives an energy resolution of 55 meV at a kinetic energy of 7.94 keV for the Fermi edge of gold measured at 20 K. In the following, we discuss a few applications of HAXPES carried out with this spectrometer.

3. Recoil effect in photoelectrons

The recoil effect is a very basic process associated with the law of conservation of momentum. It was predicted very early on that the photoelectrons emitted from an atom should also undergo the recoil effect [25], arising from the recoil energy ΔE imparted to an atom of mass M, when a photoelectron of mass m is emitted from an atom. Based on a simple picture of an atom at rest in vacuum, if the emitted photoelectron has a kinetic energy E_K, the recoil energy is estimated to be

$$\Delta E = E_K \left(\frac{m}{M} \right) \tag{1}$$

This recoil energy ΔE should show up as an apparent increase of the binding energy (BE) of the photoelectron emitted from an atom. For a solid, the recoil energy can be expected to be absorbed by the phonon bath, and thereby result in the excitation of phonons. HAXPES experiments were carried out on graphite to check for the recoil effect. The C 1*s* core level of graphite was measured in normal emission using several photon energies ($h\nu$ = 340 eV, 870 eV, 5950 eV and 7940 eV) and the experimental data are shown in Fig. 2(a). The C 1*s* spectrum at $h\nu = 870$ eV shifts first to lower BE compared to the $h\nu = 340$ eV spectrum. This is known to be due to a surface component occurring at a higher BE compared to a bulk component at lower BE. This change does not reflect the recoil effect. On increasing the energies to hard X-rays ($h\nu = 5950$ eV and 7940 eV), the C 1*s* BEs shift to higher values again and this is due to the recoil effect. Using Eq. (1), the calculated value of ΔE is 360 meV for $h\nu = 7940$ eV in close agreement with the experimental shift of 340 meV. Theoretical calculations of the recoil effect were carried out in the adiabatic approximation, taking into account an anisotropic Debye model which is known to be valid for explaining the phonon density of states of graphite [26]. The calculated spectra for normal emission are shown in Fig. 2(b) and they reproduce the experimental shift and shape of the core level spectra, including the asymmetric line shape on the high BE side. Further, it could be shown that the emission angle dependence from a shallow angle (30° from grazing incidence) to nearly normal emission (85°) also showed a good correspondence between experiment and theory for the shape of the core level spectra [26]. These results showed the recoil effect of photoelectrons in the C 1*s* core level spectra of graphite.

In a subsequent study, the role of recoil was investigated for the electrons constituting the Fermi edge of elemental metals

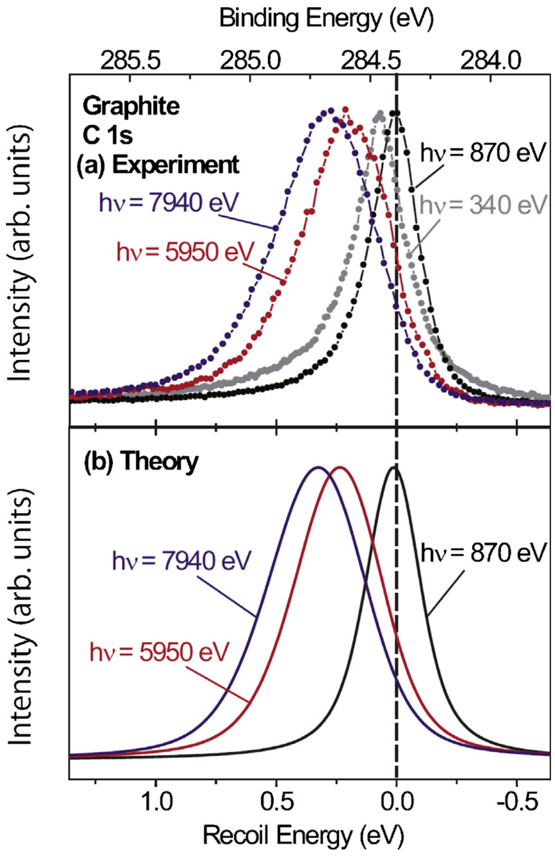

Fig. 2. (a) Photon energy dependence ($h\nu$ = 340 eV, 870 eV, 5950 eV and 7940 eV) of the normal emission C 1*s* core level spectra of graphite. (b) Theoretical spectra obtained by taking into account the recoil effect in a Debye model shows a very good match to the experimental data [26].