Journal of Electron Spectroscopy and Related Phenomena 208 (2016) 100–104

Contents lists available at ScienceDirect

Journal of Electron Spectroscopy and Related Phenomena

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

High-energy photoemission spectroscopy for investigating bulk electronic structures of strongly correlated systems

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ARTICLE INFO

Article history:
Received 13 July 2015
Received in revised form 4 February 2016
Accepted 19 February 2016
Available online 28 February 2016

Keywords:
Soft and hard X-ray photoemission
Synchrotron radiation
Linear dichroism
Electronic structure
Strongly correlated electron systems

ABSTRACT

Progress of high-energy photoemission spectroscopy for investigating the bulk electronic structures of strongly correlated electron systems is reviewed. High-resolution soft X-ray photoemission has opened the door for revealing the bulk strongly correlated spectral functions overcoming the surface contributions. More bulk-sensitive hard X-ray photoemission spectroscopy (HAXPES) enables us to study the electronic structure with negligible surface contribution. The recent development of the polarization-dependent HAXPES is also described in this short review.

1. Introduction

Photoemission spectroscopy of solids is often considered to be a very surface-sensitive probe of electronic states, which are often deviated substantially from the bulk electronic structure, as a consequence of the photoelectron inelastic mean free path. On the other hand, valence-band photoemission has been recognized as a unique tool for directly probing the one-particle spectral function or the imaginary part of the retarded Green's function, which is important for investigating many-body problems in strongly correlated electron systems [1,2]. Probing the bulk electronic structure of the strongly correlated materials by photoemission has thus been a worthwhile challenge. Within these two decades, photoemission techniques have been much improved by virtue of utilization of high-brilliance undulator radiations and/or an UV laser, overcoming the surface sensitivity.

As widely known, the photoelectron inelastic mean free path as a function of kinetic energy in solids exhibits a minimum at kinetic energies of 20–100 eV [1–7], corresponding VUV excitations, as schematically shown in Fig. 1. Note that this photoelectron kinetic energy would deviate from that in vacuum, as directly detected in the actual photoemission measurements. Of course the difference in kinetic energy of photoelectrons between vacuum and solids is negligibly small when the excitation energy is higher than several tens eV. Therefore, one way for improving the photoemission as a bulk-sensitive probe is clearly to go to high-energy excitations with fairly keeping the overall energy resolution. Here, a brief review of the photoemission study of the strongly correlated electron systems concerning the bulk and surface contributions in the spectra is described. In particular, improvements in high-energy-excitation photoemission within a couple of decades, which are mainly focused on hard X-ray photoemission (HAXPES) [8–30], are reviewed.

2. Probing bulk electronic structure before HAXPES

Instrumental photoelectron energy resolutions for solids have been rapidly improved after the discovery of so-called high-temperature superconducting cuprates for observing their momentum-dependent superconducting gaps [31]. At the same time, detailed investigations of the electronic structures of strongly correlated transition metal oxides with locally similar structures with those for the cuprates have been extensively performed [32,33]. In general, the strongly correlated electronic states are much influenced by U/W, where U denotes the on-site Coulomb repulsion energy and W stands for the strongly correlated bandwidth. Among them, "unusual" temperature dependence of the valence-band photoemission spectra by using a He discharge lamp

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http://dx.doi.org/10.1016/j.elspec.2016.02.001
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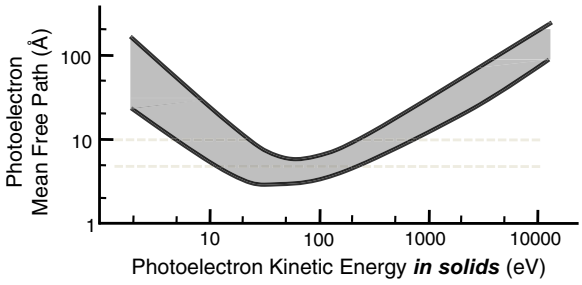

Fig. 1. Schematically drawn photoelectron mean free path as a function of its kinetic energy in solids on the basis of so far reported many literatures.

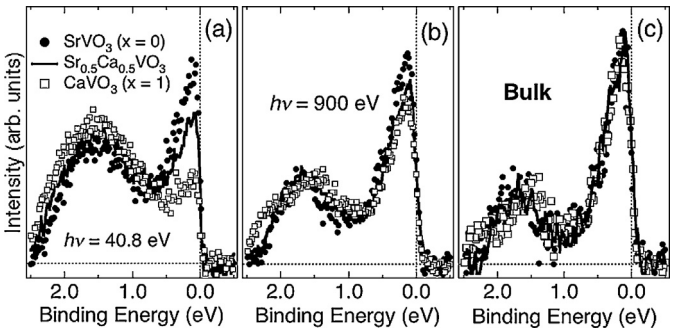

Fig. 2. (a) V 3d angle-integrated photoemission spectra of $Sr_{1-x}Ca_xVO_3$ measured at $h\nu = 40.8$ eV. (b) Same as (a), but measured at $h\nu = 900$ eV. (c) Bulk V 3d photoemission spectra deconvoluted from the spectra measured at $h\nu = 275$ and 900 eV. The bulk contribution is then estimated as ~64% (<30%) for the spectrum at $h\nu = 900$ (40.8) eV.

has been reported by Sarma et al. [34]. On the other hand, a serious difference in the strongly correlated electronic states between bulk and surface has been early recognized for Yb metal [35] and compounds [36–38]. High-resolution valence-band photoemission spectra at $h\nu \sim 100$ eV have been successfully deconvoluted into narrow bulk Yb 4f peaks and broad surface/subsurface 4f structures [37]. For Ce compounds, remarkable differences in the 4f spectral functions between the surface-sensitive 4d–4f ($h\nu \sim 120$ eV) and relatively bulk-sensitive 3d–4f ($h\nu \sim 880$ eV) have been pointed out [39–41]. Maiti, Mahadevan and Sarma [42] have shown that the strongly correlated 3d spectral functions have been markedly different from the spectra measured at the low energy excitation for a doped Mott insulator $La_{1-x}Ca_xVO_3$.

The door of the bulk-sensitive high-energy-excitation photoemission has been opened by the successful high-resolution Ce 3d–4f resonance photoemission studies performed at BL25SU in SPring-8 [43], where the overall energy resolution of ~100 meV for the photoemission measurements has been achieved at the excitation energies of ~1000 eV. Such a high-resolution soft X-ray photoemission has been feasible owing to the combination of the varied-line-spacing plane monochromater and the twin-helical undulator in the third-generation synchrotron radiation facility [44]. Then, many rare-earth (Ce, Pr and Yb) bulk 4f spectral functions have been clarified by the 3d–4f resonance or non-resonance high-resolution photoemission [43,45–50].

The different electronic structures of the three-dimensional strongly correlated electron systems between bulk and surface originate mainly from difference in W, since the nearest-neighbour coordination number of hopping paths is significantly reduced in the surface. Therefore, it has been natural to consider that the bulk spectral functions of the transition metal oxides would be different from those so far reported by low-energy excitation photoemission. Actually, the bulk 3d spectral functions have been re-examined for metallic $Sr_{1-x}Ca_xVO_3$ at BL25SU in SPring-8 [51] although Maiti et al. has reported the photon energy dependence of the spectra [52]. Fig. 2 shows the photon energy-dependent V 3d spectra among $x = 0$, 0.5 and 1 as well as the extracted bulk 3d spectral functions. The photoemission spectra at $h\nu = 275$ (not shown here) and 900 eV were measured by using a GAMMADATA-SCIENTA SES-200 spectrometer whereas the data at $h\nu = 40.8$ eV (He II) were recorded by using a VG CLAM4 spectrometer in Osaka University. Clean surfaces were obtained by fracturing the single-crystalline $SrVO_3$ and $Sr_{0.5}Ca_{0.5}VO_3$, and polycrystalline $CaVO_3$ in situ at the measuring temperature of 20 K. In all spectra, the peak seen near the Fermi level (E_F) and the broad peak centred at about 1.6 eV are corresponding to the quasi-particle (QP) band crossing E_F and lower Hubbard band representing the localized 3d character, respectively. On going from $CaVO_3$ to $SrVO_3$, the QP band is clearly enhanced in the low-energy PES spectra at $h\nu = 40.8$ eV as shown in Fig. 2(a). This tendency is consistent with the previous low-energy PES studies [53,54]. However, this spectral difference among the compounds becomes noticeably smaller in the spectra measured at $h\nu = 900$ eV in Fig. 2(b). The extracted bulk 3d spectral functions as shown in Fig. 2(c), obtained from the data $h\nu = 275$ and 900 eV, are almost equivalent among the three compounds, in contrast to the so far reported previous photoemission spectra. This is consistent with the thermodynamic properties [55] while the considerable × dependence of the electronic state originates from the surface region. This result has shown the power of the high-energy-excitation photoemission for revealing the bulk electronic structure of the strongly correlated electron systems.

3. Hard X-ray photoemission spectroscopy (HAXPES)

As shown in Fig. 2(b) and (c), there are quantitative differences between the spectra at $h\nu = 900$ eV and the "bulk" spectral functions, which are due to the surface contributions (about 30%) even in the soft X-ray excited photoemission spectra. Therefore, it is natural to go to a higher photon-energy excitation photoemission called as HAXPES, which gives a spectrum more highly reflecting the bulk electronic structure. In 2000s, several HAXPES end-stations have been commissioned and started for experiments [8–21]. For a crystal monochromator utilizing the Bragg reflections, the resolving power $\Delta\lambda/\lambda$ (λ: wavelength of the excitation light) is given by

$$\frac{\Delta\lambda}{\lambda} \simeq \sqrt{\Delta\omega^2 + \Delta\theta^2}\cot\theta_B, \quad (1)$$

where θ_B is the Bragg angle and $\Delta\omega$ stands for the width of the rocking curve of the diffraction depending on θ_B and the structure factor of the crystal whereas $\Delta\theta$ is the divergence angle of the incident beam [2]. Therefore, low-emittance synchrotron radiations with smaller $\Delta\theta$ are preferable for effective high-resolution HAXPES measurements. The actually obtained resolving power with enough high throughput for HAXPES by using a Si channel-cut crystal is on the order of 10^{-5}–10^{-6} at $h\nu = 6$–8 keV corresponding the photon energy resolution of ~100 meV. At BL19LXU of SPring-8 with a long (25-m) undulator, the gold Fermi cut-off has successfully been measured at $h\nu = 7.9$ keV with the overall energy resolution of 65 meV as shown in Fig. 3. For this measurement, the incident light has been monochromatized by a Si (6 2 0) reflection and the acquisition time has been 30–40 min using a MB Scientific A1-HE hemispherical photoelectron spectrometer. By using higher order reflection such as (4 4 4) and (5 5 1) reflections at $h\nu \sim 8$ keV, the photon energy resolutions become better although the throughputs become worse.

Here, the example of photoemission data indicating the highly bulk-sensitive property of HAXPES is demonstrated. Fig. 4 shows the comparison of the Yb^{2+} 4f photoemission spectra near E_F between $h\nu = 700$ [56] and 8180 eV [20] for a Kondo semiconductor YbB_{12} at 20 K with the comparable energy resolution