L-01

RECENT PROGRESS IN SYNCHROTRON RADIATION PHOTOEMISSION SPECTROSCOPY OF SOLIDS : APPLICATIONS OF VUV, SOFT AND HARD X-RAY RADIATION

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The Hiroshima Synchrotron Radiation Center is a common facility for both research and education in the field of synchrotron radiation science. The role of the center is to promote original research, training of young scientists, international exchange and cooperative research with neighboring universities, public organizations and industries. The formal operation of the light source was started from March 1998. The storage ring can be operated at 700 MeV with a critical energy of 873 eV. The machine has a racetrack shape with a circumference of 22 m, and has 14 photon beam ports on the bending sections with an opening angle of 20 mrad and 2 on the straight sections with one linear and one helical undulators. The maximum operational current is 300 mA at present, and the lifetime of the beam is longer than 6 hours at 200 mA.

Of total 13 beamlines introduced so far, three beamlines are dedicated to photoemission spectroscopy (PES). BL1 [1] is a linear undulator beamline with a grazing incidence monochromator. An available photon-energy range is $h\nu$ = 26-300 eV. A hemispherical photoelectron analyzer is equipped at the end station. Total energy resolution has been achieved to ~15 meV at $h\nu$ = 100 eV. BL9A [2] is also a helical undulator beamline. A normal-incidence monochromator and a hemispherical photoelectron analyzer are used to measure PES spectra. The photon-energy range is $h\nu$ = 4-40 eV and total energy resolution is ~4.5 meV at $h\nu$ = 7 eV. On the other hand, BL7 is a bending beamline with a grazing incidence monochromator, which covers $h\nu$ = 20-380 eV region. Although total energy resolution has been achieved to ~25 meV at $h\nu$ = 80 eV, we usually carry out the conventional PES experiments. On these three beamlines, angle-resolved PES (ARPES) is also available.

In the PES experiments at $h\nu$ = 20-300 eV, we have to distinct the surface- and bulk-derived components from the spectra since the probing depth (λ) is relatively small in this energy range. The PES spectra taken at $h\nu$~7 eV provide bulk-sensitive information on the conduction-band electrons such as *sp* states. In order to investigate the bulk-originated electronic structure of the *d* and *f* electron systems, which is important to study the highly correlated systems, we started the hard x-ray PES experiments ($h\nu$ = 6 keV) [3] with a total energy resolution of ~270 meV, in collaboration with SPring-8 since 2002. Thus, we promote the research project with use of light in a wide energy-range between 7 eV - 6 keV.

1) Unusual energy gap formation in the Kondo semiconductor CeRhAs

CeRhAs is known as a Kondo semiconductor and has attracted much interest for its unusual energy gap formation or metal-to-insulator transition as temperature decreases [1]. The narrow energy gap is assumed to be formed by the temperature dependence of the *c-f* hybridization. By means of high-resolution low-temperature resonant PES, we could observe a clear energy-gap structure in the Ce 4*f* states [1]. In order to clarify the origin of the energy-gap formation, it is indispensable to examine conduction-band states at the Fermi level (E_F) responsible for the *c-f* hybridization. In order to observe As 4*p* state and Rh 4*d* state, we have measured the PES spectra at $h\nu$ = 7.9 eV, 40 eV and 6 keV, which reflect almost the As 4*p*, Rh 4*d* and As 4*p* states, respectively, due to the photon-energy dependence of photoionization cross-section. In particular, the spectra at $h\nu$ = 7.9 eV and 6 keV also provide bulk-sensitive information. From the spectra at $h\nu$ = 7.9 eV, we could clearly see that the density of states (DOS) near E_F decreases with lowering temperature, followed by an opening of small energy gap. It is fully consistent with the Ce 4*f* DOS, deduced from the Ce 4*d*-4*f* resonant PES ($h\nu$~122 eV), also decreases with lowering temperature. The 40-eV spectrum, indicating Rh 4*d* partial DOS, shows also energy gap structure near E_F. This similar temperature-dependent behavior indicates that the hybridization between the Ce 4*f* and conduction-band states is essentially important in CeRhAs [4]. We can, thus, reveal behaviors of each orbital for the gap formation with use of the energy-dependent PES spectra.

2) Valence transition in $YbInCu_4$ [5]

$YbInCu_4$ has attracted great interests because of an isostructural first-order valence transition at T_V = 42 K

[6]. In accordance with the valence transition, abrupt changes in the lattice volume, magnetic susceptibility and the other physical properties are observed. Thermodynamic data have shown that the Yb valence changes from z~3 (high-temperature phase) to z~2.9 (low-temperature phase), while Yb L_{III}-edge x-ray absorption spectroscopy (XAS) experiments from z~2.9 to z~2.8. In order to investigate the change of the Yb 4f and conduction-band states near the valence transition, the PES spectra have been measured at hν = 7 eV - 6 keV.

The spectra of $YbInCu_4$ measured at hν = 21.2 - 180 eV show the peak-structure derived from the Yb^{2+} $4f_{7/2}$ states at ~39 meV below E_F, in spite of the Yb states close to trivalent in the high-temperature region. Although the peak intensity increases with lowering temperature, the change is rather gradual and the sharp change is not observed. As one of reasons, the small λ of PES has often been pointed out. Reinert *et al*. proposed an existence of a subsurface region, physical properties of which are different from the bulk, in $YbInCu_4$ within λ [7].

Actually, the PES spectra taken at hν = 7 eV, which are bulk-sensitive compared to those at hν = 21.2 - 180 eV and reflect conduction-band states such as the In 5*sp* and Cu 4*s* states, exhibit a drastic change between 50 and 40 K. The spectral feature at the top 150 meV region is almost flat above 50 K. With lowering temperature to 40 K, the structure suddenly appears around 47 meV and the feature is unchanged down to 20 K. This experimental result shows that an amount of hybridization between the Yb 4*f* and conduction-band states abruptly increases in the low-temperature phase and is consistent with the change of the Kondo temperature T_K in accordance with the valence transition; T_{K+}~25 K and T_{K-}~400 K.

In order to investigate the Yb 4*f* states under the bulk-sensitive condition, we have measured the PES spectra at hν = 6 keV. The intensity of the Yb^{2+} 4*f*-derived peak is negligibly small above 50 K and the peak is remarkably enhanced through the valence transition. Such a drastic change of the valence-band PES spectra of $YbInCu_4$ has not been presented so far. The Yb 3*d* PES spectra also show a sharp change at the valence transition. With the increase of λ, the change of the spectral feature becomes sharp and the Yb valence derived from the PES spectra becomes close to trivalent. As pointed out by Reinert *et al*., the λ–dependent PES spectra suggest an existence of the subsurface region, where the transition temperature would be higher than that of the bulk, in $YbInCu_4$.

3) Many body effect in Ni(110)

Metallic ferromagnetism of Ni has attracted much interest for a long time. Electron correlation plays an important role for the narrowing of the Ni 3*d* bands and the appearance of the spin-polarized 6 eV satellite in photoemission spectra. In order to examine manybody effects in the ferromagnetic Ni 3*d* bands, we have done high-resolution ARPES study of Ni(110) using hν = 21-29 eV [8]. We set the total energy resolution at ΔE = 11 meV and angular resolution $\Delta\theta$ = 0.15°. In the intensity plot of the ARPES spectra of Ni(110) taken at hν = 29 eV, the Σ_1 up- and down-spin bands crossing E_F are observed. From the width of an angular-distribution curve (ADC) at E_F, which traces the ARPES intensity at a constant binding energy as a function of *k*-vector, we can estimate mean-free paths of quasi-particles at E_F with up- and down-spins. By quantitative line shape analyses, we found that up-spin electrons has shorter mean-free path compared with down-spin electrons. The present experimental result is consistent with the results that the up-spin band is strongly renormalized compared with the down-spin band [9,10]. We could also evaluate the real and imaginary parts of the self-energy, in which information on the many-body effects is included. We can, thus, discuss electronic structure quantitatively by means of the high-resolution ARPES experiments using synchrotron radiation. A great amount of information can be deduced from the high-resolution PES spectra, which provides us with new insight into the origin of the physical properties of solids.

4) Others

Other than three subjects above mentioned, the PES results have been obtained for the carbon nanotubes (BL1) [11], the Kondo semiconductor YbB_{12} (BL1 and BL9A) [12], the superconducting interlayered nitrides β-HfNCl (BL7) [13]. In addition to PES, linear and circular dichroison (LD and CD) experiments are available at BL14. Recently, we have measured the LD in the Ti 2*p*-3*d* absorption spectra of the Mott insulator $YTiO_3$ [14]. The experimental LD is well reporoduced by the theoretical one calculated with the assumption of the orbital order in $YTiO_3$.

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