



Core-level photoemission revealing the Mott transition

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Abstract

Ru 3d core-level X-ray photoemission spectra of various ruthenates are examined. They show in general two-peak structures, which can be assigned as the screened and unscreened peaks. The screened peak is absent in a Mott insulator, but develops into a main peak as the correlation strength becomes weak. This spectral behavior is well explained by the dynamical mean-field theory calculation for the single-band Hubbard model with the on-site core-hole potential using the exact diagonalization method. The new mechanism of the core-level photoemission satellite can be utilized to reveal the Mott transition phenomenon in various strongly correlated electron systems.

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Electron correlation effect has been considered to be weak in 4d transition-metal compounds (TMCs) because 4d orbitals are fairly delocalized, and RuO₂, for example, is traditionally classified as a band metal [1]. However, recent studies revealed that many ruthenates such as Ca_{2-x}Sr_xRuO₄ [2] and pyrochlores [3,4] have various interesting properties related with the correlation effect among Ru 4d electrons. Ru 3d core-level XPS spectra also show some hint of the strongly correlated nature of Ru 4d electrons revealing a

two-peak structure [5]. Here, we show that the two-peak structures in the Ru 3d core-level XPS spectra of ruthenates are the manifestation of satellite structures expected for the Mott–Hubbard system by calculating the core-level spectra of a single-band Hubbard model with core-hole potential Q using the dynamical mean-field theory (DMFT) based on the exact diagonalization method [6].

Fig. 1 shows core-level and valence-band spectra of a ten-site half-filled model obtained by the modified Lanczos method changing the ratio of the band width to the Coulomb interaction (W/U) from a Mott insulator regime to a good metal regime to show the behavior of spectral weights in

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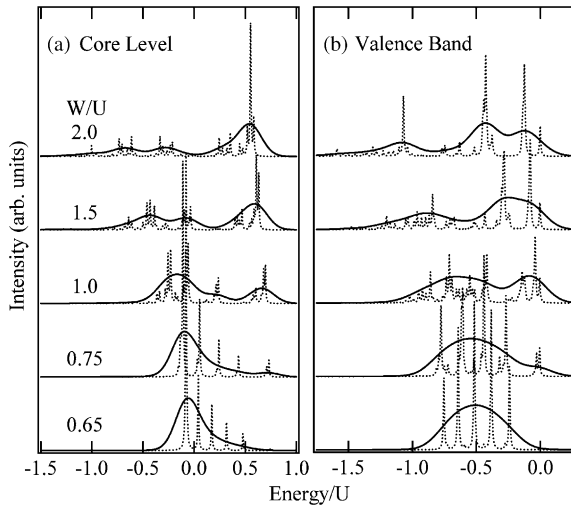


Fig. 1. Core-level (left panel) and valence-band (right panel) spectra of a half-filled Hubbard model calculated by the DMFT using the exact diagonalization method for $N_s = 10$ and $Q/U = 1.25$ varying W (core-hole energy is set to Q). Solid lines are guidelines obtained by broadening dotted lines with a Gaussian of $0.25U$ full-width at half-maximum to remove discreteness due to the finite size.

the bandwidth-controlled metal–insulator transition. The core-level spectra are mainly composed of two peaks and their behavior with W/U is quite similar to that of the valence-band spectra and, moreover, the intensity of the screened peak at lower binding energy is found to be nearly proportional to the quasiparticle weight, which implies that the two-peak structure is strongly related with the Mott transition. In a Mott insulator ($W/U = 0.65$) we can see a broad single peak, and as the coherent peak grows with the increase of W in the valence-band spectra, a sharp shake-down satellite structure appears in the core-level spectra in the positive energy side and eventually becomes a main peak with an asymmetric low-energy tail. By analyzing a four-site model, where all the configurational components of each peak can be tracked down, it can be shown that the unscreened peak originates from the configuration d^1 ($\equiv d^1 L^2 C^1$, for $N_s = 4$), while the screened peak from the configurations $d^2 C$ and $d^2 L$, where d denotes the “impurity” level and C (L) denote the coherent peak (lower Hubbard band) in the DMFT framework [6].

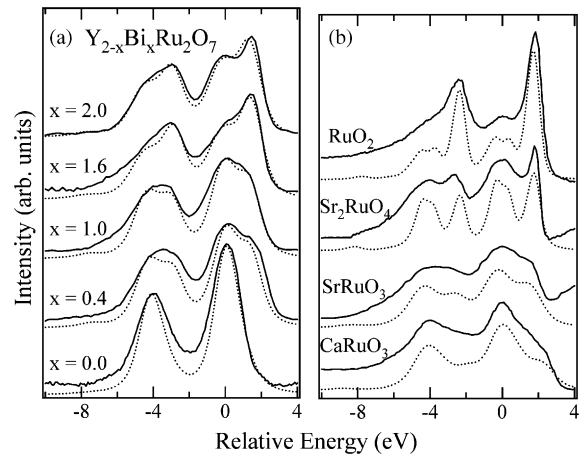


Fig. 2. Comparison of the experimental Ru 3d XPS spectra (solid lines) of (a) $Y_{2-x}Bi_xRu_2O_7$ and (b) $CaRuO_3$, $SrRuO_3$, Sr_2RuO_4 and RuO_2 (after Ref. [5]) with the present model calculations (dotted lines). All the spectra are aligned by the unscreened peak position.

To test the validity of the present model, we made a systematic study of the Ru 3d core-levels in $Y_{2-x}Bi_xRu_2O_7$ system which is known to be a bandwidth-controlled Mott–Hubbard system from theoretical calculation [4], transport properties [3] and valence-band photoemission spectra [7]. Experimental Ru 3d XPS spectra of $Y_{2-x}Bi_xRu_2O_7$ are shown in Fig. 2(a) with solid lines. We can see the systematic behavior that the weight of the screened peak becomes larger with x . This tendency is strongly correlated with the transport properties and valence-band photoemission spectra.

Using the present model, these experimental core-level spectra of $Y_{2-x}Bi_xRu_2O_7$ series could be reproduced by changing only W -value with fixed $U (= 1.7 \text{ eV})$. We also fit the spectra of other ruthenates [5] by freeing U , and Table 1 summarizes all the parameter values. The results (dotted lines) are plotted over the experimental spectra in Fig. 2 for (a) $Y_{2-x}Bi_xRu_2O_7$, and (b) other ruthenates. The fitting results are quite satisfactory and all the spectral features are well reproduced. Rather surprisingly, RuO_2 , which was believed to be well described by band calculations [1], should be reconsidered as a strongly correlated metal according to our fitting result ($W/U = 2$).

Table 1

Parameter values (in eV) obtained from fitting Ru 3d XPS spectra of ruthenates and $Q/U = 1.25$

x in $Y_{2-x}Bi_xRu_2O_7$	U	W		U	W
0.0	1.7	1.2	CaRuO ₃	2.7	2.6
0.4	1.7	2.1	SrRuO ₃	2.15	2.6
1.0	1.7	2.15	Sr ₂ RuO ₄	2.15	2.8
1.6	1.7	2.9	RuO ₂	1.8	3.6
2.0	1.7	2.7			

Although the present model does not include such terms as Ru 4d-orbital degeneracy and also the density of states of Ru 4d(t_{2g}) bands is far from a semi-elliptical shape assumed in the calculations, it is quite successful in describing the two-peak structure of the core-level spectra, which confirms that the Mott–Hubbard mechanism is the most important factor. But, the role of O 2p electrons cannot be neglected, as seen in recent works on 3d TMCs [8], for more accurate quantitative analysis.

We also note that the appearance of a sharp screened peak coincides with the metallic behavior, and can be easily utilized as a fingerprint for distinguishing metallic from insulating regions in

spectro-microscopic techniques such as scanning photoemission microscopy by taking advantage of the strong signals of the core-level XPS.

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