THEORY OF Cu 2p XPS AND 3p RESONANT XPS IN OXIDE SUPERCONDUCTORS

K. Okada, A. Kotani

JOURNAL DE PHYSIQUE
Colloque C8, Supplément au n° 12, Tome 49, décembre 1988

THEORY OF Cu 2p XPS AND 3p RESONANT XPS IN OXIDE SUPERCONDUCTORS

K. Okada and A. Kotani

Department of Physics, Tohoku University, Sendai 980, Japan

Abstract. – We have analysed Cu 2p-XPS and 3p resonant XPS spectra of $(La_xSr_{1-x})_2\,CuO_4$ (LaCuO), consistently by using the impurity Anderson model. To take account of the symmetry of Cu site, five filled valence bands are introduced. Comparison between LaCuO, $YBa_2Cu_3O_{7-\delta}$ and CuO is also made.

1. Introduction

So far the mechanism of high T_c superconductivity in $(La_xSr_{1-x})_2\,CuO_4$ (LaCuO) and $YBa_2Cu_3O_{7-\delta}$ (YBaCuO) has been studied [1]. Photoemission study, in particular, resonant XPS, is one of the most direct way to obtain information on electronic states. Our purpose is to analyse consistently the Cu 3p resonant XPS [2] and 2p XPS [2] by using the impurity Anderson model with five filled valence bands. The single filled band version [3] of this model have already succeeded in describing the photoemission spectra of the Ce compounds. As it is well-known that the photoemission spectra of LaCuO and YBaCuO resemble those of CuO [4] in many respects, comparison between them is also a major subject.

2. Model

We concentrate on the Cu site on the so-called CuO_2 plane which is commonly contained in LaCuO and YBaCuO. We describe the system by using the impurity Anderson model so as to take account of the strong electron correlation on Cu atom. It is given by

$$\begin{aligned} H = & \sum_{\Gamma,\sigma}\sum_{k=1}^{N}\varepsilon_{\Gamma k}n_{\Gamma k\sigma} + \sum_{\Gamma,\sigma}\varepsilon_{d\Gamma}n_{\Gamma\sigma} + \\ & + U\sum_{(\Gamma\sigma)\neq(\Gamma'\sigma')} n_{\Gamma\sigma}n_{\Gamma'\sigma'} \\ & + \sum_{\Gamma,\sigma}\sum_{k}\frac{V_\Gamma}{\sqrt{N}}\left(a^+_{\Gamma k\sigma}d_{\Gamma\sigma} + d^+_{\Gamma\sigma}a_{\Gamma k\sigma}\right) \\ & - U_{dc}\sum_{\Gamma,\sigma} n_{\Gamma\sigma}\left(1 - a^+_c a_c\right), \end{aligned} \tag{1}$$

In equation (1), Γ represents the symmetry of the Cu 3d orbital states, A_1, B_1, B_2 and E, which are irreducible representations in the D_{4h} point group symmetry, and the first term describes the valence band states (with the band width W_Γ) which couple to Cu 3d states. This treatment of the valence band is an extension of the filled band Anderson model [3] to take account of the symmetry of Cu 3d state in a phenomenological way, where the emphasis is put on the effect of the local symmetry of oxygen atoms around the Cu atom, but the translational symmetry of oxygen atoms in the relevant crystal is not literally taken into account. The index k, which corresponds to the wave number in the radial direction, describes the energy distribution in each Γ band. The second, third and fourth terms describe the 3d states, the d-d Coulomb repulsion and the hybridization, respectively. The fifth term is a core hole potential acting on 3d electrons.

Even when the holes are doped to La_2CuO_4, for example, its effect on Cu 2p-XPS and the valence band XPS (v-XPS) as a first approximation seems to be negligible [2]. We assume nominally divalent Cu ions in the CuO_2 planes and assume that the hole state of those Cu ions is of B_1 $\left(x^2-y^2\right)$ symmetry in the ground state, which is natural in explaining the easy plane of the spins. We describe the ground state of the system by a linear combination of d^9 and $d^{10}\underline{L}$ electron configurations:

$$\left|d^9\left(\Gamma\right)\right\rangle = d_\Gamma\left|d^{10}\right\rangle \tag{2}$$

and

$$\left|d^{10}\underline{L}\left(\Gamma,k\right)\right\rangle = a_{\Gamma k}\left|d^{10}\right\rangle, \tag{3}$$

where $\Gamma = B_1$ and $\left|d^{10}\right\rangle$ describes the state where both of d level and valence bands are occupied fully. The average energy difference $E\left(d^{10}\underline{L}\left(\Gamma\right)\right) - E\left(d^9\left(\Gamma\right)\right)$ in the limit of vanishing V_Γ is defined as Δ_Γ.

The states (2) and (3) describe also the final states of 2p-XPS. In the case of v-XPS, the final states are described by the states which are obtained by annihilating a d electron or a valence band electron from the states (2) and (3). The intermediate state of the resonant XPS is $\left|d^{10}\right\rangle$.

3. Calculated results

We take $\varepsilon_{\Gamma k} = \varepsilon_{d\Gamma} - \Delta_\Gamma + W_\Gamma/2 - W_\Gamma\left(k-1/2\right)/N$ for $k = 1 \sim N$ with a finite number N, so that the wave functions are described by a finite number of the

basis wave functions. Therefore we can diagonalize the Hamiltonians numerically. We take $\varepsilon_{d\Gamma} = \varepsilon_d$ (a constant) for all Γ 's.

Figure 1 shows a calculated result of 2p-XPS with $\Delta(B_1) = 2$ eV, $V(B_1) = 2.5$ eV and $W(B_1) = 5$ eV. Except the observed multiplet structure which is not taken into account in our calculation, it reproduces well the observed peak separation in energy and the intensity ratio, I_s/I_m, between the main and satellite peaks.

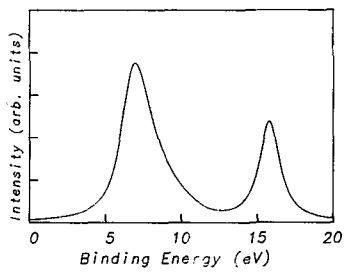

Fig. 1. – Cu 2p XPS of La_2CuO_4. The abscissa is the relative binding energy.

Figure 2 shows a calculated d electron photoemission spectrum for La system at the energy of off-resonance. It consists of the broad main peak around $E_B = 4$ eV and the satellite peak around $E_B = 12.5$ eV. The satellite originates mainly from the d^8 final state and its intensity shows Fano-type resonance at the 3p core excitation threshold, as shown in the inset of figure 2. The main peak originates mainly from the $d^9\underline{L}$ final state, and its intensity also shows resonance behavior at the threshold, which is caused by the resonance of the satellite through the strong mixing $V(B_1)$. Large energy separation between two peaks means large U of

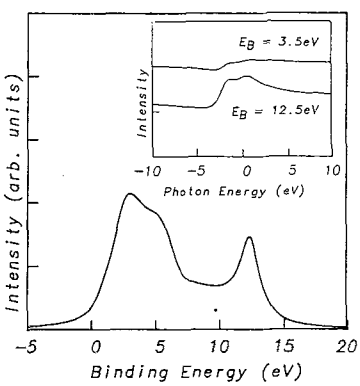

Fig. 2. – Valence band XPS of La_2CuO_4 at the energy of off-resonance. The origin of the abscissa is the Fermi energy. The inset shows CIS spectra for two peaks in VB-XPS, where the origin of the photon energy is the $3p_{1/2}$ excitation threshold.

up to 7 eV. Although the satellite intensity in figure 2 appears to be somewhat stronger than the observed result, it will be improved by taking account of the O 2p electron emission.

From a viewpoint of the symmetry of hole state, the final states with B_1 and E holes have the largest contribution to the total v-XPS spectrum because of their multiplicity. Therefore the shape of the main peak is strongly dependent on the parameters $V(E)$ and $\Delta(E)$. In the present case, we assume that $V(E) = 1$ eV, $\Delta(E) = 2$ eV and $W(E) = 3$ eV.

4. Discussion

Our theory explains the 2p-XPS and 3p resonant XPS well. Strong mixing $V(B_1)$ gives the mixed valent nature of the ground state of the undoped system. Moreover, estimated large U almost excludes the double hole occupancy of Cu site in the doped system.

When we compare the 2p-XPS for LaCuO, YBaCuO and CuO, the peak separation is similar between them while I_s/I_m is larger in CuO than in LaCuO and YBaCuO. In our calculation, this fact is explained mainly by taking slightly larger $\Delta(B_1)$ for CuO. Since the 2p-XPS is very similar between LaCuO and YBaCuO [2], $\Delta(B_1)$ and $V(B_1)$ should be almost the same between them. However, it appears that the main peak in v-XPS is somewhat different in shape between LaCuO, YBaCuO and CuO. As mentioned above, it depends remarkably on $V(E)$ and $\Delta(E)$ so that it is concluded that these parameter values will be considerably different between them.

Thus the strong electron correlation and the anisotropic electron transfer are important, and this situation becomes clearer in understanding the recent study on the polarization dependence of L_3 XAS [5].

Acknowledgement

This work is partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture, Japan.

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