HIGH T_c SUPERCONDUCTORS

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Electronic Structure

roceedings of the International Symposium on the Electronic Structure of High T_c Superconductors, Rome, 5–7 October 1988

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Preface

This volume arose from an international symposium on the "Electronic Structure of High T_c Superconductors" sponsored by the Associazione Amici dell' Accademia dei Lincei, Europa Metalli-LMI, Commission of European Communities, Consiglio Nazinale delle Ricerche and ENEA. It was held October 5 to 7, 1988, at "La Farnesina" in Rome. The venue was the renaissance villa decorated by Raphael in 1517, and seige of the National Academy of Lincei. The Accademia dei Lincei was founded by Federico Cesi in 1603 and G. Galilei joined the company of Lynceans in 1611.

The most active groups working on the electronic structure of the new cuprate perovskites that exhibit high T_c superconductivity have presented the results of a wide range of spectroscopies such as photoemission, infrared reflectivity and absorption, photoinduced absorption, Raman spectroscopy, magnetic scattering, nuclear magnetic resonance, μSR, electron energy loss, x-ray emission, extended x-ray absorption fine structure and x-ray absorption near edge structure.

The experimental results are compared with the theoretical results of the most distinguished theorists of the electronic structure of these materials. The experimental data are needed today to verify the large number of theories of high T_c superconductivity that have been proposed.

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CHARACTER OF DOPED HOLES AND LOW-ENERGY EXCITATIONS IN HIGH-T_C SUPERCONDUCTORS: ROLES OF THE APEX OXYGEN ATOMS

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ABSTRACT

Using the results of photoemission spectroscopy and cluster-model calculations, we have studied the location and symmetry of doped holes and the nature of low-energy (0.1-0.5 eV) excitations in the Cu-oxide superconductors. Even though the doped holes may be located predominantly in the CuO_2 planes, appreciable real and virtual transfer of the holes to the apex oxygens is show to occur, which may be important in the hole doping process. The strong antiferromagnetic coupling between the holes and Cu spins, which has been suggested to favor attractive interaction between the holes, is accompanied by this charge transfer and may be coupled to other charge fluctuations such as plasmons and optical phonons.

KEYWORDS

High-T_c superconductivity; photoemission; cluster model; doped hole; phonon softening.

INTRODUCTION

In order to elucidate the mechanism of high-T_c superconductivity in the Cu-oxide systems, understanding of the electronic structure is an essential first step. By means of photoemission (e.g., Fujimori *et al.*, 1987a,b; 1989) and other high-energy spectroscopies (Bianconi *et al.*, 1987; Tranquada *et al.*, 1987), the following basic picture has been established: (a) Electron correlation is strong (U ~ 5-7 eV) for the Cu 3d electron; (d) The Cu 3d and O 2p levels are close to each other and are strongly hybridized; (c) Doped holes are O 2p-like. Although the superconductivity mechanism is still far from understood, at least the ordinary BCS theory based on one-electron band theory is irrelevant to this class of compounds. This situation necessiates the use of correlated two-band models such as extended Hubbard and periodic

Anderson models which include both Cu 3d and O 2p states explicitly. These models have lead to many proposals of spin (Emery, 1987; Imada, 1988) and charge fluctuation mediated (Varma *et al.*, 1987; Hirsch *et al.*, 1988. Tachiki and Takahashi, 1988) superconductivity mechanis. In most theoretical studies based on the two-band models, the properties of the CuO_2 planes have been investigated. The importance of the BaO planes adjacent to the CuO_2 planes was first pointed out by Takayama-Muromachi *et al.* (1988b) in the study of the $La_{1+x}Ba_{2-x}Cu_3O_{7\pm\delta}$ system, in which a small amount of oxygen vacancies in the BaO planes are shown to suppress T_c dramatically. Bianconi *et al.* (1988) studied polarized Cu L_3-edge x-ray absorption in $YBa_2Cu_3O_{7-\delta}$ and pointed out the possibility that the doped holes enter the BaO planes. It has also been controversial within the CuO_2 planes whether the holes are in the $p\sigma_{x,y}$ (Emery, 1987; Imada, 1987), $p\pi_{x,y}$ (Aharony *et al.*, 1988), or $p\pi_z$ (Johnson *et al.*, 1988) orbitals (Fig.1). The magnetic coupling between the $p\sigma_{x,y}$ holes and the Cu d^9 spins is antiferromagnetic and extremely strong, whereas the $p\pi$ orbitals as well as the $p\sigma_z$ orbitals in the BaO planes are ferromagentically coupled to the Cu d^9 spins relatively weakly. The symmetry of the holes is therefore of particular importance in the studies of spin fluctuation mediated mechanisms (Imada *et al.*, 1988; Shiba and Ogata, 1988).

In order to get insight into the character of the doped holes and their coupling to other spin or charge degrees of freedom, we have performed configuration-interaction calculations on CuO_n clusters combined with photoemission spectroscopy. Our results suggest that, even if the holes are predominantly distributed within the CuO_2 planes, there exist significant virtual and real charge transfer between the in-plane and apex oxygens, implying a coupling of the holes to some charge fluctuation such as plasmons and optical phonons.

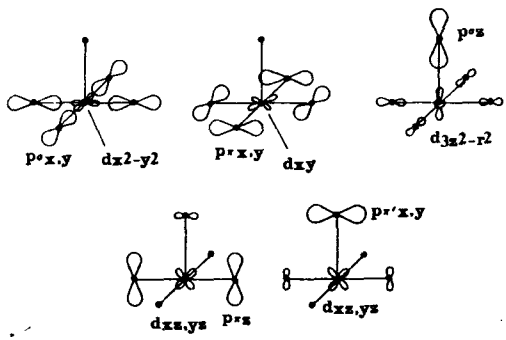

Fig. 1 Various types of oxygen p orbitals for the CuO_5 cluster. Also shown are Cu 3d orbitals which are hybridized with these p orbital

CLUSTER MODEL

We consider a CuO_5 or an elongated CuO_6 cluster depending on the local geometry around the Cu atom. The ground state of the undoped cluster (N-electron system) is represented as

$$\psi_g = \alpha \mid d^9\rangle + \beta \mid d^{10}\underline{L}\rangle, \qquad (1)$$

where $\underline{L}$ denotes a ligand hole. The first term in Eq. (1) represents the purely ionic (Cu^{2+}, O^{2-}) configuration, and the second term a p-to-d charge-transfer state. Energy levels of the N-electron system are characterized by the charge-transfer energy, $\Delta \equiv E(d^{10}\underline{L}) - E(d^9)$, and the p-d hybridization, $T \equiv \langle d^{10}\underline{L}|H|d^9\rangle$. Figure 2 shows schematically these energy levels. The p-d hybridization in the ground state is restricted to the CuO_2 plane and does not involve apex oxygen orbitals because of the x^2-y^2 symmetry of the unoccupied orbital.

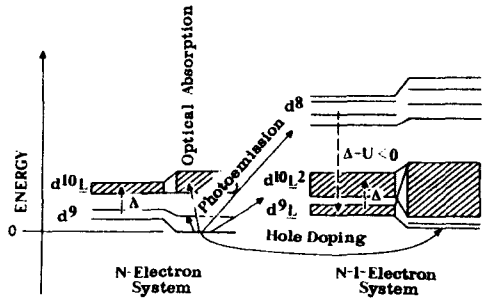

Fig. 2 Schematic energy-level diagram of the CuO_n cluster.

When a valence electron is removed by doping with an extra hole or by photoemission, we explicitly consider energy levels of the N-1-electron system instead of the N-electron system (Fig.2). Eigenstates of the N-1-electron system are given in the form (Fujimori and Minami, 1984)

$$\psi_f = \alpha'_f \mid d^8\rangle + \beta'_f \mid d^9\underline{L}\rangle + \gamma'_f \mid d^{10}\underline{L}^2\rangle \qquad (2)$$

Here, the energy differences between the configurations are parameterized as $E(d^9\underline{L}) - E(d^8) = \Delta - U$ and $E(d^{10}\underline{L}^2) - E(d^9\underline{L}) = \Delta$.

As the extra hole may not be necessarily in the $p\sigma_{x,y}$ orbitals, we include p orbitals on the apex oxygen. We introduce a new parameter $\Delta\varepsilon_p$, the energy difference between p orbitals in the

CuO_2 plane and on the apex oxygen, i.e., $\Delta\varepsilon_p \equiv \varepsilon(p\sigma_z) - \varepsilon(p\sigma_{x,y})$. In order to evaluate the off-plane p-d and p-p hybridizations, they are assumed to scale with $R^{-3.5}$ and R^{-2}, respectively, where R is the interatomic distance (Harrison, 1980). Thus the relative interatomic distance for the out-of-plane Cu-O bond to the in-plane one, r, has been taken as another independent parameter, which is determined from crystallographic data.

Due to the strong intra-atomic correlation (U) as compared to the interatomic interaction (band effects) for the Cu 3d states, single impurity models such as the cluster and the impurity Anderson models provide a good starting point. As for the band-like O 2p states, their finite bandwidths are explicitly taken into account in the impurty Anderson model, whereas in the cluster model the O 2p band is treated as a set of molecular orbitals derived from the oxygen ligand orbitals. Nevertheless, these two models are virtually equivalent concering the ground states of insulators and also for their spectroscopic properties as far as gross spectral features are concerened. Here, it shoul be noted that the cluster model describes the lowest energy states of the N-1-electron system as correctly as the impurity Anderson model does if these states are split off from the $d^9\underline{L}$ continuum to form bound states. This is indeed the case for the Cu oxides because of the large p-d hybridization (Eskes and Sawatzky, 1988).

SPECTROSCOPIC DETERMINATION OF PARAMETERS

The parameters introduced above can in principle be determined by fitting the calculated photoemission spectra to the experimental ones. Indeed, the spectral shapes are sensitive to T, U, and Δ, but unfortunately are rather insensitive to $\Delta\varepsilon_p$. It is therefore practically impossible to determine $\Delta\varepsilon_p$ by this procedure as can be seen from Fig. 3. Although $\Delta\varepsilon_p$ does not affect the spectral shape appreciably, it does determine the symmetry of the lowest binding energy feature, namely, the symmetry of the extra holes. In Fig. 4, calculated spectra are compared with experiment for $La_{2-x}Sr_xCuO_4$ and $Bi_2(Sr,Ca)_3Cu_2O_{8+\delta}$ (Fujimori *et al.*, 1989). Best fits have been obtained with U = 6.5 eV, Δ = 1-2 eV, and T = 2.2-2.4 eV.

We have also utilized the Cu 2p core-level photoemission spectra to estimate the parameters. The Cu core-hole state is given by

$$\Psi_f = \alpha'_f \,|\, \underline{c}d^9\rangle + \beta'_f \,|\, \underline{c}d^{10}\underline{L}\rangle \qquad (3)$$

where $\underline{c}$ denotes a core hole. The energy difference between the two configurations is $E(\underline{c}d^{10}\underline{L})-E(\underline{c}d^9) = \Delta-Q$, where -Q is the Coulomb interaction between the core hole and a d electron.

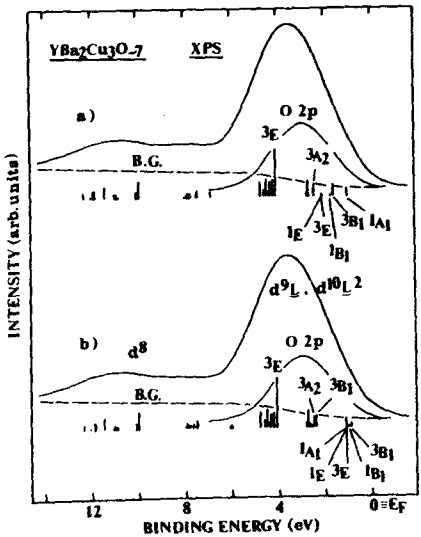

Fig. 3 Calculated valence-band x-ray photoemission spectra of $YBa_2Cu_3O_{-7}$. U=7.0 eV, Δ=1.2 eV, and T=2.3 eV. (a): $\Delta\varepsilon_p$=0.7 eV; (b): $\Delta\varepsilon_p$=1.7 eV (Fujimori, 1988).

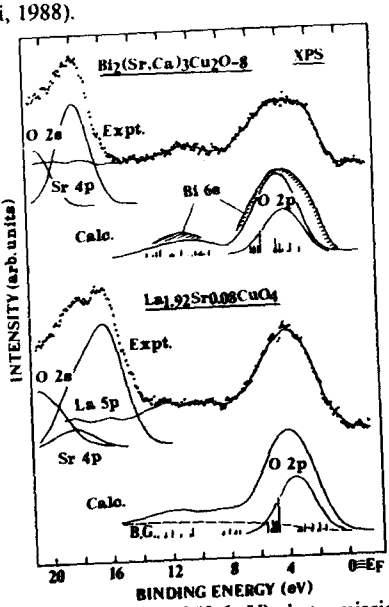

Fig. 4 Valence-band x-ray (hν = 1253.6 eV) photoemission spectra of single-crystal $La_{2-x}Sr_xCuO_4$ and $Bi_2(Sr,Ca)_3Cu_2O_{8+\delta}$ compared with those calculated using the cluster model (Fujimori *et al.*, 1989).

Thus two peaks are observed in the spectrum corresponding to the $\underline{c}d^9$ and $\underline{c}d^{10}\underline{L}$ final-state configurations as shown in Fig. 5. Then it is possible to obtain Δ, T, and Q from the energy separation and the relative intensities of the two peaks following the procedure given by van der Laan *et al.* (1981). Parameter values thus determined are listed in Table I (Fujimori *et al.*, 1989).

Table I Parameters Δ, T, U, and Q evaluated from analyses of the photoemission spectra. Energies are in eV.

	Δ	T	Q	U
$Bi_2(Sr,Ca)_3Cu_2O_{8+\delta}$	2.0 ± 0.5	2.4 ± 0.2	8.1± 0.2	7.5± 0.3
$YBa_2Cu_3O_{7-\delta}$	0.7 ± 0.2	2.6 ± 0.2	7.3± 0.1	7.0± 0.3
$La_{1.92}Sr_{0.08}CuO_4$	0.4 ± 0.3	2.7 ± 0.2	6.5± 0.1	6.5± 0.3

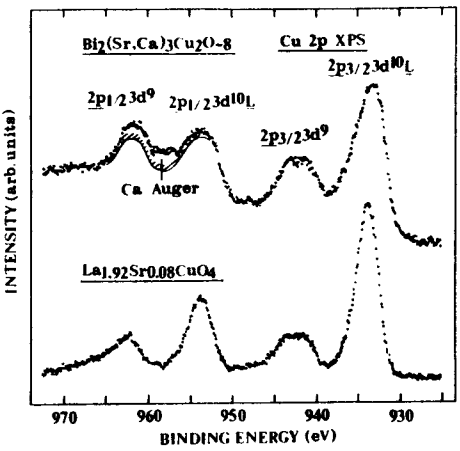

Fig. 5 Cu 2p core-level x-ray photoemission spectra of single-crystal $La_{2-x}Sr_xCuO_4$ and $Bi_2(Sr,Ca)_3Cu_2O_{8+\delta}$ (Fujimori *et al.*, 1989). Each spin-orbit component is further split into the main ($\underline{c}d^{10}\underline{L}$) and satellite ($\underline{c}d^9$) peaks.

We find that Δ is indeed smaller than U, which classifies the Cu-oxide systems in the charge-transfer regime (Zaanen *et al.*, 1985) . Also, Δ is small as compared to T, leading to highly covalent character in the Cu-O bond.

CHARACTER OF DOPED HOLES AND LOW-ENERGY EXCITATIONS

The symmetry of the ground state of the hole-doped CuO_5 cluster has been explored, and it is found that only $^1A_1$- and $^3B_1$ -symmetry states are possible for a reasonable renge of the parameters as shown in Fig. 6 (Fujimori, 1988). In the $^1A_1$ state, the doped hole is in an x^2-y^2-symmetry molecular orbital consisting of in-plane oxygen $p\sigma_{x,y}$ orbitals and forms a singlet with the Cu spin; In the $^3B_1$ state, the hole is in a $3z^2$-r^2-symmetry molecular orbital consisting of the apex oxygen $p\sigma_z$ as well as of the in-plane $p\sigma_{x,y}$ orbitals (Fig. 1) and is coupled to the Cu spin ferronagnetically.

Low-lying excited states of the doped cluster for realistic T, U, and Δ values are plotted as functions of $\Delta\varepsilon_p$ in Fig. 7. In the case of the $^1A_1$ ground state (small $\Delta\varepsilon_p$), the $^3B_1$-$^1A_1$ splitting

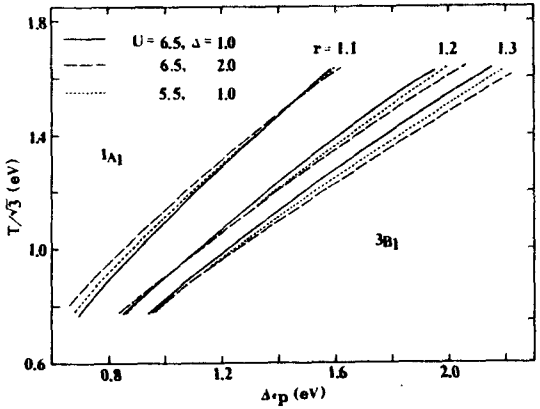

Fig. 6 Boundaries between the $^1A_1$ and $^3B_1$ ground states for the hole-doped CuO_5 cluster in the T-$\Delta\varepsilon_p$ plane (Fujimori, 1988).

represents the magnitude of the antiferromagnetic coupling J_{pd}. This splitting depends on $\Delta\varepsilon_p$ (and on r) and can become huge (J_{pd} ~ - (0.2-0.5) eV) for small $\Delta\varepsilon_p$ (or large r). In the case of the $^3B_1$ ground state (large $\Delta\varepsilon_p$), the $^3B_1$-$^1B_1$ splitting yields the ferromagnetic J_{pd}, which only weakly depends on $\Delta\varepsilon_p$ and r and is relatively small (J_{pd} ~ 0.07 eV). It is also noticed form Fig. 7 that a ^3E state is located only ~0.2-0.4 eV above the $^3B_1$ state. As the ^3E state is mainly derived from $p\pi_{x,y}$ orbitals of the apex oxygen ($p\pi'_x$ in Fig. 1), this state can be the ground