Symmetry of Hole States in Superconducting Oxides: Correlation with T_c

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(Received 17 January 1991)

Despite their small occupancy, the apical oxygen p_z states have the indirect effect of modifying the relative occupancy of holes in states with different local symmetries in the CuO$_2$ planes. A well-defined correlation is found between the maximum critical temperature $T_c^{\max}$ of various cuprates and the excess of holes in states with local a_1 symmetry with respect to the doping $\delta^{\max}$ at which $T_c^{\max}$ is obtained for each compound. Implications for superconductivity models are discussed.

PACS numbers: 74.65.+n

It is commonly accepted that the high-T_c copper oxides[1] are charge-transfer insulators at half filling with one hole per cell occupying predominantly the $d_{x^2-y^2}$ orbital of copper on the CuO$_2$ planes. These planes are surely the most relevant structures in these materials and, upon doping, the added holes, due to a strong ($\sim$8–12 eV) Hubbard repulsion on copper orbitals, mainly reside on surrounding oxygen p orbitals. This is coherent with the proposal of a three-band extended Hubbard model[2,3] including both planar p orbitals and $d_{x^2-y^2}$ orbitals. Polarized x-ray absorption spectroscopy[4] (XAS) and electron-energy-loss spectroscopy[5] (EELS) show a sizable [$\sim$(10–15)%] occupancy of Cu $d_{3z^2-r^2}$ orbitals in all the investigated superconducting materials. To account for the observed presence of these states and their possible role in high-T_c superconductivity, the three-band extended Hubbard model must be further enlarged by including the $d_{3z^2-r^2}$ orbitals of copper.[6,7] However, the models entirely restricted to the CuO$_2$ planes hardly discriminate between the different high-T_c compounds. In the actual crystals pyramidal or octahedral structures are present with apical oxygen ions above or/and below the copper ions. Several experimental findings (including Raman spectroscopy,[8] where a softening of the mode related to the motion of the apical oxygen was revealed when the temperature was lowered below T_c) indicate that also these out-of-plane oxygens can play a relevant role despite their small occupancy revealed by EELS (Ref. 5) experiments. This conclusion is also supported by a recent analysis[9] of the isotope effect and by semiphenomenological analyses of the relation between crystal structure and the maximum critical temperature in the various high-T_c cuprates. A clear correlation has been found between $T_c^{\max}$ and the Cu bond valence sum which is almost entirely due to variation in bonding of the copper ion to the apical oxygen.[10] Similarly a correlation[11] has been shown between $T_c^{\max}$ and the position of the atomic level ε_p^z of the p_z orbitals of the apical oxygen.

In this Letter we relate the above findings concerning the apical oxygen to the electronic structure of the cuprates. We perform a band-structure analysis in the presence of strong local correlations. In addition to the most relevant planar orbitals ($d_{x^2-y^2}$, $d_{3z^2-r^2}$, p_x, and p_y), we include also the p_z orbital of the apical oxygen, which tunes the occupancy of states with different local symmetries and enables us to differentiate between the various cuprates.

Within the context of the three-band model, Zhang and Rice[12] proposed that the holes on $d_{x^2-y^2}$ orbitals form singlets with the holes on planar oxygen in the molecular orbital combination of local b_1 symmetry $(1/\sqrt{4})(p_{x_1}-p_{y_2}-p_{x_3}+p_{y_4})$ by means of a hopping integral $2t$ ($t\sim 1.3$ eV) (the phases of the orbitals have been chosen with the same standard convention used in Ref. 7). This gives rise to a singlet band inside the charge-transfer gap; the equivalent result in the mean-field slave-boson approach is a quasiparticle band of predominantly b_1 symmetry crossing the Fermi level.[13] The additional $d_{3z^2-r^2}$ orbital in the four-band model mixes with the a_1-symmetry orbital combination $(1/\sqrt{4})(p_{x_1}+p_{y_2}-p_{x_3}-p_{y_4})$ of the planar oxygen via a hopping term $2t/\sqrt{3}$. This gives rise[7] to a second band of predominantly a_1 symmetry above the first, mainly b_1 symmetric, band, which also confers a sizable a_1 character to the occupied (hole) states via an overall hybridization of the two bands.

This electronic structure is affected by the apical oxygen ions. As it turns out, the p_z orbitals hybridize rather effectively with the underlying $d_{3z^2-r^2}$ orbitals of copper and with the a_1 combination of the p_x and p_y orbitals of the oxygen ions on the planes. This hybridization lowers the energy of the second lowest band, the one with mostly a_1 character, enhances the mixing of the two bands, and increases the a_1 contribution to the states occupied by holes. It must be emphasized, however, that the main effect of the apical oxygen is indirect: The p_z orbitals modify the occupancy of planar orbitals with a_1 symmetry while keeping their own occupancy rather small [less than a few percent, in agreement with the EELS (Ref.

5) experiments].

The Hamiltonian of the model is

$$
\begin{aligned}
H = {} & \varepsilon^0_{d_x}\sum_{i,\sigma} d^\dagger_{x_{i,\sigma}} d_{x_{i,\sigma}} + \varepsilon^0_{d_z}\sum_{i,\sigma} d^\dagger_{z_{i,\sigma}} d_{z_{i,\sigma}} + \sum_{j,\sigma;\alpha=x,y,z} \varepsilon^\alpha_p (p^\dagger_{\alpha_{j,\sigma}} p_{\alpha_{j,\sigma}}) + 2t_p \sum_{k,\sigma} \alpha_k (p^\dagger_{x_{k,\sigma}} p_{y_{k,\sigma}} + \text{H.c.}) \\
& + \frac{U_d}{2} \sum_{\substack{i,\sigma,\sigma' \\ (\alpha,\beta)=x,z}} d^\dagger_{\alpha_{i\sigma}} d_{\alpha_{i\sigma}} d_{\beta_{i\sigma'}} j d_{\beta_{i\sigma'}} (1-\delta_{\sigma\sigma'}\delta_{\alpha\beta}) + \sum_{\substack{i,j,\sigma \\ \alpha=x,y}} \left[t_{ij} (d^\dagger_{x_{i,\sigma}} p_{\alpha_{j,\sigma}} + \text{H.c.}) + \frac{t_{ij}}{\sqrt{3}} (d^\dagger_{z_{i,\sigma}} p_{\alpha_{j,\sigma}} + \text{H.c.}) \right] \\
& + \frac{4t'}{\sqrt{6}} \sum_{k,\sigma} (d^\dagger_{z_{k,\sigma}} p_{z_{k,\sigma}} + \text{H.c.}) + 2t'_p \sum_{k,\sigma;\alpha=x,y} \sin(k_\alpha)(p^\dagger_{\alpha_{k,\sigma}} p_{z_{k,\sigma}} + \text{H.c.}) \\
& + \sum_{\substack{i,j,\sigma,\sigma' \\ \beta=x,z;\alpha=x,y}} (V_\beta d^\dagger_{\beta_{i,\sigma}} d_{\beta_{i,\sigma}} p^\dagger_{\alpha_{j,\sigma'}} p_{\alpha_{j,\sigma'}}) + \sum_{\substack{i,\sigma,\sigma' \\ \beta=x,z}} (V'_\beta d^\dagger_{\beta_{i,\sigma}} d_{\beta_{i,\sigma}} p^\dagger_{z_{i,\sigma'}} p_{z_{i,\sigma'}}) ,
\end{aligned}
\tag{1}
$$

with $\alpha_k \equiv \cos[(k_x+k_y)/2] - \cos[(k_x-k_y)/2]$ and $t_{ij} = \pm t$. We work in the hole representation in which the vacuum state is the $3d^{10}$ configuration for copper and the $2p^6$ for oxygen. The $d_{x_{i,\sigma}}$ and $d_{z_{i,\sigma}}$ ($d^\dagger_{x_{i,\sigma}}$ and $d^\dagger_{z_{i,\sigma}}$) operators are annihilation (creation) operators for holes in the $3d_{x^2-y^2}$ and $3d_{3z^2-r^2}$ orbitals of the Cu atoms, while $p_{x_{j,\sigma}}$, $p_{y_{j,\sigma}}$, and $p_{z_{j,\sigma}}$ ($p^\dagger_{x_{j,\sigma}}$, $p^\dagger_{y_{j,\sigma}}$ and $p^\dagger_{z_{j,\sigma}}$) are the corresponding operators for the $2p_x$, $2p_y$, and $2p_z$ orbitals on the O sites. σ labels the spin. The subscripts i and j indicate the O or Cu sites. The first three terms specify the bare atomic levels $\varepsilon_p = \varepsilon_p^{x,y}$, ε_p^z, and $\varepsilon^0_{d_x}, \varepsilon^0_{d_z}$ for planar O, apical O, and Cu, respectively. The fourth term gives the dispersion of the planar-p band. The U_d term is the strong Hubbard repulsion on Cu sites. We neglect the local and nearest-neighbor (nn) oxygen-oxygen repulsions. The following term is the in-plane p-d hybridization while the terms with t' and t'_p describe the hybridization with the apical oxygen. The remaining terms give the nn Coulombic repulsions. Since the $p_{x,y}$ orbitals overlap more with the $d_{x^2-y^2}$ orbitals than with the $d_{3z^2-r^2}$ ones, we assume $V_x > V_z$. Typical values[14] are $V_x \sim 0.5$ and $V_z \sim 0.25$ eV. For the same reason we consider two different values $V'_x < V'_z$ ($V'_x \sim 0.1$ and $V'_z \sim 0.5$ eV) for the repulsions between holes in the p_z orbitals and holes in the $d_{x^2-y^2}$ or $d_{3z^2-r^2}$ orbitals, respectively.

The strong Hubbard repulsion U_d forbids double hole occupancy on the copper. This has been formalized by means of the slave-boson approach,[15] which, in the limit $U_d \to \infty$, leads to $b_i^\dagger b_i + n_{d_{xi}} + n_{d_{zi}} = 1$, where $b_i^\dagger$ and b_i are the slave-boson operators of the standard replacement of the d and $d^\dagger$ operators $d^\dagger \to d^\dagger b$, $d \to b^\dagger d$. The constraint is then implemented by a Lagrange multiplier field λ_i. The V terms are decoupled via Hubbard-Stratonovich transformations which introduce six complex conjugate auxiliary fields. At the mean-field level we set all these fields, including b_i and λ_i, equal to their average values independent of the site. To get these (not all independent) mean-field parameters, we solve numerically the self-consistency equations together with the equation for the chemical potential which fixes the average number of particles per cell to the value $n = 1+\delta$, δ being the doping. Once the mean-field parameters are obtained they can be inserted into the Hamiltonian and its diagonalization gives the band structure. Except for the values of the V's, we choose all the other input parameters according to the structural data of Ref. 11, where they have been collected for all the different cuprates. The bare atomic levels are derived from the Madelung potentials in the ionic model with dielectric screening, while the hopping matrix elements are based upon a tight-binding fit to a local-density-approximation calculation for La_2CuO_4, and then rescaled for variation in distance according to appropriate power laws.

The band structures we calculated typically show two low-lying bands. The lowest band, which crosses the Fermi level, has predominantly b_1 symmetry, but with sizable a_1 admixture. For the second lowest band, slightly above the Fermi level, the situation is reversed. It should be noted that our slave-boson approach, taking into account the strong local interaction in a rather effective way, gives bandwidths and general features of the band structure which are in qualitative agreement with angle-resolved photoemission (ARPES) experiments.[16]

The calculated densities of holes in the various orbitals as a function of doping are reported in Fig. 1(a) with the input parameters pertaining to $Pb_{0.5}Tl_{0.5}Sr_2CaCu_2O_7$, which has its maximum critical temperature $T_c = 110$ K at $\delta = 0.25$, and in Fig. 1(b) for $La_{2-x}Sr_xCuO_4$, which attains its maximum $T_c = 38$ K at $x = \delta = 0.2$. Values for the occupancy n_z of the $d_{3z^2-r^2}$ orbital consistent with the XAS data are obtained in both cases, as well as the observed slight increase of n_z with δ, while the $d_{x^2-y^2}$ occupancy n_x is slightly decreasing. Also shown is n_{a_1}, the total occupancy of all states with local a_1 symmetry, i.e., resulting from $d_{3z^2-r^2}$, from the apical oxygen p_z orbital, and from the a_1-symmetric combination of the planar p_x, p_y oxygen orbitals. The most evident difference between the high-T_c compound and the low-T_c compound resides in a much larger n_{a_1} for the second one. The total occupancy of the p orbitals in the plane is accordingly reduced because of the larger values of n_z and n_p^z.

We have also systematically studied the variations of the band structure and the occupancies with the input

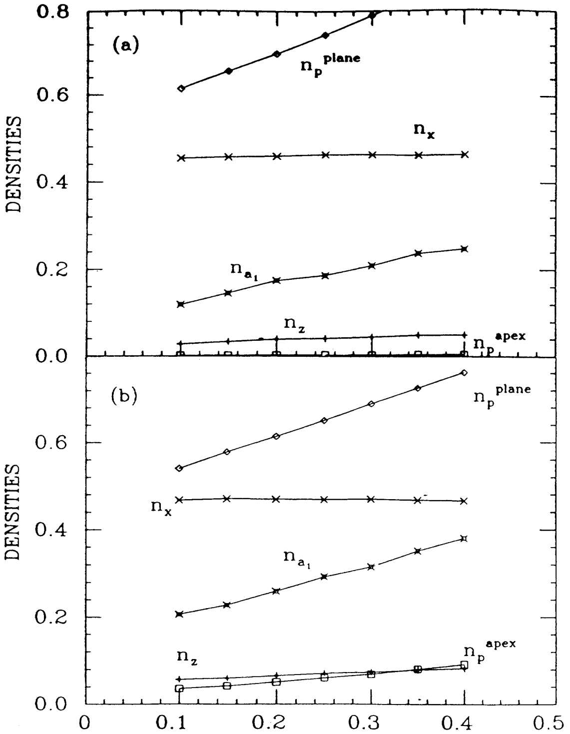

FIG. 1. Hole densities for (a) a Pb$_{0.5}$Tl$_{0.5}$Sr$_2$CaCu$_2$O$_7$ sample with $T_c=110$ K and input parameters $t=1.102$, $t_p=0.48$, $t'=0.403$, $t_p'=0.304$, $\varepsilon_p-\varepsilon_{d_x}^0=2.77$, $\varepsilon_p^z-\varepsilon_p=3.152$, $\varepsilon_{d_z}^0-\varepsilon_{d_x}^0=0.29$, and (b) La$_{1.85}Sr_{0.15}CuO_4$ with $T_c=38$ K and $\delta=0.15$, and parameters $t=1.13$, $t_p=0.49$, $t'=0.425$, $t_p'=0.315$, $\varepsilon_p-\varepsilon_{d_x}^0=3.26$, $\varepsilon_p^z-\varepsilon_p=-0.25$, $\varepsilon_{d_z}^0-\varepsilon_{d_x}^0=0.2$. All the energies are in eV.

parameters, in particular those referring to the apical oxygen. Lowering the level ε_p^z or increasing the hoppings t' and t_p' sufficiently (variation of the repulsions V_x' and V_z' having virtually no effect) makes, above a certain value of doping δ_c, the second band with mainly a_1 symmetry cross the Fermi level. However, we find that this never occurs for physically reasonable values of the input parameters. Of course, a dynamic and/or doping-dependent change of the position of the apex oxygen could induce a nonlinear increase of its effects allowing for a crossing of the second band. The high polarizability of the medium may favor this phenomenon.[17] The ARPES experiments,[16] on the other hand, do not give conclusive indications on the presence of a second band at the Fermi level. We also find significant changes in the occupancies, in particular a large increase in n_{a_1} at the expense of the density in the orbitals of b_1 symmetry if ε_p^z is lowered or t' and t_p' are increased. These changes with parameters (i.e., between compounds) are more pronounced than the variation with doping for fixed parameters (i.e., within one compound).

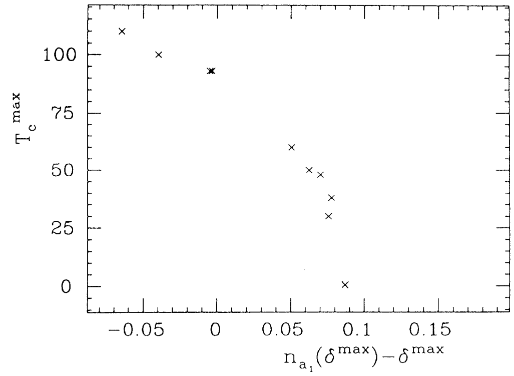

FIG. 2. Maximum critical temperature $T_c^{\max}$ of various of superconducting cuprates plotted vs the corresponding excess density $n_{a_1}(\delta^{\max})-\delta^{\max}$ of holes with a_1 symmetry at the doping $\delta^{\max}$ at which $T_c^{\max}$ is attained. The input parameters are obtained from Ref. 11 for the compounds La$_2$SrCu$_2$O$_6$ ($T_c^{\max}=0$ K), La$_{1.85}$Sr$_{0.15}$CuO$_4$ ($T_c^{\max}=38$ K), La$_{1.85}$Ba$_{0.15}$CuO$_4$ ($T_c^{\max}=30$ K), (Ba$_{0.67}$Eu$_{0.33}$)$_2$(Eu$_{0.67}$Ce$_{0.33}$)$_2$Cu$_3$O$_{8.78}$ ($T_c^{\max}=48$ K), Y$_{0.8}$Ca$_{0.2}$Ba$_2$Cu$_3$O$_{6.11}$ ($T_c^{\max}=50$ K), YBa$_2$Cu$_3$O$_{6.5}$ ($T_c^{\max}=60$ K), YBa$_2$Cu$_3$O$_7$ ($T_c^{\max}=93$ K), Pb$_{0.5}$Tl$_{0.5}$Sr$_2$CaCu$_2$O$_7$ ($T_c^{\max}=110$ K), TlBa$_2$CaCu$_2$O$_7$ ($T_c^{\max}=100$ K), Bi$_2$Sr$_2$Ca$_{0.9}$Y$_{0.1}$Cu$_2$O$_{8.24}$ ($T_c^{\max}=93$ K).

From the above observations related to two compounds with high and low T_c we are led to look at the total occupancy of states with local a_1 symmetry, n_{a_1}, as a feature in the electronic structure that may differentiate among the various cuprate superconductors despite their similarity. We therefore consider ten sets of parameters calculated from the structural data of Ref. 11. They are representative of compounds with maximum critical temperature ranging from 0 to 110 K. For each of them we have calculated n_{a_1} from our self-consistency equations *at the value* $\delta^{\max}$ corresponding to $T_c^{\max}$. It must be emphasized, however, that *no apparent correlation between* $T_c^{\max}$ *and* $n_{a_1}(\delta^{\max})$ *is obtained:* In order to separate the effect of crystal structure from that of doping one has to correct for the differences in doping at which $T_c^{\max}$ occurs between the various compounds. We therefore consider $n_{a_1}(\delta^{\max})-\delta^{\max}$, the excess of holes with local a_1 symmetry with respect to the doping itself. In Fig. 2, $T_c^{\max}$ is plotted versus this quantity and it is evident that a well-defined trend exists: *The higher* $n_{a_1}(\delta^{\max})-\delta^{\max}$ *is, the lower* $T_c^{\max}$ *is.* We made several tests: Such a correlation shows up so clearly only for $n_{a_1}(\delta^{\max})-\delta^{\max}$ or for the complementary quantity specifying the occupancy of states with local b_1 symmetry ($n_{a_1}-\delta\approx 1-n_{b_1}$). We have also tested the robustness of this correlation by rescaling some of the parameters of each set by the same factor for all the compounds. Looking at the input parameters, we finally point out that the variation of $n_{a_1}(\delta^{\max})-\delta^{\max}$ between compounds is largely due to the differences in $\varepsilon_p^z-\varepsilon_p$, i.e., in Madelung potential on the oxygen ions, rather than to differences in the hoppings t' and t_p', in agreement with Ref. 11.

Finally we point out some implications of our results: (i) If the pairing mechanism is related to the existence of Zhang-Rice singlets, then it is natural that a higher occupancy of b_1 states produces a higher T_c. The excess of a_1 holes simply reflects a low occupancy of b_1 states, which in turn would produce a low $T_c^{\max}$. The same conclusion was put forward in Ref. 11. (ii) All the models[18] which could qualitatively be described by mobile holes interacting with a locally antiferromagnetically correlated substrate could be supported by the above findings if one assumes that $T_c^{\max}$ is larger for those systems where it is possible to add a large amount of holes (in a_1 states) without spoiling the locally magnetically correlated (mostly b_1 symmetric) substrate. This substrate most effectively provides the pairing potential when one hole (spin) per substrate cell is present. In this case a high $T_c^{\max}$ is not obtained when n_{b_1} is as large as possible, as in case (i), but rather when $n_{b_1} \sim 1$.[19] Only further experimental analysis can distinguish between the two cases. (iii) A class of models exists where, due to the nn interaction, charge-transfer fluctuations play a crucial role in the superconducting pairing mechanism.[3,6,20] As we observed above, the strongest nn interaction occurs between holes in the $d_{x^2-y^2}$ Cu orbital and in the planar oxygen p orbitals (V_x). A high value of $n_{a_1}(\delta^{\max}) - \delta^{\max}$ corresponds to a large occupancy of $d_{3z^2-r^2}$ at the expense of the occupancy of $d_{x^2-y^2}$ and effectively reduces the nn interaction[21] ($V_x \to V_z$) and consequently the pairing potential due to charge-transfer modes.

A systematic experimental analysis of the relative occupancies of states with different symmetry as a function of doping for various cuprates and a more precise assignment of the band structure via ARPES are required to provide more stringent indications on pairing mechanisms within the present approach. In the mean time, however, the established correlation between $T_c^{\max}$ and $n_{a_1}(\delta^{\max}) - \delta^{\max}$ gives at least one clear indication that all the effective models with planar orbitals only can efficiently give rise to pairing mechanisms, but hardly reproduce systematic variations between different materials and the suppression of T_c above a certain doping. The increase of the effect of the apical oxygen with doping could explain this latter phenomenon provided it is further supported by experimental findings.

We would like to thank Professor C. Castellani, Professor A. Bianconi, and Professor M. F. H. Schuurmans for many interesting discussions and suggestions. This work has been supported by the European Economic Community under Contract No. SC1* 0222-C(EDB).

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[21] We thank Professor C. Castellani for bringing this point to our attention.