Implications of crystal-field and intra-atomic interactions for the electronic structure of high-T_c superconductors

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The energies of Cu $3d$ and O $2p$ ion orbitals in the ion-lattice potentials of La_2CuO_4 and $YBa_2Cu_3O_7$, and the intra-atomic energies of various Cu^{3+} $(3d)^8$ configurations, are calculated. The results suggest that electrons removed from the CuO_2 layer to accommodate doping in La_2CuO_4 or the $YBa_2Cu_3O_7$ stoichiometry come not from the Cu $3d_{x^2-y^2}$'s and their O $2p\sigma$ bonding partners but from otherwise filled π-bonding orbitals. The resulting two types of bonds and/or bands may be important for superconductivity.

Despite intense research activity stimulated by discoveries of superconductivity at 30 K and 40 K, respectively, in Ba- and Sr-doped La_2CuO_4,[1-4] and above 90 K in $YBa_2Cu_3O_7$,[5] the superconducting mechanism(s), remains uncertain and controversial.[6,7] Determining the initial vacuum state of the system is an important aspect of the problems as this will both suggest and limit possible mechanisms. Many of the proposed mechanisms involve different vacuum states, with one class of theories assuming the electrons of the CuO_2 layer are in delocalized band states,[8-12] while other theories assume localized electron spins on the Cu atoms, in which spins are either paired in generalized valence bond states[13-15] or are antiferromagnetically coupled.[16-18]

Here, we suggest that useful insights into the initial-state problem and other features of superconductivity models may be obtained by recognizing that these materials are primarily ionic crystals that would be insulators (as suggested by others[13-18] and this work for pure La_2CuO_4) except for the introduction of a relatively small number of charge carriers by doping in La_2CuO_4 or nonstoichiometry in $YBa_2Cu_3O_{7-\delta}$ for $\delta < 0.5$. Thus, given the reasonable assumption that screening effects of this low concentration of mobile charges can be neglected in modeling the initial state, the mobile valence electrons or holes in these materials, whose bonding and/or banding interactions are of paramount importance for conductivity and superconductivity, move in the framework of the ionic lattice under the influence of an effective potential determined primarily by the Madelung potentials at the various ions and the atomic potentials of these ions. The contribution to this effective potential from the ion core repulsions, although considered to some extent, is believed to be considerably less important for several reasons. First, the core-repulsion energy (E_R) is only a small fraction ($\approx 10\%-15\%$) of the Madelung energy[19] (E_M) and changes in E_R due to motions of the mobile electrons are thus likely to be small compared to the corresponding changes in E_M. Furthermore, E_R should not depend strongly on the mobile electrons because E_R results from overlaps of filled ion orbitals and, as discussed later, an important aspect of our results is that the different pairs of Cu and O ion orbitals which are likely to host the

mobile electrons have very similar overlap integrals. Finally, small changes in the ion positions can often reduce any increase in the short-range core repulsions incurred by the electrons moving so as to reduce the intra-atomic and long-range Madelung energies.

The Madelung potentials at the various ions in La_2CuO_4 and $YBa_2Cu_3O_7$ are calculated using the Evjen method[20] with the unit cell determining the electrically neutral groups summed over. It is unimportant that the reference or zero-level of these potentials depends on the neutral group used[20] because only differences in potential are important here. Mixtures of Cu^+, Cu^{2+}, and Cu^{3+} cations or partial holes on the O^{2-} anions are readily simulated by appropriate variation of the ionic charges. A spherical harmonic expansion of the Madelung potential in the vicinity of the ith ion, $V_i(\mathbf{r}_i)$, is obtained by introducing the spherical harmonic expansion of $1/|\mathbf{r}_i - \mathbf{r}_L|$ where $\mathbf{r}_L$ is the vector from this ion to the Lth lattice site, and summing the terms of this series over L. The result is

$$V_i(r_i, \theta_i, \phi_i) = \sqrt{4\pi} \sum_k \sum_{m=-k}^{k} C_{k,m}(i) Y_k^m(\theta_i, \phi_i) r_i^k ,$$

where r_i, θ_i, and ϕ_i are the polar coordinates of $\mathbf{r}_i$, and here and elsewhere the x, y, and z molecular axes correspond to the a, b, and c, crystallographic axes, respectively.

The results for La_2CuO_4, assuming it has the $La_{1.85}Ba_{0.15}CuO_4$ crystal structure,[8] which is the material of interest here, and is pure ionic, i.e., $La_2^{3+}Cu^{2+}O_4^{2-}$, are given in Table I.

The results for $YBa_2Cu_3O_7$ in Table II were calculated using the crystal structure of David et $al.$[21] with their suggested ionic assignments: Y^{3+}, Ba^{2+}, O^{2-}, $Cu(1)^{3+}$, and $Cu(2)^{2+}$, where Cu(1) and Cu(2) are the Cu ions in the one-dimensional (1D chains) and two-dimensional (2D planes) CuO networks, respectively. The ionic binding energy of this structure is 2.7 eV/molecule greater than that of the structure with the Cu^{3+} ions in the 2D plane. This energy difference is much less, however, if only a fraction (f) of the Cu^{3+} ions are in the 2D planes (0.25 and 0.65 eV/molecule for $f=0.2$ and 0.4), and, delocalization of the Cu^{3+} holes should yield a greater resonance

energy here than in the 1D chains. Thus, the 2D layer should have some Cu^{3+}, and probably also O^-, character, which is consistent with recent single-crystal results showing the superconductivity is associated with the 2D layer.[22]

These calculations have several interesting implications. In discussing them we use the following conventions. The term hole(s) denotes an unoccupied orbital(s) in a hypothetical reference structure where all ions have closed shells, i.e., Cu^+ and O^{2-}, so undoped La_2CuO_4 has one hole per Cu atom. Also, an ionic orbital is σ or π with respect to another ion according to whether or not it is partly directed along the corresponding interionic axis.

First, in the pristine 2D CuO_2 layer of either pure La_2CuO_4, or $YBa_2Cu_3O_7$ with all Cu^{3+} ions in the 1D chain, the electron transfer process $Cu^{2+}...O^{2-} \rightarrow Cu^+...O^-$, which is essential to forming a band of Cu$-$O hybridized orbitals, requires a large energy given by the following equation:

$$E(Cu^{2+}...O^{2-} \rightarrow Cu^+...O^-) = |e| [C_{0,0}(O) - C_{0,0}(Cu)] - I(Cu^+) + A(O^-) - e^2/R .$$

Here, $I(Cu^+) = 20.3$ eV is the Cu^+ ionization potential,[23] $A(O^-) = -8.4$ eV is the electron (dis)affinity of O^-, estimated from the energy of 6.9 eV for the exothermic process $O^{2-}(g) \rightarrow O(g) + 2e$,[19] and the 1.5 eV electron affinity of the O atom,[23] and $-e^2/R$ is the energy of the resulting electron-hole pair. In La_2CuO_4 ($R = 1.89$ Å) this energy is a forbiddingly large 13.2 eV, and it is only slightly less in $YBa_2Cu_3O_7$. (A calculation of the total atomic and Madelung energy as a function of the Cu and O charges in the CuO_2 plane, i.e., q in $La_2^{3+}Cu^{(2-q)+}O_{2,in}^{(2-0.5q)-}O_{2,out}^{2-}$, shows in a mean-field sense, that this result would not be changed if the electrons were mobile and could move collectively.) Core repulsions are unlikely to change this result significantly, since these are not only inherently small as discussed previously, but this electron transfer simply relocates a repulsive filled orbital from the O to the Cu ion. A more important consideration is that the O^- ion and its other Cu^{2+} neighbor can share their unpaired electrons to form a covalent bond or antibond according to whether their spins are in a singlet or a triplet configuration. This bond energy should be comparable to the Cu$-$O transfer integral ($t \simeq -1.6$ eV)[11] and thus will not change $E(Cu^{2+}...O^{2-} \rightarrow Cu^+...O^-)$ much,

but it may play a role in superexchange coupling between Cu^{2+} ions. Thus, in pure La_2CuO_4 the CuO_2 layer should consist largely of Cu^{2+} and O^{2-} ions with the unpaired Cu^{2+} electron spins possibly being antiferromagnetically coupled, as recent experiments suggest.[24,25]

Second, the additional holes introduced into the 2D CuO_2 layer by Ba or Sr doping of La_2CuO_4 or inherently present in $YBa_2Cu_3O_7$ should be highly mobile over both the Cu and O ions as required to form a conduction band. This is readily seen by calculations of the Madelung energy combined with ion formation energies (the ionization potentials of Cu^{2+} and Sr^{2+} are 36.8 and 43.6 eV, respectively)[23] for various assignments of the ionic charges in $La_{1.85}Sr_{0.15}CuO_4$, and similar results have been obtained for $YBa_2Cu_3O_7$. These show that the structure with 15% Cu^{3+} character is only slightly more stable, by 0.50 and 0.33 eV/molecule, respectively, than structures with 7.5% in and out of plane O^- character, whereas the structure with Sr^{3+} is considerably less stable by 1.2 eV/molecule. Thus, the additional holes should be largely in the 2D layer where their delocalization over the CuO_2 plane will yield a stabilizing resonance energy.

Finally, these additional holes are likely to be in orbitals

TABLE I. Nonzero coefficients of the spherical harmonic expansion of the ion lattice potentials at the various ions in La_2CuO_4. O(1) is the oxygen in the CuO_2 plane. Units are $|e|/Å^{k+1}$ and the x, y, and z axes of the expansion are the crystallographic $a \equiv b$ and c axes, respectively, with $x\|$ [Cu$-$O(1)].

Ion	Cu	O(1)	O(2)	La
$C_{0,0}$	-1.7122	1.7307	1.6709	-1.6682
$C_{1,0}$	0.0000	0.0000	0.0566	-0.0075
$C_{2,0}$	0.1424	-0.0260	0.0287	-0.0346
$C_{2,\pm2}$	0.0000	0.0624	0.0000	0.0000
$C_{3,0}$	0.0000	0.0000	0.0436	0.0182
$C_{3,\pm2}$	0.0000	0.0000	0.0000	0.0000
$C_{4,0}$	-0.0643	0.0025	0.0304	-0.0047
$C_{4,\pm2}$	0.0000	-0.0815	0.0000	0.0000
$C_{4,\pm4}$	-0.0614	0.0406	-0.0121	0.0056

TABLE II. Nonzero coefficients of the spherical harmonic expansion of the ion lattice potentials at the various ions in $YBa_2Cu_3O_7$ for the case where Cu^{3+} ions occupy the Cu(1) sites. Ion numbers follow the crystallographic notation. Units are $|e|/Å^{k+1}$ and the x, y, and z axes of the expansion are the crystallographic a, b, and c axes, respectively.

Ion	Cu(1)	O(1)	O(4)	Cu(2)	O(2)	O(3)	Ba	Y
$C_{0,0}$	-2.1304	1.8030	1.5648	-2.0642	1.2607	1.2541	-1.2590	-2.3693
$C_{1,0}$	0.0000	0.0000	0.3002	0.0057	-0.0335	-0.0449	0.1198	0.0000
$C_{2,0}$	-0.1737	-0.1793	0.1585	0.1489	-0.0495	-0.0404	0.0194	-0.0176
$C_{2,\pm2}$	0.1383	-0.1336	0.0217	-0.0066	0.0585	-0.0496	-0.0137	0.0000
$C_{3,0}$	0.0000	0.0000	0.0814	-0.0581	0.0111	0.0117	0.0015	0.0000
$C_{3,\pm2}$	0.0000	0.0000	0.0134	0.0033	0.0411	-0.0388	-0.0083	0.0000
$C_{4,0}$	-0.0828	0.0300	0.0662	-0.0434	-0.0055	-0.0067	-0.0020	0.0256
$C_{4,\pm2}$	-0.0378	0.0878	0.0096	0.0014	-0.0587	0.0588	-0.0075	-0.0022
$C_{4,\pm4}$	-0.0259	0.0348	-0.0110	-0.0515	0.0386	0.0367	0.0058	-0.0163

FRANK J. ADRIAN

other than Cu^{2+} $3d_{x^2-y^2}$, whose choice for the initial Cu^{2+} hole is determined primarily by Madelung energy considerations, and its O^- $2p\sigma$ (relative to the Cu) bonding partners. This is so, first, because the additional intra-atomic energy required to place the two Cu^{3+} holes in the same orbital is greater than the saving in Madelung energy, and, second, the Madelung energy is optimum for a $p\pi$ rather than a $p\sigma$ O^- hole. This is readily seen from Fig. 1(a) which gives the calculated crystal-field splittings of the Cu^{3+} $3d$ and in-plane O^- $2p$ holes[26] in La_2CuO_4 (similar results are obtained for $YBa_2Cu_3O_7$), and comparison of the former with Fig. 1(b) which gives the Cu^{3+} atomic term energy splittings calculated for various combinations of two directed $3d$ holes[26] using the LS coupling formalism.[27] Note that the atomic energies of those Cu^{3+} states with holes in different orbitals were calculated for uncorrelated spins (i.e., a random mixture of singlet and triplet spin states), even though pure triplets would have lower energies by Hund's rule, because this maximizes the ability of these orbitals to form bonds with other ions. This could have interesting consequences for the electronic structure of the high T_c superconductors, if, as is next discussed, different pairs of Cu and O orbitals have comparable bonding power.

This bonding power of the various Cu and O ion orbitals, and the related core repulsion energies, can be estimated from the corresponding overlap integrals calculated using Hartree-Fock orbitals of the neutral $Cu^+...O^-$ pair.[26] (The $Cu^{2+}...O^{2-}$ pair with a potential-stabilized O^{2-} $2p$ orbital[28] gave similar results.) These overlaps and the corresponding binding are of two types: σ and π according to the previously defined orbital types. The Cu $3d_{x^2-y^2}$ and $3d_{z^2}$ orbitals each have σ overlaps with the four nearest O ions of the CuO_2 layer, whose magnitudes at the Cu—O distance of 1.89 Å are $0.866\langle Cu,d\sigma|O,p\sigma\rangle = 0.069$ and $0.5\langle Cu,d\sigma|O,p\sigma\rangle = 0.043$, respectively. Thus, the Cu $3d_{z^2}$ bonding power in the CuO_2 layer is relatively weak compared to that of $3d_{x^2-y^2}$ but it could have a strong localized interaction with the O ions in the Ba layer [O(4)] of $YBa_2Cu_3O_7$. The $3d_{xy}$, $3d_{xz}$, and $3d_{yz}$ orbitals all form π bonds with the corresponding overlap integral being $\langle Cu,d\pi|O,p\pi\rangle = 0.071$, although different O π orbitals are involved. The $3d_{xy}$ orbital interacts with the $2p_{(x,y)\pi}$ orbitals of each of its four O neighbors in the CuO_2 layer while the equivalent $3d_{xz}$ and $3d_{yz}$ orbitals each interact with the $2p_{z\pi}$ orbitals of two nearest O ions lying along the in-plane x and y axes, respectively. Thus, the bonding power, and core repulsions, of both these orbital types should be comparable to that of the $3d_{x^2-y^2}$ orbital.

Consequently, not only are all of these Cu^{3+} uncorrelated spin configurations energetically preferable to the $^1(d_{x^2-y^2})^2$ even if their Madelung energies are slightly higher, but there is a strong likelihood of additional stabilization from the existence of both σ and π bond and/or band forming interactions with the O ions. Most importantly, interactions within and between these σ and π electronic structures could provide novel superconducting mechanisms. An obvious possibility, noted in several early proposals for raising superconducting transition temperatures,[29,30] is superconducting pairing of mobile π electrons
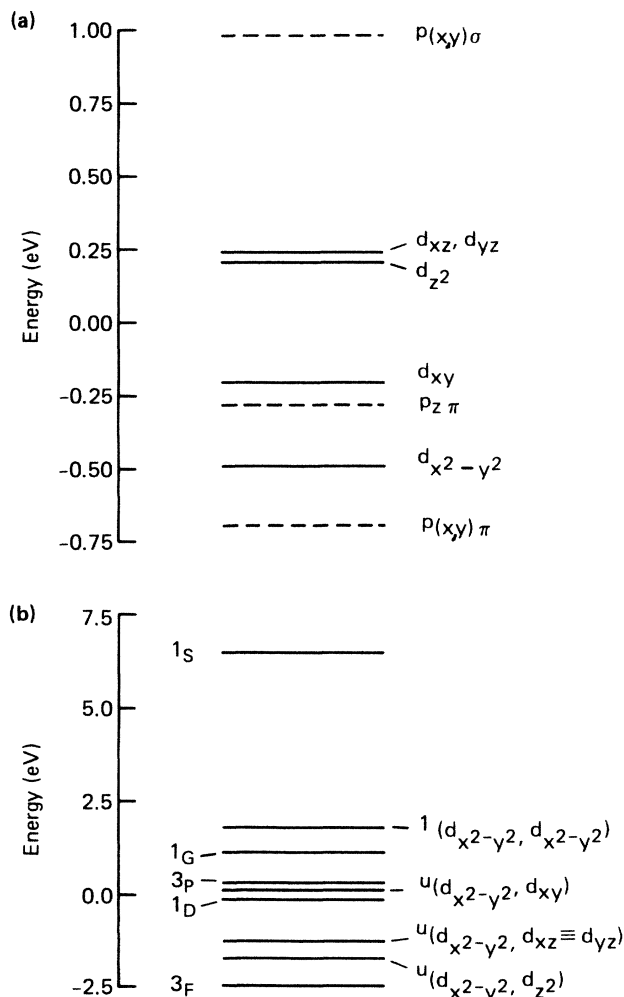

FIG. 1. (a) Crystal-field splittings of the Cu^{3+} $3d$ (solid lines) and the in-plane O^- $2p$ holes (dashed lines) in La_2CuO_4. The x, y, and z axes correspond to the crystallographic $a \equiv b$ and c axes and σ and π denote O^- holes directed toward and perpendicular to the nearest Cu. (b) Cu^{3+} $(d)^8$ atomic term energies and energies of various configurations of the two $3d$ holes in this ion. u denotes the hole spins are uncorrelated.

via scattering interactions with a localized σ charge transfer state[12] or vice versa. Also, models based on pairing of oxygen holes by interaction with antiferromagnetically ordered Cu spins[16-18] might benefit if the O and Cu hole orbitals were of different symmetry. The strong spin dependence of O hole movement via the Cu atoms, which is an essential feature of these models, would now be provided by the large singlet-triplet splittings in the intermediate Cu^{3+} (d^8) state, cf. Fig. 1(b), but strong bonding or antibonding interactions between adjacent Cu and O holes, which might disrupt the antiferromagnetically ordered Cu spin system, would no longer be present. Clearly, further work is needed to substantiate the model and explore its possibilities, but, given the unique challenge presented by high T_c superconductivity, such an effort seem well worth undertaking.

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