Tendency towards Local Spin Compensation of Holes in the High-T_c Copper Compounds

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Using an Anderson impurity description of the high-T_c superconductors, we study the character of the states closest to the Fermi level. In a kind of phase diagram involving the Cu d-d Coulomb interaction (U), the charge-transfer energy (Δ), and the hybridization (T), we show under which conditions the singlet, triplet, or delocalized ligand hole states are closest to the Fermi level. For reasonable values of T the lowest-energy hole states are local singlets ($^1A_{1g}$) of primarily $d^9\underline{L}$ character for $U > \Delta$ and local triplets ($^3B_{1g}$) of primarily d^8 character for $U < \Delta$.

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One of the most sought after basic aspects of the high-temperature superconductors concerns the nature of the states closest to the Fermi level. There seems to be a general consensus that these states are strongly localized on the CuO_2 planes. Realizing that the first ionization states in, e.g., insulating La_2CuO_4 would be the holes present in substituted and superconducting $La_{2-x}Sr_xCuO_4$, it is interesting to try to determine the nature of these first ionization states. There are strong spectroscopic[1-5] indications that these states are of primarily O-$2p$ character or holes in the oxygen band in the substituted materials. This would put the insulators in the B (charge-transfer gap) region of the Zaanen-Sawatzky-Allen[6] diagram which would move towards region D (ligand hole conduction) upon substitution. This would imply that the Cu d-d Coulomb interaction (U) is stronger than the O-$2p$–Cu-$3d$ charge-transfer energy (Δ). This experimental evidence coupled with the arguments given by Zaanen, Sawatzky, and Allen lead us to believe that important information concerning the nature of the charge carriers can be obtained by studying the Anderson impurity Hamiltonian in which the translational symmetry of the Cu ions is neglected. In this paper we present the results of such a study and address especially the questions concerning the origin, sign, and size of the exchange coupling between the doping induced O-$2p$ holes with the already present Cu-$3d$ holes. It turns out that this exchange is always ferromagnetic in octahedral symmetry (O_h point group) but for a large range of parameters strongly antiferromagnetic in square planar coordination (D_{4h} point group), forming local singlet states. Such a singlet state has in fact been assumed to be present in several theoretical investigations of the high-T_c material.[7-16] We note that in the use of a single (s-like) band Hubbard model, one also assumes local singlet states in that the spin is zero for other than single occupation. Zhang and Rice[17] have shown that such a singlet state with primarily O-$2p$ hole character is not inconsistent with a resonating-valence-bond description[7] of the high-T_c materials. In addition such a local singlet character could be the reason for the rapid disappearance of magnetic order with substitutions.

In the calculations we consider the Cu-$3d$ states as independent impurities hybridizing with an O-$2p$ band.[18] Although there is both theoretical[19] and experimental[5] evidence for substantial O-$2p$–O-$2p$ interactions (4–7 eV), we can safely neglect these in the low-hole-density limit considered here. The resulting Anderson impurity Hamiltonian ($H = H_0 + H_1$) is given by

$$H_0 = \sum_m \int d\epsilon\, \epsilon c^\dagger_{\epsilon m} c_{\epsilon m} + \sum_m \epsilon_m d^\dagger_m d_m + \sum_m \int d\epsilon [T(m) d^\dagger_m c_{\epsilon m} + \text{H.c.}],$$

$$H_1 = \sum_{m,m',n,n'} U(m,m',n,n') d^\dagger_m d_{m'} d^\dagger_n d_{n'}.$$

Here $c^\dagger$ creates electrons in the ligand (oxygen) band with energy ϵ. The operators $d^\dagger$ create Cu-$3d$ electrons. The indices m, m', n, and n' denote the spin and orbital quantum numbers. H_0 describes the (one-particle) interaction between the Cu-$3d$ and O-$2p$ orbitals, and H_1 the Cu-$3d$ Coulomb repulsion.

The ground state is given by one hole in a $3d$ orbital (d^9) with some mixed in ligand hole band character ($d^{10}\underline{L}_k$). Removal of an extra electron by means of doping or photoemission leaves us with a two-hole problem which is exactly solvable. To calculate the ionization states of Cu in square planar coordination of oxygen, we use the formalism developed by Zaanen and Sawatzky[18] to calculate ground states, band gaps, and spectral line shapes of transition-metal compounds.

In square planar symmetry the labels m are, aside from spin, taken to be the b_{1g} ($d_{x^2-y^2}$), a_{1g} ($d_{3z^2-r^2}$), b_{2g} (d_{xy}), and e_g (d_{xz},d_{yz}) orbitals which are the irreducible representations spanned by a d hole in a D_{4h} point group. The ligand hole wave functions used are taken to be linear combinations of O-$2p$ orbitals with the above symmetries. If we take $T(m)$ to be the nearest-neighbor matrix element coupling d_m with $\underline{L}_m$ as defined above, it is easy to show that $T(a_{1g}) = T(b_{1g})/\sqrt{3}$ and $T(e_g) = T(b_{2g})/\sqrt{2}$. Since, in general, π bonding is about $\frac{1}{2}$ of the σ bonding,[20] we take $T(b_{2g}) = T(b_{1g})/2$. These differences in $T(m)$ yield the ligand field splitting and the fact that T for b_{1g} is the largest causes the ground state to be that with one hole in an (antibonding) orbital of b_1 ($d_{x^2-y^2}$) symmetry which has predominantly Cu (d^9) character for a large charge-transfer energy (Δ).

The ground state is the lowest-energy pole of the one-hole Green's function

$$g_d^d(m,z) \equiv \langle \Phi | d_m^\dagger \frac{1}{z-\delta+H_0} d_m | \Phi \rangle$$
$$= [z-\delta+\epsilon_m - T^2(m)\Gamma(z-\delta+\Delta)]^{-1},$$

where

$$\Gamma(z) = \int_{-\infty}^{\infty} \frac{\rho(\epsilon)}{z+\epsilon} d\epsilon,$$

and the vacuum state $|\Phi\rangle$ is taken to be the state with a full O-2p band and Cu in a d^{10} configuration. Taking $\epsilon_m = \epsilon(b_{1g}) = 0$, we get a ground state stabilized by hybridization by an amount

$$\delta = T^2(b_{1g}) \int \frac{\rho(\epsilon)}{\delta-\Delta-\epsilon} d\epsilon,$$

where $\rho(\epsilon)$ is the O-2p band density of states.

The d-electron-removal (photoelectron) spectrum is given by the solutions of an also exactly solvable two-hole Green's function.[21] However, now we must take into account the d-d Coulomb and exchange interactions defined by the A, B, and C Racah parameters. The d^8 states span singlet and triplet irreducible representations in D_{4h} for which the Coulomb and exchange matrix elements and basis functions are given in Ref. 18.

An exact expression for a two-particle problem can be written in terms of the T matrix by use of $G = G_0 + G_0 T G_0$ and $T = H_1 + H_1 G_0 T$. The matrix elements of H_1 are determined by the A, B, and C Racah parameters.[18] The d-electron-removal spectrum is determined by

$$G_{dd}^{<}(m,m';z) \equiv \langle \text{g.s.} | d_m^\dagger G d_{m'} | \text{g.s.} \rangle,$$

where $|\text{g.s.}\rangle$ is the (one hole) ground state and $G = (z-\delta+H)^{-1}$.

It is easy to show that in terms of the two-hole irreducible representations Γ_I

$$G_{dd}^{<}(m,m';z)$$
$$= \sum_I \langle b_{1g}m |\} \Gamma_I \rangle \langle \Gamma_I |\} b_{1g}m \rangle G_{dd}^{<}(m,m',z;\Gamma_I),$$

$$G_{dd}^{<}(m,m',z;\Gamma_I)$$
$$= g_d^d(m,z)\delta_{mm'} + g_d^d(m,z)\langle n_d \rangle T_{b_{1g}m}^{b_{1g}m'}(\Gamma_I) g_d^d(m',z),$$

where $\langle b_{1g}m |\} \Gamma_I \rangle$ is the fractional parentage.

To solve these equations we used a semielliptical O-2p band of total width W, the free-ion Racah $B = 0.15$ and $C = 0.58$ parameters,[22] and treated the Racah A parameter, Δ, and $T(b_{1g})$ as variables.

In Fig. 1 an example of a d spectral distribution as calculated for $W = 4.4$ eV, $T(b_{1g}) = 2.35$ eV, $A = 7.6$ eV, and $\Delta = 2.75$ eV (Ref. 23) is shown. Also shown is the decomposition of the d spectral distribution into the various final-state irreducible representations. We see that the hybridization is strong because the spectral weight of all of them is spread out over a large energy range. Of most interest is the first peak which is of pure $^1A_{1g}$ character.[24]

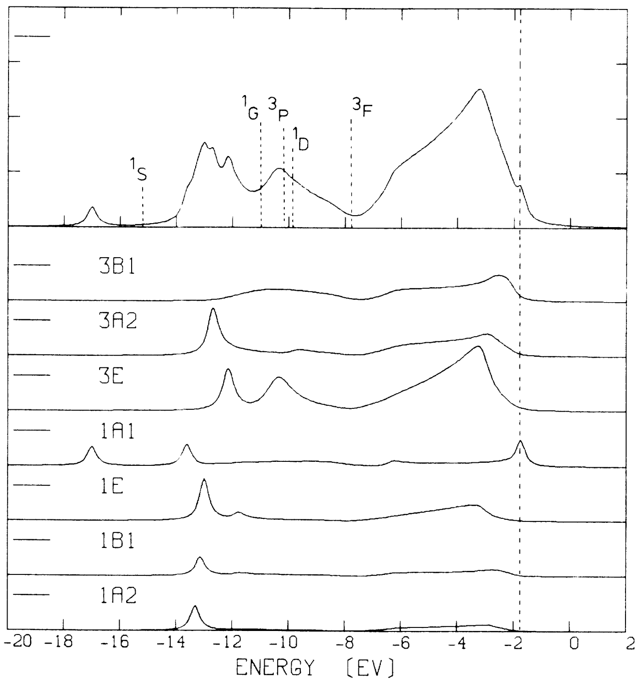

FIG. 1. The d-electron-removal spectral weight calculated for $A = 7.6$ eV, $\Delta = 2.75$ eV, $T(b_{1g}) = 2.35$ eV, and $W = 4.4$ eV. Also shown are the contributions from the various irreducible representations.

In Fig. 2 we show, in a $A - \Delta$ (Ref. 25) against $T(b_{1g})$ diagram for $W = 4.4$ eV (solid curves) and $W = 2.0$ eV (dashed curves), the various possible types of first ionization states. The curves drawn give the boundaries for obtaining, respectively, $^1A_{1g}$ or $^3B_{1g}$ bound states as indicated. The hatched regions marked I, II, and III refer to $W = 4.4$ eV. In region I there are no bound states. In region II the $^3B_{1g}$ discrete state is the first ionization state whereas in region III the singlet ($^1A_{1g}$) state is the lowest in energy. From this figure we see that for sufficiently large $A - \Delta$ and $T(b_{1}g)$ a local singlet is the lowest ionization state. These limits are well below the values generally accepted from experimental data for the high-T_c materials strongly indicating that these lie in region III. McMahan, Martin, and Satpathy[19] have recently calculated values for the parameters which upon translation to our notation become $A - \Delta \simeq 4.5$ eV and $T(b_{1g}) \simeq 3.2$ eV. We have included in Fig. 2 this point which lies well into region III.

It is also interesting to note that for $A \leq \Delta$, in which case the first ionization state would be of primarily Cu^{3+}

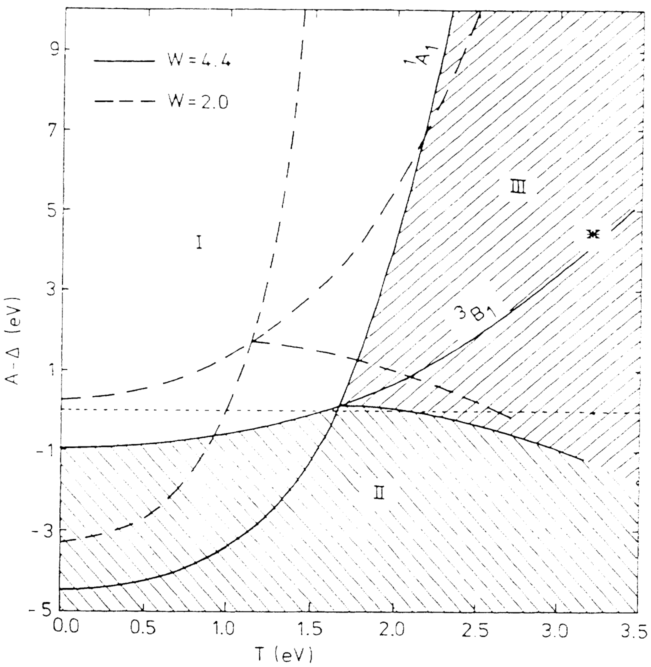

FIG. 2. A plot showing the parameters $A-\Delta$ and $T(b_{1g})$ for which the $^1A_{1g}$ and the $^3B_{1g}$ states just form discrete states and a division into regions corresponding to the following: I, no discrete state; II, $^3B_{1g}$ discrete state; and III, $^1A_{1g}$ discrete state as the lowest-energy states. The solid lines are drawn for $W=4.4$ eV and the dashed lines for $W=2$ eV. The calculations are done with $\Delta=2.75$ eV. The asterisk is the position obtained from the parameters of Ref. 19.

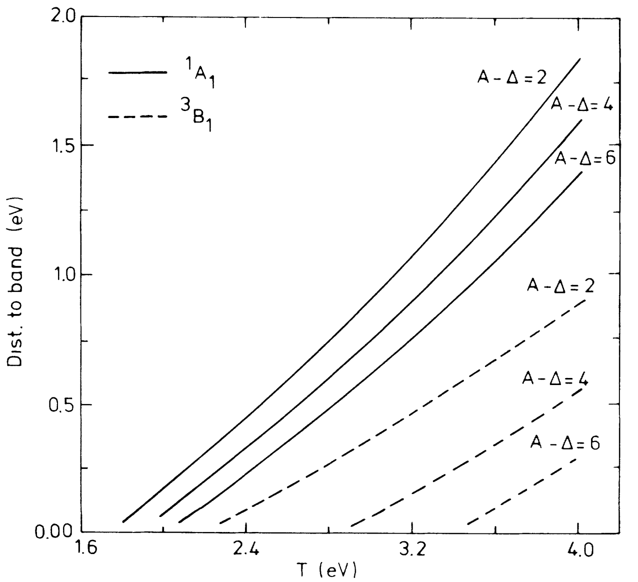

FIG. 3. The energy above the band of the $^1A_{1g}$ and $^3B_{1g}$ discrete states as a function of $T(b_{1g})$ for various values of $A-\Delta$.

(d^8) character, the *triplet and not the singlet state* would be the lowest for any reasonable value of $T(b_{1g})$, *so if* Cu^{3+} (d^8) *were present it would be high spin.*

The same calculation can be repeated for O_h symmetry, for which the $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ orbitals hybridize equally strongly with the ligand states. Since the triplet d^8 states ($d^{\uparrow}_{x^2-y^2}d^{\uparrow}_{3z^2-r^2}$) are lower in energy than the singlet state ($d^{\uparrow}_{x^2-y^2}d^{\downarrow}_{x^2-y^2}$) (Hund's rule), the lowest-energy state pushed out of the band will always be a triplet.

For the parameters used for Fig. 1, which are close to expected values for the high-T_c materials, we find that the first ionization state is a singlet ($^1A_{1g}$). It is split from the band because of hybridization with the d^8 ($^1A_{1g}$) state but it in fact has only 4% d^8 character although, as is evident from Fig. 1, it has considerable Cu-d spectral weight (18%) because both the d^8 and $d^9\underline{L}$ can be reached from the ground state by d emission. Because of the small amount of d^8 character in the first ionization state, it seems quite reasonable to neglect this and use a model Hamiltonian with $U_{dd}\rightarrow\infty$. However, it is then extremely important to include a ligand hole–Cu d hole antiferromagnetic exchange interaction as well as a strongly reduced ligand hole dispersional bandwidth and a Cu interatomic antiferromagnetic superexchange. An estimate of the ligand hole–Cu d hole exchange is given by the energy separation of the $^1A_{1g}$ and $^3B_{1g}$ discrete states or the $^1A_{1g}$ separation from the band. This is shown in Fig. 3 for various values of $A-\Delta$ as a function of T for $W=4.4$ eV. We see that for $A-\Delta=4$ eV (which would correspond to $A\simeq7$ eV, $\Delta\simeq3$ eV) and $T=2.4$ eV the exchange defined as above is about 0.3 eV.[26] The exchange interaction using the calculated parameters of McMahan, Martin, and Satpathy[19] is even larger ($\simeq0.8$ eV). These values are at least an order of magnitude larger than the Cu-Cu superexchange and therefore would tend to break up antiferromagnetic long-range order in preference to local singlet formation.

In conclusion, we have shown that the lowest ionization states of the CuO_2 layers in the high-T_c materials are, using an impurity model, most likely discrete singlet states. This conclusion is not very sensitive to the choice of the O-2p band shape or width for parameter sets suitable for the high T_c's. These states correspond to a d hole and a ligand hole of combined singlet ($^1A_{1g}$) character which is lowest in energy because of the hybridization with much higher lying Cu-d^8 states of $^1A_{1g}$ character. The lowest-energy state is of primarily b_{1g}^2 character although some a_{1g}^2, b_{2g}^2, and e_g^2 characters are mixed in. The order of the unhybridized d^8 states $^1A_{1g}$ and $^3B_{1g}$ is inverted for the $d^9\underline{L}$ state in D_{4h} but not in O_h symmetry, showing the importance of the low symmetry for the high T_c's. This inverted ordering, resulting in a singlet lowest-energy state, appears only for $U>\Delta$ for reasonable values of the transfer integral. We are of the opinion that these states, upon inclusion of translational symmetry, form the quasiparticle states responsible for the conductivity and superconductivity in the high-T_c materials.

After submission of this paper, we were informed of the calculation by McMahan, Martin, and Satpathy[19] who also obtained a singlet for the lowest-energy ionization state of La_2CuO_4.

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[1] Zhi-xun Shen, J. W. Allen, J. J. Yeh, J. S. Kang, W. Ellis, W. Spicer, I. Lindau, M. B. Maple, Y. D. Dalichaouch, M. S. Torikachvili, J. Z. Sun, and T. H. Geballe, Phys. Rev. B **36**, 8414 (1987).

[2] N. Nücker, J. Fink, J. C. Fuggle, P. J. Durham, and W. M. Temmerman, Phys. Rev. B **37**, 5158 (1988).

[3] A. Fujimori, E. Takayama-Muromachi, Y. Uchida, and B. Okai, Phys. Rev. B **35**, 8814 (1987).

[4] P. Steiner, S. Hüfner, V. Kinsinger, I. Sander, B. Siegwart, H. Schmitt, R. Schulz, S. Junk, G. Schwitzgebel, A. Gold, C. Politis, H. P. Müller, R. Hoppe, S. Kemmler-Sack, and C. Kunz, Z. Phys. B **69**, 449 (1988).

[5] D. v. d. Marel, J. v. Elp, G. A. Sawatzky, and D. Heitmann, to be published.

[6] J. Zaanen, G. A. Sawatzky, and J. W. Allen, Phys. Rev. Lett. **55**, 418 (1985).

[7] P. W. Anderson, G. Baskeran, Z. Zou, and T. Hsu, Phys. Rev. Lett. **58**, 2790 (1987).

[8] T. M. Rice, Z. Phys. B **67**, 141 (1987).

[9] L. J. de Jongh, Solid State Commun. **65**, 963 (1988).

[10] M. Imada, J. Phys. Soc. Jpn. **56**, 3793 (1987).

[11] I. Afflect and J. B. Marston, to be published.

[12] C. M. Varma, S. Schmitt-Rink, and E. Abrahams, in *Proceedings of the International Conference on New Mechanisms of Superconductivity, Berkeley, California, 1987,* edited by V. Kresin and S. Wolf (Plenum, New York, 1987).

[13] A. E. Ruckenstein, P. J. Hirschfeld, and J. Appel, Phys. Rev. B **36**, 857 (1987).

[14] S. A. Trugman, Phys. Rev. B **37**, 1597 (1987).

[15] J. E. Hirsch, Phys. Rev. Lett. **59**, 228 (1987).

[16] R. H. Parmenter, Phys. Rev. Lett. **59**, 923 (1987).

[17] F. C. Zhang and T. M. Rice, Phys. Rev. B **37**, 3759 (1988).

[18] J. Zaanen and G. A. Sawatzky, to be published, and Can. J. Phys. **65**, 1262 (1987); G. A. Sawatzky, in Proceedings of the Eleventh Taniguchi Conference, edited by A. Kotani, Springer Series in Solid State Sciences (Springer-Verlag, New York, to be published).

[19] A. K. McMahan, R. M. Martin, and S. Satpathy, Phys. Rev. B (to be published).

[20] L. F. Mattheiss, Phys. Rev. B **5**, 290 (1972).

[21] M. Cini, Solid State Commun. **24**, 681 (1977); N. Vos, D. v. d. Marel, and G. A. Sawatzky, Phys. Rev. B **29**, 3073 (1984).

[22] J. S. Griffith, *The Theory of Transition Metal Ions* (Cambridge Univ. Press, Cambridge, England, 1961).

[23] Note that Δ is defined from the center of the O-2p band. The equivalent cluster value of Δ would be about 0.5–1 eV.

[24] Note that we have taken the point-charge contributions to the crystal field to be zero so that for zero hybridization the d^8 states are those of the free ion (dashed lines in Fig. 1).

[25] In Figs. 2 and 3 the value of Δ plays a role only via the $d^{10}\underline{L}$ band. The positions of the singlet and triplet bound states are therefore only weakly dependent on Δ and depend mainly on $A-\Delta$.

[26] For an oxygen bandwidth of 2 eV, the exchange defined above is even larger. For the same parameters we find 0.5 eV as compared to 0.3 eV for $W=4.4$ eV.