RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 40, NUMBER 4 1 AUGUST 1989

Electronic Hamiltonian and antiferromagnetic interactions in La_2CuO_4

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(Received 17 April 1989)

A many-body Hamiltonian for La_2CuO_4 with *ab initio* parameters is solved numerically using embedded-cluster approximations. The results give an antiferromagnetic insulator with a 2–3 eV energy gap, consistent with spectroscopic measurements, NMR chemical shifts, and the spin-wave velocity. The Néel state has a significant frustration due to second-neighbor interactions, $J_2/J_1 \approx 5\%$–8%. Two competing states are found for holes introduced by doping, with primarily in-plane oxygen p_σ and out-of-plane oxygen p_z character.

A crucial step in understanding the new high-temperature superconductors is to identify the appropriate model Hamiltonian for the electrons, which may be among the wide variety of possible Hamiltonians that have been proposed.[1-6] In order to derive parameters in the many-body Hamiltonian, detailed calculations have been carried out for La_2CuO_4 by McMahan, Martin, and Satpathy[7] (MMS) and Hybertsen, Schlüter, and Christensen[8] (HSC). MMS solved their Hamiltonian in an Anderson impurity approximation and found general agreement with experiments,[9-11] in particular, a magnetic ground state, a gap at the Fermi level, and a $d^9 \rightarrow d^8$ satellite in photoemission, which are not present in the usual single-particle band calculations.[9]

The purpose of this Rapid Communication is to show that a wide range of spectroscopic and magnetic measurements on La_2CuO_4 can be understood using the many-body parameters of MMS and HSC and the resulting correlated wave functions. Furthermore, we use the present comparison with experimental quantities to limit the allowed ranges for two key parameters, the O_I $2p$ to Cu $3d$ level separation, $\varepsilon_{pI} - \varepsilon_d$, and hopping matrix element t_{pd}. A wide range of different values for these parameters has been proposed by various authors[11-13] based upon comparison to different experimental results. The quantities that we calculate include the gap at the Fermi level for insulating La_2CuO_4, the nature of the highest-lying hole states, the gaps for neutral excitations, the copper NMR chemical shift tensor, the magnitude of the copper moments, the Heisenberg interactions, and the spin-wave velocity. The latter particularly limits the allowed range of the many-body parameters. We also show that for the entire parameter range the spin lattice has significant frustration because of second-neighbor interactions. This is due to the large oxygen-oxygen overlap emphasized by MMS.[7] Frustration of the spin lattice has relevance for a number of recent theories in which the ordered Néel state is replaced by a spin-liquid or resonant-valence-bond state.[1,14-17]

Ab initio parameters for a microscopic many-body Hamiltonian for La_2CuO_4 were derived by MMS and HSC from constrained density-functional theory. This uses the local-density approximation (LDA) to find ground-state energies of the system subjected to external constraints.[18,19] The many-body interaction parameters derived in this way can describe cases where the usual LDA fails, for example, the electronic and magnetic properties of Mott insulators such as NiO,[19,20] PrO_2,[18] or La_2CuO_4. In this latter case the energy differences are calculated with constrained occupancy of the copper d shell, giving the copper site energy ε_d and Coulomb interaction U_d. Similarly constrained oxygen occupancy is used to calculate U_p and U_{pd}. The oxygen-derived energy bands give estimates of the oxygen-oxygen hopping matrix elements t_{pp} and site energies ε_{pI} and ε_{pII}. The Cu-O hybridization t_{pd} can be found using the LDA matrix elements. The parameters obtained in this way by MMS are summarized in the first column in Table I. The large oxygen-oxygen hybridization is a consequence of the ~6-eV-wide oxygen bands found by MMS and has also been noted recently by Park *et al.*[21] and by Yu, Massida, and Freeman.[22] In addition to these parameters, in our calculations we have also included a direct Hartree-Fock exchange interaction K (-0.36 eV) between the copper and oxygen sites, as proposed by Stechel and Jennison.[12] This has a small but significant effect on the calculated exchange constants J.

There is some degree of uncertainty in the above calculations of the many-body parameters, primarily due to the differences between the linear muffin-tin-orbital (LMTO) basis functions and the true Wannier orbitals. The most sensitive parameter is the copper-oxygen energy difference, $\varepsilon_{pI} - \varepsilon_d$. For example, if equal sized copper and O_I spheres are used, this parameter is found to be ~2 eV larger than given by MMS while other parameters change by only ~10%. For comparison with our results in Table I we have listed in the second column the parameters obtained by HSC. These values were also obtained in con-

TABLE I. Constrained density-functional parameters for holes in La_2CuO_4. Column 1 is from McMahan, Martin, and Satpathy (Ref. 7), column 2 is from Hybertsen, Schlüter, and Christensen (Ref. 8). All energies are given in eV. When a range of values occurs the preferred values are given in parentheses. Where no values are given in column 2 we have used the same values as in column 1. The hopping matrix elements are derived from the Slater-Koster parameters by $t_{pp}=(V_{pp\pi}-V_{pp\sigma})/2$, $t_{pd}=\sqrt{3}/2V_{pd\sigma}$.

	MMS	HSC
$\varepsilon_{p\mathrm{I}}-\varepsilon_d$	1.3–3.3(2.3)	2–4(3.6)
$\varepsilon_{p\mathrm{I}}-\varepsilon_{p\mathrm{II}}$	1.8	
U_d	8.5	9–11(10.5)
U_p	4.1–7.3(6)	3–8(4)
U_{pd}	0.6–1.3(1)	0.7–1.7(1.2)
$V_{pd\sigma}$	1.85	1.50
$V_{pd\pi}$	−0.75	
$V_{pp\sigma}$	−1.0	
$V_{pp\pi}$	0.3	
t_{pd}	1.6	1.3
t_{pp}	0.65	0.65

strained density-functional theory, but implementing the constraints with a Lagrange multiplier method (unlike MMS), and by fitting matrix elements to the full LDA band structure rather than using the constrained oxygen-only bands. The ranges of parameters are very similar, although their preferred fit (given in parentheses in Table I) has $\varepsilon_{p\mathrm{I}}-\varepsilon_d\sim 3.6$ eV which is near the upper limit of the range given by MMS, and they have t_{pd} 20% smaller than MMS. The range of parameters shown in Table I is consistent with a number of estimates obtained by using experimental data,[6,12,13] although these estimates vary widely.

The many-body Hamiltonian obtained above is an extended Hubbard model[2,3,12,13] for which it is necessary to make some approximations in order to obtain solutions. Since the copper Coulomb interaction U_d is large compared to t_{pd}, we have chosen an Anderson impurity-type approach in which we set $t_{pd}=0$ on all but one or two copper sites. Furthermore, since the solutions to this model are bound states localized near the copper sites, it is only important to include the Coulomb interactions U_p, U_{pd}, and K for their nearest-neighbor oxygens. The remaining atoms in the oxygen lattice ($\sim$5000 atoms in the full three-dimensional La_2CuO_4 structure) are assumed noninteracting ($U_p=U_{pd}=K=0$). Within this approximation we can calculate the bound-state eigenvalues exactly by numerical diagonalization. The method we use is to first apply the block recursion (or Lanczos) algorithm of Nex[23] to transform the single-particle Hamiltonian to a block tridiagonal form. The many-body Hamiltonian is then constructed using this new basis set and diagonalized by a further application of the Lanczos algorithm. The bound-state eigenvalues converge quickly with respect to basis set size and with number of Lanczos iterations. The calculations presented here use the tight-binding parametrization of the Hamiltonian discussed above. We have verified that for the single impurity model, this gave numerical results almost identical to those described previously by MMS.

We first consider the five-atom cluster of a copper site and its four oxygen nearest neighbors embedded in the oxygen lattice. The eigenvalues are summarized in Table II as a function of the key parameters $\varepsilon_{p\mathrm{I}}-\varepsilon_d$ and t_{pd}. We find that the ground state is a single hole bound to the copper site by 2–4 eV relative to the oxygen band edge. This state has x^2-y^2 symmetry and is strongly localized, at least 98% of its weight on the copper d state and the four nearest oxygen atoms. The weight on the copper site itself, $\langle n_d\rangle$, is 60%–70%, which is consistent with the observed Néel state staggered magnetization[24] of 0.48 $\pm 0.15\mu_B$, where the moment is reduced from $1.14\mu_B$ expected for Cu^{2+} by both hybridization and by $\sim$60% because of quantum fluctuations[25] (here μ_B is the Bohr magneton). As a further experimental test we have calculated the chemical shift tensor of copper nuclear magnetic resonance (NMR), which is sensitive to both the ground and excited states. Evaluating the paramagnetic chemical shifts[26] using the embedded-cluster wave function and taking[27] $\langle d|r^{-3}|d\rangle=6.3a_0^{-3}$ gives the values shown in Table II. The experimental value has been estimated for the CuO_2 plane site in $YBa_2Cu_3O_{7-\delta}$ giving $K_{xx}=0.44\%$, $K_{zz}=1.69\%$,[27] or $K_{xx}=0.24\pm 0.02\%$, $K_{zz}=1.35\pm 0.08\%$,[28] which are consistent with the calculated values in columns 2–4.

There is an energy gap E_{gap} of 2–3 eV between the energies to add or remove a hole from the cluster, as shown in Table II. This gap is consistent with that observed experimentally in combined photoemission and bremsstrahlung isochromat spectroscopy experiments.[10] Furthermore, the size of the gap and the fact that the two-hole state is predominantly of $d^9\underline{L}$ character (here $\underline{L}$ denotes ligand hole) is in accord with the observations of Cu x-ray-absorption edge spectroscopy for doped and undoped La_2CuO_4 by Bianconi *et al.*[29] In our calculation two states have almost degenerate energy for the added hole. These states are a singlet state with x^2-y^2, x^2-y^2 ($^1A_1$) symmetry, and a triplet state with x^2-y^2, $3z^2$-r^2 ($^3B_1$) symmetry. The former is energetically favored by the larger in-plane Cu-O hybridization while the effects of U_p and U_{pd} favor the latter, hence resulting in energies which are the same to within $\sim$0.1 eV.[30,31] Our LMTO calculations indicate that the CuO_2 layer in-plane π states discussed by Guo, Langlois, and Goddard[5] and by Aharony *et al.*[6] lie $\sim$0.7 eV above the bottom of the O-hole continuum because of hybridization effects with La states neglected by these authors. The added hole states in Table II, on the other hand, are 0.3–0.7 eV below the bottom of the O-hole continuum, and are thus the likely levels for the doped holes.

The single copper site calculations described above showed the existence of spin-$\frac{1}{2}$ Cu^{2+} local moments in La_2CuO_4; we now calculate the exchange interactions between these spins J_1 and J_2 where

$$\hat{H}=J_1\sum_{\langle i,j\rangle}\mathbf{S}_i\cdot\mathbf{S}_j+J_2\sum_{\langle i,k\rangle}\mathbf{S}_i\cdot\mathbf{S}_k\ ,$$

and the sums over $\langle i,j\rangle$ and $\langle i,k\rangle$ denote all pairs of

TABLE II. Embedded-cluster results for La_2CuO_4, calculated with parameters from Table I. All energies are given in eV. The ground-state energy is measured relative to the oxygen band edge. The neutral excitation energies are, for example, $\Delta_{3z^2-r^2}=\varepsilon_{3z^2-r^2}-\varepsilon_{x^2-y^2}$, and the added hole energies are the lowest gap, $E_{\rm gap}$, and the differences in energies to add holes in $3z^2-r^2$ and x^2-y^2 states, $E_{x^2-y^2}-E_{3z^2-r^2}$. J_1 and J_2 are the first- and second-neighbor exchange interactions and c is the spin-wave velocity in eV Å.

	1	2	3	HSC
$\varepsilon_{p1}-\varepsilon_d$	2.3	4.8	3.3	3.6
t_{pd}	1.6	1.6	1.28	1.3
Ground state				
$\varepsilon_{x^2-y^2}$	−2.32	−3.90	−2.29	−2.52
$\langle n_d\rangle$	0.54	0.72	0.64	0.67
Neutral excitations				
$\Delta_{3z^2-r^2}$	0.99	0.94	0.77	0.78
Δ_{xy}	2.23	1.60	1.38	1.34
Δ_{xz}	2.26	1.71	1.48	1.45
Added hole				
$E_{\rm gap}$	1.90	3.20	1.99	2.25
$E_{x^2-y^2}-E_{3z^2-r^2}$	−0.03	+0.15	−0.12	−0.12
NMR chemical shift				
K_{zz}	0.61%	1.38%	1.29%	1.42%
K_{xx}	0.15%	0.33%	0.30%	0.33%
Exchange parameters				
J_1	0.362	0.186	0.192	0.167
J_2	0.031	0.010	0.017	0.014
c	2.05	1.10	1.10	0.95

nearest-neighbor and next-nearest-neighbor sites, respectively. We calculate J_1 using an embedded cluster consisting of two nearest-neighbor copper sites and the intermediate oxygen site, and J_2 using an embedded cluster of two second-neighbor copper sites and the four intermediate oxygens. The method used is the same as for the single copper site problem, i.e., exact diagonalization of the one- and two-hole eigenproblems using the Lanczos method. The exchange interaction J is given by the difference between the lowest triplet and singlet eigenvalues for two holes. Our results for the exchange constants are summarized in Table II. Notice in particular that the second-neighbor interactions J_2 are quite large, $J_2/J_1\sim 5\%$–8%, arising from the oxygen-oxygen overlap t_{pp}. This shows that undoped La_2CuO_4 has a substantial degree of frustration of its antiferromagnetic order. If this frustration, J_2/J_1, is large enough [estimates vary from 13%,[14] 25%,[16] 40%,[15] to ~50% (Ref. 17)] it may destroy the Néel long-range order giving rise to a disordered state, possibly of the resonant valence-bond type. Holes introduced by doping will also frustrate the spin lattice,[1] possibly explaining why small dopant concentrations destroy the antiferromagnetic order.[9]

The spin-wave velocity of a frustrated $2d$ spin-$\frac{1}{2}$ antiferromagnet is given by[32]

$$c=\sqrt{8}Z_c S J_1 a\left(1-\frac{2J_2}{J_1}\right)^{1/2},$$

where a is the lattice spacing (3.81 Å) and Z_c is a renormalization factor due to quantum fluctuations estimated to be 1.158 (for $S=\frac{1}{2}$ and $J_2=0$). Our calculated values of J's give c in Table II ranging from 2.0 to 0.95 eV Å, the latter of which compares well with the experimental values or 0.74 eV Å obtained in Raman scattering,[33] or 0.6 ± 0.15 eV Å found in the neutron experiments.[34] The large values of J_1 and c found using the original MMS parameters of column 1 in Tables I and II suggest that either $\varepsilon_{p1}-\varepsilon_d$ is too small or t_{pd} is too large, and that the parameters in columns 2 and 3 are more accurate.

In summary, we have obtained a many-body Hamiltonian for La_2CuO_4 with *ab initio* microscopic parameters, which we have then solved within embedded-cluster approximations. Our calculations are consistent with the material being an antiferromagnetic Mott insulator with an energy gap of ~2–3 eV, provided that the quasiparticle band dispersion is small in the true lattice solution. Our picture agrees with a variety of spectroscopic probes[9] and with the observed moment. Two competing states are found for the dopant holes: primarily oxygen in-plane p_σ and out-of-plane p_z, respectively. By varying the parameters we have seen that reasonable values of the spin-wave velocity and of the NMR chemical shifts can be obtained with $\varepsilon_{p1}-\varepsilon_d$ from 4.8–3.3 eV and with t_{pd} in the range 1.6–1.3 eV. These parameters are consistent with those independently proposed by Hybertsen, Schlüter, and Christensen.[8] We also find that the antiferromagnetic Heisenberg Hamiltonian has considerable second-neighbor interactions, giving some degree of frustration even in the undoped material.

We thank D. Durand, C. Pennington, C. P. Slichter, S. Renn, N. Trivedi, and G. Sawatzky for helpful discussions. This work was supported by National Science Foundation Grant No. NSF-DMR86-12860.

[1]P. W. Anderson, Science **235**, 1196 (1987).
[2]F. C. Zhang and T. M. Rice, Phys. Rev. B **37**, 3757 (1988).
[3]V. J. Emery, Phys. Rev. Lett. **58**, 2794 (1988).
[4]D. M. Newns, P. C. Pattnaik, M. Rasolt, and D. A. Papaconstantopoulos, Phys. Rev. B **38**, 7033 (1988).
[5]Y. Guo, J. Langlois, and W. A. Goddard III, Science **239**, 896 (1988).
[6]A. Aharony, R. J. Birgeneau, A. Coniglio, M. A. Kastner, and H. E. Stanley, Phys. Rev. Lett. **60**, 1330 (1988).
[7]A. K. McMahan, R. M. Martin, and S. Satpathy, Phys. Rev. B **38**, 6650 (1988).
[8]M. S. Hybertsen, M. Schlüter, and N. E. Christensen, Phys. Rev. B. **39**, 9028 (1989).
[9]For a review, see K. V. Haas, in *Solid State Physics,* edited by H. Ehrenreich and D. Turnbull (Academic, San Diego, 1989), Vol. 42, p. 213.
[10]D. van der Marel, J. van Elp, G. A. Sawatzky, and D. Heitmann, Phys. Rev. B **37**, 5136 (1988).
[11]Z. Shen *et al.*, Phys. Rev. B **36**, 8414 (1988).
[12]E. B. Stechel and D. R. Jennison, Phys. Rev. B **38**, 4632 (1988).
[13]F. Mila, Phys. Rev. B **38**, 11 358 (1988).
[14]M. Inui, S. Doniach, and M. Gabay, Phys. Rev. B **38**, 6631 (1988); S. Doniach, M. Inui, V. Kalmeyer, and M. Gabay (unpublished).
[15]P. Chandra and B. Doucot, Phys. Rev. B **38**, 9335 (1988).
[16]D. S. Rokhsar (private communication).
[17]E. Dagotto and A. Moreo, Phys. Rev. B 39, 4744 (1989).
[18]A. K. McMahan and R. M. Martin, in *Narrow Band Phenomena,* edited by J. C. Fuggle, G. A. Sawatzky, and J. W. Allen (Plenum, New York, 1988), p. 133.
[19]M. R. Norman and A. J. Freeman, Phys. Rev. B **33**, 8896 (1986).
[20]G. A. Sawatzky and J. W. Allen, Phys. Rev. Lett. **53**, 2339 (1984).
[21]K. T. Park, K. Terakura, T. Oguchi, A. Yanase, and M. Ikeda, J. Phys. Soc. Jpn. **57**, 3445 (1988).
[22]J. Yu, S. Massida, and A. J. Freeman, Physica C **152**, 273 (1988).
[23]C. M. M. Nex, in Proceedings of the MSI Workshop on Practical Iterative Methods for Large Scale Computations, 1988 (unpublished).
[24]D. Vankin, S. K. Sinha, D. E. Moncton, D. C. Johnston, J. M. Newsam, C. R. Safinya, and H. E. King, Jr., Phys. Rev. Lett. **58**, 2802 (1987).
[25]J. D. Reger and A. P. Young, Phys. Rev. B **37**, 5978 (1988).
[26]C. P. Slichter, *Principles of Magnetic Resonance* (Springer-Verlag, Berlin, 1978).
[27]C. H. Pennington, D. J. Durand, C. P. Slichter, J. P. Rice, E. D. Bukowski, and D. M. Ginsberg, Phys. Rev. B **39**, 2902 (1989).
[28]M. Takigawa, P. C. Hammel, R. H. Heffner, Z. Fisk, J. L. Smith, and R. Schwarz, Phys. Rev. B **39**, 300 (1989); M. Takigawa, P. C. Hammel, R. H. Heffner, and Z. Fisk, Phys. Rev. B **39**, 7371 (1989).
[29]A. Bianconi, J. Budnick, A. M. Flank, A. Fontaine, P. Lagarde, A. Marcelli, H. Tolentino, B. Chamberland, C. Michel, B. Raveau, and G. Demazeau, Phys. Lett. A **127**, 285 (1988).
[30]A similar conclusion was reached by A. Fujimori, Phys. Rev. B **39**, 793 (1989).
[31]Previous calculations found the $^1A_1$ state energetically favorable, because either they did not include the Coulomb interactions on the oxygen sites, e.g., MMS and H. Eskes and G. A. Sawatzky, Phys. Rev. Lett. **61**, 1415 (1988), or they did not explicitly include the $3z^2-r^2$ copper d orbital (Refs. 3 and 12). Two further effects have not been included in the values in Table II: first, including the full Racah coefficients for the copper Coulomb interaction, as suggested by Eskes and Sawatzky, favors the $^3B_1$ state by $\sim$0.1 eV. Second, our LMTO calculations indicate that $V_{pd\sigma}$ falls off with distance faster than the $r^{(-L-L'-1)}$ that we have assumed in our tight-binding calculations; this effect reduces the Cu-O_{II} hybridization and shifts the $^3B_1$ state up by $\sim$0.2 eV, again resulting in almost degenerate states.
[32]P. W. Anderson, Phys. Rev. **86**, 694 (1952); T. Oguchi, *ibid.* **117**, 117 (1960).
[33]K. B. Lyons, P. A. Fleury, J. P. Remeika, A. S. Cooper, and T. J. Negran, Phys. Rev. B **37**, 2353 (1988).
[34]R. J. Birgeneau, M. A. Kastner, A. Aharony, G. Shirane, and Y. Endoh, Physica C **153–155**, 515 (1988); C. J. Peters *et al.*, Phys. Rev. B **37**, 9761 (1988).