Magnetic Phase Diagram and Magnetic Pairing in Doped La_2CuO_4

Amnon Aharony,[1-3] R. J. Birgeneau,[2] A. Coniglio,[1,4] M. A. Kastner,[2] and H. E. Stanley[1]
[1]*Center for Polymer Studies and Department of Physics, Boston University, Boston, Massachusetts 02215*
[2]*Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139*
[3]*School of Physics and Astronomy, Beverly and Raymond Sackler Faculty of Exact Sciences, Tel Aviv University, Tel Aviv 69978, Israel*
[4]*Dipartimento di Fisica, Università degli Studi de Napoli, I-80125, Napoli, Italy*
(Received 1 December 1987)

We discuss the temperature-concentration phase diagram of doped La_2CuO_4. The addition of holes introduces a local ferromagnetic exchange coupling between Cu spins. The resulting frustration destroys the 3D Néel state characterizing pure La_2CuO_4, and generates a new 3D spin-glass phase. In the paramagnetic phase, the strongly correlated Cu spins in the planes are canted by the holes, yielding an oscillating dipole-dipole attraction between holes. The possible relevance to superconductivity is discussed.

PACS numbers: 75.50.Ee, 74.70.Hk, 74.70.Jm, 75.40.Cx

The quaternary compounds $La_{2-x}(Sr,Ba)_xCuO_{4-y}$ and related materials exhibit dramatic behavior, including structural, antiferromagnetic (AF), insulator-metal (I-M), and superconducting transitions.[1-4] All of these transitions depend strongly on the dopant concentration x (or the oxygen deficiency y). In the first part of this paper we discuss the temperature-concentration (T-x) phase diagram, shown schematically in Fig. 1. It contains the following details: (A) *Antiferromagnetism:* Pure La_2CuO_4 exhibits 3D AF ordering of Heisenberg-coupled Cu spins at a Néel temperature $T_N \simeq 300$ K. Above T_N the spins are ordered over large distances two dimensionally, but there exists no measurable time-averaged staggered moment.[4] Upon doping, T_N drops quickly to zero when y is changed by about 0.03.[5] The Cu-Cu AF exchange coupling in the CuO_2 planes is of order 1300 K, yielding large in-plane correlation lengths, ξ_{2D}, even in the samples that do not have 3D long-range order.[4] (B) *I-M transitions:* The pure and slightly doped materials display hopping conductivity, indicating localization of the electronic states at the Fermi energy.[3] This conductivity is attributed to holes, resulting from the doping. With use of the variable-range hopping data and the density of states, the localization length l_0 was estimated to be of order 2-3 lattice constants.[6] As x, the concentration of holes, is increased, the system undergoes an I-M transition at $x \simeq 0.05$. (C) *Structural transition:* Pure La_2CuO_4 undergoes a tetragonal (T) to orthorhombic (O) transition at $T_{TO} = 533$ K. T_{TO} decreases to zero at about $x \simeq 0.2$.[7] (D) *Superconductivity:* The metallic material becomes superconducting at $T \leq T_c$, and $T_c(X)$ increases with x reaching a plateau at about 40 K (Refs. 1 and 7) and dropping sharply for $x > 0.2$.[6]

Concerning the I-M transition, we believe that the localization of the holes results from the random potential introduced by the dopant atoms and other quenched impurities and defects. The holes become mobile at around $x \simeq 0.05$, probably because their density becomes high enough to screen the random potential. We do not believe that the localization is due to self-trapping of the holes, as might be expected from a nonrandom translationally invariant single-band Hubbard model.[8]

Given the experimental fact that the holes are localized at small x, we next show they they generate a local ferromagnetic (F) exchange interaction between the (otherwise antiferromagnetically coupled) Cu ions. The resulting frustration gives rise to the sharp decrease in T_N, and yields a spin-glass phase (Fig. 1). Several very recent experiments, brought to our attention after the present theory was completed, support the existence of this new phase. In the second part of the paper we show that the same frustration effects also yield an effective attractive interaction between static holes. The possible relevance of this new pairing mechanism to the superconductivity in the lanthanum cuprates is then discussed.

Pure La_2CuO_4 has an AF ground-state ordering of the Cu^{++} spins. The in-plane exchange coupling ($-J$) is strong ($\simeq 1300$ K),[4] while that between planes ($-J'$) is weak. Each Cu ion couples to four nearest-neighbor Cu ions in the plane above its own and four below. In the T

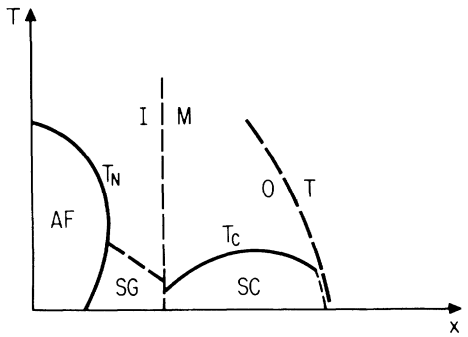

FIG. 1. Schematic phase diagram, as a function of hole concentration x. AF=antiferromagnetic; SG=spin-glass; I=insulator; M=metal; SC=superconductor; O=orthorhombic; T=tetragonal.

phase, the distances to each of these neighbors are exactly the same. If the four neighbors order antiferromagnetically in the Néel ground state, the sum of their spins vanishes and the net coupling between neighboring planes also vanishes.[9] This is the reason for the magnetic structures observed[9] in the isostructural K_2NiF_4, and for the excellent fit to 2D Ising behavior. This exact cancellation is removed in the O phase, in which, indeed, the spins order antiferromagnetically in the *ac* planes. If we assume that the exchange increases with decreasing separation, then, since $a<c$, $J'<0$. The 3D AF transition in orthorhombic La_2CuO_4 is thus driven by J' and one has $kT_N \sim J'\xi_{2D}^2$.[4]

Emery[8] and others[10] have argued that doping creates holes on the O^- sites in the CuO_2 planes. This has now been fully supported by x-ray photoemission spectroscopy.[10] Since the exchange interaction between the two Cu ions is mediated via the O ions, the extra spin of a hole localized on the O^- will have a drastic local effect. If we denote the spins of the two neighboring Cu^{++} ions by $\mathbf{S}_1$ and $\mathbf{S}_2$, and that of the O^- ion by σ, the relevant Hamiltonian for a static hole is $H_{12}=-J_\sigma(\mathbf{S}_1+\mathbf{S}_2)\cdot\sigma$. Since $|J_\sigma|$ results from overlap integrals over the Cu-O distance, it is expected to be much larger than the original AF Cu-Cu exchange ($-J$). For $J_\sigma>0$ (or <0), σ would thus like to be parallel (antiparallel) to both $\mathbf{S}_1$ and $\mathbf{S}_2$. Thus, for either sign of J_σ, $\mathbf{S}_1$ and $\mathbf{S}_2$ prefer a state in which they are parallel to each other. If the spins were classical, then one could easily perform the exact trace over σ in the partition function, and generate an effective Hamiltonian $\bar{H}_{12}=K\mathbf{S}_1\cdot\mathbf{S}_2$, with $K=O(|J_\sigma|)\gg|J|$. For the quantum mechanical $S=\frac{1}{2}$ case, this transformation is not exact. However, since $|J_\sigma|\gg|J|$, one should first diagonalize H_{12} and only then add the coupling to the other Cu spins.[11] The eigenstates of H_{12} are characterized by the total spin S and its z component S_z and by the total spin of the two Cu ions, S_{12}. One finds the eigenstates $|\frac{3}{2},S_z,1\rangle$ $|\frac{1}{2},S_z,1\rangle$ and $|\frac{1}{2},S_z,0\rangle$, with eigenenergies $-J_\sigma/2$, J_σ, and 0, respectively. For example,

$$|\tfrac{1}{2}\,\tfrac{1}{2}\,1\rangle = \tfrac{2}{3}\sqrt{3}|{+}{-}{+}\rangle-\tfrac{1}{6}\sqrt{6}|{+}{+}{-}\rangle-\tfrac{1}{6}\sqrt{6}|{-}{+}{+}\rangle$$

(where the signs indicate the z components of the Cu-O-Cu spins). Thus, the ground state has $S=\frac{3}{2}$ (or $\frac{1}{2}$) and energy $-J_\sigma/2$ (or J_σ) if $J_\sigma>0$, F (or <0, AF). In both cases, $S_{12}=1$, i.e., $\mathbf{S}_1\cdot\mathbf{S}_2=\frac{1}{4}$; the two Cu spins tend to be parallel to each other. This tendency remains when the coupling J is introduced perturbatively. Recent work[12], in fact, suggests that the $S=\frac{3}{2}$ state is lowest in energy.

It has recently been shown[13] that the instantaneous spin-spin correlations in the 2D $S=\frac{1}{2}$ Heisenberg model exhibit the same behavior as those of the corresponding classical spin model, but with renormalized coupling constants. In view of this, we replace the Cu spins by classical spins, and replace the Cu-O-Cu complex by the effective F term, $K\mathbf{S}_1\cdot\mathbf{S}_2$. Since a strong F bond in a CuO_2 plane will tend to destroy the local AF order, it will also destroy the near cancellation of the coupling to the neighboring planes, and generate an effective Cu-Cu F interplanar interaction K'.

In the insulating phase, the holes are localized. We thus start by considering an instantaneous configuration of the holes, in which they occupy a fixed fraction p ($\sim x$) of the Cu–Cu bonds in the CuO_2 planes. This implies that a fraction p of the bonds in the plane have exchange K and a fraction p' ($\sim x$) of interplane bonds have exchange K'. Adding holes, which then adds F exchange couplings, lowers both ξ_{2D} and the effective J', and thus lowers T_N. While ξ_{2D} is still fairly large, the effective J' goes to zero, eliminating 3D AF order and causing a crossover from a coherent to incoherent (that is, spin-glass) ordering of the successive planes.

Given the competing F and AF interactions, experience with many similar systems[14] leads us to predict the qualitative phase diagram shown in Fig. 1, with a relatively sharp decrease in T_N, and with a spin-glass (SG) phase that is re-entered from the AF phase upon cooling.[15] At present, there exists no detailed theory for the quasi 2D Heisenberg-model SG. In the absence of such theory, we present here two quantitative estimates of the critical concentration x_c at which the AF and the SG phases meet at $T=0$: (a) Experimentally, there exists a weak Ising anisotropy, placing the spins in the ordered phase along the c orthorhombic axis.[2] At very low temperatures, this anisotropy is expected to dominate. The ground state will then exhibit SG ordering in the CuO_2 planes. For $K=-J$, and for Ising spin interactions, the ground state loses AF long-range order when one gains energy from creating infinite domains of flipped spins. This happens at $p_c\simeq 0.09$, when the frustrated plaquettes percolate through the lattice, with next nearest-neighbor connectivity.[16] (b) In the isostructural $K_2Cu_cMn_{1-c}F_4$, the Cu-Cu exchange is F, while those of Mn-Mn and Mn-Cu are weaker and AF.[17] Ferromagnetism is lost at $c\gtrsim 0.8$, when the concentration of the weak Mn–Mn bonds is 0.01 and that of the extremely weak Mn–Cu bonds is 0.32.

Both of these estimates should be reduced in our case, for two reasons. First, the above values are based on $K=-J$, or $|K|\ll|J|$. In our case, $|K|\gg|J|$ and p_c should be lower. Second, and more important, these estimates assume a quenched distribution of the K bonds, while the hopping conductivity data show a localization length $l_0\simeq(2\text{–}3)a$, implying that each hole is shared by $\simeq 10$ oxygens. For holes in the nonbonding in-plane oxygen orbitals as discussed in Ref. 12, this movement of the hole within a localization length will not change the basic exchange Hamiltonian, $H_{12}=-J_\sigma(\mathbf{S}_1+\mathbf{S}_2)\cdot\sigma$, since J_σ is very large but it will make the effects of the hole more extended spatially. This will renormalize the

above estimates of p_c by a factor of 5 to 10, yielding $x_c \simeq 1\%-3\%$, in agreement with the observed phase diagram, which we discuss next.

Three features of Fig. 1 have been confirmed by experiment since we constructed this theory. First, Endoh *et al.*[4] found, in an oxygenated crystal of La_2CuO_4 with $T_N \cong 100$ K, that below about 25 K the Bragg intensity begins to decrease with decreasing temperature. Concomitantly 2D quasielastic ($E \cong 0$) diffuse scattering appears. This is the signature of re-entrant spin-glass behavior as observed in a number of model 3D systems.[14,15] Second, muon-precession experiments[18] in a strongly oxygenated sample show a progressive freezing of the spins at $\simeq 15$ K, suggestive of a 3D spin-glass transition in this sample. More recent muon-precession experiments[19] on $La_{2-x}Sr_xCuO_4$ show disappearance of the frozen moments at a temperature T_{SG} that decreases from $\simeq 12$ to $\simeq 6$ K when x varies from 0.02 to 0.05. A similar variation of T_{SG}, from $\simeq 12$ to $\simeq 2$ K, has also been found by recent nuclear quadrupole resonance experiments[20] on $La_{2-x}Ba_xCuO_4$.

Clearly the hole-induced frustration model is adequate to account straightforwardly for the principle features of the La_2CuO_4 magnetic phase diagram in the insulating phase. Before turning to the "metallic" phase, it is instructive to understand the spin configuration around an isolated static hole in a strongly correlated AF state. The spin Hamiltonian $H = -\sum J_{ij}\mathbf{S}_i \cdot \mathbf{S}_j$ is invariant under the gauge transformation $J_{ij} \rightarrow J_{ij}$ and $\mathbf{S}_i \rightarrow \exp[i\mathbf{Q}\cdot\mathbf{R}_i]\mathbf{S}_i$, where $\exp[i\mathbf{Q}\cdot\mathbf{R}_i] = 1$ or -1 on the two sublattices of the Néel state. It is much easier for illustrative purposes to look at the case of a F-correlated state, with F exchange $|J|$, and a single AF bond at the origin of strength $-K$. Figure 2(a) shows the numerically simulated ground-state configuration of this state, for XY classical spins, with $K/|J| = \infty$. The two spins on the AF bond are antiparallel, and perpendicular to the F background. The spins around the AF bond are canted, with a canting angle that decays as the inverse distance from the origin. More specifically, if $\mathbf{a}$ points along the AF bond, then the angle decays as $\mathbf{a}\cdot\mathbf{r}/r^2$. This decay is the same as that of the field around a dipole, in agreement with Villain's prediction based on the fact that the angles should obey Laplace's equation.[21] Since the same prediction applies for any continuous-symmetry spin model, in any dimension, we expect the same canting for the Heisenberg model. Use of the gauge transformation, and flipping the spins on one sublattice, yields Fig. 2(b). Note that the spin of the hole, which is antiparallel to those of the neighboring Cu's (if $J_\sigma < 0$), will be perpendicular to the staggered magnetization. Given the weak anisotropies[2] in La_2CuO_4, we expect this spin to order along the orthorhombic b axis. It should be noted that although the hole generates some F moment in its vicinity, the canting of the surrounding spins is not all in the same direction [Fig. 2(b)]. This is very different from the F canting which arises as a result of kinetic arguments, in order to facilitate hopping.[22]

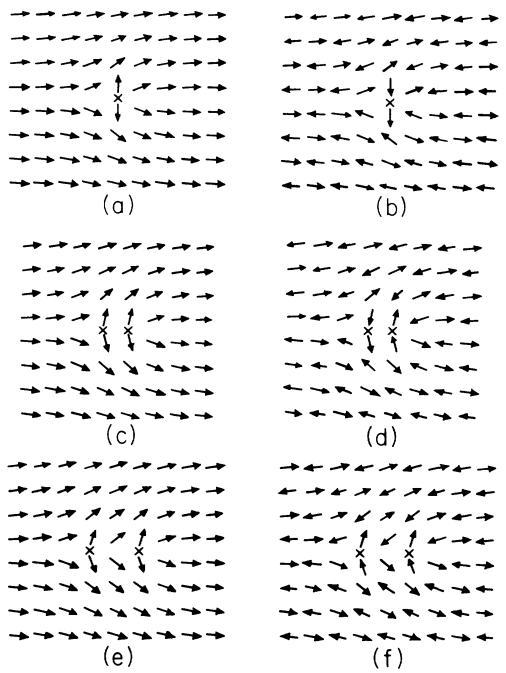

FIG. 2. XY model ground state with (a) one or (c),(e) two AF ($-K$) bonds (denoted by x) in a F background or (b) one and (d),(f) two F (K) bonds in an AF background. (a) and (b) have $|K/J| = \infty$, while the others have $|K/J| = 3$.

We next consider two holes, or two AF bonds in the F (gauge transformed) correlated region. The resulting ground-state configurations are shown, for $K/|J| = 3$, and for several distances, in Figs. 2(c) and 2(e). As anticipated by Villain,[21] the gain in energy, relative to infinite separation, is given by

$$V_d(\mathbf{r}) = -g[\mathbf{a}_1\cdot\mathbf{a}_2 - 2(\mathbf{a}_1\cdot\mathbf{r})(\mathbf{a}_2\cdot\mathbf{r})/r^2]/r^2. \quad (1)$$

Our simulations yield $g \simeq 4|J|$ for $K = \infty$, and $g \simeq |J|$ for $K/|J| = 3$.

Figures 2(d) and 2(f) show the gauge-transformed configurations, relevant to the holes in the AF. Note that the gauge-transformed holes have parallel (antiparallel) spins if the distance between them is an even (odd) number of lattice steps. We thus conclude that there is a hole-hole interaction potential of the form $V_{12}(\mathbf{r}) = \sigma_1\cdot\sigma_2 e^{i\mathbf{Q}\cdot\mathbf{r}}V_d(\mathbf{r})$. Up to this point, we assumed a fully correlated AF background. As the concentration x increases, we expect the 2D correlation length ξ_{2D} to decrease,[4] and $V_{12}(\mathbf{r})$ will be multiplied by an additional factor of order $\exp(-r/\xi_{2D})$.

So far, we ignored the Coulomb repulsion between the two holes, $V_C(r)$. In the insulating phase, one may probably use $V_C(r) = e^2/\epsilon r$, with a dielectric constant ϵ of order 10. This yields $V_C(a) \simeq 4200$ K for $a \simeq 4$ Å, of the same order as $4|J|$, since $|J|$ is of order 1300 K.[4] In

the metallic phase, the holes screen each other, and one should probably multiply $V_C(r)$ by $\exp(-\kappa r)$. A simple estimate yields $\kappa \simeq (4\ \text{Å})^{-1}$ (for $x \simeq 0.1$); hence $\exp(-\kappa a) \simeq 0.4$, and $V_C(a) \sim |J|$.

Thus, we obtain an explicit expression for an attractive static potential energy between the holes,

$$V(\mathbf{r}) = V_{12}(\mathbf{r})\, e^{-r/\xi_{2D}} + V_C(r). \tag{2}$$

This concludes the calculational part of this paper. The relevance of this attractive potential to superconductivity is a subject of current research. If the kinetic energy of the delocalized holes in the M phase is not too high, then the potential (2) would yield real-space (zero spin) bound pair states, with interpair distance r_0. These pairs would undergo a Bose condensation, at $T_c(x)$. Once r_0 becomes of the order of ξ_{2D}, this scenario would break down. This could explain the drop of T_c at larger x. An alternative description based on k-space pairing is given by Birgeneau, Kastner, and Aharony.[12]

Since our mechanism is based on classical spin interactions, it may also apply for systems with spins larger than $\frac{1}{2}$. For example, one might expect a spin-glass phase in doped La_2NiO_4 (where Ni has $S=1$), if the holes prefer the oxygen sites. In our picture, pairing and superconductivity could possibly also occur there, if there is an appropriate metallic phase.

We are grateful to V. J. Emery, P. A. Lee, G. Shirane, and P. G. de Gennes for stimulating discussions and especially to V. J. Emery for emphasizing to us the possible importance of placement of the holes on the oxygen. The work at Boston University was supported by the National Science Foundation and the U.S. Office of Naval Research, at the Massachusetts Institute of Technology by National Science Foundation Grants No. DMR 85-01856, No. 84-18718, and No. DMR 84-15336, and at Tel Aviv University by grants from the U.S.-Israel Binational Science Foundation and the Israel Academy.

[1]J. G. Bednorz and K. A. Müller, Z. Phys. B **64**, 189 (1986).

[2]D. Vaknin *et al.*, Phys. Rev. Lett. **58**, 2802 (1987); S. Mitsuda *et al.*, Phys. Rev. B **36**, 822 (1987).

[3]R. J. Birgeneau *et al.*, Phys. Rev. Lett. **59**, 1329 (1987).

[4]G. Shirane *et al.*, Phys. Rev. Lett. **59**, 1613 (1987); Y. Endoh *et al.*, Phys. Rev. B (to be published); C. J. Peters *et al.*, unpublished.

[5]D. C. Johnston *et al.*, Phys. Rev. B **36**, 4007 (1987).

[6]M. A. Kastner *et al.*, Phys. Rev. B **37**, 111 (1988).

[7]R. M. Fleming *et al.*, Phys. Rev. B **35**, 7191 (1987).

[8]V. J. Emery, Phys. Rev. Lett. **58**, 2794 (1987), and references therein. In this paper Emery first notes that placement of the holes on the oxygen will disturb the local magnetic order and thence produce a diminution of T_N. However, the idea is not developed further in this paper.

[9]R. J. Birgeneau *et al.*, Phys. Rev. B **1**, 2211 (1970).

[10]J. M. Tranquada *et al.*, Phys. Rev. B **36**, 5263 (1987); N. Nücker *et al.*, Phys. Rev. B (to be published); Z.-X. Shen *et al.*, Phys. Rev. B **36**, 8414 (1987).

[11]An alternative approach is to distribute the hole equally onto the four oxygens surrounding a Cu atom and to treat the O^- and Cu^{++} holes as a composite $S=0$ object. In that case the problem involves percolation rather than frustration. We do not believe that this latter approach is correct for large $|J_\sigma|$ since it does not treat the interaction of the O^- hole with its two surrounding Cu^{++} ions on equal footing.

[12]R. J. Birgeneau, M. A. Kastner, and A. Aharony, Z. Phys. B (to be published); Y. Guo, J.-M. Langlois, and W. A. Goddard, III, Science **239**, 896 (1988).

[13]S. Chakravarty, B. I. Halperin, and D. R. Nelson, Phys. Rev. Lett. **60**, 1057 (1988).

[14]For a recent review on spin-glasses, see, e.g., K. Binder and A. P. Young, Rev. Mod. Phys. **58**, 801 (1986).

[15]G. Aeppli *et al.*, Phys. Rev. B **25**, 4882 (1982).

[16]J. Vannimenus and G. Toulouse, J. Phys. C **10**, L537 (1977).

[17]Y. Kimishima *et al.*, J. Phys. Soc. Jpn. **55**, 3574 (1986).

[18]Y. J. Uemura, private communication.

[19]J. Budnick *et al.*, Europhys. Lett. (to be published). See also D. R. Harshman *et al.*, to be published. In this paper arguments similar to ours concerning the importance of the competing interactions arising from the holes are presented.

[20]Y. Kitaoka *et al.*, Physica (Amsterdam) B (to be published).

[21]J. Villain, J. Phys. C **10**, 4793 (1977), and Z. Phys. B **33**, 31 (1978).

[22]P. G. de Gennes, Phys. Rev. **118**, 141 (1960).