Doping dependence of antiferromagnetism in La_2CuO_4: A numerical study based on a resonating-valence-bond state

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A paramagnetic resonating-valence-bond state is modified to become a long-range-ordered antiferromagnetic state by including a staggered magnetic field as a variational parameter. At half-filling this field is shown by using variational Monte Carlo method to lower the ground-state energy of the large-U Hubbard model by 4%. A staggered moment of 0.37(1) is obtained. The antiferromagnetism is destroyed by doping with $\sim$5%–7% of holes for $t/J=\simeq 2.5$–5 and the paramagnetic state becomes stable. This result is shown to be in good agreement with experiments on La_2CuO_4-based compounds.

Since the discovery of the copper oxide superconductors[1] it has been widely recognized that the magnetic interactions between Cu spins may play an important role in our understanding of the origin of superconductivity in these materials. Antiferromagnetic (AFM) phases have been identified in undoped and lightly doped La_2CuO_4 (2:1:4) and oxygen-deficient $YBa_2Cu_3O_y$ (1:2:3) compounds[2,3] by neutron scattering, muon spin rotation, and other measurements. In particular, the phase diagram of 2:1:4 as a function of hole doping concentration has been established by magnetic resonance measurements.[4] The destruction of the AFM phase by a few percent of hole concentration is rather striking.

A number of ideas have been proposed to explain this effect. Based on the two-band Hubbard model, Aharony *et al.*[5] propose that the localization of the holes on the oxygen tends to frustrate the Cu spins into ferromagnetic coupling. This frustration causes the destruction of AFM. But using the concept of resonating-valence-bond (RVB) state proposed by Anderson[6] for the strong-coupling one-band Hubbard model, Anderson, Baskaran, Zou, and Hsu[7] and Lee, Zhang, and Chang[8] argue that the competition between the kinetic energy and spin interaction could easily favor the RVB state and the AFM long-range-ordered (LRO) state is destroyed by a polaronic effect.

Recent numerical variational Monte Carlo (VMC) calculations by Gros,[9] Yokoyama and Shiba[10] have shown that a particular kind of RVB wave function has off-diagonal long-range order in the presence of holes and that it is a superconducting state. This is also demonstrated clearly by the Gutzwiller mean-field theory of Zhang, Gros, Rice, and Shiba.[11] However, in the absence of holes the RVB state has neither AFM order nor superconducting order. The variational energy obtained is very close to the exact energy extrapolated from finite-size diagonalization by Oitmaa and Betts[12] and Horsch and von der Linden.[13] But these two finite-size calculations, renormalization-group calculations,[14] the recent Monte Carlo result of Reger and Young,[15] and the variational analysis of Huse and Elser[16] all point to a long-range ordered AFM ground state for a two-dimensional quantum Heisenberg square lattice. Hence, there are two questions to be resolved. In the absence of holes is the paramagnetic RVB state stable against the staggered magnetization? If the ground state has AFM long-range order (LRO), can we explain the experimental results of destruction of AFM by doping with a few percent of the holes?

In this paper we shall try to answer these two questions by examining the paramagnetic RVB state studied by Gros[9] and Zhang *et al.*[11] Their trial wave function is modified to simulate the presence of a staggered magnetic field. Using the VMC method we show that the paramagnetic RVB state is unstable with respect to this field. In the absence of holes, the field enhances the nearest-neighbor spin-spin correlation from the value of $-0.319(3)$ to $-0.332(4)$. This new state, referred to as the magnetized RVB state (MRVB), is a LRO AFM state with a staggered moment 0.37(1).

In the presence of mobile holes, the staggered field hinders the motion of the holes although it still gains the magnetic energy. This competition between kinetic and magnetic energies and the small energy difference between the RVB and MRVB states cause the AFM LRO to be quickly destroyed by doping with $\sim$5%–7% of holes for reasonable values of the parameters. This result is in surprisingly good agreement with the experiments.

The Hamiltonian we shall study is the large-U Hubbard model. The effective Hamiltonian considered by us has two parts,

$$H_{\rm eff}=H_1+H_2\,, \tag{1}$$

$$H_1=-t\sum_{\langle i,j\rangle\sigma}(C^\dagger_{i\sigma}C_{j\sigma}+\text{H.c.})\,, \tag{2}$$

$$H_2=J\sum_{\langle i,j\rangle}(\mathbf{S}_i\cdot\mathbf{S}_j-n_in_j/4)\,. \tag{3}$$

These two terms represent the kinetic energy of the holes and the Heisenberg spin interactions. To order of $1/U$ there is a third part H_3,

$$H_3=-t^2/U\sum_{i,\tau\neq\tau',\sigma}(C^\dagger_{i+\tau,\sigma}C^\dagger_{i,-\sigma}C_{i,-\sigma}C_{i+\tau',\sigma} - C^\dagger_{i+\tau,-\sigma}C^\dagger_{i,\sigma}C_{i,-\sigma}C_{i+\tau',\sigma})\,. \tag{4}$$

This term involves three sites and will not be considered in most of the calculations discussed below. Only at the end

of this paper we shall demonstrate that this term is negligible for our calculation. In the half-filled case, $H_{\rm eff}$ reduces to the antiferromagnetic Heisenberg Hamiltonian.

The trial wave function proposed for the RVB state[6] has a very simple form:

$$|\Psi_0\rangle = P_d \Pi_{\mathbf{k}} (u_{\mathbf{k}} + v_{\mathbf{k}} C^{\dagger}_{\mathbf{k}\uparrow} C^{\dagger}_{-\mathbf{k}\downarrow}) |0\rangle , \quad (5)$$

where the operator P_d projects out double occupancy on each site, and $u_{\mathbf{k}}$ and $v_{\mathbf{k}}$ have the BCS form

$$u^2_{\mathbf{k}} = 1/2(1 - \varepsilon_{\mathbf{k}}/E_{\mathbf{k}}), \quad v^2_{\mathbf{k}} = 1/2(1 + \varepsilon_{\mathbf{k}}/E_{\mathbf{k}}) , \quad (6)$$

$$\varepsilon_{\mathbf{k}} = -2[\cos(k_x) + \cos(k_y)] - \mu, \quad E_{\mathbf{k}} = \sqrt{(\varepsilon^2_{\mathbf{k}} + \Delta^2_{\mathbf{k}})} . \quad (7)$$

Gros[9] has shown that with the choice of $\Delta_{\mathbf{k}} = \Delta[\cos(k_x) - \cos(k_y)]$ and $\Delta = 1$, magnetic energy obtained by this function is very close to the "exact" value.[12] This state is always a singlet with no long-range AFM order. But other trial functions with AFM long-range order also have very good energy as shown in the second column of Table I. To study this question further we have examined the spin excitation spectrum of the RVB state. As shown by Lee, von der Linden, and Horsch[21] the excited states can be easily constructed by applying the spin-density operator to $|\Psi_0\rangle$. Here we shall only consider the operator $S_M = \sum_i (-1)^i S^i_z$, representing the staggered magnetization. The energy of this state, which is given by $\langle\Psi_0|S_M H_{\rm eff} S_M|\Psi_0\rangle / \langle\Psi_0|S^2_M|\Psi_0\rangle$, is found to be lower than E_0, which is given by $\langle\Psi_0|H_{\rm eff}|\Psi_0\rangle / \langle\Psi_0|\Psi_0\rangle$. Thus, the paramagnetic RVB state is unstable with respect to the staggered magnetic operator. A new trial function is needed to rid of this instability.

The new wave function we shall propose is a magnetized RVB state. It has the form

$$|\Psi_M\rangle = \exp(hS_M)|\Psi_0\rangle . \quad (8)$$

The variational parameter h might be thought of as a self-consistent staggered field. Both parameters Δ and h are to be determined by minimizing the total energy.

At half-filling, the nearest neighbor spin-spin correlation $\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle$ is evaluated for various lattice sizes, $L = 26$, 50, 82, and 122, by using VMC. The result is plotted in Fig. 1(a). Technical details of VMC can be found in Ref. 22. We chose $\Delta = 1$ for all the points shown in Fig. 1. The solid circles are for the paramagnetic RVB state[9] where $h = 0$. The triangles are the result for finite $h = h_0$. The

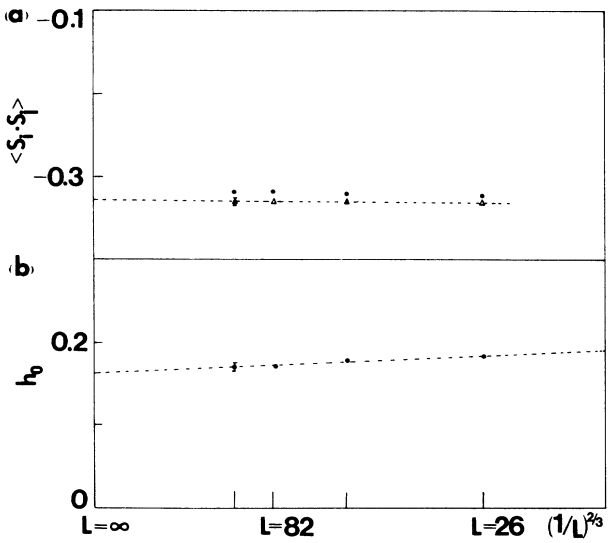

FIG. 1. Data for the half-filling case and d-wave MRVB state with $\Delta = 1$. The nearest-neighbor spin-spin correlation (a) and the staggered field h_0 that minimizes the total energy (b) are plotted as a function of $L^{-2/3}$ for lattice with a total number of sites $L = 26$, 50, 82, 122. Typical error bars are shown.

staggered field h_0 that minimizes the energy is plotted as a function of L in Fig. 1(b). Its value is about 0.17 and is rather insensitive to the size L of the lattice. Our result definitely shows that the MRVB state has lower energy than the particular paramagnetic RVB state considered by Gros.[9] The staggered moment or the order parameter extrapolated for infinite size is about 0.37(1). As shown in Table I, both energy and moment calculated by the MRVB state seem to be closer to the "exact" extrapolated finite-size result than the spin-density-wave (SDW) state used by Yokoyama and Shiba.[19] Our results are almost identical with that of the three-parameter variational calculation by Huse and Elser.[16]

In the presence of holes, the field h^* that minimizes both $\langle H_1 \rangle$ and $\langle H_2 \rangle$ is greatly reduced as the hole loses its kinetic energy $\langle H_1 \rangle$ moving in a LRO AFM background. As h^* becomes zero, the AFM LRO is destroyed and the holes regain their kinetic energy. Here, our goal is to quantitatively determine h^* as a function of the hole concentration. But the quantitative behavior will depend on

TABLE I. A comparison of the ground-state energy and sublattice magnetization for the Heisenberg model on a two-dimensional square lattice.

Author(s)	$-\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle$	$M_s/2$	Method
Anderson (Ref. 17), Kubo (Ref. 18)	0.329	0.303	Spin wave
Horsch and von der Linden (Ref. 13)	0.3219(9)	0.335	Variational
Oitmaa and Betts (Ref. 12)	0.328(3)	0.24	Finite lattice
Yokoyama and Shiba (Ref. 19)	0.321(1)	0.43	Variational SDW
Gros (Ref. 9)	0.319(1)	0	Variational RVB
Huse and Elser (Ref. 16)	0.3319	0.355	Variational
Liang *et al.* (Ref. 20)	0.3344(2)	0.375	Variational RVB
Present work	0.332(5)	0.37(1)	Variational

the ratio t/J. The total variational energy $\langle H_{\text{eff}} \rangle$ is plotted as a function of h for two different values of Δ in Figs. 2(a) and 2(b) where $t/J=5$ and 2.5, respectively. The calculation is done for two holes in a 82 sites or hole concentration $\delta=2.4\%$. For $t/J=5$, the values of Δ and h^* that give the minimum energy are about 0.55 and 0.1, respectively. For $t/J=2.5$, Δ is about 0.6 and $h^* \simeq 0.16$. In the presence of four holes in a 82 sites where $\delta \simeq 5\%$, minimum energy is obtained at $\Delta \simeq 0.6$ for both $t/J=5$ and 2.5.

In Fig. 3, h^*/h_0, which is proportional to the ratio of magnetization, is plotted as a function of hole concentration δ for several values of Δ. The solid and open circles are for $\Delta=0.6$, $t/J=5$, and 2.5, respectively. The solid and broken lines are guides for the eyes. For six holes in 82 sites where $\delta \simeq 7\%$ we found $h^*=0$ and AFM LRO is destroyed. At $t/J=5$, the reason that h^* is more sensitive to δ for $\Delta=0.6$ than 0.2 is due to the relatively smaller magnetic energy gain by h. For comparison we also plotted result for $\Delta=0.2$ and $t/J=5$ shown as the triangle in Fig. 3. The dashed and dotted lines are guides for the eyes. In this case, a very large error bar at $\delta=5\%$ is obtained because that energy is hardly varied as a function of h.

Our results clearly show that magnetic order is destroyed around $\sim 5\%$–7% of holes for $t/J=\sim 2.5\%$–5%. This is in very good agreement with experiments. In Fig. 3, the internal magnetic field determined by nuclear quadrupole measurement[4] for La-Ba-Cu-O is shown in squares. Notice that the projected spin density wave state used by Yokoyama and Shiba[19] predicted $\sim 15\%$ of holes is needed to destroy AFM for $t/J=2.5$ and mean-field theory of the weak coupling Hubbard model needs more than 25%.

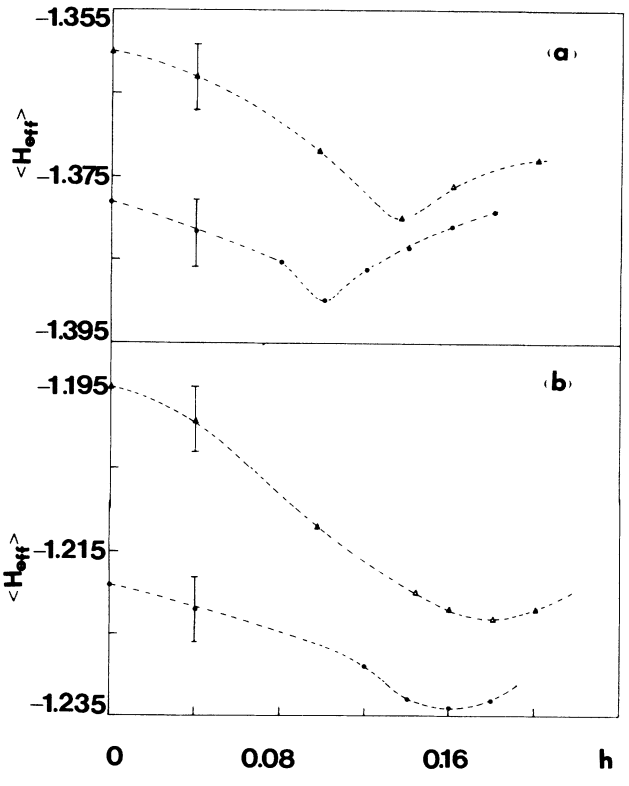

FIG. 2. Total energy per site for two holes ($N_h=2$) in a 82 sites, for $\Delta=0.2$ (triangles) and $\Delta=0.6$ (solid circles), as a function of the staggered field h in units of J. Typical error bars are shown. In (a) $t/J=5$ and in (b) $t/J=2.5$.

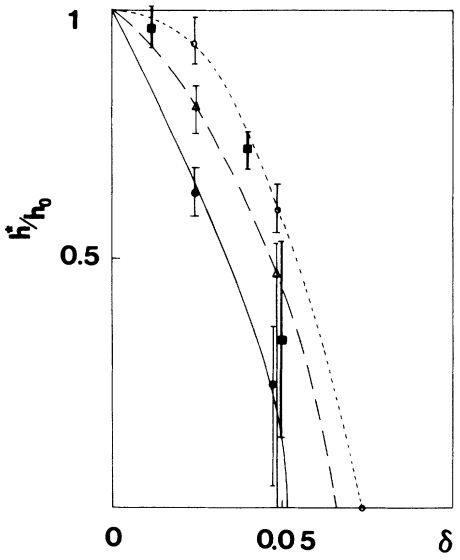

FIG. 3. Data of the ratio h^*/h_0 as a function of the hole concentration δ for $\Delta=0.6$, $t/J=5$ (solid circles), $\Delta=0.6$, $t/J=2.5$ (open circles), $\Delta=0.2$, $t/J=5$ (triangles), and internal field measurement (Ref. 4) of $(La_{1-x}Ba_x)_2CuO_4$ (squares), respectively. Typical error bars are shown.

The three-site term H_3, which we have neglected so far, gives a very small contribution to the total energy. The ratio of $\langle H_3 \rangle$ and $\langle H_{\text{eff}} \rangle$ is about 1/20 at $t/J=5$. We found negligible effect of this term in determining h^* as a function of concentration of holes. This result disagrees with the conclusion reached by Inui, Doniach, and Gabay.[23] We believe that the trial function used by them in the presence of holes has a much higher energy as discussed by Zhang *et al.*[11] and that makes H_3 more important while the kinetic energy H_1 becomes irrelevant.

Based on our wave function, the drastic reduction of AFM LRO by a small concentration of holes has a rather simple reason. The paramagnetic RVB state is only marginally unstable relative to the AFM LRO state. Because t/J is large (~ 2.5–5) and because hole moves a little bit more difficult in a LRO AFM background than in the paramagnetic RVB state, a small concentration of holes would already favor RVB state to be the ground state.

In summary, we have shown by using variational Monte Carlo method that a modified RVB state with AFM LRO has a lower energy than the paramagnetic RVB state for hole concentration less than $\sim 5\%$–7%. This result is in very good agreement with experiments on La_2CuO_4. It should be noticed that the RVB wave function chosen by us is certainly not the lowest energy RVB state. Liang, Doucot, and Anderson[20] have shown a much smaller energy difference between AFM LRO state and the paramag-

netic RVB state. It implied that a better choice of RVB wave function will probably destroy AFM even faster by doping than what we have obtained.

Our result provides additional support to applying the RVB theory to Cu-O superconductors but it also raises an interesting question about the coexistence of AFM and superconductivity. Since with holes the paramagnetic RVB state is shown to be superconducting,[9,10] our trial function for the MRVB state also would give nonzero superconducting order parameter. This coexistence phase was first proposed in the slave-boson mean-field theory.[24] At present, there is no experimental evidence for the coexistence. Whether or not this means inaccuracy in our trial wave function or other effects beyond our consideration, such as two-dimensional fluctuations, will have to be resolved in a future study.

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