Phenomenological model of the magnetic properties of $La_{2-x}Sr_xCuO_{4-y}$

Mark Jarrell, D. L. Cox, and C. Jayaprakash
Department of Physics, The Ohio State University, Columbus, Ohio 43210

H. R. Krishnamurthy*
Department of Physics, Princeton University, Princeton, New Jersey 08544
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We model $La_{2-x}Sr_xCuO_{4-y}$ for small x by assuming p_π oxygen holes are Coulombically bound to Sr (or La vacancy) acceptor defects in $2d$ hydrogenic orbitals. The holes exchange couple to the antiferromagnetically ordered copper moments. The defects are polarized due to the copper spin canting induced by the Dzyaloshinski-Moriya interaction. Within linear spin-wave analysis we obtain a defect contribution to the magnetization jump at a critical applied field H_c, and we deduce a critical defect concentration for suppression of the long-range magnetic order which is sensitive to dimensionality, defect position, and defect-defect interactions. We quantitatively account for the nonmetal-metal transition. We qualitatively explain the observed resistivity drop at H_c (for which we propose an experimental test), some anomalous muon-spin-resonance data, and the dependence of T_N on oxygen vacancies.

I. INTRODUCTION

For small x, $La_{2-x}Sr_xCuO_{4-y}$ is an antiferromagnetic semiconductor in which the long-range magnetic order is well described by a weakly anisotropic Heisenberg model. Recently, this material has been shown to display unusual magnetic properties. These include a jump in the magnetization as a function of an external field applied in the tetragonal c direction[1,2] and a coincident magnetoresistive jump.[1] Muon-spin-resonance (μSR) studies also show that the depolarization rate of the spins changes as a function of both oxygen and La vacancies, and Sr substitutional defects.[3]

Thio *et al.*[1] proposed an explanation of the jump in the magnetization based on a small antisymmetric Dzyaloshinski-Moriya (DM) interaction.[4,5]. The DM interaction causes a small canting out of the CuO_2 planes which alternates between adjacent planes due to an antiferromagnetic interplanar coupling. However, when a sufficiently strong external magnetic field is applied perpendicular to the planes, the canting in all planes aligns with the field. This causes a change in the magnetization, and a halving of the magnetic unit cell in the orthorhombic c direction which can be seen with polarized neutron scattering.[6]

Here we present a model in which defects are added to the system described by Thio *et al.* That is, the pure host has antiferromagnetic order in the CuO_2 planes, which cants out of the plane due to a small DM term. The direction of this canting alternates between the planes due to some interplanar antiferromagnetic coupling. When this material is doped, i.e., Sr^{2+} is substituted for La^{3+}, a hole is contributed to one of the planes adjacent to the ion to preserve overall charge neutrality.

Our model is similar to that proposed by Aharony *et al.*[7] to describe the precipitous drop in T_N with doping. They assume that this hole is localized on a single oxygen orbital. In contrast, in our model the hole is localized near the Sr^{2+} due to the negative charge of the Sr atom relative to the La atom. (A similar situation occurs when a La atom is replaced by a vacancy, except now there are three holes contributed to the planes adjacent to the vacancy, which may be localized by the relative -3 charge of the vacancy.) The hole occupies a two-dimensional hydrogenic orbital in the plane. We will call this combination of a substitutional defect (Sr for La) and its associated localized hole an acceptor defect. (Parenthetically, we note that a similar acceptor defect forms in the antiferromagnetic semiconductor EuTe when it is doped with Gd^{3+}, yielding similar anomalous magnetic behavior.[8,9]) The model electronic structure is shown schematically in Fig. 1.

The spin of this localized oxygen hole can interact with the copper spins within the orbital. This interaction causes an out-of-plane ferromagnetic canting of the Cu spins within the orbital, as well as a slowly decaying oscillatory canting farther away from the acceptor-defect center, as shown in Fig. 2. The net moment of this canting is strongly coupled to the oxygen hole moment, causing the oxygen spin to saturate. In the absence of any external magnetic field the net moment of the orbital defect aligns in the direction favored by the small DM term. If a sufficiently large field is applied perpendicular to a particular plane in opposition to the DM term, the saturated moment will abruptly change direction, aligning with this external field. We suggest that this may contribute to the jump in the magnetization seen in the presence of an external field.

In addition, we believe that the conduction in these materials results from variable-range hole hopping from one acceptor defect site to another. Thus, when the jump in the magnetization occurs, the resulting change of the polarization of the orbitals (Fig. 3) causes an abrupt change in the conductivity of this material. Roughly this

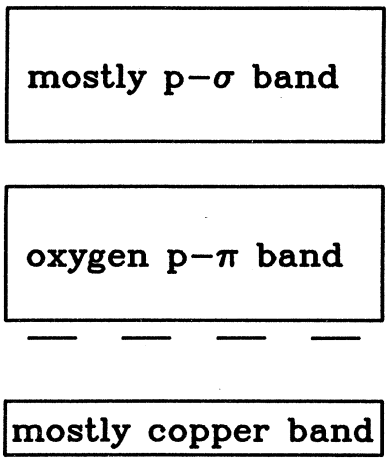

FIG. 1. Hole-energy band structure for the CuO_2 plane. The narrow lower band is a Mott-Hubbard band composed mainly of copper $d_{x^2-y^2}$ orbitals, the intermediate band of oxygen p_π orbitals, and the upper band of mostly oxygen p_σ orbitals. Because of strong correlations on the copper site, only one hole per site is required to fill the lower band, resulting in a spin moment on each site. The excess holes introduced by doping go into the p_π oxygen band. The states within the gap represent the defect orbital states.

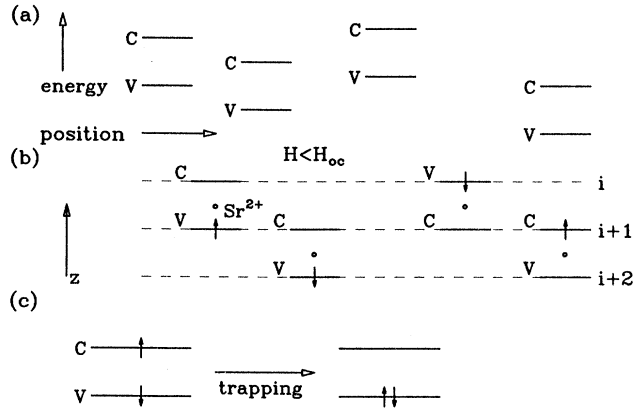

FIG. 3. Mechanism for magnetoresistance jump. (a) We assume that nominally stable vacancy (V) and excited Cu (C) defect states acquire a level distribution through the random potential, though at a given Sr^{2+} site, V states are always nominally stable. (b) Low-field regime. Intralayer $V \rightarrow C$ hopping is possible, while $V \rightarrow V$ hopping is inhibited by the Pauli principle since the defect spins are already saturated. (c) Low-field trapping. The trapping process is the dropping of a virtually occupied C state to the adjacent nominally stable V state. In high field, when all defect spins are uniformly polarized, the trapping process is frozen out.

occurs because the hole associated with a Sr^{2+} substitution can localize on either of the planes adjacent to the ion. However, due the DM term, the net spin of the acceptor-defect points in opposite directions on these two planes. So the Pauli principle does not prevent the hole from jumping from one plane to another. Thus, a hole hopping from one acceptor defect to another within a plane may suddenly jump to the adjacent plane. This trapping increases the resistivity. After the jump in the magnetization, the net moments of the acceptor defects on adjacent planes point in the same direction, the Pauli principle excludes the trapping process, and the resistivity abruptly drops.

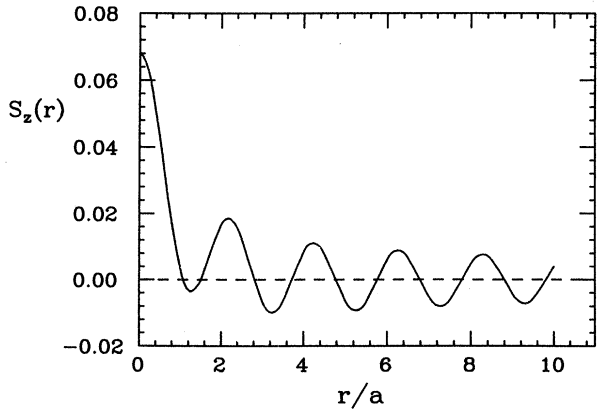

FIG. 2. Excess spin canting out of the CuO_2 plane due to a defect located at $r=0$ when $\xi_N=20a$, and $r_0=2a$, in units of the lattice spacing a, and $\delta_{pd}=-6J$. The calculation was made using Eq. (16), setting $H_0=D=0$, in the continuum approximation [i.e., using Eqs. (16) and (17)].

This model also quantitatively explains the nonmetal-metal transition and the rapid decrease of the Néel temperature T_N, both seen as a function of doping. Experimentally, $T_N \rightarrow 0$ typically when $x_c \approx 0.02$, then the nonmetal-metal transition occurs typically when $x_{\text{metal}} \approx 0.05$.[10] We believe that the antiferromagnetic order is destroyed by the slowly decaying oscillatory tail of canting surrounding the acceptor defects, as seen in Fig. 2. This tail decays with a characteristic length ξ_N, the large antiferromagnetic correlation length. Hence, each acceptor defect can have a large effect, and a small concentration of them can destroy the long-range magnetic order. The nonmetal-metal transition occurs when the defect orbitals cover a sufficient amount of the plane to complete a percolation path. Beyond the nonmetal-metal transition, the Sr^{2+} are no longer able to bind a hole. At this point we believe that a strong Ruderman-Kittel-Kasuya-Yosida (RKKY) exchange between the copper spins mediated by the itinerant oxygen holes is responsible for the inhibition of antiferromagnetism. As shown in Fig. 4, the RKKY exchange can be quite large, and for the range of doping of interest, is ferromagnetic for the first few nearest neighbors.

The majority of our results are derived within linear spin-wave theory which we will discuss in Sec. II. In Sec. III we present formulas for the magnetization of the Cu spins adjacent to the orbital defect, the binding energy of the defect orbital, and the reduction of the ordered Cu

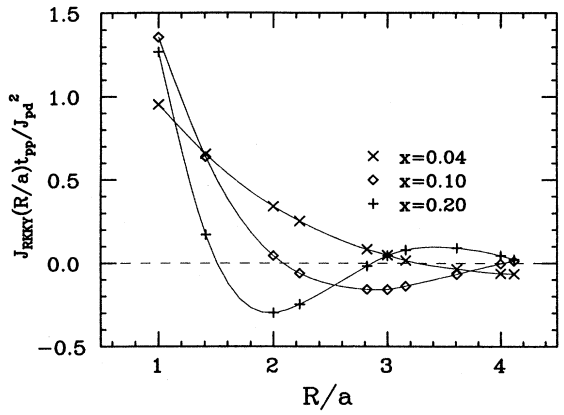

FIG. 4. Normalized RKKY exchange vs R/a. Here R is the distance between copper lattice sites, a is the lattice constant, and t_{pp} is the oxygen-oxygen hopping integral. Each data point corresponds to a copper lattice site, and data is provided out to the tenth nearest neighbor. The lines were added as a guide to the eye only. The $x=0.04$ data set roughly corresponds the doping necessary for the nonmetal-metal transition, when RKKY exchange first occurs. The doping for the other two data sets corresponds to the superconducting material. In all three cases the RKKY exchange is large and ferromagnetic for the first few neighbors.

moment. In Sec. IV we apply these formulas, and relate them to experiment. Finally, in Sec. V we summarize and conclude.

II. MODEL

The pure magnetic host. We will assume that the band structure of the CuO_2 plane is that shown in Fig. 1. In hole energies, a narrow, mostly copper Mott-Hubbard d band lies lowest, an oxygen p_π band lies above, and a mostly oxygen p_σ band lies highest. The Mott-Hubbard d band is composed mainly of copper $d_{x^2-y^2}$ orbitals, with a small admixture of oxygen p_σ orbitals. Due to large correlation energies on the copper sites, which are larger than the d-band width, the lower band will fill with a single hole per site. The band immediately above is composed mainly of oxygen p_π orbitals with a small admixture of oxygen p_σ, and the band highest in hole energies is composed mainly of oxygen p_σ, with a small admixture of copper $d_{x^2-y^2}$, and oxygen p_π orbitals. Before doping, $x=0$, the lower band is full, indicating that each copper site has a single hole and therefore, a spin moment. The small number of holes introduced by doping then go into the intermediate oxygen band. We assume that the hybridization in the band occurs mostly by hopping between adjacent p_π orbitals so that band-energy minima band fall at the corners of the zone, which is consistent with interpretations of positron-annihilation data.[11] Further, the assumption that the first excess hole per site goes onto the oxygen π orbitals is consistent with some recently proposed models[12–14] of superconductivity in $La_{2-x}Sr_xCuO_{4-y}$.

However, our model is not dependent upon the first excess hole going on to the p_π orbitals. Rather, it depends upon the presence of a magnetic exchange between the copper $d_{x^2-y^2}$ orbitals and the doped oxygen holes.

Due to the strong correlations in the full d band, each site has a magnetic moment. The resulting system can be modeled by CuO_2 layers with a weak interplanar coupling $J_\perp$. An isotropic purely two-dimensional Heisenberg system does not support long-range order at finite temperatures. However, an isotropic model with $J_\perp$ leads to a transition at T_N determined in a simple mean-field theory by $J_\perp(\xi_N/a)^2 f^2 \approx k_B T_N$, where f is the reduction in the ordered moment at $T=0$. Since $J_\perp$ is tiny ($J_\perp \approx 10^{-5} J$), it is sufficient for our purposes to investigate a two-dimensional (2D) model with long-range order at $T \neq 0$ assumed to arise from the interplanar coupling.

Thus our model will be a two-dimensional Heisenberg model where the moments interact through an antiferromagnetic superexchange mediated by the oxygen p_σ orbitals, and an antisymmetric DM term which is allowed by the orthorhombic symmetry. The DM term causes the spins to cant out of the plane.[1,6] The direction of preferred canting alternates between adjacent CuO_2 planes. In addition, there are small spin-orbit anisotropies which act to keep the antiferromagnetic order along a particular axis within the plane. These help to make the antiferromagnetic correlation length, ξ_N, finite in the pure magnetic host; however, we shall ignore their small contribution to the energy. We will separate our lattice into an A sublattice of down spins, and a B sublattice of up spins. Then if we take our coordinate system so that the z axis is perpendicular to the plane, and the x axis is in the plane in the direction of the magnetic order, then the Hamiltonian for the pure magnetic host is

$$H_{\mathrm{Cu}} = -\sum_{i\in A, j(i)} (J\mathbf{S}_i\cdot\mathbf{S}_j + \tfrac{1}{2}\mathbf{D}\cdot\mathbf{S}_i\times\mathbf{S}_j) - H_0\sum_i S_i^z , \qquad (1)$$

where $j(i)$ denotes the nearest neighbors of site i. The first term in H_{Cu} is the usual Heisenberg antiferromagnetic exchange term ($J<0$), the second is the DM term ($\mathbf{D}=D\mathbf{y}$, the sign of D alternates between planes), and the last is due to an external magnetic field.

The origin of the jump in the magnetization is not obvious from Eq. (1). In order to understand the jump, as discussed by Thio *et al.*,[1] one must include the effects of the small planar anisotropy, and $J_\perp$. Both the anisotropy and the DM contribution to the energy of the ordered planar state are degenerate under a rotation of 180° which reverses the direction of canting. The degeneracy is broken by the interplanar coupling $J_\perp$ which favors alternation of the canting direction between adjacent planes, and by an external magnetic field applied perpendicular to the planes which favors alignment of the canting. Thus, when an external field becomes sufficiently large [at $T=0$, $H_0 > H_c \approx 2J(J_\perp/D)$] all the canted planes align in the same direction accompanied by a 180° rotation of the spins in half of the planes.[26]

The defect orbital. We next discuss the effect of impurities introduced into the magnetic host. These impurities can be elemental impurities, including Sr^{2+}, Ba^{2+}, Ca^{2+}

divalent ions, or defects in the local stochiometry, including La and oxygen vacancies. We assume that even "pure" La_2CuO_{4-y} has some concentration of La vacancies in quantities of at least one part per thousand Cu. Further, we will assume that all divalent defects are quantitatively similar, and that La vacancies, which bind an odd number of holes, are at least qualitatively similar to divalent acceptor defects in their effect upon the magnetic host. The La vacancy cannot localize all three holes on one plane due to the mutual repulsion of the holes. However, it may localize two holes on the nearest plane, and one on the next-nearest plane. If the two holes on the nearest plane bind into a singlet, then they will have no net spin, and hence will not affect the magnetic properties of the host. However, the single spin localized on the next-nearest plane will have the same effect as the hole localized by a Sr substitutional defect. In addition, the two-hole singlet will be less tightly bound due to the mutual hole repulsion. Thus oxygen vacancies, which remove holes, may strip some of these holes from the La acceptor defect. In this phenomenological model we will discuss Sr acceptor defects, and assume that other divalent defects, and La vacancies, affect the magnetic host in a similar way.

When a Sr^{2+} is substituted into this system, the corresponding hole goes into the oxygen band. We will assume that it is spatially bound to the defect by a Coulombic interaction which is screened by the lattice dielectric polarization. The hole can then go into one of the two adjacent CuO_2 planes. The Sr^{2+} is located above a square of four copper sites in the nearest plane (~ 2.4 Å away), and directly above a single copper atom in the next-nearest plane (~ 3.6 Å away). It is not clear which plane the hole will localize on. The interplanar conductivity is low and there is little evidence from band structure for significant c-axis dispersion. Thus it is an excellent first approximation to assume that, in the absence of any external perturbations, the hole will localize on one of the two planes. If the hole localizes in the nearest plane, then we will call the acceptor defect "vacancy centered" (labeled "*V*" in Fig. 3), and if the hole localizes in the farther plane, then we will call it "Cu centered" (labeled "*C*" in Fig. 3).

The dielectric constant ϵ in this type of system can be quite large,[15,16] so that the size of the orbital will be larger than the distance between the copper atoms, and also larger than the displacement of the Sr^{2+} ion from the plane. Thus we will ignore the lattice fine structure and the displacement of the ion from the plane, and assume that the appropriate wave function for the defect orbital is the continuum ground-state wave function of the two-dimensional hydrogen atom multiplied by the appropriate Bloch states[17]

$$\Psi(\mathbf{r})=\sqrt{N}\,\psi(r)\phi(\mathbf{k}^*,\mathbf{r}) , \tag{2}$$

where

$$\psi(r)=\left[\frac{2}{\pi r_0^2}\right]^{1/2} e^{-r/r_0} , \tag{3}$$

and

$$\phi(\mathbf{k},\mathbf{r})=\frac{1}{\sqrt{2N}}\sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}}[\varphi^x(\mathbf{r}-\mathbf{R})-\mathrm{sgn}(k_x k_y)e^{-i(k_x-k_y)a/2}\varphi^y(\mathbf{r}-\mathbf{R})] . \tag{4}$$

Here, $\varphi^x(\mathbf{r}-\mathbf{R})$ and $\varphi^y(\mathbf{r}-\mathbf{R})$ are, respectively, the oxygen p_x and p_y Wannier functions for basis site $\mathbf{R}$ composed of a copper and two oxygen orbitals. The value of $\mathbf{k}^*$ is chosen to correspond to the energy minimum of the oxygen band.[17] With our assumed band structure

$$\mathbf{k}^*=\mathbf{Q}=\left[\pm\frac{\pi}{a},\pm\frac{\pi}{a}\right] ,$$

one of the four equivalent points at the corners of the Brillouin zone. The orbital radius r_0 will be treated as a variational parameter, determined by minimizing the binding energy of the defect orbital using the Coulombic potential which accounts for the displacement of the Sr^{2+} ion from the plane.

The combined defect-copper spin system. The spin of the oxygen hole interacts with the antiferromagnetically ordered copper spins in the plane. If we assume that the acceptor-defect orbital changes slowly over the unit cell, then the spin moment of the bound oxygen hole interacts with the copper spins through an exchange interaction of the form[18]

$$H_{0c}=-\mathcal{J}_{pd}S_0^z\sum_i a^2|\psi(R_i)|^2S_i^z . \tag{5}$$

Here a is the lattice constant, and $\mathbf{S}_0$ denotes the oxygen moment. We have assumed that the only finite component of $\mathbf{S}_0$ is that along the z axis since the DM interaction provides a preferred canting direction.

The form of Eq. (5) is found by evaluating the exchange integral between the copper $d_{x^2-y^2}$ orbital and the defect orbital Eq. (4). The value and sign of $\mathcal{J}_{pd}$ can vary greatly with the composition and symmetry of the oxygen band. Since we assume that the oxygen band is composed from π bonded oxygen orbitals, then $\mathcal{J}_{pd}$ is roughly $2J_{pd}$, where $J_{pd}>0$ is the exchange integral between the $d_{x^2-y^2}$ orbital and a single oxygen orbital. We will also assume that $\mathcal{J}_{pd}$ can be quite large $\mathcal{J}_{pd}\gg|J|$.[7]

To see the effects of this interaction we will treat the combined system with linear quantum spin-wave theory (see, for example, Ref. 19). We separate the copper lattice into A and B sublattice lattices and rotate the spins

on the B sublattice by 180° around the z axis. We then make the linear-spin-wave substitutions:

$$S_i^x \to s - n_i \ ,$$
$$S_i^y \to is(a_i^\dagger - a_i) \ , \tag{6}$$
$$S_i^z \to s(a_i^\dagger + a_i) \ ,$$

where $s = \frac{1}{2}$ is the spin magnitude, and the operators $a_i^\dagger$, and a_i, respectively, create and destroy a boson at site i. After Fourier transforming, the spin-wave Hamiltonian for the magnetic host with a single acceptor defect located at the origin is

$$H = -J \sum_{\mathbf{k}} [2a_{\mathbf{k}}^\dagger a_{\mathbf{k}} + (\gamma_{\mathbf{k}} a_{\mathbf{k}}^\dagger a_{-\mathbf{k}}^\dagger + \text{H.c.})] - [S_0^z \mathcal{J}_{pd}(\mathbf{k}) + \sqrt{N}\,\delta_{k0}(H_0 - D)]\tfrac{1}{2}(a_{\mathbf{k}}^\dagger + a_{\mathbf{k}}) - H_0 S_0^z \ , \tag{7}$$

where

$$\gamma_{\mathbf{k}} = \tfrac{1}{4} \sum_{j(i)} e^{i\mathbf{k}\cdot(\mathbf{R}_j - \mathbf{R}_i)} \tag{8}$$

and

$$\mathcal{J}_{pd}(\mathbf{k}) = \frac{1}{\sqrt{N}} \mathcal{J}_{pd} \sum_i a^2 |\psi(\mathbf{R}_i)|^2 e^{-i\mathbf{k}\cdot\mathbf{R}_i} \ . \tag{9}$$

Note that as a result of the linear approximation, the DM term now enters the Hamiltonian exactly like the external field H_0. From now on, we will refer to both of these terms as uniform field terms.

Equation (5) may be diagonalized with a Bogoliubov transformation

$$a_{\mathbf{k}} = \cosh(u_{\mathbf{k}}\beta_{\mathbf{k}}) + \sinh(u_{\mathbf{k}}\beta_{-\mathbf{k}}^\dagger) - \frac{[S_0^z \mathcal{J}_{pd}(\mathbf{k}) + \sqrt{N}\,\delta_{k0}(H_0 - D)]}{4J(1+\gamma_{\mathbf{k}})} \ , \tag{10}$$

where

$$\tanh(2u_{\mathbf{k}}) = -\gamma_{\mathbf{k}} \ . \tag{11}$$

The resulting Hamiltonian is

$$H = \sum_{\mathbf{k}} \omega_{\mathbf{k}} (\beta_{\mathbf{k}}^\dagger \beta_{\mathbf{k}} + \tfrac{1}{2}) + \sum_{\mathbf{k}} \frac{[S_0^z \mathcal{J}_{pd}(\mathbf{k}) + \sqrt{N}\,\delta_{k0}(H_0 - D)]^2}{4J[1+\gamma_{\mathbf{k}} + (a/2\xi_N)^2]} - H_0 S_0^z \ , \tag{12}$$

where

$$\omega_{\mathbf{k}} = -2J[1 - \gamma_{\mathbf{k}}^2 + 2(a/2\xi_N)^2]^{1/2} \ ,$$

and $\beta_{\mathbf{k}}^\dagger$ and $\beta_{\mathbf{k}}$ are boson creation and destruction operators, respectively. We have added a finite correlation length to Eq. (12) which we regard as a phenomenological parameter. Formally, the effect of a staggered field along the direction of ordering contributes a term of the same effect, where $(a/2\xi_N)^2 = \frac{1}{2} H_{\text{staggered}}$.

III. PROPERTIES OF THE MODEL

Using the canonical Bogoliubov transformation we may also calculate the ground-state energy

$$E = + \sum_{\mathbf{k}} \frac{\langle [S_0^z \mathcal{J}_{pd}(\mathbf{k}) + \sqrt{N}\,\delta_{k0}(H_0 - D)]^2 \rangle}{4J[1+\gamma_{\mathbf{k}} + (a/2\xi_N)^2]} + \tfrac{1}{2} \sum_{\mathbf{k}} \omega_k - H_0 \langle S_0^z \rangle \ , \tag{13}$$

and the canting angle,

$$S^z(\mathbf{R}) = -\frac{1}{\sqrt{N}} \sum_{\mathbf{k}} \frac{[\langle S_0^z \rangle \mathcal{J}_{pd}(\mathbf{k}) + \sqrt{N}\,\delta_{k0}(H_0 - D)]}{4J[1+\gamma_{\mathbf{k}} + (a/2\xi_N)^2]} \times e^{i\mathbf{k}\cdot\mathbf{R}} \ . \tag{14}$$

The reduction in the ordered moment is given by the number of bosons in the ground state

$$\langle n_i \rangle = \frac{1}{N} \sum_{\mathbf{k}} \frac{\langle [S_0^z \mathcal{J}_{pd}(\mathbf{k}) + \sqrt{N}\,\delta_{k0}(H_0 - D)]^2 \rangle}{16J^2[1+\gamma_{\mathbf{k}} + (a/2\xi_N)^2]^2} + \frac{1}{N} \sum_{\mathbf{k}} \sinh^2 u_{\mathbf{k}} \ . \tag{15}$$

In Eqs. (13)–(15) the angular brackets $\langle\ \rangle$ indicate a trace over the oxygen degrees of freedom.

The integrands in Eqs. (13)–(15) all have a similar form, consisting of some power of a field term

$$[\langle S_0^z \rangle \mathcal{J}_{pd}(\mathbf{k}) + \sqrt{N}\,\delta_{k0}(H_0 - D)]$$

multiplied by some power of the response function

$$[1 + \gamma_{\mathbf{k}} + (a/2\xi_N)^2]^{-1} \ .$$

The response function is easily characterized. It is smallest at the center of the Brillouin zone but has a divergence at the zone corners which is cut off by the correlation length. The form of the field term is determined by $\mathcal{J}_{pd}(\mathbf{k})$ except at the zone center. $\mathcal{J}_{pd}(\mathbf{k})$ is peaked at the zone center. When only the small $\mathbf{k}$, i.e., zone-center, behavior of $\mathcal{J}_{pd}(\mathbf{k})$ is important, we will use the continuum approximation,

$$\mathcal{J}_{pd}(\mathbf{k}) \approx \frac{\mathcal{J}_{pd}}{\sqrt{N}} \left[1 + \left[\frac{kr_0}{2} \right]^2 \right]^{-3/2} \ , \tag{16}$$

which is quantitatively accurate for small k, and has the correct qualitative property of being finite at the zone corner.

The binding energy and size of the defect orbital. The energy integral, Eq. (13), is logarithmically dependent on the momentum cutoff ξ_N/a, due to the cutoff divergence of the response function at the corner of the zone. This is a weak dependence which makes little contribution to the integral, and hence may be neglected. Thus we can approximate the integral by replacing $\mathcal{J}_{pd}(\mathbf{k})$ by its continuum approximation, Eq. (16), and the response function by

$$\frac{1}{[1+\gamma_{\mathbf{k}} + (a/2\xi_N)^2]} \approx \frac{1}{2 - (ka)^2/4} \ . \tag{17}$$

Then

$$E \approx \frac{1}{4J}\mathcal{J}_p \langle S_0^z \rangle (H_0 - D) + \frac{1}{8J} N (H_0 - D)^2 + \frac{\langle S_0^{z2} \rangle a^2 \mathcal{J}_{pd}^2}{16 J \pi r_0^2} . \quad (18)$$

Only the last term, which depends on r_0, contributes to the binding energy of the defect orbital. This is because the other terms, which are independent of r_0, are unchanged if the acceptor-defect hole becomes unbound ($r_0 \to \infty$).

The radius of the defect orbital is determined by minimizing the net orbital energy, ε

$$\varepsilon \approx \frac{\hbar^2}{2mr_0^2} + \frac{\langle S_0^{z2} \rangle a^2 \mathcal{J}_{pd}^2}{16 J \pi r_0^2} - 2\pi \int r\, dr \frac{e^2}{\epsilon (r^2 + z^2)^{1/2}} |\psi(r)|^2 , \quad (19)$$

where z is the distance from the plane to the Sr site. Here, the first term is the kinetic energy, the second is the energy gained by the polarization of the copper spins described above, and the last is the Coulombic potential energy. If we take $\epsilon = 15$, $z = 2.4$ Å, $\mathcal{J}_{pd} = -6J = 7200$ K, and minimize ε numerically, then we find the orbital radius $r_0 \approx 7$ Å, which is approximately $1.8a$ in units of the lattice spacing a. A defect orbital of this size would encompass approximately ten spins within r_0.

We note that in our model it is possible to make $\mathcal{J}_{pd}$ large enough so that the spin will localize adjacent to a single Cu site as is assumed by some authors.[7] Roughly, this occurs when the second term in Eq. (19) becomes large enough to overcome the kinetic barrier.[20] With the same parameters used above, we find that this first occurs when $|\mathcal{J}_{pd}| = 25\,000$ K. A value of $|\mathcal{J}_{pd}| > 25\,000$ K is consistent with the assumption that the lower oxygen band is composed of in-plane σ-bonded orbitals, since these are the only oxygen orbitals which strongly hybridize with the $d_{x^2-y^2}$ Cu orbitals. This hybridization can lead to a very strong antiferromagnetic superexchange between the hole occupying the copper $d_{x^2-y^2}$ orbital and those on the oxygen σ-bonded orbitals.[21,22] Thus if $|\mathcal{J}_{pd}| > 25\,000$ K, then it is likely that the hole will localize on the four oxygen orbitals adjacent to a single copper site in the manner described by Zhang and Rice.[21]

The copper spin polarization. The copper spin polarization is specified by Eq. (14). If the integrand is expanded it yields

$$S^z(\mathbf{R}) = \frac{H_0 - D}{8J} - \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} \frac{\langle S_0^z \rangle \mathcal{J}_{pd}(\mathbf{k})}{4J[1 + \gamma_{\mathbf{k}} + (a/2\xi_N)^2]} e^{i\mathbf{k}\cdot\mathbf{R}} , \quad (20)$$

where the first term is the canting due to the uniform fields, and the second is the excess canting due to the copper-oxygen-hole spin interaction.

If we replace $\mathcal{J}_{pd}(\mathbf{Q})$ by the continuum approximation, Eq. (16), then the excess canting appears as in Fig. 2. There is a small region of ferromagnetic response of radius $\approx r_0/2$. In this region, the canting angle falls off exponentially like $|\psi(r)|^2$. Farther from the acceptor defect, there is a region of antiferromagnetic canting out of the plane. The envelope of this canting falls off like $K_0(r/\xi_N)$, where K_0 is a modified Bessel function of the second type. The net magnetization of the acceptor defect is

$$M_{\text{defect}} = -\frac{\langle S_0^z \rangle \mathcal{J}_{pd}}{4J} + 2\langle S_0^z \rangle . \quad (21)$$

If $\mathcal{J}_{pd} = -6J$ and the oxygen spin is fully polarized, then this is roughly the magnetization of 1.75 copper moments.

Many of the properties of the acceptor-defect depend upon the polarization of the bound oxygen hole. In the absence of a uniform field, H_0 or D, there is no preferred direction for the oxygen spin to point, so $\langle S_0^z \rangle = 0$. When the uniform field is nonzero, $\langle S_0^z \rangle$ has a finite value. Through $\mathcal{J}_{pd}$, the oxygen spin further polarizes the copper spins. This feedback can result in the saturation of $\langle S_0^z \rangle$. At finite temperatures, $\langle S_0^z \rangle$ is given by

$$\langle S_0^z \rangle = \tfrac{1}{2} \tanh \left[\beta \left[H_0 - \frac{\mathcal{J}_{pd}(H_0 - D)}{4J} - \langle S_0^z \rangle \frac{\mathcal{J}_{pd}^2 a^2}{16 J \pi r_0^2} \right] \right] . \quad (22)$$

We assume that

$$-\frac{\beta \mathcal{J}_{pd}^2 a^2}{16 J \pi r_0^2} \gg 2$$

so that $|\langle S_0^z \rangle| \approx \frac{1}{2}$.

The reduction of the ordered moment. In spin-wave theory, the ordered Cu moment is given by $s - \langle n_i \rangle$. Thus, Eq. (15) gives the reduction of the ordered copper moment. The first term is the reduction due to both the constant fields and the acceptor defects. The effect of a small concentration of acceptor defects is much larger than that of the constant fields. Thus, we will ignore the constant fields in Eq. (15). If we assume that there is a very small concentration of uncorrelated acceptor defects in the material, then each impurity contributes independently to the reduction of the ordered moment. Then the reduction of the moment which comes solely from the acceptor defects is given by

$$\langle n_i \rangle_{\text{defects}} = x \sum_{\mathbf{k}} \frac{\langle S_0^{z2} \rangle \mathcal{J}_{pd}(\mathbf{k})^2}{16 J^2 [1 + \gamma_{\mathbf{k}} + (a/2\xi_N)^2]^2} . \quad (23)$$

The integrand increases strongly at the corners of the Brillouin zone so that the result is totally dominated by this region of integration. Thus,

$$\langle n_i \rangle_{\text{defects}} \approx x \frac{N \mathcal{J}_{pd}(\mathbf{Q})^2 \langle S_0^{z2} \rangle}{\pi J^2} \left[\frac{\xi_N}{a} \right]^2 . \quad (24)$$

This result is sensitive to the dimensionality of the material. For example, in three dimensions $\langle n_i \rangle_{\text{defects}} \propto (\xi_N/a)$. The second term in Eq. (15) may be evaluated numerically. It represents the reduction due to quantum

fluctuations alone, which reduces the moment by

$$\langle n_i \rangle_{\text{quantum}} \approx 0.19 \ . \tag{25}$$

IV. CONNECTION WITH EXPERIMENT

We believe that many of the properties of the magnetic semiconducting phase of $La_{2-x}Sr_xCuO_{4-y}$ can be explained by the presence of acceptor defects. Among these are the nonmetal-metal transition, the suppression of the antiferromagnetic order, a contribution to the jump in the magnetization in the presence of an external field and the coincident magnetoresistance, and the μSR depolarization rate which changes as a function of Sr doping and La and oxygen vacancies.

Nonmetal-metal transition. $La_{2-x}Sr_xCuO_{4-y}$ undergoes a transition from a semiconductor-insulator to a weakly conducting metal when $x \approx 0.05$. We assume that the transport in $La_{2-x}Sr_xCuO_{4-y}$ is predominantly intralayer. In some semiconductors, like phosphorus doped Si,[23] the nonmetal-metal transition is believed to be a Mott-Hubbard transition. However, since the DM interaction polarizes the spins of the acceptor defect holes, hopping (which conserves spin) cannot doubly occupy a site without violating the Pauli principle. Thus, in our model, the nonmetal-metal transition cannot be a Mott-Hubbard transition. We believe that the transition is due to percolation. The critical concentration can be obtained by estimating when a percolating conduction path is formed by defect orbital overlap. Obviously, this ignores quantum effects, but should provide a reasonable estimate. In a two-dimensional lattice, tiled by nonoverlapping defect orbitals, this threshold occurs when the tiling fraction reaches 50%. Thus

$$x_{\text{metal}} \approx 0.5 \frac{a^2}{\pi r_0^2} \ . \tag{26}$$

If $r_0 = 1.8a$, then $x_{\text{metal}} \approx 5\%$. In the real material x_{metal} will be increased by the overlapping of adjacent defect orbitals, and oxygen vacancies, which strip holes from the acceptor defects.

The suppression of the ordered moment. The ordered magnetic moment vanishes before the nonmetal-metal transition occurs. At zero temperature, the ordered moment typically vanishes when $x \approx 0.02$. Within spin-wave theory, the antiferromagnetic order is destroyed when the average moment $s - \langle n_i \rangle$ becomes zero. From a simple linear extrapolation of Eqs. (24) and (25), which neglect the correlations between the acceptor defects, the corresponding formula for x_c is

$$x_c \approx \frac{0.31 J^2 \pi}{N \mathcal{J}_{pd}(\mathbf{Q})^2 \langle S_0^{z2} \rangle} \left[\frac{a}{\xi_N} \right]^2 . \tag{27}$$

As we mentioned above in connection with Eq. (24), this result is quite sensitive to the dimensionality of the material. For example, in three dimensions $x_c \propto (a/\xi_N)$. Thus the large value of ξ_N in these materials,[24] and the quadratic sensitivity of Eq. (27) to ξ_N due to the planar nature of $La_{2-x}Sr_xCuO_{4-y}$, ensure that x_c will be small.

Equation (27) is also sensitive to $\mathcal{J}_{pd}(\mathbf{Q})$, which is difficult to calculate. From Eq. (9) it is clear that $\mathcal{J}_{pd}(\mathbf{Q}) = 0$ for vacancy centered defects in a tetragonal lattice. This is because the contribution from up-spin sites exactly cancels that from down-spin sites equidistant from the defect. However, in the real material, $\mathcal{J}_{pd}(\mathbf{Q})$ is finite for at least three reasons. First, $La_{2-x}Sr_xCuO_{4-y}$ is orthorhombic. The orthorhombic distortion displaces the spins, destroying any possible cancellation. Second, other charged defects may distort the defect orbital. This will have the same effect as the orthorhombicity since then in Eq. (9) sites equidistant from the orbital will be weighted differently by $|\psi|^2$. Finally, if the acceptor defects are Cu centered, then $\mathcal{J}_{pd}(\mathbf{Q})$ is finite regardless of lattice symmetry since all the spins equidistant from the center contribute constructively to $\mathcal{J}_{pd}(\mathbf{Q})$.

Any calculation of $\mathcal{J}_{pd}(\mathbf{Q})$ must involve an explicit lattice sum, since a continuum approximation is only good for long-wavelength (zone-center) behavior. For example, if the acceptor defects are copper centered and $r_0 = 1.8a$, then an explicit lattice sum yields

$$\mathcal{J}_{pd}(\mathbf{Q}) = 0.085 \mathcal{J}_{pd} / \sqrt{N} \ .$$

Thus if $\mathcal{J}_{pd} = -6J$ and $\xi_N = 30a$, then $x_c \approx 1.7\%$. Of course, this value depends sensitively upon the chosen parameters. For example, if we chose $r_0 = 2a$ with all other parameters the same, then $x_c \approx 3.3\%$. In addition, if the material has some concentration of oxygen vacancies which strip holes from the acceptor defects, then the critical concentration x_c will increase. This effect has been seen in $La_{2-x}Sr_xCuO_{4-y}$, where T_N actually increases when oxygen vacancies are introduced.[25,2,3] The same effect is seen in μSR studies which can directly measure the ordered moment, as discussed below.

Physically, it is the long-range oscillatory tail of the canting out of the plane (Fig. 2) which destroys the magnetic moment. This tail extends out from the acceptor defect with a range given by the antiferromagnetic correlation length ξ_N, and the effect is to disrupt the antiferromagnetic order once a sufficient number $x = x_c$ of acceptor defects have been introduced.

RKKY interaction. It is well known that in $La_{2-x}Sr_xCuO_{4-y}$ $x_c \approx 0.02$, and that $x_{\text{metal}} \approx 0.05$. In the doping region (roughly $0.05 < x < 0.30$), where the material is superconducting, there is no evidence for long-range antiferromagnetic order. Thus, if the mechanism described above, which is based on localized holes, depresses T_N, then one must naturally ask why the material does not become antiferromagnetic once the holes completely delocalize in the metal. We believe that the RKKY interaction which results when the oxygen holes delocalize will be sufficient to suppress the antiferromagnetism.

Using standard techniques (e.g., see Mattis[19]) we have calculated the RKKY exchange using the appropriate form factors for the CuO_2 planar lattice. As we show in Fig. 4, the RKKY exchange, $J_{\text{RKKY}}(R/a)$, is strong and ferromagnetic between the first few nearest-neighbor copper spins. For example, consider the nearest-neighbor RKKY exchange. If we take

$$J_{\mathrm{RKKY}}(R=a)t_{pp}/J_{pd}^2=1\ ,$$

and if $t_{pp}=0.65$ eV and $J_{pd}=0.36$ eV, then

$$J_{\mathrm{RKKY}}(R=a)=0.200\ \mathrm{eV}\ ,$$

easily canceling the near-neighbor superexchange $J\approx 0.1$ eV. The material does not become ferromagnetic due to the frustrating nature of the RKKY interaction, however; it could very well exhibit spin-glass behavior.

The μSR precession and depolarization rates. In $La_{2-x}Sr_xCuO_{4-y}$, the μSR depolarization rate changes with the quantity and type of defects introduced into the magnetic host.[3] In this experiment, spin-polarized muons are introduced into the system. They thermalize quickly, retaining their polarization, and come to rest near the ordered plane. They then begin to precess due to the magnetic field of the ordered copper spins. The depolarization rate measures how fast the precession of different muon spins becomes uncorrelated. Budnick *et al.*[3] find that, for $T<T_N$, the depolarization rate increases with the introduction of both La vacancies and Sr defects. They provide a consistent interpretation of the data in terms of static inhomogeneities in the magnetization of the material. We believe that the acceptor defects produce the magnetic field inhomogeneities by polarizing the copper spins in their vicinity. Budnick *et al.* also found that the depolarization rate decreased when oxygen vacancies were introduced. The introduction of an oxygen vacancy into $La_{2-x}Sr_xCuO_{4-y}$ removes two holes, which must come from the acceptor defects, rendering them unable to polarize the Cu spins. Budnick *et al.* also measured the μSR precession frequency in La_2CuO_{4-y} which is proportional to the ordered moment. They find that samples with oxygen vacancies have the largest ordered moment, whereas samples with a large concentration of La vacancies have the smallest. Both of these effects are consistent with our discussion of the reduction of the ordered moment above.

The acceptor-defect moment, and the jump in the magnetization. When a sufficient magnetic field is applied perpendicular to the CuO_2 planes, then $La_{2-x}Sr_xCuO_{4-y}$ exhibits a small but a rapid rise in the magnetization, and a coincident decline in the resistivity. Earlier, in Eq. (22), we showed that $\langle S_0^z\rangle$ would quickly saturate when a uniform field breaks the symmetry. The strong copper-oxygen spin coupling $\mathcal{J}_{pd}$ amplifies the effect of the uniform fields. In fact if $J=-1200$ K, $\mathcal{J}_{pd}=-6J$, and $r_0=1.8a$, then

$$2\langle S_0^z\rangle=\tanh\left[\frac{\beta}{2}[H_0-1.25(H_0-D)+\langle S_0^z\rangle 530\ \mathrm{K}]\right]\ . \tag{28}$$

Thus, when $H_0=0$, then $\langle S_0^z\rangle$ saturates along the direction of **D**. When H_0 first exceeds H_c, then the magnetic moment of each acceptor defect in the planes in which the effect of D and H_0 are in opposition, abruptly changes sign. Thus the acceptor defect contribution to the change in magnetization is given by

$$\Delta M=\tfrac{1}{2}xN\left[-\frac{\mathcal{J}_{pd}}{4J}+2\right]\ . \tag{29}$$

Here the factor of $\frac{1}{2}$ reflects the fact that the jump occurs in only half the planes, those for which H_0 and D are in opposition. Oxygen vacancies, which strip holes from the acceptor defects, will reduce this contribution to the jump.

Magnetoresistivity. Coincident with the jump in the magnetization as a function of the applied magnetic field is a sharp drop in the resistivity of $La_{2-x}Sr_xCuO_{4-y}$. Both above and below the critical field the resistivity is relatively flat as a function of the field. In what follows we will assume that the vacancy-centered acceptor defects are energetically more stable than Cu-centered acceptor defects, and that intraplane variable-range hopping dominates the transport. The second assumption is consistent with the zero-field data which do not clearly distinguish between 2D or 3D variable-range hopping: over the limited range of temperature for which data is available, a $T^{-1/3}$ exponent provides as plausible a fit as a $T^{-1/4}$ exponent.[26]

Then, a possible (though incomplete) picture for understanding the planar magnetoresistance within the same scenario is as follows: The basic features are illustrated in Fig. 3. Below the critical field H_c at which the magnetization jumps, the spins of the bound holes are fully polarized by the DM interaction in opposite directions on adjacent planes. The Pauli principle excludes intraplane hopping between occupied vacancy-centered defect orbitals (labeled V in Fig. 3). However, intraplane hopping is possible to the nominally empty Cu-centered orbitals (labeled C in Fig. 3). This can indeed occur since the random potential created by the defects themselves, as well as other sources of disorder (twinning, oxygen defects, copper defects, etc.), randomize the V and C levels such that there is some overlap of the spectra. We note that such intraplane hopping costs no magnetic polarization energy since the ambient canting of the plane is preserved.

The description for $H<H_c$ is as follows: It is possible for a C orbital defect spin in, say, a down plane to hop to the up-plane V orbital immediately above or below, as shown in Fig. 3(c). Once this occurs, the net acceptor-defect moment vanishes, making it unfavorable for the down spin to hop within that plane because of the large mismatch of polarization energy. Hence, such local interplane transfers are essentially resonant trapping processes which contribute to the resistivity and are not dependent on H for $H<H_c$. We address the energetics of the interplane hopping now: In the improbable event that the V level is momentarily empty, then the loss of polarization binding energy (~ -200 K) from having an unfavorable defect spin orientation is largely offset by the gain in Coulombic binding energy (~ 200 K). If, as is more probable, the V level is initially occupied, we lose somewhat less polarization binding energy (~ -100 K) by going to a zero-spin defect than above but lose additional binding energy from the increase in hole-hole repulsion (~ -200 to -300 K). Again, these changes are comparable to the single-particle Coulombic binding

energy change so that the overall energy shift is not too large and the hopping process can occur.

The description for $H > H_c$ is as follows: Once the magnetic jump occurs, within our picture all defect spins are uniformly polarized. Hence, the most likely trapping processes which are hops from occupied C orbitals to already occupied, adjacent V orbitals on neighboring planes are frozen out by the Pauli principle. This suppression of trapping which impedes intraplane current flow for $H < H_c$ causes the resistance to diminish abruptly at the jump. However, since the essential intraplane hopping processes are unaffected (each plane is polarized to begin with by the DM interaction) then the magnetoresistance should show little sensitivity to fields exceeding the critical jump value.

This suppression of trapping processes will also cause a reduction of the resistance to currents flowing perpendicular to the plane. In addition, hopping to planes of similar polarization will be favored hopping to those of opposite polarization. When all the planes have the same polarization, the perpendicular resistivity should drop. Thus, the perpendicular magnetoresistance should show qualitatively similar behavior to the planar magnetoresistivity.

We would like to propose two experimental tests of our magnetoresistance model. First, if oxygen vacancy defects are introduced into $La_{2-x}Sr_xCuO_{4-y}$, then the resistivity should increase since these vacancies strip the carriers from the defect sites. Second, if pressure is applied to $La_{2-x}Sr_xCuO_{4-y}$ in the orthorhombic c direction, then this should increase the overlap of the C and V defect sites.[27] This would increase the effectiveness of the trapping, hence, increasing the jump in the planar resistivity coincident with the jump in the magnetization.

V. SUMMARY

We have proposed a model which can explain much of the phenomenology of the magnetic phase (low doping) of $La_{2-x}Sr_xCuO_{4-y}$ in terms of magnetic acceptor defects in an antiferromagnetic host. The defect orbital forms when a donor ion contributes a hole to the bottom of the conduction band, which we assume to be formed from the overlap of the π-bonded oxygen orbitals. This hole is localized near the donor ion by a Coulombic attraction, and interacts with the ordered magnetic moments of the copper sites through a ferromagnetic exchange.

Our model gives a possible explanation for the jump in the magnetization in an external field, the coincident drop in the resistivity, the μSR depolarization, and the reduction of the ordered moment and the nonmetal-metal transition both seen as a function of doping, all properties of $La_{2-x}Sr_xCuO_{4-y}$ for small x. Thus, we believe that our model provides a consistent explanation of many of the low doping properties of $La_{2-x}Sr_xCuO_{4-y}$.

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*Permanent address: Physics Department, Indian Institute of Science, Bangalore 560012, Mysore, India.

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