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Reentrant antiferromagnetism in oxygen-doped cuprates

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The reentrant behavior of the sublattice magnetization in the doped cuprates La_2CuO_{4+x} and $YBa_2Cu_3O_{6+x}$ is explained by a model which assumes that the localized holes reduce the sublattice magnetization more strongly than the mobile holes. Good agreement with the experiments is obtained, using the measured temperature dependence of the localized hole density, which is characterized by the (measurable) hole excitation energy $E(x)$, and the difference between mobile and localized holes, described by a single x-dependent parameter. The theory also accounts for the absence of the reentrant behavior in highly doped samples. At higher temperatures we find additional corrections, due to a renormalization of the spin waves by the impurities.

The parent materials for high-temperature superconductors, La_2CuO_4 and $YBa_2Cu_3O_6$, are layered antiferromagnets (AF) with high Néel temperatures $T_N = 320$ and 410 K.[1–4] For doped samples, La_2CuO_{4+x} (LCO) and $YBa_2Cu_3O_{6+x}$ (YBCO), the Néel temperature T_N decreases with increasing x, and it is convenient to identify samples by the values of T_N.[1–5] The long range AF order disappears ($T_N = 0$) when $x \approx 0.02$ in LCO and $x \approx 0.4$ in YBCO, and a transition to a spin glass state was observed at least in LCO.[6,7]

In the pure samples, the temperature dependence of the staggered magnetization, $M(T,x)$, was explained[2] in terms of a generalized Schwinger boson mean field theory.[8] However, the temperature dependence of M in the doped cuprates is unusual.[1–4,9] In LCO with $T_N = 190$ K, M has a large plateau at $T < 0.4T_N$ (see Fig. 1 of this paper).[2] A plateau is also seen in samples with $T_N \approx 150$ and 220 K (Ref. 10). When x is further increased, with a corresponding decrease of T_N to 90 K, M reveals a reentrant behavior (Fig. 1). It exhibits a maximum at some temperature $T_m \ll T_N$, followed by a decrease at lower T. Finally, when $T_N = 50$ K, M decreases monotonically with increasing T.[11] A similar maximum in $M(T,x)$ has also been observed in YBCO,[3,4] in samples with $x = 0.3$, $T_N = 350$ K; $x = 0.33$, $T_N = 300$ K (see Fig. 2); and $x = 0.37$, $T_N = 180$ K. At higher impurity concentration ($x = 0.38$, $T_N = 150$ K) the T dependence is monotonic.

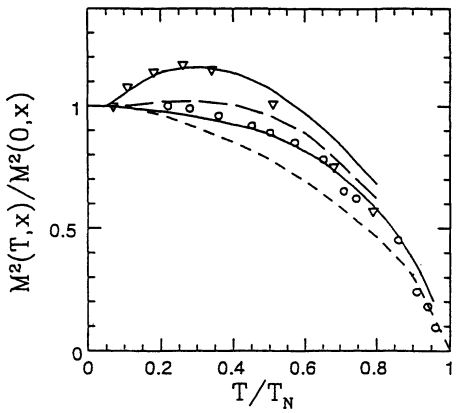

FIG. 1. The temperature dependence of the normalized square of the sublattice magnetization, M^2/M_0^2, in LCO. $\circ - T_N = 190$ K; $\triangledown - T_N = 90$ K; the dashed (lower) line $-x = 0$, $T_N = 325$ K (from Ref. 2). The solid lines represent the theoretical fit to Eq. (3). The broken (upper) line gives the prediction for the sample with $T_N = 150$ K.

In this paper we discuss two mechanisms which affect the x dependence of $M(T,x)$. Figures 1 and 2 show our theoretical results, from the first mechanism, based on the difference between mobile and localized holes. The theory, which involves an x-dependent parameter $\beta(x)$ (see below), clearly reproduces the observed plateaus and the maxima. The further reduction of $M(T,x)$ at $T > T_m$ is explained in the second part of the paper, via the scattering of spin waves.

Shender and Rammal[12] described the disorder in the antiferromagnet by a model of local noninteracting magnetic two-level systems (see also Ref. 13) with a wide distribution of the energy splitting $P(\epsilon)$. This model results in a reentrant behavior of the sublattice magnetization if $P(\epsilon \leq T) \geq J^{-1}$, where J is the in-plane exchange interaction between neighboring Cu spins, and if P does not scale with the defect concentration. The authors did not

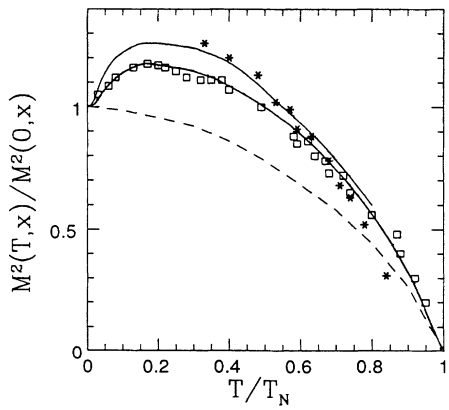

FIG. 2. Same as Fig. 1 for YBCO. $\square - x = 0.30$; $* - x = 0.33$; the dashed line $-x = 0.20$ (from Refs. 3 and 4). The solid lines represent the theoretical fit to Eq. (3).

make a detailed comparison with the experiment.

The reentrant behavior of M observed in the doped cuprates resembles that of magnets exhibiting a reentrant transition to a spin glass state.[14] Therefore Aharony *et al.*[6] and Endoh *et al.*[9] related the maximum in M with the spin glass ordering.[7] It has been argued,[6] that at low doping the holes are localized on the oxygen sites in the CuO_2 planes, introducing a large effective ferromagnetic interaction between the two Cu spins neighboring the oxygen hole. The two spins connected by the frustrated bond are perpendicular to the sublattice magnetization and act on the AF background as a dipole. The spins around the ferromagnetic bond are canted, by an angle which decays at large distances r from the origin as r^{-1} (Refs. 6 and 15). Thus the defect induced decrease of the order parameter diverges as $\ln L$ in the limit $L \to \infty$, where L is the sample size. This means that an arbitrary small number of defects destroys the long range order. In real cuprates, the range of the r^{-1} dependence is restricted to $r < r_0$ by the in-plane anisotropy (with a spin wave gap $\epsilon_g \simeq 1$ meV,[16] in LCO) or by the interplane exchange interaction $J_\perp$ (in YBCO). A simple generalization of Villain's[15] arguments shows that the range of the r^{-1} dependence is of the order of $r_0 = J/\epsilon_g \approx (J/J_\perp)^{1/2} \approx 10^2$ in the lattice constant units. Thus each localized hole lowers the sublattice magnetization in a finite but large ($r_0 \gg 1$) range, and the sublattice magnetization decays quickly when the doping increases.

Recent experiments[5,17] show that the acceptors in LCO and YBCO are relatively shallow. In pure LCO with $T_N = 320$ K, the acceptor level energy is $E(x = 0) = 35$ meV$> T_N$. Upon doping, $E(x)$ drops quickly, faster than $T_N(x)$ (Fig. 3). Since the fraction of mobile holes is[5,18] $n(T,x) = \exp[-E(x)/T]$, the number of localized holes decreases substantially as T increases in the range $0 < T < T_N$. The activation energy in slightly doped YBCO is also about 30 meV.[5]

In some models,[19,20] the mobile holes move as polarons in pure conductance bands. The effect on $M(T,x)$ is then minimal. In other models,[21] the hole is described as a moving vacancy in the quantum AF. The spins around the hole are canted in a dipolelike way. In the cuprates, the hopping energy t obeys $t \gg J$. In that case, the hopping is faster than the spin dynamics, and the hole "hops through a frozen spin background."[21] It is thus reasonable to assume that mobile holes cause less disruption of the AF order than localized ones. Therefore the delocalization of the holes with increasing T should cause an increase in M.

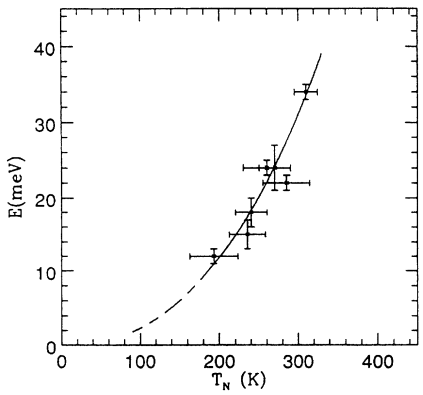

FIG. 3. The hole activation energy in LCO as a function of the doping (Refs. 5 and 17). T_N is used to label the doping. The solid line is a guide for the eye, and the dashed line shows the extrapolation to low T_N.

To separate the two effects addressed in this paper, we write

$$M(T,x) = M_{sw}(T,x) - m_c(T,x). \quad (1)$$

Here $M_{sw}(T,x)$ describes the temperature dependence of the magnetization due to the spin wave excitations. The disorder affects this function only via the renormalization of the spin wave spectrum. Therefore $M_{sw}(T,x)$ is independent of x for $T \to 0$. The effects of hole delocalization are contained in $m_c(T,x)$, and $m_c(T,0) = 0$. Thus, $M_{sw}(0,x) = M_{sw}(0,0) = M(0,0)$. We now consider $m_c(T,x)$ in two limits. At $T = 0$, all the holes are localized [$n(T = 0,x) = 0$], and we define $\delta_0 = m_c(0,x)/M_{sw}(0,x) = [M(0,0) - M(0,x)]/M(0,0)$. In the other limit, of high T, all the holes become mobile, and we denote the limit of $m_c(T,x)/M_{sw}(T,x)$ when $n(T,x) \to 1$ by δ_1. δ_1 is T independent: the temperature dependence of $m_c(T,x)$ is caused only by the spin wave excitations. Since the main contribution to $m_c(T,x)$ comes from spins with small canting angles, the function $m_c(T,x)$ is proportional to $M_{sw}(T,x)$.

In the intermediate temperature range, when $0 < n(T,x) < 1$, we write

$$m_c(T,x)/M_{sw}(T,x) = [1 - n(T,x)]\delta_0 + n(T,x)\delta_1. \quad (2)$$

Equations (1) and (2) yield

$$\frac{M(T,x)}{M(0,x)} = \frac{M_{sw}(T,x)}{M(0,0)} \times \left[1 + \beta(x)\frac{\Delta M(0,x)}{M(0,x)} \exp\left(\frac{-E(x)}{T}\right)\right], \quad (3)$$

where $\Delta M(0,x) = M(0,0) - M(0,x)$, and $\beta(x) = (\delta_0 - \delta_1)/\delta_0$. Basically, Eq. (3) contains the single x-dependent parameter $\beta(x)$ which represents the difference between mobile and localized holes. We expect $\beta(x)$ to decrease with the increase of x, since the localization range of the hole increases and the difference between localized and delocalized holes decreases.

We first compare Eq. (3) with the experiments for LCO. Ignoring the renormalization of spin waves (see below), we approximate $M_{sw}(T,x)/M(0,0)$ by the function $M(T,0)/M(0,0)$, known from neutron measurements.[2] The magnetization decay $\Delta M(0,x)/M(0,x)$ is also known from the experiment.[10] The energy $E(x)$ has been determined from Hall measurements of the hole concentration for a number of LCO samples.[5,17] The dependence of E on T_N according to these data is given in Fig. 3. Thus we are left with one adjustable parameter, β. For the sample with $T_N = 190$ K, and $E(x) = 140$ K (Fig. 3), Fig. 1 shows a very good fit to Eq. (3) with

$\beta(x) = 0.26$. A similar fit was found for $T_N = 220$ K (from Ref. 10), with $\beta = 0.30$. For $T_N = 90$ K, we extrapolate $E(T_N)$ in Fig. 3 and estimate $E(x) = 21$ K. Figure 1 shows that Eq. (3) with $\beta = 0.13$ reproduces the data very well, especially near the maximum. Indeed, β decreases with increasing x. In both cases, the fit becomes worse at higher T, due to the x dependence of $M_{\rm sw}(T,x)$ (see below). Figure 1 also shows Eq. (3) with $T_N = 150$ K, $E = 70$ K, and $\beta = 0.18$, which we choose by interpolation between the parameters found above. The resulting graph exhibits a plateau, similar to the data of Ref. 10. However, the scatter in the latter does not allow a quantitative comparison.

There are no experimental data for $E(x)$ in YBCO. We therefore used both $E(x)$ and $\beta(x)$ as adjustable parameters when comparing Eq. (3) with the experiments. We approximated the function $M_{\rm sw}(T,x)/M(0,0)$ in Eq. (3) by the measured[3,4] function $M(T,0.20)$ rather than by $M(T,0)$. The reason is that $M(T,0.20)$, like $M(T,0)$, does not exhibit any peculiarities (see Fig. 2), i.e., $M(T,0.20) \approx M_{\rm sw}(T,0.20)$. It is natural to suggest that the function $M_{\rm sw}(T,0.20)$ is closer to the functions $M_{\rm sw}(T,x)$ for $x \geq 0.30$, than $M_{\rm sw}(T,0)$. It is seen from Fig. 2 that the theoretical line with $E = 25$ K and $\beta = 0.54$ follows closely the experimental points for YBCO with $x = 0.3$ ($T_N = 350$ K) in the whole temperature range $0 < T < T_N$. $E = 15$ K and $\beta = 0.32$ give a good fit for the sample with $x = 0.33$ at $T < 0.7T_N$ (Fig. 2). However, the comparison in this case is less conclusive, since there are no experimental points in the region of the maximum.

As mentioned above, the sample with $x = 0.37$ ($T_N = 180$ K) also reveals the reentrant behavior. Nevertheless, the overall temperature dependence of $M(T,x)$ for this sample differs substantially from that in the above samples with a lower doping level: the line $M(T,0.37)$ at $T > T_m$ is concave rather than convex. This means that the frustrating impurities affect strongly the function $M_{\rm sw}(T,x)$, and our assumption that this function behaves as $M_{\rm sw}(T,0.20)$ ceases to be valid. Therefore we have not tried to fit Eq. (3) to the data in this case.

We can now understand why $M(T,x)$ exhibits a maximum only at some intermediate range of x. When x is small, E is large, of the order of T_N. Thus the increase of M due to the delocalization of the holes, which is most pronounced at $T \approx E$, is depressed by the fast decay of M due to the thermal fluctuations near T_N. In the highly doped samples the difference between the localized and delocalized states is small, i.e., $E(x)$ and $\beta(x)$ go to zero. Therefore there is no reason to expect an increase of M, when the number of delocalized holes rises. The relation between $E(x)$ and $T_m(x)$ has been noted in Ref. 3.

We now turn to our second effect, involving the difference between the temperature dependence of $M_{\rm sw}(T,x)$ for a doped crystal and $M_{\rm sw}(T,0)$ for the pure one. For small x we consider a simple model of the impurities: frustrated noninteracting bonds. We can thus consider a single frustrating bond, connecting the spins $\vec{S}_{1f}$ and $\vec{S}_{2f}$. The Hamiltonian of the system is $H = H_0 + H_{\rm int} + H'_{\rm int}$, where $H_0 = J\sum_{\langle ij\rangle} \vec{S}_i \cdot \vec{S}_j$ is the Hamiltonian of the undoped antiferromagnet, with nearest neighbors $\langle ij\rangle$. $H_{\rm int}$ describes the interaction of the spins $\vec{S}_{1f}$ and $\vec{S}_{2f}$ with their neighbors. Assuming a strong ferromagnetic coupling between $\vec{S}_{1f}$ and $\vec{S}_{2f}$, these spins are parallel to each other, perpendicular to the staggered moment. Thus

$$H_{\rm int} = J\sum_i \vec{S}_{1f}\cdot\vec{S}_i + J\sum_i \vec{S}_{2f}\cdot\vec{S}_i \tag{4}$$

contains sums over the three neighbors of $\vec{S}_{1f}$ (excluding $\vec{S}_{2f}$) and similarly for $\vec{S}_{2f}$, and

$$H'_{\rm int} = -J\sum_{\langle ij\rangle} \vec{S}_i \cdot \vec{S}_j, \tag{5}$$

where the sum is over the seven bonds connecting $\vec{S}_{1f}$, $\vec{S}_{2f}$ and their six neighbors. Note that for simplicity we neglect the canting of all the spins except for $\vec{S}_{1f}$ and $\vec{S}_{2f}$.

In the usual linear spin wave theory the Hamiltonian (4) describes the interaction of the spin waves with a pair of canted spins. For low energy spin waves, this is analogous to the interaction of phonons with a local distortion or magnetic ion (see, e.g., Ref. 22):

$$H_{\rm int} = S_f^+ \sum_{\vec{q},\lambda=1,2} V_{\vec{q}f}\alpha^\dagger_{\vec{q}\lambda}\exp(i\vec{q}\cdot\vec{R}_f) + \text{H.c.} \tag{6}$$

Here $\alpha^\dagger_{\vec{q}\lambda}$ creates the spin wave with polarization λ, and $S_f^+ = S_f^x + iS_f^y$ represent the joint spin $\vec{S}_{1f} = \vec{S}_{2f} = \vec{S}_f$ (the sublattice magnetization is along z). The interaction energy is $V_{\vec{q}f} \propto J^{3/2}q(\omega^0_{\vec{q}})^{-1/2} \propto Jq^{1/2}$, where $\omega^0_{\vec{q}} = c_0 q$ is the spectrum of the undoped antiferromagnet.

The spin wave self-energy which follows from (6), after the averaging over the impurity bonds with concentration x, is

$$\Sigma(\omega,\vec{q}) \sim x \mid \bar{V}_{\vec{q}} \mid^2 \chi(\omega), \tag{7}$$

where the overbar means averaging over the orientations of the frustrated bonds. The retarded Green's function of the spin $\vec{S}_f$, $\chi(\omega)$, is proportional to the susceptibility of the impurity spin, which is (under sufficiently general conditions) a Lorentzian.[23] The width Γ of the Lorentzian is determined by the dipole-dipole interaction (mediated in our case by the spin waves[6,15]) of the randomly distributed impurity spins or by the interaction of the spin with the matrix degrees of freedom (spin-phonon, spin-magnon interactions, etc.). Thus at low frequencies $\omega \ll T$ we have

$$\chi(\omega) = -\frac{i\Gamma\mu^2}{T(\omega+i\Gamma)}, \tag{8}$$

where the effective dipole moment μ represents the spin $\vec{S}_f$, taking into account phenomenologically that the real defect is more complicated than the model considered here.[24]

Writing the renormalized spin wave spectrum

$$\omega_{\vec{q}} = \omega^0_{\vec{q}} + \text{Re}\Sigma(\omega_{\vec{q}},\vec{q}), \tag{9}$$

and using Eqs. (7)–(9) for $\omega \ll \Gamma$, the renormalized spin

wave velocity becomes

$$c = c_0(1 - UT^{-1}), \qquad \omega_{\vec{q}} \ll \Gamma, \tag{10}$$

where $c_0 \sim J$ and $U \sim J\mu^2 x$.

The spin wave contribution to M_{sw} in a quasi-two-dimensional antiferromagnet is of the order of $Ac^{-2}T \ln(T/\omega_c)$,[25] where ω_c is a lower cutoff energy determined by the in-plane anisotropy or the interplane exchange interaction and A is a constant. Thus if $\Gamma \ll \omega_c$ the part of the spectrum with renormalized spin wave velocity (10) does not contribute to the magnetization, but if $\Gamma \gg \omega_c$ we find that with logarithmic accuracy:

$$\frac{M_{sw}(0,x) - M_{sw}(T,x)}{M_{sw}(0,x)} = \frac{AT}{c_0^2(1 - UT^{-1})^2}. \tag{11}$$

For $T \gg U$, the right-hand side becomes $A(T + 2U + 3U^2T^{-1} + \cdots)/c_0^2$. The leading correction, AU/c_0^2, lowers $M_{sw}(T,x)$ at high T, in qualitative agreement with Figs. 1 and 2.

Equation (11) has a maximum at $T_0 = 3U$. Thus, one might think that it could replace Eq. (3) in reproducing Figs. 1 and 2. However, fits to Eq. (11) failed to reproduce the data with plateaus, and Eq. (11) fails at $T < T_0$.

The Hamiltonian (5) describes the interaction of the spin waves with a defect consisting of two neighboring vacancies. Qualitatively the effect of such a defect on the spin wave spectrum should be the same as that of one site vacancy, which has been investigated for many years (see Ref. 26 and references therein). The renormalization of the spin wave spectrum due to this scattering does not depend on the temperature at $T \ll T_N$. It softens the magnetic system and therefore, as mentioned above, it also sharpens the decay of $M_{sw}(T,x)$ with the increase of T. However, it does not affect the structure observed in Figs. 1 and 2. Thus we see that the renormalization of the sublattice magnetization due to spin wave scattering on the frustrated bonds improves the agreement of Eq. (3) with the experiment at high temperatures, but the anomalies of the magnetization at lower temperatures are mainly due to the second factor in Eq. (3).

In conclusion, we presented a model that explains the reentrant behavior of the sublattice magnetization in doped cuprates LCO and YBCO. The model is based on the single assumption that the moving holes destroy the long range order less than the localized ones. Using measured parameters, we found a good agreement with the experimental data for both LCO and YBCO.

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