Evolution of Magnetic Properties of Lightly Doped Copper Oxides

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ABSTRACT

We study how doping destroys the AF order in the layered cuprates within the framework of the charge-transfer insulator concept. We use the criterion of stability of the AF background to show that the stability problem is one of the main issues in any correspondence between results for the $t - J$ model and, say, the three–band model for the lightly–doped layered oxides. Provided a phenomenological conduction band is chosen to satisfy the criterion of stability, a detailed picture of how dopants influence the spin wave spectrum at $T = 0$ is presented. The critical concentration $x_c$ for the destruction of the AF long range order is due to the Cherenkov effect when the Fermi velocity first exceeds the spin wave velocity. We then discuss the overall spectrum of spin excitations and find that the spin wave attenuation for $x < x_c$, $T = 0$ due to Landau damping appears in the range of magnon momenta $k(x) = 2m^*s \pm \alpha \sqrt{x}$. We also argue that in the presence of superconductivity, the Cherenkov effect is eliminated due to the gap in the spectrum. This may restore the role of the AF fluctuations as the main source of dissipation at the lowest temperatures.

PACS #: 74.70Vy, 75.30.-m, 73.20.Dx
We address the issue of how the conduction and magnetic properties of the HTSC oxides evolve with doping starting from Mott’s insulator state. The system best studied experimentally so far is $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$. The properties of the AF insulating state for the parent compound, $\text{La}_2\text{CuO}_4$, are by now reasonably understood in terms of the 2D Heisenberg model (see [1] for a review). The origin of magnetism is commonly ascribed to the copper $d^9$ configuration (i.e. one hole in the closed $d^{10}$ Cu shell). The Hund’s rule in the atomic limit would provide $S = 1$ for the configuration $d^8$, which is costly in energy (7–10 eV), so that the so-called “Hubbard U”, the repulsion between two holes located at the “same Cu site”, can safely be taken equal to infinity ($U_{Cu} = \infty$).

An enormous literature exists by now regarding properties of lightly doped 214–materials ($\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$). The vast majority of theoretical papers treat the hole motion in terms of the $t-J$ model. In this model doping is represented by the removal of charges originally located on Hubbard centers. On the contrary, as is known, the actual situation is the opposite (at least for 214 compounds) – Sr$^{2+}$ ions add charge (holes) into the system. The resolution of the seeming contradiction with the assumption of infinite U comes if one remembers that the new materials are charge-transfer insulators [2], i.e., in addition to Hund’s energy, there exists a lower energy scale. Indeed, transfer of electrons from an oxygen site, $\epsilon_p$, to close up the copper $d$-shell ($d^{10}$) $\epsilon_d$, costs in energy only $|\epsilon_p - \epsilon_d| = 2$ to 2.5 eV (see [2] for a review). Without doubt, in the complicated $\text{La}_2\text{CuO}_4$ unit cell all orbitals become mixed, or hybridized. Although the description in terms of ionic copper or oxygen orbitals serves mostly as a convenient language, it contains the physics underlying the essential properties of these materials.

There is a belief that the above-mentioned controversy concerning adding holes by doping in real materials and its simulation in terms of “holes” formed in the half-filled background of the $t-J$ model may be eliminated by a one-to-one mapping in terms of the Zhang-Rice
singlet picture [3]. In this view a hole introduced by Sr\(^{2+}\) goes to oxygen orbitals where it forms a singlet bound state (in the three-band model [4]) of the oxygen orbitals with one of the neighboring localized Cu spins. Such a picture is not obvious. Its applicability has already been the subject of a discussion [5,6]. Our considerations have also led us to the conclusion that any search for such a correspondence simply misses the main physics here.

A more crucial question is whether the dynamic properties of mobile holes in HTSC materials and their impact on the magnetic behavior can nevertheless be simulated by the \(t - J\) model. It seems obvious that the physics becomes richer if the extra electronic degrees of freedom connected with the lower oxygen levels are taken into account. On the other hand, at low doping and low temperatures some characteristics of doped oxides may be model independent and can be treated phenomenologically. Therefore, in the first part of this paper we discuss these general features as they can be derived for the lightly doped Mott state from the charge–transfer point of view. For this purpose, there is no need to go through all the complications of, say, the three band model [4, 6, 7]. Instead, we adopt a more phenomenological point of view. Namely, we assume that, in addition to the localized Cu states where the electron correlations are most crucial, the manifold of other (“oxygen”) orbitals provides a set of itinerant bands of a common character to which the doped holes go. In such an approach [7] the standard Anderson Hamiltonian is adequate for the description of the behavior of holes:

\[
H = \sum_{i\sigma} \epsilon_d d_{i\sigma}^d d_{i\sigma} + \sum_{\vec{p}\sigma} \epsilon(\vec{p}) a_{\vec{p}\sigma}^d a_{\vec{p}\sigma} + t_0 \sum_{i\vec{p}} (d_{i\sigma}^i a_{\vec{p}\sigma} e^{i\vec{p} \cdot \vec{r}_i} + \text{h.c.})
\] (1)

Here \(\epsilon_d\) is the localized (Cu) level, \(\epsilon(\vec{p})\) the dispersion law of the itinerant band. Let us also assume that \(\epsilon(\vec{p}) \sim p^2/2m\) near \(\vec{p} = 0\). Then \(W = 4/(ma^2)\) is a scale for the bandwidth (we use units such that \(\hbar = 1\) and \(a\) is the lattice constant), while \(t_0\) is responsible for hybridization, i.e., for transitions between localized and delocalized states separated by the
charge transfer gap $\epsilon_p - \epsilon_d \sim \Delta$, and double occupancy of the copper sites is forbidden ($U_{Cu} = \infty$). The virtual processes then immediately provide a "Kondo-like" exchange interaction between the spin of a conduction hole and the spins of localized levels $\vec{S}_i$:

$$j'(\vec{S}_i \cdot \vec{\sigma}) ; \quad j' = \frac{2t_0^2}{\Delta}$$

(2)

In higher order the Heisenberg exchange between nearest neighbor localized spins appears:

$$H_{ex} = \sum_{\langle i,k \rangle} J_{ik} \vec{S}_i \cdot \vec{S}_k$$

(3)

The nearest neighbor exchange interaction is nonvanishing for this model only for a finite bandwidth $W$. In the case that $W \ll \Delta$ we have

$$J_{ik} = J = \frac{t_0^4}{2\Delta^3} \left( \frac{W}{\Delta} \right)^2$$

(3')

With both $\Delta$ and $J$ known experimentally ($\Delta \simeq 2.0$ eV, $J \simeq 0.15$ eV) one estimates (assuming $W \simeq \Delta$) for $\left( \frac{t_0^2}{\Delta^2} \right) \simeq 0.4$. (The three-band model may involve different factors in eqs. (1,2); see refs. [4,5] and below).

The value for $J \simeq 1500$ K is rather large and the common belief is that to describe doping, at least for small enough $x$, the antiferromagnetic background is always to be taken into account first. Rewriting the effective Hamiltonian (2) and (3) in the momentum space:

$$H_{eff} = \sum_{\vec{p}\sigma} \epsilon(\vec{p}) a_{\vec{p}\sigma}^\dagger a_{\vec{p}\sigma} + \frac{j'}{\sqrt{N}} \sum_\vec{q} \vec{S}_\vec{q} \cdot \left( a_{\vec{p}+\vec{q}\rho}^\dagger \vec{\sigma}_{\rho \rho'} a_{\vec{p}+\vec{q}\rho'} \right) + \sum J(\vec{q}) \vec{S}_\vec{q} \cdot \vec{S}_{-\vec{q}}$$

(4a)

and after introducing (at $T = 0$ in the 2d case) the average staggered magnetization: $\vec{\mu} = \mu_B \langle \vec{S}_{\vec{Q}_0} \rangle \neq 0$, where $\vec{Q}_0 \equiv (\pi/a, \pi/a)$, the total Hamiltonian (4a) may then be reduced to a simpler form, since for small concentrations $x$ only the bottom of the conduction band is important. In the vicinity of $\vec{p} = 0$ and in the presence of a staggered magnetization the
behavior of a single hole is described by the Hamiltonian:

$$H_{\text{eff}} = \sum_{\vec{p}\sigma} \frac{p^2}{2m} a_{\vec{p}\sigma}^\dagger a_{\vec{p}\sigma} + \frac{1}{\sqrt{N}} \sum_{\vec{p},\vec{q}} \left[ j' S_{\vec{q}} + iB \vec{f}(\vec{p},\vec{q}) \cdot \vec{q} \vec{j}_s \right] \cdot \left( a_{\vec{p}-\vec{q}\rho}^\dagger \vec{\sigma}_{\rho\rho'} a_{\vec{p}\rho'} \right)$$ \hspace{1cm} \text{(4b)}$$

The coefficient $B$ is $a^2j'^2/8W$ (we assumed $W \gg j',J$ for simplicity), and the momentum dependent form factor $\vec{f} \equiv \vec{p} - \vec{q}/2$. The term with $\vec{j}_s \equiv (\vec{\mu} \times \vec{S}_{\vec{Q}_0-\vec{q}})/\mu_B$ appears as a perturbation due to opening of an AF gap in the new band spectrum at $\vec{p} = \vec{Q}_0/2$. One sees that eqn. (4b) has the same form as that derived in [8,9] from the $t - J$ model in the nonlinear $\sigma$ model approximation. The distinction between the two pictures is that in the above the number of localized spins is conserved. Secondly, in such an approach there are no special relation between $m$ (or $W$), $J$ and $j'$ and, finally, doping adds new fermionic degrees of freedom, which are now responsible for conduction.

At the derivation of eq. (4b) (near $\vec{p} = 0$) it was assumed that only the long wave components of spin degrees of freedom are relevant. Those are the spin waves and can be introduced either phenomenologically, or derived explicitly by use of the Dyson – Maleev transformation [10]. For our immediate needs we write down only the second term in eq. (4b):

$$\frac{j'}{\sqrt{N}} \sum_{\vec{p},\vec{q}} \frac{\sqrt{qa}}{2^{3/4}} \left[ (\alpha_q + \beta_{-q}^\dagger) a_{\vec{p}-\vec{q}\uparrow}^\dagger a_{\vec{p}\uparrow} + (\alpha_{\vec{q}}^\dagger + \beta_{-\vec{q}}) a_{\vec{p}-\vec{q}\downarrow}^\dagger a_{\vec{p}\downarrow} \right].$$ \hspace{1cm} \text{(5)}$$

Together with the Hamiltonian for spin-waves

$$H' = \sum \Omega_{\vec{q}} \left( \alpha_{\vec{q}}^\dagger \alpha_{\vec{q}} + \beta_{\vec{q}}^\dagger \beta_{\vec{q}} \right)$$ \hspace{1cm} \text{(6)}$$

one arrives at the well-studied problem of an electron interacting with long wave excitations having the linear dispersion law $\Omega(\vec{q}) = sq$ (see [11] for a review). This allows one to reexamine the self-consistency of the basic assumption that the motion of holes takes place in the AF background. The problem is that the hole described by Hamiltonian (4b) and
interacting with spin waves may be unstable with respect to a sort of polaron formation. If spin frequencies remain low compared with the hole bandwidth \((W >> J)\) the problem may be investigated quasi–classically in the spin wave occupation numbers \((\alpha^{\dagger}\alpha, \beta^{\dagger}\beta \sim j'^2/(J^2qa) \gg 1)\). It is possible to minimize the sum of eqs. (4b) and (6) to eliminate the spin wave operators. The result is the familiar Deigen-Pekar functional for the ground state of the hole “dressed” by spin fluctuations:

\[
H = \frac{1}{2m} \left\{ \int \sum_{\sigma} \left| \nabla \psi_{\sigma} \right|^2 - 4c \left| \psi_{\downarrow} \right|^2 \left| \psi_{\uparrow} \right|^2 d^2r \right\}
\]

where \(\psi\) is the hole wave function and

\[
c \equiv \frac{mj'^2(qa)a^2}{2\sqrt{2} \Omega_q},
\]

where \(\Omega_q\) is the spin wave energy.

In ordinary semiconductors the functional (7) determines the height of the barrier for formation of self-trapped states. The property specific to the 2\(d\) physics is that in this case such a barrier does not exist. Instead, as has first been shown in [12] the system either remains stable if

\[
c < 2.88
\]

or has a saddle point (i.e. the functional (7) has no minimum) if \(c\) exceeds the limit (9). The third term in (4b) does not add much to these considerations. Provided the parameters of the model are such that AF background remains essentially intact, this term may provide a helical structure in the doped antiferromagnet [9].

Having this criterion, we first discuss its implications for, say, the three–band model. We have considered whether this model can be reduced to the form of eq. (4a). (The results will be published in detail elsewhere). It turns out that the truncation of the three-band Hamiltonian done in refs. [3] and [5] to a sole singlet-like component essentially oversimplifies
the results. Actually, this model, after the nonzero staggered magnetization is taken into account, becomes highly degenerate and possesses dispersionless bands. To eliminate these artifacts, it is necessary to account for a number of realistic features like the interaction between two holes placed on an oxygen site (we assume a finite Hubbard $U_O$, for double occupancy of oxygen sites). Then we would obtain:

$$j' = -\frac{4t_0^2 U_O}{\Delta(\Delta + U_O)} < 0$$

(10)

and, for the effective mass of the lowest band with dispersion

$$(m^*)^{-1} = 2a^2 \left(1 - (\mu/\mu_B)^2\right) t,$$

(11)

where $t = t_0^2/2\Delta$.

For the three band model with an “on–oxygen” $U_O$, the antiferromagnetic interaction (3) turns out to be

$$J = 4 \frac{t_0^4}{\Delta^2(2\Delta + U_O)}$$

(3’’)

The criterion for stability for this band would then be

$$\frac{1}{(1 - (\mu/\mu_B)^2)} \frac{U_O^2}{t_0^2} \frac{\Delta(2\Delta + U_O)}{(\Delta + U_O)^2} < 2.88$$

(12)

We see that the criterion depends on all three parameters $t_0, \Delta$ and $U_O$, so that (as before) in eqs. (3’’, 9) we need an additional experimental parameter to determine whether it is satisfied or not. If, however, one starts from the model assumed in [7] ($W \gg \Delta$), the band width, $W \gg j' \gg J$, then $c \ll 1$ and the criterion (9) for the stability of the AF state is fulfilled. We may analyze the $t - J$ model results from the same point of view. While the phenomenological Hamiltonian (4b) has the same form in both cases as it is noted above, the parameters are quite different. For the orthodox $t - J$ model $t$ is expected to be large
$t \gg J$. To get the kinetic energy, one is to account at least partially for fluctuations. The issue of the bandwidth remains a controversial one (see ref. [9]), however it seems that $W$ is of the order of $J$. Though no adiabatic approximation is justified any more, the criterion would still point toward instability if $W \sim J \ll j' \sim t$. Therefore, in our opinion, the problem is not at all whether the one-to-one correspondence between the three–band picture and the $t-J$ model can be established. It is that if $j' \gg J$ the system may become unstable and, as it is easy to estimate, the instability would be resolved by the formation of large magnetic “polarons” (or textures) of the size $r_0$, such that $r_0^2/a^2 \sim j'/J \gg 1$, so that any correspondence would lose any meaning. Indeed, the criterion (9) can now be understood better from this end, at least qualitatively. Let us overlook for a moment the kinetic energy term in eqn. (4b). Then the interaction $j'$ tends to align the surrounding spins in a parallel way. It produces a “potential well” of depth of the order of $j'$ to a distance less than $r_0$. The well has a finite size $r_0$ because there is an energy cost of the order of $J(r_0/a)^2$ due to the destroyed AF state within the well. One now realizes that the criterion (9) indicates the provision that due to the kinetic energy terms one may or may not have a bound state in this effective potential well. The onset of an instability may mean either the creation of a number of textures or even “phase separation” [13].

Assume now that, in accordance with eqn. (9), with the appropriate values for the parameters $W, j', J$ the AF ground state remains stable. We address now another problem, namely how doping would destroy the AF order ($T \equiv 0$). For finite concentration of dopants sitting at the bottom of the band (near $\vec{p} = 0$) there are corrections to the spin wave spectrum shown diagrammatically in Fig. 1. The straightforward calculation of the polarization operator gives rise to the following expression for the renormalized spin wave
velocity $\vec{s}$ ($\vec{q} \to 0$):

$$\vec{s} = s + \frac{j^2 a}{\sqrt{2}\pi W} \int \frac{(\vec{q} \cdot \vec{v}_F) \, d\phi}{qs - (\vec{q} \cdot \vec{v}_F) - i\delta}$$  \hspace{1cm} (13)

(Recall that the long range AF order implies (and vice versa) a Goldstone mode in $\vec{q}$ at $q \to 0$). The expression in brackets can be calculated explicitly. For $v_F < s$ one has:

$$\vec{s} = s \left\{ 1 + \frac{c}{2\pi} \left[ \frac{1}{\sqrt{1 - (v_F/s)^2}} - 1 \right] \right\}, \hspace{1cm} (13')$$

where $c$ is as in eqn. (8). The remarkable feature in eqn (13') is that the attenuation of the spin waves at $q \to 0$ takes place abruptly in the form of the inverse square root singularity at $v_F \geq s$. The mechanism (the Cherenkov effect) is so pronounced due to the dimensionality ($d = 2$). We can now write down the critical concentration $x_c$ of dopants destroying the AF long range order by this mechanism (the doping parameter $x = (ap_F)^2/2\pi$):

$$x_c = \left( \frac{am^* s}{2\pi} \right)^2 \sim \left( \frac{J}{W} \right)^2 \ll 1$$ \hspace{1cm} (14)

A few comments are in order in connection with eqs. (13), (13') and (14). First, one sees from (13), (13') that at very low concentrations $v_F < s$ the stiffness of the spin wave mode at very low $q$ increases with doping. This is unexpected, but it seems it can be interpreted as a reduction of quantum fluctuations due to doping for a stable AF background. Let us now discuss in more detail how doping would influence the AF state as a whole. The short wavelength part of the spin wave spectrum remains of course untouched by either finite temperature ($T < \omega(\vec{q})$, $T \ll J$), or doping (at $x \ll 1$). At $T = 0$ the role of doping is then clarified by a more careful study of the divergence in Fig. 1 at arbitrary $\vec{q}$. Here we summarize the results. At $x \to 0$, the attenuation in $\omega(\vec{q})$ first appears around $q^* \equiv 2ms$. At finite $x < x_c$ the imaginary part in $\omega(\vec{q})$ is non–zero in the range $2ms - 2p_F < q < 2ms + 2p_F$ (Landau damping). Taking $(\xi^*)^{-1} = 2\pi q^* = 4\pi(ms + p_F)$, the beginning of attenuation
from the side of larger $q$, we get what we might call a coherence length

$$(\xi^*)^{-1} = 4\pi \left( m_s + \sqrt{2\pi} \frac{x^{1/2}}{a} \right)$$

Comparing this with $2\pi q_T \sim 2\pi T/s$ we see that the Heisenberg like AF fluctuations would become “saturated” at

$$T^* \simeq 2\sqrt{2\pi \frac{x^{1/2}}{a}}$$

In the presence of disorder introduced by dopants (Sr$^{+2}$-ions) the conduction holes experience scattering by defects. Taking the mean free path $l$ for holes into account one would get an additional source of attenuation of the spin waves. At $ql \ll 1$ this effect on the diagram in Fig. 1 is known to be to substitute for the factor under the integral in eq. (13):

$$\int \frac{(\vec{q} \cdot \vec{v}_F) d\phi}{qs - (\vec{q} \cdot \vec{v}_F) - i\delta} \rightarrow \int d\phi \frac{-iDq^2}{\omega + iDq^2}$$

For $\omega > Dq^2$ we get

$$\omega(\vec{q}) = s \left( q - i\frac{c}{2\pi} \frac{Dq^2}{s} \right)$$

as it should be in the hydrodynamic regime. This result ignores any spin–flip scattering by defects.

Both the Green’s functions (i.e. $m$) and the vertices (i.e. $j'$) in the diagram shown in Fig.1 are renormalized by quantum corrections in accordance with the Hamiltonian (5). It is easy to verify that the main corrections are of the order of $c$, i.e. they would not seriously change the estimate (16) provided (9) is satisfied.

To summarize, the spin density wave spectrum which is responsible for the spin fluctuations in doped systems acquires an attenuation at $q^* = 2ms$ (Landau damping). There is a sharp threshold due to the Cherenkov effect (eqs. (13–13′)), which describes the disappearance of the AF long range order at $T = 0$ as manifested by the dissappearance of the
Goldstone mode at $q \to 0$. Most remarkable is that for the Cherenkov effect to show up, a sharp Fermi surface at zero temperature is needed. Therefore if the superconducting gap were present for $x > x_c$, the mechanism (13′) would disappear as if a restoration of some AF order had taken place. Of course, the effects of the mean free path for hole scattering from defects would also smear out the Fermi surface edge. Unfortunately, the whole analysis carried out for $T = 0$ cannot be immediately extended to an analysis of the system’s temperature behavior, and the points above need further investigation.

One of us (LPG) acknowledges the extensive discussions with J. R. Schrieffer at the beginning of this work and the valuable comments by E. I. Rashba on the stability problem in semiconductors. LPG was supported by the National High Magnetic Field Laboratory through the NSF cooperative agreement # DMR-9016241 and the State of Florida. VNN and PK were supported by a grant from U. S. D. O. E., DEF G05-91-ER45462.
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FIGURE CAPTION

Fig. 1: Diagram that contributes to the renormalization of the spin wave velocity to lowest order.