Statistical mechanics of CuO_2 plane in the presence of localized holes

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Both La_2CuO_4 and $YBa_2Cu_3O_6$ are antiferromagnetic insulators, becoming less so as holes are introduced on individual oxygen bonds. We evaluate the free energy of a single CuO_2 plane in the Ising representation. Beyond a critical concentration $x_0=0.29289$ holes per CuO_2 cell, antiferromagnetism is replaced by a paramagnetic phase having short-range order only. The *ground-state entropy* is 0 at $x=0$, 0.0697 per CuO_2 cell at $x=x_0$, and 0.6931 (i.e., ln2) at $x=1$.

La_2CuO_4 and $YBa_2Cu_3O_6$ have a layered structure in common, each containing planes of CuO_2 with spins on the Cu^{2+} ions antiferromagnetically disposed.[1] Far from being superconductors, at stoichiometry, these materials are in fact excellent insulators. With increasing dopant concentration (Sr or O vacancies in $La_{2-x}Sr_xCuO_{4-y}$ or oxygens in $YBa_2Cu_3O_{6+y}$) the antiferromagnetism decreases as the number of positive charge (hole) carriers increases, ultimately giving way to the high-temperature superconducting phase spectacularly evinced by[2] $La_{1.85}Sr_{0.15}CuO_4$ and[3] $YBa_2Cu_3O_{6.9}$.

It is worthwhile to examine the statistical mechanics associated with the doping. Recently, Aharony *et al.*[4] outlined *all* the magnetic interactions and derived therefrom a phase diagram which agrees in many respects with experimental observations. To supplement their qualitative analysis, I wish to show that at least one aspect of the problem can be analyzed. Moreover, by making a simple assumption concerning the localization of holes in the insulating phases of the magnetic materials, it can be analyzed exactly.

It will be shown that in the Ising representation, with neglect of any interplanar interactions, the statistical mechanics is that of a "decorated" two-dimensional Ising model.[5] It is this model which is exhibited here, without pretentions of modeling physical reality, both for its own interest (it is exactly soluble) and for whatever guidance it may ultimately provide. For completeness, we present *two* models, each based on slightly different physics. In the first, denoted the "defective-bond model" or DB model, a fraction $x/2$ of the original antiferromagnetic bonds $+J$ are replaced by ferromagnetic bonds $-Jg$. Both J and g can be computed using ordinary "superexchange" theory,[6] which yields J an energy of the order of 0.1 eV, and g a number typically $\gg 2$. In the second "localized hole model," or LH model, a fraction $x/2$ of the original bonds are missing; at each defect site, the spins of two copper ions are now each connected to a third spin—that of the hole located on the intervening oxygen ion—instead of to each other. There are more dynamical variables in the LH model than in the DB model, and it is a more accurate representation of the physics. Indeed, in the full Heisenberg model formulation of the problem, these two models are quite distinct. But in the Ising formulation, they turn out to be virtually identical.

The variables in the DB model are S_i, the copper ion's spins, $n_{ij}=0$ (no hole on the bond $+J$ connecting nearest-neighbor spins S_i and S_j) and $n_{ij}=1$ ($J\rightarrow -gJ$ in the presence of the hole). With g and the hole concentration x as the only parameters, we shall define a function $J_{\rm eff}(T)$ and $\beta_{\rm eff}\equiv J_{\rm eff}/kT$, with which to map the physical system onto a reference Ising model (antiferromagnetic if $\beta_{\rm eff}$ is positive, ferromagnetic if negative). All thermodynamic properties of the physical system at a given $\beta\equiv J/kT$, g and x, can be obtained from the reference model at $\beta_{\rm eff}$.

The DB Hamiltonian for N CuO_2 *cells* (1 site, 2 bonds per cell) is

$$H=J\sum_{(i,j)}[(1-n_{ij})-gn_{ij}]S_iS_j-\mu\sum_{(i,j)}n_{ij}\,, \tag{1}$$

with (i,j) signifying nearest-neighbor pairs, and μ adjusted to yield

$$x=2\langle n_{ij}\rangle_{TA}\,, \tag{2}$$

where x is the specified number of holes per CuO_2 cell (per copper site). The hole concentration can vary in the range $0\le x\le 2$, with superconductivity known to replace antiferromagnetism for x exceeding some[2] $x\approx 0.05$–0.1 in $La_{2-x}Sr_xCuO_4$ (superconducting to as high as ≈ 40 K) or starting at[3] $x\ge 0.3$ (the precise value depending on somewhat ambiguous valency assignments) in $YBa_2Cu_3O_{6+x}$ (superconducting to as high as ≈ 90 K, depending on x). In evaluating the partition function Z, it is helpful to perform traces over all n_{ij} first, obtaining

$$Z=(\chi^2-\lambda^2)^N{\rm Tr}\left[\exp\left[\beta_{\rm eff}\sum_{(i,j)}S_iS_j\right]\right]\,, \tag{3}$$

where the remaining trace is over the copper's spins (each $S_i=\pm 1$), and $\tanh\beta_{\rm eff}=\lambda/\chi$, i.e.,

$$\beta_{\rm eff}(T)\equiv J_{\rm eff}(T)/kT=\tfrac{1}{2}\ln[(\chi+\lambda)/(\chi-\lambda)]\,, \tag{4a}$$

where λ and χ are

$$\chi\equiv[\cosh(\beta)+e^{\mu/kT}\cosh(g\beta)]\,,$$
$$\lambda\equiv[\sinh(\beta)-e^{\mu/kT}\sinh(g\beta)]\,. \tag{4b}$$

We have thus found f, the free energy per CuO_2 cell,

$$f\equiv -kT\ln Z=-kT\ln(\chi^2-\lambda^2)+f_I(J_{\rm eff})\,. \tag{5}$$

Here, $f_I(J_{\rm eff})$ is the free energy per cell of a reference Ising model, at temperature T, in the absence of an external

field, on an *homogeneous* square lattice having *all bonds* $J_{\rm eff}(T)$. Equation (2) is equivalent to

$$x=-\partial f/\partial\mu$$
$$=kT\{\partial[\ln(\chi^2-\lambda^2)]/\partial\mu+w_I(\beta_{\rm eff})\partial(\beta_{\rm eff})/\partial\mu\}\,, \quad (6)$$

where $w_I(\beta_{\rm eff})$ is related to the internal energy per site of the reference model $u_I(\beta_{\rm eff})$,

$$w_I(\beta_{\rm eff})=-(J_{\rm eff})^{-1}u_I(\beta_{\rm eff})\,. \quad (7a)$$

Now making use of Onsager's[7] formula for u_I we obtain

$$w_I(\beta_{\rm eff})=\coth(2\beta_{\rm eff})[1+(2/\pi)k_2K(k_1)]\,, \quad (7b)$$

where $k_1=2\sinh(2\beta_{\rm eff})/\cosh^2(2\beta_{\rm eff})$, $k_2=[2\tanh^2(2\beta_{\rm eff})-1]$, and $K(k)$ is the complete elliptic integral $K(k)=\int_0^{\pi/2}d\theta(1-k^2\sin^2\theta)^{-1/2}$.

We eliminate μ in Eq. (6) by the use of (4):

$$e^{\mu/kT}=\sinh(\beta-\beta_{\rm eff})/\sinh(\beta g+\beta_{\rm eff})\,, \quad (8)$$

with $\beta\geq 0$ and $e^{\mu/kT}\geq 0$ translating into requirements $\beta>\beta_{\rm eff}$ (if $\beta_{\rm eff}>0$) and $\beta>|\beta_{\rm eff}|/g$ (if $\beta_{\rm eff}<0$). Then,

$$x=[1+w_I(\beta_{\rm eff})/2]F_+ +[1-w_I(\beta_{\rm eff})/2]F_-\,, \quad (9)$$

where

$$F_\pm=[1+e^{\pm\beta(1+g)}\sinh(\beta g+\beta_{\rm eff})/\sinh(\beta-\beta_{\rm eff})]^{-1}\,. \quad (10)$$

This formula contains the complete solution of the stated problem, and is our principal result. It can be used in several ways. If we fix β (or T) it determines $\beta_{\rm eff}$ for given g,x and allows the evaluation of the free energy [Eq. (5)], of μ [Eq. (8)], and of all related thermodynamic functions such as ground-state entropy.

To locate the critical points $\beta_N=1/kT_N$, and $\beta_F=1/kT_F$ (if any), we set $\beta_{\rm eff}=+\beta_c$ in (10), the critical point in the reference Ising antiferromagnet. We know[7] $\tanh\beta_c=\sqrt{2}-1$, i.e., $\beta_c=0.44069\ldots$, $w_I(\beta_c)=\sqrt{2}$, and $|\partial w_I/\partial\beta_{\rm eff}|_c=\infty$.

The following flows immediately from Eq. (9): Starting from $T_N=T_c$ at $x=0$, T_N decreases with increasing x, ultimately vanishing at—and beyond—a concentration $x_0=1-1/\sqrt{2}$ (independent of g). The behavior is relatively insensitive to g for $g\gg 1$. In this physically important and illustrative limit, Eq. (9) reduces to the simple formula

$$x=x_0(1-e^{-2(\beta_N-\beta_c)})\,,$$

i.e.,

$$T_N/T_c=[1-(1/2\beta_c)\ln(1-x/x_0)]^{-1}\,, \quad (11)$$

with $x_0=0.29289$ and $1/2\beta_c=1.1346$.

The critical point in the reference ferromagnetic (F) model lies at $\beta_{\rm eff}=-\beta_c$ [in Eq. (10)], with $w_I(\beta_c)=-\sqrt{2}$ [in Eq. (9)]. After these slight modifications, Eq. (9) yields a maximum $T_F=gT_c$ at $x=2$, decreasing to $T_F=0$ as x is decreased to $x_0=1+1/\sqrt{2}=1.7071$ (once again, independent of g).

The critical point x_0 could have been guessed from mean-field arguments, upon noting that each hole affects 7 bonds in its immediate neighborhood. Thus, when $x>\frac{2}{7}=0.2857$, we expect antiferromagnetism (AF) to be squelched, which is within 3% of the exact Ising result. Studies[1,4,8] of $YBa_2Cu_3O_{6+y}$ have found the tetragonal phase[8] and antiferromagnetism[1,4] to persist only for $y\leq 0.31$. This supplies experimental confirmation of our results, if oxygen ions have valency -2 and are supplied solely to the basal plane, and if antiferromagnetism always persists in the tetragonal phase. As the resulting holes are presumably shared by the two CuO_2 planes of the triplet "sandwich" structure, this scenario implies $x=y$; hence, $x_0=0.31$.

For concentrations *intermediate* between x_0(AF) $=0.29289$ and x_0(F) $=1.7071$, $|\beta_{\rm eff}|$ remains $<\beta_c$ at all T and there is no phase transition. There, the DB model maps only onto the high-temperature, paramagnetic (disordered) phase of the reference Ising model and never acquires long-range order.

The optimum antiferromagnetic short-range correlation function $G(R)$ here is always that of nearest-neighbor spins S_1,S_2. It is $G(R_{12})=\langle S_1S_2\rangle_0=-1$ at $T=0$ and $x=0$. Increasing x to x_0(AF) causes the correlation to become less antiferromagnetic and $G(R_{12})$ to rise to $-1/\sqrt{2}=-0.7071$. Increasing x further causes the ground-state correlation $G(R_{12})$ to vanish at precisely $x=1$, independent of g. For $x>1$, the correlations are ferromagnetic, $G(R_{12})\geq 0$. The point $x=1$ (half the bonds are occupied by holes) is thus the limiting point for antiferromagnetic behavior. At $x=1$ there is *total absence* of correlations among individual copper ions' spins even at $T=0$, and the ground-state entropy per cell is $\mathcal{S}_0=k\ln 2$. For x exceeding 1, correlations are ferromagnetic, with long-range ferromagnetic order setting in beyond 1.7071. As the ferromagnetic regime lies outside the physically interesting range of $0\leq x\leq 1$, it is perhaps only of academic concern.

We now turn to the slightly more involved but physically more relevant LH model. A hole represents the absence of one electron on a specified oxygen ligand ion, the spin-doublet ion O^{1-}. The antiferromagnetic bond J associated with O^{2-} is replaced by *two* antiferromagnetic bonds gJ, connecting the hole's spin σ_{12} with those on each copper ion. Thus, in the presence of the hole, $H_{12}=JS_1S_2$ is *replaced* by $H_{12}=gJ\sigma_{12}(S_1+S_2)$. (In the Ising scenario adopted here, all operators σ,S are restricted to the values ± 1.) As previously noted, J is an energy of the order of 0.1 eV and g a number typically $\gg 2$. We again define a function $J_{\rm eff}(T)$ and $\beta_{\rm eff}\equiv J_{\rm eff}/kT$, with which to map the physical system onto a reference Ising model. The bond variables are now $n_{ij}=0$ and 1, and $\sigma_{ij}=\pm 1$ (the spin orientation of the hole if and only if $n_{ij}=1$). The total Hamiltonian for N CuO_2 cells (1 site, 2 bonds per cell) is

$$H=J\sum_{(i,j)}\{S_iS_j(1-n_{ij})+gn_{ij}\sigma_{ij}(S_i+S_j)\}-\mu\sum_{(i,j)}n_{ij}\,, \quad (12)$$

with μ satisfying Eq. (2).

In evaluating the partition function Z, one traces over all n_{ij},σ_{ij} first, obtaining Z in exactly the form of Eq. (3). Once again $\tanh\beta_{\rm eff}=\lambda/\chi$ as in Eq. (4a). Although f retains the precise form of Eq. (5), the functions λ and χ are

no longer given by (4b), but by

$$\chi \equiv (\cosh\beta + 2e^{\mu/kT}\cosh^2 g\beta)\,,$$
$$\lambda \equiv (\sinh\beta - 2e^{\mu/kT}\sinh^2 g\beta)\,. \quad (13)$$

Combining Eqs. (4a), (6), and (13) eliminates μ and results in Eq. (9) once again. Replacing $F_\pm$ of Eq. (10) we now have

$$F_+ = [1 + e^{\beta} L(\beta,\beta_{\rm eff})]^{-1}\,,$$
$$F_- = [1 + e^{-\beta} L(\beta,\beta_{\rm eff})/\cosh(2\beta g)]^{-1}\,, \quad (14)$$

where

$$L(\beta,\beta_{\rm eff}) \equiv [\sinh\beta_{\rm eff}\cosh^2\beta g + \cosh\beta_{\rm eff}\sinh^2\beta g]/\sinh(\beta - \beta_{\rm eff})\,. \quad (15)$$

On the antiferromagnetic side, at small x the behavior of the LH model is virtually identical to the DB model. It becomes independent of g for $g \gg 1$, and Eq. (11), connecting T_N with x, applies without modification. On the ferromagnetic side, for $g \gg 1$, long-range order appears for $x > 1 + 1/\sqrt{2} = 1.7071$ as before, with T_F increasing from $T_F = 0$ at this point to a maximum $T_F = T_c \times 0.5766g$, at $x = 2$.

With the exception of such details in the ferromagnetic regime, the statistical mechanics and the phase diagrams of both models are virtually identical. They predict four phases: (I) an antiferromagnetic phase at hole concentrations $0 < x < x_0(\mathrm{AF})$, (II) a paramagnetic phase (annealed spin glass?) with short-ranged antiferromagnetic correlations persisting for $x_0(\mathrm{AF}) < x < 1$, (III) a similar paramagnetic phase with ferromagnetic short-ranged correlations at $x > 1$, and (IV) actual ferromagnetism at $x > x_0(\mathrm{F})$. Comparison with Ref. 4 suggests that phase II is the prime candidate for superconductivity.

The *ground-state entropy* per unit cell, $\delta_0 \equiv -\partial f/\partial T|_0$, can be obtained from Eq. (5) and is found to be

$$\mathcal{S}_0(x) = \mathcal{S}_I(\beta_{\rm eff}^0) - 2[1 - w_I(\beta_{\rm eff}^0)]\beta_{\rm eff}^0\,, \quad (16)$$

in units $k = 1$, with $\beta_{\rm eff}^0$ being the value of $\beta_{\rm eff}$ at $T = 0$. As x increases, so does $\mathcal{S}_0(x)$, quickly reaching a plateau $\mathcal{S}_0(x_0) = 0.0697$ in the vicinity of x_0, increasing thereafter to a maximum $\mathcal{S}_0(1) = \ln 2 = 0.6931$ at $x = 1$.

The decrease in antiferromagnetism with increasing hole concentration appears in accord with experiment. However, we have ignored a number of physically important phenomena. A list of them includes: (1) coupling between adjacent CuO_2 planes, (2) quantum fluctuations of spins, and (3) hopping of holes. Once the last is permitted, it is the Pauli principle and not the Boltzmann factor which plays a major role in determining the distribution of the bonds. In ignoring hopping, the present work turns the issue of superconductivity into a moot point, of course. Nevertheless, we find two important results: a lack of long-range antiferromagnetic correlations in phase II, *even in an Ising formulation* which ordinarily promotes long-range order, and the persistence of nonzero entropy, even at $T = 0$ indicative of magnetic frustrations.

It is possible to implement some modest improvements. Concerning point (1), the Ising formulation can evidently be extended to three dimensions, although that will not effect a qualitative change. With the correct use of *vector* spins, this point acquires more significance, as the two-dimensional Heisenberg model has no phase transitions, whereas its three-dimensional counterpart does. Note that by manipulation of the Baker-Hausdorff expansion it is possible to approximately formulate a "decorated" Heisenberg model (although the calculation of the free energy here is another matter). Concerning points (2) and (3): recently, Pan, Lin, and the present author,[9] working in the $x \to 0$, $T = 0$ limit, have studied the $S = \frac{1}{2}$ Heisenberg antiferromagnet in the presence of 1 and 2 hopping holes, taking due account of the Pauli principle, and finding spin correlations not unlike the present results in the $x \to 0$ limit.

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