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Extinction of antiferromagnetism by holes in CuO_2

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The introduction of a sufficient number of holes into antiferromagnetic planes of CuO_2 in La-Cu-O and Y-Ba-Cu-O causes antiferromagnetism to disappear at a critical density x_c, beyond which superconductivity occurs. We investigate two competing tendencies, which determine the dependence of x_c on the bandwidth of the holes.

INTRODUCTION

The parent compounds of many high-temperature superconductors, e.g., La-Cu-O (Ref. 1) and Y-Ba-Cu-O,[2] are antiferromagnetic insulators. The Néel temperature $T_N(x)$ depends upon the hole-doping concentration x. It decreases with increasing doping, until, at a critical concentration x_c, T_N vanishes and the high-temperature superconducting phase appears. One premise of the phase diagram proposed by, among others, Aharony *et al.*[3] for the high-temperature superconductors, was that the holes reside on oxygen atoms ("ligands") where they transform the (relatively weak) antiferromagnetic superexchange interaction between neighboring coppers into a (relatively stronger) ferromagnetic bond. This "frustrates" the magnetic lattice sufficiently that, beyond some critical density of holes, the antiferromagnetic ordering can no longer be sustained.

One of the challenges in the quest for the origins of high-temperature superconductivity is the calculation of x_c from first principles. The various bond strengths have been measured[4] and the geometries are known, so the problem of computing $T_N(x)$ and comparing with experimental observations might appear relatively straightforward. Nevertheless, it represents a formidable task which, to our knowledge, has not yet been seriously undertaken. The first major difficulty, not yet overcome, arises in formulating the statistics (fermions, bosons, anyons?) and the corresponding dynamical correlations in the nonsuperconducting phase, for a finite density of holes in two-dimensional conductors.

If, however, one neglects the motion of the holes then, *ipso facto,* their statistics become irrelevant. In that limit, there does already exist an exactly solved[5] model; it is the "annealed" imperfect Ising antiferromagnet.[6] This model assumes that the given, small fraction x of ferromagnetic bonds are distributed within the antiferromagnet in such a manner as to minimize the free energy at each temperature. Calculations for two dimensions[5,6] show that $x_c = 1 - 1/\sqrt{2} = 0.2929\ldots$. Thus, taking account of the fact that there are two oxygens per unit CuO_2 cell, this theory predicts the loss of antiferromagnetism after 14.64% of the oxygen atoms have taken on a hole. Although the calculated value of x_c turns out to be almost totally independent of the parameters or other details of the model,[5] experimentally, x_c is not so rigorously constant.[7]

Thus, one must consider additional physical variables which might vary from material to material, such as the motion of the holes. For example, if instead of being assigned to particular oxygen atoms the holes were allowed to wander, the number of copper atoms with which each comes into interaction would be increased, and there would result a greater number of ferromagnetic bonds per hole. This reasoning predicts x_c will be decreased, by an amount dependent on the holes' bandwidth. On the other hand, one might argue with equal justification that wandering holes do not contribute to frustration. In that case, increasing the hole bandwidth should cause x_c to rise nearer to the percolation limit ($x = 1$). Which is the correct answer? The present investigation examines this issue.

THE MODEL AND ITS SOLUTIONS

The exact formulation of the interaction of a number of holes with a lattice of spins compounds a difficult problem, that of the Heisenberg antiferromagnet, with an even more abstruse many-body problem, that of the "Kondo" lattice. We opt for a more transparent model, a simple extension of the models of Ref. 5. With J the strength of nearest-neighbor antiferromagnetic bonds, $-gJ$ that of ferromagnetic bonds, $\mu \equiv \nu J$ the chemical potential with which to adjust the concentration of holes, and t a parameter proportional to their bandwidth, the starting basis of our theory is the Hamiltonian $H = H_0 + H_t$, where

$$H_0 = J \sum_{(i,j)} \{[(1-n_{ij}) - g n_{ij}] S_i S_j - \nu n_{ij}\} , \tag{1}$$

$n_{ij} = h_{ij}^{\dagger} h_{ij}$ being the occupation-number operator for a hole on the oxygen atom linking nearest-neighbor copper-ion spins S_i and S_j. In the Ising model, each S_i takes on the values ± 1.

The hopping of a hole at a given bond at (i,j) brings it to any of the six nearest-neighbor bonds. By virtue of the fluctuation-dissipation theorem, such electrical conduction is associated with charge fluctuations on the relevant links. While it is the former which causes the technical difficulties, it is the latter which physically relates to the

fluctuations between antiferromagnetic and ferromagnetic links, the feature in which we are most interested.

One way of simulating the relevant phenomenon without becoming involved in details of quantum transport theory is to allow the holes to hop in and out of additional artificial "reservoir" sites, associating one reservoir state with each link. Under this assumption the hopping Hamiltonian is bond local, and takes the form

$$H_t = -t \sum_{(i,j)} (h_{ij}^{\dagger} c_{ij} + \text{H.c.}) , \tag{2}$$

where $c_{ij}, c_{ij}^{\dagger}$ are the field operators of the reservoir sites; it will be convenient to set $t \equiv J\eta$, and adopt J as the unit energy in this problem.

Because the individual links are now independent, their Hamiltonians are trivially diagonalized. Upon summing over the link variables, the partition function Z for the spins assumes the form

$$Z = A^N \text{Tr} \left[\exp \left[\beta_{\text{eff}} \sum_{(i,j)} S_i S_j \right] \right] . \tag{3}$$

With $\beta \equiv J/kT$, the various relevant quantities are

$$\begin{aligned} A &= \exp(\beta\nu)\cosh[(\beta/2)(a+b)^{1/2}]\cosh[(\beta/2)(a-b)^{1/2}] , \\ \exp(2\beta_{\text{eff}}) &= \exp[\beta(1-g)]\cosh[(\beta/2)(a+b)^{1/2}]/\cosh[(\beta/2)(a+b)^{1/2}] , \end{aligned} \tag{4}$$

in which $a = (1+g)^2 + \nu^2 + 4\eta^2$ and $b = 2\nu(1+g)$.

The chemical potential is adjusted to yield any desired hole concentration by setting

$$x = (1/\beta)\frac{\partial \ln Z}{\partial \nu} . \tag{5}$$

Except for the multiplicative factor A_N, Z is the partition function of an Ising antiferromagnet (we anticipate $\beta_{\text{eff}} < 0$ for x in the range $0 \le x \le x_c$), having all bonds equal to $J_{\text{eff}} = kT\beta_{\text{eff}}$. In two dimensions, long-range order disappears at $\tanh(|\beta_c|) = \sqrt{2} - 1$ and derivatives of Z are explicitly known.[8] Thus, our equations allow us to examine the range of variables which makes $\beta_{\text{eff}} = -|\beta_c|$.

Performing algebraic manipulations similar to those if Ref. 5, we obtain

$$\begin{aligned} x_c = 1 + \tfrac{1}{2}\{ &(1-\sqrt{\tfrac{1}{2}})\tanh[(\beta/2)(a+b)^{1/2}](\nu+1+g)/(a+b)^{1/2} \\ &+ (1+\sqrt{\tfrac{1}{2}})\tanh[(\beta/2)(a-b)^{1/2}](\nu-1-g)/(a-b)^{1/2}\} . \end{aligned} \tag{6}$$

Given the temperature $T = J/(k\beta)$ and the parameters g and η, this yields the concentration of holes at which antiferromagnetic orders disappears.

Figures 1 and 2 display the resulting curves $T_N(x)$: Fig. 1, at various values of $g = \eta$ (these parameters *are* typically of the same magnitude), and Fig. 2, as function of the hole-hopping parameter η, with g held fixed at (an arbitrarily chosen) large value $g = 15$. Figure 2 shows x_c decreasing with increasing η up a minimum x_c at $\eta \approx 5$. Increasing η beyond this value causes x_c to rise once more.

Figure 3 further explores this feature. It shows that at any $g > 2$ there is an optimum value of η yielding a minimum x_c; exceeding this optimum η causes x_c to rise once again. The optimum η is ≈ 5 at $g = 15$, drops to ≈ 2.5 at $g = 5$, to $\eta \approx 1$ at $g = 3$, and sticks at 0 for $g \le 2$. For $g \le 2$, any nonzero η causes x_c to rise, ultimately to approach the percolation limit $x_c \to 1$ at sufficiently large η.

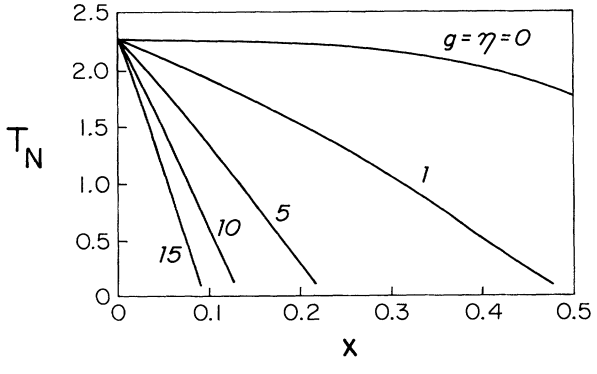

FIG. 1. $T_N(x)$ for various $g = \eta$. T_N (in units of J/k) plotted vs hole concentration x per unit CuO_2 cell, for $g = \eta = 0$, 1, 5, 10, and 15.

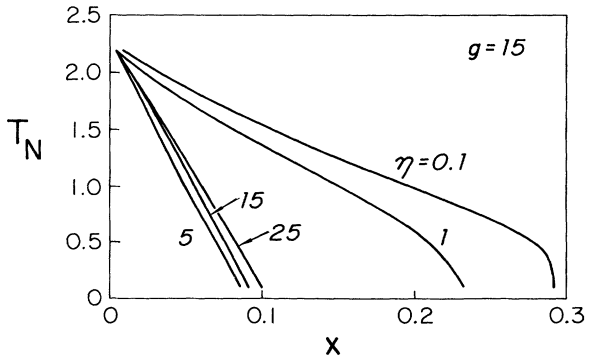

FIG. 2. $T_N(x)$ at fixed $g = 15$. T_N plotted vs x for $\eta = 0.1$, 1, 5, 15, and 25.

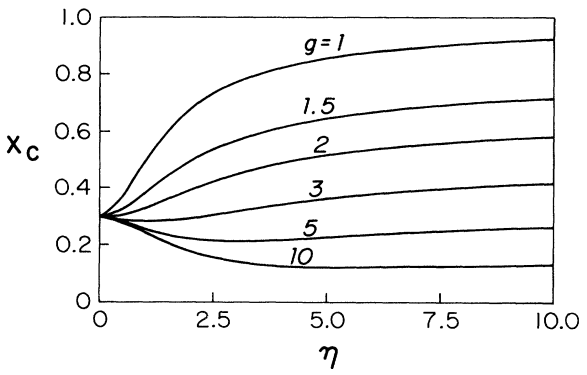

FIG. 3. x_c as a function of η. x_c is plotted vs η for $g=1$, 1.5, 2, 3, 5, and 10. Note the qualitative differences between curves for $g \leq 2$ and $g > 2$ (see text).

CONCLUSIONS

In summary, we have shown (Figs. 1 and 2) that for large g the charge fluctuations inherent in a finite bandwidth of the holes cause x_c to drop from 0.29 (14.6% holes per oxygen atom) to as little as 0.1 (5% holes per oxygen atom). Figure 3 confirms this tendency for $g > 2$, but it also indicates that for $g < 2$ the charge fluctuations can have the opposite effect, enhancing x_c *to as much as 3 times its original value.* Thus, *in principle,* either of these opposing tendencies might be operative.

However, in the physical situations of present interest, we may reasonable assume $g > 2$. Thus, to the extent that the present model corresponds to reality, the generic dependence of x_c on the hole bandwidth parameter $t = \eta j$ should resemble that of the lower curves shown in Fig. 3: As the bandwidth η is increased, x_c decreases to a point where it attains a minimum—from which, upon further increase of $\eta = t/J$, it rises slowly.

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[2]K. B. Lyons *et al.*, Phys. Rev. Lett. **60**, 732 (1988); J. H. Brewer *et al.*, *ibid.*, **60**, 1073 (1988); N. Nishida *et al.*, Jpn. J. Appl. Phys. Pt. 2, **26**, L1856 (1987); J. M. Tranquada *et al.*, Phys. Rev. B **38**, 2477 (1988).

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[4]For example, $J = 950$ cm^{-1} in Y-Ba-Cu-O: see K. B. Lyons *et al.*, Ref. 2.

[5]D. C. Mattis, Phys. Rev. B **38**, 7061 (1988); R. J. V. dos Santos *et al.*, *ibid.* **40**, 4527 (1989).

[6]The thermodynamics of Ising models with randomly distributed interaction (including one of the models studied in Ref. 5) was solved by M. F. Thorpe and D. Beeman, Phys. Rev. B **14**, 188 (1976), some time before high-temperature superconductivity was discovered; see their Fig. 2, and their references to earlier work.

[7]x_c ranges from just a few percent in La-Cu-O to well over 30% in Y-Ba-Cu-O; see, e.g., phase diagrams in Ref. 3 and also Fig. 5 in Tranquada *et al.*, Ref. 2, and Fig. 3 in J. H. Brewer *et al.*, Ref. 2.

[8]See Refs. 5, 6, or Table 3.2 in D. C Mattis, *The Theory of Magnetism II, Thermodynamics and Statistical Mechanics* (Springer, Berlin, 1985), p. 137.