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1e and 2e superconductivity in spin liquids and spin crystals

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The recent, unexpected discoveries of superconductors with reported transition temperatures as high as 123 K have renewed the search for mechanisms with higher transition temperatures. Among the resulting proposals is one by Anderson in which an odd-electron insulator in a resonating valence-bond or quantum-spin-liquid state becomes superconducting via pair condensation when sufficiently doped. However, Kivelson, Rokhsar, and Sethra have suggested that doping such a state introduces singly charged boson defects which form a superconducting state via Bose-Einstein condensation. We resolve this apparent contradiction by pointing out the possible existence of a remarkable transition between superconductivity with an elementary charge of the supercurrent of e to superconductivity with an elementary charge of $2e$ with increased doping. Moreover, both kinds of superconductivity occur, even in the spin-crystal or Néel state.

The discovery of superconductivity in the La-Ba-Cu-O system ($T_c = 30$–40 K),[1] the La-Sr-Cu-O system ($T_c \sim 50$ K),[2] and the Y-Ba-Cu-O system ($T_c = 90$–120 K) and its various derivatives[3] has sparked an enormous, world-wide surge of activity. Theorists have renewed the debate over whether the conventional theory of superconductivity, the Bardeen-Cooper-Schrieffer (BCS) theory with the attractive interaction between pairs provided by the virtual exchange of phonons, can encompass such high transition temperatures. All of the theories proposed to date can be divided into two categories, electron-pair condensation as in the BCS theory, and Bose-Einstein condensation of charged elementary excitations or defects. The pair theories can be further subdivided into those in which pairing and condensation both occur at T_c as in the BCS theory and into those in which pairs are already present above T_c and condensation occurs at T_c. The boundary between these two categories is blurred by superconducting fluctuations above T_c in low-dimensionality materials. In the first category, an attractive interaction normally drives the pairing and pair condensation, but gapless superconductivity can be induced by a purely repulsive interaction of appropriate form.[4] In the second category, condensation can occur with or without interaction of either sign.

A guide as to where one might search among these many possibilities is provided by a crystal structure[5] and electronic structure studies[6] of the high-T_c materials. A structural element common to all of these materials is planar (or near-planar) arrays of Cu and O with Cu at the corners of squares and O at the edge centers. The Fermi surface intersects a σ-antibonding band made up of Cu $d_{x^2-y^2}$ orbitals hybridized with O p orbitals. In the prototypic compound La_2CuO_4, that band is half full, and the material is an odd-electron insulator. Incorporating experience derived from earlier studies of oxide superconductors, Anderson[7] observes that superconductivity tends to occur in such materials near a metal-insulator transition into an odd-electron insulator with peculiar magnetic properties. He hypothesizes that the insulating phase is a resonating valence-bond[8] or quantum-spin-liquid state with all electrons tied up in nearest-neighbor singlet pairs. Sufficient doping (e.g., substitution of Ba for La) then forces these pairs to move, and an attractive residual exchange between pairs drives condensation into a superconducting state at a high T_c, a theory of the first category.[9] Kivelson, Rokhsar, and Sethna[10] have pointed out, however, that doping at low levels produces mobile charged defects which are bosons with a hard-core repulsion. These then undergo Bose-Einstein condensation into a superconducting state, the sole theory in the second category. In the present paper, we resolve this apparent contradiction and point out as well that both kinds of superconductivity can occur in the antiferromagnet or Néel state as well.

We start by discussing the phases of the half-filled Hubbard model. In that model, there is a nearest-neighbor electron transfer matrix element t and an on-site repulsion U between electrons of opposite spin. When $t=0$, there is a 2^N-fold–degenerate ground state at energy zero, and there are excited states at energies vU, where N is the total number of electrons and v is the number of doubly occupied sites. At finite t, the exact effective Hamiltonian within this ground-state manifold is $H_{\text{eff}} = V_{GT}(E - H_{DD})^{-1} V_{DG}$, where E is the energy of the state in question, G refers to the ground-state manifold, and D is the excited-state manifold. By examining the convergence of the expansion of the propagator $(E - H_{DD})^{-1}$ in powers of t/U, one can establish that the Mott-Hubbard metal-insulator transition occurs when $\alpha(t/U)_c = 1$, where α is infinite for the simple square lattice and becomes finite as soon as electron transfer occurs in the third dimension. Similar considerations demonstrate the existence of a superexchange interaction between spin pairs in the ground-state manifold which has

an exponential asymptotic separation dependence with range

$$R=[2\ln(U/at)]^{-1}\sim[(2/a)(U/t-(u/t)_c)]^{-1}\ .$$

When $t=0$, the individual electrons are confined to a single site. For finite t they spread out, the localization length L becoming $L=2R$.

Suppose now that the ground state for finite t is that of a Néel antiferromagnet or a *spin crystal*. If so, all exchange interactions between spins on the same sublattice are frustrated. It is possible that the spin crystal is unstable and melts into a *spin liquid*. There are three tests for stability of the spin crystal: (1) all spin-wave energies must be positive to prevent a condensation; (2) all spin-wave energies must be real to prevent exponential growth of fluctuations; and (3) the ground-state energy must be lower than that of the spin liquid. The first stability requirement is met for all spin waves and all t/U within the insulating phase. The second stability requirement, that of local stability, is violated at higher values of t/U than is the third, that of thermodynamic stability, implying that spin melting is a first-order phase transition, occurring within the Mott-Hubbard, odd-electron insulating phase.

Both transitions, the metal-insulator transition and spin melting, are very sensitive to disorder. The real materials are not strictly two dimensional. The metal-insulator transition thus becomes a line on the (t/U)-W phase plane (zero temperature), where W is an appropriate measure of the disorder, as indicated in Fig. 1. It corresponds to an Anderson transition[11] at W_c for large t/U and a Mott-Hubbard transition[12] at $(t/U)_c$ for small W. Disorder reduces the localization length L in the insulating phase and therefore the range R of the exchange, stabilizing the spin crystal relative to the spin liquid as shown in Fig. 1.

We now consider the effects of doping, for example, by substituting divalent Ba or Sr in La_2CuO_4 to form

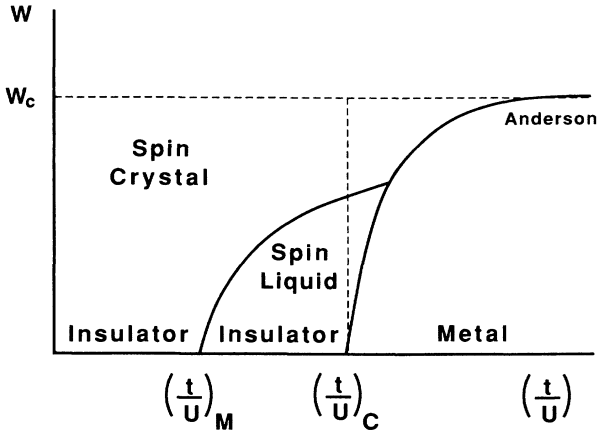

FIG. 1. Electric and magnetic phase diagram for a half-filled, quasi-two-dimensional Hubbard model. W is a measure of the disorder, e.g., the variance of a random site potential, t is the nearest-neighbor electron transfer matrix element, and U is the on-site repulsion between electrons of opposite spin. The metal-insulator transition is continuous, and the spin melting transition is first order.

$La_{2-x}Ba_xCuO_4$. Thus, x electrons per Cu atom are removed from the previously half-filled band. As the acceptor ions are presumably randomly distributed on the trivalent ion sites, doping is accomplished by a substantial disorder potential. We shall simplify our discussion, however, by supposing that x and W are subject to indepenednt control and deal here only with cases in which disorder is unimportant. We turn first to the doping of a spin liquid. Kivelson, Rokhsar, and Sethna[10] have pointed out that the lowest-energy configuration for a single electron removed is that of an electron deficiency spread over a range b of sites which moves freely in solitonlike fashion.

The following determination of b differs from that of Kivelson *et al.*[10] The problem is closely analogous to that of the acoustic polaron in d dimsnions.[13] The part of the energy of localization dependent on b is, approximately, $t(a/b)^2$, and that of the exchange energy is $-\frac{1}{2}(t^2U)(a/b)^d$, where a is the lattice constant. Minimizing their sum with respect to b yields[14] $b/a=(dt/4U)^h$, where $h=1/(d-2)$. Thus, for $d>2$, the solitons become sharply defined, particularly in the quasi-two-dimensional cases of interest here.

For small but finite doping, there will be a number density n_0x of these charged solitons, where n_0 is the electron density in the undoped case. Between the regions of charge deficiency, the wave function is identical to that of the undoped spin liquid. It is a wave function with moving holes. The wave function is unaffected by exchange of hole position, so that these solitons are bosonlike. They depart from bosons in that two electrons cannot be removed from the same site. They can nevertheless be treated as bosons after adding to their Hamiltonian a repulsive pseudopotential interaction which becomes an infinite contact repulsion when the internal size of the soliton shrinks to a single site. These solitons undergo Bose-Einstein condensation so that at x values low enough for the statistical and Coulomb interactions to be ignored, they are superconducting with a $T_c\sim x^{2/3}$. As the entities which condense have a charge of e, all experiments which yield the charge of the carriers of the supercurrent will show e in place of the usual $2e$.

As the doping increases, either the zero-point kinetic energy $25.6x^{5/3}t$ per site of the solitons arising from their short-range repulsion increases to the point where it is too costly to maintain the ground-state wave function in its undoped spin liquid from between the holes of cheese deficiency, or the solitons overlap, $b\approx r_s=(3/4n_0x)^{1/3}$, and became unstable. Either way, there is a phase transition to the ground state described by Anderson and coworkers[7-9] at a critical doping value, x_c. The electron deficiency spreads out and becomes uniform, the pairs become free, and they condense. The appropriate theory is that of preformed pairs which Bose condense at T_c, as in the mean-field theory of Baskaran, Zou, and Anderson.[9] We thus predict the remarkable phenomenon of a change of the elementary charge of the supercurrent from e to $2e$ with increased doping, as illustrated in Fig. 2. While T_c may be low in the e domain, such a phase would nevertheless be of great interest, and these materials should be studied at low doping levels despite the lower T_c's.

We now turn to the spin crystal. The existence of anti-

ferromagnetism within the Mott-Hubbard insulating state changes nothing essential within the argument of Kivelson *et al.*[10] concerning the defects in the ground state generated by doping. An electron can be stripped away from a site on either sublattice. There are thus two kinds of singly charged bosons, one carrying Ising spin $-\frac{1}{2}$ on the up sublattice and the other Ising spin $+\frac{1}{2}$ on the down sublattice. In the simplest case of small t/U in which the solitons are compact, each propagates on its own sublattice via a nearest-neighbor transfer matrix element t_s equal to half the intersublattice superexchange interaction J, $t_s=-(1/2)J=-2r^2/U$. Thus, for the simple square lattice, each has a band structure given by

$$\varepsilon(\mathbf{k})=2t_s[\cos(k_\xi 2^{1/2}a)+\cos(k_\eta 2^{1/2}a)]+2t_\perp\cos(k_z c)\ , \tag{1}$$

$$|k_\xi|,|k_\eta|\le\frac{\pi}{2^{1/2}a},\ k_z\le\frac{\pi}{c}\ ,$$

where, to allow for Bose-Einstein condensation, we have explicitly included three-dimensionality in the motion, with $t_\perp \ll t_s$. The solitons are compact, confined primarily to a single site with a shape independent of J. The condensation temperature is

$$k_B T_c=4.17(J^2 t)^{1/3}x^{2/3}\ . \tag{2}$$

Because of their compactness, the zero-point energy, 16.2 $Jx^{5/3}$ may play the more important role in destabilizing the soliton gas, and once the critical concentration x_c is reached, the electron deficiencies cease to be localized and spread out uniformly over all sites. The theory of Baskaran, Zou, and Anderson is then applicable and is readily modified to incorporate the spin polarization on each sublattice. There results a theory of BCS form but with certain important differences. First, each member of a pair resides on a different sublattice. This has the effect of enhancing superconductivity by substantial reduction of the direct Coulomb interaction through spatial separation, an enhancement mechanism suggested by us 20 years ago.[15] Second, the predominant attractive interaction driving the condensation is the superexchange. An interesting aspect of the theory is that the terms representing the product of two spin deviations usually neglected in spin-wave theory play a central role in the superconductivity. Finally, the cutoff is of order of the bandwidth. The resulting transition temperatures can be very high, as in Anderson's picture.[7,9]

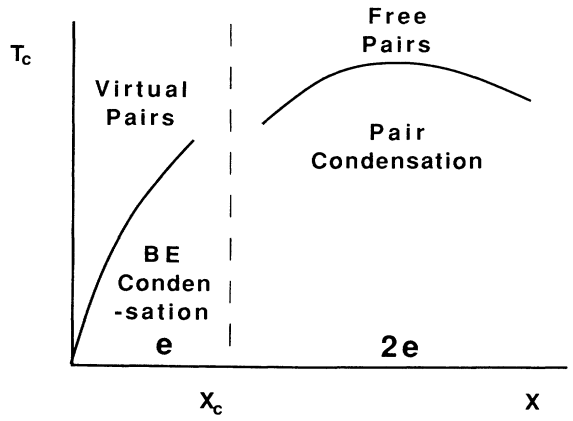

FIG. 2. Superconducting transition T_c temperature as a function of doping x. At x_c there is a transition from superconductivity via the Bose-Einstein (BE) condensation of singly charged solitons and to superconductivity via the condensation of the singlet pairs forming the resonating valence bonds.

The above discussions can be applied to doping by donors, such a oxygen vacancies, simply by substituting everywhere doubly occupied sites for empty sites.

We conclude with a note of caution. Rich in possibilities as the nearly filled Hubbard model is, it is simpler and less rich than any tight-binding model accurately describing the essential features of the electronic structures of the real materials.

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