Resonating–Valence-Bond Theory of Phase Transitions and Superconductivity in La_2CuO_4-Based Compounds

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We identify the mysterious high-T "twitch" transition in La_2CuO_4 with the mean-field resonating-valence-bond transition of the Heisenberg model of Baskaran, Zou, and Anderson. The structure distortions are caused by Coulomb correlations of the pair wave function. In the pure compound the pseudo-Fermi surface of the spin soliton nests and antiferromagnetism occurs at 240 K. We briefly discuss superconductivity and the nature of excitations in the system.

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The new high-T_c superconductors based on rare-earth–copper oxides have been described at length in the public and the scientific press.[1] Almost none of their properties correspond to those of previously known superconductors except for a very small class of equally peculiar compounds such as TlTe, $Ba(Pb,Bi)O_3$, and $LiTi_2O_4$, and we start from the premise that a wholly new theory is necessary.

In approaching any new many-body or quantum-field problem, the basic question is to identify the appropriate "vacuum" or reference state: the Fermi and Bose liquids of Landau, for instance, for ^{3}He and ^{4}He, or the QCD vacuum of Callan, Dashen, and Gross,[2] in which nucleon "bags" reside. In this instance the appropriate reference state was hypothecated in 1973 by Anderson[3] and called the "resonating valence bond" (RVB) state of two equivalent models, the Heisenberg, $S=\frac{1}{2}$ antiferromagnet and the Mott insulating half-filled Hubbard model. The 1973 paper proposed this state for the triangular layer lattice, but was written in response to the mysterious (and probably only now understandable) scarcity of $S=\frac{1}{2}$ antiferromagnets in general.

The RVB state is a mixture of singlet pairings of the electrons on the different sites i in a specific way. It is a precise singlet, has no obvious long-range order, and is a fluid in that it has quantum transport of spin excitations. The proof of gaplessness for the $S=\frac{1}{2}$ linear-chain Heisenberg model due to Lieb and Mattis[4] applies without modification to this case, and hence it contains zero-energy spin excitations.[5]

In our previous papers[6,7] we assumed that the mean-field BCS transition we derived for the RVB state in the insulating Hubbard model was only a crossover because the Mott-Hubbard gap condition of zero charge fluctuation required that we average locally over phases in the gap function at every site. Thus the RVB transition seemed to break no symmetry. This is true in one dimension, as is confirmed by the identity of 1D RVB and Gutzwiller wave functions.[8]

In more dimensions there are more phases in the RVB-BCS function than there are Mott-Hubbard conditions and the relative phasing of the different bonds is relevant. Thus a true phase transition can exist which we identify with the mysterious high-T crystal distortion of La_2CuO_4,[9] which we have called the "twitch" transition (see *Note added.*).

As pointed out by Kivelson, Rokhsar, and Sethna,[10] the excitations of the RVB state are of three kinds: fermion spin solitons, which we call "spinons"; boson holes with charge e; and true electrons or holes, which are the product of the two.[11] In contradiction to Kivelson, Rokhsar, and Sethna, we believe the spinon-state spectrum to be gapless, having a pseudo-Fermi surface, even in the presence of electron-phonon interaction not strong enough to cause spin-Peierls instability.[12] For small doping, superconductivity arises from Bose condensation of holes.

In the pure La_2CuO_4, the pseudo-Fermi surface has perfect nesting and the residual interactions between pseudofermions (or spinons) cause the pure material to become antiferromagnetic at $\simeq 240$ K[13] through the pseudo-Fermi-surface instability. This is not incompatible with the symmetry left behind the RVB condensation, which has a "black-red" degeneracy in the square lattice.[10]

Doping of the pure La_2CuO_4 in the RVB state is compensated not by displacement of the pseudo-Fermi surface as in a conventional insulator but by the creation of boson "hole" excitations, as long as the system remains in the RVB state. A very small percentage ($\sim 1\%$ or less) of holes will destroy antiferromagnetism because, as pointed out by Brinkman and Rice,[14] the kinetic energy of holes is much reduced in the antiferromagnetic state. For conventional $S>\frac{1}{2}$ antiferromagnets this leads to double exchange[15] and ferromagnetism, but for $S=\frac{1}{2}$ the RVB state satisfies both the antiferromagnetic J and the requirements of the hole kinetic energy, since holes are almost free in the RVB state. The three-site example shown in Fig. 1 illustrates this. The amplitude for transition from state I to state III is $\sim\sqrt{2}t$, which suggests that the hopping integral of the hole is $\propto t$. Hence the RVB state is the equilibrium state. The holes can undergo Bose condensation and make a superconductor. Holes can have only off-diagonal long-range order and

$$|\downarrow\uparrow\circ\rangle - |\uparrow\downarrow\circ\rangle \quad \text{I}$$

$$|\downarrow\circ\uparrow\rangle - |\uparrow\circ\downarrow\rangle \quad \text{II}$$

$$|\circ\downarrow\uparrow\rangle - |\circ\uparrow\downarrow\rangle \quad \text{III}$$

FIG. 1. A hole hops with the free-electron matrix element (Hubbard-model t) while preserving singlet correlation of electron pairs. Arrows stand for electrons while the circles stand for a hole.

not true macroscopic coherence, since we can have no physical amplitude[11] $\langle 0|b|0\rangle$, but they can undergo Bose condensation without binding into pairs, and their Bose condensation temperature is roughly the degeneracy temperature. The hole amplitude then drives true electron-pair amplitudes via the hole-pair amplitude which has the same symmetry as a bound electron pair. As T_c approaches the RVB transition, the hole amplitude becomes relatively smaller and BCS-like superconductivity ensues.[8] Between T_c and $T_{\rm RVB}$, conduction is mainly by holes, with Hall constant[16] $1/n_h ec$; above $T_{\rm RVB}$, by electrons, with $R \lesssim 1/(1+n_h)ec$.

Let us formally substantiate some of the above statements. As in Ref. 3, we write the Heisenberg second-order Hamiltonian with $J=4t^2/U$, t and U the Hubbard model parameters:

$$\mathcal{H} = -J\sum_{\langle ij\rangle} b_{ij}^\dagger b_{ij}, \tag{1}$$

with

$$b_{ij}^\dagger = (C_{i\uparrow}^\dagger C_{j\downarrow}^\dagger - C_{i\downarrow}^\dagger C_{j\uparrow}^\dagger)/\sqrt{2} \tag{2}$$

creating a valence-bonded pair $\langle ij\rangle$. After projection with the Mott-Hubbard condition $n_{i\uparrow}+n_{i\downarrow}=1$, the $C_{i\sigma}^\dagger$ turn into "spinon" degrees of freedom $S_{i\sigma}^\dagger$ which have no true kinetic energy. In the RVB state we can ascribe all the kinetic energy to the hole degrees of freedom which carry the charge, and treat the $S_{i\sigma}$ as strictly neutral,[11] even for $n_i \neq 1$, but in discussing the phase transition the Baskaran-Zou-Anderson (BZA) mean-field theory using true electron fermions is probably a good model. Hence, in what follows we will use the electron operators in place of the spinon operators.

In the square lattice there is a perfect black-red symmetry and there are two kinds of $C_{i\sigma}$ for $i=b$ (black) or r (red), and four kinds of bonds

$$b_{ij}^\dagger = (C_{i\uparrow}^\dagger C_{j\downarrow}^\dagger - C_{i\downarrow}^\dagger C_{j\uparrow}^\dagger)/\sqrt{2}$$

ending on the four r sites surrounding a b site, i.e., two per site (Fig. 2). In a BCS theory we have four order parameters corresponding to the four bonds

$$\Delta_l^\dagger = J\langle b_l^\dagger\rangle \tag{3}$$

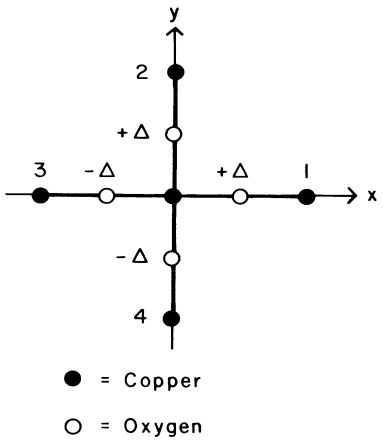

FIG. 2. Relative phases among the four valence bonds connecting a black site to its four neighboring red sites. The phases for two of the bonds are chosen as + and the other two have real physical meaning (see text).

with $l=1,2,3,4$,

$$\langle b_l^\dagger\rangle = \sum_k e^{i\mathbf{k}\cdot\boldsymbol{\tau}_l}\langle C_{k\uparrow}^\dagger C_{-k\downarrow}^\dagger\rangle. \tag{4}$$

Let $l=1$ and 3 be in the $\pm x$ direction and 2 and 4 in the $\pm y$ directions. The phases of any two Δ's may be chosen arbitrarily, but then those of the other two are real physical variables. (Self-consistency allows the four to be chosen at will.) Physically, these phases control the shape of the "correlation hump"[17,18] in the density-density correlation function $\langle\rho(r)\rho(r')\rangle$. In particular, there will be a term in the charge-charge correlation function

$$\langle\rho_\downarrow(r)\rho_\uparrow(r')\rangle = \text{const} + [\phi_i(r)\phi_j(r)][\phi_i(r')\phi_k(r')]\langle b_{ij}\rangle\langle b_{ik}^\dagger\rangle, \tag{5}$$

that is, a hump proportional to the product of the corresponding "overlap charges" $\rho_{ij}(r)$ and $\rho_{ik}(r')$, where ϕ_i's are Wannier orbitals. Since the d-p hybridization is quite strong, the overlap charge will be concentrated on the oxygen ion in the Cu—Cu bond. The energies involved are not negligible; we realize that unlike the usual BCS case, $\langle b_{ij}\rangle$ is of order unity, since the order parameter and the bandwidth are identical, while overlaps of 20% are reasonable, and so we are talking about charges of $(0.1$–$0.2)e$ or more. If we choose $\Delta_1=\Delta_2=\Delta=-\Delta_3=-\Delta_4$, the correlation humps are repulsive between O ions in the $+x$ and $+y$, and $-x$ and $-y$ directions, and attractive for the $+x$ and $-y$ and the $-x$ and $+y$. This will lead to the observed atom displacements seen in the 550-K transition.[19] Note that the mean interaction is zero and that therefore the energy involved comes only from the atom displacements and is fourth order in Δ; the correlation effect does not affect T_c but determines the specific form of the gap function, as in ^{3}He.

The best we can do for a mean-field theory of this

RVB transition is the Gutzwiller-projected BCS theory of BZA. As we see from their Fig. 1 (reproduced here in more detail as Fig. 3), the dependence of T_c on δ is remarkably like that of the "twitch" transition; any close resemblance is, of course, coincidental because of the unknown effects of projection and of dimensionality and fluctuations (we suspect these act in opposite directions). Taking BZA seriously, we may estimate $J \simeq 0.2$ eV and bandwidth $2W = 4$ eV ($t = 0.5$ eV), both reasonable values, implying $U \sim 5$ eV.

The spinon quasiparticle energy is now

$$E_k = \Delta |\sin k_x + \sin k_y|, \tag{6}$$

which still nests, of course, but with a mean k value reflecting the doubling of the new unit cell. (The size of the Brillouin zone reduces to half of the original one.)

For the discussion of other phase transitions, let us assume ourselves to be well below the RVB transition. In this region we believe that it is correct to separate out the two kinds of soliton excitations, the spinon and the hole. For both excitations, we imagine leaving all of the electrons in the substrate paired up in singlets, so that the substrate is a precise singlet with one site (say i) eliminated. For the spinon, we fill the empty sites with an electron of spin σ, so that the state $S_{i\sigma}\Psi_0$ is a state with spin $\frac{1}{2}$ and no free charge. The motion of spinons is mediated entirely by the exchange energy $J\sum_{\langle ij\rangle}\boldsymbol{\sigma}_i \cdot \boldsymbol{\sigma}_j$, and they are the single-particle excitations of the BZA mean-field theory. In fact, we can think of the RVB states as a BCS condensate of spinons.

For a hole excitation $b_i^\dagger$, the site i is simply empty, and $b_i^\dagger\Psi$ is a state with spin 0 and charge $+e$. Holes have an effective mass essentially equal to that of a free electron. The simplest way to see this is that we can move a hole about in the lattice without changing the net number of nearest-neighbor singlet pairs. Figure 1 shows a singlet-preserving next-neighbor hop to the nearest "r" site.

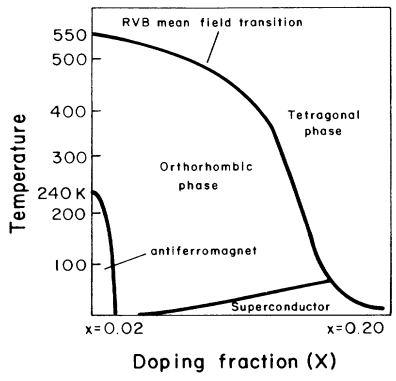

FIG. 3. RVB mean-field transition temperature as a function of doping parameter x as calculated by BZA (see Ref. 7). This transition is identified with the tetragonal-orthorhombic phase transition in La_2CuO_4-based compounds. The transition at 240 K is the observed antiferromagnetic ordering, which is destroyed upon a small percentage of doping ($x < 0.02$).

A single hole injected into the antiferromagnetic state will create around itself a bubble of RVB whose size M is determined by a balance of the gain in kinetic energy $-t(1-M^{-2/3})$ against the energy difference between RVB and antiferromagnet (AF), which is

$$M \times (\Delta E)_{\text{AF-RVB}} \simeq M \times (200\ \text{K}).$$

With $t \simeq 1$ eV, this leads to $M \simeq 50$, or $\lesssim 2\%$ of holes will suppress antiferromagnetism. It will be interesting to see whether careful purification of other systems, such as CuO or $BaBiO_3$, will lead to antiferromagnetism.

The hole and the spinon have an attractive interaction of order J, since it is more favorable energetically to have one fewer broken bond around each soliton. This is not strong enough to bind the very light holes to the spinons, and thus true "electronic excitations" are not stable. Doping with Ba, Sr, etc., will introduce one hole per dopant. The first few presumably will occupy localized states, but long-wavelength light bosons are hard to localize and screen out potential fluctuations very effectively and at a very small δ they will become mobile. We see no reason not to use rarified-Bose-gas statistics for the holes, similarly to He in Vycor, so that we expect

$$T_c \simeq (2\pi\hbar^2/m^*)(n - n_c)$$

if we use the two-dimensional density. When we allow that the three-dimensional transition temperature can be somewhat reduced, and that m^* for a hole may be bigger than the band-structure mass, T_c's of ~ 100 K at a few percent are still very reasonable. In fact, the observed T_c's seem to be too low and higher values for better materials are not out of the question. The ideal region physically will be that of relatively low doping but still large enough to eliminate antiferromagnetic order. Here we expect the holes to exhibit a rotonlike spectrum with a minimum energy at $k \sim n^{1/2}$. Long-wavelength bosons couple to plasma oscillations and will have a very high frequency. The observed gap for doped excitations in tunneling will be the roton gap, since the missing spin can be compensated by a low-energy spinon. The density of states will not be BCS-like; for single-particle tunneling one expects the convolution of the roton $(E-E_0)^{1/2}$ spectrum with constant behavior. The roton gap might be rather larger than the BCS value as observed.

The clearest indication that this RVB superconductivity is present is that it will not have a gap for neutral-spinon excitations. This will appear most clearly in a linear low-temperature specific heat with a large, more or less conventional, metallic γ. Such behavior will also be visible in neutron elastic scattering, NMR relaxation, Knight shift (of normal metallic type and value), etc. The problem of the infrared spectrum is complex; in principle, spinons will not be infrared active but they can couple to phonons which are. A very striking prediction for the normal state is the conductivity properties of the

boson holes. Bosons with long wavelengths as $T \rightarrow 0$ are very hard to scatter, and even normal elastic potential scattering gives $\rho \propto T^{1/2}$ (3D) or T (2D). A T-dependent resistivity is *not* necessarily inelastic (contrary to Lee and Read[20]). At reasonable temperatures a strong scattering mechanism will be spinons, which are present in an amount $\propto T$ and may lead to $\rho \propto T$. The most striking experimental fact confirming the presence of bosons is the absence of an extrapolated residual resistivity for reasonably good samples.

Finally, let us discuss interference phenomena. The charge-e boson will not appear in Josephson experiments because it is a soliton with accompanying ground-state structure. Only the boson-pair amplitude, equivalent to an electron-pair amplitude, can exist globally for a sample grain as a whole.

We are not clear whether $\hbar c/e$ fluxons will exist inside individual grains. Carrying a hole around a circuit displaces the bonding structure in the underlying RVB state. We have to recognize that actually the "holes" can be thought of as merely a bookkeeping device for keeping track of the valence-bond pairing in the underlying RVB state, and that every time a hole moves two spaces a valence-bond pair moves one space (see Fig. 1). If we think of the valence-bond pair as the true reality, they can constructively interfere around a half quantum of flux. The problem is not unlike that of the θ vacuum in field theories, and remains to be resolved.

In conclusion, we would like to elaborate on the hypotheses of the present work. As we mentioned before, when we dope the insulator the pseudo-Fermi surface of spinons is not displaced as in a conventional metal and soliton holes are produced. They act like independent systems except for the local charge restrictions. In the lowest order the holes only renormalize the parameters of the BZA theory of the half-filled band and the Gutzwiller-projected half-filled band is a good description of the system as far as spin excitations are concerned. The twitch transition is mainly driven by the spin-dependent electrostatic interactions between the overlap charges among the oxygen atoms. We are unaware of any experimental data which contradict this picture.

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Note added.—We have shown[21] that this theory is equivalent to a U(1) lattice gauge theory which Polyakov[22] shows has a deconfining transition in ≥ 4D, but only a crossover for physical dimensionality. What couples to the lattice strain is not yet clear.

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