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Topology of the resonating valence-bond state: Solitons and high-T_c superconductivity

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We study the topological order in the resonating valence-bond state. The elementary excitations have reversed charge-statistics relations: There are neutral spin-$\frac{1}{2}$ fermions and charge $\pm e$ spinless bosons, analogous to the solitons in polyacetylene. The charged excitations are very light, and form a degenerate Bose gas even at high temperatures. We discuss this model in the context of the recently discovered oxide superconductors.

In a recent paper, Anderson[1] proposed that La_2CuO_4 is in a "resonating valence-bond" (RVB) state, and that the high-T_c superconductivity observed in the material[2] when doped with Ba or Sr must be understood in terms of this unusual insulating state. We show here that the resonating valence-bond state has topological long-range order, and characterize its topological excitations. We propose an exotic mechanism for superconductivity.

Our paper draws three main conclusions. (1) We argue that electron-phonon interactions can stabilize a resonating valence-bond state. A highly simplified schematic of this state is shown in Fig. 1(a). The state does not possess a broken symmetry, but on a bipartite lattice it has a topological long-range order. It has a gap to both spin and charge excitations. (2) The elementary electronic excitations[3] in the RVB state have reversed charge statistics and charge-spin relations: There are neutral spin-$\frac{1}{2}$ fermions and charge $\pm e$ spinless bosons. At finite temperatures, these topological solitons destroy the long-range order (see Fig. 2). (3) The bosons have a mass on the order of the electron mass, and a binding energy set by electronic energy scales, so they will exist and be highly degenerate even at high temperatures. Naively, one might think that the condensation of charge $\pm e$ bosons would lead to flux quantization in units of hc/e. However, the solitons are topological, and hence can only be created or destroyed in pairs; this seems to imply that if flux quantization occurs, the quantum is $hc/2e$, consistent with Yang's[4] general analysis of off-diagonal long-range order. It is plausible that this RVB state occurs in Sr- or Ba-doped La_2CuO_4, and that in the doped material condensation of the charge-e bosons could occur at high temperatures.

The active electronic states in La_2CuO_4 are associated with the two-dimensional square lattice of Cu ions. Each Cu has one active orbital and (in the undoped insulator) has one associated electron. Exchange between Cu ions is mediated by the oxygen atom midway between them;

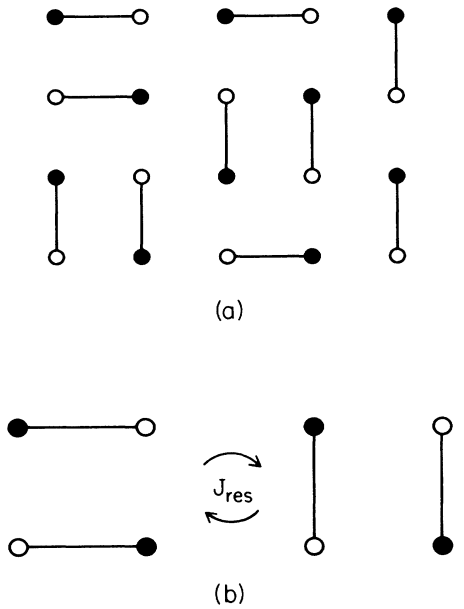

FIG. 1. (a) To first approximation, the resonating valence-bond state is a coherent superposition of states like the one depicted here. Lines denote strong "valence" bonds, across which the electrons form singlet pairs; each site is strongly bonded to precisely one neighbor. The real RVB state is "dressed" by virtual soliton-antisoliton pairs. (b) An elementary resonance between two valence-bond configurations. This resonance lowers the energy of the superposition by J_{res}.

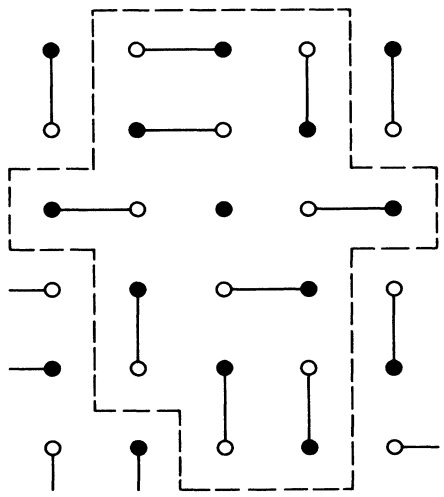

FIG. 2. The existence of a topological defect (here, a black soliton) can be deduced from a large loop enclosing it.

there is thought to be a large Coulomb energy associated with placing two electrons on the same copper. The natural model for this material is the half-filled Hubbard model. There is a structural transition in the insulating state at 533 K,[5] in which the intermediate oxygen atoms buckle out of the plane; initial experiments suggest[6] that the superconducting state is associated with the suppression of this lattice distortion. Thus we are led to look at Hubbard-Peierls models for phases without broken translational symmetry but with a gap to charged excitations. (Our analysis of the statistics of the elementary excitations is, however, independent of the mechanism by which the RVB state is stabilized.)

Figure 1(a) shows a highly simplified schematic of the resonating valence-bond state, which should be interpreted as a snapshot in a path integral. Each lattice site is occupied by a single electron (large Hubbard U), and participates in one singlet "valence bond" with a nearest-neighbor site. Associated with each valence bond is a lattice deformation which increases the hopping energy across that bond; these phonons stabilize the RVB state with respect to the Néel state (which cannot take advantage of lattice deformations to lower its energy). The RVB state is a coherent superposition of the various arrangements of valence bonds; the resonance energy from tunneling between these arrangements stabilizes the RVB phase with respect to the spin-Peierls phase (which is a crystalline arrangement of bonds).

To examine the competition between the Néel and the RVB states, consider the Heisenberg Hamiltonian (describing the Hubbard model in the large U limit) including the effects of lattice deformations:

$$H=\sum_{\langle i,j\rangle}\left[\frac{4(t_0-au_{ij})^2}{U}\mathbf{S}_i\cdot\mathbf{S}_j+\frac{K}{2}(\mathbf{u}_i-\mathbf{u}_j)^2\right], \quad (1)$$

where $\mathbf{u}_i$ is the displacement of the ith atom, u_{ij} is the change in the length of the bond between sites i and j, t_0 is the electron hopping matrix element, a is the electron-phonon coupling constant, U is the on-site repulsion between electrons, and K is the spring constant. The naive energy for the Néel antiferromagnetic state (i.e., ignoring quantum corrections) is $-2t_0^2/U$ per site. The naive energy for our RVB state is obtained by balancing the strain energy against the gain in electronic energy; the RVB energy is lower than the Néel state when $a^2/KU>\frac{1}{9}$, at which point the strong-bond hopping matrix element is $\frac{4}{3}t_0$. Quantum corrections (spin waves versus resonance) further favor the RVB state.[7,8]

The RVB state is a quantum liquid of valence bonds.[7] Under what conditions is it lower in energy than crystalline arrangements of valence bonds (i.e., spin-Peierls states)? The most natural spin-Peierls state looks like a stack of antiferromagnetically aligned polyacetylene chains: All bonds are aligned along the same axis, with no next-nearest-neighbor bond pairs. Presumably, this crystalline arrangement minimizes the energy for large ion mass, but without breaking bonds it cannot resonate with any other valence-bond configuration. A typical valence-bond configuration has a large density of next-nearest-neighbor bond pairs. These pairs can resonate between horizontal and vertical configurations (Fig. 2), which lowers the energy of the appropriate superposition by an effective tunnel splitting $J_{\rm res}$. If the difference in energy density between the spin-Peierls state and a single typical valence-bond configuration is less than order $J_{\rm res}$, the RVB phase will be preferred. In the adiabatic limit, a simple WKB (Wentzel-Kramers-Brillouin) estimate (ions of mass M tunneling a distance u through a barrier of height $aut/U\gtrsim\hbar\omega^*$) gives

$$J_{\rm res}\approx\omega^*\exp[-A(t^2/U)/(\hbar\omega^*)],$$

where A is a constant of order unity and $\omega^*=\sqrt{a^2/KU}\sqrt{K/M}$ is the renormalized phonon frequency.[9] (This estimate suggests $J_{\rm res}$ is small. In the absence of phonons, $J_{\rm res}$ would be of order t^2/U. Doping can also stabilize[10] the RVB state by a delocalization resonance energy of order xt_0, where x is the soliton density.)

We can see already a schematic of the RVB state's topological long-range order. Color the lattice sites alternately black and red, in a checkerboard pattern; each bond connects two sites—one black, one red. Consider a large loop which cuts no bonds. For a perfect valence-bond configuration,[11] the number of enclosed red and black squares must be the same, independent of the size of the loop. Unbonded sites (dangling bonds) are the topological defects. So long as the loop passes through perfect regions, the difference between the number of black and red squares enclosed is equal to the difference between the number of black and red defects (Fig. 2): Dangling bonds (free spins) on black squares act as antiparticles to dangling bonds on red squares.

These dangling bonds are entirely analogous to the neutral solitons in polyacetylene.[9] They have spin $\frac{1}{2}$ and charge 0, are created in pairs by breaking a bond, and (because the RVB state has no crystalline long-range order) act as free particles. As in polyacetylene, the defect will presumably extend over several sites, and be quite mobile. Upon doping, the added electrons or holes will bind to the free spins, forming a charged soliton. (In the absence of electron-electron interactions, charge conjugation symmetry implies that a dangling bond has a midgap state; the charged soliton binding energy is then of order $2au$. With interactions, these states will split apart, but the extra electron will presumably prefer to avoid breaking an extra bond, giving a binding energy of order $2t^2/U$.) The charged defect has spin 0 and charge $\pm e$. The charged defect will certainly delocalize over several sites; its size R is determined by balancing the delocalization energy (of order $-t[1-(a/R)^2]$) against the exchange energy [of order $(t^2/U)(R/a)^d$ per site], so $R/a\sim(U/t)^{1/(d+2)}$.

If the many-body wave function has a quasiparticle interpretation, the statistics of the quasiparticles can be determined by considering the transformation of the wave function under the exchange of two solitons as follows. Turn on an external potential which localizes the solitons near points Q_0 and R_0. Schematically, the quasiparticle wave function should be approximately of the form

$$\Psi(Q,R)=[\Phi(Q-Q_0)\Phi(R-R_0)\pm\Phi(Q-R_0)\Phi(R-Q_0)]/\sqrt{2},$$

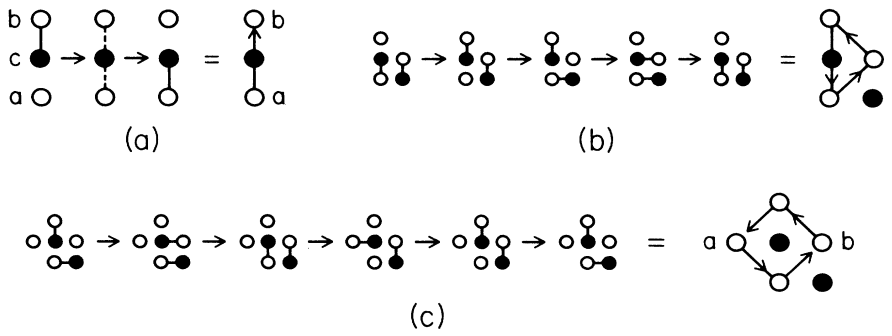

FIG. 3. Quasiparticle statistics: Statistics are usually determined by the change in the sign of the wave function when the identities of two particles are permuted. Statistics can also be determined by adiabatically dragging two identical quasiparticles along a path which exchanges their positions (Ref. 12), and examining the resulting change in the phase of the many-body wave function. (a) An elementary step which adiabatically transports a soliton from site a to site b. The electron hopping matrix elements t_{ac} and t_{cb} are slowly changed from their initial values ($t_{cb} \gg t_{ac}$) to their final values ($t_{cb} \ll t_{ac}$); this moves the valence bond from cb to ac and the soliton from site a to site b. The sign change in the wave function is unambiguous only if the solitons transverse a closed loop. However, keeping the wave function real and using the most natural sign convention, we find that charged solitons pick up a $+1$ per move and neutral solitons pick up a -1 per move (calculated analytically for $U=0$ and numerically for the $U\neq 0$ Hubbard model). (b) Transporting *single* neutral solitons around loops produces phase changes. We carry a single red soliton around a closed path which encloses one plaquette. If the soliton is charged $\pm e$, the phase of the wave function is unchanged; however, if the soliton is neutral, the change in the sign of the wave function is $(-1)^N$, where N is the number of moves of the type shown in (a). (The final move, which takes two horizontal bonds to two vertical bonds, must be done carefully to avoid a degeneracy in the many-body ground state. When this is done, it yields no phase change.) The neutral solitons therefore behave like particles with a negative hopping matrix element. This sign change can also be written (for a loop) as $(-1)^{N'}$ where N' is the number of enclosed plaquettes, as if the neutral soliton were in an external gauge field with half a flux quantum per plaquette. (c) In this path, we exchange two red solitons in such a way that the bonds return to their initial configuration. One soliton moves from a to b along the top path, and the other moves from b to a along the bottom. If the solitons are charged, the wave function is unchanged; if the solitons are neutral, the wave function changes sign. (This path encloses an even number of plaquettes; as noted above, neutral solitons following paths enclosing an odd number of plaquettes will pick up an extra factor of -1.)

where Q and R are the quasiparticle coordinates. By slowly varying this external potential the quasiparticles can be moved adiabatically along a path which exchanges Q_0 and R_0 [Fig. 3(c)]; before and after exchange the Hamiltonian is the same. From the net sign change of the wave function we have determined that the charged solitons are bosons and the neutral solitons are fermions, as described in Fig. 3.

How are these considerations related to high-T_c superconductivity? First, the scale of the binding energy of the elementary bosons is no longer set by the phonon Debye frequency, but rather by an electronic energy, $\sim 2t_0^2/U$. Second, just as for solitons in polyacetylene,[9] the effective mass of the bosons can be very small, making for large quantum effects.[13] In two dimensions,[14] the adiabatic effective mass of a soliton is proportional to the square of the lattice deformation: $M^* \approx M(u/a)^2$. To estimate M^*, we use parameters for La_2CuO_4. We take $t_0=0.5$ eV and $\alpha \sim 3$ eV/Å from band-structure calculations.[15] These parameters imply that a lattice displacement $u_c = t_0/(6\alpha) = 0.03$ Å is needed to stabilize the RVB state with respect to the Néel state. The Cu-Cu distance is $a=3.79$ Å, so at critical coupling $M^*/M \approx 5\times 10^{-5}$. Thus, as in polyacetylene, the soliton mass is comparable to an electron mass; at optimal doping densities bosons of this mass would still be highly degenerate at the measured T_c. The large binding energy and degeneracy temperature of our charged solitons, both several hundred K, make this a promising starting point for a complete theory.[16]

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[1] P. W. Anderson, Science, **235**, 1196 (1987); see also L. Pauling, *The Nature of the Chemical Bond* (Cornell Univ. Press, Ithaca, NY, 1960).

[2] J. G. Bednorz and K. A. Müller, Z. Phys. B **64**, 188 (1986);

S. Uchida, H. Takagi, K. Kawasaki, and S. Tanaka, Jpn. J. Appl. Phys. Lett. (to be published); R. J. Cava, R. B. van Dover, B. Batlogg, and E. A. Rietman, Phys. Rev. Lett. **58**, 408 (1987); C. W. Chu, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, and Y. Q. Wang, *ibid.* **58**, 405 (1987).

[3]These topological excitations certainly do not exhaust the degrees of freedom. In particular, there will be neutral, transverse phononlike excitations of the RVB degrees of freedom.

[4]C. N. Yang, Rev. Mod. Phys. **34**, 694 (1962).

[5]V. B. Grande, Hk. Müller-Buschbaum, and M. Schweizer, Z. Anorg Allg. Chem. **48**, 120 (1977); J. M. Longo and P. M. Raccah, J. Solid State Chem. **6**, 526 (1973).

[6]Peter Littlewood (private communication).

[7]P. W. Anderson, Mater. Res. Bull. **8**, 153 (1973).

[8]P. Fazekas and P. W. Anderson, Philos. Mag. **30**, 432 (1974).

[9]W. P. Su, J. R. Schrieffer, and A. J. Heeger, Phys. Rev. B **22**, 2099 (1980); A. J. Heeger, S. Kivelson, J. R. Schrieffer, and W. P. Su (unpublished).

[10]G. Baskaran (private communication); S. A. Kivelson, D. S. Rokhsar, and J. P. Sethna (unpublished).

[11]The true RVB ground state will certainly contain an admixture of virtual soliton-antisoliton pairs. However, topological long-range order, similar to that in the XY model, may survive.

[12]M. V. Berry, Proc. R. Soc. London, Ser. A **392**, 45 (1984); D. P. Arovas, J. R. Schrieffer, and F. Wilczek, Phys. Rev. Lett. **53**, 722 (1984).

[13]J. P. Sethna and jS. Kivelson, Phys. Rev. B **26**, 3513 (1982); A. Auerbach and S. Kivelson, *ibid.* **33**, 8171 (1986).

[14]We are assuming that the dispersion relation is not completely changed by the exotic order of the RVB state. Also, our analysis is substantially unchanged in discussing three-dimensional cubic systems, except that the mass of the solitons will be larger. The binding energy of the charged soliton is not strongly dependent on dimension; thus the possibility exists that bosons could exist above their condensation temperature in three dimensions.

[15]L. F. Mattheiss, Phys. Rev. Lett. **58**, 1028 (1987).

[16]Both interlayer couplings and attractive interactions between charged solitons (mediated, for example, by exchange of neutral solitons) should allow Bose condensation, which, strictly speaking, will not occur in a noninteracting two-dimensional system.