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Nature of the pairing in a resonating-valence-bond superconductor

S. Kivelson
Department of Physics, State University of New York at Stony Brook, Stony Brook, New York 11794
and Department of Applied Physics, Stanford University, Stanford, California 94305-4090
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One of the most striking features of the recently reported experimental data on the new high-temperature copper-oxide superconductors is the apparent disagreement between the photoabsorption and some of the tunneling measurements of the superconducting gap. It is argued here that this may not be an experimental artifact, but rather reflects the novel nature of the pairing in the resonating-valence-bond state: The lowest-lying quasiparticle excitations consist of pairs of neutral solitons. Thus, the superconducting gap can be measured in tunneling, but not in the photoabsorption. The nature of the expected absorption spectrum, and the analogy with doped polyacetylene is also discussed.

A striking feature of the recently reported experimental data on the new high-temperature copper-oxide superconductors is the apparent discrepancy between the superconducting gap measured by tunneling[1-5] and infrared absorption.[6-9] On the one hand, tunneling measurements imply large values of the gap. While some measurements can be interpreted in terms of a gap with a low-temperature value $2\Delta_0/k_BT_c \simeq 4-5$ and a smoothly rising density of states in the gap, the most striking measurements reveal an extremely clean gap with $2\Delta_0/k_BT_c = 10-12$, and a temperature dependence[2] which implies $2\Delta \rightarrow 0$ as $T \rightarrow T_c$. (It has been suggested[5] that the smaller gaps are an artifact of the higher current densities in these experiments.) The tunneling density of states has particle-hole symmetry, as in conventional superconductors, with the threshold for particle and hole injection at $V = \Delta/e$ and $-\Delta/e$, respectively. Subsidiary thresholds are observed[1] in some samples at $V = \pm 3\Delta/e$ and $\pm 5\Delta/e$. On the other hand, the infrared absorption obtained by Kramers-Kronig transformations of the reflectivity[6] shows no clear threshold that can be clearly identified as the superconducting gap; a characteristic energy[6,9] below which the absorption is somewhat lower in the superconducting than the normal state has been taken to imply a gap of order $2\Delta/k_BT_c \sim 3-4$. However, there are dramatic absorption features which are associated with doping (i.e., removing electrons from the highest lying Cu-O band so that it is less than half filled); there is an infrared active "charged phonon" mode with an energy in $La_{2-x}Sr_xCuO_4$ of about $\hbar\omega \sim 0.02$ eV and an electronic transition[7,8] which produces a broad absorption peak centered at about $\hbar\omega \sim 0.5$ eV. However, there is no evidence of any feature in the optical absorption at an energy corresponding to $\hbar\omega = 2\Delta_T$ where $2\Delta_T$ is the gap inferred from tunneling.

It is, of course, possible that this discrepancy is an experimental artifact having to do with differences in sample preparation, sample inhomogeneity, or misinterpretation of the experimental data. However, it is the purpose of this note to show that this discrepancy is to be expected if the superconductivity results from the formation of a resonating-valence-bond state (RVB) of the sort proposed by Kivelson, Rokhsar, and Sethna[10] (KRS) based on the original proposal of Anderson.[11] Moreover, the analysis reveals a rather fundamental feature of the RVB state, namely that it can be thought of as a condensate of Cooper pairs of charge-neutral spin-$\frac{1}{2}$ fermions. It also highlights an important difference in the properties of the RVB state inferred by KRS on the basis of an analysis of a strong-coupling limit of the model, and the properties infered by Baskaran, Zou, and Anderson[12] (BZA) from a mean-field theory analysis. In particular, KRS found that there is a gap in the spin excitation spectrum of the RVB state,[13] while BZA found that the spectrum was gapless. In this paper I will develop the idea that neutral solitons are the spin excitations, and that the RVB state is analogous to a BCS condensate of neutral solitons. Finally, I will describe how the spectroscopic features that are observed in infrared absorption can be understood by making the analogy with the absorption spectrum of doped polyacetylene.

It is not strictly correct to think of the BCS ground state as a Bose condensate of Cooper pairs due to the large overlap between pairs.[14] Nonetheless, there is a real sense in which the condensate consists of pairs of electrons in that when a pair is broken, a pair of quasielectrons of opposite spin are produced as excitations. The nature of the excitation produced upon photoexcitation can be viewed as breaking one pair producing two quasiparticles. Since the ground state is a Bose condensate with an indeterminate number of pairs, the energy associated with this is simply twice the quasielectron creation energy 2Δ. The particle-hole symmetry of the tunneling density of states is also a consequence of the pairing nature of the ground state. When an electron is added to the superconductor, it forms a quasielectron. The threshold energy is, thus, the quasielectron creation energy Δ. When an electron is removed from a superconductor, a pair is broken, and one electron is removed, leaving behind one quasielectron. Again, because the ground state has an indeterminate number of pairs, the energy required is the quasielectron creation energy Δ.

The nature of the RVB state has been discussed extensively by several authors.[10-13,15] The results that are germaine to the present study can be readily summarized.

Following Anderson,[7] we assume that the electronic properties of the copper-oxide superconductors can be modeled in terms of a large-U Hubbard model $U \gg t$, in which each site (representing a unit cell with one Cu and two O) is neutral when the Wannier function is singly occupied (i.e., the band is half filled). We also imagine[10] that there is a moderately strong electron-phonon interaction which modulates the electron hopping matrix t, and hence, serves to stabilize the RVB state. A valence bond implies a strong nearest-neighbor bond (i.e., the lattice is distorted such that t is greater than average) and a pair of electrons associated with the bond in their singlet ground state. For the half-filled band, each site is involved in exactly one valence bond; for a less-than-half-filled band, there are necessarily some unoccupied nonbonded sites. These sites are the charge e, spin-0 solitons characterized by KRS, and, as they showed, they are bosons [see Fig. 1(b)]. The RVB, then, is a coherent superposition of all valence-bond states of given mean band occupancy, and hence is a Bose condensate of valence bonds. For a less-than-half-filled band, this also implies that it is a Bose condensate of charged solitons. The lowest-lying spin excitations of the system are the neutral solitons, shown schematically in Fig. 1(a), which consist of a singly occupied nonbonded site. KRS showed that these can be treated as spin-$\frac{1}{2}$ charge-0 fermions. In the strong-coupling limit, the neutral soliton creation energy Δ is one-half the energy to break a strong bond. More generally we identify the neutral soliton creation energy with the superconducting gap parameter Δ since 2Δ is the minimum energy needed to break one valence-bond pair. Conversely, it is in this sense that the RVB state can be thought of as a Bose condensate of Cooper pairs of neutral solitons.

Before we discuss the specific implications of this picture, it is useful to make a few general observations. First, it seems unlikely that the RVB state is ever the true ground state for the half-filled band on a square lattice;[10] either a Néel state or a spin-Peierls state is likely to have lower energy. Even if it were the true ground state, it would not be strictly superconducting since it carries no charge.[11,15] However, when the system is less-than-half-filled, the charge solitons can stabilize the RVB,[10,15] and render it superconducting. In the normal BCS pairing, the large size of the Cooper pair (and, concomitantly, the time-retarded nature of the interaction) is important to avoid strong Coulomb repulsion between the electrons which constitute the pair.[14] In the current model (because of the large value of U), the pairing is between neutral quasiparticles. Hence, the pair (valence bond) need not be large, and pairing is not opposed by the long-ranged Coulomb repulsion. In general terms this is what is responsible for the high T_c. Finally, the charged boson in particular is necessarily an extended object, since the energy to localize a hole on a single site is $\sim t$, while the energy to break a bond is $2\Delta < t^2/U \ll t$. Thus, the charge soliton consists of a region of strong uniform bonds which can be viewed as a polaronic distortion of the lattice plus a cloud of virtual neutral soliton pairs which locally melt the RVB order as shown in Fig. 1(c). This is analogous to the finite extent of the soliton in polyacetylene.[16] KRS estimated this radius to be of order $R/a \sim (U/t)^{1/4}$, and the soliton effective mass to be of order a few electron masses. Finally, KRS showed that a strong and precise analogy exists between the solitons in polyacetylene and the solitons in the RVB state.

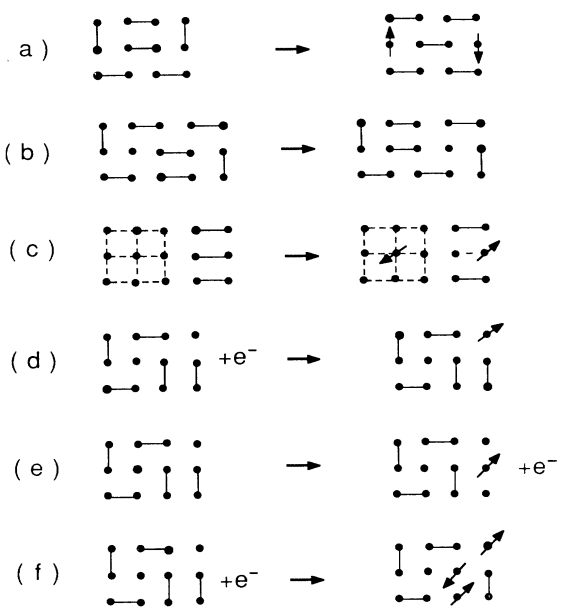

FIG. 1. The solid lines represent valence bonds and hence, have two electrons associated with them. The nonbonded sites are solitons; when unoccupied they represent charged solitons and when occupied by an arrow they represent neutral solitons of the indicated spin. All figures are schematic; the solitons are actually extended objects [see (c)] and the difference between strong and weak bonds is probably, at most, a few percent effect. (a) A process whereby a pair of neutral solitons is created from an ideal valence-bond state. (b) A process in which a charged soliton translates by one bond length. (c) On the left is a schematic representation of a charged soliton. The dashed lines represent "melted" bonds. There is one fewer electron than sites in this melted region, and the hole is delocalized over the entire region. The process shown in the figure is one in which the soliton is ionized with the lattice essentially frozen. (d) The lowest-energy process in which an electron is added to the superconductor. (e) The lowest-energy process in which an electron is removed from the superconductor. (f) A higher-order process in which an electron is added and three quasiparticles are generated.

With these observations in mind, we are in a position to understand the relation between the tunneling and absorption spectra. The particle-hole symmetry of the tunneling spectrum is, again, a consequence of the pairing nature of the wave function. Figures 1(d) and 1(e) schematically show the lowest-energy excited states created when an electron is added or removed from the superconductor. When an electron is added, it must go on an unoccupied site, i.e., a charged soliton. Thus, the final state consists of one quasiparticle (neutral soliton) excitation and nominally one fewer charged solitons. Since the superconductor is a Bose condensate of charged solitons, this latter change is unobservable. Thus, the energy required to add an elec-

tron is Δ. Similarly, when an electron is removed, a bond must be broken, leaving behind an extra neutral soliton and an extra charged soliton. Again, the change in the number of charged solitons is unobservable. Thus, the energy required is Δ.

As discussed above, and as shown schematically in Fig. 1(a), the minimum energy required to create a quasiparticle excitation without changing the number of electrons is simply 2Δ, the soliton pair creation energy. However, since the neutral solitons are neutral, there is no optically allowed transition from the superconducting ground state to the two quasiparticle state. This statement can be made formally, as in polyacetylene:[17,18] The Hamiltonian is charge-conjugation symmetric. Both the RVB ground state for the half-filled band and the soliton-pair state are charge-conjugation even, while the current operator is charge-conjugation odd. Thus, the transition is an optically forbidden one. The absence of a feature in the infrared absorption at 2Δ reflects the fact that the pairing occurs between neutral solitons. The gap should be observable in inelastic neutron scattering or Raman scattering. This is the main point of this paper.

Finally, we are led to some speculation concerning the spectroscopic features that are actually observed in the copper-oxide superconductors. Because of the analogy with the solitons in polyacetylene, we are guided by what is known in that system.[17] There are two distinct classes of optically active modes associated with the introduction of charged solitons: (1) There are charged "phononlike" modes associated with the soliton translation,[19] as shown in Fig. 1(b). There is one such mode corresponding to each optical-phonon branch that is coupled to the soliton charge. The in-phase translation of all the components of soliton lattice distortion is the Goldstone mode associated with the fact that the soliton breaks the translational invariance of the lattice, and hence, this mode occurs at zero frequency in the absence of disorder pinning (i.e., it gives rise to Drude absorption in the normal state); the out-of-phase translation of the different components of the lattice distortion produce finite frequency modes.[20] The oscillator strength associated with these modes is large due to the soliton's small effective mass. (2) There is a "midgap" absorption associated with ionizing the charged soliton, as shown in Fig. 1(c). The oscillator strength associated with this transition is large due to the large size of the soliton.[21]

In the copper oxides I speculate that the Drude absorption[5] above T_c and the phononlike absorption peak[4] at $\hbar\omega \sim 0.02$ eV are associated with the soliton translation modes. (Below T_c, the Drude absorption moves to $\omega = 0$.) From the oscillator strength associated with the Drude absorption,[5] I deduce an effective mass for the charged soliton of $m^* \simeq 7m_e$ in $La_{2-x}Sr_xCuO_4$, which is roughly consistent with the effective mass deduced from the low-temperature London penetration length.[22] The observed broad absorption peak[8] at $\hbar\omega = 0.45$ eV with $\Delta\hbar\omega = 0.3$ eV in the $La_{2-x}Sr_xCuO_4$, and at $\hbar\omega = 0.65$ eV with $\Delta\hbar\omega = 0.3$ eV in $YBa_2Cu_3O_{7-\delta}$ I associate with the ionization energy of an isolated charged soliton. (Essentially, this is the same assignment of the modes that was made in Ref. 5.) From the oscillator strength, an optical effective mass of $m^* = 0.4\ m_e$ can be associated with this transition, or roughly the band effective mass $m^* = \hbar^2/(2ta^2) \sim 0.5m_e$ for $t = 0.5$ eV, as estimated from band-structure calculations.[23] This suggests that the soliton radius is not more than a couple lattice constants. Lastly, the multiple thresholds in the tunneling spectra seem to imply a non-negligible amplitude for producing multiple additional quasiparticles, as shown schematically in Fig. 1(f). While such a process is possible in a conventional superconductor, it is always strongly suppressed due to the large size of the Cooper pair $\xi_0 \gg a$. The large amplitude for this process in the high-temperature superconductors probably reflects a small size for the effective Cooper pair $\xi_0 \sim a$; such a small size for the Cooper pair is possible only due to the fact that they are formed of neutral quasiparticles. The small size of ξ_0/a also, seemingly, implies unprecedentedly strong coupling, and the possibility of concomitantly high values of $2\Delta/k_BT_c$.

Note added. It has recently been reported that in single-crystal films[4] the mid-gap peak is not observed in either infrared or Raman. (This is reminiscent of the same effect which occurs when polyacetylene is doped in excess of 5%.) Since the midgap peak is a property of an isolated soliton, this observation could be understood if we postulate that the observed midgap absorption is associated solely with relatively isolated, trapped solitons that occur in the noncrystalline material. The midgap peak is likely to be washed out for a dense array of solitons, as it is in polyacetylene, due to the formation of a soliton band which broadens the midgap absorption to such an extent that it becomes essentially unobservable.[24]

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