Antiferromagnetic singlet pairs, high-frequency phonons, and superconductivity

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The properties of a model of electrons interacting through an on-site Hubbard repulsion U, and coupled to intersite lattice vibrations, are discussed. It is argued that the antiferromagnetic singlet pairs induced by U will condense into a superconducting state in the presence of coupling to high-frequency phonons, or, equivalently, that an on-site U strongly enhances the electron-phonon coupling giving rise to superconductivity. It is proposed that this model describes the essential features of the high-T_c oxide superconductors.

In a recent Letter,[1] it was pointed out that an effective attractive interaction between nearest-neighbor antiparallel spins arises in the non-half-filled repulsive Hubbard model for strong U, and suggested that these singlet pairs could condense into a superconducting state. It was also found within weak-coupling perturbation theory that antiferromagnetic spin fluctuations induce a tendency to even-parity singlet pairing, particularly near a spin-density-wave instability.[2] While numerical evidence on two-dimensional small lattices was found to support the existence of this nearest-neighbor attraction,[1] it did not unequivocally point toward a superconducting state at low temperatures in the pure Hubbard model. The question of whether in the pure Hubbard model the antiferromagnetic singlet pairs will condense into a superconducting state at sufficiently low temperatures is still open.

Anderson has suggested that the oxide superconductors can be described by a Hubbard model.[3] He proposed that the insulating phase in these systems is a "resonating-valence-bond" state, which when doped would give rise to a superconducting state when the pre-existing singlet pairs condense. While his condensation of the singlet pairs is clearly related to the above-mentioned picture, we believe that the resonating-valence-bond insulating state probably does not exist in the pure Hubbard model on a square lattice. This is based on the fact that Monte Carlo simulation results for the pure half-filled Hubbard model clearly point to the existence of long-range antiferromagnetic order for all U.[4] In the presence of coupling to phonon degrees of freedom, the the ground state is likely to be an insulating spin-Peierls state, as discussed below.[5]

We will consider in this Brief Report the properties of the Peierls-Hubbard Hamiltonian

$$H=\sum_i \frac{p_i^2}{2M}+\tfrac{1}{2}K\sum_{\langle i,j\rangle}(q_i-q_j)^2-\sum_{\langle i,j\rangle}t_{ij}(c_{i\sigma}^{\dagger}c_{j\sigma}+\text{H.c.})+U\sum_i n_{i\uparrow}n_{i\downarrow},\quad t_{ij}=t-\alpha(q_i-q_j)\ , \tag{1}$$

with $\langle i,j\rangle$ nearest neighbors on a bipartite lattice. In particular, we have a two-dimensional square lattice in mind, with possibly a weak coupling in the three-dimensional direction. In a one-dimensional geometry, it has been recently shown that in the presence of coupling to low-frequency intermolecular vibrations, an on-site repulsion U will strongly *enhance* the tendency of the system towards dimerization.[6,7] The largest enhancement was found to occur for U approximately equal to the bandwidth. That is, the antiferromagnetic singlet pairs induced by U couple more strongly to the intermolecular lattice vibrations than uncorrelated electrons. The enhancement of dimerization by U was qualitatively explained by Mazumdar and Dixit[6] in terms of U providing a barrier to resonance between states differing by a lattice translation. Clearly the same mechanism can be invoked in a two-dimensional square lattice. The square lattice has also a nested Fermi surface in the half-filled-band case, and additionally a logarithmic singularity in the density of states which should enhance the instability further.[8] Moreover, in one dimension it was shown that the dimerized state is stable against quantum fluctuations for arbitrary phonon frequency.[9] This should be even more so in two dimensions. These considerations strongly suggest to us that the two-dimensional half-filled Peierls-Hubbard Hamiltonian will exhibit a spin-Peierls ground state for arbitrary parameters. This is not inconsistent with fairly extended antiferromagnetic spin correlations, as has been shown in Monte Carlo simulations in the one-dimensional case.[7] Finally, a small nearest-neighbor repulsion was found to enhance the lattice instability further in the one-dimensional case,[7,10] and this is also likely to carry over to two dimensions.

It is easy to see that an on-site U will enhance the electron-phonon interaction that occurs through modulation of the intersite hopping t. Consider a simple two-site system: In the absence of U, one has up and down electrons that resonate independently between the two sites, while in the presence of U the processes become coherent, as depicted in Fig. 1. The coherent hopping process couples more strongly to a modulation of the hopping t: The fractional change in the energy of this two-site system under a change in the hopping is

$$\frac{1}{E}\frac{dE}{dt}=-\frac{8t}{\sqrt{(U^2/4)+4t^2}}\,\frac{1}{U/2-\sqrt{(U^2/4)+4t^2}}\ , \tag{2}$$

which is an *increasing* function of U, going from 2 to 4 as

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$$|\uparrow\rangle|0\rangle \xleftrightarrow{t} |0\rangle|\uparrow\rangle$$
$$|\downarrow\rangle|0\rangle \xleftrightarrow{t} |0\rangle|\downarrow\rangle$$
(a)

$$|\uparrow\rangle|\downarrow\rangle \xleftrightarrow{t^2/U} |\downarrow\rangle|\uparrow\rangle$$
(b)

FIG. 1. (a) For $U=0$, up and down electrons resonate independently between two neighboring sites. (b) For large U, only correlated hoppings occur.

U increases from zero to infinity. The extra factor of 2 in the large-U limit arises from the fact that the effective coupling is t^2/U. PP In the large-U limit, the effective Hamiltonian for the half-filled Hubbard model is a Heisenberg Hamiltonian with coupling t_{ij}^2/U, which in one dimension is unstable toward dimerization (spin-Peierls transition). The instability is stronger than the Peierls one, since the relevant susceptibility diverges linearly in $1/T$ rather than logarithmically.[11] This will yield a transition temperature that goes *linearly* with the coupling constant rather than exponentially. For any finite U the corresponding instability toward bond charge-density-wave order (BCDW), is found to have the same divergence as in the large-U limit from numerical simulations.[12] It is also likely that in two dimensions the spin-Peierls instability is stronger than the Peierls one, although it has not yet been verified directly.

For non-half-filled-band cases, however, and in the presence of high-frequency phonons, we expect the dominant instability to be toward a superconducting state, and it should also be enhanced by a Hubbard U. For the non-half-filled Hubbard model, one can write an effective Hamiltonian in strong coupling with interaction:[1]

$$V_{\text{eff}} = -\frac{2t^2}{U}\sum_{\langle i,j\rangle}(n_{i\uparrow}n_{j\downarrow}+n_{i\downarrow}n_{j\uparrow}) - \frac{2t^2}{U}\sum_{\langle i,j\rangle}(c_{i\uparrow}^\dagger c_{j\downarrow}^\dagger c_{i\downarrow}c_{j\uparrow}+c_{i\downarrow}^\dagger c_{j\uparrow}^\dagger c_{i\uparrow}c_{j\downarrow}) , \quad (3)$$

which suggests that there is a tendency to a pairing of nearest-neighbor electrons with antiparallel spins. The appropriate order parameter is[1,13]

$$\Delta_{ij} = \frac{c_{i\uparrow}c_{j\downarrow} - c_{i\downarrow}c_{j\uparrow}}{\sqrt{2}} , \quad (4)$$

with i,j nearest neighbors, in terms of which

$$V_{\text{eff}} = -\frac{4t^2}{U}\sum_{\langle i,j\rangle}\Delta_{ij}^\dagger\Delta_{ij} . \quad (5)$$

Although the forms of Eqs. (3) and (5) suggest pairing,[1,14] they do not prove that the system will become superconducting. First, there are other terms in the effective interaction involving three sites that were omitted;[1] in addition, the kinetic energy itself of the effective Hamiltonian does not describe free particles. This question will probably be settled only by nonperturbative numerical calculations.

We can also obtain an effective interaction arising from the phonon part of the Hamiltonian Eq. (1) in the limit of high-frequency phonons:

$$V_{\text{eff}}^{(\text{ph})} = \frac{2\alpha^2}{K}\sum_{\langle i,j\rangle}(n_{i\uparrow}n_{j\uparrow}+n_{i\downarrow}n_{j\downarrow}) - \frac{2\alpha^2}{K}\sum_{\langle i,j\rangle}(c_{i\uparrow}^\dagger c_{j\downarrow}^\dagger c_{i\downarrow}c_{j\uparrow}+c_{j\uparrow}^\dagger c_{i\downarrow}^\dagger c_{j\downarrow}c_{i\uparrow}) - \frac{2\alpha^2}{K}\sum_{\langle i,j\rangle}(c_{i\uparrow}^\dagger c_{i\downarrow}^\dagger c_{j\downarrow}c_{j\uparrow}+c_{j\uparrow}^\dagger c_{j\downarrow}^\dagger+c_{i\downarrow}c_{i\uparrow}) . \quad (6)$$

The last term represents the hopping of pairs of electrons on the same site and can be neglected for large U. The first term is a nearest-neighbor repulsion between electrons of parallel spin, and the second term gives rise to pairing of antiparallel electrons on the bonds, stabilizing further the pairs that appear in the pure Hubbard model.

Figure 2 shows in a simple example how the electron-phonon interaction stabilizes the pairs. In the absence of it, Fig. 2(a), two pairs next to each other can transform into a single pair and two isolated electrons; in the presence of electron-lattice coupling this pair-breaking mechanism is inhibited by the fact that the lattice distorts where the singlet pairs are, making it energetically unfavorable to break the pairs. In addition, the effective nearest-neighbor repulsion between parallel electrons in Eq. (6) will inhibit pairs from occupying nearest-neighbor sites.

To investigate the competition between superconductivity and bond CDW order in this model requires a detailed calculation. Some insight can be gained by considering a related model describing intramolecular vibrations (Holstein model) and with an *attractive* Hubbard U. That model is well understood both in strong and weak coupling,[15,16] and it is found that low-frequency phonons favor a charge-density-wave state and high-frequency phonons a superconducting state. As one approaches the half-filled-band case, the CDW state becomes more favorable for fixed phonon frequency, and at exactly half filling it dominates for any phonon frequency. An attractive U enhances both instabilities. It is likely that the repulsive Hubbard model with intermolecular vibrations has identical properties, both models being connected by a duality transformation that interchanges sites and bonds (the on-site repulsive U gives an effective attractive $-t^2/U$ on the

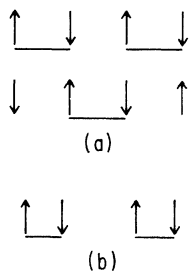

FIG. 2. (a) In the absence of electron-lattice coupling, it is easy to break two pairs to form a single pair plus two unpaired electrons. (b) If the lattice distorts, the pairs are stabilized.

bonds). The details of this mapping will be discussed elsewhere. Here, we will infer the qualitative behavior of the Peierls-Hubbard Hamiltonian by considering the appropriate susceptibilities in the noninteracting case. The susceptibility toward bond CDW order in the x direction is

$$\tilde{N}(q)=\frac{1}{N}\int_0^B d\tau\sum_{i,j}e^{iq(R_i-R_j)}\langle[c_{i\sigma}^{\dagger}(\tau)c_{i+\delta x,\sigma}(\tau)+\text{H.c.}](c_{j\sigma}^{\dagger}c_{j+\delta x\sigma}+\text{H.c.})\rangle=\frac{1}{N}\sum_k\frac{f(\varepsilon_{k+q})-f(\varepsilon_k)}{\varepsilon_k-\varepsilon_{k+q}}[1+\cos(q_x+2k_x)]\ , \tag{7}$$

and toward pairing on bonds in the x direction

$$P=\frac{1}{N}\int_0^{\beta}d\tau\sum_{i,j}\langle\Delta_{i,i+\delta x}(\tau)\Delta_{j,j+\delta x}^{\dagger}(0)\rangle$$
$$=\frac{2}{N}\sum_k{}'\cos^2k_x\frac{\tanh(\beta\varepsilon_k/2)}{2\varepsilon_k} \tag{8}$$

We assume that there is a cut-off frequency ω_0 for the pairing interaction so that the sum in Eq. (8) is restricted to $|\varepsilon_k|<\omega_0$. The cutoff does not affect the CDW instability.[16]

At one-half band filling, both susceptibilities diverge as $\ln^2T$.[8] The strong divergence is due to the log singularity in the density of states, and for $\tilde{N}(q)$ to the fact that the Fermi surface is nested. As we move away from half-filled band ($\rho=1$), P diverges as $\ln T$ and $\tilde{N}$ is no longer divergent. However, at intermediate temperatures $\tilde{N}$ may still be larger than P so that bond CDW order can occur first. Figure 3 shows the susceptibilities for two temperatures as functions of band filling. For $\beta=4$, bond CDW order dominates for band filling $\rho\gtrsim0.8$, and superconductivity for $\rho<0.8$. As T is lowered, superconductivity dominates up to $\rho=0.92$ for $\beta=8$. If we decrease the cutoff frequency ω_0, bond CDW order occurs over a larger range of band fillings and the superconducting T_c decreases. In Fig. 4 we show critical temperatures obtained within the random-phase approximation assuming the same coupling $\lambda=2$ for both instabilities. Superconductivity dominates for band filling $\lesssim0.9$, and T_c decreases rapidly as the band filling decreases and as the cutoff frequency decreases.

Finally, one should remark that if the singularity in the density of states occurs at a point where there is no nesting, one will obtain strongly enhanced superconductivity dominating over the bond CDW instability. This has been discussed in detail elsewhere,[8] and may be of relevance to the oxide superconductors.

In summary, we have discussed the interplay between bond CDW order (spin-Peierls instability) and superconductivity from condensation of nearest-neighbor singlet pairs in the two-dimensional Peierls-Hubbard model. We have shown that a Hubbard U enhances the effective electron-phonon coupling. We argued that away from half-band filling, the dominant instability is toward superconductivity due to condensation of the nearest-neighbor singlet pairs, and that as we approach the half-filled-band case T_c increases until the superconductivity is preempted by the condensation of the singlet pairs into a spin-Peierls state. Higher phonon frequency favors superconductivity over spin-Peierls. While we do not yet have a quantitative theory, these considerations suggest that a Hubbard model coupled to high-frequency intermolecular vibrations may contain the essential features to describe the high-T_c oxide superconductors.

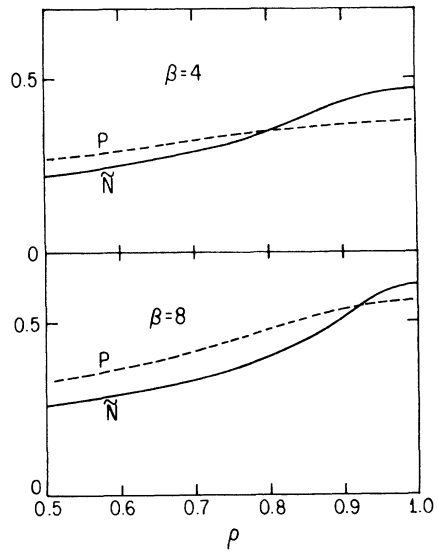

FIG. 3. Bond CDW (full line) and bond pairing susceptibilities as functions of band filling for $\beta=1/T=4$ and 8, in units where $t=1$. The cutoff is $\omega_0=2$.

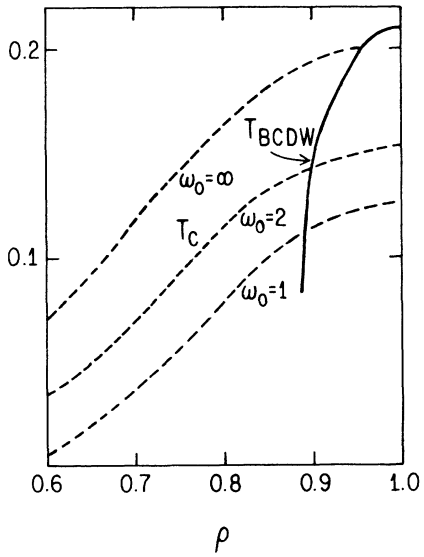

FIG. 4. Transition temperatures toward spin-Peierls (full line) and superconducting state (dashed lines) vs band filling for $\lambda=2$ and several values of ω_0.

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