Finite Systems Studies and the Mechanism of High T_c

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I discuss results of exact and Monte Carlo calculations of models for the oxide superconductors. These results show that magnetic mechanisms are highly unlikely to lead to high temperature superconductivity. A Cu-O charge-transfer excitation is found to be a possible mechanism for pairing of oxygen holes, if the parameters are right. However, the body of experimental results and our results from small systems point to another, novel and highly universal mechanism for superconductivity in these and other materials.

I. Introduction

Recent experimental developments [1] have in my view delivered a fatal blow to theories based on magnetic mechanisms as the origin of high T_c superconductivity. The discovery of 30° K superconductivity in $Ba_{1-x}K_xBiO_3$, a material with no traces of magnetism, rules out magnetic mechanisms unless one assumes that the origin of superconductivity in Cu and non-Cu oxides is entirely different. I believe that ascribing entirely different mechanisms to two classes of oxide materials with largely similar properties and both having T_c's substantially higher than what was known before 1986 defies common sense.

Numerical work on model Hamiltonians, however, had already indicated that magnetic mechanisms will not give rise to high T_c [2,3]. Within a model with one orbital per O and one orbital per cation [4], these calculations suggested instead a charge-transfer excitation mechanism [3,5,6]. This mechanism can operate both in Cu and non-Cu based compounds, and thus the recent discovery mentioned above does not invalidate it. An attractive feature of this mechanism is that certain structural and other features that are specific to the oxide materials (both with and without Cu) are required for it to be feasible [3,5]. On the other hand, the parameter regime where this mechanism is found to be effective is somewhat restricted and it may require too large Coulomb interaction between nearest neighbors. In the first part of this paper (Sects. II and III) we review our work and conclusions on these issues.

On the other hand, if we abandon the single-orbital per atom model another, highly universal mechanism involving charge fluctuations suggests itself as compelling [7]. In the last part of this paper we discuss the evidence that points towards this mechanism and some numerical work on an effective Hamiltonian to describe the essential physics.

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II. Magnetic Mechanisms

Soon after the discovery of high T_c superconductivity, ANDERSON [8] put forward the two-dimensional Hubbard model as the model to describe the essential physics of the phenomenon. A large amount of theoretical work followed that supported this point of view. SCHRIEFFER and coworkers [9] proposed a spin-bag picture to describe the properties of the two dimensional Hubbard model that would also lead to superconductivity in this system. Previous numerical and theoretical work [10] had also suggested superconductivity in the two-dimensional repulsive Hubbard model.

However, numerical work has so far not confirmed any of the above pictures. Detailed numerical work has been performed on the two-dimensional Hubbard model in the past two years. In the half-filled band, it has now been convincingly established that the model exhibits antiferromagnetic order that is not destroyed even by strong charge fluctuations (small Hubbard U) [11]. The magnetic properties are well described by spin-wave theory [11-14], and thus far from being described by a "resonating valence bond" (RVB) insulating state, as originally proposed [8]. Comparison with experiment [14,12] suggests that the model is appropriate to describe the *magnetic* properties of the Cu-O materials.

When the model is doped away from half-filling, results of Monte Carlo simulations [2] indicate that no tendency to superconductivity exists down to temperatures a fraction of J, the antiferromagnetic coupling, where there are very strong antiferromagnetic spin fluctuations. Although the numerical work cannot rule out superconductivity at exponentially smaller temperatures, this is unlikely to occur and would anyway not be relevant for the high T_c phenomenon in oxides. In addition, exact diagonalization results on 8-site clusters [2] showed no tendency to superconductivity down to zero temperature. While boundary effects could play an important role in such a small system, one usually does see at least a tendency to other instabilities in such small systems when expected such as antiferromagnetism, Spin-Peierls, charge-density wave and superconductivity (the latter in an attractive Hubbard model or an electron-phonon model). In addition, we should recall that the coherence length in the high T_c materials is believed to be only a few lattice spacings. The combined evidence of Monte Carlo and exact diagonalization studies of the Hubbard model in my view convincingly establishes that it is not the right model to explain superconductivity in the oxide materials. Furthermore, our simulations of a 3-band model for CuO_2 planes with a Hubbard U on the Cu [3] also failed to show enhanced tendency to pairing, indicating that a Hubbard U by itself cannot induce superconductivity [15].

III. Cu-O Charge Transfer Mechanism

Within a model describing a single orbital on the cation and the anion, the tight-binding Hamiltonian for electrons or holes in a plane is:

$$H = \sum_{\langle i,k\rangle} t(d^+_{i\sigma}c_{\ell\sigma} + h.c.) + (\epsilon-\mu)\sum_{\ell\sigma} c^+_{\ell\sigma}c_{\ell\sigma} - \mu\sum_{i\sigma} d^+_{i\sigma}d_{i\sigma} + t'\sum_{\langle\ell\ell'\rangle}(c^+_{\ell\sigma}c_{\ell'\sigma} + h.c.)$$

$$+ U\sum_i n_{i\uparrow}n_{i\downarrow} + U_p\sum_\ell n_{\ell\uparrow}n_{\ell\downarrow} + V\sum_{\langle i\ell\rangle} n_i n_\ell + V_{00}\sum_{\langle\ell\ell'\rangle} n_\ell n_{\ell'} \qquad (1)$$

where we have included interactions and hoppings up to a distance $\sqrt{2}a$, with a the cation-anion distance, and neglected longer-ranged terms. The operators $c^{+}_{i\sigma}$ create holes in the $2p^6$ band of O^{--}, and $d^{+}_{i\sigma}$ creates holes in the $3d^{10}$ shell of Cu^{+} or $6s^2$ shell of Bi^{3+}. We omit orbital angular moments labels thus restricting the occupation of these orbitals to 0, 1 and 2 holes. ϵ is the energy difference between anion and cation single particle levels. It is determined by the cation and anion as well as the over-all structure.

Consider some bare parameters for the Hamiltonian (1). The on-site repulsion on O sites [16] $U_p = E(O^{--}) + E(O) - 2E(O^{-}) = 10.2$eV, which is surprisingly large due to the fact that O^{--} is a highly unstable species. The reason O^{--} exists is of course that it is stabilized by electrostatic energy in ionic solids. The on-site repulsion on the cations is not much larger: for Cu [17], $U = E(Cu^{+++}) + E(Cu^{+}) - 2E(Cu^{++}) = 16.5$eV, and for Bi, $U = E(Bi^{3+}) + E(Bi^{5+}) - 2E(Bi^{4+}) = 10.7$eV. Therefore, it is unrealistic to assume that U_p can be omitted in models where U plays an essential role [18]. U_p is, however, unimportant for magnetic properties: the lattice structure of the planes favors an antiferromagnetic state with the moments centered around the cation sites when there is one hole per unit cell; the strength of the antiferromagnetic exchange is determined mainly by U, with U_p playing a secondary role. The bare Coulomb repulsion between two neighboring holes is $V = e^2/a = 7.4$eV for the nearest-neighbor distance on Cu-O planes, clearly not negligible compared to the on-site interactions.

The basic pairing mechanism in this model in the strong coupling limit is illustrated in Fig. 1 [3]: two added O holes can have a lower energy if they are on the same O atom and polarize their environment:

$$E_2 = 2V + 4\epsilon + U_p \tag{2}$$

rather than far apart from each other, each with energy:

$$E_1 = \epsilon + 2V \tag{3}$$

if the parameters are such that the effective interaction:

$$U_{eff} = E_2 - 2E_1 = -2V + U_p + 2\epsilon \tag{4}$$

is negative. For the bare parameters of CuO_2 given above, U_{eff} is negative for $\epsilon < 4.7$eV. This argument implicitly assumes that U on the cations is much larger than ϵ; otherwise the added holes go predominantly onto the cations rather than anions and the

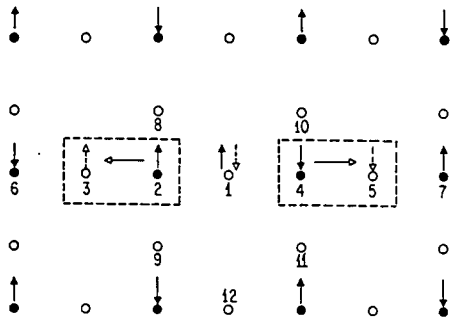

Fig. 1. Schematic illustration of pairing mechanism in 3-band model [3]. As holes are added to the center O ion, holes on neighboring cations are pushed away onto O ions. The dashed lines enclose the two polarizable "side units" to the center O ion that produce the effective attractive interaction on that O

pairing mechanism described becomes ineffective. A similar argument can be used for pairing of O holes on nearest neighbor O atoms [19]. The strong coupling analysis there, however, yields an effective interaction $U_{eff} = \epsilon - V + 2V_{00}$. If we assume the bare electrostatic value $V_{00} = V/\sqrt{2}$ we find always a positive U_{eff} under these conditions. Nevertheless, this process does help in reducing the value of the bare nearest-neighbor repulsion substantially.

Note that the lattice structure with doubly coordinated anion and higher coordinated cation is crucial to this argument. Consider instead, for example, a square lattice structure as in the BaO planes in $BaBiO_3$. If we attempt to move charge from Ba to a neighboring O when we add holes to an O (analogously to Fig. 1), this has to overcome the repulsion of 3 rather than 1 nearest-neighbor Ba, and thus it is always energetically unfavorable. Thus, that structure does not allow for the polarization mechanism described above.

The Coulomb interaction parameters in the real material will not be given by these bare values but are going to be screened by processes involving orbitals not included in the Hamiltonian (1). Many calculations suggest that the intra-atomic parameters are reduced by roughly a factor of 2 [20]. To estimate the inter-atomic repulsion is more difficult, and estimates vary.

For finite hopping t, we can obtain semiquantitative estimates for the effective interaction by diagonalizing the two-site units involving the motion of the holes that are pushed away by the added holes (sites 2 and 3, and 4 and 5 in Fig. 1) [21]. Due to the existence of V_{00}, the motion of the hole on the left is going to be predominantly between sites 2 and 3 rather than including also sites 8 and 9, and similarly on the right. One finds, for example, that there is an optimum value for ϵ which increases with V. For the unit on the left, it is determined approximately by the condition $(V + \epsilon)n_6 \sim V$ which causes the effective energy of sites 2 and 3 to be equal (i.e. maximum resonance) when the first hole is added. The effective frequency of these polarizable side units is $\Delta E \cong 2\sqrt{(\epsilon/2)^2 + t^2}$, which is of the same order of magnitude as the band width, so that for small levels of doping ($\epsilon_F \ll \Delta E$) the effective interaction is essentially instantaneous.

Extensive cluster calculations in one- and two-dimensional geometries give detailed information on the parameter range where pairing will exist [5], and show that pairing can also occur for significantly smaller values of V than the previous analysis would suggest. Figure 2 shows one example of a phase diagram obtained from diagonalization of

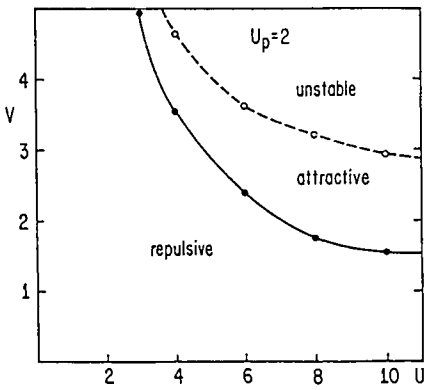

Fig. 2. Phase diagram obtained from diagonalization of a (12)-site Cu-O cluster with Hamiltonian (1). $t = 1$, $\epsilon = 0$, $V_{00} = t' = 0$

a twelve-site cluster [5]. The unstable region is defined as the region where a *third* added particle has a lower energy than if added elsewhere, indicating a tendency to clustering rather than superconductivity. We expect the region of attractive interaction to grow as the cluster size increases. It is difficult to assess whether the parameter regime where pairing is found in this model is realistic for the oxide materials. As we discuss in what follows, we believe there is another primary mechanism for pairing that is operative.

IV. A New Mechanism

Let us step back for a moment and evaluate the situation. Our numerical results have shown that magnetic mechanisms don't work, and that an anion-cation charge transfer mechanism is feasible in certain parameter ranges but perhaps much too specific. Many other specific models have been proposed, involving Cu d-d excitations, out-of-plane polarization, etc. And yet the experimental information that is accumulating suggests that the mechanism is not specific but rather universal. Let us consider the following selected experimental findings (most of which were highlighted at this meeting):

1. Spectroscopic evidence strongly suggests that holes are predominantly on O sites.
2. NMR results have beautifully shown that BCS-like superconductivity is due to O holes and that Cu sites are essentially *decoupled* as far as the superconductivity is concerned.
3. Hall coefficient measurements indicate that these materials are superconductors when the conductivity is hole-like, and non-superconductors when it is electron like.
4. Transient high temperature superconductivity has been observed in the past in CuCl and CdS.

These findings suggest that the essential physics of high T_c is contained in the simple fact that *conduction in these materials occurs through holes in anions with filled shells. Anions that normally do not form conductors but highly insulating solids.*

When theorists write down model Hamiltonians such as (1) they do not usually differentiate between electrons and holes. And yet nature makes an enormous difference between them. Recall that elements with one *electron* added to a closed shell ion are simple metals, while elements with one *hole* added to a closed shell ion are halogens that solidify onto a molecular, highly insulating solid. What is it that breaks particle-hole symmetry in nature and causes these two kinds of elements (say Na and F) to behave so differently?

A simple explanation is that an electron added to a closed-shell ion changes very little its "background," the states of the other electrons in the ion. A hole added to a closed-shell ion affects substantially its "background," by modifying the states of all the remaining electrons of the outer shell. This rearrangement of electrons in the outer shell is what causes F to solidify as a molecular insulating solid rather than as a simple metal like Na. It is also, I believe, the key to high temperature superconductivity.

Imagine one could create a monatomic solid with closed-shell ions (O^{--}, Cl^{-}, S^{--}, etc.) in a regular lattice structure (one atom per unit cell) and dope the system with a few holes. I claim the resulting system will obviously be a high temperature superconductor. The pairing interaction will arise from polarization of the outer shell by the holes, just as in the usual electron-phonon interaction case but inverted: the conducting particles have positive charge, and the background that provides the pairing (the outer filled shell) has negative charge. The dominant interaction is the *local atomic polarization* of the outer shell by the hole that goes into that same shell. Both interaction strength and energy scale are two orders of magnitude larger than for the electron-phonon case. As we discuss elsewhere [7], I believe there is substantial evidence that suggests that this basic mechanism is not restricted to high T_c oxides but plays also an essential role in "conventional" superconductors [22].

A Hamiltonian that contains the essential physics of high T_c has to describe this interaction of the hole with the outer filled O^{--} shell. The basic components will be the kinetic energy of the holes, a Coulomb interaction between holes, and the interaction between the hole and the outer filled shell. To a first approximation, the hole-ion interaction can be neglected. The Hamiltonian is then:

$$\begin{aligned} H &= \sum_{n,\sigma} \epsilon_k c^+_{k\sigma} c_{k\sigma} + \sum_{kk'q} V(q) c^+_{k+q\uparrow} c^+_{k'-q\downarrow} c_{k'\downarrow} c_{k\uparrow} \\ &+ \sum_{kk'\lambda} I^\lambda_{k-k'} c^+_{k'\sigma} c_{k\sigma} (b_{k'-k,\lambda} + b^+_{k-k',\lambda}) + \sum_{q\lambda} \omega_k b^+_{q\lambda} b_{q\lambda} \end{aligned} \tag{5}$$

where $c^+_{k\sigma}$ creates a hole in the outer O^{--} shell, and $V(q) = 4\pi e^2/q^2$ is the Coulomb repulsion between holes. $b^+_{i\lambda}$ creates an excitation in the outer filled shell, describing a transition of an electron to an orbital in the next shell, and λ labels the different excitations of the outer shell. Off-site interactions will be much smaller than on-site interactions so that the q dependence of I^λ_q is small. The Hamiltonian (5) is formally identical to an electron-phonon Hamiltonian but the parameters are electronic energies, of order several eV. Within the conventional theory of superconductivity we can derive an effective interaction

$$V_{eff}(q,\omega) = \frac{V(q)}{\epsilon(q)} + \sum_\lambda \frac{|I^\lambda_q|^2 \omega_\lambda}{\omega^2 - \omega^2_\lambda} \tag{6}$$

with $\epsilon(q)$ the dielectric constant of the hole gas, and a critical temperature using Eliashberg theory. Because the energy scale is large, however, it is not obvious that vertex corrections will not be important. We have found, however, in recent simulation studies [23] that Eliashberg theory gives reasonable answers even for phonon frequencies of the same order as electronic energies.

An even simpler model that contains the essential physics is obtained by modelling the states of the outer filled shell of the anion by a two-level system. The holes, when they are on a given anion, induce transitions between these polarization states of the cloud. The Hamiltonian is:

$$H = \sum t_{ij} (c^+_{i\sigma} c_{j\sigma} + h.c.) + \alpha \sum_{i\sigma} \sigma^i_x n_{i\sigma} + \omega \sum_i (\cos\theta \sigma^i_x + \sin\theta \sigma^i_z) + U_0 \sum_i n_{i\uparrow} n_{i\downarrow}. \tag{7}$$

Estimates for ω, α and θ can be obtained from atomic physics calculations. ω and α are of order several eV. θ is an important parameter because it determines the band-narrowing due to the hole-cloud interaction, similarly to the situation for small polarons: for $\omega \ll \alpha$, the bare hopping of holes through the O^{--} network t_{ij} is renormalized to $\tilde{t}_{ij} = t_{ij} \cos^2 \theta/2$. The direct O-O hopping has been estimated by McMAHAN et al. [20] to be 0.65 eV, and there will be an additional contribution from hopping through the cations. For definiteness we will take $\theta = \pi/2$ in what follows. U_0 is the bare Coulomb repulsion between two holes on the same anion.

The effective interaction for two holes on the same anion is:

$$U_{site} = E_0^1(2) + E_0^1(0) - 2E_0^1(1) + U_0 \tag{8}$$

with

$$E_0^1(n) = -\sqrt{\omega^2 + \alpha^2 n^2 + 2\omega\alpha n \cos\theta} \tag{9}$$

and we know from atomic physics that $U_{site} > 0$ for any anion, in particular, as mentioned, the bare $U_{site} \sim 10$eV for O. However, when we allow the holes to hop between different anions the effective interaction between holes can be negative for parameters where $U_{site} > 0$. We have diagonalized the Hamiltonian (7) on lattices of size 2, 4 and 8 sites [24]. Figure 3 shows one example of the effective interaction between 2 holes

$$U_{eff} = E_0(2) + E_0(0) - 2E_0(1) \tag{10}$$

for various cases. We find that there is a wide range of parameters where the effective interaction is attractive, even for large on-site repulsion (up to $U_0 \sim 3\alpha$ on the 8-site system for some ω's). An extra added particle is found not to bind so that the system is stable.

The fact that the effective interaction becomes more attractive as the cluster size increases suggests that this mechanism is most effective for small doping: in our 8, 4 and 2-site clusters two particles correspond to band filling $\rho = 0.25$, 0.5 and 1 respectively. We also find that as more particles are added to the 8-site cluster the range of parameters where the effective interaction is attractive decreases [24]. This suggests that superconductivity will be lost for too high doping.

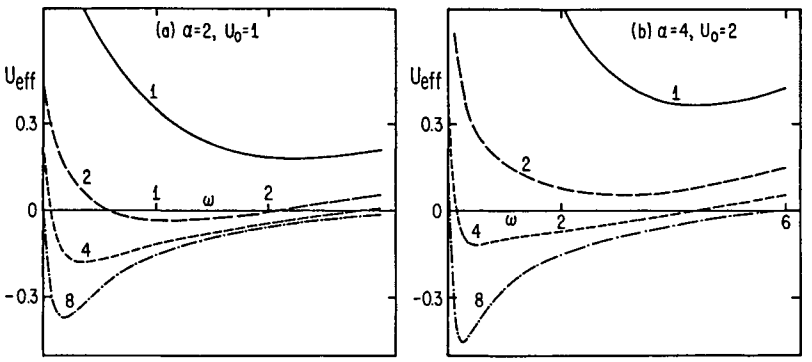

Fig. 3. Effective interaction for 2 particles for the Hamiltonian (7) on clusters of various sizes (indicated by the number next to the curve). $t = 1$, $\theta = \pi/2$

For small levels of doping and large energy scale ω we can model the system by an even simpler Hamiltonian, the Hubbard model with an *attractive* instantaneous interaction $U < 0$. Monte Carlo simulations of the two-dimensional attractive Hubbard model show large enhancement of the s-wave pair susceptibility

$$P = \int_0^\beta d\tau \langle \Delta(\tau)\Delta^+(0)\rangle \tag{11}$$

$$\Delta = \frac{1}{N}\sum_k c_{k\uparrow}c_{-k\downarrow} \tag{12}$$

as U becomes more negative, as expected, although not as large as predicted by BCS theory. An example is shown in Fig. 4(a), for band filling $\rho = 0.5$ and interactions $U = 0$, -2 and -4 (in units where the hopping is 1). Figure 4(b) shows the behavior of P for different values of the chemical potential and hence band filling for the case $U = -4$. To extract the two-dimensional critical temperature is difficult and requires simulations on larger lattices. However, we can obtain the transition temperature for three-dimensional superconductivity in the presence of a weak hopping between planes $t_\perp$ within a random phase approximation from the condition [25] $1 = (2t_\perp^2/|U_{eff}|)P$, where P is the in-plane pair susceptibility, (11). The inset in Fig. 4(b) shows the critical temperature versus doping obtained in this fashion for one case. Although the parameters are not realistic it illustrates the general behavior: T_c increases as $n^{1/2}$ with doping. As mentioned above, however, for too high doping the effective interaction itself will cease to be attractive and T_c will drop. Another consequence of high doping is of course that when two holes are on the same O^{--} they yield neutral O that tends to leave the sample, rendering the system unstable.

We expect also the normal state properties to be significantly altered by the hole-cloud interaction; in particular, for $\theta \to \pi$ in (7) significant band narrowing will occur, leading to a small "electronic polaron." SCALAPINO et al. [26] have discussed in detail how a polaron model can explain several of the normal state properties of the high T_c oxides.

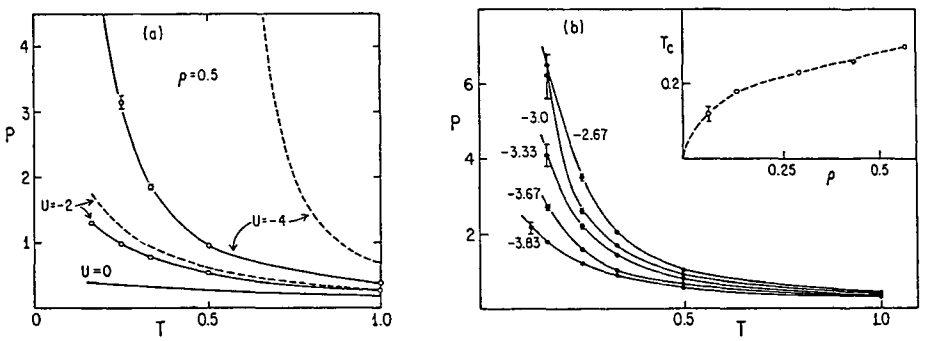

Fig. 4(a). S-wave pair susceptibility P versus temperature for an attractive Hubbard model on a 6 × 6 lattice, 1/4 filled band. The dashed lines are results of BCS theory. (b) P versus temperature for various band fillings for $U = -4$. The number next to each curve indicates the chemical potential. The inset shows T_c versus band filling (doping) obtained from these data as described in the text for the case $t_\perp/t = 0.9$

To summarize, we believe that the experimental evidence points towards a model of the high T_c materials where conduction occurs via holes in the O network and the only role of the cations is to make this situation possible by stabilizing an otherwise unstable structure. We have argued that conduction by holes in closed-shell anions will necessarily lead to high temperature superconductivity, and discussed some results of model calculations. We also argued that the model can explain the anomalous normal state properties of the high T_c oxides. It will be difficult to prove this model to be correct over a variety of other models involving charge fluctuations, but I believe just its simplicity and universality make it compelling. Perhaps the most convincing proof will come only when material scientists find high T_c superconductivity in a wide variety of materials whose only common characteristic will be that conduction occurs through holes in closed shell anions of elements in the right portion of the periodic table.

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