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VALENCE-FLUCTUATION SCENARIO FOR CUPRATE SUPERCONDUCTIVITY: THE FINITE-U PAIRING MECHANISM

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INTRODUCTION

The idea that the normal state of cuprate superconductors is a valence-fluctuation (VF) state is appealing for a number of reasons. We are exploring this scenario quantitatively,[1] focussing especially on the finite-U mechanism[2] for s-wave pairing. The calculations employ a many-body variational technique developed previously for VF and heavy-fermion materials.[3] We are presently exploring the effects of (a) varying the Hamiltonian parameters away from the values obtained from photoemission data analysis,[1] (b) various simple assumptions for the band structure and hybridization k-dependence, and (c) corrections to the Gutzwiller approximation. These are the topics to be discussed in this report.

ARGUMENTS FOR A VALENCE-FLUCTUATION PHASE

There are several good reasons to expect that the electronic state of a cuprate superconductor above T_c may be a valence-fluctuation state. At the outset, we note an obvious lesson from band theory and general solid-state chemistry: The 3d and 2p electrons are *both* close to the Fermi level, so it is appropriate to consider both types of orbitals explicitly within the model Hamiltonian. This leads to an Anderson lattice model (or multi-band Hubbard model), similar to the usual starting point for VF or heavy fermion studies. This immediately suggests the VF phase as a candidate to be explored. (It should be noted that the heavy fermion state is basically the same as the VF state, but in a region of parameter space where the effective mass enhancement is considerably larger.)

The VF picture leads directly to a *normal Fermi liquid*, for the state above T_c, with quasiparticles satisfying the Luttinger sum rule. Futhermore, this involves a "renormalized band" or "renormalized hybridization" type of effective band structure, for the quasiparticle spectrum. Many physical properties should therefore be interpretable via the conventional band theoretic recipes, perhaps with minor modifications due to the renormalization.

There are two ways to qualitatively understand this normal Fermi liquid result. One way is to argue that a large U generates local moments on the copper ions, and then the oxygen 2p electrons cancel these moments by Kondo screening. One then obtains a normal Fermi liquid because there are, effectively, no local moments to disrupt the elementary Bloch periodicity. Although quite correct, this description has the disadvantage of suggesting that we are dealing with an exotic scenario. We now want to argue that this is not so.

An equivalent but very pedestrian way to visualize this result is to start with the $U=0$ solution of the Anderson lattice Hamiltonian. This gives an elementary band-theoretic state, which is obviously a Fermi liquid. We then invoke the idea of Luttinger continuity, i.e., we suppose that U is switched on adiabatically, and that the system evolves continuously without any phase change. The result is therefore a strongly-correlated normal Fermi liquid -- the valence-fluctuation state. The large number of known VF and heavy-fermion materials demonstrate that this scenario is physically reasonable. It must be admitted, however, that there are no well-established previous examples of the VF state in which 3d electrons are the active ingredient.

With either version of the argument, one can see that the 2p orbitals play an essential role in promoting the assumed normal Fermi liquid state. The itinerancy or metallic aspect is provided by the 2p's, because the various models typically neglect any direct hopping between the 3d Wannier orbitals. On the other hand, the Anderson lattice model is flexible enough to permit formation of local moments, and even a Mott-insulator state (at proper stoichiometry), if this is what the system would prefer.

Experimentally, one of the most striking features of the cuprate superconductor materials is the existence of a Fermi surface in close agreement with the prediction of conventional band theory, as revealed by angle-resolved photoemission. Band theory is not fully successful, however, because this data also indicates weaker dispersion in the vicinity of ϵ_F, i.e. some "heaviness." The band-theoretic Fermi surface, together with some heaviness, is a typical signature for the known VF and heavy-fermion materials. In addition, there are a number of other physical properties for which striking parallels have been found between cuprate superconductors and heavy-fermion materials. These have recently been reviewed by Levin and co-workers.[5] All together, this experimental evidence supports the VF picture very strongly. Recent calculations by Newns and co-workers[6] have also demonstrated quantitative consistency of this picture with a number of cuprate properties, in a fairly *ab initio* manner.

The assumed absence of local moments should be contrasted with the physics of the t-J model, where the use of the J parameter presumes the existence of local moments. This contrast leads to a further implication of the present scenario: There should probably be a first-order phase boundary between the local-moment phase of $La_{2-x}Sr_xCuO_4$ at small doping, and the VF phase at higher doping. This is not seen experimentally, however, at least not clearly. We presume that this is due to local inhomogeneity in the Sr concentration, leading to a range of doping x with both phases coexisting on a microscopic scale. This might, for example, be the explanation for the so-called spin glass region. We note that other speakers at this workshop have also suggested coexisting phases on a microscopic scale, although with differences in the details.[7] Our present scenario envisages just one phase, essentially homogeneous, throughout the region of well developed superconductivity.

THE FINITE U PAIRING MECHANISM

Possible mechanisms for pairing within the VF phase have long been studied, with the goal of understanding the heavy fermion superconductors. Apart from some phonon proposals, most of this work has been based on the 1/N or slave boson expansion. However, the resulting mechanisms involving exchange of one slave boson[8] $[O(N^{-1})]$ or two slave bosons[9] $[O(N^{-2})]$ can provide d or p wave pairing, but *not* s wave pairing. There is only one known electronic mechanism which can produce s wave pairing within the VF phase, the "two hole resonance" mechanism of Newns,[2] so this is the one we are studying. This arises because of the *finiteness* of U, i.e.,

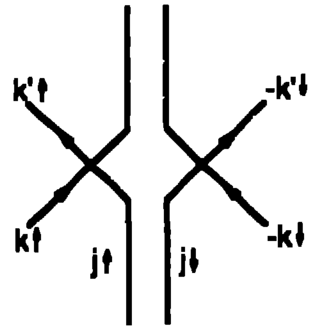

Figure 1. Diagram illustrating the finite-U mechanism for s-wave pairing.

the fact that in a real material $U^{-1} \neq 0$. (In contrast, nearly all of the 1/N expansion work has assumed that $U=\infty$, $U^{-1} = 0$.) This Newns mechanism also has a very convenient feature -- it arises already at the "mean field" or "renormalized band" stage of approximation, corresponding to $(1/N)^0$ or no slave-boson exchanges. This is a welcome simplification, which in practice should enhance the reliability of the numerical results.

This finite-U pairing mechanism is illustrated in the diagram of Fig. 1. Here the vertical lines represent occupied $d(x^2\text{-}y^2)$ Wannier orbitals (of spin ↑ and ↓) at a copper site j. (The other eight d orbitals are assumed to be inert and fully occupied.) The sloping lines represent "conduction" orbitals, in the language of VF theory. These are Bloch functions constructed from the oxygen 2p orbitals. In the present case these 2p Bloch functions are components (projections) of Landau-Luttinger quasiparticle states, so this diagram represents an interaction between quasiparticles. The quantum numbers shown for these quasiparticles correspond to annihilation of one Cooper pair $(k\uparrow, -k\downarrow)$, and creation of another pair $(k'\uparrow, -k'\downarrow)$ so this process constitutes a pairing interaction $V_{k'k}$.

One can see here that the d^8 intermediate state plays the role of an exchanged boson. From another point of view this might be described as a charge-transfer mechanism, because it involves p-d transitions, but it is essential to recognize that this involves the *correlated* action of two electrons (of spin ↑ and ↓) doing this simultaneously. Hence the name "two-hole resonance."

Letting M denote the effective matrix element for the two electron dd →(k, k) transition, the net effect of the second order process shown is $|M|^2$/(negative denominator) : *attractive*, as desired. This is quite appealing. But this also presents a problem. The mechanism appears to work "too well," suggesting that high temperature superconductivity should be a common phenomenon. We shall see, however, that this process is accompanied by an opposing mechanism, and that it is not at all easy for the Newns pairing to win in the resulting competition.

RENORMALIZED HYBRIDIZATION

Our present version of the Anderson lattice Hamiltonian is

$$H = \sum_{k\sigma} \varepsilon_k \hat{n}_{k\sigma} + \varepsilon_d \sum_{j\sigma} \hat{n}_{j\sigma} + U \sum_j (1-\hat{n}_{j\uparrow})(1-\hat{n}_{j\downarrow})$$

$$+ \sum_{kj\sigma} (v_{kj}\, \eta^{\dagger}_{k\sigma}\, \eta_{j\sigma} + h.c.)\,, \tag{1}$$

where $\hat{n}_\alpha = \eta^{\dagger}_\alpha \eta_\alpha$ is a number operator. Here $\alpha = k\sigma$ refers to a "conduction" Bloch orbital composed of oxygen 2p orbitals, with a dispersion width for ε_k amounting to several eV due to the considerable direct pp orbital overlap. On the other hand, $\alpha = j\sigma$ refers to a $d(x^2\text{-}y^2)$ Wannier orbital for a copper ion at site j. The direct dd overlap is surely small, and is neglected. Note that the Hubbard U is assumed to act between 3d *holes*, so it is the d^8 (two-hole) configuration energy which is raised by U. (We start with a Wannier representation for the d's to facilitate the treatment of U, but the resulting recipe is later transformed to the Bloch representation.)

As already mentioned, the solution of this Hamiltonian is elementary when U=0. This becomes a simple two-band hybridization problem, in which the 3d's constitute a band of zero width. The hybridization matrix element connecting the p and d Bloch basis states is $V_k = N^{-1/2} \sum_j e^{-ik\cdot R_j} v_{kj}$, where this N is the number of copper sites. In the mean-field approximation, the effect of replacing U=0 by U=∞ is to leave this simple picture intact, but to renormalize the input parameters:

$$\varepsilon_d \rightarrow \tilde{\varepsilon}_d\,, \tag{2}$$

$$V_k \rightarrow \tilde{V}_k = V_k\, Z^{1/2}\,, \tag{3}$$

where $0 < Z < 1$.

Unfortunately, the VF literature has presented two recipes for the renormalization parameter Z, without providing a compelling reason for choosing either one over the other. These rivals are the so-called mean field recipe,

$$Z_{mf} = 1 - n_f\,, \tag{4}$$

and the Gutzwiller recipe,

$$Z_G = (1-n_f)/(1-n_{f\sigma})\,. \tag{5}$$

(Here we use the familiar notation of the VF literature, referring to the f electrons of a cerium compound. For cuprates, the average f *electron* number n_f, at a single site, should be replaced by the d *hole* number.) We have studied this problem in considerable detail,[10] and have concluded that the Gutzwiller version (5) is physically more correct. This conclusion was obtained, independently, from a variety of separate studies, including (a) exactly-solvable test cases, (b) few-site systems, (c) combinatoric analysis, (d) diagrammatic analysis, and (e) the requirement of correct behavior in the $U \rightarrow 0$ limit. Since we are now concerned with the effects of finite U, the last of these considerations seems particularly significant. In terms of actual calculations, however, the diagrammatic approach has proved to be most useful.

Using a linked cluster diagrammatic analysis,[11] we had previously obtained the mean field version (4) by ignoring the restriction that in a diagram with several sites, all of the site indices (j, j′, j″, ...) must be distinct. We later managed to incorporate this site exclusion feature, and thereby obtained the extra factor $(1-n_{f\sigma})^{-1}$ seen in (5).[10] Still later, this recipe was extended to the case of finite U.[1] For finite U this recipe for Z differs somewhat from previous Gutzwiller treatments of the Anderson lattice, but ours has the virtue of summing a well-defined class of diagrams. Examination of the diagrams still omitted shows that this recipe is generally still inexact, although this does become exact in some special cases.

The choice between recipes (4) and (5) has profound consequences for the understanding of cuprate superconductivity. In the mean-field version (4), there is ***no*** interaction between the quasiparticles when U=∞, and finite U then provides superconductivity. [However, the 1/N correction (exchange of one slave boson) opposes s-wave superconductivity, so the final outcome is still not trivial.] In the Gutzwiller version (5), the explicit spin dependence in the $(1-n_{f\sigma})^{-1}$ factor leads to a very strong Stoner enhancement of the magnetic susceptibility, and this "Gutzwiller magnetism" tendency now strongly opposes the "Newns pairing" tendency. (This agrees, of course, with the general experience that magnetism is bad for s-wave superconductivity.) The result is that we now find it rather difficult to obtain superconductivity.

STRATEGY AND CALCULATION TECHNIQUE

We are considering only isotropic band models, in which the ε_k and V_k depend only on the magnitude $|k|$ and not the direction $\hat{k}$. This is convenient here because the "Gutzwiller magnetism" and "Newns pairing" aspects then ***both become purely s-wave effects***, in the sense of Landau. The net result of their competition can therefore be described by means of a single parameter, the Landau F_o^a. The static magnetic susceptibility takes the form

$$\chi = \frac{\mu_B^2 \rho_{qp}(\varepsilon_F)}{1 + F_o^a} , \tag{6}$$

and thus through study of χ we can determine F_o^a. Now suppose that F_o^a turns out to be positive. If we further assume that the effective pairing matrix element $V_{kk'}$ is constant throughout the Brillouin zone, and likewise that the quasiparticle state density is independent of energy, we obtain the simple result

$$k_B T_c \approx \frac{1.14}{\rho_{qp}(\varepsilon_F)} e^{-\frac{1}{F_o^a}} . \tag{7}$$

This recipe for T_c is admittedly very crude, and of course it can be refined. (We have made some progress here.) This does show, however, that for initial exploration it makes sense to merely calculate χ and $\rho_{qp}(\varepsilon_F)$, and see whether the resulting F_o^a is positive. This F_o^a should be reliable as a guide to track whether various parameter changes or other modifications are beneficial or harmful for the superconductivity. A lot can be learned by guiding F_o^a from an initially large negative value towards a positive value.

The actual calculations are based on a many-body variational technique.[1,3] This is patterned after the variational approach of BCS, although we adapt and apply the technique to the assumed ***normal*** Fermi liquid VF ground state. A trial many-body wavefunction Ψ is constructed in which there is one free parameter for each Bloch state kσ within the Brillouin zone, plus one extra parameter to control the amount of d^8 component in the ground state.[1] We then obtain an analytic expression for ⟨H⟩ via partial summation of a linked cluster diagrammatic expansion.[11] Although there are approximations in the choice of Ψ and in the evaluation of ⟨H⟩, the subsequent steps of optimizing the variational parameters, followed by the evaluation of χ, are carried out exactly, i.e. with no further approximations. This aspect is significant in view of the strong-coupling nature of the present problem.

RESULTS AND DISCUSSION

The F_o^a results in our initial publication[1] are, unfortunately, invalid due to a bug in this part of the program. When corrected, the F_o^a remained strongly negative (and usually <1, implying magnetic instability) for all reasonable choices of inpu parameters.

This could of course be a sign that the present approach is simply wrong or inappropriate for the cuprate superconductors. We doubt this conclusion, for several reasons: (1) For the conceptual and experimental reasons already discussed, it appears most likely that the normal state (above T_c) is actually a VF state. (2) The many-body variational technique is quite refined, and appears to be adequate for the task at hand. (3) If one grants that we are dealing with a VF state, which arises from a substantial U parameter, then $(-F_o^a) > 0$ corresponds to the effective or screened Coulomb parameter μ^* of the McMillan formula. Thus, a large negative F_o^a would constitute a serious obstacle which any other mechanism (e.g. phonons) would be required to overcome. It is therefore quite inappropriate to simply give up and ignore this problem.

A further motivation is the fact that rare-earth intermetallic compounds typically have local moments, which is consistent with a large negative value for F_o^a. Nevertheless, the nonmagnetic (Pauli paramagnetic) VF and heavy-fermion materials demonstrate that this is not always the case. One of the main problems remaining for VF theory is to explain how this magnetic-nonmagnetic phase boundary is determined, or in terms of the present study, what it is that can counteract the Gutzwiller magnetic tendency. The previous understanding of this phase boundary has been based on the competition between two effects[12]: the Kondo screening (included here), which opposes magnetism, and the RKKY coupling (omitted here), which promotes magnetism. [An RKKY interaction arises from the model Hamiltonian (1), via the $(1/N)^2$ correction.[9] In reality, however, part of the effective coupling between the 3d's and 2p's is due to the Fock exchange between these orbitals, which is omitted from (1).] We now emphasize that the Gutzwiller magnetism and Newns pairing tendencies are *also* very important for this issue, as well as emphasizing that this issue is related to cuprate superconductivity.

Our first stratagem to resolve the numerical discrepancy was to study corrections to the Gutzwiller approximation (5). We identified the leading diagrams omitted from our finite-U version of the Gutzwiller renormalization, and included them in the parameter self-consistency and the evaluation of χ. Their effect was rather small, and of the wrong sign.

We next observed that the assumed band structure model for these studies was extremely crude: V_k independent of k, and $\rho(\varepsilon_k)$ = constant (rectangular state density for the ε_k's). This model has often been used in VF studies, because the required Brillouin-zone integrals become elementary. It turns out that a number of other simple band models can also be integrated analytically, and we are presently exploring some of these. In an actual CuO_2 layer, most of the antibonding band dispersion is due to the k-dependence of V_k, rather than to the ε_k dispersion. Some of the simple models are obtained by attributing *all* of the quasiparticle dispersion to a sinusoidal k-dependence for V_k, using ε_k = constant. [There is more than one model of this type, due to different possible assumptions for the density of states $\rho(k)$.] This modification greatly improved the results. Further refinement in this vein is possible, including for example a logarithmic singularity in the state density to mimic the van Hove singularity. We expect this to make the pairing interaction matrix element a bit more attractive (or less repulsive), besides increasing its state density prefactor. Our general variational method can in principle deal with a real band structure, to be integrated numerically (as for example in Ref. 6), but it seems premature to take this step.

We have also varied the Hamiltonian parameters away from the values obtained by analyzing CuO photoemission data.[13] It is very helpful to make both U and Δ much smaller. ($\Delta = \varepsilon_d - \varepsilon_p$ is the "charge-transfer energy," where ε_p is the centroid of the hybridizing 2p band states.) Our present inclination is that $U \approx 3.5$ eV and $\Delta \approx 4$ eV may be reasonable values here, even though our photoemission analysis[13] gave U = 7.0 eV, Δ = 7.55 eV. We attribute most of this major difference in U to the effect of metallic screening in the VF phase. (CuO is a Mott insulator.) We attribute this also, to a much lesser extent, to a screening renormalization from the eight other d orbitals which are omitted from the model of Eq. (1). Metallic screening should also tend to reduce Δ, but it is difficult to estimate by how much. The present guess for Δ is simply the value obtained phenomenologically by Newns and co-workers,[6] and is not much greater than values obtained from band-theoretic supercell calculations.[14] (We measure Δ from the centroid of the $b_{1g} = x^2 - y^2$ hybridization strength distribution for the oxygen 2p's, about 1 eV above the 2p band center, while other authors refer Δ to the center or to the top of the 2p band.)

Another parameter change appears to be essential here. To obtain sufficient satellite intensity in the CuO photoemission analysis, we found it necessary to assume a stronger hybridization interaction ($t_{pd\sigma} = -1.9$ eV) for the d^8-d^9 transitions than for the d^9-d^{10} transitions ($t_{pd\sigma} = -1.45$ eV). Sawatzky and co-workers[15] had earlier found photoemission evidence for such a charge-dependence of $t_{pd\sigma}$, and Martin[16] had also found this in his *ab initio* cluster calculations. By taking Martin's value for d^8-d^9 ($t_{pd\sigma} = -2.3$ eV), the U and Δ values just mentioned, and a band model with V_k dispersion, we have finally obtained attractive pairing of a reasonable magnitude. This work is still in a preliminary stage, however, and we are not ready to claim that these values are realistic.

Two other issues should be mentioned. In Ref. 1 we mentioned the finding of Houghton and Sudbø,[17] that coupling to the *bonding* quasiparticle band influences the pairing interaction, namely, the effective interaction between the quasiparticles of the *antibonding* band (the band which intersects ε_F). It turns out that our variational treatment takes care of this automatically, so no correction is needed on this account. Secondly, the previous Anderson-lattice studies[8,9] have found that the $(1/N)^1$ correction (from exchange of one slave boson) has a very significant effect on χ. Specifically, this 1/N correction amounts to $\delta F_0^a \approx -0.5$. Such a large and negative shift of F_0^a could be very difficult to cope with in the present scenario. We note, however, that this result was obtained for U=∞, with a highly simplified band structure, and without considering any Gutzwiller factors of the $(1-n_{f\sigma})^{-1}$ type. A more realistic evaluation of the 1/N correction could conceivably give a quite different result. We intend to explore this.

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REFERENCES

1. B. H. Brandow, Solid State Commun. **69**, 915 (1989).
2. D. M. Newns, Phys. Rev B **36**, 2429 and 5595 (1987); D. M. Newns, M. Rasolt, and P. C. Pattnaik, *ibid.* **38**, 6513 (1988).
3. B. H. Brandow, Phys. Rev. B **33**, 215 (1986) and **37**, 250 (1988).
4. B. H. Brandow, J. Solid State Chem. **88**, 28 (1990).
5. K. Levin, Ju H. Kim, J. P. Lu, and Qimiao Si, to appear in Physica C.
6. D. M. Newns, P. C. Pattnaik, and C. C. Tsuei, Phys. Rev. B **43**, 3075 (1991).
7. See the reports of R. S. Markiewicz, J. C. Phillips, and J. M. Tranquada, this proceedings.
8. A. Auerbach and K. Levin, Phys. Rev. Lett. **57**, 877 (1986); M. Lavagna, A. J. Millis, and P. A. Lee, *ibid.* **58**, 266 (1987).

9. A. Houghton, N. Read, and H. Won, Phys. Rev. B **37**, 3782 (1988).
10. B. H. Brandow, unpublished.
11. B. H. Brandow, J. Magn. Magn. Mat. **63-64**, 264 (1987).
12. S. Doniach, Physica **91B**, 231 (1977).
13. B. H. Brandow, J. Solid State Chem. **88**, 28 (1990).
14. A. K. McMahan, R. M. Martin, and S. Satpathy, Phys. Rev. B **38**, 6650 (1988); A. K. McMahan, J. F. Annett, and R. M. Martin, *ibid.* **42**, 6268 (1990); M. S. Hybertsen, M. Schluter, and N. E. Christensen, *ibid.* **39**, 9028 (1989).
15. J. Ghijsen *et al.*, Phys. Rev. B **42**, 2268 (1990).
16. R. L. Martin, Physica B **163**, 533 (1990), and private communication.
17. A. Houghton and A. Sudbø, Phys. Rev. B **38**, 7037 (1988).