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HIGHLY ANISOTROPIC BUT NODELESS GAP FROM A VALENCE-FLUCTUATION PAIRING MECHANISM

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ABSTRACT - We have refined and quantitatively explored a valence-fluctuation pairing mechanism, the finite-U mechanism introduced by Newns. This can provide an s-like (nodeless) gap. We use an Anderson-lattice Hamiltonian, with realistic parameter values derived from photoemission and BIS data. The Landau-Luttinger quasiparticle spectrum and the pairing interaction are obtained from a many-body variational formalism. Adequate pairing attraction is obtained, together with band narrowing (mass enhancement) and an extremely short coherence length, in reasonable agreement with experiment. These fully self-consistent results were obtained with an isotropic approximation to the band structure of a single CuO₂ plane. Now, using a simplified treatment for a more realistic band structure, we find that the gap has strong in-plane anisotropy, although it should probably still remain nodeless. This conclusion is consistent with a variety of data.

Keywords: gap anisotropy, valence-fluctuation mechanism

INTRODUCTION

We have explored and developed a valence-fluctuation (VF) scenario for cuprate superconductivity (Brandow 1989, 1993). This is based on the finite-U pairing mechanism introduced by Newns (1987, 1988), which can provide s-like (nodeless) pairing. This approach is supported by strong experimental evidence (described below) that the "normal" (above-T_c) state of the cuprate superconductors should actually be a VF or heavy-fermion-like state. An important conclusion from this study is that the gap should have very strong in-plane anisotropy, although it should probably still remain nodeless. There is considerable experimental evidence that the gap does have this form.

Our quantitative work is based on an Anderson lattice Hamiltonian for a single CuO₂ plane, with realistic parameters deduced from photoemission and BIS data (Brandow 1990, 1992). The Landau-Luttinger quasiparticle spectrum and the pairing interaction are obtained from a variational many-body formalism (Brandow 1986), and the gap equation of BCS is then solved with these ingredients. A second-order perturbation argument (to order 1/U) is easily seen to provide an attractive pairing interaction. However, a self-consistent treatment at the mean-field or (1/N)⁰ level of approximation reveals that this pairing tendency is overwhelmed by a strong magnetic tendency arising from a Gutzwiller form of hybridization renormalization, so that pairing does not seem possible for realistic input parameters. Motivated by this failure, together with the indications that the basic scenario is sound, we have recently extended this finite-U lattice treatment to formal order (1/N)¹ (Brandow 1993). We discovered that the lattice aspect plays a major and unexpected role here. In a suitable parameter regime this leads to a strong suppression of the magnetic tendency, and thus we are now able to obtain adequate pairing attraction for realistic Hamiltonian parameter values. Other important results are an adequate band narrowing (mass enhancement or heaviness), and an extremely short coherence length (~ 4 lattice spacings), in reasonable agreement with experiment. We also find a strong quasiparticle interaction at the Fermi surface, consistent with the high normal-state resistivity. Other recent studies have demonstrated that such a strong quasiparticle interaction, together with the proximity of the Fermi level to the van Hove singularity, can account for the remarkable linearity of the resistivity (Pattnaik *et al.* 1992, Gopalan *et al.* 1992).

These favorable results were obtained with a fully self-consistent treatment, based on an isotropic approximation to the band structure for a single CuO₂ plane. The resulting gap was therefore isotropic. Subsequently, using a simplified treatment for a more realistic band model, we have found that the gap should actually have very strong in-plane anisotropy. It appears that the gap should still remain nodeless, although our present treatment is too crude to make this a firm prediction.

A curious and intriguing correlation (T_c ~ n/m*) has been found between the cuprate superconductors and a number of other "exotic" superconductors, by Uemura *et al.* (1991). (These other exotics include oxides without copper, and A-15, Chevrel, C₆₀, organic, and heavy-fermion compounds.) Although we do not understand this specific Uemura correlation, we note that the typical features of these other

superconductors include remarkably short correlation lengths and anomalously high resistivities. We therefore suggest that the same mechanism may be active in all of these other exotic superconductors, in addition to the conventional phonon mechanism.

Most of this work is described elsewhere (Brandow 1993). After an overview we therefore focus here mainly on the gap anisotropy, and how this emerges from the present mechanism, since this was only briefly mentioned previously.

OVERVIEW: THE SCENARIO AND THE THEORY

It is well known that angle-resolved photoemission has revealed Fermi surfaces in generally good agreement with conventional band theory. In contrast, however, the quasiparticle dispersions near ϵ_F are considerably smaller than in band theory. This combination of features is a typical signature of the VF or heavy-fermion state. In our view this is the strongest and most direct evidence for the VF state, as the above- T_c state from which the superconductivity emerges. There is also much supporting evidence from similarities in many other properties (Levin *et al.* 1991), and there has also been considerable progress in explaining some of these other properties within the VF framework. It is also noteworthy that the VF state can be viewed as the adiabatic transform or analytic continuation of the conventional band-theoretic state, as the Hubbard U is switched on gradually. We therefore argue that the VF state is the *least exotic* of the various strongly-correlated states which have been proposed. We regard this as an important plausibility argument.

Some further aspects of this scenario should be mentioned: (1) There is a major discrepancy between the strong electron-phonon coupling ($\lambda \sim 1.5$) obtained from band-theoretic calculations, and the weak coupling ($\lambda \sim 0.3$) deduced from the lack of saturation of the resistivity at high temperatures. This paradox is at least partially resolved by the finding that λ is considerably reduced by the strong (U -induced) correlations within the VF state (Kim *et al.* 1991). (2) The large and linear resistivity can be explained within the present framework, as already mentioned, so this need not be viewed as evidence for a fundamental failure of Fermi liquid theory. (3) Using $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ as a prototype, we find $1+x$ holes in the VF state, in contrast to the x holes with respect to the Mott (insulating and magnetic) parent state. This striking difference leads us to expect a first-order transition with respect to x . This is not seen experimentally, however. We attribute this to inhomogeneity in the Sr distribution, leading to a limited range of x in which these two phases coexist on a microscopic scale.

For a quantitative many-body treatment we use a variational approach, which is applied to an assumed *normal* ground state. This involves the following steps: (a) A trial many-body wavefunction Ψ is chosen to describe the normal ground state. (b) An analytic expression is obtained for $\langle H \rangle$, as a function of the variational free parameters, by means of an approximate diagrammatic summation. (c) The free parameters are all fully optimized, by an analytic and numerical method. (d) A functional differentiation with respect to quasiparticle occupation numbers provides the quasiparticle energy spectrum, according to the Landau definition $E_{k\sigma} = \delta \langle H \rangle / \delta n_{qp}(k\sigma)$. (e) A second differentiation provides the $f(k\uparrow, k'\downarrow)$ quasiparticle interaction, for all k, k' in the Brillouin zone. Finally, the pairing interaction $V_{kk'}$ is deduced from this Landau interaction, and the BCS gap equation is solved using this $E_{k\sigma}$ and $V_{kk'}$. We emphasize that steps (c), (d), and (e) are done exactly, subject only to the approximations in steps (a) and (b). This self-consistency feature is important because of the strong-coupling nature of this problem. The formal order in $1/N$ enters here through the choice of configurations allowed in Ψ ; we follow the finite- U classification scheme of Gunnarsson and Schonhammer (1985) here, since our work can be viewed as a lattice version of their treatment for a single Anderson impurity.

Our Anderson lattice Hamiltonian is based on the $[3d(x^2-y^2), 2p_x, 2p_y]$ tight-binding band model. For the fully self-consistent calculations we have simplified this band structure, using a *single* (orbitally nondegenerate) $2p$ band representing the combination of p_x, p_y orbitals (p - p antibonding) which hybridizes with the $3d$'s. This single band (the "conduction" band in VF terminology) is fitted to the corresponding p_x, p_y band along the $(1,1)$ direction. Its dispersion is therefore $\epsilon_k = \epsilon_p^0 + W_p S_k^2$, where $S_k = \sin(k\pi/2)$, and the dimensionless k ranges from 0 to 1. Its hybridization coupling to the $3d$ Bloch state is $V_k = V_0 S_k$. This band structure (ϵ_k, V_k) is then assumed to be isotropic in the plane. To obtain a reasonable one dimensional representation we introduce a k -state density $d(\# \text{ } k \text{ states}) = d(S_k^2)$, to mimic the linear-in- k behavior of the actual planar state density near $k \approx (0,0)$ and $k \approx (1,1)$.

The resulting quasiparticle energy spectrum is very similar to the corresponding tight-binding band theory. The main difference is a reduced bandwidth, now of order 1.0 - 1.5 eV, instead of the 3.5 eV typical of conventional band calculations for the p-d antibonding band.

GAP FUNCTION AND GAP ANISOTROPY

The pairing interaction obtained from this isotropic band model is approximately of the form $V_{\mathbf{k}\mathbf{k}'} = -a + bS_{\mathbf{k}}S_{\mathbf{k}'}$, with a and b positive and quite large (several eV). The resulting gap function is therefore of the form $\Delta_{\mathbf{k}} = a' - b'S_{\mathbf{k}}$ (a' and b' positive), being positive and large (~ 0.2 eV) at $\mathbf{k} = 0$, and having a node slightly above k_F . The roughly linear behavior, $|\Delta_{\mathbf{k}}| \sim |\mathbf{k} - \mathbf{k}_F|$, over much of the Brillouin zone, leads to the striking result that $\Delta_{\mathbf{k}}/E_{\text{BCS}_{\mathbf{k}}}$ is distributed rather uniformly throughout the entire Brillouin zone. (There is of course a peak at k_F , and also a node where $\Delta_{\mathbf{k}}$ vanishes, but this "non-uniform" region occupies only a fraction of the zone.) This has the important consequence that the pair wavefunction (the Fourier transform of $\Delta_{\mathbf{k}}/E_{\text{BCS}_{\mathbf{k}}}$) has a rapidly decaying envelope, thereby leading to a very short Pippard coherence length ξ_0 , consistent with experiment. With hindsight, we note that this argument can also be inverted. The fact that ξ_0 is only about four lattice spacings (in-plane), in YBa₂Cu₃O_{7- δ} , seems to actually *require* such a roughly linear behavior for $\Delta_{\mathbf{k}}$ far from k_F . We therefore argue that the extremely short ξ_0 is important evidence in favor of the present mechanism.

Our goal now is to determine the implications of these results for the gap anisotropy, when using a more realistic (anisotropic) band structure for the CuO₂ plane. For typical cuprate superconductors (123, 214, and now apparently also for Bi-2212), the Fermi surface lies *above* but close to the van Hove singularity. The strong $\mathbf{k}$ -dependence in $V_{\mathbf{k}\mathbf{k}'} = -a + bS_{\mathbf{k}}S_{\mathbf{k}'}$ therefore suggests that, due to the larger $|\mathbf{k}|$ for the Fermi surface region near the $\mathbf{k} = (1,0)$ point, $V_{\mathbf{k}\mathbf{k}'}$ should be less attractive here, and therefore the gap should be smaller in this neighborhood, as compared to the gap along the (1,1) direction. But this is opposite to the result from angle-resolved photoemission (Shen *et al.* 1993), which shows that Δ is *maximum* in the Fermi surface region closest to (1,0). There is, however, also an opposing effect to be considered here.

The net or average attraction in $V_{\mathbf{k}\mathbf{k}'}$ is found to increase quite strongly with increasing charge-transfer energy Δ_{CT} , for Δ_{CT} near the threshold value required to obtain pairing. (Here $\Delta_{CT} = \epsilon_d - \langle \epsilon_k \rangle$, in "electron" notation, where $\langle \epsilon_k \rangle$ is the "conduction" band centroid.) In reality the "conduction" band is highly anisotropic, with its energy at (1,0) far below its energy for the same $|\mathbf{k}|$ along the (1,1) direction. This is due in part to the p_x - p_y interaction, which raises ϵ_k along (1,1) but has no effect along (1,0). Of comparable importance, however, is the effect of the copper 4s orbitals, which overlap very strongly with the $2p_x$, $2p_y$'s. Although the 4s "conduction" hybridization vanishes at (0,0) and (1,1), it has often been overlooked that this interaction becomes very strong at (1,0) and depresses ϵ_k here by several eV. It is quite plausible that the effect of this ϵ_k lowering should be similar to an increase of Δ_{CT} . We therefore expect that $V_{\mathbf{k}\mathbf{k}'}$ should be more attractive (or less repulsive) for $\mathbf{k}$ and/or $\mathbf{k}'$ in the vicinity of (1,0), and therefore that $\Delta_{\mathbf{k}}$ should be more positive in this region.

We have explored this effect in a two-dimensional model with a suitably warped form for $\epsilon_{\mathbf{k}}$, namely

$$\epsilon_{\mathbf{k}} = 2 [W_p S_x^2 S_y^2 + E_{px} (S_x^2 - S_y^2)] / (S_x^2 + S_y^2) . \quad (1)$$

Here $S_x = \sin(k_x \pi/2)$, $W_p = 2.6$ eV is the value used previously, and E_{px} is a strongly negative parameter (~ -2.5 eV) adjusted to have the normal-state quasiparticle Fermi surface intersect the (1,q) line at $q \sim 0.15$. The corresponding hybridization interaction is given the form

$$V_{\mathbf{k}} = V_0 (|S_x^2 + S_y^2 + \gamma_{sd}(2 - S_x^2 - S_y^2)| / 2)^{1/2} . \quad (2)$$

Here $\gamma_{sd} = 0.17$ represents an estimate of the effect of the $3d(x^2-y^2)$ mixing with planar oxygen 2s rather than 2p. Our assumed single "conduction" band thus now approximately incorporates oxygen 2s as well as copper 4s effects. The present $\epsilon_{\mathbf{k}}$ and $V_{\mathbf{k}}$ are now used where these functions enter explicitly in our (quite complicated) expression for $V_{\mathbf{k}\mathbf{k}'}$, while all other parameters in this expression are taken from the "most physical" results for the preceding isotropic model. Because of the lack of self-consistency here, the present results are merely indicative. The main conclusion is that the 4s effect

dominates over the simple k -dependence effect, so that the gap is much larger near the (1,0) point than it is along the (1,1) direction. This agrees with the above-mentioned result from angle-resolved photoemission. We also find that the gap is nodeless, and that $\Delta_{\max}/\Delta_{\min} \sim 4$, although these conclusions are obviously sensitive to details that we do not have under good control. We describe the result as an "s + g" ($l=4$) gap, or as a very strongly distorted s gap.

On the experimental side, a good case can be made for this form of gap. Several experiments clearly establish a strong anisotropy, such as the rapid drop in NMR relaxation (opposite to Hebel-Slichter behavior) just below T_c , and the linear behavior of the London penetration depth at lower temperature ($T < T_c/2$) (Hardy *et al.* 1993). On the other hand, this precision penetration-depth data shows a clearly different behavior below 15K. There it appears to be activated, as expected for the present gap form. Much of the tunneling data for 123 also suggests a minimum gap value, with $\Delta_{\max}/\Delta_{\min} \sim 4$ (Geerk *et al.* 1989, Gurvitch *et al.* 1989). [This "s + g" form of gap was in fact suggested previously (Mahan 1989), on the basis of earlier tunneling data.] Two recent phenomenological studies (Li and Joynt 1993, Dickinson and Doniach 1993) have also concluded that Δ should be nodeless but highly anisotropic, although there are differences of detail in the assumed variation of the gap near its minimum value (degree of V-shape vs. U-shape).

Finally, we mention a striking phenomenological correlation between the T_c 's of many different cuprates and the Madelung potentials of their apical oxygen ions (Ohta *et al.* 1991). Our mechanism provides a qualitative explanation for this. A high electron energy (low Madelung potential) for an apical oxygen p_z orbital means that this orbital should interact more strongly with the copper $4s$, thereby effectively raising the latter's energy and weakening its effect on the (1,0) energy, of ϵ_k . This should decrease the average attraction of $V_{kk'}$, and therefore lower T_c , in agreement with observation. Furthermore, the physical removal or elimination of an apical oxygen ion corresponds here to replacing its Madelung potential by $+\infty$, which is quite beneficial for the superconductivity. This helps to explain how $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ is able to superconduct, even though its charge-carrier concentration is so far from being optimum. The more isotropic gap in this material (Wu *et al.* 1993) is also to be expected, since the larger electron number keeps the Fermi surface farther away from the (1,0) point.

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REFERENCES:

- B.H. Brandow, Phys. Rev. B **33** (1986) 215 and **37** (1988) 250; Solid State Commun. **69** (1989) 915;
J. Solid State Chem. **88** (1990) 28; in High-Temperature Superconductivity, edited by
J. Ashkenazi *et al.*, World Scientific, Singapore, 1992, p. 583; (1993) preprint.
- P.H. Dickinson and S. Doniach, APS Bulletin **38** (1993) No. 1, Abstract J23 9.
- J. Geerk *et al.*, Physica C **162-164** (1989) 837.
- S. Gopalan *et al.*, Phys. Rev. B **46** (1992) 11798.
- O. Gunnarsson and K. Schonhammer, Phys. Rev. B **31** (1985) 4815.
- M. Gurvitch *et al.*, Phys. Rev. Lett. **63** (1989) 1008.
- W.N. Hardy *et al.*, (1993) preprint, and this proceedings.
- J.H. Kim *et al.*, Phys. Rev. B **44** (1991) 5148.
- K. Levin *et al.*, Physica C **175** (1991) 449.
- Q.P. Li and R. Joynt, Phys. Rev. B **47** (1993) 530.
- G.D. Mahan, Phys. Rev. B **40** (1989) 11317.
- D.M. Newns, Phys. Rev. B **36** (1987) 2429 and 5595; *ibid.* **38** (1988) 6513 and 7033.
- Y. Ohta *et al.*, Phys. Rev. B **43** (1991) 2968.
- P.C. Pattnaik *et al.*, Phys. Rev. B **45** (1992) 5714.
- Z.-X. Shen *et al.*, Phys. Rev. Lett. **70** (1993) 1553.
- Y.J. Uemura *et al.*, Phys. Rev. Lett. **66** (1991) 2265; Nature **352** (1991) 605; Physica C **185-189** (1991) 733.
- D.H. Wu *et al.*, Phys. Rev. Lett. **70** (1993) 85.