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LA-UR--89-3037

DE90 000603

TITLE SUPERCONDUCTIVITY FROM FINITE-U VALENCE FLUCTUATIONS

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SUBMITTED TO: Proceedings of the International Conference on the Physics of
Highly Correlated Electron Systems, Santa Fe, NM
September 11-15, 1989.
To be published in a special volume of Physica

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SUPERCONDUCTIVITY FROM FINITE -U VALENCE FLUCTUATIONS

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The finite- U pairing mechanism of Newns is explored by an adaptation of our previous $U = \infty$ variational treatment of the Anderson lattice. This pairing mechanism is found to be opposed by a magnetic tendency arising from Gutzwiller renormalization of the hybridization. This competition restricts superconductivity to the parameter regime $\Delta \gtrsim U$, and this also reproduces the parabolic rise and fall of T_c in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ with increasing x . Re-analysis of the photoemission and BIS data for CuO reveals that indeed $\Delta \gtrsim U$ for this compound, contrary to previous work.

Most of this study has been reported elsewhere in more detail.¹ We shall outline the main features, and then describe the main result of a new analysis of photoemission data for CuO. Contrary to previous analyses, this indicates that cuprate materials have parameters favorable for the present theory.

The conceptual picture of valence fluctuations or “heavy fermions” has a priori appeal, for a non-phononic theory of superconductivity, for several reasons. First, a variety of evidence suggests that oxygen 2p orbitals are somehow playing an important role, in addition to the copper 3d orbitals. This view is supported by band-structure calculations, by a wealth of experience with related transition-metal compounds, and, more recently, by valence-band photoemission experiments.² These considerations lead to a model Hamiltonian of the Anderson lattice form, which is the standard starting point for valence fluctuation (VF) theory. Another reason is that the VF picture immediately provides a normal Fermi liquid, with Landau quasiparticle states which provide an ordinary Fermi surface and satisfy the Luttinger sum rule.³ This permits much of the BCS theory to be taken over directly, and it may also serve to explain the normal-state transport properties.⁴ This picture also provides some “heaviness” or enhancement of state density at ε_F , which seems to be required for several properties, including the magnetic susceptibility above T_c , and the specific heat jump at T_c .

In the presumed VF phase of the superconducting cuprates above T_c , the 2p electrons provide Kondo screening of the copper local moments, thereby enabling the existence of a normal (nonmagnetic) Fermi liquid. This role of the 2p electrons is so different from that assumed in the Mott insulating “parent” compound, and in the associated lightly-doped materials, that we expect these contrasting phases to be separated by a first order transition. This transition is presumably masked experimentally by sample inhomogeneities, leading to a range of doping with both phases present.

Pairing mechanisms within the framework of VF theory have been recognized for some time at the $(1/N)^1$ and $(1/N)^2$ orders of the $1/N$ expansion (which generally presumes that $U = \infty$); these mechanisms lead to p or d-wave pairing. [It is the $(1/N)^2$ process which corresponds to “paramagnon” or spin-fluctuation exchange, as in liquid ^3He .] We are focusing instead on a third mechanism, the “two-hole resonance” mechanism of Newns.⁵ This arises already at the $(1/N)^0$ or “mean field” stage of approximation, and it gives s-wave pairing. In the present case of VF theory the Landau quasiparticles involve fluctuations between d^9 and d^{10} configurations; these occur already when $U = \infty$. A pairing attraction between these quasiparticles can then arise from fluctuations into d^8 (“two-hole resonance”), but this is possible only when U is finite ($U < \infty$). We note that this mechanism has a simple diagrammatic interpretation.¹ We presume, as de Newns *et al.*⁵ that this mechanism contributes also to the superconductivity of the non-cuprate bismuth materials, via Bi 6s orbitals playing a role similar to the (orbitally nondegenerate) x^2-y^2 3d orbitals of Cu.

Our method of analysis differs from that of Newns. We have extended our previous variational treatment³ to the case of finite U . By analytic and numerical methods all of the variational parameters are fully optimized, i.e., they are fully self-consistent. The calculations therefore do not require any of the Hamiltonian parameters, or combinations of parameters, to be small; the calculations remain sensible throughout all of the Hamiltonian parameter space.

Our theory also differs physically in one major respect from that of Newns. At the “mean field” or $(1/N)^0$ level of approximation, it is well known that the Landau quasiparticles are described by a simple effective hybridization model,³ in which the 2p-3d hybridization interaction V_k is renormalized into $V_k \rightarrow V_k \sqrt{q}$. Unfortunately, however, there are at present two different recipes for the renormalization factor q . Newns and co-workers have used the so-called mean field recipe, $q_{mf} = 1 - n_f$, where n_f refers to the f-electron occupation number for a VF cerium compound. (For a cuprate, this n_f becomes

the 3d *hole* number, per Cu ion.) However, we have recently become convinced that the Gutzwiller form, $q_G = (1-n_f)/(1-n_f\sigma)$, is more correct. (This conclusion is based on a variety of evidence⁶: exactly-solvable test cases, combinatoric analysis, diagrammatic analysis, and the requirement of correct behavior as $U \rightarrow 0$.) We therefore use the Gutzwiller form, suitably generalized for the finite- U case.¹

This difference in the renormalization has major consequences. The explicit spin dependence of the Gutzwiller q causes a strong tendency towards magnetism, and this effect opposes the Newns pairing mechanism. One result is that we do not find superconductivity unless $\Delta [\equiv E(d^{10}\underline{L}) - E(d^9)]$, the charge-transfer energy parameter of Sawatzky,⁷ is made considerably larger than the numerical values typically obtained from analyses of photoemission data.^{8,9} Instead of $\Delta \ll U$, as typically found, this theory requires that $\Delta \gtrsim U$, or in other words that $E(d^8) \lesssim E(d^9\underline{L}) \ll E(d^{10}\underline{L}^2)$. This is very different from the prevailing picture, in which $E(d^8) \gg E(d^9\underline{L}) < E(d^{10}\underline{L}^2)$. Nevertheless, there is a further reward for this assumption. When we increase the doping level x of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, we find that T_c first increases, and then decreases and terminates, following an inverted parabola, in qualitative agreement with the data of Torrance *et al.*¹⁰ This behavior results here from the competition between the pairing and magnetic tendencies. We consider this a significant success for the present theory.

Motivated by the foregoing, and by other arguments in Ref. 1, we have now carefully re-analyzed the CuO photoemission and BIS data of Sawatzky and co-workers.⁹ We have basically followed their method of analysis (including the full crystal field-multiplet structure, and all of the associated charge transfer configurations), but with several differences of detail. In particular, we have carefully calculated the intensity distribution for oxygen 2p electron removal, in addition to the 3d removal spectrum. This 2p intensity has significant structure, and much of this spectrum is unaffected by the p-d hybridization. The use of this spectrum, together with the 3d spectrum, therefore permits a clear and unambigu-

ous determination of Δ . We find that indeed $\Delta \gtrsim U$, as anticipated in Ref. 1. Besides supporting the present theory, this result has a number of further implications which we shall discuss elsewhere, together with the details of this analysis. One of these implications is to refute the common assertion that the holes resulting from doping are accommodated almost entirely in oxygen 2p orbitals. We find¹ that these doping holes are shared between the 2p and 3d orbitals with quite similar probabilities. This is consistent with recent data on photoemission near ε_F in superconducting cuprates.² The present configuration-energy ordering is also consistent with quantum-chemistry cluster calculations.¹¹

In conclusion, it should be noted that this theory focuses attention on two parameters as being particularly significant for the attainment of high T_c 's. One is the concentration of "doping holes," e.g., the x in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$. The other is the effective electronegativity difference between the copper and oxygen sites, as measured by the parameter Δ . It has recently been emphasized that this parameter is sensitive to the Madelung - potential effects of the ions between the active CuO_2 layers, and especially to the presence or absence of apical oxygens.¹² Another possible route¹ for modifying Δ would be to replace the in-plane oxygens by fluorine or chlorine, with other substitutions to maintain the nominal copper valence near 2.2. A hypothetical example of such substitutions would be $\text{K}_2\text{CuF}_{4-x}\text{O}_x$, with $x \approx 0.2$.

ACKNOWLEDGMENT

This work was supported by the U.S. Department of Energy.

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