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Pairing state of cuprate superconductors containing double CuO_2 planes

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This paper examines the viability of the "Efetov-Larkin" state (*s* wave, spin triplet, odd between layers) as an identification of the pairing state of those cuprate superconductors that contain double CuO_2 planes. It is concluded that most of the NMR and other data are consistent with this assignment but there are one or two obvious difficulties.

As is well known, the recently discovered high-temperature superconductors[1] (HTS) all contain well-separated CuO_2 planes, or pairs or triples of such planes. Most discussions of the nature and the symmetry of the superconducting state have either treated[2] the superconductivity as a property of the single individual planes, assisted by some kind of weak, Josephson-type interplane coupling, or have assumed[3] that the electron states involved are fully three-dimensional (3D) and that the possible symmetries of the superconducting state can be classified accordingly. In this paper we focus on the possibility that the *pairs* of planes which occur in a number of the HTS [$YBa_2Cu_3O_{7-\delta}$, (YBCO) $Bi_2Sr_2CaCu_2O_8$] might play a special role. Needless to say, if this were to turn out to be correct it would be necessary to examine the implications for those HTS ($La_{2-x}Sr_xCuO_4$, Bi 2:2:2:3) where either only single planes or triples occur, but we shall not do this here.

The rationale for focusing on pairs of planes is twofold. First, while a number of arguments, both experimental and theoretical, suggest[4] that there is no coherent electron transfer in the normal state, between *well-separated* CuO_2 planes (i.e., those in different unit cells, spaced by ~10–12 Å), recent de Haas–van Alphen experiments on YBCO (Ref. 5) seem to favor the hypothesis (which is not implausible *a priori*) that the behavior is coherent between the pairs of planes *within* a unit cell (spacing ~2 Å). If so, this needs to be taken into account in the classification of the possible superconducting states. Second, as we shall see, some of the experimental properties of the superconducting state suggest that the states accessible within a single plane may not possess enough degrees of freedom to explain them.

In the following we shall assume that the principle underlying the phenomenon of superconductivity in the HTS is, as in the "old-fashioned" superconductors, the formation of Cooper pairs, though we shall make no specific assumptions about the mechanism of attraction involved. The problem then reduces to identification of the symmetry of the Cooper-pair state (order parameter). Now the interesting thing is that while most of the experimental low-temperature properties of the HTS suggest[3] that the energy gap has no nodes and therefore point *prima facie* to an "*s*-wave-like" state, there are some features of the NMR behavior,[6] in particular the Cu(2) *c*-axis Knight shift and the absence of a Hebel-Slichter peak, which are intriguingly suggestive of spin triplet pairing. Within the context of a model without intercell coherence in the *c* direction there are at least two ways to resolve this dilemma.[7,8] One, which does not rely on the occurrence of double planes, is simply to postulate a *p* wave, "equal-spin-pairing" (ESP) spin triplet state such as, for example, the two-dimensional analog of the "ABM" state believed to describe superfluid ^{3}He-*A*;[9] for a 2D Fermi surface it is not necessary that the energy gap in such a state has nodes. The properties of such a state may be straightforwardly obtained[3] as a special case of the general theory of spin triplet pairing, see Refs. 8 and 9, and will not be discussed here. The second possibility, which *is* peculiar to the double-layer situation, is to invoke the pairing state first investigated in a different context by Efetov and Larkin,[10] in which the pair wave function is *s*-wave-like within each plane, a triplet in spin space and *antisymmetric* with respect to the interchange of the two layers within the unit cell. It is this latter state, which we shall refer to as the Efetov-Larkin (EL) state, whose properties will be investigated and compared with experiment on YBCO and Bi 2:2:1:2 in this paper.

Before starting a discussion of this model, we briefly mention the experiments on the Josephson current observed between conventional superconductors and high-T_c materials.[3] Theoretically,[11] the Josephson coupling to the Efetov-Larkin state would (in the presence of strong spin-orbit coupling) not vanish for a tunneling current parallel to *c* axis but would vanish for a tunneling current parallel to *a* or *b* axis. One experiment has the opposite results among conflicting reports.[12] However, the observed critical current is between 1 and 3 orders of magnitude smaller than expected for a conventional Josephson junction, and the possibility of proximity-effect-induced coupling is not ruled out.

For the moment we neglect the finite single-electron matrix element for transfer between the two planes. Then the "plane" degree of freedom may be thought of as essentially equivalent to an "isotopic spin" $\hat{\tau}$ of $\frac{1}{2}$, with the eigenvalues $\tau_z = \pm\frac{1}{2}$ representing localization on one plane or the other. The EL state is a product of space, spin and "isospin" wave functions:

$$\Psi_{\text{total}} = \Psi_{\text{orb}}\Psi_{\text{spin}}\Psi_{\text{isospin}} \tag{1}$$

with in-plane angular momentum $l = 0$, total spin $S = 1$, and total isospin $\tau = 0$. In terms of the **d**-vector notation conventionally employed[9] to describe spin triplet pairing, this state corresponds to $\mathbf{d}(\mathbf{n}) = $ const over the (2D) Fermi surface; for simplicity of presentation we shall for the moment take $\mathbf{d}$ to be real and to lie along the z axis, corresponding to a Cooper-pair spin configuration with $S_z=0$. Note that the z axis may be chosen by convention in an arbitrary direction without affecting the results.

In accordance with the generalized pairing notation conventional in nuclear physics,[13] we write the ground-state wave function in the form

$$|\text{ground}\rangle=\prod_{\alpha>0}(u_\alpha+v_\alpha c_\alpha^\dagger c_{\bar\alpha}^\dagger|\text{vacuum}\rangle \tag{2}$$

so that the appropriate Bogoliubov transformation is

$$\begin{aligned}\gamma_\alpha&=u_\alpha c_\alpha-v_\alpha c_{\bar\alpha}^\dagger\\ \gamma_{\bar\alpha}^\dagger&=u_\alpha c_{\bar\alpha}^\dagger+v_\alpha c_\alpha\end{aligned} \tag{3}$$

where c, $c^\dagger$ $(\gamma,\gamma^\dagger)$ are annihilation and creation operators for particles (quasiparticles), and $|u_\alpha|^2+|v_\alpha|^2=1$. Fermi statistics requires that $u_{\bar\alpha}=u_\alpha$, $v_{\bar\alpha}=-v_\alpha$. For s-wave pairing u_α, v_α are defined as usual:[14] $|u_\alpha|^2=\frac{1}{2}[1+\varepsilon_\alpha/(\varepsilon_\alpha^2+\Delta^2)^{1/2}]$, $|v_\alpha|^2=\frac{1}{2}[1-\varepsilon_\alpha/(\varepsilon_\alpha^2+\Delta^2)^{1/2}]$, where ε_α is the kinetic energy of particles measured from chemical potential and Δ is gap. For the EL state we have $\alpha=(\mathbf{k},s,\tau),\bar\alpha=(-\mathbf{k},-s,-\tau)$ and

$$\begin{aligned}u_{\mathbf{k},s,\tau}&=u_{\pm\mathbf{k},\pm s,\pm\tau}=u_{\mathbf{k}}\,,\\ v_{\mathbf{k},s,\tau}&=v_{\pm\mathbf{k},\pm s,\tau}=-v_{\pm\mathbf{k},\pm s,-\tau}=v_{\mathbf{k},\tau}\,.\end{aligned} \tag{4}$$

The transformation inverse to (3), subject to condition (4), is

$$\begin{aligned}c_{\mathbf{k},s,\tau}&=u_{\mathbf{k},s,\tau}\gamma_{\mathbf{k},s,\tau}+v_{\mathbf{k},s,\tau}\gamma_{-\mathbf{k},-s,-\tau}^\dagger\,,\\ c_{\mathbf{k},s,\tau}^\dagger&=u_{\mathbf{k},s,\tau}\gamma_{\mathbf{k},s,\tau}^\dagger+v_{\mathbf{k},s,\tau}\gamma_{-\mathbf{k},-s,-\tau}\,.\end{aligned} \tag{5}$$

We now apply Eq. (5) in the standard way to calculate the coherence factors, etc., which occur in the expressions for various experimental quantities.

Nuclear spin relaxation. The EL state has a characteristic anisotropy in spin space, and we should therefore expect the nuclear spin relaxation to be anisotropic, i.e., to depend on whether the applied field $\mathbf{H}$ is parallel or perpendicular to the vector $\mathbf{d}$. If we assume that the spin relaxation rate T_1^{-1} is dominated by an isotropic contact interaction of strength A (anisotropy due to lattice structure is unimportant since we use a nodeless s-wave pairing model), then the general form of the expression for T_1^{-1} is

$$T_1^{(i)-1}=A^2\sum_{\mathbf{k},\mathbf{k}'}C_i(\mathbf{k},\mathbf{k}')f_{\mathbf{k}}(1-f_{\mathbf{k}'})\delta(E_{\mathbf{k}'}-E_{\mathbf{k}}-\omega)\,, \tag{6}$$

where i refers to the parallel ($\parallel$) or perpendicular ($\perp$) directions of $\mathbf{H}$ with respect to $\mathbf{d}$, and $C_i(\mathbf{k},\mathbf{k}')$ is the relevant coherence factor; f is the Fermi distribution function, and $E_{\mathbf{k}}=(\varepsilon_{\mathbf{k}}^2+\Delta^2)^{1/2}$ is the quasiparticle energy. A straightforward calculation gives

$$C_\perp=(u_{\mathbf{k}}u_{\mathbf{k}'}+v_{\mathbf{k}}v_{\mathbf{k}'})^2,\ C_\parallel=(u_{\mathbf{k}}u_{\mathbf{k}'}-v_{\mathbf{k}}v_{\mathbf{k}'})^2\,, \tag{7}$$

i.e., the coherence factor for $\mathbf{d}$ perpendicular to $\mathbf{H}$ is the same as for a simple BCS s-wave state, leading to the expectation of a "Hebel-Slichter peak," while that for $\mathbf{d}$ parallel to $\mathbf{H}$ is the same as the BCS coherence factor for ultrasound attenuation, leading to the absence of a peak. Note that the result (7) is *opposite* to what we would expect from a naive argument based on the fact that for $\mathbf{d}\parallel\mathbf{H}$ we have "opposite spins paired" as in the simple BCS state.

Longitudinal ultrasound attenuation and electromagnetic absorption. The coherence factors in the expressions for these quantities are identical to those occurring for a simple BCS s state; the derivation is straightforward and will not be given here.

Knight shift. To obtain this, or rather the electronic spin susceptibility χ to which (part of) it is proportional, we proceed exactly as in the standard theory of a spin triplet p-wave superfluid;[9] it is clear that the different orbital (and isotropic spin) symmetry does not change the formal expressions at all. The result is, for no Fermi-liquid corrections,

$$\chi_\perp\cong\chi_n,\ \chi_\parallel=\chi_n Y(T)\,, \tag{8}$$

where χ_n is the normal-state susceptibility and $Y(T)$ the Yoshida function, which is of course given by the original[15] expression appropriate for a BCS s state, since as there the gap is isotropic. If the $\mathbf{d}$ vector is varying in space, for example, because of domain structures enforced by crystalline imperfections, then we should expect that the macroscopically observed susceptibility tensor should be of the form

$$\chi_{\alpha\beta}=\chi_n\{\delta_{\alpha\beta}-[1-Y(T)]\overline{d_\alpha d_\beta}\}\,. \tag{9}$$

However, it is not clear that the observed Knight shift (or more precisely the contribution of the electronic spin susceptibility to it) should be given by simply multiplying (9) by the appropriate constant factor; one might argue that in these circumstances one would see, for any given field direction, a *distribution* of Knight shifts corresponding to the orientation of $\mathbf{d}$ in the different domains.

To interpret the results of the calculations of the Knight shift and nuclear spin relaxation rate one needs to know which orientation of $\mathbf{d}$ is likely to be favored. While we cannot exclude effects arising from spin-orbit coupling at the one-electron level, the most obvious orienting effect is the simple electromagnetic dipole-dipole interaction. By a calculation along the lines of Ref. 9, Sec. X.A, we have shown that for the state (1) this interaction tends to favor an orientation of $\mathbf{d}$ in the ab plane with an associated energy which is $\sim 10^{-8}$ J/m^2. Another orienting effect is the magnetic field which tends to align $\mathbf{d}$ perpendicular to $\mathbf{H}$. When $\mathbf{H}$ is along c axis there is no competiton since $\mathbf{H}$ also align $\mathbf{d}$ in the ab plane. When $\mathbf{H}$ is in the ab plane the associated energy is $\sim 10^{-8}$ H^2 J/m^{2}T^2. Hence the dipole-orienting effect is dominant for fields up to ~ 1 T. Thus, for moderate fields we should expect $\mathbf{d}$ to lie in the ab plane.

We now briefly comment on the effect of taking into account the finite matrix element for single-electron interplane tunneling. We are now more or less forced to do the calculation in a single-electron basis classified, apart from the momentum $\mathbf{k}$ in the plane, by the parity $(+,-)$ of the single-electron states with respect to interchange between the planes, and it is clear that for given $\mathbf{k}$ there will be an approximately $\mathbf{k}$-independent splitting J between those two states, the + state lying lower. Thus, the form of the Hamiltonian as regards the isotopic-spin degree of freedom is formally identical to that of the (true) spin degree of freedom for a BCS superconductor in a magnetic field, and just as there we should expect that for a large enough value of J we get the possibility of a "pseudo-Fulde-Ferrell" type of state[16] in which $(\mathbf{k},+)$ can be paired with $(-\mathbf{k}+\mathbf{q},-)$. A realistic calculation of this possibility would require attention to the specific in-plane density of states realized in the HTS, in particular to the degree of nesting. For small enough J (crudely speaking, $J < k_B T_c$) we should expect the results derived above to apply unmodified.

We now turn to the comparison of these predictions with experiments. We first briefly comment on the argument of Monien and Pines[17] which concludes that the existing Knight-shift data[18] on the Cu(2) nuclei alone are adequate to exclude a general class of spin triplet states, which includes the EL state if we assume that the correct expression for the Knight shift involves an average over the direction of **d** as in Eq. (9), and that **d** is distributed randomly in the *ab* plane. The argument is essentially that any such state would have a theoretical *ab*-plane Knight shift at $T=0$ which is half of the normal-state value; since the *total* (experimentally observed) magnetic shift at $T=0$ is in fact just about half the normal-state value, this would mean that the *orbital ab*-plane contribution would have to be very close to zero. On the other hand, the theoretically expected value of the orbital *ab*-axis contribution is about 25% of the *c*-axis orbital contribution, leading to a contradiction. While this is a strong argument, there is one possible loophole in it: In the presence of Fermi-liquid effects, the predicted[19] *ab*-plane Knight shift at $T=0$ may be different from $\frac{1}{2}$, and in fact a value of the Landau parameter F_0^a of 1.4 would be sufficient to reconcile the inferred value of the orbital *ab*-plane susceptibility with theoretical expectations.[20]

As a matter of fact, the question of the *ab*-plane Cu(2) Knight shift has been complicated by measurements[21] which seem to show a *distribution* of shifts (or more accurately a considerable broadening of the NMR line). Qualitatively this is what one would expect if each nucleus "sees" the **d** vector in its own neighborhood and the effective χ is given by the unaveraged form of Eq. (8); however, alternative explanations are clearly possible. To resolve this question it would obviously be very useful to have Knight-shift data for untwinned specimens.

A probably more serious objection to the identification of the pairing state of YBCO with the EL state is the behavior of the O^{17} and Cu(1) Knight shifts; both of which drop off rapidly below T_c for *all* directions of the field.[18,22,23] It seems difficult to reconcile this behavior with the EL hypothesis without invoking a two- or multiple-band scenerio, which would detract somewhat from the appeal of that hypothesis. However, the very different width of the O^{17} and Cu^{63} lines in the experiment of Takigawa *et al.*[21] tend to confirm that the O sites are indeed, in some way not currently understood, "different."

Regarding the NMR relaxation rate, we note that a result of the above discussion was that for **d** perpendicular to **H** the coherence factor, and hence the temperature dependence, has its BCS form; whereas for **d** *parallel* to **H** the formula, when normalized to its value at T_c, is identical to the BCS expression for the *ultrasonic attenuation*. This is intriguing, since some experiments on the temperature dependence of the relaxation rate indeed seem to show this correspondence.[24] However, one would expect *prima facie* that in a powder or twinned single-crystal sample one would see a distribution of relaxation rates ranging from the "parallel" to the "perpendicular" rate; it is unclear why the experimentally observed behavior should (if the above explanation is correct) be dominated by the *slowest* rate. Furthermore, while the EL model (with **d** assumed to lie in the *ab* plane, cf. above) is qualitatively consistent with the observed[6,25] drop of the ratio W_{1a}/W_{1c} just below T_c [$W_{1c\,(1a)}$ is the *c*-axis (*ab*-plane) relaxation rate], it apparently cannot explain the rise of the ratio above its normal-state value at low temperature.

We mention the conductivity peaks observed in recent experiments.[26] These peaks are possibly coherence peaks if high-T_c superconductors were in the Efetov-Larkin pairing state. Since in this state NMR and conductivity could have different coherence factors.

We conclude that while there are certainly one or two fairly major discrepancies, many of the qualitative features of the superconducting-state behavior of the double-layer cuprates appear consistent with an EL pairing state. In view of the present lack of "smoking-gun" evidence for alternative models such as *d*-wave pairing,[27–29] we feel that it would be premature to discard this possibility entirely. A definitive resolution could almost certainly be achieved by NMR measurements on single untwinned crystals, should this be possible.

Finally we want to mention the relationship of our work to that of Klemm and Liu.[30] They used a mixed singlet-triplet order parameter and the Ginzburg-Landau free-energy functional to make some interesting observations on the gap anisotropy and the competition between intralayer pairing and interlayer pairing. In particular, they assumed the existence of the band structure along the *c* axis, while we do not. We concentrated on triplet pairing only and considered different aspects of the experimental consequences.

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[1]See, for example, *Physical Properties of High Temperature Superconductors*, edited by D. M. Ginsberg (World Scientific, Singapore, 1990), Vols. I and II.

[2]*High Temperature Superconductivity: Proceedings*, edited by K. S. Bedell *et al.* (Addison-Wesley, Reading, MA, 1990).

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