The Superconducting State of YBa$_2$Cu$_3$O$_{7-\delta}$

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Many low temperature properties of high $T_c$ superconductors deviate significantly from the detailed predictions of BCS theory. Here we discuss whether these effects could be caused by either: (a) an unconventional pairing state, or (b) local randomness in the gap function due to the intrinsic disorder. We review recent experiments pertinent to these questions: Josephson effects in (001) oriented planar junctions between YBa$_2$Cu$_3$O$_{7-\delta}$ and classic superconductors and the temperature dependence of the a-b plane electro-magnetic penetration depth at low temperatures. We also calculate the density of states of s-wave superconductors with local quenched disorder in the gap function so as to determine whether s-wave pairing could be consistent with the low energy quasiparticle excitations seen in many experiments.

1. INTRODUCTION

The high temperature superconductor YBa$_2$Cu$_3$O$_{7-\delta}$ exhibits many surprising physical properties which are presently not well understood. Not only is there still no widely accepted explanation of the high transition temperature itself, but both the normal and superconducting states show unusual behavior. The superconducting state is anomalous since many measurements appear quite different from the predictions of s-wave BCS theory. In particular, although there is structure in the density of states similar to the BCS energy gap, $\Delta$, there appears to be no energy, however low, where there is a complete absence of excitations. For example, Raman scattering finds a

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broad continuum of electronic states throughout the gap region, infrared measurements always show non-zero optical absorption, while tunneling measurements also see a non-zero density of states at all energies. Consistent with this picture one also finds that both nuclear magnetic relaxation rates and microwave surface resistance exhibit anomalous temperature dependence. The latter data are also consistent with thermal conductivity data below $T_c$, if the dominant contribution is assumed to be electronic rlap. The thermal conductivity data and the temperature dependence of the relaxation rate are explicable assuming that there are nodes in the gap. Even the electromagnetic penetration depth has temperature dependence at low temperatures which appears inconsistent with a full energy gap in the spectrum. All of these results are difficult to explain in s-wave BCS theory where there is expected to be a gap minimum $\Delta_{\text{min}}$ below which, at zero temperature, there are no single particle excitations, even taking into account gap anisotropy, strong coupling, disorder and weak inelastic scattering.

In this contribution we shall discuss two alternative possible explanations for these anomalous superconducting state properties: (a) an unconventional pairing state, and (b) s-wave pairing, but with strong quenched local disorder in the superconductor order parameter. Firstly we shall review the current evidence for and against an unconventional pairing state in YBa$_2$Cu$_3$O$_{7-\delta}$; we concentrate especially on evidence from recent measurements of Josephson effects in planar junctions and from the temperature dependence of the a-b plane electromagnetic penetration depth. These two sections represent a report (albeit incomplete) of new developments since the publication of our earlier review article. A more complete review would discuss the quasi-particle relaxation rate and the thermal conductivity.

Finally we shall discuss the effects of strong local disorder on the density of states of s-wave superconductors. Here we show that disorder can give rise to an exponential Lifshits band-tail of states inside the BCS energy gap. However, only if the disorder is sufficiently strong can this exponential tail be qualitatively similar to the density of states observed in YBa$_2$Cu$_3$O$_{7-\delta}$.

2. RECENT EVIDENCE FOR AN UNCONVENTIONAL SYMMETRY STATE

Perhaps the most fundamental characteristic of any superconducting or superfluid state is symmetry. At least in principle, the symmetry of the superconducting state can be determined experimentally without assuming any particular microscopic theory. Assuming only that the superconductivity is described by a Ginzburg-Landau free
energy functional close to $T_c$, or that there exist Gorkov pairing correlation functions below $T_c$,

$$
F_{\alpha\beta}(\vec{r}_1, t_1, \vec{r}_2, t_2) = \left\langle \hat{T} c_{\alpha}(\vec{r}_1, t_1) c_{\beta}(\vec{r}_2, t_2) \right\rangle
$$

(1)

where $\hat{T}$ is the time ordering operator, it is possible to use group theoretic methods to enumerate all the symmetry distinct superconducting states in a given crystal structure. Such a symmetry classification has been carried out for the tetragonal and orthorhombic crystal groups appropriate to $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and related compounds.\textsuperscript{[9]} We use the term “conventional” superconductivity for any state which is spin singlet and which possesses the full symmetry group of the crystal, while conversely “unconventional” states are not invariant under all space group or spin rotation operations. With this nomenclature the s-wave BCS state is conventional. Note that a conventional pairing state need not imply the BCS pairing mechanism or any other similarity to BCS theory other than the overall symmetry.

The most powerful class of experimental constraints on the symmetry of the order parameter are those which rely purely on symmetry properties and do not depend upon the microscopic theory in any way. As we have discussed previously in ref.\textsuperscript{9} experimental constraints of this kind include: (1) fluctuation specific heat, diamagnetism and conductivity close to $T_c$, (2) possible splitting of the phase transition under applied strain or magnetic field, (3) angular dependence of upper critical field $H_c2$, and (4) vanishing of Josephson or proximity effects in planar junctions with particular crystallographic orientations. At present 1-2 remain inconclusive for reasons discussed in ref.\textsuperscript{9}. Experiments of type 3 have apparently still not been carried out, presumably because of the difficulty of measuring $H_c2$ reliably. Therefore the Josephson effect measurements appear to offer the best available tests of the superconducting state symmetry at present and for the near future.\textsuperscript{[11]}

Josephson effects between $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and other superconductors are a powerful probe of the order parameter symmetry, provided that the junction is planar and perpendicular to a crystallographic symmetry direction. For example suppose that the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ was a singlet ‘d-wave’ state with $x^2 - y^2$ symmetry (1$B_{1g}$ in the notation of ref.\textsuperscript{10}). Fabricating a planar junction with Nb perpendicular to the c-axis, one would expect to observe no Josephson effects. This is because there can be no matrix elements coupling the two order parameters in the two superconductors, since the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ order parameter changes sign upon a 90° rotation about the c-axis while the the Nb order parameter is invariant.\textsuperscript{[10,11]} This is an extremely powerful test, since it does not depend in any way upon the details of the pairing mechanism but depends only upon the existence of order parameters or pairing functions such as equation (1). If the junctions are not ideal but have imperfections which break the ideal
crystallographic symmetry, then the Josephson coupling matrix elements can be non-zero and there is no clear conclusion possible from the experiment. It is therefore very important to control the junction quality, and if possible, monitor the magnitude of the Josephson coupling as the junction quality is improved. If the coupling becomes weaker as the junction quality is improved than we may infer that it would vanish in an ideal junction, while if it becomes stronger or remains unchanged then the coupling would be finite for an ideal junction.

A number of experiments have been performed to determine Josephson effects in oriented junctions between YBa$_2$Cu$_3$O$_{7-\delta}$ and Nb or Pb. We shall especially concentrate on the results for c-axis (001) junctions and a-axis (100) junctions since these impose important symmetry constraints on the order parameter. First, Greene et al.\textsuperscript{[12]} using YBa$_2$Cu$_3$O$_{7-\delta}$-Au-Pb junctions perpendicular to the YBa$_2$Cu$_3$O$_{7-\delta}$ c-axis, observed weak Shapiro steps in the junction characteristic indicating a non-zero Josephson coupling in these (001) junctions. The steps vanish above the transition temperature of Pb, and $I_c R \approx 1\mu V$. These authors also searched for a proximity effect in the c direction, but were unable to observe it. Kwo et al.\textsuperscript{[13]} also observed Shapiro steps in (001) oriented junctions and $I_c R$ values of a roughly 0.5 mV. On the other hand Akoh et al.\textsuperscript{[14]} measured Shapiro steps in a number of (103) oriented YBa$_2$Cu$_3$O$_{7-\delta}$-Au-Nb sandwich junctions, but found no Josephson effects in (001) oriented junctions. This latter result was also found by Yoshida et al.\textsuperscript{[15]} who observed dc Josephson effects in (103), (100) and (110) oriented junctions, but found none in (001) junctions. Finally, Lee et al.\textsuperscript{[16]} found supercurrent characteristics in the IV curves for (100) films, but none for (001) or (103). The Lee et al. experiments were performed on smaller junction areas than the other measurements and the (001) faces were well characterized by X-ray diffraction and atomic force microscopy (AFM) suggesting an almost ideal junction geometry. The (103) faces were found to be effectively (001) faces in the latter experiments, due to the “tipping over” of the a – b planes at the surface.\textsuperscript{[17]} However, these authors did not demonstrate that the observed Josephson effects vanished above the transition temperature of Pb, so it is not possible to conclude definitively that there is coupling in those directions between Pb and YBa$_2$Cu$_3$O$_{7-\delta}$.

Nevertheless, taking the experimental results at face value, it would appear that a Josephson effect is present on (100) oriented junctions. If confirmed, this in itself rules out a large number of candidate pairing states (for example $A_2g$, $B_{2g}$, and $E_g$ states in table 5 of ref. 10). In fact if we assume that the YBa$_2$Cu$_3$O$_{7-\delta}$ pairing is singlet, as suggested by NMR Knight shift measurements.\textsuperscript{[14],[15]}
and use the approximately tetragonal point group for YBa$_2$Cu$_3$O$_{7-\delta}$, then only two distinct states are possible: conventional ‘s-wave’ (or more correctly, $^1A_{1g}$) or $x^2 - y^2$ ‘d-wave’ ($^1B_{1g}$). If a (001) Josephson effect exists, as suggested by the observations of Shapiro steps by Greene et al.\textsuperscript{[12]} and Kwo et al.\textsuperscript{[13]} then ‘s-wave’ is the only possible pairing state. On the other hand if the (001) Josephson coupling vanishes, as suggested by the work of Akoh et al.,\textsuperscript{[14]} Yoshida et al.,\textsuperscript{[15]} Lee et al.,\textsuperscript{[16]} and the failure to observe c-axis proximity effect\textsuperscript{[17]} then only the $d_{x^2 - y^2}$ pairing state is possible. Given these conflicting results and the importance of the conclusion they imply, it is important to clarify with further experiments precisely which junction orientations exhibit Josephson coupling and which do not, and to compare junctions of different qualities to see if the coupling becomes larger or smaller as the junction quality is improved.

3. ELECTROMAGNETIC PENETRATION DEPTH

There have been several developments in this area since our review article\textsuperscript{[9]} appeared. Existing data has been reanalysed\textsuperscript{[8,6]} and new data has become available.\textsuperscript{[19,20]} Given that the penetration depth directly measures the superfluid density, rather than the excitations of the condensate, it is in principle a clean probe of the superconducting state. However, only the asymptotic low temperature behaviour – exponential versus power law – is a qualitative measure of the presence or absence of nodes in the gap.

Until very recently, the only data with small scatter which extended to low temperature was that taken on thin films using kinetic inductance, by Fiory et al.\textsuperscript{[21]} Although the overall temperature dependence could be fitted to that of weak-coupling BCS theory, later analysis\textsuperscript{[6]} revealed that at low temperatures, the data follow

\[
\frac{\Delta \lambda(T)}{\lambda(0)} = B \left( \frac{T}{T_c} \right)^2 + O(T^3),
\]

where $\lambda(T)$ is the $a - b$ component of the penetration depth tensor, and $\Delta \lambda(T) = \lambda(T) - \lambda(0)$. The coefficient $B$ was found to be 0.63 for a film of thickness 300$\AA$ and 1.6 for a film of thickness 2000$\AA$.

More recently, Pond et al.\textsuperscript{[13]} observed similar behaviour and moreover found that over the entire temperature range, including low temperatures, the data were very well fit by the empirical form

\[
\lambda(T) = \frac{\lambda(0)}{\sqrt{1 - (T/T_c)^2}}.
\]

This result was independently found by Bonn et al.\textsuperscript{[6]} and us, analysing data from Anlage et al. (see below), and also confirmed
for the 500Å film data of Fiory et al. The data of Pond et al. only extend down to about 20 K unfortunately, so it is unclear whether their experiment is really in the asymptotic low temperature regime.

Perhaps the most complete of the recent experimental results are those of Anlage et al., performed by measuring the phase velocity of a microwave signal propagating along a thin film of superconductor, acting like a transmission line. These data extend down to reduced temperature \( t = T/T_c = 0.09 \). By suitable adjustment of their baseline zero temperature phase velocity, these authors were able to fit their data to the s-wave BCS exponential form with a zero temperature gap given by \( 2\Delta(0)/k_B T_c = 2.5 \pm 0.3 \). However, this fit extended all the way up to \( t = 1/2 \), and so may not be representative of the asymptotic behaviour. In fact, the same analysis applied to Nb and NbCN gave values of \( 2\Delta(0)/k_B T_c \) which were in disagreement with known results. Anlage’s data were independently analysed by Bonn et al. and by us. Both of these studies found that the raw data for the phase velocity \( v_p \) at low temperatures varies as

\[
\frac{c^2}{v_p^2} = 5.32 + 0.0636t^2
\]

which implies that \( \lambda(T) = \text{const} + 0.5t^2 \) in this temperature range. Note that in (4) there has been no subtraction of baseline performed. This behaviour is simply the low temperature limit of (3). It was also found that for \( 0.11 < t < 0.16 \), the data could be fit to the s-wave BCS form, with \( 2\Delta(0)/k_B T_c \approx 1.0 \). For temperatures \( t < 0.11 \), the data of Anlage et al. exhibit too much scatter to be reliably interpreted, although there is a possible indication of a change of behaviour. At temperatures below \( t = 0.11 \), we are not aware of data other than that of Fiory et al.; a detailed study at temperatures \( t < 0.1 \) is required to resolve the current situation.

Other measurements of the penetration depth have been made by \( \rho SR \), and are reported by Bonn et al.. These authors have obtained the most complete data at temperatures below \( t = 0.5 \), and find that the temperature variation is consistent with (3), and is certainly stronger than predicted by s-wave BCS theory. However, the scatter in the data together with the relatively large number of assumptions needed for the interpretation, render any conclusion from this technique open to question.

4. EXPONENTIAL TAILS IN THE DENSITY OF STATES

While the evidence for unconventional pairing in YBa\(_2\)Cu\(_3\)O\(_{\gamma-t}\) remains inconclusive it is important to test whether conventional pairing models can also explain the anomalous experimental results. In particular, is it possible for an s-wave BCS type pairing theory to give a non-zero quasiparticle density of states in the ’gap’ region
as implied by much of the experimental data\textsuperscript{1-8}. Of course gapless s-wave superconductivity is a well known possibility when there is large magnetic or inelastic scattering. However the scattering rate determined experimentally falls three orders of magnitude as the temperature is lowered and is much smaller than the value $\Delta/h$ required for standard gapless superconductivity. We must therefore turn to a quite different mechanism to explain the non-zero density of states in the gap region. We now show that order parameter disorder can give a density of states which is non-zero through the gap region, qualitatively similar to experimental observations in YBa$_2$Cu$_3$O$_{7-\delta}$.

Quenched randomness in the order parameter plausibly exists in YBa$_2$Cu$_3$O$_{7-\delta}$ and similar materials for several different reasons. Firstly, the attractive pairing interaction may itself be spatially random if it is associated with oxygen or other defects.\textsuperscript{25,26} In this case the usual BCS gap equation would give rise to a spatially varying gap function, $\Delta(\mathbf{r})$. Secondly, even if the pairing interaction itself is not associated directly with defects, localized impurities can give rise to a spatially varying gap function near the defect.\textsuperscript{26} Finally, if the superconducting state is in a ‘vortex glass’ phase due to trapped vortices the gap function will also be spatially non-uniform.\textsuperscript{26} Such trapped vortices could be present even for nominally zero field cooled samples because of the very low $H_{c1}$.

In order to model the density of states in superconductors with order parameter disorder we shall use a Bogoliubov-de Gennes Hamiltonian:

$$\hat{H} = \sum_{i,j,\sigma} H_{ij} c_{i\sigma}^+ c_{j\sigma} + \sum_i \Delta_i c_{i\uparrow}^+ c_{i\downarrow}^\dagger + h.c.$$ \hfill (5)

where $c_{i\sigma}^\dagger$ creates an electron of spin $\sigma$ in orbital $i$ and so on. For simplicity we shall only consider one orbital per unit cell of the copper-oxide plane, and so $H_{ij}$ is a simple nearest neighbor hopping Hamiltonian on a square 2d lattice. We choose the Fermi level as the zero of energy. Now if the gap function is a constant $\Delta$ at all sites, then there are no eigenstates of (5) between $-\Delta$ and $+\Delta$; this is the usual BCS energy gap. Even if the single particle Hamiltonian $H_{ij}$ is spatially random and the single particle states are in the strongly localized limit the gap in the spectrum remains. This can be proved easily from equation (5) by pairing time reversed single particle eigenstates.\textsuperscript{27} On the other hand, consider the spectrum of the Hamiltonian (5) if the order parameter is spatially random, with a probability distribution $\mathcal{P}$ with mean

$$\langle \Delta_i \rangle = \Delta_0$$ \hfill (6)

and variance

$$W^2 \equiv \langle \Delta_i^* \Delta_i \rangle - |\langle \Delta_i \rangle|^2 \neq 0.$$ \hfill (7)
If $\mathcal{P}(\Delta) = 0$ for $|\Delta| < \Delta_{\text{min}}$, with $\Delta_{\text{min}} \neq 0$, then we expect that the quasiparticle spectrum has a gap from $-\Delta_{\text{min}}$ to $+\Delta_{\text{min}}$. This may be shown in a one dimensional lattice using transfer matrix methods. If the probability distribution of the gap function, $\Delta_i$, has no minimum value, e.g. a uniform distribution $0 \leq \Delta_i \leq \Delta_{\text{max}}$ or a Gaussian distribution, then it is possible that there may be quasiparticle states at all energies, and there will be no true gap in the energy spectrum. In fact Ziegler\textsuperscript{[34]} proved that the density of states at the Fermi level, $\rho(E_F)$, becomes non-zero even for arbitrarily small amounts of disorder in the gap function. This extends earlier work of Oppermann, who had argued that $\rho(E_F)$ would remain zero unless the disorder, $W$, exceeded a critical value.\textsuperscript{[29]}

In order to gain a more detailed understanding of the effects of quenched order parameter disorder we have numerically computed the density of states from the disordered Bogoliubov-de Gennes equation (5). For simplicity we considered a spatially uniform single particle Hamiltonian, with nearest neighbor hopping $t = -0.125$eV and diagonal site energy $\epsilon_0 = +0.06$eV relative to the Fermi level. This corresponds to about 20\% doping relative to a half filled band. The gap function $\Delta_i$ was chosen to be real, with mean $\Delta_0 = 25$meV, and a Gaussian probability distribution of width $W$ ranging from 0 to 50meV. The results we present here were obtained with a statistically independent gap function at each site, however the results are qualitatively similar for correlated disorder. The density of states was computed by the recursion method\textsuperscript{[30]} using 1024 x 1024 lattices with periodic boundary conditions. To improve convergence the recursion was actually computed using $\tilde{H}^2$ with 360-400 recursion levels and an ensemble of ten or more statistically independent lattices.

Figure 1 shows the computed integrated density of states

$$N(E) = \int_{-E}^{E} \rho(\epsilon)d\epsilon$$

for energies, $E$, up to the mean gap energy, $\Delta_0 = 25$meV, with disorder distributions of width $W = 0, 12.5$meV, 25meV and 50meV. Clearly, as the disorder increases the gap gradually fills with states, and the density of states becomes non-zero at all energies. Overall the behavior of the density of states is similar to that in disordered normal metals where the density of states develops an exponential 'band-tail' at the band edge.\textsuperscript{[21]} The full curves in figure 1 for $W = 12.5$meV, 25meV and 50meV correspond to a fit to the exponential form:

$$N(E) = a\exp\left(-b(E_0 - E)^\nu/W\right)$$

motivated by the corresponding asymptotic density of states in normal metals.\textsuperscript{[22]} The fit shown corresponds to $\nu = 2, E_0 = \Delta_0$, and shows that this functional form gives a good agreement in the
Fig. 1. Calculated integrated density of states \( N(E) \) for a Gaussian distributed gap function, with \( \Delta_0 = 25\text{meV} \) and \( W = 0, 12.5\text{meV}, 25\text{meV} \) and \( 50\text{meV} \). Asymptotic limit \( E \to 0 \) (the small oscillations in the numerical \( N(E) \) are an artefact of a finite recursion calculation). Fits with \( \nu = 3/2 \) were also reasonable in this limit, while fits with \( \nu = 1 \) were not. Note that in order to keep the number of fitting parameters to a minimum we have not attempted to include any pre-exponential factors in the fit.

In conclusion, our calculations show that 'gapless' s-wave superconductivity can occur without magnetic or inelastic scattering provided there is disorder in the gap function. However, as can be seen in figure 1, the disorder must be relatively strong, \( W > \Delta_0 \), before the density of states becomes significant throughout the whole gap region. Whether such a strong randomness is reasonable depends upon the role of defects in the electronic structure and pairing interactions in \( \text{YBa}_2\text{Cu}_3\text{O}_{7-\delta} \). If such a large disorder is not present, then the most reasonable explanation for the non-zero density of states seen in many experiments \(^{9-10} \) is that the superconductivity corresponds to a d-wave \( x^2-y^2 \) state. Such a pairing state could be consistent with the observed \( T^2 \) temperature dependence of the electromagnetic penetration depth at low temperatures.\(^{11} \) Hopefully experiments searching for Josephson effects in (100) and (001) axis junctions with Pb or Nb, and other experiments currently underway, will be able to determine unambiguously the pairing state symmetry in the near future.

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REFERENCES

6. D.A. Bonn et al., unpublished
7. R.C. Yu et al., University of Illinois preprint.
17. Mark Lee, private communication.
33. See (e.g.) M. Prohammer and J.P. Carbotte, *Phys. Rev. B.* 43, 5370 (1991).