Experimental Constraints on the Pairing State of the Cuprate Superconductors: an Emerging Consensus

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ABSTRACT

We present a critical discussion of recent experimental probes of the pairing state of the high temperature superconductors, focusing primarily, but not exclusively, on $YBa_2Cu_3O_{7-\delta}$, where the best data currently exist. Penetration depth measurements near T_c give no indication of an extra transition, indicating that the pairing state is a one-dimensional representation of the crystal symmetry. Penetration depth measurements at low temperatures provide strong evidence for a change in sign of the gap function over the Fermi surface. Quantum mechanical phase interference experiments generally confirm this and in addition show that the nodal positions are consistent with a $d_{x^2-y^2}$ pairing state. This pairing state is consistent with photoemission measurements of the gap function, Raman scattering, the effect on T_c of impurities, and many other data (reviewed by two of us previously) which indicate the presence of low lying excitations in the superconducting state. We also discuss evidence that apparently does not fit in with a $d_{x^2-y^2}$ pairing state, and we describe possible alternative scenarios.

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1. Introduction

The pairing state symmetry of the high temperature superconductors is a topic that over the last 5 or 6 years has moved from the wings to centre stage. Although the star billing in the tragicomical history of high temperature superconductivity must surely go to the mechanism for pair formation, the identification of the pairing state may well be a bit part that has stolen the show. Indeed no other aspect of the high temperature superconductors has ignited as much controversy; and some of the most elegant and sophisticated experiments in condensed matter physics have been performed to illuminate this issue.

In 1990, writing in Volume II of this series, Annett, Goldenfeld and Renn (hereafter referred to as AGR)[1,2] presented a lengthy review of the experimentally determined properties of the superconducting state of $YBa_2Cu_3O_{7-\delta}$, in which they described a variety of anomalous features which would be naturally explained if the pairing state were an unconventional singlet state with line nodes. These features included the presence of low energy excitations in NMR, Raman scattering, infra-red absorption and the absence of a Hebel-Slichter coherence peak. On the other hand, AGR were prevented from concluding that a d-wave state was indeed indicated, because of the apparent close agreement between the best available measurements[3] of the temperature dependent penetration depth $\lambda(T)$ below 20 K and the exponential form for this quantity expected for a pairing state without nodes. In contrast, a clean unconventional singlet state with line nodes would have yielded a linear dependence on temperature for the quantity measured. Thus, AGR's original article ended with the paragraph

> In summary, given the presently available data, it appears that triplet states are ruled out by the Knight shift anisotropy, and singlet states with line nodes seem to be ruled out by the temperature dependence of the penetration depth. If both of these tentative results stand up to further scrutiny, then the only remaining candidate state would be the conventional one.

The caution expressed by AGR has, in a sense, been vindicated by developments, especially by two key sets of experimental results. First, the data of Ref. 3 were re-analysed[4] and shown, in fact, to be inconsistent with an exponential temperature dependence; the actual dependence of the penetration depth on temperature was found to be quadratic, known to be consistent with an unconventional singlet state subject to impurity scattering. This finding was followed by a series of decisively accurate and controlled experiments on very clean $YBa_2Cu_3O_{7-\delta}$ single crystals by Hardy, Bonn and co-workers at the University of British Columbia (see their Chapter in the present Volume for a detailed survey

of these developments),[5] which indicated a strong temperature dependence of the penetration depth below 20 K, consistent with a linear behaviour, and clearly ruling out the much weaker dependence expected for a nodeless superconductor. Subsequent experimental and theoretical developments, discussed in detail below, add support to the interpretation that the superfluid density has a temperature dependence at low temperatures which is inconsistent with the simplest s-wave pairing state models, but consistent in a semi-quantitative manner with the generic predictions of a $d_{x^2-y^2}$ pairing state.

The intense interest that these discoveries provoked resulted in a flurry of experimental results which bore more or less directly on the identification of the pairing state. The second key set of experimental results are a series of elegant measurements of phase interference effects associated with the sign change of the gap function at the Fermi surface, beginning with the paper (describing the experiment referred to below as UIUC I) by Wollman, Van Harlingen, Lee, Ginsberg and Leggett.[6] As we discuss in detail below, the observation of these interference effects can only be reconciled with s-wave pairing under hypotheses that we regard as either already ruled out or extremely implausible.

These key developments, augmented by the many other experimental observations consistent with nodes in the energy gap, such as photoemission determinations of the gap function symmetry, have lead to what many, including the present authors, believe to be a compelling case for the $d_{x^2-y^2}$ pairing state. Nevertheless, it is only fair to point out that there are still grounds for caution, based upon two experimental results which, if taken at face value, do not conform in an obvious way to the d-wave pairing picture. These are the apparent observation of c-axis tunneling currents between a conventional superconductor and a cuprate superconductor[7] and the observation of a non-zero critical current across a closed grain-boundary junction loop.[8]

The purpose of this Chapter is to discuss these developments in some depth, highlighting the logical connections between the experimental findings and their theoretical interpretation. Rather than attempting a comprehensive review of all the experimental findings that may be taken as evidence for or against d-wave pairing, we shall concentrate on those experiments which, in our view, are most decisive. Also, we shall not repeat discussion of experiments which were already reviewed extensively in AGR, unless there have been major changes since 1991.

The layout of this Chapter is as follows. Firstly, in Section 2, we shall very briefly review the assumptions which underly the classification of different pairing states in superconductors. Then, in Section 3, we show how very general symmetry and thermodynamic considerations limit the possible superconducting states, especially mixed symmetry states such as $s + d$, $s + id$. In Section 4, we shall

discuss the specific symmetries involved in the high T_c materials. In particular we discuss the symmetry implications of their highly layered structures, the existence of chains, and the orthorhombic distortions of the CuO_2 planes. In Section 5 we discuss the evidence for sign changes in the superconducting gap function $\Delta(\mathbf{k})$. This includes penetration depth and photoemission experiments among others. Phase sensitive interference experiments providing evidence for a macroscopic order parameter with $d_{x^2-y^2}$ symmetry are discussed in Sections 6 and 7. Section 6 discusses the general principles underlying this type of experiment, while Section 7 discusses the specific experiments which have been performed to date. In Section 8, we briefly discuss the effects of impurities, since the extreme sensitivity of unconventional superconductors to non-magnetic impurity scattering is often cited as an objection to d-wave pairing in the high T_c materials. Finally, our conclusions present our synthesis of the overall experimental situation as it currently stands.

2. Basic Assumptions: Pairing and ODLRO

In discussing the symmetry of the superconducting state in the high T_c materials we want to make as few assumptions as possible about the nature of the superconductivity or of its mechanism. At first sight this might appear to be especially difficult in the high T_c superconductors since there is not even a universally agreed upon picture of the normal state. If the normal state were generally agreed to be a Fermi liquid, as is the case in ^{3}He and the heavy Fermion materials, then one could develop the theory of possible superconducting states arising from attractive interactions among the quasiparticles. The instabilities of the Fermi liquid to Cooper pairing in various channels would lead to a system of BCS-like gap equations, whose solutions would be the various possible pairing states of the system. The difficulty of applying this procedure to the high T_c superconductors is that it is by no means clear that the normal state above T_c is a Fermi liquid, or that any form of BCS-like gap equation is valid below T_c.

In fact, it is not necessary to assume that the normal state is a Fermi liquid in order to understand the symmetries of possible superconducting states. The only assumption which it is necessary to make is to assume that *pairing* and *off diagonal long range order* (ODLRO) occur in the superconducting state. In other words, one must assume that T_c corresponds to the temperature at which the following correlation function first becomes non-zero:

$$\langle \psi_\alpha^*(\mathbf{r}_1,t_1)\psi_\beta^*(\mathbf{r}_2,t_2)\psi_\gamma(\mathbf{r}_3,t_3)\psi_\delta(\mathbf{r}_4,t_4)\rangle \begin{cases} = 0 & T > T_c \\ \neq 0 & T < T_c \end{cases} \qquad (2.1)$$

where $\mathbf{r}_1$ and $\mathbf{r}_2$ are taken to be macroscopically distant from $\mathbf{r}_3$ and $\mathbf{r}_4$. Here

$\psi_\alpha^*(\mathbf{r}, \mathbf{t})$ and $\psi_\alpha(\mathbf{r}, \mathbf{t})$ are the usual electron creation and annihilation operators, for an electron of spin α at point $\mathbf{r}$ and time t. The existence of such ODLRO will ensure the rigidity of the thermodynamic state under weak applied magnetic fields, and hence follows flux quantisation, zero resistivity and the Meissner effect.[9] Whether or not the state above T_c is a Fermi liquid is clearly irrelevant in considerations solely of properties of the state below T_c. Possibly if other kinds of long range order are also present above or below T_c, then these may alter the physics, but this is not the case for the majority of the non-Fermi liquid normal states proposed to date, such as a gas of pre-formed pairs,[10] or the short ranged RVB spin liquid.[11,12]

Of course ODLRO could in principle also occur in other forms besides (2.1). For example, a charge e condensate is not ruled out *a priori*.[13] However, for reasons discussed extensively in AGR[1] we believe there is overwhelming evidence for a conventional $2e$ ODLRO in the cuprates. As well as the value of the flux quantum, the evidence includes the existence of ac and dc Josephson effects in cuprate-cuprate junctions and in junctions with ordinary superconductors such as Pb and Nb, and the observation of Andreev reflection. Therefore from now on we shall take it as given that the onset of superconductivity at T_c corresponds to the formation of a condensate of electron pairs. At this point we do not need to make any assumptions about the nature of the state above T_c; for example it could equally well be a Fermi liquid, a marginal Fermi liquid,[14] a Luttinger liquid[15] or a gas of bound pairs which are not Bose condensed.[10]

The existence of a condensate of electron pairs below T_c also implies that the order parameter for superconductivity corresponds to the appearance (i.e. non-zero value) of Gor'kov type off-diagonal Green functions

$$\mathcal{F}(\mathbf{r}_1, t_1, \mathbf{r}_2, t_2; \alpha\beta) = \langle \psi_\alpha(\mathbf{r}_1, t_1)\psi_\beta(\mathbf{r}_2, t_2)\rangle, \qquad (2.2)$$

in an appropriate grand canonical ensemble. We shall assume (apart from one exception discussed below) that there exists a Ginzburg-Landau order parameter $\Psi(\mathbf{r}_1, \mathbf{r}_2; \alpha, \beta)$ identified with the equal time, $t_1 = t_2$, limit of (2.2) (the zero-frequency limit is essentially equivalent). The observation of three dimensional critical scaling in the XY universality class[16] and the existence of a λ-transition-like specific heat anomaly near T_c which is consistent with that of the ^{4}He universality class[17] is evidence for the existence of a (two component) Ginzburg-Landau order parameter, at least in the scaling limit as $T \to T_c$.

As soon as the Green function $\mathcal{F}(\mathbf{r}_1, t_1, \mathbf{r}_2, t_2; \alpha\beta)$ is non-zero, the electron self-energy must also develop anomalous, or off-diagonal, terms, corresponding to the BCS gap function $\Delta(\mathbf{r}_1, t_1, \mathbf{r}_2, t_2; \alpha\beta)$. If the normal state is a Fermi

liquid, then Δ determines the gap in the quasiparticle spectrum in the usual way. However, if the normal state is not a Fermi liquid, then there may be no direct correspondence between Δ and the quasiparticle spectrum. For example in the pre-formed pairs scenario the quasiparticle spectrum has become gapped even above T_c.[10] There is also no reason to suppose that Δ obeys a mean field equation such as the BCS gap equation.

By the *symmetry of the pairing state* we mean the transformations of the function $\mathcal{F}(\mathbf{r}_1, t_1, \mathbf{r}_2, t_2; \alpha\beta)$ under the various symmetry operations of the crystal and spin symmetry groups. Clearly these symmetries can be defined equally well whether or not the cuprates have a Fermi liquid normal state. Many of the experimental tests of the pairing state symmetry which we discuss below (such as the Josephson experiments) are also completely independent of Fermi liquid assumptions. Other tests, such as the evidence for a node in the gap function from penetration depth data, do have to make some Fermi liquid-like assumptions. In particular it is necessary to assume the existence of a Fermi surface. In practical terms a "pseudo" Fermi surface should be sufficient, namely a surface in momentum space where the electron distribution function, $n(\mathbf{k})$, has a cusp, rather than a full Fermi liquid discontinuity.[14,15] The positron annihilation and angle resolved photoemission experiments[18] both show that such a Fermi surface exists (at least in the ab-plane) of the cuprates, whether or not the quasiparticle lifetimes are Fermi liquid, marginal or Luttinger.

With regard to general symmetry properties, almost all of the non-Fermi liquid models of the cuprates will behave similarly. One of the few exceptions to this rule is the anyon theory of superconductivity.[19] This is because, unlike the marginal or Luttinger liquid models, this state has a symmetry which is different from a normal Fermi liquid: broken time reversal symmetry, T. However, even broken T symmetry in the normal state does not significantly change the symmetry analysis outlined in the next two Sections. In particular the considerations of Section 3 imply that two separate phase transitions are to be expected in the proposed $d_{x^2-y^2} + id_{xy}$ anyon superconducting state, whether or not T is broken in the normal state. In any case, to date there appears to be no strong signature of a broken T state in $YBa_2Cu_3O_{7-\delta}$.[20]

3. Mixing of Different Symmetries: Thermodynamic Constraints

In the previous Section we introduced the general idea of a superconducting order parameter:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2; \alpha\beta) \equiv \langle \psi_\alpha(\mathbf{r}_1)\psi_\beta(\mathbf{r}_2) \rangle. \tag{3.1}$$

In this Section we will discuss to what extent thermodynamic or related observations enable us to infer constraints on the behaviour of the expression (3.1) under the (exact or approximate) symmetry operations of the crystal Hamiltonian. In particular we will emphasize the conditions under which the pairing state belongs to a single irreducible representation of the symmetry group, and the conditions under which it becomes a "mixed" state involving two or more representations. As we show below, simple thermodynamic considerations place quite strong restrictions on the conditions for such mixed states to occur. It should be emphasised that the considerations of this Section are very general and do not in themselves exclude e.g. that the equilibrium Ψ has nontrivial transformation properties under the crystal translation group, i.e. that the translational symmetry is spontaneously broken in the superconducting state, although in the rest of this Chapter we should usually assume that it is not.

Consider first the group G of *exact* symmetries of the Hamiltonian for a given crystal. This is the direct product of the gauge group $U(1)$, the crystal lattice translation group T_ℓ and the crystal point group H:

$$G = U(1) \otimes T_\ell \otimes H \tag{3.2}$$

As remarked above, we will normally assume that Ψ transforms as the identity representation of T_ℓ, in which case we can simply take G to be given by $U(1) \otimes H$; however, we may as well keep (3.2) for generality. We now expand Ψ in the irreducible representations $\chi(\mathbf{r}_1 \mathbf{r}_2; \alpha\beta)$ of the group G:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2; \alpha\beta) = \sum_l \sum_{m=0}^{D_l} \psi_{lm} \chi_{lm}(\mathbf{r}_1, \mathbf{r}_2 : \alpha\beta) \tag{3.3}$$

where D_l is the dimension of the l-th irreducible representation and the ψ_{lm} are coefficients which are in general complex. Note that it is not assumed, anywhere in this argument, that ψ is constant as a function of the centre of mass variable $\mathbf{R} \equiv (\mathbf{r}_1 + \mathbf{r}_2)/2$.

We now proceed, in the spirit of Ginzburg and Landau, to express the free energy F as a multiple power series in the coefficients ψ_{lm}, using the principle that F must be invariant under all operations of G (and moreover must be real). It is immediately clear that invariance under U(1) implies that all terms containing an odd number of ψ_{lm}'s vanish identically, while the rest must contain an even number of ψ_{lm}'s and ψ_{lm}^*'s. Moreover, the second-order terms must have the form $\sum_l \alpha_l(T) \sum_m |\psi_{lm}|^2$, where the $\alpha_l(T)$ are functions of T which, barring

pathology, will be different for different l. At fourth order the generic term is

$$\frac{1}{2}\sum \beta_{l_1 m_1 l_2 m_2 l_3 m_3 l_4 m_4}\psi^*_{l_1 m_1}\psi^*_{l_2 m_2}\psi_{l_3 m_3}\psi_{l_4 m_4}. \tag{3.4}$$

For the tetragonal and orthorhombic symmetry groups relevant to the high T_c superconductors the relevant representations and Ginzburg-Landau expansions up to fourth order are well known.[21] However, such symmetry analyses usually assume that only a single irreducible representation, say l, is relevant. Instead, let us examine terms in the Ginzburg-Landau expansion which couple two or more representations.

The quartic terms can be grouped, for reasons which will become apparent, into what we shall call "mixing" and "non-mixing" terms. The non-mixing terms are those in which for each representation the ψ_{lm}'s enter to even order, and mixing terms are the rest. The non-mixing terms are thus the terms such as $|\psi_{l_1 m_1}|^2 |\psi_{l_2 m_2}|^2$ and $(\psi^*_{l_1 m_1})^2 (\psi_{l_2 m_2})^2$ + c.c., while the mixing terms are of the form $\psi^*_{l_1 m_1}\psi^*_{l_2 m_2}\psi^2_{l_1 m_1}$. The usefulness of this separation into mixing and non-mixing terms lies in the fact that in all orthorhombic and tetragonal superconductors, such as the cuprates, simple symmetry arguments imply that the mixing terms are absent.[21] Thus the general form of the Ginzburg-Landau expansion up to fourth order is:

$$\begin{aligned}
F(T) = \sum_{lm} &\left(\alpha_l(T)|\psi_{lm}|^2 + \frac{1}{2}\beta_{l,m_1,m_2,m_3,m_4}\psi^*_{lm_1}\psi_{lm_2}\psi_{lm_3}\psi_{lm_4} \right) \\
&+ \sum_{l_1,l_2,m_1,m_2,m_3,m_4} \frac{1}{2}\beta_{l_1 l_2 m_1 m_2 m_3 m_4}\psi^*_{l_1 m_1}\psi_{l_1 m_2}\psi^*_{l_2 m_3}\psi_{l_2 m_4} \\
&+ \sum_{l_1,l_2,m_1,m_2,m_3,m_4} \frac{1}{2}\kappa_{l_1 l_2 m_1 m_2 m_3 m_4}\psi^*_{l_1 m_1}\psi^*_{l_1 m_2}\psi_{l_2 m_3}\psi_{l_2 m_4},
\end{aligned} \tag{3.5}$$

plus terms involving three or four distinct representations, l. For the purposes of the present argument, we may neglect the sixth- and higher-order terms, which do not affect the results qualitatively. In fact there are no mixing terms to *any* order[21] unless three or four distinct representations are mixed. General results from non-truncated Ginzburg-Landau expansions have also been developed by Gufan *et al.*[22] for p- and d-wave superconductors.

At a sufficiently high temperature all the $\alpha_l(T)$ are positive, and minimisation of the free energy is achieved by setting all ψ_{lm} equal to zero, i.e. the system is in the normal phase. As the temperature falls, there comes a point, $T_c^{l_0}$, where one α_l corresponding (e.g.) to $l = l_0$, becomes negative while (in the absence of

pathological coincidence) all other α_l remain positive. We first consider the case (actually not very likely to be relevant to the high temperature superconductors) where the irreducible representation l_0 is multidimensional. In this case, for T just below $T_c^{l_0}$, some or all of the corresponding $\psi_{l_0 m}$ will be nonzero; the weights with which the various m are represented will be controlled primarily by the fourth-order terms, and may in principle depend on T through the β's (or through the omitted higher-order terms). Thus it is possible that the "configuration" (i.e. the relative weight of the various m) undergoes either a continuous or a discontinuous change below $T_c^{l_0}$; an example of the latter is the A-B transition in superfluid ^{3}He.

We turn to the case, probably more relevant to the high temperature superconductors, that the irreducible representation l_0 is one-dimensional. The crucial question is: What is the condition that below $T_c^{l_0}$ some ψ_{lm} corresponding to *other* values of l are nonzero? It is clear that if the mixing terms are nonzero this can happen in a continuous way (even if all other α_l are positive for all T). But let us consider the case that the mixing terms vanish, corresponding to the high T_c superconductors. For simplicity of notation, we shall specialise to the case where there is only one relevant irreducible representation besides l_0 and it is moreover also one-dimensional (the generalisations are straightforward). In this case we note that we can always minimise the free energy by choosing $\arg(\psi_{l_0 m_0}\psi_{lm})$ to be either 0 or π; having done this, and changing the notation for convenience ($l_0 \to 1$, etc.), we can write

$$
\begin{aligned}
F(T) = &F_0(T) + \alpha_1(T)|\psi_1|^2 + \alpha_2(T)|\psi_2|^2 + \\
&\frac{1}{2}\beta_1(T)|\psi_1|^4 + \frac{1}{2}\beta_2(T)|\psi_2|^4 + \kappa(T)|\psi_1|^2 \cdot |\psi_2|^2.
\end{aligned}
\tag{3.6}
$$

For purposes of illustration we shall choose the temperature dependences of the coefficients to have the simple Ginzburg-Landau form

$$
\begin{aligned}
\alpha_1(T) &= \alpha_1(T - T_{c_1}), \\
\alpha_2(T) &= \alpha_2(T - T_{c_2}), \\
T_{c_2} &\leq T_{c_1} \quad (\text{and possibly } T_{c_2} < 0), \\
\beta_1(T) &= b_1, \\
\beta_2(T) &= b_2, \\
\kappa(T) &= \kappa
\end{aligned}
\tag{3.7}
$$

where b_1, b_2, and κ are constants, and where stability requires[23] that $\beta_1, \beta_2 > 0$, $\kappa > -\sqrt{\beta_1 \beta_2}$. The qualitative results are independent of this ansatz.

The phase diagram of a system with a free energy of the form (3.7) is discussed in detail by Imry.[24] For our purposes it is sufficient to know the following: For T above the "upper" transition T_{c_1}, it is clear that $\psi_1 = \psi_2 = 0$ (normal phase). For T just below T_{c_1}, the free energy is minimised by the choice

$$\psi_1 = (\alpha_1/\beta_1)(T_{c_1} - T)^{1/2}, \qquad \psi_2 = 0. \tag{3.8}$$

At lower temperatures there are various possibilities, depending on the ratios of the parameters.[24] However, it is clear that if ψ_2 is ever to obtain a finite value, one of two things must happen: either it must jump discontinuously from zero to this value, which evidently corresponds to a first-order phase transition with an actual discontinuity in the value of various physical quantities, or there must be a second second-order phase transition at a temperature T^* given by

$$T^* - T_{c2} = \lambda(T^* - T_{c1})$$
$$\lambda = \kappa\alpha_1/\alpha_2\beta_1 \tag{3.9}$$

This second possibility requires $\lambda \leq T_{c2}/T_{c1}$. In this case it is straightforward to show that the (positive) specific-heat discontinuity at T^* is given by the expression

$$\Delta c_v^* = (a_2^2/b_2)\frac{(1-\lambda)^2}{1 - \kappa^2/b_1b_2} \geq (a_2^2/b_2)\frac{[(T_{c1} - T_{c2})/T_{c1}]^2}{1 - \kappa^2/b_1b_2} \tag{3.10}$$

Thus, assuming that the ratio $(a_2^2/b_2)/(a_1^2/b_1)$ is not pathologically small, the anomaly at T^* is comparable to that at T_c ($\equiv T_{c1}$) unless T_{c2} is extremely close to T_{c1} (and quite likely even then). A second quantity of interest is the change in slope at T^* of the "total" order parameter $|\psi|^2 \equiv |\psi_1|^2 + |\psi_2|^2$; crudely speaking, many physical quantities such as the mean-square energy gap are likely to be roughly proportional to this. We find for the *relative* change in slope δ^* at T^* the expression

$$\delta^* = \frac{(1-\lambda)(1 - \lambda a_2/a_1)(a_2b_1/a_1b_2)}{1 - \kappa^2/b_1b_2} \tag{3.11}$$

In simple BCS-type theories it turns out that $a_j \propto T_{cj}^{-1}$, and thus (in view of the constraint on λ) the quantity δ^* is positive in such theories and of order one except possibly for T_{c2} very close to T_{c1}.

It is clear that the above results, derived for the explicit form (3.6) of the free energy, should generalise qualitatively to more realistic "non-mixing" forms, with the sole caveat that if the temperature T^* is very low compared to T_c the anomalies δc_v^* and δ^* are likely to be correspondingly reduced. With this caveat,

therefore, we draw the following very important conclusion: If the order parameter is a superposition of two functions from different irreducible representations of the crystal symmetry group and symmetry considerations forbid "mixing" of these functions in the free energy (as in the cuprates), then *there must inevitably be a second phase transition at some temperature below* T_c. Unless the relevant irreducible representations have transition temperatures which are very close, both the entropy and other physical quantities will undergo either discontinuities or substantial changes in slope. The almost complete absence (see Section 5.1), to date, of any suggestion of such phenomena in the cuprate superconductors is a very strong argument against this type of superposition.

For completeness we should briefly discuss what happens when, owing perhaps to some small breaking of the symmetry (such as may be constituted, for some at least of the high temperature superconductors, by the orthorhombic crystalline anisotropy) the mixing terms are small but not zero. We first note that any "quadratic" mixing, that is, any term in the free energy of the form

$$\gamma(\psi_1 \psi_2^* + c.c.) \tag{3.12}$$

can always be eliminated by a re-diagonalisation of the quadratic terms; however, the quartic terms will then contain terms of the form $\psi_1^3 \psi_2$ and $\psi_2^3 \psi_1$, whose coefficients will be proportional to $\gamma/|\alpha_1 - \alpha_2|$ when this is small. We note that in most cases these coefficients will not be strongly T-dependent; in particular, in BCS theory, because of the special form of the $\alpha_j(T)$, $|\alpha_1 - \alpha_2|$ is approximately $T(T_{c2}^{-1} - T_{c1}^{-1})$. There may in addition be "direct" fourth-order mixing terms. In the following, let T^* be the temperature at which a second second-order phase transition would have occurred in the absence of a mixing term.[25] For small mixing, the term in $\psi_1 \psi_2^3$ will have little effect for $T \geq T^*$, so we shall neglect it. Suppose now that the coefficient of $\psi_2 \psi_1^3$ is of order of magnitude ξ. Then for $T < T_{c1}$ and not too close to T^*, the effect of the mixing term is that ψ_2 is non-zero, increasing as $T(T_{c1} - T)^{3/2}$:

$$\psi_2 \sim \xi \psi_1^3 |\alpha_2'(T) \sim \xi(\alpha_1/\beta_1)^{3/2}(T_{c1} - T)^{3/2}/\alpha_2'(T), \tag{3.13}$$

where $\alpha_2'(T) \equiv \alpha_2(T)(1 - \lambda)$.

Well below T^*, on the other hand, the mixing will have only a small effect and ψ_2 will increase approximately as $[-(\alpha_2'(T)/\beta_2) \cdot (1 - \kappa^2/\beta_1\beta_2)^{-1}]^{1/2}$. We may obtain an estimate of the order of magnitude ΔT of the crossover region by equating the value of the first expression at $T^* + \Delta T$ to that of the second at

$T^* - \Delta T$; because $\alpha'_2 \equiv \alpha_2(1 - \lambda)(T - T^*)$, this gives

$$\Delta T = \left(\frac{\xi}{\beta_2}\right)^{2/3} \left(\frac{\alpha_1\beta_2}{\alpha_2\beta_1}\right) \left(\frac{T_{c1} - T^*}{1 - \lambda}\right) \left(1 - \kappa^2/\beta_1\beta_2\right)^{1/3} \qquad (3.14)$$

Thus for ξ/β_2 non-zero but $\ll 1$ (and λ not too close to 1, etc.) the vestige of the second second-order transition persists in the form of a sharp kink in the thermodynamic properties near T^*, as we should expect intuitively; the absence of observation of such behaviour may be used to put limits on ξ in any specific case of interest.

Finally, what about the quartic terms in the Ginzburg-Landau expansion which involve three or four distinct representations? In this case the "mixing" terms need not vanish. For example, mixing terms such as $\psi^*_{l_1m_1}\psi^*_{l_2m_2}\psi_{l_3m_3}\psi_{l_4m_4}$ are symmetry-allowed in a tetragonal crystal with $l_1 = A_{1g}$ $l_2 = A_{2g}$, $l_3 = B_{1g}$, $l_4 = B_{2g}$ (in the notation of Ref. 21). However, mixing terms of this kind do not lead to a continuous mixing of representations of the ground state, and thus do not change the qualitative observations given above, regardless of how many α_l's go negative. Again a second phase transition below $T_c^{l_0}$ is required if a mixed symmetry state is to exist at low temperatures.

4. Classification of Pairing States in the Cuprates

The basic principles of the symmetry classification of superconducting states are well known,[26−30] and have been reviewed for the high T_c symmetry groups in Ref. 21. However, there are several issues which potentially complicate the situation in the high T_c materials. We have already discussed the possibility that the normal state is not a Fermi liquid. Another complication is the strongly two-dimensional nature of the crystals, with possibly no coherent single electron motion between planes. Further complications are the existence of chains and other orthorhombic distortions, and the bilayers and trilayers present in these materials.

From now on we shall restrict our attention to singlet pairing states since, as discussed in AGR,[1] the Knight shift experiments in $YBa_2Cu_3O_{7-\delta}$ imply that the superconducting state has no unpaired spins at $T = 0$. More recent Knight shift experiments on $La_{2-x}Sr_xCuO_4$ and on the one-, two- and three-layer systems, $Tl_2Ba_2CuO_{6+y}$, $TlSr_2Ca_2Cu_2O_{7-\delta}$, and $Tl_2Ba_2Ca_2Cu_3O_{10-\delta}$, all indicate that the spin susceptibility vanishes at zero temperature (except possibly for a small impurity induced contribution) and hence that these are all singlet superconductors.

At first sight, singlet pairing would imply, by the Pauli principle, that the orbital parity must be even. However, at this point we should note a possible loophole in this argument: as pointed out originally by Berezinskii[35] in the context of superfluid ^{3}He, and explored more recently by Balatsky and Abrahams[36] in the context of heavy-fermion and other superconductors, states can exist which are odd in *frequency*, so that the Gor'kov Green function $\mathcal{F}(\mathbf{r}_1, t_1, \mathbf{r}_2, t_2; \alpha\beta)$ is an odd function of $t_1 - t_2$. This precludes having a non-zero pairing amplitude at equal times, $t_1 = t_2$, or at zero frequency and hence the order parameter cannot be defined as in (3.1). For these odd frequency states, spin singlet superconductivity corresponds to odd parity pair pairing, while triplet pairing states will have even parity, opposite to the usual situation. Furthermore since the gap function, $\Delta(\mathbf{k}, \omega)$ (or for triplets $\mathbf{d}(\mathbf{k}, \omega)$) must vanish at $\omega = 0$, these superconductors have gapless excitations at every point on the Fermi surface. This does not appear to be compatible with the experimental situation in the cuprates where, although there are gapless excitations (as evidenced by the temperature dependence of the penetration depth) much of the Fermi surface appears to have a well developed energy gap (for example as seen in the photoemission experiments discussed below). We shall therefore not consider these odd frequency states further in this Chapter.

4.1. Possible Pairing States in a Plane Square Lattice

Because of the highly layered nature of the cuprates, we first consider the possible pairing states of the electrons confined to a single CuO_2 plane with a square lattice structure. Thus we assume until further notice that in Eqn. (3.1) $\mathbf{r}_1$ and $\mathbf{r}_2$ lie in the same CuO_2 plane.

For the case of a single square CuO_2 plane the relevant crystal point group is simply the group of the square, C_{4v}. The symmetry operations are: (a) rotation through $\pi/2$ about the $\langle 001 \rangle$ (z) axis, $\hat{R}_{\pi/2}$ (b) reflection in a $\langle 100 \rangle$ (x/y) crystal axis, $\hat{I}_{axis}$, and (c) reflection in a $45°$ or $\langle 110 \rangle$ axis, $\hat{I}_{\pi/4}$. Since for an even-parity state the only allowed eigenvalue of $\hat{R}_{\pi/2}^2$ is $+1$, and quite generally the only allowed eigenvalue of $\hat{I}_{axis}^2$ is $+1$, it immediately follows that the even-parity irreducible representation of the group C_{4v} can be uniquely labeled by the possible eigenvalues ± 1, of $\hat{R}_{\pi/2}$ and $\hat{I}_{axis}$ ($\hat{I}_{\pi/4}$ is not independent). These four representations correspond to the tetragonal states A_{1g}, A_{2g}, B_{1g}, and B_{2g} in standard group-theoretical notation.[21] These four possible states transform under the symmetry operations as the identity, $xy(x^2 - y^2)$, $x^2 - y^2$ and xy, respectively. These four states are shown in Fig. 1. (Notice that there are no E representations (d_{xz}, d_{yz}) because of our assumption of a single CuO_2 plane, rather than a full tetragonal crystal). It should be emphasised that these "representative" functions

are typical only as regards the symmetry of the pair state in question, and may give a very poor indication of the actual nodal structure of the gap function. For example, a possible s state is $\Delta(\mathbf{k}) = A + B\cos 4\theta$, $(\theta = \tan^{-1} k_x/k_y)$ which for $|B| > |A|$ has 8 nodes. (This is sometimes called an "extended s-state").

In the following discussion it will be convenient to use a more informal, and perhaps intuitively more appealing, nomenclature for these four states. We shall call any state which is even under $\hat{R}_{\pi/2}$ an "s-state" and any which is odd a "d-state". To distinguish the two "s" states we shall use superscripts $+/-$ for states which are even and odd under $\hat{I}_{axis}$. Thus in this simplified notation the four states are just s^+, s^-, $d_{x^2-y^2}$ and d_{xy}, respectively, with the properties summarised in Table 1 and Fig. 1. (Note that because of the C_{4v} symmetry the "g-wave" state $xy(x^2-y^2)$ is invariant under $\hat{R}_{\pi/2}$, i.e. it has the same rotational properties as an s state, and is only distinguished from s by its mirror reflections. Hence we use the nomenclature s^- rather then g for this state.)

Informal name	Group-theoretic notation	$\hat{R}_{\pi/2}$	$\hat{I}_{axis}$	Representative state
s^+	A_{1g}	$+1$	$+1$	const.
s^- ("g")	A_{2g}	$+1$	-1	$xy(x^2-y^2)$
$d_{x^2-y^2}$	B_{1g}	-1	$+1$	$x^2 - y^2$
d_{xy}	B_{2g}	-1	-1	xy

Table 1: The four singlet pairing states of a single plane with square symmetry.

A point which will be absolutely crucial to the argument of this review is that because of the structure of the group C_{4v}, all terms in the Ginzburg-Landau free energy which involve two of these irreducible representations must be "non-mixing" in the sense of Section 3. Mixing type terms involving four of these distinct irreducible representations are possible in principle, but do not allow "mixing" with a single second-order phase transition. We conclude that for single square CuO_2 planes the existence of a "mixed" order parameter, i.e. of two or more components transforming according to different irreducible representations of the symmetry group, (such as $s^+ + id_{x^2-y^2}$) is incompatible with the observed absence of more than one phase transition (see Section 5.1). Unless fluctuation effects are very much more dominant than they are usually assumed to be in the cuprates (in which case the very use of a Ginzburg-Landau free energy analytic in the order parameter components might be regarded as dubious), it seems to

us very difficult to avoid this important conclusion.

4.2. EFFECTS OF ORTHORHOMBICITY

As is well known, the CuO_2 planes in most of the cuprates, with the exception of the Tl- and Hg-based compounds, are not exactly tetragonal but have an orthorhombic structure; in addition to the slight difference (usually $< 2\%$) of the a- and b-crystal axes, the "buckling" of the planes usually picks out a special axis. In the case of YBCO (both "1237" and "1248") a more substantial anisotropy of the crystal lattice as a whole is induced by the presence of chains in the b-direction; although one's immediate instinct is that most of the "action" as regards to superconductivity is likely to be in the CuO_2 planes and the chains should therefore be a relatively minor perturbation, the fact that the penetration depth is observed[37,38] to be appreciably anisotropic ($\sim 50\%$) in the ab-plane shows that this "perturbation" cannot necessarily be neglected.

The presence of the orthorhombic anisotropy means that the relevant symmetry group is no longer the group of the square but a subgroup of it. However, it is important to appreciate that this subgroup is not the same for all the cuprate superconductors. In the case of YBCO, the a- and b- crystal axes become inequivalent, but each remain a twofold axis and a mirror plane: thus $\hat{I}_{axis}$ remains a symmetry operation while $\hat{R}_{\pi/2}$ and $\hat{I}_{\pi/4}$ are no longer so. The effect is to permit mixing of what were in a square lattice the s^+ and $d_{x^2-y^2}$ states, and likewise the pair s^- and d_{xy}; however, there can for example still be no mixing of $d_{x^2-y^2}$ and s^-. On the other hand, in LSCO and BSCCO it is the two orthogonal $45°$ axes which become inequivalent, while remaining mirror planes; thus $\hat{I}_{\pi/4}$ is still a good symmetry operation but $\hat{R}_{\pi/2}$ and $\hat{I}_{axis}$ are not, and the members of the pairs (s^+, d_{xy}) and (s^-, $d_{x^2-y^2}$) can mix. These considerations have important consequences for the structure of the gap function (a "local" quantity which is defined separately in each twin domain, see below): while in YBCO the nodes of the gap, if it is "$d_{x^2-y^2}$ like" (cf. below) may now occur at an angle different from $45°$, in LSCO and BSCCO it must still occur at exactly $45°$.

In many of the experiments conducted on the orthorhombic cuprates to determine the symmetry of the order parameter, the samples have been heavily twinned; untwinned samples are the exception. To describe the general nature of the order parameter within a single twin domain we shall adapt the following terminology: in YBCO, an order parameter which is even under $\hat{I}_{axis}$ will be called "s^+ - like" or "$d_{x^2-y^2}$ - like" according as it has the same or opposite sign on the x- and y-axes. Similarly, an odd state will be called "s^- -like" or "d_{xy} -like" depending on whether its value at some arbitrary angle, say $30°$, does or does not change sign under $\pi/2$ rotation; while in LSCO and BSCCO an order parameter

which is even under $\hat{I}_{\pi/4}$ will be called "s^+ like" or "d_{xy} - like" according as it has the same or opposite sign under a $\pi/2$ rotation.

Where we come to discuss the heavily twinned samples used in most experiments, an extremely important question arises: how does the order parameter behave as we cross a twin boundary? The alternatives for the $d_{x^2-y^2}$ like state, are illustrated in Fig. 2. In Fig. 2(a), the "+" and "-" signs follow the a- and b-axes, while in Fig. 2(b), they remain oriented with respect to the "absolute" North-South-East-West ("NSEW") axes, a behaviour we refer to as "gyroscopic." *We believe there are extremely strong considerations which favour the conclusion that the behaviour is gyroscopic.* In the first place, the critical current of twinned samples does not, as far as is known, differ markedly from that of untwinned ones, and this would seem to indicate that the coupling of the order parameter across twin boundaries, in contrast to that across grain boundaries, is comparable to that in bulk. If so, then since there is no obvious reason for the sign of the coupling between two neighbouring "NS" lobes of the order parameter on different sides of the twin boundary to be different from that between two lobes in the same grain, the gyroscopic configuration is favoured by a large energy. This argument could possibly fail in a strongly orthorhombic crystal such as YBCO, if for example the coupling across the twin boundary should turn out to be dominated by the chains[39] (something for which as far as we are aware there is currently no evidence either for or against). However, we believe an even stronger argument for gyroscopic behaviour (in YBCO) is the observation of a reproducible phase shift of zero in the UIUC I[6] and Maryland control experiments[40] (see Section 7 below), both of which were performed on heavily twinned (as well as, in the case of UIUC I, untwinned) samples. Were the "non-gyroscopic" hypothesis correct it would be impossible to understand this reproducibility. Although we have gone through this argument explicitly for the case of $d_{x^2-y^2}$ pairing, it is clear that similar considerations apply to the d_{xy} and s^- states (for the s^+ state, the question clearly does not arise).

In light of the above, it is convenient to define a "twin-averaged" order parameter, that is the order parameter averaged over the two possible twin-orientations on the assumption that it behaves gyroscopically across the boundary between them. It is clear that the possible symmetries of this "twin-averaged" order parameter are exactly those already found for the case of pure tetragonal (square) symmetry. Moreover, when we come to discuss the Josephson experiments (Section 7 below), it will turn out that in the "thermodynamic limit" (by which we mean the limit in which the number of twin domains in the area of the relevant junction tends to infinity and there is no systematic bias in favour of one orientation) and with the "gyroscopic" assumption, it is only this "twin-averaged"

order parameter which is relevant. In addition, it is clear that, given the above assumptions, the bulk Ginzburg-Landau free energy, averaged over the twins, can be expressed in terms of the twin averaged order parameter, and the arguments about mixing then go through exactly as in the tetragonal case. Thus to a large extent (though not entirely, see Section 7.1) in the context of the Josephson experiments the whole issue of orthorhombic anisotropy is irrelevant. Of course, it cannot be neglected when analyzing experiments such as ARPES, which probe the "local" gap and do not average over a large number of twin domains.

4.3. Bilayer and Trilayer Structures

Up to now, we have assumed that all pairing states take place within a single plane, i.e. that in the expression (3.1) for the order parameter, $\mathbf{r}_1$ and $\mathbf{r}_2$ lie in the same CuO_2 layer. We must now face up to the complications associated with the fact that many of the cuprates, including YBCO, possess double or in some cases triple CuO_2 planes; and that even for single-layer materials such as Tl 2201,[41] it is not obvious that there cannot be pairing between electrons in different layers.

Let us first dispose of the latter complication. What we are fundamentally interested in throughout this review is the symmetry of the order parameter in the ab-plane, and given that $\Psi(\mathbf{r}_1, \mathbf{r}_2; \alpha\beta) = \langle \psi_\alpha(\mathbf{r}_1)\psi_\beta(\mathbf{r}_2) \rangle$ is non-zero for $\mathbf{r}_1$ and $\mathbf{r}_2$ within the same CuO_2 layer, we can analyze this symmetry as in subsection 4.1 and 4.2 above, quite irrespective of whether Ψ is also non-zero for $\mathbf{r}_1$ and $\mathbf{r}_2$ in different layers. Thus the only circumstance which would render the analysis of Sections 4.1 and 4.2 invalid is if $\Psi(\mathbf{r}_1, \mathbf{r}_2; \alpha\beta)$ were to vanish for $\mathbf{r}_1$ and $\mathbf{r}_2$ in the same plane. While this hypothesis is not incompatible with the existence of a superconducting state, we believe its plausibility in single-layer materials is so low that it is legitimate to neglect it in the present context. Thus, for such materials the analysis of Sections 4.1 and 4.2 is adequate as it stands.

For double- or triple-layer materials such as YBCO or BSCCO 2223 it is less obvious *a priori* that the hypothesis of "exclusively inter-layer" pairing can be excluded. Let us focus for definiteness on a bilayer material such as YBCO. If the order parameter is symmetric with respect to interchange of the "layer" indices of $\mathbf{r}_1$ and $\mathbf{r}_2$ (a possibility which actually seems pathological if there is to be no intra-layer pairing) then it is clear that the analysis of subsections 4.1 and 4.2 goes through unchanged. If on the other hand it is antisymmetric (and we continue to assume, as in subsection 4.1, spin singlet even-frequency pairing), then the symmetry with respect to inversion within the ab-plane must be odd rather than even, and we have to deal with a set of irreducible representations different from those of Fig. 1. We will not explore this possibility further here, since (a) in view of the general qualitative similarity between the superconducting behaviour

of various classes of cuprates, it seems to us extremely unlikely that the pairing state is radically different in one- and two-layer materials,[43] and (b) a state with odd parity in the ab-plane seems difficult to reconcile with the existence of a reproducible (a- or b-direction) Josephson effect with ordinary s-wave superconductors (cf. Section 6, below). Thus we conclude that within a single CuO_2 plane the order parameter is finite and can be classified as in Fig. 1. Given this state of affairs, it is still a nontrivial question how the order parameter behaves (a) under reflection in the symmetry plane "spacing" the two layers (e.g. in the case of YBCO, the plane containing the Y atoms), and (b) under translation up the c-axis from one unit cell to the next. With regard to (b), the "natural" assumption is that the order parameter is identical both in magnitude and (in the absence of superflow) in phase from one unit cell to the next, (i.e. behaves according to the identity representation of the translation group T_ℓ), and any assumption different from this would seem to complicate the picture gratuitously without helping in any way to resolve the apparent experimental inconsistencies we shall comment on below (indeed, in many cases it would exacerbate them). We will therefore make the "natural" assumption from now on. (The same comment applies to the behaviour of the order parameter within the ab-plane).

Finally, what is the behaviour of the order parameter under reflection in the "spacing" plane? Evidently the irreducible representations are even or odd under this operation, and thus are "non-mixing" in the language of Section 3. Thus, by the arguments of that Section, the absence of more than one phase transition in the bilayer materials is strong evidence in favour of one and only one irreducible representation being realised. Now if it is the odd representation that occurs, it is difficult, if not impossible, to understand the existence of an (a- or b- direction) Josephson effect with ordinary superconductors (the argument is essentially that of Section 6.1, slightly generalised). Thus we conclude that the symmetry under reflection is even, and it is then clear that we can for many (though not all) purposes neglect the bilayer structure entirely, i.e. treat each bilayer as effectively a single layer.

It is clearly possible to give a similar discussion of trilayer structures, but since few if any of the crucial experiments have been done on trilayer materials, there seems no point in doing so here.

4.4. The energy gap

While the existence of the two-particle anomalous average (order parameter) defined by Eqn. (3.1) is of course fundamental to the whole of our discussion, none of the results we have obtained so far depend in any way on any specific assumptions about the mechanism of its generation; in particular, they are completely independent of its relation to the single-particle elementary excitations of the crystal (if such exist). This point should be emphasised, since an important class of theories of superconductivity in the cuprates starts from the premise that in the effectively two-dimensional systems formed by the individual CuO_2 planes no "single-particle" excitations in the usual sense of Fermi-liquid theory exist. If this should turn out to be the case, then it is not obvious that any of the microscopic concepts of BCS theory apply to the superconducting states, and in interpreting the experimental data on (e.g.) specific heat, penetration length and ARPES one must start again from scratch in the light of the concepts of the specific alternative theory under consideration. For the purposes of the present review, we shall take the point of view that the apparent signature of a Fermi surface in the normal-phase ARPES data,[18] plus the qualitative similarity of many of the superconducting-state data to what is predicted in (generalisations of) BCS theory, make it reasonable to discuss the microscopic properties in what is essentially a "BCS-like" picture. That is, we shall assume in this subsection that, at least for the purposes of discussing the superconducting state, a description of the normal state in terms of a Fermi-liquid type of picture is adequate, and will then go on in Section 5 to interpret various "microscopic" experiments in light of the description of the superconducting state so obtained. It should be emphasised that even if the assumptions which underlie the work of this subsection and Section 5 should eventually turn out to be false, none of the other results obtained in this review will be affected.

In a "Fermi-liquid-like" picture of the normal state of a typical "3D" metallic crystal, the low-lying single-particle excitations are Bloch waves $\phi_{n\mathbf{k}}(\mathbf{r})$ characterised by a crystal momentum $\mathbf{k}$, a band index n and a spin index s, and have an energy $\epsilon_{n\mathbf{k}}$ which becomes arbitrarily sharply defined as $\mathbf{k}$ approaches the Fermi surface of band n. (This would also be true in the marginal Fermi liquid and Luttinger liquid pictures.[14,15]) In the very simplest microscopic model of superconductivity (essentially the original BCS picture) one considers only a single band n, and one forms (spin singlet) Cooper pairs by pairing electrons with momentum-spin values $\mathbf{k} \uparrow$ and $-\mathbf{k} \downarrow$: see e.g Ref. 44. In such a theory the single-particle excitation energies $E_{\mathbf{k}}(T)$ are given by the familiar BCS formula

$$E_{\mathbf{k}}^2(T) = \epsilon_{\mathbf{k}}^2 + |\Delta_{\mathbf{k}}(T)|^2 \qquad (4.1)$$

where the quantity $\Delta_{\mathbf{k}}(T)$ is usually known as the "energy gap." As discussed in Section 2, a non-zero value for the Gor'kov off-diagonal Green function (2.2) implies the existence of an anomalous self-energy $\Delta_{\mathbf{k}}$ whether or not the normal state is a Fermi liquid. However this BCS quasiparticle energy formula (4.1) is only guaranteed to be valid in a Fermi liquid picture. In this case, there is a simple relation between $\Delta_{\mathbf{k}}(T)$ and the order parameter $\Psi(\mathbf{r}_1, \mathbf{r}_2)$ (we suppress the spin indices, assuming as always spin singlet pairing):

$$
\begin{aligned}
\Psi(\mathbf{r}_1, \mathbf{r}_2; T) &= \sum_{\mathbf{k}} \frac{\Delta_{\mathbf{k}}(T)}{2 E_{\mathbf{k}}(T)} \tanh\left(E_{\mathbf{k}}(T)/2T\right) \phi_{\mathbf{k}}(\mathbf{r}_1) \phi_{\mathbf{k}}(\mathbf{r}_2) \\
&\equiv \sum_{\mathbf{k}} \Psi_{\mathbf{k}}(T) \phi_{\mathbf{k}}(\mathbf{r}_1) \phi_{\mathbf{k}}(\mathbf{r}_2)
\end{aligned}
\tag{4.2}
$$

In the case of the cuprates we have to decide whether to treat the Bloch waves as three-dimensional or as defined only within the plane (cf. refs. 45, 46). In the former case we can take over formula (4.2) as it stands, for arbitrary values of $\mathbf{r}_1$ and $\mathbf{r}_2$: in the latter we should consider only values of $\mathbf{r}_1$ and $\mathbf{r}_2$ lying in the same plane or bilayer, etc. (but see below), and the sum over $\mathbf{k}$ then goes only over values in the ab-plane.

For a single band the Bloch wave function and energies must respect the crystal symmetry, in the sense that $\epsilon_{n\mathbf{k}} = \epsilon_{n\hat{R}\mathbf{k}}$ and $\phi_{n\mathbf{k}}(\mathbf{r}) = \phi_{n\hat{R}\mathbf{k}}(\hat{R}\mathbf{r})$, where $\hat{R}$ is any symmetry operation of the crystal point group. Since all the irreducible representations relevant to our problem (i.e. those of Fig. 1) are one-dimensional, it follows immediately from (4.1) and (4.2) that whenever $\Delta_{\mathbf{k}}(T)$ transforms according to a single irreducible representation of the crystal group, then $\Psi(\mathbf{r}_1, \mathbf{r}_2)$ transforms according to that same irreducible representation. Note that this conclusion is independent of any consideration concerning the details of the dynamics. Is the converse also true? It will certainly be so, if the condition which determines how $\Delta_{\mathbf{k}}(T)$ transforms can be written in the form of a generalised BCS gap equation, i.e. in the form

$$
\Delta_{\mathbf{k}}(T) = \sum_{\mathbf{k}'} V_{eff}(\mathbf{k}, \mathbf{k}') \Psi_{\mathbf{k}'}(T).
\tag{4.3}
$$

For, even if $V_{eff}(\mathbf{k}, \mathbf{k}')$ is itself a function of $\Delta_{\mathbf{k}}(T)$, analyticity arguments similar to those employed in the discussion concerning the Ginzburg-Landau free energy, show that it can depend only on $|\Delta_{\mathbf{k}}(T)|^2$ and must therefore (in the case of a 1D representation) continue to respect the crystal symmetry. It immediately follows that if $\Psi(\mathbf{r}_1, \mathbf{r}_2)$ transforms according to a given single irreducible representation then so does $\Delta_{\mathbf{k}}(T)$.

It should be emphasised that the above arguments do not prove that the Fourier transform of the order parameter, $\Psi(\mathbf{k})$, is simply proportional to $\Delta_\mathbf{k}(T)$ in its complete dependence on the direction $\hat{\mathbf{k}} \equiv \mathbf{k}/|\mathbf{k}|$, even for a single irreducible representation (let alone for the "mixed" case). However, in the so-called weak coupling limit in which the effective cutoff energy in the sum over $\mathbf{k}'$ is much greater than typical values of the gap, the effect of the nonlinearity in Eqn. (4.3) is small and the two quantities should be approximately proportional. (cf. the related discussion for the case of O(3) symmetry.[47]) Irrespective of this, we note from (4.2) that the nodes of $\Delta_\mathbf{k}(T)$ and $\Psi(\mathbf{k})$ coincide even when they are not symmetry-determined. Thus for most purposes it should not be too bad an approximation to take the two quantities to be proportional.

When we allow for more than one band to be involved in the process of Cooper pair formation, things become more complicated. If we define operators $c_{n\mathbf{k}}$ for the Bloch waves $\phi_{n\mathbf{k}}$ in the standard way, the quantity $\langle c_{n\mathbf{k}} c_{n'\mathbf{k}'} \rangle$ and hence the "generalised gap function" $\Delta_{nn'\mathbf{k}}(T)$ may be a matrix with respect to the band indices. (cf. the related problem of pairing in a spin triplet state ($S = 1$) when all the Zeeman substates are represented.[48]) An extreme case of this situation is a scenario recently proposed by Tahir-Kheli,[49] in which the pairing is exclusively "inter-band," i.e., the diagonal elements of $\Delta_{nn'\mathbf{k}}(T)$ are zero. In general the formula for the energy spectrum and hence the experimental properties in such models are considerably more complicated than in the one-band case. However, we emphasize that these complications in no way invalidate the conclusions we have already reached about the possible symmetries of the order parameter; in fact, the form of the quantities $\Delta_{nn'\mathbf{k}}(T)$ must respect these conclusions, so that for example in a square lattice the occurrence of only one phase transition constrains all the elements $\Delta_{nn'\mathbf{k}}(T)$ to belong to the same representation.

As a matter of fact, the "multi-band" case most likely to be of practical interest arises in the context of bi- or multilayer systems. Considering the bilayer case for definiteness, we have two obvious limiting cases, depending on our hypothesis about the nature of the electronic state in the normal phase. If one-electron hopping between the two component layers of the bilayer is coherent, with hopping matrix element, $t_\perp$, then the bands are split into even and odd bands, with $\epsilon_{\pm\mathbf{k}} = \epsilon_{0\mathbf{k}} \pm t_\perp$. Furthermore, if the pairing interaction is sufficiently weak that $k_B T_c \ll t_\perp$, then the pairing matrix will be diagonal in the band indices (although the equation for the gaps may couple them[50]). In the opposite limit, where the normal-state hopping is completely incoherent, or coherent but with a very small matrix element (compared to the effects of the (intra-layer) pairing interaction $t_\perp \ll k_B T_c$), pairing is likely to be diagonal in the layer indices, with a subsequent Josephson-type coupling between the layers. The case

in which the normal-state inter-layer contact is completely incoherent is particularly fascinating, since Chakravarty *et al.*[15] have argued that in this case the pair tunneling in the superconducting state can raise the transition temperature very substantially.

In the intermediate case ($t_\perp \sim k_B T_c$) the gap matrix is likely to be diagonal neither in the "layer" nor in the "even-odd" representation. We reemphasise, however, that irrespective of these complications the conclusions reached earlier still obtain; in particular, in a bilayer cuprate superconductor with a square lattice and a single phase transition, even if there is more than one "energy gap" all gaps must transform under ab-plane operations according to the same representation[51] (though they need not, of course, have an identical dependence in detail on $\mathbf{k}$).

5. Evidence for a Sign Change in the Gap Function

In this Section, we discuss the experimental evidence for a sign change in the gap function at the Fermi surface. These data include a systematic investigation of the low energy excitations in the superconducting state, some of which was discussed in AGR. Here we focus primarily on the electromagnetic penetration depth and the photoemission results. These two probes are perhaps the most direct measures of the superconducting state, and with a minimum of theoretical interpretation yield useful information about the pairing state. The penetration depth provided perhaps the first strong indication that the pairing state was not s-wave. Photoemission directly probes the symmetry of the gap function, and potentially can disprove a d-wave scenario. Indeed, as we shall see, until very recently, it did seem that the photoemission data were inconsistent with a d-wave pairing state.

5.1. Electromagnetic Penetration Depth

The electromagnetic penetration depth is a powerful probe of the superconducting state because the data, if taken at face value, directly reflect the response of the condensate to electromagnetic perturbations. Thus, the penetration depth is a measure of the superfluid density tensor. In general, a detailed understanding of the superconducting state is required to interpret correctly penetration depth data. Details of many factors, including the coupling between the electrons and the pairing bosons, electronic structure and disorder can all quantitatively modify the predictions based upon a simple BCS-type theory.

In the absence of a detailed microscopic theory, it behoves one to examine the universal qualitative behaviour of the penetration depth, which with relatively weak assumptions can be usefully interpreted, independent of the mechanism of superconductivity. Two such regimes are available in the cuprate superconductors.

The first is the asymptotically low temperature regime, which we will discuss extensively below, and which can directly test hypotheses about the existence or non-existence of a change in sign of the gap function over the Fermi surface. This regime is also available in classic superconductors. At low temperatures, it should be possible to distinguish a superconductor with a non-zero gap function minimum from one that has nodes by the presence or absence of exponential behaviour as a function of temperature. As discussed (*e.g.*) in AGR, different varieties of nodal structure give rise to a temperature dependent penetration depth tensor whose components approach their zero temperature value as a power law function of temperature, with an exponent that is related (but not in a one-to-one correspondence) to the pairing state.

The second universal regime is that near T_c, where fluctuation effects become important.[52] Although it has been generally accepted for some time that weak Gaussian fluctuations about mean field theory are observable in the cuprates, it is only recently that genuine critical fluctuations have been observed.[16] This critical fluctuation regime is not accessible in other three dimensional superconductors, and arises in the cuprates because the Ginzburg-Landau correlation length extrapolated to low temperatures is of order the unit cell dimensions.

Summary of experimental observations

During the last 6 years, experimental data have become available on better characterised samples than previously. The salient experimental findings have been reviewed by D.A. Bonn and W.N. Hardy in this Volume, and the results can be summarised as follows:

(1) Measurements[5,53,54] of the $a - b$ plane penetration depth $\lambda(T)$ in twinned single crystals of $YBa_2Cu_3O_{7-\delta}$ indicate a linear temperature dependence with a slope of about 4Å/K, from about 1K to about 30 K. These results have now been reproduced by a variety of different groups using different techniques, including microwave and μSR techniques.

(2) Measurements[55] of $\lambda(T)$ in high quality twinned thin $YBa_2Cu_3O_{7-\delta}$ films epitaxially grown on MgO or $LaAlO_3$ substrates also exhibit the linear behaviour mentioned under (1). These measurements agree quantitatively with those obtained on the single crystals, with the exception that $\lambda(0)$ was found to be 1750 ± 160Å, slightly larger than the value of 1400 ± 50Å

usually quoted for crystals. Linear behaviour has also been observed on $YBa_2Cu_3O_{7-\delta}$ films grown by evaporation onto a $SrTiO_3$ substrate.[56]

(3) Measurements[55, 57−60] on lower quality twinned thin $YBa_2Cu_3O_{7-\delta}$ films yield a temperature dependence for λ that varies as T^2. In Ref. 55, the films whose temperature dependence was quadratic were found to have a value for $\lambda(0)$ of 3600Å, whereas in the other references cited, where a value can be deduced, it is of order 1700Å. The nominally pure films exhibited a quadratic temperature dependence at temperatures below 25K, but between 25K and 40K the temperature dependence matched that measured on single crystals[5] very well.[60] The authors of Ref. 60 were able to plot the coefficient of the quadratic term against $\lambda(0)$ and found agreement with the d-wave theory of Hirschfeld and Goldenfeld.[61]

(4) The anisotropy of the penetration depth[37, 62] and surface resistance[62] of untwinned $YBa_2Cu_3O_{7-\delta}$ crystals has been measured using microwave cavity perturbation techniques[62] and far infra red spectroscopy.[37] It is found that the temperature dependence of the principal components of the penetration depth tensor (i.e. in both the a and b directions) is similar to that found in the average penetration depth observed in twinned crystals. For present purposes, the quantity that is of interest is σ_{00}, the limiting value of the real part of the complex conductivity, extrapolated to zero frequency. A surprising prediction is that in a d-wave superconductor, σ_{00} is independent of the scattering rate, and takes a value of approximately 0.3 times the dc conductivity at T_c. The observed values for the residual conductivity (that is, the conductivity extrapolated to zero temperature) are consistent with this prediction.

(5) Twinned single crystals of $YBa_2Cu_3O_{7-\delta}$ similar to those which give a linear temperature dependence for $\lambda(T)$ at low temperatures were systematically doped with Zn and Ni impurities.[63] These impurities substitute for the Cu(2) atoms (in the CuO_2 planes) so that the sequence of crystals studied were $YBa_2(Cu_{1-x}A_x)_3O_{6.95}$, where A stands for Zn or Ni, $x = 0.0015$ and 0.0031 for Zn and $x = 0.0075$ for Ni. The Zn-doped crystals experience a strong T_c suppression,[64] $\partial T_c/\partial x \approx -1260$K, whereas the Ni-doped crystals (and thin films)[65] experience much less of a suppression in T_c: $\partial T_c/\partial x \approx -390$K. This is seemingly at odds with the observation[65] that the dc resistance at T_c is increased to roughly the same extent by both Ni and Zn. The influence on the low temperature behaviour is quite dramatic. The Zn doping[63] causes the penetration depth to exhibit a quadratic variation with temperature below a crossover temperature T^*, and a linear variation with temperature above T^*. That is, if one considers only the

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temperature interval over which the nominally pure crystals exhibit a linear temperature dependence, this interval becomes divided into two regions. The Ni doping shows very little effect on the penetration depth, although the barely discernible trend is qualitatively similar to that for the Zn doping. These data could be sensibly fit to an interpolation formula derived from the theory of impurity scattering in d-wave superconductors.[61]

(6) Ni and Zn dopants were added to $YBa_2Cu_3O_{7-\delta}$ films[66] but in much greater concentrations than in the single crystal experiments described above. The values of x for both Ni and Zn ranged from 2% to 6%, corresponding to a substitution of 3% to 9% of the plane copper atoms. As with the single crystals, it was found that Ni and Zn have approximately the same scattering rate, as determined from infrared reflectivity measurements, but that Zn depresses T_c about three times more rapidly than Ni. The penetration depth was determined from kinetic inductance measurements and the variation of $\lambda(0)$ with doping concentration analysed and compared with a theory of Kim $et\ al.$[67] which is an extension of Ref. 61 to high concentrations. The agreement is not very good, with the reduction in the zero temperature superfluid density $n_s(0)$ being severely underestimated by as much as a factor of 10 (Ni at 6% doping).

(6) The c-axis penetration depth has been measured[68] and a linear temperature dependence obtained.

(7) Near T_c, the penetration depth diverges as $\lambda(T) \propto (1 - T/T_c)^{-y}$ with $y \approx 0.33$. This behaviour has been observed in $YBa_2Cu_3O_{7-\delta}$ single crystals[16, 69] and $La_{2-x}Sr_xCuO_{4\pm\delta}$ thin films.[70]

(8) The low temperature behaviour[71] of $\lambda(T)$ for thin films and single crystals of the $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ compound exhibits an exponential temperature dependence with $2\Delta(0)/k_BT_c \approx 4.1$. This material seems to be exceptional, because it is the only known cuprate which appears to be an s-wave superconductor. Presumably this is associated with the fact that it is electron-doped as opposed to hole-doped.

Evidence for one complex order parameter

The observed critical behaviour of the penetration depth is consistent with the three dimensional (3D) XY universality class. In Ref. 16, the authors checked this interpretation in a number of ways, apart from the value of the exponent for the penetration depth. First, the observed exponent was not altered by the presence of Zn impurities; generically, disorder would be expected to affect the universality class of the phase transition, but in the case where the specific heat exponent is negative, such as the 3D XY model, the Harris criterion predicts that

weak disorder should be irrelevant in a renormalisation group sense. Secondly, Kamal *et al.* used hyperscaling relations to calculate the correlation length in the c-axis; thus they were able to verify that the system was indeed in a regime where the fluctuations would be expected to be three dimensional, showing that the analysis was self-consistent.

The observed behaviour has several implications. First, no evidence for a second transition is observed. Gross thermodynamic measurements on single crystals away from T_c have failed to indicate any anomalies or discontinuities. The measurements of Ref. 16 exhibit scaling phenomena over two decades of reduced temperature $t \equiv (T_c - T)/T_c$ over the range $0.001 < t < 0.1$, setting a bound on how close to the upper value of T_c a putative second transition would have to be, assuming that it did indeed affect the penetration depth by causing an anomaly in the superfluid density. In light of the thermodynamic arguments in Section 4, *we conclude that an order parameter consisting of a mixture of irreducible representations does not occur.* Secondly, the observation of 3D XY scaling strongly indicates that *the order parameter is a single complex number* and hence is a one dimensional irreducible representation.

Evidence for nodes

The observation of linear temperature dependence of λ at low temperatures is certainly a striking departure from the s-wave prediction of a flat or exponential temperature dependence, and is stronger evidence for a d-wave interpretation than the earlier observations of quadratic temperature dependence. The latter could conceivably have been an artifact of several proposed mechanisms, but within the context of an s-wave pairing scenario: these mechanisms include trapped vortices,[72] vortex pair nucleation at defects[73] and low frequency phonons.[74,75] However, none of these mechanisms was shown to account quantitatively for the experimental evidence for the quadratic temperature dependence observed in thin films.

The linear temperature dependence observed more recently is in accord with the arguments of Ref. 4, which showed that *both* principal components of the a-b plane penetration depth tensor should grow linearly with temperature if YBa$_2$Cu$_3$O$_{7-\delta}$ were a singlet unconventional superconductor. There are two main scenarios in which this interpretation could be incorrect. First, the theoretical prediction concerns the asymptotic low temperature behaviour of the penetration depth. It is conceivable that the gap function is strongly anisotropic, but with a gap minimum that is not zero but nonetheless very small compared with $k_B T_c$, for example of order 1mK. In this case, the asymptotic low temperature behaviour would be exponential, but would not be observed until $T \sim 1$mK. For temperatures greater than this, but still much less than T_c, the temperature dependent

penetration depth would resemble that of a genuine d-wave superconductor. This scenario can never be entirely eliminated (by penetration depth measurements alone), even by taking data at much lower temperatures. An s-wave multilayer proximity effect coupling model of $YBa_2Cu_3O_{7-\delta}$ has been presented,[76] which is able to fit the nominally pure data of Ref. 63 by appropriate choice of the parameters in the model. However, this model predicted that the temperature dependence of $\lambda_c(T)$ should be strongly exponential, in clear disagreement with subsequently measured data of Ref. 68.

The second scenario is the proposal that phase fluctuations may be important in the high temperature superconductors,[77] and could account for the linear temperature dependence of the penetration depth.[78−80] However, it is hard to see how this proposal could account for the observed crossover to a quadratic temperature dependence in the presence of impurities. In addition, the theory generically predicts that $d\log\lambda(T)/dT$ extrapolated to zero temperature should increase and be proportional to $\lambda(0)^2$ as this latter quantity is increased by impurity doping. However, the experimental result[56] is that the zero temperature extrapolated value of $d\log\lambda(T)/dT$ decreases with increasing $\lambda(0)$. Moreover, the observed trend is qualitatively consistent with the node scenario, because isotropising or filling in of the density of states will tend to reduce the temperature dependence of $\lambda(T)$. Thus, it seems very unlikely that phase fluctuations are making an important contribution to the low temperature penetration depth, so they cannot account for the observed behaviour.

Probably the strongest grounds for associating the observed low temperature behaviour of the penetration depth with nodes in the gap is the behaviour in the presence of small amounts of doping, discussed in other contexts in Section 8. Assuming that one can use the standard Abrikosov-Gor'kov theory for impurity scattering in superconductors[81,82] and that the unitary scattering limit is relevant, it is straightforward to show that the penetration depth in a superconductor with line nodes (in three dimensions) gives rise to a penetration depth that crosses over from linear to quadratic temperature dependence.[61, 83] The crossover is accompanied by an increase in the zero temperature value of the penetration depth, which can also be computed[61,67] and observed by extrapolation of the data. The theory predicts that for small impurity concentrations, the limiting low temperature behaviour should be quadratic, crossing over to a linear temperature dependence at higher temperatures but still in the regime $T \ll T_c$. The observed crossover temperatures T^* are in reasonable agreement with estimates made from the theory. For example, the theory predicts that $T^* \approx 0.83\sqrt{\Gamma\Delta_0}$, where Γ is the impurity scattering rate, which is estimated from conductivity measurements for the 0.31% Zn-doped single crystals of Ref. 63 to be 5K, and Δ_0 is the gap function amplitude, taken to be of order $3k_BT_c$; thus T^* should

be of order 31K, which compares favourably with the observed value of 28K for this concentration. Although the theory does not include a variety of effects which may be important, such as taking proper account of the electronic structure along the c-axis, van Hove singularities and localisation effects, it is expected to be a reasonable indicator of the main trends, and should be useful in a semi-quantitative way.

Another question is the use of the unitary limit in the scattering calculation. The motivation for this was two-fold: first to ensure that the impurities did not rapidly reduce T_c to unobservably low values, and second because of the observation[84] of a crossover in the thermal conductivity to linear behaviour below about 300mK. Not taking the unitary limit would ensure that T_c would decrease too rapidly with doping to be consistent with experiment; but with the unitary limit in place, there is no reason to believe that the theory would give a proper account of phenomena near T_c: for example, inelastic scattering is neglected. Nevertheless, the theory focuses on the most important physics at low temperatures, where it was intended to be used.

The doping dependence of the penetration depth contrasts sharply with what one would expect for a state without nodes, for which the addition of impurities would be expected to increase the minimum of the gap function[85,86] leading to a more obvious exponential behaviour. Thus, even if for some accidental reason, the nominally pure samples had a gap function that went to zero or nearly vanished at the Fermi surface (thus simulating a d-wave superconductor from the point of view of exhibiting a linear temperature dependence), the doped samples would exhibit an exponential temperature dependence in disagreement with experiment.

<u>Conclusion</u>

What do these observations and the fitting with simple theoretical models enable us to conclude about the pairing state? First, unless there is a very weak secondary transition below the threshold of detection, we can rule out a state with two order parameters. Second, the superconducting state of YBa$_2$Cu$_3$O$_{7-\delta}$ and at least one of the La materials is a one-dimensional representation in the universality class of the 3D XY model, consistent with a s, d or mixture of $s + d$ states in an (untwinned) orthorhombically-distorted tetragonal copper-oxide plane. The linear temperature dependence down to about 1K places an upper bound on any minimum in the gap function, and the observed crossover to quadratic behaviour, even at relatively high levels of doping, are consistent with nodes, but do not completely remove the possibility that the minimum in the gap function is accidentally very small in the nominally pure samples, so that any exponential temperature dependence occurs at temperatures well below those at

which measurements have been made. In the $s + d$ state that is permitted in the orthorhombically-distorted tetragonal plane, the node positions are shifted away from the Brillouin zone diagonal; the theoretical predictions are unchanged, except that there is the logically allowed possibility that at high doping the gap function will have become so isotropic that it no longer changes sign at the Fermi surface, a possibility that cannot occur in a pure d-wave state. The fact that T_c can be driven to zero with enough electron irradiation[87] indicates that this possibility does not seem to occur, at least in $YBa_2Cu_3O_{7-\delta}$. Finally, it is reasonable, but of course unproven, that the quadratic temperature dependence observed in BSCCO films is a reflection of disorder imposed on an underlying d-wave state, just as is the case with YBCO.

5.2. Angle Resolved Photoemission

Angle resolved photoemission spectroscopy (ARPES) is potentially one of the most powerful techniques for elucidating the superconducting gap function over the whole Brillouin zone. Unlike other probes of the energy gap, if the gap function has nodes then the ARPES experiment should be able to pinpoint exactly where on the Fermi surface the nodes lie. This should clearly distinguish superconducting states which have "accidental" nodes, such as extended s-wave states, from those which have symmetry determined nodes, such as $d_{x^2-y^2}$. Unfortunately the interpretation of the photoemission data is not quite as straight forward as would appear at first sight, and this has led to some controversy about which pairing state is actually indicated by the experiments. First we shall discuss the current state of the experiments, and then we shall make some comments on the theory of photoemission from superconductors and some possible interpretations of the experiments.

Experiments

Photoemission only became a viable probe of the the superconducting gap after the discovery that $Bi_2Sr_2CaCu_2O_8$ could be cleaved in vacuum to produce a good quality surface with a sharp photoemission Fermi edge. The first measurements, by Imer et $al.$,[88] showed a significant temperature dependence of the spectra at the Fermi edge, between 105K and 15K. The changes were not just the sharpening of the Fermi edge expected from the Fermi-Dirac distribution but the clear pile up of states below the BCS gap. They found that the spectrum was roughly consistent with a BCS density of states convolved with instrumental broadening. They estimated the gap to be 30 ± 5 meV, assuming a Gaussian broadening with a 20meV full-width-half-maximum. In contrast to these results for $Bi_2Sr_2CaCu_2O_8$, photoemission measurements on $YBa_2Cu_3O_{7-\delta}$ show relatively poor evidence for a superconducting energy gap. Indeed only rare surface

cleaves show a sharp metallic Fermi edge at all.[89−91] For this reason we shall concentrate mostly on the $Bi_2Sr_2CaCu_2O_8$ spectra here. Very recently ARPES measurements of the superconducting gap in $YBa_2Cu_3O_{7−\delta}$ have also become available,[92] and these agree quite closely with the BSCCO data. A more extensive review of photoemission results in high T_c superconductors is also available elsewhere.[93,94]

Angle resolved photoemission experiments on $Bi_2Sr_2CaCu_2O_8$ were first measured by Manzke *et al.*[95] and Olson *et al.*,[96] who reported energy gaps of 30meV and 24meV respectively. The first systematic study of the angular dependence of the gap appeared to support an isotropic energy gap,[97] although this interpretation was based upon only a limited set of sampling points in the Brillouin zone. The first evidence for gap anisotropy was obtained by Dessau *et al.*[98] and by Wells *et al.*[99] who reported that the gap decreased by roughly a factor of two on going from the ΓM line to the ΓX line in the zone. From the leading edges of the spectra, the gap function $\Delta(\mathbf{k})$ is much bigger nearer the ΓM line than the ΓX line. Fitting the spectral shape, Wells *et al.* reported that the gap was about 15meV along ΓX compared to 24meV along ΓM. Note that because the $Bi_2Sr_2CaCu_2O_8$ crystal axes are rotated by 45° relative to the Cu-O bond directions, the ΓX direction corresponds to the nodal point of a $d_{x^2−y^2}$ energy gap, using the usual nomenclature appropriate to the square Brillouin zone of a single isolated CuO_2 plane.

The first evidence that the gap might actually vanish at the $d_{x^2−y^2}$ nodal line was reported by Shen *et al.*[100] They showed that for points in the zone along ΓY the gap was very small, and the data could be consistent with a gap node at this point. A gap node would be expected along ΓY if $Bi_2Sr_2CaCu_2O_8$ were a $d_{x^2−y^2}$ superconductor. Shen *et al.* found that the gap at ΓY inferred from the data was strongly sample dependent. At many of the experimental ΓY points Δ was as small as 2meV, while at others it was as large as 12meV. Interestingly the gap remained highly anisotropic, even in an oxygen depleted sample which had a reduced T_c of 78K and a much smaller gap at ΓM of 12meV. Shen *et al.* argued that their data supported a $d_{x^2−y^2}$ order parameter or a mixed symmetry state with a large $d_{x^2−y^2}$ component, and that it was qualitatively incompatible with extended s-wave states. The recent results of Schabel *et al.*[92] show a predominantly $d_{x^2−y^2}$ gap anisotropy in YBCO which is essentially identical to the behaviour found in BSCCO.

Subsequently the debate has focused on whether or not the gap is truly zero in the ΓX and ΓY directions. Ding *et al.*[101] found that the gap was small and consistent with zero along both ΓX and ΓY. Kelley *et al.*[102] found that the gap was non-zero but only $1 − 2$meV along ΓY, while it was larger, $4 − 8$meV,

along ΓX. The ΓX and ΓY lines would be equivalent in a tetragonal crystal, but are rendered inequivalent in $Bi_2Sr_2CaCu_2O_8$ by the slight difference in a and b lattice constants of 5.4095Åand 5.4202Å.[103] The a and b axes are also inequivalent because of the incommensurate superstructure in the Bi-O planes.[104]

Ma et $al.$[105] measured the temperature dependence of both the ΓX and ΓM gaps. They found strong coupling BCS-like behaviour near T_c for the large gap $(14-18\text{meV})$ at ΓM, but a much weaker temperature dependence for the smaller gap (of $7-11\text{meV}$) at ΓX. For quite a wide range of temperatures below T_c the gap at ΓX is indistinguishable from zero, only becoming clearly non-zero below about $0.8T_c$. This behaviour appears to suggest that a model with more than one order parameter component might be required, for example one in which the order parameter at T_c has pure $d_{x^2-y^2}$ symmetry, while a second order parameter component (such as s or d_{xy}) becomes non-zero below T_c.

Ding et $al.$[106] measured the angular dependence of the photoemission spectrum at a large number of points on the Fermi surface. They found non-zero gap values along both ΓX and ΓY, with values similar to those reported by Kelley et $al.$[102] Furthermore, they also claimed that the gap was actually a local maximum at both ΓX and ΓY, and that it went to zero at about $10-15°$ around the Fermi surface from the $d_{x^2-y^2}$ gap node. This surprising result would be incompatible with even mixed symmetry states such as $d_{x^2-y^2}+s$ and $d_{x^2-y^2}+id_{xy}$, but seemed to indicate an extended s-wave state with no $d_{x^2-y^2}$ component. However a subsequent polarisation analysis by Norman et $al.$[107] has suggested that that non-zero gap observed at ΓX could be due to Umklapp scattering events caused by the incommensurate modulation. They argued that in the absence of this Umklapp scattering the gap in the ΓX quadrant would be identical to that in the ΓY quadrant. Hence the gap is very small (of order 2meV or less) at the $d_{x^2-y^2}$ node point in both the ΓX and ΓY quadrants. Indeed, apart from one data point, the ΓY gap is zero within experimental error near the $d_{x^2-y^2}$ nodal point.

If these sometimes conflicting results are not disturbing enough, photoemission experiments also present one further puzzle. This is that the total area of the photoemission spectrum appears to be temperature dependent. This was first reported by Dessau et $al.$[98] who observed that the total spectral area appeared to decrease (increase) as a function of temperature along ΓM(ΓX). Ma et $al.$[105] measured the detailed temperature dependence of this change in the spectral area. In fact there are no sum rules which constrain this occupied spectral area (unlike the total occupied+unoccupied spectral area). It is only in weak coupling BCS theory that the occupied spectral area remains unchanged below T_c. Thus the change in spectral area could be due to strong coupling effects, or other

many-body effects such as quasiparticle renormalisation or non-Fermi liquid effects. It is not clear at present how the anisotropy of the area change relates to the gap anisotropy.

Finally, the work of Kelley *et al.*[108] indicated that a polarisation analysis of the photoemission spectra at ΓX and ΓY was incompatible with either s-wave or $d_{x^2-y^2}$ pairing, and implied either a $d_{xz}+d_{yz}$ or p_x+p_y state. The interpretation of the spectra appears to be flawed, however, since the presence or absence of a peak in the spectrum was taken to indicate the presence or absence of a condensate. No such simple relationship exists between the photoemission spectral shape and the condensate.

Interpretation and Theory

In the above discussion, we have taken the various gaps quoted by the experimental groups at face value. However, at least some of the discrepancies between quoted results appear to be due to different methods of determining the gap function from the experimental photoemission spectra. For this reason it is worth reexamining the theoretical basis of the photoemission experiments, in order to put the various experimental claims in a proper context.

The many body theory of photoemission was formulated by Schaich and Ashcroft,[109] who showed that the photoelectron current was given by a Kubo response theory, in terms of a three-current correlation function. In practice one neglects effects such as interactions between the photoelectron and the hole it leaves behind in the solid, yielding a simpler formula due to Pendry[110]

$$I(\mathbf{K}, E_i + \hbar\omega) \propto \mathrm{Im} \left\langle \mathbf{K}, z | G^+ H' G_h H'^+ G | \mathbf{K}, z \right\rangle. \tag{5.1}$$

Here $|\mathbf{K}, z\rangle$ is an electron state with momentum $\hbar\mathbf{K}$ parallel to the surface at the plane of the detector, z, outside the surface. G is the propagator for the photoelectron with energy $E_i + \hbar\omega$. H' is the electron-photon interaction Hamiltonian

$$H' = \int d^3r \mathbf{A}(\mathbf{r}, t) \cdot \mathbf{J}(\mathbf{r}) \tag{5.2}$$

where $\mathbf{J}(\mathbf{r})$ is the current operator. G_h is the propagator for the hole which is excited inside the solid, at energy, E_i. In the Pendry theory the propagators G and G_h are fully dressed by the appropriate self-energy, so many-body effects are included, as well as the full surface electronic structure.[111]

In the analysis of photoemission data of the high T_c superconductors several critical assumptions are usually made:

(1) It is assumed that the photoelectron propagator, G, is unchanged by the superconductivity, because of its high energy, and so the effects of superconductivity are entirely contained in the hole propagator G_h.

(2) The photoelectrons are assumed to be excited sufficiently far inside the surface that the electronic structure and superconducting order parameter are essentially bulk-like.

(3) Any dependence of the matrix elements of the current operator with momentum around the Fermi surface, or with initial state energy, is neglected. With this assumption the angle resolved photoemission spectrum intensity becomes proportional to the single particle spectral weight function, $A(\mathbf{k}, E_i)$.

(4) For the cuprates, the electronic structure is assumed to be essentially two-dimensional, and so the observed spectrum as a function of the parallel momentum $\mathbf{K}$ is assumed to be indicative of the full Fermi surface and gap function, neglecting any possible band dispersion and gap modulation along the c-axis.

(5) Various fitting schemes are used to extract the angle-dependent gap function $\Delta(\mathbf{k})$ from the spectra, using either the leading edge of the spectrum or a fit to a strong coupling theory lineshape. It seems that differences in fitting procedures, as well as variation among samples (e.g. oxygen content) accounts for the differences in numerical gap values found by the various groups. It is also important to point out that these fits neglect possible angular dependences in other relevant quantities, such as the quasiparticle lifetime, $\tau(\mathbf{k})$. An angular dependent $\tau(\mathbf{k})$ could lead to increased sharpening of the spectral edge at some points in the zone, hence leading to systematic errors in the extracted values of $\Delta(\mathbf{k})$. One should therefore be very wary of quoted measurement error bars, since these do not take into account possible systematic errors.

While each of the above points may have its justifications, together they raise several questions about whether the experiments are indeed determining the gap parameter, $\Delta(\mathbf{k})$, with the precision usually implied. Such uncertainties may explain why quoted gap values from different groups sometimes have non-overlapping error bars. Of course varying sample and surface qualities may also be a factor, as is clear from the work of Shen *et al.*[100] In particular they bear on the key question of whether $\Delta(\mathbf{k})$ vanishes at the $d_{x^2-y^2}$ nodal lines, or is merely small there. At the present time, in our opinion, all that can be said is that the photoemission data appears to be *consistent* with a pure $d_{x^2-y^2}$ order parameter. The experiments *cannot rule out* a small non $d_{x^2-y^2}$ component, such as s or d_{xy}, or a highly anisotropic s-wave state such as that of Ref. 112. Any

such anisotropic gap must vary in magnitude by a factor of at least two (and probably more like a factor of 10) between ΓM, ΓX and ΓY.

More work on the theory of photoemission in superconductors is certainly warranted. The prospect that the detailed spectral shapes for $A(\mathbf{k}, E_i)$ may be used to determine the McMillan $\alpha^2 F$ function is very exciting.[113] However, the observed spectrum is highly convolved, with instrumental broadening in both energy and momentum in addition to the strong coupling self-energy effects.[114] It seems unlikely that any deconvolution process will be able to extract the full angle-dependent strong coupling $\Delta(\mathbf{k}, \omega)$ with an accuracy of more than $\pm 1 - 2\text{meV}$, given the typical instrumental energy broadening of $15 - 20\text{meV}$. This would be sufficient to eliminate pure $d_{x^2-y^2}$ pairing if the gap were found to be non-zero within this error bar at the nodal lines. However it is unlikely ever to be possible to completely eliminate the possibility of small ($< 2\text{meV}$) non-zero gap values at the $d_{x^2-y^2}$ nodes using ARPES experiments.

5.3. Neutron Scattering

The possibility that neutron scattering could be used to probe the pairing state in unconventional superconductors was first suggested, to our knowledge, by Lu in 1992.[115] Because the neutron scattering intensity is essentially the spin susceptibility,

$$S(\mathbf{q}, \omega) = \left(1 + \frac{1}{e^{\hbar\omega/k_B T} - 1}\right) \text{Im}\chi(\mathbf{q}, \omega), \qquad (5.3)$$

neutron scattering obtains information which is very similar to NMR $1/T_1$ measurements. However Lu pointed out that neutron scattering could provide a very clean cut test of unconventional superconductivity because of the experimental freedom to tune precisely the wave vector and frequency, unlike NMR which is wave-vector integrated and in the limit $\hbar\omega \to 0$. The neutron scattering intensity $S(\mathbf{q}, \omega)$ should be significantly affected by superconductivity provided $\hbar\omega < \Delta$. In unconventional superconductors with nodes in the gap function, Lu predicted that sharp $\mathbf{q}$ dependent resonances would occur in $S(\mathbf{q}, \omega)$ because of scattering between states at the gap nodes, as illustrated in Fig. 3. In principle, by measuring the positions of the resonance peaks in $S(\mathbf{q}, \omega)$ one could unambiguously determine precisely where on the Fermi surface the gap nodes occur, and hence the pairing state. Lu pointed out that the conditions for the appearance of these resonances: $T < \omega < T_c < \Delta$, were experimentally realisable in the high T_c superconductors.

Experimental neutron scattering work on the cuprate superconductors has been active ever since their discovery. See, for example, the excellent review

by Birgeneau and Shirane in Volume 1 of this series[116] or any of the more recent reviews.[117,118] Much of this work has focused on the magnetic properties of the antiferromagnetic phases of the materials, and on the antiferromagnetic fluctuations (paramagnons) in the normal metallic state. It has been difficult to obtain spectra in the superconducting state because of the necessity of growing large enough single crystals which are doped homogeneously. Nevertheless superconducting state neutron scattering spectra are now available, for example, in $La_{1.85}Sr_{0.15}CuO_4$ with $T_c = 37K$[119] and for $YBa_2Cu_3O_{7-\delta}$ crystals with T_c of 93K.[120] The neutron scattering results from the 214 and 123 materials are quite different from each other, in both the normal and the superconducting state. In both materials there is evidence of strong antiferromagnetic spin fluctuations in the normal state, showing up at peaks in $S(\mathbf{q}, \omega)$ near $\mathbf{q} = (\pi/a, \pi/a)$. However in the 214 materials these fluctuations are incommensurate, peaking at wavevectors $\mathbf{q} = (\pi/a, \pi(1 \pm \delta)/a)$ and $\mathbf{q} = (\pi(1 \pm \delta)/a, \pi/a)$ with $\delta \sim 1/4$, while in 123 they remain commensurate at $(\pi/a, \pi/a)$. In 123, as a function of frequency and temperature $S(\mathbf{q}, \omega)$ shows evidence for a gap of order $3.5k_BT_c$. However this gap is usually believed to be a magnetic gap in the paramagnon spectrum, i.e. a spin gap, rather than a superconducting gap. In 214, by contrast, there is no such gap and there is evidence for low energy excitations at least down to $1 - 2meV$.[121−123]

Let us now consider in detail the superconducting state neutron scattering in the 214 materials, and the constraints it places on the superconducting pairing symmetry. As already mentioned, $S(\mathbf{q}, \omega)$ is strongly peaked at the four incommensurate vectors $\mathbf{q}_\delta = (\pi/a, \pi(1 \pm \delta)/a)$ and $(\pi(1 \pm \delta)/a, \pi/a)$. These vectors clearly do *not* connect the gap nodes of a d-wave superconductor as in Fig. 3, since these would be of the form $(1 \pm \epsilon)(\pi/a, \pm\pi/a)$. Instead the incommensurate peaks must be associated with nesting vectors of the Fermi surface[122] and the peaks are clearly a normal state property since they are present both above and below T_c. On cooling the sample into the superconducting state the incommensurate peaks remain at the same position, $\mathbf{q}_\delta$, and have essentially unchanged width in $\mathbf{q}$.[122] Thurston *et al.*[121] and Matsuda *et al.*[123] found that at the peak maximum $Im\chi(\mathbf{q}_\delta, \omega)$ remained independent of temperature below T_c for $1.5 \leq \omega \leq 6meV$. In contrast Mason *et al.*[122] found a gradual decrease in intensity below T_c. Despite this disagreement, in either case, it is clear that the spectra are *inconsistent with an isotropic gap*. The considerable intensity in $Im\chi(\mathbf{q}_\delta, \omega)$ at low frequencies and below T_c implies the presence of excitations with energies well below the expected isotropic BCS gap of $\Delta \sim 10meV$. Mason *et al.*[122] argued that these low energy excitations could not be taken as direct evidence for $d_{x^2-y^2}$ pairing, because the wave vector dependence of $S(\mathbf{q}, \omega)$ was the same in the normal and superconducting states.

The most recent experiments on $La_{1.85}Sr_{0.15}CuO_4$ by Yamada *et al.*[119] have clarified this picture somewhat. They found that the incommensurate peak intensity, $Im\chi(\mathbf{q}_\delta, \omega)$, was essentially independent of T for $\hbar\omega \geq 4.5$meV, and decreased below T_c for $\hbar\omega \leq 3$meV. This implies that there *is* an energy gap at the wave vector $\mathbf{q}_\delta$ and that it is close to 3.5meV. Since the neutron scattering intensity at wave vector $\mathbf{q}$ depends on electronic excitations from $\mathbf{k}$ to $\mathbf{k} + \mathbf{q}$,[115] one can define a $\mathbf{q}$ dependent effective gap as

$$\Delta_{eff} = \min_{\mathbf{k}} |E_+(\mathbf{k} + \mathbf{q}) - E_-(\mathbf{k})|, \qquad (5.4)$$

where as usual $E_\pm(\mathbf{k}) = \pm\sqrt{(\epsilon(\mathbf{k})^2 + |\Delta(\mathbf{k})|^2)}$. Yamada *et al.* noted that if one assumes a $d_{x^2-y^2}$ gap function

$$\Delta(\mathbf{k}) = (\Delta_0/2)(\cos k_x a - \cos k_y a), \qquad (5.5)$$

then the effective excitation gap at the incommensurate vector $\mathbf{q}_\delta$ will be about 3.5meV if $\Delta_0 = 10$meV. This value of Δ_0 would be consistent with several theoretical predictions based upon models of $d_{x^2-y^2}$ pairing.[119]

Of course, these observations could not be said to completely rule out an anisotropic s-wave state, whether with gap nodes or not. Any gap function with $\Delta_{eff} = 3.5$meV at $\mathbf{q}_\delta$ should also give similar behaviour. What would be needed to distinguish clearly $d_{x^2-y^2}$ pairing from the anisotropic s-wave states is a more detailed analysis of the neutron scattering intensities precisely at the gap node wave vectors (as shown in Fig. 3), rather than at the nesting vectors $\mathbf{q}_\delta$. In this case one would have to see $\Delta_{eff} = 0$ for a $d_{x^2-y^2}$ pairing state. Mason *et al.*[122] did scan along a line $\mathbf{q} = (1 \pm \epsilon)(\pi/a, \pi/a)$ in the superconducting state, where one might expect to see $d_{x^2-y^2}$ gap nodes, but the intensity was rather featureless. If the sharp resonances predicted by Lu in Ref. 115 are present, then they have a relatively low spectral weight compared to the strongly enhanced antiferromagnetic scattering around $\mathbf{q}_\delta$. Future experiments with higher resolution may be able to search more closely for these peaks. It should also be noted that Lu's theoretical predictions did not include the effects of strong electron-electron interactions, or of disorder. It is quite likely that disorder would smear out the sharp $\mathbf{q}$ structure he predicted, although one should still see $\Delta_{eff} = 0$ in a $d_{x^2-y^2}$ superconductor.

As mentioned above, the neutron scattering data in the $YBa_2Cu_3O_{6+x}$ compounds differs considerably from that in $La_{2-x}Sr_xCuO_4$. The structure factor $S(\mathbf{q}, \omega)$ has a broad, commensurate, peak around $\mathbf{q}_{AF} = (\pi/a, \pi/a)$. In contrast to the lanthanum cuprate there does not appear to be a continuum of low energy

excitations at this wave vector, but rather there exists an energy gap, E_g.[118] The gap is around $33-35$meV in fully oxygenated samples, and decreases as the oxygen content is reduced, roughly following $E_g \sim 3.5 k_B T_c$. The exact nature of this gap is controversial, but it is generally believed to be associated with a gap in the spin wave spectrum which develops because of the loss of long range antiferromagnetic order in the metallic state. It is apparently not directly associated with the superconducting gap, although it is generally of the same order of magnitude. Interestingly, if we assume that $YBa_2Cu_3O_{7-\delta}$ is a $d_{x^2-y^2}$ superconductor with a gap given by eq. (5.5) with $\Delta_0 = 25$meV as found in photoemission,[92] then the effective excitation gap Δ_{eff} in Eq. (5.4) for the antiferromagnetic wave vector $\mathbf{q}_{AF}$ is expected to be around 30meV, for the Fermi surface and gap function found in Ref. 92. Unfortunately it appears probable[118] that for $YBa_2Cu_3O_{6+x}$ there are two distinct gaps, one magnetic and one superconducting, which have similar magnitudes at $\mathbf{q}_{AF}$. This considerably complicates the interpretation of the neutron scattering data and makes an unambiguous identification of the pairing state difficult.

A second feature of the neutron scattering spectra — a resonance at $\hbar\omega = 41$meV — is more clearly associated with the superconductivity.[124] This peak in $S(\mathbf{q}, \omega)$ above the "spin gap" appears only in optimally oxygenated samples at $\mathbf{q}_{AF}$. It is quite sample dependent[117] and occurs at an oxygen content of $O_{6.9}$-O_7. The peak intensity increases suddenly below T_c and then saturates for $T \ll T_c$, clearly following the opening up of the superconducting gap. A detailed study of this resonance was carried out by Fong et $al.$[120] They observed that the peak had both magnetic and non-magnetic (phonon) contributions, and it was the sudden appearance of the magnetic scattering below T_c which led to the increase in intensity. They argued that the appearance of magnetic scattering in this channel was strong evidence for a sign change in the gap function, such as one expects in $d_{x^2-y^2}$ pairing. The argument is based upon the BCS coherence factor for neutron scattering exciting electrons from $\mathbf{k}$ to $\mathbf{k}+\mathbf{q}$. It is most clearly demonstrated by considering the weak coupling BCS spin susceptibility given by Lu:[115]

$$\chi(\mathbf{q}, \omega) = \sum_k \frac{1}{4} \left\{ 2\chi_1 + \chi_2 + \chi_3 \right\}, \tag{5.6}$$

where

$$\chi_1 \equiv \left(1 + \frac{\epsilon(\mathbf{k}+\mathbf{q})\epsilon(\mathbf{k}) + \Delta(\mathbf{k}+\mathbf{q})\Delta(\mathbf{k})}{E(\mathbf{k}+\mathbf{q})E(\mathbf{k})}\right)\left(\frac{f(\mathbf{k}+\mathbf{q}) - f(\mathbf{k})}{\omega - [E(\mathbf{k}+\mathbf{q}) - E(\mathbf{k})] + i\Gamma}\right)$$

$$\chi_2 \equiv \left(1 - \frac{\epsilon(\mathbf{k}+\mathbf{q})\epsilon(\mathbf{k}) + \Delta(\mathbf{k}+\mathbf{q})\Delta(\mathbf{k})}{E(\mathbf{k}+\mathbf{q})E(\mathbf{k})}\right)\left(\frac{1 - f(\mathbf{k}+\mathbf{q}) - f(\mathbf{k})}{\omega - [E(\mathbf{k}+\mathbf{q}) + E(\mathbf{k})] + i\Gamma}\right)$$

$$\chi_3 \equiv \left(1 - \frac{\epsilon(\mathbf{k}+\mathbf{q})\epsilon(\mathbf{k}) + \Delta(\mathbf{k}+\mathbf{q})\Delta(\mathbf{k})}{E(\mathbf{k}+\mathbf{q})E(\mathbf{k})}\right)\left(\frac{f(\mathbf{k}+\mathbf{q}) + f(\mathbf{k}) - 1}{\omega + [E(\mathbf{k}+\mathbf{q}) + E(\mathbf{k})] + i\Gamma}\right)$$

$$(5.7)$$

In the $T \to 0$ limit, the first term dominates, and either $E(\mathbf{k}+\mathbf{q})$ is above the Fermi level and $E(\mathbf{k})$ is below the Fermi level, or vice versa. In either case the product $E(\mathbf{k}+\mathbf{q})E(\mathbf{k})$ is negative. Precisely on the Fermi surface $\epsilon(\mathbf{k}+\mathbf{q}) = \epsilon(\mathbf{k}) = 0$, and thus the prefactor for the scattering process is:

$$1 - \frac{\Delta(\mathbf{k}+\mathbf{q})\Delta(\mathbf{k})}{|\Delta(\mathbf{k}+\mathbf{q})\Delta(\mathbf{k})|}. \tag{5.8}$$

Clearly this vanishes if $\Delta(\mathbf{k}+\mathbf{q})$ and $\Delta(\mathbf{q})$ have the same sign, as in s-wave pairing, but is non-zero if they have different signs, as in $d_{x^2-y^2}$ pairing. Unfortunately, since the exact nature of this 41meV peak remains uncertain, this argument must be treated with some caution. In particular the resonance appears to be associated with the bi-layer structure of $YBa_2Cu_3O_{7-\delta}$,[124] which leaves open the question of which Fermi surface sheets correspond to the initial and final states $\mathbf{k}$ and $\mathbf{k}+\mathbf{q}$. An s-wave gap which changed signs between the two Fermi surfaces might also be compatible with the existence of the 41meV peak.[125−127]

In summary, the neutron scattering data have not proved as simple a test of unconventional pairing in the cuprates as originally thought. The difficulty arises from the combination of several factors, most importantly the interaction between the particle-hole excitations of the superconductor and the magnetic fluctuations present in both normal and superconducting states. This implies that weak coupling BCS calculations,[115] will not capture the full physics of $\text{Im}\chi(\mathbf{q},\omega)$; instead calculations are necessary which explicitly take into account the strong correlations. Many groups have carried out such calculations using a variety of techniques[128−131] but it is beyond our scope to discuss them in detail. However, good qualitative, and sometimes quantitative, agreement with the neutron scattering data can be obtained in both the normal and superconducting states assuming a single band Hubbard model or bilayer Hubbard model. Furthermore if this calculated spin susceptibility is used as the pairing interaction, usually in an Eliashberg type formalism, a self-consistent picture of superconductivity appears to emerge. In a single layer this pairing state must always be $d_{x^2-y^2}$, while in the bilayer both $d_{x^2-y^2}$ and s-wave solutions appear with similar values of T_c. This s-wave state has a gap function which changes sign between the two

Fermi surface sheets.[125−127] At present the netron scattering appears to *be consistent* with a $d_{x^2-y^2}$ pairing state in both $La_{1.85}Sr_{0.15}CuO_4$ and $YBa_2Cu_3O_{7-\delta}$ but *cannot unambiguously rule out* some of these other alternatives.

In the future we hope that the neutron scattering data will put more precise limits on the possible pairing states. One key issue is whether or not there is a true gap in the spectrum $S(\mathbf{q}, \omega)$, or whether there is a tail of low energy excitations corresponding to the d-wave gap nodes. It is surprising that such low energy excitations have not been seen in neutron scattering in $YBa_2Cu_3O_{7-\delta}$ unlike $La_{1.85}Sr_{0.15}CuO_4$, especially when there is plenty of other evidence for gapless behaviour as seen in Raman scattering, infra-red response penetration depth and so on. It is possible that the relevant region of the $\mathbf{q}$, ω space ($\mathbf{q} \sim (1 \pm \epsilon)(\pi/a, \pi/a)$, $\hbar\omega \ll \Delta_0$) has not been searched thoroughly enough on good quality samples, or that the intensity of these excitations is just much weaker than the strong antiferromagnetic fluctuations near $(\pi/a, \pi/a)$ and they are lost in the background. Mook *et al.*[124] did see a weak tail of low energy excitations below the "spin gap", but other groups generally consider these to be part of the background.[118] A clarification of this issue would considerably strengthen the claims that the neutron scattering supports the $d_{x^2-y^2}$ pairing hypothesis.

5.4. Raman Scattering

Raman scattering provided some of the first strong evidence for nodes in the superconducting gap in $YBa_2Cu_3O_{7-\delta}$, as reviewed by AGR. The data available by 1988 clearly showed that the continuum of electron-hole pair excitations extended well down below the superconducting "gap", which appeared as a broad edge in the spectra. The interpretation of the continuum as due to electron-hole pair excitations was clear cut because of the Fano lineshapes of several of the phonon modes.[132] Monien and Zawadowski[133] argued (based on a specific microscopic model) that this spectrum was consistent with a d_{xy} state among others, but not with $d_{x^2-y^2}$ or s-wave.

Since then, the superconducting state Raman measurements have been extended from $YBa_2Cu_3O_{7-\delta}$ to, for example, $Bi_2Sr_2CaCu_2O_{8+\delta}$,[134] again showing the continuum of excitations extending well below the nominal gap.

Clearly this continuum is *prima facie* evidence against an isotropic gap, such as isotropic s-wave or $d_{x^2-y^2} + \alpha i d_{xy}$ with $\alpha \sim 1$, and in this sense is consistent with the photoemission results described above. In order to ask whether the data place stronger constraints on the gap function it is necessary to predict the Raman spectra for various anisotropic gaps, such as $d_{x^2-y^2}$, or anisotropic s-wave states. Such a calculation has recently been provided.[135,136] The results

showed very good quantitative agreement for the Raman spectra *including its polarisation dependence* for $d_{x^2-y^2}$ while both isotropic and anisotropic s-wave were qualitatively inconsistent. Of particular interest is the observed ω^3 low frequency power law of the B_{1g} spectrum (note here B_{1g} etc. labels the symmetry of the excitations measured, and is not the pair state symmetry), compared to the linear power law for A_{1g} and B_{2g} spectra. It is important to realise that this change in power law is not just a density of states effect, but arises from the BCS-like coherence factors in the Raman scattering intensity. Thus the calculated $d_{x^2-y^2}$ spectra is completely different from the spectra calculated with the $\Delta(\mathbf{k}) \sim |d_{x^2-y^2}|$ gap function proposed by Chakravarty *et al.*[15] even though it has exactly the same density of states. In our view these results not only strongly support the overall picture emerging from photoemission that $|\Delta(\mathbf{k})| \sim |k_x^2 - k_y^2|$ but also *force us to the conclusion that* $\Delta(\mathbf{k}) \sim k_x^2 - k_y^2$. It is also interesting to note that the calculation clearly distinguishes $d_{x^2-y^2}$ from d_{xy} states, since the absolute orientation of the crystal axes is known and the B_{1g} and B_{2g} spectra are inequivalent.

6. Quantum Phase Interference: General Principles

In the last couple of years a new class of experiments has been developed which looks *directly* at the symmetry of the order parameter as a function of its arguments.[137] Experiments of this type were originally proposed in the context of heavy-fermion superconductors such as UPt$_3$ which were suspected of forming pairs in a p-state, but were never successfully conducted (or indeed as far as we know attempted) there; this is probably not an accident, given that there is an important difference between the p- and d-wave cases. The principle of the experiment is based on the Josephson effect, so we start with a brief review of the latter.

Imagine a pair of classic (isotropic BCS) superconductors 1 and 2 joined by some "weak link," e.g. a thin, clean layer (~ 10 Å) of oxide ("ideal tunnel oxide junction"). The order parameter in each of the bulk superconductors has no interesting dependence on relative coordinate and may for the moment be characterised in each case by a single complex number $\Psi_1(\Psi_2)$. Now the junction can transmit, in some intuitive sense, not just quasiparticles but also Cooper pairs, and one might therefore imagine that there could be a term in the free energy which involves both Ψ_1 and Ψ_2. The lowest-order such term of interest must, by gauge invariance, be of the form

$$E_J^{(2)} = -\text{const.}(\Psi_1^*\Psi_2 + c.c.) \equiv -J\cos\Delta\varphi, \tag{6.1}$$

where $\Delta\varphi \equiv \arg(\Psi_1/\Psi_2)$ is the relative phase of the Cooper pairs on the two sides and J is a function of T which turns out to be related to the critical supercurrent I_c of the junction by the formula

$$|J| = I_c\varphi_0/2\pi$$
$$(\varphi_0 \equiv h/2e = \text{flux quantum}).$$

(6.2)

It is usually assumed (cf. below) that J is positive, (and this is almost certainly the case for an ideal tunnel oxide junction), but in principle there can be types of weak link for which it is negative,[138] in which case the junction is called a "π-junction" (since the equilibrium value of the relative phase $\Delta\varphi$ is π). The existence of a coupling energy of the form (6.1) has a number of well-known consequences, most of them already pointed out in Josephson's original 1962 paper:

(1) Under zero dc voltage the junction can carry a dissipationless current (supercurrent) of any magnitude up to the critical current I_c (Eqn. (6.2)).

(2) Since the time-dependence of $\Delta\varphi$ is given by the Josephson relation

$$d\Delta\varphi/dt = 2eV/\hbar \equiv 2\pi V/\varphi_0,$$

(6.3)

under a finite dc voltage the junction will carry an ac supercurrent at frequency $2eV/\hbar$., which can be detected by its resonance with a superimposed ac field ("Shapiro steps").

(3) If a uniform magnetic field B is applied in the plane of the junction, then the total critical current through the latter shows a "Fraunhofer" modulation as a function of the quantity $\Phi_J = BA_{eff}$, where A_{eff} is the "effective area" of the junction:

$$I_c(\Phi_J) = I_c \left| \frac{\sin(\pi\Phi_J/\varphi_0)}{(\pi\Phi_J/\varphi_0)} \right|.$$

(6.4)

The "effective area" A_{eff} is given by the product of the length perpendicular to the field times the quantity $(d + \lambda_1 + \lambda_2)$, where d is the thickness of the junction and λ_1, λ_2 are the London penetration depth of the two bulk superconductors.

(4) If the junction is inserted in a bulk superconducting ring (thickness $\gg$ London penetration depth: "rf SQUID" configuration), the quantity $\Delta\varphi$ must satisfy the condition $\Delta\varphi = 2\pi\Phi/\varphi_0$ (modulo 2π), where Φ is the total flux trapped through the ring. In the limit of a "strong" junction

($J \gg \varphi_0^2/2L$, where L is the ring self-inductance) minima with respect to Φ occur close to integral multiples of φ_0, so the trapped flux is *quantised* in units of φ_0.

(5) Most importantly in the present context, suppose we incorporate two junctions in a ring, as part of a circuit, and trap a flux through the ring ("dc SQUID" configuration). Then the *difference* between the phase differences across the individual junctions will be $2\pi\Phi/\varphi_0$, and since the elements act in parallel the total critical current will have maxima at integral values of Φ/φ_0, including zero, and minima at half-integral values. Note that this conclusion rests crucially on two implicit assumptions:

(a) there are no sources of phase difference "around the ring" other than the trapped flux, and

(b) the junctions are both "normal" (or both "π," but not mixed).

Note also that the flux which enters the result is the *trapped* flux, which may not necessarily be equal to that applied externally as the ring may set up its own circulating currents.

We next consider the case of a junction where one or both of the bulk superconductors involved shows "unconventional" pairing. The possible forms of the bilinear term in the free energy analogous to (6.1) are now strongly constrained by symmetry considerations: The relevant expression must be invariant under any transformation under which the Hamiltonian describing the junction is invariant (Principle A).[21, 139] For example, if the junction Hamiltonian (6.1) is invariant under rotation in spin space, it cannot give rise to bilinear coupling between a spin triplet order parameter on the one side and a spin singlet one on the other. Independently of this, if the junction is invariant under inversion then an odd-parity order parameter cannot couple to an even-parity one. This latter result has immediate application to the case of UPt$_3$ and possibly other heavy-fermion systems: although it is very unlikely that the junction is strictly invariant under parity at a microscopic level, it is likely to be much more so after macroscopic averaging, and therefore any overall Josephson coupling between an odd-parity superconductor and a conventional one is likely to be (a) small and (b) random in sign (that is, the predominant coupling of the (single) order parameter of the conventional superconductor is as likely to be to the "incoming" lobe of the p-wave order parameter as to the "outgoing" one). It is therefore not surprising (if one believes UPt$_3$ is indeed odd-parity) that there has been no reliable observation of a Josephson effect between this material and any conventional superconductor: moreover one would predict that even if we were to learn how to make junctions which give a finite effect, the SQUID experiments proposed for this system would in real life give random and hence not very convincing results.

By contrast, the predictions for Josephson contact between a d-wave superconductors and an s-wave one are clear-cut. First consider the case where the junction is parallel to the ab-plane, and assume that the junction itself is invariant under $\pi/2$ rotation. Then *no* d-wave state can show a bilinear coupling to the s-wave state and one should get no Josephson supercurrent (or more accurately no lowest-order one, see below). In addition, even in orthorhombic symmetry no coupling can occur between the s^- or d_{xy} states and the s-state of the conventional superconductor (if the junction is invariant under reflection in the orthorhombic crystal axes). By contrast, if the plane of the junction is perpendicular to the ab-plane then there is no symmetry argument which forbids coupling of the s-wave order parameter predominantly to (e.g.) the d-wave lobe which is oriented perpendicular to the junction, so that the existence of a finite Josephson current between YBCO and classic superconductors in this geometry (which has been long known) is perfectly compatible with d-wave pairing in the former. (It should be emphasised that the above symmetry arguments constrain only the terms in the free energy which are *bilinear* in the Ψ's. In most cases one cannot exclude the possibility that effects of higher order in the Ψ's may give rise to a finite Josephson supercurrent. However, in such cases the periodicity observed in e.g. the ac Josephson radiation or the flux trapping behaviour (or the Fraunhofer diffraction pattern, cf. below) would be φ_0/n, where n is an integer greater than 1. Most of the experiments to be discussed have explicitly checked that the periodicity is indeed φ_0 and thus discounted this possibility, so we will assume in the following that any Josephson effect observed is indeed bilinear).

Let us now consider the general case. In the following we shall, in common with most if not all of the existing literature on this subject, assume that the dependence of the order parameter on the center-of-mass coordinate $\mathbf{R}$ is important only in so far as it affects the overall phase. More specifically, we shall assume that the (spin singlet) order parameter $\Psi(\mathbf{r}_1, \mathbf{r}_2)$ can for our purposes be written in the form

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = F(\rho)f(\mathbf{R}), \tag{6.5}$$

where ρ is the relative coordinate $\mathbf{r}_1 - \mathbf{r}_2$. The quantity $F_{\mathbf{k}}$ is defined as just the Fourier transform of $F(\rho)$. We emphasize that the assumption (6.5) is made only for the purposes of simplifying the notation in the ensuing argument; those results below which follow from pure symmetry arguments are completely unaffected by a relaxation of the assumption, and the (non-symmetry-based) results of microscopic theory are likely to be only weakly sensitive to it.

Consider a given Josephson junction between bulk superconductors 1 and 2, and suppose that the order parameter in superconductor 1 (2) may in general be a combination of various irreducible representations $j(j')$. (In the case of an

orthorhombic crystal, we take those to be the irreducible representations of the tetragonal group.) For each j or j' we choose a basis function $Y_j^{(1)}(\mathbf{k})$, $Y_{j'}^{(1)}(\mathbf{k})$, which, as well as transforming appropriately, reflects the detailed $\mathbf{k}$-dependence of the order parameter, so that we can write

$$
\begin{aligned}
F_{\mathbf{k}}^{(1)} &= \sum_j \psi_j^{(1)} Y_j^{(1)}(\mathbf{k}) \\
F_{\mathbf{k}}^{(2)} &= \sum_{j'} \psi_{j'}^{(2)} Y_{j'}^{(2)}(\mathbf{k}).
\end{aligned}
\tag{6.6}
$$

Then, from gauge invariance, the lowest-order Josephson coupling energy can be written in the form

$$
\begin{aligned}
E_J^{(2)} &= -\operatorname{Re} \sum_{jj'} A_{jj'} \psi_j^{(1)} \psi_{j'}^{(2)} \\
&= -\operatorname{Re} \sum_{jj'} A_{jj'} |\psi_j^{(1)}| |\psi_{j'}^{(2)}| \cos\left(\varphi_j^{(1)} - \varphi_{j'}^{(2)} \right)
\end{aligned}
\tag{6.7}
$$

where the quantity $A_{jj'}$ will in general depend on the properties of the junction.

In the application of our analysis to circuits including more than one Josephson junction a crucial role is played by the choice of phase convention for the $Y_j(\mathbf{k})$. In our opinion by far the simplest and most natural choice is so that for any one bulk superconductor the form of $Y_j(\mathbf{k})$ is real and is defined *relative to absolute space*: e.g. for a crystal oriented with axes along the NS and EW directions in "absolute" (laboratory) space, we define a $d_{x^2-y^2}$-like basis function so that its + signs are always on the NS lobes and the − signs on the EW ones. (For a twinned crystal we apply this definition to the "twin-averaged" order parameter, see Section 4). Note that even in cases where various bulk regions are made of the same superconductor (e.g. YBCO), if the crystal axes are differently oriented the definitions of the $Y_j(\mathbf{k})$ will be different in different regions and the relative phase convention may be arbitrary; this however causes no difficulty provided we keep the accounting straight.

With the above choice of phase convention, the quantity $A_{jj'}$ may depend not only on the "intrinsic" properties of the junction *but also on its orientation*, and in particular may be negative for some combinations j, j'. For example, if we define the phase convention for a $d_{x^2-y^2}$ state as above, and consider a junction with an ordinary s-wave superconductor with the junction plane (edge) in the NS-direction, then since the natural assumption is that the exterior s-wave couples more strongly to the lobe of the order parameter which is perpendicular

to the junction than to the "parallel" one, it is plausible that A_{sd} is in this case negative. We see more generally that with our convention, for a single irreducible representation in each bulk superconductor the lowest-order Josephson coupling can always be written in the form

$$E_J^{(2)} = -J \cos \Delta\varphi \tag{6.8}$$

where however J may have either sign. In the recent literature junctions for which J is negative are sometimes referred to as "π-junctions"; however, this seems to us very confusing, since the fact that J is negative has nothing to do with the intrinsic properties of the junction as such but is entirely a consequence of our choice of phase convention. We urge that in future the term "π-junctions" be reserved for junctions of the type discussed in Ref. 138, or more generally for those junctions which induce half-quantum flux quantisation in a single-junction SQUID ring with uniform bulk crystal orientation. To make quite sure that there is no ambiguity, in the rest of this review, we shall use the term "intrinsic π-junctions" for such a case.

In the case where more than one irreducible representation occurs in one or both superconductors we need to invoke a very important general consideration (cf. Section 3): In the absence of pathology, the relative phase of the different ψ_j occurring in each of the bulk superconductors is uniquely fixed by the energetics (see the form of the fourth-order terms in Eqn. (3.5)). Let us then choose one particular irreducible representation j, j' on each side, and (with the general phase convention above) define the phases $\varphi_j(\varphi_{j'})$ of the other components relative to $\psi_{j0}(\psi_{j'0})$. We then define, conventionally, the "total" phase difference $\Delta\varphi$ across the junction as the difference between the phases of ψ_{j0} and $\psi_{j'0}$. Then we can write the lowest-order Josephson coupling energy in the generally valid form

$$E_J^2 = -J \cos(\Delta\varphi + \alpha) \tag{6.9}$$

with J, α real and

$$J e^{i\alpha} \equiv \sum_{jj'} A_{jj'} |\psi_j| \cdot |\psi_{j'}| \exp i(\varphi_j - \varphi_{j'}). \tag{6.10}$$

We note explicitly that the quantity α need not be 0 (or π). For example, if (contrary to the arguments of Section 4) the twin-averaged order parameter of YBCO is of the $s + id$ form, then we expect that for certain junctions α would vary continuously from 0 to $\pi/2$ as the "d-wave" component is increased.

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In the context of a determination of the symmetry of the order parameter the crucial question is: What do we know for sure about the coupling constants $A_{jj'}$ in (6.10), and what may we reasonably surmise? It is essential to appreciate that the only totally reliable knowledge of the $A_{jj'}$ which is independent of a particular microscopic model is that which follows from symmetry arguments. We will assume that when averaged over scales large compared to a typical "correlation" length, which is in general of an atomic order of magnitude or, at least, very much smaller than the transverse dimensions of the junction, the properties of the latter itself are invariant under appropriate symmetry operations ($\pi/2$ rotations about the normal, reflection in the plane defined by the normal and a bulk crystal axis, etc.). This then immediately implies that the Josephson energy $E_J^{(2)}$ must be invariant under the appropriate operations when applied simultaneously to the junction and the bulk superconductors, and this will in general determine (a) which of the $A_{jj'}$ must be zero ("principle A"), and (b) to some extent, how these quantities transform when the orientation of the junction is changed. It is clear that when the bulk samples are heavily twinned (and we assume no correlation in the twinning across the boundary), then in the thermodynamic limit (only!) these arguments can be applied to the $A_{jj'}$ defined in terms of the "twin-averaged" order parameters. We already saw an example of (a): if the plane of a junction between a tetragonal cuprate superconductor and (e.g.) Pb is normal to the c-axis, and the properties of the junction are invariant under $\pi/2$ rotation, then $A_{s,d_{x^2-y^2}}$ must be zero. An example of (b) is exploited in the "type-II" experiments of Section 7: for two junctions between Pb and a tetragonal cuprate with normals lying in the ab-plane and at right angles the sign of $A_{s,d_{x^2-y^2}}$ must be different. We will exploit some rather more complicated applications of these principles in Section 7.

Can we obtain any further information about the coupling coefficients $A_{jj'}$ over and above what is implied by symmetry? To do so, we clearly need (a) a microscopic model of the formation of Cooper pairs in bulk, and (b) a microscopic model of the processes in the junction which give rise to the Josephson coupling. As regards (a), while a few calculations[140] have been done for the case of "exotic" (non-Fermi-liquid-based) models of the bulk superconductivity, to the best of our knowledge those have all assumed simple s-wave symmetry; since the main relevant differences of those models from the standard BCS one appears to lie mainly in the energy-dependence of the single-particle propagators, it seems unlikely that the behaviour of the $A_{jj'}$ in (anisotropic versions of) such models would be quantitatively different from what it is in BCS-type theories. However, we should caution that while these existing calculations have produced a Josephson coupling with the conventional sign, we can see no compelling *a priori* argument to exclude the possibility that in such models "intrinsic π-junctions"

(in the sense defined above) might be the norm, between two cuprate supercon-
ductors and/or between a cuprate and a classic superconductor such as Pb. As
regards point (b), while the literature of the last thirty years contains hundreds
or perhaps thousands of papers which work out the details of the Josephson ef-
fect in the various different known types of junction (tunnel oxide barriers, SNS
junctions, microbridges, point contacts...) the vast majority of these not only
deal with s-wave superconductors but neglect the details of the directional prop-
erties of tunnelling matrix elements (as is legitimate in the s-wave case) so that
the generalisation to unconventional pairing is not obviously trivial.[141] One case
where one can write down such a generalisation is that of a simple tunnel oxide
junction described by the simple Bardeen-Josephson Hamiltonian

$$\hat{H}_T = \sum_{\mathbf{kq}\sigma\sigma'} (T_{\mathbf{kq}\sigma\sigma'} a^+_{\mathbf{k}\sigma} b_{\mathbf{q}\sigma'} + \text{H.C.}) \tag{6.11}$$

where $a^+_{\mathbf{k}\sigma}(b^+_{\mathbf{q}\sigma'})$ create an electron in Bloch-wave state $\mathbf{k}(\mathbf{q})$ and spin $\sigma(\sigma')$ in
bulk superconductor 1 (2). For a simple BCS-like picture of the bulk state of
both superconductors the calculation of the second-order Josephson coupling
energy is a straightforward generalisation of the original one of Ambegaokar and
Baratoff[142] for the s-wave case: for simplicity of notation we state it under the
simplifying assumptions[143] of zero temperature and a matrix element $T_{\mathbf{kq}\sigma\sigma'} = T_{\mathbf{kq}}\delta_{\sigma\sigma'}$ which is proportional to a unit matrix in spin space and is moreover
time-reversal invariant $T^*_{\mathbf{kq}} = T_{-\mathbf{k}-\mathbf{q}}$ but is otherwise arbitrary:

$$E_J^{(2)} = -2\text{Re} \sum_{\mathbf{k},\mathbf{q}} \frac{|T_{\mathbf{kq}}|^2 F_{\mathbf{k}}^{(1)} F_{\mathbf{q}}^{(2)*}}{E^{(1)}(\mathbf{k}) + E^{(2)}(\mathbf{q})}, \tag{6.12}$$

where $F_{\mathbf{k}}^{(j)} \equiv \Delta^{(j)}(\mathbf{k})/2E^{(j)}(\mathbf{k})$, $j = 1, 2$.

For the case of s-wave pairing, Ambegaokar and Baratoff showed that the
critical current $I_c \equiv 2\pi E_J/\varphi_0$ which follows from Eqn. (6.12) is related to the
normal state resistance R_n of the junction by the formula

$$I_c R_n = \frac{\pi \Delta^{(1)}}{2e} f(\Delta^{(1)}/\Delta^{(2)}), \tag{6.13}$$

where f is a specified function of the gap ratio, taking the value one when its
argument is unity. We will refer to the right hand side of Eqn. (6.13) as the
"Ambegaokar-Baratoff" value of the product $I_c R_n$, and denote it by $(I_c R_n)_{AB}$.

Expression (6.12) respects the symmetry principle we have called "principle A." We can therefore rewrite it in the form (6.10), with the $A_{jj'}$ given by the formal expression

$$A_{jj'} \propto \int \frac{d\Omega}{4\pi} \int \frac{d\Omega'}{4\pi} |\tilde{T}(\hat{\mathbf{n}}, \hat{\mathbf{n}}')|^2 \tilde{Y}_j(\hat{\mathbf{n}}) \tilde{Y}_{j'}(\hat{\mathbf{n}}') \qquad (6.14)$$

where $\tilde{Y}_j(\hat{\mathbf{n}})$ and $\tilde{T}(\hat{\mathbf{n}}, \hat{\mathbf{n}}')$ are respectively the energy-averaged value of $Y_j(\mathbf{k})$ and a quantity which, while in general not simply related to $T_{\mathbf{kq}}$, respects its symmetries and its qualitative features (in particular, if $T_{\mathbf{kq}}$ is sharply peaked for $\mathbf{k}$ and $\mathbf{q}$ normal to the junction plane, then so is $\tilde{T}(\hat{\mathbf{n}}, \hat{\mathbf{n}}')$).

As already stated, the expression (6.12) (and hence (6.14)) has been derived for the anisotropic case only for a simple oxide tunnel junction described by the Hamiltonian (6.11). However, it seems plausible to guess that it would apply more generally, with however $T_{\mathbf{kq}}$ replaced by some "effective" matrix element which, for example, in the case of an SNS junction would depend strongly on the properties of the normal-metal layer (including its temperature). Unfortunately, for most types of junction both our theoretical and our experimental information on the detailed angular dependence of $|T_{\mathbf{kq}}|^2$ (or its average) is rather poor. For an SNS junction, and to a somewhat lesser extent for a simple tunnel oxide barrier, it seems very plausible that $|T_{\mathbf{kq}}|^2$ (hence also $\tilde{T}(\hat{\mathbf{n}}, \hat{\mathbf{n}}')$) is strongly peaked in the normal direction ($\mathbf{k}$ and $\mathbf{q}$ both close to the junction normal $\hat{\mathbf{n}}_0$). If this is the case, then for those types of junction $A_{jj'}$ is a direct measure of the product $Y_j(\hat{\mathbf{n}}_0) Y_{j'}^*(\hat{\mathbf{n}}_0)$. However, in the case of junctions formed by grain boundaries (which not only tend to be "jagged" but also to act as sinks for various chemical impurities etc.) it would seem optimistic to expect that the $A_{jj'}$ have this simple form.

Finally, if we not only make the assumption of the last paragraph but assume that the $d_{x^2-y^2}$ irreducible representation has literally that form (i.e. $Y_j(\hat{\mathbf{n}}) = \hat{n}_x^2 - \hat{n}_y^2$), we obtain the expression written down by Sigrist and Rice[144] for the coupling energy of two differently oriented YBCO grains each described by a $d_{x^2-y^2}$ state:

$$E_J^{(2)} \propto \cos 2\theta_1 \cos 2\theta_2 \cos(\varphi_1 - \varphi_2) \qquad (6.15)$$

where θ_1 and θ_2 are the angles made by the positive lobe of the order parameter in superconductor 1 and 2 respectively with the boundary normal. While this "Sigrist-Rice" ansatz for the coupling energy has of course the correct symmetries, we would caution that it may be dangerous to take it too seriously as the exact form of $A_{dd}(\hat{\mathbf{n}})$, in particular in the case of a grain boundary junction.

To complete our analysis, we need to consider the behaviour of the order parameter in the bulk superconductor, whether the latter be classic or unconventional. We will postpone for the moment possible complications associated with twin boundaries, corners, etc., and assume the superconductor in question to be homogeneous (though not necessarily infinite in spatial extent). We now invoke a very important general consideration: in all models of the pairing in the high temperature superconductors currently considered, the only unbroken *continuous* symmetry is the U(1) gauge symmetry. Thus to deform the components of the order parameter continuously in any way other than by an overall phase rotation will cost a bulk free energy density of order $\alpha^2 F_c$, when F_c is the bulk thermodynamic condensation free energy and α is a number which is in general of order unity; while for special cases α could be much smaller than 1, it is very unlikely to be of the order of the inverse sample size. On the other hand, the "bending" energy density associated with variation of the components in space over a distance L, turns out to be quite generically of the order of $F_c(\xi(T)/L)^2$, where $\xi(T)$ is the correlation length: in BCS-type theories this is of order $\hbar v_F/\Delta(T)$, and quite generally is expected to be of the order of the pair size except close to T_c. Thus any deviation of the order parameter from its equilibrium value (such as, for example, a "soliton" in which the lobes rotate *geometrically* in **k**-space from one axis to another) will have a typical length scale of order $\xi(T)/\alpha$ and cost an energy per unit area of order $\alpha F_c(T)\xi(T)$. The upshot of this is that for any reasonable sample size the creation energies for such solitons, etc., will be so enormous relative to $k_B T$ that their probability of existence in thermodynamic equilibrium is essentially zero except very close to T_c; and while in principle this kind of "defect" could be generated during the quenching through the phase transition, it seems likely in the cases of physical interest that it would be topologically unstable and disappear as soon as T falls appreciably below T_c. Thus the *only* kind of variation of the order parameter over macroscopic distances which we need to consider in the bulk superconductor is the overall phase variation corresponding to the U(1) gauge symmetry. (The case of ordinary s-wave superconductivity is a rather trivial special case of this general result).

From rather general considerations we can say that if the overall phase $\varphi(\mathbf{R})$ varies in space, the associated "bending" free energy density has the form

$$F = \rho_s(T)\frac{\hbar^2}{8m}(\nabla\varphi - 2e\mathbf{A}(\mathbf{R})/\hbar)^2 \qquad (6.16)$$

and the supercurrent is given by

$$\mathbf{J}_s = \rho_s(T)\frac{\hbar e}{2m}(\nabla\varphi - 2e\mathbf{A}(\mathbf{R})/\hbar), \qquad (6.17)$$

where the superfluid density $\rho_s(T)$ defined by (6.16) may in general be a tensor

in Cartesian space. In any given geometry the equilibrium form of the order parameter must be found by minimising the sum of (a) the Josephson energies (6.9) associated with any junctions in the circuit (b) the "bending" energy (6.16), and (c) the usual electromagnetic energy

$$F_{em} = \frac{1}{2\mu_0} \int (\nabla \times \mathbf{A}(\mathbf{r}))^2 d^3\mathbf{r}. \tag{6.18}$$

For an arbitrary geometry this minimisation problem may be quite complicated (cf. below). However, in most cases (though not all) of experimental relevance a major simplification is possible. The problem contains three characteristic energies:

(1) The energy E_{kin} which would be necessary to produce one quantum of circulation (with $\mathbf{A} = 0$) *with flow over the whole bulk volume.*

(2) The self-inductance energy E_{ind} of the corresponding circulating current (note that for most experimentally interesting geometries, this is not particularly sensitive to the actual distribution of the current, and in any case we are interested only in orders of magnitude).

(3) The phase-locking energy E_J of any Josephson junctions involved.

Using (6.16) and standard results of electrical circuit theory, we obtain the order-of-magnitude estimates

$$E_{kin} \sim \rho_s \frac{\hbar^2}{2m} \frac{A_B}{L}, \qquad E_{ind} \sim \frac{(h/e)^2}{\mu_0 L}, \qquad E_J \sim I_c(\hbar/e), \tag{6.19}$$

where A_B is the cross-sectional area of the bulk superconductor(s), and L is the circumference of the circuit. The condition for E_{kin} to be large compared to E_{ind} is $A_B \gg \lambda_L^2(T)$ where $\lambda_L(T)$ is the bulk London penetration depth; this condition is fulfilled for essentially all geometries of experimental interest. The condition $E_{kin} \gg E_J$ is generally fulfilled, in particular when the cross-sectional area of the junction is small compared to A_B; however, in certain special "two-dimensional" geometries E_J may be comparable to or even larger than E_{kin}. Now, if E_{kin} is indeed the largest energy in the problem, it will be important to get rid of it by forcing the current to flow only over a strip of thickness of order $\lambda_L(T)$ on the surface of the bulk superconductor (the usual Meissner effect). If furthermore, the thickness of the bulk is itself $\gg \lambda_L(T)$ (a condition which is, of course, compatible with but not guaranteed by the condition $A_B \gg \lambda_L^2(T)$), then we will be able to argue as in the standard account of flux quantisation that since

the current is screened out within the bulk, the phase difference $\Delta\varphi$ accumulated *within the bulk regions* as we go around a circuit is given by

$$\Delta\varphi = \frac{2e}{\hbar} \int \mathbf{A} \cdot \mathbf{dl} = 2\pi\Phi/\varphi_0, \qquad (6.20)$$

where Φ is the total flux through the circuit (it is assumed here that the contribution of the junction regions to the flux is negligible). Moreover, for a single circuit the sum of the energies E_{kin} and E_{ind} then has the simple expression (Φ_{ext}=externally applied flux, L=self-inductance of circuit)

$$E_{ind}(\Phi) = \frac{1}{2}LI^2 = (\Phi - \Phi_{ext})^2/2L. \qquad (6.21)$$

We now choose a particular component j_0 of the order parameter (it does not matter which) in each bulk region and define the phase difference $\Delta\varphi_i$ across the i-th junction as described above. Since the total phase difference accumulated by the phase as we go around the complete circuit must be $2n\pi$, we have from (6.20) the central result

$$\sum_i^{(c)} \Delta\varphi_i = -2\pi\Phi/\varphi_0 \; (+2n\pi), \qquad (6.22)$$

where the (c) indicates that we must sum over all the junctions in the circuit as we traverse it in a consistent sense. Further, the total energy of the (closed) circuit is given by the expression

$$E_{tot}(\Phi) = (\Phi - \Phi_{ext})^2/2L - \sum_i E_i^{(J)}(\Delta\varphi_i), \qquad (6.23)$$

where $E_i^{(J)}(\Delta\varphi_i)$ is the Josephson coupling energy of the i-th junction. It should be noted that Eqn. (6.23) applies only for a circuit with no external leads (or in the (unphysical) case of exact symmetry, cf. Section 7.3). We refer to the combination of eqns. (6.22) and (6.23) as "principle B."

From here on the analysis proceeds essentially as in the case of a normal circuit with only s-wave order parameters and "normal" junctions. Let us focus in particular on the case (realised in most experiments) that the critical currents of all the junctions involved are large compared to φ_0/L. Then the second term in (6.23) dominates, and the value of *total* flux Φ through the circuit is simply $(\varphi_0/2\pi)\Delta\varphi_{tot}$ where $\Delta\varphi_{tot} \equiv \sum_i \Delta\varphi_i$ is the value which minimises the sum of

the Josephson couplings. Thus in this limit the current circulating in the ring is given by the simple expression

$$I = \left(\Phi_{ext} - (\varphi_0/2\pi) \cdot \Delta\varphi_{tot} \right) / L \qquad (6.24)$$

of which the s-wave result ($\Delta\varphi_{tot} = 0$) is of course a special case. Moreover, in the case of a two-junction ring set up with external leads in the "dc-SQUID configuration", the critical current, which with our sign convention for the $\Delta\varphi_i$ is $I_{c1}\sin\Delta\varphi_1$, is easily seen to be periodic in the trapped flux Φ with period φ_0, and maxima at $\Phi = \varphi_0(n + \Delta\varphi_{tot}/2\pi)$. For the special case $I_{c1} = I_{c2}$ the formula is

$$I_c = 2I_c \left| \cos\left(\frac{\pi\Phi}{\varphi_0} - \frac{\Delta\varphi_{tot}}{2} \right) \right| \qquad (6.25)$$

but for unequal junctions the minima are finite. Note that it is the *total trapped flux* Φ, not the external flux Φ_{ext}, which appears in this formula: we return to this point in Section 7.3.

The upshot of all this is that either a direct measurement of the circulating current as a function of Φ_{ext}, or (with caveats) a measurement, in the 2-junction case, of the parallel critical current as a function of Φ, will determine the quantity $\Delta\varphi_{tot}$, and hence allow us to infer something about the $E_i^{(J)}$ and thus the symmetry of the order parameter. Two important points should be noted: (1) unless time-reversal symmetry is spontaneously broken (which requires, as a minimum, the mixing of two different irreducible representations) the quantity $\Delta\varphi_{tot}$ must be either 0 or π; (2) experiments of this type cannot by themselves ever exclude the presence of components of the order parameter which, for symmetry or other reasons, do not contribute to the individual $E_i^{(J)}$.

7. Quantum Phase Interference: Experiments

At the time of this writing (late 1995) there are about a dozen experiments in the literature which attempt to exploit the Josephson effect systematically to determine the symmetry of the order parameter. With one exception they are all on YBCO, usually pure but in one case also Pr-doped. It is convenient to classify them into three groups:

I. Experiments involving a single Josephson junction between YBCO and a conventional superconductor such as Pb, in the "c-axis" geometry. These exploit only principle A.

II. Experiments involving a SQUID-type circuit or something related, the bulk ingredients of the circuit again being YBCO and a conventional superconductor. These experiments exploit (directly) only principle B.

III. Experiments on a circuit whose bulk elements are entirely YBCO (or some other high temperature superconductor), with the different bulk regions having different crystal orientations. As we shall see, these experiments in some sense exploit both of the principles A and B.

In reviewing the experiments we shall focus primarily on the application to them of the general principles enunciated in Section 6 above, with particular attention to the possible complicating effects of the orthorhombic structure of YBCO. For those considerations which are specific to the particular experimental geometry or method used, such as the possibility of unwanted trapped flux, we refer the reader to the original papers and the subsequent exchanges in the literature.

Type I experiments

To date there have been experiments reporting a finite Josephson current by two groups: Sun *et al.*[7] followed by Katz *et al.*[145] being one, and Iguchi and Wen[146] being the other. We will refer to those as the UCSD and Tsukuba experiments respectively. It should be mentioned that a number of groups had previously tried and failed to observe a Josephson current in this geometry.[2]

In the UCSD experiments the authors etched single (but heavily twinned) crystals of $YBa_2Cu_3O_{7-\delta}$ and $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ so as to expose faces parallel to the ab-plane, and fabricated junctions by evaporating on to the exposed surface first about 10Å of Ag (to prevent formation of too thick an insulating barrier) and then a 1μm thick Pb film. Since there is probably a thin material insulating barrier formed at the YBCO surface, the resulting junction is probably best described as of SINS (superconductor-insulator-normal-superconductor) type.

For our purposes the salient result of this experiment is that a finite critical current I_c was obtained between the YBCO and the Pb. However, the magnitude of the product I_cR_n was considerably less than the (s-wave) "Ambegaokar-Baratoff" value (see Section 6), which is calculated for a Pb-YBCO junction as 8.0 meV. In fact, the ratio $I_cR_n/(I_cR_n)_{AB}$ varied from about 0.025 to 0.11, being highest for the pure YBCO samples. Since the effective dimensions[147] of the junctions were reasonably well known, it could be checked that the Fraunhofer modulation pattern obtained in a magnetic field applied in the plane of the junction is not only of the conventional type but corresponded to a field scale defined by the usual flux quantum $h/2e$ (and not, e.g., $h/4e$), thus establishing that the Josephson effect seen is indeed the usual lowest-order one (see Section 6). No

anomalous Fraunhofer patterns were reported.

The Tsukuba experiments employ a geometry which, at least at the macroscopic level, is similar to the UCSD one: they used c-oriented YBCO and Pb films as the electrodes, while the barrier was either "natural" or an MgO layer (and sometimes an Ag overlayer) a few nm thick. In this experiment too, finite critical currents were observed, with however a value[148] of $\alpha = I_c R_n / (I_c R_n)_{AB}$ in the range $0.01 - 0.025$, thus smaller than in the UCSD experiment. In addition, the authors report two intriguing further features: First, the critical current is a nonmonotonic function of temperature; it rises steeply below the T_c of Pb, reaches a maximum at around 5K and then decreases until at 2K it is about half the maximum value. Secondly, in some cases the Fraunhofer pattern is "split," i.e. shows a minimum at zero applied field (see Fig. 2 of Ref. (146)); as we shall see below, similar behaviour is seen in the UIUC II experiment. However, at low temperatures the critical current appears to be only weakly dependent on the field. The Fraunhofer patterns seen are often asymmetric under reversal of the field or the current or both.

Let us first try to interpret these data on the hypothesis of simple s-wave pairing in the YBCO. Clearly the UCSD data are qualitatively consistent with this assignment; while the value of α is surprisingly small, there are various scenarios which could explain it, e.g. normal-metal "shorts" which contribute to R_n^{-1} but not to I_c. Indeed, it is not totally implausible that the even smaller value of α seen in the Tsukuba experiments could be accounted for in this way. However, the Fraunhofer data in the latter are more difficult to explain on an s-wave hypothesis: while the obvious explanation of the frequent asymmetry of the patterns is as some kind of trapped-flux effect, it seems difficult to account for the "split" patterns in this way without invoking a rather implausible degree of coincidence. However, this does not seem to us a conclusive argument against the s-wave scenario.

Now let us ask whether the data are compatible with any assignment other than simple s-wave. For pedagogical clarity let us first pretend that the crystal symmetry of YBCO is pure tetragonal, so that the competing possibilities are s^-, $d_{x^2-y^2}$ and d_{xy}. Now the Cooper pairs in Pb are known with a high degree of confidence to form in a simple s-state, i.e. are even under $\pi/2$ rotation and under inversion in a crystal axis; further, it seems a natural assumption that the junctions themselves are isotropic in the ab-plane, at least where averaged over a few atomic distances (but see below). Given this state of affairs, and the experimentally verified fact that the Josephson effect is seen in lowest order, principle A immediately rules out[149] all YBCO pairing symmetries other than s^+.

It should be emphasised that this conclusion (drawn for the case of tetragonal symmetry, which is of course not realised for real-life YBCO) is a great deal more robust than one might think at first sight. For example, it is tempting to try to think up mechanisms by which the bulk d-wave order parameter of YBCO might have some s-wave component mixed into it as we approach the surface, so that this component could couple to the Pb order parameter and give a finite lowest-order Josephson effect. However, any such effect must still come from a bilinear coupling of the bulk order parameters in the Pb and the YBCO, so that the general symmetry principle still rules it out.

Once the orthorhombic anisotropy of real YBCO is taken into account, the situation becomes a good deal more complicated. (For the moment we still assume that the surface is smooth.) Indeed, it is immediately clear that an *untwinned* single crystal of orthorhombic YBCO with $d_{x^2-y^2}$ pairing can show a lowest-order Josephson effect in the UCSD/Tsukuba geometry with an s-wave superconductor such as Pb,[150] in fact it can even have a value of α of order unity. However, the UCSD and (presumably, though it is not stated) the Tsukuba samples were heavily twinned. The subsequent analysis depends crucially on the behaviour assumed for the order parameter on crossing a twin boundary. If it behaves "non-gyroscopically" as defined in Section 6 above, then the critical currents of the different twin domains add up in phase and the α-value for the whole junction will be essentially the same as for an untwinned sample. However, we argued in Section 6 that there are compelling reasons to believe that the order parameter behaves "gyroscopically," i.e. keeps its + and − signs relative to "NSEW." In this case neighbouring twins will tend to interfere destructively, and one would expect that the α-value for the macroscopic junction will be of order $N^{-1/2}\alpha_0$, where α_0 is the "untwinned" value, and N is (at least for the moment: but see below) the number of twin domains in the area of the junction.

The crucial question now is: Is the value of N which is likely to have been realised in the UCSD and Tsukuba experiments small enough that the predicted α would be as large as observed? In the Tsukuba experiment this seems not implausible: the largest value of α observed was about 0.025, and if we assume that the twinning of the sample was comparable to that in the UCSD experiment and use the estimates of the latter authors, there should have been $\approx 10^3 - 10^4$ twin domains in the junction area. Thus, provided α_0 is of order 1, reconciliation is possible. Actually there is in any case a complication connected with the nature of the sample surface which may help here: see below.

It is more difficult to explain the UCSD results in this way; the number of twin domains as quoted by the authors is comparable, but the values of α, as we see, are larger, up to 0.11. Thus even with $\alpha_0 \sim 1$ the predicted value of α is too

small by at least a factor of 4, unless the estimate of N is for some reason badly wrong.

A further complication concerns the microscopic nature of the nominal "ab" surface. In the above argument it was assumed to be microscopically flat, so that all tunnelling is literally in the c-direction; however, in real life this is unlikely to be so. Indeed, the authors of the Tsukuba experiment note explicitly that their surface carries a large number of "micrograins" (protrusions) whose height and lateral dimension they estimate at 2-5 nm and 10-100 nm respectively; moreover, they postulate that all or most of the tunnelling actually takes place across the *side* faces of these micrograins and is therefore in the a- and/or b-direction. Rather similar phenomena may occur in the UCSD experiment, with a/b tunnelling occurring across the vertical sides of the etch pits. Does this affect the arguments used above?

It should be strongly emphasised that *provided* (a) all surface inhomogeneities are on average isotropic with respect to the laboratory ("NSEW") axes and (b) the order parameter behaves gyroscopically across twin boundaries, the generic symmetry argument *still* rules out states other than s^+ in the thermodynamic limit (area of junction $\rightarrow \infty$). The only difference is that the "thermodynamic limit" may be less easy to attain. Suppose for example it turns out that (perhaps because of the contribution of the chains) tunnelling in the b-direction is appreciably easier then in the a-direction. The effect is (a) to make α_0 of order 1, (rather than the smaller value it is likely to have for a truly planar ab-interface), and (b) to replace, in the calculation of α, the factor $N^{-1/2}$ by the excess number of ac-interfaces normal to (say) the NS axis, which should be of order $N_r^{-1/2}$ where N_r is the total number of "rugosities" (micrograins and/or etch pits) in the junction area. Since N_r could well be an order of magnitude or so smaller than N, this may make it easier to reconcile the observed value of α with a d-wave scenario. While this may be an important effect in the Tsukuba experiment,[151] its relevance to the UCSD results is thrown in doubt by the reported observation that a systematic study of the effects of different degrees of etching showed no systematic dependence of I_c on the latter.

We should finally note that the Tsukuba authors cite the observation of "split" Fraunhofer patterns as evidence for a d-wave scenario, interpreting them as the result of the interference of tunnelling through the a- and b- faces of a single micrograin (cf. the discussion, below, of the UIUC II experiment). However, it seems to us that (since N_r, while smaller than N, seems unlikely to be of order two or three!) such an interpretation would require a high degree of coincidence of the dimensions of the different micrograins contributing to I_c, which seems difficult to reconcile with the quoted spread of values. Thus, this feature of the

Tsukuba experiments, as well as the anomalous temperature-dependence of I_c,[152] remains to us puzzling.

In sum, the UCSD experiment is clearly compatible with a simple s-wave scenario and appears, at least, very difficult to reconcile with a $d_{x^2-y^2}$ picture (or indeed any unconventional one). As to the Tsukuba experiment, while the existence of a critical current of the observed magnitude is compatible with either d- or s-wave behaviour (and if anything would seem to favour the former), other features of the experimental results appear puzzling on any symmetry assignment. If we are prepared to disregard the thermodynamic argument against "mixing" either experiment could of course accommodate a real or imaginary mixture of s^+ and $d_{x^2-y^2}$.

Type-II experiments

To date there are four experiments of type II in the literature; they are reported in Wollman *et al.*,[6] Brawner and Ott,[153] Mathai *et al.*[40] and Wollman *et al.*[154] We shall refer to them as respectively the UIUC I, ETH, Maryland and UIUC II experiments. The circuit arrangements used in the first three are essentially the same, the differences lying mainly in the techniques used to infer the device's current-flux relation and the precautions taken against the possible effects of trapped flux; the UIUC II experiment uses a modification of the circuit arrangement. All four type-II experiments were done on $YBa_2Cu_3O_{7-\delta}$, with δ in the range $0-0.1$, and all are interpreted by their authors as incompatible with any s-wave order parameter (i.e. as favouring a d-state, though not necessarily pure $d_{x^2-y^2}$). In addition, the Maryland group claim to exclude violation of time-reversal invariance at any level above about 5%.

The prototype geometry of these experiments is that of UIUC I (see Fig. 4). For pedagogical clarity we start by discussing an idealised version, in which the circuit (including the two junctions) is exactly symmetric under reflection in the diagonal axis. The analysis is then extremely straightforward and is simply a generalisation of that given originally by Geshkenbein *et al.*[155] for the case of p-wave pairing: cf. Sigrist and Rice.[144] We first assume for the moment that the YBCO pairing state corresponds to a single irreducible representation, and note that the mere fact that a finite critical current is observed across either junction individually then implies, by principle A, that this representation must be invariant under reflection in a crystal axis; this implies that as regards the bulk YBCO the operations of rotation through $\pi/2$ and inversion in a 45° axis are equivalent and we may use either in our argument. We choose for reasons of subsequent convenience to consider $\pi/2$ rotation; in any case, the relevant pairing symmetries are only s^+ and $d_{x^2-y^2}$.

We can now apply the analysis of Section 6 directly. If the pairing state is s^+, then the circuit is just the standard symmetric dc-SQUID circuit described in textbooks of superconducting electronics; the quantity $\Delta\varphi_{tot}$ is zero and all the usual results hold. If on the other hand the pairing state is $d_{x^2-y^2}$, then the symmetry under $\pi/2$ rotation implies that the couplings $A_{jj'}$ across the two junctions ($j = s$, $j' = d_{x^2-y^2}$) have opposite sign: $A_{sd}^{(2)} = -A_{sd}^{(1)}$. Thus $\Delta\varphi_{tot} = \pi$, and the current-flux relation has an offset of half a flux quantum. This is the basic principle used in all the type-II experiments.

Let us now discuss the realistic case. This is complicated by (a) the orthorhombic bulk asymmetry of YBCO, (b) the lack of identity of the junctions, and (c) the asymmetry of the bulk external circuit (and the points of attachment of the junctions, etc.). In addition one might ask (d) how the above argument, which implicitly assumes that the faces to which the junctions are attached are exactly perpendicular to the crystal axis, would be affected if this is not rigorously the case. In view of the fact that the authors of all the type-II experiments report or infer a current-flux relation corresponding to $\Delta\varphi_{tot} = \pi$, we shall discuss only the question of whether any of the above considerations allow this result to be compatible with the assignment of a single YBCO pairing state other than $d_{x^2-y^2}$. For the moment we ignore complication (d) and assume a single irreducible representation; then the above application of principle A goes through and the only alternative to $d_{x^2-y^2}$ is the simple s^+ state. Do considerations (a)-(c) allow a loophole for this assignment?

It is immediately clear that consideration (a) is completely irrelevant, i.e. it in no way changes the predictions for an s-state[156] (many existing dc SQUIDS use classic superconductors whose crystal symmetry is not tetragonal!). Consideration (b) is relevant, in the sense that were a single experiment to come out in favour of the conclusion that $\Delta\varphi_{tot} = \pi$, one might try to reconcile it with an s-wave scenario by postulating that one of the junctions involved was normal and the other an ("intrinsic") π-junction. However, quite apart from the fact that to our knowledge no experimentalist has ever reliably seen an intrinsic π-junction, the UIUC I experiment in particular relies on statistics obtained with a very large number of different pairs of junctions, and it stretches credulity that the preponderance of "normal-π" pairs in the nominally random ensemble could be sufficient to explain the results.

Complication (c) is by far the most annoying in practice. For a strictly symmetric "s-wave" dc SQUID circuit (meaning that not only the inductances, but also the critical currents of the two junctions are identical) the maxima and minima of the critical current occur rigorously at integral and half-odd-integral values of Φ_{ext}/φ_0 respectively, and this remains true even in the presence of finite

self-inductance effects. (This statement follows essentially from the conditions of time-reversal invariance and periodicity of I_c in Φ_{ext} and the experimental observation that $I_c(\Phi_{ext})$ is monotonic over a half-cycle). However, an asymmetry in any of the circuit parameters will in general invalidate this result, since (e.g.) even for $\Phi_{ext} = 0$, by the time the critical current is reached there will in general be a finite current *circulating* in the "ring," and this will produce its own flux. Thus a naive measurement of the dependence of I_c on the "applied" flux will in general give totally misleading results. We refer the reader to the original papers (cf. also Ref. 157) for the various ingenious experimental procedures which have been devised to circumvent this problem; one of them, that of UIUC II, will be discussed further below.

Next we turn to complication (d), and the related question of the possible occurrence of "mixed" representations: note that although in Section we have given strong *a priori* arguments based on thermodynamic considerations for excluding this possibility, it is still of interest to subject it to direct experimental test. We first note that if we ignore for the moment consideration (d), i.e. assume all junction planes are rigorously normal to the crystal axes, etc., then none of the existing type-II experiments can exclude an arbitrary admixture of the s^- or d_{xy} states, since those are odd under reflection in the crystal axes and hence by principle A cannot contribute to the single-junction coupling energy. (However, as suggested in Ref. 158, future experiments using faces cut at $45°$ could in principle do so.)

Next, what are the consequences of a very small misalignment of the (macroscopic) junction plane with the crystalline axes? In principle, if the misalignment is accurately known, this might put some constraints on the s^- and d_{xy} admixture, but those are likely to be exceedingly weak. A more interesting question is whether such misalignment provides a loophole for the simple s-wave (s^+) scenario. It is clear that the answer is no, unless the state is so extremely anisotropic that it actually changes sign (eight times) as we go around the Fermi surface (perimeter). Even with this extreme assumption it would appear to require an almost pathologically violent variation of the order parameter and/or the tunnelling matrix elements with angle. We shall therefore not discuss this theoretical possibility further here.

The most interesting "mixed" possibility, if we are prepared despite the thermodynamic counter-argument of Section 4 to consider such states,[159] is a mixture of s^+ and $d_{x^2-y^2}$ with some definite relative phase: schematically, the (twin-averaged) order parameter would be

$$\Psi \sim d_{x^2-y^2} + \beta e^{i\varphi} s^+. \tag{7.1}$$

This ansatz has the attraction that it could apparently explain the UCSD experiment (in which the $d_{x^2-y^2}$ component is irrelevant). (It is more commonly written schematically, for $\varphi = \pi/2$, as "$s+id$".) It may be seen that such a state leads, in the "standard" type-II geometry, to a total phase shift $\Delta\varphi_{tot}$ given by the expression

$$\Delta\varphi_{tot} = \tan^{-1}\left(\frac{-2\gamma\sin\varphi}{1-\gamma^2}\right), \tag{7.2}$$

where $\gamma \equiv \beta A_{ss}/A_{sd}$. All the type-II experiments indicate that $\Delta\varphi_{tot}$ is close to π, and in particular the Maryland experiments are reported as indicating that $\Delta\varphi_{tot}$ differs from π by no more than about 5%. Since there seems no good reason to believe that the quantities $|A_{ss}|$ and $|A_{sd}|$ are different in order of magnitude, this would then indicate that the *imaginary* part of any s-wave admixture cannot be much greater than this.

We finally review a couple of miscellaneous features of the type-II experiments which are relevant to points raised elsewhere in this review. First, both the UIUC I and the Maryland experiments included "control" experiments in which the two junctions, rather than being attached in the standard "corner" geometry of Fig. 4, were attached to the same edge (UIUC I) or the opposite edge (Maryland) of the YBCO crystal. In both experiments the data indicate that $\Delta\varphi_{tot}$ is equal or close to zero in this geometry. Since all the Maryland samples and some of the UIUC I samples were heavily twinned, this can be reconciled with the $d_{x^2-y^2}$ assignment required by the "corner" data if and only if the order parameter behaves gyroscopically across a twin boundary; we already used this conclusion heavily in Section 4.

Secondly, we note that the UIUC II experiment was done not on a true SQUID geometry, but on a single junction attached at the corner of the YBCO plate, so that the current flowing across the "NS" and "EW" edges was roughly equal. Under these conditions a simple extension of the theory of the Fraunhofer modulation quoted in Section 6 leads, for an s-wave state, to the same expression (6.4) as for an "edge" junction, while for a $d_{x^2-y^2}$ state it predicts a symmetrical but "split" Fraunhofer peak (i.e. the critical current is a minimum at $\Phi = 0$). For the case of exact symmetry with respect to the diagonal through the corner the formula which replaces (6.4) is

$$I_c(\Phi) = I_c\left|\frac{\sin(\pi\Phi/2\varphi_0)}{(\pi\Phi/2\varphi_0)}\right|. \tag{7.3}$$

A major advantage of this arrangement over that of UIUC I is that the effective self-inductance of the "circuit" is much smaller and thus we can essentially replace

Φ in the Fraunhofer formula by the external flux Φ_{ext} which is directly measured. The UIUC II experiment shows a split Fraunhofer pattern which is incompatible with formula (6.4) and reasonably close to (7.3); the residual discrepancy can be reasonably accounted for by the lack of exact reflection symmetry.

To sum up, all the type-II experiments indicate that the order parameter of YBCO, or at least a substantial component of it, has $d_{x^2-y^2}$ symmetry; they are incompatible with an s^+ component such that $A_{ss} > A_{sd}$, and in addition the Maryland experiment excludes an *imaginary* admixture at a level much greater than 5%.[160] No experiment of this class can *by itself* (i.e. without appealing to the thermodynamic argument of Section 4.1) exclude an arbitrary admixture of s^- and/or d_{xy}.

Type-III experiments

As mentioned above, type-III experiments involve a circuit whose bulk elements are entirely composed of some high-temperature superconductor epitaxial films, separated by grain boundaries so that different bulk regions have different crystal orientations. To date there are three such experiments on YBCO in the literature which are reported in refs. 8, 161 and 162; those will be referred to as the IBM I, IBM II and TCSUH experiments respectively. Very recently, the IBM II experiment has been repeated on Tl 2201.[163]

In the IBM II experiment (Fig. 5) a ring was constructed out of three different bulk regions of (heavily twinned) YBCO, with the crystal axes and grain boundary orientations as indicated in the Figure. The system was placed in zero external field and the flux generated by circulating currents spontaneously induced in the ring was measured; those were found to be finite and to correspond closely to the result expected if the ring is "spontaneously" generating a half-odd-integral number of flux quanta. In a control experiment,[161] rings containing zero or two grain boundaries were found to show integral trapped flux, as did also a three-junction experiment[164] with the junctions differently oriented in relation to one another and the crystal axes (the so-called "zero-ring" experiment). In a more recent experiment by the same group,[165] the hole in the ring was in effect removed, and vortices carrying a half-quantum of flux were found to occur at the "tricrystal point" where the three grain boundaries meet (see Fig. 5).

The TCSUH experiment used the geometry shown in Fig. 6. This is conceptually quite close to the geometry of the more recent IBM experiment, and in fact one would expect that under certain circumstances, in an expanded version of this geometry (or one with a hole in the middle), a "half-quantum" vortex would be generated around the tricrystal point. In fact the dimensions are too small (in the principal experiment) for this to happen, and rather than look for spontaneously induced flux the authors measured the critical current of the device as a

function of the external flux applied to the microbridge region. As they remark, it is possible to regard this experiment as analogous to UIUC II, (with the role of the Pb in the latter being played by region III). As in UIUC II, a "split" Fraunhofer pattern was observed, i.e. the critical current is a (local) *minimum* for zero applied flux. In a second experiment using a much wider microbridge (40μ rather than 3μ) the Fraunhofer pattern was of the "normal" type. It should be noted that unlike in the IBM II experiments, the characteristic angles are not close to multiples of $30°$ (the significance of this will become clear below).

Finally, in the IBM I experiment the Josephson critical current was measured between a hexagon of YBCO separated from an outside YBCO region by grain boundaries and oriented at approximately $45°$ with respect to it (see Fig. 7). The measurement was first made for the complete hexagon and then repeated after the various hexagon faces (grain boundaries) had been "chopped away" one by one by laser ablation (leaving barriers which are essentially completely insulating). The salient results for our purposes are that (1) a finite critical current is observed for the complete hexagon, and (2) this current decreases, as the various faces are chopped away, approximately in proportion to the remaining length of face.

In the discussion of the implications of these experiments implicit assumptions have often been made which are not a consequence of basic symmetry considerations. Let us start our own discussion by stating a few conclusions which rely only on very general principles. In doing so, we assume that the applied fluxes, critical currents etc which the authors quote are the "true" ones (e.g. there are no trapped-flux effects). We further assume that the junctions are all in the thermodynamic limit with respect to the twinning and are statistically identical, and moreover (for the moment) that "defrustration" can be neglected. First, it is clear that neither the IBM II nor the TCSUH results are compatible with the conjunction of (a) an order parameter which is everywhere real and of the same sign (i.e. a nodeless s^+ state) with possibly small admixtures of other symmetries, and (b) junctions which are all of "normal" type (i.e. not (intrinsic) π-junctions). This is because under these circumstances it is straightforward to verify that we can choose our phase conventions so as to make all the Josephson coupling energies E_J positive, and the circuit in question will then behave exactly like a "textbook" circuit made of (say) Al, and will show neither a spontaneous flux nor a split Fraunhofer pattern. Since we regard the occurrence in nature (let alone in these experiments!) of (intrinsic) π-junctions as problematical, we would regard this conclusion as effectively disposing of the possibility of a real nodeless order parameter, and in particular of a nodeless s^+ state.

Secondly, while the IBM I experiment is clearly compatible with (and sug-

gests) an s-wave order parameter, we want to emphasise that, *taken by itself* and without additional thermodynamic or other considerations, it *does not* rule out the possibility of a d-state (cf. the remark below Eqn. (2) of Ref. 8). Indeed, any experiment using a circuit in which the bulk components are YBCO only which can be explained by an s-wave order parameter can equally well be accounted for by the hypothesis that the order parameter is of the form $d_{(x+iy)^2}$ (i.e. $\Delta(\mathbf{k}) \sim (k_x + ik_y)^2$). (In essence this is because the only way, in this case, in which the order parameter depends on direction is a phase *which is independent of the crystal axis orientation* and therefore cancels between the order parameters on the two sides of the junction.) While, in view of the evidence for rather strong crystal lattice effects, we would not regard the $d_{(x+iy)^2}$ state itself as particularly plausible, it is clear by continuity that a mixture of the two different irreducible representations $d_{x^2-y^2}$ and d_{xy} of the form

$$d_{x^2-y^2} + i\alpha d_{xy} \qquad (7.4)$$

with α close to 1, would also replicate the s-wave behaviour at least to a good approximation. We note that such a state is not excluded by the type-II experiments; in fact the only compelling arguments against it are the thermodynamic considerations reviewed in Section 4, and the existence of a node in the gap function as described in Section 5.

The further conclusions drawn by the authors of the cited papers[8,163] appear to us mostly to rest on the explicit or implicit assumption of a very specific form of the Josephson coupling as a function of the orientation of the crystal axes along the two sides, namely the Sigrist-Rice expression (6.15) or, at least, the "forward-scattering" ansatz. For the reasons given in Section 6, we would therefore regard these arguments as suggestive rather than compelling.

However, provided we disregard the small deviation ($\sim 3°$) of the actual angles in these experiments from (what we take to be) the "design" angles, it is still possible to draw some conclusions from symmetry arguments alone. Let us for example consider the three junctions of the IBM II experiment: for clarity we omit the hole in the ring and bring them together to a point as in the later experiments of this group. The crucial point is that, to the extent that the actual angles approximate to the design angles, the three grain boundaries *plus* the bulk crystal domains on either side are related to one another by simple symmetry operations, and are therefore "equivalent" provided we do the accounting of the axes right. Suppose first that only a single irreducible representation is represented in the (twin-averaged) YBCO order parameter. There it is clear that $\Delta\varphi_{tot}$ must be zero or π according as to whether this irreducible representation is even or odd under the product of $\pi/2$ rotation and inversion in a crystal axis,

i.e. under inversion in a 45° axis (note that this conclusion does not assume that the area of the three junctions is the same). Thus, the experimental observation that $\Delta\varphi_{tot}$ is (close to) π limits the possible single irreducible representation to $d_{x^2-y^2}$ or s^-. *The IBM II experiment by itself, without further assumptions about tunnelling matrix elements cannot distinguish between these two possibilities.*

If, despite the thermodynamic arguments, we allow for more than one irreducible representation, things become a good deal more complicated: since the individual grain boundaries have no special symmetry relative to both the bulk regions, any of the four possible irreducible representations in one bulk region can couple to any in the other, giving 16 independent possible coupling constants $A_{jj'}$ (note that the matrix $A_{jj'}$ is not in general symmetric). The value of $\Delta\varphi_{tot}$ is then determined by minimisation of the total Josephson energy

$$E_J = -\sum_i \sum_{jj'} A_{jj'}^{(i)} \psi_j \psi_j^* \tag{7.5}$$

where i labels the various junctions, and in general $\Delta\varphi_{tot}$ need not be 0 or π. The observation that $\Delta\varphi_{tot}$ is in fact close to π then merely tells us, crudely speaking, that the Josephson coupling is dominated by irreducible representations which change sign under inversion in the 45° axis, i.e. by $d_{x^2-y^2}$ and/or s^- ; it cannot exclude finite admixtures of s^+ and d_{xy}.

A similar analysis can be applied to the IBM I experiment, with the slight simplification that the rather higher degree of symmetry puts some restrictions on the individual $A_{jj'}$. We see immediately from Fig. 7 that since the complete hexagon is invariant under simultaneous reflection of the inside grain in a crystal axis and the external one in a 45° axis, it would follow from an argument similar to that applied to the IBM II experiment that if the order parameter corresponds to a single irreducible representation it must be even under the product of these two operations, or equivalently even under $\pi/2$ rotation–that is, it must be either s^+ or s^-. It is convenient, however, to split this symmetry argument into two parts: supposing that the only irreducible representation represented is odd under the product of $\hat{I}_{axis}$ and $\hat{I}_{\pi/4}$, then (a) faces 1 and 4 must individually give zero contribution to the Josephson current, and (b) faces 5 and 6 (and 2 and 3) must cancel one another. As to point (a), the fact that face 1 alone gives a non-zero current (see Fig. 2 of Ref. 8) seems to rule out s^-, leaving only s^+.

As regards point (b), an important observation has been made by Millis:[166] The argument for cancellation depends critically on the assumption that there are no currents in the "bulk" inside the grain (so that in the absence of a vector potential the phase is constant throughout this grain as in Eqn. (6.20)). That is, it requires, *inter alia*, that in (6.19) the kinetic energy E_{kin} is much larger

than the Josephson energy E_J. Millis points out that this is probably not so in the actual experiment, and that assuming the order parameter is d-wave, the system will then try to "defrustrate" by allowing the phase to vary throughout the internal region.[167] Unfortunately, while this argument can certainly explain how the total Josephson coupling can be nonzero even if the pairing state is pure $d_{x^2-y^2}$, it does not by itself account for the fact that the contribution from faces 1 and 4 appears to be finite (and more generally that the total critical current is found to be simply proportional to the layer exposed). Millis' own tentative explanation, which is based on the possible "jaggedness" of the grain boundaries which form the junctions, seems to us to require that the scale of this jaggedness is so great that we are not in the "thermodynamic limit", which seems rather unlikely. In view of the poorly understood nature of the grain boundary, one cannot entirely exclude explanations of this general nature.

Once we consider the possibility of more than one irreducible representation, there are few useful conclusions we can draw from the IBM I experiment; in particular, as already noted, it cannot exclude a state of the form $d_{x^2-y^2} + i\alpha d_{xy}$ with α fairly close to 1.

Finally, we note that the analysis of the TCSUH experiment, in which there appears to be no particular equivalence between the various grain boundaries, apparently cannot be carried out as above, but would require a specific hypothesis about the form of the Josephson matrix elements. The same applies to the "zero-ring" experiment of Kirtley *et al.*[164]

Summary

To summarize our conclusions concerning the Josephson experiments: (1) If, relying on the thermodynamic argument of Sections 3 and 4.2, we allow only a single irreducible representation of C_{4v} for the (twin-averaged) order parameter, then the conclusions which appear, *prima facie*, to follow from the various Josephson experiments are, on symmetry grounds alone, not mutually compatible: under this hypothesis the UCSD experiment allows only s^+, the IBM I experiment only s^+ or s^-, the IBM II experiment only $d_{x^2-y^2}$ or s^- and the four type-II experiments only $d_{x^2-y^2}$. The only obvious way to reconcile the various experiments is to assume that neither in the UCSD nor in the IBM I experiment was the "thermodynamic limit" realised, but we have seen above that this is not obviously plausible. (2) If we allow more than one irreducible representation, then to explain all the experiments we require as a minimum a mixture of s^+ and $d_{x^2-y^2}$, with some s^- and/or d_{xy} component as an "optional extra." However, the Maryland experiment excludes an $s^+ + d_{x^2-y^2}$ mixture with relative phase close to $\pi/2$ (assuming a reasonable amplitude for each component). Hence the most plausible assignment would seem to be a real mixture of s and d. This would be

compatible with the IBM I experiment if the contribution of the d-wave component is largely washed out by scattering at the grain boundary. We emphasize that it is the twin-averaged order parameter which must have this character, and that therefore the mechanism for producing it can have nothing to do directly with the orthorhombic asymmetry of YBCO, which as we have mentioned above is (given the gyroscopic assumption) in the Josephson context largely irrelevant.

8. Effects of Impurities

One of the most commonly-expressed doubts about the reality of d-wave pairing in high temperatures superconductors is the presumed extreme sensitivity of a d-wave superconductor to dirt. It is natural to suppose that a small amount of impurity would generate enough s-wave scattering as to completely destroy the superconducting state even at the nominal levels of dirt surely present in even the best samples of the high temperature superconductors. This naive argument does not fully take into account the very short coherence length of the cuprates, and needs to be investigated quantitatively before any conclusion can be drawn. Fortunately, an elegant series of experimental measurements have recently been completed, which shed considerable light on this important issue.

We have chosen to discuss several experiments below, which have the feature that their interpretation is to a large extent model-independent. Perhaps the strongest assumptions are the correctness and applicability of the standard theory of disordered superconductors, about which more will be said below. The experiments fall into two classes: impurity doping,[65, 168,169] usually with Zn or Ni, and planar oxygen displacement by electron irradiation.[170,171 ,87]

8.1. Doping studies

It is generally believed that Ni and Zn are the only substitutes for Cu which reside on the CuO_2 planes, although Al also resides on both planes and chains. Naively, one would expect Zn to behave as a non-magnetic impurity, whereas Ni would behave as a magnetic impurity. Early measurements[172] as well as the more recent measurements[168] of the nuclear spin-lattice relaxation time T_1 and the ^{63}Cu Knight shift in Zn-doped $YBa_2Cu_3O_{7-\delta}$ indicated that the low temperature Knight shift increases with Zn content, and that the relaxation rate becomes Korringa-like at low temperatures. Both of these results are consistent with the notion that there is a non-zero density of states at the Fermi surface in the doped crystal, as would be expected for an unconventional singlet state. The Ni doping does not produce the same results: the Knight shift is essentially unchanged, and the relaxation time saturates at low temperature, rather than

obeying the Korringa behaviour found in the Zn-doped samples. Thus, it seems that Ni induces localised magnetic moments. The origin of the difference between these two behaviours is not well-understood. Nevertheless, these results appear inconsistent with an s-wave pairing state.

The effects of Ni doping on $YBa_2Cu_3O_{7-\delta}$ films have been explored by infra-red measurements.[65] At the high concentrations studied, namely 4 at. %, the elastic scattering rate is observed to increase in the normal state to such an extent that if the same scattering is assumed to be present in the superconducting state, a large absorption onset would have been visible in the infra-red reflectance. This was not observed, suggesting that there is indeed no gap function minimum in the $YBa_2Cu_3O_{7-\delta}$ films studied. Similar results were later confirmed for the Zn-doped films.[169]

The changes in T_c with doping have been extensively studied by many groups. For a review see, for example, Ref. 173. What is immediately striking about the data is that T_c decreases *linearly* with dopant concentration in almost all cases, especially in the concentration $\rightarrow 0$ limit. Obviously one must be cautious in interpreting this result since there is no generally accepted theory of T_c itself in the pure material. Nevertheless it would be hard to understand this behaviour in an isotropic s-wave picture, since as is well known, elastic (s-wave) non-magnetic impurity scattering has no effect on T_c for s-wave superconductors,[174] a result which is usually known as "Anderson's theorem". In s-wave superconductors T_c decreases linearly with magnetic impurities only. The linear decrease in T_c with impurity concentration is thus not surprising for the magnetic impurities (Ni and Fe) but was unexpected for a non-magnetic impurity such as Zn. However, this result is not hard to understand in qualitative terms. "Anderson's theorem" relies upon a cancellation that occurs only if the gap is exactly isotropic. In an anisotropic superconductor (whether anisotropic s-wave or d-wave) this cancellation does not occur, and in general T_c will decrease linearly with impurity concentration. The results are thus qualitatively consistent with either d-wave pairing, or anisotropic s-wave, and they cannot be said to provide any stronger constraints on the pairing state than to eliminate isotropic s-wave.

8.2. IRRADIATION STUDIES

Irradiation studies are possibly a more clear cut test of the sensitivity of the superconductivity to disorder, since unlike doping studies there is no danger of substantially altering the electronic structure at the same time as introducing disorder. Basov *et al.*[175] measured the evolution of the infra-red optical conductivity in a $YBa_2Cu_3O_{7-\delta}$ crystal both before and after irradiation with low-energy He ions. The irradiation suppressed T_c from 93.5K to 80K. Basov *et al.* observed that

after irradiation the optical conductivity was finite at all frequencies, and even developed a Drude-like low frequency peak. Recently, detailed calculations of the far-infra-red conductivity were performed for a $d_{x^2-y^2}$ superconductor with both elastic and inelastic scattering.[176−178] These calculations show that the qualitative evolution of the spectra with increasing disorder, including the Drude-like peak, could be understood naturally in a d-wave picture. In contrast the optical conductivity of disordered isotropic s-wave is qualitatively different.[179] It is particularly noteworth that, at least within the Eliashberg formalism of the calculations, there is a reasonable *quantitative* agreement between the decrease in T_c under irradiation, and the observed spectral shape.[176] In other words, there is a consistent choice of parameters such that the same defect scattering rate leads to both the observed T_c decrease and the spectral shape. Carbotte *et al.* emphasize that the calculated spectral shape would be essentially the same for any gap function $\Delta(\mathbf{k})$ with a node, including extended s-wave states, but would be inconsistent with states in which $\Delta(\mathbf{k})$ does not change sign (such as $|k_x^2 - k_y^2|$). Thus, we conclude that the d-wave pairing state accounts qualitatively (and possibly even quantitatively) for the experimentally observed features of the far infra-red conductivity. Perhaps the main question about the theoretical calculations for this comparison is the use of the Eliashberg theory: it is by no means obvious that this is applicable, given that there is presently no understanding of the microscopic mechanism, and hence no justification to assume Migdal's theorem applies. Nevertheless we believe that the comparison is probably qualitatively correct, in the sense that it is hard to see how a more detailed theory could restore agreement between the s-wave calculations and the experimental observations.

A very elegant technique to explore the effects of impurities on the cuprates is to use electron irradiation to displace atoms from the crystal lattice. These studies[87,171] were performed on high quality, detwinned single crystals, and the electron energy was chosen so as to selectively remove the planar oxygens O(2,3); a careful study was undertaken to demonstrate that this had in fact occurred. The resulting defects do not contribute a Curie-Weiss tail to the normal state susceptibility, neither do they affect the plasma frequency nor the carrier concentration. Thus, the resulting samples contained non-magnetic defects in the CuO_2 planes, without any change in carrier concentration or plasma frequency, at least to the extent that could be determined experimentally. The a-axis resistivity, measured as a function of irradiation dose, indicates clearly that for 4.1% displacement of planar oxygens, the superconducting transition temperature is zero, or at least less than 12K, the lowest temperature attained in the experiment. If we follow the authors, and assume that T_c actually is zero, or would have become zero at the appropriate extrapolated irradiation dose, then it appears that these data are in sharp contrast to the expectation based upon

a s-wave state and non-magnetic scattering, viz. an originally anisotropic s-wave state would become isotropised by the impurity scattering, leading to a non-zero value of T_c above some critical concentration of impurities. We conclude two things: first, the pairing state must have nodes, but could be either d-wave or an extended s-wave state (with 8 nodes). The latter state is ruled out by (*e.g.*) the photoemission data on gap anisotropy. Secondly, the d-wave state may have a small admixture of s, but not so much that the gap function symmetry reverts to s-wave before the superconductivity is destroyed. Thus, this experiment places an upper bound on any non-zero value for the gap function integrated over the Fermi surface.

The results of electron irradiation experiments agree qualitatively with the earlier study of Sun *et al.*[180] who also found that T_c gets driven to zero in both Pr-doped and ion-beam damaged $YBa_2Cu_3O_{7-\delta}$ single crystals. These authors did not attempt to determine if the resulting impurity scattering was magnetic or not. In both experiments, taken in isolation from the body of other data described in this Chapter, it would be conceivable that the pairing state is s-wave, and that there is a small magnetic component to the scattering: a quantitative comparison of the T_c dependence and the experimentally implied upper bounds on magnetic scattering would be needed to explore this possibility. A potentially serious issue for the $d_{x^2-y^2}$ scenario, which is still not resolved, is the large quantitative discrepancy between the observed T_c in the experiments of Sun *et al.* and calculations based on Eliashberg theory combined with the observed residual resistance at T_c.[180, 181]

There are three logically distinct points at which any of the above arguments could fail. Firstly, the applicability of Abrikosov-Gor'kov theory to the cuprates is certainly not obvious *a priori*. It should be emphasised that the Abrikosov-Gor'kov theory is in essence a variational calculation, which compares the free energy of one possible kind of pairing state, namely that in which pairs form in plane-wave states, despite the fact that these are no longer eigenstates of the single-particle Hamiltonian in the presence of impurities, with the normal-state free energy. While it is clear that some obvious alternatives, e.g. pairing in the basis of single-particle eigenstates, do worse than the Abrikosov-Gor'kov ansatz,it is not entirely obvious that there is no possible alternative which might do better in the rather unusual environment of the high temperature superconductors, and this must remain a caveat with respect to conclusions drawn on this basis.

Secondly, as mentioned earlier, Eliashberg theory itself is dubious in the cuprates since it is unlikely that Migdal's theorem is valid if the pairing mechanism is either purely electronic (e.g. spin fluctuation exchange) or involves the lattice (e.g. bipolaron theories).

Thirdly, even assuming that the above two points can be dealt with, it is far from clear that all the conclusions of Abrikosov-Gor'kov theory are then strictly valid in a disordered two-dimensional system. In particular Wenger and Nersesyan[182] have shown that the vertex corrections are large for two-dimensional d-wave superconductors, and hence Abrikosov-Gor'kov theory may fail for the quasiparticle states near the gap-node. In particular they also found[183] a density of quasiparticle states near the d-wave gap node of the form $\rho(\omega) \sim |\omega|^\alpha$ as $\omega \to 0$ with $\alpha < 1$ which is qualitatively different from the d-wave Abrikosov-Gor'kov result $\rho(\omega) \sim$ const. On the other hand, numerical calculations[184] of the density of states in a disordered two-dimensional d-wave superconductor were qualitatively similar to the Abrikosov-Gor'kov predictions (cf. Ref. 184, Fig. 8).

9. Conclusions

No single pairing state, whether a pure irreducible representation or a mixture, is consistent with all of the experimental results, taken at face value, which we have described above. Nevertheless we feel that a clear picture is definitely emerging from the data taken as whole. In fact there is a remarkable degree of consistency between quite different experiments performed on the whole range of the cuprate superconductors (except the Nd compounds). The temperature dependence of the penetration depth clearly indicates that the gap function has nodes on the Fermi surface, and furthermore, that $\Delta(\mathbf{k})$ changes sign there. On the other hand the angle resolved photoemission experiments show that $|\Delta(\mathbf{k})|$ is small or zero at (or very close to) the $d_{x^2-y^2}$ nodal position. Taken together these two results alone imply that the pairing state is predominantly $d_{x^2-y^2}$ with possibly small admixtures of s^+, s^-, or d_{xy}. Any such admixtures could be real or imaginary, but in either case would appear to be no more than 10% of the $d_{x^2-y^2}$ gap function. A wide range of other experimental observations, such as: the electronic Raman scattering, the infra-red conductivity, and the neutron scattering, all can be understood naturally in the context of such a gap function. There appear to be no spectroscopic experiments which cannot be understood within this framework. Also the extreme sensitivity of d-wave pairing to impurities is consistent with such a gap function, since the impurity dependence of such a state is indeed at least qualitatively consistent with what is observed. Some of these spectroscopic measurements, for example the photoemission, could also be consistent with a gap which did not change sign, such as $|k_x^2 - k_y^2|$, but such a state would not agree with either the impurity dependence of penetration depth of infra-red conductivity, or the Raman scattering. The spectroscopic evidence, taken as a whole, is thus quite clearly in favour of a predominantly $d_{x^2-y^2}$ gap function.

As to the Josephson experiments taken at face value, we have seen in Section 7 that if we use the thermodynamic argument of Section 4 to exclude the possibility of more than one irreducible representation, then there is no single assignment of pairing states which will account for all the data. However, the preponderance of the evidence clearly points to a $d_{x^2-y^2}$ pairing state. If we relax the thermodynamic constraint so as to allow a mixed pairing state, the data can all be accommodated by a real mixture of s^+ and $d_{x^2-y^2}$, with possibly also an admixture of s^- and d_{xy}. It should be emphasised that this possibility does *not* arise from the orthorhombic distortion of YBCO; nevertheless, it would clearly be valuable to repeat the type-I and and type-II experiments on the purely tetragonal Tl compound.

In conclusion, the only type of state which is compatible with all the experiments we have reviewed is, then, a mixed state with an appreciable $d_{x^2-y^2}$ component. The most plausible candidate is a real mixture of $d_{x^2-y^2}$ and s^+, with the former being the dominant component. This case would require there to be a second transition, for which there is presently no evidence in single crystal samples. Given this, the pairing state which is compatible with by far the highest proportion of experiments to date on YBCO and similar compounds (but not the Nd compound) is the pure $d_{x^2-y^2}$ state.

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150. Note however that pure s^- and d_{xy} are still excluded.

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FIGURE CAPTIONS

Fig. 1. The four singlet irreducible representations possible in a single square CuO_2 plane.

Fig. 2. The two possible behaviours of the $d_{x^2-y^2}$ order parameter at a twin boundary in YBCO.

Fig. 3. Resonances in neutron scattering intensity, $S(\mathbf{q}, \omega)$ for a $d_{x^2-y^2}$ superconductor. For $\hbar\omega < k_B T_c$ the intensity $S(\mathbf{q}, \omega)$ should show sharp peaks at the wave vectors drawn. Taken from Ref. 115.

Fig. 4. Geometry of the UIUC I experiment of Wollman *et al.*[6].

Fig. 5. The geometry of the IBM II experiment, as reported in Ref. 161.

Fig. 6. Geometry of the TCSUH experiment, after Ref. 162.

Fig. 7. Geometry of the IBM I experiment[8]