Pairing symmetry of the high temperature superconductors

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May 13, 1999

A review of relevant experiments that favour an unconventional pairing symmetry in high temperature cuprates is made. Results of magnitude sensitive techniques are discussed and then tests which probe directly the phase of the order parameter are presented in more detail. Josephson effect and its relevance to this problem is described. Consensus resulting from compelling arguments for a $d_{x^2-y^2}$ symmetry of the order parameter is presented as a conclusion

1 Introduction

Since 1986 many materials, mostly in the class of cuprates were found to exhibit superconducting properties at high temperatures. Apart from the challenge of the interesting and still unsolved physical phenomena taking place, there has been the hope of finding room temperature superconductors. The maximum critical temperature that has been achieved is 165 K.

The microscopic mechanism governing high temperature materials is different from that characteristic of low temperature superconductors, where Bardeen-Cooper-Schrieffer (BCS) theory can be applied. However, the large amount of the experimental data acquired so far allows us to conclude that high T_c superconductivity is intrinsically connected to the existence of Cooper pairs. To set the things clear from the outset, throughout this essay unconventional superconductors and pairing state means materials where BCS theory is not applicable and the order parameter (O.P.) has a symmetry which is different from the 's' isotropic Cooper pair. In the 's' case, both the magnitude and phase of the O.P. have the same values for a given $k = |\vec{k}|$.

Symmetry arguments go beyond the microscopic details of a particular system and this is why their generality is often extremely useful in getting 'a priori' information. Important knowledge about the physical problem is thus acquired before trying to do any calculations. In this respect, establishing the pairing symmetry is a central problem in high T_c materials. Its unambiguous determination may help rule out some of the proposed microscopic mechanisms driving superconductivity at such high temperatures. The excitation spectrum as well as the macroscopic quantum-mechanical nature of the superconductors depend on the type of the pairing state.

Because the intention of this paper is to bring to light phenomena which support a $d_{x^2-y^2}$ symmetry, let us take a look at the functional form of the gap function in $\vec{k}$ space:

$$\Delta(\vec{k}) = \Delta_0[\cos(k_x) - \cos(k_y)] \tag{1}$$

We can note that it it has nodes along $|k_x| = |k_y|$ lines (conventionally known as as ΓX, ΓY lines). It changes sign and has the maximum value of its modulus along k_x or k_y lines (ΓM line). The sign change indicates a relative phase difference of π in the superconducting condensate wavefunction for Cooper pairs with orthogonal relative momenta. For the 's' wave symmetry the gap is roughly constant in k space (only small variations are induced by the system anisotropy) and there is no phase change.

Roughly speaking, we can talk about two kinds of experiments for establishing the nature of the pairing state: Those which are essentially sensitive to the magnitude $|\psi|$ of the order parameter, and phase sensitive techniques. Tests of the phase anisotropy are a direct way to probe the pairing symmetry and, as we will see later, to bring evidence for a 'd-wave' state. However, a warning that this distinction is not so sharp is mandatory. This is because some of the 'magnitude sensitive' experiments, under a careful analysis, turn out to be subtly related to direct probing of the symmetry, as for instance electromagnetic penetration depth results. The focus of this paper is on the so called 'phase sensitive' tests. To conclude this introductory part, in the following a short discussion is made about results of some techniques which belong to the first category.

1. Tunneling measurements, by a renormalized plot of the dynamical conductance versus voltage, reveals the presence of a subgap density of states (DOS), which means that the gap in the case of unconventional materials is not fully formed by contrast with the case of conventional superconductors, as can be seen from Figure 1.

2. Nuclear magnetic resonance (NMR), which was one of the crowning evidence that led to the acceptance of BCS theory, also suggests unconventional pairing. In a metal the electrons are the coupling agent of the nuclei spins and thus a drastic change should be expected in the spin lattice relaxation rate $\frac{1}{T_1}$, at and below T_c, because of the coherent state in which the electrons are locked. The Hebel-Slichter peak appearing in low T_c materials as soon as the gap arises at T_c, can no longer be seen in high T_c materials. Cuprates exhibit a power law dependence of $\frac{1}{T_1}$ on temperature at low temperatures instead of an exponentially activated behavior.

3. Knight shift is another aspect which provides powerful evidence for singlet pairing. The shift in the usual NMR resonance frequency $\omega = \gamma H_0$ (where γ is the nuclear gyromagnetic factor) has a component which is the effect of the interaction of nuclear spins with the spin paramagnetism of the electrons. Proportionality of the interaction with the Pauli spin susceptibility makes the T-dependence of the the Knight shift be directly related to χ_s. For a singlet superconductor χ is isotropic and tends to zero as the temperature goes to zero; the triplet state breaks the rotational invariance and χ becomes a tensor. In this case, if the diagonal elements satisfy $\chi_{aa} = \chi_{bb}$, we have that at $T = 0$ K, χ_{aa} cannot be smaller than half of the normal state susceptibility. Vanishing susceptibility as the temperature approaches zero and measurements of the total shift in the NMR resonance frequency, seems to definitely rule out triplet pairing.

4. Angle resolved photoemission spectroscopy (ARPES) is a very powerful technique in this respect. However the data are not so straightforward to analyze. Some of the assumptions in the analysis are that the electronic structure is essentially two dimensional and the excited electrons are sufficiently far from the surface so that the the structure probed is bulk-like. Nonetheless, the data clearly shows an anisotropy in the gap along different directions in $\vec{k}$ space. A decrease in the gap is seen when going from ΓM line to ΓX, ΓY lines, which are the nodal directions for a d wave symmetry. ARPES precision could have easily ruled out this symmetry if that had been the case. Instead the data is consistent with $d_{x^2-y^2}$ symmetry, but cannot eliminate other components.

5. Raman scattering means inelastic scattering. The continuum in the Raman spectra below a broad edge (which can be roughly identified with a 'superconducting gap') prove the existence of low frequency electron-hole excitations. In the presence of a definite non-zero gap, a sharp edge at the frequency $\omega = 2\Delta_{min}$ should have been expected. Calculations of Raman spectra for various symmetries have been made and there is quantitative agreement with a $d_{x^2-y^2}$ wave. The calculations could rule out some other close symmetry like $|d_{x^2-y^2}|$, although it provides the same DOS.

6. The temperature dependence of the **electromagnetic penetration depth** λ_L also supports this idea. Through the dependence on the fraction of the superfluid component, we expect an exponential behavior for an 's' symmetry. Measurements on high quality pure single crystals show a linear dependence of λ_L on T, which is consistent with a gap with nodes. Moreover results in doped YBCO (Zn impurities) in the range of linear dependence of undoped superconductors put in evidence a crossover temperature T^*. The dependence is quadratic below T^* and linear above. This is an important issue because it is in agreement with theories of impurity scattering in d-wave superconductors.

The conclusion is the existence of unconventional pairing and form of the energy gap in high T_c materials. As pointed out above, some of this methods are not only probes of the magnitude of the order parameter, but also sensitive to phase anisotropy.

2 Phase sensitive experiments

2.1 Josephson effect

There are methods which can probe directly the symmetry of the order parameter. Let us take a look first at the basic principles an phenomena lying behind them, namely the d.c Josephson effect and macroscopic quantum phase interference. Complicated issues and complications from the ideal case will be discussed at the end.

Let us consider a pair of conventional superconductors (1 and 2) and a thin layer of normal material between them. The layer can be for the time being either an insulator (SIS junction) or just a metal in the normal state (SNS junction). Assume that the superfluid component in each of the superconductors is described by a simple complex number ψ_i , with $i = 1, 2$, and the weak link between them allows not only a transfer of electrons but can also transmit Cooper pairs. One expects that the tunneling of the condensed pairs is dissipationless, namely the junction allows a d.c. current to flow through the junction without any voltage drop developed across it. The current vs voltage characteristic is the one presented in Figure 2. There is a maximum current which the junction can support, called the critical current. Above the critical current the dependence on voltage is the usual one as reflected in the first figure.

The essential features of this phenomenon can be realized by writing a set of two Schrodinger-like coupled equations applied to the amplitudes of the order parameters in the 2 superconductors:

$$i\hbar\frac{\partial\psi_1}{\partial t} = \hbar\hat{T_{12}}\psi_2 \qquad i\hbar\frac{\partial\psi_1}{\partial t} = \hbar\hat{T_{12}}\psi_2 \tag{2}$$

where $\hbar T$ is the transfer interaction and

$$\psi_{1,2} = (n_{1,2})^{\frac{1}{2}}\exp(i\theta_{1,2}) \tag{3}$$

here n_j with j=1,2 is the density of Cooper pairs in the superconductor 'j'.Solving the set of coupled equations for the densities and phases we get that:

$$\frac{\partial \delta}{\partial t} = 0 \quad \text{where} \quad \delta = \theta_2 - \theta_1$$

$$\frac{\partial n_1}{\partial t} = -\frac{\partial n_2}{\partial t} \propto 2\hat{T}(n_1 n_2)^{\frac{1}{2}} \sin(\delta) \tag{4}$$

The main point is that the superconducting current is given by:

$$I_s = I_c \sin(\phi_{12}) \tag{5}$$

because the current is proportional to the time derivative of the density of Cooper pairs. The current in the junction is thus proportional to the transfer interaction and to the sinus of the phase difference between the O.P. in the 2 weakly connected superconductors. ϕ_{12} is not just a constant but depends on the biasing current in the junction. Intuitively the coupling is induced by the applied current and thus the phase difference is zero for zero bias.

The current is a gauge invariant quantity while the phase is not. The expression for the current density:

$$\vec{j} = -\left[\frac{2e^2}{m}\vec{A} + \frac{e\hbar}{m} \bigtriangledown \phi\right] |\psi|^2 \tag{6}$$

allows us to overcome this difficulty by replacing ϕ_{12} by the gauge invariant quantity

$$\gamma_{12} = \phi_{12} + \frac{2e}{\hbar}\int_1^2 \vec{A} d\vec{l} \tag{7}$$

In the same time we can write the phase difference of ψ between two points in a superconductor as:

$$\phi_2 - \phi_1 = -\frac{2e}{\hbar}\left[\int_1^2 \left(\vec{A} + \frac{m}{2e^2|\psi|^2}\vec{j}\right)\right] d\vec{l} \tag{8}$$

Having these tools, straightforward calculations lead us to two key points in our discussion. One of them is how the critical current is modulated by a uniform magnetic field present in the barrier region (taking into account that $\oint \bigtriangledown \times \vec{A} d\vec{l} = \int_\Sigma \vec{B} dS$). For a planar junction we have:

$$I_c = I_{co}\left|\frac{\sin\left(\frac{\pi\Phi}{\Phi_0}\right)}{\left(\frac{\pi\Phi}{\Phi_0}\right)}\right| \tag{9}$$

If there is an intrinsic phase difference of π between two directions in the crystal (as $d_{x^2-y^2}$ symmetry imposes on the $\vec{a}$ and $\vec{b}$ directions), in a symmetric corner junction geometry as the one represented in Figure 3., we have for the critical current:

$$I_c = I_{co}\left|\frac{\sin^2\left(\frac{\pi\Phi}{2\Phi_0}\right)}{\left(\frac{\pi\Phi}{2\Phi_0}\right)}\right| \tag{10}$$

In (9) and (10), I_{co} is the critical current in the absence of the field, $\Phi_0 = \frac{h}{2e}$ is the flux quantum and $\Phi = Bw(t + \lambda_1 + \lambda_2)$ where w is the width of the barrier, t is its thickness and $\lambda_i's \quad (i = 1, 2)$ are the London penetration depths of the two superconductors $w(t+\lambda_1+\lambda_2)$ is thus the effective area penetrated by magnetic flux.

The key point is that while in (9) we have a maximum for zero value of flux and minima occurs for integral multiples of Φ_0, in (10) the critical current is null for $\Phi = 0$ and the flux modulation period is twice as big.

The second important issue is that in a circuit consisting of two parallel junctions connected by a superconducting ring as presented in Figure 4. (which is a d.c. SQUID configuration) the modulation of the critical current is also drastically different according to the (non)-existence of an intrinsic phase shift of the order parameter. In such a macroscopic quantum phase interference device we have:

$$I = I_{c1} \sin(\gamma_1) + I_{c2} \sin(\gamma_2) \tag{11}$$

where $I_{c1,2}$ are the critical currents in the two branches of the circuit, and for the total current

$$I_c = 2I_{co} \left| \cos\left(\frac{\pi\Phi}{\Phi_0} + \frac{\delta}{2} \right) \right| \tag{12}$$

Here the critical currents in each part I_{co} are assumed to be the same, and δ, in our cases of interest could be 0 ('s' wave) or π ($d_{x^2-y^2}$ wave). Note that as the modulation period remains the same, the variation of $\frac{I_c}{2I_{co}}$ with Φ is shifted by $\frac{\Phi_0}{2}$ in the 2 cases.

In any geometry the equilibrium form of the order parameter is found by minimizing the total energy. The entering factors are the kinetic term, the magnetic term (given by the self inductance of the circuit) and the Josephson coupling energies. The kinetic term is directly related to the London penetration depth λ_L. If the thickness of the bulk is much larger than λ_L we can assume that the current is screened out of the bulk and also that we can choose paths inside such that the phase difference around the loop is given by $\nabla\phi = \frac{2e}{\hbar} \oint \vec{A} d\vec{l} = \frac{2\pi\Phi}{\Phi_0}$. If $LI << \Phi_0$, the coupling energy between the two superconductors dominates and that the circulating supercurrent which has to insure the phase coherence in the loop is given by:

$$IL = -\Phi_{ext} + \frac{\delta}{2\pi}\Phi_0 \tag{13}$$

and at the same time the flux through the the junction is approximately equal to the applied flux.

The upshot of all this is that we can conclude from (9)-(11) that either measuring the critical current as a function of external field, or measuring the circulating supercurrent can determine the intrinsic phase shift in the order parameter and give thus evidence for a particular symmetry.

2.2 Possible symmetries of the order parameter

Up to now we discussed only about two possible symmetries in the gap function, namely 's' (conventional isotropic symmetry) or $d_{x^2-y^2}$. The symmetry of the gap in the $\vec{k}$ space should be related to the symmetry operations under which off-diagonal matrix elements of the form $< \psi_\alpha(\vec{r_1}, t_1), \psi_\beta(\vec{r_2}, t_2) >$ remain invariant. These in turn should reflect the symmetry operations under which the real crystal is invariant. The structure of CuO_2 planes can in first approximation be considered a 2-dimensional square lattice. The point group of the square leads to four singlet (recall the conclusion of Knight shift measurements) pairing states: s^+, s^-, $d_{x^2-y^2}$ and d_{xy}. The 's' and 'd' states are those which are even and respectively odd under a $\pi/2$ rotation around the c axis, and s^+, $d_{x^2-y^2}$ and s^-, d_{xy} differ in the parity under reflection along the (1,0,0) axis (a-axis). The form of these four irreducible representations (ireps) is sketched in Figure 5. Mixing of more than one ireps should lead to a splitting of the transition. But all the experimental observations could detect so far only one second order transition to the superconducting state. Thus an order parameter which does not have only one 'pure' symmetry for a square symmetry seems improbable from group theory considerations taken together with the experimental data.

A non trivial question is what are the effects of orthorombicity, i.e. the deviations from the tetragonal symmetry of the crystal. This fact allows mixing of different ireps which however depends on the type of cuprates. For instance, in YBCO, $s^+ + d_{x^2-y^2}$ and $s^- + d_{xy}$ are permitted, while for LSCO or BSCCO the combinations allowed are $s^+ + d_{xy}$ and $s^- + d_{x^2-y^2}$. This is basically due to the fact that the remaining symmetry operations are defined according to the 3-dimensional crystal structures, and these differ for the above mentioned classes of cuprates.

Another problem is whether or not the sign of the order parameter changes across a twin boundary, i.e. the $\vec{a}$ and $\vec{b}$ directions are interchanged. The independence and reproducibility of the critical currents and the shifts due to magnetic field strongly suggest a 'gyroscopic' behavior, which means that the '+' and '-' signs in the gap remain the same with respect to an 'absolute' laboratory reference. The effect of multi-layered structure cuprates seems not to be an essential point. The symmetry of $< \psi_\alpha(\vec{r_1}), \psi_\beta(\vec{r_2}) >$ can be analyzed independently whether $\vec{r_1}$ and $\vec{r_2}$ are in the same or different layers as long as we are dealing with a superconducting state in the planes. Antisymmetry with respect to changing the 'layer indices' of $\vec{r_1}$ and $\vec{r_2}$ is also unlikely because of the Josephson coupling to ordinary s-wave superconductors, and a drastic difference between pairing states in adjoint layers is implausible.

2.3 Experiments

In the following a few 'prototype' experiments probing directly the phase of the O.P. are described, using the notation in [3].

1) UIUC I experiment:

The basic experimental scheme for this experiment consists of a d.c. corner SQUID as shown in Figure 4. The measurements were made on YBCO single crystals. The tunneling direction is in a plane perpendicular to the $(\vec{a}, \vec{b})$ plane. The loop is closed by a conventional superconductor, lead, because its properties are well known and its critical temperature is higher ($\sim$ 7 K) than those of the most BCS superconductors. The tunneling barrier is made of normal gold. Aside from corner junctions, measurements were made on control edge SQUID's, in which both of the Josephson junctions are on the same crystal face.

The fact that a finite critical current is observed across both junctions individually implies that the symmetries which are relevant in this case are only s^+ and $d_{x^2-y^2}$. Intuitively this can be understood by inspecting the four irreducible representations, and noticing that, because of the change of sign in the order parameter along the directions studied, the couplings with positive and negative lobes should cancel each other in the other cases. This argument has behind it the fact that tunneling is directional so that each junction senses the order parameter in the direction perpendicular to the crystal face. This takes place not only for SIS junctions but also for SNS junctions.

We are now dealing with the case described by relation (12) which is analogous to a two-slit interference experiment in optics. Measurements were made on both untwinned and heavily twinned samples. The differences in the results are very small and hence twinning sees to be of no significant importance. Orthorombicity is also not important because the intrinsic phase difference should be the same even if the lobes have different sizes. In twinned samples, the order parameter has effective tetragonal symmetry because of averaging over many twin domains.

The results of these experiments are extremely sensitive to the presence of any magnetic flux. The ambiental magnetic field was reduced by shielding the samples. Magnetic vortices trapped in the loop were eliminated to a high degree by cooling the samples several times. The remaining trapped flux could account for 5-10 percents of the shifts in modulation patterns but these values are small enough to permit distinction between s and d symmetry. The sharp corners of the SQUID's are found not to constitute a singularity region for the supercurrent flow (moreover it is argued that the corners are rounded in a real sample).

Maybe the most annoying of all this deviations from the ideal case are the asymmetries between the critical currents across each junction and also in the closed loop. The general equation for the supercurrent reads:

$$I = I_{c1} \sin \phi_1 + I_{c2} \sin \phi_2 \tag{14}$$

They can produce shifts, suppression and distortions in the modulation patterns. Besides, the asymmetry in the critical currents increases with the biasing current, coupling a larger field to the loop for finite inductances.

Modulation of the dynamical resistance as a function of the applied flux was done with different values of the bias current. Oscillatory dependence was obtained and high sensitiveness was accomplished by biasing the sample in the noise-rounded region of the dynamic vs. current characteristic, as presented in Figure 6. The phase shifts show a liner bias current dependence because of asymmetries as expected, but the intercepts with the ϕ axis of minimum resistances (which correspond, according to (12) to maximum values of supercurrents) is at $\frac{\Phi_0}{2}$ for corner SQUID's and at zero flux for control edge SQUID's, which is consistent with $d_{x^2-y^2}$ symmetry.

Plots of minima in the modulation curves extrapolated at 0 current, for different samples, are shown in Figure 7. Although the intercepts are distributed around $\Phi = 0$ (edge SQUID's) and $\Phi = \frac{\Phi_0}{2}$ (corner SQUID's) because of asymmetries and trapped flux, the picture however clearly makes a distinction between the two cases and brings evidence for a π shift between the two orthogonal directions.

2) UIUC II experiment:

In this case the circuit looks like the one in Figure 3. The phenomenon used in this kind of experiments is the modulation period of individual Josephson-junction critical currents by a magnetic field threading this time the normal metal barrier and not a superconducting loop. The analogy in this case goes perfectly with a Fraunhofer single-slit interference pattern in optics. Theoretical modulation patterns can be easily pictured in mind from relations (9) and (10). In this experiment edge control junctions are also used.

This method has certainly some major advantages if compared to the previous one. An obvious one is the easier fabrication. In this case just a single junction is needed instead of two required for the SQUID's setup. Asymmetries of the currents in different parts of the junction do not create a phase shift. What actually happens is a sort of transition from the 'd' to the 's' pattern. Thus this technique is very sensitive to the presence of an s-wave component. Moreover a finite fraction of 's' component leads to a shift and imbalance in the peak heights. The effects of trapped and residual flux are smaller because the adimensional parameter $\frac{\Phi}{\Phi_0}$ is build with the same flux quantum. The area of the junction is much smaller, so the scaling in this case is much smaller. Presence of any unwanted flux is clearly evidenced by distortion and breaking the symmetry of the modulation pattern.

The measurements seem clearly capable to distinguish the edge junctions from corner junctions. A pronounced dip at zero field is seen for corner junctions while a maximum at zero field is observed in the other case. Unambiguous comparison of the separation period of minima (which is twice larger for a d-wave) is however not possible. Figure 8. presents the the actual results of the measurements and shows an obvious difference between the two cases, as expected from theory. Thus we can conclude that 'd' symmetry is strongly supported by single junction experiments too.

3) IBM II experiments:

A beautiful idea of applying the Josephson effect and flux quantization led to an experiment in which rings with two and three grain-boundary Josephson junctions were used to test the pairing symmetry. The experimental arrangement is the one shown in Figure 9.

The samples are again YBCO thin film loops deposited onto a $SrTiO_3$ tri-crystal. The substrate is oriented in such a way that the orientation of the $(\vec{a}, \vec{b})$ planes is rotated by 30 degrees in each region. Sigrist and Rice derived an expression for the supercurrent at such grain boundaries:

$$I_s^{ij} = (A^{ij}\cos(2\theta_i)\cos(2\theta_j))\sin(\bigtriangledown\phi_{ij}) = I_c^{ij}\sin(\bigtriangledown\phi_{ij}) \tag{15}$$

In (5), θ_i, θ_j are the angles of the crystallographic axes (for an orthorhombic symmetry these are equivalent to k_x, k_y directions) with respect to the interface between superconductors 'i' and 'j'.

Although the sign of the current is chosen usually by convention if just a single junction is considered, the key point is that a ring with an odd number of 'π' junctions will always exhibit a spontaneous magnetization inthe limit $LI_c >> \Phi_0$, if we choose the sign in a consistent way. The generated flux has a value which is an odd number of half flux quanta: $\frac{(2k+1)\Phi_0}{2}$. This can be shown starting from equation (8), which has as an immediate consequence flux quantization in a superconducting ring.

$$I_s L + \Phi_{ext} + \frac{\Phi_0}{2\pi}\sum_i \phi_i = n\Phi_0 \tag{16}$$

For the particular case of three junctions is enough to consider just one negative critical current. The π phase shift which appears in a form like (13) can be included by convention in the sign of the current as stated, because $I_c \sin\phi = -|I_c|\sin(-\pi+\phi)$. Thus, from the previous relation we get:

$$I_s L = \frac{(2n+1)\pi}{\frac{2\pi L}{\Phi_0} + \sum_i \frac{1}{I_{ci}}} \simeq \frac{(2n+1)\Phi_0}{2} \tag{17}$$

Imaging the flux was done with the help of scanning SQUID whose basic working principles were presented previously. The 'search' for a $\frac{\Phi_0}{2}$ spontaneous magnetization was succesfull, and the results can be seen in Figure 10. We can note the values for the ring flux corresponding to odd number of half flux quanta threading the 3 junction rings compared to the 0-junction control ring. The points correspond to 12 runs in the experiment and the dotted line is a correction for tip wear.

Although the authors of this experiment were positive about establishing d-wave symmetry, a comment is necessary. While it is clear that this experiment rules out symmetries for which the order parameter is everywhere positive, the symmetry in the problem allows, if we take into account just symmetry considerations, for a spontaneous magnetization in case of s^- symmetry. This is because the π value of $\triangle\phi_{tot}$ is permitted by s^- because apart from rotations connecting the orientation of grain boundaries which do not play the essential role, this symmetry is odd under inversion in a 45° axis. However, the effort to reconcile these results with other phase sensitive tests makes this experiment a proof for d-wave pairing.

4) UCSD and Tsukuba experiments

In these two experiments, Josephson tunneling measurements along c-axis were performed. The weak link consisted essentially from an insulator barrier between YPrBCO-Pb superconductors. Although these experiments are in similar in principle, their interpretation was totally different. Let us focus first on the UCSD experiment, which was the most proeminent proof against a d-wave symmetry.

The finite value of the critical current along c-axis seemed to rule out any symmetry other than s^+. That is because the pairs in lead are conventional s singlets and the YBCO crystals were heavily twinned. Thus even the orthorombicity of the cuprate (which could have made the the inequality in the positive and negative lobes play an important role) was rendered not relevant because of averaging out the differences. Thus, the expected canceling out of the the supercurrents in a d-wave scenario was contradicted. Moreover, possible tunneling in $(\vec{a}, \vec{c})$ or $(\vec{b}, \vec{c})$ planes was not relevant because Josephson coupling showed no systematic dependence on the degree of etching (which increases the number of protrusions and the exposure to 'orthogonal tunneling'). The modulation pattern was conventional and the period of modulation was Φ_0 and not $\Phi_0/2$ as in UIUC II experiment. Another control test was the determination of the electromagnetic penetration depth from the modulation patterns in YBCO-Pb and Pb-Insulator-Pb junctions. Recall that the effective area of the junction is $w(t+\lambda_1+\lambda_2)$ as pointed out in the comment of relation (10). The results are in quantitative agreement with previous measurements.

Although all these facts constituted compelling arguments for an s-wave symmetry let us examine the so called Tsukuba results. The diffraction patterns were very close to those presented in Figure 3. corresponding to a d-wave. By atomic force microscopy (AFM) the growth of a large number of micrograins was generally observed. It is reasonably argued that tunneling in $\vec{a}, \vec{c})$ and $(\vec{b}, \vec{c})$ planes should have observable effects. So each possible route of a pair would have its own contribution. But provided that we have isotropic micrograins and there is no 'preference' for a pair for $(\vec{a}, \vec{c})$ vs. $(\vec{b}, \vec{c})$ tunneling, the combined effect still cancels out. However, the contribution of the oxygen chains which lay along $\vec{b}$ direction make tunneling perpendicular to $(\vec{a}, \vec{c})$ plane easier. This fact can explain the finite value of the critical current obtained in both experiments.

Another issue supporting unconventional pairing in YBCO is the nonmonotonic dependence of the critical current on T. It raises below the Pb critical point, reaches the maximum at about 4.2 K and then decreases until 2 K. In the case of an s-wave superconductor, a constant increase in I_c is expected with lowering temperature.

The d-wave assumption is thus 'rescued' again. And not only that but all these experiments and a lot of others working on the same basic principles can be reconciled within the d pairing symmetry scenario.

3 Conclusion

As was stated from the very beginning, symmetry arguments are sometimes extremely powerful. Symmetry of the order parameter is one of the predictions of some proposed microscopic theories for superconductors. The $d_{x^2-y^2}$ symmetry is a concrete possibility in models of strongly correlated systems as those characteristic of high T_c cuprates, namely by calculations of pairing mechanisms involving antiferromagnetic spin fluctuations.

Great effort has been done in this field and overall, the huge amount of data not only suggests but brings compelling evidence for unconventional microscopic mechanisms governing these materials. Not all the high T_c's behave like this. For instance $Nd_{2-x}Ce_xCuO_4$ are thought to be s-wave from measurements of electromagnetic penetration depth. There are also some low temperature compounds as UPt_3 or UBe_{13} where although the gap is anisotropic it may have 'p','d' or a combination of more than one symmetries.

For cuprates the examples given here in short or in more detail can be reconciled by a 'd' symmetry. Among the most significant, ARPES measurements indicate vanishing gap at the nodal directions in a d-wave, and the same is the case with the temperature dependence of λ_L which is consistent with theory. The 'phase sensitive tests' contributed in this respect decisively to the evidence already brought by previous experiments. Absence of a split transition in these materials is consistent with the existence of only one symmetry. That $d_{x^2-y^2}$ symmetry characterizes the order parameter is a consensus to which debates have emerged.

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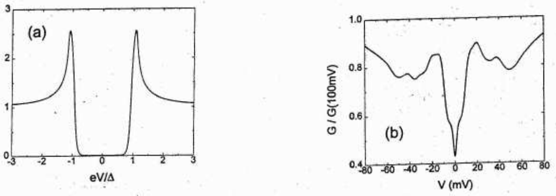


Figure 1

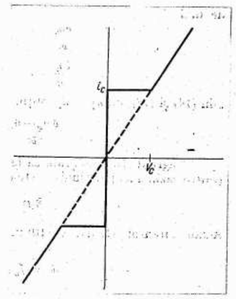


Figure 2

Figure 3

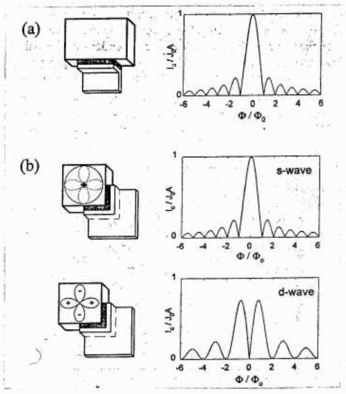
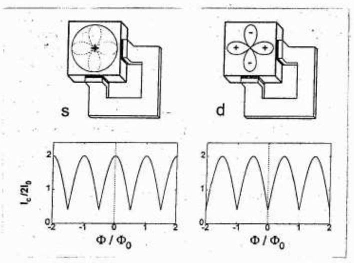


Figure 4



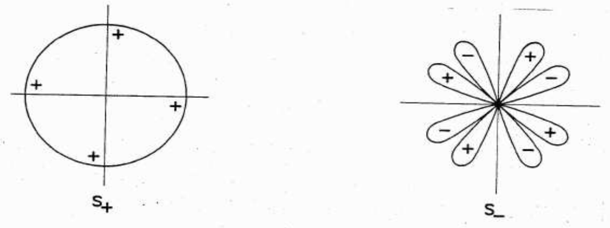
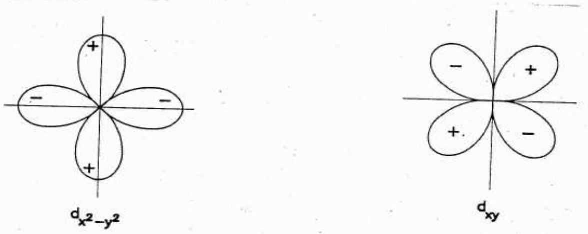
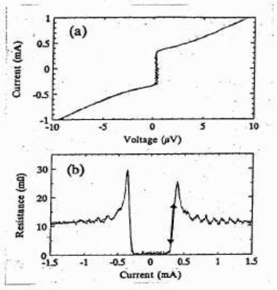


Figure 5





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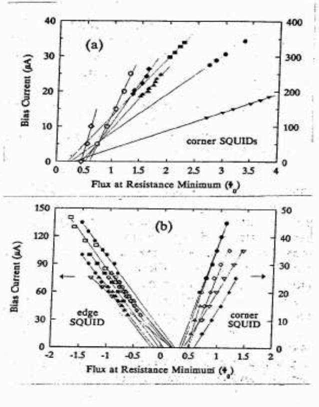

Figure 7

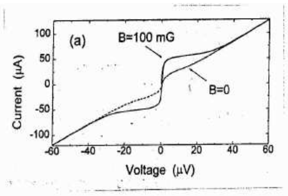

Figure 8

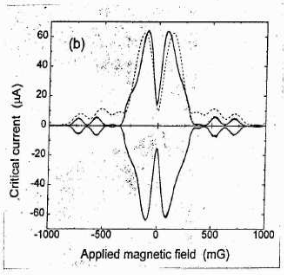

Figure 9

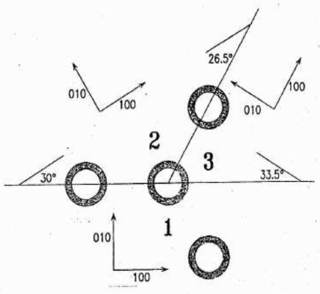

Figure 10