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Experimental Constraints on Theories of High–Transition Temperature Superconductors

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Recent experiments have revealed several key features of the unique nature of the new, high–transition temperature cuprate superconductors. These results provide an easily understandable, physical picture of the structure and behavior of the charge carriers in these materials, and point to the mechanism responsible for their existence. These experiments are now placing strong constraints on possible theoretical models of the phenomenon.

THE RECENT DISCOVERIES OF SUPERCONDUCTIVITY IN $La_{2-x}Sr_xCuO_4$ (*1*) with a transition temperature, T_c, above 30 K, and of superconductivity in $YBa_2Cu_3O_7$ (*2*) above 90 K, have come as a shock to most physicists familiar with superconductivity. These cuprate ceramics superconduct at temperatures many times higher than any other materials. Superconductivity had been discovered in 1911 by Kammerlingh Onnes in mercury at 4.2 K, but prior to 1985 the highest transition temperature observed among the thousands of alloys prepared was only 23.2 K. The physics community has now been presented with an existence proof of high-temperature superconductivity. In response, a flood of theories have come forth, which range from modest additions to the Bardeen, Cooper, and Schrieffer (BCS) theory (*3*) which had explained so successfully conventional superconductors, to theories suggesting the existence of a totally new type of metal. It is not yet clear, even to the experts, how valid or applicable many of these are. It is even more difficult for the nonexpert to appreciate the subtleties of this complex phenomenon.

While the theorists were rethinking the problems of superconductivity, the experimentalists have been busy. A huge amount of work has been done during the past 18 months studying the electronic, magnetic, thermal, structural, and optical properties of these materials. Included in this study are a few basic experiments, which have established some strong constraints on the possible theoretical explanation of the phenomenon. My purpose is to present these and to discuss their implications from a general point of view for physicists, chemists, materials scientists, and molecular biologists. I will begin by considering the nature of the charge carriers and then show how the study of these reveals something of the interactions responsible for the superconductivity.

The Charge Carriers

For a material to exhibit the essential features of superconductivity—persistent currents, perfect diamagnetism, or quantum interference behavior—a finite fraction of all the charge carriers must be in the same quantum state (*4*). The reason is that this single state must make a significant contribution to the total free energy of the system, which, in turn, requires that it have a macroscopic occupation.

The charge carriers in a normal metal are electrons, which obey the Pauli exclusion principle. One and only one such particle can be in any one state at a time. So the charge carriers in the superconducting state cannot be single electrons but must be composite particles, of an even number of electrons. These then are bosons, and obey Bose-Einstein statistics, which allows an arbitrary number of particles to be in the same state. The wave function of such a composite particle is a linear combination of products of single-particle states. Many such composite particles can be in the same state because, although each is described by the same linear combination, the same terms in the linear combination in different particles are never occupied by electrons at the same time. Thus the exclusion principle is obeyed by the individual electrons but the composite particle as a whole behaves as a boson.

In conventional superconductors the bosons are pairs of electrons—the "Cooper Pairs" of the BCS theory. This was established by the beautiful flux quantization experiments of Deaver and Fairbank (*5*) and Doll and Nabauer (*6*) in 1962. In these experiments it was shown that the magnetic flux trapped in a hollow superconducting cylinder was an integral multiple of a fundamental unit of flux, $hc/2e$. Here h is Planck's constant, c the velocity of light, and e the charge of the electron. The presence of the factor of 2 in the denominator shows that the carriers are pairs. Similar and related experiments on a large number of conventional superconductors show, without exception, that the charge carriers in these also are pairs. Are the charge carriers in the cuprates pairs, as in the BCS theory, or quartets or more complex structures?

A clean and elegant answer to this question was given by a flux quantization experiment done by Gough *et al.* (*7*) in Birmingham. The values of the flux trapped in a superconducting ring of

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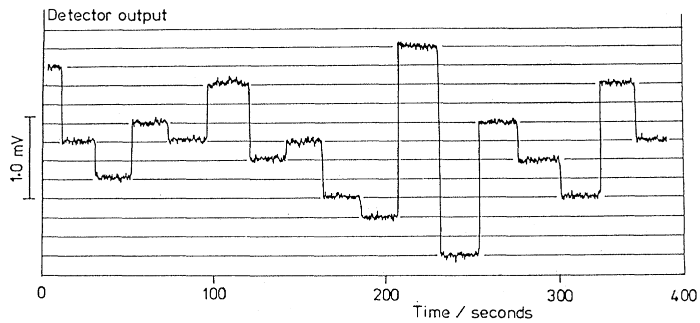

Fig. 1. Output of SQUID magnetometer showing small integral numbers of flux quanta jumping in and out of a ring of $Y_{1.2}Ba_{0.8}CuO_4$. Step heights provide proof of existence of pairs. [Courtesy C. Gough (7), reprinted with permission of *Nature*, copyright 1987, Macmillan Journals Ltd.]

$Y_{1.2}Ba_{0.8}CuO_4$ was measured as shown in Fig. 1. The observed values of the steps in the detector output were found to give 0.97 ± 0.04 $(hc/2e)$ for the flux quantum (*8*). The predicted value for pairs would be $hc/2e$, and for quartets, $hc/4e$, that is, $0.5hc/2e$. This shows that the charge carriers are indeed pairs.

An experiment on the ac Josephson effect supports this observation. It had been shown by Josephson (*9*) in 1962 that if two superconductors are separated by an insulating gap a few angstroms thick, Cooper pairs could tunnel from one to the other. If, in addition, a potential V is maintained between the two, then the passage of a current would be accompanied by the emission of radiation. The frequency ν of this radiation is determined by the Planck condition for a particle of charge $2e$ falling through a potential difference V, that is, $h\nu = 2$ eV. This has been observed in many conventional superconductors. The same result can be obtained by irradiating a junction with microwaves when a current is passed from one superconductor to the other; then, the voltage across the junction can be sustained at integral multiples of the corresponding voltages given by the Planck condition. Such an experiment has been done by Niemeyer, Dietrich, and Politis at Karlsruhe for a junction between $YBa_2Cu_3O_7$ and an alloy of Pb and Sn (*10*). This gave voltage steps of $V = 0.994 \pm 0.007$ $(h\nu/2e)$, confirming again, through the factor of 2, that the charge carriers in $YBa_2Cu_3O_7$ are electron pairs as before. Consider next the structure of the pair wave function.

The Pair Wave Function

Let the wave functions of the two electrons, which are to form a pair, be $\phi_k(\mathbf{r}_1,s_1)$ and $\phi_{k'}(\mathbf{r}_2,s_2)$, where $\mathbf{r}$ represents the spatial coordinates of the particle and s, the spin. If these are bound to form a composite particle then the pair function will have the form:

$$\Psi(\mathbf{r}_1,s_1;\mathbf{r}_2,s_2) = \Psi(\mathbf{R})\Phi(\rho)\chi(s_1,s_2) \qquad (1)$$

where $\mathbf{R} = (\mathbf{r}_1 + \mathbf{r}_2)/2$ is the coordinate of the center of mass, $\rho = (\mathbf{r}_1 - \mathbf{r}_2)$ is the relative coordinate, and $\Psi(\mathbf{R})$, $\Phi(\rho)$, and $\chi(s_1,s_2)$ are the wave functions of the center of mass, relative, and spin coordinates, respectively.

Each of the three functions $\Psi(\mathbf{R})$, $\Phi(\rho)$, and $\chi(s_1,s_2)$ contains information on the mechanism of the superconductivity. I have already discussed the flux quantization. It can be shown that this results from the boundary conditions on $\Psi(\mathbf{R})$. I have deduced from this that the charge carriers are pairs.

We can represent the wave function of the internal structure of the pair in terms of spherical harmonics $Y_{lm}(\Theta,\varphi)$ and a radial function $R(\rho)$, where ρ is now the scalar separation of the particles:

$$\Phi(\rho) = \sum_{lm} c_{lm} Y_{lm}(\theta,\varphi) R(\rho) \qquad (2)$$

We would like to know whether the pairs are bound in *s*-, *p*-, or *d*-states, the spatial extent of the radial wave function $R(\rho)$, and whether the spins form a singlet or triplet state. The total wave function of the pair must be antisymmetric to the exchange of the two electrons because they are fermions, so the singlet state must be associated with the *s*- or *d*-states and the triplet associated with the *p*-state.

Singlet or Triplet Pairs?

A number of experiments now provide evidence that the pairs in $YBa_2Cu_3O_7$ and $La_{2-x}Sr_xCuO_4$ are singlet pairs in an *s*-state (*11*), as postulated in the standard BCS theory. One such experiment is the observation of the dc Josephson effect between $YBa_2Cu_3O_7$ and a Pb/Sn alloy as I will explain below.

It had been pointed out by Akhtyamov (*12*) in 1966 that tunneling of the Josephson type is impossible between a triplet and a singlet state superconductor, or between any two superconductors in which the symmetry of the pair states differ. This can be seen from Fig. 2. If the superconductor on the left has singlet pairs and the superconductor on the right triplets, then, if a pair from the right is to tunnel to the left, some means is needed to absorb the excess angular momentum. This would require the flip of an electron spin or the generation of a spin wave. In general, this would be irreversible so that the passage of a current from one side to the other would not be free of dissipation. However, in the dc Josephson effect a dc current is observed at zero voltage and hence occurs with no dissipation. The same argument applies to pairs that are in the same spin state on each side of the barrier but that differ in regard to the angular momentum state of the pairs on each side.

The dc Josephson effect recently has been observed between $YBa_2Cu_3O_7$ and a Pb/Sn alloy by Niemeyer, Dietrich, and Politis (*10*). The significance of this is that both Pb and Sn are classic BCS superconductors with pairs in the singlet, *s*-state. Hence the pairs in $YBa_2Cu_3O_7$ must be of the same symmetry as those in Pb and Sn, that is, singlet pairs in an *s*-state.

My argument so far has ignored spin-orbit coupling, which makes the clean separation between spin and spatial parts of the wave function impossible. However, it has been shown by Volovik and

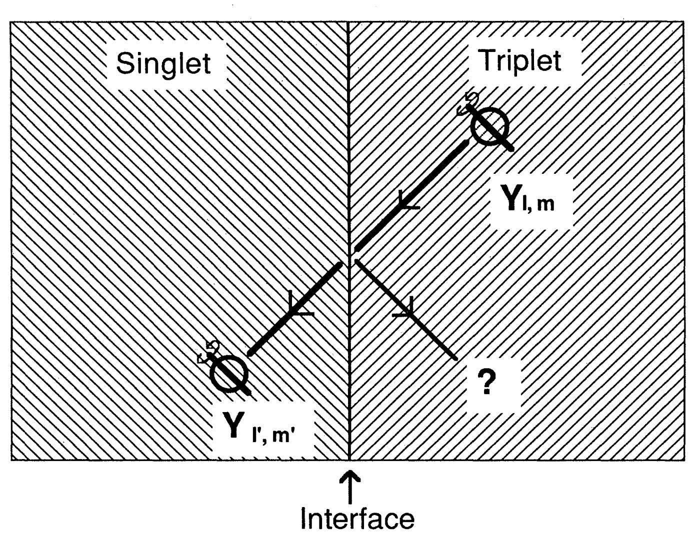

Fig. 2. Schematic representation of tunnel junction between a singlet and a triplet superconductor. Triplet pair must change spin momentum to become a singlet pair on the other side.

Gorkov (*13*) that in many cases it is possible to define a "pseudospin" index to describe the pair, which for most purposes allows one to treat the pseudospin as ordinary spin, as discussed by Millis, Rainer, and Sauls (*14*).

Further evidence that the pairs in $YBa_2Cu_3O_7$ are singlet pairs in an *s*-state comes from data on the effect of impurities on T_c. Suppose the pairs were in a *p*-state, instead; then the amplitude of the pair function in one direction in the crystal would be positive, but negative in the opposite, as for any atomic *p*-state. The effect of impurities is to scatter the electrons, mixing the states in the forward and backward directions. Because the amplitudes of these are opposite in sign in a *p*-state, destructive interference occurs and causes a depression of the amplitude of the pair state and of T_c. In general, chemical impurities depress T_c in *p*- and *d*-wave superconductors because of mixing of different lobes but have little effect upon *s*-wave superconductors (*15, 16*), which have the same amplitude in all directions. Magnetic impurities, on the other hand, flip the spin, causing destructive interference in the spin function in a singlet superconductor. Usually 1 or 2% is sufficient to suppress T_c.

If the pairs in $YBa_2Cu_3O_7$ or $La_{2-x}Sr_xCuO_4$ were in *p*- or *d*-states then we could expect impurities or vacancies of a few percent to cause a similar strong depression. This is not observed. In particular, for $La_{2-x}Sr_xCuO_4$ the presence of Sr causes disorder in the lanthanum lattice, yet with increasing Sr content (over a limited range) T_c goes up, not down (*17*). Likewise for $YBa_2Cu_3O_7$, the compound may be prepared deficient in oxygen, which introduces vacancies that act as scattering sites. Although this does reduce T_c, this depression in T_c is related to the reduction in the number of oxygen holes, which are responsible for the conductivity, and not to scattering (*18*).

On the other hand, one could argue that the introduction of magnetic ions at the yttrium sites in, for example, $HoBa_2Cu_3O_7$ should depress T_c if the pairs are in the singlet state, and this is not what is observed. However, as band calculations have shown (*19*), the conduction electrons do not have a significant amplitude at the magnetic ion sites. This is important because, strictly speaking, it is not the magnetic interaction that causes the flip of the electron spin but rather the exchange interaction. This interaction requires a significant overlap of the orbitals of the conduction electrons with the spin orbital. This overlap for *f*-orbitals is weak, and is particularly small in these layered materials. Hence we should not see a significant depairing as a result of the presence of the magnetic ions, in agreement with what is observed.

Further evidence for *s*-wave pairing in $YBa_2Cu_3O_7$ comes from experiments done at the TRIUMF cyclotron facility in Canada by Harshman *et al.* of the temperature dependence of the depolarization rate with the predictions of the BCS theory gave excellent agreement, implying that the pairs are indeed of the *s*-wave variety.
tor. Such fields can exist in type II superconductors because they behave as perfect diamagnets up to a lower critical field H_{c1}, but above this field, the field penetrates and the charge carriers are forced to organize their motion into an array of vortices. The magnetic field is strongest down the core of these vortices and hence varies from place to place within the material. If the pairs are in a *p*-wave state rather than an *s*-state then the wave function of the pair would vanish at certain nodal points or lines. A different internal field distribution would then result. A careful comparison by Harshman *et al.* of the temperature dependence of the depolarization rate, with the predictions of the BCS theory gave excellent agreement, implying that the pairs are indeed of the *s*-wave variety.

These and other experiments (*21, 22*) give convincing evidence that the pairs in both $YBa_2Cu_3O_7$ and $La_{2-x}Sr_xCuO_4$ are singlet pairs in an *s*-state as in the original BCS theory. This result makes it necessary to reconsider the assumptions of those theories that conclude that the pairs are in the triplet state (*23, 24*) or have *d*-wave pairs (*25*). In particular, Chen and Goddard's paper (*23*), which has received a great deal of media attention recently, predicts triplet pairs and a magnon exchange coupling mechanism. Both of these appear to be ruled out by these experiments and the experiments (*21, 22*) discussed below.

Table 1. Properties of BCS Superconductors in weak coupling.

Observation	Value or ratio	
Transition temperature, T_c	kT_c	$= 1.14\ \hbar\omega \exp(-1/\lambda)$
Discontinuity in specific heat	$\Delta C/\gamma T_c$	$= 1.43$
Gap $\Delta(0)$ at $T = 0$	$2\Delta(0)/kT_c$	$= 3.53$
Thermodynamic critical field, $H_c(0)$	$\gamma T_c^2/H_c(0)^2$	$= 0.169$

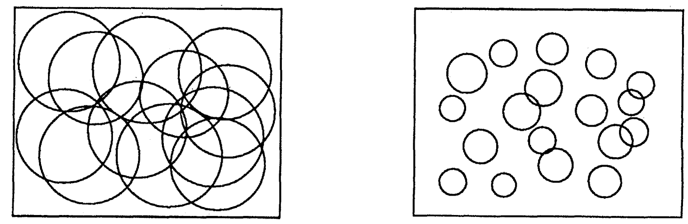

Fig. 3. Illustration of the distinction between BCS types of pairs (left), where many pairs overlap and share the same region of space; and, preexisting tightly bound bosons (right), whose separation is large compared to their size.

The Size of the Pairs

Superconductivity or superfluidity, which is the analogous phenomenon to superconductivity for uncharged particles, can come about in two ways. In the BCS theory it results from the coherent attractive interaction between pairs, which keeps a finite fraction of the electrons paired in the same state for T below T_c. Such condensation of particles into a single state can also occur for statistical reasons, in the absence of interactions. This occurs in Bose-Einstein condensation of a noninteracting gas of Bose particles (*26*). As the temperature of such a gas is lowered the number of particles in the lowest kinetic energy states gradually increases until at some T_c the more or less continuous distribution of momentum states can no longer contain all the particles and the excess number overflow and fill the single, lowest state. The macroscopic occupation of this state gives the system superfluid or, for a gas of charged particles, superconducting properties. Thus there can be two kinds of superconductors—the BCS type where the pairs are formed at T_c and the Bose-Einstein type where the pairs preexist, and only condense at T_c. One would like to know which type it is in the cuprates. A guide to this can be found from the size of the pair.

An estimate of the size is complicated by the fact that the structure of these cuprates is laminar. In both $YBa_2Cu_3O_7$ and $La_{2-x}Sr_xCuO_4$ the conduction electrons lie in planes formed by the Cu–O sheets. There is only weak coupling between these sheets in the perpendicular direction. The pairs therefore tend to be confined to these planes, forming flat, disk-like structures. I can estimate the radius of these disks from the upper critical field H_{c2} applied perpendicular to the sheets. The upper critical field is the maximum magnetic field at which a type II superconductor can superconduct. As mentioned earlier, when one exceeds the lower critical field H_{c1}, the magnetic field penetrates the superconductor and the pairs form themselves into vortices. Each vortex, which may involve many pairs, encloses exactly one unit of flux ($\phi_0 = hc/2e$). As the field is increased further, the number of these vortices increases to accommodate the increased flux of the magnetic field through the sample. The vortices are pushed closer together until they become separated by little more than the size of a pair. At this point no more vortices can be accommodated and the sample reverts to the normal state. In this case $H_{c2}(0) = \phi_0/(2\pi\xi^2)$, that is, the cross-sectional area of the vortex times the applied field is about equal to the flux quantum. Here ξ is a length (the coherence length), which is closely related to the size of the pair, and $H_{c2}(0)$ is measured at $T = 0$ K.

A recent measurement of $H_{c2}(0)$ by Yamagishi *et al.* (*27*) for a single crystal of $EuBa_2Cu_3O_7$ (similar to $YBa_2Cu_3O_7$) gives a clean measurement of ξ both in the plane and perpendicular to the plane. They obtained 35 Å for ξ in the plane and 3.8 Å perpendicular to the plane. The pair is thus a flat pancake-shaped structure lying in the Cu–O planes. To understand whether these pairs are BCS-like or preexisting bosons, we compare their size to the interparticle spacing.

Hall-effect measurements (*28, 29*) give a carrier density at 100 K for $YBa_2Cu_3O_7$ of 3.0×10^{21} per cubic centimeter. A similar result can be expected for $EuBa_2Cu_3O_7$. The radius of a spherical volume containing one carrier is then about 4.3 Å. Similar results are found for the other cuprate superconductors. The size of the pair is such that several will overlap one another and coexist in the same volume. This is characteristic of a BCS model and is in contrast to the model of preexisting tightly bound bosons (Fig. 3).

I come now to the question, "What holds the pair together?" To answer this I turn first to theory.

Strong or Weak Coupling?

The BCS theory (*3*), as originally presented, considered a system of electrons in which an instantaneous attraction was assumed to exist between electrons with energies within $\pm\hbar\omega_D$ of the Fermi surface, where $\hbar\omega_D$ was the Debye energy of the lattice. This emulated the attraction induced by phonons. As one electron moves, it puckers the lattice of positive ions near it, and a second electron is attracted to this locally increased density and thus to the first electron. The distortion of the lattice can be described by the phonon coordinates. Implicit in this treatment is the assumption that the interaction is weak.

Within this weak coupling approximation, the BCS theory makes a number of predictions in regard to T_c, an energy gap Δ, and a thermodynamic critical field $H_c(0)$. These various factors are related to one another and to the factor γ in the specific heat ($C_V = \gamma T$) of the electrons in the normal state. Table 1 shows the relations among these properties as predicted by the BCS theory.

As the interaction with the lattice becomes stronger, the distortion that accompanies the electron becomes larger. The particle becomes part electron and part phonon. Normalization causes a reduction in the weight of the electron-like part as a result of the addition of the phonon part. To take these renormalization effects into account, Eliashberg (*30*) reformulated the BCS theory to allow it to be applied when the interactions are strong. These equations take into account explicitly the exchange of the phonon in the attractive interaction.

The Eliashberg theory is sufficiently general to allow one to consider interactions that are not mediated by phonons alone but by other types of excitations. In particular, it allows one to take into account electronic excitations of a type that I had proposed many years ago (*31–33*). I had shown that an attractive interaction could arise from the polarization of an electron subsystem, rather than the lattice, and that under appropriate circumstances this should lead to superconductivity near room temperature. A simple explanation of this is that, in such a system, the Debye energy, $\hbar\omega_D$ in the BCS expression $kT_c = 1.14\,\hbar\omega_D \exp(-1/\lambda)$, is replaced by a much larger electronic energy $\hbar\omega$, and, consequently, if the coupling constant λ is the same, the transition temperature will be raised accordingly.

To identify the excitation responsible for the attraction, it is helpful first to determine whether the coupling is weak or strong. If it is weak then the ratio of kT_c to $\hbar\omega$ will be small, whereas if it is strong it will be larger. Hence, from a knowledge of T_c and the regime, one can estimate the magnitude of $\hbar\omega$ and identify it from spectroscopy.

A valuable step in this direction has been provided by Geilikman and Kresin (*34*) and Kresin and Parkhomenko (*35*), who calculated the numerical ratios of those factors given for weak coupling in Table 1 and for strong coupling using the Eliashberg equations. Similar calculations have been made by Marsiglio and Carbotte (*36*). The results obtained for $2\Delta(0)/kT_c$, $\Delta C_V/\lambda T_c$, and $\lambda T_c^2/H_c(0)^2$ can be expressed in terms of $kT_c/\hbar\omega$. Careful measurement of these ratios tells us whether the coupling is strong or not and gives an estimate of $\hbar\omega$.

The Ratios

Although early results from tunneling and infrared spectroscopy gave a wide range of values for $2\Delta(0)/kT_c$, more recent experiments have given more consistent results. Their common feature is that each measures a property of the material that is uniquely associated with the superconducting state.

The first experiment is the observation of Andreev reflection, which makes use of a point contact to inject electrons into a normal metal that is backed by the superconductor. If the injected electron has an energy less than the gap Δ, it cannot enter the superconductor as a quasiparticle because the superconductor has no states in this energy range. However, it can condense with another electron of opposite spin and momentum (if the pairs are at rest in a singlet state) to form a Cooper pair. The hole that is created then will move back in exactly the same direction from whence the first electron came (Andreev reflection), giving rise to an excess current in the junction. By varying the energy of the injected electron one can measure the voltage at which Andreev reflection ceases. Hoevers *et al.* (*37*) have succeeded in observing this effect in $YBa_2Cu_3O_7$, finding a value for $\Delta(0) = 12.5 \pm 2$ meV. They have also observed classic superconductor-insulator-superconductor (SIS) tunneling between superconducting grains in the same sample, with zero

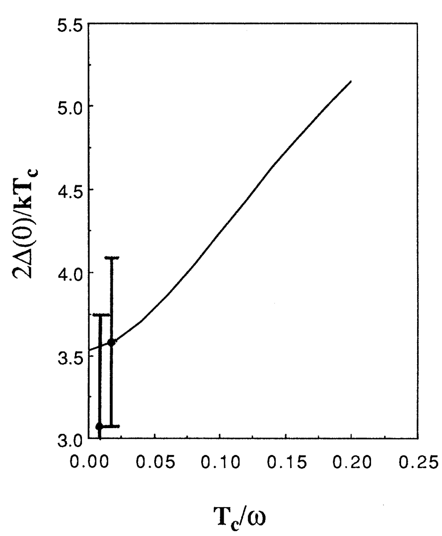

Fig. 4. Plot of $2\Delta(0)/kT_c$ versus T_c/ω from strong coupling theory (*34–36*). Error bars represent the uncertainty in the measured values of $2\Delta(0)/kT_c$ (*37, 38*), indicating that $T_c/\omega \approx 0.02$ (T_c/ω is dimensionless with $h = k = 1$). Solid line is strong coupling prediction of BCS.

current below $eV = 2\Delta$, which allowed again a clean measurement of the gap of $\Delta(0) = 14 \pm 2$ meV. The two results give 3.22 ± 0.51 and 3.60 ± 0.51, respectively, for the ratio $2\Delta(0)/kT_c$, consistent with weak coupling (Fig. 4). The two phenomena, Andreev reflection and zero tunneling current, are uniquely associated with superconductivity.

A third series of experiments involves the reflection of infrared light. Light with a photon energy less than 2Δ cannot be absorbed by a superconductor at low temperatures, and consequently is perfectly reflected. Usually, however, the sample surface is marred by normal inclusions, insulating layers, and so on, which exhibit a reflectivity less than 100%. Thomas and co-workers (*38*) recently have observed the temperature-dependent reflectivity at these long wavelengths of two specimens of $YBa_2Cu_3O_{6-\delta}$ with reduced oxygen content with T_c's of 50 K and 70 K, which at the lowest temperatures gave reflectivities within 1% of 100%. The sharp onset of this perfect reflectivity allowed a determination of 2Δ in each case. The results for this and earlier experiments on $YBa_2Cu_3O_7$ and $La_{2-x}Sr_xCuO_4$ are plotted in Fig. 5. The solid line is the weak-coupling BCS prediction $2\Delta(0)/kT_c = 3.53$. Again the result is consistent with weak coupling.

A second ratio that gives a measure of the strength of the coupling is $\Delta C_V/\gamma T_c$. The change in C_V at T_c is small, but Junod *et al.* (*39*) have shown that ΔC_V can be measured to a few percent (see inset in Fig. 6). The above ratio needs also a knowledge of γ. This has been estimated from the magnetic susceptibility, χ, by a number of workers (*40, 41*) using a free electron model. The ratio obtained is plotted in Fig. 6 on the strong coupling curve of Marsiglio and Carbotte. Again this points to weak coupling. However, there is considerable uncertainty in the value of γ because of unknown Stoner and mass enhancement factors, which relate χ to γ but which are not included in the error bars. Nevertheless, independent evidence of weak coupling comes from another observation of Junod *et al.* (*39*).

Although an excellent correlation exists between $\Delta C_V/T_c$ and χ from different samples, T_c is independent of these variations. This can be understood if one is in the weak coupling regime, for then $\hbar\omega >> kT_c$, and $\hbar\omega$ is of the order of 1 eV. Then T_c is determined through the gap equation by the density of states averaged over a region within ± 1 eV of the Fermi surface. On the other hand, χ and γ are both determined by the density of states much closer to the Fermi surface. Hence, the different behavior of T_c and χ and γ can be understood.

The ratio $\gamma T_c^2/H_c(0)^2$ also gives a measure of the strength of the coupling, but here one needs a more precise measurement of $H_c(0)$ than is available at present. If this can be obtained then the product of $\Delta C_V/\gamma T_c$ and $\gamma T_c^2/H_c(0)^2$ would yield a ratio, which would not depend upon the less well known quantity γ.

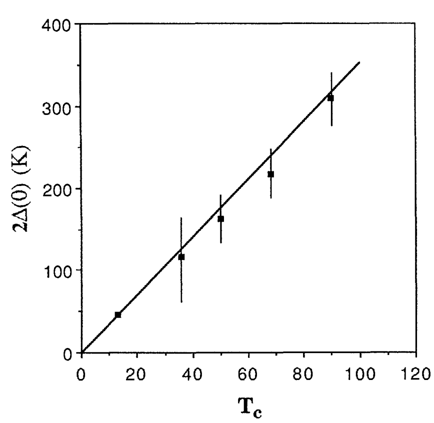

Fig. 5. Plot of $2\Delta(0)$ versus T_c from recent measurements of infrared reflectivity of several cuprates with different T_c's. Point at 13 K is of related compound $Ba(Pb_{1-x}Bi_x)O_3$. Solid line is weak coupling prediction of BCS.

The above ratios suggest (Figs. 4 and 6) that the excitations responsible for the attractive interaction have an energy, $\hbar\omega > 0.30$ eV, which would suggest that they are electronic.

The Nature of the Excitation: Magnetic or Charge?

Both La_2CuO_4 and $YBa_2Cu_3O_6$ are antiferromagnetic, but with a small amount of doping of La_2CuO_4 with Sr, or the addition of oxygen to $YBa_2Cu_3O_6$, the superconducting state is obtained. The close proximity of this magnetic state has led to many theoretical models, which take it as their starting point. The resonant valence bond theory (*42*) is one such, whereas other theories have invoked the exchange of magnons (*23*) or spin fluctuations (*24*) to provide a more conventional BCS attractive interaction. The expected strong magnetic correlations should also show themselves in the normal state. But Yamagishi *et al.* (*27*) have measured the resistivity of the normal state down to low temperatures and find a classic Bloch-Grüneisen curve with the usual residual resistivity. Several experiments have attempted directly to determine the presence of magnetic fluctuations.

Brückel *et al.* (*21*) measured the magnetic neutron scattering cross section of $YBa_2Cu_3O_7$ and established that the total intensity of magnetic fluctuations in the energy region below 25 meV was zero to within one standard deviation. Indeed, it was so low as to eliminate in their opinion all magnetic mechanisms for the occurrence of superconductivity! The absence of any magnetic scattering also argues against the existence of triplet pairs. Nuclear magnetic and quadrupole resonance show no evidence of static moments on the copper sites in $YBa_2Cu_3O_7$ nor any evidence of magnetic interactions. Indeed, Furo *et al.* (*22*) report that the relaxation rate of ^{65}Cu, which has the larger magnetic moment but smaller quadrupole moment, is smaller than ^{63}Cu, showing that the relaxation is not of magnetic origin.

These experiments sample only the lower energy spectrum of magnetic excitations. Lyons *et al.* (*43*), on the other hand, have reported the results of inelastic light scattering experiments that do give evidence of spin pair excitations near 0.3 eV in both insulating La_2CuO_4 and $YBa_2Cu_3O_6$. However, as one approaches the superconducting state (with the creation of O holes) the scattering cross section decreases rapidly, suggesting that the magnetic terms are competing with superconductivity rather than being responsible for it.

Yet another experiment argues against magnetic effects being responsible for the superconductivity. This is the discovery of superconductivity near 30 K by Cava *et al.* (*44*) in $Ba_{0.6}K_{0.4}BiO_3$, which is a perovskite-type oxide structure similar to the cuprates. This is well above the T_c's of conventional metals, but, unlike the cuprates, this compound contains no magnetic ions. If, as seems reasonable, the origin of the superconductivity in this and the cuprates is the same, then it cannot be in the magnetism.

If it is not an interaction of magnetic origin, then what can it be? Several types of charge excitations have been suggested, including excitons, plasmons, and *d*-mons. Of particular interest is a suggestion of Weber (*45*), who noted that in addition to the spin degrees of freedom in the cuprates there are valence-conserving charge degrees of freedom. These correspond to *d*-*d* excitations of the Cu^{2+} ion, which represent oscillations of the shape of the *d*-shell. These would play the role of the polarizable electron subsystem in our model. Evidence for such excitations at 0.6 eV and 1.4 eV has recently been found by Geserich *et al.* (*46*) in the optical spectra of thin films of superconducting $YBa_2Cu_3O_7$. This model appears to require anisotropy in the local environment of the polarizable shell.

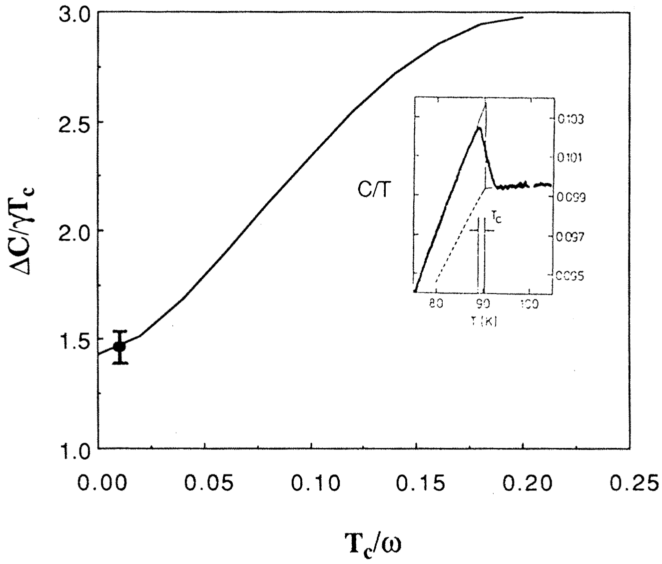

Fig. 6. Plot of $\Delta C/\gamma T_c$ versus T_c/ω from strong coupling theory. Point with error bar represents recent measurement of $\Delta C/\gamma T_c$, again indicating that T_c/ω is small. Inset shows clear discontinuity in specific heat at T_c for $YBa_2Cu_3O_7$ as observed by Junod *et al.* (*39*). (Inset reproduced with permission; copyright 1988, North-Holland)

The existence of superconductivity in $Ba_{0.6}K_{0.4}BiO_3$, which appears to be cubic, therefore poses a similar problem to that for the magnetic models unless this symmetry is lost at lower temperatures.

The acid test of how much a particular excitation contributes to the superconductivity is whether it leaves an imprint on the energy dependence of the gap function Δ. In principle, this can be determined from tunneling or from infrared reflectivity data but thus far this has proved impossible for a variety of experimental reasons. Collman and I have recently suggested a new technique, gap modulation spectroscopy (*47*), which may be able to yield these data even for samples of poor quality. With this information in hand, a positive identification of the mechanism of superconductivity should be possible.

The cluster of experiments described above impose severe constraints on any theoretical model of the superconductivity of the cuprates. They require a theory having virtually all the attributes of the BCS theory—a gap, a discontinuity in the heat capacity, singlet pairs in an *s*-state, and type II behavior in a magnetic field—in addition the coupling strength should be relatively weak and the normal state like that of most other metals. The one difference from a conventional BCS superconductor appears to be the mode of coupling. Evidence suggests that some charged excitation, with an energy several times that of phonons, provides this coupling. This remains to be identified.

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11. Note that I use the conventional, but imprecise, use of the term "*s*-state," to imply a state with no nodes but one that is not spherical in Cartesian coordinates. The superconducting cuprates are highly anisotropic and the coherence lengths in, and perpendicular to, the planes are very different. In a coordinate system in which length is measured in units of the coherence lengths, an *s*-state would be approximately spherical. Similar caveats apply to the *p*- and *d*-states.
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