

Distinguishing *d*-wave superconductors from highly anisotropic *s*-wave superconductors

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Systematic impurity doping in the Cu-O plane of the hole-doped cuprate superconductors may allow one to decide between unconventional (“*d*-wave”) and anisotropic conventional (“*s*-wave”) states as possible candidates for the order parameter in these materials. We show that potential scattering of any strength always increases the gap minima of such *s*-wave states, leading to activated behavior in temperature with characteristic impurity concentration dependence in observable quantities such as the penetration depth. A magnetic component to the scattering may destroy the energy gap and give rise to conventional gapless behavior, or lead to a nonmonotonic dependence of the gap on impurity concentration. We discuss how experiments constrain this analysis.

Introduction. A number of recent experiments on hole-doped cuprate superconductors have provided evidence for a superconducting state with very large anisotropy, consistent with actual gap nodes on the Fermi surface.^{1–4} The set of experimental results indicating the existence of low-energy quasiparticle excitations have been interpreted in terms of an *unconventional*, “*d*-wave” pairing state, where we use the term *unconventional* to mean that the superconducting order parameter breaks additional symmetries of the normal state beyond the usual gauge symmetry.⁵ Such an order parameter Δ_k^d has a nontrivial phase variation over the Fermi surface and changes sign at the node. Since the quantities measured in these experiments usually depend on the order parameter only through the quasiparticle energy $E_k = (\xi_k^2 + |\Delta_k|^2)^{1/2}$, where ξ_k is the single-particle energy measured relative to the Fermi level, it is easy to see that an identical result would be obtained by a measurement on a hypothetical state with order parameter $\Delta_k^s = |\Delta_k^d|$, which would vanish at the same nodal points but never change sign. Since the nodal points in this case are accidental rather than being enforced by symmetry, it is more realistic to consider a highly anisotropic *s*-wave state with very deep gap minima but no nodes. Such an order parameter has in fact been proposed by Chakravarty *et al.*,⁶ and is quite difficult to distinguish from a similar *d*-wave state if the experiment does not measure temperatures substantially below the gap minima and is not sensitive to the gap phase variation.

As a consequence of these ambiguities, methods of distinguishing between unconventional states and anisotropic conventional states are of great importance. Josephson tunneling experiments are sensitive to the order parameter phase and therefore, in principle, capable of deciding this question.^{7,8} At present, however, different Josephson experiments of slightly different concept and design have reached differing conclusions regarding the order parameter symmetry.^{4,9,10} We have therefore reexamined the well-studied problem of dirty superconductors with an eye towards designing further tests which may be capable of distinguishing *d*-wave and highly anisotropic *s*-wave states. We find that systematic impurity doping experiments are indeed sensitive to the

order parameter phase, albeit indirectly, and can provide important evidence toward the resolution of this question.

Model—potential scattering. For illustration’s sake we consider a $d_{x^2-y^2}$ state over a cylindrical Fermi surface, $\Delta_k = \Delta_0 \cos 2\phi$, and a hypothetical *s*-wave state $|\Delta_0 \cos 2\phi|$. Norman¹¹ has shown that weak potential scatterers eliminate the nodes in the *s*-wave case at the points $\phi = \pi/4, 3\pi/4, \dots$, increasing the gap in these directions monotonically with impurity concentration. It was in fact argued in Ref. 11 that the dependence of angle-resolved photoemission (ARPES) data on sample aging² may be construed as evidence for *s*-wave superconductivity, but there are alternative explanations peculiar to the ARPES configuration.² Here we consider these two states further, and investigate the effects of strong scattering as well as spin scattering, and try to make predictions for bulk thermodynamic and transport experiments.

The properties of a $d_{x^2-y^2}$ state in the presence of elastic impurity scattering have been extensively investigated in recent months,^{12,13} but are in fact generic to states with lines of nodes on the Fermi surface in three dimensions (3D) (point nodes in 2D) investigated in the context of heavy fermion superconductivity.^{14,15} An infinitesimal number of impurities suffice to make the density of states at the Fermi level nonzero,¹⁴ giving rise at low temperatures $T \ll T_c$ to contributions which vary with temperature as their normal state analogues, but with a smaller prefactor which scales with impurity concentration. The penetration depth, which does not have a normal state analogue but varies as $\sim T/\Delta_0$ in the pure *d*-wave state, is known to cross over to a T^2 behavior in this so-called “gapless” regime.^{12,16} At the same time, the actual energy gap in the angle-resolved density of states remains zero along the nodal directions. All these characteristics may be understood as consequences of the exact vanishing of the anomalous impurity self-energy which occurs in most—but not all—unconventional states.

The essential differences between *s*- and *d*-wave states may be understood by examining the single particle matrix propagator \underline{g} averaged over impurity positions, given by¹⁷

$$\underline{g}(\mathbf{k}, \omega_n) = (\tilde{\omega}_T^0 + \tilde{\xi}_k \tau^3 + \tilde{\Delta}_k \tau^1) / (\tilde{\omega}^2 - \tilde{\xi}_k^2 - |\tilde{\Delta}_k|^2) \quad (1)$$

where the τ^i are the Pauli matrices and $\tilde{\Delta}_k$ is assumed to be a unitary order parameter of s - or d -wave type in particle-hole and spin space. The propagator (1) has the form of the propagator for the pure system with renormalized frequency $\tilde{\omega} = \omega - \Sigma_0(\omega)$, single-particle energy $\tilde{\xi}_k = \xi_k + \Sigma_3(\omega)$, and order parameter $\tilde{\Delta}_k = \Delta_k + \Sigma_1(\omega)$, where the self-energy due to s -wave impurity scattering has been written $\underline{\Sigma} = \Sigma_i \tau^i$. For the particle-hole symmetric systems we consider here, renormalization of the single-particle energies can be important for arbitrary scattering strengths, but are small in either the weak or strong scattering limit. We will neglect them in what follows.

As alluded to above, in odd-parity states and states with certain reflection symmetries like $d_{x^2-y^2}$, the off-diagonal self-energy Σ_1 vanishes identically and the gap is unrenormalized ($\tilde{\Delta}_k = \Delta_k$). Potential scatterers are then pairbreaking, in “violation” of Anderson’s theorem,¹⁸ but the angular (e.g., nodal) structure of the gap is not changed. By contrast, in the anisotropic s -wave case the order parameter Δ_k is *always* renormalized by a positive shift which is independent of \mathbf{k} in the s -wave scattering approximation. This leads to a smearing of the energy gap anisotropy leading eventually to an asymptotically isotropic gap in the dirty limit, as implied by Anderson¹⁸ and calculated explicitly by various authors.¹⁹

In the absence of ξ_k renormalizations, the self-energies are given in a t -matrix approximation by $\Sigma_0 = \Gamma G_0/D$; $\Sigma_1 = \Gamma G_1/D$, where $\Gamma \equiv n_i/(\pi N_0)$ is a scattering rate parameter depending only on the concentration of defects n_i and the density of states at the Fermi energy, N_0 , while the strength of a single scattering is characterized by the cotangent of the scattering phase shift, c . Here $D \equiv c^2 + G_1^2 - G_0^2$ is the denominator determining the bound state spectrum, and the $G_\alpha \equiv (1/2\pi N_0) \sum_k \text{Tr}[\tau^\alpha \underline{g}]$ are components of the integrated, disorder-averaged propagator. The Born limit corresponds to $c \gg 1$, so that $\Gamma/c^2 \simeq \Gamma_N \equiv \Gamma/(1+c^2)$, where Γ_N is the scattering rate in the normal state due to impurities. The unitarity or strong scattering limit corresponds to $c = 0$.

Order parameter, critical temperature, and energy gap. We first solve the Dyson equation for the renormalized propagator (1) together with the gap equation, $\Delta(k) = T \sum_n \sum_{k'} V_{kk'} \text{Tr}(\tau_1/2) \underline{g}(k', \omega_n)$, where $V_{kk'} \equiv V_{d,s} \Phi_{d,s}(\hat{k}) \Phi_{d,s}(\hat{k}')$ is the phenomenological pair interaction assumed. The order parameter is $\Delta_k = \Delta_0^{d,s} \Phi_{d,s}(\hat{k})$, with $\Phi_{d,s} = \cos 2\phi, |\cos 2\phi|$ for d and s wave, respectively. The initial slope of T_c suppression, $dT_c/d\Gamma_N = -\chi\pi/4$, where $\chi \equiv [(\Phi_s^2) - \langle \Phi_s^2 \rangle] / \langle \Phi_s^2 \rangle$ is 1 - 8/ π^2 for the s -wave and 1 for the d -wave state considered. In the d -wave case the critical temperature continues to drop rapidly to zero at a critical concentration of $n_i^c = \pi^2 N_0 T_{c0} / 2e^\gamma$, whereas the decrease becomes more gradual as the gap is smeared out in the s -wave case, finally varying¹⁹ as $T_c \sim T_{c0} [1 - \chi \ln(1.154 \Gamma_N / \pi T_{c0})]$.

It is important to recognize that the renormalized order parameter $\tilde{\Delta}_k$ in the s -wave case is only indirectly related to the actual energy gap Ω_G in the system, given by

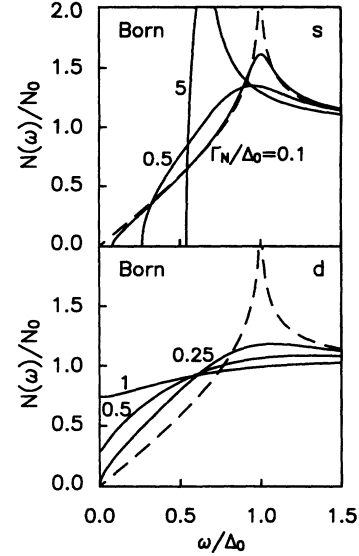


FIG. 1. Normalized density of states $N(\omega)/N_0$ for s - and d -wave order parameters vs reduced frequency ω/Δ_0 , shown for various potential scattering rates Γ_N/Δ_0 in Born approximation.

the maximum frequency ω such that the angle-resolved density of states $N(\mathbf{k}, \omega) \equiv \text{Im Tr} [g(\mathbf{k}, \omega)] / \pi = 0$ for all \mathbf{k} . A simple estimate shows that for small scattering rates, $\Omega_G \sim \Gamma$ (Γ_N in Born limit). In the dirty limit $\Gamma \rightarrow \infty$, the s -wave superconductor becomes isotropic with a BCS density of states $N(\omega) = \text{Re} [\omega / (\omega^2 - \Delta_{\text{avg}}^2)^{1/2}]$, as shown in Fig. 1. In contrast to a d -wave superconductor, the self-energies obtained in the Born approximation and in the resonant scattering limit are almost equivalent in the highly anisotropic s -wave system. This insensitivity to larger phase shifts arises because of off-diagonal self-energy corrections which prevent the occurrence of poles in the t matrix, $c^2 - G_0^2 + G_1^2 \simeq \mathcal{O}(1)$ for all $c \lesssim 1$. Densities of states for both types of states in the limit of resonant scattering are shown in Fig. 2.

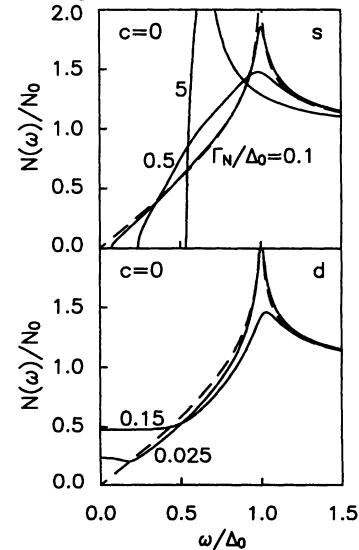


FIG. 2. Normalized density of states $N(\omega)/N_0$ for s - and d -wave order parameters vs reduced frequency ω/Δ_0 , shown for various potential scattering rates Γ/Δ_0 in unitarity limit, $c = 0$.

London penetration depth. The opening of the energy gap with increasing impurity concentration is an indelible signature of s -wave superconductivity. It will obviously give rise to activated behavior for $T \ll \Omega_G$ in a wide range of thermodynamic properties, of which we have chosen to discuss only one for purposes of illustration, the temperature-dependent magnetic penetration depth. For the model states and Fermi surface under consideration, this may be expressed as $[\lambda_0/\lambda(T)]^2 = \int d\omega \tanh \beta\omega/2 \int d\phi/2\pi \operatorname{Re} \tilde{\Delta}_k^2/(\tilde{\omega}^2 - \tilde{\Delta}_k^2)^{3/2}$ where λ_0 is the pure London result at $T = 0$. The penetration depth in a d -wave superconductor (Fig. 3, bottom half) is known to vary as $\lambda(T) \simeq \tilde{\lambda}_0 + c_2 T^2$ at the lowest temperatures,^{16,12} over a temperature range which widens with increasing impurity concentration. The coefficient c_2 decreases, as Γ^{-1} in the Born limit and $\Gamma^{-1/2}$ in the resonant scattering case. The corresponding activated behavior in the anisotropic s -wave case is easy to distinguish from the d -wave case when plotted against $(T/T_c)^2$ as also shown in Fig. 3. The important experimentally relevant signature is of course not simply the exponential behavior, but the increase in the activation gap with impurity concentration.

Spin scattering. A simple defect like a vacancy or Zn ion in the CuO_2 plane may not behave simply as a potential scatterer, as assumed above. In the presence of large local Coulomb interactions, a magnetic moment may form around the defect site, giving rise to spin-flip scattering of conduction electrons.²⁰ This poses the most serious obstacle for the direct application of the principle distinguishing d -wave from anisotropic s -wave systems outlined above, since magnetic scattering will lead to gapless superconductivity as in the usual Abrikosov-Gor'kov theory. Furthermore, even if a gap remains, strong spin-flip scattering may lead to bound states within it^{21,22} which may give rise under the proper circumstances to a residual density of states $N(\omega \rightarrow 0)$

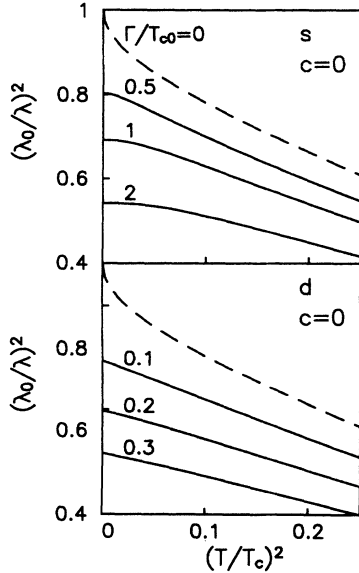


FIG. 3. Temperature dependence of normalized magnetic penetration depth $[\lambda_0/\lambda(T)]^2$ for s - and d -wave order parameters vs reduced temperature $(T/T_c)^2$, shown for various potential scattering rates Γ/T_{c0} in unitarity limit, $c = 0$.

as in the d -wave case. Here we investigate the competition between the opening of the energy gap in the s -wave state due to potential scattering and gapless behavior due to magnetic scattering. To this end we add a term $J\mathbf{S} \cdot \boldsymbol{\sigma}$ to the Hamiltonian, where \mathbf{S} is a classical spin representing the impurity and $\boldsymbol{\sigma}$ is the conduction electron spin density, and study the system in an average t -matrix approximation analogous to the one applied to the pure potential scattering case. The self-energies found in the presence of both types of scattering reduce in the isotropic s -wave case to those given by Shiba,²² but are complicated and will be given elsewhere. We find that until the dimensionless exchange JN_0 becomes of $\mathcal{O}(1)$, the results for the s -wave system are very similar to those obtained in the simpler Born approximation, as discussed above. In this case, $\Sigma_0 = (\Gamma_N + \Gamma_N^s)G_0$ and $\Sigma_1 = (-\Gamma_N + \Gamma_N^s)G_1$,¹⁷ where $\Gamma_N^s \equiv n_i J^2 S(S+1)\pi N_0$. The induced gap, Ω_G , in the s -wave system may then be shown to vary as $\Omega_G \simeq \Gamma_N - \Gamma_N^s \geq 0$, but the effects of self-consistency rapidly become important as the concentration is increased. In Fig. 4, we plot Ω_G as a function of the impurity concentration through the parameter Γ_N for various assumptions about the scattering character of the impurity ion, where the quantity Γ_N^s/Γ_N specifies the relative amount of magnetic scattering. The destruction of the induced gap takes place because the system becomes insensitive to large amounts of potential scattering, but magnetic impurities continue to break pairs also at large concentrations. The gap is nevertheless found to persist into the very dirty limit even for systems where the magnetic scattering is nearly as strong as the potential scattering.

For weak spin scattering, the bound state in the t -matrix approximation is found to lie at $\omega \gg \Omega_G$, just below the average order parameter Δ_{avg} deep in the continuum, and thus plays no role. Stronger spin scattering does not change this qualitative behavior at low concentrations until $JN_0 \simeq 1$ when the bound state lies at the Fermi level in the classical spin approximation.²² In this case the Kondo effect, neglected here, also becomes important. It is known from other analyses²³ that the bound state lies near the Fermi level, and will therefore give rise to a residual density of states $N(\omega \rightarrow 0)$, only

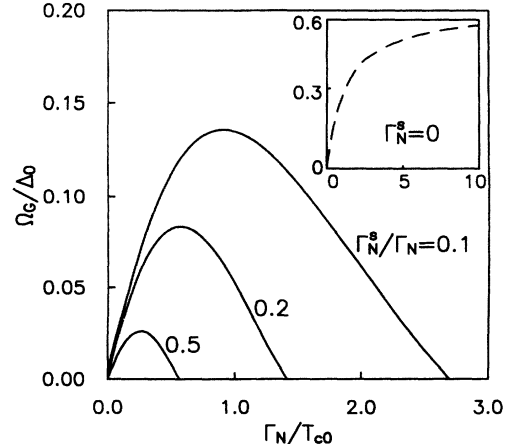


FIG. 4. Induced energy gap normalized to clean gap maximum, Ω_G/Δ_0 , vs potential scattering rate Γ_N/T_{c0} for different ratios, Γ_N^s/Γ_N of magnetic to potential scattering rates.

when $T_K \simeq T_c$. For any other ratio of T_K/T_c , the bound state will lie at an energy corresponding to an appreciable fraction of the *average* gap in the system, and hence be irrelevant for our purposes.

Clearly a quantitative estimate of the relative size of Γ and Γ_N^s is required to decide whether spin scattering plays a role in real high- T_c materials with simple defects. Walstedt and co-workers estimated $JN_0 \simeq 0.015$ for a Zn ion in Y-Ba-Cu-O (YBCO), implying that Zn is a nearly pure potential scatterer in this system.²⁴ On the other hand, Mahajan *et al.*²⁵ estimate $JN_0 \simeq 0.45$. For a 1% Zn concentration, a magnetic moment of $0.36\mu_B$ for Zn in fully oxygenated YBCO (Ref. 25) and a density of states of $1.5/\text{eV}$,²⁵ we find $\Gamma_N^s \simeq 1 \times 10^{-4}$ eV. From the residual resistivities of Zn-doped YBCO crystals,²⁶ we estimate that a 1% Zn sample corresponds to a *total impurity* scattering rate of $\Gamma_N^{\text{imp}} \simeq 2 \times 10^{-3}$ eV, assuming that the inelastic and elastic contributions to the scattering rate add incoherently. This suggests that potential scattering must dominate the total elastic rate, $\Gamma_N^s \ll \Gamma$. On the other hand, the large value of $JN_0 \simeq 0.45$ deduced for a Zn ion²⁵ means that the Kondo effect may be important, and that we cannot completely rule out the possibility that a bound state sits very close to the Fermi level.

Conclusions. There is by now a considerable body of experimental data supporting the picture of gapless superconductivity in the cuprate high- T_c materials, with a residual density of states and low-temperature behavior varying qualitatively according to the *d*-wave plus resonant scattering model.^{1,27} This data stands in apparent contradiction to the well-known effect of small amounts of potential scatterers on anisotropic *s*-wave superconductors, namely the smearing of energy gap anisotropy. This continues to hold even for extremely anisotropic systems

with nodes, as illustrated by the simple theory presented here for a representative order parameter. We believe that this data strongly suggests that the pairing is unconventional in these materials, but the above analysis does not as it stands allow one to distinguish among possible candidate unconventional states (e.g., $d_{x^2-y^2}$ and d_{xz}) without further quantitative comparison. It should be noted that time-reversal breaking unconventional states with a gap will become gapless in the presence of pure potential scattering.

As we have briefly discussed, the major difficulty inherent in such an analysis is the possibility that even an apparently "inert" impurity such as Zn or a vacancy in the Cu-O planes may induce local spin correlations in the strongly interacting electron system, leading to spin-flip scattering. Ruling out gapless superconductivity induced by magnetic scattering then becomes a quantitative problem. Gapless behavior in films suggests that a resonant scattering mechanism of some type must be present in order to induce a significant residual density of states with comparatively little T_c suppression. We have shown, however, that resonant potential scattering does not take place in *s*-wave systems, and argued that low-energy resonant spin-scattering is much less likely than in the isotropic case. We have furthermore made a crude estimate of the importance of spin-flip scattering in Zn-doped YBCO crystals which indicates these materials are dominated by potential scattering and should therefore exhibit an induced gap if the superconducting state is *s* wave.

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