Why is T_c of the Oxide Superconductors So Low?

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An analysis of the resistivity above T_c in the oxide superconductors shows that the inelastic-scattering rate is several times kT. This inelastic scattering yields pair breaking which suppresses T_c relative to the energy gap. The large energy scale in the problem suggests an electronic pairing mechanism, which we believe leads to d-wave pairing. The inelastic scattering has contributions from electron-phonon and from electron-electron scattering in a two-dimensional square lattice near half filling. In the latter case, the pair breaking can be reduced in a more three-dimensional structure.

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The oxide superconductors share an unusual feature in that their resistivity ρ is relatively large ($\approx 250\ \mu\Omega$ cm) just above T_c, and is linear from T_c up to room temperature with a slope $d\rho/dT \approx 1.7$–$2.5\ \mu\Omega$ cm/K.[1] The fact that ρ is temperature dependent indicates that the electrons are being scattered inelastically. We can estimate the transport scattering time τ_{Tr} from the formula $\sigma = e^2 N_0 D(m/m^*)$, where $D = \langle v_F^2 \rangle \tau_{\mathrm{Tr}}/2$ is the diffusion constant in 2D, N_0 and v_F are the density of states and Fermi velocity from band calculations, and m^*/m is a many-body mass enhancement relative to the band mass to be discussed below. As a result of the perfect nesting of the Fermi surface in a half-filled 2D square lattice, most scattering processes involve $2k_F$ scattering across the Fermi surface which dissipates momentum efficiently. Consequently, the inelastic-scattering rate is $\tau_{\mathrm{in}}^{-1} \simeq \tau_{\mathrm{Tr}}^{-1}/2$. We assume that the band structure can be modeled by a tight-binding band

$$\epsilon(\mathbf{k}) = -2t(\cos k_x a + \cos k_y a). \tag{1}$$

By expanding the tight-binding fit[2] to the hybridized Cu-O band near the Fermi level, we find $t = 0.46$ eV. In this model N_0 has a logarithmic singularity at half filling, and we assume that doping puts the Fermi level at a point very close to half filling where $N_0 = 0.2/tV$ per spin,[3] where V is the volume per unit cell. This value of N_0 produces a specific heat γ of 2 mJ/mole K^2. We can also compute $\langle v_F^2 \rangle = (2ta/\hbar)^2$. Within this sample model we find that

$$\hbar/\tau_{\mathrm{in}} = 8(d\rho/dT)(m/m^*)kT, \tag{2}$$

where $d\rho/dT$ is in units of $\mu\Omega$ cm/K.

Recent analysis[4] of γ and magnetic susceptibility χ of $La_{2-x}Sr_xCuO_4$ suggests that $m^*/m \approx 5$. With this mass enhancement, we estimate that $\hbar/\tau_{\mathrm{in}} \approx 3kT$. The value of τ_{in} should be directly measurable in optical experiments. The frequency-dependent conductivity should have the Drude form with a reduced spectral weight, $\sigma(\omega) = (e^2 nm/m^*)\tau/(1+\omega^2\tau^2)$, plus higher-energy excitations which represent the effects of correlation. An analogous situation exists for the heavy-fermion metals.[5]

We expect τ^{-1} to equal τ_{in}^{-1} and therefore to be linear in T for $\omega < T$ and to become linear in ω for $\omega > T$. The reduced spectral weight can be understood either as n electrons with heavy mass m^* where n is nearly one electron per copper, or n^* holes in the lower Hubbard band with the band mass m, where n^* is one hole per Sr in $La_{2-x}Sr_xCuO_4$. The latter picture was used in the interpretation of the Hall effect.[6]

Even as pure phenomenology, the observation that $\hbar/\tau_{\mathrm{in}}$ exceeds kT already yields important information about the superconductivity. Essentially when $\hbar/\tau_{\mathrm{in}}$ exceeds kT, kT is no longer a relevant energy scale. The logarithmic singularity responsible for the superconducting instability is cut off by $\hbar\tau_{\mathrm{in}}^{-1}$, not by kT. Thus we expect the onset of superconductivity to be roughly given by the criterion

$$\Delta \approx \hbar\tau_{\mathrm{in}}^{-1}(T_c) \tag{3}$$

instead of the usual BCS equation, $2\Delta = 3.5kT_c$. The fact that superconductivity can survive such strong inelastic scattering indicates that the basic pairing energy is very large. Recent tunneling measurements[7] indeed showed direct evidence of a very large zero-temperature gap $2\Delta \approx 13kT_c$. This is consistent with the large τ_{in}^{-1} and Eq. (3), given the approximate nature of our estimates. It should be pointed out that a number of other groups reported smaller gap ratios of 10.5,[8] 4.8,[9] and 4.5.[10] While the experimental situation needs clarification, there is a consensus that the tunneling gap exceeds the BCS value. We also note that recent tunneling measurements on an organic superconductor[11] also found $2\Delta \approx 14kT_c$. In these materials ρ is also temperature dependent above T_c and the same pair-breaking mechanism may hold in this case, even though the mechanism which leads to a large inelastic rate may be different.

A large τ_{in}^{-1} should be directly observable experimentally by looking for Lorentzian broadening of the gap in tunneling measurements just below T_c. An analogous situation exists in the sites of superconductivity near the metal-insulator transition.[12]

In metals, $\hbar\tau_{in}^{-1} \approx \lambda kT$ for $kT \geq \hbar\omega_D$ as a result of electron-phonon scattering, where λ is the electron-phonon coupling and ω_D is the Debye frequency. For $kT \ll \hbar\omega_D$, the temperature dependence of τ_{in}^{-1} is usually T^2 because of electron-electron collision or even higher power due to phonon scattering. Specific-heat measurements[13] show that $La_{2-x}Sr_xCuO_4$ cannot be described as a simple Debye solid, and neutron determination of the phonon density of states[14] shows a first maximum at approximately 11 meV (≈ 130 K) with considerable structures up to 50 meV. Some of the higher-energy phonons are the oxygen breathing modes which are believed to couple strongly to the electrons. The usual arguments require that τ_{in}^{-1} due to phonons is linear in temperature only if kT exceeds all the phonon modes that couple strongly to the electrons. Thus, it would be difficult to understand how phonon scattering can lead to a linear behavior of τ_{in}^{-1} down to 40 K as is the case in $La_{2-x}Sr_xCuO_4$. However, we must keep in mind that empirically, the resistivity of a Debye solid becomes linear in T for T greater than $0.2\omega_D$. Thus phonons would contribute to the τ_{in}^{-1}, especially at higher temperatures, but we are not certain whether they alone would account for the linear T dependence or the large magnitude. In the following we suggest a novel alternative contribution.

It turns out that as a result of special features of the van Hove singularities in a 2D square lattice near half filling, τ_{in}^{-1} due to electron-electron scattering is proportional to kT. This is most readily seen by considering the q- and ω-dependent susceptibility for noninteracting electrons,

$$\chi_0(q,\omega) = \sum_k \frac{f(\epsilon_{k+q}) - f(\epsilon_k)}{\omega - (\epsilon_{k+q} - \epsilon_k) - i\eta}. \tag{4}$$

If we write $\chi_0 = \chi' + i\chi''$, it is known that at half filling,[3] for $\mathbf{q} = \mathbf{Q}^*$ where $Q^* = (\pm\pi/a, \pm\pi/a)$, $\chi_0'(Q^*,\omega) \sim \ln^2|\omega|$. This is due to the perfect nesting of the Fermi surface plus the existence of saddle points at the Fermi level in 2D. From the Kramers-Kronig relation, we immediately see that $\chi_0''(Q^*,\omega) \sim \ln|\omega|$ is needed to produce the singularity in χ_0'. A direct analysis of Eq. (4) shows the approximation relation

$$\chi_0''(q,\omega) \approx -\ln[(|\omega| + v_F|\mathbf{q} - \mathbf{Q}^*|)/t] \tag{5}$$

for $\mathbf{q}$ near $\mathbf{Q}^*$. The important feature of Eq. (5) is that χ_0'' approaches a constant as $\omega \to 0$ for all $\mathbf{q}$ near $\mathbf{Q}^*$. This is due to the existence of saddle points at the Fermi level at $\mathbf{k} = (\pm\pi/a, 0)$ and $(0 \pm \pi/a)$, in the vicinity of which the band is very flat. Thus a particle-hole excitation with momentum connecting these saddle points can be at arbitrarily low energy. In contrast, in usual Fermi-liquid theory, $\chi''(q,\omega) \sim \omega/v_F q$ vanishes linearly with ω.

The inelastic-scattering rate can be calculated by our considering the process where an electron is scattered to an unoccupied state across the Fermi surface while exciting a particle-hole pair, i.e., it is an integral of $\chi''(q,\omega)$ over a set of allowed q and ω. The allowed range of ω is kT. Usually $\chi'' \sim \omega$ immediately produces the standard Fermi-liquid result $\tau_{in}^{-1} \sim T^2/\epsilon_F$. The unusual behavior of Eq. (5) (after we note that the allowed $\omega < |\mathbf{q} - \mathbf{Q}^*|$) yields instead

$$\hbar\tau_{in}^{-1} = \alpha kT, \tag{6}$$

where α is proportional to the interaction strength squared and can be greater than unity.

As the filling deviates from half filling ($x \neq 0$ in $La_{2-x}Sr_xCuO_4$), the Fermi energy moves away from the saddle point by an amount ϵ_0, and the electron-electron scattering rate gradually crosses over from T to T^2. We expect the crossover to begin when $\epsilon_0 \approx kT$. This occurs when $x \approx x_c$, where $x_c \approx 2N_0\epsilon_0 m^*/m$, where N_0 is the single spin density of states per particle as plotted in Ref. 3 and has a value $\approx 0.3/t$ in the region of interest. Setting $\epsilon_0 \approx 100$ K and $m^*/m = 5$, we obtain an estimate of $x_c \approx 0.06$. This rough estimate indicates that scattering due to saddle points gradually diminishes for $x > 0.06$, but it seems possible that even at $x = 0.15$, it contributes in an important way to the observed τ_{in}^{-1}. In the following we examine further implications of our picture.

The most important conclusion we draw (and this is independent of the mechanism responsible for the large τ_{in}^{-1}) is that the superconductivity in these systems involves a very high energy scale, so that the zero-temperature gap is of order several hundred kelvins. Our analysis makes clear that this is a bulk property, so that the reservations made in Ref. 7 that the large gap may be a surface feature can now be removed. This implies that we must abandon the phonon mechanism and look to electronic mechanism as a cause of the superconductivity. Anderson[15] has emphasized the importance of correlation in these materials and proposed that the Hubbard model should be a good starting point. There is a growing suspicion among theorists that the ground state of the nearly half-filled Hubbard model is an anisotropic superconductor, at least near the antiferromagnetic (or spin-density wave) phase boundary. Hirsch[16] has numerical evidence from Monte Carlo studies in 2D, and he argued that the antiferromagnetic exchange favors singlet pairing on neighboring sites. Anderson[15] has proposed the resonant valence-bond idea if the half-filled problem is somehow frustrated from forming a Néel state. Both these pictures view the problem from the large-U limit.[17] An alternative viewpoint is to start from the small-U limit where one expects the formation of a spin-density wave. A number of workers[18-20] have suggested that near an antiferromagnetic instability, d-wave pairing is favored by the exchange of antiferromagnetic spin fluctuations. In particular, Scalapino, Loh, and Hirsch[20] have shown that within the random-phase approximation, a weak attraction $\lambda \simeq 0.1$ is found for d-

wave pairing near the spin-density wave instability. These discussions have not taken lifetime effects into account and must be reexamined, at least in 2D. Thus both the large-U and small-U considerations point to an anisotropic superconducting ground state. In the large-U limit, the resonant valence-bond approach attempts to describe the ground-state wave function directly. It seems to us that even in this limit, the elementary excitations can be described by heavy quasiparticles with residual interaction and the resulting anisotropic superconductor can be described by BCS pairing of quasiparticles near the Fermi surface. The oxide superconductors appear to be in an intermediate-U regime with modest mass enhancement[4] ($m^*/m=5$). If we approach the problem from the large-U limit, the energy scale is set by $J \approx t^2/U$ and is maximized for intermediate U.

Thus, we believe that d-wave pairing via antiferromagnetic spin-fluctuation exchange with a modest coupling constant and a large energy scale can explain the superconductivity of the oxides. In particular, our explanation of the large tunneling gap in terms of pair breaking removes the necessity of appealing to some exotic strongly coupled state. Incidentally, the organic superconductor[11] is also found near a spin-density wave phase boundary, and may well belong to the same class as the oxide superconductors, except with an overall reduction in energy scales.

Next we discuss how the existence of d-wave pairing can be determined experimentally. In the heavy-Fermion superconductors, d-wave pairing implies lines of zeros in the energy gap on the Fermi surface, leading to power-law T dependence in the specific heat, in the nucleation spin relaxation rate T_1^{-1}, and in transport properties such as ultrasonic attenuation and thermal conductivity.[21] The observations of these power-law behaviors are convincing evidence that one does not have the standard s-wave pairing. In the present case the situation is complicated by the fact that in two dimensions and for an isotropic Fermi surface, the d-state gap function is $\Delta_{\pm}(\mathbf{k})=\Delta_0\exp(\pm i2\phi_{\hat{\mathbf{k}}})$ where $\phi_{\hat{\mathbf{k}}}$ is the angle of the $\hat{\mathbf{k}}$ vector. The energy gap is proportional to $|\Delta_{\pm}(\mathbf{k})|$ and is fully isotropic. If the Fermi-surface anisotropy introduced by the square lattice is sufficiently weak, it is possible to form a low-temperature d state with a weakly anisotropic gap and no zeroes.[22] Thus the observation of low-temperature activated behavior does not rule out d-wave pairing.

On the other hand, when the Fermi energy is near half filling so that the anisotropy of the Fermi surface is strong, or when the temperature is just below T_c, the gap function is

$$\Delta(\hat{\mathbf{k}})=\Delta_0\cos2\phi_{\hat{\mathbf{k}}}=\Delta_0(\hat{\mathbf{k}}_x^2-\hat{\mathbf{k}}_y^2), \tag{7a}$$

or

$$\Delta(\hat{\mathbf{k}})=\Delta_0\sin2\phi_{\hat{\mathbf{k}}}=\Delta_0 2\hat{k}_x\hat{k}_y. \tag{7b}$$

These states have nodes in the gap at four points. We expect Eq. (7a) to be favored so that the troublesome saddle points are fully gapped. In this case the quasiparticle energy is given by $E(\mathbf{k})=\{|\Delta(\hat{\mathbf{k}})|^2+[\epsilon(k)-\mu]^2\}^{1/2}$, where $\Delta(\hat{\mathbf{k}})$ and $\epsilon(\mathbf{k})$ are given by Eq. (7a) and Eq. (1), respectively. In the vicinity of the saddle points $\mathbf{k}^*=(\pm\pi/a,0),(0,\pm\pi/a)$, the energy gap equals Δ_0, and for $\mu=0$, the density of states per saddle point is given by

$$N^*(\omega)=-\frac{1}{4\pi^2}\frac{1}{t}\frac{\omega}{(\omega^2-\Delta_0^2)^{1/2}}\ln\left[\frac{(\omega^2-\Delta_0^2)^{1/2}}{t}\right]. \tag{8}$$

The additional logarithmic factor compared with the standard BCS formula is a consequence of the flat band at the saddle point. This leads to a sharpening of the density of states at the gap edge. Furthermore, the presence of sharp features at the gap edge leads to a sharp structure for the onset of particle-hole pair creation at $2\Delta_0$, and it is possible that a quasiparticle at energy $E(\mathbf{k})$ plus one or more particle-hole pairs are created at the saddle points, leading to structures at energies $E(\mathbf{k})+2n\Delta_0$, $n=1,2,\ldots$. The existence of these structures is another indication of the strong scattering of quasiparticles by particle-hole excitations at the saddle points. Structures of this type were reported in Ref. 7 but have not been confirmed by other investigators.

While the observation of a T^2 term in the low-temperature specific heat and the nuclear relaxation rate $(T_1T)^{-1}$ would be proof of anisotropic pairing, it is not ruled out by the absence of these power laws for reasons described earlier. One common feature of anisotropic pairing is that ordinary impurity scattering is pair breaking. In this sense the present structure is ideal in that the dopant ions are not part of the conducting Cu-O bonding network and the extrapolated residual resistivity is surprisingly low. Another signature is the possibility of transition between different pairing states such as the nodeless state at low temperature and a state described by Eq. (7) near T_c.

In this paper we have pointed out that the observed linear resistivity above T_c in oxide superconductors implies a short inelastic lifetime which is pair breaking. It is interesting to remark that in ordinary strong-coupled superconductors, the enhancement of the ratio $2\Delta/kT_c$ can be interpreted as inelastic scattering suppressing T_c more effectively than it suppresses Δ, while both are the product of electron-phonon coupling. In the present situation, we believe that phonons are not responsible for the pairing interaction, so that strong electron-phonon coupling is detrimental to high-temperature superconductivity. At the same time, we have identified at least one source of scattering which is specific to the 2D square lattice near half filling and which is not directly related to any of the proposed pairing mechanisms. Thus, it will

be interesting to suppress the electron-electron scattering by going away from 2D. One could do it gradually by increasing the interlayer coupling by applying uniaxial stress or even hydrostatic pressure, since in an anisotropic structure, pressure most likely would affect the interlayer spacing more than the Cu-O planes. It is interesting that T_c in $La_{2-x}Ba_xCuO_4$ is significantly enhanced under pressure,[23] and it will be interesting to correlate this enhancement with $d\rho/dT$. Alternatively, one could abandon the 2D structure entirely and go to a 3D structure which models a 3D half-filled Hubbard model. An example would be the cubic perovskite $A_{1-x}T_xCuO_3$ where A is a +4 ion and T is a +3 ion so that when $x=0$, Cu is +2, i.e., a single d hole per site. However, in the cubic structure the crystal field leaves a twofold orbital degeneracy d_{z^2} and $d_{x^2-y^2}$ and ends up with a Hubbard model with orbital degeneracy. Unless this degeneracy is lifted by distortion, this is quite different from the 2D situation. Alternatively, it will be interesting to investigate cubic perovskite with a nondegenerate s orbital and this leads us back to the oxide superconductor $BaPb_{1-x}Bi_xO_3$. The compound that is the 3D analog of $La_{2-x}Sr_xCuO_4$ would be $Ba_{1-x}A_xBiO_3$ where A is an alkali atom or $Ba_{1-x}T_xPbO_3$ where T is trivalent. However, unlike La_2CuO_4, $BaBiO_3$ has a strong lattice distortion, which makes the analogy incomplete.

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