Band-theory analysis of anisotropic transport in La_2CuO_4-based superconductors

Philip B. Allen* and Warren E. Pickett
Condensed Matter Physics Branch, Naval Research Laboratory, Washington, D.C. 20375-5000

Henry Krakauer
Department of Physics, College of William and Mary, Williamsburg, Virginia 23185
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The anisotropic resistivity ρ_{aa} and Hall coefficient $R_{a\beta\gamma}$ of $La_{2-x}M_xCuO_4$ are analyzed as a function of x, using a rigid-band treatment of the previously given linearized augmented plane-wave bands of tetragonal La_2CuO_4. The experimental $\rho_{xx}(T)$ is used to extract $\lambda_{tr} \approx 3.8$, which permits a conventional electron-phonon interpretation of the high T_c. The Hall coefficients are qualitatively explained, including sign discrepancies in published measurements.

In cubic metals, band theoretic analysis of transport properties has given insight into electron-phonon interactions and superconducting properties.[1,2] Here we present a similar analysis for the new superconducting materials based on La_2CuO_4 with $T_c \approx 40$ K. A new feature of this analysis is that, unlike materials studied previously, these have highly anisotropic transport behavior. Our conclusion is that a consistent picture of both transport and superconductivity can be based on the standard electron-phonon model, using available density-functional band structures.[3,4] This conclusion agrees with the calculations of Weber,[5] and Pickett, Krakauer, Papaconstantopoulos, and Boyer,[4] and is not directly contradicted by any experimental evidence.[6]

The Bloch-Boltzmann theory of transport properties,[7] like the BCS-Eliashberg theory of superconductivity,[8] rests on the Migdal approximation[8,9] and is believed to be quantitatively reliable provided three circumstances hold; (1) the dominance of electron-phonon (as opposed to Coulomb) interactions, (2) the availability of the correct quasiparticle band structure, and (3) the smallness of the parameters $N(\varepsilon_F)\hbar\omega_D$ and $N(\varepsilon_F)\hbar/\tau$, where $N(\varepsilon_F)$ is the Fermi-level density of states, ω_D is a characteristic phonon frequency, and $1/\tau$ the electronic scattering rate. The degree of success of our calculation serves as a test of the conjecture that circumstance (1) and (2) hold; circumstance (3) is directly checked later in the paper.

The free-electron formulas $\sigma = ne^2\tau/m$ and $R_H = -1/ne$ are meaningless except in the cases where bands are parabolic, which does not apply here. On the other hand, a complete treatment using Bloch-Boltzmann theory is impossible until more is known about the phonon spectrum. Therefore, we use an intermediate level of theory, where the collision integral in the Boltzmann equation is solved variationally by the ansatz $F_k = f(\mathbf{k}+\delta\mathbf{k})$ and $\hbar\delta\mathbf{k} = -e(\mathbf{E}+\delta\mathbf{v}_k\times\mathbf{B})\tau$ and $\delta v_k = \delta\mathbf{k}\cdot\partial\mathbf{v}_k/\partial\mathbf{k}$, where F_k and f_k are the nonequilibrium and equilibrium (Fermi-Dirac) distribution functions. This model does not adequately describe effects due to inelastic or anisotropic scattering, but such effects are quite unimportant[1] except below $T = \theta_D/2$. The resulting current is[10]

$$j_\alpha = \sigma_{\alpha\beta}E_\beta + \sigma_{\alpha\beta\gamma}E_\beta B_\gamma + \cdots , \tag{1}$$

$$\sigma_{\alpha\beta} = e^2\tau(n/m)_{\alpha\beta} = (e^2\tau/\Omega)\sum_k v_{k\alpha}v_{k\beta}\delta(\varepsilon_k - \varepsilon_F) , \tag{2}$$

$$\sigma_{\alpha\beta\gamma} = -(e^3\tau^2/\hbar c\,\Omega)\sum_k v_{k\alpha}[(\mathbf{v}_k\times\nabla_k)_\gamma v_{k\beta}]\delta(\varepsilon_k - \varepsilon_F) , \tag{3}$$

where $\hbar v_{k\alpha} = \partial\varepsilon_k/\partial k_\alpha$ and Ω is the volume of the crystal. We use the body-centered tetragonal (K_2NiF_4) unit cell with $a = 3.79$ Å and $c = 13.21$ Å. The tetragonal symmetry makes $\sigma_{\alpha\beta}$ diagonal with $\sigma_{xx} = \sigma_{yy} \neq \sigma_{zz}$, and $\sigma_{\alpha\beta\gamma}$ vanishes unless the tetragonal axes α, β, γ are all different. The Onsager antisymmetry $\sigma_{\beta\alpha\gamma} = -\sigma_{\alpha\beta\gamma}$ combined with tetragonal symmetry shows that there are only two independent components, σ_{xyz} (when $\mathbf{B}$ is parallel to the c axis, $\hat{\mathbf{z}}$), and $\sigma_{yzx} = \sigma_{zxy}$ (when $\mathbf{B}$ is in the basal plane). The corresponding elements of the Hall coefficient tensor are

$$R_{xyz} = E_y/j_xB_z = \sigma_{xyz}/\sigma_{xx}\sigma_{yy} , \tag{4}$$

with $R_{yzx} = R_{zxy}$ given by cyclic permutation. The formula for τ is in general[11] quite complicated, but at temperatures of order $0.7\theta_D$ or higher, a good[1,11] approximation is

$$\hbar/\tau = 2\pi\lambda_{tr}k_BT/F_{th} , \tag{5}$$

$$F_{th} \simeq (1 - 0.038\theta_D^2/T^2)^{-1} . \tag{6}$$

Here λ_{tr} is a close approximation to the coupling constant[12] λ which fixes T_c, and F_{th} is a thermal correction factor. The value of λ_{tr} can be deduced by comparing Eqs. (2) and (5) with the experiment. In the approximation used here, τ cancels from Eq. (4) for R_H.

Energy bands ε_k were taken from Ref. 4. The effect of alloying with divalent atoms Sr, Ba in place of La was treated in rigid-band approximation by lowering the Fermi level appropriately to accommodate x holes per primitive cell according to the formula $La_{2-x}M_xCuO_4$. For small x both magnetic ordering and orthorhombic distortion occur, converting pure La_2CuO_4 into a semiconduc-

tor. The calculation was for the hypothetical tetragonal metal, which we assume closely approximates the actual structure of the superconducting phase. For purposes of performing the Brillouin-zone sums in Eqs. (2) and (3), the tetrahedron method was used on a dense mesh of ~ 1000 inequivalent k points. The values of ε_k on this mesh came from a careful Fourier interpolation based on LAPW calculations at 135 inequivalent k points.

Numerical results are shown in Fig. 1 and Table I. Noise in the Brillouin-zone sums stems from the finite number of k points at which the bands ε_k are actually computed. Unphysical oscillations in the Fourier interpolation were minimized using variations of the scheme of Koelling and Wood.[13] The remaining mild oscillations are magnified in second derivatives of ε_k, especially in the z direction where dispersion is small and sampling was sparse. Therefore, the Hall tensor (which involves second derivatives) is especially noisy, and this shows up in Fig. 1 as a discrepancy between R_{yzx} and R_{zxy}, which are supposed to be equal by symmetry. The computed R_{yzx} is quite smooth, whereas R_{zxy} (which alone involves $\partial^2\varepsilon/\partial k_z^2$) has kinks and oscillations. The magnitudes are always in quite good agreement, especially in the range near $x=0.15$ of optimum T_c. The small kinks seen in $N(\epsilon)$ in Fig. 1 line up with the large kinks in R_{zxy}, showing that these are also numerical noise.

A convenient formula, which follows from Eq. (2) and (5), is

$$\lambda_{\rm tr}/F_{\rm th}=0.842\times 10^{-3}[\rho_{aa}(295\ {\rm K})-\rho_{aa}(0)]\,\Omega_{paa}^2\ , \qquad (7)$$

where ρ is measured in $\mu\Omega$ cm, $\rho(0)$ is the residual resistance, and the Drude plasma frequency (in eV) is defined by

$$\Omega_{pa\beta}^2=4\pi e^2(n/m)_{a\beta}=4\pi e^2 N(\varepsilon_F)\langle v_{ka}v_{k\beta}\rangle/\Omega_{\rm cell}\ , \qquad (8)$$

where $\Omega_{\rm cell}$ is the volume of a unit cell, and the average over the Fermi surface denoted by $\langle\ \rangle$ is defined by comparing Eq. (8) with Eq. (2). Figure 1 shows that, whereas the density of states $N(\varepsilon_F)$ is rapidly varying as x varies (this is a 2D logarithmic saddle-point feature, broadened into a bump by the weak z direction dispersion of the band), the Drude plasma energy is smoothly varying and, thus, presumably insensitive to the minor discrepancies between the various energy-band calculations of Refs. 3 and 4. Since Ω_p is the only theoretical input needed in Eq. (7) to obtain λ from ρ, this method is especially reliable, provided single-crystal resistivity measurements are

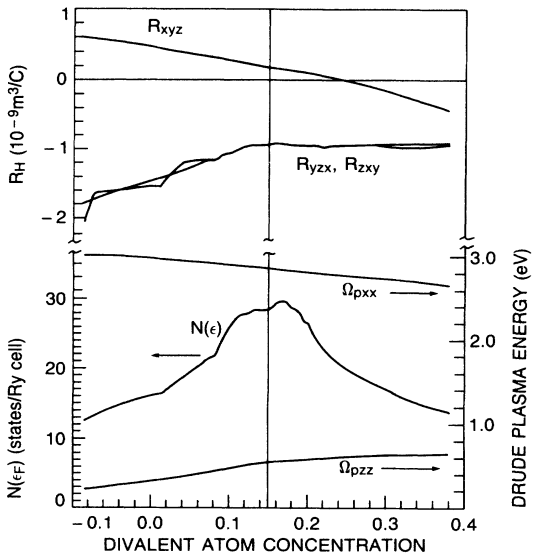

FIG. 1. Rigid-band calculations of density of states $N(\epsilon_F)$, Hall coefficients, and Drude plasma energies of $La_{2-x}M_xCuO_4$ vs x, the concentration of the divalent atom M. Negative x could be achieved by doping with a quadrivalent atom.

used. We compare with measurements by Suzuki and Murakami[14] on a thin-film single crystal of $La_{2-x}Sr_xCuO_4$ with $x=0.06$ and a superconducting transition between 15 and 23 K. The film was grown epitaxially on $SrTiO_3$ (100) and has the c axis perpendicular to the film. The measured value of $\rho_{xx}(0)$ was extrapolated to be ~ 250 $\mu\Omega$ cm, and $\rho_{xx}(295\ {\rm K})-\rho_{xx}(0)$ is ~ 450 $\mu\Omega$ cm. Taking $\Omega_p=2.9$ eV from Table I, Eq. (7) yields $\lambda_{\rm tr}/F_{\rm th}=3.2$. The thermal factor $F_{\rm th}$ is greater than 1 and probably less than 1.2, yielding $\lambda_{\rm tr}\sim 3.2$–3.8 which can easily give $T_c\sim 40$ K or higher. This conclusion is consistent with estimates made in Refs. 4 and 5. Gurvitch reported[15] a preliminary estimate of λ_{tr} using an isotropic average Ω_p^2 from Mattheiss,[4] and polycrystalline data for $\rho(T)$. His estimate of λ_{tr} was similar in magnitude. Such a large value of λ suggests proximity to a "soft-mode" instability, which can cause λ to be arbitrarily large (unfortunately, T_c does not also diverge.)

An important question is whether the measured temperature-dependent resistivity is actually caused by

TABLE I. Rigid-band calculations as in Fig. 1 at various concentrations x of divalent atoms.

x	0.00	0.05	0.10	0.15	0.20	Unit
$N(\epsilon_F)$	16.0	19.2	25.3	28.4	26.6	state/Ry cell
$\sqrt{\langle v_x^2\rangle}$	3.0	2.7	2.3	2.2	2.2	10^7 cm/s
$\sqrt{\langle v_z^2\rangle}$	0.32	0.36	0.37	0.41	0.46	10^7 cm/s
Ω_{pxx}	3.0	2.9	2.9	2.9	2.8	eV
Ω_{pzz}	0.32	0.38	0.47	0.55	0.58	eV
R_{xyz}	46.7	37.8	28.3	18.4	8.4	10^{-11} m^3/C
R_{yzx}	−151	−122	−107	−94	−96	10^{-11} m^3/C

electron-phonon interactions and can be analyzed using Bloch-Boltzmann theory. The data of Ref. 14 very strongly give the expected appearance of an electron-phonon mechanism, except that the value of ρ is larger by 10 than in other good electron-phonon metals. This magnitude is accounted for in our model by the smallness of $(n/m)_{\text{eff}}$ and the strength of the scattering as measured by λ. A test of the validity of the analysis is to compute the dimensionless ratios $N(\varepsilon_F)\hbar/\tau$ and a/l. Both are about 1 at 295 K in our analysis. This is common in good superconductors such as Nb_3Sn.[2] However, in the past whenever these ratios became as large as 1, a strong "saturation" effect[16] occurred in $\rho(T)$, indicating a failure of Bloch-Boltzmann theory, whereas no sign of saturation appears in the data of Ref. 15. A difference between La_2CuO_4 and Nb_3Sn is that in Nb_3Sn there are, for almost all k at the Fermi surface, other bands within $\hbar/\tau \sim 0.3$ eV of ε_F, which mix with the band at ε_F at higher T due to virtual-phonon scattering. In La_2CuO_4, with an even larger $\hbar/\tau \sim 0.6$ eV, there are no other bands this close for most k. Allen and Chakraborty[17] have shown how the virtual interband scattering effect provides a mechanism for the saturation effect, and this mechanism would be weakened in La_2CuO_4.

A prediction of the present calculations is the anisotropy ratio $\rho_{zz}/\rho_{xx} = (\Omega_{pxx}^2/\Omega_{pzz}^2)$, which is 28 at $x = 0.15$. This anisotropy has not yet been measured in crystals with good (Bloch-Boltzmann-like) conductivity. However, Shamoto, Onoda, and Sato[18] have reported "preliminary measurements" of the critical field (H_{c2}) anisotropy for T close to T_c, obtaining $(H_{c2\parallel}/H_{c2\perp})^2 \sim 170$ and 40 for crystals doped with Ba and Sr, respectively. This ratio should equal approximately ρ_{zz}/ρ_{xx}.

The Drude plasma frequency is, in principle, accessible to optical measurement from the formula[19]

$$\sigma_{\alpha\beta}(\omega) = \frac{\Omega_{p\alpha\beta}^2/4\pi i}{\omega[1+\lambda(\omega)]+i/\tau(\omega)} + \sigma_{\alpha\beta}^{\text{interband}}(\omega) \ .$$

For $\omega > \omega_D$, the phonon part of $\lambda(\omega)$ decays to zero and the phonon part of $1/\tau$ becomes a constant. A nonphonon (e.g., ordinary Coulomb) contribution to λ may remain at $\omega \approx \Omega_p$ however, which will affect the apparent measured value of Ω_p, as will structure in the interband part. Single-crystal infrared data have not yet been reported, but would be very useful. On polycrystalline samples, Tajima *et al.*[20] have reported a plasma edge at wavelength 1.5 μm or $\hbar\Omega_p \sim 0.83$ eV, which can be compared with our values of 2.9 eV and ~ 0.5 eV for light polarized $\perp$ or $\parallel$ to the c axis.

Finally we discuss the Hall coefficient. The only single-crystal measurement reported so far is R_{xyz}, with the **B** field perpendicular to the same film[14] on which $\rho_{xx}(T)$ was measured. The result has an interesting T dependence not contained in the simple theory of Eqs. (2) and (3). However, the accuracy of Eqs. (2) and (3) is expected to be less for R_H than for ρ. The variational principle[7] (which holds for ρ but *not* for R_H) ensures that an error of order ε in F translates only into an error of order ε^2 in ρ, but remains an error of order ε in R_H. In Nb and Cu,[10] Eqs. (2) and (3) do quite well for R_H at $T = 300$ K, while in Pd,[21] large curvature anisotropy caused an error of a factor of 2. At lower T, significant T dependence occurs in R_H of Cu, which has been explained[22] semiquantitatively by including corrections in F due to inelasticity and anisotropy. The temperature dependence of R_{xyz} reported in Ref. 15 is not entirely unlike that seen in Cu, and may be explainable as an electron-phonon effect when a more complete calculation is possible. The measured magnitude of R_{xyz} at 300 K is $+92\times10^{-11}$ m^3/C, larger by a factor 2.6 than our calculated value of 36×10^{-11} m^3/C at $x = 0.06$. This discrepancy is not much outside our previous experience in better understood metals, and the sign is correct (holelike). We predict that R_{xyz} will switch to electronlike at $x > 0.24$. This result underlines the fallacy in interpreting R_H as $-1/ne$. Such a picture would require a diverging number of holes as x increased toward 0.24, which converts instantly to a diverging number of electrons as x increases further.[23] We also predict that when the **B** field is oriented parallel to the metallic xy layers, the Hall coefficient will be electronlike. This helps explain why measurements on polycrystalline samples[24] by different workers have yielded differing signs of R_H. Experimental[25] studies of R_H vs x on polycrystals have shown a near vanishing of R_H for $x \geq 0.2$.

In summary, our results show that the biggest puzzle, the origin of the high T_c, is compatible with $\rho(T)$ and band theory in a conventional electron-phonon interpretation in La_2CuO_4-based superconductors. A new puzzle is exposed, the absence of saturation in $\rho(T)$ when $a/l \sim 1$, and a plausible resolution is offered.

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*Permanent address: Department of Physics, State University of New York, Stony Brook, NY 11794-3800.

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