Large-bipolaron transport and cuprate superconductors

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The in-plane electronic transport of large bipolarons that move within parallel conducting sheets is considered. The Coulomb interactions between the heavy bipolarons in this planar system produce a distinctive spectrum for collective excitations. Transport of the quasiparticles associated with the collective excitations is treated via the conventional Boltzmann transport theory. However, the scattering of the heavy quasiparticles by acoustic phonons is taken to be analogous to the distinctive scattering of individual large polarons. In particular, as with strong-coupling (adiabatic) large polarons, the scattering time is taken to be proportional to the quasiparticle effective mass. The resistivity, the Hall effect, and the thermoelectric power are determined with this scheme. With a constant density of carriers, the resistivity is proportional to the temperature. The Hall number, the number of carriers deduced from the reciprocal of the Hall constant, exceeds the true carrier density by a ratio that rises linearly with temperature. In addition, the thermoelectric power falls in magnitude and ultimately changes sign as the temperature is raised. These unusual transport properties, as well as the ir conductivity, are consistent with the observed behaviors of the high-T_c cuprate superconductors.

Bednorz and Müller discovered the high-T_c cuprate superconductors while searching for superconductivity in doped semiconductors with very strong electron-lattice interactions.[1] In some such situations, the carrier density (e.g., 10^{19} cm^{-3} in superconducting doped $SrTiO_3$) (Ref. 2) is too small for the superconductor to be considered a normal metal. Oxygen-related states possess an exceptionally strong short-range electron-lattice interaction. This situation arises because, unlike other divalent anions, the binding of the outer electron of an O^{2-} ion requires the presence of positive charge from neighboring cations. Thus, oxygen-related states are especially sensitive to the positions of the adjacent cations. In addition, many oxides have especially effective long-range electron-lattice interactions arising from their exceptionally displaceable ions (manifested by very large ratios of the static to optical dielectric constants, $\epsilon_0/\epsilon_\infty$). For these reasons, polarons and bipolarons have been suspected and found in many oxides. Thus, Bednorz and Müller speculated that they were observing bipolaronic superconductivity in the cuprates.[1] Since then, the theory of bipolaronic superconductivity has been developed with a distinction being made between small and large bipolarons.[3-7]

In multidimensional systems, there are two qualitatively distinct types of polaron and bipolaron.[4,5,8] "Small"-polaronic states are associated with electronic carriers that are confined to a single site. Coherent motion then requires the quantum-mechanical tunneling of atoms through distances that greatly exceed their zero-point amplitude.[9,10] As a result, the effective masses are huge, typically $>10^6$ electron masses. For this reason, small polarons (e.g., holes in the alkali halides) and small bipolarons generally localize and move by phonon-assisted hopping. By contrast, "large"-polaronic states are associated with self-trapped carriers that extend over several sites. The electronic state then adjusts continuously to atomic motion to yield an effective mass (arising from classical atomic motions) that, while large, is many orders of magnitude smaller than that of small (bi)polarons. Therefore, large polarons (e.g., electrons in the alkali halides) generally move itinerantly with substantial mobilities. For this reason, bipolaronic superconductivity is associated with large (multisite) bipolarons and not small (single-site) bipolarons.

In an ionic system, a large bipolaron can form (at least, metastably) if $\epsilon_0 > 2\epsilon_\infty$.[4,5] Furthermore, the conditions for a large bipolaron being stable with respect to separating into two large polarons become progressively easier to fulfill as $\epsilon_0/\epsilon_\infty$ is increased.[4,5] While common ionic solids in which polarons form (e.g., alkali halides) have $\epsilon_0/\epsilon_\infty \approx 2$, the insulating parent compounds of the oxides that become superconductors when appropriately doped have extraordinarily large values, between 10 and 10 000. For this reason, at least the insulating parents of the high-temperature superconductors are prime candidates for large-bipolaron formation.

The effective mass associated with the adiabatic (strong-coupling) motion of a large bipolaron is the atomic mass that is shifted in moving the self-trapped carrier. The atomic displacements nearest a large bipolaron tend to provide the largest contribution to its effective mass.[4,5] This contribution, associated with the short-range electron-lattice interaction, is of the order of E_p/s^2, where E_p is the polaron binding energy and s is the sound velocity.[5,11] With $E_p \approx 0.1$ eV, the effective mass is between 100 and 1000 electron masses, m_e. A bipolaron's mass can only be observed at frequencies well below phonon frequencies. Measurements at higher frequencies only probe the electronic response when the atoms are essentially fixed. By measuring the *low-frequency* (10^9 Hz) relaxation time, τ, and estimating the mobility, μ, on lightly doped (10^{19} cm^{-3}) La_2CuO_4, an effective mass between $300m_e$ and $1000m_e$ was found: $m = q\tau/\mu$, where q

is a carrier's charge.[12]

The scattering of a large (bi)polaron by acoustic phonons is primarily elastic.[11] Acoustic phonons with half wavelengths that exceed the diameter of the (bi)polaron, $2R$, are the most effective scatterers.[11] Since these phonons have very low momentum, $\hbar|Q| < \hbar/R$, they are ineffective in scattering a heavy, large (bi)polaron. In such scattering events, an acoustic phonon may be viewed as bouncing off the large (bi)polaron ($\mathbf{Q} \rightarrow -\mathbf{Q}$) with momentum transfer of magnitude $2\hbar|Q|$. The scattering rate for the large (bi)polaron is then $1/\tau \approx k_B T/msR$, when the density of low-energy acoustic phonons is given by its classical value ($\propto k_B T$) and the acoustic phonon dispersion relation at low frequencies is $\omega_q = s|Q|$.[11] There are two important physical features of this result. First, since the difficulty of scattering the large bipolaron increases with its mass, the scattering time is proportional to the mass. Second, the scattering rate for the heavy particle (the large bipolaron) is proportional to the density of low-momentum particles that scatter it: $1/\tau \propto k_B T$.

To treat electronic transport properly when there is a substantial density of large bipolarons requires consideration of the interactions between the large bipolarons. These interactions affect the large bipolarons' excitation spectrum, $E(\mathbf{k})$, where $\mathbf{k}$ is the excitation's wave vector. In particular, $E(\mathbf{k})$ at small $\mathbf{k}$ is associated with the (long-range) Coulomb interaction between large bipolarons. Since the self-trapped carriers move very slowly as they follow the atomic displacements, the Coulomb interaction between two bipolarons is reduced by the low-frequency dielectric constant, ϵ_0. As a result of their Coulomb interactions, the long-wavelength excitations of mobile bipolarons are plasmonlike.

In particular, consider the layered system illustrated in Fig. 1. There, large bipolarons are confined within layers that are separated from one another by the distance b. In the cuprate systems, b denotes the net separation between groups of contiguous CuO_2 layers. The spectrum for in-plane excitations of this system is[13,14]

$$E(k) = \{(\hbar\omega_p)^2 (kb/2)\coth(kb/2) + [(\hbar k)^2/2m]^2\}^{1/2}, \tag{1}$$

where $\hbar\omega_p = \hbar(4\pi n q^2/\epsilon_0 m)^{1/2}$ is the bipolarons' plasma energy, k is the magnitude of the in-plane component of $\mathbf{k}$, and n is the density of bipolarons. Four features of this dispersion relation for large bipolarons should be noted. First, as a result of the Coulomb interactions, the excitations are separated from the ground state by a gap, the plasma energy. Second, $\hbar\omega_p$ is several orders of magnitude smaller than the plasma energy of electrons in metals; for example, $\hbar\omega_p$ is 10^{-2} eV with $n \approx 10^{21}$ cm^{-3}, $\epsilon_0 = 30$, and $m = 300 m_e$. Third, with a sufficiently large effective mass, the second (free-bipolaron) contribution within the square root of Eq. (1) is of secondary importance. Finally, as shown in Fig. 2, although $E(k)$ initially rises quadratically with k, it has an extensive region of negative curvature at larger k, $kb > 2$.

Since $\hbar\omega_p$ is small, states of large k are thermally accessible. In this sense, large bipolarons are like carriers in narrow-band materials, e.g., molecular solids. Treating the large bipolarons as bosons, the large-bipolaron chemical potential μ is constrained to lie at or below the energy of the ground state: $\mu \leq 0$. Therefore, as in semiconductors, there is a gap, $> \hbar\omega_p$, albeit small, between the conducting states and the chemical potential: $E(k) > \mu$. However, unlike semiconductors, the carrier density is nonactivated.

To calculate the resistivity, the bipolarons' quasiparticle motion and scattering are treated with the customary Boltzmann approach. Since all significant vectors have the same direction, subscripts that would indicate direc-

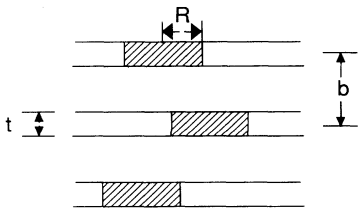

FIG. 1. A side view of bipolarons of radius R confined to conducting layers of thickness t that are separated from one another by the distance b.

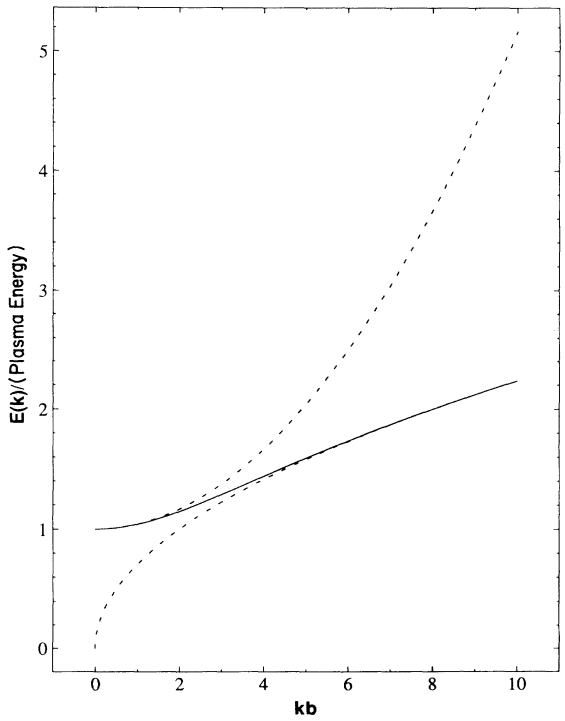

FIG. 2. $E(k)/\hbar\omega_p$ is plotted against kb (the solid curve) when the first term in the squared root of Eq. (1) dominates. Qualitative deviations from the (positive curvature) free-particle-like dispersion (the upper dashed curve) are evident as k increases. Merger with the (negative curvature) $E(k)/\hbar\omega_p = \sqrt{kb/2}$ dispersion (the lower dashed curve) is evident as k increases.

tion are dropped for simplicity:

$$\rho=\hbar/[q^2\sum_k(-\partial f_k/\partial k)(v_k\tau_k)]$$
$$=\hbar/[q^2\sum_k f_k\partial(v_k\tau_k)/\partial k]$$
$$\approx 1/[q^2\sum_k f_k(\tau_k/m_k)]\ , \tag{2}$$

where f_k is the number of boson carriers of wave vector k, the quasiparticle effective mass is defined by $1/m_k \equiv\hbar^{-1}\partial v_k/\partial k$ and (in the customary manner) the k dependence of the scattering time is assumed to be much weaker than that of the velocity. Applying the same procedure for the narrow band of collective large-bipolaron excitations as for individual bipolarons, $\tau_k/|m_k|$ is replaced by sR/k_BT. Then, $\rho=k_BT/n'q^2sR$ with $n'=\sum_k f_k\mathrm{sgn}(m_k)>0$. If the predominant contribution to the k summation occurs for positive m_k, then $n'=n$, the temperature-independent carrier density. The resistivity is then proportional to the temperature.

At finite frequencies the conductivity of large bipolarons has two distinctive features. First, since large bipolarons move itinerantly, the conductivity manifests a Drude falloff with increasing frequency. As noted above, $1/\tau$, the relaxation rate, is proportional to temperature. The magnitude of τ at room temperature will be of the order of a vibrational period if $E_p\approx k_BT$ (see below):

$$\tau\approx msR/k_BT\approx E_pR/sk_BT\approx R/s\ .$$

Second, at higher frequencies there is an absorption band arising from exciting self-trapped electronic carriers to higher levels of their self-trapping potential wells and to states that are resonant with the continuum. The density of states associated with the continuum rises with excitation energy while the matrix element for photon absorption to a resonant-continuum state of wave vector k', $M(k')$, falls when final-state wavelengths fall below the radius of the self-trapped state, R: $M(k')=[1+(k'R/2)^2]^{-3/2}$. Therefore, as with impurity states, these effects produce a nearly temperature-independent asymmetric absorption band (as phonon broadening is relatively small). The intensity of the polaronic absorption is proportional to the density of large bipolarons.

The Franck-Condon principle ensures that the threshold for this absorption exceed the binding energy of the bipolaron. For example, the threshold for absorption to resonant-continuum states is at $3E_p$ for the (hydrogenic) model of bipolaron formation considered in Refs. 4, 5, 13, and 14.[15] As a large bipolaron increases in size, its electronic levels become shallower and its absorption band narrows and shifts toward lower photon energies. In particular, increasing a bipolaron's thickness by increasing the number of contiguous CuO_2 sheets of a cuprate shifts the absorption band toward lower energies.

In the superconducting state, the Drude tail disappears (since $\tau\rightarrow\infty$) while the absorption band remains. If the threshold of the ir absorption band is about 0.1 eV, as it is in most cuprate materials, E_p is comparable to 0.03 eV, as presumed in the above numerical estimate of τ.

The Hall factor, r_H, is the ratio of the Hall coefficient to its free-carrier value, $1/nq$. A general expression for the Hall factor is obtained by solving the Boltzmann equation for a magnetic field applied in the z direction:

$$r_H=\frac{\hbar\sum_k[(\partial f_k/\partial k_y)(v_y/m_{xx})-(\partial f_k/\partial k_x)(v_y/m_{xy})](\tau_k)^2\sum_k f_k}{\left[\sum_k(\partial f_k/\partial k_x)v_x\tau_k\right]^2}\ . \tag{3}$$

Here $v_y\equiv\hbar^{-1}\partial E(k)/\partial k_y$ is the quasiparticle velocity and m_{xy} are components of the effective-mass tensor: $m_{xy}\equiv\hbar^{-2}\partial^2E(k)/\partial k_x\partial k_y$.

As in the calculation of the resistivity, the k summations of Eq. (3) (integrations) are first transformed by an integration by parts with the k dependence of the scattering time taken to be weaker than that of the velocity. If, again, $\tau_k/|m_{xx}(k)|$ is taken as k independent, Eq. (3) becomes

$$r_H=\frac{\sum_k f_k\,1-m_{xx}m_{yy}/m_{xy}m_{xy}\mathrm{sgn}(m_{xx}m_{yy})\sum_k f_k}{\left[\sum_k f_k\mathrm{sgn}(m_{xx})\right]^2}\ . \tag{4}$$

Expressing $\mathbf{k}$ in terms of the polar coordinates k and θ yields

$$1-m_{xx}m_{yy}/m_{xy}m_{xy}$$
$$=\{1+[(E''-E'/k)^2/8E''E'/k](1-\cos\theta)\}^{-1}\ , \tag{5}$$

where $E'\equiv\partial E(k)/\partial k$ and $E''\equiv\partial^2E(k)/\partial k^2$. Carrying out the θ integration from 0 to 2π then yields $4\pi(E''E'/k)^{1/2}/(E''+E'/k)$ for $E''E'>0$ and zero otherwise.[16] Since the condition that $E''E'>0$ is the same as $\mathrm{sgn}(m_{xx}m_{yy})>0$, Eq. (4) may be rewritten as

$$r_H=\frac{\sum_k{}' f_k[2(E''E'/k)^{1/2}/(E''+E'/k)]\sum_k f_k}{\left[\sum_k f_k\mathrm{sgn}(m_{xx})\right]^2}\ , \tag{6}$$

where the prime on the summation in the numerator of Eq. (6) indicates that only values of k for which $E''E'/k>0$ will be included.

The Hall number relative to the actual carrier density is the reciprocal of r_H:

$$n_H/n=\frac{\left[\sum_k f_k\mathrm{sgn}(m_{xx})\right]^2}{\sum_k{}' f_k[2(E''E'/k)^{1/2}/(E''+E'/k)]\sum_k f_k}\ . \tag{7}$$

To discuss the Hall number, first note that the square-bracketed term of the summation in the denominator of Eq. (7) is unity for $E(k) \propto k^2$. However, as k rises in the manner shown in Fig. 2, the square-bracketed term becomes progressively smaller. The square-bracketed term vanishes when E'' vanishes (near $kb=2$ in Fig. 2). Since the thermal populations of states with larger values of k increase with temperature, this effect, by itself, causes the Hall number of rise with temperature. However, at high enough temperatures, the rise of n_H with temperature will be opposed by the fall of the numerator of Eq. (7) caused by significant cancellations associated with states of negative effective mass.

Consider the case when the principal contributions to the summation in the numerator of Eq. (7) come from positive effective masses. Then

$$n_H/n \approx \frac{\sum_k f_k}{\sum_k{}' f_k[2(E''E'/k)^{1/2}/(E''+E'/k)]} \approx \frac{\int_0^\infty dE\,\rho(E)\exp(-E/k_BT)}{\int_0^{E_m} dE\,\rho(E)\exp(-E/k_BT)}, \quad (8)$$

where E_m is the energy corresponding to the cutoff of the denominator's summation. Noting that $\rho(E)$ is constant for two-dimensional motion with a quadratic dispersion, Eq. (8) yields

$$n_H/n \approx \frac{\int_0^\infty dE\,\exp(-E/k_BT)}{\int_0^{E_m} dE\,\exp(-E/k_BT)} = [1-\exp(-E_m/k_BT)]^{-1} \rightarrow k_BT/E_m, \quad (9)$$

where $k_BT > E_m$. Equation (8) indicates that the Hall number for the transport of large bipolarons has two distinctive features. First, the ratio of the Hall number to the carrier number is greater than unity. Second, the ratio of the Hall number to the carrier density rises with temperature.

The Seebeck coefficient (thermoelectric power) of large bipolarons can be very distinctive. As such, measurements of the Seebeck coefficient may be especially useful in establishing the presence of large bipolarons. For example, in a semiconductor, Seebeck-coefficient measurements can provide a means of determining whether a carrier's charge is $|e|$ or $2|e|$. In particular, in a semiconductor with itinerant charge carriers, the dc conductivity and Seebeck coefficient are approximated by $\sigma = \sigma_0 \exp(-E/k_BT)$ and $S = (k_B/q)(E/k_BT + A)$, respectively, where E is the energy for generating carriers and A is a near temperature-independent constant of order unity. Eliminating E/k_BT between these two relations yields an expression for the carriers' charge:

$$q = [A + \ln(\sigma_0/\sigma)]k_B/S. \quad (10)$$

With the limited data available on lightly doped insulating parents of the superconductors,[17,18] I find values of q close to $2.2|e|$ in La_2CuO_{4+x} and near $1.7|e|$ in $YBa_2Cu_3O_{6.25}$. These results suggest paired carriers.

The thermoelectric power (Seebeck coefficient) is the average entropy per carrier charge transported with a carrier. Thus, $S=0$ in the superconducting state where transport is determined by the resistanceless flow of carriers associated with the ground state. Above the superconducting transition temperature, T_c, the chemical potential μ moves below the ground-state energy. The ground state is then vacated, and the transport is via states for which $E(k) > \hbar\omega_p$.

The Seebeck coefficient is the average of the change of the system's entropy with the addition of a charge carrier to the state k, $[E(k)-\mu]/T$, weighted by that quasiparticle's contribution to the conductivity, Eq. (2), divided by the carrier's charge:

$$S = (1/qT)\sum_k [E(k)-\mu] f_k \,\mathrm{sgn}(m_k) \Big/ \sum_k f_k. \quad (11)$$

Here, as in Eq. (2), m_k is the diagonal component of the effective-mass tensor, $m_k = m_{xx} = m_{yy}$. With a constant density of carriers of a single sign, the magnitude of S normally rises with increasing temperature. However, if negative-mass states increasingly contribute as the temperature is raised, the magnitude of S can fall and ultimately change sign with increasing temperature.

For independent bipolarons, a domain of negative-mass states arises as the bipolaron's velocity approaches the sound velocity (since a bipolaron cannot move faster than the solid's atoms). This regime is accessible at high temperatures when the bipolaron's thermal velocity, $\sqrt{2k_BT/m}$, becomes comparable to the sound velocity, s; i.e., when k_BT becomes comparable to E_p.

Furthermore, as described by Eq. (1), the onset of a relatively high density of states with negative effective masses occurs at especially low energies for interacting bipolarons in layered systems (for $kb > 2$ in Fig. 2). In particular, for interacting bipolarons Eq. (11) is rewritten as

$$S = (k_B/q)\left\{ \frac{[\hbar\omega_p - \mu(T)]\sum_k f_k \,\mathrm{sgn}(m_k)}{k_BT\sum_k f_k} + \frac{\sum_k f_k [E(k)-\hbar\omega_p]\,\mathrm{sgn}(m_k)}{k_BT\sum_k f_k} \right\}. \quad (12)$$

With a constant carrier density, $[\hbar\omega_p - \mu(T)]/k_BT$ in the first term of Eq. (12) is positive and an increasing function of temperature. The factor $E(k)-\hbar\omega_p$ weights large-k (negative-effective-mass) terms in the second term of Eq. (12). Since the density of states of the negative-mass states increases with energy, this term tends toward an increasingly large negative value with increasing temperature.

Upon increasing temperature from T_c to 300 K in single-crystal cuprate superconductors, S for *in-plane* motion falls from the positive value expected of holes toward a negative value.[19–22] At room temperature the thermoelectric power is often negative, between -5 and

-10 μV/K. Such behavior is inconsistent with the monotonic behavior expected of a metal. However, such reports are consistent with the bipolarons' Seebeck coefficient as given by Eq. (12).

In a normal metal, the Seebeck coefficient, the entropy per charge of a carrier, is sensitive to the aligning effect of an applied magnetic field. In particular, the magnetic-field-dependent contribution to the Seebeck coefficient is $(k/2|e|)(g\mu_B H/k_B T)^2$, where μ_B is the Bohr magneton and g is the Landé g factor.[13,22] However, no magnetic-field dependence of the Seebeck coefficient is observed in the normal state of superconducting $YBa_2Cu_3O_7$ despite a predicted 300% change at 30 T.[22] This result is consistent with the charge carriers having no permanent magnetic moments, e.g., being singlet bipolarons.

In summary, the in-plane transport of a temperature-independent density of large bipolarons in a layered structure is characterized by many distinctive features. In particular, the resistivity rises *linearly* with temperature. The ir conductivity has an *absorption band* lying above a Drude falloff. The Hall number exceeds the carrier density by a ratio that *increases* with temperature. Finally, with increasing temperature the thermoelectric power of holes *falls* in magnitude and ultimately becomes *n type*. All of these features are in accord with observations on the high-T_c cuprates.

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