Quasiclassical Transport at a van Hove Singularity in Cuprate Superconductors

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The thermopower in cuprate superconductors shows a quasiclassical temperature independence rather than the T-linear behavior of a Fermi liquid, and scales in an approximately universal manner with doping. It is shown that standard transport theory at a van Hove singularity in the band structure can explain both the linear resistivity and these remarkable features of the thermopower in cuprates.

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The cuprate superconductors continue to pose a key problem as to the microscopic origin of their anomalous properties, which are presumably closely linked to their high transition temperatures. Recently a remarkable correlation was established between thermopower and transition temperature: The room temperature thermopower of five cuprate systems was found [1] to lie on a universal curve, as a function of doping, with the thermopower going through zero at the optimum doping associated with the maximum transition temperature for the materials. The temperature dependence [2–5] of the typical cuprate thermopower is also very unusual, in that it does not follow the T-linear behavior of a Fermi liquid, but is closer [5] to the T-independent behavior of an extremely narrow-band conductor with bandwidth less than the temperature [6]. But this narrow-band picture cannot be the explanation of the T-dependence observed, because the bandwidth in cuprates is known to be of order 1 eV from photoemission data [7]. Could a resolution of the paradox of the temperature-independent thermopower lie in identifying an appropriate flat feature in the band structure which duplicates "narrow-band" behavior?

High resolution angle-resolved photoemission data on high transition temperature 123 [8], 248 [8], and 2212 [9] materials have identified the presence of a saddle point (SP) in the band structure energy surface within 100–200 K of the Fermi energy, the SP being absent in the low-T_c n-type 214 material [10]. Such a SP corresponds to a logarithmic density of states singularity [van Hove singularity (VHS)]. In this paper we shall show by considering transport in the neighborhood of a SP that the VHS does provide the sharp feature needed to explain the temperature-independent thermopower, even though the overall bandwidth is of order 1 eV. As regards the doping dependence, the thermopower is found to go through zero when the Fermi level lies at the VHS. The universal relationship between the thermopower and transition temperature now receives a natural explanation in this model; as the Fermi level, controlled by doping, is swept through the SP, the density of states (DOS) at the Fermi level goes through a maximum and hence so does [11–13] T_c (e.g., the DOS dependence of the BCS formula). So we expect that the T_c maximum and the thermopower zero correspond to the Fermi level lying at the SP, and are one and the same. Confidence in this picture may be gained by noting that it is not in isolation, certain other anomalous properties, such as the marginal Fermi liquid (MFL) behavior [14], the specific heat jump [15], and the isotope shift [12] have also received an explanation in terms of the VHS.

Our approach is founded on standard transport theory, in terms of which the in-plane thermopower for tetragonal symmetry is given by [16] $S = \nu/\sigma$, where in the relaxation time approximation

$$\nu = -\frac{k_B C}{|e|}\sum_{\mathbf{k}} v_\alpha^2(\mathbf{k})\tau(\varepsilon_{\mathbf{k}})[(\varepsilon_{\mathbf{k}} - \mu)/k_B T] \times [-\partial f(\varepsilon_{\mathbf{k}})/\partial\varepsilon_{\mathbf{k}}], \quad (1)$$

$$\sigma = C\sum_{\mathbf{k}} v_\alpha^2(\mathbf{k})\tau(\varepsilon_{\mathbf{k}})[-\partial f(\varepsilon_{\mathbf{k}})/\partial\varepsilon_{\mathbf{k}}].$$

In (1) $v_\alpha(\mathbf{k})$ ($\alpha = x$ or y) is the phase velocity $\partial\varepsilon_{\mathbf{k}}/\partial\mathbf{k}_\alpha$ (in $\hbar = 1$ units) on the energy surface $\varepsilon_{\mathbf{k}}$, $\tau(\varepsilon)$ is the quasiparticle lifetime, $f(\varepsilon)$ is the Fermi function, μ is the chemical potential for electrons, and the constant $C = 2e^2/\text{volume}$.

Two opposite limits for (1) are ordinarily considered. In the Fermi liquid regime where temperature is low compared to the bandwidth, use of a Sommerfeld expansion in the integrals (1) gives thermopower proportional to temperature [17]

$$S_{\mathrm{FL}} \simeq -\frac{\pi^2}{3}\frac{k_B^2 T}{|e|}\frac{\partial \ln\sigma(\varepsilon)}{\partial\varepsilon}\bigg|_{\varepsilon=\mu}, \quad (2)$$

where $\sigma(\varepsilon) = C\sum_k v^2(\mathbf{k})\tau(\varepsilon_k)\delta(\varepsilon - \varepsilon_k)$. On the other hand, in the "classical" limit where T exceeds the electronic bandwidth, the thermopower is related to the entropy per carrier, giving the formula [6]

$$S_{\mathrm{cl}} \simeq -\frac{k_B}{|e|}\ln\left[\frac{2-f}{f}\right], \quad (3)$$

where, assuming a tight binding model with one orbital per site, f is the number of particles per site.

The experimental behavior [2–5] seen in many recent studies of cuprate thermopower is seen in Fig. 1. For

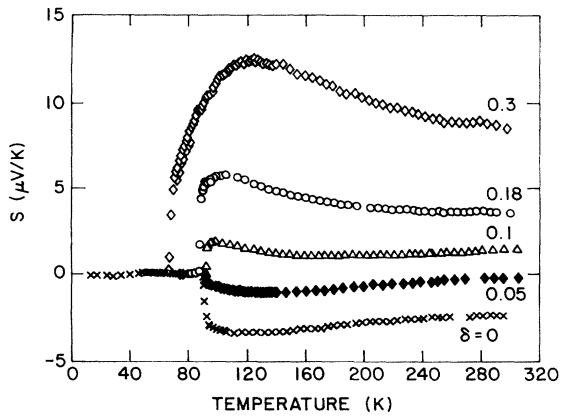

FIG. 1. Thermopower data of Cooper *et al.* on $YBa_2Cu_3O_{7-\delta}$ samples quenched from high temperature plotted as a function of temperature, for various oxygen depletions δ.

most of the temperature regime illustrated, the thermopower is nearly temperature independent or even decreasing with temperature, and this temperature-independent thermopower is strongly doping dependent (in the most oxygen-deficient sample, $\delta = 0.3$, S is, however, seen to increase with temperature at low temperatures). It should be mentioned that some data indicate the presence of a "superposition" on to this behavior of a weak T-linear component (not equivalent to the Fermi liquidlike $S \propto T$ because of the large intercepts), as, for example, in the a-axis Y-Ba-Cu-O thermopower (first part of Ref. [18]), but not in the second part of Ref. [18]. The present work is aimed at the Fig. 1 type thermopower behavior.

The thermopower in Fig. 1 clearly does not follow the Fermi liquid behavior (2) expected for the experimental regime, in which the highest temperature, 250 K, is much less than the electronic bandwidth of order 1 eV. In fact, the temperature independence of S is like that for the classical regime (3) which should only be valid when T greatly exceeds the bandwidth. We shall give a natural interpretation of this paradox in terms of transport in the neighborhood of a saddle point.

The proposal is that the saddle point is the dominant part of the band structure to be considered in the thermopower, as it is in the density of states. So to capture the essence of the problem, we evaluate the integrals (1) for the neighborhood of a single SP in the quasi-2D cuprate band structure. We take for the dispersion around a SP the model [14]

$$\varepsilon_{\mathbf{k}} = k_x k_y , \tag{4}$$

where $\mathbf{k}$ is defined within the region $|k_\alpha| \leq k_c$, k_c being a cutoff of order the Brillouin zone (BZ) dimension. Equation (4) gives a logarithmic density of states $N(\varepsilon) = (1/2D)\ln|D/\varepsilon|$ per spin, where $D = k_c^2$ is the half bandwidth.

Our calculation of the thermopower is based on the single relaxation time τ, derived from the self-energy, whose use is suggested on empirical grounds by the success of the MFL theory [19] in interpreting a wide range of cuprate properties (however, resistivity calculations for electron-electron scattering have also been based on velocity-weighted [20] and reciprocal lattice vector weighted [21] relaxation times). In the Born approximation the expression for $1/\tau$ may be written

$$1/\tau(\mathbf{k}_0) = 4\pi \sum_{\mathbf{k}_1\mathbf{k}_2} V^2(\mathbf{k}_2 - \mathbf{k}_0)[1 - f(\varepsilon_{\mathbf{k}_2})][1 - f(\varepsilon_{\mathbf{k}_1})] \times f(\varepsilon_{\mathbf{k}_1-\mathbf{k}_0+\mathbf{k}_2})[1 - f(\varepsilon_{\mathbf{k}_0})] \times \delta(\varepsilon_{k2} - \varepsilon_{k0} + \varepsilon_{k1} - \varepsilon_{\mathbf{k}_1-\mathbf{k}_0+\mathbf{k}_2}). \tag{5}$$

The model for the interaction, $V(\mathbf{q}) = W/[1 + W\prod(\mathbf{q})]$, is derived from the large-N slave boson model [12], where $\prod(\mathbf{q}) = (1/D)\ln|D/\varepsilon_q|$ is the polarizability in the charge channel, and W defines the large-q cutoff. It has been analytically demonstrated [14] in the special case of constant V, $\mu = 0$, and $T = 0$ that at low ε_k, $\tau(\mathbf{k})$ is a universal function of $\varepsilon_{\mathbf{k}}$ only, with the marginal Fermi liquid behavior [14,19], $1/\tau(\varepsilon) \propto \varepsilon$. Numerically, the $\mathbf{k}$ sums in (5) were done by implementing a four-dimensional extension of the standard tetrahedron method for calculating band structure DOS, keeping only vectors $\mathbf{k}$ inside the cutoff k_c. Calculations are done at constant particle number.

As a check on our procedure we calculate in Fig. 2 the temperature dependence of the resistivity $\rho(T) = 1/\sigma(T)$. According to MFL phenomenology [19], the linearity of scattering rate with energy, $1/\tau(\varepsilon) \propto \varepsilon$, leads to the linear resistivity $\rho(T) \propto T$. For the case $\mu = 0$ which does satisfy [14] the linearity of $1/\tau$ in ε, Fig. 2 shows that

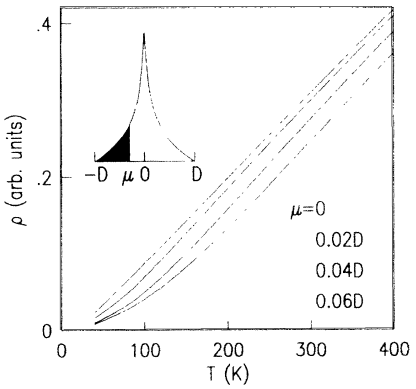

FIG. 2. Theoretical curves of resistivity vs temperature from Eq. (1) for σ, evaluating $\tau(\mathbf{k})$ in Born approximation [see Eq. (5)], with $D = 10000$ K, $W = 0.85D$. Curves labeled by different values of zero-T chemical potential μ_0 (see legend), top curve $\mu_0 = 0$, next to top curve $\mu_0 = 0.02D$, etc. Insert, DOS for model of Eq. (4), illustrating partial filling up to chemical potential μ.

a linear resistivity is indeed obtained. When μ is shifted away from the maximal T_c value $\mu = 0$, by say $\mu > 2T$, $\rho(T)$ exhibits a crossover to T^2 behavior, in accord with various data [22] on, for example, the underdoped n-type 214, 123 and Hg 1201 materials, and the overdoped Tl 2201 material.

The temperature dependence of the thermopower is illustrated in Fig. 3. Because of cancellations in Eq. (1) the thermopower is difficult to calculate accurately [16], but despite small random errors at the lowest temperatures, which could not be eliminated without prohibitively expensive calculations, the implications of the results in Fig. 3 are quite clear. The temperature behavior clearly resembles that in the experimental data (Fig. 1) very closely; the extended T-independent region in the Fig. 1 curves is well reproduced by the theory, and the curves for larger μ indeed manifest the significant T-linear region at low temperatures shown by the $\delta = 0.30$ experimental sample.

A comparison of the doping dependence of the thermopower with the experimental data is presented in Fig. 4, which is based on the universal thermopower plot [1] of Obertelli, Cooper, and Tallon (OCT). The OCT curve presents thermopower at 290 K either as (a) a plot directly in terms of doping per planar Cu derived from bond valence sums [23] (this method directly measures *planar* doping in the 123 material where the presence of chain holes complicates direct measurement) or (b) in terms of the ratio $T_c/T_c^{\max}$, where $T_c^{\max}$ is the maximum transition temperature in a given material, which is linked to doping via an empirical relationship [23]. In this plot five materials are found to lie on the same universal curve, as is clear from Fig. 4. We present the results of our thermopower calculation on the OCT plot in two ways. First, we identify the optimum hole concentration used by OCT, corresponding to the T_c maximum, $x_{\text{opt}} = 0.16$, with the point $\mu = 0$ in our model, when the relationship between μ and doping is obtainable by integrating the logarithmic DOS. In doing this one must note that the VHS only occupies a fraction of the BZ (in the specific heat work of Ref. [15] the best fit of this fraction to the data was 0.6); with the obvious *ab initio* choice of this fraction as 0.5, the dashed curve in Fig. 4 is obtained. Alternatively, we may plot thermopower versus $T_c/T_c^{\max}$, using BCS theory to calculate T_c, yielding the full curve in Fig. 4.

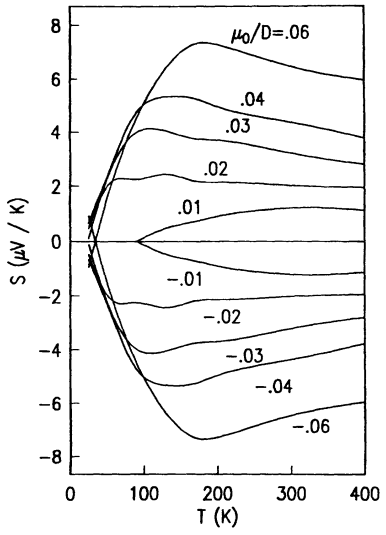

FIG. 3. Theoretical curves of thermopower vs temperature from Eq. (1), evaluating $\tau(\mathbf{k})$ from Eq. (5). Curves are labeled by the value of μ_0 in units of D; $D = 10000$ K, $W = 0.85D$.

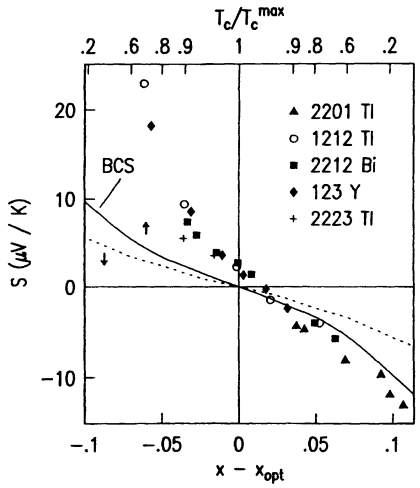

FIG. 4. Data points, universal thermopower plot [1] of Obertelli, Cooper, and Tallon (materials with hole concentration below 0.1 omitted), illustrating thermopower at 290 K plotted vs doping for materials illustrated in legend. 123 and 2223 materials plotted vs doping derived from bond valence sums (lower scale), remaining materials plotted in terms of their T_c's (upper scale), using relationship $T_c/T_c^{\max} = 1 - 82.6(x - x_{\text{opt}})^2$, with $x_{\text{opt}} = 0.16$. Dashed curve, theoretical thermopower at 280 K plotted vs doping relative to half filling of VHS (lower scale), assuming VHS occupies 50% of BZ. Full curve, plot of same quantity vs T_c (upper scale), calculated from BCS equation [12] with parameters $\omega_E = 700$ K, $D = 10000$ K, electron-phonon coupling $V_p/2D = 0.116$, $\mu^* = 0$, $T_c^{\max} = 93.9$ K.

The calculations are seen (Fig. 4) to be in agreement with, though somewhat underestimating, the data on the overdoped side of the VHS, but on the underdoped side, for dopings less than about 0.02 below optimum, the thermopower rapidly takes off exponentionally; in this heavily underdoped region it may be appropriate, due to the influence of the metal-insulator transition, to start from a quite different theoretical basis from that used here, in which the Luttinger Fermi surface no longer provides the correct underlying description of the ground state and low lying excitations. Note that, unlike an earlier approach [24] to the thermopower, the present calculation is not based on an empirical model for the mean free path, and

also does not fix the thermopower zero at the half filling (zero doping) point of the band [24] where the cuprates are insulating—a constraint incompatible with the OCT correlation which places the thermopower zero at the T_c maximum.

Another physical process which also leads to MFL behavior is nesting scattering [25]. It is interesting to speculate whether this mechanism could also reproduce the temperature-independent thermopower, but it is unclear how the universal OCT doping dependence could emerge from the nesting picture.

In conclusion, we have put forward the concept that the anomalous phase space for scattering of quasiparticles whose energy lies near a saddle point in the band structure can explain, on the one hand, the linear resistivity and its crossover to parabolic behavior, and, on the other hand, the sign, temperature dependence, doping dependence, and approximate magnitude of the thermopower in cuprates. The thermopower is a measure of scattering asymmetry about the Fermi level, and its magnitude is sensitive to the scattering potential and how it is modeled. The thermopower is also very sensitive [18] to splitting of the saddle points in materials with orthorhombic symmetry, in which the thermopower can also be explained within the present framework [26].

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