RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 51, NUMBER 9 1 MARCH 1995-I

Thermopower of the superconducting cuprates

H. J. Trodahl

*Department of Physics, Victoria University of Wellington, Wellington, New Zealand**

and Department of Physics, University of British Columbia, Vancouver, British Columbia, Canada

(Received 3 January 1995)

The normal-state thermoelectric power of the high-T_c superconducting cuprates shows a systematic but unusual dependence on temperature and on the concentration of holes in the CuO_2 planes. In this paper it is shown that the observed pattern is predicted within a conventional Fermi-liquid picture and follows from the observation, already inferred from thermal-conductivity data, that the acoustic phonons remain scattered predominantly by electrons up to room temperature.

There is an increasing body of evidence that the high-T_c superconducting cuprates can be understood on the basis of a conventional Fermi gas,[1] but a thorough understanding of all the transport properties on this or any other basis is not yet at hand. One of the most commonly measured transport coefficients which still lacks a satisfactory explanation is the thermopower.[2] Within a simple picture of conventional metals this parameter is expected to be approximately linear in temperature, with sufficiently pure metals showing a substantial "phonon drag" peak[3] below $\Theta_D/2$ (Θ_D=Debye temperature). The thermopower $S(T)$ of the high-T_c cuprates, typified by the results[4] for $Bi_2Sr_2CaCu_2O_8$ (Bi2212) in Fig. 1, differs from this simple behavior. The temperature dependence is most often linear in these materials, but the zero temperature extrapolated value (S_0) is nonzero,[2,5] as illustrated in Fig. 1(b). There is a systematic shift with increasing concentration of holes on the CuO_2 planes which is so nearly universal in these materials that it has been used as a gauge of the hole concentration.[6] It has caused some confusion that the shift is towards more negative values with increasing hole concentration, in the opposite sense than implied by the simple expectation that the thermopower has the carrier sign. This expectation is not to be trusted, for even in some simple metals (e.g., the noble metals) the sign of the thermopower differs from that of the carriers.[3] Indeed the calculated band structure of at least one member of the "hole carrier high-T_c" class, $YBa_2Cu_3O_7$ (Y123), has been shown to lead to a negative thermopower.[7]

The behavior shown in Fig. 1 is found in many of the cuprates, including all the Bi[4], Tl[5], and Hg[8] series. In these materials the thermopower is linear in temperature, and the slope is not a strong function of either the material or the hole concentration. The most prominent exception is Y123, with a temperature dependence which is both weaker and nonlinear, but the shifts still occur without large changes to that dependence.[9] Thus a set of curves $S(T)$ for samples with differing hole concentration is a set of nearly parallel lines, with the extrapolated value S_0 falling from about 20 μV/K for an underdoped sample ($T_c = T_{c\,\max}/2$) to near zero when T_c approaches 0 K on the overdoped side.[4] (The third law of thermodynamics implies that the thermopower must fall to zero at 0 K, so that even in the absence of superconductivity the curves of Fig. 1 would deviate from the linear behavior at some low temperature.) This simple behavior has not been predicted on the basis of any unconventional theory for the electron gas. It is the purpose of this paper to establish that it can be understood within conventional Fermi-liquid theory, and that the apparently anomalous behavior is simply a manifestation of the strong scattering of phonons by elec-

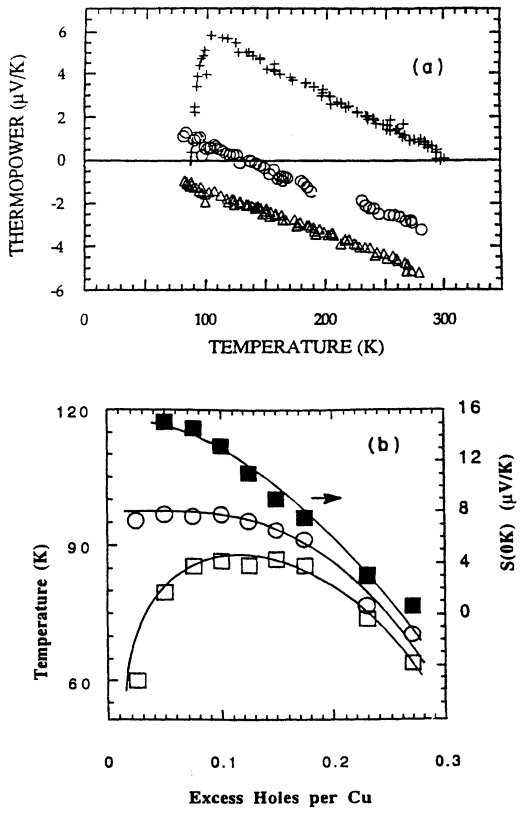

FIG. 1. (a) Thermopower of Bi2212, after Ref. 4. The various curves are for different concentrations n_h of holes on the CuO_2 planes, controlled by systematically altering the O stoichiometry. (b) shows the dependence on hole concentration of the extrapolated zero-temperature thermopower (filled squares; right scale) as well as the zero resistance and superconducting onset temperatures (open squares and circles, respectively; left scale).

trons which has already been noted in connection with the thermal conductivity of these materials.[10]

The thermopower of conventional metals is comprised of a diffusion contribution, which as suggested by the name is related to the temperature dependence of the carrier diffusion, and a phonon drag contribution resulting from the transfer of phonon momentum to the electron gas. The diffusion contribution is proportional to temperature provided there is no thermal excitation to energies at which there is structure in the quasiparticle contribution to the conductivity. The phonon drag contribution is more complex, falling at low temperatures as the phonons freeze out and at high temperatures as the excess phonon momentum is limited by phonon-phonon (anharmonic) scattering. Thus the "phonon drag peak" in conventional metals rises as T^3 below $\Theta_D/10$ and falls as T^{-1} above approximately $\Theta_D/2$. It is in part the absence of such a clear peak which has discouraged the interpretation of the cuprate thermopowers in terms of phonon drag.

It is significant in this connection that above 100 K the thermopowers of several transition metals show a close resemblance to that of the superconducting cuprates.[11] There can be little doubt that the thermopower in these entirely conventional metals is adequately described by a diffusion plus drag combination, but that the usual T^{-1} dependence is absent. Evidently the phonon-phonon scattering in these metals remains weaker than phonon-electron scattering even at room temperature. It is central to the present interpretation of the cuprate thermopowers that the same model applies to the cuprates, so that the phonons remain scattered predominantly by electrons up to 300 K. Thermal conductivity data support this model; the lack of strong temperature dependence in the thermal conductivity above T_c establishes that phonon-phonon scattering is weak and its sudden rise below T_c can be related to a reduction of a dominant phonon-electron scattering upon entering the superconducting states.[10,12]

A further argument which has been used against a phonon drag model for the cuprates is based on the weak dependence of the thermopower on impurities introduced at a level sufficient to affect the resistivity.[2] It is known from conventional metals that the phonon drag thermopower is often diminished by impurities. That sensitivity is however related to phonon, rather than electron, scattering, for it derives from a reduction in the fraction of the phonon momentum which is transferred to the electron gas. Even in conventional metals there are cases in which the introduction of *electron* scatterers leads to no change or even a small increase in the phonon drag thermopower.[3,13] Thus neither this nor the previous argument for discarding the phonon drag model apply to the superconducting cuprates, and it is shown below that the inclusion of phonon drag can explain the thermopower results within a conventional Fermi liquid.

The diffusion thermopower for an electron gas is given by the Mott formula,[3]

$$S_d(T)=\frac{\pi^2k^2T}{3e}\left(\frac{\partial \ln\sigma}{\partial\epsilon}\right)_\eta \qquad (1)$$

or on its generalization for situations in which there is structure in the quasiparticle characteristics within kT of the Fermi energy η.[7,14] If E_0 is the typical energy range over which there are changes in the parameters describing the gas then the Mott formula predicts a thermopower which is proportional to temperature,

$$S_d(T)\approx(280\ \mu\text{V/K})(kT/E_0).$$

The magnitude of the slope in Fig. 1 then yields a value of about 0.8 eV for E_0, which is the correct order of magnitude considering the narrow bands in the high-T_c cuprates.

The theory of the phonon drag thermopower is well established,[3,15,16] and the most useful expression for the present discussion, applicable in the constant relaxation time approximation, is

$$(S_g)_{xx}=\frac{-2|e|}{(\sigma_{xx}/\tau)\Omega}\sum_{qj}\left(\frac{\partial N}{\partial T}\right)\alpha_{qj}\langle\Delta v_x\rangle u_x. \qquad (2)$$

Here τ is the electron relaxation time, σ and Ω are the conductivity tensor and volume of the material, and N is the occupation number of the phonon with momentum $\mathbf{q}$ in the jth branch, $\mathbf{u}$ is the phonon velocity, and $\Delta\mathbf{v}$ is the change in the electron velocity caused by the absorption of the phonon. The change in the crystal momentum of the electron, $\Delta\mathbf{k}$, is of course equal to the phonon wave vector $\mathbf{q}$. $\alpha_{\mathbf{q}j}$ is the fraction of phonons $(\mathbf{q}\ j)$ which are absorbed by electrons, and $\langle\Delta\mathbf{v}\rangle$ is the average electron velocity change for the scattering events involving that phonon. In what follows α is set to unity, in accordance with the contention that electron scattering dominates all other phonon scattering channels.

It is important in the present context to notice that the contribution to S_g is negative if the change in the electron velocity is in the same sense as that of the absorbed phonon, and positive if the two velocities are opposed. It will be demonstrated below that the balance between the positive and negative contributions is altered systematically as the hole concentration n_h changes, which leads to the observed correlation between S_0 and n_h.

The temperature dependencies of the terms in the sum of Eq. (2) are given by the function

$$(dN/dT)=(k/\hbar\omega)(X^2/\sinh^2X),\quad X=\hbar\omega/(2kT). \qquad (3)$$

Contributions from phonons $\mathbf{q}$ in different branches are thus proportional to (u/ω), so that the acoustic branch dominates due to both the low frequency and the high speed of acoustic phonons. Inserting the frequency high in the acoustic branch (100 cm^{-1}) (Ref. 17) into Eq. (3) leads to the absolute temperature scale in Fig. 2, and it can be seen that the contribution to the phonon drag thermopower, even from this relatively high-frequency acoustic phonon, will vary by less than 15% between 100 and 300 K. Thus phonon drag will lead to a simple shift of the linear diffusion thermopower in this temperature regime, as is illustrated in Fig. 2. In this picture the extrapolated S_0 is simply the saturation value of the phonon drag thermopower.

The high-T_c cuprates are all nearly tetragonal, quasi-two-dimensional conductors, so that the surfaces of constant quasiparticle energy are approximately cylindrical with fourfold rotational symmetry about the cylinder axis.[18,19] Thus the cross section of the Fermi surface looks qualitatively as shown in the repeated zone scheme in Fig. 3. As the hole density is raised the regions of empty states expand toward

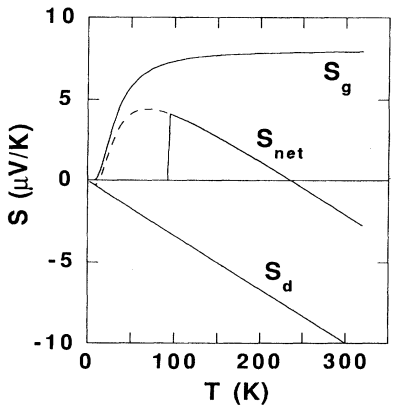

FIG. 2. The temperature dependence of a contribution to the phonon drag thermopower, labeled S_g, from a typical phonon in the acoustic branch. The diagram also shows a negative diffusion contribution (S_d) and illustrates how the observed thermopower in the cuprates results from a sum ($S_{\rm net}$) of the two contributions. The net thermopower is set to zero below a superconducting transition temperature of 90 K, where the value it would have in the absence of superconductivity is indicated by a dashed line. The magnitude of S_d has been set to reproduce the linear term observed in Bi2212, while that of S_g gives S_0 of 8 μV/K, in the center of the observed range for Bi2212 (see Fig. 1).

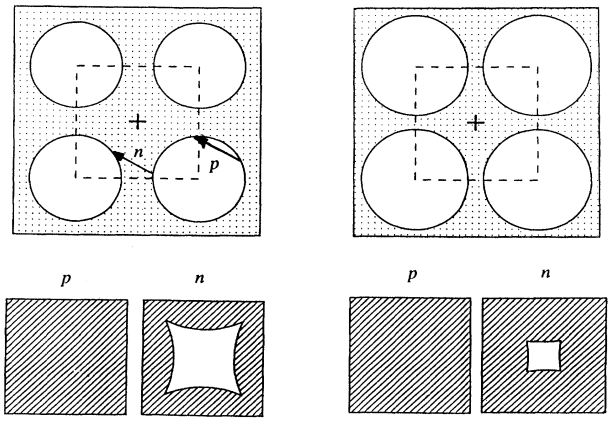

FIG. 3. Transitions in a band with a circular cylindrical Fermi surface in the repeated zone scheme. The left (right) panels correspond to a hole filling factor of 0.44 (0.60). The upper panels show filled regions of the electron Brillouin zone as filled with an array of dots; empty regions are shown clear. The first Brillouin zone is shown dotted, with Γ marked by a cross. The arrows show a set of electron transitions caused by a given phonon wave vector ($\mathbf{q}=\Delta\mathbf{k}$) and label them as contributing a positive (p) or negative (n) phonon drag thermopower. The lower panels show the regions within the *phonon* Brillouin zone which support transitions making positive and negative contributions to the phonon drag thermopower.

their neighbors, ultimately contacting them at some critical concentration (e.g., 0.79 for a circular Fermi surface). The magnitude of the phonon drag thermopower will now be estimated within such a Fermi surface.

As a start S_g is determined in the very simple model which ignores all scattering between the different cylinders in Fig. 3, in the limit of circular symmetry [$\mathbf{v}=\pm(\hbar/m)\mathbf{k}$, $\sigma=(N_c e^2\tau/m)$]. Treating the acoustic phonons in the Debye approximation [$\omega=cq$, $u_x=c(q_x/q)$, $c=$acoustic phonon speed] leads to

$$S_g=\frac{\mp C_a[1-\beta(T)]}{N_c|e|}, \tag{4}$$

where

$$\beta(T)=\frac{\sum \frac{\partial N}{\partial T}(\hbar\omega)(q_z/q)^2}{\sum\left(\frac{\partial N}{\partial T}\right)\hbar\omega},$$

and

$$C_a=\frac{1}{\Omega}\sum\left(\frac{\partial N}{\partial T}\right)\hbar\omega$$

is the heat capacity of the acoustic phonons, which is even flatter above 100 K than is the Einstein function of Eq. (3). N_c is the carrier density. $\beta(T)$ lies between zero (in strictly two dimensions) and unity. Equation (4) can be compared to the corresponding result ($2C_a/3N_c e$) for a spherical Fermi surface in three dimensions.[3] Note that ($C_a/N_c e$) $\approx k/e=86$ μV/K. This figure is a substantial overestimate in all conventional metals, for it ignores the reduced phonon speed near the Brillouin zone boundary and the contributions of opposite sign arising from umklapp events. The typical magnitude of S_0 found in the cuprates, up to a few tens of μV/K, agrees well with the model.

The competition between positive and negative contributions to S_g is affected by changes in the hole concentration. To illustrate the point Fig. 3 shows a set of transitions available for one particular phonon $\mathbf{q}$ for a circular Fermi surface. The phonon energy is too small to cause a transition to a discernibly different energy on the scale of the diagram, so that they are drawn as between points directly on the Fermi surface. For convenience the scattering events are labeled as p or n transitions according to whether they make a positive or negative contribution to S_g. (Recall that the simply connected regions contain empty states, and that the electron velocity is directed into these regions.) The regions in the Brillouin zone containing phonons which can cause n transitions differs from that for p transitions, as shown in the lower panels in Fig. 3. Large $\mathbf{q}$ phonons can cause either type of transition, and as these involve relatively distant parts of the Fermi surface they all have similarly large values of $\Delta\mathbf{v}$. I suggest that the two contributions from these high-momentum phonons approximately cancel. The contribution from lower $\mathbf{q}$ phonons is purely positive, so that the net phonon drag thermopower will be positive, as observed for the low hole-doped materials represented by the Fermi surfaces of Fig. 3.

An increase in the hole concentration is of course accompanied by an expansion of the regions in the Brillouin zone which contain empty electron states. The tubes then expand out toward their neighbors, increasing the volume in the phonon Brillouin zone which makes a negative contribution to

S_g. To illustrate this point Fig. 3 has diagrams corresponding to two different hole concentrations. Ultimately, when the hole Fermi surfaces contact, all phonons contribute to both p and n transitions, and it is then that the extrapolated value S_0 falls to near zero.

The most important consequence of the present model is that even the apparently anomalous behavior of the thermopower of the superconducting cuprates does not require an explanation based on an unconventional Fermi liquid. In addition it supports the contention that the phonon mean free path is limited by electron scattering events. The diffusion thermopower is clearly negative for all hole concentrations and proportional to the temperature for the majority of the cuprates. The exception is Y123, but in this material the strong energy dependence in the quasiparticle conductivity predicts a thermopower[7] which agrees in sign, magnitude, and temperature dependence with the diffusion thermopower implied by the data and interpreted within the present model. The complex temperature dependence for Y123 is presumably related to a competition between the portions of the Fermi surface dominated by the CuO_2 plane and the CuO chains. The simpler electron dispersion found in the other members of the high-T_c class, those without chains affecting the electronic states, can be expected to predict a more conventional temperature-linear diffusion thermopower.

This research was carried out with the support of a contract with the New Zealand Foundation for Research, Science and Technology. I am grateful for the support of the National Science and Engineering Research Council of Canada and hospitality of the Department of Physics at the University of British Columbia where some of this work was done. I have benefited from helpful discussions with A. B. Kaiser.

---

*Permanent address.

[1] W. E. Pickett, H. Krankauer, R. E. Cohen, and D. J. Singh, Science **255**, 46 (1992).

[2] A. B. Kaiser and C. Uher, in *High Temperature Superconductors*, edited by A. V. Narlikar (Nova, New York, 1991), Vol. 7, p. 353.

[3] F. J. Blatt, P. A. Schroeder, C. Foiles, and D. Greig, *Thermoelectric Power of Metals* (Plenum, New York, 1976).

[4] C. R. Varoy, H. J. Trodahl, R. G. Buckley, and A. B. Kaiser, Phys. Rev. B **46**, 463 (1992).

[5] C. K. Subramaniam, A. B. Kaiser, H. J. Trodahl, A. Mawdsley, and R. G. Buckley, Physica C **203**, 98 (1992); C. K. Subramaniam, C. V. N. Rao, A. B. Kaiser, H. J. Trodahl, A. Mawdsley, N. E. Fowler, and J. F. Tallon, Supercond. Sci. Technol. **7**, 30 (1994).

[6] S. D. Obertelli, J. R. Cooper, and J. F. Tallon, Phys. Rev. B **46**, 14 928 (1992).

[7] P. B. Allen, W. E. Pickett, and H. Krankauer, Phys. Rev. B **37**, 7482 (1988); Y. Kubo, J. Supercond. **7**, 1 (1994).

[8] C. K. Subramaniam, M. Paranthaman, and A. B. Kaiser, Physica C **222**, 47 (1994).

[9] A. Mawdsley, H. J. Trodahl, J. L. Tallon, J. Sarfati, and A. B. Kaiser, Nature **328**, 233 (1987); A. J. Lowe, S. Regan, and M. A. Howson, Phys. Rev. B **44**, 9757 (1991); A. J. Lowe, S. Regan, and M. A. Howson, J. Phys. Condens. Matter **4**, 8843 (1992); L. Cohn, E. F. Skelton, S. A. Wolf, and J. Z. Liu, Phys. Rev. B **45**, 13 140 (1992); H. J. Trodahl and A. Mawdsley, *ibid.* **36**, 8881 (1987).

[10] C. Uher, in *Physical Properties of High Temperature Superconductors*, edited by D. M. Ginsberg (World Scientific, Singapore, 1992), Vol. 3.

[11] R. Carter, A. Davidson, and P. A. Schroeder, J. Phys. Chem. Solids **31**, 2374 (1970).

[12] C. Uher, Y. Q. Liu, and J. F. Whitaker, J. Supercond. **7**, 323 (1994).

[13] C. van Baarle, Physica **33**, 424 (1967); R. P. Huebener, Phys. Rev. **171**, 634 (1968).

[14] A. B. Kaiser and G. Mountjoy, Phys. Rev. B **43**, 6266 (1991).

[15] R. D. Barnard, *Thermoelectricity in Metals and Alloys* (Taylor and Francis, London, 1972).

[16] M. Bailyn, Phys. Rev. **112**, 1587 (1958); **120**, 381 (1960); **157**, 480 (1967).

[17] W. Kress, U. Schröder, J. Prade, A. D. Kulkarni, and F. W. de Wette, Phys. Rev. B **38**, 2906 (1988); K. K. Yim, J. Oitmaa, and M. M. Elcombe, Solid State Commun. **77**, 385 (1991); A. D. Kulkarni, F. W. de Wette, J. Prade, U. Schröder, and W. Kress, Phys. Rev. B **43**, 5451 (1991).

[18] W. E. Pickett, Rev. Mod. Phys. **61**, 433 (1989).

[19] D. L. Novikov and A. J. Freeman, Physica C **212**, 233 (1993); D. J. Singh and W. E. Pickett, Physica C **203**, 193 (1992).