Thermoelectric power of the thallium-based superconductor $Tl_2Ba_2Ca_2Cu_3O_{10-\delta}$

Y. Xin, K. W. Wong, and C. X. Fan
Department of Physics and Astronomy, University of Kansas, Lawrence, Kansas 66045

Z. Z. Sheng and F. T. Chan
Department of Physics, University of Arkansas, Fayetteville, Arkansas 72701
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The temperature dependence of the thermoelectric power of the high-temperature superconductor $Tl_2Ba_2Ca_2Cu_3O_{10-\delta}$ is reported. The contribution of holes from the valence band satisfying a Fermi-liquid model gives the major part of the measured thermoelectric power. The results show that the conduction-band electrons also contribute to the total output of the thermoelectric power and the portion of the electron's contribution increases with temperature. An explicit expression for the thermolectric power of the 2:2:2:3 phase was derived based on a two-band model and the experimental data, which is given as $S(\mu V)=0.121T-(280-0.2T)e^{-550/T}$. A general formula, $S=AT+(B\lambda+CT)\exp(-\lambda/T)$, is found to give a close description of the thermoelectric power of various cuprate high-T_c superconductors.

The absolute thermoelectric power S in an excellent indicator of many fundamental aspects of charge transport in a conducting material. We can extract useful information from the characteristics of S-temperature dependency to reveal the normal-phase transport mechanism of a material. Furthermore, the sign of S can be used to distinguish the major charge carrier in the transport process. In certain regimes, S can also provide knowledge for the bandwidths and band gaps which govern the transport properties of the material.

Since the discovery of high-T_c superconductors, there have been a large number of experimental and theoretical efforts to understand the thermoelectric power of such a material. However, a satisfactory interpretation of experimental results are still lacking. $Tl_2Ba_2Ca_2Cu_3O_{10-\delta}$ is a very stable superconductor with a transition temperature above 120 K, which is the highest to date. Several groups[1-3] have studied the thermoelectric power of Tl-based compounds, including the 2:2:2:3 phase; but, unfortunately, a quantitative study is far from complete due to a lack of single phase samples. We carried out thermoelectric power study on a very pure 2:2:2:3 phase sample in a quantitative manner. Based on the experimental result, we propose a two-band (conduction CB, valence VB) conduction mechanism and give an explicit expression of the thermoelectric power of the Tl-based superconductor. This theoretical expression may also be applied to other high-T_c superconductors.

Samples used in this study were prepared by our recently developed method.[4] The sample $Tl_2Ba_2Ca_2Cu_3O_{10-\delta}$ is a pure 2:2:2:3 phase sample (no impurity being detected by powder x-ray diffraction). The thermoelectric power was measured with a modified differential method[5] in the temperature range from 300 to 100 K.

Figure 1 shows the S plot against temperature of the sample $Tl_2Ba_2Ca_2Cu_3O_{10-\delta}$. At room temperature, the value of S for this sample is 1.8 μV/K and S increases almost linearly with decreasing temperature. It has a maximum value of 12.3 μV/K at about 135 K and drops abruptly as T approaches T_c. These values are to be compared to those in Ref. 5 and will be discussed later.

The thermoelectric power-temperature dependency of $Tl_2Ba_2Ca_2Cu_3O_{10-\delta}$, as viewed from the overall behavior, is similar to those reported for $(La,Sr)_2CuO_{4-\delta}$, $RBa_2Cu_3O_{7-\delta}$ (R = rare earth), $Bi_2Sr_2CaCu_2O_{8-\delta}$, and $Tl_2Ba_2CaCu_2O_{8-\delta}$.[6-15] To explain the temperature dependence of S and the exhibition of a broad maximum above T_c for these high-T_c materials, some groups suggested a model of a strong phonon-drag effect,[16-18] while others expressed a strong doubt on this suggestion.[19,20] Based on our experimental data, there appears to be no evidence in support of phonon-drag contribution to the thermoelectric power. We found that the thermoelectric power can be simply explained from the diffusion of the charge carriers.

A specific formula for the thermoelectric power of a metal satisfying the Fermi liquid model, due to electron

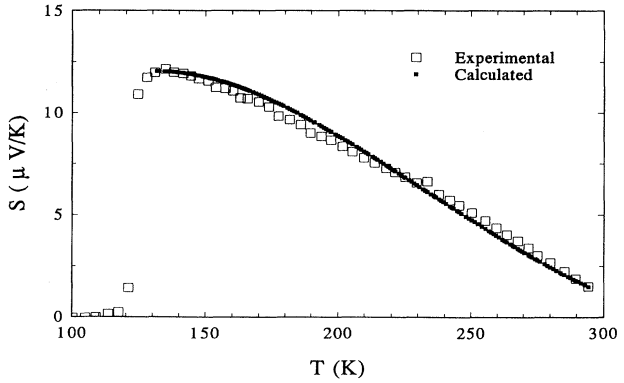

FIG. 1. Thermoelectric power vs temperature of $Tl_2Ba_2Ca_2Cu_3O_{10-\delta}$.

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diffusion is given by[21]

$$S=-\frac{\pi^2}{3}\frac{k}{e}\left[\frac{kT}{E_{F_0}}\right]\left[\frac{d\ln(E)}{d\ln E}+\frac{d\ln v^2(E)}{d\ln E}+\frac{d\ln\tau(E)}{d\ln E}\right], \quad (1)$$

where $\tau(E)$ is the relaxation (scattering) time of electronic charge carrier of energy E, e is the magnitude of the electronic charge of the carriers, E_{F_0} is the zero-temperature Fermi energy measured from the band edge (positive for electrons and negative for holes), $n(E)$ is the density of electron or hole states, and v is an average electron velocity.

The S-T relation given by Eq. (1) with a single kind of charge carrier cannot describe the S-T dependency in Fig. 1. To investigate the origin of this discrepancy, let us check the calculated band structure of $Tl_2Ba_2Ca_2Cu_3O_{10-\delta}$ in Fig. 2.[22] It is clear that the two-dimensional Cu-O antibonding bands are present along the Γ-X-Z axes (more details to the band structure can be found in Ref. 22). The number of these degenerate bands is proportional to the number of the Cu-O planes in each of the unit cells. These bands are nearly half filled; thus the valence holes carry out a metallic conduction. Cutting through these two-dimensional Cu-O bands are the broad Tl-6s O-2p bands. These Tl-O related bands extend down well below the Fermi level. However, above the Fermi level, they break with a small gap of about 0.2 eV along the Γ-D-Z direction. Since energy of the lower set bands at the broken point is almost independent of the wave vector, localized electrons can be present in these bands. Consequently, these bands can be viewed as partially filled valence bands while the empty bands above can be viewed as a empty conduction bands in a semiconductorlike structure. In the temperature range investigated, it is quite reasonable to assume that a finite number of electrons can be excited into the conduction band from the Tl-O and Cu-O valence bands. Therefore, it is plausible to establish a simplified two-band conduction mechanism for the normal-state charge transport of this material. It is worth noting that the bands generated by the Cu-O chain in $YBa_2Cu_3O_{7-\delta}$ (Ref. 22) are similar in character to those of the Tl-O in $Tl_2Ba_2Ca_2Cu_3O_{10-\delta}$. Our experimental result is therefore consistent with the assumption that the thermoelectric power comes from the combinations of both the conduction- and valence-band carriers. Because of the semiconductive character of the conduction electrons, the contribution from the valence-band holes in the Cu-O plane dominates at low temperature, although it is obvious that the contribution from the conduction-band electrons is increasing with the temperature.

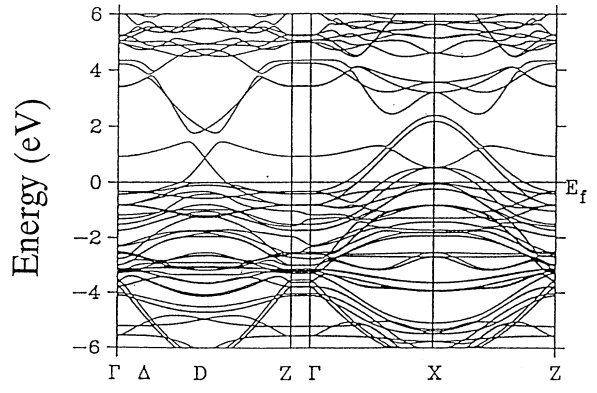

FIG. 2. Band structure of $Tl_2Ba_2Ca_2Cu_3O_{10-\delta}$.

For such a two-band model, the contribution to S can be described by[21]

$$S=(S^+\sigma^+ + S^-\sigma^-)/\sigma\ , \quad (2)$$

where $\sigma=\sigma^+ + \sigma^-$ is the sum of the conductivities from the valence and the conduction bands and S^+ and S^- are their respective Seebeck coefficients. This formula is quite general and quite independent of any specific mechanism of thermoelectric power production.

Since the valence bands of $Tl_2Ba_2Ca_2Cu_3O_{10-\delta}$ are nearly half filled, we may consider the holes in these bands as free holes described by a Fermi-liquid distribution. For a single band semiclassical model, an alternative to Eq. (1) is to write

$$S^+=-\frac{\pi^2}{3}\frac{k}{e}\left[\frac{kT}{E_{F_0}}\right]\left[\frac{d\ln\sigma^+(E)}{d\ln E}\right], \quad (3)$$

where $\sigma^+(E)$ is the electrical conductivity of the material. The p-type conduction, which is believed to be responsible for superconductivity, would be roughly given by Eq. (3). Considering the degeneracy of the Cu-O valence bands, a degenerate factor g should be added to the expression, i.e.,

$$S^+=-g\frac{\pi^2}{3}\frac{k}{e}\left[\frac{kT}{E_{F_0}}\right]\left[\frac{d\ln\sigma^+(E)}{d\ln E}\right]. \quad (3')$$

The contribution from conduction-band electrons would be given by the nondegenerate semiconductor expression[9,21]

$$S^-=+\frac{k}{e}\left[\frac{|E_c|}{kT}+\frac{d\ln\tau(E)}{d\ln E}+\frac{5}{2}\right], \quad (4)$$

$$\frac{|E_c|}{kT}=\ln\left[\frac{n}{N_c}\right],\quad N_c\equiv 2\left[2\pi m_n^*\frac{kT}{h^2}\right]^{3/2},$$

where n is the concentration of mobile electrons, and E_c is the energy measured from the center of the band gap to the bottom of the conduction band (for a typical semiconductor, this equals to E_c-E_F).

We may expect the metallic conductivity of the valence band to be proportional to the reciprocal of temperature, i.e., $\sigma^+\propto 1/T$. The conductivity of the conduction electrons, σ^-, should be described by the formula for semiconductors,

$$\sigma^-\propto e^{-E_c/kT}\ .$$

From the experimental result, we may assume that $\sigma^+ \gg \sigma^-$ in this case, then

$$\sigma^+/\sigma \approx 1 \tag{5}$$

and

$$\frac{\sigma^-}{\sigma} \propto Te^{-E_c/kT} . \tag{6}$$

From Eqs. (3) and (5), the first term in Eq. (2) is a linear term of T. We may write the term as AT, where A is a constant. The second term of Eq. (2) is more complicated. However, if we take $\lambda = E_c/k$ as a constant based on Eqs. (4) and (6), we obtain a simple form for the second term of Eq. (2):

$$(\beta\lambda + CT)e^{-\lambda/T} , \tag{7}$$

where B and C are constants. Hence the thermoelectric power of $Tl_2Ba_2Ca_2Cu_3O_{10-\delta}$ may approximately be expressed as

$$S = AT + (B\lambda + CT)e^{-\lambda/T} . \tag{8}$$

Based upon our experimental data, the constants can be best fitted to give $A = 0.121$ $\mu V/K^2$, $B = -0.509$ $\mu V/K^2$, $C = 0.200$ $\mu V/K^2$, and $\lambda = 550$ K, then the final expression for the thermoelectric power of the Tl-based 2:2:2:3 phase $Tl_2Ba_2Ca_2Cu_3O_{10-\delta}$ can be described by

$$S(\mu V) = 0.121T - (280 - 0.2T)e^{-550/T} . \tag{9}$$

We plot the calculated S along with the experimental S in Fig. 1. In the temperature range measured, the calculated values of S are in excellent agreement with the experimental data.

We now use the experimentally determined value of λ to evaluate the energy gap in the semiconductorlike band structure for the Tl-O layers of $Tl_2Ba_2Ca_2Cu_3O_{10-\delta}$. It is generally true that E_c has the same order of magnitude as that of the energy gap E_g in an intrinsic semiconductor. Usually, it is assumed that $E_c = \frac{1}{2}E_g$. According to the relation $\lambda = E_c/k$. When $\lambda = 550$ K, the magnitude of E_c is calculated as 0.05 eV. We therefore estimated that the energy gap is about 0.1 eV. This value is in the same order of magnitude as the calculated E_g value of 0.3 eV from the band structure.[22] It is worth noting that we do not exclude the possibility that the measured energy gap is the result of the presence of donor impurity states.

Another important constant A gives the measured contribution from the mobile holes in the Cu-O planes. From Eqs. (2), (3'), (5), (8), and (9), we can get

$$0.121 \times 10^{-6} = -g\frac{\pi^2}{3}\frac{k}{e}\left[\frac{k}{E_{F_0}}\right]\left[\frac{d\ln\sigma^+(E)}{d\ln E}\right] . \tag{10}$$

Taking the calculated value of $E_{F_0} = -2.41$ eV (Ref. 22) and $g = 6$ (there are six Cu-O planes in a unit cell for $Tl_2Ba_2Ca_2Cu_3O_{10-\delta}$), we get from Eq. (10) that

$$d\ln\sigma^+(E)/d\ln E = 1.99 .$$

The term $d\ln\sigma^+(E)/d\ln E$ can be rewritten as $\frac{3}{2} + d\ln\tau^+(E)/d\ln E$. The factor $\frac{3}{2}$ comes from Fermi statistics, while the hole relaxation time $\tau^+ = l/\bar{v}$, where l is the mean-free-path length. Approximately, $l \propto 1/(n_p \pi d^2)$, where n_p is the hole density and d is the interpolycrystalline grain-void average diameter. Since the energy eigenvalue of the hole inside each intergrain space is proportional to $1/d^2$, we obtain $\tau^+ \propto E^{1/2}$. Therefore the term $d\ln\sigma^+(E)/d\ln E \approx 2$. Based on this same argument we expect that the hole conductivity in the ab plane for a single crystal σ^+_{ab} would just be proportional to $E^{3/2}$. This is confirmed in Ref. 23. From Eqs. (2), (4), (6), and (9), we calculated the value of σ^-/σ, which is 0.011, 0.023, 0.075, 0.097, and 0.237 at 130, 150, 200, 300, and 800 K, respectively. This can be confirmed with the experimental results in which the resistivity shows an almost linear temperature dependency.

We also used the formula given by Eq. (8) to analyze the previously published data[5] of the thermoelectric power of a $Tl_2Ba_2Ca_2Cu_3O_{10-\delta}$ (2:2:2:3 phase $>95\%$) sample. For the best fitting to the measured curve, we have in this case $A = 0.141$ $\mu V/K^2$, $C = 0.15$ $\mu V/K^2$, $\lambda = 510$ K, and B unchanged. As mentioned above, the parameter A is related to the contribution from the mobile holes in the Cu-O planes. The change of the value of A indicates that oxygen content in the previous sample is different from the sample in the present experiment. Any oxygen deficiency would reduce the absolute value of the E_{F_0} in Eq. (10). A larger A value implies a decrease in number of holes. The λ value for the previous sample is slightly smaller than that of the sample in the present work. Since the λ depends on the energy band gap between the Tl-O band and the conduction band, the change of λ indicates the altering of this band gap. We believe that the possible cause for this alternation is the increase in impurity from the previous sample. Impurity bands lie within the gap and are near the bottom of the conduction band. We have mentioned that the sample for the present work is a very pure 2:2:2:3 sample whereas the previous one is a sample of less than 5% impurity. The presence of impurities would also affect the relaxation time of the electrons so that the C value is also changed in the previous sample. We can conclude that the quantitative values for the thermoelectric power of the $Tl_2Ba_2Ca_2Cu_3O_{10-\delta}$ material is sensitive to the oxygen content and the impurities of a sample.

We have pointed out earlier, when $T = 800$ K, σ^+ is still several times greater than σ^-, so we may still use Eq. (9) to roughly predict the S-T behavior of the Tl-based 2:2:2:3 phase at such high temperatures. Figure 3 plots the S-T curve given by Eq. (9) for $Tl_2Ba_2Ca_2Cu_3O_{10-\delta}$ within an extended temperature range from 100 to 800 K. Based on the curve, we would like to point out the basic feature of the thermoelectric power described by the general formula

$$S = AT + (B\lambda + CT)\exp(-\lambda/T) .$$

The thermoelectric power takes a maximum value at a temperature not too far above T_c and a minimum value at a higher temperature. This minimum value may be negative depending on a particular material. For Tl 2:2:2:3, the minimum is negative and occurs near 400 K.

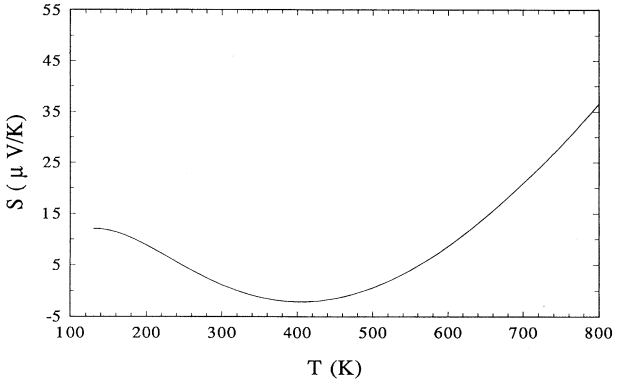

FIG. 3. Predicted S-T curve of $Tl_2Ba_2Ca_2Cu_3O_{10-\delta}$ given by $S(\mu V)=0.121T-(280-0.2T)e^{-550/T}$ in an extended temperature range.

The thermoelectric power increases rapidly with temperature after the minimum temperature. Since S can change sign over a temperature range, it points to the presence of both positive and negative carriers.

It should be mentioned that following the original model by Uher *et al.*,[6] different two-band models have been proposed. Generally, these previous treatments of the VB conduction was based on a "narrow band" Hubbard picture. However, the Hubbard model approach does not produce good fitting to the experimental data and does not give the same T dependency as Eq. (8). The most common two-band model expression with a non-Hubbard picture was $S=AT+B/T$, where the first term AT was claimed to be for the metallic hole contribution and the second term B/T for the semiconductor-like contribution. However, if the measured data is used to fit the formula, a controversy will arise, which is the sign of the constants. A must be negative and B must be positive in order to fit experimental data (the negative A and positive B were first mentioned by Yan *et al.*[24]), which conflicted with the original physical claims. Therefore, the formula $S=AT+B/T$ is not valid as a description of the thermoelectric power of high-T_c superconductors. Furthermore, there is no good fitting obtained with any of the above-mentioned proposed models, and none can show a double change of sign for S similar to that shown in Fig. 3.

In conclusion, we have investigated the thermoelectric power of a polycrystalline 2:2:2:3 phase sample $Tl_2Ba_2Ca_2Cu_3O_{10-\delta}$ and proposed a two-band conduction mechanism for this material. The Fermi-liquidlike hole conduction is dominant within a broad temperature range. The contribution from the conduction electrons can be described with a semiconductorlike expression. The derived formula $S(\mu V)=0.121T-(280-0.2T)e^{-550/T}$ is in excellent agreement with the experimental data of the Tl 2:2:2:3 phase sample. Based on this study, we believe that the general formula,

$$S=AT+(B\lambda+CT)\exp(-\lambda/T)\ ,$$

may be valid for the thermoelectric power of various cuprate high-T_c superconductors. The direction dependency of σ^+ and σ^- also allows for detail analysis of S_{ab} vs S_c as a function of T (Ref. 23) and has been shown by us to fit well with the reported experimental data measured from a single-crystal $YBa_2Cu_3O_{7-\delta}$.

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