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Anisotropic thermopower of the organic superconductor κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br

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The thermopower of the organic superconductor κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br single crystals has been measured in two crystallographic directions **a** and **c** within the most conducting organic donor molecule plane. [Here BEDT-TTF represents bis(ethylenethio)-tetrathiafulvalene.] While the thermopower in the **a** direction is positive, the thermopower in the **c** direction is negative. The drastic anisotropy in thermopower reveals that the carriers in the **a** direction are holelike, whereas the carriers in the **c** direction are electronlike. A calculation based on the tight-binding electronic band structure is able to describe the temperature dependence of the anisotropic thermopower, but with a much reduced band dispersion.

There is a renewed interest in the organic superconductors stimulated by the discoveries of new organic superconductors κ-(BEDT-TTF)$_2X$ with superconducting transition temperatures in the range 10–13 K (where BEDT-TTF represents bis(ethylenedithio)-tetrathiafulvalene; X is the anion]; with X=Cu(SCN)$_2^-$, Cu[N(CN)$_2$]Br$^-$, and Cu[N(CN)$_2$]Cl$^-$, the transition temperatures are 10.4, 11.6, and 12.8 K, respectively[1–3]). While critical-field and transport studies have revealed the quasi-two-dimensionality[4–7] of these salts, the anisotropy within the most conducting plane has been much less studied.

In this paper we report our measurements and calculations of the thermopower of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br single crystals in the **a** and **c** crystallographic directions. The thermopower in both directions was measured from 300 to 4 K. While the thermopower in the **a** direction is positive, the thermopower in the **c** direction is negative. These data reveal that the carriers in the **a** direction are holes, whereas the carriers in the **c** direction are electrons. A calculation of the anisotropic thermopower within the most conducting plane by utilizing a tight-binding model reproduced the general behavior of the thermopower, although with a much reduced band dispersion.

The κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br single crystal samples were grown at Argonne National Laboratory by an electrochemical synthesis technique, which is described elsewhere.[2] The typical geometric shape of the crystals is that of a rhombic plate with the longer diagonal axis being the **a** direction and the shorter axis being the **c** direction.[8] The typical dimensions of the single crystals is 0.8 mm for each side of the rhombus and 0.1 mm for the thickness.

The thermopower of the single-crystal samples was measured by the following technique. One end of the sample was thermally anchored to a single-crystal quartz block attached to the temperature-controlled heat sink. The other end of the sample was suspended and attached with a thin-film heater with dimensions of $1\times0.5\times0.2$ mm^3. Two junctions of a Cromel-Constantan differential thermocouple were attached to the two ends of the sample by use of GE varnish. Two 12.5-μm gold wires were attached to the two ends of the sample with silver paste, serving as the voltage leads. Another two gold leads may also be attached to the sample to allow four-terminal ac resistance measurements. The generation of a temperature gradient of 0.5 K and the measurement cycle were computer controlled, and the digitally acquired data are averaged over several cycles. The estimated uncertainty in magnitude of thermopower is less than 15%.

In Fig. 1 we show the temperature dependence of the resistance of one sample. When the temperature decreases from 300 K, the resistance increases. It reaches a peak value 50% more than the room-temperature value at 100 K. When the temperature further decreases, the resistance decreases drastically by more than an order of magnitude before the sample superconducts at about 12 K. The nonmetallic behavior of the resistance above 100 K is reminiscent of the resistivity observed in κ-(BEDT-TTF)$_2$Cu(NCS)$_2$.[1,4]

In the inset of Fig. 1, we show the resistance of the

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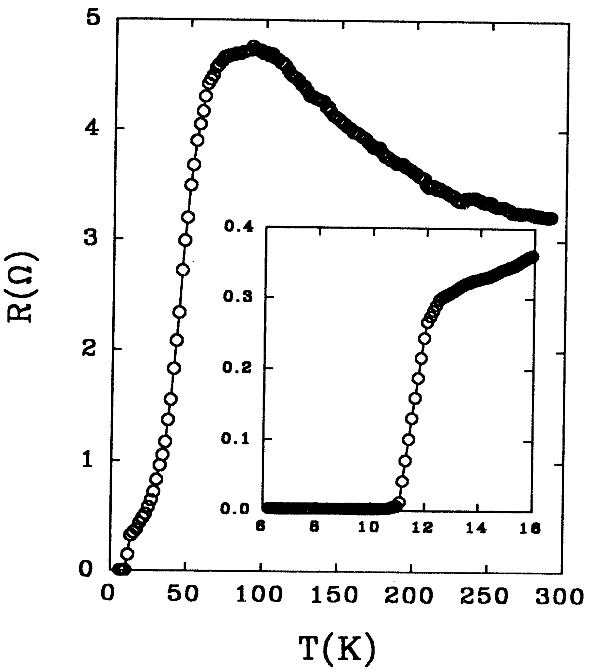


FIG. 1. Temperature dependence of the resistance of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br. In the inset is shown the resistance at the vicinity of the superconducting transition temperature.

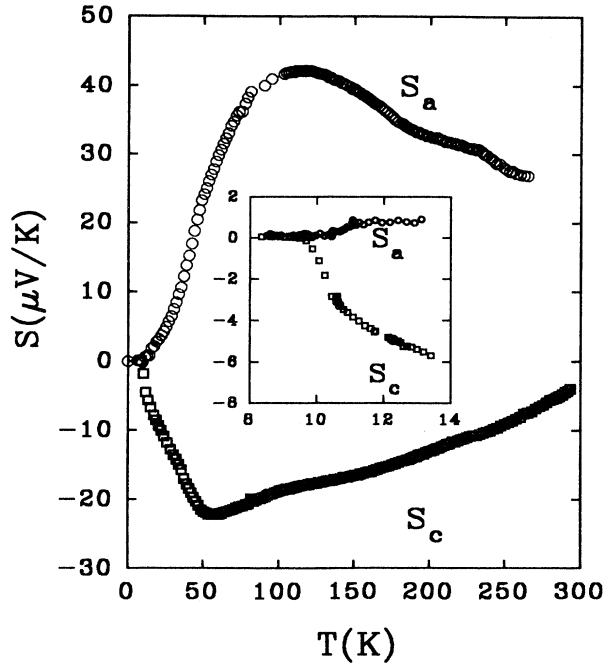


FIG. 2. Observed temperature dependence of the thermopower of κ-(BEDT-TFF)$_2$Cu[N(CN)$_2$]Br in the **a** and **c** directions from 300 to 4 K. In the inset we show the data near $T_c \sim 10.5$ K.

sample at the vicinity of the superconducting transition. The transition temperature, defined as the temperature at which the resistance reaches 50% of the normal-state resistance, is about 11.4 K.

In Fig. 2 we show the temperature dependence of the thermopower in the **a** and **c** directions. In the **a** direction, the thermopower S_a is about 25 μV/K at 270 K and increases with decreasing temperature. It reaches a maximum of about 42 μV/K at 120 K and then decreases toward lower temperature. Before the sample superconducts at 10.7 K, S_a becomes very small with a value of about 0.8 μV/K. In the **c** direction, however, the thermopower S_c is negative, with a value of -3 μV/K at 290 K, and it decreases to about -22 μV/K at 60 K before starting to increase toward the lower temperature. S_c reaches -3 μV/K before it vanishes at the superconducting transition. The midpoint transition temperature determined by the thermopower measurement is slightly lower than that determined by the resistance measurement. This discrepancy is likely due to the finite temperature gradient of 0.5 K across the sample during the thermopower measurement.

At first glance the pronounced peak at about 100 K for S_a and 60 K for S_c may be attributed to the phonon-drag effect. When electron moves in a metal, as a result of the electron-phonon interaction, the phonon system will come into equilibrium with electron system by displacing its momentum space. This corresponds to a drift of phonons which results in a lattice heat current contributing to the Peltier heat and thus to the thermopower.[9] At high temperature, the phonon-drag part of the thermopower, $S_g \sim 1/T$, and at low temperature, $S_g \sim T^3$. Hence the total thermopower at high and low temperatures is $S \sim S_d + A/T$ and $S \sim S_d + BT^3$, respectively, where S_d is the electron diffusive part of thermopower which is linear with temperature in the degenerate Fermi-liquid limit.[10] The peak in thermopower emerges when the system crosses over from high-temperature behavior to the low-temperature one. The temperature at which the peak appears is usually $\sim 1/5\Theta_D$, where Θ_D is the Debye temperature.

Although the phonon-drag effect seems to offer an explanation to the observed peak in the thermopower, it is difficult to reconcile with the observation of the peak in resistivity which occurs in the vicinity of the temperature at which the peak in the thermopower also shows up. The phonon-drag effect usually does not contribute significantly to the electric conductivity. The peak in resistivity occurring at the similar temperature as in the thermopower hints that there may be an alternate mechanism at work. We attempt to explain this peak structure in terms of the Boltzmann transport based on the tight-binding band calculation.

From the Boltzmann transport equations, the thermopower tensor $\mathbf{S}_{ij}$ is

$$\mathbf{S}_{ij} = \frac{1}{eT}\sum_{k=1}^{3}(\underline{K}_0^{-1})ik(\underline{K}_1)_{kj} \ . \tag{1}$$

In terms of the Fermi energy E_F and the Fermi distribution f^0, the matrices $(\underline{K}_0)_{ij}$, which is the inverse of $(\underline{K}_0^{-1})_{ij}$, and $(\underline{K}_1)_{ij}$ are expressed as follows:[9,11]

$$(\underline{K}_0)_{ij}=\frac{1}{4\pi^3}\frac{\tau}{\hbar}\int\int v_i v_j\left[-\frac{\partial f^0}{\partial \varepsilon}\right]\frac{dS}{v}d\varepsilon\ , \tag{2}$$

$$(\underline{K}_1)_{ij}=\frac{1}{4\pi^3}\frac{\tau}{\hbar}\int\int v_i v_j(\varepsilon-E_F)\left[-\frac{\partial f^0}{\partial \varepsilon}\right]\frac{dS}{v}d\varepsilon\ , \tag{3}$$

where the velocities v_i, v_j, and v are defined as $v_i=\partial\varepsilon/\partial(\hbar k_i)$, $v_j=\partial\varepsilon/\partial(\hbar k_j)$, and $v=(v_i^2+v_j^2)^{1/2}$. The scattering time τ is assumed to be energy independent. At the range of the temperature that we conduct thermopower measurements, most of the contribution to $\mathbf{S}_{ij}$ comes from those states within the energy range k_BT around the Fermi surface.

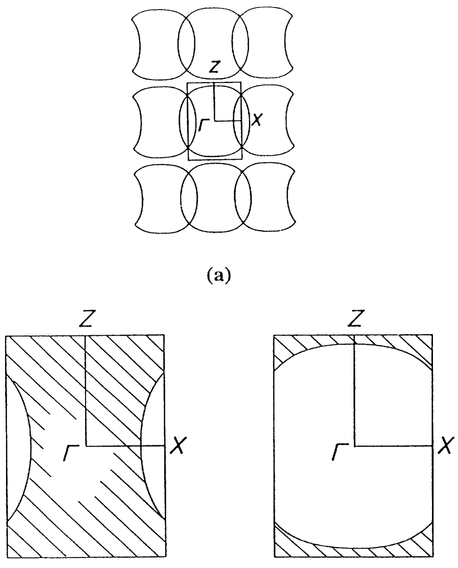
The sign of the thermopower is usually determined by the nature of the carriers. The positive sign of the thermopower in the **a** direction and the negative sign in the **c** direction indicate that the Fermi surface in the **a** direction is holelike and the Fermi surface in the **c** direction is electronlike. The band calculation of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br reveals that the highest occupied band, which is derived from the highest-occupied molecular orbitals of the donor molecules, is half-filled.[12] In Fig. 3(a) we show the schematics of the Fermi surfaces associated with the highest-occupied bands.[12] This Fermi surface is separated into the hole and electron surfaces, as shown in Fig. 3(b). Therefore, in the $\Gamma-X$ direction, namely, the crystallographic **a** direction, the thermopower should be holelike, whereas the thermopower in the $\Gamma-Z$ direction, or **c** direction, should be electronlike. This is in agreement with our experimental data.

By employing Eq. (1) and the calculated band electronic structure of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br,[12] obtained with the extended Hückel tight-binding method,[13] we calculated the temperature dependence of the thermopower along the **a** and **c** directions. We obtained the best fit of the calculated thermopower to the experimental data by adjusting the magnitude of the band dispersion.

In Fig. 4 we show the temperature dependence of the thermopower thus calculated for κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br. We can see that our calculation reproduced the general behavior of the thermopower in the **a** and **c** directions, including the sign, magnitude, and overall temperature dependence. For convenience, we denote the maximum value of S_a and the minimum value of S_c by $S_{a,\max}$ and $S_{c,\min}$, respectively. Likewise, we denote the temperature at which the $S_{a,\max}$ and $S_{c,\min}$ value occur by $T_{a,\max}$ and $T_{c,\min}$, respectively. We found that, with increase of the magnitude of dispersion of the highest-occupied band, the $T_{a,\max}$ and $T_{c,\min}$ values increase almost linearly, while the $S_{a,\max}$ and $S_{c,\min}$ values remain nearly unchanged. The calculated $T_{a,\max}$ and $T_{c,\min}$ values are in best agreement with the experimental data when the magnitude of the band dispersion is reduced by a factor of 5 from the available band calculation.

The peak in the thermopower (also in the resistivity) may be understood by the following intuitive argument. From the calculated dispersion relations of the occupied and unoccupied bands around the Fermi level,[12] we can see that there are relative flat portions of the occupied bands in the $\Gamma-X$ and $\Gamma-Z$ directions. At high temperature the contribution from those carriers excited over to an unoccupied band from these flat parts of the occupied band may dominate, as a result of the significant thermal excitation and relative large density of state at these portions of the bands. The behavior of these excited carriers would resemble a semiconductor, which diverges toward lower temperature.[9] However, at low temperature the thermal excitation is diminished and the metallic behavior recovers. The peak occurs at the temperature at which the sample crosses over from the dominant semiconducting behavior to the metallic behavior.

In order for the thermal excitation to prevail at a mod-



(a)

(b)

FIG. 3. (a) Schematics of the Fermi surface of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br. (b) The hole (left) and electron (right) pockets of the Fermi surface.

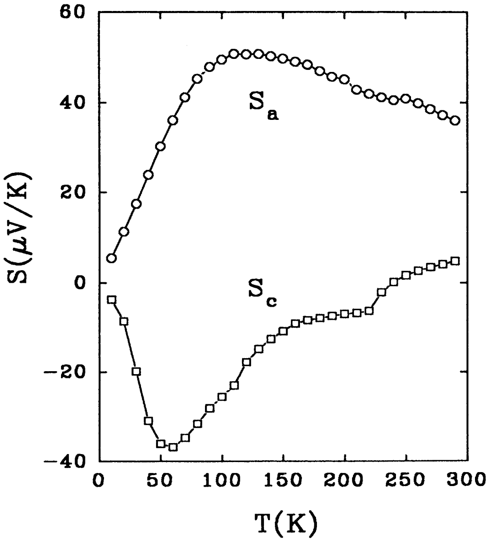


FIG. 4. Calculated temperature dependence of the thermopower of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br in the **a** and **c** directions.

est temperature of 100–300 K, the band dispersion must be significantly reduced from the available band calculation, as the above rigorous calculation points out. However, the reduction of the band dispersion from the above calculation may not imply a real small value of the band dispersion; rather, it may hint a strong enhancement of the density of states at the Fermi level. This enhancement of the density of states may be attributed to the significant electron-electron correlations. In a similar organic superconductor κ-(BEDT-TTF)$_2$Cu(SCN)$_2$, the observations of a Shubnikov–de Haas oscillation reveal that the band calculation description of the topology of the Fermi surface is not unreasonable. However, the observed cyclotron mass $m_c \sim (3.0–4.0)m_e$ (m_e is the free-electron mass), which is much larger than what is expected from the calculated bandwidth. This discrepancy has been attributed to the electron many-body effect.[14] In fact, Toyota and Sasaki[15] offered an alternative explanation for the resistance maximum in κ-(BEDT-TTF)$_2$Cu(SCN)$_2$. They proposed that the intersite Coulomb interaction symmetrically splits the band respect to the Fermi surface. When temperature decreases, the transfer integrals increase as a consequence of the lattice contraction and thus the gap between the split bands decreases. The maximum of resistance may be understood as the point when the insulator-to-metal transition occurs. Further investigations to clarify these possibilities are needed.

Previous measurements on the thermopower of κ-(BEDT-TTF)$_2$Cu(SCN)$_2$ show that, in the **c** direction, there are two maxima occurring at 140 and 50 K, respectively.[16] In fact, we also observed a similar structure in the thermopower when we measured the thermopower in the [110] direction. In Fig. 5 we show the thermopower in the [110] direction. The double-peak structure may result from the mixing of the thermopower contributed from the electron and hole pockets.

In summary, we have measured the anisotropic thermopower of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br single crystals in the most conducting plane, i.e., the organic donor molecule plane. Our data show that the Fermi surface consists of a holelike part and an electronlike part in the **a** and **c** directions, respectively. Calculations based on a tight-binding model describe the magnitude and temperature dependence of this anisotropic thermopower with a much reduced band dispersion, which hints at the possibility of a strong enhancement of the density of states at the Fermi surface due to electron-electron interactions.

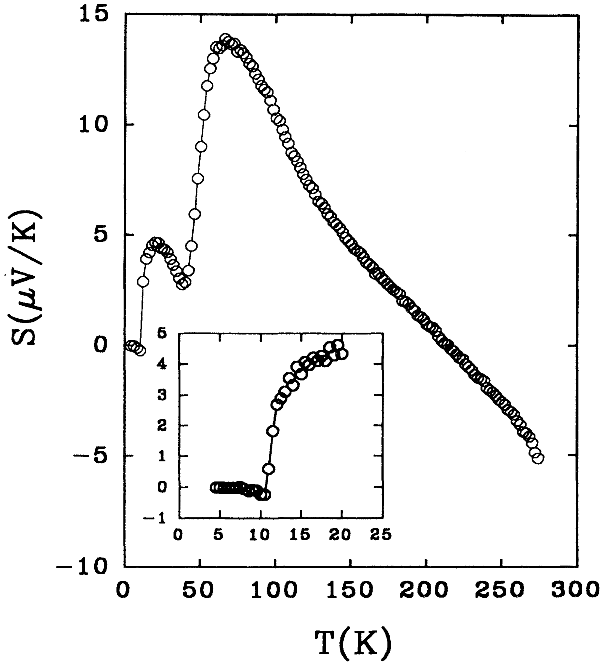


FIG. 5. Observed temperature dependence of thermopower of a κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br single crystal in the [110] direction.

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