Heat Conduction in κ-(BEDT-TTF)$_2$Cu(NCS)$_2$

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The first study of thermal conductivity, κ, in a quasi-two-dimensional organic superconductor of the κ-(BEDT-TTF)$_2X$ family reveals features analogous to those already observed in the cuprates. The onset of superconductivity is associated with a sudden increase in κ which can be suppressed by the application of a moderate magnetic field. At low temperatures, a finite linear term—due to a residual electronic contribution—was resolved. The magnitude of this term is close to what is predicted by the theory of transport in unconventional superconductors. [S0031-9007(98)07704-7]

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The superconductors of the κ-(BEDT-TTF)$_2X$ family [1] [BEDT-TTF: organic molecule bis(ethylenedithio)-tetrathiafulvalene] share a number of similarities with the high-T_c cuprates [2]. Both sets of compounds are quasi-two-dimensional with superconductivity confined to conducting planes sandwiched between insulating layers. The metallic state in both families exhibits common features such as low carrier densities, strong electronic correlations, and the proximity of an antiferromagnetic insulating state. While Shubnikov–de Haas experiments [3] have established the existence of a well-defined Fermi surface in the κ-(BEDT-TTF)$_2X$ family, this metallic state presents some more unconventional properties—such as a pseudogap in the electronic density of states in κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br [4]—which have been compared to analogous features in underdoped cuprates [2]. As for the symmetry of the superconducting order parameter, it has yet to become the subject of consensus since nowadays it is the case in the cuprates. While early penetration-depth studies on κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ led to conflicting results [5], recent NMR [6] and specific heat [7] studies on κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br provided evidence for the presence of nodes in the superconducting gap.

In this Letter we present the first study of thermal conductivity in a member of this family. According to our results, heat transport in κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ presents features which have already been detected in YBa$_2$Cu$_3$O$_{7-\delta}$ (YBCO) and other high-T_c cuprates. Notably, the observation of a residual electronic thermal conductivity at very low temperatures provides strong support for the presence of nodes in the superconducting order parameter.

We measured the thermal conductivity of five κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ single crystals using a standard one-heater–two-thermometer configuration similar to the one described elsewhere [8]. Our setup allowed us to measure, in addition to electrical and thermal conductivities, the thermoelectric power of the sample. Direct visual measurements of sample dimensions led to a gross determination of the geometric factor ($\pm 50\%$) due to irregularities in the samples' shape and thickness. Determining the absolute value of the resistivity proved to be very difficult. We found room-temperature resistivities varying from 35 to 80 mΩ cm. A comparable dispersion can be found in the technical literature on this compound. We used a unique room-temperature resistivity value (54 mΩ cm) when comparing different samples. At very low temperatures, we found that in all samples the voltage signal of the standard *IVVI* configuration was less than the *IIVV* configuration (the order of Is and Vs refers to the spatial sequence of current (I) and voltage (V) electrodes on the sample). This is a signature of a meandering charge current path characteristic of highly anisotropic superconductors with inhomogeneous contacts [9]. Therefore, we refrained from using the nominal value of resistivity in our analysis of thermal conductivity data.

Figure 1 presents the temperature dependence of the thermal conductivity for the two samples which were most thoroughly studied. The striking feature of the figure is the upturn in thermal conductivity at the onset of the superconducting transition. All of the samples studied presented such an upturn, but its intensity—reflected in the height of the consequent peak in $\kappa(T)$—was found to be strongly sample dependent. The ratio $\frac{\kappa_{\max}}{\kappa(T_c)}$ is 1.3 in sample 1 and 1.05 in sample 2. The residual restivity ratio $\frac{\rho(300K)}{\rho(T\to 0)}$ was found to be 410 in sample 1 and 250 in sample 2. Thus, as expected, the intensity of the upturn is correlated with the concentration of disorder in the sample. The positive sign of thermopower for both samples indicated that the orientation of heat current was nearly parallel to the quasi-one-dimensional sheets of Fermi surface and thus mainly implied the holelike carriers of the two-dimensional pockets [10].

A similar upturn in the thermal conductivity of high-T_c superconductors has been the subject of controversy

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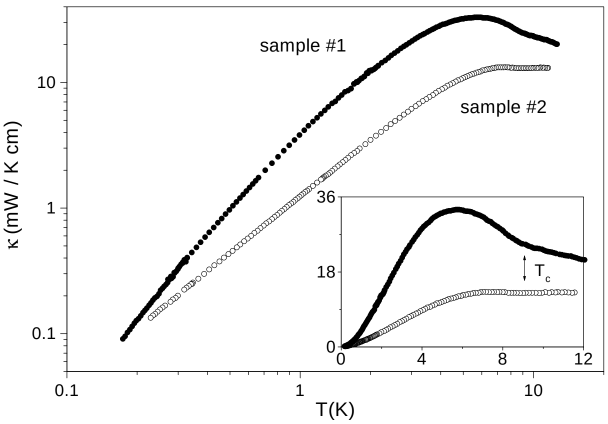

FIG. 1. Temperature dependence thermal conductivity in two different samples. Note the upturn at T_c. Inset shows a linear presentation.

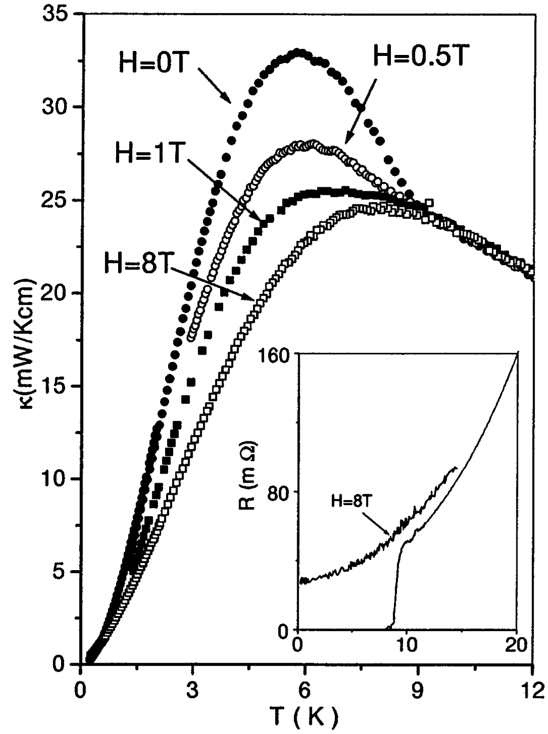

FIG. 2. The temperature dependence of the thermal conductivity in sample 1 for magnetic fields applied normal to the highly conducting planes. Inset shows the temperature dependence of the resistance of the same sample.

for several years [11]. The increase in thermal conductivity below T_c indicates that the condensation of electrons in the superconducting state strengthens heat transport by reducing the scattering of heat carriers. The debate was centered on the identity of these heat carriers. While an orthodox scenario [12] invoked an increase in the lattice conductivity due to condensation of electrons, experimental evidence for a very unusual increase in the electronic relaxation time in the superconducting state [13] led to the suggestion [11] that at least part of the upturn in κ is due to a steep increase in the electronic contribution. Strong support for the latter point of view was provided by thermal Hall effect measurements [14]. Our observation of this upturn in κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ raises the same questions. Surface resistance studies have reported an increase in the microwave conductivity of the system below T_c [15]. Compared to YBCO [13] this increase is modest, but its very existence makes it tempting to stretch the analogy with the cuprates and suggest that part of the upturn in $\kappa(T)$ reported here is due to electrons. However, the Wiedmann-Franz law (with should be employed cautiously due to the uncertainties on the absolute value of resistivity) implies that, just above T_c, the electronic contribution counts for only 5% of the total thermal conductivity. Thus, while the final issue of the question waits for thermal Hall effect measurements in the superconducting state of this compound, one can safely attribute the main part of this feature to the enhancement in the lattice conductivity consequent to a sudden decrease in electronic scattering at T_c. This very visible effect of electronic condensation on lattice conductivity indicates the strength of the electron-phonon coupling in this system, as already documented by neutron [16] and Raman [17] scattering studies. This is to be contrasted to the case of (TMTSF)$_2$ClO$_4$, where lattice conductivity was found to remain unchanged by the superconducting transition [8].

A supplementary source of information is the effect of the magnetic field. Figure 2 shows $\kappa(T)$ of sample 1 for different values of magnetic field applied normal to the highly conducting planes. The inset of the figure shows the electrical resistivity of the normal and the superconducting states. In the normal state, a magnetic field of 8 T does not affect the thermal conductivity within the experimental resolution ($<1\%$), but it induces a sizeable (15%) decrease in charge conductivity. This is an additional indication of lattice-dominated thermal conductivity in the vicinity of T_c. The peak is suppressed with the application of a moderate magnetic field. But the decrease in thermal conductivity is only monotonous at higher temperatures. This is seen in Fig. 3 which presents the field dependence of thermal conductivity for various temperatures. For temperatures higher than 2 K, thermal conductivity decreases with increasing field as a result of the reintroduction of the scattering quasiparticles by the magnetic field. A more remarkable structure appears at lower temperatures when $\kappa(H)$ exhibits a dip. This minimum indicates a competition between increasing and decreasing contributions to κ. Note that only the electronic component can be enhanced by the application of a magnetic field. Thus, the size of the jump in $\kappa(H)$ just below H_{c2} is an upper limit to the difference between electronic thermal conductivities in the normal and superconducting states. According to an early theory [18], in the vicinity of H_{c2}, the fading of a spatially inhomogeneous gap leads to a rapid enhancement in the

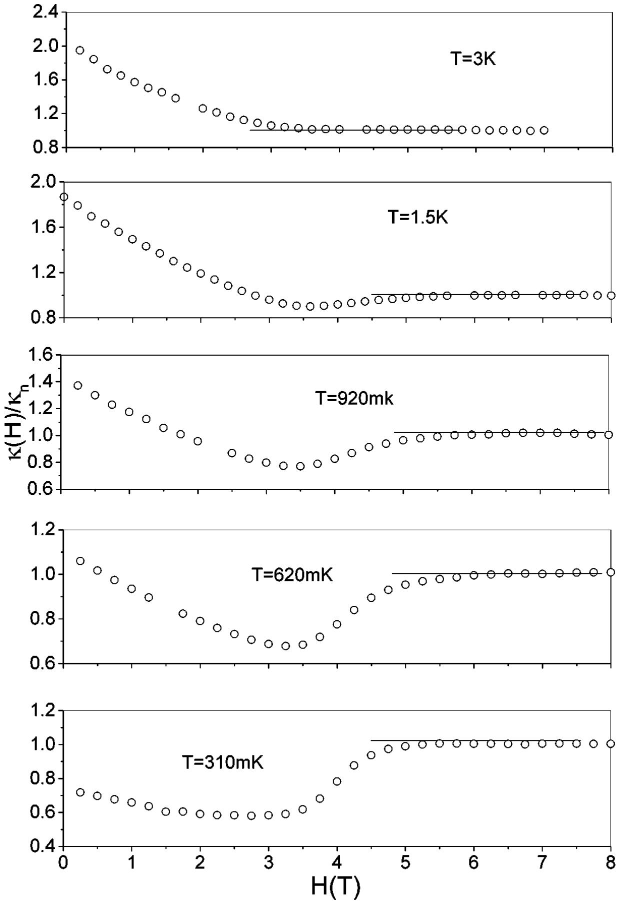

FIG. 3. The field dependence of the normalized thermal conductivity in sample 1 for different temperatures. Deviation from the horizontal line marks H_{c2}. Note the gradual apparition of a dip at low temperatures.

density of states of quasiparticles traveling perpendicular to the vortex axes. Note that, according to this bulk probe of superconductivity, H_{c2} becomes temperature independent below 1 K.

The main part of the initial field-induced decrease of thermal conductivity is due to the effect of the magnetic field on the phonon mean-free path. However, an estimation of the dominant phonon wavelength at low temperatures ($\lambda_{\mathrm{ph}} = \frac{\hbar v_s}{k_B T} \simeq 240$ nm/K) exceeds by 2 orders of magnitude the coherence length at $T = 0.62$ K so that no vortex scattering of phonons is expected. This is confirmed by the regular decrease in $\kappa(H)$ up to fields of a few teslas. The vortex scattering of heat carriers has been reported in much smaller fields with long intervortex distances [19]. Here, the observed field-induced decrease is a result of the scattering of phonons by electronic excitations including those which are extended out of the vortex cores. As first pointed out by Volovik [20], the enhancement of these latter delocalized electronic excitations by a magnetic field due to a Doppler shift in quasiparticle spectrum dominates the properties of the mixed state of unconventional superconductors [21].

Evidence for unconventional superconductivity comes from our low-temperature results. Figure 4 presents the low-temperature behavior of thermal conductivity in normal and superconducting states for the two samples. The remarkable feature of the figure is the presence of a finite linear term in the thermal conductivity of the superconducting state indicative of a residual electronic contribution. In both samples the magnitude of this term is a sizeable fraction of the normal electronic term. For sample 1, we extended our zero-field measurements down to $T = 0.16$ K and found that, for $T < 0.27$, $\kappa(T)$ presents an $aT + bT^3$ temperature dependence with $a = \kappa_e^s/T = 0.20 \pm 0.09$ mW/K^2 cm and $b = 11 \pm 5$ mW/K^4 cm. The large uncertainties are mainly due to the geometric factor. The cubic term gives an estimation of the maximum phonon mean-free path using the kinetics gas equation $\kappa_{\mathrm{ph}} = \frac{1}{3} c_{\mathrm{ph}} v_s l_{\mathrm{ph}}$, where $c_{\mathrm{ph}} = \beta T^3$ is the lattice specific heat ($\beta = 23.6$ μJ/K^4 cm^3 [22]) and v_s is the velocity of sound ($v_s = 5.10^3$ m/s [23]). This yields $l_{\mathrm{ph}} = 28$ μm which is comparable to the sample thickness ($\simeq 20$ μm). In the normal state, due to the lack of data for $T < 0.25$ K the extraction of the κ_e^n/T value at $T = 0$ is less straightforward. But one can reasonably expect that the ballistic

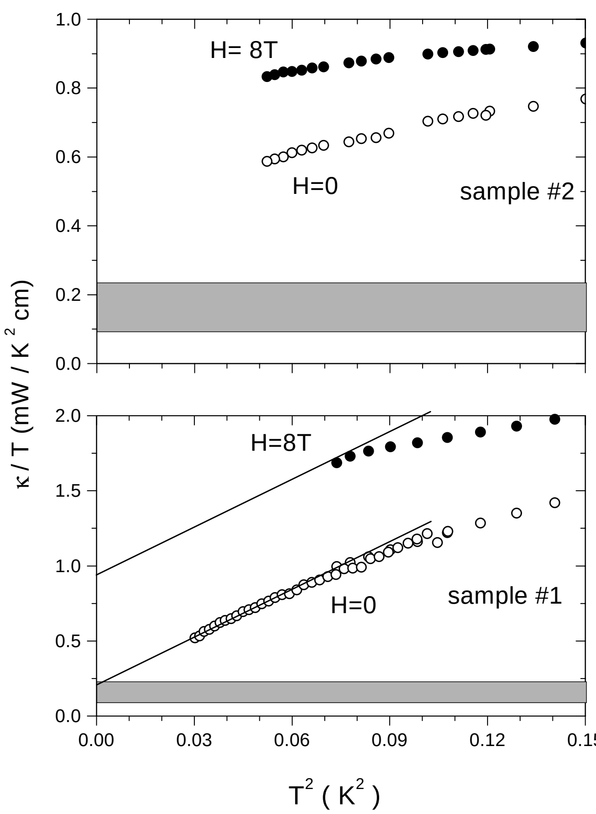

FIG. 4. The T^2 dependence of κ/T in normal and superconducting states for samples 1 and 2. The straight line for $H = 0$ is the best fit to low-temperature data. For $H = 8$ T, a parallel line schematizes the expected $aT + bT^3$ behavior (see text). The shaded area represents the universal linear term in the clean limit.

regime (with a phonon mean-free path comparable to sample dimensions) should be attained at a similar temperature range. Moreover, the magnitude of the cubic term (which depends on phonon thermodynamics and sample geometry) should be identical in the normal and superconducting states. In this way, the zero-temperature κ_e^n/T can be estimated to be 0.95 mW/K^2 cm. As expected, the difference between the electronic thermal conductivities of the normal and superconducting states is comparable to the jump in $\kappa(H)/T$ just below H_{c2} at $T = 0.31$ K, which—as argued above—is exclusively electronic and gives an estimate of $\kappa_e^n - \kappa_e^s$. In the case of sample 2, due to the lack of low-temperature data, the analysis remains qualitative.

The theory of heat transport in unconventional superconductors predicts a finite zero-temperature value for $\frac{\kappa_e^s}{T}$ due to impurity scattering of residual quasiparticles [24]. Moreover, for certain gap topologies—including the one associated with the $d_{x^2-y^2}$ symmetry—the magnitude of this linear term is universal at small concentrations of impurity: $\frac{\kappa_{00}}{T} = \frac{\hbar k_b^2 \omega_p^2}{6e^2 S}$, where ω_p is the plasma frequency and $S = \frac{d\Delta_0}{d\Phi}$ is the slope of the gap at the node. The experimental validity of this theory has been recently reported in the case of $YBa_2Cu_3O_{6.9}$ [25]. Here, using $\hbar\omega_p \simeq 0.6 \pm 0.1$ eV [26] and $2\Delta_0 = 4.8 \pm 1.1$ meV [1], and assuming a standard d-wave gap with $S = 2\Delta_0$, the predicted magnitude for $\frac{\kappa_{00}}{T}$ is 0.16 ± 0.05 mW/K^2 cm. Our experimental result is very close to this value.

We recall that this theory is based on an original work [27] on clean superconductors with an electronic relaxation time τ exceeding $\frac{\hbar}{\pi\Delta_0}$ (or equivalently $l_e > \xi_0$, where l_e and ξ_0 are, respectively, the electronic mean-free path and the coherence length). An alternative formulation of its basic statement is that, for an infinitesimal concentration of impurities, the ratio of electronic conductivities in the superconducting and normal states should extrapolate to $\frac{\hbar}{\pi\tau\Delta_0} = \frac{\xi_0}{l_e}$. Now, the electronic mean-free path can be estimated by either using the magnitude of the threshold field for the apparition of quantum oscillations (8 T) [3] or through the values of normal state conductivity (κ_e^n/T) and ω_p. Both sources yield comparable values for l_e ($\simeq$35 nm). ξ_0 can be deduced from the slope of H_{c2} at T_c ($\simeq$5 nm). Thus, our compound—still a clean superconductor—is much closer to the dirty limit than YBCO, and the expected extrapolated value for $\frac{\kappa_e^s}{\kappa_e^n}$ is as high as 0.15 ± 0.06. As seen in the lower panel of Fig. 4, the experimental ratio obtained for sample 1 is remarkably close to this value. This constitutes the first verification of the theory of transport in unconventional superconductors by directly comparing the conductivities of normal and superconducting states. Note that, according to the theory, the universal value is only expected at the extreme clean limit and the expected $\frac{\kappa_{00}}{T}$ increases with an increasing scattering rate [28]. Hence, for samples closer to the dirty limit, higher ratios of $\frac{\kappa_e^s}{\kappa_e^n}$ are expected. The upper panel of Fig. 4 suggests that this is the case for sample 2 where the extrapolated ratio tends to be higher.

In conclusion, our study of heat conductivity in κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ provides evidence for nodes in the superconducting gap, strong electron-phonon coupling and possibly an enhancement of quasiparticle scattering time below T_c.

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