

Thermal Conductivity of Superconducting $(\text{TMTSF})_2\text{ClO}_4$: Evidence for a Nodeless Gap

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We report on the first measurements of thermal conductivity in the superconducting state of $(\text{TMTSF})_2\text{ClO}_4$. The electronic contribution to heat transport is found to decrease rapidly below T_c , indicating the absence of low-energy electronic excitations. We argue that this result provides strong evidence for a nodeless superconducting gap function, but does not exclude a possible unconventional order parameter. [S0031-9007(97)04077-5]

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The $(\text{TMTSF})_2X$ family of quasi-one-dimensional conductors (the Bechgaard salts) are a well-known case of competition between superconducting and spin-density-wave ground states [1]. At ambient pressure, most of these extremely anisotropic compounds undergo a metal-insulator transition at low temperatures and have a SDW fundamental state. Under moderate pressure, the SDW instability is suppressed and replaced by a superconducting transition at a critical temperature of the order of 1 K [2]. One exception to this scheme is $(\text{TMTSF})_2\text{ClO}_4$ which is superconducting at ambient pressure. The high-field properties of these compounds—including a particular version of quantum Hall effect [3] and commensurability effects in the angular magnetoresistance [4]—have been intensely studied during the past few years. However, in spite of early speculations on a possible unconventional nature of superconductivity in this context [5], and contrary to the other families of exotic superconductors (i.e., heavy fermions and cuprates), the superconducting state has been subject to very few studies. The only attempt to explore the symmetry of superconducting order parameter in a Bechgaard salt is reported by Takigawa, Yasuoka, and Saito [6]. These authors detected a T^3 temperature dependence in the nuclear relaxation rate of proton in $(\text{TMTSF})_2\text{ClO}_4$ and concluded that the superconducting gap function should vanish along lines on the Fermi surface.

Thermal conductivity has proved to be a powerful probe of gap structure in a number of unconventional superconductors. In the case of the heavy-fermion superconductor UPt_3 , thermal conductivity measurements constitute one major source of our current knowledge on the angular distribution of nodes in the gap function [7,8]. In the case of $\text{YBa}_2\text{Cu}_3\text{O}_{6.9}$, several convincing signatures of d -wave superconductivity have been reported in a number of heat transport studies [9]. In the Bechgaard salts, measurements of thermal conductivity have been restricted to temperatures well above the superconducting instability [10]. In this Letter, we present the first study of heat transport in an organic superconducting system. Our conclusion happens to be rather surprising as we find strong evidence for a nodeless gap.

The electrical and the thermal conductivities of four $(\text{TMTSF})_2\text{ClO}_4$ single crystals—grown by standard elec-

trochemical technique—were measured with a conventional four probe method. Contacts were realized using silver paint on evaporated gold. Because of the poor conductivity of these contacts ($\sim 1 \Omega$), the heat current passing through the sample was carefully checked using an Au-Fe thermocouple connected in series with the sample. The temperature gradient along the sample was measured with two RuO_2 thermometers which were thermally coupled to the contacts through gold wires. To minimize the heat loss, each thermometer was held and measured through long tiny superconducting Nb-Ti wires which were calculated to have the required high thermal resistance in the relevant temperature range. We tested our apparatus by measuring the thermal conductivity of $20 \mu\text{m}$ wires of metallic alloys (Al and Au-Fe) and found a linear thermal conductivity in agreement with the Wiedemann-Franz (WF) law and a Lorenz ratio very close to the Sommerfeld value ($L_0 = 2.45 \times 10^{-8} \Omega \text{mK}^{-2}$). All samples studied in this work showed jumps in resistance due to appearance of cracks during the cooling process. This has been regularly reported in transport studies of Bechgaard salts with silver-paint contacts and makes the determination of the absolute value of conductivity at low temperatures very difficult. For slowly cooled samples (see below on the effect of cooling rate), the residual resistivity ratio of room temperature resistance to residual resistance [$R_0 = R(T \rightarrow 0)$] was found to vary from 10 to 440. Here we present the results for the sample with a RRR of 440 (dimensions: $1.1 \times 0.23 \times 0.07 \text{ mm}^3$) which was most thoroughly studied. But the same basic features were observed for the three other samples.

Figure 1 shows the temperature dependence of thermal conductance κ and electrical resistance. The superconducting transition leads to a sharper decrease in κ at $T \sim 1 \text{ K}$ which is coincident with the end of the resistive transition. This kink disappears with the destruction of superconductivity under a small magnetic field along the c axis. The ratio of thermal and electrical conductances at the onset of superconductivity indicates that heat transport is dominated by phonons and that the electronic contribution counts for only a small fraction of total thermal conductivity for $T > 1 \text{ K}$. In general, the separation of lattice and quasiparticle components of thermal

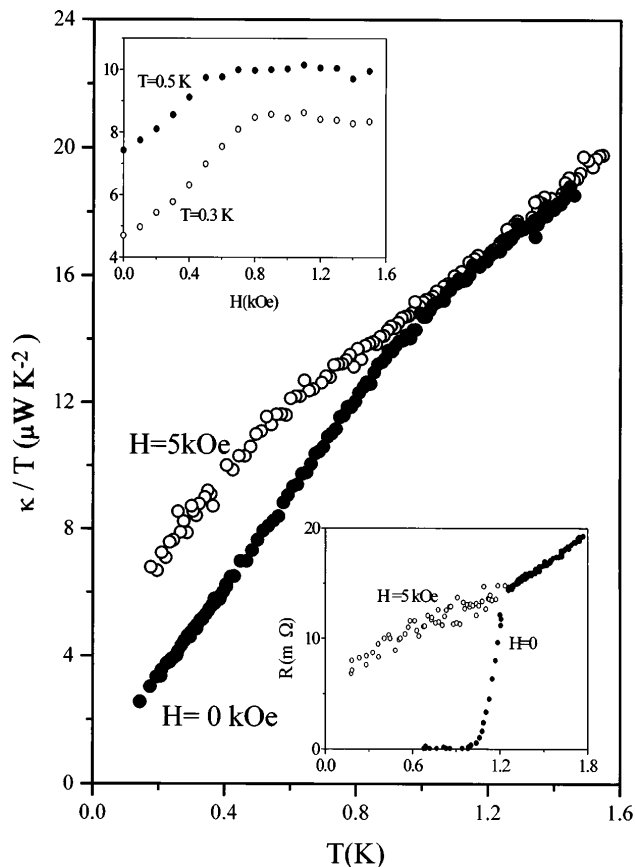


FIG. 1. Thermal conductance divided by temperature for a relaxed sample of $(\text{TMTSF})_2\text{ClO}_4$. Superconductivity is suppressed by applying a small field along the c axis. The lower inset presents the temperature dependence of the electrical resistance for the same sample. The upper inset shows the field dependence of κ/T for two different temperatures.

transport in superconductors is not straightforward, as the condensation of electrons in the superconducting state affects lattice contribution due to electron-phonon coupling [11]. To gain insight into the effect of the superconducting instability on heat carriers, we plot in Fig. 2, $\Delta\kappa/T$, the difference between the two experimental curves of κ/T (at $H = 0$ and $H = 5$ kOe), as a function of temperature. As seen in the figure, upon the entry in the superconducting state, $\Delta\kappa/T$ increases steadily with decreasing temperature before saturating at a temperature of about 0.4 K. This saturation has been observed at the same temperature for all the samples studied in this work and its value ($3.7 \pm 0.4 \mu\text{W K}^{-2}$ in this sample) was found every time to be close to (L_0/R_0) ($= 3.8 \pm 0.5 \mu\text{W K}^{-2}$ here) which is the expected maximum electronic contribution to heat transport according to the WF law.

According to recent theoretical results [12], the separation of spin and charge degrees of freedom in an interacting 1D electron gas can lead to the violation of WF law and—in certain cases—to a divergence of the

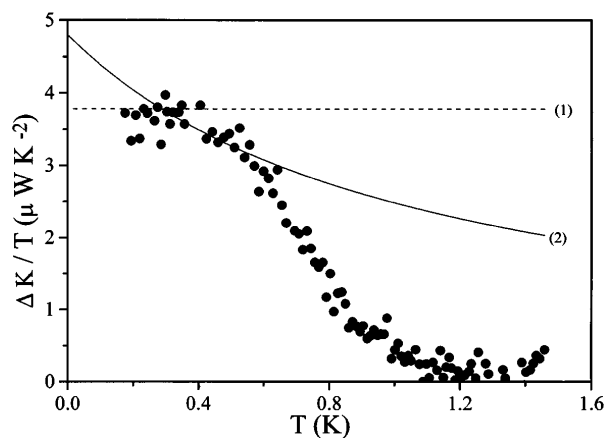


FIG. 2. The difference between the thermal conductances of $(\text{TMTSF})_2\text{ClO}_4$ at $H = 5$ kOe and $H = 0$ kOe. Note the saturation at $T = 0.4$ K. The horizontal line (1) represents L_0/R_0 ; (2) schematizes a second scenario for temperature dependence of thermal conductivity in the normal state (see text).

Lorentz number at zero temperature. Here, the correlation between the zero-temperature extrapolations of normal state resistivity and the loss in electronic thermal conductivity constitute the first confirmation of the WF law in a quasi-one-dimensional conductor. This is not very surprising, since below the temperature scale defined by the interplane coupling t_c (estimated to be a few kelvins), $(\text{TMTSF})_2\text{ClO}_4$ is expected to behave as an anisotropic 3D Fermi liquid. At finite temperatures, according to our data thermal conductivity exceeds the limit imposed by the WF law. But this additional thermal conductivity is within our experimental uncertainty on the absolute value of the Lorentz ratio. Moreover, cracks which have a less dramatic effect on thermal transport may cause a difference in the geometric factors for thermal and electrical transport. Therefore, at this stage, we will prudently remain within the boundaries of the WF law. Further studies of thermal transport in the normal state under higher magnetic field may elucidate this matter.

It can be shown that the saturation in $(\Delta\kappa/T)(T)$ constitutes a strong argument in favor of the absence of low-energy quasiparticle heat carriers. Neglecting the magnetoresistance (which is very small at 5 kOe as seen in the inset of Fig. 1), one can express this difference as

$$\frac{\Delta\kappa}{T}(T) = \left(\frac{\kappa_e^n(T)}{T} - \frac{\kappa_e^s(T)}{T} \right) + \left(\frac{\kappa_{\text{ph}}^n(T)}{T} - \frac{\kappa_{\text{ph}}^s(T)}{T} \right), \quad (1)$$

where subscripts (e , ph) stand for electronic and lattice components and superscripts (s , n) refer to superconducting and normal states. Now, a finite electron-phonon coupling would lead to an *increase* in the lattice conductivity in the superconducting state so that $\kappa_{\text{ph}}^n(T) \leq \kappa_{\text{ph}}^s(T)$ for the whole temperature range below T_c . This means that at any given temperature below T_c , $\Delta\kappa/T$ constitutes a

lower limit to the difference between the electronic conductivities of the normal and superconducting states. On the other hand, at zero temperature this difference is given by L_0/R_0 . These two constraints will allow us to extract the temperature dependence of normalized electronic thermal conductivity κ_e^s/κ_e^n from $(\Delta\kappa/T)(T)$ and compare it to what is expected for different gap structures.

In Fig. 3, neglecting the effect of electronic condensation on lattice conductivity, we consider two different scenarios for the temperature dependence of thermal conductivity in the normal state. In the first hypothesis, a constant κ_e^n/T (equal to L_0/R_0), is assumed. In the second scheme, we suppose that the electronic thermal conductivity in the normal state follows the behavior imposed by the temperature dependence of electrical resistivity and the WF law [curve (2) in Fig. 2]. The latter scenario implies a difference of 27% in the geometric factor of the sample for electric and thermal transport. As seen in Fig. 3, the normalized κ_e^s/κ_e^n curve is not very different for the two possible scenarios. It is instructive to compare them with the data on UPt_3 [7], the archetypal unconventional superconductor. The decrease in the electronic thermal conductivity within the entry in the superconducting state is much faster in $(\text{TMTSF})_2\text{ClO}_4$. At $(T/T_c) = 0.4$, for example, quasiparticle conductivity drops virtually to zero in $(\text{TMTSF})_2\text{ClO}_4$, but remains a sizable (0.38) fraction of normal state conductivity in UPt_3 . Interestingly, our data are much closer to the predictions of the conventional Bardeen-Rickaysen-Tewordt theory [13]. The BRT function was computed for different values of where $\Delta(0)/k_B T_c$, where $\Delta(0)$ is the amplitude of the superconducting gap at zero temperature. The closest fit was obtained for $\Delta(0)/k_B T_c = 2.3$. This strong-coupling value shall be compared with 1.9, which is what is expected from the size of the jump in specific heat at T_c [14]. How-

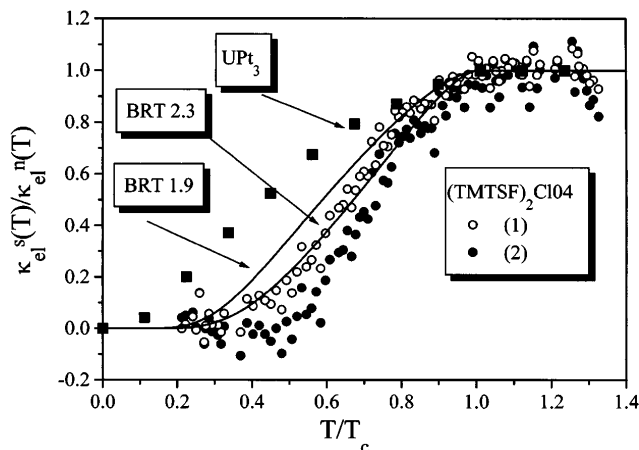


FIG. 3. Normalized electronic thermal conductivity vs normalized temperature for $(\text{TMTSF})_2\text{ClO}_4$ in two different scenarios (see text). The results are compared with the predictions of BRT theory for two different ratios of $\Delta(0)/k_B T_c$ and with the published data on UPt_3 for a heat current along the b axis.

ever, due to the neglect of electron-electron collisions in the BRT model, one shall be cautious in a quantitative comparison. Note that a finite electron-phonon coupling would lead to an even sharper decrease in κ_e^s/κ_e^n below T_c . Thus, in spite of several simplifications to obtain the plots of Fig. 3, our main conclusion is a direct consequence of the saturation presented in Fig. 2 and remains quite robust: *there is no plausible way to reconcile our data with a gap function vanishing on the Fermi surface.*

To gain further insight on lattice thermal conductivity, we studied the effect of the cooling rate on it. $(\text{TMTSF})_2\text{ClO}_4$ passes through an anion-ordering transition at 24 K. The kinetics of cooling around this temperature crucially influences the ground state. The data reported and analyzed above were obtained on a relaxed sample (cooling rate 0.6 K/h) where the relative weakness of anion disorder leads to a long mean free path both for phonons and electrons. The same sample was warmed up to 40 K in order to let the disorder fully develop and then cooled down with different cooling rates. In this way, we studied an intermediate state (25 K/h) and a quenched state (~ 60 K/min). As seen in the inset of Fig. 4, while the intermediate state still shows metallic behavior and a superconducting instability—with a lower T_c and a higher residual resistivity—the quenched state becomes insulating because of a SDW transition at 9 K. The change in the low-temperature thermal conductivity, shown in Fig. 4, is remarkable. The thermal conductivity is dramatically reduced, reflecting the sensitivity of lattice conduction to anion disorder. One can estimate the phonon mean free path in different states using the classical phonon gas equation $\kappa_{\text{ph}} = \frac{1}{3} c_{\text{ph}} v_s l_{\text{ph}}$; where $c_{\text{ph}} = \beta T^3$ is the lattice specific heat ($\beta = 58 \mu\text{J}/\text{cm}^3 \text{K}^4$ [14]), v_s is the velocity of sound [3 km/s is the reported value [15] for $(\text{TMTSF})_2\text{PF}_6$ along the a axis], and l_{ph} is the mean free path. In this picture, the $T^{2.4}$ dependence of thermal conductivity in the quenched state indicates that

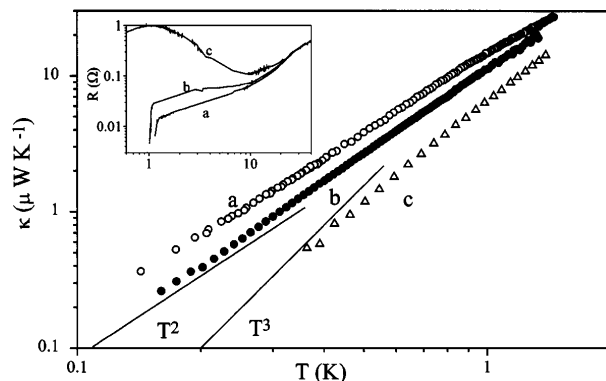


FIG. 4. Thermal conductance vs temperature for different cooling rates: Curve (a) relaxed (0.6 K/h), curve (b) intermediate (25 K/h), and curve (c) quenched (60 K/min). Inset shows the temperature dependence of electrical resistance for the three cases.

the phonon mean free path increases very slowly with decreasing temperature and can be estimated to be about $14 \mu\text{m}$ at 400 mK. This is 1 order of magnitude smaller than the maximum allowed by the sample dimensions ($\sim 150 \mu\text{m}$) and suggests that the disorderly domains of anion ordering in the quenched state [16] strongly scatter phonons. On the other hand, in the relaxed state, where the thermal conductivity shows an essentially T^2 behavior below T_c , the phonon mean-free path is estimated to be $100 \mu\text{m}$ at 200 mK. The cubic behavior of thermal conductivity associated to the ballistic regime is expected only below 130 mK. Note that the effect of cooling rate on heat transport confirms the smallness of electron-phonon scattering. Indeed, in the quenched state, the phonons are much more affected by anion disorder than the absence of electrons as scatterers.

The main outcome of this work is that the superconducting gap of $(\text{TMTSF})_2\text{ClO}_4$ has no nodes. This result is in contradiction with the conclusion of the only other experimental investigation of gap structure in this system [6]. One shall note, however, that the temperature range where the nuclear relaxation rate is reported to show a T^3 dependence is limited to $T > T_c/2$ [6]. This cannot be considered convincing evidence for nodes in a gap, as even for conventional superconductors, the exponential behavior is expected only at very low temperatures.

A nodeless gap in this compound is not necessarily associated with s -wave superconductivity. Enumerating possible gap functions for a quasi-one-dimensional conductor, Hasegawa and Fukuyama [17] showed that a pseudotriplet (i.e., odd-parity) gap with no nodes is possible in the context of Bechgaard salts (see the t_1 state in Ref. [17]). Indeed, here the order parameter can have opposite signs for antiparallel wave vectors without vanishing anywhere on the Fermi surface, due to the openness of the latter. One argument in favor of an odd-parity superconducting order parameter is the fascinating behavior of the upper critical field in the sister compound $(\text{TMTSF})_2\text{PF}_6$ [18]. When the magnetic field is oriented in the most-conducting plane, the upper critical field exceeds the Pauli limit. Insensitivity to this limit is naturally explained for Cooper pairs in a triplet state [19]. More studies are required to examine further this appealing possibility of an odd-parity gap function without nodes. From a theoretical point of view, it is highly desirable to establish all the possible gap functions for the Fermi surface of $(\text{TMTSF})_2\text{ClO}_4$. Indeed, Ref. [17] neglects triclinic symmetry of the crystal and the low-temperature shape of the Fermi surface after the opening of the anion-ordering gap. Until now, the debate on the nature of superconductivity in the organic charge-transfer salts has been centered on BEDT-TTF compounds. In the latter family, evidence for nodes in the superconducting

gap [20] as well as a strong electron-phonon coupling [21] have been recently reported.

In conclusion, we have measured the thermal conductivity of $(\text{TMTSF})_2\text{ClO}_4$ in the superconducting, metallic, and insulating states. The results are incompatible with the presence of nodes in the superconducting gap function. Moreover, electrons are found to have little effect on heat conduction by phonons.

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