LETTER TO THE EDITOR

Magnetic field dependent thermal conductivity in the organic superconductor \((\text{TMTSF})_2\text{ClO}_4\)

D Djurek†, M Prester†, D Jérome‡ and K Bechgaard‡§
† Institute of Physics of the University, Zagreb, Yugoslavia
‡ Laboratoire de Physique des Solides, Université Paris-Sud, 91405 Orsay, France

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Abstract. The thermal conductivity of the organic superconductor tetramethyltetraselenafulvalene perchlorate, \((\text{TMTSF})_2\text{ClO}_4\), has been measured between 300 K and 4.2 K. A significant monotonic decrease of the conductivity has been observed below 50 K. The low-temperature thermal conductivity is sensitive to the application of a 5 T magnetic field up to 30 K. These results are consistent with the picture of superconducting fluctuations existing far above the actual superconducting transition temperature at about 1.2 K.

\((\text{TMTSF})_2\text{ClO}_4\) is so far the only member of the family of organic conductors \((\text{TMTSF})_2\text{X}\) (Bechgaard et al 1980) which exhibits superconductivity (Bechgaard et al 1981) without the help of an applied hydrostatic pressure (Jérome et al 1980).

As these materials are quasi-1D conductors one might expect precursor effects to be important above the transition temperature where three-dimensional superconducting order sets in. The Orsay group (Jérome 1981, 1982) has suggested the existence of significant superconducting fluctuations up to temperatures which are at least ten times higher than the critical temperature for superconductivity. This point of view has been opposed by several authors (see for example Greene et al 1982).

The domain of temperatures in which intrachain short-range superconducting pairing arises must be characterised by strong collective effects (large paraconductivity) (Schulz et al 1981) and a depression of the density of states at the Fermi level (i.e. formation of a pseudo-gap in an energy interval much larger than the energy related to the establishment of 3D order).

Electron tunnelling experiments (More et al 1981) performed in \((\text{TMTSF})_2\text{PF}_6\) under pressure have led to a pseudo-gap of amplitude \(2\Delta \approx 40\) K. The present work reports an investigation of the thermal conductivity of \((\text{TMTSF})_2\text{ClO}_4\) down to helium temperature, and the effect of a magnetic field up to 5 T.

The method used for the evaluation of the thermal resistivity was previously applied to the measurement of the thermal conductivity of quasi-one-dimensional conductor \(\text{NbSe}_3\) (Djurek and Tomic 1981). The sample was positioned between the thermal link \((L)\) and the sink at temperature \(T_0\) (figure 1). The connection point \((C)\) between the sample and the thermal link was at temperature \(T_1\). The upper end of the thermal link,

§ On leave from H C Oersted Institute, DK-2100 Copenhagen, Denmark.
consisting of the chromel–constantan thermocouple was thermally connected with the sink kept at temperature $T_2$. The thermal resistance of the sample $R_s$ and of the thermal link $R_L$ are related to the temperature differences $T_1 - T_0$ and $T_2 - T_1$ as:

$$\frac{T_1 - T_0}{T_2 - T_1} = \frac{R_s}{R_L}. \quad (1)$$

An independent thermocouple, referred to as the external thermocouple is used to determine the temperature difference between the two sinks. The diameters of chromel and constantan wires were 15 and 50 $\mu$m respectively. The length of the thermocouple was 3.2 mm and the typical dimensions of samples $(\text{TMTSF})_2\text{ClO}_4$ were $0.2 \times 0.1 \times 2.5$ mm. The temperature difference $T_1 - T_0$ ranges from 0.5 K at low temperatures between 77 K and room temperature. The calorimeter was evacuated to a pressure lower than $10^{-6}$ Torr in order to avoid the possible uncontrollable side heat flow. Galvanic contact between the sample and the thermal link at the connection point C was avoided by the use of GE-warnish on the thermocouple.

The contribution of the radiation heat current from the sample to the interior of the calorimeter was estimated to be about 10 per cent of the heat current conducted along the sample. Both thermal contacts at points O and C were performed with silicone grease. The calibration of the thermal conductance of the link was carried out independently with a sample of known thermal conductivity. The accuracy of the measurement is of the order of a few per cent at low temperatures and about one per cent at temperatures above 77 K.

A superconducting magnet was used for the generation of the magnetic field. The field was swept automatically from zero up to 5 T. The sensitivity of the thermocouple to the magnetic field was controlled by the external thermocouple and a slight decrease of thermoelectric power with the magnetic field was found, in agreement with the data mentioned in the literature (von Middendorff 1971). At 5 T the thermoelectric power was about 3 per cent less than in the case of zero field. Note that the change of the voltage difference on the internal thermocouple due to the increase of the thermal conductivity of the sample is opposite to the change due to the magnetic field itself.

The magnetic field was increased and decreased several times at various temperatures, in order to control the possible hysteresis effects. No such effects of magnetic field were observed up to fields of 5 T.

The positioning of the sample in the field was imposed by the geometry of the calorimeter. Therefore the angle between the field and the sample $a$ axis was about 10 degrees.

The thermal conductivity was found to be nearly constant between room temperature
and 120 K. The data, below 120 K, are displayed in figure 2. A similar almost temperature-independent thermal conductivity has been observed in the other organic superconductor (TMTSF)\textsubscript{2}PF\textsubscript{6} under a pressure of 12 kbar (Djurek et al 1982a, b). Below 50 K a marked decrease of the thermal conductivity is observed, as shown in figure 2. Moreover, the beginning of another drop is observed around 10 K. Furthermore, the room temperature value of the thermal conductivity is similar to the value found in (TMTSF)\textsubscript{2}PF\textsubscript{6} under ambient pressure (Djurek et al 1982b).

Since organic conductors are relatively poor electronic conductors we may expect an electronic contribution to the thermal conductivity significantly smaller than the contribution usually observed in ordinary metallic conductors (Salamon et al 1975). Therefore, a large fraction of the thermal conductivity of (TMTSF)\textsubscript{2}ClO\textsubscript{4} comes from the lattice contribution. It may also be argued that the lack of exponential increase of the thermal conductivity below 77 K or so suggests that phonon–phonon Umklapp scattering is of minor importance for the thermal resistance (Djurek et al 1982a, b). Consequently, the dominant scattering centres of the phonons giving rise to thermal resistance are likely to be the electrons.

The thermal resistivity of the lattice due to this scattering may be expressed as (Berman 1978)

\[ W_L = \frac{1}{\kappa_e} \frac{\pi^2 n^2}{3} \]  

where \( n \) is the number of conduction carriers per molecule and \( \kappa_e \) is the electronic contribution to the thermal current.

\( \kappa_e / \sigma = L_0 T \)  

where in equation (3) \( L_0 \) is the Lorentz number \( \pi^2 k_B^2 / 3e^2 \). As \( \sigma T \) is known to be nearly constant in the range 150–300 K (Bechgaard et al 1981) no drastic temperature dependence of the thermal conductivity is expected in the same temperature domain.
The drop of thermal conductivity below 50 K is very strongly attenuated by the application of a magnetic field of 5 T, as shown in figure 3. In a field of 5 T the sensitivity to magnetic field vanishes above 33 K, figure 3. The error bars in figure 3 are due to the small zero offset of the nanovoltmeter (about 10 to 15% of the typical temperature difference read on the internal thermocouple). This zero offset is caused by the competition between the power radiant from the sample and the heat current conducted by the sample itself. The latter quantity is sensitive to the magnetic field and gives rise to a shift of the zero. We believe that the application of larger fields would lead to an increase of the thermal conductivity up to even higher temperatures.

A preliminary experiment has also been performed with another single crystal with the magnetic field aligned with an (unspecified) transverse direction. In such a case the sensitivity of $\kappa$ to the magnetic field is large, especially in the low-field region (figure 4). The field dependence of $\kappa$ is strongly attenuated above 2 kOe or so.
The sensitivity of the thermal conductivity to magnetic field is an essential piece of information which is provided by this work. It enables us to rule out the lattice as the origin for the drop of \( \kappa \) below 50 K. Consequently, the behaviour of \( \kappa \) must be attributed to a decrease of the electronic thermal conductivity below 50 K. Furthermore, the increase of \( \kappa \) under magnetic field cannot be explained by the Wiedemann–Franz law (equation (3)) together with the large magnetoresistance observed up to 40 K or so (Kwak et al 1982, Parkin et al 1981). Equation (3) would lead to a decrease of \( \kappa \) under magnetic field and not to the observed increase.

We are forced to conclude that the Wiedemann–Franz law does not apply below 50 K in \((\text{TMTSF})_2\text{ClO}_4\). At the moment we do not see any other reasonable explanation to the data but the progressive opening of an energy gap (or pseudo-gap) at the Fermi level below 50 K.

A pseudo-gap is expected as a one-dimensional precursor effect of the 3D ordered state. We may consider the pseudo-gap related to the two different ground states: SDW or superconductivity.

An SDW pseudo-gap could be taken into account since in some members of the \((\text{TMTSF})_2X\) series an SDW state is clearly stable at low temperature (Mortensen et al 1981, Takahashi et al 1982). However, we find the possibility of SDW 1D precursor effects rather unlikely for the following reasons:

(i) A commensurate \( \times 2 \) fluctuating SDW regime would not give rise to a very large DC conduction as observed below 50 K (Lee et al 1974).
(ii) A magnetic field stabilises the SDW state whenever it is observed in the \((\text{TMTSF})_2X\) family (Mortensen et al 1981, Takahashi et al 1982), whereas the present data show a suppression of the pseudo-gap under magnetic field.

In conclusion, the only other alternative for the origin of the pseudo-gap revealed by the magnetic field dependence of the thermal conductivity is the existence of 1D short-range superconducting order.

Several other experimental data suggest the existence of an intrachain pairing energy in the range of \( 2\Delta \approx 40 \) K in \((\text{TMTSF})_2X\) superconductors:

(i) The observation of a gap \( 2\Delta = 42 \) K in the far infrared magnetoabsorption spectrum of \((\text{TMTSF})_2\text{ClO}_4\) (Ng 1982).
(ii) The observation of a gap \( 2\Delta \approx 40 \) K in \((\text{TMTSF})_2\text{PF}_6\) at 12 kbar (More et al 1981) and also in \((\text{TMTSF})_2\text{ClO}_4\) at ambient pressure (Sorbier 1982).
(iii) The magnetic field dependence of \( N(E_F) \) in \((\text{TMTSF})_2\text{ClO}_4\) derived from the electronic specific heat data (Garoche et al 1982).
(iv) The existence of a gap 30–50 cm\(^{-1}\) wide in \((\text{TMTSF})_2\text{PF}_6\) at 25 K, as shown by far infrared reflectance spectra (Jacobsen et al 1982).

The study of the magnetothermal conductivity of \((\text{TMTSF})_2\text{ClO}_4\) suggests that the superconducting coupling in the \((\text{TMTSF})_2X\) series of superconductors is much stronger than the amplitude inferred from a \( T_c \) of about 1.2 K.

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