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D. Djurek, D. Jerome, K. Bechgaard. Thermal transport properties of organic conductors: (TMTSF) 2PF₆ and (TMTSF)₂ClO₄. *Journal of Physics C: Solid State Physics*, 1984, 17 (23), pp.4179-4192. <10.1088/0022-3719/17/23/016>. <hal-04944379>

HAL Id: hal-04944379

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Submitted on 8 Mar 2025

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Thermal transport properties of organic conductors: (TMTSF)₂PF₆ and (TMTSF)₂ClO₄

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Received 6 September 1983, in final form 9 February 1984

Abstract. The thermal conductivity of the low-dimensional organic conductors (TMTSF)₂ClO₄ and (TMTSF)₂PF₆ under pressure has been measured between room temperature and 4.2 K.

The pressure dependence of the thermal and electrical transport properties supports strong anharmonicity for this type of material. A striking violation of the Wiedemann–Franz law is observed at low temperature and under a magnetic field. It is claimed that the data are consistent with the model of superconducting fluctuations existing far above the actual superconducting transition temperature at 1.2 K.

1. Introduction

Superconductivity in organic conductors has been established by the observation of a superconducting transition at 1 K in the organic quasi-one-dimensional (quasi-1D) conductor tetramethyl-tetraselenafulvalene-hexafluorephosphate, (TMTSF)₂PF₆, submitted to a pressure of 9 kbar (Jérôme *et al* 1980). This initial discovery triggered off a vast amount of experimental and theoretical work in the family of (TMTSF)₂X salts (X = PF₆, ClO₄, ReO₄, . . .) which is reviewed elsewhere (Friedel and Jérôme 1982, Jérôme and Schulz 1982).

The study of (TMTSF)₂X salts reveals several interesting physical properties: for example a ground state that can be a superconductor or a magnetic insulator depending on the applied hydrostatic pressure or magnetic field. Other puzzling problems are the unusually large value of the conductivity observed at low temperature, the strong dependence on magnetic field and the pressure dependence of electrical transport properties at high temperature.

As three materials are quasi-1D conductors, one might expect a significant suppression of the transition temperature due to the anisotropy of the transport properties to occur and, consequently, superconducting precursor effects to be important above the transition temperature where three-dimensional superconducting order sets in. The Orsay group (Jérôme 1981, Schulz *et al* 1981, 1983) suggested the existence of superconducting fluctuations up to temperatures that are at least a decade higher than the critical temperature for superconductivity. This point of view has been opposed by several authors (Greene *et al* 1983).

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The present study reports measurements of thermal conductivity performed on two salts under conditions where the ground state is a superconductor: $(\text{TMTSF})_2\text{ClO}_4$ at ambient pressure and $(\text{TMTSF})_2\text{PF}_6$ at 12 kbar. A preliminary report of the $(\text{TMTSF})_2\text{ClO}_4$ data has been given previously (Djurek *et al* 1982a, b).

2. Experimental method

The method we used for thermal resistivity measurements is based on the simple principle of a thermal potentiometer already introduced in the measurement of the thermal resistivity of NbSe_3 . The typical dimensions of the needle-like samples used in the high-pressure work were $0.35 \times 0.25 \times 1 \text{ mm}^3$. Thermal connection between the sample (S on figure 1(a)) and the link (L) was made with polyurethane, keeping the mean distance between the sample and the link less than 0.05 mm. The temperature gradient across the thermal link and the sample was maintained by the use of a manganin heater

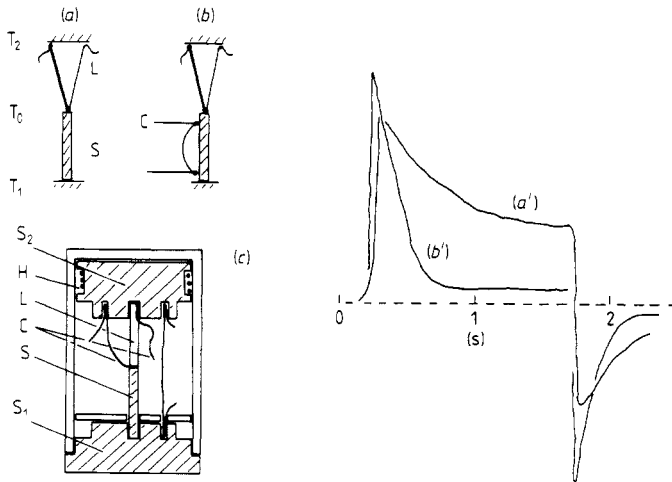


Figure 1. The experimental details for two-probe (a) and four-probe (b) thermal conductivity measurements. Also shown is the thermocouple response in two-probe measurements with the sample (a') and with a free thermocouple (b'). A high-pressure cell with a Teflon hat is shown in (c).

(H) at the upper sink (S_2) made of copper. In vacuum a simple relation connects the temperature differences $T_2 - T_0$ and $T_0 - T_1$ with the thermal resistances R_L and R_S , namely

$$(T_0 - T_1)/(T_2 - T_0) = R_S/R_L = (K_L/K_S)(A_L/A_S)l_S/l_L. \quad (1)$$

Constantan was used as the thermal link (L). Thin chromel wires (12 μm in diameter) completed the differential thermocouple for the measurement of $T_2 - T_0$. This method provides a reasonable measurement of the heat conductivity as long as the heat flow that is radiated from the sample to the side walls of the calorimeter (Q_{\perp}) can be neglected in comparison with the heat flow carried along the sample (Q_{\parallel}). The radiation losses can usually be neglected at temperatures below 100 K for most of the geometries used conventionally when $Q_{\perp}/Q_{\parallel} \approx 0.05$. However, in high-pressure work the transverse heat flow can no longer be neglected since the sample is surrounded by a pressure-transmitting medium. In the present work we use isopentane with a melting point at

about 210 K under 12 kbar. Thus, an accurate determination of the thermal conductance K_S requires a minimisation of the lateral heat flow. In the most unfavourable conditions considered, it is assumed that the transverse heat flow from the link and the sample to the side walls of the high-pressure cell is maintained by the temperature difference $(T_x - T_1)$, i.e. heat is transmitted to the side walls of the high-pressure can (diameter D) which is at the same temperature, T_1 , as the lower sink, S_1 . Then, in the case of cylindrical geometry the ratio Q_{\perp}/Q_{\parallel} becomes

$$\frac{Q_{\perp}}{Q_{\parallel}} = 2\pi \frac{K_{\text{iso}} l_S}{K_S S_S \ln(D/R)} \int_0^{l_S} (T_x - T_1) dx \quad (2)$$

where R is the sample diameter and K_{iso} is the thermal conductivity of isopentane obtained by independent measurement: $K_{\text{iso}} = 4.8 \text{ mW cm}^{-1} \text{ K}^{-1}$ at 300 K and 12 kbar. In this case the lateral heat flow from the sample is about half of the longitudinal one. By a suitable choice of thermal barrier around and on the bottom of the high-pressure cell (figure 1(c)) it is possible to reduce the transverse heat flow to the copper parts of the calorimeter by about 60%. We used a Teflon hat of wall thickness 1 mm. Teflon is a rather poor conductor of heat at low temperature with a thermal conductivity of $K_{\text{Tef}} \approx 0.05 K_{\text{iso}}$ at 4.2 K (Berman 1978). The top wall of the Teflon hat was thermally connected to the upper sink in order to maintain a fixed temperature gradient along the guard. The typical temperature difference measured between any point of the sample and the Teflon hat by a chromel–constantan differential thermocouple did not exceed 0.1 K, to be compared with $T_1 - T_2 \sim 1 \text{ K}$. Finally, the phonon mismatch between the sample contact surface and solid isopentane may appreciably reduce the remaining transverse heat flow.

The sensitivity of ratio (1) to the lateral heat flow was tested at room temperature by the use of constantan instead of the sample in the high-pressure cell. The application of 12 kbar pressure resulted in the increase of thermal conductivity of isopentane from 2.17 to 4.8 $\text{mW cm}^{-1} \text{ K}^{-1}$. Such an increase affects the ratio $(T_0 - T_1)/(T_2 - T_0)$ by about 10% and leads to an overestimate of the thermal resistance of constantan. In an independent measurement chromel was used as a standard sample for verification of the method down to 4.2 K and the thermal conductivity was found to be in good agreement with that cited in the literature. An additional measurement of the thermal conductivity of chromel and constantan in vacuum has been performed (Djurek 1981) in order to avoid errors arising from different metallurgical treatments resulting in possible discrepancies with the data taken from the literature.

In order to obtain a resolution as high as possible the length and the cross section of the thermal link were matched to the conditions for nearly equal thermal resistances of the link and the sample.

For measurements of relative values the resolution of the method described is about 5% but the estimate of the absolute thermal conductivity is uncertain by up to 20%, mainly due to errors in the determination of the true geometry of the sample and the non-linear contribution of thermal contacts. The quality of the thermal contact at the connection point C was tested independently in the dynamical pulse regime where the upper sink is subjected to a fast step-like Joule heating power. The heat current was then supplied to the sample in the ordinary way through a thermal contact at C. The time dependence of the temperature difference $T_2 - T_0$ is shown in figure 1 (curve a') for the case of good heat transport. The exponential decrease is affected by the thermal resistance of the link R_L and the sample heat capacity C_S . The heat capacity of the thermal link was usually an order of magnitude smaller than that of the sample and was

not considered in our study. For comparison the temperature response is given (curve b') for the case of a free thermocouple with no sample connected to it. This is a simulation of the poorest possible thermal contact, when there is no thermal current supplied to the sample. Finally, if the sample is replaced by a good thermal conductor (copper or silver wire) the quality of the thermal contact may be tested by comparing the temperature difference $T_2 - T_0$ to $T_0 - T_1$. For the case of good thermal contact the two values must be very nearly identical. In our measurements the typical discrepancy between the two temperature differences was about 20% of $T_0 - T_1$ at room temperature for copper used as a reference. In the zero-pressure experiments the measurements were carried out by two- and four-probe methods (figures 1(c) and (b)). Four-probe measurements usually give a higher absolute value of the thermal conductivity. For the measurements in the magnetic field we had previously checked the magnetothermal resistance of constantan (Djurek 1984) and we had found that up to 5 kg this resistance does not appreciably affect the data.

The differential thermocouple situated on the sample in the four-probe measurements was made of 12 μm chromel and constantan wires. The length was chosen so that the heat leak was less than 5% of the thermal current through the sample. The fact that the samples of $(\text{TMTSF})_2\text{ClO}_4$ are subjected to the formation of microcracks at low temperatures suggests that the thermal conductance may decrease with decreasing temperature. However we did not find, for thermal conductivity measurements, the kind of discontinuities that are well known in electrical conductivity data (Ishiguro *et al* 1983). Obtaining reproducible steady state conductance data after several temperature cycles would be very unlikely if the formation of microcracks really affects the thermal transport data. In the magnetic field measurements we made several tests in order to avoid the influence of possible spurious effects of the magnetic field in the course of the measurements. Firstly, the sensitivity to the magnetic field of the chromel–constantan thermocouple we used in our work was far below the observed effect. It even gave a signal with the opposite sign to the one reported here (Von Middendorff 1971). Furthermore, no appreciable effect on the reference thermocouple was visible. Secondly, no effect of the magnetic field was observed on replacing the sample with a chromel wire. The data were checked in the superconducting coil after the magnetic field had become well established, so there was no possibility of spurious currents induced in the thermocouple leads. The measurements of the electrical conductivity as a function of pressure were carried out by two different techniques. The standard four-probe geometry applied to $(\text{TMTSF})_2\text{X}$ compounds usually fails to give a reliable pressure dependence of the conductivity. After an initial monotonous increase of σ abrupt and non-reversible drops were observed above 3 or 5 kbar. We strongly believe that this behaviour is due to the formation of microcracks in the sample and does not represent an intrinsic effect. Furthermore two samples of the $(\text{TMTSF})_2\text{X}$ series, $(\text{TMTSF})_2\text{ClO}_4$ and $(\text{TMTSF})_2\text{ReO}_4$, have previously been pressurised successfully up to 12 kbar showing a steady increase of the electrical conductivity up to this pressure ($\sigma(12 \text{ kbar})/\sigma(0) \approx 3$) (Tomić *et al* 1982). The type of non-reproducibilities found for the four-probe technique may also be attributed to difficulties arising with regard to the contacts made between the thin gold wire leads (10 μm in diameter) and the samples, by silver dag. None of the above-mentioned experimental problems were encountered in the measurements of the thermal conductivity, K . It is therefore believed that isopentane penetrates into microcracks and causes the re-establishment of the thermal contacts inside the samples.

In order to avoid difficulties connected with the measurement of electrical conduc-

tivity at room temperature under pressure we have improved the contact-less technique of electrical conductivity measurement. This technique, successfully introduced by other authors, (see Eckert 1976) has now been adapted (Djurek and Jérôme 1984) for the low-conductivity measurements and applied to samples of $(\text{TMTSF})_2\text{PF}_6$ at room temperature under pressure. The method simply involves an inductance coil containing the sample and a capacitor connected as in a normal L - C circuit and carefully tuned to a high-frequency RF source. The typical frequency of the RF field ranged from 40 to 80 MHz. The frequency of RF field was thus continuously swept and the capacitor was adjusted in order to maintain the resonance condition, with the oscillating amplitude being very sensitive to the value of the coil inductance.

In the low-frequency regime (40 MHz) the RF field penetrates completely into the sample and is gradually expelled by the increase of the frequency (the skin effect). In the skin-effect problem both frequency and electrical conductivity enter, in the same way, the expression for the output amplitude. Thus the calibration of the output amplitude versus the frequency of the RF fields leads to the same type of calibration curve as would occur for a change of the electrical conductivity. The output amplitude was measured as a function of frequency at a constant pressure; then the pressure was changed in order to induce the variation of the electrical resistivity of the sample. In both measurements the output amplitude plays the role of common parameter and may be eliminated to give the dependence of the frequency (electrical conductivity) on pressure.

3. Experimental results and data analysis

It is well known that the transport properties of most organic conductors are strongly dependent on pressure (Jérôme and Schulz 1982). The electrical conductivity of the systematically investigated quasi-1D conductor TTF-TCNQ increases at room temperature to about four times its original value when subjected to a hydrostatic pressure of 12 kbar. A similar result holds for both $(\text{TMTSF})_2\text{PF}_6$ (figure 2) and $(\text{TMTSF})_2\text{ClO}_4$ (Greene *et al* 1982). Moreover, the onset of superconductivity in $(\text{TMTSF})_2\text{PF}_6$ occurs for applied hydrostatic pressure of above 6 kbar. The influence of pressure on many physical properties is thus of considerable interest and a number of phenomena may be elucidated by the study of the pressure effect.

The electrical and thermal conductivities of $(\text{TMTSF})_2\text{PF}_6$, displayed respectively in figures 2 and 3, show very similar pressure dependences. The thermal conductivity of

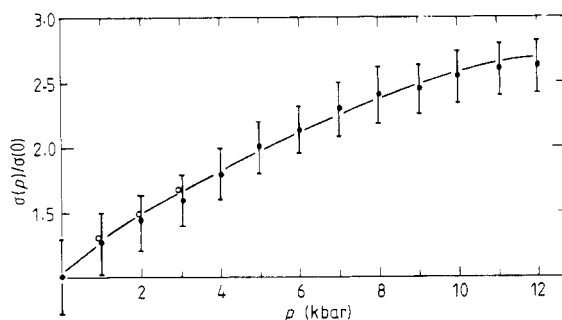


Figure 2. The pressure dependence of the electrical conductivity for $(\text{TMTSF})_2\text{PF}_6$ at 300 K obtained by the use of a contactless technique (full circles) and the usual four-probe method (open circles).

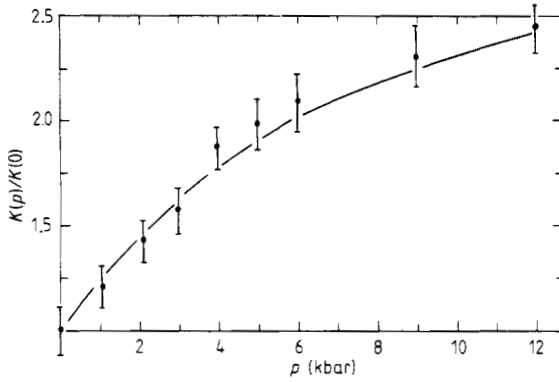


Figure 3. The pressure dependence of the thermal conductivity for $(\text{TMTSF})_2\text{PF}_6$ at room temperature (300 K).

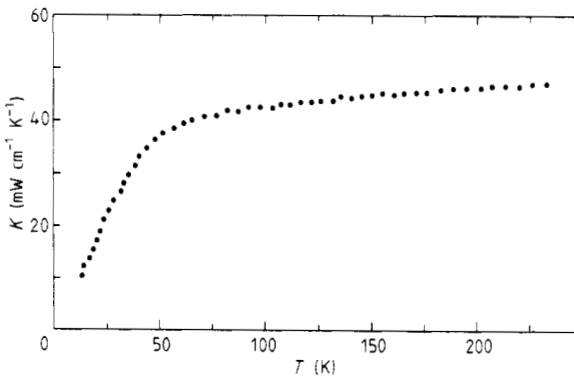


Figure 4. The temperature variation of the thermal conductivity of $(\text{TMTSF})_2\text{PF}_6$ under 12 kbar of hydrostatic pressure.

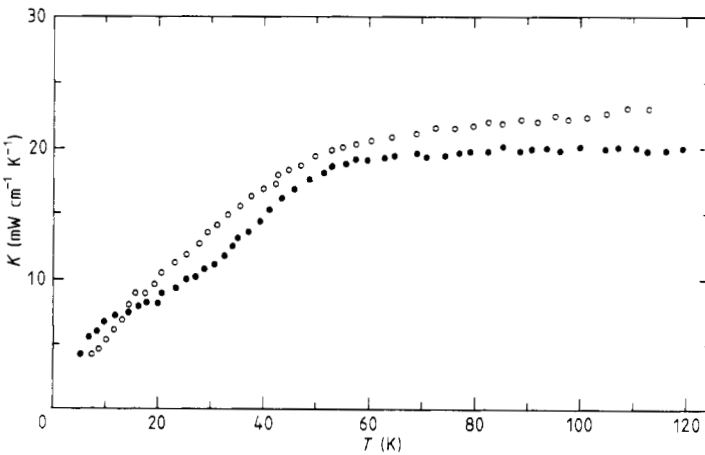


Figure 5. The temperature dependence of the thermal conductivity of $(\text{TMTSF})_2\text{ClO}_4$ at zero pressure obtained with the two-probe (full circles) and four-probe (open circles) techniques.

$(\text{TMTSF})_2\text{PF}_6$ under 12 kbar, versus temperature, is shown in figure 4. The thermal conductivity remains approximately constant at $50\text{--}60\text{ mW cm}^{-1}\text{ K}^{-1}$ down to 40 K. Below that temperature a significant drop of the thermal conductivity is observed in striking contrast with the behaviour of the electrical conductivity increasing from 10^4 to $10^5\text{ }(\Omega\text{ cm})^{-1}$ between 40 K and helium temperature. The temperature dependence of the thermal conductivity of $(\text{TMTSF})_2\text{PF}_6$ at 12 kbar is somewhat similar to the data already observed with $(\text{TMTSF})_2\text{ClO}_4$ at ambient pressure (figure 5). Even more striking behaviour is observed when a magnetic field is applied in the low-temperature regime (figures 6 and 7). The magnetic field increases the low-temperature thermal conductivity.

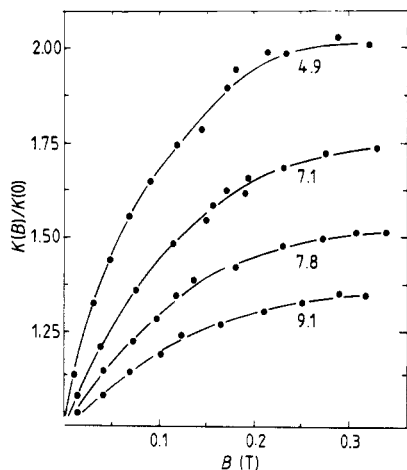


Figure 6. The magnetic field dependence of the thermal conductivity of $(\text{TMTSF})_2\text{PF}_6$ under 12 kbar pressure. Values on curves are of T in K.

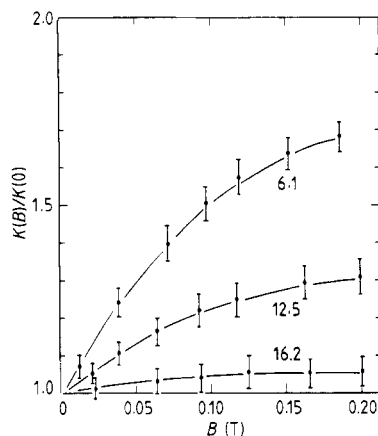


Figure 7. The magnetic field dependence of the thermal conductivity of $(\text{TMTSF})_2\text{ClO}_4$ at zero pressure. Values on curves are of T in K.

However this magnetic field effect seems to be restricted to the temperature domain up to 25 and 15 K for $(\text{TMTSF})_2\text{ClO}_4$ and $(\text{TMTSF})_2\text{PF}_6$ respectively. At helium temperature, a moderate magnetic field of a few kOe is large enough to double the value of the thermal conductance. It must be recalled that in the same temperature domain the electrical conductivity is drastically suppressed (and not enhanced) by the application of a magnetic field (positive magnetoresistance; see Jérôme 1981). For both samples the increase typical for the thermal conductivity at low temperature, with a pronounced maximum at about 20 K, of most pure metals and some dielectric solids (Berman 1978) does not occur. In the latter case the increase is principally due to the effect of phonon-phonon Umklapp scattering at low temperatures. In compounds like $(\text{TMTSF})_2\text{ClO}_4$ such an absence of increase of the thermal conductivity may be expected because of the presence of anion disorder at temperatures far above 24 K (Tomić *et al* 1982, Pouget *et al* 1983). The low-lying phonons principally responsible for the enhanced heat transport at low temperatures are strongly scattered by anion disorder and an appreciable reduction of thermal conductivity is to be expected. Similar arguments hold for irradiated samples of $(\text{TMTSF})_2\text{PF}_6$ (figure 8). Because of the defects introduced by irradiation there is no phonon-phonon Umklapp effect and the thermal conductivity exhibits no increase with decreasing temperature. The irradiation of the samples with moderate doses of x-rays results in properties being different at low temperatures. The irradiation dose for $(\text{TMTSF})_2\text{PF}_6$ was 7 h resulting in 0.08% of defects per molecule

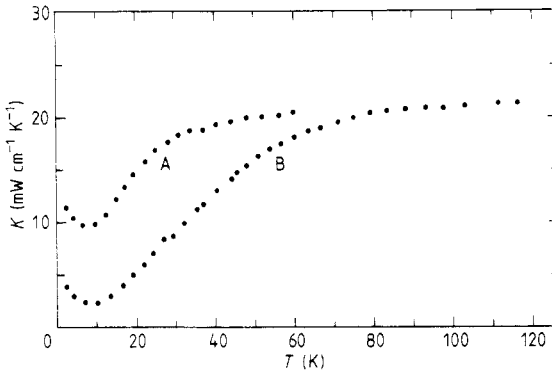


Figure 8. The temperature dependence of the thermal conductivity of irradiated samples of $(\text{TMTSF})_2\text{PF}_6$ at 1 kbar (A) and 12 kbar (B). The concentration of defects introduced by irradiation is 0.08%.

(Bouffard *et al* 1982). At room temperature the thermal conductivity of irradiated samples has a decrease that is not appreciable as compared with that for pure samples. In contrast the dependence on hydrostatic pressure is much less than in the case of non-irradiated $(\text{TMTSF})_2\text{PF}_6$ (figure 9). Upon lowering the temperature the thermal conductivity of irradiated samples exhibits a well defined minimum at about 9 K (figure 8). A similar phenomenon is well known in ionic crystals subjected to various types of irradiation (Kupperman *et al* 1973) and is attributed to a resonant scattering of phonons on quasi-localised (resonant) modes introduced by irradiation. The additional colour centres give rise to the resonant lattice thermal resistivity, with well defined maxima located between 3 and 15 K. In our samples the effect of resonant scattering is more pronounced and more than half of the thermal current is suppressed by this type of scattering mechanism.

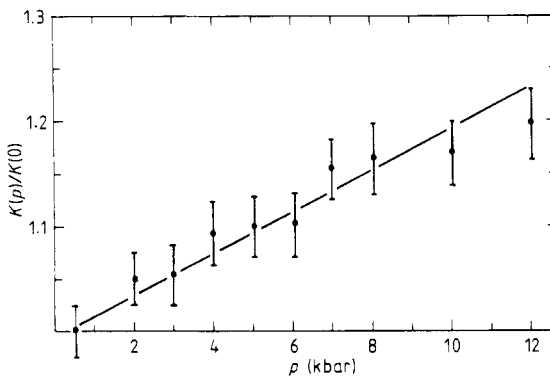


Figure 9. The pressure dependence of the thermal conductivity of irradiated samples at room temperature (300 K).

The analysis of experimental data dealing with thermal and electrical conductivity usually starts with the application of the acoustic approximation as well as with some other techniques such as the approximation of collision time. This approach may be doubtful for strongly anharmonic systems, which organic conductors are likely to be.

The coupling of a vibrating amplitude to the frequency of oscillations may result in a strong violation of ordinary dispersion relations, at least for phonons. We expect that due to the monotonic dependence of phonon frequency on wavevector (i.e., the basic analytic properties being retained) for small wavevectors the usual properties of the acoustic approximation will still hold. So far the coupling of compressibility to hydrostatic pressure has led to the renormalisation of phonon frequencies resulting in a pressure dependence of transport properties. In our simplest approach we will start with the commonly used approximation of a collision time, and for computation of the thermal resistivity introduced by irradiation we define an additional resonant scattering time τ_R for phonons. The thermal conductivity may then be expressed in the usual way by the use of the Debye thermal conductivity integral (Walker 1963):

$$K = \frac{k^4 T^3}{2\pi^2 v \hbar^3} \int_0^{\theta/T} \tau_R \frac{x^4 e^x}{(e^x - 1)^2} dx \quad (3)$$

where v stands for the sound velocity and k is the Boltzmann constant. The frequency dependence of the resonant relaxation rate at low temperatures ($T < \theta$) may generally be expressed in the form of a damped lorentzian (Pohl 1962):

$$\tau_R^{-1} = 4n\pi v^3 \delta \omega^2 / [(\omega_0^2 - \omega^2) + \delta \omega^2] \quad (4)$$

where n is the concentration of defects and the constant δ is a measure of the rate of phonon energy loss due to the friction forces caused by irradiation and free charge carriers. Such a damping affects only the narrow band of phonons with frequency near ω_0 (the resonant frequency) and may be assumed independent of frequency. The relaxation rate τ_R^{-1} is introduced into the thermal conductivity expression and for the resonant frequency we obtain by simple calculation

$$\omega_0 = (2J_4/J_2)^{1/2} T_m = 3.9 T_m. \quad (5)$$

J_4 and J_2 are Debye integrals and they saturate at temperatures $T \ll \theta$. T_m is the temperature at which the minimum of the thermal conductivity occurs.

For $T_m = 9$ K we get $\omega_0 = 35$ K. The only adjustable parameter in (3) is the sound velocity v . By simple comparison of the thermal resistivity minima ($\sim v^4$) at 1 and 12 kbar (see figure 8) it is possible to derive the change of sound velocity due to the application of a pressure of 12 kbar. A crude estimate gives $v(12 \text{ kbar})/v(1 \text{ kbar}) \approx 1.4$. This pressure dependence is in fair agreement with the reduction of the compressibility ($\sim v^{-2}$) by a factor of two that has been observed for TTF-TCNQ in the same pressure range (Filhol *et al* 1981). The applied hydrostatic pressure affects both the electronic and lattice contributions to the thermal conductivity. Using the Wiedemann–Franz law we may calculate the electronic contribution to the thermal conductivity (K_e) and obtain the lattice part by subtraction. At room temperature and zero pressure the conductivity of $(\text{TMTSF})_2\text{PF}_6$ is $21 \pm 2 \text{ mW cm}^{-1} \text{ K}^{-1}$ and for the lattice contribution K_L we have $8 \text{ mW cm}^{-1} \text{ K}^{-1}$.

From figures 2 and 3 it is evident that the ratios of electronic and phonon contributions to the thermal conductivity at room temperature are not changed by the application of hydrostatic pressure. This cannot be explained if the lattice thermal conductivity is mainly limited by phonon–phonon Umklapp scattering. On the basis of the acoustic approximation the ratio K_e/K_L should change as $K_e/K_L \sim 1/\theta$, i.e. a change of about 50% may be expected for K_e/K_L , much more than what the error bars allow. In the parent compound TTF-TCNQ the lattice thermal conductivity (Salamon *et al* 1975) at

room temperature is five times larger than it is in $(\text{TMTSF})_2\text{PF}_6$ or $(\text{TMTSF})_2\text{ClO}_4$ at ambient pressure. In this material the existence of a phonon-phonon Umklapp contribution is corroborated by the fact that thermal conductivity increases sharply at low temperatures. Thus the additional reduction of thermal conductivity in organic conductors such as $(\text{TMTSF})_2\text{PF}_6$ or $(\text{TMTSF})_2\text{ClO}_4$ may be explained as arising from the phonons scattered off the electron gas. More evidence supporting this conclusion is obtained from the fact that the thermal conductivity of $(\text{TMTSF})_2\text{PF}_6$ at room temperature is not reduced under irradiation. This is probably due to a balance effect between the heat carried by electron-scattered phonons and the heat carried by mobile electrons. In irradiated samples, electrons become less mobile (the electrical conductivity decreases under irradiation) but the scattering power of these electrons is diminished. Consequently the lattice is predominant for heat transport in irradiated samples. As far as clean samples are concerned, assuming the electrons are the main scattering centres for the phonons at 12 kbar, the lattice contribution to the thermal conductivity may be expressed as (Berman 1978)

$$1/K_L = (1/L_0 T) \sigma^2 n^2 / 3. \quad (6)$$

If $K_L = 20 \text{ mW cm}^{-1} \text{ K}^{-1}$, $L_0 = 2.4 \times 10^{-8} \text{ W cm K}^{-1}$ (the Lorentz number), σ (12 kbar, 300 K) = $1500 (\Omega \text{ cm})^{-1}$ and n stands for the number of carriers per molecule. Equation (6) gives $n \approx 0.5$ in good agreement with optical data (Jacobsen *et al* 1981) and the stoichiometry of the salts.

4. Discussion

The particular sensitivity of the thermal conductivity to magnetic field at low temperature deserves a special discussion which is undertaken in this section. Figures 4 and 10 show that a mechanism for heat transport is recovered under high magnetic field while at the same time electronic transport is strongly impeded (Jérôme 1981, Chaikin *et al* 1984). The sensitivity to magnetic field suggests that electrons are involved in the transport of heat at low temperature, a situation that is in agreement with most cases of regular metals at low temperature (Ziman 1960). Recent Hall constant measurements (Ribault *et al* 1983) performed on $(\text{TMTSF})_2\text{ClO}_4$ at low temperature do show conclusively that the Fermi surface is planar and contains 0.5 carriers per molecule, as can be inferred for a quasi-1D conductor. However the striking violation of the Wiedemann-Franz law that is observed under magnetic field shows that in spite of the extremely large conductivity at low temperature the mechanism giving rise to electron transport does not carry heat. One must go one step further since it is the destruction of the mechanism leading to high conductivity that allows the restoration of heat transport. Clearly an interpretation of the electronic properties at low temperature in terms of a single-particle Fermi sea is not satisfactory. Another interpretation has been proposed and provides an interpretation of both electronic and heat transport. This interpretation is based on the existence of precursors, at high temperature, of the superconducting ordering occurring at low temperature (Schulz *et al* 1981, 1983). It is well known that in a quasi-1D conductor the electron gas undergoes a transition to the superconducting state at a temperature that is not simply related to the strength of the Cooper pairing as it is for regular 3D superconductors. Instead the transition temperature is given (in the limit of weakly interacting electrons) by a relation such as

$$T_c \sim (J_{\perp} T_c^{\text{MF}})^{1/2} \quad (7)$$

where $J_{\perp} = t_{\perp}^2/t_{\parallel}$ is the interchain Josephson coupling and T_c^{MF} is the temperature where the phase transition should take place assuming the intrachain Cooper pairing to be isotropic (the mean-field approximation). Admittedly the reduction of the transition temperature can be drastic in a quasi-1D conductor whenever the mean-field transition temperature is large compared with the interchain coupling. In such a case the mean-field temperature has no real thermodynamic meaning. The mean-field temperature gives an order of magnitude for the temperature domain in which strong (1D) superconducting correlations begin to grow in the 1D electron gas (i.e. $t_{\perp} = 0$). The consequence of 1D superconducting correlations is twofold (J erome and Schulz 1982).

(i) Fluctuating intrachain Cooper pairs characterised by a binding energy $2\Delta \approx kT_c^{MF}$ contribute to the DC conductivity; this is a fluctuating collective mode.

(ii) The electron states contributing to the collective mode are removed from the single-particle density of states. Hence a drop of the density of states occurs at the Fermi energy over an energy width of the order of 2Δ ; this is the formation of the 1D pseudo-gap.

The formation of the pseudo-gap on cooling below T_c^{MF} is accompanied by a drop of the single-particle contribution to the DC conductivity ($\sigma_{SP} \ll \sigma$ (observed)). Therefore, the Wiedemann–Franz contribution to the thermal conduction is expected to drop at low temperature. Precursor superconducting effects can be removed by the application of a magnetic field in much the same way as regular three-dimensionally ordered superconductivity is destroyed above H_{c2} . The significant difference is, however, the much larger magnitude of the magnetic field needed to create Meissner currents in the fluctuating regime due to the weak Josephson-like interchain coupling. Accordingly, the fluctuation diamagnetism is expected to be small in the fluctuation regime (Schulz *et al* 1981) and has not been detected so far, but this is not contradictory with the observation of a significant enhancement of the conductivity since the conductivity of

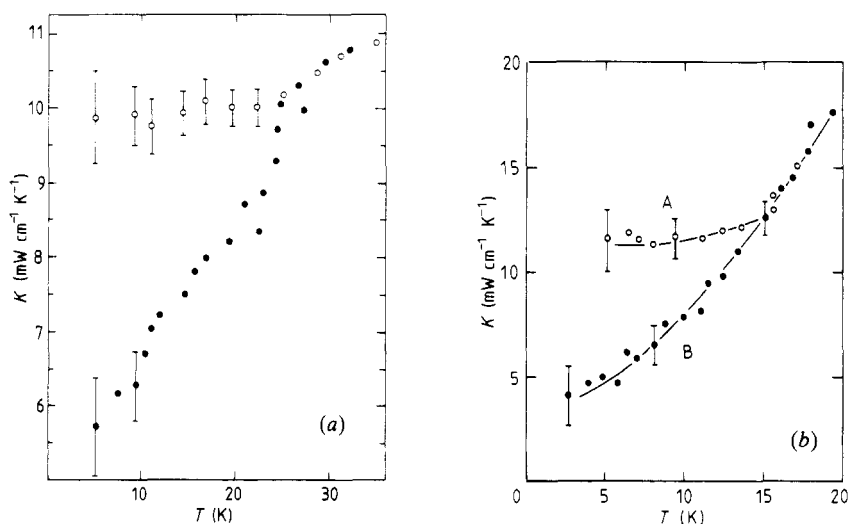


Figure 10. (a) Thermal conductivity of $(TMTSF)_2ClO_4$ at zero pressure for zero magnetic field (full circles) and for 0.2 T perpendicular to the high-conductivity axis (open circles). (b) Thermal conductivity of $(TMTSF)_2PF_6$ in a transverse field of 0.3 T (open circles) and at zero magnetic field (full circles). The pressure is 12 kbar.

single-particle origin is likely to be small at low temperature ($2000 (\Omega \text{ cm})^{-1} \leq \sigma_{\text{sp}} \leq 10\,000 (\Omega \text{ cm})^{-1}$). In short, we consider that the drop of the thermal conductivity below 30 K and its field dependence observed either in $(\text{TMTSF})_2\text{ClO}_4$ or in $(\text{TMTSF})_2\text{PF}_6$ under pressure, constitute a signature of superconducting precursor effects developing below a T_c^{MF} of about 25 to 30 K. Several arguments have been proposed against the fluctuation model. We shall briefly review and refute here the arguments related to thermal conductivity data; more exhaustive discussions are given in other articles (Jérôme 1984, Schulz *et al* 1983). It has been argued (Chaikin *et al* 1984), following the theory of fluctuations in anisotropic superconductors (Abrahams *et al* 1970), that the effect of fluctuations should enhance K and not decrease it, as observed experimentally. However the theory of Abrahams *et al* (1970) deals with the transition temperature corresponding to the onset of 3D long-range order (in the present compounds T_c would be 1.2 K) when the use of an anisotropic BCS superconductor picture becomes well justified. Therefore, the enhancement of K predicted by the Abrahams *et al* (1970) theory is restricted to a very narrow temperature domain close to T_c , namely where $(T - T_c)/T_c \sim 10^{-2}$ or thereabouts. This is definitely not the range of temperature from 4.2 to 30 K that is of interest in the present study. In the latter temperature domain low-dimensional quantum fluctuations tend to suppress $N(E)$ close to E_F and thus also the electronic thermal conduction. It has also been argued that the onset of magnetism could explain the observed field dependence of K (Kwak 1984). This argument is not relevant for the R -state of either $(\text{TMTSF})_2\text{ClO}_4$ or for $(\text{TMTSF})_2\text{PF}_6$ under pressure since a vast amount of experimental data have established the absence of a magnetic condensation in these conducting salts at low temperature and low magnetic field.

According to data in figure 8 the thermal conduction is impeded by the presence of defects. This result is in fair agreement with the drastic effects of irradiation in quasi-1D conductors which firstly suppresses superconducting fluctuations and secondly, at higher doses, decreases the single-particle conductivity through electron localisation (Bouffard *et al* 1982).

Finally we wish to comment on the data displayed in figure 11 which bear some resemblance to the temperature dependence of the critical field in a type II superconductor for which T_c would be ≈ 27 K. In a quasi-1D conductor such as $(\text{TMTSF})_2\text{ClO}_4$ the transverse overlap integral is not zero since the ratio t_{\perp}/t_{\parallel} is about 1/10 if the transverse b axis is considered. The non-zero value of t_{\perp} is the reason for the existence of long-range order at a finite temperature. At a temperature high compared with the value of t_{\perp} the quasi-1D electron gas behaves as a 1D electron gas (i.e. as if $t_{\perp} = 0$). Electron-electron and electron-hole divergences interfere closely. However this interference stops at $T \approx T_x$ (a crossover temperature) and below T_x electron states within an energy distance kT_x from the Fermi surface must be treated with the finite value of the transverse coupling whereas the rest of the electron states deeper in the Fermi sea continue to contribute to the 1D precursor effect (Bourbonnais 1984). T_x is thus the temperature that marks the beginning of transverse coherence for the small fraction of the electrons close to the Fermi level. For a free quasi-1D electron system $T_x \approx t_{\perp}/\pi$, which leads to $T_x \approx 20\text{--}30$ K taking the accepted value of $t_{\perp} \approx 0.012$ eV. As noticed by Bourbonnais (1984) the existence of interactions between electrons may depress T_x significantly. Figure 11 may therefore provide some information concerning the domain of existence of this short-range transverse ordering in magnetic field. Strong transverse correlation could start around 25 or 27 K in $(\text{TMTSF})_2\text{ClO}_4$ in zero applied field but of course true isotropic long-range order (with the full Meissner effect and zero resistance) sets in only at 1.2 K.

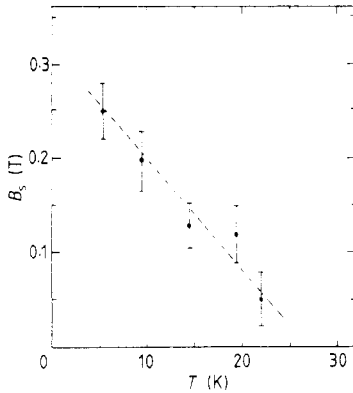


Figure 11. The saturation magnetic field for the thermal conductivity data in $(\text{TMTSF})_2\text{ClO}_4$ at zero pressure.

Acknowledgment

We thank all members of the high-pressure group who made these delicate measurements possible. One of us (DD) would like to express his gratitude to the staff of the Physics Department at UCLA who gave him the opportunity to perform four-probe measurements on $(\text{TMTSF})_2\text{ClO}_4$ samples and to M Prester for his help at an early stage of the experiment.

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