

MAGNETIC SUSCEPTIBILITY UNDER PRESSURE AND ANISOTROPY OF ELECTRICAL CONDUCTIVITY
IN QUASI-ONE-DIMENSIONAL (PERYLENE)₂(AsF₆)_{0.75}(PF₆)_{0.35} × 0.85CH₂Cl₂*

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The magnetic susceptibility and electrical conductivity of the quasi-one-dimensional organic metal (Perylene)₂(AsF₆)_{0.75}(PF₆)_{0.35} × 0.85CH₂Cl₂ was studied in the temperature range 3–300 K. The measured susceptibility can be separated into its defect χ_d , core χ_c and enhanced paramagnetic spin susceptibility χ_p components. χ_p is found to decrease upon lowering the temperature or applying pressure, in analogy with results on charge transfer compounds such as TTF–TCNQ. The conductivity ratio $\sigma_{\parallel}/\sigma_{\perp}$ also decreases with falling temperature. The present results are discussed within the context of a model which takes into account band-narrowing (electron localization) due to strong electron–phonon coupling.

1. INTRODUCTION

THE PHYSICS of quasi-one-dimensional organic metals such as TTF–TCNQ or (TMTSF)₂ClO₄ commands at the present time a great deal of interest. Difficulties in the synthesis of high purity samples, however, have restricted their preparation to but very few laboratories and could seriously hamper their production on a large scale in practical applications. On the other hand, crystals of highly conducting perylene radical salts, such as (Perylene)₂(AsF₆)_{0.75}(PF₆)_{0.35} × 0.85CH₂Cl₂, can be relatively easily prepared by the nonspecialist using standard electrocrystallization procedures [1, 2]. The room temperature conductivity for good crystals

along the needle axis σ_{\parallel} ranges typically from 500 to 1400 ($\Omega\text{-cm}$)⁻¹ and the temperature dependence of both d.c. and microwave conductivity data indicates a metallic state down to about 180 K [2]. The value $\sigma_{\parallel} \approx 1400$ ($\Omega\text{-cm}$)⁻¹ is higher than the room temperature conductivities of all known organic metals, with the exception of HMTSF–TCNQ [3, 4]. A confirmation for metallic behavior at room temperature was also obtained from optical reflectance measurements [2]. The reflectance for the electric field vector parallel to the chain axis is typical for a Drude metal with a sharp plasma edge. In contrast, the reflectance for the electric field vector perpendicular to the stack axis is rather flat without a typical plasma edge, thus demonstrating the quasi-one-dimensional character of these crystals.

In the present paper we present measurements of both the magnetic susceptibility under pressure and the anisotropy of the electrical conductivity on this perylene radical salt and compare them to analogous results on other quasi-one-dimensional organic metals.

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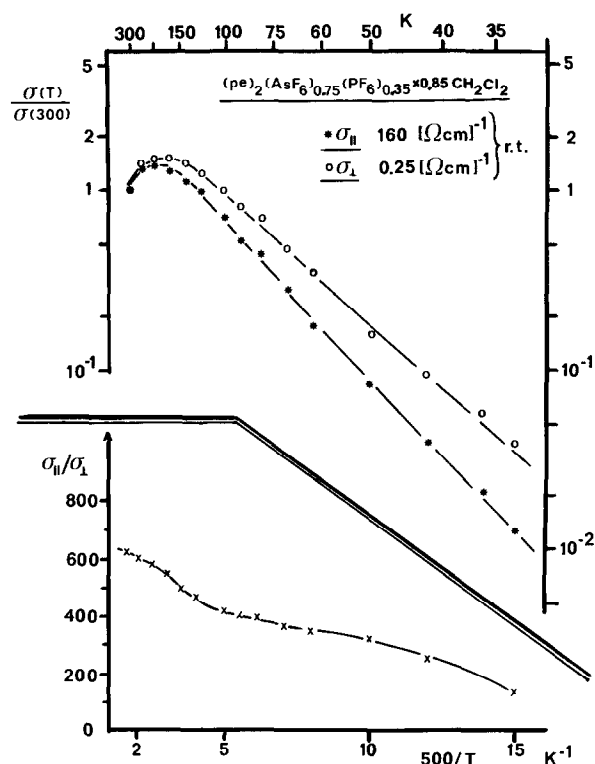


Fig. 1. *Upper*: Relative temperature dependence of the electrical conductivity σ_{\parallel} parallel to the stack (*a*)-axis and σ_{\perp} perpendicular to the stack (*b*)-axis (see [1] for crystal structure). *Lower*: Temperature dependence of conductivity ratio $\sigma_{\parallel}/\sigma_{\perp}$ exhibiting the large anisotropy.

2. ELECTRICAL CONDUCTIVITY

The quasi-one-dimensional character of the present crystals was confirmed by carrying out d.c. conductivity measurements parallel σ_{\parallel} and perpendicular σ_{\perp} to the stock axis. The Montgomery method [5] was used on relatively broad crystals (0.5–0.8 mm). In the lower half of Fig. 1 the ratio of the parallel to perpendicular conductivities $\sigma_{\parallel}/\sigma_{\perp}$ is plotted vs $500/T$. This ratio decreases from its relatively large [4] room temperature value of about 640–130 at 35 K. A similar but less dramatic decrease in $\sigma_{\parallel}/\sigma_{\perp}$ with falling temperature is observed for (TMTSF)₂PF₆ at 12 kbar [6] whereas for TTF–TCNQ it is well known that this ratio increases dramatically [7].

In the upper half of Fig. 1 the temperature dependences of σ_{\parallel} and σ_{\perp} normalized to their respective room temperature values are shown. $\sigma_{\perp}(T)$ takes on approximately the same value at room temperature in both possible directions. Both $\sigma_{\perp}(T)$ and $\sigma_{\parallel}(T)$ initially increase with decreasing temperature, showing semi-conducting behavior for $T < 180$ K. The room temperature value $\sigma_{\parallel}(300 \text{ K}) \approx 160 (\Omega\text{-cm})^{-1}$ is relatively small. This is probably due to a relatively large number of

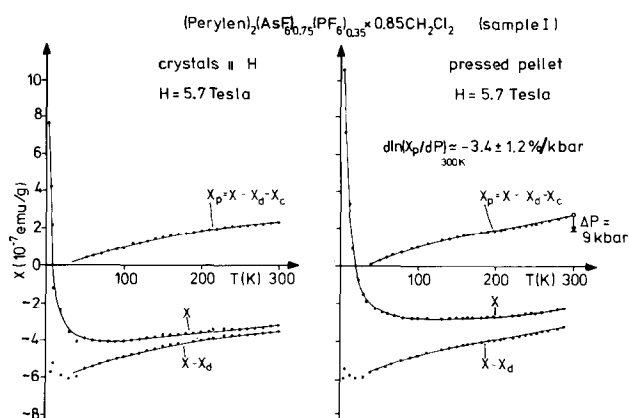


Fig. 2. Measured susceptibility χ at 5.7 T as a function of temperature for both crystalline needles and pressed pellet. χ_d , χ_c and χ_p stand for defect, core and paramagnetic susceptibilities, respectively.

imperfections in these large crystals. It is reasonable to expect that the ratio $\sigma_{\parallel}/\sigma_{\perp}$ would be even higher for more perfect crystals.

3. MAGNETIC SUSCEPTIBILITY

The static magnetic susceptibility of (Perylene)₂(AsF₆)_{0.75}(PF₆)_{0.35} × 0.85CH₂Cl₂ was measured as a function of temperature from 3 to 300 K and as a function of pressure to 9 kbar at room temperature. A Faraday magnetometer was used with the magnetic field set of 5.7 T. See [8] for a more complete description of the experimental apparatus.

To establish the dependence of the susceptibility on the condition of the sample, measurements were carried out on single-crystalline needles, a pressed pellet, and also on a sample pulverized in a mortar. The mass of the samples was approximately 70 mg. The temperature dependence of the measured susceptibility χ of a single-crystalline sample is shown in Fig. 2 where the field is applied approximately parallel to the needle axes. At room temperature χ is diamagnetic. As the temperature is lowered, this diamagnetism initially becomes slightly more negative before passing through a minimum at about 80 K and becoming paramagnetic below 10 K. If the crystalline needles are now compressed into a pellet, the paramagnetic component is enhanced at all temperatures. A further substantial increase in the paramagnetism is seen in measurements on a pulverized sample shown in Fig. 3. This increase in the paramagnetic component is particularly evident at low temperatures.

The susceptibility of many organic metals follows a power law at low temperatures, $\chi \sim T^{-n}$, with n lying between 0.6 and 1 [9]. This behavior is attributed to localized spins with random exchange coupling. To

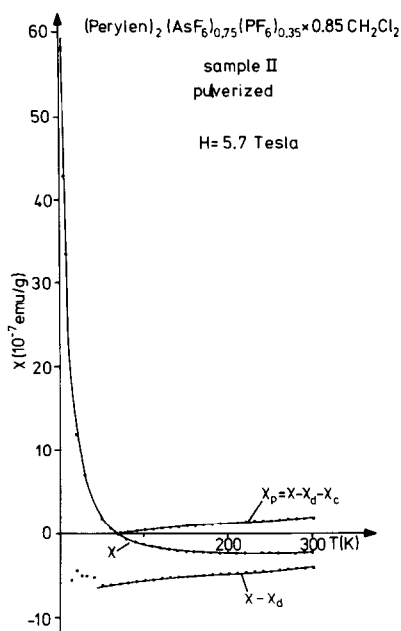


Fig. 3. Measured susceptibility χ at 5.7 T as a function of temperature for pulverized sample. χ_d , χ_c and χ_p stand for defect, core and paramagnetic susceptibilities, respectively.

estimate this defect susceptibility component χ_d we plot in Figs. 4 and 5 $\chi - \chi_c$ vs temperature on a double logarithmic scale where $\chi_c = -0.59 \times 10^{-6} \text{ emu g}^{-1}$ is the value of the core diamagnetism calculated from the appropriate Pascal constants. The low temperature ($T < 50 \text{ K}$) paramagnetic susceptibility can indeed be fit by a power law $\chi_d \sim T^{-n}$ with some variation in n . This susceptibility is smallest for the single crystals, increases for the pressed pellet, and is substantially larger for the pulverized sample. Such behavior is common and is attributed to extra paramagnetic centers produced by the mechanical crushing.

In Figs. 2 and 3 the paramagnetic tail χ_d is subtracted from the measured susceptibility χ . $\chi - \chi_d$ is seen to become more negative monotonically as the temperature is lowered, except at rather low temperatures ($T < 30 \text{ K}$) where the paramagnetic tail is so large that the value of $\chi - \chi_d$ is unreliable, being the small difference of two large quantities. The paramagnetic susceptibility of the sample χ_p is now obtained by subtracting off from the measured susceptibility both the defect and diamagnetic core contributions, i.e. $\chi_p = \chi - \chi_d - \chi_c$, as shown in Figs. 2 and 3. At room temperature the paramagnetic susceptibility χ_p is approximately equal to $+2.5 \times 10^{-7} \text{ emu g}^{-1}$ or $+9.2 \times 10^{-5} \text{ emu mole}^{-1}$. The fact that this same value is attained for all three sample forms (needles, pellets, powder) supports the correctness of the above analysis. As the temperature is lowered, χ_p is seen to decrease

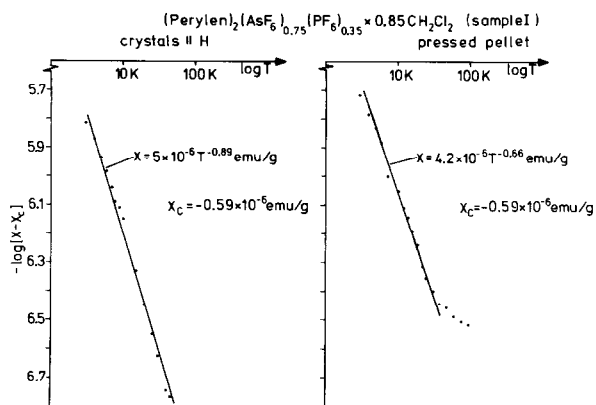


Fig. 4. Log-log plot of $\chi - \chi_c$ vs temperature for crystalline needles and pressed pellet. χ_c is core diamagnetism.

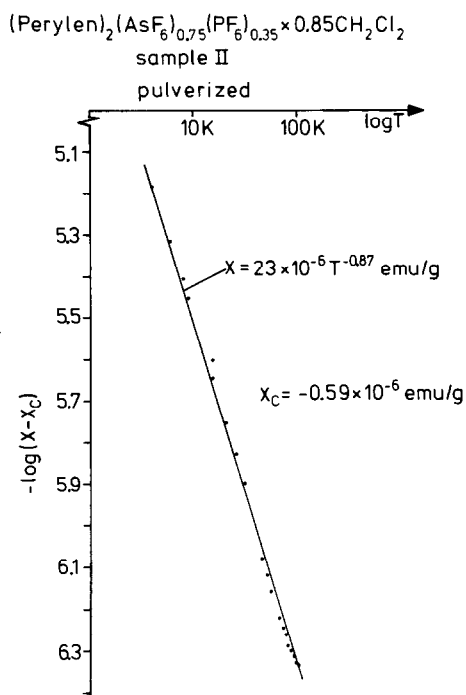


Fig. 5. Log-log plot of $\chi - \chi_c$ vs temperature for pulverized sample. χ_c is core diamagnetism.

monotonically, vanishing for temperatures below about 40 K. $\chi_p(300 \text{ K})$ also decreases under the application of hydrostatic pressure at the rate $\partial \ln \chi_p / \partial P \approx (-3.4\% \pm 1.2\%) \text{ kbar}^{-1}$, as indicated in Fig. 2.

The above results for the magnitude of the paramagnetic susceptibility, as well as its temperature and pressure dependences, are rather closely analogous to what is found for other organic metals [10, 11]. For example, the value of the susceptibility at ambient temperature often appears enhanced over the expected spin susceptibility [12]. From the measured plasma

frequency it can be estimated that the effective electron mass of the perylene compound is $m^* = 0.77m_0$ [2]. We use here the tight binding expressions $4t_{\parallel} = 2h^2/(m^*a^2)$ and $N(E_f) = (2\pi t_{\parallel} \sin k_f a)^{-1}$ for the band width and the density of states at the Fermi energy, respectively, where $a = 4.285 \text{ \AA}$ is the intermolecular separation [1] and $k_f = 0.275(\pi/a)$ is the Fermi vector for 0.55 hole charges per molecule [13] which is the case when 1.1 electrons per two perylene molecules are transferred to the (AsF₆)_{0.75}(PF₆)_{0.35} counter ions. Since $\chi_p = 2N(E_f)\mu_B^2$ we obtain here $4t_{\parallel} = 1.1 \text{ eV}$ and $\chi_p = +5.0 \times 10^{-5} \text{ emu mole}^{-1}$. If we assume a constant density of states as for free electrons in one-dimension, we find $\chi_p = +2.4 \times 10^{-5} \text{ emu mole}^{-1}$. Compared with these values, the measured ambient temperature susceptibility $\chi_p = +9.2 \times 10^{-5} \text{ emu mole}^{-1}$ is thus enhanced by a factor between *two* and *four*! This enhancement and the anomalous decrease in χ_p as the temperature is lowered are well known properties of many other organic metals, for example TTF–TCNQ [14]. In addition, the above pressure dependence of the susceptibility at ambient temperature is comparable within experimental error with that observed by Berthier *et al.* [15] for TMTTF–TCNQ, where $\partial \ln \chi_p / \partial P \simeq -6\% \text{ kbar}^{-1}$.

Two principal models have evolved in the past to account for the anomalous temperature and pressure dependence of the susceptibility of TTF–TCNQ and other charge transfer compounds. In the simplest approximation we have $\chi_p \sim N(E_f) \sim t_{\parallel}^{-1}$ from which it follows that the spin susceptibility χ_p should vary inversely as the bandwidth $4t_{\parallel}$. However, in TTF–TCNQ, from the pressure dependence of the plasma frequency [16], it has been estimated that $\partial \ln t_{\parallel} / \partial P \simeq +2.3\% \text{ kbar}^{-1}$ which would be too small to account for the above change in χ_p for TMTTF–TCNQ with pressure. Larger values of $\partial \ln \chi_p / \partial P$ would be possible if the susceptibility is exchange enhanced by the factor $S = [1 - IN(E_f)]^{-1}$, where I is the screened Coulomb interaction ($S \simeq 2$ at ambient temperature for TTF–TCNQ) [17]. In fact, if we assume $\partial I / \partial P = 0$ then it follows that $\partial \ln \chi_p / \partial P = S[\partial \ln N(E_f) / \partial P]$ so that the pressure dependence of χ_p would be enhanced over the Pauli value by the factor S . We point out, however, that in the two strongly exchange enhanced systems Pd ($S \simeq 10$) [18] and TiBe₂ ($S \simeq 70$) [18, 19] relatively little if any enhancement of $\partial \ln \chi_p / \partial P$ is believed to occur, presumably because I increases with pressure almost as fast as $N(E_f) \sim t_{\parallel}^{-1}$ decreases.

Mazumdar and Bloch [12] have recently shown that the magnitude of the effective short-range Coulomb interaction in molecular conductors can be a strong function of the degree of band filling. The enhancement of χ_p is expected to be particularly significant

for approximately half the quarter filled bands, being much less in between. This agrees with the results on the present perylene radical salt and numerous other organic metals [12].

Finally, a decrease in χ_p with falling temperature has been suggested [20] to arise via thermal contraction if a rapid decrease in I with pressure is postulated; however, no mechanism has yet been suggested for such an effect. Indeed such a decrease is opposite in sign to the above results on Pd and TiBe₂ where I is believed to increase with pressure [18, 19].

An alternate way to account for the enhanced susceptibility is to attribute it to band narrowing and the increase in the density of states resulting from the electron localization induced by strong electron–phonon coupling. Indeed, the electron mean-free-path l at ambient temperature in these organic metals is typically of the order of the intermolecular separation a . As the temperature is lowered, l increases thus reducing both the degree of localization and enhancement, i.e. χ_p decreases. One is thus dealing with a change from itinerant conductivity to hopping conductivity as the temperature is raised and l decreases. This change can be described by Holstein's polaron theory [21]. In the hopping-conductivity state the electrons are localized and the bandwidth collapsed, giving rise to an increase in the susceptibility which ultimately attains the Curie value for extreme localization.

A heuristic argument accounting for this process goes as follows: the short mean-free-path l gives rise to an uncertainty of the electron momentum of order $\Delta k = 1/l$. When we convolute a Gaussian wavepacket of this width with the electronic energy function $\epsilon(k)$, we obtain an averaged energy $E(k) = \int \epsilon(k') \exp[-(k' - k)^2 / 2(\Delta k)^2] dk'$. For a tight-binding band we have $\epsilon(k) = -2t_{\parallel} \cos ka$, from which it follows that $E(k) = 4t_{\text{eff}} \cos ka$, where the effective bandwidth is given by $4t_{\text{eff}} = 4t_{\parallel} \exp(-a/l)$. This expression is close to the one obtained by the full polaron theory [21] and also accounts well for the observed value of χ_p in TTF–TCNQ as well as the temperature and pressure dependence of χ_p in TTF–TCNQ [10, 15] and a large number of other organic metals [11].

In TTF–TCNQ the electrical resistivity decreases rapidly with pressure [22], $\partial \ln \rho / \partial P \simeq -19\% \text{ kbar}^{-1}$, which should lead to a significant decrease in both the degree of electron localization and the magnitude of the enhanced susceptibility, as found in experiment. For the present perylene-compound, accurate ambient temperature resistivity data under pressure are still lacking. However, an initial study would seem to indicate that the temperature of the metal–semiconductor transition at $\sim 180 \text{ K}$ is not strongly pressure dependent [23].

In TTF–TCNQ the rapid decrease in the conduction electron density as the temperature is lowered through the metal–semiconductor transition at ~ 60 K leads to an enhanced fall off in the spin susceptibility, in fact $\chi_p \approx 0$ for $T < 15$ K [14]. The absence of a clear anomaly in the susceptibility of the present perylene radical salts for temperatures below 180 K may be due to the broadness of the metal–semiconductor transition (see Fig. 1). We do note, however, that χ_p has fallen to nearly zero below a temperature (~ 50 K) where the increase in the sample resistivity would imply a sharp reduction in the conduction electron concentration. Also the fact that χ_p does appear to approach zero is evidence that the low temperature state of this compound is a charge density wave rather than a spin density wave.

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