

ELECTRIC CONDUCTIVITY AND THERMOPOWER OF QUASI ONE-DIMENSIONAL
 (PERYLENE)₂(AsF₆)_{0.75}(PF₆)_{0.35}·0.85CH₂Cl₂ CRYSTALS

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Résumé - La conductibilité parallèle et perpendiculaire à l'axe de la chaîne des molécules de pérylène aussi bien que la force thermique des cristaux de (pe)₂(AsF₆)_{0.75}(PF₆)_{0.35}·0.85CH₂Cl₂ sont mesurées et discutées en fonction de la température.

Abstract - The temperature dependence of the conductivity parallel and perpendicular to the stack axis as well as of the thermopower S of (pe)₂(AsF₆)_{0.75}(PF₆)_{0.35}·0.85CH₂Cl₂ crystals is reported.

Simple hydrocarbons such as naphthalene /1/, pyrene, triphenylene, perylene /2/ and fluoranthene /3/ can be used together with electrolytes like (C₄H₉)₄N⁺PF₆⁻, (C₄H₉)₄N⁺AsF₆⁻ etc. to generate conducting quasi one-dimensional crystals by electrochemical methods. Up to now especially perylene (pe) is well suited to form very stable highly conducting radical salts with room temperature d.c.-conductivities between 70-1400 (Ω cm)⁻¹ /2,4/. The perylene radical salts (pe)₂X_y⁻ with X= PF₆, AsF₆ and 1.1 ≤ y ≤ 1.5 crystallize in isomorphous orthorhombic lattices and form black needles, where the perylene molecules are arranged in segregated stacks in the direction of the needle (a-)axis with interplanar distances of about 3.4 Å and an angle of 37.7° between the bc-plane and the perylene molecules /2/. In the channels between the segregated perylene stacks the anions as well as solvent molecules (f.i. CH₂Cl₂ or THF) are arranged.

Down to about 180 K the conductivity σ of those crystals shows a metallic regime, that means the conductivity increases by lowering the temperature. Below 180 K the crystals become semiconducting probably due to a phase transition. This behaviour could be confirmed by microwave conductivity measurements at 9.3 and 23.5 GHz /4/. Optical reflectance measurements demonstrated nicely the quasi one-dimensional character of the perylene radical salts. For light in the energy range from 0.25- 4 eV and polarized perpendicular to the molecular stacks the crystals exhibit the optical behaviour of an insulating molecular crystal whereas for light polarized parallel to the perylene stacks a pronounced plasma edge at about 0.9 eV is observed /4,5/. The optical reflectance could be analyzed by a Lorentz-Drude model and on the basis of a tight binding model from the plasma frequency for the conduction band a bandwidth of 1.1 eV/5/ - 1.22 eV/4/ was obtained.

The quasi one-dimensional character of the crystals was proven now by temperature dependent measurements of the conductivity parallel $\sigma_{||}$ and perpendicular σ_{\perp} to the perylene stacks. Further the bandwidth of the conduction band was independently determined by thermopower measurements.

For the conductivity investigations relative broad (0.5 - 0.8 mm) (pe)₂(AsF₆)_{0.75}(PF₆)_{0.35}·0.85 CH₂Cl₂ (1) crystals were measured by the Montgomery method /6/. For the ratio of the electric conductivity

parallel to the stacks axis with respect to the conductivity perpendicular to the stacks(b) axis values between $400 \leq \sigma_{\parallel}/\sigma_{\perp} \leq 800$ were found. The room temperature value of σ_{\parallel} for those broad crystals was lower than usual /4/ as the example of the crystal shows in fig 1 with a value of $\sigma_{\parallel} = 160 (\Omega\text{cm})^{-1}$. This is probably due to a larger number of crystal imperfections in such broad crystals and it can be assumed that the ratio $\sigma_{\parallel}/\sigma_{\perp}$ for more perfect crystals might even be higher. Fig. 1 shows for a typical broad crystal on the bottom the ratio of the electrical conductivity $\sigma_{\parallel}/\sigma_{\perp}$ versus $1/T$. At room temperature the ratio $\sigma_{\parallel}/\sigma_{\perp}$ is about 640 and the ratio decreases by lowering the temperature to 35 K to a value of about 130. This shows that the quasi one-dimensional character of the crystals is reduced at low temperatures.

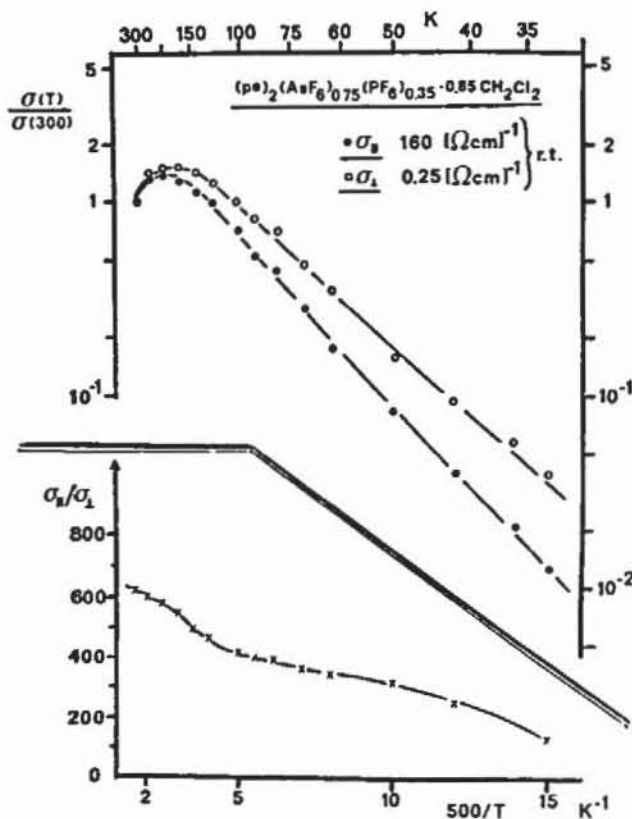


Fig. 1 - Conductivity parallel σ_{\parallel} and perpendicular σ_{\perp} to the perylene stacks as well as the ratio $\sigma_{\parallel}/\sigma_{\perp}$ versus $1/T$ (see text).

On top of fig. 1 the temperature dependence of the conductivity σ_{\parallel} and σ_{\perp} (both possible directions for σ_{\perp} show at room temperature about the same value) normalized to their room temperature values is shown. Both σ_{\parallel} and σ_{\perp} increase by lowering the temperature. Around 180 K the conductivities start to show a semiconducting behaviour. The observed band gap in this semiconducting range is about 0.038 eV as obtained from σ_{\parallel} .

Fig. 2 shows the temperature dependence of the thermopower for crystals of 1. The thermopower of organic metals yields at least as much information about the system as the electrical conductivity and the optical reflection. The measurement of the Seebeck coefficient S is often the most direct way to obtain information about the intrinsic properties because the thermopower of a metal is most sensitive to the electron transport properties. This is due to the fact that the thermoelectric power is a zero current transport measurement and therefore much less limited by breaks and defects in the one-dimensional chains than the electric conductivity unless there is also a large break in the heat flow path.

The device for the thermopower measurement was similar to that described by Chaikin and Kwak /7/. Fig. 2 shows that in the temperature

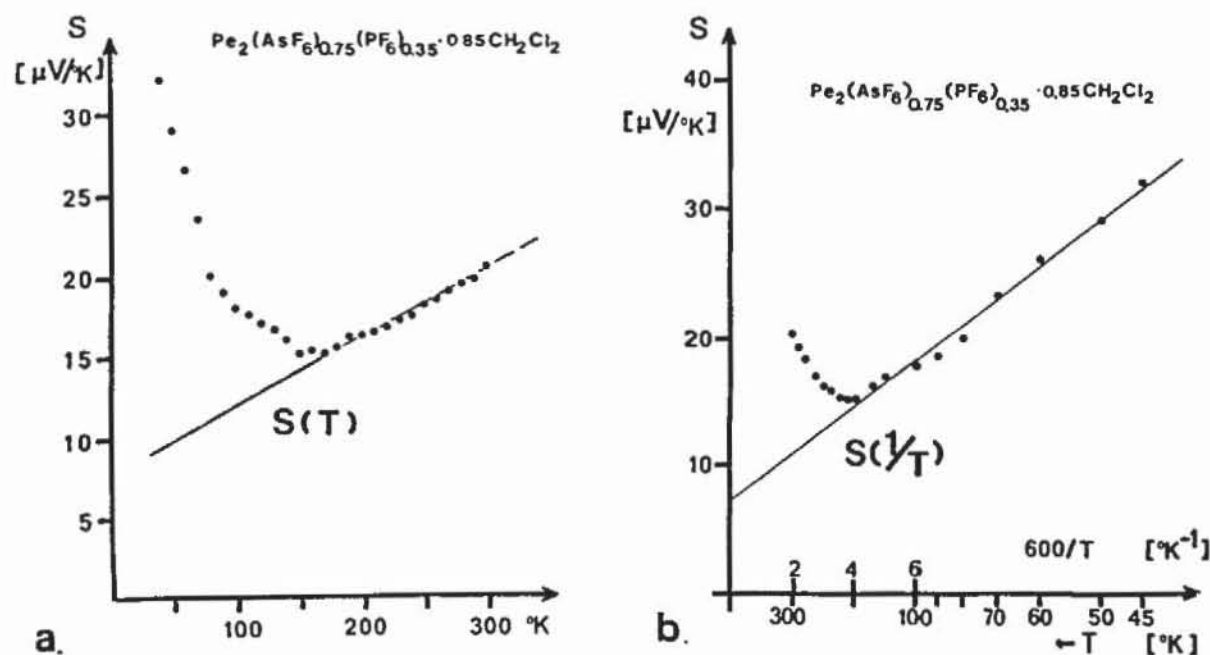


Fig. 2 - a) Temperature dependence of the thermopower S
 b) Thermopower S versus $1/T$ for crystals of 1

range between 300 and 180 K a linear temperature dependent thermopower S for crystals of 1 is found. This behaviour is characteristic for a degenerate electron gas and metallic conduction. The positive sign of S implies that the conductivity is dominated by holes as expected from crystals with a nearly $3/4$ filled conduction band. The large non-linear thermopower S below 180 K indicates that a metal insulator transition has taken place. From the slope of the linear temperature dependent part of the thermopower the bandwidth of the conduction band can be estimated.

Assuming for simplicity a single particle approach, the Seebeck coefficient S for a highly anisotropic free electron gas in a tight binding band $\epsilon_k = 1/2 W \cos(ka)$ is given /8/ by

$$(1) \quad S = \frac{2\pi^2 k_B^2}{3 e \cdot W} \cdot T \cdot \frac{\cos(\pi/2 \cdot \rho)}{\sin^2(\pi/2 \cdot \rho)}$$

Here W is the bandwidth and ρ the number of holes per site being $\rho = 0.55$ for crystals of 1. From the linearly dependent part of S in fig. 2a we obtain a bandwidth of $W = 1.2$ eV which is in very good agreement with the 1.22 eV obtained from the optical reflectance measurements /4/.

On the basis of the tight binding model the bandwidth W is related to the effective mass m^* by

$$(2) \quad W = \frac{2\hbar^2 \cdot k_F^2}{m^* a \cdot \sin(k_F \cdot a)}$$

where $a = 4.285$ Å denotes the distance between two perylene molecules in the direction of the stack axis and k_F the corresponding Fermi-vector which is given by $k_F = (\rho/2)(\pi/a) = 0.275\pi/a$. From eq.(2) a value of $m^* = 0.78m_0$ is obtained. Using a collision time $\tau = 3.3 \cdot 10^{-15}$ s and a charge carrier concentration $N_H = 1.4 \cdot 10^{21} \text{ cm}^{-3}$ /4/ leads to an intrinsic electrical conductivity $\sigma_0 = 1700 (\Omega\text{cm})^{-1}$ as obtained from eq(3).

$$(3) \quad \sigma = \frac{N_h \cdot e^2 \cdot \tau}{m^*}$$

This value is only about 20 % higher than the maximum observed value for the dc-conductivity $\sigma_{dc} = 1400 (\Omega\text{cm})^{-1}$ /4/ for crystals of 1. Using for the Fermi velocity v_F :

$$(4) \quad v_F = \frac{1}{\hbar} \cdot \left. \frac{d\epsilon(k)}{dk} \right|_{k=k_F} = 3 \cdot 10^5 \text{ m/s}$$

results at room temperature in a mean free path length $l = v_F \cdot \tau = 2.3a$. In the temperature range below 180 K the conductivity of crystals of 1 show a semiconducting behaviour. For a band semiconductor in the intrinsic range the Seebeck coefficient S can be expressed by eq.(5)/9/

$$(5) \quad S = - \frac{k_B}{e} \cdot \frac{(c-1)}{(c+1)} \cdot \left[\frac{E_g}{2kT} + 2 \right]$$

where E_g is the intrinsic gap and $c = \mu_e / \mu_h$ the ratio of the electron and hole mobilities. That means that for an intrinsic semiconductor in this case S is linear dependent on $1/T$. Fig. 2b shows S versus $1/T$ for crystals of 1. It can be seen that in fact below 180 K S is linearly dependent on $1/T$. From the slope of S versus $1/T$ we obtain an intrinsic gap $E_g = 0.05$ eV in good accordance with typical band gap values of 0.03 - 0.09 eV /2,4/ for the perylene radical salts as obtained from the conductivity measurements. For the ratio of the electron and hole mobilities a value of $c = 0.92$ is found.

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