

SPECTRAL REFLECTANCE OF THE ONE-DIMENSIONAL ORGANIC METALS
(PERYLENE)₂(PF₆)_{1.1} × 0.8CH₂Cl₂ AND (PERYLENE)₂(AsF₆)_{1.1} × 0.7CH₂Cl₂*

R. Wilckens, H.P. Geserich and W. Ruppel

Institut für angewandte Physik der Universität, D-7500 Karlsruhe, West Germany

P. Koch and D. Schweitzer

Max-Planck-Institut für medizinische Forschung, Abteilung für molekulare Physik, D-6900 Heidelberg, West Germany
and

H.J. Keller

Anorganisch-chemisches Institut der Universität, D-6900 Heidelberg, West Germany

(Received 9 October 1981 by M. Cardona)

We report on the optical reflectance of (perylene)₂(PF₆)_{1.1} × 0.8CH₂Cl₂ and (perylene)₂(AsF₆)_{1.1} × 0.7CH₂Cl₂ single crystals in the energy range from 0.25 to 4 eV. For light polarized perpendicular to the molecular stacks the crystals exhibit the optical behaviour of an insulating molecular crystal, whereas for light polarized parallel to the stacks a pronounced plasma edge at $\hbar\omega = 0.9$ eV is observed. The experimental data were analyzed by a Lorentz–Drude model in order to determine the electrical conductivity, the carrier concentration, the effective mass, the collision time, the band width, and the Fermi vector of the crystals.

THE DISCOVERY of organic charge transfer salts which behave as a quasi-one-dimensional (*1d*) metallic conductor, was the beginning of an intense and successful search for organic compounds with *1d* metallic transport properties in the early seventies [1, 2]. The main aim has been the suppression of the metal–semiconductor transition, predicted for *1d*-metals, in order to reach a superconducting state. The recent realization that the conductivity is mainly related to the partially oxidized donor stacks, led to the synthetic replacement of the organic π -acceptor molecules by symmetric inorganic counterions. Most famous examples so far are bis-tetramethyltetraselenafulvalene hexafluorophosphate (TMTSF)₂PF₆, and (TMTSF)₂ClO₄. The first of these compounds becomes superconducting under a pressure of 12 kbar at 0.9 K [3], and the latter even under ambient pressure at 1.3 K [4].

The replacement of the heterocyclic donors, as, e.g. HMTSF or TMTSF, by simple aromatic hydrocarbons would be a further step in the simplification of the preparation of such quasi one-dimensional organic metals. First experiments using hydrocarbons such as perylene (pe), pyrene, or fluoranthene are promising [5, 6]. Recently, some of us have discussed the synthesis, the crystal structure, and temperature dependence of the

electrical conductivity of new one-dimensional organic metals of the composition peryleniumylhexafluorophosphate (pe)₂(PF₆)_{1.1} × 0.8CH₂Cl₂ and (pe)₂(AsF₆)_{1.1} × 0.7CH₂Cl₂ [5]. In the present paper we report optical measurements on these compounds and their evaluation. From reflection measurements on single crystals with light polarized parallel to the axis of the molecular stacks, the electrical conductivity in the direction of the metallic axis, the collision time and the effective mass of the mobile charge carriers were determined. Further, the value of the Fermi vector and the bandwidth were computed. Under illumination with light polarized perpendicular to the axis of the molecular stacks, the crystals behave optically as insulators.

The crystals were prepared by electrocrystallization. The starting materials perylene and either tetrabutylammoniumhexafluorophosphate (Bu₄NPF₆), or Bu₄NAsF₆, were dissolved in methylene chloride (CH₂Cl₂) and filtrated into an electrochemical cell and saturated with nitrogen. The crystals were grown during three days, using a constant current of 10 μ A, resulting in a potential of about 1.9 V, at a temperature of 20°C, and under exclusion of light. Shiny black crystals in form of platelets or needles were obtained at the anode. Details about the crystal preparation may be found in [5]. Chemical analysis yielded a composition of the crystals of (pe)₂(PF₆)_{1.1} × 0.8CH₂Cl₂ and (pe)₂(AsF₆)_{1.1} × 0.7CH₂Cl₂. In contrast to the similarly

* This work was supported by Stiftung Volkswagenwerk.

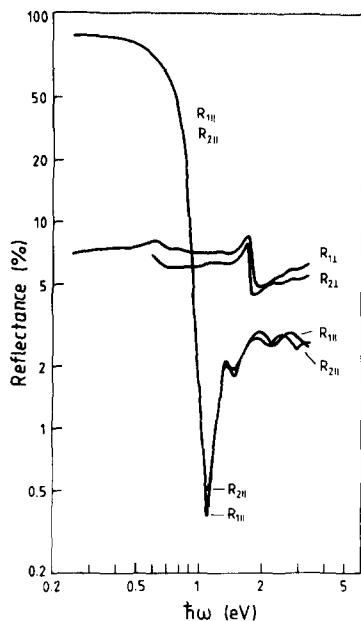


Fig. 1. Polarized reflectance spectra of needle-shaped single crystals of $(\text{perylene})_2(\text{PF}_6)_{1.1} \times 0.8\text{CH}_2\text{Cl}_2$ (index 1) and $(\text{perylene})_2(\text{AsF}_6)_{1.1} \times 0.7\text{CH}_2\text{Cl}_2$ (index 2). \parallel and \perp refer to the polarization direction with respect to the axis of the molecular stacks.

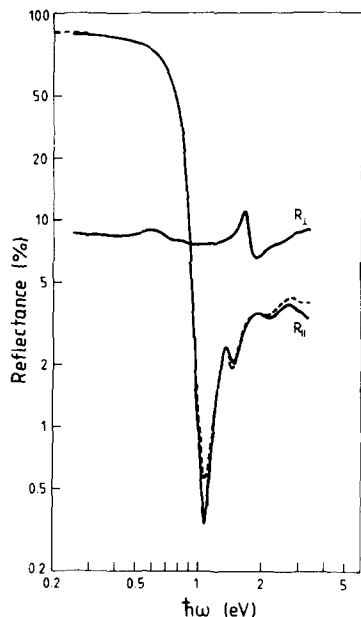


Fig. 2. Polarized reflectance spectra of a platelet-shaped single crystal of $(\text{perylene})_2(\text{PF}_6)_{1.1} \times 0.8\text{CH}_2\text{Cl}_2$. Full line: Experimental curve. Dashed line: Lorentz-Drude fit.

structured compounds of the type $(\text{TMTSF})_2\text{PF}_6$, there is no integer stoichiometric ratio of the organic donor molecules to the inorganic anions. Moreover, the crystals contain considerable amounts of the neutral solvent in the anion channels.

For the optical measurements crystals with well reflecting growth faces were selected. The reflectance data were obtained by a single-beam spectrometer especially adapted to tiny crystals. Figure 1 shows the reflectance spectra under polarized light for both compounds. They were obtained on needle-shaped specimens. If the direction of polarization is parallel to the axis of the molecular stacks, the spectrum obtained is typical for that of free carriers. The values of the reflectance reach almost 80% at low photon energies, and exhibit a steep plasma edge at 0.9 eV with a pronounced minimum. At higher photon energies the spectral distribution of the reflectivity is dominated by electronic transitions in the organic molecules. If the direction of polarization is perpendicular to the stack axis, the crystal behaves optically as a non-conducting organic compound. Differences due to the inorganic anions $(\text{PF}_6)^-$ and $(\text{AsF}_6)^-$ may not be discerned in the investigated spectral range.

After this comparison between two needle-shaped crystals with different anions, Figure 2 shows the reflectance spectrum for a $(\text{pe})_2(\text{PF}_6)_{1.1} \times 0.8\text{CH}_2\text{Cl}_2$ crystal of platelet shape. (Platelets were available only for the PF_6^- compound.) The quality of the reflecting surface of the platelet is apparently superior to that of the needles in Fig. 1, since the reflectivity is higher in the entire spectral range. While for small photon energies the difference is not significant, this difference increases with increasing photon energy. At 3.5 eV the reflectivity of the platelet exceeds that of the needle by 35%. This increase points to smaller scattering losses at the surface of the platelet. Therefore, for the quantitative evaluation of the measurements we used the reflectance spectrum R_{\parallel} obtained with the platelet. It was evaluated by a Lorentz-Drude model of the following form

$$\epsilon(\omega) = \epsilon_{\infty} + \sum_1^n \frac{\omega_{pn}^2}{\omega_{0n}^2 - \omega^2 - i\omega\Gamma_n} - \frac{\omega_p^2 \epsilon_{\infty}}{\omega^2 + i\omega\Gamma}. \quad (1)$$

The contribution to the dielectric function from vacuum polarization (unity) and from transitions beyond the measurement limit of 4 eV are lumped together in ϵ_{∞} . The ω_{0n} denote the eigenfrequencies, Γ_n the damping, and ω_{pn} the strength of the electronic transitions which are responsible for the structures between 1.3 and 4 eV. In the definition of the plasma frequency of the free carriers

$$\omega_p^2 = \frac{Ne^2}{\epsilon_0 \epsilon_{\infty} m^*} \quad (2)$$

the dielectric screening not due to electronic transitions below 4 eV is included. N , m^* , and $\tau = 1/\Gamma$ denote concentration, effective mass and collision time of the free carriers and define their contribution to the dielectric function.

The dashed line in Fig. 2 represents the best fit of the Lorentz–Drude model to the experimental data. The following values for the Lorentz oscillators are obtained:

$$\begin{aligned} \hbar\omega_{01} &= 1.38 \text{ eV} & \hbar\omega_{02} &= 2.0 \text{ eV} & \hbar\omega_{03} &= 3.0 \text{ eV}, \\ \hbar\Gamma_1 &= 0.18 \text{ eV} & \hbar\Gamma_2 &= 0.7 \text{ eV} & \hbar\Gamma_3 &= 0.9 \text{ eV}, \\ \hbar\omega_{p1} &= 0.27 \text{ eV} & \hbar\omega_{p2} &= 0.6 \text{ eV} & \hbar\omega_{p3} &= 0.7 \text{ eV}. \end{aligned}$$

For the Drude term results

$$\begin{aligned} \epsilon_\infty &= 2.55, \\ \hbar\omega_p &= 0.91 \text{ eV}, \\ \tau &= 4.4 \times 10^{-15} \text{ sec.} \end{aligned}$$

The relation

$$\sigma_0 = \omega_p^2 \epsilon_0 \epsilon_\infty \tau \quad (3)$$

yields as optical value for the electrical d.c.-conductivity $\sigma_0 = 2000 (\Omega\text{-cm})^{-1}$. This value is almost twice as large as those obtained from d.c.-measurements at room temperature [5]. Such a difference is characteristic for one-dimensional organic metals [7, 8], although there is no generally accepted unique explanation for this observation. It is plausible that d.c.-measurements are more sensitive to defects within the metallic chains than optical measurements. Following another explanation, the difference between the optical and the electrical values of the conductivity may be due to a strong electron–phonon coupling between the free charge carriers and the vibrations of the organic molecules [9]. Finally, there are many indications that in other one-dimensional metals the conductance in the direction of the stack axis in the d.c.-case is due to a sliding charge density wave, a collective phenomenon, whereas the excitation by photons gives rise to one-electron processes [10, 11]. The measurements carried out so far on the perylene compounds do not allow a distinction between these possible mechanisms. In order to elucidate this problem, further measurements of both the d.c.- and optical conductivity are intended over a larger temperature interval.

The optical data give information about the band parameters. The knowledge of the chemical composition permits an estimate of the concentration of the free charge carriers. In contrast to the charge transfer complexes of the type TTF–TCNQ with two stacks of organic molecules, the inorganic counter-ions $(\text{PF}_6)^-$ and $(\text{AsF}_6)^-$ carry a full negative charge each. This leads, based on the stoichiometric relations in the investigated crystals, to a charge deficit of $\rho = 0.55$ per organic molecule and, therefore, to a depletion of the highest occupied band by a little more than a quarter. The model of a *p*-type conductor suggests itself for the

following calculations. It yields for the carrier concentration a value of $N_p = 1.42 \times 10^{21} \text{ cm}^{-3}$.

Knowing the value of N_p , from the plasma frequency ω_p the effective mass of the free charge carriers may be computed to be $m^* = 0.9m_0$. This value is very low for an organic conductor, since organic conductors usually have narrow bands and hence high values of m^* . The effective mass of TTF–TCNQ, for example, with a value of $m^* = 3m_0$ is considerably larger [10]. The lowest value for the effective mass so far known for an organic conductor, namely that of $(\text{TMTSF})_2\text{PF}_6$, is 15% higher than the value found in this work [12]. One has to conclude that in the compounds discussed in this paper the width of the bands is of the same order of magnitude as in comparable inorganic compounds. On the basis of a tight-binding model, the bandwidth t follows from

$$t = \frac{2\hbar^2 k_F}{m^* a \sin(k_F a)}, \quad (4)$$

where $a = 4.285 \text{ \AA}$ denotes the distance between two perylene molecules in the direction of the stack axis, and k_F the corresponding Fermi vector, which can be calculated from the charge transfer ρ between donor and acceptor molecules following the relation

$$k_F = (\rho/2)(\pi/a). \quad (5)$$

With $\rho = 0.55$ a value of $k_F = 0.275\pi/a$ follows for the Fermi vector, and a value of $t = 1.1 \text{ eV}$ for the bandwidth. This value is well above the bandwidth of 0.4 eV for TTF–TCNQ but about the same as for $(\text{TMTSF})_2\text{PF}_6$ [12]. Since t is also a measure for the overlap integral, this result shows that the molecular orbitals between the donor molecules overlap much more in the perylene compounds than in TTF–TCNQ, although the distance between the mean molecular planes differs only slightly (3.40 Å in $(\text{pe})_2(\text{PF}_6)_{1.1} \times 0.8\text{CH}_2\text{Cl}_2$ [5], and 3.47 Å in TTF–TCNQ [13]).

It should be emphasized that due to the stoichiometric relations the value of the Fermi vector of the perylene compounds is incommensurate with the lattice constant. The same result has already been found for TTF–TCNQ and many other one-dimensional organic metals, although for a different reason, namely an incomplete charge transfer between the donor and acceptor molecules. In contrast, the Fermi vector in the one-stack compound $(\text{TMTSF})_2\text{PF}_6$ is commensurate with the lattice constant.

In summary the optical measurements on $(\text{pe})_2(\text{PF}_6)_{1.1} \times 0.8\text{CH}_2\text{Cl}_2$ and $(\text{pe})_2(\text{AsF}_6)_{1.1} \times 0.7\text{CH}_2\text{Cl}_2$ show that the new one-dimensional organic metals made up of radical cation aromatic hydrocarbons belong to a class of substances with comparatively strong overlap of the molecular orbitals along the stacks and

hence of a broader conduction band. Preliminary investigations on the related compounds (pyrene)₂SbF₆ and (fluoranthene)₂PF₆ even show a further shift of the plasma edge to higher energies indicating a further increase in bandwidth compared to the perylene compounds. This development tends to fill the gap between the usual narrow-band organic conductors and the large number of well-known broad-band inorganic conductors.

REFERENCES

1. See for reviews: (a) *Low-Dimensional Cooperative Phenomena* (Edited by H.J. Keller), Nato ASI-series B7. Plenum Press, New York (1975); (b) *Chemistry and Physics of One-Dimensional Metals* (Edited by H.J. Keller), Nato ASI-series B25. Plenum Press, New York (1977).
2. *Synthesis and Properties of Low-Dimensional Materials* (Edited by J.S. Miller & A.J. Epstein), *Ann. N.Y. Acad. Sci.* **313**, (1977).
3. D. Jerome, A. Mazaud, M. Ribault & K. Bechgaard, *J. Phys. Lett.* **41**, L95 (1980).
4. K. Bechgaard, K. Caneiro, M. Olsen, F.B. Rasmussen & C.S. Jacobsen, *Phys. Rev. Lett.* **46**, 852 (1981).
5. H.J. Keller, D. Nöthe, H. Pritzkow, D. Wehe, M. Werner, P. Koch & D. Schweitzer, *Mol. Cryst. Liq.* **62**, 181 (1980); *Chemica Scripta* **17**, 101 (1981).
6. C. Kröhnke, V. Enkelmann & G. Wegner, *Angew. Chemie* **92**, 941 (1980).
7. A.A. Bright, A.F. Garito & A.J. Heeger, *Phys. Rev.* **B10**, 1328 (1974).
8. C.S. Jacobsen, K. Mortensen, J.R. Andersen & K. Bechgaard, *Phys. Rev.* **B18**, 905 (1978).
9. H. Gutfreund, B. Horovitz & M. Weger, *Solid State Commun.* **15**, 849 (1974).
10. D.B. Tanner, C.S. Jacobsen, A.F. Garito & A.J. Heeger, *Phys. Rev.* **B13**, 3381 (1976).
11. D.B. Tanner, K.D. Cummings & C.S. Jacobsen, *Phys. Rev. Lett.* **47**, 597 (1981).
12. C.S. Jacobsen, D.B. Tanner & K. Bechgaard, *Phys. Rev. Lett.* **46**, 1142 (1981).
13. T.J. Kistenmacher, T.E. Phillips & D.O. Cowan, *Acta Cryst.* **B30**, 763 (1976).