

PLASMA REFLECTANCE OF THE ONE-DIMENSIONAL ORGANIC METALS OF THE TYPE
 (ARENE)₂XF₆ (ARENE=PERYLENE, PYRENE OR FLUORANTHENE ; X=P, As, Sb)^o

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Résumé - Nous avons étudié la position spectrale et la forme du seuil de réflexion due au plasma dans des sels de cations radicaux du type (arene)₂XF₆ en fonction de la nature de la molécule organique donneur et du transfert de charge entre les molécules donneurs et accepteurs.

Abstract - We have investigated the spectral position and the form of the plasma edge of different radical cation salts of the type (arene)₂XF₆ in dependence of the type of the organic donor molecule, and of the charge transfer between donor and acceptor molecules.

An important condition for the occurrence of one-dimensional metallic conduction in organic compounds is a sufficient overlap of the orbitals of adjacent molecules in the direction of the axis of the highest conductivity. In radical cation salts, consisting of organic donor molecules and inorganic acceptor molecules, the overlap of interest is that of the donor molecules in their stacking direction. In compounds containing tetrathiafulvalene (TTF) as donor molecule, it is probably mainly the size of the sulphur atoms that contributes to this overlap /1,2/. In order to enhance this overlap not particularly pronounced, one has gone two different ways. The first was the replacement of the sulphur by the larger selenium atom, as for instance in the radical cation salts which contain tetramethyltetraselenafulvalene (TMTSF) as donor molecule /3/. The other consisted in the enhancement of the number of sulphur atoms per molecule, as in the compounds with bis (ethylenedithiolo)tetrathiafulvalene (BEDT-TTF) as donor molecule /4/.

There is an entirely different, after the outlined way of reasoning surprising, possibility for the construction of one-dimensional metals. By choosing as donor molecules simple arenes, as naphthalene (Na), perylene (Pe), pyrene (Py), or fluoranthene (Fa), one desists from the bridge function of large atoms, as sulphur or selenium /5-7/. The metallic conduction in these compounds is apparently caused by the overlap of the orbitals of the relatively small carbon atoms.

In the present paper we report on optical investigations for the determination of the electronic transport parameters of these compounds as a function of the type of the donor molecule and of the amount of charge transfer between donor and acceptor.

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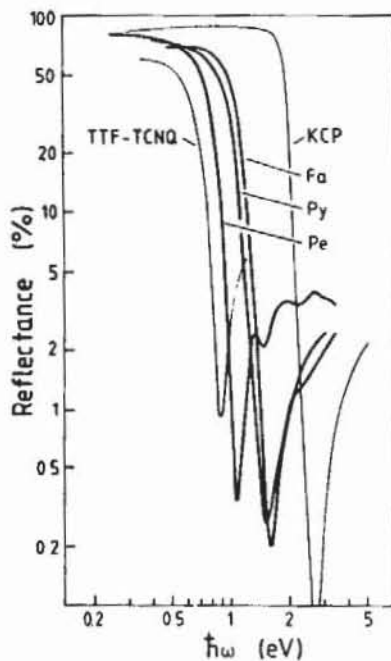
I - EXPERIMENTAL

Single crystals of the following chemical composition were grown by electrocrystallisation: $(\text{Pe})_2(\text{PF}_6)_{1.1} \times 0.8\text{CH}_2\text{Cl}_2$; $(\text{Pe})_2(\text{AsF}_6)_{0.97}(\text{PF}_6)_{0.43}$; $(\text{Py})_{12}(\text{SbF}_6)_7$, and $(\text{Fa})_2(\text{AsF}_6)_{0.2}(\text{PF}_6)_{0.8}$. The crystals were shiny black platelets or needles. Details about the crystal preparation and the crystal structure are found in ref.6-8. For the optical measurements crystals with well reflecting growth surfaces were selected. The reflectance data were obtained with a single-beam spectrometer especially adapted for tiny crystals.

II - RESULTS AND DISCUSSION

a) Variation of Donor Molecules

All crystals show reflectance spectra typical for 1d organic metals. If the direction of polarisation is perpendicular to the axis of the molecular stacks, the reflectance values are as low as those of an insulating molecular crystal. For light polarised parallel to the stack axis the reflectance spectrum, R_{\parallel} exhibits a steep plasma edge with a pronounced minimum. This is characteristic for the optical absorption by free charge carriers. Fig.1 shows that the spectral position of the



plasma edge is shifted towards higher energies, if the donor molecules are changed from perylene over pyrene to fluoroanthene. If we compare these reflectance spectra with those of the well-known 1d metals, we can draw the following conclusions: Up to now, there has been a broad gap between the spectral position of the plasma edge of organic metals, like tetrathiafulvalene-tetracyano-p-quinodimethane (TTF-TCNQ) and its derivatives including the organic superconductors on one hand /9,10/, and the spectral position of the plasma edge of inorganic 1d metals, like $\text{K}_2\text{Pt}(\text{CN})_4\text{Br}_{0.3} \times 3.2\text{H}_2\text{O}$ (KCP) and other Krogmann salts on the other hand /11/. The new 1d or-

Fig.1 - Polarised Reflectance R_{\parallel} of TTF-TCNQ; $(\text{Pe})_2(\text{PF}_6)_{1.1} \times 0.8 \text{CH}_2\text{Cl}_2$; $(\text{Py})_{12}(\text{SbF}_6)_7$; $(\text{Fa})_2(\text{SbF}_6)_{0.2}(\text{PF}_6)_{0.8}$, and KCP

ganic metals, built up from aromatic molecules, have higher plasma energies than the other 1d organic metals, and tend to fill this gap between organic and inorganic 1d metals.

For a quantitative analysis of R_{\parallel} , we use in the case of $(\text{Py})_{12}(\text{SbF}_6)_7$ and $(\text{Fa})_2(\text{AsF}_6)_{0.2}(\text{PF}_6)_{0.8}$ a simple Drude model. In the case of $(\text{Pe})_2(\text{PF}_6)_{1.1} \times 0.8 \text{CH}_2\text{Cl}_2$ this model is extended by a Lorentz term in order to take into account the electronic transitions between 1.3 and 4 eV. A fit of R_{\parallel} on the basis of these models yields the value of the plasma energy $\hbar\omega_p$, of the dielectric constant of the lattice ϵ_g , and of the mean collision time τ . Furthermore, from the relation

$$\sigma_0 = \frac{\omega_p^2 \epsilon_0 \epsilon_g \tau}{P} \quad (1)$$

optical values for the electrical conductivity may be determined. The charge transfer to the inorganic counter ions leads to a (3/4)-filled valence band and hence to p-type conductivity. Knowing the values of the carrier concentration N_p from the charge transfer ρ , we may also compute the values of their effective mass m^* from the plasma frequency ω_p according to

$$\omega_p^2 = (N_p e^2) / (\epsilon_0 \epsilon_g m^*) \quad (2)$$

On the basis of the tight-binding model follows further the bandwidth $4t$ from the overlap integral t to

$$4t = (\hbar^2 \rho \pi) / (m^* a^2 \sin \rho \pi / 2), \quad (3)$$

where a is the distance between the organic molecules in the direction of the metallic axis.

The values thus obtained for the three different compounds are compiled in Table I. For comparison, the corresponding data of TTF-TCNQ, (TMTSF)₂PF₆, and KCP are also given.

TABLE I Transport Properties of Some 1d Metals

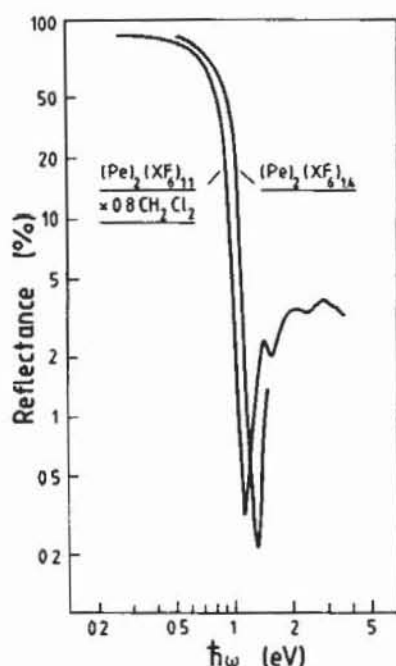
	$\hbar\omega_p$ (eV)	σ_0, opt ($10^3 \Omega^{-1} \text{cm}^{-1}$)	τ (10^{-15}sec)	N_p (10^{21}cm^{-3})	m^*/m_0	$4t$ (eV)
TTF-TCNQ	0.76	12	4	2.8	3	0.43
(TMTSF) ₂ PF ₆	0.87	11	2.7	1.4	1	1
(Pe) ₂ (PF ₆) ₁₁ x 0.8 CH ₂ Cl ₂	0.91	1.9	4.4	1.42	0.91	1.1
(Py) ₁₂ (SbF ₆) ₇	1.08	16	3.3	1.77	0.87	1.8
(Fa) ₂ (AsF ₆) _{0.2} (PF ₆) _{0.8}	1.18	1.9	2.9	1.63	0.71	2.25
KCP	1.98	7.5	4.3	1.1	0.2	

The data in the Table confirm a trend indicated by the shift of the plasma edge. The new compounds possess smaller effective masses and hence a stronger overlap of the molecular orbitals in the stacking direction than the other 1d organic metals. This is surprising because these new compounds lack the bridge function of large atoms as sulphur or selenium. As far as the widths of the valence band, given in Table I, are concerned, we note that the valence band of the fluoranthene salt is probably split into two subbands due to a slight dimerisation of the donor stacks. In the large elementary cell of the pyrene compounds, there occur even more different distances within the donor stack. Therefore, the valence band may be split into correspondingly more subbands in this case.

b) Variation of the Charge Transfer

While most radical cation salts exhibit a donor-acceptor ratio of exactly 2:1, this ratio can be varied within certain limits in the perylene salts. The explanation for this particular behaviour is found

in the possibilities for the sites of the inorganic acceptor molecules. These molecules have no fixed sites in these compounds. They are rather distributed statistically in the channels between the donor stacks. This allows for the formation of somewhat differing chemical compositions of the crystals during the electrocrystallisation process in accordance with the particular solvent employed. There are crystals with a donor-acceptor ratio of 2:1.1. These crystals contain additional neutral solvent molecules in the acceptor channels. On the other hand, crystals free of solvent have a donor acceptor ratio of 2:1.4 /6/.



In Fig.2 it is shown, that the plasma edge shifts with increasing charge excess to higher energies. As expected from equ.(2), this shift is proportional to the square root of the charge carrier concentration. This effect confirms at the same time the concept of a (3/4)-filled valence band.

Fig.2 - Polarised Reflectance R_{\parallel} of $(\text{Pe})_2(\text{PF}_6)_{1.1} \times 0.8 \text{CH}_2\text{Cl}_2$ and $(\text{Pe})_2(\text{AsF}_6)_{0.97}(\text{PF}_6)_{0.43}$

	ρ/Pe	$N_{\text{P}} (\text{cm}^{-3})$	$\hbar\omega_{\text{p}} (\text{eV})$
$(\text{XF}_6)_{1.1}$	0.55	$1.4 \cdot 10^{21}$	0.91
$(\text{XF}_6)_{1.4}$	0.7	$1.8 \cdot 10^{21}$	1.03

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