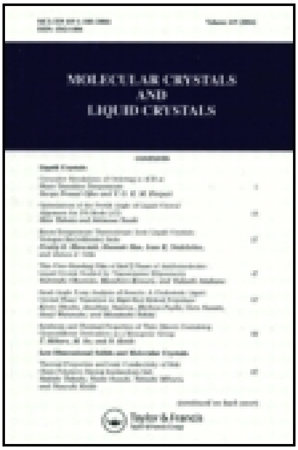

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Organic Composites Exhibiting Metallic Character: Preparation, Structure, Spectral Properties

Andre Brau [a], Imad Smirani [a], Jean-Pierre Farges [a], Victor N. Semkin [b c] & Andrzej Graja [a b]

[a] L.P.M.C., University of Nice - Sophia Antipolis, 06108, Nice, France

[b] Institute of Molecular Physics, Polish Academy of Sciences, 60-179, Poznan, Poland

[c] Ioffe Physico - Technical Institute, Russian Academy of Sciences, 194021, St. Petersburg, Russia

Version of record first published: 24 Sep 2006

Mol. Cryst. and Liq. Cryst., 2000, Vol. 354, pp. 63-70
Reprints available directly from the publisher
Photocopying permitted by license only

Organic Composites Exhibiting Metallic Character: Preparation, Structure, Spectral Properties

ANDRE BRAU[a], IMAD SMIRANI[a], JEAN-PIERRE FARGES[a], VICTOR N. SEMKIN[bc] and ANDRZEJ GRAJA[ab*]

[a]*L.P.M.C., University of Nice – Sophia Antipolis, 06108 Nice, France,* [b]*Institute of Molecular Physics, Polish Academy of Sciences, 60–179 Poznan, Poland and* [c]*Ioffe Physico – Technical Institute, Russian Academy of Sciences, 194021 St. Petersburg, Russia*

Optical conductivity spectra of the organic composite $(BEDT\text{-}TTF)_2/I_3$ obtained by direct solid-solid charge-transfer reaction between bis(ethylenedithio)tetrathiafulvalene and iodine are investigated in the infrared range. It shown that the granular structure of the composite strongly influence its conductivity for optical frequencies.

Keywords: organic composite; solid-solid charge-transfer reaction; BEDT-TTF; optical conductivity; IR spectra

INTRODUCTION

Many studies have been carried out in order to obtain conducting organic materials in a more applicable form than tiny single crystals, e.g. polycrystalline layers or compactions. The latter form has been developed since several years ago we have shown that charge-transfer (CT) reaction

* Corresponding author

between donor and acceptor moieties, could occur directly in the solid state, simply by grinding them together [1]. Recently, such a method has been employed for realising metallic organic composites BEDT-TTF/iodine, where BEDT-TTF is bis(ethylenedithio)tetrathiafulvalene [2]. These composites are simply obtained, in arbitrary amounts, from commercially available BEDT-TTF and iodine components (Aldrich). The non-limited size of a composite sample is its main advantage over single crystals. The physical properties of such composites roughly approximate the properties of $(BEDT\text{-}TTF)_2I_3$ single crystals, although they are quite different in details [2,3].

Recently, some of us have reported [2] that under appropriate conditions the composite between BEDT-TTF and iodine of stoichiometry 2 : 3 could retain metallic behaviour from 300 to 0.34 K. Below 5 K, the resistivity even starts to decrease at a more pronounced rate, thus suggesting the possible occurence of a superconducting transition in the composite at lower temperature. It was shown also that the spectral properties of the metallic composite $(BEDT\text{-}TTF)_2/I_3$ are similar to the properties of the crystalline organic metal β-$(BEDT\text{-}TTF)_2I_3$ [3].

In this paper we report optical conductivity spectra over large spectral and temperature ranges; some remarks on the physical properties of the $(BEDT\text{-}TTF)_2/I_3$ composite will be also given.

EXPERIMENTAL

Right proportions of the donor (BEDT-TTF) and acceptor (iodine) molecules are ground together during 8 hours, at room temperature, using a Retsch apparatus. The mixture is compacted under 5 kbars in the form of a disk. The samples prepared by this way are then annealed at 85° C during 2 hours and at 155° C during 2 minutes.

The reflectance spectra are taken on different small areas of the sample surface in the spectral range 550 - 7000 cm^{-1} using a FT IR Perkin Elmer

1725X spectrometer equipped with an IR microscope and a narrow band MCT detector. Width of each investigated area is about 0.1 mm and the spectral data show good overall surface homogeneity of the composite. The samples are placed into an Oxford Instruments helium cryostat (Optistat) with ITC 503 temperature controller and the spectra are recorded with unpolarized light from 300 down to 5 K.

To determine the optical conductivity, a phase shift on reflection is calculated by Kramers - Kronig transformation. The available experimental reflectivity data are supplemented with both low and high frequency extrapolations. Below 200 cm^{-1} a Hagen - Rubens extrapolation is effected, while above 40 000 cm^{-1} a standard high frequency extrapolation is assumed.

The morphology of the sample surface is investigated with an optical microscope and scanning electron microscope Jeol JEMT 300.

RESULTS AND DISCUSSION

The surface of the sample mechanically and thermally treated, although macroscopically homogeneous shows a grainy structure; it is presented in Fig. 1. The crystallites formed exhibit a typical disordered hexagonal shape which resembles that of electrochemically grown $(BEDT\text{-}TTF)_2I_3$ single crystals. The average dimension of the crystallites is about 2μm. They are randomly distributed in the sample and adjoining each other. From an analysis of the scanning electron microscope image of a $(BEDT\text{-}TTF)_2/I_3$ composite surface (Fig. 1) one can estimate a contents of the crystalline phase as about 57 %.

The infrared and near infrared reflectivity spectra of the composite (Fig. 2) are typical of the metallic phases of $\alpha\text{-}(BEDT\text{-}TTF)_2I_3$ and $\beta\text{-}(BEDT\text{-}TTF)_2I_3$ single crystals [4-7]. Common features include a plasma edge between 4800 and 5000 cm^{-1} which sharpens on cooling, a mid-infrared reflectance level which shows a strong and typical temperature dependence, and a pronounced non-

Drude structure in the range of molecular vibrations [3]. The most prominent feature in this region is a structured band centred at about 1200 cm^{-1} which is due to the activated a_g modes of BEDT-TTF involving the central C = C bond. This band is characteristic of $(BEDT\text{-}TTF)_2I_3$ salts, but some differences in its shape and assignment, caused mainly by differences in the crystal structure, are observed for the various phases of this system [8].

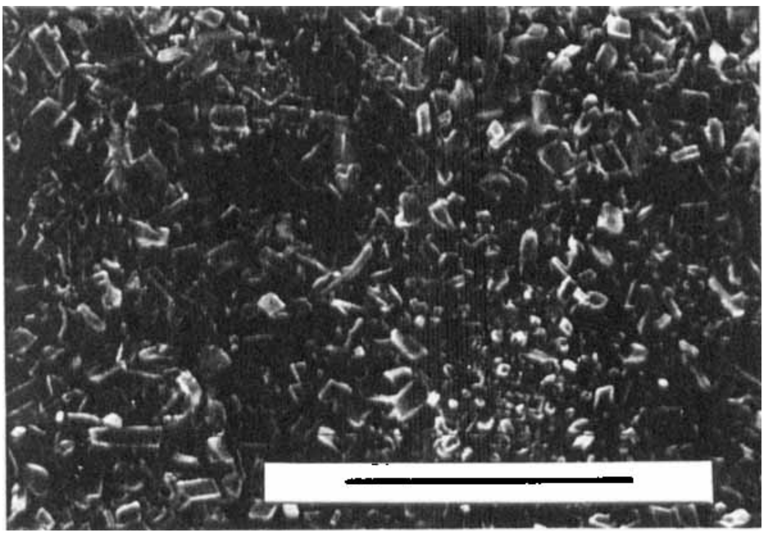

FIGURE 1 Scanning electron microscope image of a $(BEDT\text{-}TTF)_2/I_3$ composite sample surface after appropriate thermal treatment. Scale bar: 10 μm.

Recently, an analysis of the temperature dependence of the reflection spectra of the $(BEDT\text{-}TTF)_2/I_3$ composite has been performed [3]. From the analysis of the plasma-edge-like dispersion transport parameters of the composite as the optical conductivity at zero frequency $\sigma_{opt}(0)$, the plasma frequency ω_p, the optical effective mass of electrons m^*, the density of free carriers n, their mean free path Λ and Fermi velocity v_F, the relaxation rate τ, and the bandwidth 4t have all been evaluated. It was shown also, that the temperature dependence of the optical and transport parameters bear resemblance with the temperature dependence of the d.c. electrical conductivity.

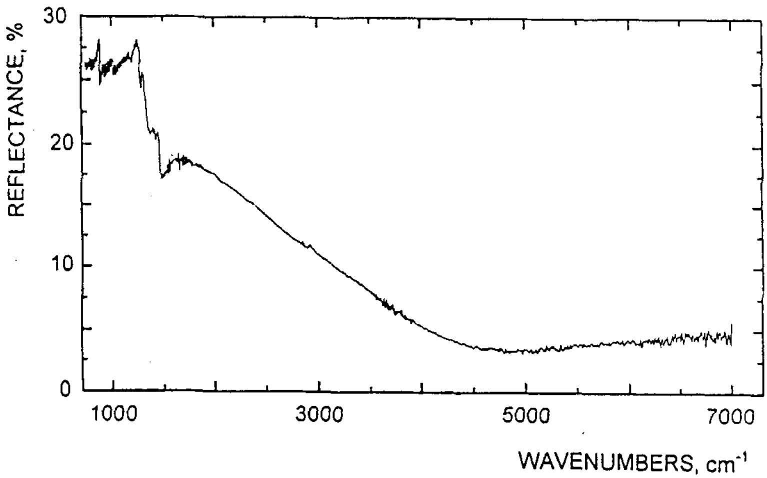

FIGURE 2 Reflectance spectrum of the composite at room temperature.

The combination of optical and electrical properties of the composite in a large temperature range, is considered also in the present investigation. The frequency dependent conductivity σ_{opt} for several temperatures is shown in the Fig.3. At room temperature the conductivity spectrum of the composite is similar to the spectrum of β-(BEDT-TTF)$_2$I$_3$ single crystals. Note that X-ray diffraction studies show that the composite consists of grains having the structure of β-(BEDT-TTF)$_2$I$_3$ [9]. A conductivity peak is observed at 2300 cm^{-1} accompanied by a strong and well structured vibrational feature at 1220 cm^{-1} which appears as the result of electron-molecular vibration (e-mv) coupling. A similar spectrum is observed for T = 5 K. The conductivity spectra for various temperatures between 100 - 150 K show different features - the conductivity peak at 2000 - 2300 cm^{-1} and partially, the vibration structure near the maximum at 1220 cm^{-1} disappear.

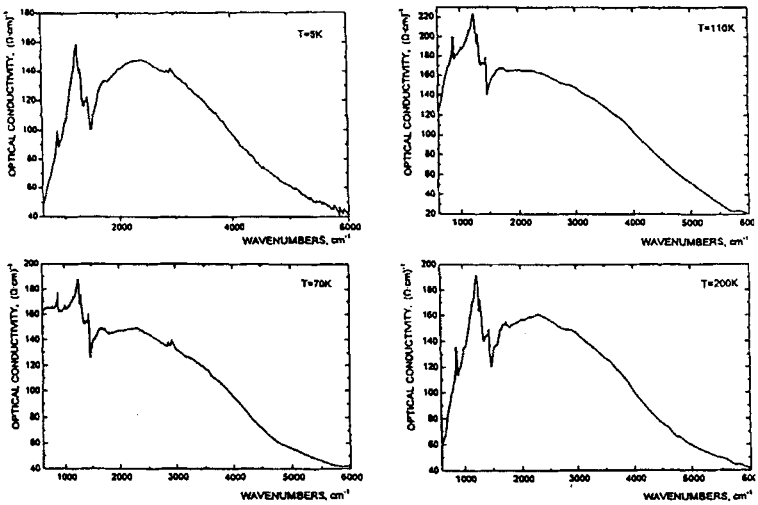

FIGURE 3 Optical conductivity spectra of the composite for several temperatures.

The spectrum in this temperature range is similar to the spectra of highly conducting, metallic BEDT-TTF salts but without the energy gap. In fact, the $(BEDT\text{-}TTF)_2/I_3$ composite is metallic over the whole temperature range, from room temperature down to 0.34 K [2]. It is not clear for a moment why the gap is seen both at low and high temperatures in spite of metallic conductivity of the composite. On the other hand the conductivity spectrum of β-$(BEDT\text{-}TTF)_2I_3$ single crystals, which shows metallic behaviours down to about 1 K, shows a gap down to lowest temperatures [5]. Similarly, the spectra of α-$(BEDT\text{-}TTF)_2I_3$ crystal, which undergoes a metal - insulator phase transition at T = 135 K, show also more or less pronounced conductivity peaks in the range of vibronic bands and an energy gap from room temperature down to 18 K [10]. A large temperature dependent semiconductor energy gap of about 1000 cm^{-1}

and a distinct charge transfer band at about 2200 cm^{-1} have been observed for κ-$(BEDT\text{-}TTF)_2Cu[N(CN)_2]Cl$ organic conductor. An intensity of this CT band increases with lowering of the temperature [11]. In an isostructural organic metal κ-$(BEDT\text{-}TTF)_2Cu[N(CN)_2]Br$ an interband transition occurs at approximately 2200 cm^{-1}, and its intensity decreases with temperature lowering [12]. Thus, temperature changes of CT band intensity are different for metallic and semiconducting materials. In $(BEDT\text{-}TTF)_2/I_3$ composite both metallic and semiconducting phases coexist and complicate temperature dependencies of the CT band as well as a corresponding energy gap.

The $(BEDT\text{-}TTF)_2/I_3$ composite shows grainy structure (Fig. 1) which determines mechanisms of electrical transport. This suggests that there are highly conducting channels in the sample, created by the metallic grains adjoined on each other - it is a form **I**. From Fig. 1 it is clear, that exists also a form **II** which consists of the same metallic grains separated by amorphous matter. The resistance of this form is determined mainly by the resistance of the amorphous borders, which are insulating. For d.c. measurements, the conductivity of the form **I** is dominant and determines as well the value as the type of conductivity. For optical frequencies, as suggest our spectral investigations, the form **II** is also conducting. Thus, we can describe the electrical conductivity of the sample for optical conductivities as a sum of metallic and semiconductive parts with appropriate contributions *a* and *b*, respectively:

$$\sigma_{opt} = a\,\sigma_m + b\sigma_{sc}$$

At low temperature the conductivity of the form **II** can be neglected.

In conclusion, it is confirmed by infrared spectral investigation of the $(BEDT\text{-}TTF)_2/I_3$ composite that charge-transfer reaction between BEDT-TTF and iodine occurs directly in the solid state; physical properties of such products approximate the properties of crystalline $(BEDT\text{-}TTF)_2I_3$ salts. The optical conductivity spectra of the $(BEDT\text{-}TTF)_2/I_3$ composite reflect a complex structure of the composite. Although the d.c. conductivity investigations show its metallic behaviour from 300 down to 0.34 K, the optical conductivity reveals clearly the twofold nature of the compactions.

Acknowledgements

One of us (A.G.) acknowledges the University of Nice - Sophia Antipolis for its hospitality. This work was partly supported by the Polish Committee for Scientific Research (Grant № 7 TO8A 003 12).

References

[1] J.P. Farges, A. Brau and P. Dupuis, *Solid State Commun.*, **54**, 531 (1985).
[2] I. Smirani, A. Brau and J.P. Farges, *Synth.Met.*, **93**, 203 (1998).
[3] V.N. Semkin, A. Graja, I. Smirani, A. Brau and J.P. Farges, *J. Mol. Structure*, (accepted).
[4] M.G. Kaplunov, E.B. Yagubskii, L.P. Rozenberg and Yu.G. Borodko, *phys. stat. sol.(a)*, **89**, 509 (1985).
[5] C.S. Jacobsen, J.M. Williams and H.H. Wang, *Solid State Commun.*, **54**, 937 (1985).
[6] R.M. Vlasova, E.A. Ivanova and V.N. Semkin, *Phys. Tverdogo Tela (Leningrad)*, **27**, 530(1985).
[7] B. Koch, H.P. Geserich, W. Ruppel, D. Schweitzer, K.H. Dietz and H.J. Keller Mol. *Cryst.Liq. Cryst.*, **119**, 343 (1985).
[8] R. Zamboni, D. Schweitzer, H.J. Keller and C. Taliani, *Z. Naturforsch.*, **44a**, 295 (1989).
[9] I. Smirani, S. Flandrois, N.B. Chanh, A. Brau and J.P. Farges, *Synth. Met.* (accepted).
[10] K. Yakushi, H. Kanbara, H. Tajima, H. Kuroda G. Saito and T. Mori, *Bull. Chem. Soc. Jpn.*, **60**, 4251(1987).
[11] K. Kornelsen, J.E. Eldridge, H.-H. Wang, H.A. Charlier and J.M. Williams, *Solid State Commun.*, **81**, 343 (1992).
[12] J.E. Eldridge, K. Kornelsen, H.-H. Wang, J.M. Williams, A.V. Strieby Crouch and D.M. Watkins, *Solid State Commun.*, **79**, 583 (1991).