TEMPERATURE STUDY OF THE POLARIZED REFLECTIVITY OF TEA(TCNQ)$_2$ SINGLE CRYSTAL

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The infrared reflection spectra of the organic quasi-one-dimensional semiconductor triethylammonium (TCNQ)$_2$ between 80 and 300 K are reported. Characteristic changes in the temperature dependencies of the bands assigned to the donor vibrations are observed. An interpretation of the electron–molecular vibration coupling in terms of the dimer theory is discussed. It is concluded that the thermal evolution of the spectrum corroborates the semiconductor–semiconductor type of phase transition attributed to the cation disorder.

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1. Introduction

Triethylammonium-tetracyanoquinodimethane (TEA(TCNQ)$_2$) ion-radical salt is one of the first organic conductors synthesized in the 1960's [1]. Though it does not belong to the group of the most conducting TCNQ salts, TEA(TCNQ)$_2$ offers a rare opportunity for the investigation of the nature and mechanism of the phase transitions, the models interpreting electron–molecular vibration (e–mv) couplings, the role of a structural disorder and so on. This is partly because it can be obtained in the form of relatively large single crystals. First of all, its tetramerized columnar structure determines the fact that this compound is a good model for studying the specific properties of a one-dimensional (1D) electron system.

A lot of papers on TEA(TCNQ)$_2$ have been published [1–22], above all by Nice's group of Brau and Farges [6–8, 10, 11, 16, 18–22]. The crystal structure of TEA(TCNQ)$_2$ has been studied by different authors [2–5]. The unit cell is triclinic. The TCNQ molecules form stacks along the crystallographic c axis and sheets of such stacks form the bc plane. TCNQ stacks consist of tetrads BAA'B' with two different molecular overlappings and three different interplanar distances of $d_{AB} = 3.22$ Å, $d_{AA'} = 3.31$ Å and $d_{BB'} = 3.33$ Å, respectively. Structural

evolution of the TEA(TCNQ)$_2$ in the wide temperature range shows that various interplanar spacings decrease with T, each to a different extent [5]. The data extrapolated down to 0 K indicate that, at this T, each column is a pile of BAA'B' tetrads which have an internal regular spacing ($d_{BB'} > d_{AA'} = d_{AB}$). At about 330 K $d_{AA'} = d_{BB'} > d_{AB}$ and a column is made of AB diads. The charge transfer estimated from bond lengths indicates a partial localization (0.6e and 0.4e) of the charge [5].

TEA(TCNQ)$_2$ is generally considered as a good 1D semiconductor ($\sigma_{RT} \approx$ 7 Ω^{-1}cm^{-1}) in which T-dependence of the longitudinal d.c. conductivity observed in a large crystal shows an anomaly in the slope of log σ vs. T^{-1} at 220 K [6, 7]. On the other hand, a number of conductivity jumps have been observed only when small single crystals have been investigated [8]. The temperature at which the first conductivity step occurs varies randomly from one thermal cycle to the next, and from one single crystal to another. It is scattered in the T-range from 268 to 196 K [8, 16]. Furthermore, some authors have postulated that this transition is of the metal–insulator type, while others tend to see a semiconductor–semiconductor mechanism.

The DSC measurements have shown a first order phase transition at 220 K attributed to the TEA disorder [16]. In fact, at 300 K, each TEA cation is randomly disordered in rotation (dynamic disorder) and, at low temperature, the disorder is only over two equipopulated positions (static disorder) sharing a hydrogen bond with either a TCNQ (A) or a TCNQ (B) anion on two adjacent TCNQ chains [4]. NMR results for TEA(TCNQ)$_2$ [17] confirm that the twofold disorder of the cation is static below 200 to 220 K and increasingly dynamic in nature as room temperature is approached. We point out that together with d.c. conductivity and DSC anomalies, presumptions of a phase transition at 220 K were observed previously in experimental results such as: the thermopower [20], the a.c. conductivity [21] and the thermal conductivity measurements [22].

The observation in TEA(TCNQ)$_2$ of a remarkable series of strong IR bands polarized in the TCNQ chain direction was reported some years ago by Kaplunov et al. [9] and, in particular detail by Brau et al. [10]. Belousov et al. [12] measured the IR spectra of TEA(TCNQ)$_2$ at two temperatures, 100 and 300 K, and analyzed them in terms of a phenomenological model of interacting oscillators. Subsequently, Rice et al. [23] fitted the phase phonon theory to the Brau's room temperature experimental data and estimated the values of e–mv coupling constants. However, a more exact description of the IR reflection spectra requires a consideration of the structure of the TCNQ stacks in the salt. It was performed by Yartsev [24]. The bands related to totally symmetric (a_g) modes of TCNQ are doublets [12, 25] or even multiples [15] in TEA(TCNQ)$_2$ at lower temperatures. The fine structure can be connected with different distribution of charge on anions in the tetramers, which leads to different frequencies of a_g modes. Steigmeier et al. [15] have interpreted TEA(TCNQ)$_2$ reflectance spectrum in terms of dimer theory, but the obtained fit is not very good, indicating the importance of interactions between dimers within a tetramer. In spite of numerous experimental studies of the polarized reflection spectra of TEA(TCNQ)$_2$, at various temperatures too, it is not possible to make a

definitive choice of the model to explain all peculiarities of the spectra. Systematic temperature studies of the polarized IR spectra of the salt are needed.

In order to shed some complementary light on the evolution of the polarized IR reflectivity and the electron–molecular vibration (e–mv) coupling in TEA(TCNQ)$_2$ vs. temperature, we investigate the spectra of the salt first of all within a phase transition region. The aim of this paper is also a discussion of the fine structure of a_g bands.

2. Experimental

TEA(TCNQ)$_2$ was prepared from TCNQ and triethylamine in acetonitrile by the method of Melby et al. [26]. The single crystals of the salt with dimensions up to $15 \times 6 \times 2$ mm^3 were prepared by slow cooling of a seeded saturated acetonitrile solution by the Nice group. The reflection spectra were taken with a Perkin Elmer FT IR 1725 X spectrometer with a microspecular reflection insert within the range 400–5000 cm^{-1}. A special cryostat was used for a sample cooling from 300 to 80 K. The sample temperature was controlled by a Cu–Cu/Fe thermocouple with an accuracy of ± 0.5 K.

The frequency-dependent conductivity $\sigma(\omega)$ was calculated from the reflection spectra using the Kramers–Kronig analysis. Since reflection spectra were measured in a restricted frequency range only, it was indispensable to make reasonable extrapolations. Between the highest measured frequency (5000 cm^{-1}) and 50000 cm^{-1} the reflectance was extrapolated on the basis of Brau et al. [10] measurements; this room temperature spectrum was used for analysis of the spectra within the whole T-range. Above 50000 cm^{-1} it was assumed that reflectivity changes as $1/\omega^4$. At low frequencies ($550 \div 20$ cm^{-1}) we used the far IR data of Brau et al. [10], and at very low frequencies, below 20 cm^{-1} it was assumed that $R = $ const. Under this assumption, the spectra in the range 600 cm$^{-1} < \omega < 4000$ cm^{-1} are rather correct and in good agreement with literature.

Some of the observed bands, in particular the a_g modes activated by e–mv coupling, show fine structure. In order to investigate their origin and thermal evolution a computer separation of the bands was performed. A standard PEAKFIT program was used for this purpose.

3. Results and discussion

The reflection spectra of the oriented TEA(TCNQ)$_2$ crystals, obtained in polarized light for a possibly broad range of frequencies render it possible to determine optical coefficients and anisotropy of the molecular system. The conductivity for IR frequencies $\sigma(\omega) = \epsilon_0 \omega \epsilon''(\omega)$ obtained by Kramers–Kronig analysis at three different temperatures is given in Fig. 1. The spectrum "a" was obtained at $T = 300$ K $> T_p$, the "b" at $T = 210$ K $\leq T_p$ and the "c" at $T = 80$ K $< T_p$. All the spectra are dominated by strong and very broad CT band at about 2300 cm^{-1} and a set of strong bands resulting from a vibronic activation of totally symmetric a_g modes of TCNQ, normally IR non-active. Some weak bands were assigned to
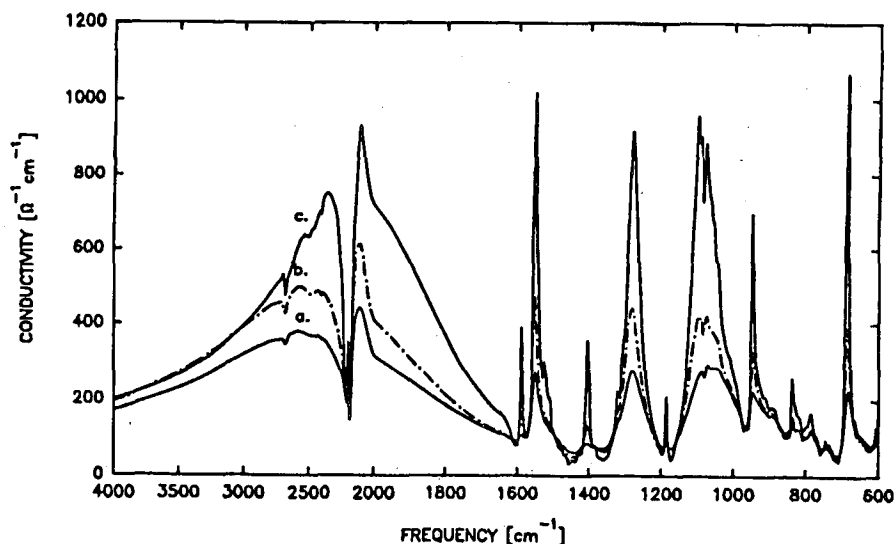
Fig. 1. Conductivity spectrum of TEA(TCNQ)$_2$ single crystal at $T = 300$ K (a), $T = 210$ K (b), and $T = 80$ K (c).

normal IR active vibrations of TCNQ$^-$ or TEA$^+$. Precise analysis of the band frequencies and bandwidths showed that the general appearance of the spectra is maintained within the whole temperature range. The spectrum of TEA(TCNQ)$_2$ is typical of semiconducting organic crystals [27] below the phase transition temperature T_p as well as above T_p. In the former T-range it is evident because the electrical transport study [6, 7] shows the semiconducting properties of TEA(TCNQ)$_2$. However, above T_p electrical conductivity is relatively high — the value of $\sigma_{d.c.}$ suggests metal-like properties of the salt. Our spectral investigations show that the phase transition in TEA(TCNQ)$_2$ is of semiconductor–semiconductor type rather than metal–insulator one.

The temperature study of the band intensities was relatively simple and precise in the case of single, well separated bands, e.g. 948 and 687 cm^{-1}. However, the majority of bands are complex and require computer separation. For this reason we decomposed the $\sigma(\omega)$ bands. For this purpose a four parameters Voigt function was used. Fitting started from the lowest temperature because the bands are best separated. Starting parameters were chosen to give a curve very close to the experimental data. For successive temperatures the procedure was almost the same, the basis being the fit obtained for a direct lower T. We decomposed the bands in as small number of components as possible, even if the quality of the fit is not excellent. It is shown in Fig. 2 where two typical band decompositions are presented. Both bands assigned to activated a_g modes of TCNQ are doublets in which wide and narrow vibronic components exist simultaneously. The doublets were observed and discussed previously for TEA(TCNQ)$_2$ [10, 15, 24, 25] and other TCNQ salts [28–30]. In some cases (e.g. the complex band between
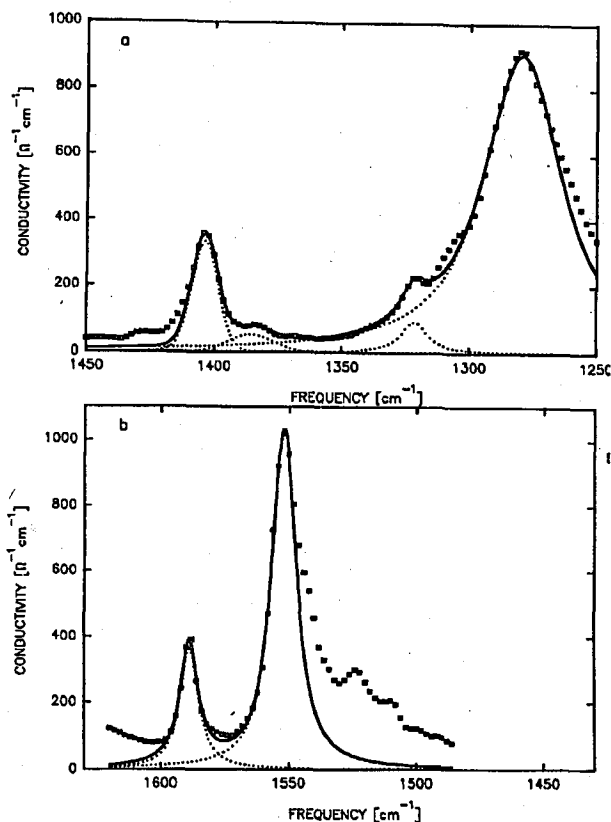
Fig. 2. Computer separation of the doublets of activated a_g modes in the regions 1404–1279 cm^{-1} (a), and 1589–1551 cm^{-1} (b).

1050–1200 cm^{-1}) more components appear. In general, the band amplitudes, A in the $\sigma(\omega)$ spectra decrease monotonically when the temperature increases. One can observe it in both the wide and narrow components (Fig. 3a), but the ratio $A(80\ K)/A\ (300\ K)$ is higher for narrow components. In the extreme case of the bands 1404 and 1279 cm^{-1} the ratio equals about 3.6 for the wide band and as much as 8.5 for the narrow, 1404 cm^{-1} band. No anomalies are observed for slope $(-dA/dT)$ variations vs. temperature for the majority of bands; it harmonizes with small and monotonic changes of structural parameters of TCNQ stacks. Few bands only, e.g. 785, 850, 1509 and 1523 cm^{-1} show other T-dependencies (Fig. 3b and 3c). The amplitude of the band 785 cm^{-1}, which is assigned to TCNQ normal mode, shows small anomaly in the T-dependence near $T = 220$ K. It is more visible in Fig. 4a, where the slope variation of the band is shown. On the other hand, the normal mode bands are weakly T-dependent; the ratio $A(80\ K)/A(300\ K) \approx 2.5$.
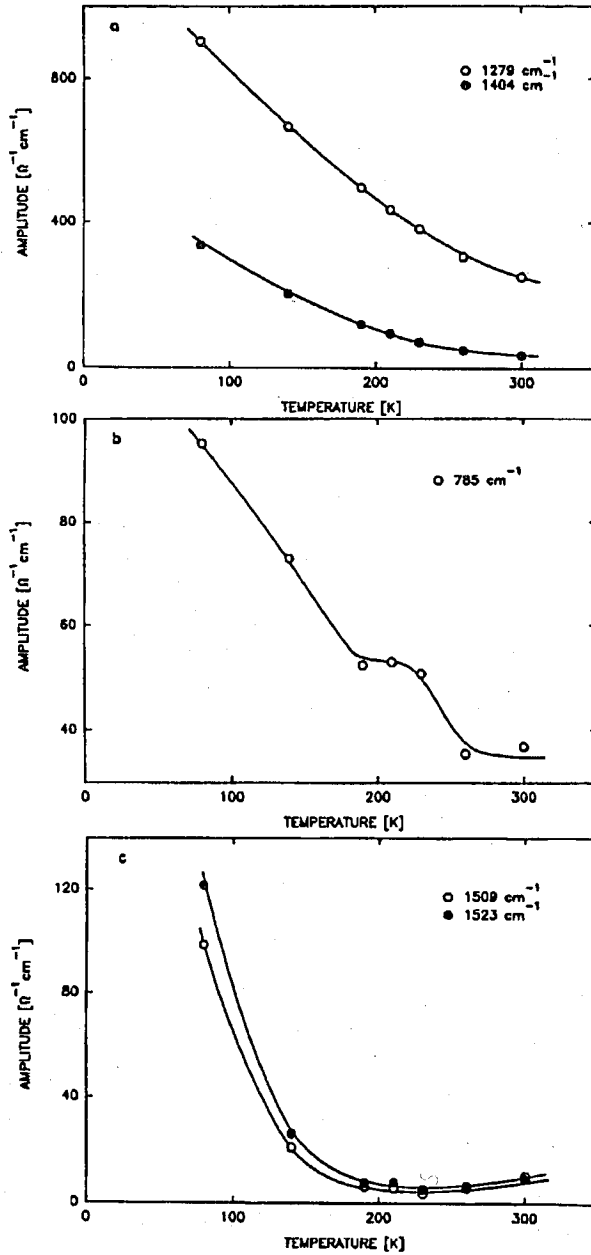
Fig. 3. T-dependencies of the band amplitudes A of the doublet at 1404–1279 cm^{-1} (a), the single band at 785 cm^{-1} (b), and the doublet 1509–1523 cm^{-1} (c).
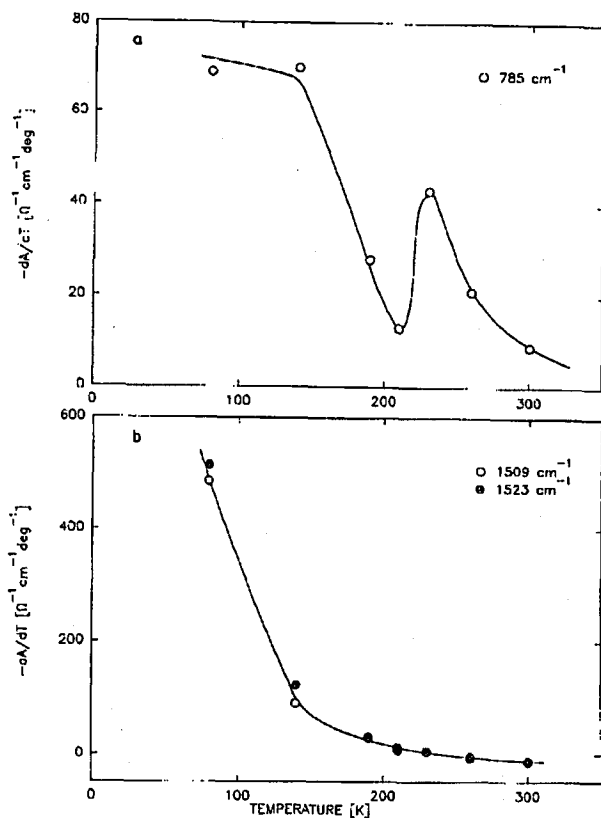
Fig. 4. T-dependencies of the curve slopes, $-dA/dT$ of the band 785 cm^{-1} (a) and the doublet 1509–1523 cm^{-1} (b).

Three remaining bands (850, 1509 and 1523 cm^{-1}) are assigned to the donor normal vibrations. Weak doublet at 1509 and 1523 cm^{-1} is given by the bending of the N–H group of the TEA$^+$ cation. These bands, as well as the band at 850 cm^{-1}, appear at low temperatures, approximately below 200 K (Fig. 4b). As it appears the presence of bands at $T < T_p$ corroborates the model of the phase transition in TEA(TCNQ)$_2$ given by Brau and Farges [16], attributing the transition to the TEA disorder. At high temperature phase the TEA cations are randomly disordered in rotation, while at low temperature phase the disorder is only over two equipopulated positions sharing a hydrogen bond with either a TCNQ(A) or a TCNQ(B) anion [4]. Above T_p the N–H group is not engaged in H-bond formation. The frequency of its bending mode is higher and coincides with a far stronger band of the activated a_g mode of the acceptor. Below the temperature of about 200 K the H-bonds with either TCNQ(A) or TCNQ(B) molecules are formed and adequate shifted bands are observed. Thus our spectral study corroborates the existence of hydrogen bonds below T_p. On the other hand, very small anomalies can be noticed for TCNQ vibrations, in particular the activated a_g modes. It means

that the phase transition occurs mainly in the cation sublattice, while the anion sublattice is not disturbed distinctly at the critical temperature. The small change in the slope of T-dependence of the 785 cm^{-1} band at the phase transition region reflects hindering of the cation rotation and establishing of the hydrogen bonds. The a_g modes are not sensitive for the H-bonds formation since their frequencies, intensities and bandwidths are determined entirely by the electron–molecular vibration couplings.

Temperature and phase transition change the interplanar spacings in the salt. Therefore, it would be interesting to study the manifestation of these changes in the model describing the electron–molecular vibration coupling. For a start we have attempted to interpret the data in terms of the dimer model derived by Rice et al. [31, 32].

We have used the model in the case of one radical electron per TCNQ dimer [32] over the whole temperature range. The interplanar distances between TCNQs (3.225 Å and 3.12 at $T = 300$ K and 80 K, respectively) and numbers of dimers per Å^3 (0.001449 and 0.001504, at both temperatures, respectively) were found from the structural data [4]. The transfer integrals $t = 151$ meV (at 300 K) and $t = 198$ meV (at 80 K), calculated according to [33], were used for the dimer fit to the experimental spectra at both temperatures. Fitting was made using the Nelder–Mead simplex algorithm for minimizing a nonlinear function of several variables. The dimer theory provides a good general fit to the 300 K data if one uses CT band parameters: $\omega_{CT} = 2042$ cm^{-1} and $\Gamma_{CT} = 1214$ cm^{-1} (Fig. 5). The
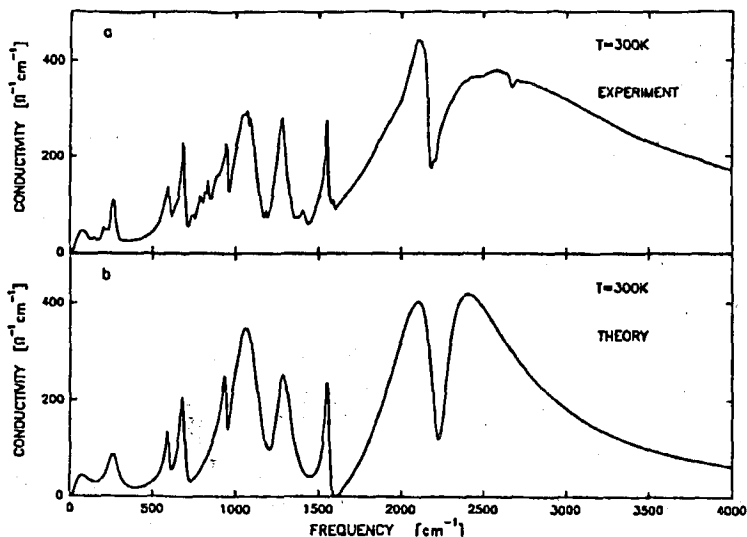

Fig. 5. Real part of the frequency-dependent conductivity of TEA(TCNQ)$_2$ as deduced by dispersion analysis of the measured reflectivity at 300 K (a) and calculated theoretically (b).

calculated values of ω_α and $\sigma(\omega_\alpha)$ are in very good agreement with the experimental data while the e–mv coupling constants g_α are reasonable [34]. A quite good general fit to the 80 K data was found for $\omega_{CT} = 1970$ cm^{-1} and $\Gamma_{CT} = 1040$ cm^{-1}. Although the fitted values of ω_α and g_α are good, the $\sigma(\omega_\alpha)$ are distinctly smaller than the experimental values. The dimer model leaves out the doublet structure of the activated a_g modes — it is the main disagreement with the experiment.

Thus, the theory of the dimer with one radical electron accounts well for the anomalous IR reflection in TEA(TCNQ)$_2$ at high temperatures, above the phase transition. On the contrary, the dimer model does not describe the spectral properties of the salt below T_p. It is an additional argument proving that the observed anomalies of the physical properties of TEA(TCNQ)$_2$ at temperatures about 220 K may arise as a consequence of the reorganization of the TCNQ stacks. The search for better models is currently under way in our laboratory [34].

4. Conclusions

We have performed an extensive investigation of the IR spectra of TEA(TCNQ)$_2$ salt. The analysis of the thermal evolution of the spectra suggests that the salt undergoes a semiconductor–semiconductor phase transition at about 220 K. It is manifested by distinct changes in the bands assigned to the cation vibrations. It means that the phase transition occurs mainly in the cation sublattice. Much smaller changes in the bands describing e–mv coupling in the anion sublattice show that also this part of the crystal undergoes some reorganization in the phase transition temperature. The dimer model, adequate for describing the high-T phase of TEA(TCNQ)$_2$, must be replaced by another one at low temperature.

Acknowledgments

References

[1] D.S. Acker, R.J. Harder, W.R. Hertler, W. Mahler, L.R. Melby, R.E. Benson, W.E. Mochel, *J. Am. Chem. Soc.* **82**, 6408 (1960).

[2] H. Kobayashi, Y. Ohashi, F. Marumo, Y. Saito, *Acta Crystallogr. B* **26**, 456 (1970).

[3] J. Jaud, D. Chasseau, J. Gaultier, C. Hauw, *C.R. Hebdomadaires des Seances de l'Académie des Sciences, Sér. C: Sciences Chimiques, Paris* **278**, 769 (1974).

[4] A. Filhol, C.M.E. Zeyen, P. Chenavas, J. Gaultier, P. Delhaès, *Acta Crystallogr. B* **36**, 2719 (1980).

[5] A. Filhol, M. Thomas, *Acta Crystallogr. B* **40**, 44 (1984).

[6] J.P. Farges, A. Brau, F. Gutmann, *J. Phys. Chem. Solids* **33**, 1723 (1972).

[7] A. Brau, J.P. Farges, *Phys. Lett. A* **41**, 179 (1972).

[8] H. Grassi, A. Brau, J.P. Farges, *Phys. Status Solidi A* **55**, K179 (1979).

[9] M.G. Kaplunov, T.P. Panova, Yu.G. Borodko, *Phys. Status Solidi A* **13**, K67 (1972).

[10] A. Brau, P. Brüesch, J.P. Farges, W. Hinz, D. Kuse, *Phys. Status Solidi B* **62**, 615 (1974).

[11] A. Brau, J.P. Farges, *Phys. Status Solidi B* **61**, 257 (1974).

[12] M.V. Belousov, A.M. Vainrub, R.M. Vlasova, *Fiz. Tverd. Tela* **18**, 2637 (1976) [*Sov. Phys.-Solid State* **18**, 1538 (1976)].

[13] R.M. Vlasova, A.I. Gutman, N.F. Kartenko, L.P. Rautian, L.D. Rozenshtein, V.N. Semkin, S.M. Khursandova, *Fiz. Tverd. Tela* **19**, 305 (1977) [*Sov. Phys.-Solid State* **19**, 176 (1977)].

[14] E.F. Steigmeier, H. Auderset, D. Baeriswyl, M. Almeida, K. Carneiro, *J. Phys. Colloq.* **44**, C3-1445 (1983).

[15] E.F. Steigmeier, H. Auderset, D. Baeriswyl, M. Almeida, *Mol. Cryst. Liq. Cryst.* **120**, 163 (1985).

[16] A. Brau, J.P. Farges, A. Filhol, H. Grassi, *Phys. Status Solidi B* **120**, 547 (1983).

[17] J.P. Travers, F. Devreux, M. Nechtschein, *J. Phys. Colloq.* **44**, C3-1295 (1983).

[18] J.P. Farges, in: *The Physics and Chemistry of Low Dimensional Solids*, Ed. L. Alcácer, D. Reidel Publ. Comp., Dortrecht 1980, p. 223.

[19] J.P. Farges, A. Brau, P. Dupuis, *Solid State Commun.* **54**, 531 (1985).

[20] J.P. Farges, A. Brau, *Phys. Status Solidi B* **64**, 269 (1974).

[21] J.P. Farges, A. Brau, *Phys. Status Solidi B* **61**, 669 (1974).

[22] H. Grassi, A. Brau, J.P. Farges, *Phys. Status Solidi B* **112**, 633 (1982).

[23] M.J. Rice, L. Pietronero, P. Brüesch, *Solid State Commun.* **21**, 757 (1977).

[24] V.M. Yartsev, *Phys. Status Solidi B* **126**, 501 (1984).

[25] M.G. Kaplunov, K.I. Pokhodniya, Yu.G. Borodko, *Phys. Status Solidi A* **71**, 649 (1982).

[26] L.R. Melby, R.J. Harder, W.R. Hertler, W. Mahler, R.E. Benson, W.E. Hochel, *J. Am. Chem. Soc.* **84**, 3374 (1962).

[27] A. Graja, *Low-Dimensional Organic Conductors*, World Scientific, Singapore-New Jersey-London-Hong Kong 1992.

[28] R. Świetlik, A. Graja, *J. Phys. (Paris)* **44**, 617 (1983).

[29] G.J. Ashwell, D.W. Allen, A. Graja, R. Świetlik, *J. Chem. Soc. Faraday Trans. II* **82**, 83 (1986).

[30] R. Świetlik, A. Graja, K.I. Pokhodnya, *Synth. Met.* **35**, 17 (1990).

[31] M.J. Rice, *Solid State Commun.* **31**, 93 (1979).

[32] M.J. Rice, V.M. Yartsev, C.S. Jacobsen, *Phys. Rev. B* **21**, 3437 (1980).

[33] G. Janssen, R. Visser, H.Th. Jonkman, J. de Boer, J. Kommandeur, *J. Phys. (Paris) Colloq.* **44**, C3-1587 (1983).

[34] I. Olejniczak, A. Graja, to be published.