

# Infrared and Raman studies of the phase transition in the organic conductor (TTM-TTP)<sub>3</sub>I<sub>3</sub>

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## Abstract

We report the polarized IR reflectance as well as Raman scattering investigations of the organic charge transfer salt (TTM-TTP)<sub>3</sub>I<sub>3</sub> as a function of temperature, below and above the metal–insulator phase transition at  $T = 160$  K. The IR reflectance was measured in the frequency region from 600 to 10,000  $\text{cm}^{-1}$ , for the electrical vector of the polarized light parallel and perpendicular to the TTM-TTP stacking axis. For the polarization parallel to stacks the IR spectra are typical for semiconducting charge transfer salts. The electronic part of IR spectra was analysed in terms of a Lorentz model and temperature dependence of the optical transport parameters was determined. For the polarization perpendicular to the stacks we observed two electronic bands at about 5000 and 8000  $\text{cm}^{-1}$ . The phase transition at 160 K has nearly no influence on the IR spectrum. The Raman scattering for different excitations ( $\lambda = 514.5, 632.6$  and 785 nm) was mainly studied within the region of C=C stretching vibrations. In this frequency range, three Raman lines at 1426, 1453 and 1486  $\text{cm}^{-1}$  attributed to TTM-TTP molecules are observed. Below 160 K a splitting of the band 1486  $\text{cm}^{-1}$  into two peaks at about 1488 and 1498  $\text{cm}^{-1}$  is found. The intensity and temperature behaviour of the split band at 1498  $\text{cm}^{-1}$  is strongly dependent on sample. The observed spectral modifications are related to an asymmetric deformation of TTM-TTP. Taking into account temperature dependence of bands attributed to the C–H stretching and SCH<sub>3</sub> bending vibrations, we suggest that the TTM-TTP deformation can exist also above the phase transition temperature. Above 160 K molecules fluctuate between distorted and symmetrical state forming non-stable domains (pre-transitional effects), but below 160 K the molecular distortion and domains are stable. The existence of electronic band at 5000  $\text{cm}^{-1}$  for the polarization perpendicular to TTM-TTP supports this picture.

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## 1. Introduction

In organic conductors the transfer integrals between neighbouring molecules in conducting stacks or layers are comparable to the on-site ( $U$ ) and inter-site ( $V$ ) Coulomb interaction energies, therefore, electron correlations play an important role in these materials. It is remarkable that conducting ion-radical salts with 1:1 composition, i.e. with half-filled energy gap, usually exhibit semiconducting prop-

erties, since considerable values of the parameter  $U$  localise electrons. The synthesis of bis-fused tetrathiafulvalene (TTF) donor molecules yielded expectations for preparation of new interesting organic conductors, since the parameter  $U$  in their dications should be reduced due to the extended molecular structure [1]. Subsequently, it was found indeed that the bis-fused TTF donors form many highly conducting radical-cation salts with metallic properties [2–7]. The first organic metal with 1:1 composition and a highly one-dimensional half-filled band was obtained by using a bis-fused TTF donor, namely 2,5-bis(4,5-bis(methylthio)-1,3-dithiol-2-ylidene)-1,3,4,6-tetrathia-pentalene (TTM-TTP) (Fig. 1),

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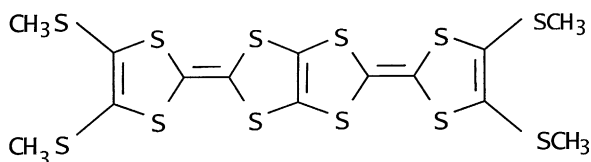


Fig. 1. Structure of TTM-TTP molecule.

and  $I_3^-$  cations [2,4,5]. Later, an organic metal with even higher oxidation degree of TTM-TTP molecules (+5/3) was discovered [6,7].

The charge transfer salt  $(\text{TTM-TTP})I_3$  exhibits metal-like behaviour with a very high room temperature conductivity (700 S/cm) and undergoes a metal–insulator phase transition at about 160 K [2,5]. The unit cell of  $(\text{TTM-TTP})I_3$  is triclinic and contains only one donor molecule. The TTM-TTP molecules are arranged in uniform stacks along the  $c$ -axis. The transfer integral along the  $c$ -axis,  $t_c = 0.26$  eV, is much larger than the interstack integrals,  $t_a, t_b < 0.01$  eV, therefore, the electronic structure is highly one-dimensional. The  $(\text{TTM-TTP})I_3$  crystals were studied as a function of temperature by various experimental methods: IR [8] and Raman [9] spectroscopy, static magnetic susceptibility [5,10,13], X-ray structure [2,5,10–12] electrical conductivity [2,5,10] ESR [5,11] and  $^{13}\text{C}$  NMR [13] measurements. From the polarized reflectance spectra by using half-filled Hubbard model, it was evaluated that the on-site repulsion  $U$  is nearly the same as the bandwidth  $4t_c$  ( $U \approx 0.57$  eV and  $t_c \approx 0.16$  eV) [8]. First measurements of the static magnetic susceptibility revealed no change at 160 K [5], but later data showed an anomaly at about 110 K [10] or 120 K [13]. The studies of Raman scattering on  $I_3^-$  anions revealed the structural phase transition at about 150 K related to the environment of  $I_3^-$  anions [9]. The first X-ray diffraction measurements suggested that the metal–insulator phase transition is not associated with any structural phase transition [5]. Subsequently, structural investigations showed the formation of  $2k_F$  superstructure below 110 K [10]. On the other hand, in Ref. [11] analogous  $2k_F$  superstructure was found below 160 K and also another structural modulation below 90–100 K, which corresponded to anomalies in the ESR spectra. The latest structural analysis showed two kinds of  $2k_F$  modulated structures below 160 K and below 100 K, most probably related to intramolecular asymmetry and stack modulation, respectively [12]. The electrical resistivity data were also rather ambiguous: in the first reports the metal–insulator transition was observed at 160 K [2,5]; but later measurements showed metallic behaviour down to about 230 K, followed by a gradual resistivity increase below this temperature and a rapid increase at about 110 K [10]. Finally, the  $^{13}\text{C}$  NMR investigations suggested that a charge ordering undergoes below about 120 K, so that at about 80 K the  $\text{TTM-TTP}^0$  and  $\text{TTM-TTP}^{2+}$  molecules are arranged alternately in the stacks [13].

Charge ordering (or charge disproportionation) phenomena can be often realised in conducting organic charge trans-

fer salts. Recently, these phenomena have attracted considerable attention as interesting states induced by electron correlations. In half-filled systems, the on-site Coulomb interaction ( $U$ ) is responsible for stabilisation of a Mott-Hubbard insulator, where charge carriers are localised at each molecular site (no charge ordering). The charge ordering effects are easily expected in quarter-filled systems with considerable inter-site interaction energies ( $V$ ). As proved by theoretical considerations, large  $V$  energies can give rise to charge ordering states both in one [14] and two-dimensional [15] organic conductors with quarter-filled band. Therefore, the  $(\text{TTM-TTP})I_3$  salt seems to be an extraordinary organic conductor: although it has a highly one-dimensional half-filled energy gap, the charge ordering was suggested by the  $^{13}\text{C}$  NMR experiment [13].

Infrared and Raman spectroscopies are useful experimental tools for investigations of the charge ordering phenomena in organic conductors [16–23]. A modification of charge distribution on molecules inside conducting columns or layers can be detected by splitting or frequency shift of suitable vibrational bands observed in IR and Raman spectra. For TTF-derivatives the C=C stretching modes are especially important for this purpose. On the other hand, modifications of the electronic structure due to charge ordering can yield considerable changes of electronic absorption in IR spectra. In particular, electronic bands due to interband transitions can be modified when a new optical energy gap is formed or/and new charge transfer bands can appear. In the present paper, we measure IR and Raman spectra of the  $(\text{TTM-TTP})I_3$  crystals as a function of temperature with the aim to study the nature of the metal–insulator phase transition. Some preliminary Raman data of  $(\text{TTM-TTP})I_3$  have been already published in Refs. [21,23].

## 2. Experimental

High-quality single crystals of the salt  $(\text{TTM-TTP})I_3$  were grown by the electrochemical method in 1,1,2-trichloroethane as described previously in Ref. [2]. The crystals selected for measurements had a shape of needles of typical size 1 mm  $\times$  0.1 mm  $\times$  0.05 mm.

Measurements of the polarized reflectance spectra were carried out on a FT-IR spectrometer Nicolet Magna 760 in the frequency region from 600 to 10000  $\text{cm}^{-1}$ . The spectrometer was equipped with an IR microscope Spectratech IR Plan. Details of the reflectance measurements were described in Ref. [24]. The reflectance spectra were measured from (1 0 0) to (0 1 0) crystal faces in two perpendicular polarizations: the electrical vector of the polarized IR beam was either parallel or perpendicular to the  $c$ -crystallographic axis (TTM-TTP stacking direction).

Optical conductivity spectra were obtained by Kramers–Kronig analysis of the reflectance data. The low-frequency data were extrapolated to zero frequency assuming a constant reflectance. The high-frequency data

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