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Infrared studies of the molecular metal [Pd(dddt)₂]Ag_{1.54}Br_{3.50} containing uniform Pd(dddt)₂ stacks

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Abstract. We present the results of studies of the polarized reflectance spectra in the frequency region from 650 cm⁻¹ to 40 000 cm⁻¹ of [Pd(dddt)₂]Ag_{1.54}Br_{3.50} single crystals at room temperature. The reflectance in the middle IR range is analysed using a Drude model. Assuming a tight-binding band suitable transfer integrals are determined. The electronic band structure is discussed.

1. Introduction

An interesting group of conducting charge transfer salts is formed by square planar metal complexes M(dddt)₂ (where: M = Ni, Pd, Pt, Au and dddt = 5,6-dihydro-1,4-dithiin-2,3-dithiolate) and various inorganic anions [1]. The M(dddt)₂ complexes are close analogues of bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF or ET) which is a well known organic donor molecule yielding many conducting and superconducting charge transfer salts [2]. Formally, M(dddt)₂ is a close structural modification of the BEDT-TTF molecule since the central C=C bond of BEDT-TTF is replaced by a metal. The salts formed by M(dddt)₂ and BEDT-TTF with the same anions possess often very similar crystal structures but their electronic band structures can be quite different. The partially filled electronic bands of BEDT-TTF salts can be well described by considering only the HOMO (the highest occupied molecular orbital); these are the so-called ‘one-band systems’. On the other hand, in the M(dddt)₂ complexes the HOMO and LUMO (the lowest unoccupied molecular orbital) exhibit relatively low splitting and the electronic band structure of their charge transfer salts can be only described when both molecular orbitals are taken into account forming the so-called ‘two-band systems’. The existence of a ‘two band electronic system’ is a characteristic feature of M(dddt)₂ conductors [3, 4].

About 13 Pd(dddt)₂ salts with various electrical properties have been synthesized [5]. The [Pd(dddt)₂]Ag_{1.54}Br_{3.50} salt is a stable molecular metal down to $T = 1.3$ K [5, 6]. The crystal structure data of the [Pd(dddt)₂]Ag_{1.54}Br_{3.50} are following: $a = 20.10(2)$ Å, $b = 6.002(5)$ Å, $c = 4.157(2)$ Å, $\alpha = 98.01(6)^\circ$, $\beta = 94.51(6)^\circ$, $\gamma = 96.39(7)^\circ$, $V = 491(1)$ Å³, space group $P\bar{1}$, $Z = 1$ [6]. The Pd(dddt)₂ cations form conducting layers alternating with the layers

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of non-stoichiometric silver bromide anions parallel to the bc plane. The conducting layers contain uniform stacks of the translationally equivalent $\text{Pd}(\text{dddt})_2$ cations along the c axis with a Pd...Pd distance of 4.157 Å; the interplanar distances between $\text{Pd}(\text{dddt})_2$ in the stacks are equal to 3.84 Å. Close S...S contacts, shorter than the sum of van der Waals radii, are only observed between the $\text{Pd}(\text{dddt})_2$ stacks (side-by-side contacts). The Ag and Br atoms are disordered in the anion layer. The electrical conductivity of the crystal measured along a diagonal in the bc plane was 12–40 S cm⁻¹ at room temperature [6]. A remarkable and exceptional feature of the crystal structure of the $[\text{Pd}(\text{dddt})_2]\text{Ag}_{1.54}\text{Br}_{3.50}$ salt is that the $\text{Pd}(\text{dddt})_2$ stacks are uniform. Since the Pd ions tend to form metal–metal bonds, the $\text{Pd}(\text{dddt})_2$ cations in charge transfer salts are usually arranged in face-to-face dimer units (dimerized stacks).

Infrared spectroscopy is a good tool to investigate electronic structure and electron–molecular vibration coupling phenomena in the conducting charge transfer crystals. The aim of this paper is to investigate the electronic structure of the $[\text{Pd}(\text{dddt})_2]\text{Ag}_{1.54}\text{Br}_{3.50}$ salt using the IR spectroscopy method.

2. Experiment

The procedure of $[\text{Pd}(\text{dddt})_2]\text{Ag}_{1.54}\text{Br}_{3.50}$ crystal preparation by the electrocrystallization method was described in [6]. Typical dimensions of the crystals in the form of elongated plates were about $1 \times 0.2 \times 0.01$ mm³. Polarized IR reflectance measurements within the frequency range from 650 to 6500 cm⁻¹ were performed on $[\text{Pd}(\text{dddt})_2]\text{Ag}_{1.54}\text{Br}_{3.50}$ crystals at room temperature by using an FT-IR Perkin-Elmer 1725X spectrometer equipped with a suitable FT-IR microscope. The incoming IR beam was polarized with a gold wire grid deposited on an AgBr substrate. Moreover, a home made microspectroreflectometer with a Glan-Thompson prism as a polarizer was used to measure the spectra in the frequency region 9000 to 40 000 cm⁻¹ at room temperature.

The reflectance spectra were measured from the best developed crystal face (100), parallel to the conducting layers, for two nearly perpendicular orientations of the electrical vector of polarized light: parallel to the step-chains formed by short S...S contacts ($E \parallel b$) and nearly parallel to the $\text{Pd}(\text{dddt})_2$ stacking direction ($E \parallel c$); these directions correspond to the maximum and nearly the minimum of reflected energy, respectively. The Kramers–Kronig analysis of reflectance data was carried out in order to obtain the dielectric function and the frequency dependent conductivity. The low-frequency data were extrapolated to zero frequency assuming a Hagen–Rubens function, a common procedure for metallic materials. Above the highest-frequency point the reflectance data were extended as $R \approx \omega^{-2}$ and above 10⁶ cm⁻¹ as $R \approx \omega^{-4}$. The extrapolation method has a slight influence on the maxima of absolute values of the dielectric function and conductivity; nevertheless the shape of calculated spectra was nearly the same.

3. Results and discussion

Figure 1 shows the polarized reflectance spectra of the (100) crystal face of $[\text{Pd}(\text{dddt})_2]\text{Ag}_{1.54}\text{Br}_{3.50}$ at room temperature with the electrical vector of the incident light parallel to the b axis ($E \parallel b$) and nearly parallel to the c axis ($E \parallel c$). The reflectance spectrum for polarization $E \parallel b$ shows a well defined plasma-edge-like dispersion, whereas for $E \parallel c$ an overdamped plasmon behaviour is observed. For both polarizations we see a vibrational feature centred at about 1200 cm⁻¹ due to coupling of electrons with internal vibrations of $\text{Pd}(\text{dddt})_2$ cations. These features are mostly related to the totally symmetric vibrations of C=C

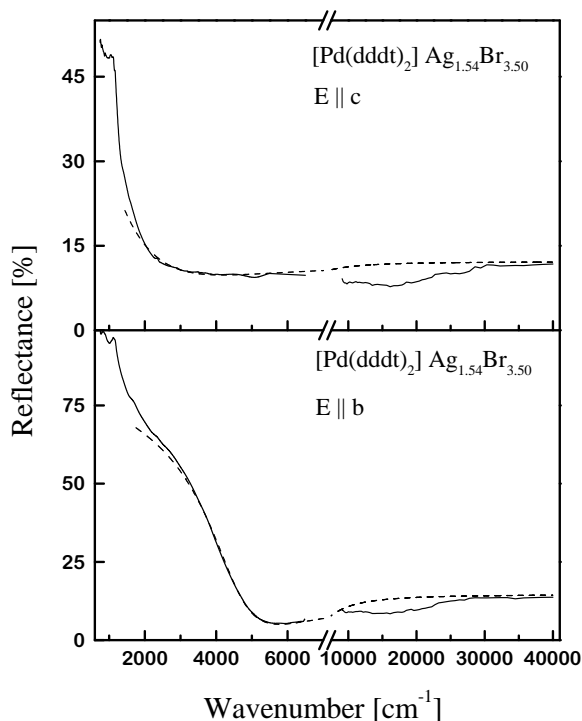


Figure 1. Room temperature reflectance spectra of $[Pd(ddd)_2]Ag_{1.54}Br_{3.50}$ crystal for polarization of the incident light along the c axis (upper panel) and along the b axis (lower panel). The least squares fits to the reflectance, based on the Drude model, are represented by dotted lines.

bonds in $Pd(ddd)_2$ cations (the so-called a_g modes). The presence of such vibrational ‘bumps’ superimposed on the electronic absorption, instead of well defined bands, is a characteristic feature of the organic conductors based on BEDT-TTF molecule, in which ‘side-by-side’ interactions between neighbouring molecules are stronger than those of ‘face-to-face’ type [7]. The reflectance data between 6500 cm^{-1} and 9000 cm^{-1} are missing. Above 9000 cm^{-1} the reflectance coefficient is low and weakly frequency dependent for both polarizations.

For both polarizations the experimental data were fitted with the reflectance calculated from the Drude model for the dielectric function:

$$\varepsilon^*(\omega) = \varepsilon_\infty - \frac{\omega_p^2}{\omega(\omega + i\Gamma)} \quad (1)$$

where: ω_p is the plasma frequency, ε_∞ is the residual dielectric constant at high frequency and Γ is the relaxation constant of free carriers. The fit was made to the reflectance data in the frequency region above 1900 cm^{-1} for $E \parallel b$ and 1600 cm^{-1} for $E \parallel c$. In the range below these frequencies the IR spectra deviate from Drude behaviour. Such deviations are usually observed in organic conductors since they are fairly strongly interacting systems with respect to the short-range electron–electron and electron–phonon interactions. However, in the analysis of IR spectra we neglect the non-Drude behaviour at low frequencies since, as was pointed out by Jacobsen in [8], the spectra near the plasmon frequency are insensitive to the detailed nature of the short-range electron–electron and electron–phonon interactions. This approach usually leads to reasonable parameters within a rather crude model of the band

Table 1. Parameters obtained from the Drude model analysis of the IR reflectance spectra of [Pd(dddtd)₂]Ag_{1.54}Br_{3.50} crystals.

Direction	ϵ_∞	ω_p (cm ⁻¹)	Γ (cm ⁻¹)	t (eV)	$\beta_{HOMO-HOMO}$ (eV) [6]
$\parallel b$	4.9	10 700	1900	0.13	0.1318
$\parallel c$	4.3	5500	4400	0.09	0.0837

structure. The best fit parameters obtained for both polarizations are listed in table 1. We tried also to fit the Drude–Lorentz dielectric function but the results were not good (see also the discussion of optical conductivity spectra).

The studied crystal should be considered as a two-dimensional one. Thus, following the procedure given in [8], we apply a simplified tight-binding band-structure model based on an orthorhombic lattice and introduce average transfer integrals t_b and t_c for directions parallel to b and c , respectively, which are weighted averages of several transfer integrals in the correct triclinic band structure. In this case the two-dimensional tight binding band is given by:

$$E(k_b, k_c) = -2t_b \cos(k_b d_b) - 2t_c \cos(k_c d_c) \quad (2)$$

where d_b and d_c correspond to the respective lattice directions. The plasma frequency is related to the band model by

$$\omega_p^2 = e^2 / \epsilon_0 \hbar \sum_{BZ} f(E_k) \partial^2 E / \partial k^2. \quad (3)$$

Here $f(E_k)$ is the Fermi–Dirac occupation number, and the derivative $\partial^2 E / \partial k^2$ is to be taken in the field direction. Then we estimate the anisotropy in the two-dimensional conducting plane. From the values of plasma frequencies given in table 1 we derive a quantity $(\omega_{pc} / \omega_{pb})(d_b / d_c) = 0.74$, where $d_b = 6.002 \text{ \AA}$ and $d_c = 4.157 \text{ \AA}$ are the respective molecular repeat distances. The anisotropy ratio $t_c / t_b = 0.72$ is estimated on basis of the numerical results given by Jacobsen *et al* [9] for the two-dimensional quarter-filled tight-binding model. This ratio indicates that the bands are nearly isotropic and the Fermi surface is expected to be closed in agreement with the band structure calculations. The estimated transfer integrals are listed in table 1. As a matter of fact the oxidation state of the silver cations can be either Ag⁺ or Ag²⁺ yielding the charge of Pd(dddtd)₂ close to +2 or +0.5, respectively. However, we have chosen $\rho = 0.5$ since this value seems to be the most probable [6].

The HOMO–LUMO gap for Pd(dddtd)₂ is equal to 0.30 eV and, as mentioned in the introduction, it should lead to the formation of the ‘two-band system’. The analysis of dispersion relations of the bands of the donor slabs in [Pd(dddtd)₂]Ag_{1.54}Br_{3.50} really shows that the HOMO and LUMO bands overlap [6]. Nevertheless, the electronic system can be considered as a ‘one-band system’, since the partially filled band is mainly built from the HOMO of Pd(dddtd)₂ donor. The tight-binding band structure calculations gave suitable interaction energies, β , for different interactions between Pd(dddtd)₂ donors [6]; however, the details of the band structure dispersion and the Fermi surface can be considerably influenced by other donor levels. The comparison of suitable $\beta_{HOMO-HOMO}$ interaction energies with the transfer integrals estimated from our reflectance spectra shows that in both directions our transfer integrals are close to calculated $\beta_{HOMO-HOMO}$ interaction energies (see table 1). This supports the previous suggestion that in the [Pd(dddtd)₂]Ag_{1.54}Br_{3.50} salt the electronic band structure is mainly built up of the HOMO of the Pd(dddtd)₂ donor and it is weakly influenced by other donor levels. In conclusion, our simplified approach has given reasonable band parameters.

The optical conductivity spectra and the real part of the dielectric function obtained by Kramers–Kronig transformation of the reflectance spectra are shown in figures 2 and 3,

respectively. In figure 2 for polarization $E \parallel b$ we observe a broad conductivity maximum centred at about 2000 cm^{-1} (0.25 eV). Such conductivity behaviour is usually considered as an indication of the energy gap existence in the electronic excitation spectrum. This broad electronic feature is surely due to a superposition of intra-band and inter-band electronic transitions. We assume that the high-frequency wing of the electronic band is weakly distorted by the inter-band transition and, consequently, the plasma frequency for $E \parallel b$, estimated on the basis of the Drude model, has a good value. The band at about 1000 cm^{-1} is a consequence of interaction between electrons and the totally symmetric C=C stretching vibrations of the $Pd(ddd)_2$ donor. When the electronic absorption overlaps with the phonon frequencies, their mutual interactions give rise to the dips or ‘antiresonances’ in the conductivity spectra [10]. This effect is readily observed on the high-frequency side of the vibrational band as a ‘notch’ in the electronic absorption. For polarization $E \parallel c$ the optical conductivity spectrum does not show any inter-band electronic transitions (figure 2). The conductivity ‘bump’ at about 1000 cm^{-1} is related to the coupling of C=C donor vibrations with electrons; this spectral feature is preceded by an ‘antiresonance’ at about 1250 cm^{-1} .

As seen in figure 3, the real part of the dielectric function, ϵ' , for polarization $E \parallel b$ is negative below about 4500 cm^{-1} , which is a characteristic feature of metallic behaviour. For metal the zero crossing of the ϵ' takes place at the plasmon frequency given by $\Omega_p = \omega_p / \sqrt{\epsilon_\infty}$. The unscreened plasma frequency, ω_p , estimated from this formula is equal to 9800 cm^{-1} and is in slightly lower than the value obtained by fitting the Drude model to the reflectance data (table 1).

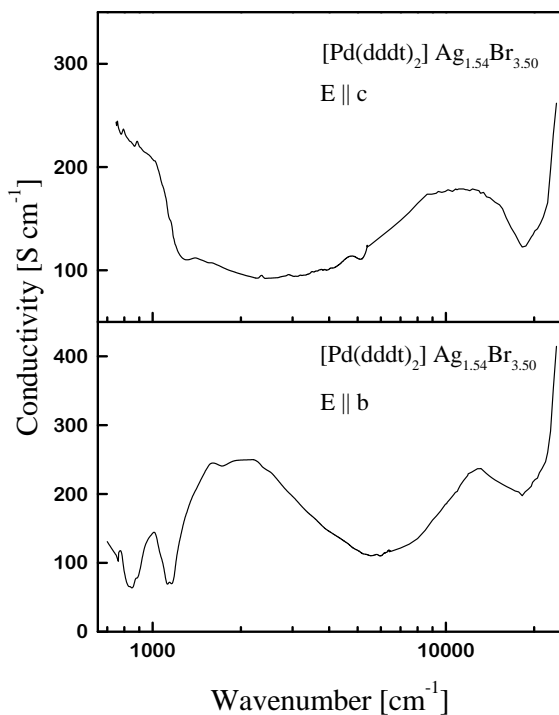


Figure 2. Optical conductivity spectra of $[Pd(ddd)_2]Ag_{1.54}Br_{3.50}$ crystal derived by Kramers–Kronig transformation (note the logarithmic frequency scale).

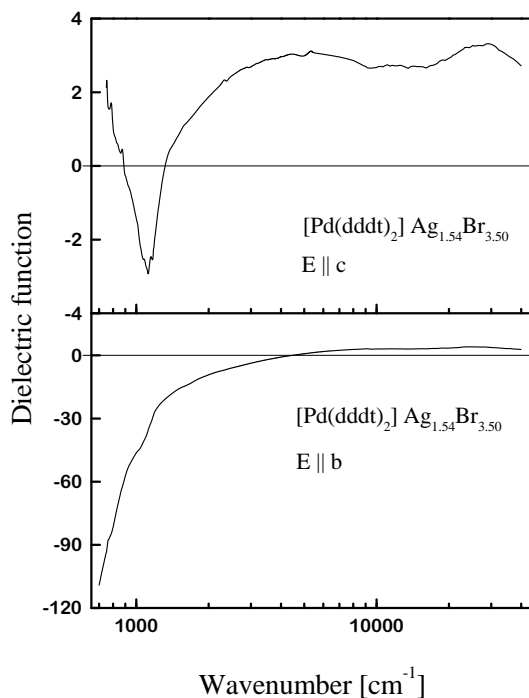


Figure 3. Real part of dielectric function of $[\text{Pd}(\text{ddd})_2]\text{Ag}_{1.54}\text{Br}_{3.50}$ crystal derived by Kramers–Kronig transformation (note the logarithmic frequency scale).

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