The temperature dependence of the infrared reflectance spectra of the organic superconductor $(BEDO-TTF)_2ReO_4 \cdot H_2O$ and the organic metal $(BEDO-TTF)_2Cl \cdot 3H_2O$

The temperature dependence of the infrared reflectance spectra of the organic superconductor (BEDO-TTF)$_2$ReO$_4$·H$_2$O and the organic metal (BEDO-TTF)$_2$Cl·3H$_2$O

M A Tanatar†‖, R Świetlik‡¶, N D Kushch§ and E B Yagubskii§

† Institute of Surface Chemistry, National Academy of Sciences of the Ukraine, 31 Prospekt Nauki, 252650 Kiev, Ukraine
‡ Institute of Molecular Physics, Polish Academy of Sciences, Smoluchowskiego 17, 60-179 Poznań, Poland
§ Institute of Chemical Physics, Russian Academy of Sciences, 142432 Chernogolovka, Russia

Abstract. The temperature dependences of the polarized reflectance spectra of two charge-transfer salts of bis(ethylenedioxy)tetrathiafulvalene, namely superconducting (BEDO-TTF)$_2$ReO$_4$·H$_2$O and metallic (BEDO-TTF)$_2$Cl·3H$_2$O, have been investigated over the 650 to 6500 cm^{-1} range. For the former salt, the first-order phase transition at about 210 K was shown to be accompanied by major relaxation rate changes, occurring preferentially in the direction normal to the crystallographic c-axis. Fluctuations within the anion layer are considered to be responsible for this peculiar relaxation rate behaviour. For the (BEDO-TTF)$_2$Cl·3H$_2$O salt, pure metallic reflectance is observed for the first time for an organic conductor, providing evidence that the electronic correlations are very weak in this system.

1. Introduction

Bis(ethylenedioxy)tetrathiafulvalene, or BEDO-TTF, is an organic donor molecule, known to produce charge-transfer salts commonly showing stable metallic resistance behaviour down to the lowest temperatures [1]. Despite this, only two of them show a transition to the superconducting state, namely (BEDO-TTF)$_3$Cu$_2$(SCN)$_3$ at nearly 1 K [2] and (BEDO-TTF)$_2$ReO$_4$·H$_2$O at 2.5 to 3.5 K [3, 4]. The reasons for this tendency for metallic state formation have been speculated to be both an ability to self-aggregate and the low ionization energy of the molecule [1]. Infrared reflectance spectra of the compounds could assist considerably in the understanding of the compounds' electron band structures, and thus help in the solving of this problem. Despite the fact that the assignment of the BEDO-TTF molecule vibrational modes, and the calculation of their electron–molecular vibration coupling constants were performed some years ago, and form a good basis for these investigations [5, 6], the single-crystal data have been limited up to now to studies of the room temperature reflectance of (BEDO-TTF)$_2$ReO$_4$·H$_2$O [7, 8]. The aim of this paper is to investigate in some detail the temperature dependences of the infrared reflectivity for both the superconducting salt (BEDO-TTF)$_2$ReO$_4$·H$_2$O and the metallic (nonsuperconducting)

‖ E-mail: kip@lab37.semicond.kiev.ua.
¶ E-mail: swietlik@ifmpan.poznan.pl.

salt $(BEDO\text{-}TTF)_2Cl\cdot3H_2O$, in an attempt to understand the electronic structure of these compounds.

2. Experimental details

Single crystals of $(BEDO\text{-}TTF)_2ReO_4\cdot H_2O$ and $(BEDO\text{-}TTF)_2Cl\cdot3H_2O$ were grown by the electrochemical oxidation technique from a BEDO-TTF solution in 1, 1, 2-trichloroethane (TCE) as described in [4]. Highly perfect distorted hexagon-shaped plates of $(BEDO\text{-}TTF)_2ReO_4\cdot H_2O$ were selected for the studies. When they were inspected under the microscope, well defined fibroid structure was observed, as had been reported previously [7]. $(BEDO\text{-}TTF)_2Cl\cdot3H_2O$ samples had the same shape. Typical sample dimensions were of the order of $1 \times 1 \times 0.1$ mm^3.

Studies of the reflectance were performed in the near-normal-incidence mode in the 650 to 6500 cm^{-1} spectral range with an FT-IR Perkin–Elmer 1725X spectrometer with the help of an FT-IR microscope. The samples were mounted, free standing, on a BaF$_2$ plate, placed on the temperature-controlled stage within an optical cryostat with KBr windows. The cryostat was filled with dried nitrogen gas, and the stage temperature was regulated and stabilized with an accuracy of the order of 1 K with a Linkam temperature controller. The incoming beam was polarized with a gold wire grid deposited on a AgBr substrate. The spectra were recorded for a number of incident beam polarizations. The reflectance maximum and minimum in the case of the $(BEDO\text{-}TTF)_2ReO_4\cdot H_2O$ were found to coincide with the directions normal to the fibroid structure and along it. On the basis of this structure, we assigned these directions as perpendicular and collinear with the c-axis within the highly conducting plane, in the crystallographic axis notation according to [7]. In the case of the $(BEDO\text{-}TTF)_2Cl\cdot3H_2O$ salt, the long and short crystal axes corresponded to the crystallographic axes a and b, respectively [9]. A very small anisotropy was typical for the $(BEDO\text{-}TTF)_2Cl\cdot3H_2O$ samples, and the directions of the extrema were in good agreement with the sample shape—that is, they were parallel to the a-axis and normal to it (i.e. parallel to the b-axis). We denote these directions as $\|a$ and $\|b$ in the following.

Table 1. Transport parameters, obtained from the Drude model analysis of the room temperature reflectance spectra of $(BEDO\text{-}TTF)_2ReO_4\cdot H_2O$.

Direction	ω_p (cm^{-1})	Γ (cm^{-1})	ϵ_∞	Reference
$\|$ to c-axis	5900	2600	2.9	This work
	7850	4600	2.8	[7]
	6400	4500	3.0	[8]
$\perp$ to c-axis	9900	2600	3.0	This work
	9900	2200	3.1	[7]
	10 600	3100	3.0	[8]

3. Results and discussion

Figure 1 shows room temperature reflectance spectra of the most perfect $(BEDO\text{-}TTF)_2ReO_4\cdot H_2O$ sample for the polarizations along and perpendicular to the crystallographic c-axis. The spectra correspond very well to those already reported [7, 8]. The spectra for both polarizations were approximated in the 2000 to 6500 cm^{-1} interval by the Drude model with three free parameters, as described in detail in [8]. The best fit of the spectra at room
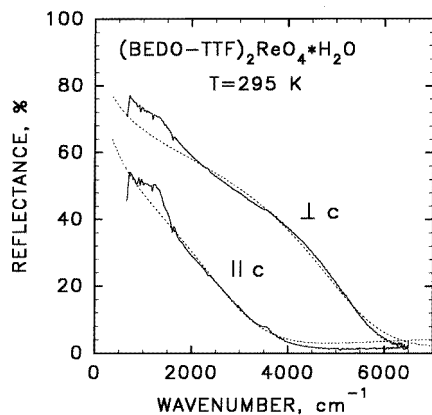
Figure 1. Room temperature reflectance spectra of $(BEDO-TTF)_2ReO_2 \cdot H_2O$ for the polarization of the incident light along ($\|c$) and perpendicular to ($\perp c$) the c-axis. The least-squares fits to the reflectance based on the Drude model are represented by dashed lines.

temperature gave the parameters listed in table 1. For the direction $\perp c$, these parameters are in good agreement with those reported in [7, 8], given also in table 1. For the direction $\|c$, the parameters obtained were little different, due probably to a slight difference in ϵ_∞ [8]. After obtaining the best fit at room temperature, the dielectric constant ϵ_∞ was fixed, and only the plasma frequency ω_p and the relaxation rate Γ were changed during the fitting process. The parameters of the fit for the polarizations of incident light parallel and perpendicular to the c-axis, and their temperature dependences, are shown in figures 2(a) and 2(b), respectively. First of all it should be noted that the reflectance of the sample increases on cooling for both polarizations, leading to the notable changes of the relaxation parameter Γ. Notable irregularity in the temperature dependence of Γ may be noticed in the vicinity of the first-order phase transition within the 205 to 220 K temperature interval. It should be noted, however, that this irregularity is very pronounced only for the polarization of the incident light perpendicular to the c-axis, while for the parallel polarization the changes are within the experimental scatter. Note also that the plasma frequency does not 'feel' the phase transition, although it leads to the twofold resistance decrease [3, 4, 10]. Our experimental finding of a preferential relaxation rate change at the phase transitions is in accordance with the conclusion of [10], based mainly on the temperature independence of the Hall constant.

The fact that ω_p, extracted from the Drude fit, is not very sensitive to temperature variation is likely simply to reflect the lack of drastic band-structure transformation at the phase transition. These changes could be rather strongly masked in such an integrated quantity as ω_p, which is related to the general band width [11], and is not very sensitive to the details of the dispersion curves in the vicinity of the Fermi energy, which are very important for the transport properties.

As regards the relaxation rate changes, they show that a rather broad spectrum of excitations is involved in the carrier scattering. The anisotropy of the relaxation change is worthy of special consideration. The nature of the high-temperature (205 to 220 K) phase transition in the $(BEDO-TTF)_2ReO_4 \cdot H_2O$ salt has been discussed in relation to the ordering process, say of the H_2O molecules and ReO_2 groups in the lattice, or in relation to the monoclinic-to-triclinic lattice symmetry change [10, 12]. As long as these processes are not directly related to the electronic system, it is hard to imagine why these processes
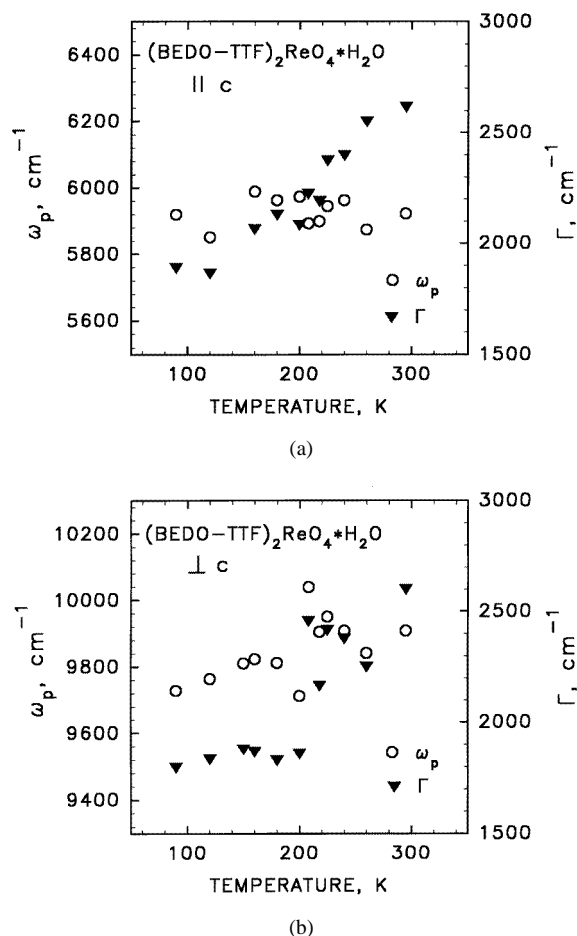
Figure 2. The temperature dependence of the plasma frequency (ω_p) and relaxation rate (Γ) of the (BEDO-TTF)$_2$ReO$_2$·H$_2$O crystal for the polarization of the incident light along (a) and perpendicular to (b) the c-axis.

would lead to such a notable and anisotropic relaxation rate change. On the other hand, according to the band-structure calculation [10], the direction of the largest relaxation rate change nearly corresponds to that of the best nesting of the Fermi surface, resulting in the incomplete spin-density-wave instability in the compound at low temperatures [4, 13]. Strong anisotropy of the relaxation time may imply then a central role of the electronic subsystem in the phase transition.

We would like now to speculate about the origin of these changes. First of all, it should be recalled that H$_2$O molecules in the crystal lattice form hydrogen bonds with the ReO$_4$ groups in the anion layer, going mostly along the direction $\perp c$ [3, 12]. So, reconstruction of these bridges can lead to the change of the anion potential, preferentially along the direction $\perp c$. In the ordered state, at temperatures below that of the phase transition, this potential may have periodicity equal to that of the lattice. In the one-dimensional systems, a process of similar kind, anion ordering [14], results in a very sharp metal-to-insulator phase transition, due to the coincidence of the anion lattice distortion wavevector k_a and the best Fermi surface (FS) nesting vector $2k_F$. In the compound under consideration, the

FS has some possibilities for nesting, as is evident from the spin-density-wave formation at low temperatures. However, this nesting does not involve the whole FS, and is likely to be incommensurate with the lattice. So, the static anion potential, which is formed at a temperature below that at which the phase transition occurs and is commensurate with the lattice periodicity, cannot map onto the FS and lead to the gap formation. However, at temperatures above that of the anion ordering, there exists a broad spectrum of the dynamic components of this potential, and some components fulfil the condition $k_a = 2k_F$. These components should be coupled rather strongly with the electron system, and create excess scattering at temperatures above that of the phase transition over a broad range of energies. Then, the dying out of the fluctuations at the phase transition must lead to a significant relaxation rate decrease, as is observed.

Table 2. Transport parameters, obtained from the Drude model analysis of the room temperature reflectance spectra of $(BEDO-TTF)_2Cl \cdot 3H_2O$.

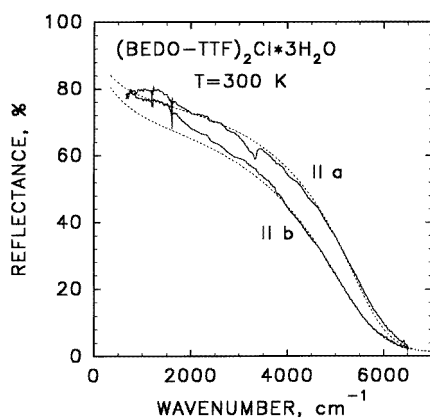| Direction	ω_p (cm^{-1})	Γ (cm^{-1})	ϵ_∞
$\parallel$ to b-axis	9800	1950	3.0
$\parallel$ to a-axis	10 750	1550	3.4

Figure 3. The room temperature reflectance spectrum of $(BEDO-TTF)_2Cl \cdot 3H_2O$ for the positions of the maximum ($\parallel a$) and the minimum ($\parallel b$) of the reflected energy of the polarized incident light. The least-squares fits to the reflectance based on the Drude model are represented by dashed lines.

Figure 3 shows the room temperature reflectance spectrum of the $(BEDO-TTF)_2Cl \cdot 3H_2O$ salt. Note that the reflectivity drop in the 3300 cm^{-1} region, especially evident for the polarization of the incident light along the direction $\parallel a$, is due to the crystalline water in the lattice. Except for this small notch, and the vibrational features below about 1500 cm^{-1}, the shape of the reflectance curves over the whole spectral interval studied can be well fitted with a simple Drude model for both polarizations at all temperatures. The Drude model was fitted to the reflectance data within the frequency region 2000–6500 cm^{-1}. Table 2 summarizes the fitting parameters for the $(BEDO-TTF)_2Cl \cdot 3H_2O$ salt at room temperature. On the basis of these parameters, we performed an estimation of the transfer integrals in the following way. The compound under study should evidently be considered as a two-

dimensional one, and in the tight-binding approximation its band structure can be represented as

$$E(k_a k_b) = -2t_a \cos(k_a d_a) - 2t_b \cos(k_b d_b) \tag{1}$$

where a and b correspond to the respective lattice directions [12]. The limiting value for the intermolecular spacing in the direction a should be taken as equal to half of the lattice parameter, due to there being two chains in the unit cell ($d_a = 4.29$ Å). We can estimate the optical anisotropy parameter $(\omega_{pb} d_a)/(\omega_{pa} d_b)$ as 0.77, and, using appropriate dependences showing anisotropic plasma behaviour from reference [15], the respective transfer integral anisotropy $p = t_b/t_a$ as 0.75 (where ω_{pa} and ω_{pb} are the plasma frequencies from table 2, and $d_b = 5.1$ Å is the intermolecular spacing in the direction b). Then, following the method described in [15] and taking the crystal volume per molecule as $V_m = 353.5$ Å^3, we find $t_a = 0.16$ eV and $t_b = 0.12$ eV. The transfer integrals calculated by Mori *et al* [16] on the basis of the extended Hückel molecular orbital model are $t_p = 0.14$ eV (t_p corresponds to the direction between the central and corner molecules in the unit cell) and $t_b = 0.10$ eV. The transfer integrals estimated from our reflectance data are slightly larger than those from reference [16].

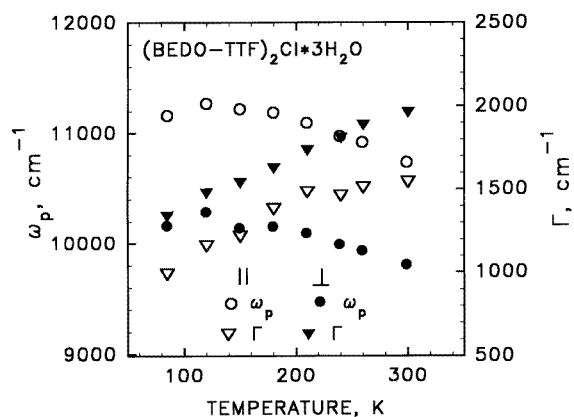**Figure 4.** The temperature dependence of the plasma frequency (ω_p) and relaxation rate (Γ) for (BEDO-TTF)$_2$Cl·3H$_2$O for polarizations $\|a$ and $\|b$ of the incident light.

The temperature dependences of the Drude model fitting parameters are shown in figure 4, and they show a smooth variation similar to the resistance temperature dependence [12]. Note that the crystalline water line in (BEDO-TTF)$_2$Cl·3H$_2$O is much more evident for the direction $\|a$, which is the same as the case for the (BEDO-TTF)$_2$ReO$_2$·H$_2$O salt, considered above. However, the Fermi surface of the (BEDO-TTF)$_2$Cl·3H$_2$O salt is of quite different shape compared to that of the (BEDO-TTF)$_2$ReO$_2$·H$_2$O salt. The Fermi surface of (BEDO-TTF)$_2$Cl·3H$_2$O was found by calculation, and confirmed experimentally [16], to have the shape of a cylinder of rotation, and no instabilities within the anion layer can map onto this Fermi surface topology. We would like to point out that a good fit of the (BEDO-TTF)$_2$Cl·3H$_2$O spectra with the simple Drude model is in strong contrast with the common outcome for organic metals [17], where a strong molecular vibration structure is typical; this indicates a very short electron residence time on the molecule. Taken in conjunction with the lack of superconductivity for most of the BEDO-TTF compounds, this leads us to suppose that strong electron correlations are likely to be essential prerequisites for the appearance of superconductivity.

4. Conclusions

The temperature dependences of the infrared reflectance spectra have been investigated for two salts of bis(ethylenedioxy)tetrathiafulvalene, namely (BEDO-TTF)$_2$ReO$_2$·H$_2$O and (BEDO-TTF)$_2$Cl·3H$_2$O. For the (BEDO-TTF)$_2$ReO$_2$·H$_2$O salt, a first-order phase transition in the 205 to 220 K temperature range was shown to be accompanied by major relaxation rate changes, mainly along the direction normal to the *c*-axis. Fluctuations of the anion ordering are considered to be responsible for this peculiar relaxation rate behaviour. For the (BEDO-TTF)$_2$Cl·3H$_2$O salt, reflectance of purely metallic type is observed, which is described very well by the simple Drude model. This simple behaviour is here observed for the first time for an organic conductor, providing evidence that the electronic correlations in the system are very small.

Acknowledgments

References

[1] Yamochi H, Horiuchi S, Saito G, Kusunoki M, Sakaguchi K, Kikuchi T and Sato S 1993 *Synth. Met.* **55–57** 2096

[2] Beno M A, Wang H H, Kini A M, Carlson K D, Geiser U, Kwok W K, Thompson J E, Williams J M, Ren J and Whangbo M-H 1990 *Inorg. Chem.* **29** 1599

[3] Kahlich S, Schweitzer D, Heinen I, Song En Lan, Nuber B, Keller H J, Winzer K and Helberg H W 1991 *Solid State Commun.* **80** 191

[4] Buravov L I, Khomenko A G, Kushch N D, Laukhin V N, Schegolev A I, Yagubskii E B, Rozenberg L P and Shibaeva R P 1992 *J. Physique* I **2** 529

[5] Pokhodnia K I, Kozlov M E, Onischenko V G, Schweitzer D, Moldenhauer J and Zamboni R 1993 *Synth. Met.* **55–57** 2364

[6] Pokhodnia K I 1995 *Acta Phys. Pol.* A **87** 815

[7] Sommer W, Moldenhauer J, Schweitzer D, Heinen I and Keller H J 1995 *Synth. Met.* **68** 133

[8] Świetlik R and Kushch N D 1994 *Phys. Status Solidi* a **142** 515

[9] Dyachenko O A 1996 private communication

[10] Kahlich S, Schweitzer D, Rovira C, Paradis J A, Whangbo M-H, Heinen I, Keller H J, Nuber B, Bele P, Brunner H and Shibaeva R P 1994 *Z. Phys.* B **94** 39

[11] Sugano T, Yamada K, Saito G and Kinoshita M 1985 *Solid State Commun.* **55** 137

[12] Schweitzer D, Kahlich S, Heinen I, Song En Lan, Nuber B, Keller H J, Winzer K and Helberg H W 1993 *Synth. Met.* **55–57** 2827

[13] Audouard A, Auban-Senzier P, Laukhin V N, Brossard L, Jérome D and Kushch N D 1996 *Europhys. Lett.* **34** 599

[14] Jacobsen C S, Pedersen H J, Mortensen K, Rindorf G, Thorup N, Torrance J B and Bechgaard K 1982 *J. Phys. C: Solid State Phys.* **15** 2651

[15] Jacobsen C S, Williams J M and Wang H H 1985 *Solid State Commun.* **54** 937

[16] Mori T, Oshima K, Okuno H, Kato K, Mori H and Tanaka S 1995 *Phys. Rev.* B **51** 11 110

[17] Graja A 1994 *Organic Conductors—Fundamentals and Applications* ed J-P Farges (New York: Dekker) pp 229–67