Materials Science-Poland, Vol. 22, No. 4, 2004

Reflectivity spectra of some conducting BETS salts

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We have measured the polarized reflectivity spectra of three BETS-based organic metals with the α-phase structure: α-$(BETS)_2NH_4Hg(SCN)_4$ (I), α-$(BETS)_2TlHg(SeCN)_4$ (II), and α-$(BETS)_2Cu_5I_6$ (III) in the range of 600–6500 cm^{-1}. The spectra exhibit a metallic-type reflection with the plasma edge about 4000–5000 cm^{-1} and high reflectivity at low frequencies. The electron-vibrational bands observed in the range of 1200–1400 cm^{-1} are due to the interaction of the intramolecular vibrational modes of BETS with conduction electrons.

Key words: *organic conductors; optical properties*

1. Introduction

Radical-cation salts of bis(ethylenedithio)tetraselenafulvalene (BETS) attract considerable attention due to unique properties (such as superconductivity or the Shubnikov–de Haas effect) of some of them ([1, 2] and refs. therein). We have studied the optical properties of three BETS-based organic metals of the α-phase structure: α-$(BETS)_2NH_4Hg(SCN)_4$ (I), α-$(BETS)_2TlHg(SeCN)_4$ (II) [1], and α-$(BETS)_2$ -Cu_5I_6 (III) [2] in the range of 600–6500 cm^{-1}.

2. Experimental

Reflectivity spectra of the compounds studied were recorded at room temperature in the range of 600–6500 cm^{-1} in polarized light by means of a Perkin-Elmer 1600 and Perkin-Elmer Spectrum BX Fourier transform spectrometers. The samples were made of one or two single crystals (of typical dimensions 1×2 mm^2 each). The spectra were taken from the plane of conducting BETS layers.

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Optical conductivity spectra were obtained from the reflectivity spectra by means of the Kramers–Kronig analysis. The result of the analysis in the range of 600–5000 cm^{-1} does not qualitatively depend on the kind of extrapolation to low and high frequencies. We suppose that the reflectivity approaches unity at low frequencies (which is typical of metals) and that it is constant at high frequencies.

3. Results and discussion

3.1. Electronic spectra

Figure 1a shows the polarized reflectivity spectra of $(BETS)_2NH_4Hg(SCN)_4$ in the range of 600–6500 cm^{-1} for the two main optical directions, x and y, for which the maximal differences in reflectivity are observed. Figure 1b shows the spectra of optical conductivity for the same main optical directions. Figure 2 shows the reflectivity and conductivity spectra of $(BETS)_2TlHg(SeCN)_4$, belonging to the same isostructural family [1]. The spectra resemble those of the analogous isostructural ET compounds $(ET)_2TlHg(SeCN)_4$ [3] and $(ET)_2NH_4Hg(SCN)_4$ [4]. Figure 3 shows the spectra of the $(BETS)_2Cu_5I_6$ salt.

The α-phase structure is characterized by the presence of stacks of BETS molecules with strong intermolecular interactions in the direction perpendicular to the stacks. The directions x and y correspond to polarizations with the electric vector perpendicular and parallel to the direction of BETS stacks [1, 3]. This means that the electronic reflectivity is greater for the polarization perpendicular to BETS stacks for all three salts studied. This fact is due to a large amount of shortened contacts between S(Se) atoms in the BETS molecules of adjacent stacks. The spectra of $(BETS)_2NH_4Hg(SCN)_4$ exhibit a pronounced plasma edge in the x direction, while in the y direction and in the spectra of $(BETS)_2TlHg(SeCN)_4$ the plasma edge is much less pronounced. The conductivity spectra of $(BETS)_2NH_4Hg(SCN)_4$, similar to those of $(BETS)_2TlHg(SeCN)_4$ and $(ET)_2TlHg(SeCN)_4$ [1, 3], do not exhibit a maximum in conductivity at about 3000 cm^{-1}, which is usual for many ET and BETS salts [3–6]. This may be an evidence of the absence of an energy gap in the spectrum of electronic states of these salts. On the contrary, the optical conductivity spectra of $(BETS)_2Cu_5I_6$ exhibit such a maximum at ca. 2300 cm^{-1}, which may be taken as an evidence of an energy gap (or pseudo-gap) in the electronic spectra of this salt.

The reflectivity spectra of the salts studied may be described in terms of the Drude–Lorentz model used for α-$(ET)_2I_3$ [5]. The obtained parameters (dielectric constant at high frequencies ε_∞, plasma frequency ω_p, electron energy gap 2Δ, electronic damping Γ) are shown in Table 1.

Carrier effective masses m_x and m_y were obtained from the equation $\varepsilon_\infty \omega_p^2 = 4\pi ne^2/m$ (e is electron charge, n is the concentration of carriers taken as

$n = 1\times10^{21}$ cm^{-3} from the structure data, supposing one electron charge per two BETS molecules in analogy with [1]) and the transfer integrals $t_x = 0.14$ eV and $t_y = 0.12$ eV were calculated from the effective masses by numerical integration in analogy with [6] (intermolecular distances were accepted as half periods along x and y directions, $a_x = 0.5$ nm and $a_y = 0.5$ nm, in analogy with [1]).

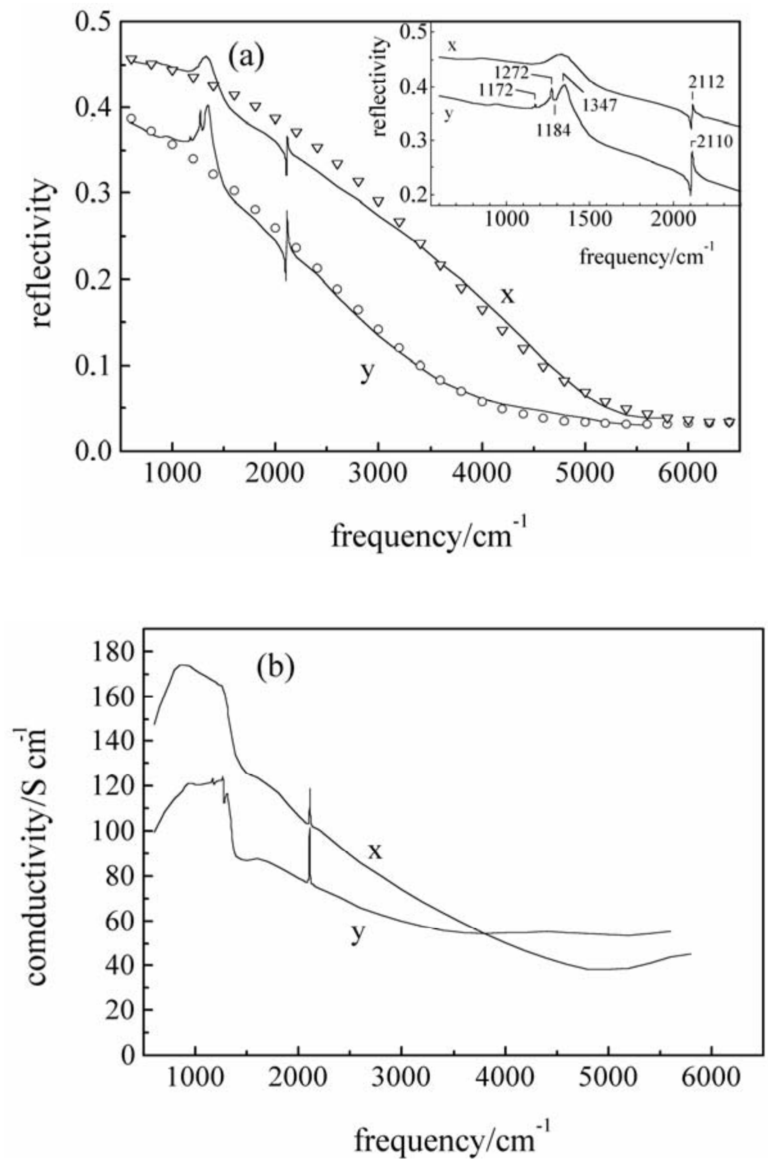

Fig. 1. Reflectivity (a) and optical conductivity (b) spectra of α-(BETS)$_2$NH$_4$Hg(SCN)$_4$ for the two main optical directions x and y. The circles and triangles show the Drude–Lorentz fit

The parameters obtained are summarized in Table 1. In all cases, the effective masses are higher and the transfer integrals lower in the *y* direction (parallel to molecular stacks). In comparison with other salts, $(BETS)_2NH_4Hg(SCN)_4$ is characterized by much lower effective masses and much larger transfer integrals (i.e., wider conduction bands).

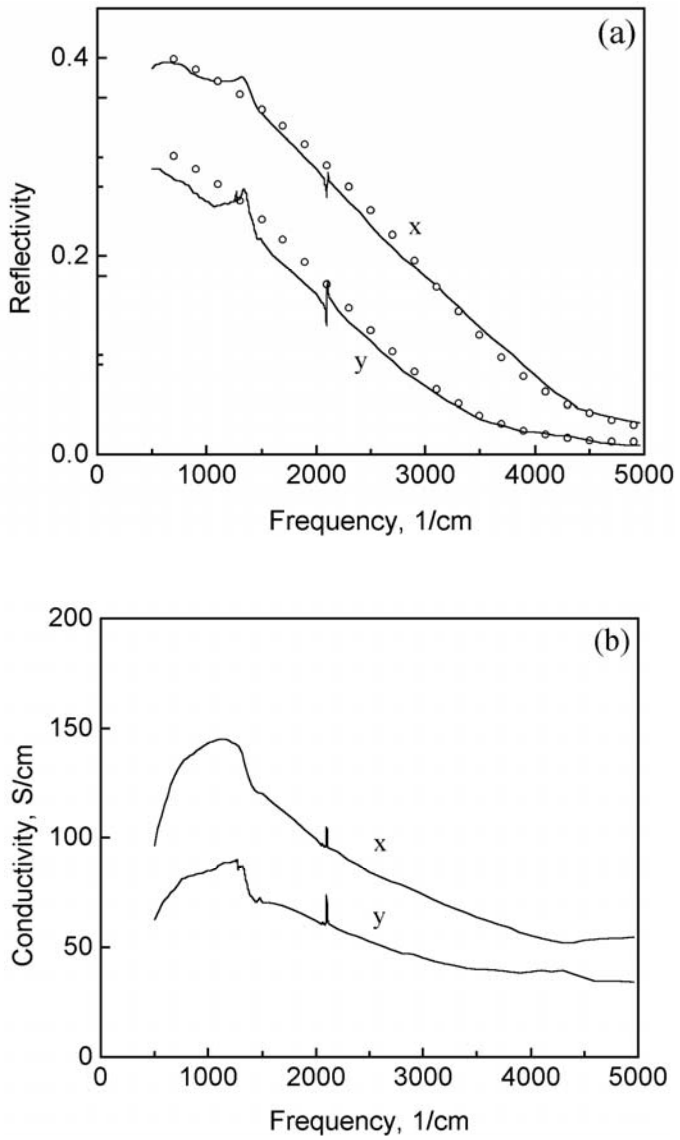

Fig. 2. Reflectivity (a) and optical conductivity (b) spectra of α-$(BETS)_2TlHg(SeCN)_4$ for the two main optical directions *x* and *y*. The circles show the Drude–Lorentz fit

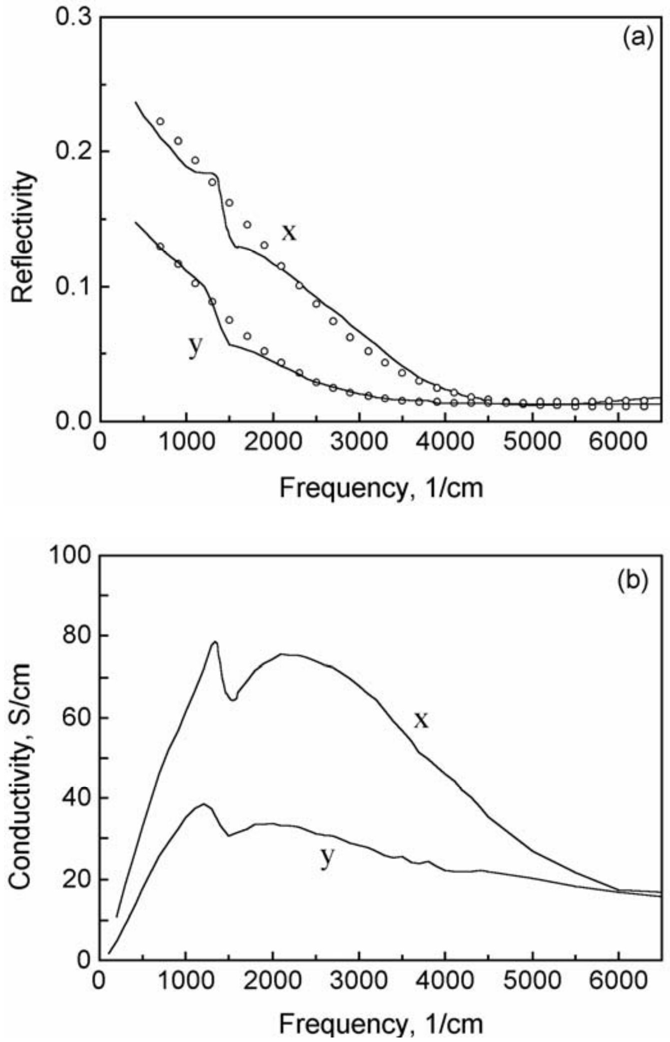

Fig. 3. Reflectivity (a) and optical conductivity (b) spectra of α-$(BETS)_2Cu_5I_6$ for the two main optical directions *x* and *y*. The circles show the Drude–Lorentz fit

Table 1. Parameters of the Drude–Lorentz fit

Parameter	α-$(BETS)_2NH_4Hg(SCN)_4$		α-$(BETS)_2TlHg(SeCN)_4$ [1]		α-$(BETS)_2Cu_5I_6$ [2]	
	x	*y*	*x*	*y*	*x*	*y*
ε_∞	3.0	2.7	2.5	2.0	1.8	1.8
ω_p, cm^{-1},	4600	3600	3850	3100	3200	2100
2Δ, cm^{-1},	1600	1400	1400	1300	1600	1500
Γ, cm^{-1}	3300	3300	3000	2850	4000	3500
m, m_e	1.4	2.6	2.4	4.7	4.8	11.3
t, eV	0.14	0.12	0.09	0.06	0.033	0.031

3.2. Vibrational spectra

The insert in Fig.1a shows the spectral range of molecular vibrations. Similar to (BETS)2TlHg(SeCN)$_4$ and (ET)2TlHg(SeCN)$_4$ [1, 3], the doublet electron-vibrational band (with a slight reflectivity minimum at 1284 cm^{-1}) is observed in the polarization parallel to BETS stacks (*y* direction), while the electron reflectivity is more intensive in the polarization perpendicular to the stacks. The maxima of this doublet are slightly shifted to higher frequencies: 1272 and 1347 cm^{-1}, vs. 1270 and 1340 cm^{-1}for $(BETS)_2TlHg(SeCN)_4$ and 1258 and 1316 cm^{-1} for the ET salt. For comparison, an analogous doublet in the κ-phase salt $(BETS)_2FeCl_4$ was observed at 1280 and 1320 cm^{-1} [7]. These bands are due to the interaction of the conduction electrons with the symmetric vibrational modes of BETS molecules [4–6], apparently including C–C stretching modes (taking into account relatively small shift between BETS and ET containing salts). For the *x* direction, only a weak, broad maximum is observed in the electron-vibrational range of 1000–1400 cm^{-1}, similar to that of $(BETS)_2TlHg(SeCN)_4$ and $(ET)_2TlHg(SeCN)_4$.

An interesting peculiarity of $(BETS)_2Cu_5I_6$ is the absence of the minimum of reflectivity at 1280–1290 cm^{-1}, observed in other salts. This may be due to the absence of centrosymmetric BETS molecules in the crystal stucture of this salt [2].

Narrow bands near 2100 cm^{-1} are due to vibrations of CN fragments in the anionic layer. The maxima of these bands are slightly shifted to higher frequencies compared with that of analogous salts: 2112 and 2110 cm^{-1} for *x* and *y* directions cf. 2110 and 2105 for $(BETS)_2TlHg(SeCN)_4$ and 2104 and 2102 cm^{-1} for $(ET)_2TlHg(SeCN)_4$ [1].

Acknowledgements

This work was supported by RFBR-DFG grant N 03-02-04023.

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Received 14 October 2004
Revised 15 November 2004