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Infrared optical properties of the new organic conductors family $(ET)_8[Hg_2X_6(C_6H_5Y)]_2$ (X, Y = Cl, Br)

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Abstract. — The polarized reflectivity spectra of the single crystals of three organic conductors $(ET)_8[Hg_2X_6(C_6H_5Y)]_2$ (X, Y = Cl, Br) have been studied. The electronic IR band with a plasma edge is observed in the spectra similar to most conducting ET compounds. However, a group of the electron-vibrational bands usual for other ET salts is not observed which has been accounted for by the peculiarities of crystal structure due to which the vibrational modes responsible for electron-vibrational interaction belong to non-totally symmetric type.

Introduction.

In previous works [1-5] we have investigated ET-based organic metals with halide-mercurate anions of the type $(ET)_4(Hg_{3-\delta}X_8)$ where X = Cl, Br, I and ET is bis(ethilenedithio)tetrathiafulvalene (in another notation BEDT-TTF). $(ET)_4Hg_{3-\delta}Cl_8$ and $(ET)_4Hg_{2.89}Br_8$ are isostructural compounds with the structure of organic sheets of κ-phase type and become superconductive at $T_c = 1.8$ K (under the pressure of 12 kbar) and $T_c = 4.3$ K correspondingly [1, 2]. Investigation of optical properties of this compounds shows a low-anisotropy metal-like IR reflection with a plasma edge and with a group of intensive electron-vibrational bands [4, 5].

Using substituted benzene as solvents in the same system of ET with halide-mercurate anions leads to a new family of iso-structural organic metals $(ET)_8[Hg_2X_6(C_6H_5Y]_2$ where X, Y = Cl, Br [6-9]. The compound $(ET)_8[Hg_2Cl_6(C_6H_5Cl)]_2$ (I) retains its metal state down to 1.5 K [7]. For $(ET)_8[Hg_2Cl_6(C_6H_5Br)]_2$ (II) the metal state is stabilized down to 10 K. Two other compounds of this family, $(ET)_8[Hg_2Br_6(C_6H_5Cl)]_2$ (III) and $(ET)_8[Hg_2Br_6(C_6H_5Br)]_2$ (IV) are metals with metal-insulator transition at 90 and 130 K correspondingly [9]. In the crystal structure of $(ET)_8[Hg_2X_6(C_6H_5Y)]_2$, ET molecules form conducting layers. Inside a layer, molecules are arranged in « ribbons » with neighbouring molecules interconnected by shortened sulphur-sulphur contacts [6-9].

In the present work, we have studied optical properties of single crystals of the three compounds from the specified family : (I), (II) and (IV). We have measured the reflectivity spectra in polarized light in the spectral range 300-5 000 cm^{-1} on Perkin-Elmer 325 spectrophotometer and in the range 4 000-10 000 cm^{-1} on SF-8 spectrophotometer. For compound (IV) with a metal-insulator transition at $T = 130$ K, we have obtained an IR spectra at $T = 300$ K and $T = 90$ K. The sample for measurements at $T = 90$ K was made from two single crystals orientated parallel to each other. In other cases, measurements were carried out on separate single crystals. The directions of polarization relative to crystallographic axes were determined according to the external shape of crystals. The reflectivity was taken from the *bc*-plane, containing conducting layers of ET molecules [6-9].

Results.

The spectra of all the three compounds at room temperature do not differ qualitatively from each other. In figure 1, the reflectivity spectra of (I), (II) and (IV) are given for the spectral region 300-8 000 cm^{-1} Above 8 000 cm^{-1}, in the range 8 000-10 000 cm^{-1}, the reflectivity, does not practically depend on frequency. Spectra are given for the two mutually perpendicular polarizations corresponding to the two principal optical directions, x and y. The principal directions were determined by a maximum difference between reflectivities at any fixed frequency. The y direction, for which IR reflectivity is minimal, approximately corresponds to the crystallographic direction [011]. The x direction (with maximum reflectivity) is close to the crystallographic direction $[02\bar{1}]$.

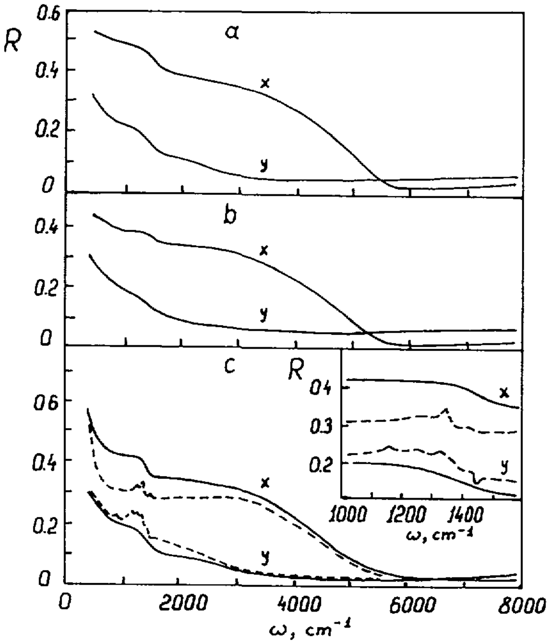

Fig. 1. — The reflectivity spectra of the compounds I (a), II (b) and IV (c) for the two principal optical directions, x and y. For the compound IV, spectra at $T = 300$ K (solid lines) and $T = 90$ K (dashed lines) are given. The insert shows the spectral region of 1 000-1 600 cm^{-1} in the enhanced scale.

In the reflectivity spectrum for the x direction, there is a plasma reflection edge at about 5 000 cm^{-1} and high reflectivity at lower frequencies, which are due to quasi-free carriers and are usual for conducting ET-compounds [10-17]. In the y polarization, the reflectivity is lower but at frequencies below 3 000 cm^{-1} it rises : this may be evidence of an electron transfer, also in the y direction.

In the spectral region of intramolecular vibrational frequencies, a weak widely dispersed maximum is observed at about 1 000-1 300 cm^{-1}. For the compound (IV) at $T = 90$ K (below the transition point of the metal-insulator transition), a fine structure appears in the region of 1 000-1 300 cm^{-1} (Fig. 1c). Besides, at low temperatures, some lowering of the electronic reflection anisotropy is observed : the IR reflectivity lowers in the x direction and rises in the y direction.

Figure 2 shows the optical conductivity spectra for (I), (II) and (IV) compounds which are obtained by a Kramers-Kronig analysis of the reflectivity spectra. It was assumed that the nearly linear growth of reflectivity observed from 800 to 300 cm^{-1} lasts at frequencies below 300 cm^{-1}. Above 10 000 cm^{-1}, the reflectivity was assumed to be constant. For all the three compounds in both polarizations, a maximum of optical conductivity is present at about 2 000 cm^{-1}. Such a maximum is usually observed for conducting ET salts and is assigned to a gap in the electronic state spectrum [10-17]. This assignment was confirmed by calculations of electronic band structures for some ET compounds [15-17].

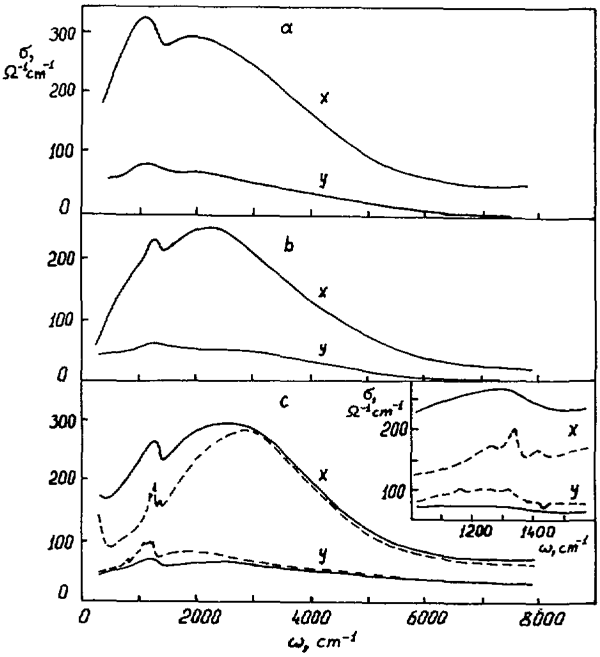

Fig. 2. — The optical conductivity spectra of the compounds I (a), II (b) and IV (c) for the two principal optical directions, x and y. For the compound IV spectra at $T = 300$ K (solid lines) and $T = 90$ K (dashed lines) are given. The insert shows spectral region of 1 000-1 600 cm^{-1} in the enhanced scale.

Discussion.

1. The anisotropy of the electronic reflection is much higher in the spectra of $(ET)_8[Hg_2X_6(C_6H_5Y)]_2$ than in another halide-mercurate containing family, $(ET)_4Hg_{3-\delta}X_8$ [4, 5] and resembles that of the β-phase of $(ET)_2I_3$ [12, 14, 16] : the reflectivity is anisotropic with a well-pronounced Drude-like plasma edge observed only in one polarization. Crystallographic data for $(ET)_8[Hg_2X_6(C_6H_5Y)]_2$ [6-9] shows that there are two directions

of intramolecular contacts in the plane of conducting layer : contacts inside a « ribbon » along the $[01\bar{4}]$ direction and those between « ribbons » along the [010] direction. The direction $[02\bar{1}]$ (corresponding to the optical direction x) is intermediate between [010] and $[01\bar{4}]$. Thus, the direction x of the maximum reflectivity corresponds to the direction of the electron transfer between ET molecules through intramolecular sulphur-sulphur contacts. In the perpendicular polarization, y, the electron transfer is much less effective than for the x but, may be, it is proved by rising reflectivity below 3 000 cm^{-1}

In the region of the plasma edge 4 000-8 000 cm^{-1}, the reflectivity for compounds (I), (II) and (IV) may be approximately described by a Drude-Lorentz relation with complex permitivity in the form :

$$\varepsilon(\omega) = \varepsilon_{\infty}\left(1 + \frac{\omega_{\mathrm{p}}^{2}}{\omega_{0}^{2} - \omega^{2} - i\omega\Gamma}\right) \tag{1}$$

where ε_{∞} is the high frequency dielectric constant (which represents the contribution of high energy electronic states), ω_{p} the plasma frequency, ω_0 the intrinsic frequency of an electronic oscillator (describing a gap in the spectrum of electronic states which approximately corresponds to the maximum of optical conductivity in Fig. 2), Γ is electron damping. The obtained values of these parameters for compounds (I), (II) and (IV) are given in table I. Besides, table I presents : (1) the effective mass of carriers, m, calculated from the equation $\varepsilon_{\infty}\,\omega_{\mathrm{p}}^{2} = 4\,\pi N e^{2}/m$ where e is the electron charge, N the carrier concentration accepted to be $N = 1.11 \times 10^{21}\ \mathrm{cm}^{-3}$ from structural data [6-9] assuming one carrier per two ET molecules (i.e. 8 carriers per elementary cell) ; m is given in units of the electron mass, m_{e}. (2) transfer integral, t, evaluated from the effective mass by the method of [4, 14] ; for the purpose of this evaluation, periods along the x and y directions were accepted to be 5.56 and 4.36 Å correspondingly. Presented in table I, values lie in the range obtained for $(\mathrm{ET})_2\mathrm{I}_3$ and some other ET compounds [12-15].

Table I. — *The parameters of the electronic spectra for* $(\mathrm{ET})_8[\mathrm{Hg}_2\mathrm{X}_6(\mathrm{C}_6\mathrm{H}_5\mathrm{Y})]_2$.

Compound	Direction	ε_{∞}	$\sqrt{\varepsilon_{\infty}}\,\omega_{\mathrm{p}}$, cm^{-1}	ω_0, cm^{-1}	Γ, cm^{-1}	m/m_{e}	t (eV)
I $(\mathrm{ET})_8[\mathrm{Hg}_2\mathrm{Cl}_6(\mathrm{C}_6\mathrm{H}_5\mathrm{Cl})]_2$	x	3	7 300	3 000	2 000	1.9	0.09
	y	2.7	4 100	1 000	3 000	5.9	0.06
II $(\mathrm{ET})_8[\mathrm{Hg}_2\mathrm{Cl}_6(\mathrm{C}_6\mathrm{H}_5\mathrm{Br})]_2$	x	2.5	6 300	3 000	2 000	2.5	0.07
	y	2.8	3 400	1 000	6 000	8.9	0.04
III $(\mathrm{ET})_8[\mathrm{Hg}_2\mathrm{Br}_6(\mathrm{C}_6\mathrm{H}_5\mathrm{Br})]_2$	x	3.3	6 500	3 400	2 000	2.4	0.07
	y	2.2	4 000	1 000	4 000	6.2	0.05

2. The rather unusual feature of $(\mathrm{ET})_8[\mathrm{Hg}_2\mathrm{X}_6(\mathrm{C}_6\mathrm{H}_5\mathrm{Y})]_2$ spectra is their behaviour in the spectral region of intramolecular vibrations. For most conducting ET compounds, the reflection bands are observed, which are connected with excitation of totally symmetric vibrational modes due to electron-vibrational interaction (electron-vibrational bands). The most intensive of these bands are observed in the spectral region of 1 100-1 300 cm^{-1} [10-13]. In the spectra of $(\mathrm{ET})_8[\mathrm{Hg}_2\mathrm{X}_6(\mathrm{C}_6\mathrm{H}_5\mathrm{Y})]_2$, such bands are absent. Instead, the region of 1 100-1 300 cm^{-1} exhibits only a weak, broad maximum.

The electron-vibrational bands have been attributed to the excitation of vibrational modes during an optical electron transfer between molecules [10-13, 18, 19]. In the case of $(ET)_8[Hg_2X_6(C_6H_5Y)]_2$, the optical electron transfer is possible. This is evident from the presence of the intense electronic reflection band with the plasma edge, but no electron-vibrational bands are observed.

3. The absence of the electron-vibrational bands for $(ET)_8[Hg_2X_6(C_6H_5Y)]_2$ may be accounted for by peculiarities of the crystal structure of these compounds. Let us consider by way of comparison, the spectra of ET compounds with the structure of the β-phase (such as β-$(ET)_2I_3$ and β-$(ET)_2IBr_2$ [12, 22]) and of the κ-phase (such as $(ET)_4Hg_{3-\delta}X_8$ and $(ET)_2Cu(NCS)_2$ [4, 5, 10, 11, 17]), which display electron-vibrational bands. In the spectra of the β-phase, such bands are observed only for one principal optical direction, namely, that with greater reflectivity. In the perpendicular polarization, these bands are absent, in spite of the presence of a relatively intensive electronic reflection which is an evidence of a possibility of electron transfer in this direction. Instead of the electron-vibrational bands, only a weak broad maximum in the region of 1 100-1 300 cm^{-1} is observed for this polarization, similar to $(ET)_8[Hg_2X_6(C_6H_5Y)]_2$ spectra. The direction of the maximum reflectivity for β-$(ET)_2I_3$ is that of ET molecular stacks [12, 20]. In this direction, the molecular interaction is of a « face-to-face » type with an overlapping of π-orbitals. In the perpendicular direction, the overlapping of molecules is absent, and they interact in a « side-by-side » manner due to shortened contacts between side sulphur atoms [20].

In the spectra of ET compounds of the κ-phase structure, the electron-vibrational bands are present for both principal optical directions [4, 5, 10, 11]. This is in accordance with the fact that in the structure of the κ-phase, overlapping of the « face-to-face » type exists for the two mutually perpendicular directions [1, 21].

For the compounds of the $(ET)_8[Hg_2X_6(C_6H_5Y)]_2$ family, the « face-to-face » interaction is absent altogether, there is only a « side-by-side » interaction [6-9]. Thus, it may be supposed that the electron-vibrational bands appear only in those cases where there exists a molecular interaction of the « face-to-face » type with the overlapping of π-orbitals.

We have not observed electron-vibrational bands in the spectra of the α-phase of $(ET)_2IBr_2$ [22]. For this compound, a very small overlapping of ET molecules of the « face-to-face » type and more strong interaction of the « side-by-side » type is also characteristic [23].

4. It is known that the electron-vibrational bands in the IR spectra of conducting organic compounds are connected with totally symmetric intramolecular vibrational modes [13, 18, 19]. For modes of other symmetries, the electron-vibrational interaction is forbidden by the selection rules. This selection is correct only in the case where neutral and ionized molecules belong to one and the same symmetry type [13]. Consider the process of arising intramolecular vibrations as a consequence of the electron-vibrational interaction. Suppose that the transition of charge takes place between a molecule and an ion due to the action of the electromagnetic radiation (the result of this consideration would not change if we considered two ionized molecules with different charges instead of a molecule and an ion). It is known that a molecule and the corresponding ion have different nuclear configurations (in particular, different bond lengths). If the charge transfer is sufficiently fast, so that the nuclear configuration does not have time to change during the transition, then after the transfer, there arise a molecule with the configuration of an ion and an ion with the configuration of a molecule. As the result of the relaxation to the equilibrium configurations, molecular vibrations will arise. If the molecule and the ion have the same symmetry, these vibrations will be totally symmetric.

Suppose now that the configurational relaxation begins already during the electron transition. This may be approved for organic conductors because the frequency of the optical electron transfer is comparable with the frequencies of intramolecular vibrations. In this case, the symmetry type of arising vibrational modes depends not only on the initial and the final state symmetry, but also on the symmetry of the intermediate states in which the transfered charge belongs to both neighbouring molecules. If we have matter with the plane molecules and the charge transfer takes place in the direction perpendicular to the molecular plane, then the conservation of symmetry in the intermediate states is quite probable, and the totally symmetric modes will thus arise.

Probably, this case is realized fo those ET salts, which contain molecules overlapping in the « face-to-face » manner in their crystal structures (for example, for the β-phase in the direction of ET molecular stacks or in the κ-phase).

However, the situation changes if the neighbouring molecules interact in the « side-by-side » manner due to the contacts of the side atoms. Now, violation of the molecular symmetry is possible during the process of charge transfer since the transferred charge may be concentrated at one end of the molecule during the transition. In this case, vibrations can also arise as the result of the configurational relaxation, but they cannot be totally symmetric already. Thus, we come to the conclusion that in the case of molecules, interacting in the « side-by-side » manner, the electron-vibrational interaction is possible only with non-totally symmetric vibrational modes. This fact evidently should lead to sufficient changes in the infrared spectra, as compared with the « usual » electron-vibrational interaction involving the totally symmetric vibrational modes.

5. In order to evaluate the character of these changes, we have made a simplifyed analysis of the reflectivity spectra using the phenomenological model introduced in reference [19], modifying it for the case of non-totally symmetric (IR active) modes. For simplification, we have considered a case of one vibrational mode.

Our analysis shows that in the case of an IR active vibrational mode, the frequency dependence of the complex dielectric permeability may be approximately expressed by the formula :

$$\varepsilon(\omega) = \varepsilon_\infty \left[1 + \omega_p^2 \frac{1 + f \cdot g/(\omega_K^2 - \omega^2 - i\omega\gamma_K)}{\omega_0^2 - \omega^2 - i\omega\Gamma - g^2/(\omega_K^2 - \omega^2 - i\omega\gamma_K)} \right] \tag{2}$$

where the parameters ε_∞, ω_p, ω_0 and Γ have the same meaning as in the formula (1), ω_K and γ_K are the intrinsic frequency and the damping of the vibrational mode, g is the electron-vibrational coupling constant connected with ω_0 and ω_K by $g^2 = \lambda \, \omega_0^2 \, \omega_K^2$ [13] (here λ is the dimensionless electron-vibrational coupling constant), f is the parameter characterizing the intensity of the intrinsic IR absorption. The expression (2) does not include the terms which are directly proportional to the oscillator strength of the vibrational oscillator because these terms are small compared with (2) and practically do not contribute to ε. This is confirmed by our numerical calculations. At $f = 0$ we obtain from (2)

$$\varepsilon(\omega) = \varepsilon_\infty \left[1 + \frac{\omega_p^2}{\omega_0^2 - \omega^2 - i\omega\Gamma - g^2/(\omega_K^2 - \omega^2 - i\omega\gamma_K)} \right] . \tag{3}$$

The expression (3) coincides with that obtained in reference [19] for the case of a totally symmetric (infrared inactive) mode.

Figure 3 shows the results of the calculation of the reflectivity spectra with the expressions (2) and (3). With the same parameters (except f), the interaction of electrons with a totally symmetric IR inactive mode ($f = 0$) gives an intensive band in the vibrational spectral region, but the interaction with an IR active mode ($f \neq 0$) gives in that region only a weak

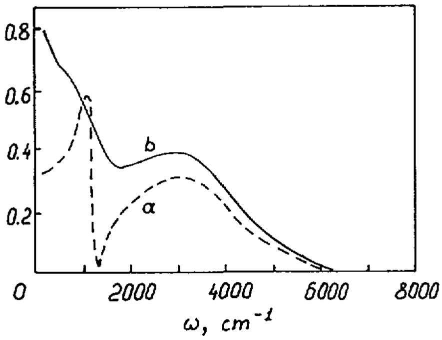

Fig. 3. — The calculated model reflectivity spectra involving the electron-vibrational interaction (see Eq. (2)) : (a) $f = 0$ (a totally symmetric IR inactive mode) ; (b) $f = 1.2$ (a non-totally symmetric IR active mode).

broad maximum, that was observed experimentally in case of $(ET)_8[Hg_2X_6(C_6H_5Y)]_2$. The parameters used in the calculation are listed in table II. The values of ε_∞, ω_p, ω_0, Γ represent the typical figures of table I. For ω_K, the value of 1 450 cm^{-1} is accepted which corresponds to the anti-symmetric C = C mode in the IR spectra of ET [12, 23]. Values of g and λ are typical for the organic conductors [10-13, 18, 19].

Table II. — *The parameters of the electron-vibrational spectra for* $(ET)_8[Hg_2X_6(C_6H_5Y)]_2$.

Parameter	Value
ε_∞	2
ω_p, cm^{-1}	6 000
ω_0, cm^{-1}	2 500
Γ, cm^{-1}	2 000
ω_K, cm^{-1}	1 450
γ_K, cm^{-1}	20
g, cm^{-1}	2 560
λ	0.5

6. In the spectra of the compound (IV) at $T = 90$ K, bands appear about 1 100-1 300 cm^{-1} resembling the « usual » electron-vibrational structure which is characteristic for other ET compounds [10-13]. This may be due to changes in the crystal structure below the temperature of metal-insulator transition which may lead to an appearance of an overlapping of the « face-to-face » type and as a consequence — the involvement of totally symmetric modes in the electron-vibrational interaction. However, changes in the electron-vibrational spectrum including non-totally symmetric modes are also possible.

Conclusion.

The study of the optical properties of $(ET)_8[Hg_2X_6(C_6H_5Y)]_2$ family shows that these compounds are anisotropic metals in which the electron transfer is possible in the two mutually perpendicular directions in the plane of the conducting layer. An original property of these compounds as compared with other conducting ET salts is the absence of the characteristic group of the electron-vibrational bands in the region of 1 100-1 300 cm^{-1}. The latter fact may be connected with the peculiarities of the crystal structure due to which the electron transfer between ET molecules takes place through the side sulphur atoms which, in turn, leads to the exclusion of the totally symmetric molecular vibrations from the electron-vibrational interaction, and the inclusion of non-totally symmetric modes to this process.

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