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Optical studies of quasi-two-dimensional organic metals $(EDT-TTF)_4[Hg_3I_8]_{1-x}$ ($x = 0$ and 0.027) — comparative analysis within the phase phononsmodel

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Reflection spectra of quasi-two-dimensional organic conductors $(EDT-TTF)_4[Hg_3I_8]_{1-x}$, are considered, which, depending on the composition, demonstrate different phase transitions: $x = 0.027$ — metal−superconductor with $T_c = 8.1$ K, $x = 0$ — metal−insulator at a temperature of $T < 35$ K. The polarized reflection spectra were analyzed using the „phase phonons"model, which takes into account the electronic-vibrational interaction. Using this model, the optical functions of both compounds were adequately described and the energy parameters of the π–electron system were obtained. It is shown that for the compound with $x = 0.027$ these parameters change monotonically with temperature, while for $x = 0$ they show a jump at the phase transition temperature. A comparison of the model parameter Δ (the value of the periodic potential) for crystals with different stoichiometric coefficients $x = 0$ and $x = 0.027$ was carried out and an assumption was made about the dependence of the periodic potential on the average charge of one EDT molecule.

Keywords: organic conductors, EDT-TTF, layered structure, reflection spectra, „phase phonons"model, electronic-vibrational interaction, optical conductivity.

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1. Introduction

In the field of molecular conductors research a great attention is paid to compounds based on the unsymmetrical donor molecule of ethylenedithiotetrathiafulvalene (EDT−TTF). In these compounds a significant change in conducting properties (from isolating to superconducting) can be observed with a small change in composition resulting in polymorphism and change in the crystal packing modulation [1,2].

Among the variety of compounds synthesized on the basis of the EDT−TTF molecule cation-radical salts with iodomercurate anions can be distinguished. Depending on stoichiometry, these compounds undergo metal/superconductor (M−SC) or metal/dielectric (M−D) transitions. Thus, the $(EDT-TTE)_4[Hg_3I_8]_{0.973}$ compound is a superconductor with $T_c = 8.1$ K, $(EDT-TTE)_4[Hg_3I_8]_{0.981}$ compound is a superconductor with $T_c = 7$ K at 0.3 kbar, and $(EDT-TTE)_4Hg_3I_8$ compound has the (M−D) transition at a temperature of $T < 35$ K [3].

An important information for the analysis of observed effects in low-dimension organic conductors can be provided from the optical studies that allow estimating the effect of both the structural features of a particular compound and the electronic-vibrational interaction (EVI) on charge localization and conductivity [4].

In [5] polarized reflection spectra of $(EDT-TTE)_4[Hg_3I_8]_{0.973}$ compound were presented, and in [6] spectra of $(EDT-TTE)_4[Hg_3I_8]$ were described. They were quantitatively analyzed within Drude−Lorentz model and the model of „phase phonons" [7] at $T = 180$ K for $x = 0.027$ and at $T = 15$ K for $x = 0$. The comparison resulted in that the model of „phase phonons", taking into account EVI, is more suitable for spectra description, in particular, in the area of the main vibrational feature at $1330\,\mathrm{cm}^{-1}$. This affords a ground to perform detailed calculations of reflection spectra of crystals with $x = 0$ and $x = 0.027$ using this model. Since metal−superconductor and metal−dielectric phase transitions are observed in these compounds at low temperatures, the polarized optical reflection spectra obtained in a wide temperature range ($T = 10-300$ K) were considered.

With the use of this model, the experimental reflection spectra are approximated throughout the entire temperature range, energy parameters for the π-electron system and interaction constants of free electrons with intramolecular vibrations are obtained. Temperature dependencies of obtained parameters for both systems are discussed.

2. Compound structure

The technique to produce and the detailed description of composition and structure of crystals by X-ray diffraction analysis at a temperature of $T = 90$ K can be found in [3]. The produced crystals of the $(EDT-TTF)_4[Hg_3I_8]_{1-x}$ group are elongated hexagonal plates with a size of ~ 0.4 mm,

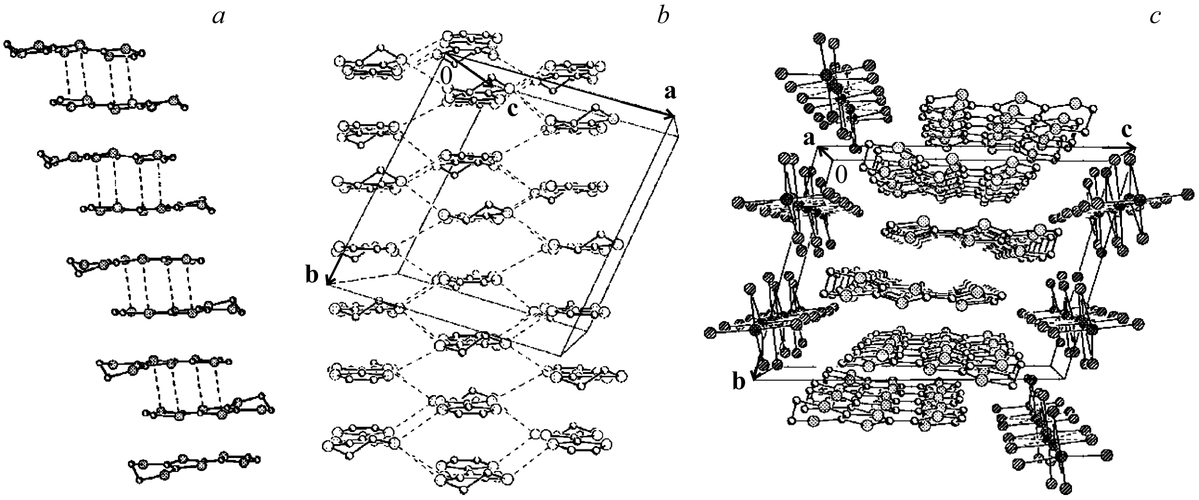

Figure 1. Crystalline structure of (EDT−TTE)$_4$[Hg$_3$I$_8$]: (*a*) — packing of cation radicals in stacks, (*b*) — packing of cation radicals in the conducting layer and the lattice cell, (*c*) — view of crystalline structure along the axis **a**. Dashed lines in Fig. 1, *a, b* — short distances between sulfur atoms of neighboring EDT−TTF molecules, thin solid line in Fig. 1, *c* shows the lattice cell.

which geometry reflects the layered structure of the compound.

According to [3], the crystalline structure of (EDT−TTF)$_4$[Hg$_3$I$_8$]$_{1-x}$ crystals is composed of conducting layers of EDT−TTF and isolating layers formed by Hg$_3$I$_8$ chains. Fig. 1, *a* shows packing of cation radicals in stacks; Fig. 1, *b* shows packing of cation radicals in a conducting layer with the lattice cell shown by dashed line; Fig. 1, *c* shows view of the crystalline structure along axis *a*.

In (M−D) compounds chains (shown dark in Fig.1, *c*) are completely ordered, while in (M−SC) compounds chains contain defects [3]. Parameters of the conducting layer structure are not so different for various x.

The structure of conducting layer (EDT−TTE)$_4$[Hg$_3$I$_8$]$_{1-x}$ has the following features.

1. Cation radicals in the plane (**ab**) form continuous stacks along the direction of (2**b** + **a**). In stacks cation radicals are packed in pairs with 180°-turning and distances between atoms of sulfur S inside the pair (3.63−3.69 Å). S−S distances between pairs are slightly longer (3.70 Å) (Fig. 1, *a*).

2. Along the direction of (**a**) the EDT−TTE cation radicals form stepped chains and there is a large number of side S−S-distances (3.37−3.43 Å) (Fig. 1, *b*).

Since these short S−S-distances along the direction of (**a**) are significantly less than those along the direction of (2**b** + **a**), the transition of electrons in the conducting layer (**ab**) is preferable along the direction of **a**, and maximum reflection was observed in the polarization of (**E** ∥ **a**) rather than anywhere else. In contrary, the transition of electrons in the direction along the stacks can be difficult, which assumes high anisotropy of the π-electron conducting system in the plane of (**ab**). Indeed, in these compounds a high anisotropy of electric conductivity of direct current was found at a room temperature. Thus, the (EDT−TTE)$_4$[Hg$_3$I$_+$8]$_{0.973}$ crystal has the electric conductivity ratio $(\sigma_{\mathrm{dc}}^{\|}/\sigma_{\mathrm{dc}}^{\perp}) \approx 750$, and $\sigma_{dc}^{\|} = 15\,\Omega^{-1}\mathrm{cm}^{-1}$ [5].

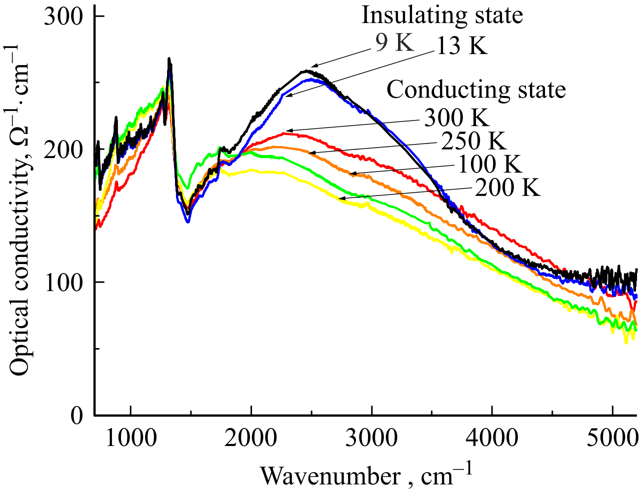

Figure 2. Optical conductivity spectra of (EDT−TTE)$_4$[Hg$_3$I$_8$] with **E** ∥ **a** polarization at different temperatures.

3. Results and discussion thereof

3.1. Optical conductivity spectra

We used the information on optical reflection of $R(\omega)$ with **E** ∥ **a** polarization presented in [5,6] to calculate optical conductivity spectra $\sigma(\omega)$ from Kramers−Kronig relationships. In this case, in the low-frequency range of spectra ($\omega < 300\,\mathrm{cm}^{-1}$) we applied Hagen−Rubens extrapolation for the „metal“ type of conductivity and $R = \mathrm{const}$ for the dielectric type. For the high-frequency extrapolation ($\omega > 10\,000\,\mathrm{cm}^{-1}$) we used the experimental data of reflection spectra $R(\omega)$ for similar materials in the range of $9000-40\,000\,\mathrm{cm}^{-1}$ [8] and the standard extrapolation at higher frequencies, $R \sim \omega^{-2}$.

The metal–dielectric phase transition in $(\mathrm{EDT-TTE})_4[\mathrm{Hg_3I_8}]$ at temperature decrease can be clearly seen in optical conductivity spectra (Fig. 2): a wide maximum is observed in the region of $2000\,\mathrm{cm}^{-1}$ for temperatures higher than the phase transition temperature, which shifts towards the region of $2500\,\mathrm{cm}^{-1}$ for temperatures below the phase transition ($T < 30\,\mathrm{K}$), that was not so clearly distinguishable in the initial reflection spectra.

At temperatures higher than the phase transition, the location of maxima shifts towards higher frequencies as temperature grows, which was not observed earlier in the spectra of quasi-one-dimensional dielectric materials with similar structure, $(\mathrm{EDT-TTF})_3[\mathrm{Hg_2Br_6}]$ [9].

It is essential that the obtained optical conductivity spectra are more illustrative in terms of the energy structure of $(\mathrm{EDT-TTE})_4[\mathrm{Hg_3I_8}]$ crystals than the initial spectra $R(\omega)$. The drop in $\sigma(\omega)$ spectra in the region of $1500\,\mathrm{cm}^{-1}$ indicates that the behavior of the conducting system in the investigated samples differs from the Drude approximation and is indicative of the presence of a „pseudogap“ in the energy spectrum of electrons. Also, it is worth to note that in the spectra of $(\mathrm{EDT-TTE})_4[\mathrm{Hg_3I_8}]$ the intensity of EVI bands increases (the region of $600-1500\,\mathrm{cm}^{-1}$) at the metal–dielectric transition.

3.2. Model of „phase phonons“

Based on the polarization studies reported in [5,6], a high anisotropy of reflection spectra of crystal group $(\mathrm{EDT-TTF})_4[\mathrm{Hg_3I_8}]_{1-x}$ can be stated. To analyze them we used the „phase phonons“model, that was initially developed for calculation of optical functions of quasi-one-dimensional conductors and took into consideration the EVI [7]. This theoretic approach considers the system of linear conducting chains of N identical organic molecules. The Hamiltonian of the system has the following form:

$$H = \sum_k E_k \Theta(E_e - |E_k|) a_k^+ a_k + V(\rho_{q_0} - \rho_{-q_0}) + \sum_n \sum_q [b_n^+(q) b_n(q) + 1/2]\omega_n(q) + N^{-1/2} \sum_n \sum_q g_n Q_n(q) \rho_{-q}. \qquad (1)$$

Here k_F, v_F, and a_k^+ denote wave vector of conduction electron at the Fermi level, its velocity and creation operator, respectively. The $\rho_q = \sum_k a_k^+ a_{k+q}$ operator corresponds to the creation of electron density fluctuations with wave vector q. The first two terms in (1) describe a system of n conduction electrons per unit length with an energy of $E_k = (|k| - k_F)v_F$, that move in the periodic potential V with wave vector $q_0 = 2k_F$. Potential V is connected with the static periodic modulation of molecular orbitals due to the presence of donor chains in the crystalline structure. Taking into consideration only the first two terms in Hamiltonian (1) corresponds to the simplest model of semiconductor without taking into account the EVI.

The third term in (1) describes a set of G non-interacting phonons, $b_n^+(q)$ and $b_n(q)$ are operators of creation and annihilation, $\omega_n(q)$ is frequency of the n-th phonon.

The bands of totally symmetric vibration modes in IR spectra are caused by the interaction of intramolecular vibrations (a set of G phonon modes n ($n = 1, 2, 3, \ldots G$)) with conduction electrons — the fourth term in (1). $Q_n(q) = b_n(q) + b_n^+(-q)$ denotes the dimensionless operator of normal mode related to the n-th phonon, g_n — the EVI constant.

According to [7], the dependence of complex optical conductivity $\tilde{\sigma}(\omega)$ in the model of „phase phonons“ is defined as follows:

$$\tilde{\sigma}(\omega) = \frac{\omega_p^2}{2\pi i \omega}[f(x) - f(0) - \lambda x^2 f^2(x) D_\varphi(x)], \qquad (2)$$

where

$$D_\varphi^{-1}(\omega) = D_0(\omega)^{-1} + 1 - V/\Delta + \lambda x^3 f(x) D_0(\omega) = -\sum_{n=1}^{N} \left[\frac{\lambda_n}{\lambda} \cdot \frac{\omega_n^2}{\omega_n^2 - \omega - i\omega\gamma_n}\right],$$

$$f(x) = \frac{ni + \ln\left(\frac{1-S}{1+S}\right)}{2Sx^2}, \quad S = \sqrt{1 - x^{-2}}, \quad x = \frac{\omega}{2\Delta},$$

$$f(0) = 1, \qquad \lambda_n = \frac{N(0) g_n^2}{\omega_n}$$

Here Δ is the gap in the energy spectrum of electrons, V is the energy gap in the absence of EVI ($V < \Delta$), ω_p is plasma frequency, λ_a are dimensionless constants of EVI, $\lambda = \sum_\alpha \lambda_\alpha$, $N(0)$ is density of electron states at the Fermi level of the initial metal zone, ω_α and γ_α are frequency and attenuation index Ag–IMV, the introduced formal parameter of electronic attenuation γ_p transforms $f\left(\frac{\omega}{2\Delta}\right)$ functions to $f\left(\frac{\omega}{2\Delta} + i\frac{\Gamma_p}{2\Delta}\right)$.

Equations for complex dielectric permittivity and reflection coefficient are:

$$\bar{\varepsilon}_{EMV}(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) = \varepsilon_\infty + \frac{4\pi i \tilde{\sigma}(\omega)}{\omega},$$

$$R_{EMV}(\omega) = \left|\frac{\sqrt{\bar{\varepsilon}_{EMV}(\omega)} - 1}{\sqrt{\bar{\varepsilon}_{EMV}(\omega)} + 1}\right|^2. \qquad (3)$$

Thus, the „phase phonon“ model leads to equation (3) for the reflection coefficient, which is the parameter that will be compared with experimental data.

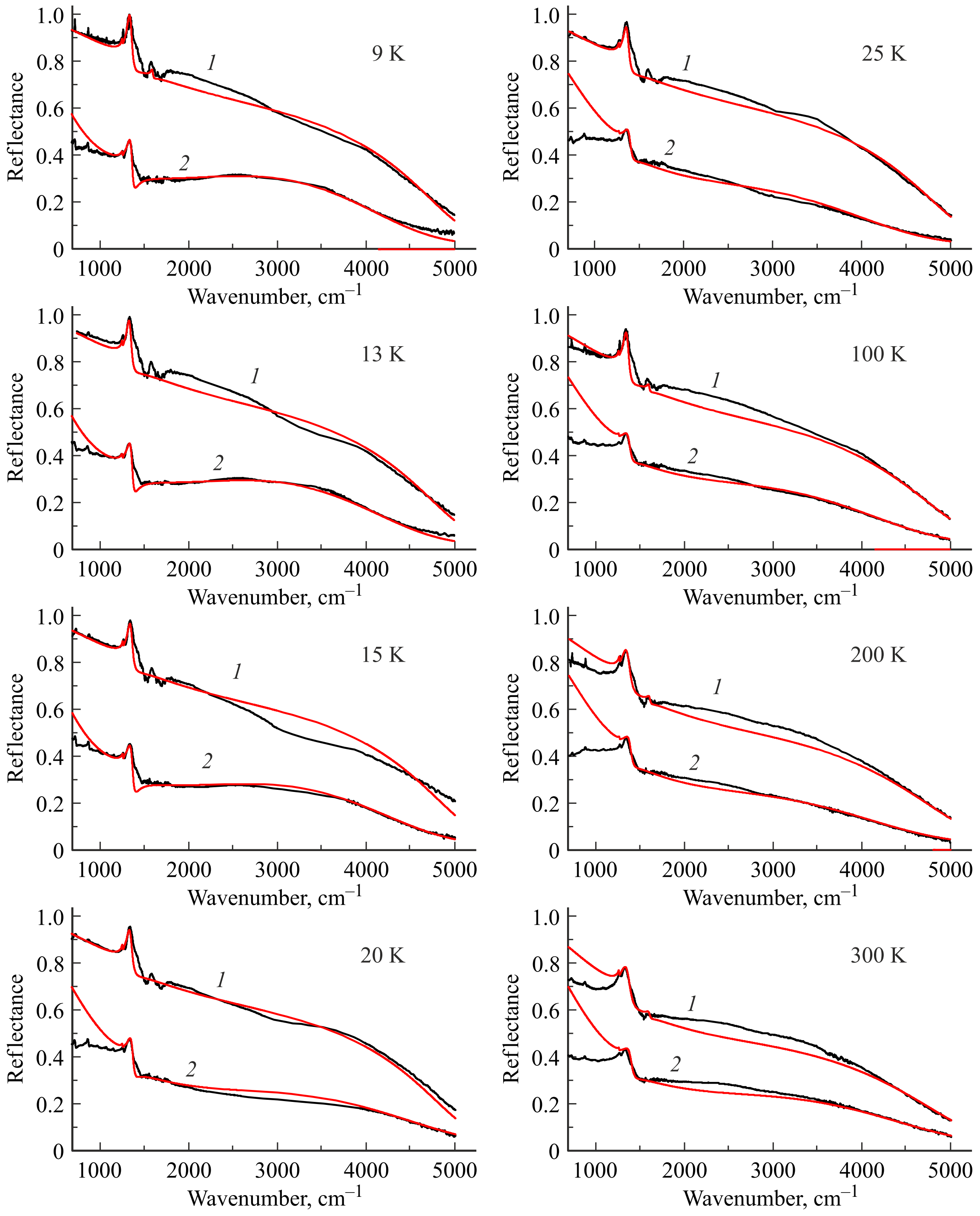

Figure 3. Experimental (black) and theoretical (red) spectra of optical reflection of (EDT−TTF)$_4$[Hg$_3$I$_8$]$_{1-x}$ crystals ($x = 0.027$ (*1*), 0 (*2*)) with **E** ∥ **a** polarization at $T = 9-300$ K.

3.3. Comparison between experimental and calculated spectra of optical reflection

To fit the calculated reflection spectra to the initial experimental spectra an algorithm was developed, which was implemented as a computer program. The method of iterative approximation of this algorithm allowed us to achieve the best matching with the experimental spectra for both the main maximum of EVI ($1330\,\text{cm}^{-1}$) and spectra in the frequency range of plasma end. In the process of fitting the energy parameters of the phase phonons model considered in section 3.2 were obtained, specifically: potentials V and Δ, $N(0)$ — density of electron states at the Fermi level, ω_p — plasma frequency, Γ_p — parameter

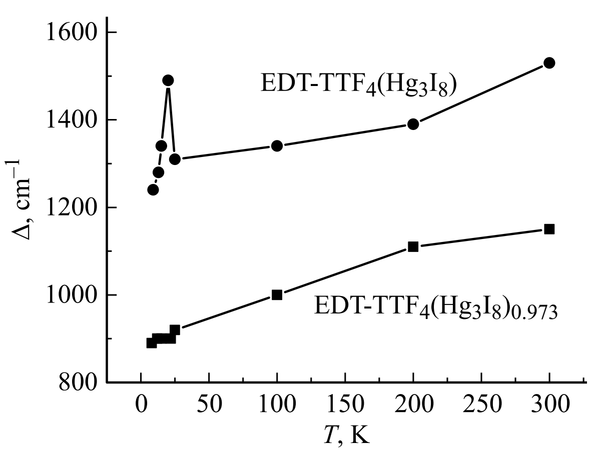

Figure 4. Parameter Δ of the „phase phonons“ model as a function of temperature.

of electronic attenuation. Results of reflection spectra quantitative analysis of $(\text{EDT}-\text{TTF})_4[\text{Hg}_3\text{I}_8]_{1-x}$ compounds in a wide temperature range are shown in Fig. 3.

As can be seen from Fig. 3, a good coincidence is obtained between theoretical and experimental spectra, especially at lower temperatures ($T = 9$, 13, 15 K). Reflection spectra at higher temperatures ($T > 25$ K) are described by the model of „phase phonons“ less well, especially the frequency region of $\omega < 1000\,\text{cm}^{-1}$. Mismatching of spectra in this region may be caused by the use of phenomenological approach in the model applied to the attenuation parameter Γ_p, where frequency (ω) is replaced by $(\omega + i\Gamma_p)$. With such approximation calculations are not so objective for frequencies $\omega \leq \Gamma_p$.

3.4. Energy parameters of the π-electron system

A good matching between experimental spectra and theoretical curves of the „phase phonons“ models allows proceeding with the analysis of energy parameters obtained as a result of the fitting. These parameters, as has been noted above, are: potential V related to the static periodic modulation of molecular orbitals; Δ — a periodic potential, which is the sum of potential V and the EVI contribution to the modulation; $N(0)$ — density of electron states at the Fermi level of the initial metal zone; Γ_p — plasma frequency; Γ_p — parameter of electronic attenuation.

For the calculations the set of ω_α frequencies and EVI constants λ_α were taken from [5], being the same for the (M–SC) compound and for the compound with (M–D) transition for all temperatures, because parameters of the lattice cell are nearly the same for all the group of $(\text{EDT}-\text{TTF})_4[\text{Hg}_3\text{I}_8]_{1-x}$.

Energy parameters of the electron system resulted from the fitting of theoretical dependencies to the experimental data are presented in the table for different temperatures.

In the process of fitting it was noted that values of the theoretical reflection $R(\omega)$ in the frequency range of $(1000-1600\,\text{cm}^{-1})$ are the most sensitive to varying the potentials V, Δ and the attenuation parameter ω_p. Thus, these values are determined from the comparison of spectra with sufficiently high accuracy. It follows from the table that for the (M–SC) compound all three precisely determined parameters change monotonously with temperature, and for the (M–D) compound their step change is observed at the phase transition temperature.

For example, Fig. 4 shows temperature dependencies of potential Δ for (M–D) and for (M–SC) crystals.

In terms of the „phase phonons“ model, the 2Δ parameter has a certain physical meaning: it is the semiconductor gap in the energy spectrum of electrons [7]. The step change in V and, as a consequence, in Δ parameters (Fig. 4) observed in spectra of $(\text{EDT}-\text{TTF})_4[\text{Hg}_3\text{I}_8]$ crystals at a temperature of 25 K, indicates a change in the structure of the conducting layer and corresponds to the metal–dielectric transition of Peierls type [10]. It?s worth noting that the energy gap that occurs at the Fermi level at $T \leq 30$ K, is a pseudogap, because the density of states in it, $N(0)$, is different from zero due to the creation of a charge-density wave in such system.

In contrary, the $(\text{EDT}-\text{TTE})_4[\text{Hg}_3\text{I}_8]_{0.973}$ superconductor has a monotonous dependency of $\Delta(T)$, that corresponds to stability of the „metal“ state in the temperature range of 10–300 K and is caused by the presence of disorder in the chains of anion layer parallel to the axis **a** [10].

We should pay attention to the growth of the Δ parameter with temperature for both (M–SC) crystals and crystals with the (M–D) transition. It is known that the bandgap of semiconductors decreases with temperature growth, and this is related to the boundary blurring between valence and conduction bands. However, $(\text{EDT}-\text{TTE})_4[\text{Hg}_3\text{I}_8]_{1-x}$ crystals have a non-zero density of states $N(0)$, and we speak about a pseudogap at the Fermi level, while the dependence of Δ on temperature is caused by other mechanisms than those in semiconductors. Perhaps the observed growth of potential is related to the equalizing of distances between EDT–TTE molecules along the direction of **a** (Fig. 1) with temperature growth, which results in a larger variability of distances between „donor“ molecules and $\text{Hg}_2\text{I}_6^{2-}$ anions.

The potential V of the (M–SC) compound at temperatures over 100 K is approximately 20% less than that of (M–D). Since in the conducting layer proportions and distances along the axis c for $x = 0$ and $x = 0.027$ are nearly the same, then, most likely, the differences in potential V are related to the different averaged charge of EDT–TTE donors: $+0.486$ for the superconductor and $+0.5$ for the dielectric material [3]. The different defectiveness of the anion layer in crystals with different stoichiometric coefficient x may result in even larger difference in V potentials.

The plasma frequency ω_p, which is inversely proportional to the effective mass of carriers, changes with temperature within the error of calculations. It follows from the

Energy parameters of the π-electron system

T, K	(EDT−TTF)$_4$(Hg$_3$I$_8$) (M−D)					(EDT−TTF)$_4$(Hg$_3$I$_8$)$_{0.973}$ (M−CP)				
	V, cm^{-1}	Δ, cm^{-1}	ω_p, cm^{-1}	Γ_p, cm^{-1}	$N(0)$	V, cm^{-1}	Δ, cm^{-1}	ω_p, cm^{-1}	Γ_p, cm^{-1}	$N(0)$
9	1080	1240	3800	1090	0.00035	730	890	4760	2100	0.0004
13	1115	1280	3800	1110	0.00038	745	900	4770	2100	0.0004
15	1160	1340	3860	1170	0.00038	750	900	4830	2100	0.0004
20	1310	1490	4120	1540	0.00025	750	900	4800	2050	0.0004
25	1170	1310	3830	1630	0.0002	770	920	4800	2080	0.0004
100	1190	1340	3950	1580	0.0002	830	1000	4780	2040	0.00036
200	1270	1420	3870	1690	0.00021	910	1110	4780	2000	0.0004
300	1370	1510	4020	1580	0.00026	960	1150	4730	1850	0.0004

table data that plasma frequency of crystals with (M−SC) transition is higher than that of (M−D) crystals.

Values of the density of states at the Fermi level $N(0)$ are determined with an accuracy of about 20%, and it is difficult to make conclusions regarding their temperature dependence.

4. Conclusion

We analyzed optical properties of crystals of the (EDT−TTE)$_4$[Hg$_3$I$_8$]$_{1-x}$ group with (M−D) and (M−SC) phase transitions for compounds with different stoichiometry ($x = 0$ and $x = 0.027$, respectively). The (M−D) transition is clearly manifested with decrease in temperature ($T \sim 30$ K) in the calculated optical conductivity spectra of compounds with $x = 0$. The observed drop in spectra in the frequency region of 1500 cm^{-1} is indicative of the presence of a pseudogap in the energy spectrum of these crystals.

To describe optical reflection spectra of the group of (EDT−TTE)$_4$[Hg$_3$I$_8$]$_{1-x}$ crystals obtained in a wide temperature range, the model of „phase phonons"was applied [7]. The reflection spectra calculated within this model were compared with the experimental data using the method of successive iterations. A good matching of spectra was achieved, especially at low temperatures. At the same time energy parameters of the „phase phonons" model were determined for both compounds at all temperatures.

The following parameters were determined with the highest accuracy: V — periodic potential related to the static modulation of molecular orbitals, Δ — periodic potential taking into account EVI, Γ_p — phenomenological attenuation coefficient. It is found that for the (M−SC) compound all three precisely determined parameters change monotonously with temperature, and for the (M−D) compound their step change is observed at the phase transition temperature.

The comparison parameter Δ for crystals with different stoichiometric coefficients $x = 0$ and $x = 0.027$ and with different conducting properties, respectively, allows us to make an assumption about the dependence of the periodic potential on the average charge of one EDT molecule.

Thus, the use of „phase phonons" model allows describing optical functions of low-dimensional organic conductors in an adequate way and obtaining energy parameters of the electron system.

Conflict of interest

The authors declare that they have no conflict of interest.

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