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Physical Properties of Some ET-Based Organic Metals and Superconductors with Mercury Containing Anions

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Abstract. — Because of mercury atoms capability of forming the compounds with various coordination, the application of the electrolytes with Hg containing anions in electrochemical oxidation of ET (bis(ethylenedithio)tetrathiafulvalene) results in the formation of ET salts with the anions of different composition. The properties of organic metals and superconductors are briefly described for three families: 1) \( \text{ET}_4\text{Hg}_3-\delta\text{X}_8 \) \((0 < \delta < 0.3, \text{X} = \text{Cl, Br})\), 2) \( \text{ET}_2\text{Hg}(\text{SCN})_3-n\text{X}_n \) \((n = 1; \text{X} = \text{Cl for} n = 1, 2)\), 3) \( \text{ET}_4[\text{Hg}_4\text{X}_{12}(\text{C}_6\text{H}_5\text{Y})] \) \((\text{X}, \text{Y} = \text{Cl, Br})\). The superconductivity of \( \text{ET}_2\text{Hg}(\text{SCN})\text{Cl}_2 \) under pressure about 9 kbar with \( T_{\text{onset}} = 2 \text{ K} \) is reported for the first time. The coexistence of two incommensurate sublattices in the salts of \( \text{ET}_4\text{Hg}_3-\delta\text{X}_8 \) family probably gives rise to their unusual physical properties such as an abnormally high anisotropy of conductivity together with its growth with temperature drop, a positive curvature of the upper critical magnetic field, \( H_{c2} \), and an exceeding of Clogston paramagnetic limit, the invalidity of Korringa law for the temperature dependence of spin-lattice relaxation rate, the growth of the temperature of a superconducting transition \( T_c \) with pressure, \( dT_c/dp > 0 \), and a series of other peculiarities. Shubnikov-de Haas oscillations were observed for some salts of \( \text{ET}_8[\text{Hg}_4\text{X}_{12}(\text{C}_6\text{H}_5\text{Y})_2] \) family. The possible types of Fermi surface are discussed for these salts.

Introduction

Shchegolev I.F. predetermined in his generalizing work “Electrical and magnetic properties of linear conducting chains” [1] (1972) further intensive development of the science field connected with the search and study of organic conductors. Since the discovery of the first organic superconductor (1979) [2] more than 70 organic superconductors have been reported [3–5]. The problem of the design of organic metals and superconductors are associated first of all with the choice of suitable organic donor or acceptor (capable to oxidizing or reducing an ion-radical state) and the choice of a corresponding counterion responsible for the processes of forming the conducting organic crystal’s part.

Most radical cation salts are now obtained by electrochemical oxidation of donor (D) molecules in different polar organic solvents (S). The electrolytes (E) used for these purposes serve

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as a source of anions (A) for radical cation salts have to be obtained

\[ D + E + S \xrightarrow{\Delta} (D^+)\dot{(\text{D}^0)\{A^\text{-}\}} \]

All electrolytes employed can be divided into two groups: stable and labile. During the reaction the anions of stable electrolytes (traditional electrolytes for electrochemistry, for example, with \( \text{BF}_4^- \), \( \text{ClO}_4^- \), \( \text{ReO}_4^- \), \( \text{PF}_6^- \) etc. anions) remain. Labile electrolytes can change during the reaction giving rise to new different anions. As rule they are metal-containing anions. A successful synthesis of new organic conductors considerably depends on the understanding of the origin of mechanism of the anions and their connection with organic conducting layers. The problem of the design of metal containing anions is a problem of coordination chemistry. Equilibrium transformations and solvents play an important role in the process of synthesis.

The last years investigations showed that the most promising metals are soft metals such as Cu, Hg and Au because of their coordinational multiplicity. Most ET-based organic superconductors are obtained with Cu-containing anions [3-6].

The chemistry of mercury salts also provides a wide possibility for creating mercury containing anions with various coordinations and structures including polymeric ones.

The chemical oxidation of ET which depends on a supporting electrolyte, solvent and reaction conditions yields some different groups of ET salts with mercury containing anions (Tab. I). It should be noted that the labile anion \( (\text{Hg}X)_3^\text{-} \) \( (X = \text{Cl}, \text{Br}, \text{I} \text{ and SCN}) \) dissociate in a solution and different combinations of dissociation products provide many different anions.

The composition and the structure of organic conductors with halomercurates obtained in the electrocrystallization are strongly dependent of a solvent, composition and concentration of a supporting electrolyte, temperature and current density.

The choice of a solvent is of a particular importance since it determines the dissociation and complex formation. Various halomercurate anions may exist in solution, hence a number of radical cation salts may be formed. The growth of the least soluble and the most highly conducting crystals has a decisive role for the electrocrystallization at the anode.

ET salts shown in Table I consist of the families of isostructural compounds that permits the comparison of their properties depending on small changes introduced in the anion part of the molecule.

Our investigations showed that the most interesting compounds are obtained with the anion \( (\text{Hg}_3\text{X}_8)^{2-} \) where \( X = \text{Cl}, \text{Br} \text{ and I} \) which can also coexist with \( (\text{Hg}X)_3^\text{-} \) in electrolyte dissociation. However because of the dissociation the former anion is unstable and its concentration in a solution is rather low. It was found that a large excess of \( \text{HgX}_2 \) is needed for a dissociation inhibition [7]. It should be mentioned that the solubility of \( \text{HgCl}_2 \) and \( \text{HgL}_2 \) differs strongly from that of \( \text{HgBr}_2 \).

A stoichiometric family of \( (\text{ET})_4\text{Hg}_{3-\varepsilon}\text{X}_8 \) where \( X = \text{Cl}, \text{Br} \text{ and I} \) was synthesized. The structure of the salt with I differs from the structures ones with Cl and Br which are isostructural, despite comparable unit cell lengths and the same space group. Their physical properties also differ strongly. The former is a semiconductor while the latter two salts are superconductors.

It was shown by X-ray analysis that the crystal structures of the salts with Cl and Br contain two incommensurate penetrating lattices with different periodicity along the crystallographic \( a \) axis [8, 9]. The first lattice is composed of ET molecules and Cl or Br atoms and the second one consists of Hg atoms. Therefore Hg-Cl bond lengths in a chloromercurate anion and Hg-Br ones in a bromomercurate anion are not constant but vary from one unit cell to another depending on each specific location of Hg atom. The stoichiometry of these salts defined from the periodicities of two incommensurate sublattices are \( \kappa-(\text{ET})_4\text{Hg}_{2.78}\text{Cl}_8 \) [10].
Table I. — Main groups of ET based radical cation salts with Hg containing anions.

<table>
<thead>
<tr>
<th>(ET)_m(HgX_3)_nS</th>
<th>(ET)_4(Hg_3-X_6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>m=1,2,3,4 E=(HgX_3)</td>
<td></td>
</tr>
<tr>
<td>n=1,2 S=TCE,THF</td>
<td></td>
</tr>
<tr>
<td>X=Cl, Br, I</td>
<td></td>
</tr>
<tr>
<td>(ET)<em>8[Hg_4X</em>{12}(C_6H_5Y)_2]</td>
<td>(ET)<em>2[Hg(SCN)</em>{3-n}X_n]</td>
</tr>
<tr>
<td>E=(HgX_3)</td>
<td></td>
</tr>
<tr>
<td>S=C_6H_5Y</td>
<td></td>
</tr>
<tr>
<td>X,Y=Cl, Br</td>
<td></td>
</tr>
<tr>
<td>E=Hg(SCN)_2+RSCN+MX</td>
<td></td>
</tr>
<tr>
<td>S=TCE</td>
<td></td>
</tr>
<tr>
<td>R=Bu_4N, Me_4N</td>
<td></td>
</tr>
<tr>
<td>X=Cl (n=1,2), F, Br, I (n=1)</td>
<td></td>
</tr>
</tbody>
</table>

and κ-(ET)_4Hg_{2.89}Br_8 [9]. (ET)_4Hg_{2.78-4}Cl_8 was the first salt with κ-ET type structure [11]. The structural peculiarities resulted in some interesting physical properties.

κ-(ET)_4Hg_{2.78}Cl_8

The room-temperature conductivity of κ-(ET)_4Hg_{2.78}Cl_8 crystals measured in ab conducting plane, ranges from 5 to 30 S/cm. The conductivity measured along c* direction is a factor of (3 - 5) × 10^4 smaller, i.e. the anisotropy of this salt is very high. The temperature dependence of conductivity is the same for both directions and is metallic down to low temperatures. There is some diversity in the resistance at the temperatures from 4 to 20 K for different crystals and the resistance begins to increase sometimes reaching a minimum. Figure 1 demonstrates the temperature dependence of resistivity at ambient and applied pressures. It is seen that the resistance is higher under applied pressure than at ambient one. However at 12 kbar the resistance increase is changed by a sharp superconducting transition with T_c = 1.8 K [11]. In a higher pressure range (about 29 kbar) the temperature dependence of the resistance changes qualitatively and the resistance abruptly decreases at 5.4 K (see insert Fig. 1) [12]. This superconducting transition is probably associated with a phase transition under high pressure.

The investigation of magnetic properties also showed some peculiarities as compared with those of other κ-type salts. The peak-to-peak linewidth ΔH of ESR observed at room temperature for all crystal orientations falls into 80 - 100 Oe range [13]. The linewidth anisotropy caused by different crystal orientations agrees well with the empirical formula characteristic of all types ET based salts:

ΔH = ΔH_m + (0.2)ΔH_m

where ΔH_m is the average value between the minimal and the maximal linewidths but the maximal ΔH value is rather higher than the known one for other κ-type salts at room temperature [4]. The large linewidth value is associated mainly with a strong spin-orbital coupling and incommensurate Hg lattice is significant as well.
Fig. 1. — Resistance vs. temperature at different pressures for ET₄Hg₂.₇₈Cl₈: (△) 1 bar, (□) 9 kbar, (○) 12 kbar, (▲) 29 kbar. The insert shows the superconducting transitions at 12 (■) and 29 (●) kbar pressures.

Figure 2 shows the temperature dependence of the linewidth ΔH for a random oriented single crystal [13]. ΔH is constant for T > 80 K whereas it decreases more than five times nearly linearly with temperature in 4 K < T < 80 K range. This temperature behaviour of ΔH differs strongly from that for the other κ-type salts for which the most distinct feature is that the peak-to-peak linewidth increases with the temperature decrease [4]. The starting point of ΔH decrease correlates with the maximum of paramagnetic susceptibility (see insert in Fig. 2) and the anomaly of the electric conductivity [11].

The static paramagnetic susceptibility is well described in terms of Bonner-Fisher model [14] with the exchange integral I = 6.4×10⁻³ eV and the parameter γ ≈ 0.7. The spin susceptibility calculated from ESR signal behaves precisely as the static one in the whole temperature range [13]. The unusual magnetic behaviour arises probably from a strong spin-orbital coupling caused by the anion and cation interaction. More additional researches for (ET)₄Hg₂.₇₈Cl₈ are obviously needed for elucidating its magnetic and superconducting properties, the pressure dependence and the structural aspects. More interesting and intricate properties are observed for the other member of the family, namely (ET)₄Hg₃₋₆Br₈.

(ET)₄Hg₂.₈₉Br₈

Like the previous salt with Cl this one contains two incommensurate sublattices. It should be mentioned that the repeating distance between Hg atoms in Hg sublattice is approximately 0.1 Å shorter than in Cl containing salt that results in a larger mercury content in
the compound. Figure 3 shows the temperature dependences of the resistance measured parallel, $\rho_\parallel$, and perpendicular, $\rho_\perp$, to the conducting $ab$ plane. It is seen that while $\rho_\parallel$ has a metallic behaviour with the temperature decrease $\rho_\perp$ increases with the temperature decrease down to $10 - 20$ K [15]. Such a behaviour of $\rho_\perp$ is unusual for organic metals for which the temperature dependences of $\rho_\parallel$ and $\rho_\perp$ behave just the same. Such $\rho_\perp(T)$ dependence for $(ET)_4\text{Hg}_{2.78}\text{Cl}_8$ implies that the crystals are quite good or the salt has a high two-dimensionality. The anisotropy of the resistance $\rho_\perp/\rho_\parallel$ shown in the insert in Figure 3, is approximately equal to 5000 at room temperature, it increases with the temperature decrease and has a maximum in 10 K range. Below 5 K both $\rho_\parallel$ and $\rho_\perp$ vanish at $\sim 3.5$ K. The midpoint for a superconductivity is $T_c \sim 4.3$ K. The resistance investigations of various crystals of this family showed the diversity of a superconductivity with somewhat lower $T_c$. This implies that some other superconducting phases could exist. The same conclusion was made in process of study of destroying the superconducting transition by high magnetic fields [15].

Upper critical magnetic fields, $H_{c2}(T)$ were studied at magnetic fields up to 15 T and the temperature down to 1.5 K [16]. Figure 4 shows the temperature dependence of the upper critical fields for two directions in the $ab$ plane of a crystal and for a perpendicular direction. One can see that $H_{c2}^\perp/\rho_\parallel > H_{c2}^\parallel$, i.e. the anisotropy of the crystal fields in $(ET)_4\text{Hg}_{2.78}\text{Br}_8$ is clearly of a quasi-two-dimensional nature.

For the temperature dependences of both longitudinal critical field $H_{c2}^\parallel(T)$ and the transverse field $H_{c2}^\perp(T)$ there is an interval with a positive curvature near 4.3 K. At lower temperatures this interval gives way to a linear interval in $H_{c2}(T)$ curves. This positive curvature is probably

Fig. 2. — Temperature dependence of a linewidth of ESR for ET$_4$Hg$_{2.78}$Cl$_8$ single crystal. The insert: a static paramagnetic susceptibility vs. temperature for ET$_4$Hg$_{2.78}$Cl$_8$. 
Fig. 3. — Temperature dependence of the resistance for ET$_4$Hg$_{2.89}$Br$_8$ measured parallel (□) and perpendicular (△) to the conducting ab plane. The insert: temperature dependence of the anisotropy of the resistance of this salt.

A result of a break of weak links between volume elements of a phase with higher $T_c$ [15]. The linear intervals in $H_c^2(T)$ and $H_c^a(T)$ curves apparently correspond to a common mechanism for the destruction of a superconductivity in the main volume of the crystal. The extrapolations of these intervals to the temperature axis approximately coincide and yield a transition temperature $T_c = 3.3$ K for the main volume of a superconductor. The slopes of the linear intervals are $dH_c^a/dT \sim 110$ kOe/K and $dH_c^a/dT \sim 5$ kOe/K. Using these derivatives and the relations of Ginzburg-Landau theory for the model of an anisotropic structure

$$H_c^a(0) = \frac{\Phi_0}{2\pi\xi^2(0)} \quad \text{and} \quad H_c^b(0) = \frac{\Phi}{2\pi\xi^b(0)\xi^a(0)},$$

in which $\Phi_0$ is flux quantum ($\Phi_0 = 2.07 \times 10^{-7}$ Oe cm$^2$), $\xi^a(0)$ and $\xi^b(0)$ are correlation lengths parallel and perpendicular to ab plane, we estimated $\xi^a(0) = 170$ Å and $\xi^b(0) = 8$ Å. The transverse correlation length $\xi^b(0)$ is roughly half a distance between the layers. However this is not enough for considering (ET)$_4$Hg$_{2.89}$Br$_8$ complex as a two-dimensional superconductor. The reason is that a necessary condition for the realization of Josephson junction between the layers is [17]

$$r = (16/\pi)[\xi^a(0)/d]^2 \ll 1$$

where $d$ is the distance between the layers. In the sample studied this relation yields $r \sim 1$. Therefore (ET)$_4$Hg$_{2.89}$Br$_8$ is a very highly anisotropic three-dimensional superconductor with a two-dimensional anisotropy.
Below 2.5 K the curves of the temperature dependence of the critical fields $H_{c2}^a(T)$ and $H_{c2}^{g'}(T)$ deviate from a linearity. For $H_{c2}^a(T)$ we found an abnormally positive curvature, while for $H_{c2}^{g'}(T)$ we observed a standard negative curvature. An extrapolation of $H_{c2}^{g'}(T)$ to an absolute zero yields $H_{c2}^{g'}(0) \sim 170 \text{kOe}$ which is nearly three times larger than Clogston paramagnetic limit in the approximation of a weak interaction, $H_p(0) = 18.4 T_c \sim 60 \text{K}$. On the other hand $H_{c2}^a(0)$ is significantly smaller than the diamagnetic effect at $T = 0$, $H_{c2}^a(0) = 0.7(dH_{c2}^a/dT)T_c \sim 250 \text{kOe}$. Considering $H_{c2}^a(0)$ as a result of the combined effect of both orbital and paramagnetic ones we estimated the paramagnetic limit $H_p(0)$ for this superconductor in accordance with the formula for a dirty superconductor [18]

$$H_{c2}^a(0) = \frac{H_{c2}^a(0)H_p(0)}{[2H_{c2}^a(0) + H_p^2(0)]^{1/2}},$$

where $H_{c2}(0)$ is an upper critical field in the absence of a paramagnetic effect. We found $H_p(0) \sim 310 \text{kOe}$ which is five times larger than the usual Clogston paramagnetic limit. There are various possibilities for understanding a great value of a paramagnetic limit. It may be associated with a triplet pairing of electrons, with a large spin-orbit scattering or with a strong electron pairing in (ET)$_4$Hg$_{2.89}$Br$_8$. We suppose that most likely interpretation for an upper critical field above a paramagnetic limit is a strong electron pairing which results in a large electron-phonon coupling constant $\lambda > 1$ [16].

Some other peculiarities are characteristic of this salt in a magnetic field, namely a spin-lattice relaxation time $T_1$ of hydrogen $H_1$ nuclei in various magnetic fields in $T < 170 \text{K}$ range.
where the dominant relaxation mechanism is the interaction of nuclei spins with the conductivity electrons [19]. Ordinary metals and organic conductors exhibit a Korringa temperature dependence \( T_1^{-1} \sim T \) in this temperature range and the relaxation rate is independent of a magnetic field. For \((\text{ET})_4\text{Hg}_{2.89}\text{Br}_8\) the temperature dependence of \( T_1^{-1} \) is nonlinear, furthermore there is a rapid increase of \( T_1^{-1} \) with \( H \) and within the studied range of magnetic fields \((7 - 21 \text{ kOe})\) the dependence \( T_1^{-1}(H) \) can be approximated by linear functions at various temperatures [19]. This field dependence of a spin-lattice relaxation rate is quite unusual for metals and organic conductors and can be explained by cross-relaxation \( \text{via} \) quadrupolar Br nuclei [20].

It was shown above that the effect of the applied pressure for the first member of the studied family, namely \((\text{ET})_4\text{Hg}_{2.75}\text{Cl}_8\) exhibits the typical decrease of \( T_c \) with the pressure increase, \( dT_c/dp < 0 \). This effect was observed for most organic superconductors [4]. However the study of superconducting transition in \((\text{ET})_4\text{Hg}_{2.89}\text{Br}_8\) under the applied pressure demonstrated an unusual behaviour for the organic superconductors, namely \( dT_c/dp > 0 \) [21,22].

Figure 5 shows the temperature dependence of the resistance for \((\text{ET})_4\text{Hg}_{2.89}\text{Br}_8\) single crystal at different pressures up to 34 kbar. With the application of a hydrostatic pressure \( T_c \) begins to increase reaching the maximum equal to \( \sim 6.8 \text{ K} \) at \( \sim (5 \pm 2) \text{ kbar} \). This \( T_c \) increase with pressure permits an unambiguous conclusion that the superconductivity is associated with the intrinsic properties of the phase rather than with the elemental mercury at the surface or in the bulk of the crystal specimen. With the further application of pressure \( T_c \)
remains almost constant and then begins to decrease slowly above 10 kbar. It was suggested in [22] that the decrease of $T_c$ with pressure indicates the changes in the structure of the phase but this is not yet confirmed by the structural studies. In 21-25 kbar pressure range the superconductivity disappeared and with the further pressure increase the salt underwent the transition to an insulating state [23]. The rate of this transition rapidly increases with pressure and $dT_{MI}/dp \sim 10$ K/kbar at a pressure about (30-34) kbar. Insert in the Figure 5 shows $T-p$ phase diagram for studied salt. It is clearly seen that the pressure, magnetic and electrical properties of the salts of this family are so unusual and complicated that much more research is needed to fully explain its nonstandard structural aspects and superconducting properties.

We obtained quite unexpected results in attempt to investigate an isotopic effect for (ET)$_4$ Hg$_2$Br$_8$ [24]. An isotope effect is used for elucidating the mechanism of superconducting electron coupling in conventional superconductors. The magnitude of the shift in $T_c$ in isotopic substitution is predicted for the electron-phonon mechanism by BCS theory. The study of the isotope effect in ET based organic superconductors led to some contradictory results which cannot be interpreted in terms of BCS theory [25,26]. We tried to synthesize a deuterated analog of (ET)$_4$Hg$_{2.89}$Br$_8$ but all the attempts were unsuccessful. Small variations of the electrolyte composition resulted in the synthesis of $\kappa$-(d$_8$-ET)$_4$Hg$_3$Br$_8$. However this salt was not a superconductor at ambient pressure. Figure 6 shows the temperature dependences of a relative resistivity of three different crystals of this salt at ambient pressure. None of these crystals is seen to undergo a superconducting transition and a large diversity in their behaviour

Fig. 6. — Relative electrical resistivity $R(T)/R(290 \text{ K})$ of three different crystals at ambient pressure for $\kappa$-(d$_8$-ET)$_4$[HgBr$_2$Hg$_2$Br$_6$] from the same batch. The insert: the same dependences for the same crystals under low pressure (~ 300 bar).
is observed. After applying a very low pressure (~ 0.3 kbar) to the crystals all of them undergo a superconducting transition (see insert in Fig. 6), however the temperatures \(T_{\text{onset}}\) for all of them are different. \(T_{\text{onset}}\) are equal to 2.0 K, 3.0 K and 4.5 K for different crystals. For some of them the transition is not complete, for one of them the midpoint corresponds to \(T_c = 3.9 \text{ K}\) [24].

It is interesting to compare the structural features of this salt with those of the organic superconductor \(\kappa-(ET)_4\text{Hg}_{2.89}\text{Br}_8\) [24, 27]. The cation layer structure corresponds to \(\kappa\)-type in both cases and Br atoms are distributed similarly in anion layers. However the locations of mercury atoms strongly differ in the anions. In \((ET)_4\text{Hg}_{2.89}\text{Br}_8\) mercury atoms are distributed in a bromine channel and form an independent sublattice whose period is incommensurate with a cation sublattice period [27]. Hg atoms form a regular linear chain in bromine channels with the distances between the nearest Hg-Hg atoms equal to 3.877 Å. The structure of \((d_8\text{-ET})_4\text{Hg}_3\text{Br}_8\) is solved in the frame of one lattice [24]. The inorganic anion layer consists of three-atomic quasi-linear \(\text{HgBr}_2\) molecules and dimeric anions \(\text{Hg}_2\text{Br}_6\). Hg atoms form a linear chain in the bromine channels which consists of Hg-Hg dimers with the distances inside them equal to 3.68 Å and Hg atom located between the dimers with the distances to the nearest Hg atoms from the dimers equal to 3.81 Å.

Thus the analysis of these two salts shows that even the deuteration and very small changes in the electrolyte result in considerable changes in the structure and properties of \((ET)_4\text{Hg}_{3-\delta}\text{X}_8\) salts. When Br was substituted for I in the process of crystal growth a new salt was obtained whose physical properties and the structure drastically differed from those of the salts with Cl and Br.

\((ET)_4\text{Hg}_3\text{I}_8\)

In contrast to \((ET)_4\text{Hg}_{3-\delta}\text{X}_8\) \((X = \text{Cl, Br})\) in which the unit cell is composed of two incommensurate sublattices, the structure of \((ET)_4\text{Hg}_3\text{I}_8\) was solved in terms of one lattice with the space group \(I_2/a\) [28]. The cation layer is located in \(ab\) plane and consists of the stacks of two types alternating along \(a\) axis. There are no shortened \(S\cdot S\) contacts between ET molecules within the stacks but those ones are between the neighboring stacks forming a two-dimensional net in \(ab\) plane. The anion layer of \((ET)_4\text{Hg}_3\text{I}_8\) consists of Hg and I atoms. Iodine atoms form slightly distorted \(\text{I}_4\) tetrahedra stretched along \(a\) axis and Hg atom is located inside each tetrahedron with positional population of 0.5.

The temperature dependence of the resistance for \((ET)_4\text{Hg}_3\text{I}_8\) single crystal measured along \(b\) axis, is presented in Figure 7. It is seen that a semiconductor-dielectric phase transition occurs in the salt at \(T = 260 \text{ K}\). At this temperature the resistivity sharply increases by 1-1.5 orders of magnitude. The activation energy is \(E_1 = 500 \text{ K}\) above the transition and \(E_2 = 5500 \text{ K}\) below it. This is the first type phase transition with the hysteresis of \(\sim 7 \text{ K}\).

The hysteresis of the similar type was observed in this salt at studying the temperature dependence of the reflectivity spectra at 900 cm\(^{-1}\) and 3200 cm\(^{-1}\) frequencies [29] (see the insert in Fig. 7). However the study of unpolarized spectra of reflectivity from the conducting \(ab\) plane recorded in 300 - 500 cm\(^{-1}\) range at room temperature and at \(T = 230 \text{ K}\), showed that they practically do not differ from each another. There is no sharpening or splitting of reflectivity band in the molecular vibration range at low temperatures as it takes place for example in \((ET)_6[\text{Hg}_4\text{Br}_{12}(\text{C}_6\text{H}_5\text{Br})_2]\) [30]. This may be explained by assuming that the structural transition is not practically concerned with ET layer (the "face-to-face" overlapping does not appear) and is due to the changes in iodomercurate anion layer. The same conclusion was drawn when the temperature behaviour of a longitudinal and a transverse conductivity was studied [28].
Fig. 7. — Relative resistivity vs. temperature for ET₄Hg₃I₈. The insert: temperature dependence of reflectivity for ET₄Hg₃I₈ at 900 cm⁻¹ (a) and 3200 cm⁻¹ (b).

The same first type phase transition was observed during the study of the temperature dependence of thermopower [28] (see Fig. 8). The thermopower is independent of temperature at high temperatures \( (S(300 \text{ K}) = +55 \text{ mcV/K}) \) and at lowering the temperature down to \( T = 260 \text{ K} \) it has a break followed by a hysteresis cycle of \( \sim 8 \text{ K} \). Right after the transition the thermopower vanishes and then sharply increases with a negative sign with the temperature decrease. The temperature independence of thermopower together with its value imply that there is spin entropy which mainly contributes to the thermopower as it is characteristic of TCNQ salts [31] with a strong Coulomb repulsion at one site. The thermopower below phase transition changes as \( \sim T^{-1} \) and is described by the formula applicable for semiconductors

\[
S = \frac{k}{e} \left( \frac{E_a}{kT} + A \right)
\]

Here the activation energy corresponds to \( E_a = 6000 \text{ K} \). This value correlates well with that of the activation energy of the conductivity below the transition temperature.

The insert in Figure 8 shows the temperature dependence of a static paramagnetic susceptibility, \( \chi_p \), of (ET)₄Hg₃I₈ [28]. At high temperatures \( (T > 50 \text{ K}) \) the \( \chi_p \) behaviour is described by Curie-Weiss law with Curie constant approximately corresponding to a localized electron per two ET molecules. Such a behaviour corresponds to the stoichiometric formula of the compound according to which the average ET charge is +0.5. The fact that Curie law is valid in \( \chi_p \) corresponds to the thermopower behaviour (at high temperatures) which suggests that electrons are localized on ET molecules because of a strong Coulomb repulsion. At the phase
transition temperature \( T \sim 260 \) K \( \chi_p \) behaviour is not very peculiar as compared with the behaviour of conductivity, thermopower and reflectivity. The low temperature behaviour of \( \chi_p \) is described by the formula
\[
\chi_p = \frac{N \mu_B^2 g^2}{kT} \left( 3 + \exp \left( \frac{2J}{kT} \right) \right)^{-1}
\]
(where \( 2J = 55 \) K) typical for the system of isolated paired sites. Here \( I \) is the exchange energy inside the pair. According to X-ray structural data ET molecules are coupled in pairs interconnected by shortened intermolecular contacts at high temperatures, while the neighbouring pairs are interconnected weaker. In terms of magnetic properties these pairs are thought to be isolated sites containing one electron per every site and interconnected into a two-dimensional network in \( ab \) plane. In the phase transition this network is assumed to undergo an alternation so that these states are coupled into pairs more or less isolated from one another.

Figure 9 exhibits the temperature dependence of conductivity for \((ET)_4Hg_3I_8\) single crystals under different hydrostatic pressures up to 26 kbar. It is seen that the first type phase transition characteristic of this salt at ambient pressure, is absent in the curve obtained at the lowest pressure. However a semiconductor-dielectric transition is realized at every pressure, the temperature of this transition being shifted to the low temperature range with the pressure increase. This transition is not suppressed even at 26 kbar pressure. The study of a pressure dependence of the resistance at the temperatures higher than 293 K showed that this salt is characterized by \( dT_c/dp > 0 \) and the first type phase transition is rapidly shifted to a high
Fig. 9. — Temperature dependence of a relative resistivity for ET₄Hg₃I₈ at different pressures. The temperature range with the pressure growth (in low pressure range) with a very high derivative approximately equal to 60 K/kbar. The insert in Figure 10 shows T – p plot for this state. Figure 10 depicts basic dependence of the resistance for ET₄Hg₃I₈ at room temperature. It is seen that there are three phase states in 10 kbar pressure range with the transitions between I-II phases in ~ 1 kbar range and those between II-III phases at ~ 5 – 6 kbar. It is obvious (see the insert in Fig. 10) that the interface between I-II phases is rapidly shifted to a high temperature range and attains the maximum in 1.5 – 4 kbar pressure range.

(ET)₂[Hg(SCN)₂₋ₙXₙ] Family

The data presented in Table I allow the conclusion that the electrochemical oxidation of ET in the presence of complex mercurate-thiocyanates and some other halide and thiocyanate compounds with crown-ethers results in the formation of new organic metals of (ET)₂[Hg(SCN)ₙ₋₃Xₙ] family where X = F, Br and I (n = 1) and X = Cl (n = 1, 2) [32, 33]. The attempts to grow the crystals with X = F suitable for X-ray analysis were not successful. As for the salts with X = Cl, Br and I all of them have κ-type packing of ET molecules in a cationic layer. There are shortened S···S contacts inside ET dimers (3.53 – 3.59 Å) in the salts except X = I. The neighbouring dimers are also connected by shortened S···S contacts (3.40 – 3.53 Å). The salt with X = I has a specific structural peculiarity which discriminates the arrangement of its cationic layers from those of the other salts of this family. An independent part of the unit cell of (ET)₂[Hg(SCN)₂I] contains [Hg(SCN)₂I] anion and two ET radical cations labeled as A and B which belong to the different radical cation layers [34]. It is shown that one radical cation layer consists only of A and the second one consists only of B. Both layers have the
Fig. 10. — Pressure dependence of resistivity at room temperature for ET₄Hg₃I₈. Three different phases are seen on pressure. The insert: $T - p$ phase diagram of I-II phase transition.

same $\kappa$-type packing but a different number of $S \cdots S$ shortened contacts: A has 6 shortened $S \cdots S$ distances and B has 8 ones. Besides these two layers have different characters of the interaction with the anion sheet.

A bidentate character of SCN ligand results in the formation of a polymerized anion, thus the anion sheets of the compounds with [Hg(SCN)$_2$X]$^-$ ($X = \text{Cl}, \text{Br}$ and $I$) form polymeric chains with two bridged SCN groups connected by shortened secondary intermolecular Hg $\cdots$ N contacts.

The synthesis of these salts was carried out at 20 °C. As for the salt with [Hg(SCN)Cl$_2$] fragment which was synthesized at 40 °C the anion forms a polymeric chain with one bridged SCN group.
The room temperature conductivity lies within $1.5 - 7 \, \text{S/cm}$ range for all salts. The fluorine containing salt behaves as metal down 4.5 K with the 100-fold increase of conductivity at this temperature. The crystals are very thin without a well-cut shape. We did not manage to obtain any X-ray data for these crystals. Three isostructural salts (two salts with Cl and one with Br) are metals at room temperature but undergo the transition to a dielectric state with the temperature decrease. The conductivity of (ET)$_2$[Hg(SCN)Cl$_2$] increases 11 times with the temperature decrease down to $T_{\text{max}} = 35$ K and that of (ET)$_2$[Hg(SCN)$_2$Cl] increases 4 times with the temperature decrease down to $T_{\text{max}} = 50$ K. Both salts transform to a dielectric state at temperatures below $T_{\text{max}}$. The only difference between these two salts is the presence of one or two bridged groups in the anion. It is interesting that the anion with a less symmetry in the former salt allows a stabilization of a metallic state at lower temperatures. The conductivity of ET$_2$[Hg(SCN)$_2$Br] increases 1.4 times to the temperature $T_{\text{max}} = 130$ K and then sharply decreases.

We studied the pressure dependence of conductivity for (ET)$_2$[Hg(SCN)Cl$_2$]. It was found (see Fig. 11) that the dielectric state below 35 K is rapidly suppressed and the salt transforms to a superconducting state with the onset temperature near 2 K in 9-12 kbar pressure range (see insert in Fig. 11). As it is usual for organic superconductors $[35,36]$ $dT_c/dp < 0$ for this salt and a superconducting drop rapidly disappears with the pressure increase. Unfortunately we had no possibility to lower the experimental temperature below 1.7 K in the pressure apparatus.
The conductivity of $\kappa$-(ET)$_2$[Hg(SCN)$_2$I] (the last salt of this family) is nearly constant down to 140 K and then it gradually decreases in a factor of 6 to $T = 5$ K. ESR study of this salt [34] showed it to differ strongly from the other $\kappa$-type ET based salts. The linewidth of ESR signal lies in 9.5-11 G range at all magnetic field directions while the linewidths of the other salts of this family lie within 60-90 G [37]. The linewidths of all $\kappa$-type salts are known to fall into 60-100 G range [4]. A narrow linewidth of this salt is associated with the peculiarities of its crystal structure. According to X-ray analysis [34] the radical cation layers consist of quasi-one-dimensional bands with shortened contacts inside the chains and a very weak interaction between the chains. Such a narrow linewidth of ESR signal is characteristic of quasi-one-dimensional organic conductors as TTF-TCNQ [38] and (TMTTF)$_2$ClO$_4$ [39].

$$(\text{ET})_8[Hg_4X_{12}(C_6H_5Y)_2], \ X, \ Y = \text{Cl}, \text{ Br Family}$$

Table I demonstrates that a solvent used in an electrochemical oxidation of ET is of great importance. The substitution of tetrachloroethylene for benzene derivatives together with the application of HgX$_3^-$ containing electrolyte results in the formation of a new type isostructural compounds with the anion which includes a solvent molecule, namely $(\text{ET})_8[Hg_4X_{12}(C_6H_5Y)_2]$ $(X, \ Y = \text{Cl, Br})$.

X-ray analysis of these four compounds showed them to be isostructural salts with the cation and anion layers alternating along a axis like most ET based compounds [40]. Figure 12 shows the crystal structure of $(\text{ET})_8[Hg_4X_{12}(C_6H_5Y)_2]$ along b axis. The anion consists of four HgX$_3^-$ groups and two molecules of the solvent C$_6$H$_5$Y bound to one another through short contacts. The cation layer can be described as a series of parallel stacks running along (b + c) direction. Four symmetric inequivalent ET molecules form B-A-C-D sequence along the stack and every stack is related to its adjacent ones through inversion centers. Shortened intermolecular S···S contacts smaller than 3.85 Å are observed for both inter- and intrastack interactions. The values of S···S distances strongly depend on the composition of the compound decreasing from Br to Cl containing salts. This is evidently associated with the decrease of the bond length in the anion at Br substitution for Cl. This results in a denser ET packing in a conducting layer.

The temperature dependences of relative resistivities of these salts are shown in Figure 13. The salt with $X = \text{Cl}, \ Y = \text{Cl}$ behaves as a metal down to 1.3 K. Its resistance decreases linearly being 100 times lower at 1.3 K. The compound with $X = \text{Cl}, \ Y = \text{Br}$ is metal down to 10 K. A metal-insulator transition below 90 K is characteristic of the compound with $X = \text{Br}, \ Y = \text{Cl}$. At this temperature the salt has a minimal resistance reduced by 5-7 times. The resistance of the compound with $X = \text{Br}, \ Y = \text{Br}$ is slightly (1.5 times) lower to 160 K and has a metal-insulator transition. Thus a consequent substitution of Br for Cl in these isostructural compounds results in the formation of shortened S···S contacts and the densification of conducting layers and as a sequence in the stabilization of a metallic state. For defining the role of different types S···S shortened contacts in transport properties of the salt with $X = \text{Cl}, \ Y = \text{Cl}$ the interaction energies of the highest occupied molecular orbitals (HOMO-HOMO) were calculated [41]. They correspond to 14 different donor-donor interactions of ET layers and fall into 0.04 - 0.3 eV range. Tight-binding band structure calculations for the room-temperature structure of the salt with $X = \text{Cl}, \ Y = \text{Cl}$ based on these values, showed the existence of closed electron and hole Fermi surfaces that is in agreement with 2D metallic conductivity.

The study of optical properties of the salts of this family showed that the specific feature of these compounds as compared with other conducting ET salts is the absence of a characteristic group of electron-vibrational bands in 1100–1300 cm$^{-1}$ range. This may be associated with the peculiarities of the crystal structure due to which the electron transfer between ET molecules
is realized through the side sulfur atom which in its turn leads to the exclusion of totally symmetric vibrations from the electron-vibrational interaction and to the inclusion of non-totally symmetric modes to this process [42].

The magnetoresistance of two salts of this family, namely (ET)$_8$[Hg$_4$Cl$_{12}$(C$_6$H$_5$Cl)$_2$] (I) and (ET)$_8$[Hg$_4$Cl$_{12}$(C$_6$H$_5$Br)$_2$] (II) in static magnetic fields up to 15 T and the temperature down to 1.5 K was investigated. For both salts Shubnikov-de Haas (SdH) oscillations were found [43,44]. Figure 14 shows SdH oscillations for I observed at a measuring current parallel to $a^*$ ($a^*$-the direction perpendicular to the conducting bc plane) and the angle $\varphi$ between the direction of a magnetic field and $a^*$ equal to 25° ($\varphi = 0$ at $H \parallel a^*$). It is seen that the curve of SdH oscillations is a superposition of different frequencies. Fast Fourier transform (FFT) of the curve $R(1/H)$ (see the insert in Fig. 14) shows that SdH oscillations at this field direction correspond at least to six different frequencies. The detailed investigation of the angular dependence of these frequencies showed all of them to be proportional to $1/\cos \varphi$. The analysis of these frequencies permits the conclusion that all of them are the combination of two fundamental $F_2$ and $F_3$ frequencies equal to 250 T and 400 T, respectively, at $H \parallel a^*$. The angular dependence of these frequencies enables the specification of Fermi surface as two cylinders with the axes parallel to $a^*$. The cross-sectional areas of these cylinders in the bc plane correspond to 13% and 20% of the cross-section of the first Brillouin zone.

Figure 15 shows the angular dependence of magnetoresistance of (ET)$_8$[Hg$_4$Cl$_{12}$(C$_6$H$_5$Cl)$_2$] single crystal at a current parallel to $a^*$. A very high anisotropy of magnetoresistance observed
is noteworthy. While \( [R(14T) - R(0)]/R(0) \) is approximately equal to 3 at the absolute minimum this ratio reaches 90 at the absolute maximum. Besides the angular dependence of magneto-resistance exhibits both SdH oscillations which are especially prominent at \( \varphi = 40 - 55^\circ \), and angular oscillations of the classical part of magneto-resistance. The minima of the latter ones are marked with arrows in Figure 15. The angles \( \varphi_n \) corresponding to these oscillations do not vary with the magnetic field thus confirming their Shubnikov origin. At \( \varphi > 0 \) the numbers of the minima of angular oscillations almost follow the law \( n \sim a^\ast \tan \varphi_n \) (see the insert in Fig. 15), while the numbers of the maxima of corresponding oscillations poorly satisfy this relation.

Such type of angular oscillations of a classical part of magneto-resistance whose minima are periodic in \( \tan \varphi \), are associated with the motion of electrons in open orbits which belong to corrugated Fermi planes characteristic of quasi-one-dimensional electron system. Such an interpretation of the electron motion from angular oscillations of the classical part of magneto-resistance contradicts the electron motion in closed orbits belonging to Fermi cylinder corrugated along its axis which was predicted by band calculations for \((ET)_{8}[Hg_4Cl_{12}(C_6H_5Cl)]_2\) [41] and the results of SdH oscillations. This problem is to be solved in the future.

As for SdH oscillations found in \((ET)_{8}[Hg_4Cl_{12}(C_6H_5Br)]_2\) fast Fourier transform shows that only one frequency is present in these oscillations for all angles between \( a^\ast \) and the field direction [44]. The dependence of SdH oscillations on \( \varphi \) is well described by \( F(\varphi) = F(0)/ \cos \varphi \) \( (F(0) = 235 \text{ T}) \) relation and corresponds to a single cylindrical sheet (or several sheets with the same section area) of Fermi surface with the axes directed along \( a^\ast \). On one hand the results obtained demonstrate that this salt differs from its isostructural analog with Cl in which at least two cylindrical sheets of Fermi surface with different cross-section areas were observed.
On the other hand these results are in a good agreement with the theoretical calculations of Fermi surface in this salt [41].

It is clear that additional research is needed to fully explain contradiction between experimental obtained Fermi surface for these two salts and the theoretical calculations of it.

Conclusion

The properties of three families of ET based organic metals and superconductors with halomercurate anions are briefly discussed. (ET)₄Hg₂.78Cl₈ and (ET)₄Hg₂.89Br₈ formed by two mutably penetrating incommensurate lattices, are superconductors with \( T_c = 1.8 \) K at \( p = 12 \) kbar and \( T_c = 4.3 \) K at \( p = 1 \) bar, respectively. Cl containing salt is characterized by the appearance of a new superconducting phase with \( T_c = 5.3 \) K at \( p = 29 \) kbar. The existence of incommensurate sublattices gave rise to a series of unusual properties for (ET)₄Hg₂.89Br₈, such as the 5-fold exceeding of a paramagnetic limit, a positive curvature of the upper critical magnetic field \( H_{c2} \), the growth of \( T_c \) with the pressure decrease, \( dT_c/dp > 0 \) and some other. The attempt to deuterate this salt for the study of an isotope effect resulted in the formation of a new commensurate phase of (ET)₄[HgBr₂Hg₂Br₆] composition which undergoes a superconducting transition at \( T_c = 3.9 \) K under \( p = 0.3 \) kbar. (ET)₄Hg₃I₈ is characterized by three phases depending on pressure at room temperature. The cooling of this salt results in the first type the phase transition at \( T = 260 \) K which is shifted to a high temperature range with a high derivative \( dT/dp = 60 \) K/kbar at pressure application.
Angular dependence of the resistance of ET$_8$[Hg$_4$Cl$_{12}$C$_6$H$_5$Cl)$_2$ at $H = 14$ T. the current parallel to $\mathbf{a}^*$ axis and $T = 1.45$ K. The minima of angle oscillations are marked by arrows. The insert: the dependence of a number minima on a tangent of the angle corresponding to $\varphi_n$.

It is shown for the first time that the salt (ET)$_2$[Hg(SCN)Cl$_2$] is transformed to a superconducting state with $T_{\text{onset}} = 2$ K at $p \sim 9$ kbar.

Shubnikov-de Haas oscillations were observed for two isostructural salts (ET)$_8$[Hg$_4$Cl$_{12}$C$_6$H$_5$ Cl)$_2$] and (ET)$_8$[Hg$_4$Cl$_{12}$C$_6$H$_5$Br)$_2$]. It was shown that the fast Fourier transform (FFT) analysis for the former salt enables the assumption of the existence of Fermi surface as two cylinders with the axes parallel to $\mathbf{a}^*$, whose cross-sections in $\mathbf{bc}$ plane correspond to 13% and 20% of the cross-section of the first Brillouin zone. The analysis of FFT for the other salt results in the conclusion on the existence of the only cylindrical Fermi surface with the cross-section equal to 13% that is in a good agreement with the theoretical calculations for this salt [41].

The results described in this paper demonstrate a quite number of unusual physical properties in every studied family but at the same time it should be noted that considerable additional studies are clearly needed for gaining insight into these unusual classes of compounds.

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