

Superconductivity of $(\text{ET})_4\text{Hg}_{2.89}\text{Br}_8$ at atmospheric pressure and $T_c = 4.3$ K and the critical-field anisotropy

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The structure of a new organic metal $(\text{ET})_4\text{Hg}_{2.89}\text{Br}_8$, which undergoes a transition to the superconducting state at atmospheric pressure and $T_c = 4.3$ K, has been identified. X-ray structural analysis data show that there are two incommensurate lattices. For the upper critical fields, H_{c2}^{\parallel} and H_{c2}^{\perp} , the curvature is typically positive and temperature dependent. The anisotropy is $(H_{c2}^{\parallel}/H_{c2}^{\perp})_{T_c} = 20$ and at low temperatures $dH_{c2}^{\parallel}/dT \approx 100$ kOe/K and $dH_{c2}^{\perp}/dT \approx 18$ kOe/K.

Among the organic conductors based on ET [ET-bis-(ethylenedithio)tetrathiofulvalene] the salts with linear anions, I_3^- , IBr_2^- , and AuI_2^- , are of most interest,^{1–3} since they can go superconducting at atmospheric pressure. In the study of many ET salts with bulk anions only the ET salts with ReO_4^- and Hg_3Cl_3^- anions⁵ were found to go superconducting at pressures of 7 and 12 kbar, respectively. We have recently reported⁶ the results of a study of an ET compound with a bromomercurate anion with a broad superconducting transition at atmospheric pressure. This compound apparently is a mixture of several superconducting phases. We have not identified in this system a superconducting phase with $T_c = 4.3$ K. In this letter we describe the characteristic features of the structure, the superconducting transition, and the anisotropy of the upper critical fields of this phase.

The results of an x-ray structural analysis show that a more accurate composition of this compound corresponds to the formula $(\text{ET})_4\text{Hg}_{2.89}\text{Br}_8$. The main packing motif is the alternation of two-dimensional layers of organic ET molecules and layers of inorganic anions, as is typically the case for all ET salts. The distinguishing feature of this superconductor, as that of the superconductor with a chloromercurate anion,⁵ is that its crystal structure is described by two incommensurate monoclinic lattices with the lattice constants (I): $a = 11.219(3)$, $b = 8.706(2)$, $c = 37.105(7)$ Å, $\beta = 90.97(4)^\circ$, space group $I2/c$; (II): $a = 3.877(1)$, $b = 8.706(2)$, $c = 37.141(7)$ Å, $\beta = 87.30(4)^\circ$, space group $I2$. Collection and analysis of the two corresponding independent sets of experimental data from one crystal (DAR-UM diffractometer, $\text{CuK}\alpha$, 1945 and 388 reflections for data sets I and II, structures I and II were determined more precisely within $R = 0.070$ and 0.074 , respectively) showed that lattice I is comprised of ET and Br atoms and lattice II consists of Hg atoms and that the periodicity of Hg atoms differs from that of ET and Br atoms. An important conclusion can be drawn from the discrepancy in the lattice constants of different atoms of the same molecule in the superconductor under study: The Hg-Br bond lengths in a bromomer-

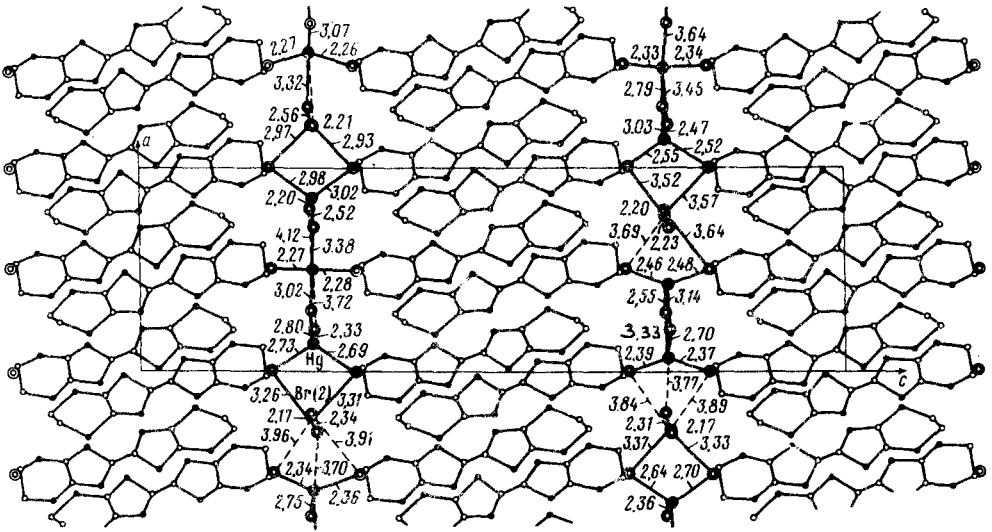


FIG. 1. Projection of the structure of the salt $(\text{ET})_4\text{Hg}_{2.89}\text{Br}_8$ along the b direction. The ET layers alternate with the anion layers. ●—Hg; ○—Br.

curate anion and the spacing between the Hg and ET atoms are not constants, as is usually the case in crystal chemistry, but are instead values that vary from one unit cell to another, depending on each specific position of the Hg atom (Fig. 1). The morphology of the diamond-shaped crystals is linked with the direction of the crystallographic axes: the a axis is directed along the long diagonal of the diamond and the b axis is directed along the short diagonal.

The longitudinal resistivity (ρ_{\parallel}) of the crystal decreases only slightly upon cooling it from room temperature to liquid-helium temperature. For various crystals, for example $R_{300}/R_6 \approx 5-10$. These values are 1.5-2 orders of magnitude lower than those for ET salts with linear anions.^{1,7,8} Such behavior of the resistivity apparently is related to the presence of incommensurate lattices and the specific packing of the ET molecules in the cation layer. The transverse resistivity (ρ_{\perp}) of the crystal, which increases

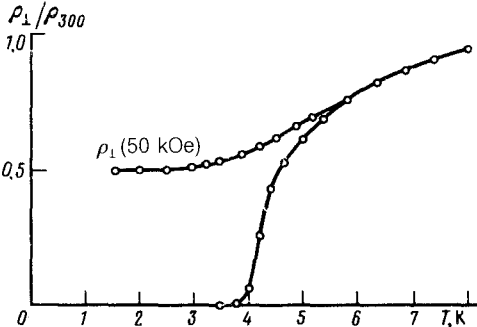


FIG. 2. Temperature dependence of the resistivity ρ_{\perp} in the fields $H = 0$ and $H = 50$ kOe.

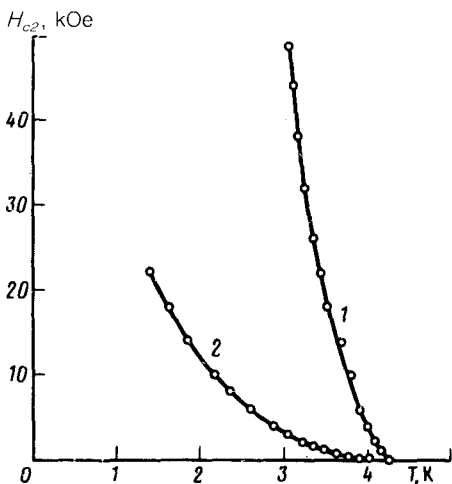


FIG. 3. Temperature dependence of the upper critical fields, H_{c2}^{\parallel} and H_{c2}^{\perp} . 1—The magnetic field H is directed parallel to the ab plane of the crystal; 2— $H \perp ab$.

slightly upon lowering the temperature, has a broad peak at 40–60 K. Below 20 K, both ρ_{\parallel} and ρ_{\perp} decrease rapidly and at $T = 3.8$ K the resistivity vanishes in both directions. Figure 2 shows the behavior of ρ_{\perp} in the absence of a field and in a 50-kOe field applied perpendicular to the plane of the crystal. We see that the superconducting transition begins at $T \approx 5.0$ K and that its midpoint lies at $T_c = 4.3$ K.

In determining the upper critical fields the magnetic field was directed perpendicular to the ab plane of the crystal (H_{c2}^{\perp}) and along various directions parallel to the ab plane (H_{c2}^{\parallel}). Under these conditions we measured ρ_{\perp} . At T_c the critical fields H_{c2}^{\parallel} and H_{c2}^{\perp} were determined from the midpoints of the superconducting transitions on the $\rho_{\perp}(T)$ curves in fields that were held constant. The curves that we measured are shown in Fig. 3. Note that there is no anisotropy of the H_{c2} fields for various directions of H in the ab plane. Figure 3 shows that the $H_{c2}(T)$ curves have a positive curvature for various field directions.

In the case of the previously studied organic superconductors based on ET (Refs. 7–10) and TMTSeF (Ref. 11), the upper critical fields have a linear temperature dependence and the positive curvature was detected only in the β -8 phase of the $(ET)_2I_3$ salt for the H_{c2}^{\perp} field.^{12,13} Of the two possible effects—the orbital effect and the spin effect, which determine the influence of the magnetic field on the superconductivity, the orbital effect is the most important one for the ET and TMTSeF salts. The spin effects, which are associated with the Pauli paramagnetism, are unimportant, since the experimentally observed critical fields lie below the fields characteristic of the Chandrasekhar-Clogston paramagnetic limit.^{7–11}

On the basis of the Ginzburg-Landau theory for the model of an anisotropic band structure we estimate the correlation lengths ξ_{\perp} and ξ_{\parallel} (in the perpendicular and parallel directions to the ab plane) for the salt we are studying from the relations

$$H_{c2}^{\perp}(0) = \frac{\phi_0}{2\pi \xi_{\parallel}^2(0)} \text{ and } H_{c2}^{\parallel}(0) = \frac{\phi_0}{2\pi \xi_{\parallel}(0) \xi_{\perp}(0)}.$$

The critical fields in the ab plane are assumed to be isotropic and the values of $H_{c2}^{\perp}(0)$ and $H_{c2}^{\parallel}(0)$ are found through a linear extrapolation of the $H_{c2}(T)$ curve near T_c . At $T=0$ we found $\xi_{\parallel}(0) = 343 \text{ \AA}$ and $\xi_{\perp}(0) = 17 \text{ \AA}$ for the Ginzburg-Landau correlation lengths. Near T_c the anisotropy of the critical fields is $H_{c2}^{\parallel}/H_{c2}^{\perp} = \xi_{\parallel}/\xi_{\perp} \approx 20:1$. This anisotropy is the same as the field anisotropy of the β -(ET) $_2$ I $_3$ salt.⁷ The correlation length corresponding to the direction across the layers of the anion and cation is half the value of the lattice constant in this direction. The anisotropy of the conductivity estimated from the anisotropy of the critical fields ($\mu \approx 400$ near T_c) is at variance with the anisotropy of the conductivity found from the measurements of the longitudinal and transverse conductivities ($\mu \approx 3000$ – 6000 at room temperature, and it increases with decreasing temperature). Such a discrepancy apparently stems from the fact that a (ET) $_4$ Hg $_{2.89}$ Br $_8$ salt must be regarded as a “dirty” superconductor.

On the other hand, we have estimated $H_{c2}^{\perp}(0)$ to be ≈ 50 kOe and $H_{c2}^{\parallel}(0)$ to be ≈ 400 kOe through a linear extrapolation of the low-temperature part of the $H_{c2}(T)$ curves to $T=0$. We see that $H_{c2}^{\parallel}(0)$ is much greater than the paramagnetic limit, $H_p = 18.4 \cdot T_c \approx 79$ kOe. If this is in fact the case, then this difference may stem from the strong influence of the spin-orbit scattering on the paramagnetic effect.¹⁴ The ratio dH_{c2}^{\parallel}/dT was estimated from the low-temperature part of the $H_{c2}(T)$ curve. We have thus obtained a record value for organic superconductors: $dH_{c2}^{\parallel}/dT \approx 100$ kOe/K. In a similar way, we found dH_{c2}^{\perp}/dT to be ≈ 18 kOe/K.

Accordingly, the temperature dependence of ρ_{\parallel} and ρ_{\perp} , the Ginzburg-Landau correlation lengths, the large anisotropy, and the positive curvature of the temperature dependence of the upper critical fields, which is a “universal property”¹⁵ of layered compounds, lead us to assume that the (ET) $_4$ Hg $_{2.89}$ Br $_8$ compound is a two-dimensional superconductor.

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