Upper critical field five times the Clogston paramagnetic limit in the organic superconductor $(\mathrm{ET})_4\mathrm{Hg}_{2.89}\mathrm{Br}_8$

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The temperature dependence of the upper critical fields has been studied in the organic superconductor $(\mathrm{ET})_4\mathrm{Hg}_{2.89}\mathrm{Br}_8$. For the longitudinal critical field, a value five times the Clogston paramagnetic limit $H_p(0) = 18.5\,T_c$ has been observed. The temperature dependence of the transverse critical field has a positive curvature. Both these facts are linked with the possibility of a strong electron–phonon coupling in this superconductor.

The organic superconductor $(\mathrm{ET})_4\mathrm{Hg}_{2.89}\mathrm{Br}_8$, where ET is *bis*(ethylenedithio)tetrathiafulvalene, is an extremely interesting entity for a study of upper critical fields. The interest stems primarily from its layered structure: The ET molecules form conducting layers in the *ab* plane, which are separated along the c^* direction by $\mathrm{Hg}_{2.89}\mathrm{Br}_8$ anions. The conductivity along c^* is lower than that along a or b' ($b' \perp ac^*$) by more than three orders of magnitude (Ref. 1). With a structure of this sort, one does not rule out a Josephson interaction of the superconducting layers, which would have a strong effect on the behavior of the upper critical field along the layers.[2,3] Previous research[1] in a narrow interval of magnetic fields, up to 50 kOe, has revealed a record high value (for organic superconductors) of the derivative $dH^a_{c_2}/dT$ specifically, ~ 100 kOe/K ($H^a_{c_2}$ is the second critical field along a), at the highest fields attainable experimentally. This research has thus revealed a tendency toward a surmounting of the Clogston paramagnetic limit. An experimental test of this tendency is important because (first) a critical field significantly above the paramagnetic limit has been seen only in the organic superconductor $\beta_H - (ET)_2I_3$ (Ref. 4) and (second) a critical field above this limit might lead to practical applications of organic superconductors. In the present letter we are reporting a study of the upper critical fields in the compound $(ET)_4Hg_{2.89}Br_8$ in magnetic fields up to 150 kOe.

The value of the second critical field was determined at the middle of the superconduction transition on the temperature dependence of the resistance along c^* in various magnetic fields. The resistance was measured by the standard four-terminal method in a copper Bitter solenoid,1) which was capable of reaching a field of 150 kOe. A study was made of rhombiform single crystals of $(ET)_4Hg_{2.89}Br_8$. The large diagonal of the rhombus coincided with the crystallographic a direction. The resistivity of

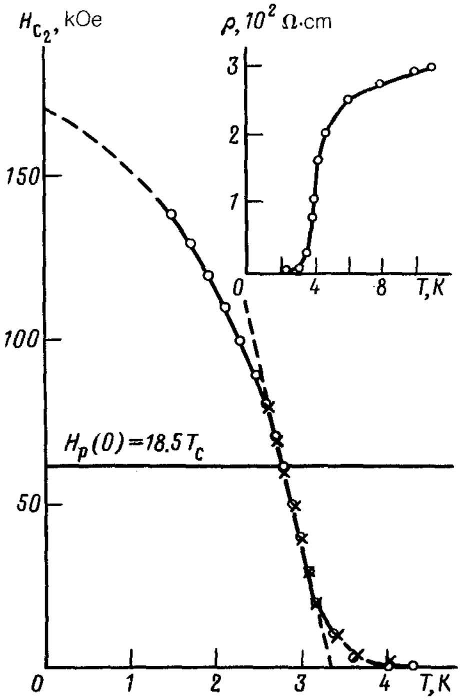

FIG. 1. Temperature dependence of the upper critical fields $H^a_{c_2}$ and $H^{b'}_{c_2}$ parallel to the ab plane, of an $(ET)_4Hg_{2.89}Br_8$ single crystal. ●—H‖a; ×—H‖b′. The inset shows the temperature dependence of the resisitivity ρ^a of the same sample, at $H=0$ in the region of the superconducting transition.

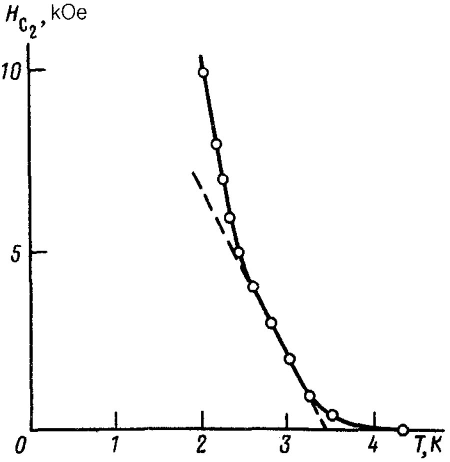

FIG. 2. Temperature dependence of the upper critical field $H_{c_2}^{c^*}$ perpendicular to the *ab* plane, of an $(\mathrm{ET})_4\mathrm{Hg}_{2.89}\mathrm{Br}_8$ single crystal.

the samples along the *a* direction at room temperature was $\rho^a_{300\mathrm{K}} \approx 0.1\text{–}0.5\ \Omega\cdot\mathrm{cm}$. When the sample was cooled to liquid-helium temperature, ρ^a decreased by a factor of 5–10, and the sample went superconducting at $T_c = 4.3$ K (see the inset in Fig. 1).

Figures 1 and 2 show the temperature dependence of the upper critical fields of an $(\mathrm{ET})_4\mathrm{Hg}_{2.89}\mathrm{Br}_8$ single crystal for various directions of the magnetic field. We see $H^a_{c_2} \approx H^{b'}_{c_2} \gg H^{c^*}_{c_2}$. The anisotropy of the crystal fields in $(\mathrm{ET})_4\mathrm{Hg}_{2.89}\mathrm{Br}_8$ is thus clearly of a quasi-two-dimensional nature, just as one would expect on the basis of the structural data.

For the temperature dependence of both the longitudinal critical field $H^a_{c_2}(T)$ and the transverse critical field $H^{c^*}_{c_2}(T)$ there is a region with a positive curvature near 4.3 K. At lower temperatures, this region gives way to a linear region on the H_{c_2}(T) curve. In all probability, this positive curvature results from a breaking of weak links between volume elements with higher values of the transition temperature. The linear regions on the $H^a_{c_2}$(T) and $H^{c^*}_{c_2}(T)$ curves apparently correspond to the usual mechanism for the destruction of superconductivity in the main volume of a crystal. Extrapolations of these regions to the temperature axis for the transverse and longitudinal critical fields approximately coincide and yield a transition temperature $T_c = 3.3$ K for the main volume of the superconductor. The slopes of the linear regions are $dH^a_{c_2}/dT \approx 110$ kOe/K and $dH^{c^*}_{c_2}/dT \approx 5$ kOe/K. From them, we can calculate the correlation lengths in the conducting layers and perpendicular to these layers. We find $\xi^{ab}(0) \approx 170$ Å and $\xi^{c^*}(0) \approx 8$ Å, respectively. The transverse correlation length ξ^{c^*} is roughly half the distance between layers. This circumstance, however, is not a sufficient basis for regarding the $(\mathrm{ET})_4\mathrm{Hg}_{2.89}\mathrm{Br}_8$ complex as a two-dimensional superconductor. The reason is that a necessary condition for the realization of a Josephson junction between layers is[3]

$$r = (16/\pi)[\xi^{c^*}(0)/d]^2 \leqslant 1,$$

where d is the distance between layers. In the samples which were studied, in contrast, the relation $r \sim 1$ held. Consequently, $(\mathrm{ET})_4\mathrm{Hg}_{2.89}\mathrm{Br}_8$ is a highly anisotropic three-dimensional superconductor with a two-dimensional anisotropy.

Below 2.5 K the curves of the temperature dependence of the critical fields $H_{c_2}^{c*}(T)$ and $H_{c_2}^{a}(T)$ deviate from linearity. For $H_{c_2}^{c*}(T)$ we find an anomalous positive curvature, while for $H_{c_2}^{a}(T)$ we find a normal negative curvature. An extrapolation of $H_{c_2}^{a}$ (T) to absolute zero yields $H_{c_2}^{a}(0) \approx 170$ kOe, which is nearly three times the Clogston paramagnetic limit in the approximation of a weak interaction, $H_p(0) = 18.5\ T_c \approx 60$ kOe. On the other hand, $H_{c_2}^{a}(0)$ is significantly smaller than the diamagnetic effect at $T = 0$, $H_{c_2}^{a(d)}(0) = 0.7(dH_{c_2}^{a}/dT)T_c$ kOe. Treating $H_{c_2}^{a}(0)$ as the result of the combined influence of orbital and paramagnetic effects, we can estimate the paramagnetic limit for this superconductor in accordance with Ref. 5. We find $H^{(p)}(0) \approx 310$ kOe, which is five times the usual Clogston paramagnetic limit. This large value of the paramagnetic field could hardly be attributed to a triplet pairing of electrons. The reason is that this pairing is unstable in dirty superconductors,[3] and the superconductor $(\mathrm{ET})_4\mathrm{Hg}_{2.89}\mathrm{Br}_8$ is apparently dirty, since it has a large internal disorder due to the existence of two incommensurate lattices in its structure.[1] A consequence of this disorder is the large value of the resisitivity of these samples at low temperatures, $\rho_{6\mathrm{K}}^{a} \approx 0.03\ \Omega\cdot\mathrm{cm}$. In dirty superconductors, spin-orbit scattering is usually regarded as the main reason for the suppression of the paramagnetic effect. However, studies of the g-factor in $(\mathrm{ET})_4\mathrm{Hg}_{2.89}\mathrm{Br}_8$ reveal no evidence of a strong spin-orbit coupling in this compound.[6] In our opinion, the most likely explanation for an upper critical field above the paramagnetic limit is a strong electron pairing in $(\mathrm{ET})_4\mathrm{Hg}_{2.89}\mathrm{Br}_8$, with the result that the superconducting gap is larger than the BCS gap $\Delta(0) = 1.76\ kT_c$. In this case, it would become possible to explain, at least at a qualitative level, the strong paramagnetic field along a and the positive curvature of $H_{c_2}^{c}(T)$ at low temperatures.[7] [We cannot rule out the possibility that the temperature dependence $H_{c_2}(T)$ is being affected by a resistive state in fields[8] $H_{c_1} < H < H_{c_2}$.] In contrast, a *quantitative* comparison of the results found on $H_{c_2}^{a}$ with the theory of Ref. 7, with allowance for an effect of strong pairing on the orbital field, yields values for the electron-phonon coupling constant which are not very realistic, $\lambda \gtrsim 10$. On the other hand, it seems quite probable that the gap in $(\mathrm{ET})_4\mathrm{Hg}_{2.89}\mathrm{Br}_8$ is exceeded by a factor of five, since tunnel experiments on the superconductor $(\mathrm{ET})_2\mathrm{AuI}_2$ have revealed a gap more than four times the BCS gap.[9]

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