Anomalous pressure dependence of the critical parameters of the organic superconductor $(ET)_4Hg_{2.89}Br_8$

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We have investigated the effect of pressure on the temperature of the superconducting transition and the second critical field of the organic superconductor $(ET)_4Hg_{2.89}Br_8$. We observed a maximum in the pressure dependence of the critical parameters at the pressure $p \sim 6$ kbar. This maximum is probably associated with a phase transition. Another metal–insulator phase transition occurs in the pressure range $p \sim 23$ kbar, and the temperature of the transition into the insulator state increases rapidly with pressure.

The family of salts based on ET (ET = bis-(ethylene dithio)tetrathiofulvalene) with mercuric halide anions occupies a special place among organic superconductors, of which there are now more than 35. This is because these salts contain two incommensurate sublattices.[1] This feature of the structure of the salt $(ET)_4Hg_{2.89}Br_8$ is probably responsible for a number of properties which are unusual for organic metals, for example, significant exceeding of the paramagnetic limit,[2] failure of Korringa's law, dependence of the spin-lattice relaxation rate on the frequency of the NMR signal,[3] and positive pressure derivative dT_c/dp.[4,5] In the present work we investigated the combined effect of a magnetic field and high pressures on the critical parameters of the organic superconductor $(ET)_4Hg_{2.89}Br_8$.

Orthorhombic single crystals were obtained by electrochemical oxidation of a solution of ET in trichloroethane using the electrolyte $k(n\text{-}Bu_4NHgBr_3 + HgBr_2)$. The temperature measurements were performed under hydrostatic pressure on two different setups: 1) using a four-contact method on dc current and pressures up to 34 kbar (Ref. 6) and 2) using an inductive method at modulation frequencies of 330–100 kHz and pressures up to 16 kbar.[7] In the second case a magnetic field of up to 20 kOe was applied to the sample. The modulation and external fields were parallel to one another and perpendicular to the conducting plane *ab* of the crystal. The superconducting transition temperature was determined from T(onset) on the curve of the real part of the magnetic susceptibility versus the temperature. According to inductive measurements, the width of the superconducting transition was equal to $\Delta T_c \sim 0.7$ K and, within the limits of accuracy of measurement, was independent of the pressure.

The temperature dependence of the upper critical field H_{c2}, presented in Fig. 1, has a positive slope in the entire range of temperatures and pressures studied. It is obvious that weak fields ($H < 1$ kOe) easily destroy the superconducting state. As noted previously,[2] this is probably associated with the breaking of weak links between volume elements having higher values of T_c. The rapid growth of the critical field at lower temperatures corresponds to destruction of superconductivity in most of the volume of the crystal. The derivative $-dH_{c2}/dT$, determined on the part of the temperature dependence $H_{c2}(T)$ corresponding to the highest fields, is equal to ~ 33 kOe/K and, within the accuracy of the measurements, it is independent of the pressure.

Investigation of the dependence of the superconducting transition temperatures in a magnetic field, T_c^H (for $H = 5$ kOe), on the modulation frequency (Fig. 2) showed that T_c^H increases with the frequency, and the $T_c^H(\ln f)$ dependence has the largest positive slope. This nature of the $T_c^H(f)$ dependence agrees qualitatively with the behavior of high-T_c superconductors with weak pinning.[8] Under pressure the $T_c^H(\ln f)$ curves are displaced practically parallel with an insignificant change in the slope.

Figure 3a shows the pressure dependence of the superconducting transition temperature. As one can see from the figure, the $T_c(p)$ curve for the salt $(ET)_4Hg_{2.89}Br_8$ has a quite unusual form. After rising rapidly, the curve has a maximum at a pressure of 6 kbar,after which T_c decreases almost linearly. This increase in T_c with pressure[4,5] is not characteristic of organic superconductors of the family ET. For many salts in this family it has been shown that the derivative dT_c/dp is, as a rule, large and negative.[9]

We note that the behavior of the $T_c(p)$ curves in the presence of magnetic fields ($H > 2$ kOe) differs significantly from the behavior of $T_c(p)$ in the absence of a field: At pressures $p > 8$ kbar the pressure derivative at $H = 0$ is quite large, $dT_c/dp = -0.4$ K/kbar, and at $H = 5$ and 10 kOe

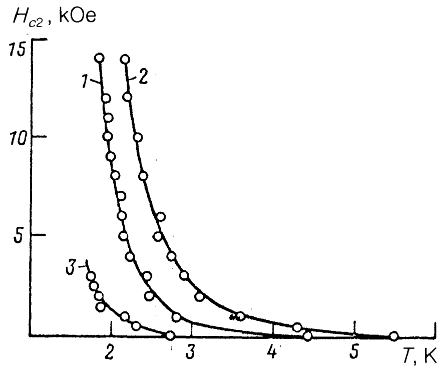

FIG. 1. $H_{c2}(T)$ curves for different pressures $p = 3.4$ kbar (1), $p = 6.1$ kbar (2), and $p = 13.2$ kbar (3).

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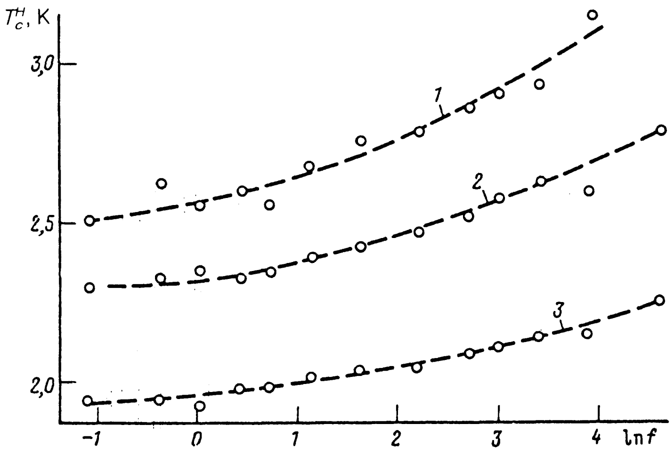

FIG. 2. Superconducting transition temperature in a constant field ($H = 5$ kOe) versus the frequency (f, kHz): $p = 6.1$ kbar (1), $p = 8.4$ kbar (2), and $p = 9.3$ kbar (3).

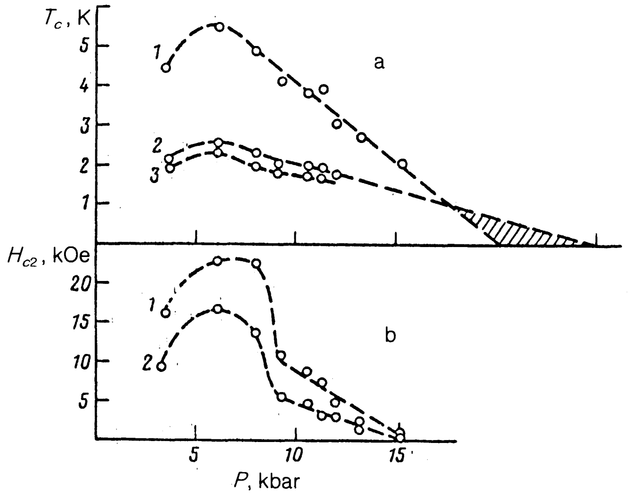

FIG. 3. Pressure dependence of the critical parameters: a) superconducting transition temperature [$H = 0$(1), $H = 5$ (2), and $H = 10$ kOe (3)] and b) second critical field [$T = 1.8$ K (1) and $T = 2.0$ K (2)].

dT_c/dp is equal to -0.12 and -0.1 K/kbar, respectively. There are several reasons for such a significant difference in the pressure derivatives: First, several superconducting phases, whose high-pressure behavior in weak and strong magnetic fields can be different, can coexist[10] and, second, weak links, which are easily destroyed by a magnetic field and by the motion of vortices (Ref. 8), can probably affect the pressure dependence $T_c(p)$. If several superconducting phases, which react differently to a magnetic field, do indeed exist, then for this superconductor a very unusual situation can, in principle, arise: suppression of superconductivity by high pressure in the absence of a magnetic field and restoration of superconductivity by application of a magnetic field. The region of such behavior is obtained by extrapolating the curves $T_c(p)$ in different fields to the abscissa axis (Fig. 3a, hatched part). In order to reach this region experimentally, temperatures $T < 1$ K and pressures $p > 20$ kbar are required.

The $H_{c2}(p)$ curves at fixed temperatures were constructed on the basis of the $H_{c2}(T)$ temperature dependence obtained at different pressures (Fig. 3b). The $H_{c2}(p)$ curves also have a maximum at $p \sim 6$–7 kbar. The form of the $H_{c2}(p)$ curve is somewhat different from that of the $T_c^H(p)$ curves: The maximum in them is somewhat more pronounced. As the pressure is increased ($p > 9$ kbar) the dependence becomes close to linear. An estimate of the pressure derivative of the second critical field (for $p > 9$ kbar)

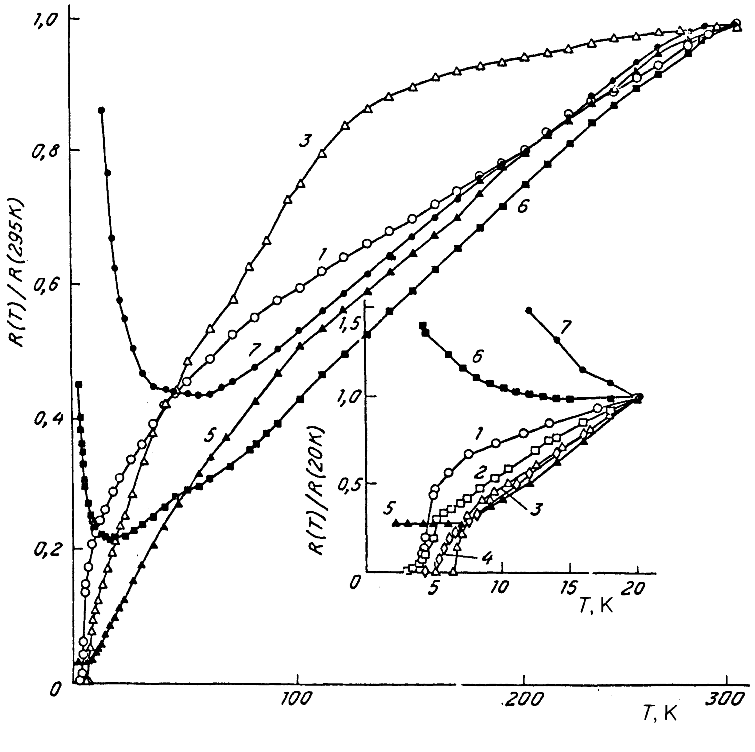

FIG. 4. Temperature dependence of the resistance of the single crystal $(ET)_4Hg_{2.89}Br_8$ at different pressures (inset: same at low temperatures): 1—1 bar (○), 2—4 kbar (□), 3—7 kbar (△), 4—13 kbar (◇), 5—23 kbar (×), 6—30 kbar (+), and 7—34 kbar (*).

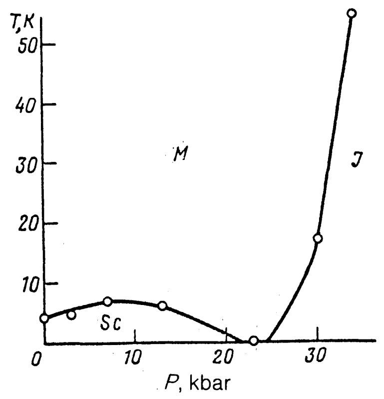

FIG. 5. T–p phase diagram for $(ET)_4Hg_{2.89}Br_8$.

gives $dH_{c2}/dp = -0.9$ kOe/kbar ($T = 2$ K) and -1.9 kOe/kbar ($T = 1.8$ K).

For a large number of organic superconductors belonging to the ET family the $T_c(p)$ dependence is described by a linear function[9] and, for this reason, by extrapolating $T_c(p)$ at $H = 0$ to the abscissa axis (Fig. 3a) we find that superconductivity in $(ET)_4Hg_{2.89}Br_8$ should be suppressed at $p = 21$ kbar.

Figure 4 shows the temperature dependence of the resistance at pressures up to 34 kbar. These measurements were performed on a different setup using a four-contact method and dc current. It is evident from the inset in the figure (low-temperature range) that T_c increases with pressure up to $T_c = 6.8$ K at pressures of 5–7 kbar and then decreases to zero at pressures of 21–23 kbar. Increasing the pressure further results in rapid dielectrization of the salt $(ET)_4Hg_{2.89}Br_8$. Figure 5 shows the T–p phase diagram for the organic superconductor $(ET)_4Hg_{2.89}Br_8$ at pressures up to 34 kbar. The increase in T_c with increasing pressure confirms the fact that in this salt and in the chlorine salt isostructural with it[11] superconductivity is realized in the compound itself and not along the mercury in the interior or on the surface of the crystal. The maximum value $T_c = 6.8$ K at 5–7 kbar is quite high for organic superconductors. High values of T_c have been obtained only for β_H- $(ET)_2I_3$ (8 K), $(ET)_2Cu(NCS)_2$ (10.4 K), and $(ET)_2Cu[N(CN)_2]Br$ (11.6 K).[12] The existence of a maximum in the $T_c(p)$ curve probably indicates a phase transition in this pressure range;[5] a different transition (metal–insulator) occurs at pressures near 23 kbar.

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