Critical magnetic fields of β-(BEDT–TTF)$_2$I$_3$ in the high-temperature superconducting phase

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The dependence $H_{c2}(T)$ has been studied in the β-H high-temperature superconducting phase of β-$(ET)_2I_3$. The $H_{c2}(T)$ curve has a pronounced positive curvature. This behavior implies that a non-BCS version of superconductivity, e.g., a strong-coupling superconductivity, may occur in the β-H phase.

It has now been established that the organic superconductor β-$(BEDT\text{–}TTF)_2I_3$ [β-$(ET)_2I_3$ for short] can exist in two phases. The temperature of the superconducting transition for one of these phases is 1.3–1.5 K, while that for the other is 7.5–8.0 K. These phases are called "β-L" and "β-H." The phase β-H can be reached in various ways: by imposing a small hydrostatic pressure on β-L crystals[1,2] (the β-H phase is metastable) or by heating iodine-rich $(ET)_4(I_3)_2I_8$ crystals in a vacuum.[3] A circumstance which has attracted much interest is that the β-L and β-H phases, while identical in chemical composition and nearly the same in crystal structure (the differences which have been established consist of the presence of an incommensurate superstructure and a disorder in the arrangement of the ethylene groups in the β-L phase and the absence of such groups in the β-H phase), have critical temperatures that differ by a factor of five.

In this letter we report a study of the critical magnetic fields of the β-H phase. We compare the results with corresponding results[4] on β-L, and we draw some conclusions about the properties of these phases.

The β-H phase is produced in these experiments by imposing a hydrostatic gas pressure up to 500 bar on a sample in the β-L phase and then lowering the pressure to standard pressure at $T = 90$–100 K. The metastable state of the β-H phase is preserved in this process.[2] All measurements of the critical magnetic fields are carried out at standard pressure; the minimum temperature $T = 0.5$ K is reached through the pumping of He^3 vapor. The superconducting transition is identified on the basis of the change in the electrical resistance measured by the method described in Ref. 2.

Figure 1 shows curves found for the superconducting transitions in magnetic fields of various strengths. Figure 2 shows curves of $H_{c2}(T)$ for β-H samples with $\vec{H}\parallel\vec{c}^*$ and $\vec{H}\parallel\vec{b}^*$. The open circles are data from the present experiments [the value of T_c in the field of 40 kOe was found by extrapolating the corresponding $R(T)$ curve to the value $R = 0.5R_{res}$]. Shown along with our results are results of several groups who have studied the $H_{c2}(T)$ curves of a β-H phase reached by imposing pressure on the β-L phase.[5,6] The dashed lines show results on β-L from our earlier study.[4] It should be noted that all the measurements of $H_{c2}(T)$ with $\vec{H}\parallel\vec{c}^*$ are in fairly good agreement, although the values of the resistivity at room temperature reported by the different

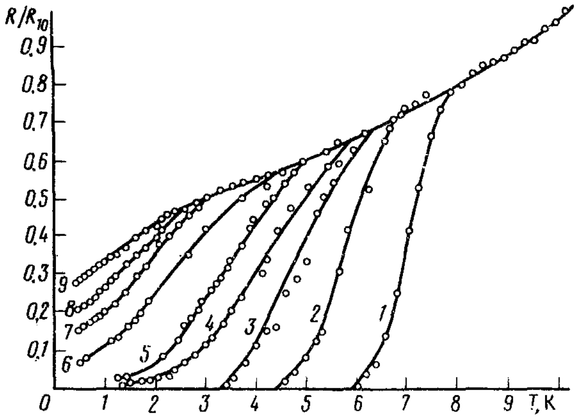

FIG. 1. Curves of the superconducting transitions in a magnetic field for a β-$(ET)_2I_3$ sample in the β-H phase, with $\vec{H}\|\vec{c}$. 1—$H=0$; 2—5 kOe; 3—10 kOe; 4—15 kOe; 5—18 kOe; 6—25 kOe; 7—30 kOe; 8—35 kOe; 9—40 kOe.

investigators differ by a factor of three to seven. From the curves in Fig. 2 we found the values $dH_{c2}/dT|^{\perp}_{T_c} = 4$ kOe/K (the magnetic field is perpendicular to the conducting layers and parallel to the $\vec{c}$* axis) and $dH_{c2}/dT|^{\|}_{T_c} = 48$ kOe/K (the magnetic field is parallel to the $\vec{b}$* axis).

Using the familiar relation

$$dH_{c_2}/dT|^{\perp}_{T_c} = \phi_0/2\pi\xi^2_{\|}(0)T_c,$$

we can determine the superconducting correlation length at $T=0$: $\xi_{\|}(0)$. For β-H we have $\xi_{\|}(0) = 100$ Å, while for β-L we have $\xi_{\|}(0) = 8\times10^2$ Å. Estimates of the electron mean free path l in the two phases made on the basis of the free-electron approximation, from the relation $\sigma_{\|} = e^2N(0)v^{\|}_F l^{\|}$ (which incorporates the two-dimensional nature of this compound), show that for β-L we have $l_{\|} = 70$ Å, while for

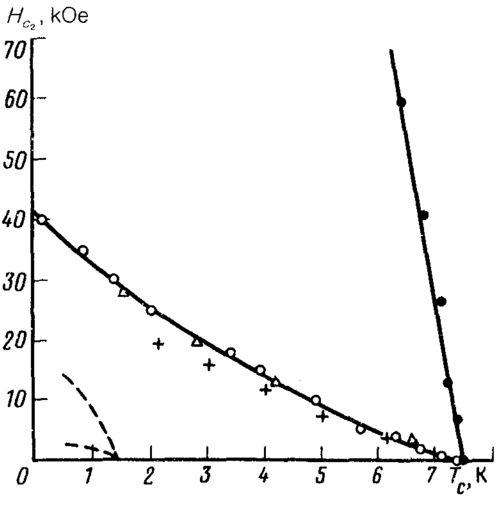

FIG. 2. Curves of $H_{c2}(T)$ for β-$(ET)_2I_3$ samples. ○, ●—Data from the present experiments on the β-H phase for the field directions $\vec{H}\|\vec{c}$ and $\vec{H}\|\vec{b}$, respectively; △—data of Ref. 5; +—data of Ref. 6 for the β-H phase with $\vec{H}\|\vec{c}$; dashed lines—curves of $H_{c2}(T)$ for β-L from Ref. 4.

β-H we have $l_{\parallel} = 200$ Å. The value of the state density at the Fermi surface, $N(0) = 0.37 \times 10^{34}$ erg$^{-1}\cdot$cm^{-3}, was found from data on the coefficient (γ) of the electron component of the specific heat[7]; the velocity at the Fermi surface, $v_F = 1.3 \times 10^7$ cm/s, was found from optical measurements in Ref. 8; and the values of the conductivity $\sigma_{\rm res}$ are 2.2×10^4 S/cm and 7.5×10^3 S/cm for the β-H and β-L phases, respectively.[9] We thus have $l_{\parallel} > \xi_{\parallel}(0)$ for β-H, and this is a purely superconducting phase; for β-L we have $l_{\parallel} < \xi_{\parallel}(0)$, and this phase is a dirty superconductor. Confirmation that the β-L phase is indeed "dirty" comes from the satisfaction of the Gor'kov relation, written with allowance for the anisotropy:

$$\gamma = 2,2 \cdot 10^{-5} \rho_{\parallel}^{-1} dH_{c_2}/dT \,|_{T_c}^{\perp} .$$

This relation holds for specifically dirty superconductors; it does not hold for the β-H phase.

From Fig. 2 we can also estimate the anisotropy of $H_{c2}(T)$ for the β-H phase and the ratio $(dH_{c2}/dT)^{\parallel}/(dH_{c2}/dT)^{\perp} = 12$. It was shown in Ref. 10 that the magnitude of the anisotropy of the resistance in the β-H phase is $\rho_c/\rho_a = 200 \pm 50$ and changes only slightly with the temperature. We know that the anisotropy of the electrical resistance and that of the critical magnetic field are related by the relation $(dH_{c2}/dT)^{\parallel}/(dH_{c2}/dT)^{\perp} = (\rho_{\perp}\,\rho_{\parallel})^{1/2}$. This relation agrees well with the experimental data from the present experiments and from Ref. 10.

We see from Fig. 2 that the $H_{c2}(T)$ curve for β-H has a pronounced positive curvature. A positive curvature on the curve of $H_{c2}(T)$ for $\vec{H} \parallel \vec{c}^*$ was also noted in Ref. 3, in a study of the β-H phase found from the ϵ phase of the iodide (ET).

Figure 3 shows curves of $f(T/T_c) = H_{c2}(0)/(dH_{c2}/dT)T_c$ for the β-L and β-H phases in a field $\vec{H} \parallel \vec{c}^*$. The curve of $f(T/T_c)$ for the β-L phase conforms to the BCS model, and in the limit $T \to 0$ we find $f(T/T_c) = 0.62$, in good agreement with the theoretical value of 0.69. The course of this curve for the β-H phase is completely different, and in the limit $T \to 0$ we find $f(T/T_c) = 1.4$. We note in this connection

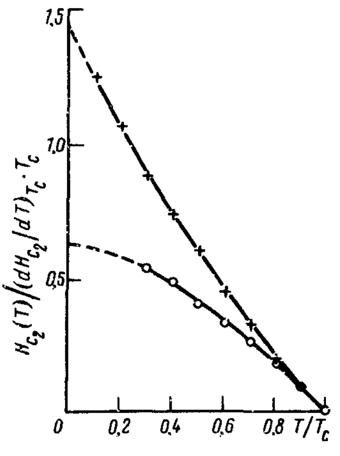

FIG. 3. Plot of $H_{c2}(0)/(dH_{c2}/dT)_{T_c} T_c$ versus the reduced temperature for β-$(ET)_2I_3$. ●—β-L phase; +—β-H phase, $\vec{H} \parallel \vec{c}$.

that experimental data on the size of the superconducting gap $\Delta(T)$ in β-$(ET)_2AuI_2$, given in Ref. 11, show that the value of $\Delta(0)/T_c$ differs from the corresponding value according to the BCS model by a factor of more than four. Consequently, the measurements of $H_{c2}(T)$ and also the measurements of $\Delta(T)$ from Ref. 11 imply that some version of superconductivity different from the BCS superconductivity, e.g., a superconductivity with strong coupling, may be operating in the β-H phase of β-$(ET)_2I_3$ and β-$(ET)_2AuI_2$.

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[1]V. N. Laukhin, E. É. Kostyuchenko, Yu. V. Sushko, I. F. Shchegolev, and É. B. Yagubskiĭ, Pis'ma Zh. Eksp. Teor. Fiz. **41**, 68 (1985) [JETP Lett **41**, 81 (1985)].
[2]V. B. Ginodman, A. V. Gudenko, I. I. Zasavitskiĭ, and É. B. Yagubskiĭ, Pis'ma Zh. Eksp. Teor. Fiz. **42**, 384 (1985) [JETP Lett. **42**, 472 (1985)].
[3]A. V. Zvarykina, P. A. Kononovich, V. N. Laukhin, *et al.*, Pis'ma Zh. Eksp. Teor. Fiz. **43**, 257 (1986) [JETP Lett. **43**, 329 (1986)].
[4]V. B. Ginodman, A. V. Gudenko, and L. N. Zherikhina, Pis'ma Zh. Eksp. Teor. Fiz. **41**, 41 (1985) [JETP Lett. **41**, 49 (1985)].
[5]F. Creuzet, G. Creuzet, and D. Jerome, J. Phys. (Paris) **46**, L1079 (1985).
[6]M. Takumoto, K. Murata, H. Bando, *et al.*, Solid State Commun. **54**, 1031 (1985).
[7]G. R. Stewart, J. O. Bourke, F. Bross, and K. Andres, Phys. Rev. B **33**, 2046 (1986).
[8]H. Tajima, K. Yakushi, H. Kuroda, and G. Saito, Solid State Commun. **55**, 137 (1985).
[9]V. B. Ginodman, A. V. Gudenko, P. A. Kononovich, *et al.*, Pis'ma Zh. Eksp. Teor. Fiz. **44**, 523 (1986) [JETP Lett. **44**, 673 (1986)].
[10]L. I. Buravov, M. V. Kartsovnik, P. A. Kononovich, *et al.*, Zh. Eksp. Teor. Fiz. **92** (1987).
[11]M. E. Hawley, K. E. Gray, B. D. Terris, *et al.*, Phys. Rev. Lett. **57**, 629 (1986).

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