Effect of twinning on the superconducting transition temperature in β-$(ET)_2X$ organic metals

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It is shown that the organic isostructural metals β-$(ET)_2X$ where $X = I_3$, IBr_2 and AuI_2, can undergo plastic deformation by twinning. An increase in the superconducting transition temperature T_c is then observed which can reach 30% of T_c for the original specimen, while in the β-$(ET)_2I_3$ compound with $T_c \approx 1.3$ K the formation and stabilization of the high pressure phase with $T_c \approx 8$ K takes place at normal pressure.

Organic superconductors based on bis(ethylene dithiolo)tetrathiofulvalene (ET) are of considerable interest. During the last four years it has been possible to raise the superconducting transition temperature (T_c) of these compounds from 1.4 K for β-$(ET)_2)I_3$ (Ref. 1) to 10.5 K for $(ET)_2Cu(SCN)_2$ (Ref. 2). The complex $(ET)_2I_3$ occupies a special place as it can crystallize in four (α,β,θ, and K) polymorphic modifications, three of which (β,θ, and K) are superconductors,[3–5] with the β phase being able to exist in two superconducting states: with $T_c \approx 1.4$ K (β_L phase) at normal pressure[1] and $T_c \approx 7.5$ K (β_H phase) at elevated pressure.[6] The existence of a step in the region of $T = 7$–8 K on curves of the temperature dependence of the resistance $R(T)$ indicated[7,8] the existence of a superconducting state with $T_c \approx 8$ K at normal pressure in some crystals of the β_L type obtained by the electrocrystallization method. X-ray diffraction studies of such crystals then showed in general the existence of twins in them. Specimens of the β phase obtained as a result of a solid-state conversion from ε phase crystals have a complete superconducting transition with $T_c = 6$–7.5 K at normal pressure, which is stable at room and higher temperatures and are mosaic twins.[9]

One of the possible reasons for the appearance at normal pressure of a state with high T_c can be stabilizations of the β_H phase[6] produced by internal local strains which arise on the formation of twins. But it is also not impossible, for example, that localized superconductivity arises near twinning planes.[10] For large concentrations of twin boundaries such superconductivity can have a bulk nature.

In this connection it is interesting to elucidate the role of twins in the raising of T_c for organic superconductors. For this purpose we have studied the influence of twinning on T_c for both the compounds β-$(ET)_2I_3$ and for β-$(ET)_2IB_2$ and β-$(ET)_2AuI_2$ which are isostructural with β-$(ET)_2I_3$, but in them there is no phase transition to a new superconducting state under pressure.

Crystals of β-$(ET)_2I_3$ with $T_c \approx 1.4$ K were obtained by oxidizing ET with elementary iodine in a solution of nitrobenzene with a molar ratio ET:I_2 = 1:0.5. They were separated from the reaction mixture by slow cooling from 80 °C to room temperature at a rate of 1.5 or 0.5 deg·h^{-1}. The yield was then 81.5%. Crystals of β-$(ET)_2IBr_2$ with $T_c \approx 2$ K were obtained both by the electrocrystallization method[11] and by chemical oxidation of ET in a chlorobenzene solution. Crystals of β-$(ET)_2AuI_2$ were obtained by electrochemical oxidation of ET in TCE in the presence of n-$(But\text{-}_4N)AuI_2$ for a current density $I = 0.5\,\mu A \cdot cm^{-2}$ (Ref. 12).

Single-crystals of these compounds were subjected to plastic deformation by twinning on non-uniform compres-

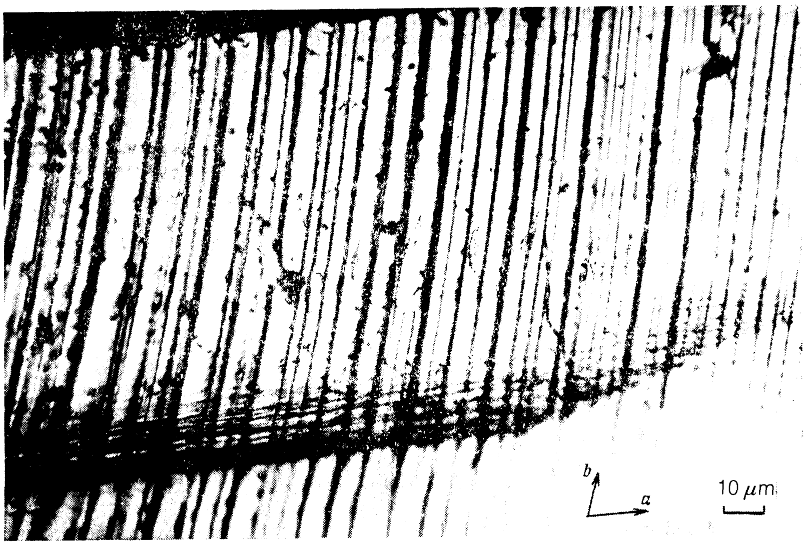

FIG. 1. Microphotograph of the *ab* plane of a specimen of β-$(ET)_2I_3$ deformed by uniaxial compression along the **a** axis at $T = 295$ K.

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sion which was both uniaxial (along the **a** axis) and all-sided but not hydrostatic, and was carried out up to a pressure of several tens of kbar at $T \approx 295$ and 78 K. After this the pressure was totally removed, the chamber with the specimens was warmed up to room temperature, the crystals were extracted, washed and fixed onto a four-terminal module for measuring the conductivity at constant current. Such a deformation was accompanied by the appearance on the surfaces of the crystal of a banded structure characteristic of twinning (Fig. 1), with different orientations and band density for the various compounds and twinning conditions. The existence of twins was confirmed by x-ray diffraction. Uniaxial deformation of single crystals with typical dimensions $1 \times 0.4 \times 0.2$ mm was carried out under a microscope only at room temperature using a specially constructed manipulator. All-sided non-hydrostatic compression was carried out in the high-pressure chamber under conditions such that the pressure-transmitting liquid GKZh-94 solidified on cooling to 78 K or as a result of applying a sufficiently high pressure ($\sim$50–60 kbar) at room temperature. A "piston-cylinder" or "toroid" type of chamber was used to obtain the pressure.

It turned out surprisingly that β-$(ET)_2I_3$ crystals deformed easily by twinning without fracturing both at room and at low temperatures. At the same time twinning was not observed in β-$(ET)_2IBr_2$ and β-$(ET)_2AuI_2$ crystals on uniaxial compression up to appreciable forces which even led to fracture of the specimens. It was only possible to produce twins in them, with the formation of the characteristic banded picture on the surfaces, at low temperatures ($\approx$78 K).

Typical curves of the transition to the superconducting state for β-$(ET)_2I_3$ crystals are shown in Fig. 2 before and after various treatment with non-uniform pressure. It can be seen that for a specimen with the usual superconducting transition at $T_c \approx 1.3$ K in the initial, state (curve 1), a step appears in the region of 6–7 K after uniaxial compression (curve 2). As the specimen becomes saturated with twins the step becomes more marked and shifts in the direction of high temperatures while the fraction of the β_L phase decreases (curve 3). Finally, after deformation at large pressures ($\approx$50 kbar) specimens are obtained with a very high concentration of twins of different orientation and a complete superconducting transition at $T_c \approx 8$ K (curve 4).

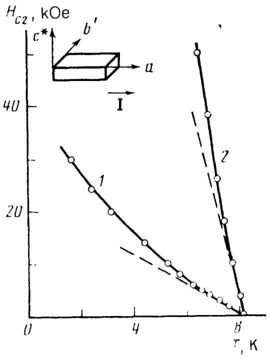

FIG. 3. Temperature dependence of the upper critical field for a β-$(ET)_2I_3$ crystal deformed at $P \approx 50$ kbar and $T = 295$ K: 1—**H**‖**c***; 2—**H**‖**b**′.

It should be pointed out that the two-dimensional nature of the properties of β-$(ET)_2X$ crystals is preserved on twinning. The temperature dependences of the upper critical magnetic fields H_{c2} are shown in Fig. 3 for **H**‖**c*** and **H**‖**b**′ (**b**′ is a vector lying in the *ab* plane and perpendicular to the **a** axis; **c*** is a vector perpendicular to the *ab* plane), corresponding to the center of the resistive transition, for a β-$(ET)_2I_3$ crystal deformed under a pressure of $\approx$50 kbar. The characteristic anisotropy in H_{c2} is clearly visible, with $H_{c2}^{(b)} \gg H_{c2}^{(b*)}$. The values of the derivative $(dH_{c2}/dT)_{T_c}$ for the **b**′ and **c*** directions are equal to 20 and 2.7 kOe·K^{-1} respectively and their ratio is equal to $\approx$7.4. The values of T_c and $(dH_{c2}/dT)_{T_c}$ and also the observed positive curvature of the $H_{c2}(T)$ dependence for both field directions are thus close to the analogous characteristics both for the β phase specimens obtained as a result of the solid phase ε-β transformation[9] and for the β_H phase.[13] From this it can be proposed that the increase in the transition temperature from 1.3 to $\approx$8 K in the present β-$(ET)_2I_3$ specimens is connected with the fact that at least part of the specimen, deformed in the way described above, is in the same state as that which has $T_c \approx 7.5$ K and only arises on raising the pressure.[6] We note that in the case of uniform gas pressure only $P \approx 300$ bar is necessary[14] for the formation of the β_H

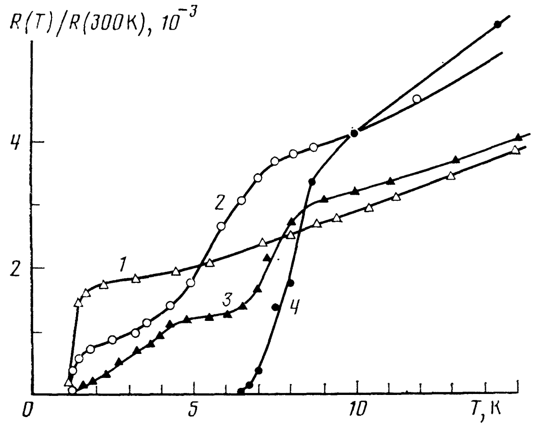

FIG. 2. Temperature dependence of the resistance of initial and deformed specimens of β-$(ET)_2I_3$ in the region of the superconducting transition: 1—undeformed specimen; 2—after uniaxial compression at $T = 295$ K; 3—after non-uniform deformation at $P \approx 15$ kbar and $T = 78$ K; 4—after non-uniform deformation at $P \approx 50$ kbar and $T = 295$ K.

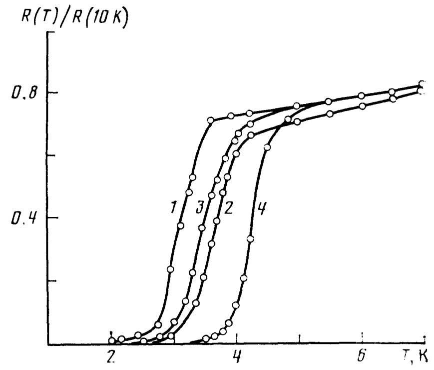

FIG. 4. Superconducting transitions for a β-$(ET)_2AuI_2$ specimen: 1—initial crystal, 2—after deformation at 78 K; 3—after repeat deformation at 78 K; 4—the crystal annealed at 120 °C for 7 h after the repeat deformation.

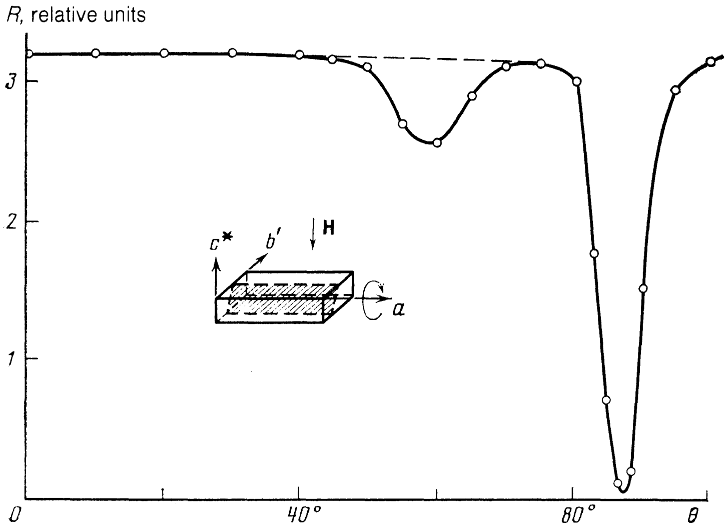

FIG. 5. Dependence of the resistance of a β-$(ET)_2AuI_2$ crystal on the angle between the **c*** axis and the magnetic field direction **H**⊥**a** ($H = 26$ kOe) in the initial (dashed line) and deformed (full line) states. The crystal was rotated around the **a** axis. The proposed twinning plane is shown shaded, since in the given crystal the bands which appear on the *ab* plane as a result of twinning were generally parallel to the **a** axis.

phase with $T_c \approx 7.5$ K. It is therefore difficult in β-$(ET)_2I_3$ crystals to separate the effects in the raising of T_c produced by twinning and by the appearance of the β_H phase.

The effect of twinning on T_c can be followed for β-$(ET)_2IBr_2$ and β-$(ET)_2AuI_2$ crystals which, as mentioned above, are isostructural with β-$(ET)_2I_3$ crystals but do not have a phase transition into a new superconducting state under pressure. Figure 4 shows curves of the superconducting transitions of β-$(ET)_2AuI_2$ crystals before and after deformation, as a result of which various kinds of defects arise in the crystal, including twins. The deformation of this crystal was carried out under a pressure of 10–20 kbar at $T \approx 78$ K. After the first deformation cycle the superconducting transition shifted to higher temperatures (curve 2). After the second similar cycle T_c, on the contrary, decreased (curve 3), but after annealing this crystal at 120 °C for 7 hours the superconducting transition temperature again increased (curve 4) with the final increase in T_c amounting to about 30% of T_c for the initial specimen. Similar results were obtained for β-$(ET)_2IBr_2$ crystals.

The results given point to an appreciable influence of mechanical defects on T_c of organic superconductors of the β-$(ET)_2X$ series. In general the defects of themselves can both raise and lower the superconducting parameters while it is a lowering of T_c which is characteristic for organic superconductors on introducing all kinds of impurities and defects.[15] It can thus be suggested that some reduction in T_c on repeated deformation of a β-$(ET)_2AuI_2$ crystal (curve 3 in Fig. 4) is associated with a growth in the concentration of, for example, dislocations. The annealing of deformed crystals leads to a partial relaxation of internal strains and reduces the concentration of slip defects while the number of twins, as is well known, is then preserved and can even increase.[16] The rise in T_c on annealing deformed specimens thus gives evidence of the significant role of twinning.

The results of resistance measurements in a magnetic field also point to the influence of twinning on superconductivity. Since two-dimensional anisotropy of the properties is characteristic for the organic β-$(ET)_2X$ superconductors, as noted above, then on rotating such specimens around the **a** or **b**′ axis in a magnetic field, **H**⊥**a** or **H**⊥**b**′ respectively, where $H_{c2}^{(a)} \approx H_{c2}^{(b')} > H > H_{c2}^{(c^*)}$ (see Fig. 3), we usually obtain the dependence of the resistance on the angle θ between the **c*** axis and the direction of the field **H** with one clearly marked minimum in the resistance (Fig. 5, dashed curve). On the similar dependence of a deformed β-$(ET)_2AuI_2$ specimen (the crystal is rotated around the **a** axis **H**⊥**a**), in addition to the sharp minimum corresponding to the field along **b**′ with a maximum value for H_{c2}, an additional minimum is observed (Fig. 5, full curve), most likely due to systems of mutually parallel twinning planes arising, one of which is shown schematically as shaded in the inset to Fig. 5.

On mechanical twinning, T_c of β-$(ET)_2I_3$ thus rises from 1.3 to ≈ 8 K at the same time that for the isostructural crystals β-$(ET)_2AuI_2$ and β-$(ET)_2IBr_2$ the increase in T_c is 20–30%, roughly the same as in Nb (Ref. 17).

It can be concluded from everything that has been said above that twins evidently directly play the chief part in the raising of T_c on plastic deformation of β-$(ET)_2IBr_2$ and β-$(ET)_2AuI_2$ crystals. As regards the compound β-$(ET)_2I_3$, the sharp increase in T_c here is associated with the β_H phase arising and stabilizing thanks to local strains which arise on plastic deformation. Mechanical twins, which already arise in the β_H phase on deformation, lead to an increase in the temperature of the start of the superconducting transition for the β_H phase from 8 to ≈ 9 K.

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