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Superconductivity at Normal Pressures of Some Organic Metals of (BEDT-TTF)-I System

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I. INTRODUCTION

The discovery by K. Bechgaard, D. Jerome et al.[1] in 1980 of the first organic superconductor, $(TMTSF)_2PF_6$, was, in some sence, the final step of a long way to organic superconductivity begun about ten years earlier. Although the existence of a number of organic metals was well established already by 1975, till 1978 there was no assurance that organic superconductors may exist. Because all first organic metals were of 1d type, and their metallic properties did not conserve at low enough temperatures.

Two ways were employed for diminishing the one-dimensionality. The chemical one consisted in introduction of heteroatoms in molecules forming the conduction chains in order to increase the transverse overlap and in using small inorganic counterions in order to bring chains together. And the physical way was the using of the hydrostatic pressures.

The metallic phase stable at $T \to 0$ was firstly observed in $(TSeT)_2Cl$ at pressures $P \gtrsim 5$ kbar[2]. A year later the suppression of the MI transition at $P \gtrsim 10$ kbar was found in TMTSF-DMTCNQ. In both cases the high pressure metallic phases turned out to be non-superconducting. However, their stability at $T \to 0$ clearly pointed to the possibility of organic superconductors.

In 1980 K. Bechgaard has synthesized[4] a series of compounds based on TMTSF in which the MI transition is suppressed at $P \gtrsim 10$ kbar, and in most of them in the high pressure metallic phase the superconducting transitions were observed.[5] Finally, it has been reported in 1981[6] that one of Bechgaard's salts, $(TMTSF)_2ClO_4$, being cooled very carefully, may be transferred into the superconducting state at normal pressure. Since then, the chemistry and the physics of Bechgaard's superconductors have been the subject of much investigation.

In this report we present some data on the properties of another type of organic metals exhibiting the superconducting transitions at the normal pressure, those of (BEDT-TTF)-I family.

BEDT-TTF was synthesized in 1978.[7] Recently, a number of compounds has been obtained on its basis[8,9] with using Bechgaard's anions ClO_4, ReO_4, PF_6. One of them, $(BEDT\text{-}TTF)_4(ReO_4)_2$, has been reported to become superconducting at pressures above 4 kbar.[9] We have found[10-12] that BEDT-TTF forms with iodine a number of phases with properties of 2d metals. Some of them become insulating with cooling down to 140–150 K, and others remain in the metallic state at normal pressures and exhibit the superconducting transformation at temperatures between 1.5 and ~7 K.

2. β-PHASE: $(BEDT\text{-}TTF)_2I_3$

The crystal of the β-modification may be obtained both chemically and electrochemically. The electrochemical oxidation of BEDT-TTF has been carried out on a platinum anode in the benzonitrile or tetrahydrofuran solution (10^{-3} mole/ℓ) using the constant current regime (~20 μA/cm^2). Bu_4NI_3 has been used as an electrolyte (10^{-1} mole/ℓ). At these conditions the crystals of the β-phase are obtained in mixture with crystals of its polymorphic modification (α-phase) which exibits the sharp MI transition near 140 K. Very small admixture of the α-phase may be obtained by working with trichlorethane at 60°C.

Chemically, BEDT-TTF has been oxidized by I_2 in the benzonitril solution or by Bu_4NI_3 in trichloroethane at molar ratios 1 : 1 and 1 : 10, respectively.

The crystals grow both in the form of platelets of 20–30 μ thick and ~3 × 3 mm^2 area and in the form of needles with the typical dimensions of 0.01 × 0.05 × 2 mm^3. The room temperature conductivity measured along the needle axis and in arbitrary direction in the platelets (*ab*) plane is of the same order of 30 Ohm^{-1}cm^{-1}. The conductivity in the direction perpendicular to the *ab*-plane (close to the *c*-axis) is about 50 times less.

The temperature dependence of the (normalized) resistivity of two platelets and two needles at temperatures below 30 K is shown in Fig. 1. The platelets were found to be always less perfect than the needles. Their transition is often shifted to lower temperatures.

The suppression of the superconductivity by the magnetic field directed roughly along the *b*-axis at right angles to the measuring current flowing along the *a*-axis is shown in Fig. 2. It is seen that the

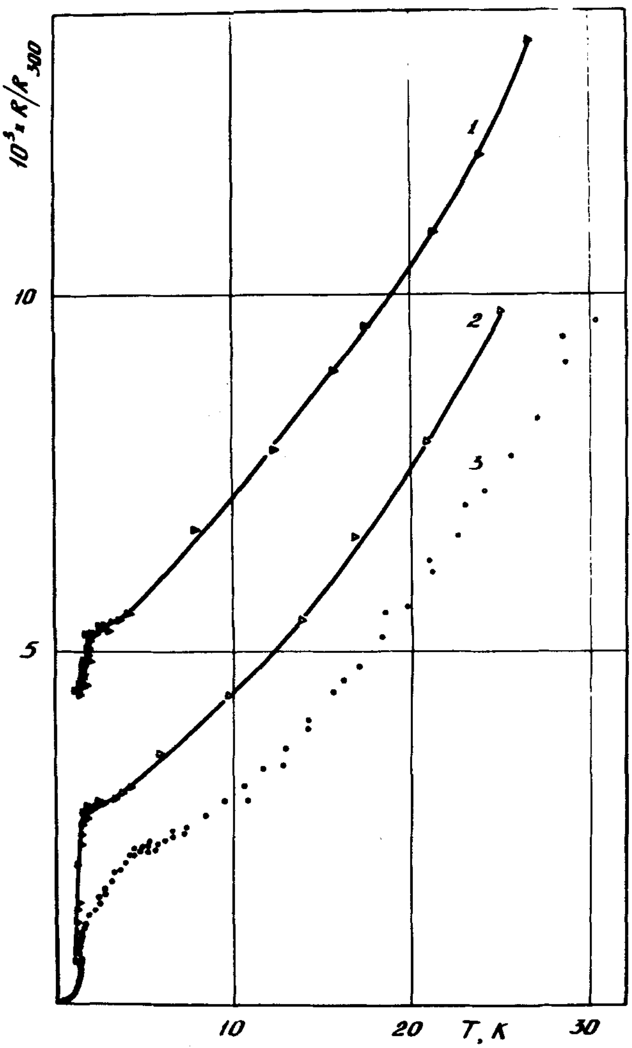

FIGURE 1 Temperature dependence of resistivity of the β-phase △, ▲—platelets; ○, ●—needles.

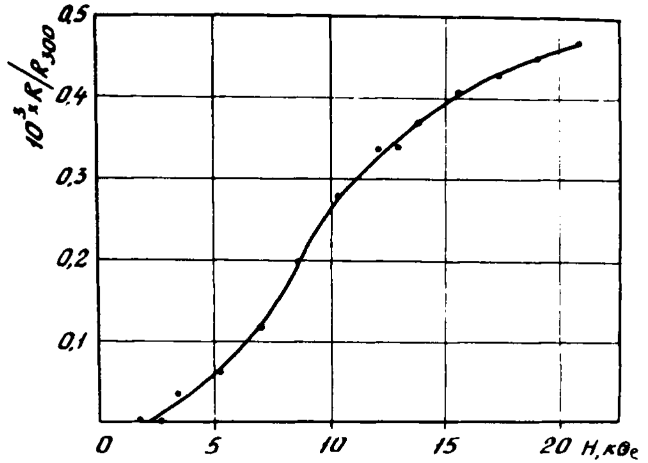

FIGURE 2 Suppression of the superconductivity in the β-phase by magnetic field at $T = 0.15$ K.

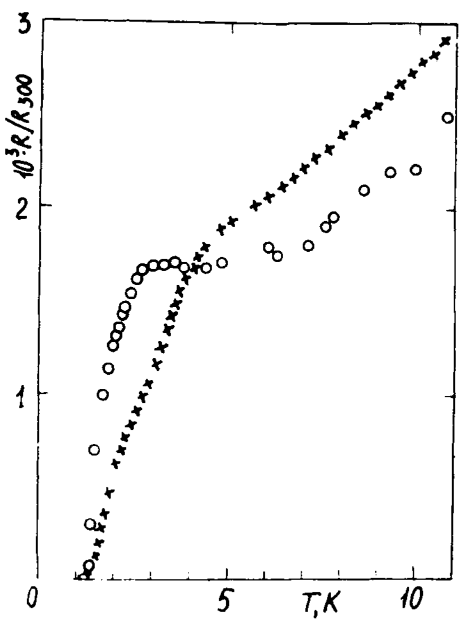

FIGURE 3 Two crystals with almost the same RR exhibit different pre-transitional behaviour.

traces of the resistivity appear at 2-2.5 kOe, but the transition is not completed up to 25 kOe.

So, the β-phase, $(BEDT\text{-}TTF)_2I_3$, is a normal pressure superconductor with $T_c = 1.5 \pm 0.1$ K. Attention should be drawn to the fact that the resistivity of many needles often falls below 4 K more rapidly than at slightly higher temperatures. Such a behaviour is not related unambigously with the perfection of the crystals measured by the value of the resistance ratio $RR = R_{300}/R_{4.2}$. As exemplified by Fig. 3, two crystals with almost the same RR may behave in different manner. We will turn to this question in Sec. 4.

3. γ-PHASE: (BEDT-TTF)I_x

Upon varying the conditions of the electrochemical synthesis by using different solvents and operating currents a number of other modifications of (BEDT-TTF)-I family may be obtained. The crystals of the γ-phase were grown by the electrochemical oxidation of BEDT-TTF in the trichloroethan solution (10^{-3} mole/ℓ) in the galvanostatic regime (~64 μA/cm^2) with Bu_4NI_3 as an electrolyte (10^{-1} mole/ℓ). The same phase may be also obtained chemically upon oxidation of BEDT-TTF by I_2 or Et_4ClI_4 in benzonitrile at the molar ratios 1 : 2 and 1 : 1, respectively. The crystals have the form of thin platelets with typical dimensions of $2 \times 0.2 \times 0.01$ mm^3.

The crystal structure of the γ-phase is not yet established, so that we do not yet know its real composition. It will be seen that its physical properties point to the 2d type of its structure. For brevity, we will designate the platelet plane as *ab*-plane with *a*-axis along the needle axis, and the perpendicular direction as *c*-axis.

The room temperature conductivity in the *ab*-plane averaged over a number of crystals is rather small, about 20 Ohm^{-1}cm^{-1}. In the *ab*-plane the conductivity is nearly isotropic and about 20–30 times bigger than that in the *c*-direction.

The temperature dependence of the (normalized) *a*-axis resistivity for 5 crystals is shown in Fig. 4. The insert shows in more details the low-temperature behaviour.

It is seen that the "humps" appearing on some curves at temperatures near 120 K have no influence on T_c. The size of the "hump" affects only the residual resistivity, whereas the value of T_c determined by the middles of the corresponding curves lies between 2.4 and 2.6 K.

A striking example of lacking correlations between the "hump"

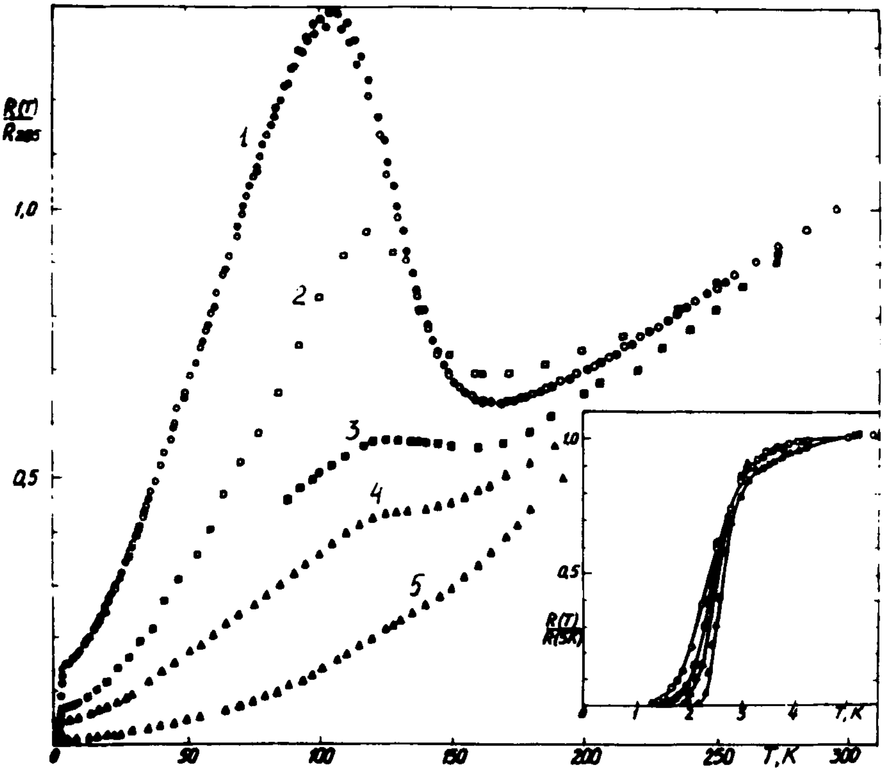

FIGURE 4 Temperature dependence of the resistivity for 5 crystals of γ-phase.

size and T_c is shown in Fig. 5. As a consequence of an increase of a factor close to 14 on the $R(T)$ curve in the vicinity of 100 K the sample resistance at 4.2 K is 2.5 times higher than that at 300 K. Nevertheless, the nearly complete superconducting transformation takes place in the crystal at the same temperature of 2.5 K.

The superconducting transition curves of crystal 5 in the magnetic field directed along *a*-axis are presented in Fig. 6. In the insert the temperature dependences of the critical fields are shown for each of 3 directions. The critical field is smallest in the *c*-direction. In the *ab*-plane its value is more than one order of magnitude bigger and close to the paramagnetic limit. Indeed, the transition temperature of 2.5 K corresponds to a gap $\Delta \sim 10$ K$\sim$70 kOe while the *ab*-plane critical field is of the order of 30 kOe at temperatures only 1.5 times below T_c.

The suppression of the superconductivity at $T = 1.5$ K by magnetic fields oriented in 3 different directions is shown in Fig. 7. In the

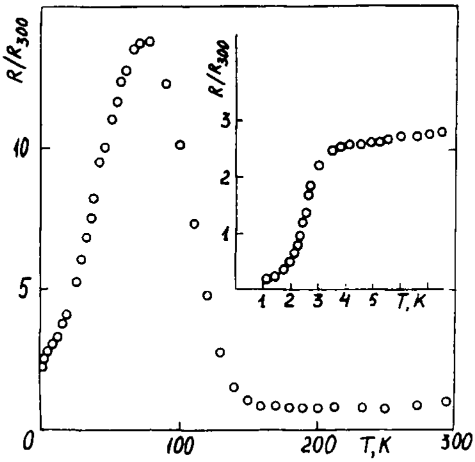

FIGURE 5 Superconducting transition in a γ-phase crystal with big "hump".

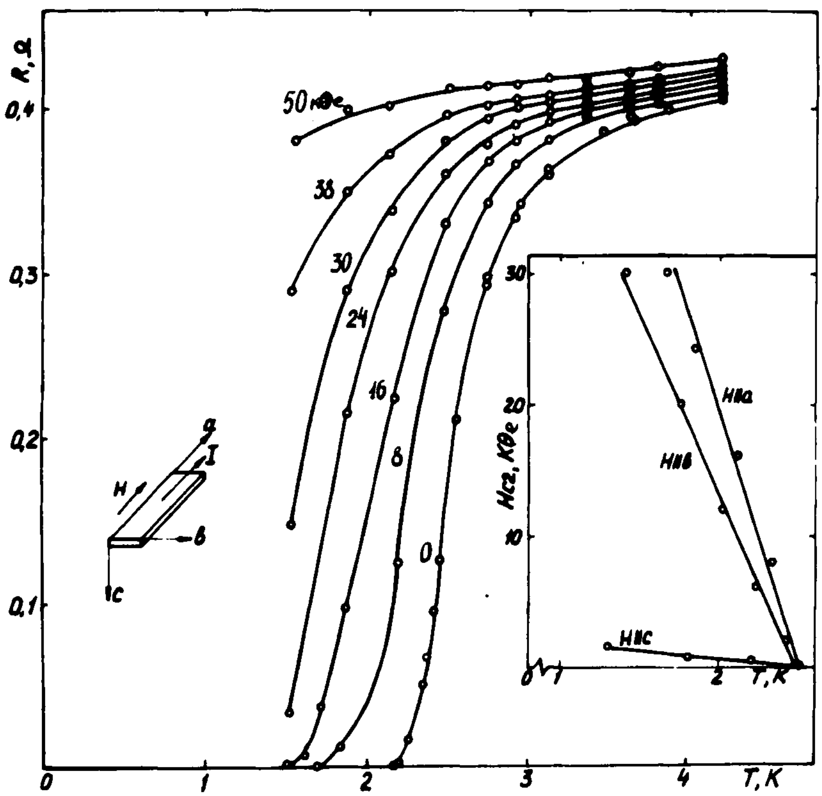

FIGURE 6 Superconducting transition curves in magnetic field $H \| a$ for crystal of the γ-phase. In insert temperature dependence of critical fields is shown.

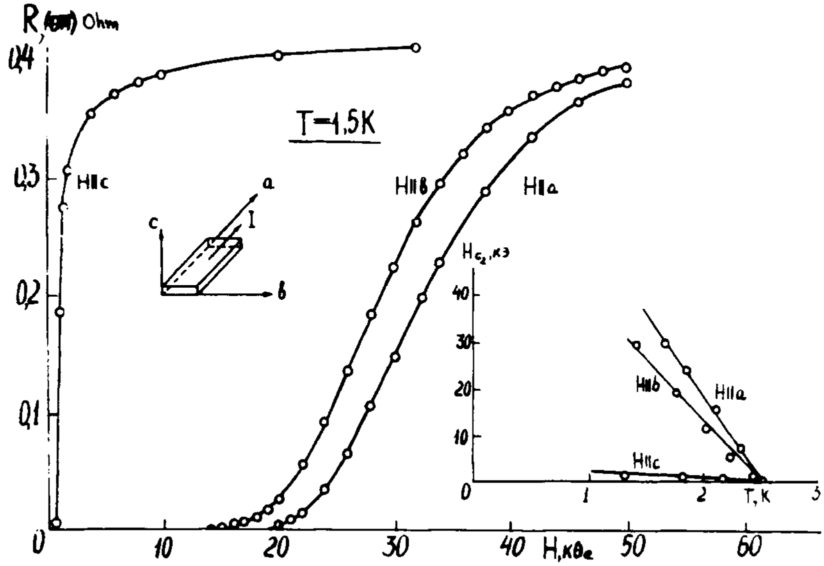

FIGURE 7 Suppression of the superconductivity by magnetic field at $T = 1.5$ K. A crystal of the γ-phase.

longitudinal fields the transition is rather broad: the resistance traces appear at 15–20 kOe, and the end of the transition lies at H 50 kOe.

The big anisotropy of the critical fields, the closeness of the *ab*-plane critical fields to the paramagnetic limit and the broadness of the field induced transition with fields in the *ab*-plane all point to the 3d character of the γ-phase.

A number of experimental facts indicate that the γ-phase crystals are rather inhomogeneous. Firstly, the lack of correlation between the "hump" size and the value of T_c suggests that the "humps" are not an intrinsic property of the γ-phase. It has been found, moreover, that different parts of a crystal may behave in markedly different manner. It has happened that one part of the crystal became insulating at temperatures below 140 K, whereas the other has passed with cooling through the "hump" and exhibited the superconducting transformation.

Further, it has been found that, by varying the conditions of the synthesis, T_c of the γ-phase may vary considerably, ranging from 2.2 K to 3.3 K. It should be noted that the superconducting transition is not complete for every crystal. An example of such an incomplete transition with T_c = 3.3 K is presented in Fig. 8 together with data on its suppression by the magnetic field.

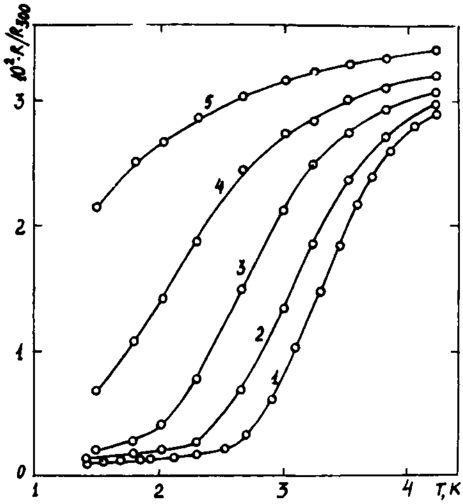

FIGURE 8 An example of incomplete transition at $T_c = 3.3$ K. 1 – $H = 0$, 2 – $H = 6$ kOe, 3 – $H = 16$ kOe, 4 – H = 30 kOe, 5 – $H = 50$ kOe.

The scattering of T_c in crystals of the γ-phase obtained from different synthesis may be associated with the existence of a range of iodine concentrations within which limits the γ-phase is stable. Such a range of variable concentration was observed earlier in $TTT_2I_{3-\delta}$.[13]

4. ORGANIC SUPERCONDUCTIVITY WITH $T_c = 7$K?

It has been mentioned in Sec. 2 that the characteristics feature of many crystals of the β-phase is the fact that their resistivity does not approache the residual value before the superconducting transition. On the contrary, the resistivity begins often to fall more rapidly a few Kelvins to T_c. In some crystals it happens from ~4 K, but there are also crystals whose resistivity fall is accelerated beginning from ~8 K. In every cases the application of the magnetic field suppresses this falling.

Such a behaviour is exemplified by Fig. 9 in which the temperature dependence of the resistivity are shown in two fields, $H = 0$ and H = 50 kOe, for two crystals of the β-phase obtained in two different synthesis. In Fig. 10 the field dependences of the resistivity of one of theese samples are shown for temperatures above 4 K. Attention is drawn to initial portions of theese curves with relatively quick increas-

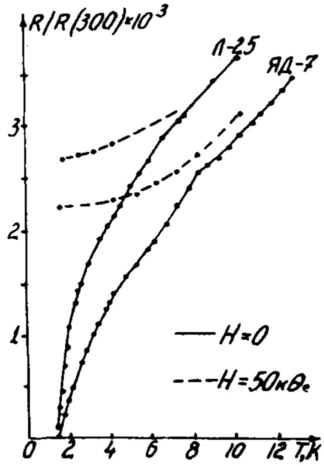

FIGURE 9 Influence of the magnetic field on the resistivity of two crystals of β-phase at $T \gg T_c$.

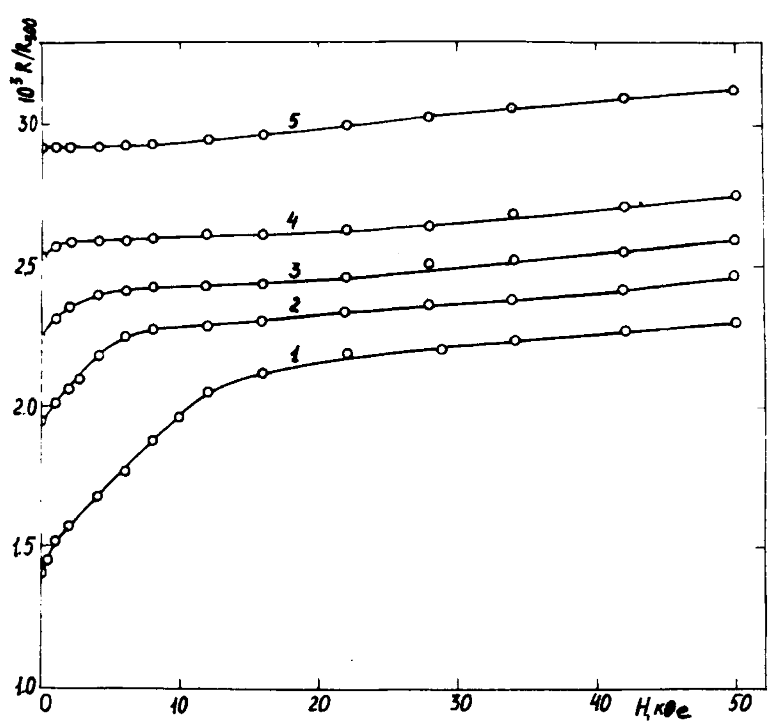

FIGURE 10 Field dependences of resistivity at $T > 4$ K.

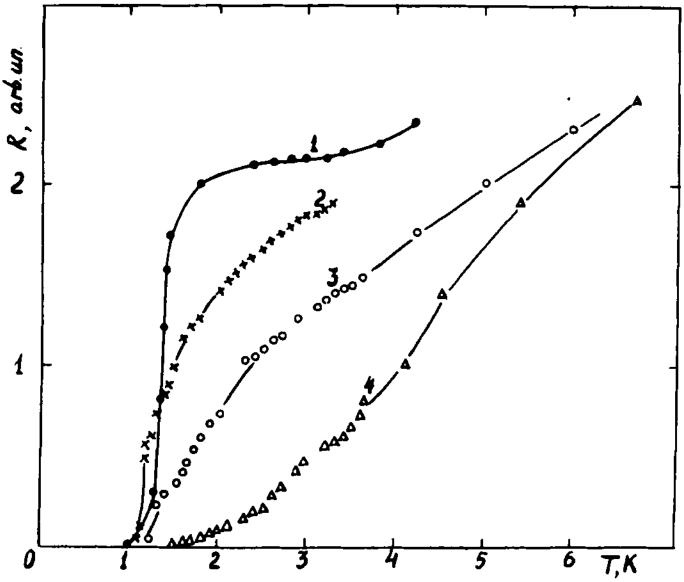

FIGURE 11 Variations in the low-temperature resistivity coarse produced by cycling.

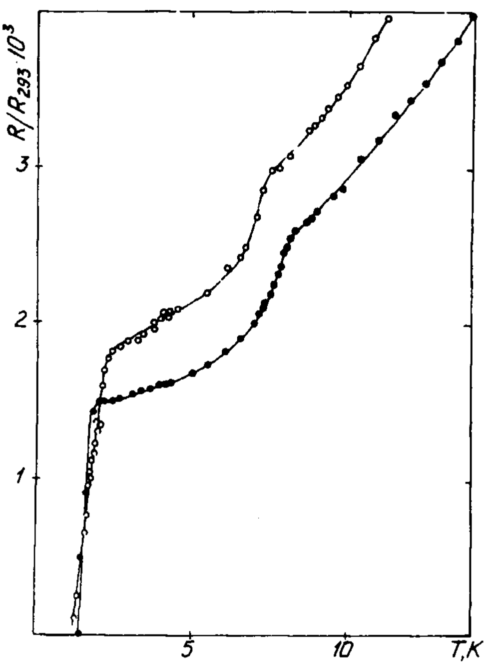

FIGURE 12 Two-stage superconducting transition in crystals of the β-phase.

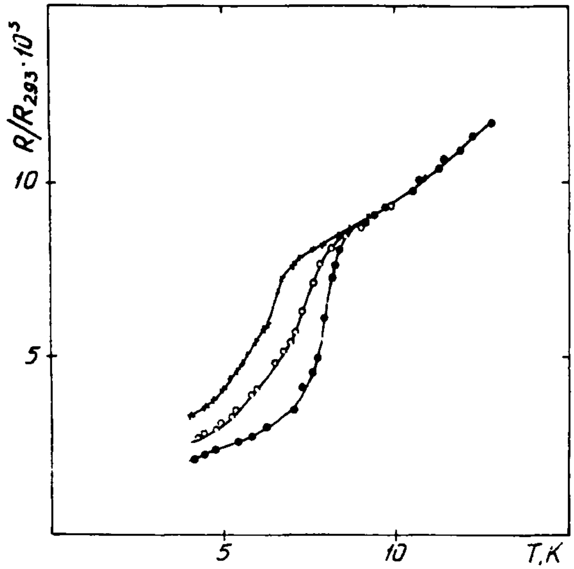

FIGURE 13 Is it the superconductivity at 7 K?

ing the resistivity. Theese portions diminish with increasing the temperature and disappear above 8 K.

It has been found that such a behaviour of the resistivity may be sometimes stimulated by the temperature cycling of the sample. An example of the stimulation is given in Fig. 11 on which 4 passages of the same crystal are shown from the room temperature down to 1 K.

And, finally, it has been found that in some crystals, instead of continuous decrease of the resistivity below 7–8 K, the superconducting transformation takes place in two stages, one at 7–8 K and another at 1.5 K. Two examples of such a behaviour are shown in Fig. 12.

The 7 K step may be sometimes considerable and its size may change with the temperature cycling. The sizeable step and its shift in the magnetic fields are shown in Fig. 13. It is possible that we are concerned here with a superconducting transition.

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