Direct detection of the β-1.5⇌β-8 phase transition in β-dibis(ethylenedithio)tetrathiofulvalene triiodide, β-$(ET)_2I_3$

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The phase transition β-1.5⇌β-8 in β-$(ET)_2I_3$ has been detected for the first time, on the basis of jumps on the $R(T)$ and $R(P)$ resistance curves. The β-8 phase is found to be more ordered than the β-1.5 phase. A possible form of the T–P phase diagram of β-$(ET)_2I_3$ is discussed.

It was found in Refs. 1 and 2 that β-$(ET)_2I_3$ has, in addition to a superconducting phase[3] with $T_c = 1.5$ (the β-1.5) phase, yet another superconducting phase, with $T_c \simeq 7$–8 K (the β-8 phase), at pressures in the kilobar range. So far, however, there has been no report of a direct detection of the phase transition β-1.5⇌β-8. In the present letter we report the detection of this transition, on the basis of jumps on the $R(T)$ and $R(P)$ curves.

The samples are compressed in a bomb with gaseous helium,[4] which makes it possible to produce strictly uniform pressures down to the temperature at which helium solidifies. The resistance is measured by means of squeezing contacts of the type described in Ref. 5. The customary method of attaching contacts with conduction paste proved totally unacceptable in this case, since it frequently results in nonreproducible jumps in the resistance because of deformations that occur near the contacts. We studied two β-$(ET)_2I_3$ single crystals with a ratio $R_{300}/R_{4.2} \simeq 550$ which showed no traces of any sort of the pretransition phenomena at 7–8K, which were reported in Refs. 4 and 6. These crystals did not exhibit the thermal-cycling effects described in Refs. 6 and 7.

Figure 1 shows some examples of the observed jumps in the resistance for one of the samples. The vertical parts of these curves correspond to a change in the resistance of the sample over time at fixed values of T and P.

Curve 1 in Fig. 1 shows $R(T)$ during cooling and heating of a sample at $P = 1$ bar. Curve 2 shows the same dependence in step e) of the following cycle: a) $T = 300$ K, $P = 1 \to 400$ bar; b) $P = 400$, $T = 300 \to 60$; c) $T = 60$, $P = 400 \to 1$; d) $P = 1$, $T = 60 \to 4.2$; e) $P = 1$, $T = 4.2 \to 200$; f) $P = 1$, $T = 200 \to 4.2 \to 200$. From the low-temperature parts of both curves (in the coordinates R, T^2), shown in the inset, we see that in the first case the sample is in β-1.5 phase, while in the second it is in the β-8 phase. The cooling of the sample in step f) shows that the behavior of its resistance at low temperatures corresponds to curve 1, not curve 2. The jump on curve 2 at 124 K thus corresponds to the phase transition β-8→β-1.5.

Curves 3 and 4 in Fig. 1 show the behavior $R(T)$ in steps b) and e), respectively,

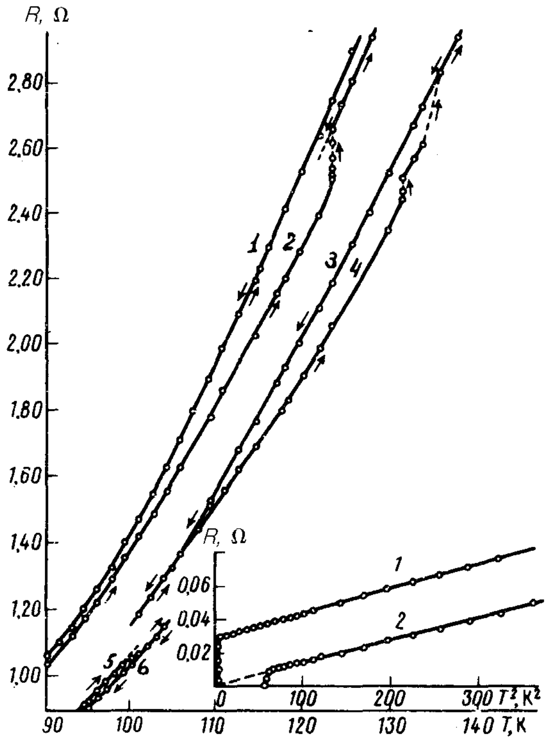

FIG. 1. Temperature dependence of the resistance of β-$(ET)_2I_3$ in the β-1.5 and β-8 phases. 1,2—$P = 1$ atm; 3,4—$P = 200$ atm; 5,6—$P = 400$ atm. The inset shows the low-temperature parts of the curves 1 and 2 for the β-1.5 and β-8 phases, respectively (see the text proper for an explanation).

of the following cycle: a) $T = 200$ K, $P = 1 \rightarrow 200$ bar; b) $P = 200$, $T = 200 \rightarrow 100$; c) $T = 100$, $P = 200 \rightarrow 1$; d) $T = 100$, $P = 1 \rightarrow 200$; e) $P = 200$, $T = 100 \rightarrow 200$.

It must be assumed that above 134 K the sample is in the β-1.5 phase, since no structural features of any sort are observed on the $R(P)$ curves at these temperatures. Below 110 K, in contrast, the sample is in the β-8 phase, since after the pressure is removed in step c), the temperature dependence of the resistance follows curve 2. At $P = 200$ bar, cooling in the region 110 ± 2 K is accompanied by the transition β-1.5$\rightarrow\beta$-8, while heating at 134 ± 2 K is accompanied by the transition β-8$\rightarrow\beta$-1.5.

Figure 2 shows $R(P)$ in compression-decompression cycles at several temperatures. At the beginning of each cycle, the sample is in the β-1.5 phase. The jumps on the $R(P)$ curves correspond to the transitions β-1.5$\rightleftharpoons\beta$-8.

Curves 1 and 2 in Fig. 3 show the temperatures and pressures of the transitions observed on the basis of the jumps on the $R(T)$ and $R(P)$ curves. Curve 1 corresponds to the transition β-8$\rightarrow\beta$-1.5 during heating (decompression). This curve intersects the $P = 0$ axis at 124 K, in good agreement with the result of Ref. 8. Curve 2 corresponds to the formation of the β-8 phase during cooling (compression). We see that the β-8 phase during cooling (compression). We see that the β-8 phase can be reached at pressures well below the pressures of 0.5–1 Kbar, which were reported previously.[1,2,4,9] Nevertheless, curve 2 clearly does not reach the ordinate axis, since we know

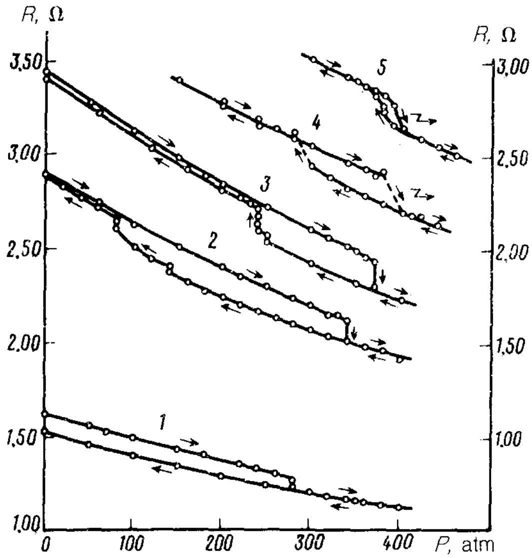

FIG. 2. Pressure dependence of the resistance for β-$(ET)_2I_3$ at various temperatures. 1—$T=104.5$ K; 2—$T=128.5$ K; 3—$T=1.36.5$ K; 4—$T=140$ K; 5—$T=151$ K.

that the β-1.5 phase exists at standard pressure at all temperatures. There is the interesting question of just how far along the pressure scale this phase can be preserved when the sample is compressed at temperatures below, say, 110 K.

The results of a corresponding experiment are shown by curves 1 in Fig. 2. We see that at $T=104.5$ K an irreversible transition β-1.5$\rightarrow$$\beta$-8 occurs at $P\simeq280$ bar. This

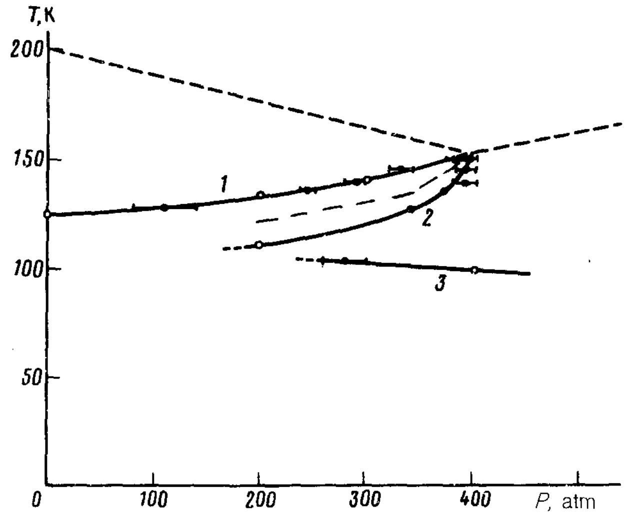

FIG. 3. Part of the T,P phase diagram of β-$(ET)_2I_3$. Solid lines: boundaries of the region of stable (curves 2 and 3) and metastable (curve 1) existence of the β-8 phase. Dashed lines: suggested lines of equilibrium transitions (see the text proper for an explanation).

point is plotted on curve 3 in Fig. 3. The second point on this curve was found in the isobaric cycle shown by curves 5 and 6 in Fig. 1. Curve 5 corresponds to the β-1.5 phase, reached by compression to $P = 400$ bar at 20 K, while curve 6 corresponds to the β-8 phase. We see that in this case the β-1.5$\rightarrow\beta$-8 transition occurs at $T = 100 \pm 2$ K.

From the outline of the T,P diagram in Fig. 3, we see that the region of stable existence of the β-8 phase is bounded by curves 2 and 3. Lines 1 and 2 are hysteretic branches of the transition β-1.5$\rightarrow\beta$-8. The disappearance of the hysteresis near $T \simeq 150$ K, $P \simeq 400$ bar may indicate a change in the nature of the transition. This change may be a consequence of the existence of a triple point in this region, reached by a line of a second-order superstructural transition in the β-1.5 phase, which was found in Ref. 10 at standard pressure near 200 K. The third line here may correspond to an ordering of the ethylene groups of the ET molecule, which was detected in Ref. 11 at $T = 300$ K and $P = 9.5$ kbar.

It was suggested in Ref. 12 that the high value of T_c in the β-8 phase is due to a suppression of this superstructural transition. Although a superstructure in β-8 was not actually observed,[9] the suggestion of Ref. 12 is difficult to reconcile with the circumstance that no substantial changes in electronic properties are observed at this superstructural transition.[13-15]

It follows from the data shown in the inset in Fig. 1 that the β-8 state is more ordered than the β-1.5 state. In both phases we have $R(T) = R_0 + AT^2$; the values of A are approximately the same, while the values of R_0 differ by a factor of more than 30. If this circumstance is responsible for the pronounced difference between the values of T_c for the β-1.5 and β-8 phases, we conclude that either the disorder of the β-1.5 phase is so pronounced that this phase is near an Anderson transition or we are dealing with a triplet superconductivity, since the presence of a slight disorder does not affect the value of T_c in the case of singlet pairing.

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