Superconductivity in β-di[bis(ethylenedithio)tetrathiafulvalene]-triiodide [β-(BEDT-TTF)$_2$I$_3$] annealed at 104 K

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The title compound has recently been found to exhibit two superconducting transitions at 2 and 7.5 K when annealed at 100–120 K at ambient pressure. We have investigated the development of the two phases as a function of annealing time (at 104 K) by complex susceptibility measurements. At the initial stage of annealing, both the 2- and 7.5-K superconducting phases appear, but, with further annealing, the 7.5-K transition grows to a considerable fraction of the complete diamagnetism. The present results suggest that the 7.5-K phase is the most stable state at ambient pressure. The profile of the evolution is discussed in terms of both the real and imaginary parts of the susceptibility.

The organic superconductor β-di[bis(ethylenedithio)-tetrathiafulvalene]triiodide, β-(BEDT-TTF)$_2$I$_3$, has two different superconducting states: At ambient pressure, the superconducting transition temperature is 1–1.5 K (the low-T_c state), while it exhibits superconductivity at much higher temperatures, 7–8 K (the high-T_c state), under soft pressures (above 0.4 kbar).[1,2] It is known that there is a structural difference between these two phases. An incommensurate lattice modulation with slight molecular displacements occurs below 175 K in the low-T_c state,[3] but is suppressed in the high-T_c state under pressure.[4] In addition, the conformation of the ethylene groups in the BEDT-TTF molecules is also different; in the former state the so-called *A* and *B* conformations coexist, while the latter state is believed to contain only the *A* conformation.[5] It was found later that the high-T_c phase can be stabilized at ambient pressure by releasing pressure at low temperatures.[6] The high-T_c phase is believed metastable at ambient pressure. A pressure-temperature phase diagram taking account of the metastability has been proposed.[7]

The structural metastability of this compound was further studied by the recent detailed x-ray measurements by Kagoshima *et al.*[8] They observed that the wave number of the superstructure was gradually reduced ($\sim$10%) when the sample was held in the temperature range of 100–120 K for several tens of hours. Moreover, their subsequent studies revealed that the well-annealed sample with this structural change exhibited two superconducting transitions at 2 and 7.5 K.[9] From resistivity and dc susceptibility measurements, they concluded that the 2-K phase occupies most of the sample volume, while the 7.5-K phase only occupies a small portion. The 2-K transition was assumed to be a phase different from the low-T_c phase.

In this work, we have investigated the development of superconductivity in β-(BEDT-TTF)$_2$I$_3$ at ambient pressure as a function of the annealing time, by complex susceptibility measurements. We give evidence that the 2-K transition is actually indicative of another superconducting phase, as suggested in the earlier work. In addition, we show drastic growth of the 7.5-K phase in our annealing condition, which suggests that the high-T_c state is the most stable state.

Single crystals of β-(BEDT-TTF)$_2$I$_3$ were prepared by the usual electrochemical method. The dimension of the crystal used in the present measurement is $1.7\times1.2\times0.1$ mm^3. The complex susceptibility was measured in the temperature range between 1.6 and 10 K with a Hartshorn-type mutual inductance bridge, the resolution of which is 5 nH. The ac magnetic field of 195 Hz was applied perpendicular to the conducting *ab* plane of the crystals. The sample temperature was measured with a calibrated carbon glass resistor.

The present experiments consist of the repetition of annealing and measurement: First, the crystal was cooled down to the liquid He temperature with the usual cooling rate of 0.3$\sim$0.7 K/min. After the first measurement, the sample temperature was raised up to 104.4$\pm$0.3 K and held constant for 8 h. Then the sample was cooled again and the susceptibility was measured. This sequence of annealing and measurement was repeated. Before annealing, there observed no superconductive diamagnetism in the measured temperature range ($T>1.6$ K).

The temperature dependence of the real part of the susceptibility at the field of 358 mOe is shown in Fig. 1 with the total annealing time as a parameter. It is clear in the figure that two superconducting transitions with onsets of 7.5 and 2.3 K are induced by annealing. The annealing has an accumulative effect on growth of the superconducting phases. The initial appearance of both transitions is followed by rather rapid growth of the 2.3 K transition. Then the 7.5 K transition finally becomes predominant over the 2.3 K transition. According to a rough estimate of the absolute value of the susceptibility, the complete diamagnetism corresponds to the full scale

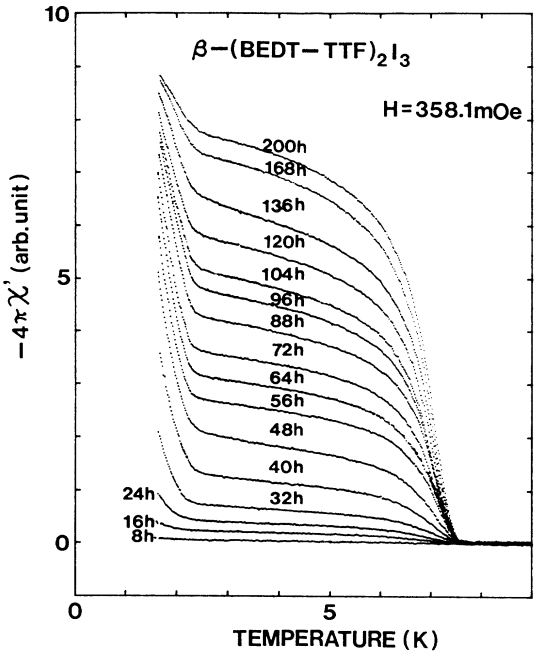

FIG. 1. Real part of complex susceptibility at low temperatures when the sample was annealed at 104.4 K. Figures on each curve indicate the accumulated annealing time.

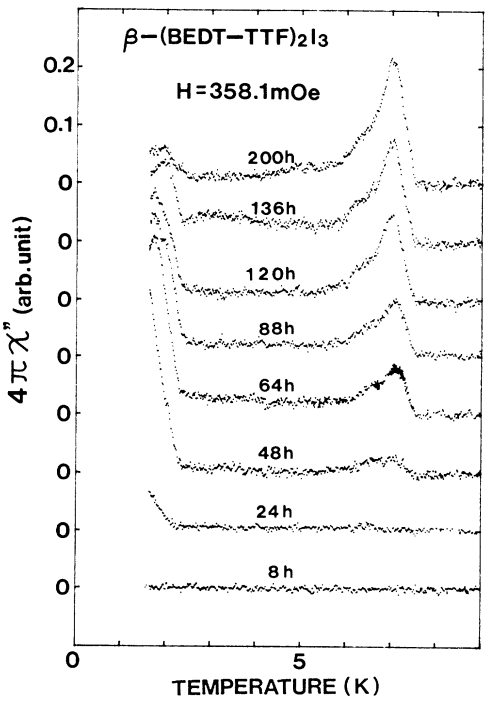

FIG. 2. Imaginary part of complex susceptibility at low temperatures when the sample was annealed at 104.4 K. Figures on each curve indicate the accumulated annealing time.

of Fig. 1; that is, nearly complete diamagnetism is achieved after 200 h annealing. In the intermediate range between 2.3 and ~6 K, χ' is weakly temperature dependent.

Results of the imaginary part, χ'', are shown in Fig. 2. One can see that nonvanishing χ'' appears below 2.3 K and at 6–7.5 K corresponding to the two superconducting transitions. The peak at the higher temperatures grows monotonously with annealing time. On the other hand, the peak at the lower temperature grows rapidly at the early stage of annealing, but, after 50–60 h, the peak starts to diminish; this implies again the progressive occupation of the 7.5-K phase.

The onset temperature of the lower transition stays constant (2.3 K) at any stage of annealing process, as seen in Figs. 1 and 2. Since the lowest temperature in the present measurement is limited to 1.6 K, we could not see the saturation of diamagnetism. However, the peak of χ'' usually appears at the midpoint of superconducting transition; in the present case, the midpoint is considered as 1.8–1.9 K at the field of 358 mOe. The transition is somewhat broadened by the external field. Actually, a slightly narrower transition was observed at a smaller ac field of 116 mOe, where a peak of χ'' appears at 2.0 K. This transition temperature is different from the accepted values of T_c (1.0–1.5 K) for the low-T_c phase, implying the existence of a new superconducting phase. These results agree well with those reported by Kagoshima *et al.*[9]

The annealed β-(BEDT-TTF)$_2$I$_3$ must be considered as an inhomogeneous superconductor consisting of 7.5 K grains embedded in the lower-T_c region (2.3 K or the low-T_c phase). In various types of composite superconductors including granular systems, two-step diamagnetic transitions similar to the one observed in the present work are often observed. Indeed, the observed profile in Fig. 1 has a strong resemblance to that of fine multifilamentary NbTi wires, where an interfiber transition occurs by the coupling due to proximity effect, below the individual intrafiber transition.[10] In this case, the transition at lower temperature does not mean the existence of another superconducting phase but indicates the formation of overall phase coherence among the superconducting grains. Therefore, it is not a trivial problem whether the lower transition at 2.3 K in our system means another superconducting phase or not.

Generally speaking, the phase coherence transition takes place when the thermal disturbance k_BT becomes less than the coupling energy. Therefore, the transition temperature should be quite sensitive to the strength of the coupling. Turning attention to our system, it is reasonable to expect that the couplings between 7.5 K grains, if any, should become stronger as the volume fraction increases with annealing. On the other hand, the onset temperature (2.3 K) stays constant at any stage of annealing process, as mentioned earlier. This fact evidences that the 2.3 K transition is not a phase-coherence one but is of bulk nature.

The onset temperature of the 7.5 K transition also remains unchanged through the development of this phase. This means that a well-defined phase nucleates from the initial stage of annealing. To see the time evolution of the 7.5-K phase, the value of χ' at 5 K is plotted as a function of annealing time in Fig. 3. One can see that the time evolution of χ' is not simple: The increase in χ' is rather slow at the initial stage (<30 h) and then

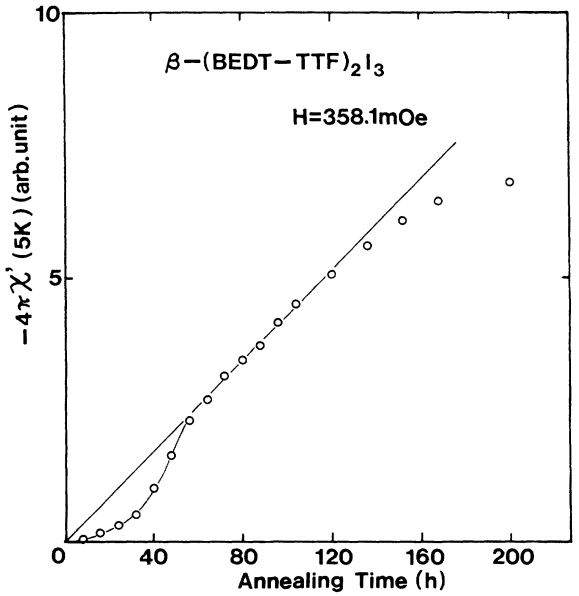

FIG. 3. Growth of the real part of the susceptibility at 5 K as a function of annealing time. The solid lines are guides to the eye.

accelerates. From 50 to 120 h, χ' increases linearly, following a straight line passing through the origin. Finally χ' tends to saturate for further annealing. The saturation value appears to reach a considerable fraction of the complete diamagnetism.

It is, however, difficult to get a reliable estimate of the volume fraction of the 7.5 K phase from these results. One of the difficulties is that no one knows the actual shape of the grains. Therefore, (i) the demagnetization effect cannot be corrected. (ii) Field penetration must be considered when the grain size is small compared with the penetration depth. Another difficulty comes from (iii) the possibility of shielding effect due to intergrain couplings. In spite of these ambiguities, one may consider that the evolution of χ' roughly corresponds to that of the superconducting volume fraction. This is valid when (i) the morphology of the grains does not change so much in the annealing process, (ii) the grain has a macroscopic size larger than the penetration depth, and (iii) the intergranular shielding diamagnetism can be neglected. The observed linear time evolution of χ' seems to be consistent with this picture. The deviation from the linearity at the initial annealing (0–50 h) can be explained by the magnetic-field penetration into the small grains. The London penetration depth of this material is estimated as ~ 330 nm from the reported values of the effective mass and carrier density (in the high-T_c phase).[11] The typical grain size should be larger than this value after 50 h annealing in this picture.

However, the shielding effect due to intergrain coupling is difficult to rule out. If the shielding diamagnetism has a dominant contribution to the observed data, an alternative interpretation is required. In this case, χ' is expected to increase with a higher power than linear and diverge at a percolation threshold.[12] Thus it is likely that the system annealed for 0–50 h is in this regime; superconducting paths percolate at 50 h. The system is considered as an ensemble of clusters with finite size before 50 h, and as an infinite network percolating over the sample after 50 h. As far as the diamagnetic response is concerned, the system in the latter regime behaves as an effective superconducting medium as a whole. The effective penetration depth of magnetic field is known to be of macroscopic size,[13] comparable with the sample size. This explains the fact that even above the percolation threshold (at 50 h) the susceptibility is appreciably reduced from the complete diamagnetism. Moderate increase of χ' after 50 h is reasonably interpreted as the decrease in the effective penetration depth of field due to the further growth of 7.5-K phase network.

We cannot tell which of the two situations mentioned above is the case for the present system and cannot make a quantitative estimate of the superconducting volume fraction. (The observed χ' was not very sensitive to the amplitude of ac field, at least for 0.1–1 Oe. This may be suggestive of the validity of the former picture because the weakly-coupled network is expected to show strongly field-dependent diamagnetism.) For either case, however, it is concluded that the 7.5 K phase develops into a considerable portion of the volume, and is not a by product. The present results are in contrast to the previous reports where annealing was made at higher temperature by several kelvin.[8,9]

At present, it is not clear what is going on during the annealing process. Here, we point out that the importance of the conformation of the ethylene groups. It should be noted that one hundred kelvin is a characteristic temperature for freezing of thermal motions of the ethylene groups, probably between the two conformations, as shown by the measurements of ^{1}H NMR relaxation and lineshape.[14] Therefore, rapid cooling through this temperature region will result in disorders of the ethylene conformations, while the annealing at temperatures in that region will realize the best conformation in a stable state. The coupling of the conformational change to the superconductivity is an important ingredient but its relation to the 2.3 and 7.5 K superconductivities is still an open question. In any way, since the low-T_c state is metastable at low temperatures, the transition to the real ground state (very probably, the high-T_c state) should be brought about by thermal activations through a finite energy barrier. Therefore, the relative occupations and thermal relaxation rate between the metastable and the ground state are expected to be strongly temperature dependent. This may suggest the sensitivity to the annealing temperature and explain the discrepancy between the present and the previous results. Experiments under different annealing conditions are now in progress. Preliminary results have shown a strong temperature dependence.

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