

TWO SUPERCONDUCTING PHASES IN THE ORGANIC CONDUCTOR: β -(BEDT-TTF) $_2$ I $_3$

F. CREUZET, C. BOURBONNAIS, G. CREUZET, D. JEROME, D. SCHWEITZER and H. J. KELLER

Laboratoire de Physique des Solides, Université Paris-Sud, 91405 ORSAY (France)

We have investigated the nature and the stability of the high- T_c (~ 8 K) and low- T_c (~ 1.5 K) superconducting phases (respectively called β -H and β -L) of the organic conductor β -(BEDT-TTF) $_2$ I $_3$. First, by resistivity measurements and following a well-defined temperature-pressure cycling process, we show that the β -H phase is stabilized at ambient pressure and low temperature, exhibiting a very sharp and complete superconducting transition at 8.1 K and 1 bar. Secondly, an AC-susceptibility study reveals that this state is stable and exhibits bulk superconductivity at high T_c and ambient P as long as the sample is not warmed above 125 K. Finally, we present NMR results on the 1 H spin-lattice relaxation rate behaviour in both the β -H phase and the β -L phase.

INTRODUCTION

The series of organic conductors based on the (BEDT-TTF)molecule has provided new interesting compounds ¹. In particular, the β -modification of the trihalide salt exhibits the highest superconducting transition temperature (T_c) ever reported in organic compounds ^{2,3}. More precisely, T_c lies around 1.5 K at ambient pressure ⁴ and is raised up to 7.5 K under a pressure of 1.3 kbar ^{2,3}. Two groups have claimed the observation of superconductivity around 7 K at 1 bar either after temperature cycling ⁵ or after the release of a high pressure at room temperature ⁶. However, this claim is based on 4-probe resistivity measurements which exhibit a two-steps like transition extending over the broad temperature domain 2-8 K. Furthermore, the Meissner expulsion, characteristic of bulk superconductivity, could not be detected at ambient pressure after the cyclings of ref ^{5,6}, while it was under pressure ⁷.

EXPERIMENTAL

Single crystals of β -(BEDT-TTF) $_2$ I $_3$ have been prepared by electrochemical method ¹⁰. The high pressure was provided by helium gas hydrostatic medium, so that it was possible to monitor the pressure, even at low pressure, in the T-P domain where helium remains fluid. The first step of this work was achieved via 4-probe conductivity measurements on single crystals using the standard low-frequency technique. The bulk character and the metastability of the superconducting transition were studied by an AC susceptibility detection: a powdered sample was filling the tank circuit of a Robinson oscillator ¹¹ so that a rapid increase of the resonance frequency was expected, if a bulk superconducting transition occurs. Finally, standard measurements of 1 H spin-lattice relaxation rate (T_1^{-1}) were per-

formed at 6.1 kG and 2.9 kG, using the usual saturation comb pulse sequence.

RESULTS

a. Conductivity

By resistivity measurements, we have defined the basic features of the temperature-pressure cycling which we call the Orsay process. At room temperature, we applied pressure up to 1.5 kbar; then at constant pressure, we cooled the sample down to 33.8 K (arbitrary chosen above 20 K, the freezing point of helium at this pressure). At this regulated temperature, we released the pressure down to its atmospheric value. With further cooling at 1 bar, we observe the very sharp and complete superconducting transition displayed in fig.1. The onset temperature is about 8.5 K,

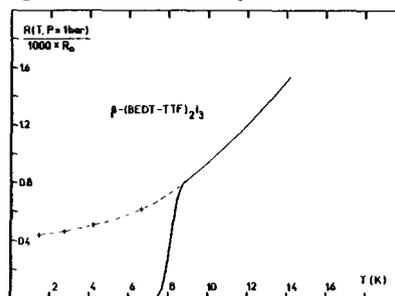


Fig. 1. Superconducting transition at ambient pressure.

while the transition temperature, evaluated by the middle of the resistive transition, amounts to 8.1 K. Magnetic field applied along c^* destroys the superconducting state (typically, the upper critical field H_{c2} is 3.5 T at 1.5 K); the resistivity in the normal state is sketched out by crosses in fig.1. In a second run, the sample was warmed up to 250 K, kept at this temperature for 30 minutes, and then cooled down again to low temperature, without any pressure supply. Consequently, an anomalous resistive behaviour,

occurring at 8 K and suppressed by magnetic field, gives some evidences that traces of superconductivity still remain after this annealing process¹².

b. AC susceptibility

First, we have detected the superconducting transition under pressure. According to the Meissner expulsion observation⁷, the sharp increase of the resonance frequency starting at 8 K (fig.2.a) is the signature of the true bulk superconducting transition. Then, the Orsay process leads to the same characteristic signal (fig.2.b), supporting the fact that the high T_c superconducting state stabilized at ambient pressure exhibits the bulk character. The following runs (various annealings) essentially show that the superconducting phenomenon is unchanged if the annealing temperature at ambient pressure doesn't exceed 121 K (the AC susceptibility response corresponds to that of fig.2.b) while the annealings above 131 K destroy superconductivity, in the sense that no signal could be detected around 7 K (fig.2.c). In the last run, we annealed the sample up to 125 K at ambient pressure, keeping it at this temperature for about 5 minutes. At the same onset temperature ($T \approx 8$ K), a much weaker decrease of the signal was observed (fig.2.d), the overall shift being only 25 % of the other superconducting signals. Very recently¹³, resistivity experiments have given similar conclusions for all these treatments.

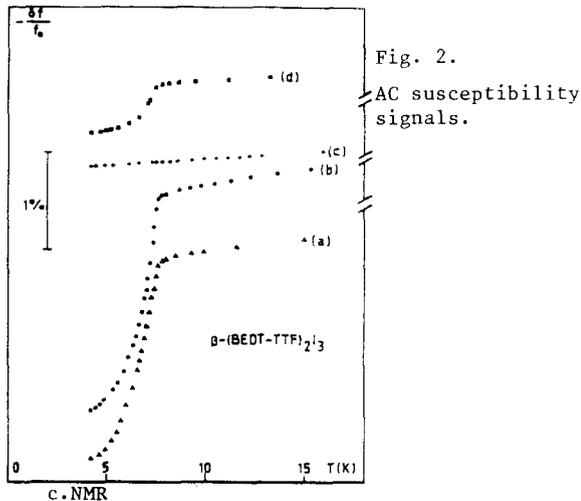
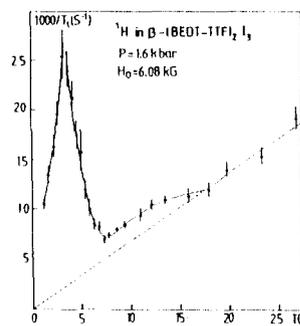


Fig. 2. AC susceptibility signals.

Concerning the NMR results, we focus on the large enhancement of the proton spin-lattice relaxation rate (T_1^{-1}) at the superconducting transition¹⁴. First, the measurements were performed under a pressure of 1.6 kbar. The results at 6.1 kG are displayed in fig.3. The continuous change of T_1^{-1} with temperature breaks down at 7.5 K where a rapid enhancement occurs while decreasing the temperature down to 3.5 K. Due to

the anisotropy of the critical field in this class of materials¹⁵, the temperature domain 3.5 - 7.5 K corresponds to a broad superconducting transition for the powdered sample, each crystal becoming superconductor depending on its orientation with respect to the applied magnetic field. In the condensed state ($T < 3.5$ K), T_1^{-1} decreases but does not tend towards zero; T_1^{-1} that is not an impurity effect since the ambient pressure data reveal a significant long T_1 ($1000/T_1 = 1.8 \text{ s}^{-1}$ at 1.2 K) at the same field in the normal state. At lower field (2.9 kG, fig.4), this behaviour (dashed line) is not modified except in the temperature domain 3.5-7.5 K. The onset temperature for the enhancement (7.5 K) appears to be field independent and lies very near the expected transition temperature in zero field. Moreover, the T_1^{-1} enhancement occurs in a reduced temperature window (5.7-5K) to reach a much higher value at 5 K, and then decreases to meet the high field data at 3.5 K. It is easy to imagine that the zero field limit T_1^{-1} behaviour would be a very sharp increase at $T_c = 7.6$ K, followed by a smooth decrease in the condensed state, what resembles very closely a lambda-like anomaly.

Secondly, at ambient pressure, we have prepared the sample in the high- T_c superconducting state, following the Orsay process: no deviation of the NMR relaxation properties from those obtained under pressure could be detected. On the other hand, the annealing at 250 K suppresses the peak of relaxation and no anomaly occurs around 8 K¹⁴; moreover, a reduction of the high temperature Korringa constant is observed and amounts to about 25%.



DISCUSSION

The superconducting phase stabilized at 8.1 K and atmospheric pressure after the Orsay process cannot be distinguished from the one observed under pressure:

- i) the resistivity drops to zero in a very narrow temperature domain.
- ii) the AC susceptibility signal, compared to one at 1.6 kbar where Meissner effect has been observed⁷, show its bulk character.
- iii) the NMR T_1^{-1} peak, which will be related to superconductivity later, occurs in the same way as under pressure.

On the contrary, all the broad resistive anomalies reported around 7 K at 1 bar either after temperature cycling⁵ or the release of a high pressure at room temperature⁶ do not lead to a zero resistance and are not related to any volume effect⁷; that is corroborated by the absence

of AC susceptibility signal in our experiments. These two well-defined situations lead us to assume that the high- T_c (β -H) and low- T_c (β -L) phases are crystallographically different and correspond to the phase stable at room temperature and either to the modulated structure 9 or to the superstructure 8 at low temperature (there is still a controversy on the exact structure of this phase). Therefore, we suggest that the structural phase transition is suppressed under the moderate pressure of 1.3 kbar. Nevertheless, the phases are energetically close to each other and β -H can be frozen at low temperature and atmospheric pressure after appropriate cyclings. Then, the β -H state gradually converts into β -L if the sample is warmed up at ambient pressure. After annealing above 131 K, the modification is rapid and the incomplete resistivity drops around 7 K do not involve more than 3% of the sample volume kept in the β -H state (within the accuracy of the AC susceptibility detection). Moreover, the observation of an intermediate superconducting signal without change of the onset temperature, after annealing up to 125 K, strongly suggests that these two phases may coexist at low temperature. In this case, β -H converts rather slowly into β -L at 125 K and finally amounts to about 25% of the total volume after 5 minutes; that might explain the resulting zero resistance observed below 8 K in similar conditions¹³. We want to emphasize that in the T-P phase diagram of the structurally identified β -H phase, the superconducting domain begins at 8.1 K under ambient pressure and reveals no break at 1.3 kbar.

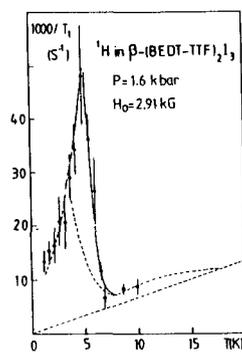


Fig. 4

We comment briefly on the T_c^{-1} divergence near T_c . For an isotropic singlet superconductor, as T_c is approached from above, Maniv and Alexander (MA)¹⁶ have shown that the first-order fluctuations contribution to T_c^{-1} is logarithmically singular in ω_N , the nuclear Larmor frequency. For an anisotropic organic conductor, this gives a critical enhancement $(T_c^{-1})_{cr}$ over the normal Korringa-like contribution $(T_c^{-1})_K$ which can be calculated¹⁴ using band structure cal-

culations¹⁷. At T_c and for fields considered, this gives the order of magnitude for the enhancement $(T_c^{-1})_{cr}/(T_c^{-1})_K$ within a factor 3 to 10. At 1 bar, the ratio of Korringa constants in the β -L and β -H states is not large enough to explain the ratio of the critical temperature by a density of states effect. Therefore, we suggest that the crystallographic modification is changing the effective pairing interaction.

CONCLUSION

We have shown the first stabilization of homogeneous superconductivity in the β -phase of $(BEDT-TTF)_2I_3$ at high temperature and ambient pressure. We propose that the crystallographic transition occurring at 1 bar is responsible of the striking reduction of T_c if no pressure is applied. However, the phase corresponding to the room temperature structure (called β -H) is the only one giving rise to the high- T_c superconductivity and can be frozen at low temperature and atmospheric pressure after the Orsay process. It is worth noting that organic superconductivity is very sensitive to slight changes of physical parameters.

REFERENCES

1. For a review, see for example the proceedings of ICSM 84, Mol.Cryst.Liq.Cryst.119 (1985).
2. V.N. Laukhin et al, Soviet Physics J.E.T.P. Lett.41 (1985), 81.
3. K. Murata et al, J.Phys.Soc.Japan 54,(1985), 1236.
4. E.B. Yagubskii et al, Sov.Phys.JETP Lett.39 (1984) 12.
5. J.F. Schegolev et al, Mol.Cryst.Liq.Cryst. 126 (1985) 365.
6. M. Tokumoto et al, Solid State Commun.54 (1985) 1031.
7. H. Veith et al, Solid State Commun.56 (1985) 1015.
8. K. Angermund et al, reported at the "Ninth European Crystallographic Meeting", 1985, Torino (Italy).
9. T.J. Emge et al, Phys.Rev.B 30 (1984), 6780.
10. K. Bender et al, Liq.Cryst.108 (1984) 359.
11. P. Deschamps et al, Rev.Sci.Instrum.48 (1977) 664.
12. More details can be found in: F.Creuzet et al, J.Physique Lett.46, (1985) L-1079.
13. An analog study of the metastability has been performed by B.Hamzic and G.Creuzet, private Communication.
14. More details can be found in: F.Creuzet et al, Europhys.Lett 1 (1986), 467.
15. M.Tokumoto et al, J.Phys.Soc.Japan 54 (1985) 869.
16. T.Maniv et al, Sol.State Commun.18 (1976), 1197.
17. P.Grant, unpublished.