THERMAL EXPANSION OF THE ORGANIC CONDUCTOR β-(BEDT-TTF)$_2$I$_3$

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We report high resolution thermal expansion measurements between 1.2 and 300 K along the c*-axis in the organic conductor β-(BEDT-TTF)$_2$I$_3$ where the superconducting properties are strongly dependent on the way the system is prepared in the pressure-temperature diagram. We clearly observed a strong anomaly at 172 K related to the structural phase transition and the resistivity anomalies reported by several groups. The temperature analysis in the low temperature regime is coherent with a phonon dominant contribution. Finally, the presence of small hysteresis in a large region around the transition seems to indicate why both the pressure and the temperature cycling may stabilize small regions of the high-T_c phase of the system, as observed.

INTRODUCTION

β-(BEDT-TTF)$_2$I$_3$† is the first ambient pressure sulfur based organic superconductor [1, 2]. (BEDT-TTF)$_2$I$_3$ compound can crystallize in several different crystallographic phases with very different physical properties [3]. At ambient pressure, the β-phase remains metallic at low temperature and becomes superconducting (SC) below 1.2 K [1, 2]. It has been found that SC transition temperature T_c is very sensitive to the applied pressure, T_c first decrease from 1.2 K with pressure, then suddenly increases to about 7.5 K at a pressure of 1.3 kbar [4, 5] and decrease again with further pressure increasing [4]. Furthermore, the stabilization of superconductivity around 7 K at ambient pressure has also been observed either after temperature cycling [6] or after the release of a high pressure at ambient temperature [7]. However these two ways to prepare the system lead to the same incomplete transition: after a first step around 7–8 K, clearly related to superconductivity (i.e. destroyed by a magnetic field), the resistivity reaches zero around 2–3 K. This "two-step" superconductivity can be understood with the simple picture of a mixture of small quantities of a high-T_c phase in a sample where the low T_c phase is dominant. The fact that both pressure and temperature cycling induce such a mixed state

increase the interest of thermal expansion measurements in order to understand the mechanism which stabilizes the high-T_c state. More recently, F. Creuzet et al. [8] report the observation of a complete superconducting transition at 8.1 K and ambient pressue after a well-defined process: first a pressure of 1.5 kbars is applied at room temperature, followed by cooling down to 33.8 K at constant pressure, and finally the release of the pressure down to one atmosphere at this fixed temperature. This first evidence, using 4-probe resistivity technique, has been confirmed by an a.c.-susceptibility study [9] which first shows that the high-T_c state is stabilized if the pressure is released at any temperature below 110 K; secondly, annealing experiments show that the high-T_c (say β-H) state remains stable at low temperature as long as the annealing temperature does not exceed 125 K.

Around this characteristic temperature of 125 K, Mortensen et al. [10] and more precisely Henning et al. [11] reported the observation of a break in the slope of the thermopower data, suggesting that a phase transition may occur at this temperature, but no crystallographic evidence of a transition had been obtained. Furthermore, the crystallographic situation of β-(BEDT-TTF)$_2$I$_3$ is still controversial. Emge et al. [12] detected by neutron scattering the existence of an incommensurate distortion below 220 K. On the other hand, Ravy et al. [13] observed the same distortion by X-ray diffuse scattering but only below 175 K. However, a pronounced distortion of the triiodide chain giving rise to a commensurate

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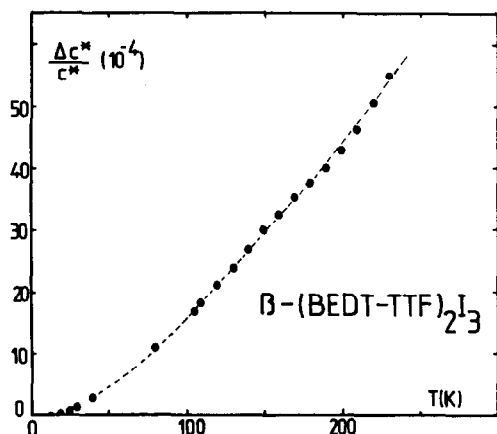†BEDT-TIF: Bis (ethylenedithio) tetrathiofulvalene

Fig. 1. Thermal expansion of β-(BEDT-TTF)$_2$I$_3$ between 1.2 and 300 K.

superstructure has also been reported at 100 K [14]. Finally, small anomalies were observed on the a-axis conductivity by Douglas-Carlson *et al.* [15] around 220 K and more recently on the c*-axis conductivity by Cooper *et al.* [16] at lower temperature.

In organic conductors, thermal expansion was only measured, as far as we know, in the (TMTSF)$_2$X series [17]. In (TMTSF)$_2$PF$_6$, the results were analyzed in terms of a dominant phonon contribution. With the same background, in (TMTSF)$_2$ClO$_4$ which exhibits an anion ordering transition around 24 K, a negative contribution was clearly measured, proportional to the superstructure peak intensity. High resolution thermal expansion then appears very useful to study the crystallographic transitions in organic compounds.

EXPERIMENTAL

In order to measure the thermal expansion with a high sensitivity of a few 10^{-8} for $\Delta l/l$, we used a capacitance technique. Details of the method can be found elsewhere [18]. In the high temperature region, because of small mechanical and thermal fluctuations, the sensitivity changes to about 10^{-6} for $\Delta l/l$. Single crystals of β-(BEDT-TTF)$_2$I$_3$ have been prepared by electrochemical method as reported previously [19]. The β-crystals were separated from the α-ones by their shape and this identification was checked by the EPR at room temperature. Single crystals with typical dimensions $0.50 \times 0.35 \times 0.25$ mm^3 were mounted in the thermal expansion cell with the measurement direction along the c*-axis. We measured two samples between 1.2 and 300 K and results were reproducible.

RESULTS AND DISCUSSION

Figure 1 shows the thermal expansion in the whole range of measurement. β-(BEDT-TTF)$_2$I$_3$ present a
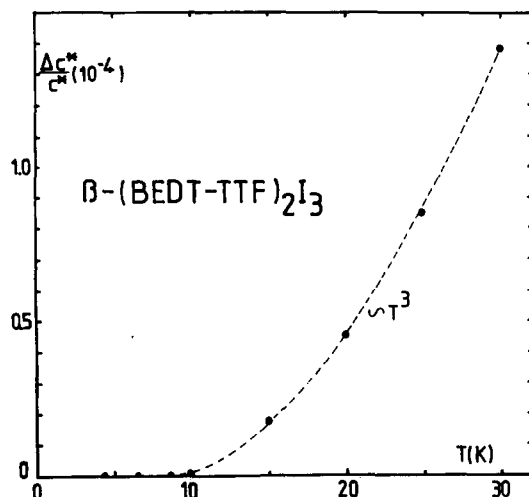

Fig. 2. Low temperature part of the thermal expansion of β-(BEDT-TTF)$_2$I$_3$.

relative change $\Delta c^*/c^*$ of about 1% between helium and room temperature, which is quite large compared with pure Cu (about 0.3% in the same temperature interval) and similar to the results in (TMTSF)$_2$X [17,18].

The low temperature behaviour is given in Fig. 2. Below 40 K, we found a T^3 dependence which changes to T^4 below 12 K. A similar behaviour was found in (TMTSF)$_2$PF$_6$ [17, 18] along a-axis and similarly here it can be ascribed to a dominant large phonon contribution. As a matter of fact, the thermal expansion coefficient $\alpha = 1/c^*$ $\partial c^*/\partial T$ is related to the specific heat C through the well-known thermodynamic relation $\alpha = \gamma K C$, where K is the compressibility and γ the Grüneisen coefficient. Neglecting in a first approximation the temperature variation of K and γ at low temperature, a T^4 behaviour of the thermal expansion correspond to a T^3 dominant phonon term in the specific heat, as recently observed [20].

Figure 3 shows the high temperature thermal expansion. The main behaviour is quite linear, which is again coherent with a dominant phonon contribution above the Debye temperature [21]. The most important point is the clearly observed change in contraction of the lattice at 172 K, temperature which is exactly the occurrence of the structural phase transition observed by Ravy *et al.* [13] on the same crystals. The insert shows the thermal expansion coefficient where the transition temperature is emphasized. From these results, we can evaluate the change of thermal expansion coefficient at the transition $\Delta \alpha \approx 10^{-5}$. K^{-1};

We did temperature cycling in an attempt to detect some difference in thermal expansion behaviour. We found that the phase transition at 172 K remain quite sharp and that it does not depend on the thermal cycling rate. However a very small "hysteresis" in thermal
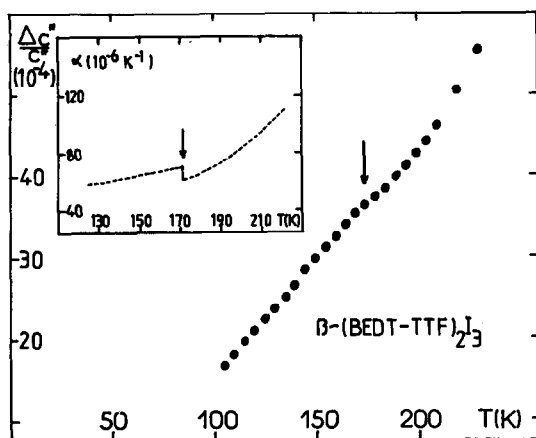
Fig. 3. High-temperature part of the thermal expansion of β-(BEDT-TTF)$_2$ I$_3$. The anomaly around 172 K is emphasized in the insert which shows the thermal expansion coefficient.

expansion was observed in the range 140–210 K. This effect is almost within the limit of experimental error in this temperature region, e.g. the maximal difference between $\Delta c^*/c^*$ values was about 5%. In spite of that the "hysteresis" was reproducible in the way that when raising a given temperature and inversing the thermal variation direction the lattice parameter always follows a curve just above the preceding one. This might be indication that during the temperature cycling procedure strains develop in the crystal leading to the apparition of small amount of high-T_c (β-H) SC phase in the crystal.

As suggested by F. Creuzet et al. [8, 9] the β-L and β-H phases may be energetically close to each other, but separated by a barrier which is temperature and pressure dependent in such a manner that following the "Orsay process" [8] one can freeze the system in the β-H state [22] which seems not to be the lowest energy state from direct ambient pressure measurements where β-L is observed [1, 2]. In such a phenomenological picture, it is easy to understand from the observation of small hysteresis in the thermal expansion why both temperature cycling [6] or pressure cycling at room temperature before cooling [7] can give rise to a mixed state where very small quantities of β-H phase can be present in a β-L sample, so the resistivity appear with a "two-step" behaviour as discussed above.

Finally, it is also important to mention that, within our sensitivity, we did not find any anomaly around 100 K where from X-ray analysis [14] the existence of a phase transition was deduced. Moreover, the same remark can be made around 125 K which is the highest annealing temperature of the β-H state [9] and where an anomaly was observed in thermopower measurements [10, 11].

CONCLUSION

The thermal expansion of β-(BEDT-TTF)$_2$ I$_3$ is mainly due to phonon contribution. We have observed an anomaly at 172 K, clearly related to the structural phase transition where an incommensurate distortion develop below this temperature. In addition some small hysteresis in a large region around the transition may induce internal strains which can be at the origin of poor high-T_c superconductivity observed after temperature cycling.

REFERENCES

1. E.B. Yagubskii, I.F. Schegolev, V.N. Laukhin, P.A. Kononovich, M.V. Karatsovnik, A.V. Zvarykina & L.I. Buravov, *JETP Lett.* **39**, 12 (1984).
2. G.W. Crabtree, K.D. Carlson, L.N. Hall, P.T. Copps, H.H. Wang, T.J. Emge, M.A. Beno & J.M. Williams, *Phys. Rev.* **B30**, 2958 (1984).
3. For a review, see for example the proceedings of ICSM'84, *Mol. Cryst. Liq. Cryst.* **119** (1985).
4. V.N. Laukhin, E.E. Kostyuchenko, Yu.V. Sushko, I.F. Schegolev & E.B. Yagubskii, *JETP Lett.* **41**, 81 (1985).
5. K. Murata, M. Tokumoto, H. Anzai, H. Bando, G. Saito, K. Kajimura & T. Ishiguro, *J. Phys. Soc. Japan* **54**, 1236 (1985).
6. I.F. Schegolev, E.B. Yagubskii & V.N. Laukhin, *Mol. Cryst. Liq. Cryst.* **126**, 365 (1985); V.B. Ginodman, A.V. Gudenko & L.N. Zherikhina, *JETP Lett.* **41**, 49 (1985).
7. T. Tokumoto, K. Murata, H. Bando, H. Anzai, G. Saito, K. Kajimura & T. Ishiguro, *Solid State Commun.* **54**, 1031 (1985).
8. F. Creuzet, G. Creuzet, D. Jérome, D. Schweitzer & H.J. Keller, *J. Phys. Lett.* **46**, L1079 (1985).
9. F. Creuzet, D. Jérome, D. Schweitzer & H.J. Keller, *Europhys. Lett.* 1 461 (1986).
10. K. Mortensen, C.S. Jacobsen, K. Bechgaard, K. Carneiro & J.M. Williams, *Mol. Cryst. Liq. Cryst.* **119**, 401 (1985).
11. I. Henning, K. Bender, D. Schweitzer, K. Deitz, H. Endres, H.J. Keller, A. Gleitz & H.W. Helberg, *Mol. Cryst. Liq. Cryst.* **119**, 337 (1985).
12. T.J. Emge, P.C.W. Leung, M.A. Beno, A.J. Schultz, H.H. Wang, L.M. Sowa & J.M. Williams, *Phys. Rev.* **B30**, 6780 (1984).
13. S. Ravy, R. Moret & J.P. Pouget, private communication.
14. K. Angermund, H. Endres, R. Heinen, M. Hiller, H.J. Keller, C. Krüger, D. Schweitzer & A. Weber, reported at the *Ninth European Crystallographic Meeting*, Torino, Italy, (1985); K. Angermund, H. Endres, H.J. Keller, C. Krüger & D. Schweitzer, to be published.
15. K. Douglas Carlson, G.W. Crabtree, L.N. Hall, P. Thomas Copps, H.H. Wang, T.J. Emge, M.A. Beno & J.M. Williams, *Mol. Cryst. Liq. Cryst.* **119**, 357 (1985).

16. J.R. Cooper *et al.*, private communication.
17. C. Gaonach, G. Creuzet & A. Moradpour, *Mol. Cryst. Liq. Cryst.* **119**, 265 (1985); C. Gaonach, G. Creuzet & C. Noguera, to be published.
18. C. Gaonach, *Thesis*, Orsay, 1985, unpublished.
19. K. Bender, I. Henning, D. Schweitzer, K. Dietz, H. Endres & H.J. Keller, *Mol. Cryst. Liq. Cryst.* **108**, 359 (1984).
20. G.R. Stewart, J. O'Rourke, G.W. Crabtree, K.D. Carlson, H.H. Wang, J.M. Williams, F. Gross & K. Andres, *Phys. Rev.* **B33**, 2046 (1986).
21. This Debye temperature has been evaluated to 195 ± 5 K fron [20] but from the beginning of the linear thermal expansion law it seems to be lower. Note that the same problem occur in the (TMTSF)$_2$X series [18] and may be due to the determination of such a high θ_D from the low temperature T^3 part of the specific heat.
22. More precisely from resistivity measurements one can only say from the observation of a complete SC transition at 8 K that enough β–H phase is present in the system to allow such domains to percolate.