Charge-Carrier Drift Mobilities and Phase Transition in Tetrakis(octylthio)tetrathiafulvalene, TTC_8-TTF, Crystal

Yongfang Li, Chikako Nakano, Kenji Imaeda, Hiroo Inokuchi,* Yusei Maruyama,*
Naoko Iwasawa,† and Gunzi Saito†
Institute for Molecular Science, Myodaiji, Okazaki 444
†Institute for Solid State Physics, Tokyo University,
Roppongi, Tokyo 106
(Received September 4, 1989)

Temperature dependence of the charge-carrier mobility in tetrakis (octylthio)tetrathiafulvalene crystals has been observed in the temperature range of −100—45 °C by the time-of-flight measurement of transient photocarriers. The mobility shows a clear jump at the crystal phase transition which is found in the electrical conductivity measurement. This fact may lead a quantitative analysis of the correlation between the conductivity jump and the phase transition.

The relatively high electrical conductivities in the series of tetrakis(alkyl-thio, -seleno, -telluro)tetrathiafulvalenes, TXC_n-TTF (X=T(S), Se, Te,), have recently been gathering a keen interest in the study of organic semiconductors.[1] The strong dependence on n, the number of alkyl carbons, in the various physical properties of these compounds has lead the concept of "molecular fastener effect".[2] In the case of $TTeC_1$-TTF, on the other hand, the unusually short distance and the unidirectional alignment in the intermolecular tellurium atom configuration are suggestive of a substantial inclusion of covalency in the intermolecular tellurium atoms bonding in addition to the conventional van der Waals interaction.[3]

The reduction of intermolecular distances due to these two effects should result in the increase of the charge-carrier mobility in these crystals, and some preliminary measurements for drift mobilites indicated that it is actually the case.[3,4] In this report, we describe the temperature dependence of the mobility in TTC_8-TTF (Fig. 1) single crystals focusing on the correlation between the carrier mobility and crystal structure especially at the crystal phase transition.[5] TXC_nTTF crystals are known to show somewhat typical solid-state phase transitions.[6] One type of TTC_8-TTF crystals undergoes a crystal phase transition at a temperature just below its melting point (47.6 °C), and its electrical resistivity jumps to 10^2 higher value around the transition.[7] Our aim of this exteriment is to find out the origin of the resistivity jump from the view points of charge-carrier mobility and crystal structure.

Experimental

TTC_8-TTF crystallizes in the two crystal forms depending on the conditions of preparation; plate-like crystals of lower-resistivity (1.2×10^5 S^{-1} cm at r.t.) were obtained from a cold (<−5 °C) hexane–ethanol solution, and needle-like crystals of higher-resistivity (7.0×10^7 S^{-1} cm at r.t.) from a room temperature (>0 °C) solution. The former undergoes a sharp resistivity jump and crystal phase transition around 33 °C, and it essentially turns to a latter crystal.[7]

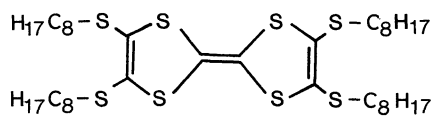

Fig. 1. Molecular structure of TTC_8-TTF.

A plate-like crystal was set in a sandwich-type mobility-measurement cell of which electrodes were a tin oxide coated quartz plate and a copper foil. A pulsed nitrogen laser, PRA LN1000, was used for photo-excitation source, and the time-evolution of photocurrents was detected by a storage-type ocilloscope, Tektronix 7834, through a cascade-preamplifier Tektronix 7A26. Sample temperature was controlled in a conventional thermo-regulated cryostat.

Results and Discussion

Figure 2 indicates a typical photocurrent time-evolution curve of a TTC_8-TTF crystal (0.125 mm thick) which was observed for holes on applying 200 volts and with a 100 ohm input resistance at room temperature. We can recognize a deflection point from the flat part to long tail at ca. 140 ns after the initial

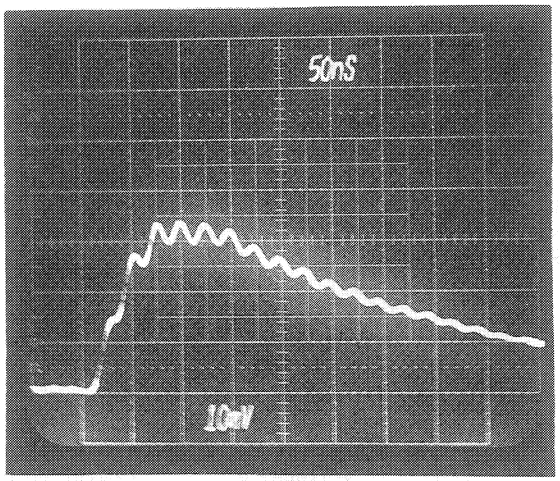

Fig. 2. Photocurrent time-evolution of TTC_8-TTF crystal (0.125 mm thick) for holes at room temperature. Each division on the horizontal axis represents 50 ns.

rising point if we smooth out the high-frequency noises which might come from the amplification unit. If we plot the photocurrent in natural logarithmic scale vs. time, we can identify such points more definitely as shown in Fig. 3. The reciprocals of transit-time, t_d, determined in such a way are almost proportional to the applied electric field up to 2.4×10^4 V cm^{-1} at various temperatures (Fig. 4). The electron and hole mobilities at room temperature are 6.8 and 6.4 cm^2 V^{-1} s^{-1}, respectively, which are substantially higher than a conventional mobility value, μ, for organic crystals, $\mu\leqslant1$ cm^2 V^{-1} s^{-1}, at room temperature.[8]

At lower temperatures, from room temperature down to −100 °C (173 K), the mobilities increased monotonously with decreasing temperature. At higher temperatures, especially around the phase transition point, 33 °C, there exists a sharp drop in the mobilities and it is just corresponding to the resistivity jump at this temperature. A typical photocurrent curve after the phase trandition is shown in Fig. 5, which seems to be drastically changed after the transition. This change might be cuased by the crystal-form or defect-state change or temperature effects as well as the change of time-range in the observation.

All obtained data in the range of −100—45 °C are summarized in Table 1, and they are plotted against absolute temperature, T, in both logarithmic scales in Fig. 6. From the slope in the low temperature region (173—295 K), we can evaluate −1.8 as for the negative exponent n in the relation of $\mu\propto T^n$;

$$\mu\propto T^{-1.8},$$

and this is just consistent with a conventional value for usual organic crystals, $|n|<3$.[8] The amount of decrease in the mobility after the phase transition is about one order of magnitude. Such a clear change in

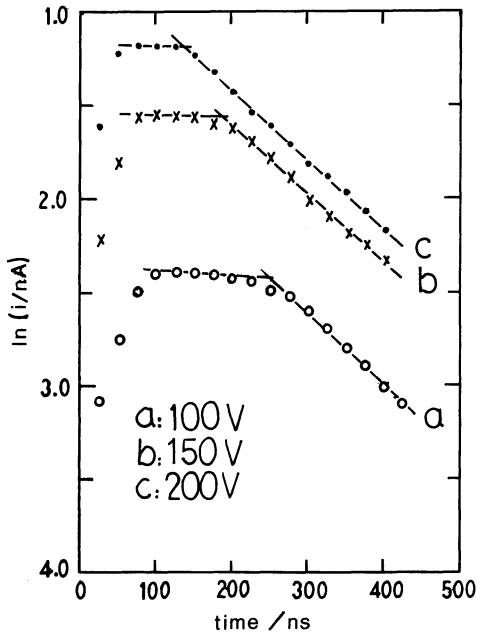

Fig. 3. The natural logarithms of the photocurrent are plotted against time for various applied voltages at room temperature.

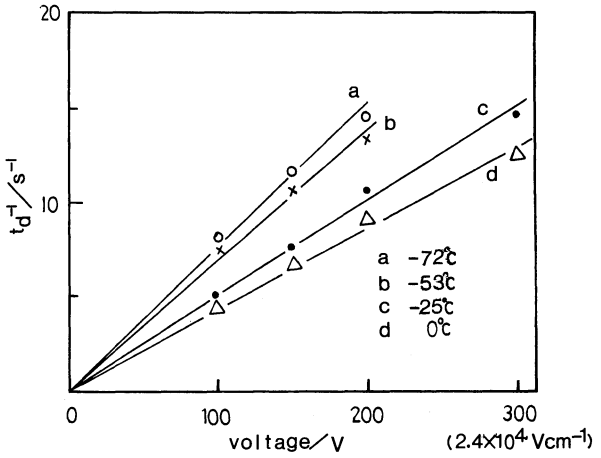

Fig. 4. The reciprocals of transit-time, t_d, are plotted against the applied electric fields at various temperatures.

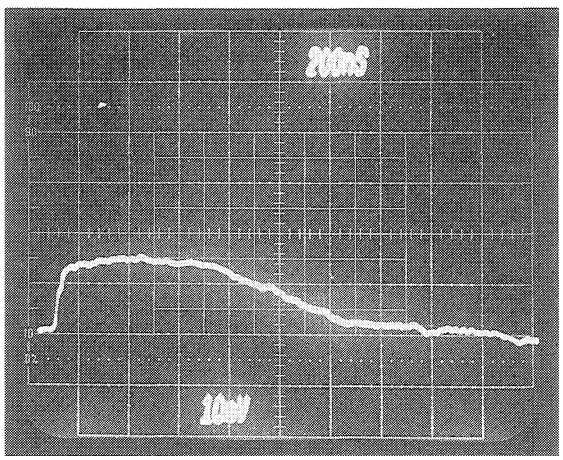

Fig. 5. Photocurrent time-evolution at 45 °C. Each division on the horizontal axis represents 200 ns.

Table 1. Charge-Carrier Mobilites in a TTC$_8$-TTF Crystal at Various Temperatures

Temperature		Mobilities/cm^2 V^{-1} s^{-1}	
t/°C	T/K	μ_{hole}	$\mu_{electron}$
−100	173	16.58	18.20
−72	201	11.88	12.22
−53	220	10.86	10.93
−25	248	7.75	8.41
0	273	6.72	7.59
22	295	6.40	6.78
31	304	4.34	6.01
37	310	1.93	2.54
45	318	0.77	1.33

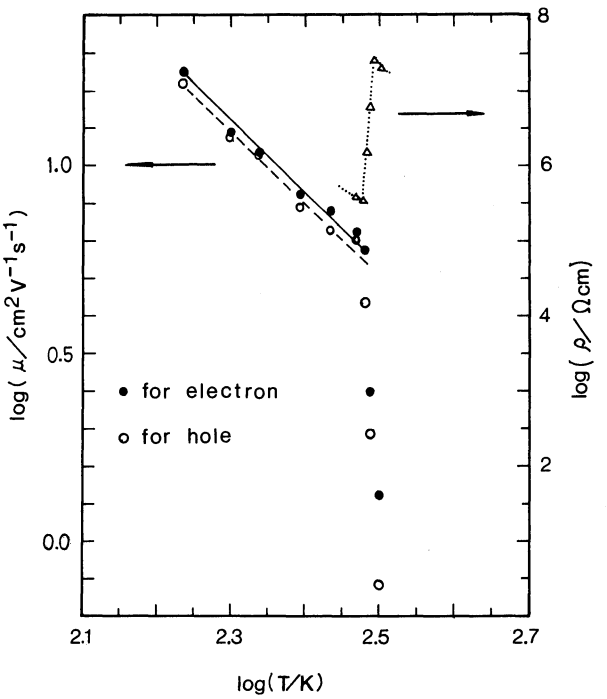

Fig. 6. The logarithms of the mobilities, μ, are plotted against the logarithms of T. Open and full circles are for holes and electrons, respectively. The resistivities are also indicated by open triangles.

the charge-carrier mobility according to a crystal phase transition has been reported in very few cases. The resistivity jump is about two orders of magnitude ($\approx 10^2$), thus we may conclude that the anomalous sharp reduction in mobility is strongly responsible to the jump in the resistivity.

The intermolecular alignment of some alkyl chains seems to become loose after the phase transition based on the result of the crystal structure analysis for both phases.[5] Accordingly the intermolecular interaction between TTF moieties should be weaker after the transition, and this change may result in the reduction of the mobilities and the increase of the band-gap energies. The details of the crystal structure analysis and overlap integral calculation will appear elsewhere soon.[5]

References

1) K. Imaeda, T. Enoki, Z. Shi, P. Wu, N. Okada, H. Yamochi, G. Saito, and H. Inokuchi, *Bull. Chem. Soc. Jpn.*, **60**, 3163 (1987).

2) H. Inokuchi, G. Saito, P. Wu, K. Seki, T. B. Tang, T. Mori, K. Imaeda, T. Enoki, Y. Higuchi, K. Inaka, and N. Yasuoka, *Chem. Lett.*, **1986**, 1263.

3) H. Inokuchi, K. Imaeda, T. Enoki, T. Mori, Y. Maruyama, G. Saito, N. Okada, H. Yamochi, K. Seki, Y. Higuchi, and N. Yasuoka, *Nature (London)*, **329**, 39 (1987).

4) Y. Maruyama, unpublished results.

5) C. Nakano et al., to be submitted.

6) P. Wang, T. Enoki, K. Imaeda, N. Iwasawa, H. Yamochi, H. Urayama, G. Saito, and H. Inokuchi, *J. Phys. Chem.*, **93**, 5947 (1989).

7) K. Imaeda, C. Nakano, H. Inokuchi, and G. Saito, 3rd China-Japan Joint Symposium on Conduction and Photoconduction in Organic Solids and Related Phenomena, 1989, Abstr., p. 51.

8) Y. Maruyama, *Mol. Cryst. Liq. Cryst.*, **171**, 287 (1989).