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Charge Carrier Trapping in Organic Crystals†

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Abstract—Studies on the carrier trapping characteristics of anthracene, chrysene and tetracene crystals using thermally stimulated current (TSC) techniques and space-charge-limited-trap-limited current (SCLTLC) techniques are described.

TSC studies on melt-grown, vapor-grown and radiation damaged anthracene crystals, melt-grown chrysene crystals and vapor-grown tetracene crystals have shown that a TSC peak at 255–265 °K (trap depth 0.6–0.8 eV) is obtained for all these crystals and appears to be relatively insensitive to the physical state of the crystals.

SCLTLC measurements on many high purity melt-grown and thick ($\sim$ 1–2 mm) vapor-grown anthracene crystals using a liquid hole injecting contact ($AlCl_3$-anthracene/nitromethane), gave trap densities ranging from 10^{14} to 10^{19} traps cm^{-3} for both types of crystals. Hole trap densities did not correlate with the density of dislocations emerging through (001), indicating that the hole traps in these crystals are not directly related to the dislocation content.

1. Introduction

Although the existence of charge carrier trapping has now been well established in organic solids, the physical nature of carrier traps is still uncertain. In some cases evidence has accumulated which indicates that impurities are a major cause of carrier trapping.(1) In this case it is generally considered that discrete level traps are

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introduced by impurity molecules. In other studies, results have indicated that physical or structural defects in the crystal lattice can also act as carrier trapping centers.(1,2) Such traps can be considered to arise from " perturbed " molecules in the crystal lattice causing local polarization energy changes which introduce both hole and electron traps. Since, in general, there will be a distribution of perturbed molecules, it is usually considered that distributions of traps, both below the conduction band and above the valence band, will be introduced by this mechanism.

In order to shed further light on hole trapping in molecular crystals, trapping parameters have been evaluated for pure melt-grown, vapor-grown and irradiated anthracene crystals by means of thermally stimulated current (TSC) techniques(3) and limited-trap-limited-current (SCLTLC) techniques.(4,2d) TSC studies have also been carried out on vapor-grown tetracene crystals, melt-grown chrysene crystals and Teflon samples for comparison.

2. Experimental

Anthracene and chrysene crystals were obtained and characterized by methods described previously, the total impurity content not exceeding 10 ppm in any crystal.(2b,c,5) Samples were irradiated using a 4000 Curie 150 C γ-beam unit supplied by Atomic Energy of Canada, Limited. Tetracene crystals were obtained by subliming pre-purified material at 225 °C in a stream of nitrogen (0.3 cu ft h^{-1}). The starting material was purified by column chromatography(6) and two sublimations. Four impurities were detected by gas chromatography, the total impurity content in this case amounting to 0.3%.

TSC studies were carried out using methods described previously.(3) Blocking electrodes were employed.(3a,c) Measurements were carried out on crystals having approximately the same electrode area (0.25 cm^2) and thickness (1 mm) with an applied voltage of 200 volts. Thinner crystals were employed in the case of tetracene (100 μ).

SCLTLC studies were carried out in an arrangement similar to that described previously.(7) A Cary 31/31V vibrating reed electrometer and a Keithley 240 power supply were employed for current measurement.

3. Results and Discussion

Single peak TSC maxima were generally obtained indicating discrete trap levels. Typical thermally stimulated current plots at several heating rates are shown in Fig. 1 for a melt-grown anthracene crystal. The TSC peak magnitude at the same heating rate was used as an approximate measure of trap density and the trap depth was evaluated from the variation of the TSC peak maximum (T_m) with heating rate.(8) Data on three types of anthracene crystals are summarized in Table 1. Trap depth was also determined by Grossweiner's method.(9) An average value of 0.6 eV was obtained for several heating rates, in good agreement with the data in Table 1. In general, TSC data were quite similar for the different types of anthracene crystal within experimental error. The trap depth was in the range 0.6–0.8 eV for all the crystals in agreement with previous studies.(3) The TSC magnitude was also similar for all crystals, being slightly lower for the irradiated crystals. The reduction in TSC peak intensity observed in irradiated anthracene crystals may be due to the introduction of traps at deeper levels than 0.6–0.8 eV. The effect of high energy radiation may thus be similar to mechanically deforming anthracene crystals in this respect.(3c,12) Any deep traps introduced in this way were not observed in the present study, however, since the temperature range investigated did not allow detection of traps deeper than 1.0 eV. Since lower dislocation densities are generally found in vapor-grown crystals(2c,d) it is unlikely that the carrier traps revealed by TSC studies are directly associated with dislocations emerging through (001). Previous workers have arrived at substantially the same conclusion.(3c)

Similar TSC peaks were found in melt-grown chrysene and vapor-grown tetracene crystals. Table 2 summarizes TSC data for several

TABLE 1 Thermally Stimulated Current for Anthracene Crystals (6–8°/min)

Crystal type	Peak current (Amp × 10^{13})	Peak temp. (°K)	Trap depth (eV)
Melt-grown	5.3	257	0.6
Vapor-grown	5.2	256	0.8
Irradiated melt-grown (10^7 rad)	2.2	257	0.6

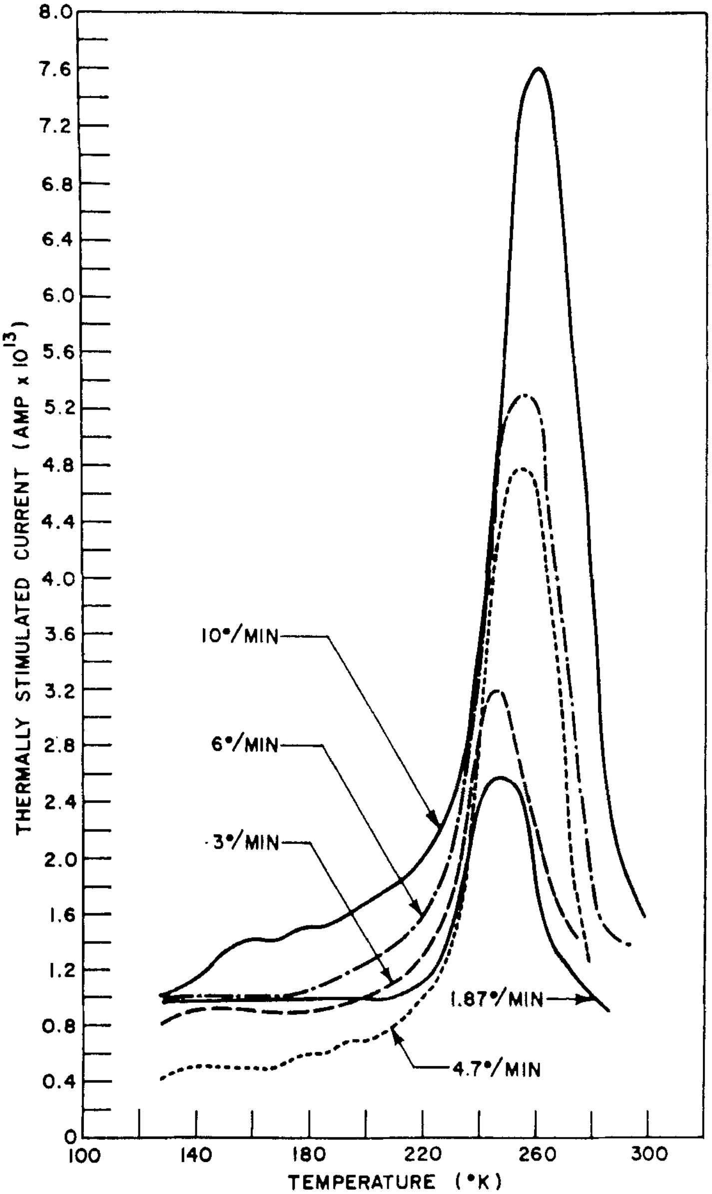

Figure 1. Thermally stimulated currents in melt-grown anthracene.

TABLE 2 Thermally Stimulated Current in Several Solids (5–7°/min)

Solid	Peak current (Amp)	Peak temp. (°K)
Tetracene (vapor-grown)	4.2×10^{-11}	263
Chrysene (melt-grown)	4.6×10^{-13}	256
Teflon	2.2×10^{-13}	240

substrates at the same heating rate. The molecular crystal substrates anthracene, tetracene and chrysene gave TSC peaks located within a few degrees of each other. Tetracene gave a higher current peak due to the thinner crystals employed. A TSC peak was also obtained in a Teflon substrate. However, the peak was generally lower in magnitude and located at a lower temperature than those found in the molecular crystals. The similarities in the data obtained on molecular crystal substrates suggests that the same physical phenomenon is responsible for the deep, discrete level trap revealed by TSC studies in all these crystals. It is unlikely that a common dissolved impurity is responsible for the effect. Some common physical defect is a possibility, since anthracene and chrysene both crystallize in the monoclinic system and the triclinic tetracene crystal structure is closely related to a monoclinic structure.(10) This may explain why the TSC peak observed in Teflon specimens is farther removed from the molecular crystal TSC peaks. Teflon is a more complex physical system consisting of both crystalline and amorphous regions. However, the similarity of the TSC data in several substrates also suggests that an atmospheric effect involving trace quantities of adsorbed oxygen may be responsible, as suggested originally by Bree and Kydd.(11) In this case the differences between the Teflon data and the molecular crystal data are not readily explained.

Typical current–voltage characteristics obtained for an anthracene crystal with a hole-injecting solution electrode, the same electrode evaporated to dryness and conducting silver paint electrodes, are shown in Fig. 2. Superlinear current–voltage characteristics were generally obtained for the solution contact with the contact biased positive ($J \alpha V^n$, with $n \geq 2$). When the contact was evaporated to dryness, the current level was found to be lower and almost linear

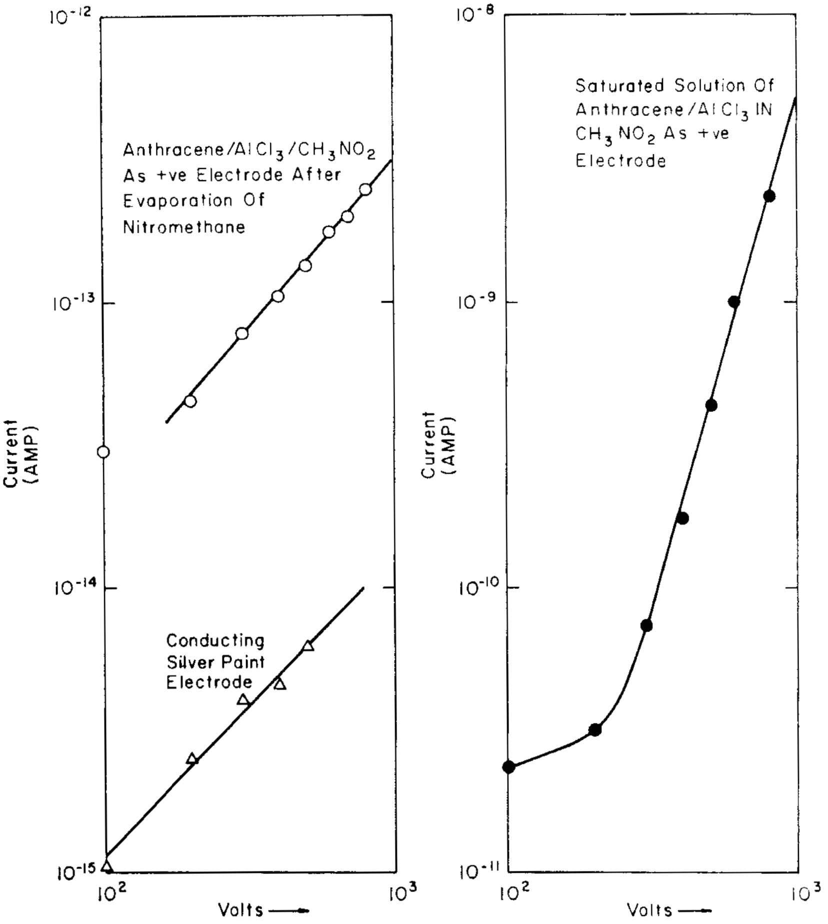

Figure 2. J–V characteristics for anthracene.

with applied voltage. The current level was higher than that obtained with silver paint electrodes, however. The current in the superlinear region was found to depend upon d^{-m} with $m \geq 3$. Since the solution contact more clearly satisfied the criteria for SCLTLC, these contacts were generally employed to investigate anthracene crystals.

In the majority of crystals evaluated it was found that J depended upon V with $n > 2$. It was concluded, therefore, that in both melt- and vapor-grown crystals of high purity, the observed SCLTLC characteristics are best interpreted in terms of an exponential hole trap distribution.(4) The trapping parameters H and kT_c were evaluated from the current–voltage characteristics employing the usual relationship.(4,2d) Values for a range of melt- and vapor-grown crystals are listed in Table 3. Values of H ranged from 10^{14} cm^{-3} to 10^{19} cm^{-3} for both types of crystal showing no obvious correlation with either dislocation density or impurity content.(2c) This is in contrast with previous SCLTLC studies where a correlation was observed between trap density and dislocation density.(2d) kT_c varied over the range 0.04 eV to 0.09 eV, showing again no obvious dependence upon crystal type. If traps of this nature are associated with molecules perturbed to varying degrees from their lattice positions it is not too surprising that a direct correlation between H and dislocation density is not found. Many of the perturbed molecules in the crystal lattice will be associated with dislocations but not necessarily all of them. H should be related to the total number of perturbed molecules in the crystal lattice per unit volume and kT_c to the relative contributions of slightly perturbed and highly perturbed molecules. An interpretation in these terms of trap distribution parameters in anthracene crystals is presented elsewhere.(13) An attempt was made to evaluate the effect of high energy radiation (10^7 rad) on the trapping parameters. Crystals so treated did not exhibit SCLTLC characteristics, however, and no conclusions could be drawn regarding the effect of high energy radiation on trap distribution parameters.

TABLE 3 Trapping Parameters for Anthracene Crystals

	Melt-grown			Vapor-grown	
	kT_c (eV)	H (cm^{-3})		kT_c (eV)	H (cm^{-3})
1.	0.041	1.5×10^{18}	1.	0.057	1.2×10^{17}
2.	0.065	1.6×10^{15}	2.	0.069	3.1×10^{15}
3.	0.075	2.3×10^{15}	3.	0.048	1.1×10^{18}
4.	0.034	2.7×10^{17}	4.	0.065	3.6×10^{15}
5.	0.087	1.5×10^{14}			
6.	0.042	1.7×10^{19}			

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