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Charge-carrier Drift Mobility in Pyrene Single Crystals

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Synopsis. The charge-carrier drift mobility in highly pure pyrene single crystals was measured. Observed values were $(3.8\pm0.1)\times10^{-3}$ cm^2 V^{-1} s^{-1} for electrons and $(3.3\pm0.4)\times10^{-3}$ cm^2 V^{-1} s^{-1} for holes at 345 K. The mobilities increased with the temperature between 333—374 K with an activation energy of 0.43 ± 0.01 eV for electrons.

Measurements of charge-carrier drift mobility in organic crystals have given the most important information in the studies of their electrical conduction processes. A few years ago, we observed rather small carrier mobilities in perylene single crystals and analyzed the obtained results taking the excimer-like excess electron state into consideration.[1)]

In this note, we will report the behavior of carrier drift mobility in pyrene single crystals in which the "dimeric structure" in an unit cell is also realized and in which its effect results in a pronounced excimer emission. In order to confirm the hypothetical transport model based on the "dimeric structure" in a perylene crystal,[1)] a similar type of measurement should be done using a dimeric pyrene crystal.

Highly pure pyrene was obtained by a careful zone-refining technique after conventional chemical and physical treatments. A single crystal ingot was grown using a pulling-down method in a Bridgman furnace from which disk-like, single crystals were carefully cleavaged out in a size of ≈10 mm × 10 mm × 0.5 mm (in thickness). Electron and hole drift mobility in the c′-direction were measured using the previously reported measuring system,[1)] but with the air-gap-discharge light pulser replaced by a xenon flash tube (Ushio Denki) as an exciting light source. Since the photocurrent sensitivity was not high enough at room temperature, the drift mobilities were observed in the temperature range of 333—374 K.

The typical photocurrent pulses observed are shown in Fig. 1 under the conditions specified in the caption. The observed electron or hole mobility was almost independent of the electric field between 1×10^4—2×10^4 V cm^{-1}, the mean value in the c′-direction was $(3.8\pm0.1)\times10^{-3}$ cm^2 V^{-1} s^{-1} for electrons and $(3.3\pm0.4)\times10^{-3}$ cm^2 V^{-1} s^{-1} for holes at 345 K. These values are smaller by about one order than those in a perylene crystal.[1)] The electron mobility increased with the temperature between 345—374 K. Plots of the logarithm of the mobility *vs.* T^{-1} in Fig. 2 show an almost straight line of 0.4 eV in this temperature range. The hole mobility also showed a similar temperature dependence.

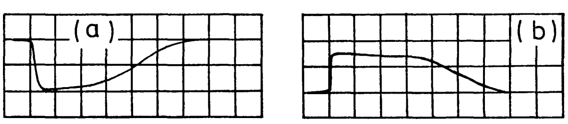

Fig. 1. Typical photocurrent *vs.* time curves.
(a) Electron current, (b) hole current, at 345 K, 0.2 ms/division (abscissa).

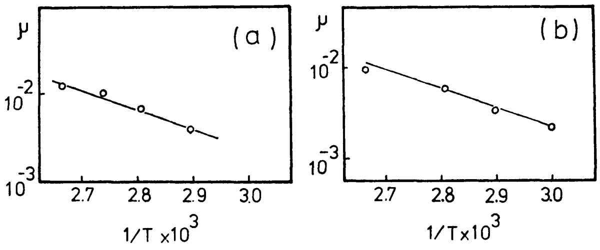

Fig. 2. Temperature dependence of drift mobility.
(a) Electron, (b) hole.

In order to elucidate the experimentally obtained characteristic of the electron drift mobility in the c′-direction, we display the relevant transfer integral values in Table 2, comparing them with the corresponding ones in a perylene crystal[1)] and an anthracene crystal.[3)]

Table 2. A comparison of the electron-transfer integrals in the c′-direction in a pyrene crystal with those in a perylene or an anthracene crystal in units of 10^{-4} eV

Molecule-pairs	Pyrene	Perylene	Anthracene
1— 8	74.3	3.57	0.38
1—11	− 0.60	0.84	0.67
1—13	−13.4	0.13	0.38

The physical situation in a pyrene crystal seems to be qualitatively similar to the case of perylene when we compare the values indicatied in Table 2 with the observed mobility. In the pyrene crystal, an excess electron on a dimeric point may be somewhile localized. through the formation of an excimer-like electronic state between two molecules. The excimer state in pyrene crystals is known to be located 0.4 eV below the mutually independent molecular lowest excited state.[4)] The relative displacement between dimeric molecules due to an excimer formation was estimated by Birks to be ~0.2 A.[4)] These two effects may cause the fluctuation in the transfer integrals and also the activation process in the electron-transport procedure. This type of fluctuation should be significant in determining the drift mobility value in this case.

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molecular crystals may be determined mainly by means of the intermolecular resonance integrals or transfer integrals, which can be evaluated from the molecular wavefunctions, taking the crystal structure into consideration. The crystal structure of pyrene was analyzed by Robertson and White.[2]

The transfer integrals for each pair of molecules in a pyrene crystal were calculated using Hückel-type molecular orbitals, in which a single Slater orbital exponent, 3.08×10^8 cm^{-1}, was employed. Only the two center integrals were considered, the other procedures in the calculation were almost the same as those reported by Katz *et al.*[3]

In Table 1 we display the transfer integrals calculated between the molecule at Position 1 and the several neighboring molecules, the numbering of which is shown in Fig. 3. The same formalism as that shown in Ref. 1 will lead to the drift mobility in the c′-direction, 1.4×10^{-4} cm^2 V^{-1} s^{-1} at 345 K, using the formulae deduced by Gosar and Choi[5] and the activation energy of 0.44 eV.

Although the agreement between the calculated value, 1.4×10^{-4} cm^2 V^{-1} s^{-1}, and the observed value, 3.9×10^{-3} cm^2 V^{-1} s^{-1}, at 345 K is not so good as in the perylene crystal (0.015 cm^2 V^{-1} s^{-1} and 0.017 cm^2 V^{-1} s^{-1} respectively), the validity of the proposed electron-transfer mechanism may seem to be confirmed.

TABLE 1. INTERMOLECULE TRANSFER INTEGRALS IN UNITS OF 10^{-4} eV

Molecule number	Electron	Hole
2	99.5	76.7
3	−13.5	38.1
4	− 4.07	1.06
5	−13.5	38.1
6	3.58	14.2
7	− 4.07	1.06
8	74.3	−79.6
9	0.30	0.0
10	− 0.31	0.33
11	− 0.60	−1.03
12	74.3	0.16
13	−13.4	0.14

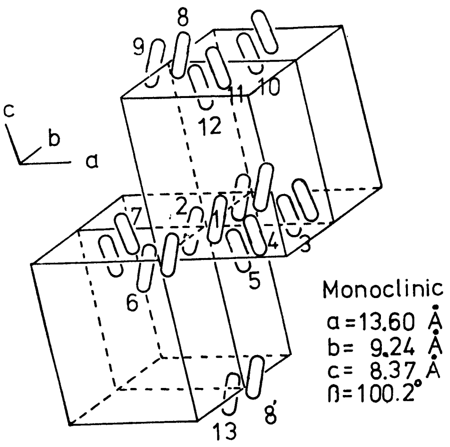

Fig. 3. Schematic representation of the pyrene unit cells, showing the numbering of the molecules used in this paper.

The large discrepancy between the previously reported value[6] and the present one may be partly due to the difference in the purity of the specimen and also partly to that in the crystal growth method. The former crystals were grown from a solution.

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