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NOTE

Hole Mobilities and Anomalous Current Transients in Crystalline Naphthalene

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Hole mobilities in naphthalene have been measured in the range 200–350 K. In addition to "normal" current transients, it is found that current can be carried along the (oxidized?) surface of naphthalene crystals, yielding well-defined mobilities of a few $cm^2/Vsec$.

INTRODUCTION

Drift mobilities of electrons and holes in crystalline naphthalene have been measured several times in the last fifteen years: Silver *et al.*,[1] Spielberg *et al.*,[2] and Mey and Herrmann,[3] obtained results in fair but imperfect agreement (see Table I). In addition, one quite different set of values had been measured several years ago in this laboratory.[4]

All these results were obtained by the well-known time-of-flight method,[5] in which the drift mobility in the direction of the applied field is deduced from the measurement of a transit time t_r equated to $L^2/\mu V$ (or $0.79\ L^2/\mu V$ in SCL conditions). As μ is generally assumed to be independent of the electric field in organic solids, the relation $t_r \propto V^{-1}$ is usually taken as the criterion of a good measurement of μ. Differences in values of μ measured by different workers can often be explained by the occurrence of shallow trapping, the evidence being an exponential temperature dependence of μ in this case, in place of T^{-n} dependence in the absence of trapping. In general, different measurements of μ on the same material yield, after

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TABLE I

Hole mobilities in naphthalene (cm^2/Vsec) and temperature dependence $\mu^+ \propto T^{-n}$

Applied field direction	a		b		c'	
	μ^+	n	μ^+	n	μ^+	n
This work	0.9 ± 0.1	3 ± 0.5	1.4 ± 0.1	2.8 ± 0.3	0.35 ± 0.05	1 ± 0.2
Ref. 1	0.9		1.4		0.4	
Ref. 2	0.8		1.2		0.55	
Ref. 3	0.81	1	1.41	0.8	0.99	2.1
Ref. 7					0.4	

correction for shallow trapping, much better agreement[5] than in the present case.[1,4] Mobilities in naphthalene have therefore been reinvestigated, in an attempt to understand the origin of the dependence.

EXPERIMENTAL SETUP

Naphthalene single crystals were grown by the Bridgman method from zone-refined scintillation-grade material. More elaborate purification methods have been proposed but, as one of the purposes of this work was a comparison with the results of Ref. 4, the sample preparation techniques as in Ref. 4 were used. Electron trapping being severe and electron yields small, only hole transients were studied.

Samples 1 to 3 mm thick were cut along (*ab*), (*ac'*) and (*bc'*) planes, polished on benzene-soaked tissue, and mounted between semitransparent electrodes of Al on quartz plates, in a copper crystal holder which temperature could be adjusted by circulation of a thermostated fluid. The sample holder could be placed under vacuum or under any atmosphere (usually pure N_2 or air were used).

The excitation was provided by a discharge in Hg vapor (General Electric BH6 lamp), delivering a 1.5 μsec pulse at 2850 Å, selected by an interference filter. At this wavelength, light is strongly absorbed by the naphthalene crystal: $\varepsilon > 5 \cdot 10^4$ cm^{-1},[6] but the photon energy is smaller than the band-gap, and only carrier generation processes involving several quanta, such as singlet–singlet annihilation are possible.[7,8] Light intensities were too low for this process to be effective, and only extrinsic processes such as carrier detrapping by excitons or assisted injection were active, hence the large difference between hole and electron yields.

The current transients were amplified (Keithley 102B), displayed on a Tektronix 545 oscilloscope and photographed.

RESULTS AND DISCUSSION

1) Freshly cleaved crystals, mounted and studied in a pure N_2 atmosphere, gave good hole transients. The temperature dependence of $\mu^+ \propto T^{-n}$ above 250 K is indicative of intrinsic mobility (Fig. 1). These results (0.9; 1.4 and 0.35 $cm^2\ V^{-1}\ s^{-1}$ respectively along $\vec{a}$, $\vec{b}$, and $\vec{c}$, axis) are compared to those obtained by others[1-3,7] on Table I. Below 250 K, μ^+ decreases exponentially, indicating the presence of shallow traps, with a concentration of about 10^{-10} and a depth $E_t = 0.45 \pm 0.05$ eV. Successive experiments

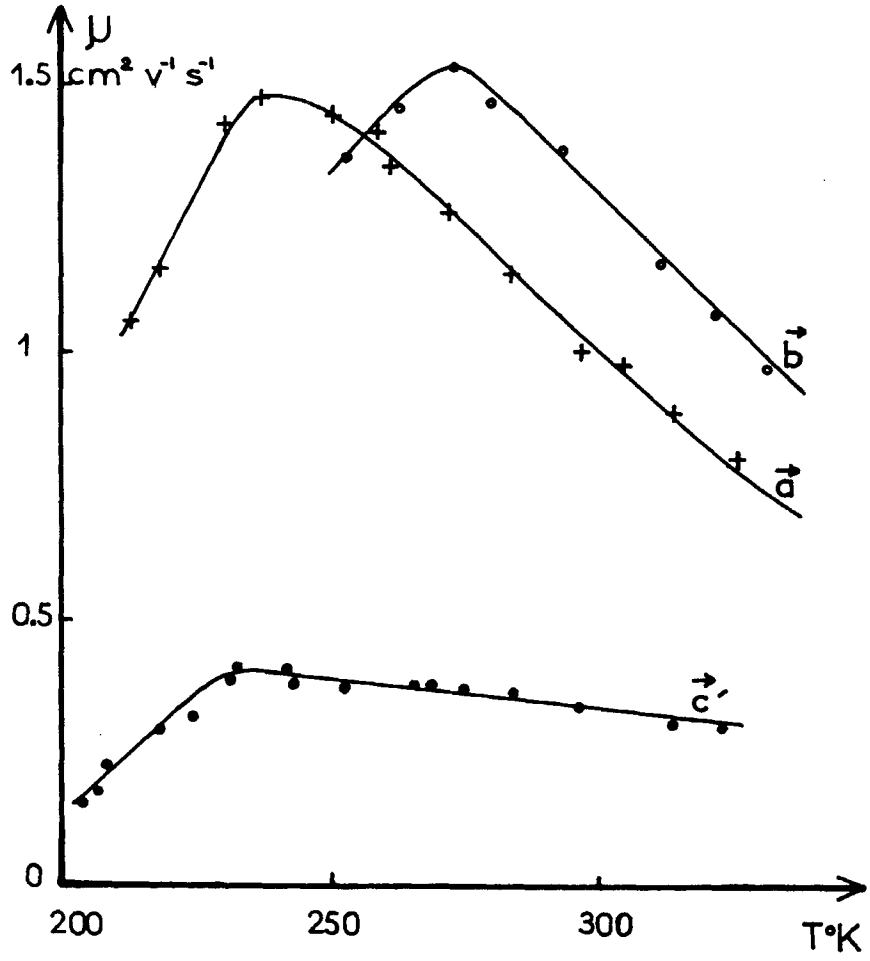

FIGURE 1 Temperature dependence of hole mobilities, for electric field applied along *a*, *b* and *c'* axes.

yielded the same mobilities, as long as the sample remained under N_2 gas.

2) After a crystal had given such results, it was placed and studied in air (or O_2). After a few pulses at 2850 Å, the hole transient current changed, and two transients appeared simultaneously (Fig. 2), the longer corresponding to an unchanged mobility. A second, larger, mobility, which value is approximately twice the first, can be deduced from the new transient (whose length is $\propto V^{-1}$), slowly increasing with T over the whole temperature range explored from 220 to 325 K (Table II).

This additional current can also be generated by light at wavelengths longer than naphthalene absorption, showing that it is associated to photochemical reaction products. If the exciting beam is diaphragmed, and care is taken to avoid any excitation of the sample's lateral surfaces, this current disappears. Presumably, it corresponds to a surface current flowing through a photooxidized surface region. The chemical composition and crystal structure of this region are unknown. If it is distorted, it is surprising that carriers are more mobile there than in naphthalene single crystal. Could it be a different phase stabilized by a small amount of impurity? There is no obvious way by

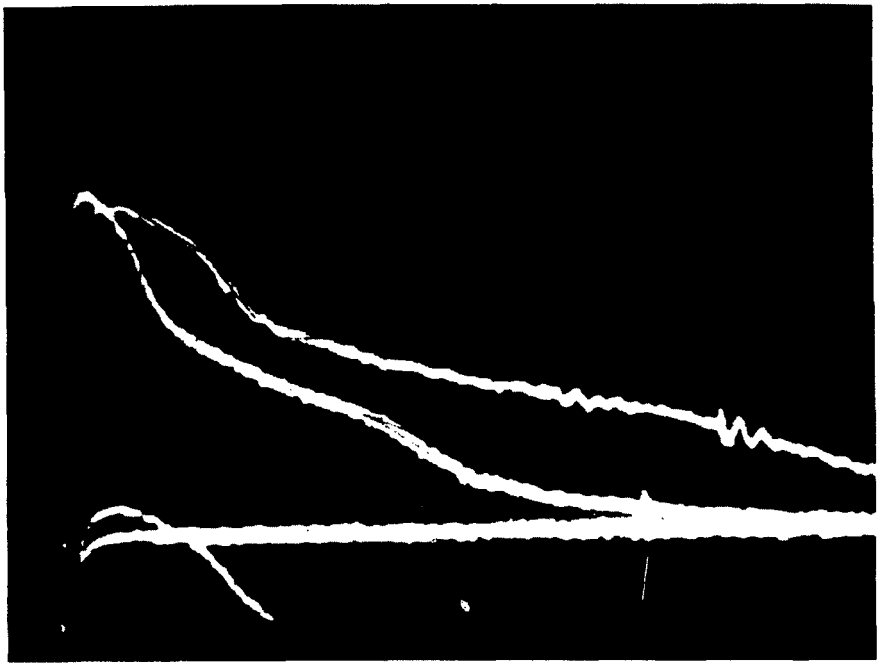

FIGURE 2 A typical current transient showing the two transit times. The two transients are obtained in the same experimental conditions, with different time bases (50 μs/div. and 100 μs/div.)—300 V applied to a 2.4 mm thick crystal, along a axis. $T = 335$ K.

TABLE II

"Surface" mobilities for electric field applied along various crystal directions

Direction of applied field[a]		a	b	c'
Holes	This work	2.1	2.1	
	Ref. 4	2.1	5.5	3.9
Electrons	This work	2.15	2.15	
	Ref. 4	3.6	3.6	3.4

[a] Relative to naphthalene crystal axes.

Note that, since the structure of the surface layer is not known, the orientation of the applied field relative to it is not known.

which a single crystal of a photoproduct could grow at the expense of the naphthalene crystal. Transport properties of naphthoquinone are not known, but carrier mobilities in anthraquinone are small.[9]

3) The new "mobilities" obtained in the present experiments are still smaller than those measured previously,[4] also reported on Table II. The temperature dependence also are different; in Ref. 4 $\mu \propto T^{-n}$ above room temperature and is limited by shallow trapping on relatively deep traps below 300 K. Transient SCL currents were observed in Ref. 4, allowing to estimate the cross-section through which the "new" current flowed; it was found to be $\sim 10^{-4}$ the geometrical cross-section of 5 mm^2, in agreement with current flow in a surface region approximately 1 micron thick. Although we believe that the same basic phenomenon was observed in Ref. 4 and here, the origin of the difference in results is not known.

4) Evidence that naphthalene crystals can be inhomogeneous has been presented by Dresner *et al.*,[10] who studied SCL currents in the dark. They found that their results could not be explained by the usual theory of SCL currents, and also that, above the trap-filled limit the current was still four orders of magnitude smaller than the trap-free SCL current. They propose that filamentary unipolar conduction occurs. This is a possibility—filamentary double injection is often observed in organic solids—but, since no guard electrode was used, it is equally possible that surface conduction was observed in Ref. 10 as well.

5) The present results should serve as a warning. In transport experiments on materials which must be excited in the ultraviolet, photoproducts, which absorb at longer wavelengths, and are therefore easier to excite than the host, may interfere with the results, and not only by introducing trapping

centers. In experiments involving current flow along a surface, the transport properties investigated may be different from those of the bulk; an example would be some photo-Hall experiments.[11]

References

1. M. Silver, J. R. Rho, D. Olness, and R. C. Jarnagin, *J. Chem. Phys.*, **38**, 3030 (1963).
2. D. H. Spielberg, A. I. Korn, and A. C. Damask, *Phys. Rev.* **B**, **3**, 2012 (1971).
3. W. Mey and A. M. Hermann, *Phys. Rev.* **B**, **7**, 1652 (1973).
4. M. Heritier, Thèse de 3e cycle, University of Paris, unpublished (1969).
5. N. Karl, *Festkörperprobleme XIV*, 261, Pergamon Viceveg (1974).
6. A. Bree and T. Thirunamachandran, *Mol. Phys.*, **5**, 397 (1962).
7. G. Castro, *I.B.M. J. Res.*, **15**, 27 (1971).
8. C. L. Braun and G. M. Dobbs, *J. Chem. Phys.*, **53**, 2718 (1970).
9. Z. Burshtein and D. F. Williams, *Mol. Cryst. Liq. Cryst.*, **43**, 1 (1977).
10. J. Dresner, M. Campos, and R. A. Moreno, *J. Appl. Phys.*, **44**, 3708 (1973).
11. J. Dresner, *Phys. Rev.*, **143**, 558 (1966).