ANISOTROPY AND TEMPERATURE DEPENDENCE OF THE DRIFT MOBILITY OF HOLES IN CRYSTALLINE IODOFORM

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Time-of-flight studies of the drift mobility of holes in crystalline iodoform are reported. The mobilities were measured along the crystal six-fold axis (c) and in the direction perpendicular to c. Mobility values above 270 K follow a T^{-n} dependence with $n \approx 0.3$ and 1.5 for the two directions, respectively. Below 270 K the mobilities are temperature activated.

1. Introduction

Recent studies of the steady-state [1] and two-photon-induced photoconductivity [2] in iodoform (triiodomethane) single crystals have shown that iodoform exhibits a high photogeneration yield when excited with light of wavelengths shorter than ≈340 nm, or, by a two-photon absorption, between 480 and 640 nm. The present paper supplements these investigations with data on time-of-flight measurements in iodoform crystals providing information on the drift mobility of charge carriers.

2. Experimental

Iodoform was purified by multiple vacuum sublimation, the initial sublimation step being carried out through activated carbon. Single-crystalline boules were grown from the vapour phase by the method described in ref. [3]. The purification and crystal growth steps were carried out in the dark to avoid decomposition of the material (cf. refs. [4,5]). Plane-parallel samples, typically 0.4–1.3 mm thick and 10–25 mm^2 in area were cut with a wire saw. Sample surfaces were gently polished on a tissue soaked either with a mixture of ethyl ether and chloroform or with tetrahydrofuran. Such a procedure was found essential for obtaining good-quality current transients.

Iodoform crystallizes in the hexagonal system [6–9], thus the mobility tensor has only two independent components: that corresponding to the direction of the six-fold axis (the crystallographic c axis) and that perpendicular to it. Hence, the determination of the complete tensor requires, in principle, that the mobilities be measured only in these two crystallographic directions. Accordingly, the samples were cut in only two orientations which could readily be checked with a polarizing microscope.

Measurements of the drift mobility were carried out by a standard time-of-flight technique using apparatus similar to that described in ref. [10]. The duration of employed polychromatic light pulses produced by air sparks was ≈2 μs and the overall time constant of the circuitry was below 1 μs. Special care was taken to avoid the build-up of space charge in the material, hence low-intensity light pulses were employed to generate the carriers and the bias field was applied to the samples only immediately before each transient. Consequently, we believe that the measurements were taken under the small-signal regime [11].

3. Results

Polychromatic pulses of light used in this study have been found to generate photocurrents of both signs, i.e. for both polarities of the illuminated surface.

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Transient currents which could be attributed to electrons or holes, respectively, did, however differ considerably in shape. While positive (hole) photocurrents exhibited a behaviour resembling that of an ideal trap-free transient, negative (electron) photocurrents showed the existence of rapid deep trapping (fig. 1). In both cases the build-up of signals exceeded significantly the response time of the measuring system, possibly indicating the influence of shallow surface traps (cf. ref. [12]).

In most cases the peak magnitudes of electron photocurrents were about an order of magnitude lower than those of hole photocurrents. This difference is much less pronounced than that observed for the steady-state photocurrents [1]. and, in view of rapid deep trapping of electrons, does not contradict the assumption made in our previous papers [1,2] that the photogeneration in iodoform is an intrinsic process.

Measurements of the temperature dependence of the photogenerated charge showed that the activation energy of the photogeneration amounts to ≈0.01–0.03 eV within the range 290–360 K. The charge was found to be a linear function of the electric field up to 2.5 × 10^4 V/cm, as observed in the two-quantum photogeneration experiments [2].

Mobilities of holes (μ) were calculated from the equation

$$\mu = L^2/t_f U, \tag{1}$$

cusps on the current transients being taken as the transit times t_f. In the above equation L stands for the sample thickness and U for the voltage applied. The mobilities were found field independent within the whole range of the fields employed, i.e. plots of t_f^{-1} versus U were always linear and, as a rule, exhibited zero intercepts. Average values of room-temperature hole mobilities were found to be ≈0.20 ± 0.04 and 0.85 ± 0.10 $\mathrm{cm^2/V\,s}$ for the directions parallel and perpendicular to the six-fold axis, respectively.

Typical results of the temperature dependence of the mobility are shown in fig. 2. Above ≈270 K the mobilities in both crystallographic directions are descending functions of temperature whereas below 270 K the mobilities become temperature activated. Temperature dependences were interpreted assuming that

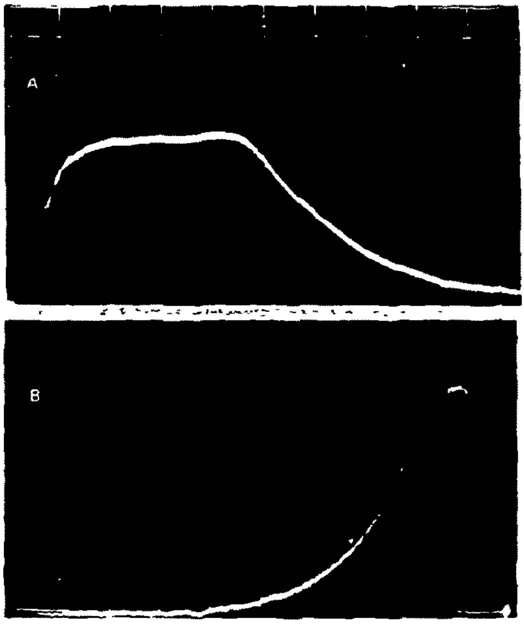

Fig. 1. Typical photocurrent transients of holes (a) and electrons (b). (a) $T = 290$ K, time basis 5 μs/div, $U = 400$ V, $L = 0.46$ mm; (b) $T = 290$ K, time basis 5 μs/div, $U = 700$ V, $L = 0.46$ mm.

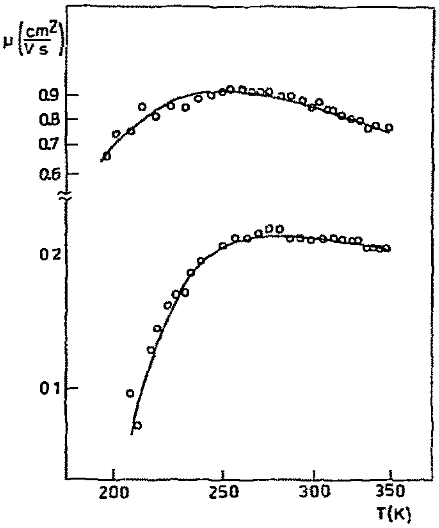

Fig. 2. Typical temperature dependences of the hole mobility measured parallel (lower data set) and perpendicular to c (upper data set). Circles denote experimental points. Full lines are the fits to eq. (2). The fit parameters are as follows: $\mu^0 = 2.87 \times T^{-0.447}$, $E_t = 0.276$ eV, $N_t/N_c = 4.45 \times 10^{-7}$ – parallel to c; $\mu^0 = 490 \times T^{-1.10}$, $E_t = 0.136$ eV, $N_t/N_c = 3.84 \times 10^{-4}$ – perpendicular to c.

the "lattice" mobility of holes (μ^0) in both directions follows a T^{-n} dependence throughout the whole temperature range. The temperature-activated behaviour of the mobility has been commonly interpreted in terms of the shallow-trapping controlled carrier transport. Initially we followed this approach, and the following formula was adopted [13]

$$\mu = \mu^0(T)[1 + N_t/N_c \exp(E_t/kT)]^{-1}, \qquad (2)$$

where N_t and E_t stand for the concentration and the depth of traps, respectively and N_c is the density of conducting states. Least-squares fits to the experimental data allowed us to evaluate the temperature dependence of μ^0 as well as N_t/N_c and E_t for a series of samples cut in both crystallographic directions.

Average values of n amount to 0.3 ± 0.3 and 1.5 ± 0.5 for the directions parallel and perpendicular to c, respectively. It was also found that both the concentrations and depths of traps differ considerably when determined from measurements taken along these two directions. The best-fit procedure yielded E_t and N_t/N_c amounting to 0.27 ± 0.04 eV and $\approx 10^{-6}$, and 0.13 ± 0.02 eV and $\approx 10^{-4}$, for the directions parallel and perpendicular to c, respectively. We shall return to these, rather unusual, results in section 4.

4. Discussion

The values of the mobilities determined in this work fall in the range of values expected and measured in other molecular crystals. Assuming that the temperature behaviour of the hole mobility at elevated temperatures reflects that of the "lattice" mobility, one finds that a stronger temperature dependence (a higher value of n) occurs for the direction of higher mobility — as is also the case e g. for the mobility of electrons in anthracene [14]. It is worth noting that the anisotropy of the mobility may be rationalized taking into account the packing of molecules in the crystal lattice of iodoform [6–9], and assuming the overlap of iodine orbitals to be a decisive factor determining the electron transfer rate. Indeed, the distances between iodine atoms on the ab plane are distinctly shorter than those between the planes (i.e. along the c direction).

Deep trapping of electrons observed in our measurements is possibly due to traces of either iodine, which may be formed by the decomposition of iodoform, or oxygen, as might be expected from the comparison of appropriate electron affinities.

The temperature dependence of the hole mobility observed in the low-temperature region and interpreted tentatively as due to shallow trapping needs more comment. A striking feature in this case is a marked anisotropy of both depths and concentrations of traps. This result puts in doubt the applicability of eq. (2) and hence the physical meaning of the parameters thus obtained which should be scalar in terms of the commonly employed models of shallow-trap-controlled transport.

It should be mentioned that available crystallographic data on the structure of iodoform crystals indicate the existence of an orientational disorder of molecules. As reported in refs. [7,8], the direction of the C–H bond may be either parallel or antiparallel to the c axis. The disorder is likely to be a function of temperature. The disordered structure and the associated structural traps might lead to an explanation of the unusual temperature behaviour of the mobilities reported in this paper. Further studies are, however, necessary to draw final conclusions.

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