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Space charge limited transport and time of flight measurements in tetracene single crystals: A comparative study

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We report on a systematic study of electronic transport in tetracene single crystals by means of space charge limited current spectroscopy and time of flight measurements. Both I–V and time of flight measurements show that the room-temperature effective hole mobility reaches values close to $\mu \simeq 1 \text{ cm}^2/\text{V s}$ and that, within a range of temperatures, the mobility increases with decreasing temperature. The experimental results further allow the characterization of different aspects of the tetracene crystals. In particular, the effects of both deep and shallow traps are clearly visible and can be used to estimate their densities and characteristic energies. The results presented in this article show that the combination of I–V measurements and time of flight spectroscopy is very effective in characterizing several different aspects of electronic transport through organic crystals. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1631079]

I. INTRODUCTION

Organic devices for electronic applications are usually based on thin film technology.[1,2] This is particularly advantageous, as thin films of organic molecules and polymers can be manufactured easily and cheaply in different ways. Over the past few years, an intense research effort has resulted in rapid improvement of the manufacturing processes, which has allowed the commercialization of products based on organic devices, i.e., organic electronics.

In spite of the rapid progress that has taken place on the applied side, the rather low chemical and structural purity of the thin films used in device fabrication has so far prevented a systematic study of the intrinsic electronic properties of organic semiconductors. That is because, for these films, it is the defects that determine the behavior observed experimentally.[3] As a consequence, our basic understanding of the electronic properties of organic materials is still limited.

Improved chemical and structural purity in organic conductors can be obtained by using single crystals of small conjugated organic molecules. Electronic transport through single crystals of different organic molecules has been investigated in the past by means of time of flight (TOF) measurements.[4,5] It has been found that the hole mobility is approximately $1 \text{ cm}^2/\text{V s}$ at room temperature, increasing up to values in excess of $100 \text{ cm}^2/\text{V s}$ with decreasing temperature. Since these observations have been reported only in the highest-purity crystals, it is believed that this is the *intrinsic* behavior of charge carrier mobility in organic conductors. So far, however, this intrinsic behavior has never been observed in conventional dc transport measurements.

In this article we report an experimental study of dc transport through a tetracene single crystal and show that our results exhibit some of the features expected for the intrinsic behavior of organic conductors. Our investigations are based on the study of the current-voltage (I–V) measurements in the space charge limited current regime and on their comparison to TOF measurements performed on identically grown crystals. As we will show, we find overall agreement between the results obtained with the two different methods. In particular, both I–V and TOF measurements show that the room-temperature effective hole mobility reaches values close to $\mu \simeq 1 \text{ cm}^2/\text{V s}$. Both measurement techniques also show that, within a range of temperatures, the mobility increases with decreasing temperature. For the best samples probed by I–V measurements this range extends down to approximately 200 K, below which a structural phase transition known to occur in tetracene causes a sudden drop of the mobility. The experimental results further allow the characterization of different aspects of the tetracene crystals. In particular, we observe the effect of both deep and shallow traps.[6] For the former, the measurement of the I–V characteristics give us an upper bound on their bulk density ($N_t^d < 5 \times 10^{13} \text{ cm}^{-3}$) and an estimate of their depth ($E_t^d \approx 700 \text{ meV}$ relative to the edge of the valence band). The concentration of shallow traps is substantially larger and only a very rough estimate can be obtained from TOF experiments.

The paper is organized as follows. We first describe the most important aspects of the tetracene crystal growth and of the sample preparation (Sec. II). The behavior of the measured I–V curves is presented in Sec. III. In this section we also discuss the basic aspects of the theoretical concepts necessary to interpret the experimental data. Section IV is devoted to TOF experiments. Finally, in Sec. V we summarize and compare the outcome of TOF and dc transport measurements and present our conclusions.

II. CRYSTAL GROWTH AND SAMPLE PREPARATION

Tetracene single crystals are grown by means of physical-vapor deposition in a temperature gradient (see Fig.
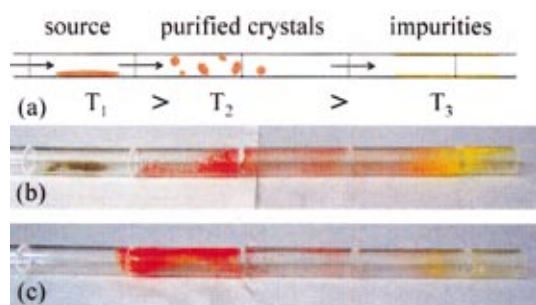
FIG. 1. (Color) (a) Schematic overview of tetracene crystal growth system. Tetracene sublimes at temperature T_1, is transported through the system by the carrier gas (indicated by the arrows), and recrystallizes at temperature T_2. Heavy impurities (with a vapor pressure lower that of tetracene) remain at the position of the source material. Light impurities (with a vapor pressure higher than that of tetracene) condense at a lower temperature $T_3 < T_2$, i.e., at a different position from where the crystals grow. Therefore, the crystal growth process also results in the purification of the material. (b) Result after first regrowth of as-purchased tetracene. Purified tetracene crystals are visible in the middle; the dark residue present where the source material initially was and the light (yellow) material visible on the right are due to impurities. (c) At the end of the second regrowth no dark residue is present at the position of the source material, which demonstrates the purifying effect of the growth process.

1), in the presence of a stream of carrier gas, using a setup similar to that described in Ref. 7. Both Ar and H_2 were used. All experiments discussed in this article are performed on Ar grown crystals on which we obtained the highest values of charge carrier mobility. Crystal growth is performed in the dark to minimize possible photoactivated chemical reaction of tetracene with remnant O_2. These photoinduced reactions with O_2 are known to occur for most polyacenes[8] and result in chemical impurities that can act as traps for charge carriers.

The source material for the first crystal growth is 98% pure tetracene purchased from Sigma-Aldrich. Crystals grown from as-purchased tetracene are used as source material for a subsequent growth process. For the first and second growth steps the results of the growth processes are shown in Fig. 1. Note the large residues of impurity molecules clearly visible after the first process [Fig. 1(b)] but not after the second [Fig. 1(c)], which directly demonstrates the usefulness of the second regrowth process.

Tetracene crystals grown by physical-vapor deposition are large platelets, with surfaces parallel to the ab plane. Typical dimensions range from a few square millimeters to 1×1 cm^2 or larger. For crystals grown by letting the growth process proceed overnight, the typical crystal thickness ranges between ~ 10 μm and ~ 200 μm. We have performed x-ray structural studies on a few of our thickest crystals and found a structure consistent with known literature data.[9,10]

Multiply regrown crystals are inspected under an optical microscope with polarized light. As is typical for many organic conjugated molecules, tetracene crystals are birefringent. This allows us to select single crystals to be used for transport experiments by choosing those samples that become uniformly dark when changing the orientation of cross polarizers.[11]

All I–V and TOF measurements discussed in this paper have been performed in the direction perpendicular to the crystal ab plane, using electrical contacts on the two opposite faces of crystals. Electrodes for I–V measurements are fabricated by connecting gold wires to the crystal surface using a two-component, solvent-free silver epoxy, so that the epoxy is in direct contact with the crystal. The contact area is measured under the microscope and it is typically of the order of 0.1 mm^2. We use silver epoxy Epo-Tek E415g, which hardens at room temperature in a few hours. This contact fabrication method is very quick and it was chosen because it allows the investigation of many samples in a relatively short time. Other types of contacts were tested as well, i.e., metal evaporated contacts and colloidal graphite paint contacts, but they did not result in any improvement of the observed electrical properties. For TOF measurements we used silver electrodes prepared by thermal evaporation through a shadow mask.

III. dc TRANSPORT THROUGH TETRACENE SINGLE CRYSTALS

In this section we discuss the results obtained by studying the I–V characteristics of approximately 100 tetracene single crystals. We have found that the measured I–V curves exhibit large sample-to-sample deviations so that particular care has to be taken in the interpretation of the experimental data. For this reason, we first discuss how the charge carrier mobility can be estimated using concepts of space charge limited current theory of general validity, i.e., not sensitive to the detailed behavior of our samples. After presenting the experimental results in terms of the concept previously introduced, we discuss the role of deep traps present in the bulk of the crystals and at the metal/organic contact interface. We argue that the latter provide the most likely explanation of the large sample-to-sample variation observed in the measured I–V characteristics.

A. Estimate of the carrier mobility

Since the band gap of tetracene is approximately $E_g \simeq 3$ eV,[12] high-purity tetracene crystals containing a negligible amount of dopants essentially behave as insulators. It is still possible to pass a current through tetracene crystals by applying a sufficiently large voltage, which acts both to transfer charge from the electrodes into the crystal and to accelerate that charge. When the charge injected from the contacts is larger than the charge present in the material in equilibrium, the I–V characteristics become nonlinear and transport is said to occur in the space charge limited regime.[13]

For materials in which current is carried by only one carrier type (holes in our tetracene crystals; see Sec. IV B), there exists an upper limit to the current that can be carried in the space charge limited regime. This is due to electrostatics which, at any given voltage V, fixes the maximum amount of charge that can be injected into the material. For the geometry used in our experiments, the resulting maximum current that can flow in the space charge limited regime in the presence of an applied voltage V is[13]

$$I = A \frac{9\epsilon\epsilon_0 \mu V^2}{8L^3}, \qquad (1)$$

with A and L, respectively, the electrode area and separation, and ϵ the relative dielectric constant of the material ($\epsilon \simeq 3$ for tetracene). This upper limit is *intrinsic* and is not sensitive to any of the specific sample details that determine the shape of the $I-V$ curves. For any applied voltage, contact effects, defects, or traps can only reduce the current below the value given by Eq. (1).

We use these considerations to obtain experimentally a lower limit μ_{min} for the mobility of charge carriers, by measuring the current I induced by a voltage V and by "inverting" Eq. (1). We obtain

$$\mu_{min} = \frac{8IL^3}{9A\epsilon\epsilon_0 V^2}. \qquad (2)$$

If μ_{min} is very low—e.g., at room temperature, much lower than the intrinsic value $1\ cm^2/V\ s$ typical of organic semiconductors—this approach does not provide any useful information. However, if the value of μ_{min} is close to $1\ cm^2/V\ s$, this analysis indicates that the quality of the crystal is high (since the intrinsic mobility $\mu > \mu_{min}$).

B. Measurements of $I-V$ characteristics

All the measurements of $I-V$ characteristics of tetracene crystals discussed in this paper have been performed in vacuum ($P < 10^{-5}$ mbar) and in the dark, in a two-terminal configuration. We used a Keithley 237 source-measure unit that permits to apply of up to 1100 V across our samples and to measure currents as small as 10 fA. Measurements at lower temperature were performed in the vacuum chamber of a flow cryostat. Approximately 100 samples were measured at room temperature. Temperature dependent measurements were performed on most samples in which a high value for μ_{min} (0.1 $cm^2/V\ s$ or better) was found and on a few of the others.

The precise shape of the $I-V$ characteristics measured on different samples exhibits large deviations, whose possible origin is discussed in the next section. Here, we focus on some important common features observed in many of the samples investigated ($\simeq 100$). In particular, we often observe that in the lower-voltage range ($V < 10-100$ V, depending on the sample) the current increase with voltage is approximately quadratic.[14] At higher voltage, the current increases by many decades (typically six to eight, depending on the sample) for a one-decade increase in voltage (Fig. 2). In most cases samples fail as the voltage is increased in this part of the $I-V$ curve, either because too much power is dissipated through the crystals (samples with high μ_{min}) or because the electrical contacts detach from the crystal (samples with low μ_{min}). In a few cases, however, we have observed that the rapid current increase terminates by crossing over into an approximately quadratic dependence on voltage (Fig. 2, inset).

The value of the current measured at the maximum applied voltage is used to calculate μ_{min} from Eq. (2). The calculation requires knowledge of the crystal thickness,
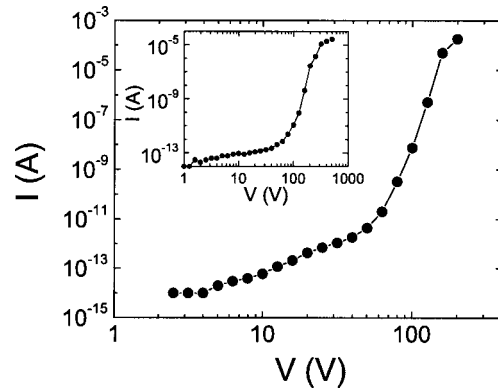
FIG. 2. Typical result of a dc $I-V$ measurement perpendicular to the *ab* plane of a tetracene single crystal, with a thickness $L = 30\ \mu m$ and a mobility $\mu_{min} = 0.59\ cm^2/V\ s$. The inset shows a similar measurement on a different crystal ($L = 25\ \mu m$, $\mu_{min} = 0.014\ cm^2/V\ s$), in which a crossing over into an approximately quadratic dependence on voltage is visible at high voltage. In both cases, a very steep current increase occurs around or just above 100 V that we attribute to filling of deep traps. We observed a steep increase in current in most samples studied.

which, in this geometry, corresponds to the electrode separation L. The measurement of L is done by inspecting the crystals under an optical microscope. The uncertainty of L (typically 10–20 %) is rather large and is due to the difficulty of the measurement and to the opposite crystal surfaces not being parallel to each other. In calculating μ_{min} we have used lower estimates of L, in order to be sure not to overestimate the crystal mobility.

The histogram shown in Fig. 3 provides an overview of the values of μ_{min} obtained from all measured samples. The spread in the calculated values of μ_{min} is large, as a consequence of the large deviations observed in the measured $I-V$ characteristics. In what follows we concentrate on those samples for which the lower limit to the mobility is $\mu_{min} > 0.1\ cm^2/V\ s$.[15]

For most high-quality samples that did not fail during the room-temperature measurements we have performed $I-V$ measurements at different temperatures. We reproducibly find that μ_{min} increases upon lowering the temperature in all the samples in which $\mu_{min} > 0.1\ cm^2/V\ s$ at room temperature (Fig. 4). The same behavior has also been observed in a few samples in which $\mu_{min} \simeq 0.01\ cm^2/V\ s$, although
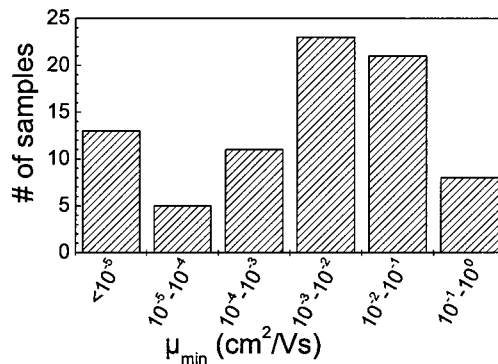
FIG. 3. Histogram of values for μ_{min} calculated from dc $I-V$ measurements performed on approximately 100 tetracene single crystals.
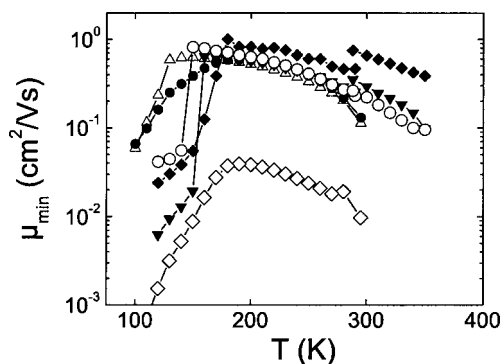
FIG. 4. Temperature dependence of the lower limit to the mobility, μ_{min}, measured for several tetracene single crystals. Note the abrupt drop in mobility occurring at different temperatures below $\simeq 180$ K, originating from a known structural phase transition (Ref. 16).

normally samples for which $\mu_{min} < 0.1$ cm²/V s at room temperature exhibit a decrease in current as the temperature is lowered. We conclude that samples in which the room-temperature mobility is sufficiently close to the value of 1 cm²/V s exhibit the behavior expected for high-quality organic semiconductors, i.e., *an increasing mobility with decreasing temperature*, in simple two-terminal dc $I-V$ characteristics.

In all the high-mobility samples measured we observe that below $T \simeq 180$ K μ_{min} starts to decrease when the temperature is decreased further. In most samples, the change in the temperature dependence of μ_{min} is very sharp (Fig. 4). This suggests that the origin of this change is a structural phase transition, which is known to occur in tetracene in this temperature range.

Past studies of this transition[16] have shown that the precise transition temperature depends on details, such as the stress induced by the adhesion between a crystal and the substrate on which the crystal is mounted.[17] These studies have also shown that the phase transition does not occur uniformly, with two different crystalline structures coexisting in different parts of the same crystal in a large interval of temperatures below the transition. The coexistence of different crystal phases is detrimental for transport, since it introduces grain boundary junctions and regions with different bandwidths that can trap large amounts of charge carriers. This explains the observed temperature dependence of the mobility. The observation of the effect of this structural phase transition on the transport properties of tetracene provides one additional indication that the crystal quality is high and that we are probing intrinsic effects in the material.

C. Deep traps in the bulk and at the contacts

The interpretation of experimental data in terms of μ_{min} is of general validity and does not require any assumption regarding the sample characteristics. Additional information can be extracted from the measurements if one considers the behavior of the measured $I-V$ curves in more detail. Here we consider the effect of deep traps present in the bulk of the tetracene crystals and at their surface.

In general, deep traps suppress current flow by localizing charge carriers. In the space charge limited transport regime, it can be easily shown[13] that when the applied voltage V is approximately equal to

$$V_{TFL} = \frac{N_t^d e L^2}{\epsilon \epsilon_0} \qquad (3)$$

the charge injected by the contacts is sufficient to fill all the traps and transport occurs in the so-called trap-filled limit. At this point (i.e., on increasing V from below to above V_{TFL}) the measured current exhibits a large sudden increase given by

$$\frac{N_v}{N_t^d} \exp\left(\frac{E_t^d}{k_B T} \right). \qquad (4)$$

In this expression, N_v is the number of states in the valence band, which we take to be of the order of one state per molecule.[13]

Essentially all samples exhibit a large, steep increase in current around a given (sample dependent) voltage (Fig. 2), which we interpret as due to the transition to the trap-filled limit. Using Eq. (3) we obtain $N_t^d \simeq 5 \times 10^{13}$ cm⁻³. We find that different samples all give comparable values. Introducing this value for N_t^d in Eq. (4), we then find, taking the magnitude of current increase measured on samples with the highest value of μ_{min}, $E_t^d \approx 700$ meV.

The estimate of N_t^d is based on the assumption, not usually emphasized in the literature, that the deep traps are uniformly distributed throughout the entire crystal bulk. In actual samples, due to the contact preparation process, it is likely that more traps are present at the crystal surface under the electrodes. A small amount of traps located close to the surface can have a large effect in suppressing current flow. This is because charges trapped at the surface can substantially affect the electrostatic profile in the bulk of the crystal, which determines the current flow in the space charge limited current regime.

To make this point more explicit, consider a 20 μm thick crystal in which no traps are present except in the first monolayer of molecules close to the surface. Suppose that, in this monolayer, one deep trap per every 1000 molecules is present. This will result in a very large current suppression, as populating these traps results in an electric field through the crystal which corresponds, in the case considered, to approximately 1000 V applied between the electrodes. For an $I-V$ measurement this would imply that, as the voltage across the electrodes is increased, the surface traps are initially filled and no current flows until more than 1000 V are applied. For comparison, for a 20 μm thick crystal with no surface traps and a bulk density of traps of 5×10^{13} cm⁻³, transport already occurs in the trap-free limit when 200 V are applied across it. For this reason, our estimate of N_t^d is a higher limit to the bulk density of deep traps.

The strong sensitivity of the $I-V$ curves to traps located at the metal/organic interface makes these traps a logical explanation for the large sample-to-sample variation observed in the experiments. Evidence for the relevance of contact effects is provided by the rather good sample-to-sample

reproducibility observed in TOF measurements (see Sec. IV B) as compared to dc transport measurements.

IV. TOF EXPERIMENTS ON TETRACENE SINGLE CRYSTALS

A. Technical aspects of TOF experiments

Time of flight spectroscopy is based on two fundamental steps. First, by photoexcitation electron-hole pairs are generated near the crystal surface. Second, in the applied electric field the charge carriers move to the electrodes and the corresponding displacement current is measured.[12] Therefore, studies of the transport behavior are free of contact effects and the technique is selective with respect to the type of charge carrier by choice of the polarity of the external voltage.

For the TOF measurements the tetracene crystals are covered on both sides by a thin layer of Ag thermally evaporated and, afterwards, mounted on a Cu support acting as back electrode as well as thermal contact for the temperature dependent studies. The 15–20 nm thick Ag contacts show almost bulk conductivity but are still sufficiently transparent for photoinduced generation of charge carriers at the front electrode. As light source for the charge carrier generation, a nitrogen laser in single shot mode ($\lambda = 337$ nm, pulse width 0.76 ns) is used. The suitability of the used wavelength for photoexcitation has been proved by UV-visible absorption measurements on the crystals. In addition, from the TOF pulse shape and the absorption spectra we can conclude that charge carrier generation takes place mainly in the topmost fraction of the crystals i.e., the depth of charge carrier generation (several micrometers) can be neglected with respect to the thickness of the crystals ($\sim 100 \ \mu$m).

The displacement current is measured as a voltage drop across a resistor connected in parallel to the crystal. The resistor is chosen in such a way that the time constant of the RC part is much smaller than the transit time τ. TOF studies in the range from room temperature up to 450 K were carried out in a heating stage at ambient pressure, the upper temperature limit being caused by sublimation of tetracene at around 450 K.[18]

B. Measurement of TOF transients

Temperature dependent TOF measurements have been performed on three different single crystals giving essentially identical results. The room-temperature mobility values obtained from the different crystals were very close to each other (ranging from 0.5 cm^2/V s to 0.8 cm^2/V s) and their temperature dependence was qualitatively identical. This is in clear contrast with the large sample-to-sample variations observed in dc transport measurements. From the outcome of the TOF experiments we conclude that the quality of the grown crystals is rather reproducible and that the sample-to-sample variations observed in the dc I–V curves originates from irreproducibility in the contact preparation.[19] This is consistent with the fact that TOF experiments are not very sensitive to the contact quality whereas dc I–V measurements are.
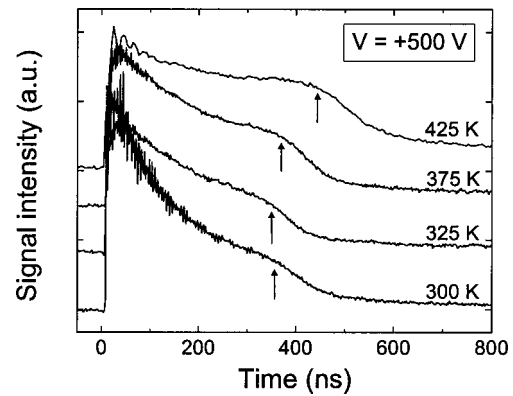

FIG. 5. Hole TOF pulses measured at different temperatures in the range from room temperature to 150 °C. The applied voltage is +500 V. The arrows point to the transit times.

Representative TOF pulses for positive charge carriers measured at various temperatures in one of the three tetracene single crystals are shown in Fig. 5, from which the transit time τ can be easily extracted. In contrast to these well-defined TOF pulses measured for hole transport, only dispersive transport is observed for electrons throughout the measured temperature range. This indicates strong trapping for electrons, which is why in Sec. III we have used single carrier space charge limited current theory to interpret the behavior of the measured I–V curves.

Assuming a constant electric field E across the crystal, the mobility of the holes is related to the transit time and to the crystal thickness L by

$$\mu = \frac{L}{E\tau}. \tag{5}$$

For the values of electric field used in our studies τ^{-1} depends linearly on E (see Fig. 6) so that μ does not depend on electric field. All the mobility values discussed in this paper have been estimated from this Ohmic regime only.

In the absence of traps Eq. (5) represents the intrinsic mobility μ of the organic material, which typically varies as an inverse power of temperature, i.e., $\mu \propto T^{-n}$ ($n \simeq 2-3$ depending on the specific organic molecules[12]). If shallow traps[20] are present, however, the measured mobility is just an "effective" mobility μ_{eff} related to the μ by[12]
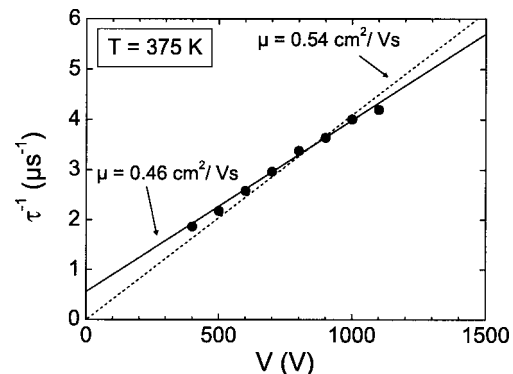

FIG. 6. Transit time of hole TOF pulses versus applied voltage estimated at 375 K showing a linear (Ohmic) dependence. The continuous and dotted lines represent, respectively, the best linear fit and the best linear fit passing through the origin. The corresponding difference in the μ values gives a measure of the uncertainty in the extracted mobility.
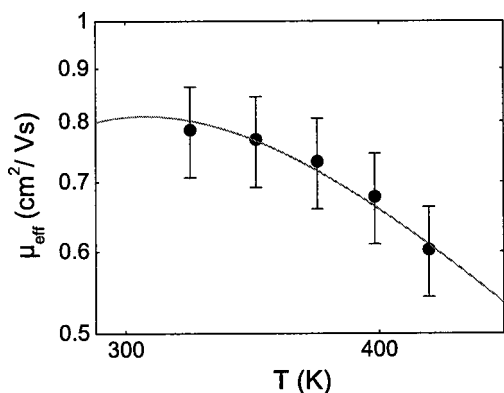
FIG. 7. Temperature dependence of the hole mobility (full circles). The fit (straight line) is described by Eq. (6) using an exponent $n=2$, a mobility of 1.4 cm^2/V s, a trap energy of 0.13 eV, and a density ratio between shallow traps and tetracene molecules of 5×10^{-3}.

$$\mu_{\text{eff}}(T) = \frac{\mu(T)}{1 + (N_t^s/N_v)\left[\exp(E_t^s/k_B T) - 1\right]}, \qquad (6)$$

where N_t^s/N_v is the density ratio between shallow traps and organic molecules in the crystal, and it is assumed that all the shallow traps have the same energy depth E_t^s relative to the valence band. A plot of the measured μ_{eff} versus T is shown in Fig. 7. The saturation with decreasing temperature is a characteristic signature of shallow traps.

The effect of shallow traps is visible not only in the temperature dependence of the mobility, i.e., of the transit time of TOF pulses, but also in their shape. Specifically, Fig. 5 shows that the signal intensity increases with increasing temperature and that the pulse becomes more rectangular. Both effects are due to reduced trapping at elevated temperature, which makes the sample behavior conform more closely to the ideal trap-free condition.

We have attempted to use Eq. (6) to fit the measured temperature dependence of μ_{eff} and to determine the values of N_t^s and E_t^s. However, the limited temperature range which is experimentally accessible, the uncertainty in the intrinsic room-temperature mobility of tetracene and the unknown value of n determining its temperature dependence make it impossible to determine trap density and concentration precisely. Even when we set $\mu(300\text{ K}) = 1$ cm^2/V s and $n=2$, we find that different combinations of N_t^s and E_t^s produce a satisfactory fit of our data. From this analysis we can, however, roughly estimate that $N_t^s \approx 10^{18}$ cm^{-3} and $E_t^s \approx 100$ meV. A more precise determination of these parameters would require extending the temperature dependent measurements over a wider temperature range. In practice, however, the temperature range is limited by sublimation of tetracene ($T > 450$ K) on the high end and by the blurring of the TOF pulse on the low end ($T < 300$ K).

V. SUMMARY

Systematic dc transport measurements and TOF experiments have been performed on identically grown *single crystals* of organic molecules and overall agreement was found in comparison of the results obtained with the two techniques. Specifically, from both measurement techniques we

conclude that the room-temperature hole mobility is close to 1 cm^2/V s and that its temperature dependence is nonmonotonic.[21] For TOF measurements on tetracene, this behavior had been observed previously.[22] On the contrary, an increase in mobility with decreasing temperature observed by measuring the dc $I–V$ curves in the space charge limited transport regime has not been reported previously for tetracene or, to the best of our knowledge, for any organic undoped semiconductor. This observation, together with the observed effect of the structural phase transition on the hole mobility, indicates that signatures of the intrinsic electronic properties are visible in the $I–V$ measurements, which demonstrates the high quality of the crystals.

In spite of the crystal quality, the effect of imperfections is still clearly visible. In particular, $I–V$ and TOF measurements provide complementary information about the presence of deep and shallow traps. $I–V$ measurements allow us to infer an upper limit for the bulk density of deep traps and their activation energy (see Sec. III C). For shallow traps the observation of a maximum in mobility in TOF measurements around room temperature indicates that the typical activation energy is ~ 100 meV, but a more precise value as well as a reliable estimate of the density cannot be presently obtained. We believe that these shallow traps originate from local deformations of the crystals, such as those due to mechanical stress or to electrically inactive chemical impurities as well as from chemical impurities interacting only weakly with the surrounding host molecules. Within a conventional band picture it is easy to see that these deformations would have an important effect, as they can locally change the band gap of tetracene and form spatially localized "pockets" of holes. This mechanism could account for a fairly large density of shallow traps and for a trapping energy of ~ 100 meV,[23] which corresponds to only a few percent change in the 3 eV tetracene gap.

Not only the similarities but also the differences between $I–V$ and TOF measurements provide useful information. Particularly noticeable is the reproducibility of TOF measurements in contrast to the large sample-to-sample deviations observed in the $I–V$ characteristics. Three out of three crystals studied by means of TOF gave $\mu \approx 0.5–0.8$ cm^2/V s, whereas out of approximately 100 samples measured only 5–10 % gave a mobility larger than 0.1 cm^2/V s. The reproducibility obtained in TOF measurements indicates that different tetracene crystals grown in our setup exhibit only minor differences in their properties and that these differences cannot account for the large spread of $I–V$ characteristics observed experimentally.

We conclude that the large sample-to-sample variations observed in the measurement of $I–V$ characteristics mainly originate from the quality of the electrical contacts. As mentioned above, this is critically important for $I–V$ measurements, but not for TOF measurements. Since the large values of μ_{min} obtained in the best samples indicate that it is possible to fabricate "high-quality" contacts using silver epoxy, we infer that the effects determining the contact quality in our samples are mainly of *extrinsic* nature. Our estimates suggest that deep traps present under the contacts at the crystal surface (introduced during the contact fabrication) play an

important role. This is because even a very small surface density of these traps can substantially perturb the electrostatic profile in the crystal bulk that determines the current flow in the space charge limited transport regime.

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[21] Although the general trend in the T dependence of the mobility is similar in both the $I-V$ and TOF experiments, the temperature at which the mobility reaches its optimum value is different. We suggest that the cause of this difference is that, in the case of $I-V$ measurements, a much larger amount of charge is being injected, so that more (shallow) traps are filled.
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