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M. Pope [a] & W. Weston [a]

[a] Chemistry Department and Radiation and Solid State Laboratory, New York University, Washington Square, N.Y., 10003

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Voltage Dependence of Unipolar Excess Bulk Charge Density in Organic Insulators

M. POPE and W. WESTON

Chemistry Department and Radiation and Solid State Laboratory, New York University, Washington Square, N.Y. 10003

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The voltage dependence of the average total excess charge density in anthracene single crystal at room temperature is reported using a hole injecting contact of 0.1M Ce^{4+} in 7.5M H_2SO_4 and a neutral contact of H_2O. These results were obtained from precise measurements of the change in the delayed fluorescence lifetime ($\Delta\beta/\beta_0$) as charge was injected into the crystal. Regimes of diffusion assisted, space charge limited, and quasi-saturation currents have been identified. A theoretical fit to the data in the quasi-saturation region results in a calculated value of 0.0083 $cm^{\frac{1}{2}}V^{-\frac{1}{2}}$ for the Schottky coefficient. Using the value of the charge density at the electrode, a lower limit to the work function of the Ce^{4+}/Ce^{3+} electrode was calculated to be 5.2 eV. Preliminary findings on electrical conduction in anthracene single crystal using a hole injecting contact of Au and a neutral contact of Hg are briefly discussed.

The flow of a steady, unipolar, injected current in a solid insulator has been the subject of theoretical analysis for several decades [1-4]. These theories differ essentially in their choice of the trap distribution and boundary conditions. Theoretical studies have also shown that idiosyncratic spatial distribution of traps can significantly alter the current-voltage (*J-V*) response [5,6], making it difficult to interpret this basic measurement in an unequivocal manner. It would be of considerable value to know the voltage and temperature dependence of the spatial distribution of charge inside the insulator[7], and this paper deals with the first phase of an attempt to carry out such a measurement. We report here the voltage dependence of the average total excess charge density in anthracene crystal provided with a hole-injecting contact.

The method used to measure the charge density is a simple refinement of the method used to measure the bimolecular interaction coefficient γ between a triplet exciton and a free (γ_{Tf}) or trapped (γ_{Tt}) carrier[8]. The principle of the technique is to measure the delayed fluorescence (DF) lifetime as a function of the applied voltage. The DF is produced by the radiative fusion of two triplet excitons, and the applied voltage changes the DF lifetime by forcing into the crystal charge carriers which act as triplet exciton quenchers. It can be shown[8] that for the interaction of triplet excitons with trapped carriers,

$$\frac{\beta\text{-}\beta_o}{\beta_o} = \gamma_{Tt} <n_t> \tau_o \tag{1}$$

where β_o ($= 1/\tau_o$), β, $\langle n_t \rangle$, γ_{Tt} are respectively, the triplet exciton decay rate in the absence of an applied voltage V, the decay rate in the presence of V, the average trapped carrier density, and the bimolecular interaction coefficient. A similar equation would hold for the interaction of triplet excitons with free carriers, using γ_{Tf} and $\langle n_f \rangle$ in place of γ_{Tt} and $\langle n_t \rangle$. If free and trapped carriers are present, then (1) would be modified to include both contributions, suitably weighted to reflect the appropriate carrier concentrations. The refinement introduced in this work is to make DF lifetime measurements precise to within 0.3%. This makes possible the calculation of $\langle n_t \rangle$ to a precision of about 5% when $\Delta\beta/\beta_0$ is about 0.05 (i.e. a value of 0.05 could be depended on to be 0.05 ± 0.003) and to a precision of about 3% when $\Delta\beta/\beta_0$ is 0.1.

EXPERIMENTAL

Anthracene crystals were purchased from Princeton Organics of Princeton, New Jersey. These crystals were cleaved in the *ab* plane and polished so that the final thickness of the samples was about 200μ. The triplet exciton lifetime in these crystals was about 20 msec before polishing and 10 msec after polishing. Upon annealing[9], the triplet lifetime rose to 19 msec. A modified Pope-Kallmann[10] cell was used to hold the crystal. A chopped He-Ne laser beam was used to generate triplet excitons in the bulk of the crystal, and the delayed fluorescence (DF) was monitored with a single photon counting apparatus feeding into a multichannel analyzer. DF lifetime measurements could be made reproducibly to within 0.3% (typically less than 0.2%).

The injecting anode solution was 0.1M in $Ce(SO_4)_2$ and 7.5 M in H_2SO_4[11]; the cathode was deionized distilled water. In making $J-V$ measurements, three minutes were allowed at each V before the J reading was taken.

RESULTS

The complete $J-V$ dependence is shown in Figure 1, and the complete $\Delta\beta/\beta_0$ versus V dependence is shown in Figure 2. Figure 3 demonstrates the behavior of

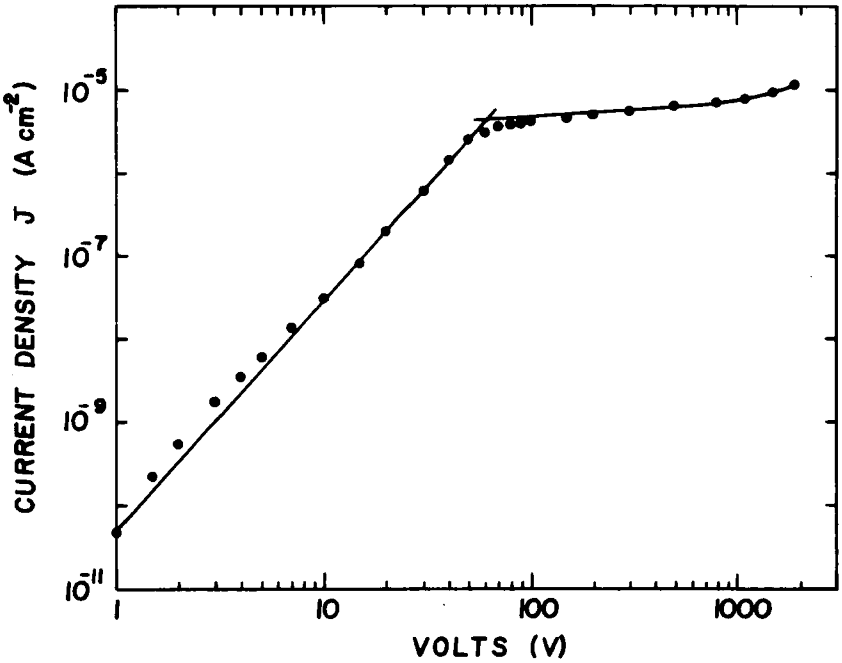

FIGURE 1 Voltage dependence of hole current density through a 230μ thick anthracene crystal. Electrodes: 0.1M Ce^{4+} in 7.5M H_2SO_4 (anode) and H_2O (cathode). Electrode area is 1.6×10^{-2} cm^2.

$\Delta\beta/\beta_0$ at very low voltages (these measurements were performed on the same crystal but at a different time). The reverse current was about 10^{-5} that of the forward current for most of the voltage range. There are several interesting features shown in Figure 2 and 3. In Figure 3, it may be seen that for voltages less than 5V, $\Delta\beta/\beta_0$ lies slightly above the line going through the origin. Although the displacement of $\Delta\beta/\beta_0$ from the line is small, it is reproducible and we feel that its reflects the contribution of diffusion current to the drift current. In a crystal with a higher trap density it appears that the upward displacement of $\Delta\beta/\beta_0$ from the straight line is distinctly greater. It should be kept in mind that the reference lifetime for calculating changes in DF lifetime is that measured in the crystal *before* the electrolyte solutions are applied. It is found generally that upon contacting the crystal with the electrodes, the DF lifetime drops slightly. This can be due to charge injected at zero applied field or to a specific quenching effect exerted by the electrode. With increasing voltage, $\Delta\beta/\beta_0$ approaches the straight line that represents the $Q \simeq CV$ curve, where Q is the total injected carrier population, and C is the geometric capacitance. Corresponding to the slightly elevated values of $\Delta\beta/\beta_0$ in the region $V < 5$ volts, one notices that the

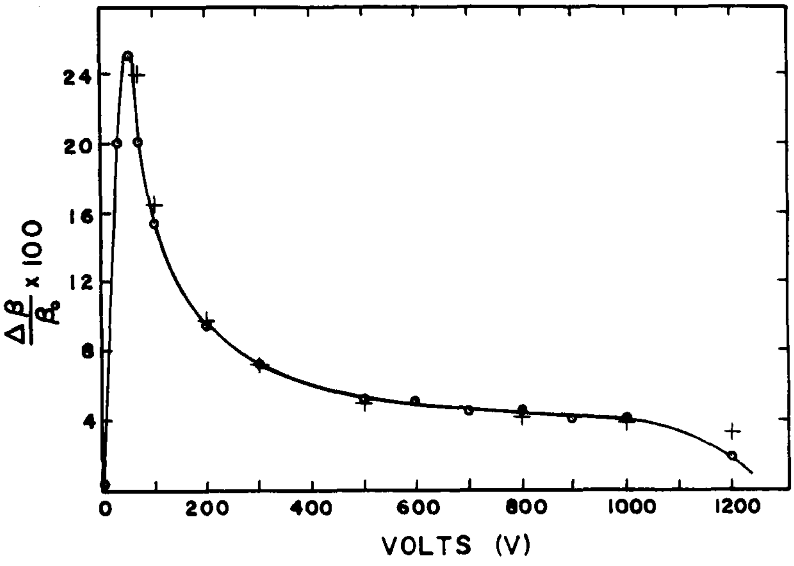

FIGURE 2 Voltage dependence of average excess total charge density, $n_{tot} \propto \Delta\beta/\beta_0$, in a 230$\mu$ thick anthracene crystal. Electrodes: 0.1M Ce^{4+} in 7.5M H_2SO_4 (anode) and H_2O (cathode). O Experimental. + Theoretical using equation (3) to determine $\langle n_f \rangle$ and normalizing at $V = 300$ volts with $\beta = 0.0083$ cm$^{\frac{1}{2}}$V$^{-\frac{1}{2}}$

slope of the $J-V$ curve for this voltage region (Figure 1) is higher than in the rest of the curve. This is characteristic of the $J-V$ dependence in a diffusion current assisted regime.[3]

In the voltage range 5 to 50V, $\Delta\beta/\beta_0$, and hence Q, is linearly proportional to V, characterizing the appearance of space charge limited current (SCLC). The current goes as $J \propto V^{2.7}$ which, according to the theory of SCLC as described by Helfrich and Mark[7], implies that the trapping levels in the crystal have a quasi-exponential distribution on energy in some energy interval. The SCLC portion of the $\Delta\beta/\beta_0$ versus V dependence has been well studied by several laboratories in the course of evaluating the constants γ_{Tt}[12] and γ_{Tf}[8]. For this particular crystal, it is found that the bimolecular rate constant is ~ 6 x 10^{-11} cm^3 sec^{-1} as compared with a published value of $\gamma_{Tt} = 7 \pm 3 \times 10^{-12}$ cm^3 sec^{-1} [11]. However, we have also measured a value of 3×10^{-12} cm^3 sec^{-1} for another crystal in which the triplet lifetime was about 16 msec instead of 20 msec. We have two brief remarks to make about these values. First, we feel that our value of 6×10^{-11} cm^3 sec^{-1} contains a contribution due to free carriers; and second, it should be kept in mind that a determination of γ_{Tt} as measured by changes in the DF lifetime will not be strictly valid if the sites that trap the carriers are triplet exciton quenchers even in the absence of a trapped carrier[13]. In other words γ_{Tt} (DF measurements) $\leqslant \gamma_{Tt}$ (true). It is likely that deep traps quench triplet excitons even if no carrier is present in those sites, and that shallow traps do not necessarily quench triplet excitons unless carriers are present in those sites. Since there are more shallow traps than deep traps, there will tend to be more agreement between the values obtained by different investigators using different crystals than might at first have been expected.

Turning to Figure 1, it may be seen that there is no sign of a traps-filled-limit region and that saturation of the current commences at about 60 volts. In Figure 2 there exists no data point at 60 volts; however, in another experiment using the same crystal, the voltage at which current saturation commenced was accurately bracketed by the $\Delta\beta/\beta_0$ values. It can be concluded that immediately prior to the onset of saturation, $\Delta\beta/\beta_0$ will experience a maximum. At the extremum, $\frac{d}{dV}\left\{\frac{\Delta\beta}{\beta_0}\right\} = 0$ or $n_{tot} = \text{constant}$. For a short voltage interval, Ohm's law holds as is to be expected when the current shifts from SCLC towards saturation,[1,4] and $n_f = \text{constant} = n_f(0)$ where $n_f(0)$ represents the density of the free charge at the anode. This permits the calculation of a lower bound to the work function of the Ce^{4+}/Ce^{3+} electrode, as will be shown below.

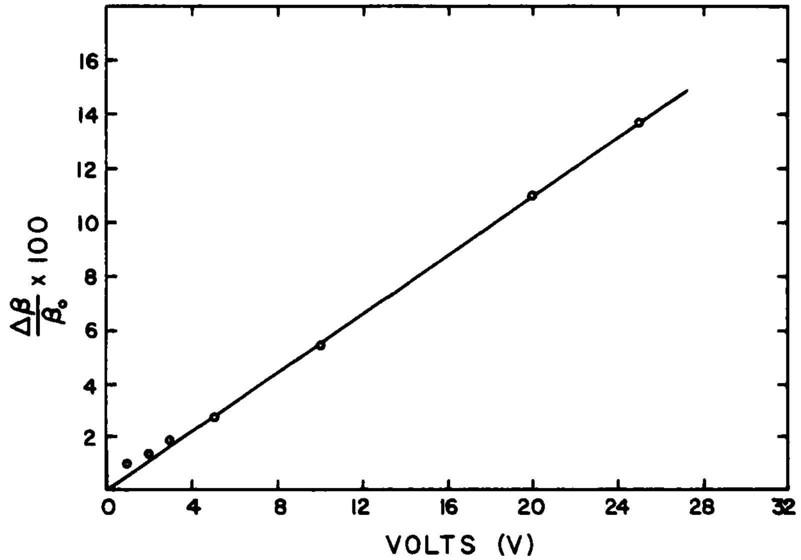

FIGURE 3 Voltage dependence of average excess total charge density, $n_{tot} \propto \Delta\beta/\beta_0$, in a 230$\mu$ thick anthracene crystal. Electrodes: 0.1M Ce^{4+} in 7.5M H_2SO_4 (anode) and H_2O (cathode). Measured value of τ_0 is 19 msec; calculated value of γ_{eff} is 5.5×10^{-11} cm^{3}sec^{-1}. (See eg. 6a)

For $V > 60$ volts, a quasi-saturation region is entered as described by Bonham and Lyons [14,15] in which

$$J = J_s + J_0 \exp\left(\beta L^{-\frac{1}{2}} V^{\frac{1}{2}}\right) \tag{2}$$

where J_s is the saturation current density, J_0 is a constant, β is the Schottky constant $\left\{\beta = e/kT \left(\frac{e}{4\pi\epsilon\epsilon_0}\right)^{\frac{1}{2}}\right\}$, and L is the crystal thickness. According to Lampert[16] the field throughout most of the crystal is approximated by V/L, so we can write

$$J = J_s\left\{1 + \frac{J_0}{J_s}\exp\left(\beta L^{-\frac{1}{2}} V^{\frac{1}{2}}\right)\right\} = \langle n_f \rangle e\mu\, V/L \tag{3}$$

where e is the electronic charge, and μ is the carrier mobility. Assuming that $n_f/n_t = \theta =$ constant at least for $V < 1000$ volts, one can calculate theoretical values of $\Delta\beta/\beta_0$ as a function of V using (1) and (3). These results are shown in Figure 2. The $V = 300$ volts point was chosen for normalization purposes and in the evaluation of the constant J_0. J_s was taken at the junction of the extrapolated slopes shown in Figure 1 rather than on the curve itself because space charge effects tend to round off the experimental curve[17]. The agreement between the predictions of (3) and experiment is fairly good over the voltage range that corresponds to the saturation region. The calculated value of β was $0.0083\ \text{cm}^{\frac{1}{2}}\text{V}^{-\frac{1}{2}}$ as compared with the theoretical Schottky coefficient of $0.0082\ \text{cm}^{\frac{1}{2}}\text{V}^{-\frac{1}{2}}$ for anthracene with $\epsilon = 3.4$. This agreement is somewhat fortuitous because the choice of J_s is in some sense arbitrary. With small variations in the constants in (2), the fit to the data of Figure 2 can be improved.

Referring to Figure 2, let us call the straight line passing through the origin the SCLC line since it corresponds to the relation $Q \simeq CV$ that characterizes the SCLC regime[4]. In a previous paper, Pope and Kallmann[18] pointed out the expected voltage dependence of the total excess charge Q ($\propto \Delta\beta/\beta_0$):

$$\begin{array}{ll} \text{a)} & Q > CV \text{ for } V < V(\text{SCLC}) \\ \text{b)} & Q = CV \text{ for } V(\text{SCLC}) \leqslant V < V_{\text{sat}} \\ \text{c)} & Q < CV \text{ for } V > V_{\text{sat}} \end{array} \tag{4}$$

As may be seen in Figure 2 and 3, this prediction is borne out, yielding the following values; $V(\text{SCLC}) = 5$ volts marks the onset of the SCLC regime and the termination of any significant diffusion current contribution to the total current. $V_{\text{sat}} = 60$ volts marks the depletion of the reservoir at the contact and the beginning of a modified Schottky regime. There is an ohmic region of small extent centering about 60 volts. For $V > 1000$ volts electroluminescence is observed and the interpretation of $\Delta\beta/\beta_0$ becomes more difficult.

One can make several calculations from the data. From the slope of the experimental SCLC curve in Figure 1, one can calculate $\ell = 1.7$ using the approximate relation[8]

$$J = N_{\text{eff}}\,\mu\, e \left(\frac{\epsilon\epsilon_0}{He}\right)^{\ell} \frac{V^{\ell+1}}{L^{2\ell+1}} \tag{5}$$

where N_{eff} is the effective density of states within kT of the upper edge of the valence band in anthracene ($\sim 4 \times 10^{21}\ \text{cm}^{-3}$) , and H is the total density of traps in the crystal. At 10V, $L = 230 \times 10^{-4}$ cm, $J = 3 \times 10^{-8}$ A cm^{-2} and using the relations[8]

$$\begin{aligned} \langle n_{\text{tot}}\rangle &= 3/2\,\frac{\epsilon\epsilon_0}{e}\; V/L^2, \\ \theta &= \frac{N_{\text{eff}}\, n_{\text{tot}}^{\ell-1}}{H^{\ell}}\,, \end{aligned} \tag{6}$$

one obtains

$$\begin{aligned} &\langle n_{\text{tot}}\rangle = 5 \times 10^{10}\ \text{cm}^{-3} \\ &\theta = n_f/n_t \sim 0.1 \\ &H \simeq 4 \times 10^{17}\,\text{cm}^{-3} \\ &n_f(\text{SCLC}) \sim 5 \times 10^{9}\,\text{cm}^{-3} \\ &n_f(\text{ohmic}) \sim 8 \times 10^{9}\,\text{cm}^{-3} = \text{n}(0)\ \text{(calculated at 60 volts,} \end{aligned}$$

using $J = n_f\, e\, \mu\, V/L$)

From the ratio $\theta \simeq 0.1$, and using the published values of γ_{Tf}[8] and γ_{Tt}[12], we can calculate an effective bimolecular rate constant from (1)

$$\gamma_{\text{eff}} = \left(\Delta\beta/\beta_0\right)\left(\langle n_{\text{tot}}\rangle\tau_0\right)^{-1} = 0.1\,\gamma_{\text{Tf}} + 0.9\,\gamma_{\text{Tt}} \simeq 10^{-10}\,\text{cm}^3\,\text{sec}^{-1} \tag{6a}$$

which compares reasonably well with our measured value of $6 \times 10^{-11}\ \text{cm}^3\ \text{sec}^{-1}$ for γ_{eff}.

One can calculate a lower limit to the work function of the Ce^{4+}/Ce^{3+}, electrode from the value of $n_f(0)$. Since[1]

$$n_f(0) = N_{\text{eff}} \exp\left(-\varphi/kT\right) \tag{7}$$

where φ is the potential energy step between the Fermi level in the electrode and the valence band edge in the solid, one gets $\varphi \simeq 0.7$ eV and using a band gap E_g for anthracene of of 4eV[19], and a crystal ionization energy I_c of 5.9eV[20], one gets the work function of the Ce^{4+}/Ce^{3+} electrode to be 5.2eV. This work function depends on the concentration ratio of Ce^{4+}/Ce^{3+} at the contact and will probably change if the solution is stirred. In addition, as was shown by

Adirovich[2] and Kallmann and Pope[21], $n_f(0)$ may decrease with increasing applied voltage, so the value of $n_f(0)$ shown in (7) that was calculated at the saturation voltage of 60 volts should be less than the thermal equilibrium value that should properly be used in (7). Indeed, a value of 5.9eV for the work function of Ce^{4+}/Ce^{3+} was obtained by Lohmann and Mehl[21], although this value was calculated using different estimates for I_c and E_g.

Preliminary measurements have been made on anthracene provided with a Au anode and a Hg cathode. The $J-V$ response on a 94μ crystal shows an approximate V^3 dependence for $V < 300$ volts followed by a steeply rising current ($J \propto V^{18}$) commencing at $V > 300$ volts and attaining a value of 10^{-5} A cm^{-2} at 500 volts. The steeply rising portion could easily have been taken as evidence for a traps-filled-limit (TFL)[4], but $\Delta\beta/\beta_0$ is zero over the entire voltage range measured, whereas it should have been at least 50% at 500 volts. At least for this particular case, there is no doubt that the steeply rising current is not evidence of a TFL but of a high field effect or double injection. This work is mentioned here to provide an indication of the power of the techniques described in this paper and will be reported on at greater length shortly.

Summarizing, it can be seen that the lifetime of the DF produced by the fusion of triplet excitons can be used to provide a qualitative and quantitative measure of the voltage dependence of the excess carrier density in an insulator, which in turn opens an entirely new window into the study of electrical conductivity in insulators. Since the observable is an optical signal and the triplet exciton is unaffected by the electrical field, changes in the charge density can be measured precisely and without reference to the internal or external field. For relative charge density changes, no assumption is necessary to connect $\Delta\beta/\beta_0$ and V; for absolute measurements, some reliable relation between n_{tot} and V must be known, such as is shown in (5) and (6). In addition, recent work in our laboratory has shown that the carrier density gradient can be determined as indicated in Ref. 7 and also by measuring the wavelength dependence of DF lifetime. This work will be reported on shortly.

Acknowledgements

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