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Electron time-of-flight measurements in sulfur interpreted via an extra surface mobility channel

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Time-of-flight measurements were carried out in orthorhombic sulfur for various fields, ranging from -2 to -20 kV/cm. No dependence of the mobility with the electric field was found but the current, normalized by the initial current, showed an electric field dependence at small times, decaying faster for larger electric field. After the failure of the usual models in explaining the results—including the assumption of depth-dependent density of traps—a model assuming an extra mobility channel near the surface provided a reasonable set of parameters independent of the electric field. The measurements were carried out at 8.5, 29, 53, 68, and 79 °C.

I. INTRODUCTION

Time-of-flight (TOF) experiments allow us to access the mobility as well as the trapping characteristics of a homogeneous material under study. In the analysis of the results a theory must be invoked, the usual one taking trapping and detrapping parameters as primary concepts. With such a model, the reduced current, that is, the ratio of the current at a time t (smaller than the transit time) to the value at zero time, should be, at each temperature, a universal function of time, that is, independent of the applied voltage. This holds as long as the charge in the transit is kept much smaller than the charges at the electrodes and no anomalous dependence of the mobility with the field[1,2] is detected.

In the following we report electron TOF measurements carried out in orthorombic sulfur along the [111] direction for various voltages and five differents temperatures for which that universality was found not to hold in the initial part of the transport process. Indeed, our results seem to show that a perturbation is effective near the illuminated surface, as already observed in anthracene.[3] It is indeed remarkable that some aspects of the charge transport and trapping in these materials remain unclear despite the large number of TOF works devoted to them.

A number of known and new models were checked concerning their ability in explaining that lack of universality and in the most successful one (of course a possibility is not excluded that another model may also fit our results) a near-surface mobility anomaly (and not simply a near-surface trapping anomaly) had to be assumed. It goes as follows: Negative carriers are created in two channels. One is regular, extending uniformly through the bulk, and its constant mobility is directly accessed through transit time results. The other is characterized by an exponentially decreasing mobility from the surface into the bulk, of yet unknown origin. Both channels lose carriers to deep traps (deep for the time scale of the TOF experiment) thoroughly characterized by a single trapping time.

We would like to mention that other models were found to lead to the same, or nearly the same, time dependence of the observed current. However, they were discarded on physical grounds. For instance, in one model the anomalous band would have associated with it a set of traps distributed in distance hyperbolically from the surface and having a trapping time that is electric field dependent, such as in one- or quasi-one-dimensional conductors.[4] However, the electron mobility tensor has been measured in sulfur and found to be isotropic in one instance,[5] and with a factor of 3 between the smallest and the highest mobility value elsewhere.[6] One such weak anisotropy seems unable to turn the trapping time electric field dependent,[4] and on this ground the model was rejected.

Besides leading us to the mentioned extra "surface" band, the observed traces also indicate an anomalous opening of the carrier packet, resulting in a broader tail around the transit time. This subject is planned to be treated in a forthcoming publication, but we may advance that we agree with the Mort-Scher[7] suggestion that such an opening is due to a small spread in the mobility value, around 5% (perhaps due to the spread on the hopping distance).

Least mean-square techniques were used to get the best set of parameters whenever an analytical expression was at our disposal, but computer integration of the set of partial equations describing the transport of carriers was also performed (see end of Sec. III) to properly take into account space-charge effects.

II. EXPERIMENT

The measurements were carried out in air, with the conventional setup. Quartz platelets, slightly metallized, were used as transparent electrode. A xenon nanopulser 437A was used for a light flasher. The sulfur samples were grown by evaporating a satured solution of sulfur in carbon sulfide[8] and platelets were prepared having 1.0 cm^2 of area and thickness around 1 or 2 mm. The current traces shown in the article were carried out with a 2-mm thick crystal, but the analysis of the results were consistently made in crystals of different thickness. In order to prevent space-charge accumulation in traps, the sample was discharged in short circuit with either sunlight or with a tungsten lamp, after each current trace was obtained. Both faces of the sample gave essentially the same results.

A coil around the sample holder was filled with hot or cold water for getting the desired temperature (8.5–79 °C). A filter with band transmission from 250 to 360 mm was used (only uv light) in order to reduce the light intensity, Oriel neutral filters of optical density 1.5 (3.16% of transmitivity) were used.

The ratio of the charge in the pulse to CV never exceeded 0.1 (C is the sample capacitance and V the applied voltage), what is called the small signal case (see, however, the end of Sec. III). Current and its time derivative were registered using a transient recorder (Datalab model DL 912).

III. NUMERICAL ANALYSIS TECHNIQUES

Least mean-square techniques[9] were employed to obtain the best set of parameters fitting the analytical expression being tested, for instance, the one corresponding to the small signal case[10] for times smaller than the transit time. The fitting was considered good when no visual difference between the computed curve and the corresponding experimental curve could be detected.

In order to better realize the influence of the space charge on the current and also to obtain the current beyond the transit time (here, analytical expressions are indeed available in some cases but they are too cumbersome) the complete set of partial differential equations[11] describing the charge transport in insulators (with unsaturable traps) were used, incorporating eventually specific changes due to the previously mentioned anomalous channel. The finite difference was the method employed throughout which, however, makes the tail markedly rounded near the transit time. Therefore our computed solutions are not good in this region. In order to take advantage of the information brought by the tail shape, coming from comparison between measured and calculated current shapes, we developed a method of integration, using the characteristic lines of the system of partial equations,[12] which by itself, excludes the above-mentioned rounding, although, of course, using more computer time. With it we could conclude that the observed tails were broader than we could expect from the theory.

These numerical integrations allowed us to observe that trapping times may decrease as much as 15% when space-charge effects are considered. This is due to the accumulative effect of space charge, enhancing the current at larger times.

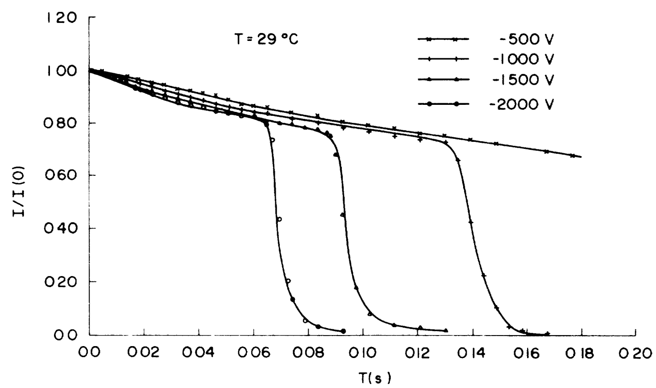

FIG. 1. Normalized current traces for different voltages at 29 °C.

IV. EXPERIMENTAL RESULTS

No initial spike was observed when 1.5 optical density filter was interposed. Therefore, those spikes described in Ref. 13, which also may appear in sulfur, were avoided. This allowed us to find the ratio r of the current at the time t to its value at $t=0$, shown in Figs. 1 and 2 for measurements performed at 29 and 79 °C and for a series of different voltages. It is clear that universality does not

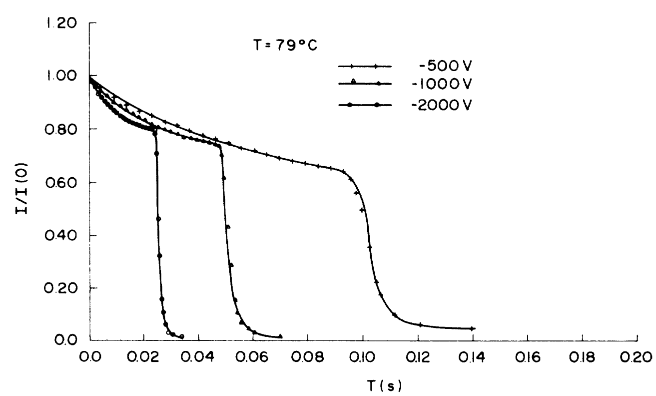

FIG. 2. Normalized current traces for different voltages at 79 °C.

hold and that the ratio r drops more with the time for higher voltages than for lower ones. Taking the transit time at the maximum of the time derivative of the current we found the mobility to be field independent, with a value of 3.6×10^{-4} cm^2/V s at 29 °C, with an activation energy of 0.19 eV, in accordance with previous results.[14]

A comparison of the traces in Fig. 1 and 2 shows an interesting feature: The values of r are higher at lower temperatures, thereby indicating a less severe trapping. We also note a relatively sharp tail followed by a long-lived small decaying current.

We have observed that the beginning of the current traces after several shots, followed by the white light cleaning, become rounded. Keeping the sample at 80 °C for many hours under a 1-torr vacuum has no effect on the current trace. However, cleaning the surface with benzene, with 1% reduction of the sample thickness, is able to recuperate the shape of the trace.

We have also observed that the beginning of the current trace is sensitive to previous small sliding between sample and front electrode. Because of this, the whole series of measurements was carried out without handling the system.

V. ANALYSIS OF THE RESULTS

Table I shows the results obtained when attempting to fit the results at 29 °C with a two-trap-level scheme, one shallow, with τ_1 and τ_{e1} as trapping and detrapping times, and the other deep, with τ_2 as trapping time.[10] Although a good fitting is achieved for every current trace, a large variation of the shallow trap parameters with the voltage is observed. This comes from the lack of universality displaced by r in Figs. 1 and 2. On the other hand, the deep trap parameter τ_2 gave consistent results.

Space-charge effects tend to increase the currents at later times.[15] In order to be sure that no perturbation was responsible for the observed behavior, the integration of the system of partial equations with the same set of traps (one shallow, and one deep) was performed. No difference with the small signal case analytic solution in the whole voltage range was detected, aside from the change for the larger trapping time mentioned at the end of Sec. III.

It could be that only a fraction of the carriers created by the flash were instantaneously injected, a larger one for higher fields, the remaining of the charge being continuously injected afterwards. Such a model could, in principle, explain our results,[16] since the delayed component would increase the current for smaller voltages at later times. We tested the model assuming an exponential time decrease of the trapped surface charge as well as other laws, together with the two bulk trapped levels already used. Here, again the numerical integration of the partial differential equation was carried out allowing us to obtain the current after the transit time. No good fitting was obtained and, besides this, a larger long-lived tail was found (due to the delayed injection) opposite the modest one actually observed.

We have also tried an exponential distribution of deep traps in depth $s(x)$ (Ref. 17) such as

$$s(x)=N_t[1+B(e^{-x/x_0}+e^{-(l-x)/x_0})]$$

with a single deep trapping time τ. Again no consistent set of parameters (τ, B, and x_0) came out of the calculation. In the above formula, N_t, B, and x_0 are constants, x is the depth, and l is the thickness of the sample.

VI. PROPOSED MODEL

Other models were tried without success, but we will not dwell on this any more. The one leading to reasonably good results is as follows: light creates carriers in two channels. The first (numbered 1) has a constant mobility μ_1, and the second (numbered 2) an exponentially decreasing mobility, as $\mu_2 e^{-\alpha x}$, α being a constant and x being the distance from the surface. Both interact with a deep trap level of trapping time τ.

The velocity of the carriers in level 1, within the high-field approximation, is μ_1,E, and therefore the position x_1 of the layer of carriers (a δ function) at the time t is $x_1=\mu_1 Et$ (E is the "external" electric field and μ_1 the mobility in channel 1). On the other hand, the velocity of the carriers on level 2 is given by $\mu_2 e^{-\alpha x}E$, μ_2 being the initial mobility of carrier at the channel 2. Therefore we have

$$\frac{dx_2}{dt}=\mu_2 E e^{-\alpha x}$$

leading to $x_2=(1/\alpha)\ln(1+\mu_2\alpha Et)$ as the position of the corresponding δ function. The density of charge on the two layers, $\rho_1(x,t)$ and $\rho_2(x,t)$ may be written as

$$\rho_1(x,t)=q_1 e^{-t/\tau}\delta(x-x_1(t)) ,$$

$$\rho_2(x,t)=q_2 e^{-t/\tau}\delta(x-x_2(t)) ,$$

q_1 and q_2 being the initial charge content in each channel. Now, the external current I may be found integrating the total current density through the sample thickness l (times the area S of the sample)

TABLE I. Trapping parameters obtained with a two-trap-level scheme.

V (V)	τ_1 (s)	τ_{e1} (s)	τ_2 (s)
−2500	0.17	0.01	0.49
−1800	0.21	0.023	0.48
−1400	0.20	0.020	0.45
−1000	0.34	0.025	0.49
−7000	0.70	0.047	0.49
−400	0.86	0.058	0.47

TABLE II. Parameters of the Sec. VI model obtained by fitting at various voltages, for $T=29$ °C, with $\mu_2\alpha=5.3\times10^{-3}$ cm/V s fixed.

V (V)	A	τ (s)	
−2500	0.13	0.51	
−1800	0.12	0.56	
−1400	0.14	0.50	$\mu_2\alpha=5.3\times10^{-3}$ cm/V s
−1000	0.14	0.56	
−700	0.1	0.52	

TABLE III. Parameters of the Sec. VI model, obtained at various temperatures (overall results).

T (°C)	A	$\mu_2\alpha$ (cm/V s)	τ (s)
8.5	0.10	4.0×10^{-3}	0.71
29	0.13	5.3×10^{-3}	0.54
53	0.10	1.04×10^{-2}	0.43
68	0.23	1.45×10^{-2}	0.32
79	0.21	2.07×10^{-2}	0.27

$$Il = S\left[\int_0^l \mu_1\rho_1(x,t)E\,dx + \int_0^l \mu_2\rho_2(x,t)E\,dx\right],$$

resulting in the following expression for the external current:

$$I = I_0\left[(1-A)e^{-t/\tau} + \frac{Ae^{-t/\tau}}{1+aVt}\right],$$

where I_0 is the current at zero time, V the applied potential, and

$$A = \frac{\mu_2 q_2}{\mu_1 q_1 + \mu_2 q_2}, \quad a = \frac{\alpha\mu_2}{l}.$$

A few points should be noted: first, that a hyperbolic decay results from the exponential x-dependent mobility; second, that only the product $\alpha\mu_2$ related to the "anomalous" process is relevant to our results, and also that three parameters should be determined from the fitting A, a, and τ. To this end, we first allowed the three parameters to vary freely, and the best mean-square fit was achieved. After this, the mean value of a was found and fixed, the other two being again determined by the mean-square fit. We show the results corresponding to 29 °C in Table II, and the overall results for other temperatures in Table III. To save space, figures comparing fitted and measured currents are not shown, but the agreement was quite good.

VII. DISCUSSION

The values appearing in Table II look reasonable. The relative intensity of the anomalous component A does not change with the field and is smaller than the normal one (0.13 as compared with 0.87). The determined trapping time is $0.54 + 0.04$ s at 29 °C. The results at other temperatures, Table III, show that A sharply increases from 0.13 to 0.22 in the range 53–68 °C. On the other hand, the trapping time decreases with increasing temperature, a behavior known to hold whenever the mobility (let us think here of the normal μ_1 mobility) is shallow trap modulated. Table III shows that the mobility μ_2 grows more than τ decreases (respectively, 5 and 4 times from 8–79 °C). Alternatively, the decrease in τ could be explained assuming the trapping act to be activated, a possibility discussed by Schmidlin.[2] This last explanation should be preferred, since the mobility is believed to be due to electron hopping through the lattice[18,19] (see however, Ref. 20). Before continuing, a few words are in order about the spreads in Table II. We agree that they are not small, but the point to be stressed is the lack of correlation between the values of the parameters and the electric field variation, a result not achieved with the other models.

A simple proportionality is found between the parameter $a = \alpha\mu_2/l$ and the mobility μ_1. Since α should be only weakly dependent on the temperature, this would indicate the same temperature behavior for both and μ_1 and μ_2. Within the scope of the model no reason could be advanced to explain the result.

Concerning the depth of the surface states ($1/\alpha$), it is concealed in the product $\mu_2\alpha$. We first thought that the perturbing surface effect obtained in Fig. 5 of Ref. 5 by the interrupted field technique, giving a surface thickness of 40 μm, could be related to our extra surface channel. But a closer examination shows that this is not the case since both channels have the same trapping time. However, we should note that, opposite to our measurements, the current traces in Ref. 5 exhibit large initial spikes, indicative, perhaps, of large surface trap density.

Values obtained by the fitting procedure leading to data in Table II could now feed the system of partial differential equations to be computer integrated. In Fig. 3 we show a fitting using the finite difference method (points are experimental results). As previously mentioned (Sec. III) this integration method introduces uncertainties near the transit time and therefore a region near it should not be considered. The general agreement is good even after the transit. It shows that the long-lived current tail is due to the anomalous current, a quite unexpected result. On the other hand, it should be noted that the parameters used to fit the curve of Fig. 3 do not duplicate exactly the mean values in Table II, as mentioned in Sec. III. The incorporation of space-charge effects lowers the trapping time even at the low injection level employed here. We gave to α the value of 250 cm^{-1}, but the plot is quite insensitive to the individual values of α and μ_2, only the product being effective.

Concerning the nature of the states or centers leading to the anomalous mobility, they could be related either to surface states or impurities. But experiments we carried out in a vacuum (10^{-2} torr), at low light intensity, gave essentially the same results as in ambient air. Yet this is

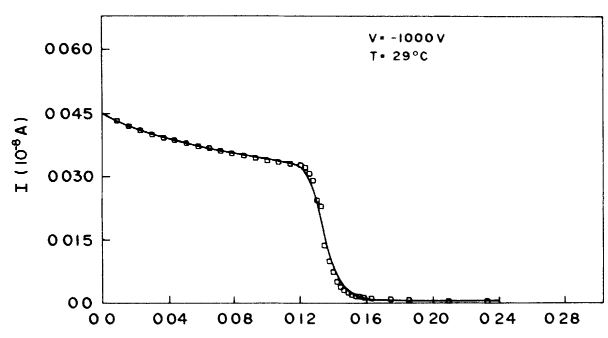

FIG. 3. Current trace obtained with integration of the transport equations using the finite difference $\mu_1 = 3.6\times10^{-4}$ cm^2/V s, $\mu_2 = 2.1\times10^{-5}$ cm^2/V s, $\alpha = 250$ cm^{-1}, $A = 0.13$.

not conclusive. On the other hand, a conduction band above but near (0.8 eV) the hopping electron band has been predicted by Chen,[21] and it is possible that it may in some way be related to the observed anomalous channel.

VIII. FINAL REMARKS

We think that our hypothesis about "surface" states is important in the sense of incorporating near-surface anomalies detected long ago (persistent internal polarization[22,23]) in the realm of TOF analysis. Trapping near the surface is enhanced over the normal value due to the contribution to it brought by the extra channel component. In this respect it should be stressed that the simpler and, at first sight, more natural model of a single mobility and a decreasing trapping distribution from the surface on[17] failed to fit the results and forced us to define a second mobility, restricted to the surface region. New research work is necessary for a better understanding of these results.

IX. ACKNOWLEDGMENTS

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