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Evidence for a linear low-voltage space-charge-limited current in organic thin films. Film thickness and temperature dependence in alpha-conjugated sexithienyl

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Résumé. — Les caractéristiques courant-tension (I - V) de structures Au/ α -sexithiényl/Au ont été mesurées. Les courbes I - V présentent deux régimes : à tensions élevées, on observe la loi en V^2 correspondant au courant limité par la charge d'espace (CLCE) ; la variation linéaire à faible tension est généralement attribuée au courant ohmique dû aux porteurs libres en volume. Une étude du courant linéaire en fonction de l'épaisseur de l'échantillon montre deux comportements. Le modèle standard s'applique aux films épais, dont la conductivité calculée à partir de la pente des courbes I - V est indépendante de l'épaisseur. Dans les films minces (moins de 2 μm), on obtient une conductivité dépendante de l'épaisseur. Ceci s'explique dans le cadre du modèle développé par Bonham et coll., dans lequel on tient compte de la diffusion des porteurs injectés thermiquement. La densité en volume de ces porteurs injectés croît quand l'épaisseur est réduite, et peut devenir plus grande que celle des porteurs libres déjà présents dans le film. Les résultats expérimentaux sont en bon accord avec les prédictions du modèle. On a pu calculer la mobilité effective du α -sexithiényl (α -6T) à partir du régime quadratique des courbes I - V . On a également effectué des mesures en fonction de la température. On trouve une mobilité thermiquement activée, ce que l'on interprète par l'existence d'un piège peu profond situé à 0,3 eV au-dessus du sommet de la bande de valence.

Abstract. — The current-voltage (I - V) characteristics of Au/ α -sexithienyl/Au sandwich structures have been measured. The I - V curves present two regimes : at high voltages, the square law corresponding to the space-charge-limited current (SCLC) is observed ; the linear variation occurring at low voltages is generally attributed to the ohmic current due to bulk free-carriers. A study of the linear current as a function of the sample thickness shows that two behaviors are encountered. The standard model is followed on thick films, where the conductivity calculated from the slope of the I - V curve does not depend on the thickness. In thin films (less than 2 μm), a thickness dependent conductivity is obtained. This is explained within the frame of the model developed by Bonham and co-workers, in which the diffusion of carriers thermally injected is taken into account. The bulk density of these injected carriers increases when the thickness is reduced, and may become higher than that of bulk free-carriers already present in the film. Experimental results are in good agreement with the predictions of the model. The effective mobility of α -sexithienyl (α -6T) could be calculated from the quadratic regime of the I - V curves. Measurements as a function of temperature were also carried out. The mobility is found to be thermally stimulated, which is interpreted as due to a shallow trap located 0.3 eV above valence band edge.

Introduction.

Organic semiconductors have received a renewed attention since they have been used as the active component in electronic devices, Schottky diodes and more recently field-effect transistors (FET's). Organic FET's have been fabricated with conjugated polymers, polyacetylene [1, 2] and various polythiophene derivatives [3, 4], metallophthalocyanines [5], and α -sexithienyl (α -6T) [6], an alpha-conjugated oligomer of thiophene that is currently studied in our laboratory as a model molecule of its homologue polymer. The improvement of these organic devices requires a better understanding of the charge-carrier transport mechanism in these materials.

Organic compounds [7] generally present very low electrical conductivities. Raising the conductivity to the semiconducting range can be obtained by doping, i.e. introducing small amounts of electron donating or accepting impurities. Unfortunately, impurities in organic semiconductors act more often as traps rather than dopants. A probable reason for this is the low electron affinity of organic compounds, as compared to that of covalently bound inorganic crystals. The question arises of the origin of the carriers in non-intentionally doped materials. Most experimental information comes from the current-voltage (I - V) characteristic of films sandwiched between two metal electrodes, which usually presents at high applied voltages a superlinear dependence in V^n , $n \geq 2$ [8]. This is an evidence for a space-charge-limited current (SCLC) resulting from carriers injected by the metallic electrodes. The linear variation at low biases is generally attributed to an ohmic current due to bulk free carriers, coming from some doping agent present in the material. However, as has been shown in theoretical papers [9-12], this linear current may also arise, in the case of thin films, from charges injected from the contact electrodes.

Experimental results on α -6T films of various thicknesses are presented here to illustrate these previous models. It is shown that the actual ohmic current is not observed but on samples thicker than several micrometers. The very low density of doping impurities already found in polythiophene [13] is confirmed here.

Experimental.

Alpha-conjugated sexithienyl was synthesized from α -terthienyl (Aldrich) according to the method described earlier [14].

The current-voltage measurements were carried out on sandwich structures. A 500 nm gold layer was first sputtered on glass slides. α -6T was then evaporated by heating the powdered material in a tungsten crucible under a pressure of 5×10^{-3} Pa. The front contact was realized by evaporating gold dots (area : 0.00018 cm², thickness : 25 nm) through a mask on top of the organic layer. The current was measured in a metal box which provided a capacitive and inductive shielding. Tungsten microprobes were used to contact the metal dots. The I - V characteristics were obtained with a Hewlett-Packard 4140B pA meter/d.c. voltage source, monitored with a HP 310 desk computer.

Low temperature measurements were made under reduced pressure ($< 10^{-1}$ Pa) in a Displex DE 202 (Air-Product) close-cycle cryostat. The temperature was adjusted within ± 0.1 K with a APD-E temperature controller.

Results and discussion.

VARIATION WITH THICKNESS. — The I - V characteristics of Au/ α -6T/Au sandwich structures with various thicknesses have been measured in ambient air and temperature (300 K). Results are shown in figure 1. For the sake of clarity, only four I - V curves, out of the six measured,

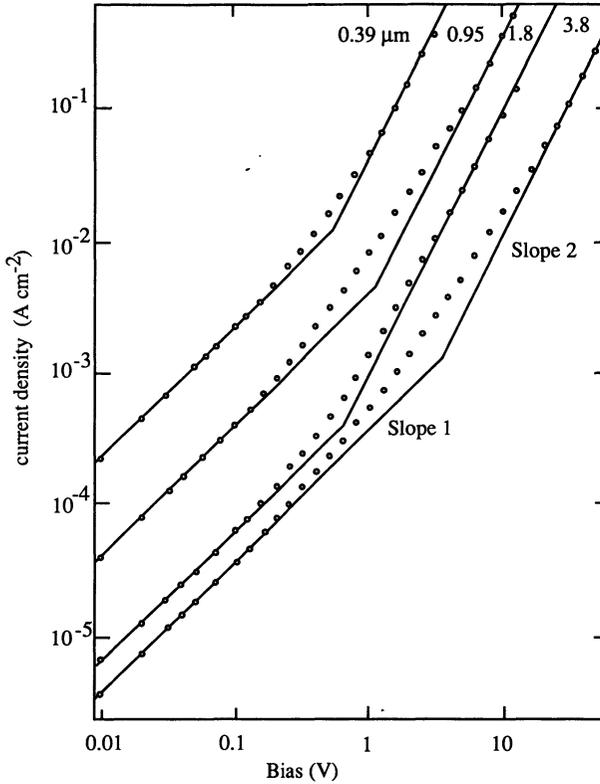


Fig. 1. — Log-log plot of the current-voltage characteristics of Au/ α -sexithienyl/Au structures for various thicknesses of the organic layer. The straight lines are least-square adjustment to the experimental points, with a slope of 1 at low biases, and 2 at high biases (SCLC).

are shown in figure 1. In all cases, the variation of the current density is linear at low voltages and quadratic at high voltages. The straight lines drawn in figure 1 correspond to least-square adjustments to the experimental points with slopes of 1 and 2.

The linear regime can be characterized by a low voltage conductivity :

$$\sigma = L(j/V) . \quad (1)$$

Here, j is the current density and L the thickness of the film. The variation of σ as a function of L is shown in table I and figure 2. If the linear current was due to the bulk free carriers, one should not expect it to vary when changing the film thickness. Obviously, this behavior is not followed for thicknesses lower than about 2 μm .

The standard space-charge-limited current density for shallow trapping j_{sc} obeys

$$j_{sc} = (9/8) \varepsilon \theta \mu V^2 / L^3 . \quad (2)$$

Here ε is the dielectric constant ($\varepsilon = \varepsilon_r \varepsilon_0$, with a relative dielectric constant $\varepsilon_r = 2$ for α -6T), and μ the mobility. θ is the fraction of the total charges free to move, which depends on the trap density and temperature, and will be explicated further. In the trap-free case $\theta = 1$, but usually the majority of the injected charges is immobilized in traps and $\theta \ll 1$. The intercept voltage V_i where the linear line crosses the SCLC curve is obtained by

Table I. — Parameters of the current voltage characteristics of Au/ α -6T/Au sandwich structures with various thicknesses of the organic layer. The low voltage conductivity σ is deduced from the slope of the linear region, j_{sc} and the effective mobility $\theta\mu$ from the quadratic regime of the characteristics. A relative dielectric constant of 2 was taken. V_i is the intercept bias between the linear and quadratic regimes.

Sample #	Thickness μm	σ S cm^{-1}	j_{sc} (at 1 V) A cm^{-2}	$\theta\mu$ $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$	V_i V
PR1	0.39	8.60×10^{-7}	3.89×10^{-2}	0.012	0.57
005	0.49	5.19×10^{-7}	1.20×10^{-2}	0.007	0.90
01	0.93	3.78×10^{-7}	3.24×10^{-3}	0.013	1.25
1	1.8	1.14×10^{-7}	9.12×10^{-4}	0.027	0.69
03	2.8	1.31×10^{-7}	2.09×10^{-4}	0.023	2.24
04	3.8	1.40×10^{-7}	1.00×10^{-4}	0.028	3.68

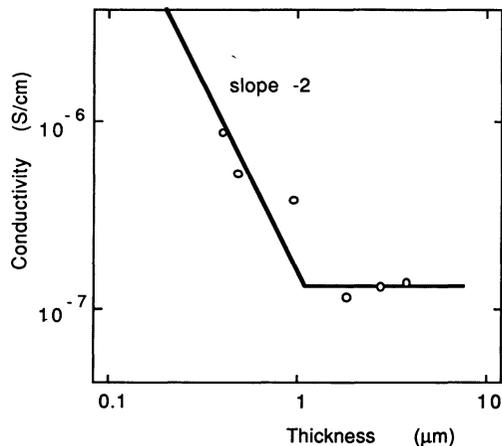


Fig. 2. — Variation of the low voltage conductivity σ as a function of thickness, deduced from a least-square adjustment of the I - V curves in figure 1 at low voltages.

equating equations (1) and (2)

$$V_i = (8/9)(\sigma/\varepsilon\theta\mu) L^2 \quad (3)$$

where σ is the low voltage conductivity. A log-log plot of the variation of V_i as a function of the thickness is shown in figure 3. Again, the standard behavior predicted by equation (3) is not observed at thicknesses lower than 2 μm .

Because there is no analytical solution to the general single-carrier conduction problem, the standard SCLC theory has been derived by neglecting the carrier diffusion. More complete analytical or numerical resolutions already reported [9-12] have shown that at low voltages, a linear current also arises from carriers injected from the contacts. As stated in a previously published paper [12], the density of injected carrier $n(x)$ at a distance x of one electrode is

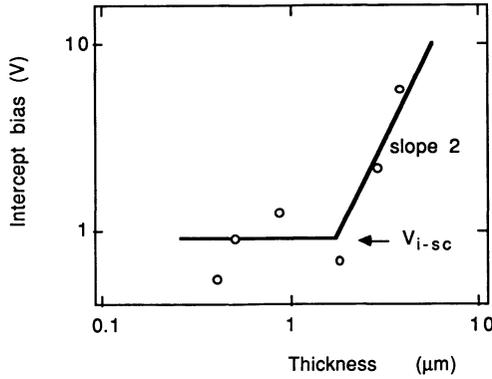


Fig. 3. — Variation of the intercept bias between linear and quadratic regime of the I - V curves, as a function of sample thickness. V_{i-sc} correspond to the theoretical value for thin films.

given, in the case of two perfectly injecting contacts, by

$$n(x) = 2 \pi^2 \varepsilon kT / [qL \sin(\pi x/L)]^2 \tag{4}$$

where q is the charge of the carriers. Equation (4) shows that there exists a concentration of charge thermally injected by the contacts without any applied voltage, the minimum value of which is $n_{min} = 2 \pi^2 \varepsilon V_T / qL^2$ (here, the thermal voltage $V_T = kT/q$, which controls the injected space charge, appears explicitly in the formula). This voltage independent charge density gives rise to a linearly varying current at low applied voltages. Importantly, this concentration increases when the thickness L decreases, and may become higher than the density of the free carriers already present in the bulk. The linear current will then correspond to a conductivity σ_i resulting from injected carriers :

$$\sigma_i = 2 n_{min} q\mu = 4 \pi^2 kT \varepsilon \theta \mu / qL^2 \tag{5}$$

which can be compared to the ohmic conductivity σ_Ω generated by ionised bulk acceptor impurities :

$$\sigma_\Omega = n_\Omega q\mu \tag{6}$$

where n_Ω is the density of non-injected bulk free carriers. The variation of the conductivity of α -6T as a function of thickness, given in figure 2, is now well described by equations (5) and (6) : it decreases as L^{-2} (slope -2 in a log-log plot) for thicknesses lower than ca. $2 \mu\text{m}$, and is thickness independent beyond this value. The actual ohmic conductivity corresponds to the thickness independent value, namely $1.3 \times 10^{-7} \text{ S cm}^{-1}$.

For shallow trapping the parameter θ is given by [8] :

$$\theta = (N_V/gN_t) \exp[-(E_t - E_V)/kT] \tag{7}$$

for a dominant trapping level at energy E_t and density N_t . N_V is the density of state on top of the valence band at E_V , g the degeneracy factor (generally taken as 2). Carriers originating from acceptors of density N_a are also trapped and contribute to the free carrier density by

$$n_f = (N_V/gN_t) \exp[-(E_t - E_V)/kT] N_a = \theta N_a \tag{8}$$

and the ohmic conductivity can be written as :

$$\sigma_{\Omega} = \theta N_a q \mu . \quad (9)$$

The value of the product $\theta \mu$ deduced in table I from the quadratic SCLC regime gives a density of acceptors $N_a = 3.2 \times 10^{13} \text{ cm}^{-3}$, which is extremely low. One tentative explanation would be that the density of doping centers is much lower than the total concentration of impurities, most of which behave as trapping centers [13].

A most interesting outcome of the space charge model including diffusion is the prediction that the intercept voltage $V_{i\text{-sc}}$ between the space-charge-limited linear (Eq. (5)) and quadratic (Eq. (2)) regimes, given by [12] :

$$V_{i\text{-sc}} = (32/9) \pi^2 kT/q \quad (10)$$

is independent of the transport properties (i.e. mobility μ), the thickness of the sample, the nature of the material (i.e. its dielectric constant), and its trapping parameters (i.e. $\theta(N_t, E_t)$). It is only proportional to the temperature. This comes from that in both regimes, the charge density involved is the injected space charge. For the linear dependence, the *thermally* injected effective free density is (in the case of shallow trapping) :

$$n_T = 4 \pi^2 \theta \varepsilon V_T / qL^2 = 4 \pi^2 \theta \varepsilon kT / q^2 L^2 . \quad (11)$$

In the standard space-charge regime, the *field* injected effective free density is :

$$n_{sc} = (9/8) \varepsilon V / qL^2 . \quad (12)$$

By equating the two charge densities, equation (10) is obtained. At room temperature (300 K) $V_{i\text{-sc}} = 0.91 \text{ V}$. These two important tests, namely the thickness independence of the intercept voltage, and its absolute value close to 1 V, are both verified in figure 3 for thin films (L less than $2 \mu\text{m}$). Conversely, when the low-voltage linear regime is due to non-injected free carriers of density n_{Ω} , the intercept voltage is given by equating this density with the field injected density n_{sc} (Eq. (12)) to give :

$$V_{\Omega, sc} = (8/9) qL^2 n_{\Omega} / \theta \varepsilon = (8/9) qL^2 N_a / \varepsilon \quad (13)$$

which is dependent on the thickness, the nature of the material, and the amount of dopant. Again, the variation of the intercept voltage of α -6T films (Fig. 3) is in good agreement with this model.

More accurate numerical computations made by Bonham and Jarvis [11] have shown that, in fact, neither the linear nor the quadratic laws are good approximations around the intercept bias. Their calculated curve greatly resembles the experimental I - V plots of figure 1. For a trap-free material (or a material with only shallow traps) the standard SCLC square law is only verified at voltages higher than about 5 V. A consequence of this wide intermediate regime is a poor accuracy in the determination of the intercept bias. This could explain the scattering of the values obtained on thin films, as can be noticed in figure 3.

At higher voltages, the current predicted by the complete theory merges with the standard quadratic SCLC. It can be seen in figure 4 that the variation of the space-charge-limited current on our samples follows a L^{-3} law all over the whole thickness range. Similarly, the effective mobility deduced from equation (2) is roughly independent of the thickness, as shown in table I. A decrease of the mobility as the thickness is lowered has already been reported from I - V measurements on α -6T and casted poly(3-hexylthiophene) field-effect

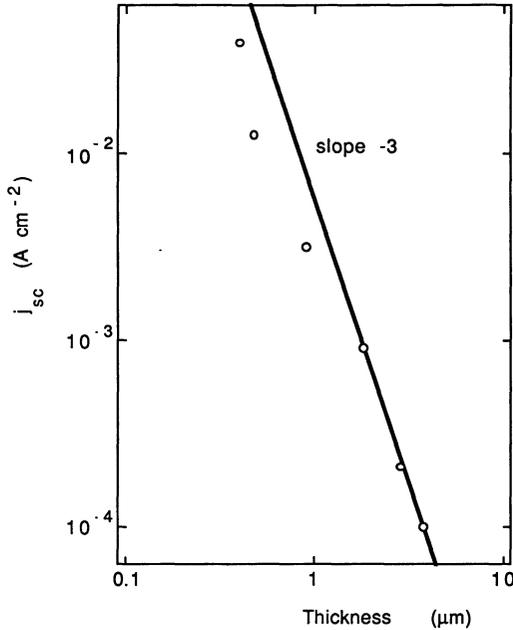


Fig. 4. — Log-log plot of the space-charge-limited current vs. sample thickness. A slope of -3 corresponds to the standard SCLC theory.

transistors [4, 6]. Such a decrease could account for the deviation from the straight line in figure 4 at low values of L .

VARIATION WITH TEMPERATURE. — The variation of the I - V characteristics as a function of temperature is given in figure 5 and table II. The thickness is $1.8 \mu\text{m}$ (sample $\neq 1$). It must be noted that the measurements at low temperatures were carried out under reduced pressure. We have previously reported that, in this case, an undoping of α -6T occurs [6], which explains the lowering of the low voltage conductivity. However, a mere undoping cannot account for the concomitant lowering of the SCLC, which does not depend on the dopant induced bulk carrier density. The global lowering of the current could be due to an *increase* of the trap density. One possible explanation for this behavior is that oxygen acts as a trap-killer. Its presence in films exposed to ambient atmosphere would then result in a *decrease* of the trapping efficiency. Conversely, the decrease of the oxygen content when the films are put in vacuum would result in an increase of the density of traps. Due to this increased trapping, the linear regime of the I - V curve is now space-charge limited (Eq. (7)), as indicated by the value of the intercept bias, which is close to the theoretical value (0.91 V at 300 K). As was stated above, V_{i-sc} is independent of the thickness and the nature of the material, but it is linearly dependent on the temperature. A plot of V_i vs. temperature is shown in figure 6. The straight line corresponds to the theoretical value (Eq. (10)). A fair agreement is found for temperatures higher than 240 K; the slight difference can be ascribed to poor accuracy in determining V_i , as noted above. At lower temperatures, a strong departure from the calculated curve is observed. Up to now we have assumed that the SCLC was characterized by a quadratic variation with the applied voltage. Such a variation is valid for a trap-free material, and can be extended to materials with shallow trap levels. When deep traps are present, their gradual filling as the voltage increases results in a variation of the current as V^n , with $n > 2$ [8]. A closer look at the I - V curves in figure 5 shows that the slope of

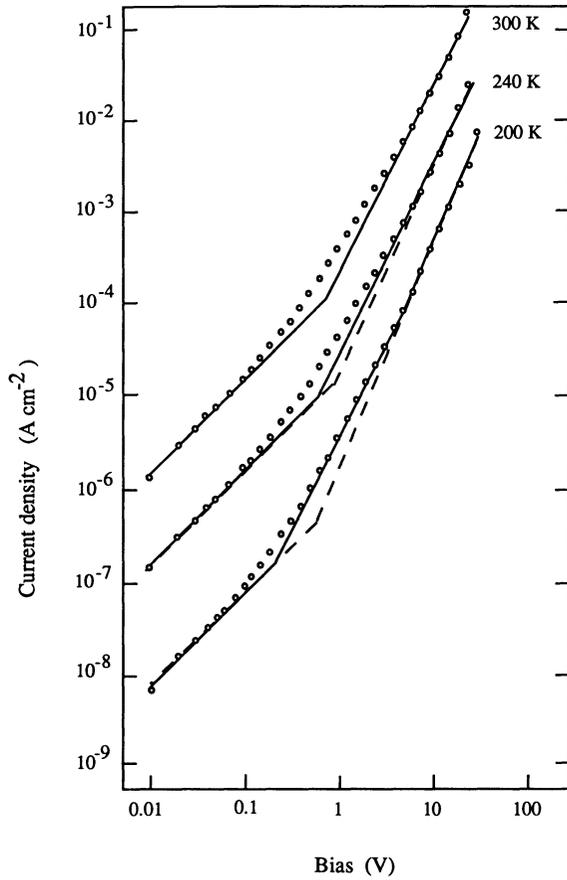


Fig. 5. — Log-log plot of the I - V characteristic of sample # 1 ($1.8 \mu\text{m}$) under reduced pressure ($< 10^{-1} \text{ Pa}$) at different temperatures. The experimental points are adjusted to straight lines with a slope of 1 at low voltages, and 2 at higher biases (full lines). The dashed lines correspond to ajustements with slopes greater than 2.

Table II. — Variation of the parameters deduced from current voltage characteristics as a function of the temperature. Sample # 1, Au/ α -6T/Au, thickness : $1.8 \mu\text{m}$. See table I for the meaning of symbols.

Temperature K	$\sigma \text{ S cm}^{-1}$	$\theta \mu \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$	$V_i \text{ V}$
300	2.73×10^{-8}	7.34×10^{-3}	0.77
270	1.47×10^{-8}	4.43×10^{-3}	0.69
240	2.75×10^{-9}	1.03×10^{-3}	0.55
220	3.13×10^{-10}	2.85×10^{-4}	0.23
200	1.32×10^{-10}	1.28×10^{-4}	0.21
180	2.38×10^{-11}	3.17×10^{-5}	0.15

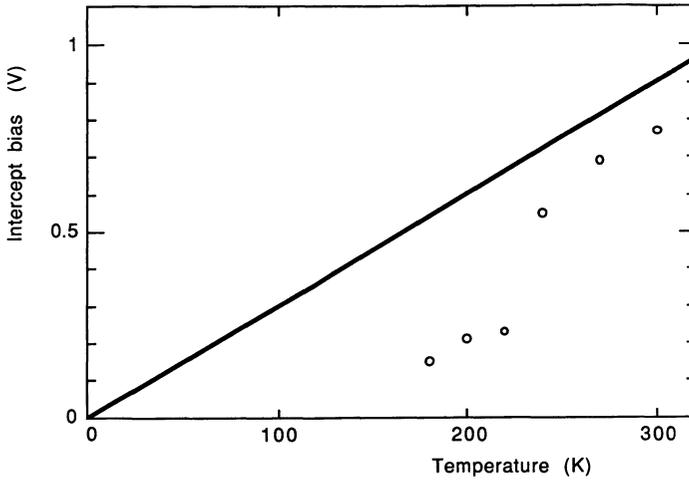


Fig. 6. — Variation of the intercept bias between linear and quadratic regimes for sample # 1 vs. temperature. The variation predicted by our model is indicated by the full line.

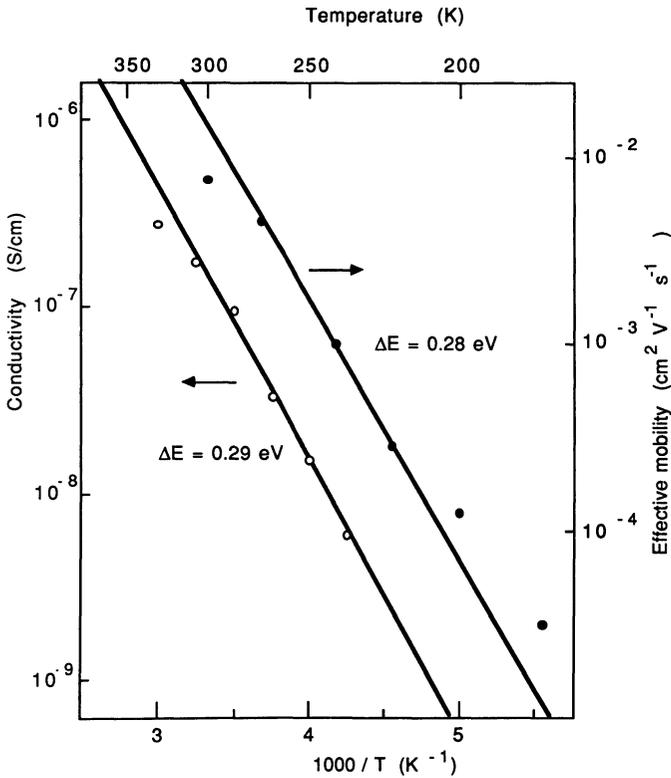


Fig. 7. — Arrhenius plot of the effective mobility, calculated from SCLC on sample # 1, and conductivity, measured on a α -sexithienyl layer with two gold contacts separated by 90 μm .

the SCLC increases slightly when the temperature decreases, indicating that the shallow traps are filling as the Fermi level approaches the valence band edge. Consequently, an intercept bias calculated from straight lines with a slope of 2 is no longer valid when the temperature decreases below 240 K.

The presence of traps can be shown by an Arrhenius plot of the effective mobility $\theta\mu$ where θ is given by equation (7) (Fig. 7). Also drawn in figure 7 is the variation of the conductivity. Since the bulk conductivity cannot be deduced from the linear regime of the I - V curves, it was measured on a film with two gold contacts on the same side, separated by 90 μm . With this configuration, the I - V curves were linear up to ± 100 V. The Arrhenius plot of σ is parallel to that of the effective mobility, and gives an almost equal activation energy, roughly 0.3 eV. This shows that the same dominant trapping level at 0.3 eV controls the free carrier density in both cases, in agreement with equation (8). A similar feature has been reported on metal-free phthalocyanine single crystals [15], and was attributed to a donor level located at the same distance from the conduction band edge as the shallow trap level (in this particular case, metal-free phthalocyanine was found to behave as a n -type semiconductor). In fact, in equation (9) the factor θ can be indifferently assigned either to N_a , giving in this case a free carrier density $n_f = \theta N_a$ moving with a microscopic mobility μ , or to the mobility, in which case one assumes that all the acceptors of density N_a are ionized and that the carriers move with an effective mobility $\mu_{\text{eff}} = \theta\mu$. The latter approach is the most often used in papers dealing with the SCLC, simply because the field dependent density of injected carriers does not appear explicitly in equation (2). However, it should be kept in mind that, basically, the concept of effective mobility mirrors the fact that an electric current is the result of two distinct phenomena — carrier generation and recombination, including trapping, on the one hand, and charge transport on the other hand — which cannot be separated from I - V measurements alone. The determination of the microscopic mobility, and its temperature dependence, requires other kinds of experiments, e.g. Hall effect, time of flight, etc. Such an independent measurements would also be necessary for calculating the density of traps.

Conclusion.

Although its limitations have been noticed for more than a decade, the standard SCLC model is still commonly used for interpreting the I - V curves of weakly conducting materials. We have presented here a set of experimental data obtained on Au/ α -6T/Au sandwich structures, which substantiate the validity of the model developed by Bonham and co-workers [11] where the effects of diffusion was calculated. The variation of the low voltage conductivity as a function of sample thickness establishes the existence of two regimes. For thicknesses larger than a few micrometers, the classical behavior is followed, and the conductivity is thickness independent. When the thickness decreases, σ becomes proportional to the reversed square thickness, which is consistent with thermal space charge injection. The actual conductivity could be deduced, and a density of acceptors of $3.2 \times 10^{13} \text{ cm}^{-3}$ at 300 K was calculated.

Although fundamental in nature, voltage independent thermal injection is scarcely taken into account in interpreting experimental I - V characteristics. However, analytical [12] and numerical [11] calculations, together with our experimental results, clearly show that the contribution of thermal injection may be dominant at low applied voltages in thin films.

The variation of the I - V curve as a function of temperature shows that the effective mobility is thermally activated. This can be attributed to a shallow trap level, the distance of which from the valence band edge corresponds to the activation energy : 0.28 eV.

Experimental results will be presented in the near future, in order to extend the model to the case of unsymmetrical contacts.

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