Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Space Charge Limited Current in Naphthalene Single Crystals

M. Campos [a] [b]

[a] Physics Department, Esxola de Engenharia São, Carlos, S. Paulo, Brazil

[b] Dartmouth College, Department of Chemistry, Hanover, New Hampshire, 03755, U.S.A.

Version of record first published: 21 Mar 2007.

To cite this article: M. Campos (1972): Space Charge Limited Current in Naphthalene Single Crystals, Molecular Crystals and Liquid Crystals, 18:2, 105-115

To link to this article: http://dx.doi.org/10.1080/15421407208083254

Molecular Crystals and Liquid Crystals. 1972. Vol. 18, pp. 105–115

Printed in Great Britain

Space Charge Limited Current in Naphthalene Single Crystals†

M. CAMPOS‡

Physics Department, Escola de Engenharia
São Carlos, S. Paulo, Brazil

Received December 14, 1971

Abstract—Measurements of the current in naphthalene single crystals, as a function of the voltage, showed space charge limited current characteristics. Using this theory we found for the trap density of this material, values between 10^{16}–10^{17} cm^{-3}. The mean depth was about 0.65 eV, the capture cross section, 10^{-17} cm^2 and the frequency of escape, 10^9 sec^{-1}. For the current range encountered in this work, it is shown that silver paste behaves as an injecting contact for electrons.

1. Introduction

The study of space charge limited currents (SCLC) has been the object of investigation in different materials, by many researchers. A detailed study can be found in the book of Lampert and Mark.[1] This theory allows the determination of the trap density N_t of the material by two different procedures. We can calculate the density of traps from the voltage V_{tfl} where the trap-free region starts, using the equation:

$$N_t = 10^{-13}(\epsilon V_{tfl})/(el^2) \tag{1}$$

where ϵ is the dielectric constant of the solid, l is the separation between electrodes and e the electron charge. Or, we can calculate N_t from the curve $d\theta/dT$;

$$\theta = n/n_t = (N_c/N_t)\exp(-E_t/kT) \tag{2}$$

where n/n_t is the ratio of free electrons to trapped electrons, E_t is the trap depth of traps with density N_t and N_c is the effective

† Work supported by National Research Council of Brazil, Foundation for the Research of São Paulo (FAPESP) and Bank of National Development (BNDE).

‡ Present address: Dartmouth College, Department of Chemistry, Hanover, New Hampshire 03755, U.S.A.

density of states in the conduction band. However, as we shall see, Eq. (1) does not provide the real trap density of the material.

The main difficulty in making measurements on organic crystals has been making Ohmic contacts for these crystals. In the specific case of naphthalene, some attempts have been made, without great success.[2,3] More recently, Lohmann and Mehl[4] studied the double injection of electrons and holes in naphthalene crystals grown from solution, using contacts of sodium–potassium eutectic for the electron injection and Ag^{2+}/Ag^{+} in 7.5n HNO_3, for hole injection. They observed no injection currents for crystals grown by fusion and solidification.

Recently, Williams and Campos[5] observed a behavior typical of SCL currents in naphthalene single crystals, charged with negative corona discharge and with silver as the anode. In that work it was not clear whether conduction was due to electrons from the negatively charged surface or to holes injected by the anode. We show here that conduction is due to electrons.

2. Experimental

Single crystals of re-sublimed naphthalene were grown by the fusion and solidification process, described in Ref. 6. An electric field was applied normally to the *ab* crystallographic plane. The crystal was mounted so as to permit temperature variation in an apparatus previously described.[6] Electrodes and guard ring consisted of silver paint. The thicknesses of the crystals varied from 0.07 to 0.32 cm, and their areas were 1.0 and 1.7 cm^2. Electric fields ranging between 87 V/cm and 5×10^4 V/cm were applied to these crystals. Measurements were made at temperatures between 243 and 323 °K.

For some measurements, one electrode was removed and the surface charged by a negative corona discharge. After the discharge, the electrode was again applied, and the sample was placed in the measuring system.

3. Results

To distinguish between injection of electrons or holes, we used as one of the electrodes, silver paint and for the other, a very thin

teflon sheet. We could observe then that for voltage pulses in the injection regime the current due to electrons was about 30 times greater than that due to holes. However, if the applied potential was within the Ohmic region, where there is no injection, the current values were equal. This shows that the injection currents are due to electrons.

A typical result observed for the current, as a function of voltage, is shown in Fig. 1. We can see from this figure several well-defined regions. The first is Ohmic, followed by a square-law region, another with large-slope of the I–V curve and finally a quadratic region of magnitude 10^4 smaller than a trap-free SCL current. This behavior is characteristic of multiple discrete trapping levels.

A theoretical trap-free SCLC I_0 for a sample with known constants can be calculated from the equation:

$$I_0 = (10^{-13}\epsilon\mu V^2 A)/l^3 \tag{3}$$

μ is the mobility of the carriers in cm²/V-sec, V is the applied voltage in volts, A is the area of the sample in cm². From the ratio of the current in the low voltage quadratic region to the calculated trap-free value, we obtain $\theta = 4.2 \times 10^{-8}$. From Fig. 1 we can see that at room temperature the transition from Ohmic to quadratic behavior occurs at $V_t = 160$ V. From this transition voltage:

$$V_t = 10^{13} n_0 e l^2 (\epsilon\theta)^{-1} \tag{4}$$

we then calculate the concentration of free carriers $n_0 = 1.1 \times 10^3$ cm^{-3}.

The density of traps in this sample can be calculated using the value of $V_{tfl} = 2600$ V in Eq. (1), giving $N_t = 4.5 \times 10^{11}$ cm^{-3}. With this value in Eq. (2), we find $E_t = 0.99$ eV, for the distance in energy, below the conduction band, at room temperature.

Figure 2 illustrates the dependence of the current-voltage curve on he temperature. The trap depth was then calculated from $\mathrm{d}\theta/\mathrm{d}T$ giving $E_t = 0.65$ eV. This is shown in Fig. 3. Supposing that N_c and N_t are not functions of the temperature, we find from the intercept at $1/T = 0$, $N_t = 4.5 \times 10^{16}$ cm^{-3}, a value five orders greater than calculated by V_{tfl}. From the definition $\theta = n/n_t$ and from the measured current, it is possible to calculate the trap depth in an independent way. Such values are shown in Table 1. Using the

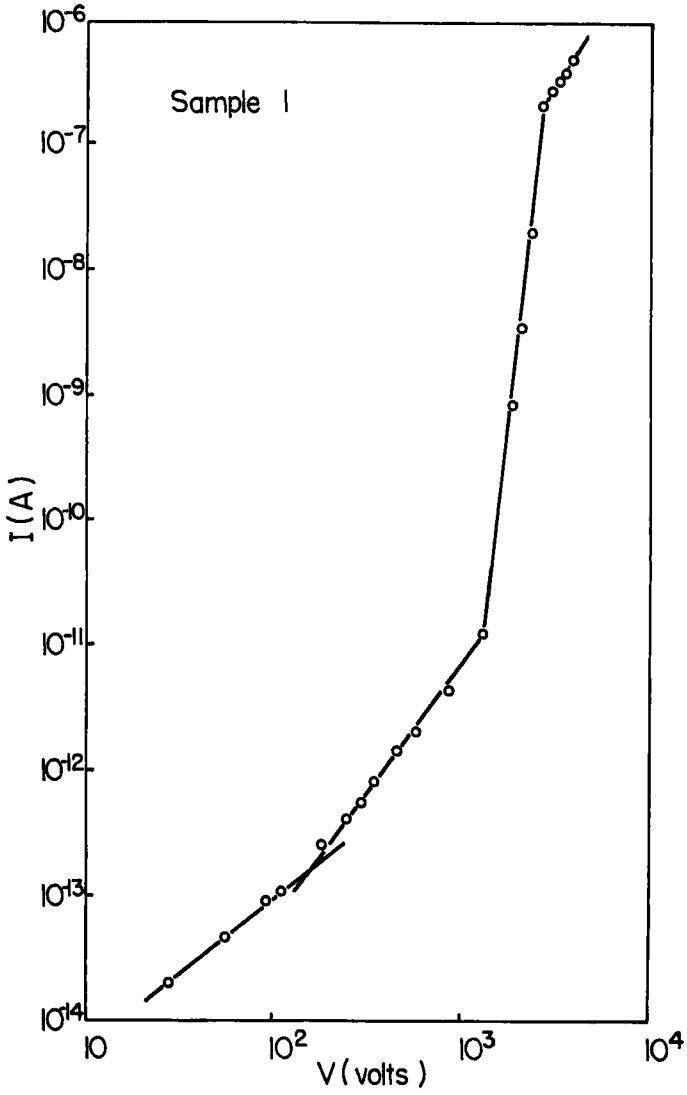

Figure 1. Current as a function of voltage, at room temperature, for sample 1, thickness 0.10 cm.

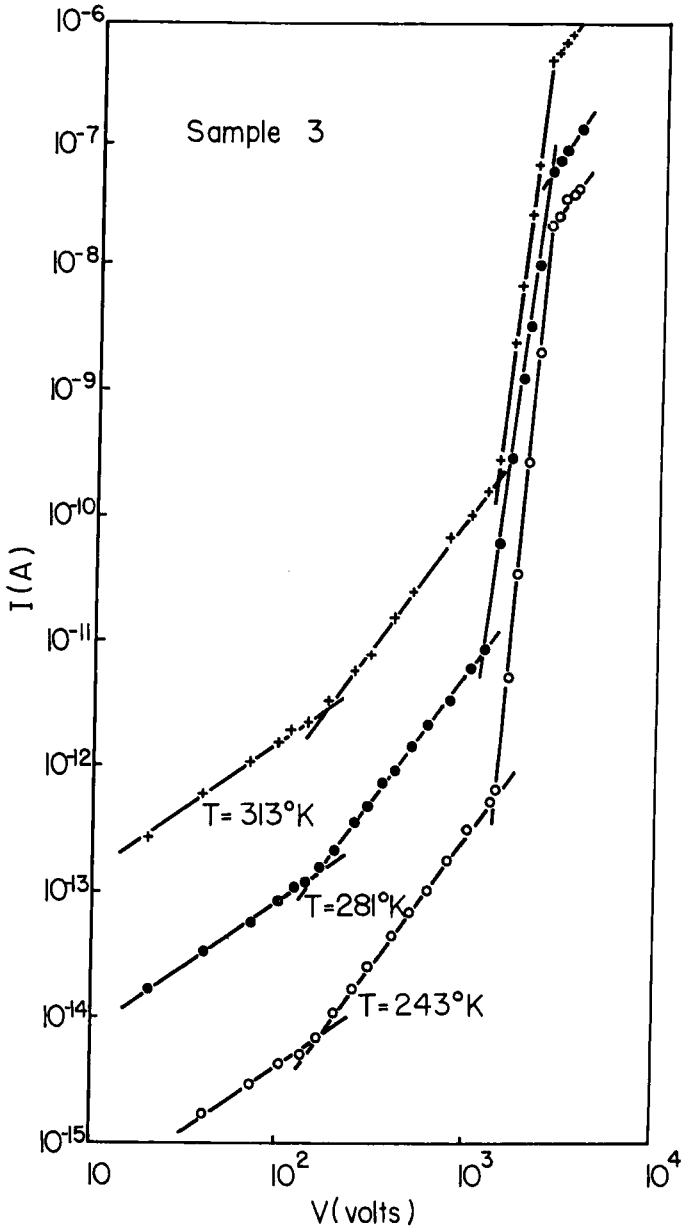

Figure 2. Variation of current with applied voltage at three different temperatures.

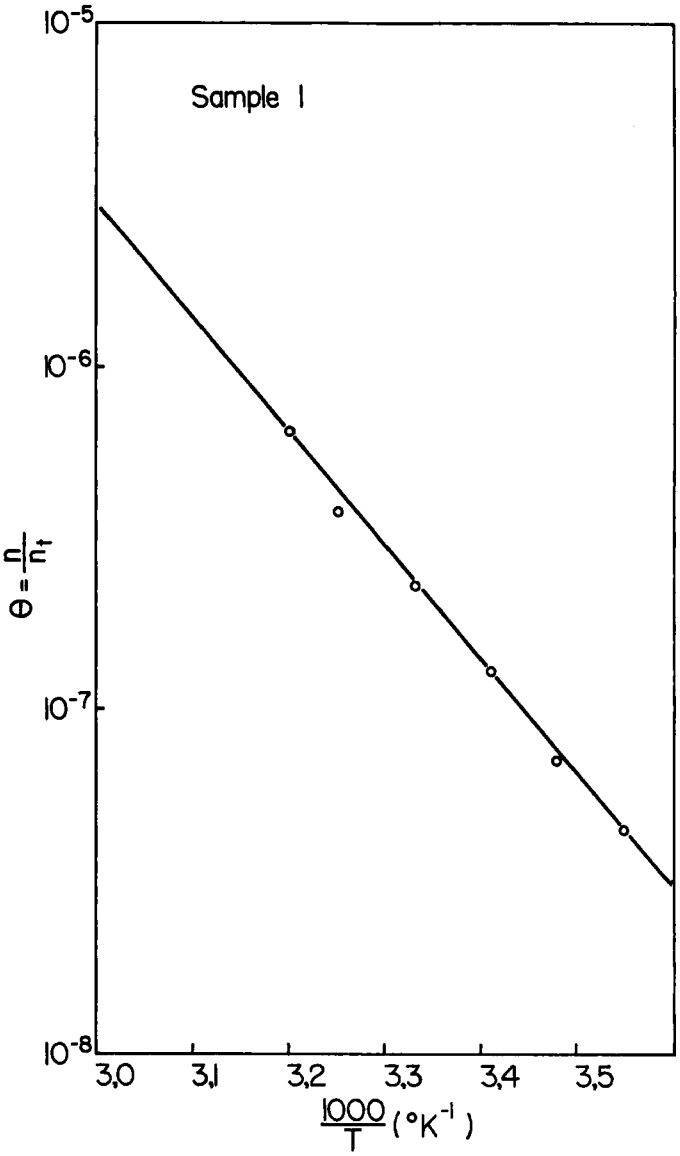

Figure 3. Plot of $ln\theta$ vs. $1/T$ to determine E_t and N_t from Eq. (2).

TABLE 1 Trap parameters based upon $N_t = 4.5 \times 10^{16}$ cm^{-3} and $V = 1300$ volts

T(°K)	n(cm^{-3})	n_t(cm^{-3})	E_f(eV)	E_t(eV)
243	19.8	1.45×10^{10}	0.95	0.67
281	0.56×10^{3}	1.47×10^{10}	1.01	0.69
300	2.27×10^{3}	1.64×10^{10}	1.05	0.70
313	6.81×10^{3}	1.47×10^{10}	1.06	0.71

expression[7] $n_0 = N_c \exp(-E_f/kT)$ we can as well calculate the position of the Fermi level for each temperature at constant voltage $V = 1300$ V. The values obtained are also shown in Table 1. We can see from this table the consistency of the values of n_t with the values of N_t found from Fig. 3. The table shows also the agreement between the value of E_t at room temperature calculated in this way, with that calculated from the data of Fig. 3. Values obtained for n_0, N_t, E_t for a series of samples, at room temperature, are shown in Table 2. From this table, we can point out that in spite of the samples having been all made according to the same process, some variations occurred in the calculated values of N_t, although the values of E_t are approximately constants.

Since the trap depth and trap density have been determined, we can calculate, approximately, its cross section. Assuming that the mean free path is larger than the diameter of the capture centers, we can write[8]

$$\tau \simeq 1/N_t v S \tag{5}$$

where τ is the trapping time, v the thermal velocity, N_t the density of traps and S the cross section. Taking $\tau = 10^{-5}$ sec and $v = 10^5$ cm/sec, values found by Silver *et al.*[9], we find $S = 2.2 \times 10^{-17}$ cm^2.

TABLE 2 Trap parameters calculated from Eq. (2)

Samples	n_0(cm^{-3})	N_t(cm^{-3})	E_t(eV)
1	1.1×10^{3}	4.5×10^{16}	0.65
2	3.9×10^{3}	3.1×10^{17}	0.62
3	2.7×10^{3}	1.6×10^{17}	0.60
4	8.2×10^{2}	1.5×10^{17}	0.62
5	9.3×10^{2}	4.0×10^{16}	0.68

We can verify the agreement of the value of S, using the value calculated from the expression:[3]

$$\frac{\nu}{S} = N_c v = 10^{26}\ \text{cm}^{-2}\ \text{sec}^{-1} \tag{6}$$

The frequency ν can be calculated independently by

$$\nu = \frac{\theta}{\tau}\exp(E_t/kT) \tag{7}$$

where τ has the meaning already stated. We find then $\nu = 1.31 \times 10^9\ \text{sec}^{-9}$ and $S = 1.31 \times 10^{-17}\ \text{cm}^2$ at room temperature, in agreement with Eq. (5). However, if we use $N_t = 4.5 \times 10^{11}\ \text{cm}^{-3}$, we obtain $\nu = 2 \times 10^{14}\ \text{sec}^{-1}$ a value much larger than the highest frequency of optical phonons $10^{13}\ \text{sec}^{-1}$. Thus the low value of N_t found from V_{tfl} cannot represent the true concentration of traps, while the higher value of N_t obtained from $\mathrm{d}\theta/\mathrm{d}T$ maintains internal consistency for the analysis above.

The mobility μ in our samples can also be determined, with the help of the equation

$$I = 10^{-13}\theta(V^2\mu\epsilon/l^3) \tag{8}$$

where we have considered for the current the trap-free region. From this equation, we get $\mu = 0.28\ \text{cm}^2/\text{V-sec}$, in good agreement with the value of $0.4\ \text{cm}^2/\text{V-sec}$ found experimentally by Silver.[9]

Results of a corona discharge previous to the application of the field, are shown in Fig. 4. We notice that the square-law region has disappeared, also a shift of the voltage of the transition from the quadratic region to the region that shows a sudden increase of the current. This change, as we shall see, can be ascribed to the electrons coming from the corona discharge.

4. Discussion

The trap density, calculated from the value of V_{tfl} does not agree with the one obtained through the variation of θ with the temperature. This shows consequently that in the assumed trap-free region, not all traps are filled, indicating therefore that the fast current increase is not due to the filling of the traps. This has already been previously observed by Bube,[10] who assumed that probably it was due to trap ionization. However this does not seem very likely,

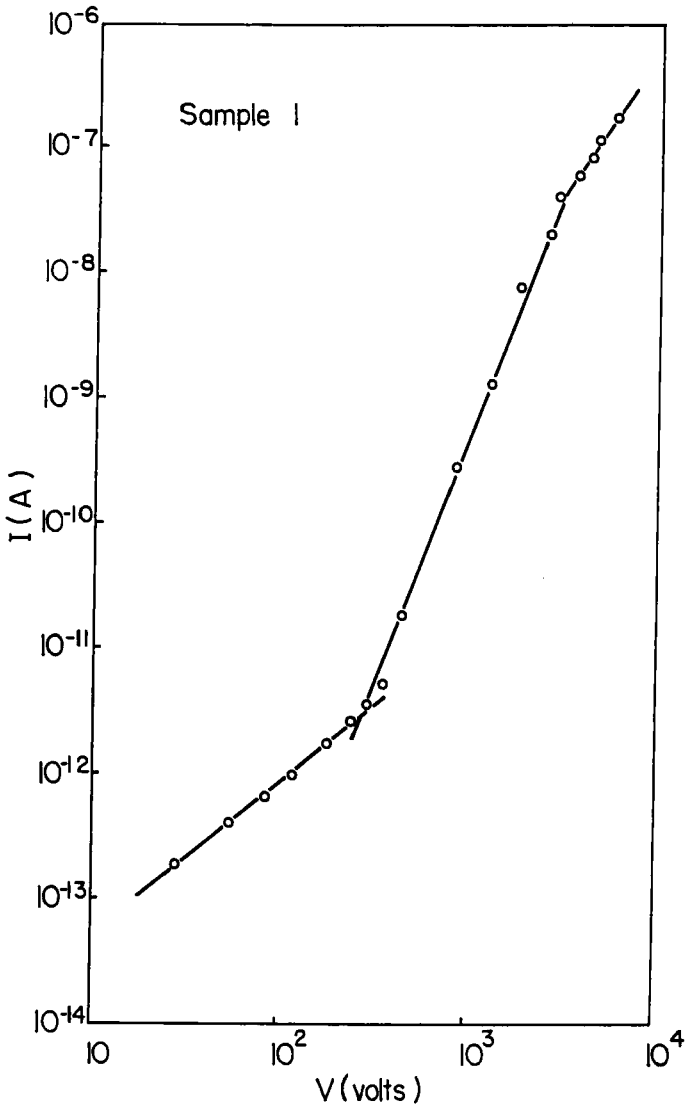

Figure 4. Variation of current with applied voltage, after a corona discharge.

since the field is of the order of 10^4 V/cm and therefore not enough for that.

For very low fields, where injection does not dominate, we observe an Ohmic current, arising from the free carriers. However if we corona-charge the cathode-free surface before applying the electrode, the behavior is completely different. In this case, the negative oxygen ions chemisorbed on the surface can inject their negative charge into the crystal. For this reason even for small values of the field, there exists a space-charge prior to application of the electrode, with the traps partially filled. This is the reason why we do not see a square-law region in this case, although the value of V_{tfl} is the same for both cases. We notice also that, according to Eq. (4), the transition voltage must increase, when the number of free carriers increases, as is observed.

5. Conclusions

SCLC theory has been shown to be applicable to naphthalene with silver contacts. However, the values obtained with such theory for the density and depth of traps do not agree with the values obtained by the dependence with temperature of the factor θ. This seems to indicate that the fast increase of the current is not due to filling the traps. These traps were well characterized; values were determined for density, depth, cross section and frequency of escape.

Acknowledgement

The author would like to express his thanks to Dr. J. Dresner for several helpful discussions and for reading and commenting on the manuscript.

REFERENCES

1. Lampert, M. A. and Mark, P., *Current Injection in Solids*, Academic Press, New York, 1970.
2. Kallmann, H. and Pope, M., *J. Chem. Phys.* **32**, 300 (1960).
3. Mark, P. and Helfrick, W., *J. Appl. Phys.* **33**, 205 (1962).
4. Lohmann, F. and Mehl, W., *J. Chem. Phys.* **50**, 500 (1969).
5. Williams, R. and Campos, M., *J. Appl. Phys.* **41**, 4138 (1970).
6. Campos, M., Leal Ferreira, G. and Mascarenhas, S., *J. Electrochem. Soc.* **115**, 338 (1968).

7. Rose, A., *Phys. Rev.* **97**, 1538 (1955).
8. Rose, A., *Concepts in Photoconductivity and Allied Problems*, John Wiley Sons, New York, 1963.
9. Silver, M., Rho, J. R., Olness, D. and Jarnagin, R. C., *J. Chem. Phys.* **38**, 3030 (1963).
10. Bube, R. H., *J. Appl. Phys.* **33**, 1733 (1962).