

SPACE-CHARGE LIMITED CURRENT IN *p*-CHLORANIL CRYSTALS
MEASURED USING THE LIQUID ELECTRODES

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The negative steady-state space-charge limited currents in *p*-chloranil crystals were measured using the liquid electrodes. The magnitude of the current has been found to be independent of the nature of the carrier-injecting electrode used. The data obtained from the current-voltage characteristics enabled to calculate the electron mobility and the space density of traps. The electron mobility amounts to about 5×10^{-8} cm²/V · sec. The concept of the conduction band is incompatible with such a low value of mobility.

Introduction

Kallmann and Pope [1–4] have shown that the injection of the charge carriers into semiconducting organic crystals is due to the redox reaction on the semiconductor — electrolyte interface. The electrolyte acts in this case as a liquid electrode. Helfrich and Mark [5–7] and Mehl [8] used the liquid electrodes to investigate the positive space-charge limited currents in anthracene, *p*-terphenyl and *p*-quaterphenyl crystals. Recently Mehl and Büchner [9, 10] and Helfrich and Schneider [11, 12] used solutions of alkali metals in organic solvents to inject the negative carriers into anthracene.

In the present work the negative space-charge limited currents (SCLC) in *p*-chloranil crystals were measured at 20 and 40°C using the liquid electrodes. The results obtained have shown that the current-voltage characteristics do not depend on the electrode used provided that the electrode can inject the charge carriers into the crystal.

Because of low density of free carriers in organic semiconductors, the electric fields of rather low intensities applied to a semiconductor crystal result in an uncompensated excess charge extending sufficiently far into the crystal. This charge has an important influence on the magnitude and shape of the current-voltage characteristics.

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Single-carrier SCLCs in the crystals of semiconductors and insulators have been discussed by Rose [13] for a trap-free crystal and by Lampert [14] for a crystal with the single trap level. Helfrich and Mark [5, 7] have given the relationship between SCLC and the applied voltage for a crystal with exponentially distributed traps.

If the electrode injecting the carriers into the crystal is ohmic (that is, if it acts as a reservoir of free carriers), at sufficiently high voltage applied the density of the current is limited by the space charge of the injected carriers and is given by the equation:

$$j_c = \frac{9}{8} u \varepsilon \frac{V^2}{d^3}, \quad (1)$$

where: u — mobility of carriers,
 ε — dielectric constant,
 V — applied voltage,
 d — crystal thickness.

This is the known Child's law for solids. Relationship (1) was derived for a trap-free crystal, that is when all injected carriers participate in the charge transport. When traps are present, some carriers are captured by them and do not participate in conduction process. If the distribution of trap states in the crystal is given by the equation:

$$h(E) = \frac{H}{kT_c} \exp \left(- \frac{E}{kT_c} \right), \quad (2)$$

where: $h(E)$ — trap density per energy unit,
 H — total space density of traps,
 T_c — characteristic temperature of the trap distribution,

the SCLC in the crystal obeys the equation:

$$j_t = a N_0 u e_0^{1-l} \left(\frac{\varepsilon l}{H(l+1)} \right)^l \left(\frac{2l+1}{l+1} \right)^{l+1} \left(\frac{V^{l+1}}{d^{2l+1}} \right), \quad (3)$$

where: a — numerical factor close to unity accounting for the change in the position of the Fermi level with temperature,
 N_0 — effective density of states in the conduction band,
 e_0 — elemental charge
 $l = T_c/T$,
 T — temperature of the crystal.

When the voltage increases, more and more carriers are injected into the crystal and fill the traps. At a certain voltage value all traps are filled and the current obeys the Child's equation. The value of the threshold voltage amounts to:

$$V_{TFL} = \frac{e_0 d^2}{\varepsilon} \left[\frac{9H^l}{8N_0} \left(\frac{l+1}{l} \right)^l \left(\frac{l+1}{2l+1} \right)^{l+1} \right]^{\frac{1}{l-1}}. \quad (4)$$

At sufficiently high voltage the depletion of the reservoir of the carriers occurs at the interface and the current tends to a saturation value (*cf.* [4, 8]).

Experimental part

Chloranil (FOCh, Gliwice) was purified by two-fold sublimation in vacuo. Diethylamine (Schuchardt-Munich) was purified chromatographically on Al_2O_3 . Hydroquinone (FOCh) was purified by the zone melting method. $\text{Na}_2\text{S}_2\text{O}_3$ pro analysi (FOCh), Na_2SO_4 (FOCh) pro analysi, SnCl_2 (FOCh) pro analysi were used without previous purification.

The measurements were made on the circuit presented schematically in Fig. 1. The voltage has been applied from a d.c. stabilised supply unit ZWN-2.5 (BUTJ, Warsaw). The current was measured using a vibrational electrometer TR-1501 (Orion, Budapest). A measuring cell similar to that described by Kallmann and Pope [15] was used. In order to avoid the disturbances resulting from the change of outer electric fields both the leads and the measuring cell were thoroughly screened.

Chloranil crystals have been grown from the purified commercial product by slow resublimation under reduced pressure. Their thickness was determined by measuring the

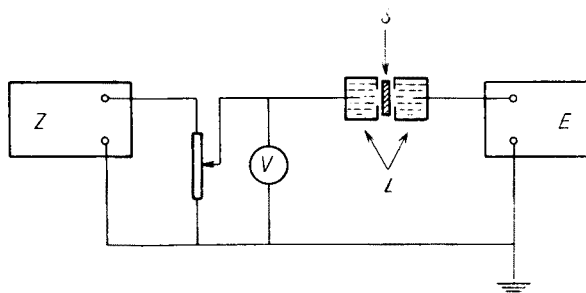


Fig. 1. The circuit. Z — d. c. supply unit, V — voltmeter, S — sample, L — liquid electrodes, E — electrometer

area and weighing. A selected crystal was then stuck to the front wall of the measuring cell with silicone grease.

Aqueous solutions of diethylamine, hydroquinone, $\text{Na}_2\text{S}_2\text{O}_3$ and SnCl_2 were used as an injecting electrode (cathode). 0.1 M Na_2SO_4 , inert with respect to the crystal, was used each time as anode. The voltage was applied through platinum wires immersed in solutions.

Results

In this work the electrochemically injected SCLC was investigated. It was found that the current-voltage characteristics does not depend on the nature of the cathode used, although the reactions accompanying the charge injection are quite different in each case. A typical plot is shown in Fig. 2. The values of the parameter l and of voltage at which the traps are filled (V_{TFL}) were determined from the diagrams and then the parameter H was calculated from equation (4). The effective density of states was assumed to be equal to the double number of molecules in unit crystal volume in view of low carrier mobility found in *p*-chloranil (*cf.* [6]). On account of the rough approximation made, and rather great spread of the results the parameter a in equation (4) was neglected. The electron

mobility was calculated from equation (1) for the applicability range of Child's law. The results with various electrodes are given in Tables I and II.

Attempts to determine the electron mobility in chloranil at 0°C have failed presumably because of flaws formed in crystals in the course of cooling. The uncontrolled diminution

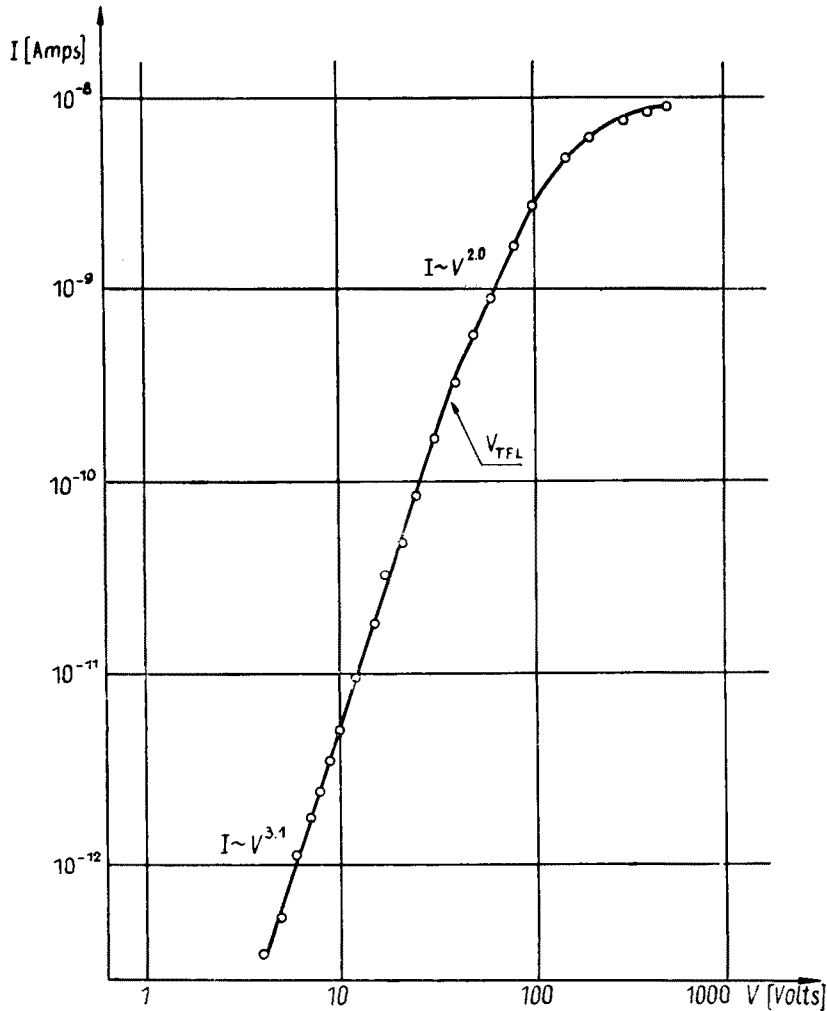


Fig. 2. Space-charge limited current in *p*-chloranil. Crystal thickness 20 microns, injecting electrode $3 \times 10^{-2}M$ $Na_2S_2O_3$ solution

of effective crystal thickness resulted in a decrease of the breakdown voltage and unreliably high mobility values found in the experiments. It was however possible to determine from the current-voltage characteristics the parameter l , a quantity independent of the crystal thickness. It amounted to 2.4 ± 0.1 . From its values at various temperatures the characteristic temperature T_c was calculated (see equations (2), (3)). The results are presented in Table III.

TABLE I
Ambient temperature 20°C

Crystal thickness (microns)	Injecting electrode	l	$H \times 10^{-17} \text{ (cm}^{-3}\text{)}$	$u \times 10^8$ ($\text{cm}^2/\text{V} \cdot \text{sec}$)
15	Diethylamine $3 \times 10^{-2} \text{ M}$	2.4	3.8	1.3
18	Diethylamine $3 \times 10^{-2} \text{ M}$	2.0	3.2	1.6
48	Diethylamine $3 \times 10^{-2} \text{ M}$	2.2	5.3	3.6
18	Diethylamine $3 \times 10^{-2} \text{ M}$	2.1	3.0	8.4
38	$\text{Na}_2\text{S}_2\text{O}_3$ $3 \times 10^{-2} \text{ M}$	1.9	3.3	13.0
20	$\text{Na}_2\text{S}_2\text{O}_3$ $3 \times 10^{-2} \text{ M}$	2.3	4.7	8.4
36	$\text{Na}_2\text{S}_2\text{O}_3$ $3 \times 10^{-2} \text{ M}$	2.4	3.9	5.0
15	Hydroquinone $3 \times 10^{-2} \text{ M}$	2.2	2.3	1.3
46	Hydroquinone $3 \times 10^{-2} \text{ M}$	2.0	3.6	5.0
52	SnCl_2 10^{-2} M in HCl	2.4	5.1	3.0
20	SnCl_2 10^{-2} M in HCl	2.0	3.4	5.7
	Mean values	2.2 ± 0.1	3.8 ± 0.4	5.1 ± 1.3

TABLE II
Ambient temperature 40°C

Crystal thickness (microns)	Injecting electrode	l	$H \times 10^{-17} \text{ (cm}^{-3}\text{)}$	$u \times 10^8$ ($\text{cm}^2/\text{V} \cdot \text{sec}$)
46	Diethylamine $3 \times 10^{-2} \text{ M}$	1.9	3.5	5.4
18	Diethylamine $3 \times 10^{-2} \text{ M}$	2.2	5.3	4.1
21	Diethylamine $3 \times 10^{-2} \text{ M}$	2.1	4.7	8.7
	Mean values	2.1 ± 0.1	4.5 ± 1.0	6.1 ± 2.2

TABLE III

T (deg. K)	273	293	313
l	2.4 ± 0.1	2.2 ± 0.1	2.1 ± 0.1
T_c (deg. K)	655 ± 30	645 ± 30	657 ± 30

Discussion

Measurements of SCLC in *p*-chloranil crystals have been earlier made by Reucroft, Rudyj and Labes [16]. They used crystals 0.3—1 mm thick, grown from solution, with silver paste electrodes fixed on them. When the electric field applied to the crystal exceeded $4 \times 10^3 \text{ V/cm}$, the current was limited by space charge and was proportional to the square of voltage. Assuming the band model with a single trap level and the value of $0.1 \text{ cm}^2/\text{V} \cdot \text{sec}$ for the carrier mobility, the authors have estimated the space density and the depth of traps. The current-voltage characteristics for chloranil reported later by Reucroft and coworkers [17] are however different, being similar to those obtained in the present work.

The applicability of the band model to organic semiconductors has been hitherto discussed almost exclusively on the basis of measurements made on anthracene crystals. According LeBlanc [18], the band model may be applied to anthracene but the width of the conduction band is small and hence the mobility of carriers low ($1 \text{ cm}^2/\text{V}\cdot\text{sec}$ approximately). Nevertheless it is by seven orders of magnitude greater than the mobility found by us in *p*-chloranil. Such a low value of the electron mobility implies that the band model could not be applied here.

It should be noticed, however, that both the concept of SCLC and equation (1) are not attached to any particular conduction mechanism. They are also compatible with the hopping or tunneling mechanisms of carrier motion which seems to be more adequate in this case. In deriving equation (3) an assumption of exponential distribution of traps was made. This assumption does not seem to be on contradiction with the above models. The nature of trapping centres remains however obscure. The reasonable constancy of the *H*-values for different crystals and the correct dependence of *l* on temperature support the above discussion. The rather great spread of mobility values is presumably due to errors in evaluating the crystal thickness.

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