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

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Version of record first published: 21 Mar 2007.

To cite this article: Haruhisa Shimoda , Mitsunori Sukigara & Kenichi Honda (1973): The Sign and the Lifetime of Charge Carriers in Auramine under Photoconduction, Molecular Crystals and Liquid Crystals, 20:2, 165-175

To link to this article: http://dx.doi.org/10.1080/15421407308083309

Molecular Crystals and Liquid Crystals. 1973. Vol. 20, pp. 165–175

Printed in Great Britain

The Sign and the Lifetime of Charge Carriers in Auramine under Photoconduction

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Received July 31, 1972; *and in revised form September* 8, 1972

Abstract—An experiment for determining the sign and the mean lifetime of the majority carriers in photoconduction is described. The method is similar to one of those for measuring a drift mobility and uses an electric pulse and a light pulse. Auramine hydrochloride crystal which was grown from an ethanol solution is measured with this method and it is found that the majority carriers are holes and their mean lifetime is about 0.2 μsec at -74 and -50 °C under 10^{-8} Torr. The upper limit of the drift mobility of holes is estimated to be less than 2 cm²/V-sec.

1. Introduction

In a previous paper[1] we dealt with the electric conduction characteristics of a sandwich type cell using evaporated films of aluminium and auramine hydrochloride and suggested that the charge carriers of dark conduction were electrons and those of photoconduction were holes. It was also shown that the activation energy in a low temperature range was nearly 0 eV in dark conduction and about 0.4 eV in photoconduction.[1] This result coincides with that of n-type SnO_2-auramine hydrochloride-Al sandwich type cell[2] where electric characteristics were considered to be largely influenced by the nature of the interface.

Meier classified the dark conduction of auramine into electron conduction by the fact that the dark conductivity was suppressed by the introduction of oxygen gas.[3] On the other hand, Terenin

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reported that the majority carriers of auramine in photoconduction were holes from the measurement of contact potential change under illumination.[4] These experiments were done under steady state condition, so it would be difficult to get information for the lifetime of photogenerated carriers. In addition, charge carriers passed through the interface of electrode and auramine layer in their experimental conditions, so the electrical characteristics of the interface might significantly influence the results. Therefore we made an electrically blocked sandwich cell and measured the sign and the lifetime of charge carriers of photoconduction in the bulk of auramine by using a light pulse and an electric pulse.

2. Method of the Measurement

The principle of the method of measuring the sign and the lifetime of charge carriers is described here. In Fig. 1, A and B denote the electrodes of a blocking cell and these electrodes are connected to a cell of voltage V through a resistance R. If the B side is illuminated

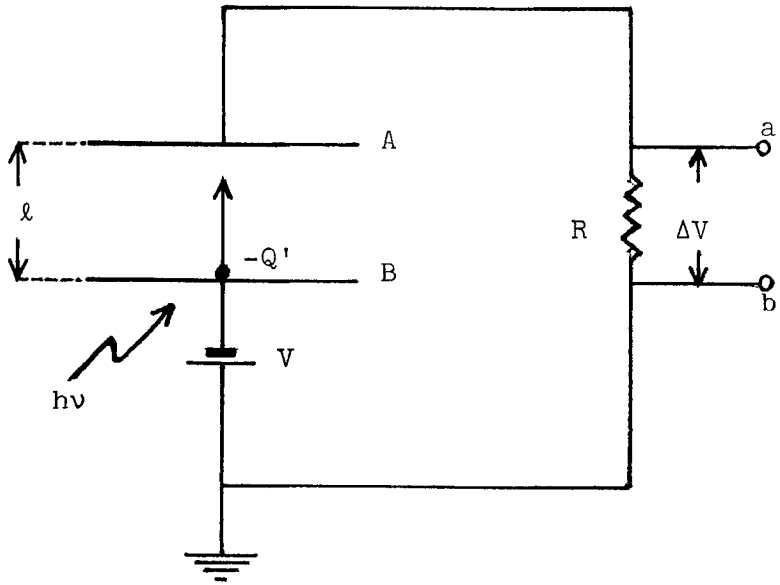

Figure 1. A diagram of the electric circuit for the measurement of lifetime. A and B denote the surfaces of a sample.

by a sufficiently short light pulse, photogenerated carriers drift to the A side and a voltage corresponding to this phenomenon appears between a and b. It would be concluded that the majority carriers are electrons, if a signal is observed only when the bias direction is as that shown in Fig. 1. The shape of the observed signal between a and b will be considered as follows. Here, the consideration is made only for electrons, since the same treatment can be applied for holes. We suppose that a charge Q' drifts along the electric field with a velocity v from the electrode B to A. Then, the current caused in the outer circuit is given by[5]

$$I = Q' \frac{v}{l}, \tag{1}$$

where l is the distance between A and B. Accordingly the charge,

$$Q = \int_0^t Q' \frac{v}{l} \mathrm{d}t, \tag{2}$$

flows in the outer circuit in the direction from A to B during the time t. If the value of R is sufficiently large and the time constant of the circuit is much longer than the time T in which the charge Q' reaches A from B, voltage V appears between a and b corresponding to the charge Q in Eq. (2).

$$V = -\frac{Q}{C} = -\frac{1}{C}\int_0^t Q' \frac{v}{l} \mathrm{d}t. \tag{3}$$

Here, C is the capacitance of the cell. In a real crystal the photogenerated carriers contribute to the current only in their lifetime. If the lifetime and the number of photogenerated charge carriers are τ and n_0 respectively, the number of free carriers is supposed to decrease as,

$$n = n_0 \exp(-t/\tau), \tag{4}$$

then, Q' is expressed as follows.

$$Q' = n_0 q \exp(-t/\tau). \tag{5}$$

Here, q is the unit charge of an electron. By substituting Eq. (5) into Eq. (3),

$$\begin{aligned} \Delta V &= -\frac{1}{C}\int_0^t n_0 q \exp(-t/\tau) \frac{v}{l} \mathrm{d}t \\ &= -\frac{n_0 q v \tau}{lC}(1 - \exp(-t/\tau)). \end{aligned} \tag{6}$$

this voltage appears between a and b. However, the flow of the carriers stops at the time T when they arrive at the surface of A side, and the voltage ΔV becomes constant. ΔV is expressed by Eq. (6) if $t < T$, but if $t > T$ it becomes the constant value,

$$\Delta V = -\frac{n_0 q v \tau}{lC}(1 - \exp(-T/\tau)). \tag{7}$$

Figures 2(a) and (b) show the $\Delta V - t$ curves when $t \ll T$ and $\tau \gg T$, respectively. It is supposed that $CR \gg T$. Supposing the electric

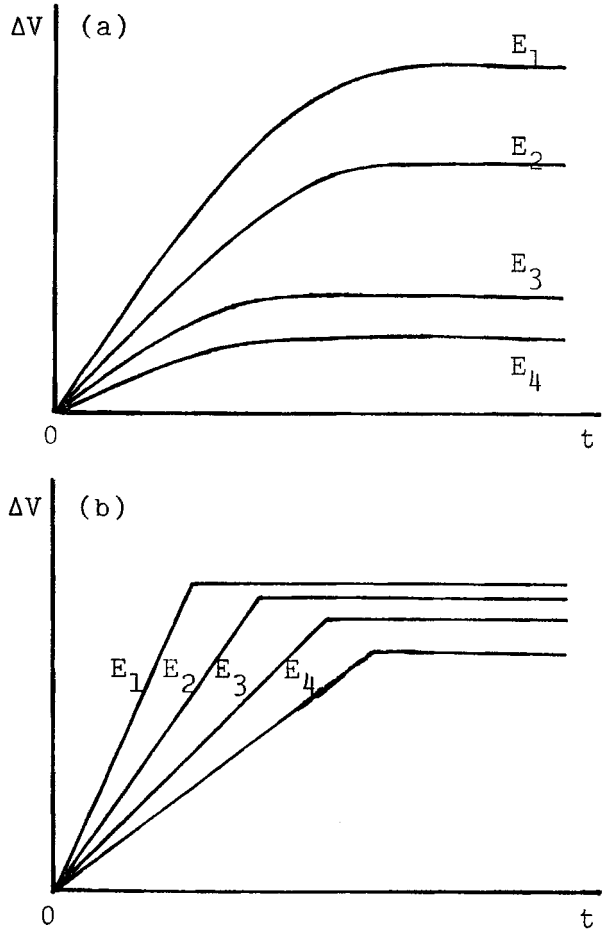

Figure 2. The electric field dependence of $\Delta V - t$ curve.
$|E_1| > |E_2| > |E_3| > |E_4|$
(a) $\tau \ll T$; (b) $\tau \gg T$.

field to be constant through the crystal, T is given by

$$T = l/v = l/\mu E. \tag{8}$$

Here, μ is the mobility of the carriers and E is the electric field. Therefore, when $\tau \gg T$ the folding point of $\Delta V - t$ curve comes shorter with the increase of the electric field (Fig. 2(b)). On the contrary, when $\tau \ll T$, no definite folding point appears, but the saturation value of ΔV increases with the increase of the electric field (Fig. 2(a)). Thus, by choosing the voltage range in which $\tau \ll T$, the lifetime τ can be obtained by analysing the curves in Fig. 2(a).

3. Experimental

In the actual measurement, electric pulses were used to avoid influences of dark current and the polarization by the electric field in the crystal, and a differential circuit was used to cut the dc component. This method is the same in principle as the method for measuring the drift mobility of photogenerated charge carriers in semiconductors.[6] Figure 3 shows the structure of the cell. The sample was an auramine hydrochloride crystal grown from an ethanol solution. The thickness of the crystal† was 50 μm and its diameter

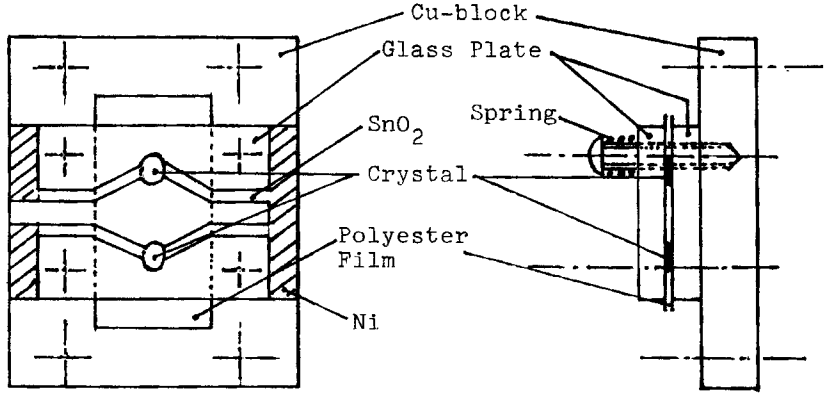

Figure 3. The structure of the blocking cell with two auramine crystals.

† Auramine hydrochloride, bought from E. Merck Co., was recrystallized three times from an ethanol solution. Then the crystals were grown from an ethanol solution in a dried atmosphere at 20 °C.

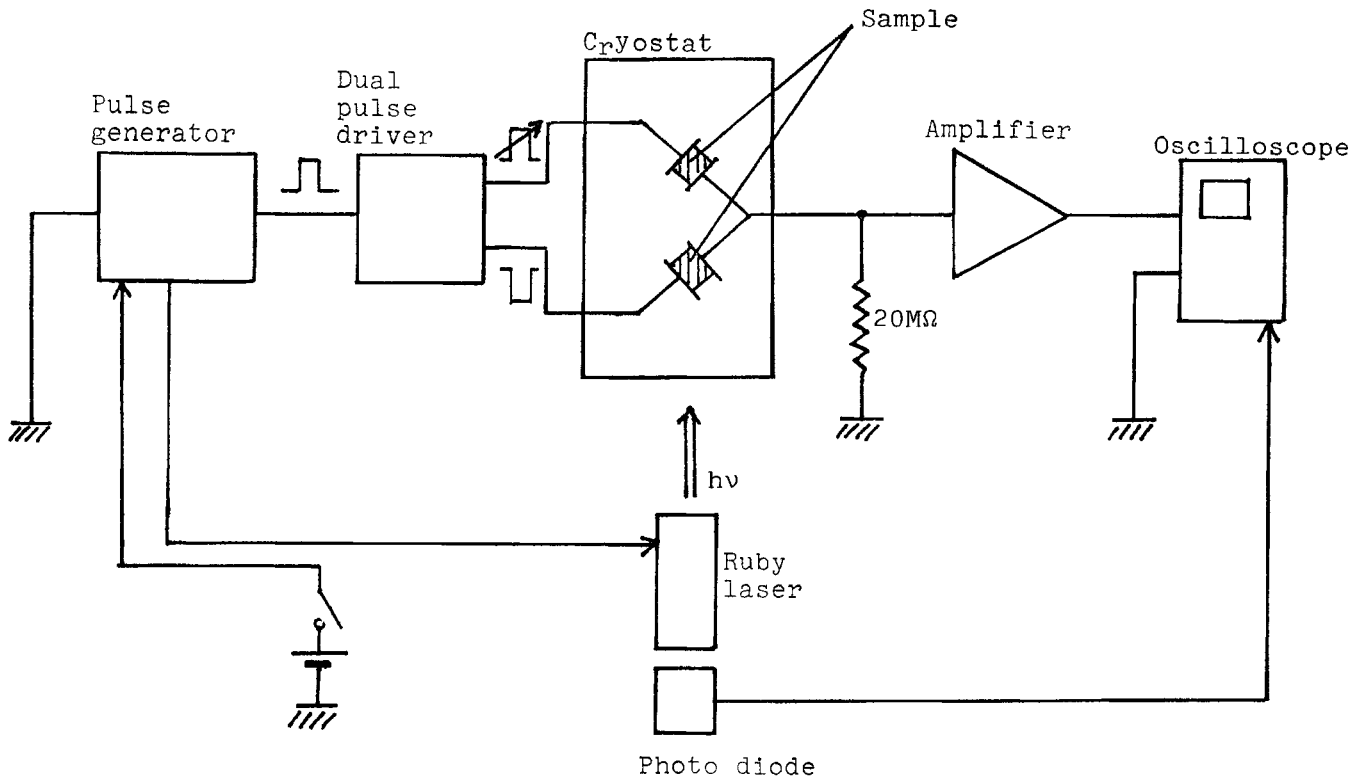

Figure 4. The block diagram of the measuring circuit.

was 3 mm. The electrode was made by photoetching an SnO_2 coated glassplate. Polyester films were put on the electrodes and two crystals having almost the same shapes were inserted between the electrodes. This cell was fixed with four bolts and nuts with springs, then attached to a Cu plate which was set in a cryostat. The measurements were made under vacuum (10^{-8} Torr) at the temperatures $-74\,°C$ and $-50\,°C$. Temperature was controlled with an electronic regulator within the accuracy of $\pm 0.1\,°C$. Figure 4 shows the block diagram of the measuring circuit. Two pulses having opposite polarities were respectively supplied to the crystals. These dual pulses were supplied with a dual pulse driver which was made by one of the authors and a single pulse generator, and the amplitudes of the pulses were chosen to show no dc component. The resistance and the capacitance of the circuit were $20\,M\Omega$ and 10 pF, respectively, so the time constant of the circuit was about 0.2 m sec. The pulse width was about 3 msec and the pulse height was changed between 0–40 V. An amplifier with input impedance of $10^{17}\,\Omega$ and output impedance of $50\,\Omega$ was made by one of the authors using a MOSFET. The response time of the amplifier was less than 0.1 μsec. The light pulse was a second harmonics from a giant pulse ruby laser and its wavelength was 3472 A. The peak output energy of the light pulse was about 50 kW, and the duration time was about 40 nsec. An oscilloscope for recording signals was triggered with an NEC avalanche photodiode, APD 200. In the experiment, only one of the samples was irradiated with the light pulse.

4. Results and Discussion

A photogenerated signal was observed only when the illuminated electrode was positively biased. This fact indicates that the majority carriers in photoconduction are holes, and this result coincides with the assumption in a previous paper.[1] The lifetime dealt with in this paper is the lifetime of free carriers from the nature of the measurement. For the sake of continuing the discussion briefly, we consider a simple model with a single type of recombination center and monochromatic trapping level. The following equation is derived from the transport equation for holes neglecting influence of space charge and diffusion, and assuming that the rate of the

thermal excitation of holes from traps is very slow.

$$\frac{dp}{dt} = -\left(\frac{1}{\tau_r} + \frac{1}{\tau_t}\right) p = -\frac{p}{\tau}. \tag{9}$$

Here, τ_r is the time required for capturing the free holes by the recombination centers, $1/\tau_t$ is the rate constant of trapping free holes, and p is the density of free holes which was generated by an illumination. By setting the initial condition as $p = p_0$ at $t = 0$, the solution of Eq. (9) comes to

$$p = p_0 \exp(-t/\tau). \tag{10}$$

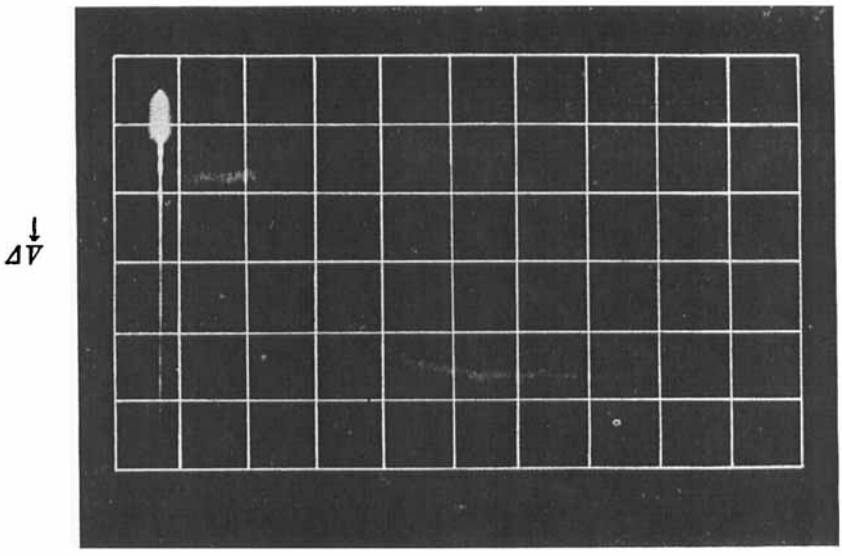

Figure 5. A typical shape of the observed signal at -50°C. $E = 2.0 \times 10^3$ V/cm, scanning speed = 0.2 μsec/div.

Equation (10) is consistent with the Eq. (4). Figure 5 shows an example of the measured signals. Logarithm of $(\Delta V - \Delta V_\infty)$ is plotted against time in Fig. 6, where ΔV_∞ is the saturation value of ΔV and corresponds to $n_0 q v \tau / lC$ in Eq. (6). Figure 7 shows the

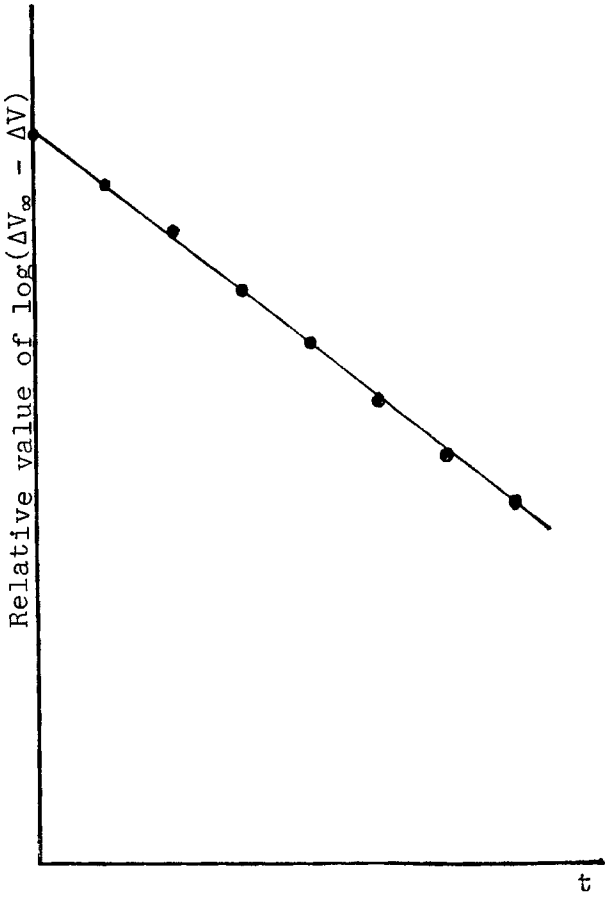

Figure 6. Change of $(\Delta V_\infty - \Delta V)$ with time after the auramine crystal was excited with a light pulse.

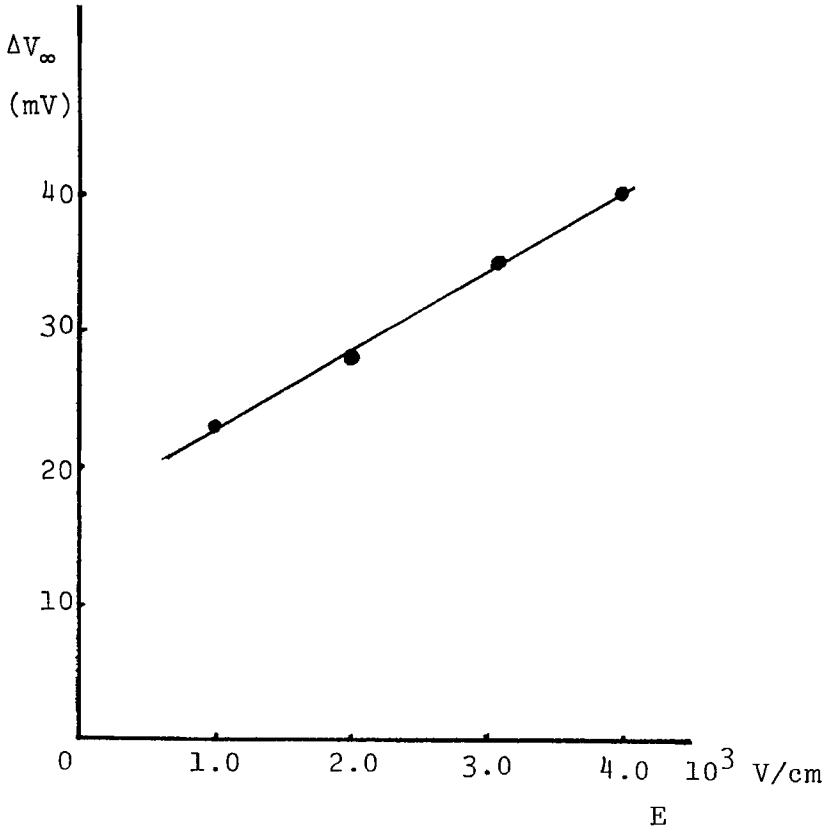

Figure 7. A linear relation of ΔV_∞ with electric field in the auramine crystal.

ΔV_∞–E curve. These two curves are straight lines denoting that the Eq. (6) is valid. By supposing the dielectric constant of the insulator and crystal to be ϵ_1 and ϵ_2, respectively, the thickness of the crystal to be l and that of the insulating film to be $d/2$, the electric field, E, in the crystal is expressed as,

$$E = \frac{\epsilon_1 V}{\epsilon_1 l + \epsilon_2 d}. \tag{11}$$

These modified values of electric field are used in Fig. 7. The measured lifetimes are shown in Table 1. By substituting the value of the time t_∞, which corresponds to ΔV_∞, to T in Eq. (8), μ is calculated to be about 2 cm²/volt sec, and the drift mobility of auramine

TABLE 1 The Measured Values of Lifetime

Temp.	−74 °C	−50 °C
$\tau^{(a,b)}$	0.2 μsec	0.2 μsec

(a) These values are mean values of five time measurement.
(b) The supplied electric fields are 1.0, 2.0, 3.1, 4.0 $\times 10^3$ V/cm and a mean value of these fields was taken.

is estimated to be less than this value from the discussions above. That is, the actual value for μ could be an order of magnitude lower.

Acknowledgement

The authors wish to thank Mr. Kazuo Sugaya for his help in experiments and also to Mr. Yoshihiro Aikawa for his valuable discussions.

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