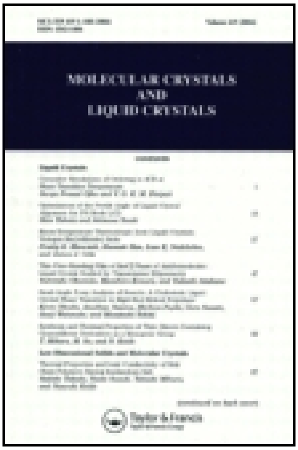

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TEMPERATURE AND FIELD DEPENDENCE OF HOLE TRANSPORT IN CHLOROALUMINUM PHTHALOCYANINE DETERMINED BY TIME-OF-FLIGHT MEASUREMENTS

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Abstract Using the time-of-flight technique, drift mobility measurements were performed on the p-type semiconductor chloroaluminum phthalocyanine (ClAlPc). The field dependence of the hole mobilities was examined at different temperatures, and the results were found to be interpretable within the context of the disorder formalism developed by H. Bässler and coworkers. In the region of low applied fields the mobilities are seen to first decrease with increasing field, for all the temperatures in the range studied. The mobility then reaches a distinct minimum at intermediate fields which is followed by an increase at higher fields. The high field behaviour for all temperatures studied shows a linear dependence of ln μ vs $E^{1/2}$, the slope of which decreases with increasing temperature with values ranging from $9.15\text{x}10^{-3}$ $(\text{cm/V})^{1/2}$ at 265 K to $5.25\,\text{x}10^{-3}$ $(\text{cm/V})^{1/2}$ at 330 K. Mobilities at all applied fields were found to increase with rising temperatures showing a linear dependence of ln μ vs T^{-2}. At each temperature, measurements were taken for applied fields of $2.5\text{x}10^{4}$ V cm^{-1} to $1.9\text{x}10^{5}$ V cm^{-1}. The mobilities at the highest applied field ranged from $6.05\text{x}10^{-5}\text{cm}^{2}\text{V}^{-1}\ \text{s}^{-1}$ at 265K to $1.15\text{x}10^{-4}\ \text{cm}^{2}\ \text{V}^{-1}\ \text{s}^{-1}$ at 330K.

In view of the apparent consistency of this system's behaviour with that predicted by the disorder formalism, the relevant constants were calculated and their relationships examined to better determine the correlation with the proposed model. From $\mu\ (E=0) = \mu_0 \exp\text{-}(T_0/T)^2$ and the appropriate plot, the values for μ_0 and T_0 are $2.5\text{x}10^{-3}\ \text{cm}^{2}\ \text{V}^{-1}\ \text{s}^{-1}$ and 777 K respectively. This yields a distribution width σ of 0.1 eV and corresponding $\hat{\sigma}$ values varying from 3.5 to 4.415 within the temperature range studied. Finally the parameter related to off-diagonal disorder, Σ, was found to be 1.58.

Keywords: phthalocyanine, photoconductivity, mobility, hole transport

INTRODUCTION

Phthalocyanines are among the most studied organic semiconductors, their photoconductivity being widely utilized in electrophotography [1,2]. Besides this main industrial application, the photoactivity of phthalocyanines is also studied in photovoltaic[3,4] and photoelectrochemical cells[5-7]. Phthalocyanines are hole transport materials due to their interaction with oxygen[8-12], which is also beneficial to the photoconductivity of these compounds[12-14].

Recently, our group has focused its attention on chloroaluminum phthalocyanine (ClAlPc). Through chemical and structural modifications of ClAlPc in contact with salt solutions, performing photocathodes were obtained that are able to yield about 2mA/cm^2 under 100 mW/cm^2 white light irradiation[15,16]. It is interesting to study now the transport properties of the same pigment.

In a previous study on unmodified ClAlPc, drift mobilities were measured at room temperature by the time-of-flight technique[17]. It was found that the dependence of the drift mobilities on applied field was best described by a model based on disorder due to Bässler and coworkers[18-21]. In the present work, the time-of-flight technique is further employed to study the effect of temperature on the mobility-field relationship and the measurements are analyzed within the framework of the disorder formalism. The analysis supported the presence of both energetic and positional disorder and yielded results consistent with the model's predictions.

EXPERIMENTAL

The synthesis of ClAlPc was performed according to a previously published procedure[15,16]. The material was purified by sublimation in vacuum twice, at a temperature of 375°C and a vacuum of 10^{-5} Torr, which yields a high-purity material as was determined by elemental analysis.

Thin films of ClAlPc (1μm) were used, having been incorporated in an Al - ClAlPc - Al "sandwich cell" structure. The experimental set-up is as previously described[17] with some modification for temperature control: the cell is mounted on a refrigerator/heater platform inside a vacuum chamber, with the top semi-transparent aluminum electrode facing the chamber window. Light impinges on the sample through this top electrode, after applying to it a pulse of positive polarity. The bottom aluminum electrode connects to the measuring system. The electrodes form blocking contacts with the film. The sequence of events with a typical response is depicted in Figure 1.

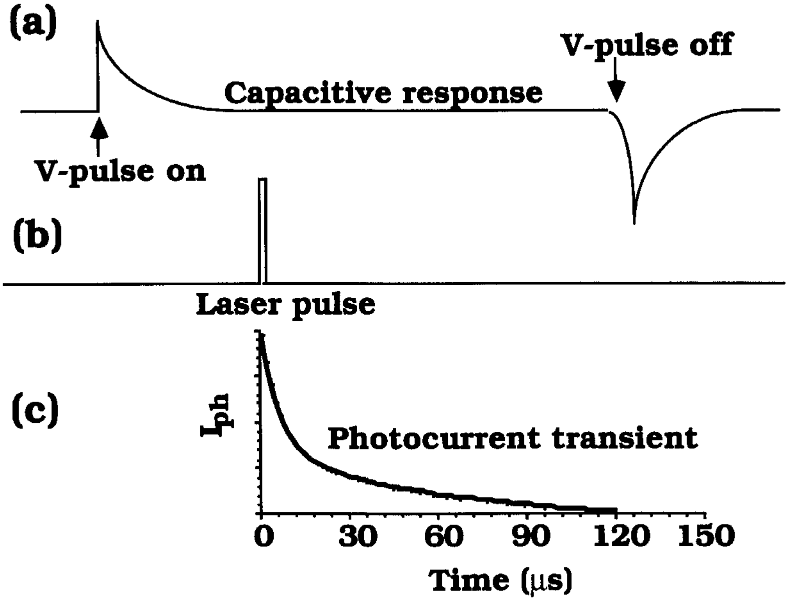

FIGURE 1 Sequence of events in time

The laser produces pulses of 200 ns duration, which are much shorter than the time regime of the transit times (μs). The wavelength of irradiation is chosen at 690 nm because of its close coincidence to the S_0 - S_1 absorption peak of ClAlPc[15,16]. Strong absorption at this wavelength ensures that the thickness of the photogenerated charge layer (<0.2 μm) is small compared to cell thickness. Further precautions taken in order to achieve clear and interpretable results were:(i) removing space-charge, that may accumulate from one reading to the next, by short-circuiting the cell in between readings while applying light to it repeatedly; (ii) adjusting the variable resistor, R, across which photovoltage is measured, such that R<R(cell)/1000; (iii) ensuring that the total charge photogenerated is no greater than 5% of

the CV product of cell capacitance times applied voltage; (iv) obtaining an average of 5 readings at each field setting, and (v) scaling up and down in temperature for each set of measurements, verifying the continued integrity of the sample.

RESULTS AND DISCUSSION

As can be seen in Fig. 1c, the obtainable photocurrent transients are typically featureless, so the current is plotted versus time in a log-log representation, from which the transit time, t_T, is obtained as the intersection of the two tangents shown in Fig.2 .

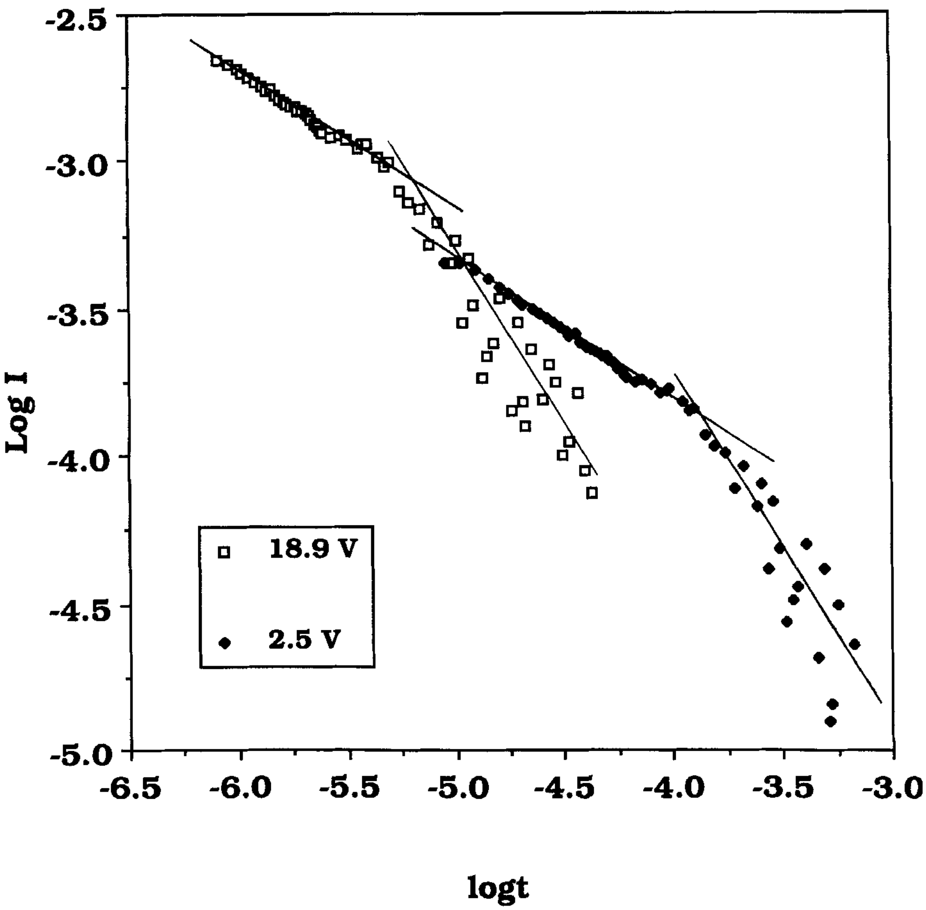

FIGURE 2 Log I_{ph} vs. log t at 300 K, at the two limiting voltages

Measuring the film thickness then leads to a determination of the drift mobility according to the fundamental relation of drift mobility measurements : $t_T = L / \mu E$, where L = sample thickness, E = applied field and μ = drift mobility.

In Fig. 2 two photocurrent transients can be seen in their log-log representations obtained at the voltage limits for one of the temperatures investigated, The fields applied ranged from 2.5×10^4 V/cm to 1.9×10^5 V/cm, limited at the low end by signal-to-noise considerations and at the high end by dielectric breakdown. The temperature range was 265 K to 330 K .

In Table I, which shows transit times parametric in voltage, the transit time is observed to decrease (μ increases) with increasing field at the higher field range. A decrease is expected if measurements are representative of charge transport. This has been verified in previous work on this material[17] where the transit time was found to scale linearly with sample thickness.

TABLE I Transit times parametric in voltage at 300 K

Field applied ($\times 10^{-4}$ V/cm)	Transit time (μs)
2.5	83.2
4.3	93.3
6.0	72.0
8.1	40.0
10.1	36.3
12.2	17.4
14.3	11.7
16.4	7.4
18.5	5.1

The increase in transit time seen at the lowest voltages is predicted by the disorder formalism where at sufficiently low fields a reversal in the classic trend of drift mobility with field is postulated.

In Table 2, which shows transit times paramentric in temperature, the t_T is seen to also decrease with increasing temperature, as expected for drift mobility measurements on an organic film .

TABLE II Transit times parametric in temperature for $1x10^5$ V/cm

Temperature (K)	Transit time (μs)
265	42.5
275	35.5
285	29.1
300	26.3
310	24.0
320	22.1
330	19.5

A previous examination of the actual form of the relationship between μ and applied E at room temperature yielded the first indications that the disorder formalism applies to this charge transport material and pointed to the following study over a range of temperatures to verify whether the model provides a self-consistent description of the results for ClAlPc.

In Fig. 3 can be seen plots of the logarithm of the mobility vs. the square root of field over the temperature range employed. According to the model, transport that is subject to both energy ("diagonal") disorder and disorder of intersite coupling ("off-diagonal" disorder) can result in a mobility with a field dependence given as $\exp(bE^{1/2})$. This behaviour is indeed observed at the high field end in Fig. 3 and coincides with the model's prediction of the high-field mobility as given by:

$$\mu(\hat{\sigma},\Sigma,E) = \mu_0 \exp\left[-\left(\frac{2}{3}\hat{\sigma}\right)^2\right] \cdot \begin{cases} \exp C\cdot\left(\hat{\sigma}^2 - \Sigma^2\right)\cdot E^{1/2}, & \Sigma \geq 1.5 \\ \exp C\cdot\left(\hat{\sigma}^2 - 2.25\right)\cdot E^{1/2}, & \Sigma < 1.5 \end{cases} \tag{1}$$

where $\hat{\sigma} = \sigma/kT$ characterizes energetic disorder, $C = 2.9x10^{-4}$ $(cm/V)^{1/2}$ and Σ is a parameter accounting for variations of intersite coupling due to random variations of both intersite distances and wave function overlap. Furthermore, the decrease in slope with increasing temperature is also observed in other systems described by this model and tends towards a reversal of sign for the slope, S, at high enough temperature[22-24].

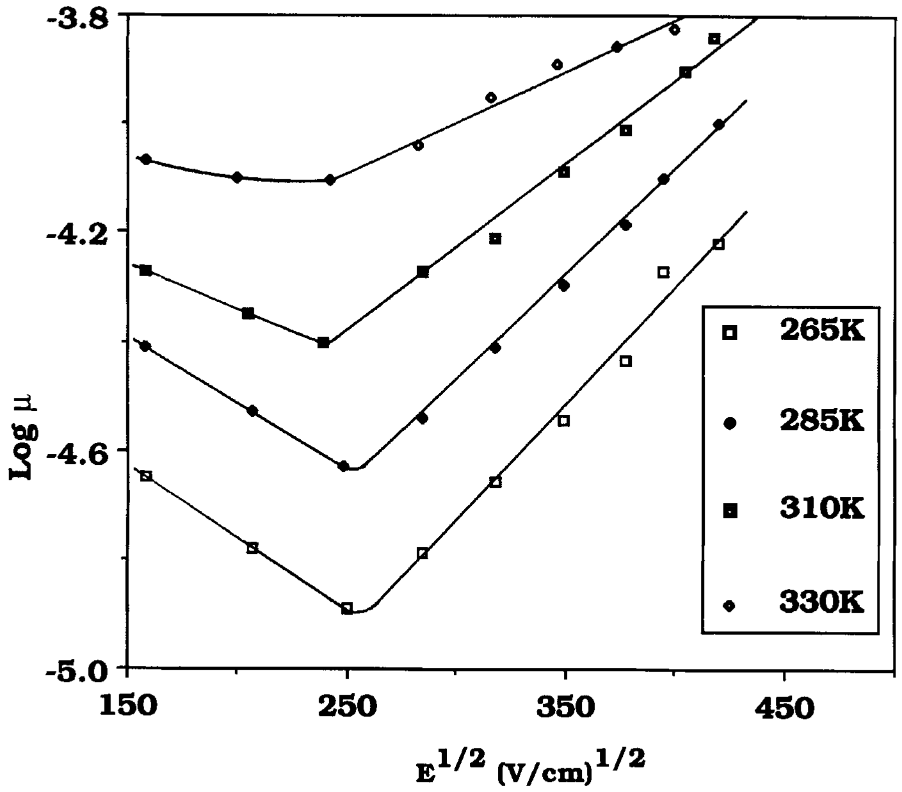

FIGURE 3 Log μ vs $E^{1/2}$, parametric in temperature

Consideration of the lower and mid-field mobility again shows its behaviour coinciding with the model's predictions according to which, at sufficiently low fields a negative field dependence of the mobility is expected. The field dependence of μ over the temperature range studied follows therefore the trends postulated by the disorder formalism and results were further analyzed in the context of the model to obtain the

Extrapolation of the linear part in Fig.3 to zero yields the zero-field mobility. The logarithm of this mobility can be plotted against the inverse of the temperature, 1/T, or against $1/T^2$ as shown in Fig.4 . Both provide adequate fits so that the model's prediction of a $1/T^2$ dependence according to

$$\mu\ (E = 0) = \mu_0 \exp - (T_0/T)^2 \tag{2}$$

is seen to be applicable, though not exclusively.

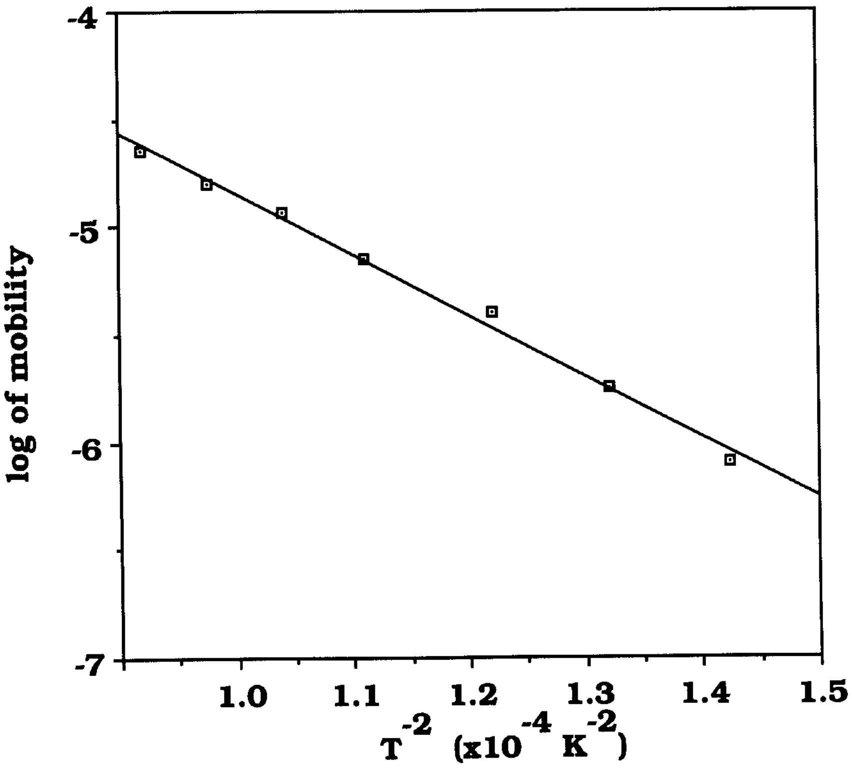

FIGURE 4 Log μ (at E = 0) vs. $1/T^2$

From this plot therefore the prefactor μ_0 is found to be : 2.5×10^{-3} cm^2 V^{-1} s^{-1} and the slope yields the characteristic temperature T_0 as 777K. As T_0 relates to the energy width of the density of states distribution by $T_0 = 2\sigma/3k$, σ is obtained as 0.1 eV. The parameter $\hat{\sigma}$ at each temperature is then given by $\hat{\sigma} = \sigma/kT$. Finally, the slopes, S, of the linear portion of the logμ vs. $E^{1/2}$ graphs are plotted vs. $\hat{\sigma}^2$ (shown in Fig. 5), from which the intercept at S=0 yields the parameter $\Sigma = 1.58$.

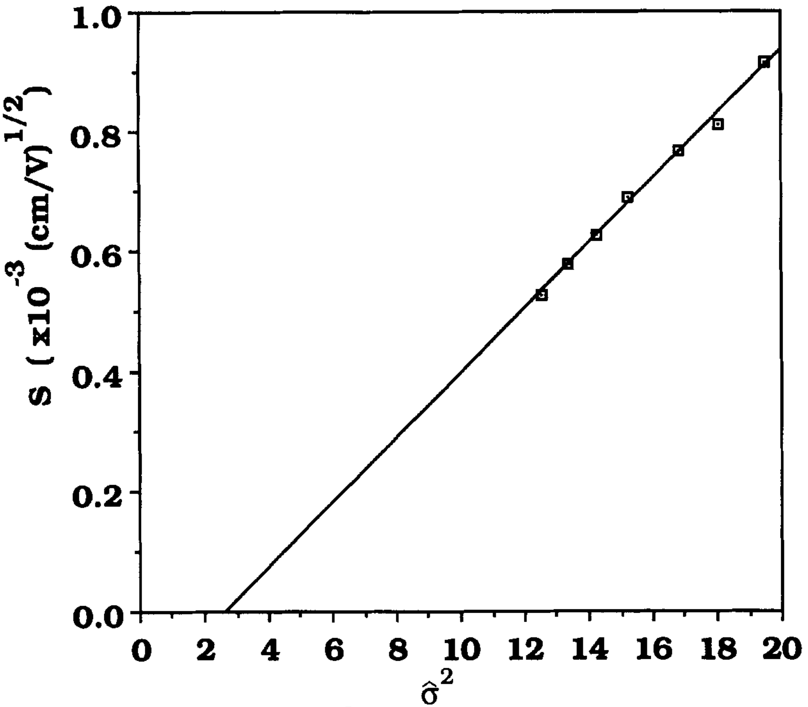

FIGURE 5 Slopes, S, vs $\hat{\sigma}^2$

CONCLUSIONS

The above results follow the trends and relationships predicted by the disorder formalism, allowing the calculation of all the parameters involved in the model which then yields reasonable values for physical constants of this system such as the 0.1eV energy width of the distribution of states. An expansion of the temperature range may be used to further explore the charge transport properties of ClAlPc and any limits to their description by this model. Such studies are currently under way. Furthermore, drift mobility studies on a related compound, oxotitanium phthalocyanine, will also explore the applicability of this model.

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