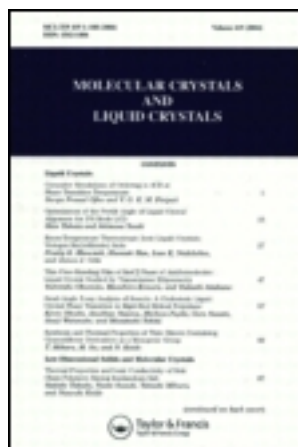


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Drift Mobility Measurements in Copper Phthalocyanine Single Crystals

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Abstract—The drift mobilities of holes in copper phthalocyanine were observed to be 0.2–0.5 cm²/V.sec. The mobilities increase exponentially with temperature with the activation energy of 0.1 eV.

1. Introduction

The measurement of drift mobilities in organic molecular single crystals has been a matter of considerable interest. The drift mobilities and the temperature dependences can help one to understand mechanisms of charge transfer on these crystals under the influence of applied electric fields.

Transient current measurements of mobilities have been successful in a number of organic crystals.^(1,2,3)

The phthalocyanine single crystals are a particularly interesting class of organic compounds because of their stability and versatility.⁽⁴⁾

Drift mobilities for amorphous films of copper and metal free phthalocyanine have been already measured by several authors.^(5,6,7) However, for the investigation of the conduction mechanism in molecular crystals the measurements of drift mobilities for single crystals are important. Drift mobilities of metal free phthalocyanine single crystals were recently carried out by N. N. Usov *et al.*⁽⁸⁾ and are about 0.5 cm²/V.sec.

Copper phthalocyanine has been studied in great detail because it has a relatively high Hall mobility of about 15–75 cm²/V.sec^(4,9,10) which is much larger than that of 0.1–0.4 cm²/V.sec of metal free

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phthalocyanine,⁽¹¹⁾ but its drift mobility and the temperature dependence have not been observed.

In this paper drift mobilities of copper phthalocyanine single crystals and the temperature dependence are reported.

2. Experimental

Single crystals of Cu phthalocyanine were grown by sublimating the material in a two zone furnace, using nitrogen gas as a carrier after purifications of 5 times by sublimation. Thin flat crystals with 70–120 μm thickness were used for measurements.

Drift mobilities were observed by a crystal counter technique using a giant pulse ruby laser as shown in Fig. 1. The time constant of the output circuit is made large compared to the duration of the photoconductive transient so that the circuit acts as an integrator.

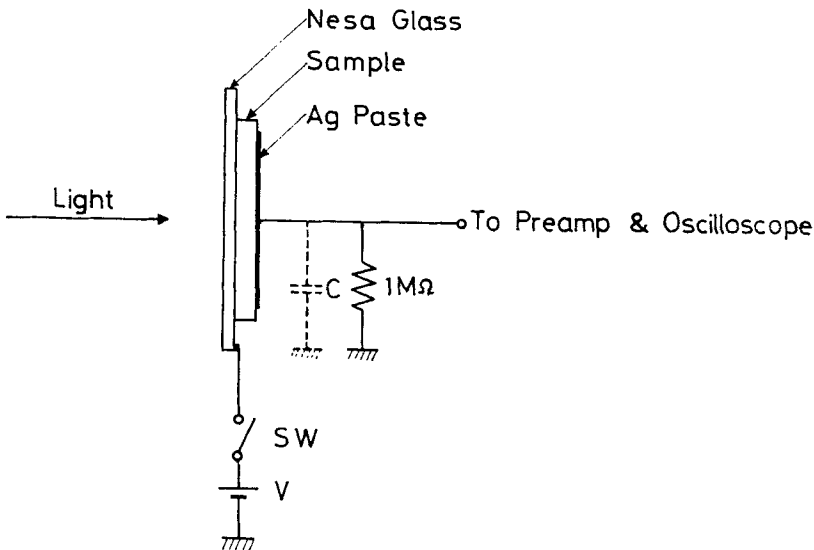


Figure 1. Schematic of the drift mobility measurement.

In our experiment the electrodes are placed on the ac-plane of the crystal. To avoid crystal surface damages by the illumination the weak laser excitation intensity was used.

3. Results and Discussion

Figure 2 shows the typical applied voltage dependence of collected charge which is linear with voltage for low voltages and saturates at high voltages. This behavior is referred to as "Hecht behavior" and this shows that carriers arrive at the unilluminated electrode.

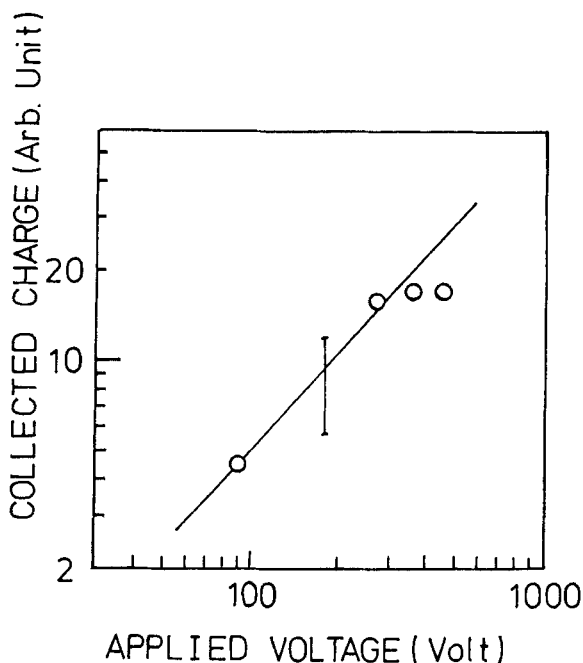


Figure 2. Typical applied voltage dependence of the collected charge.

Figure 3 shows the displacement of the break point corresponding to the transit time with increasing applied voltage V . The observation of a sharp break point in the curves suggests that trapping is small and the field remains uniform during one transit time.

The absorption coefficient of phthalocyanine at the wavelength of the ruby laser radiation is greater than 10^5 cm^{-1} .⁽¹²⁾ This suggests that carriers are generated at the surface.

The measurement of the transit time T_{tr} allows one to compute the drift mobility from the relation

$$\mu = d^2/VT_{tr}.$$

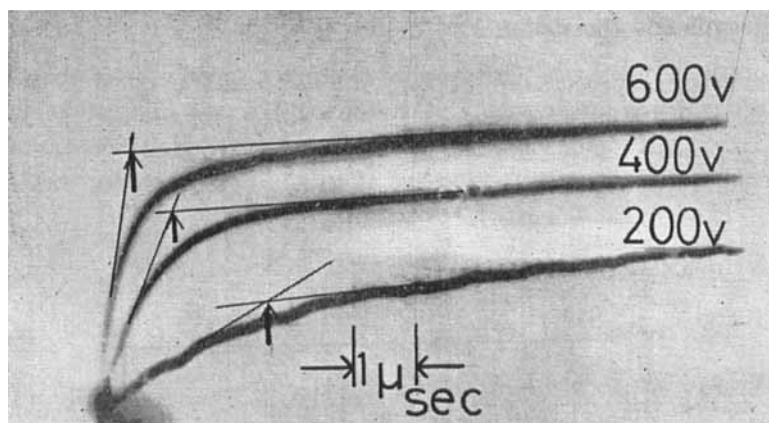


Figure 3. Photoresponses for several values of V . The arrow marks indicate the value of T_{tr} .

Observed displacement is proportional to $1/V$ as shown in Fig. 4. The mobility is calculated by obtaining the slope of the plot of T_{tr} vs. $1/V$. Values of mobilities obtained from the slopes are shown in Table 1. In our experiment the drift mobility of electrons could not be estimated because sharp break point is not observed in electron currents. This suggests that the drift mobility of electrons is less than that of holes.

Observed drift mobilities of holes are the same order as those of anthracene and metal free phthalocyanine but are much smaller than Hall mobilities. The ratio of the Hall mobility to the drift mobility is about 30 and is the same order as that observed in anthracene by M. Schott *et al.*⁽¹³⁾ The origin of the large ratio is discussed by many authors^(14,15) but has not been clarified.

Figure 5 shows that the hole mobility increases exponentially with temperature as written in followings,

$$\mu = \mu_0 \exp(-E/kT),$$

where E is the activation energy and is 0.1 eV. The exponential dependence of the mobility suggests that the thermal activation process in charge transfer is important.

Values of μ at $1/T = 0$ are about 17–43 $\text{cm}^2/\text{V}\cdot\text{sec}$ which are the same order as values of Hall mobilities and are much larger than

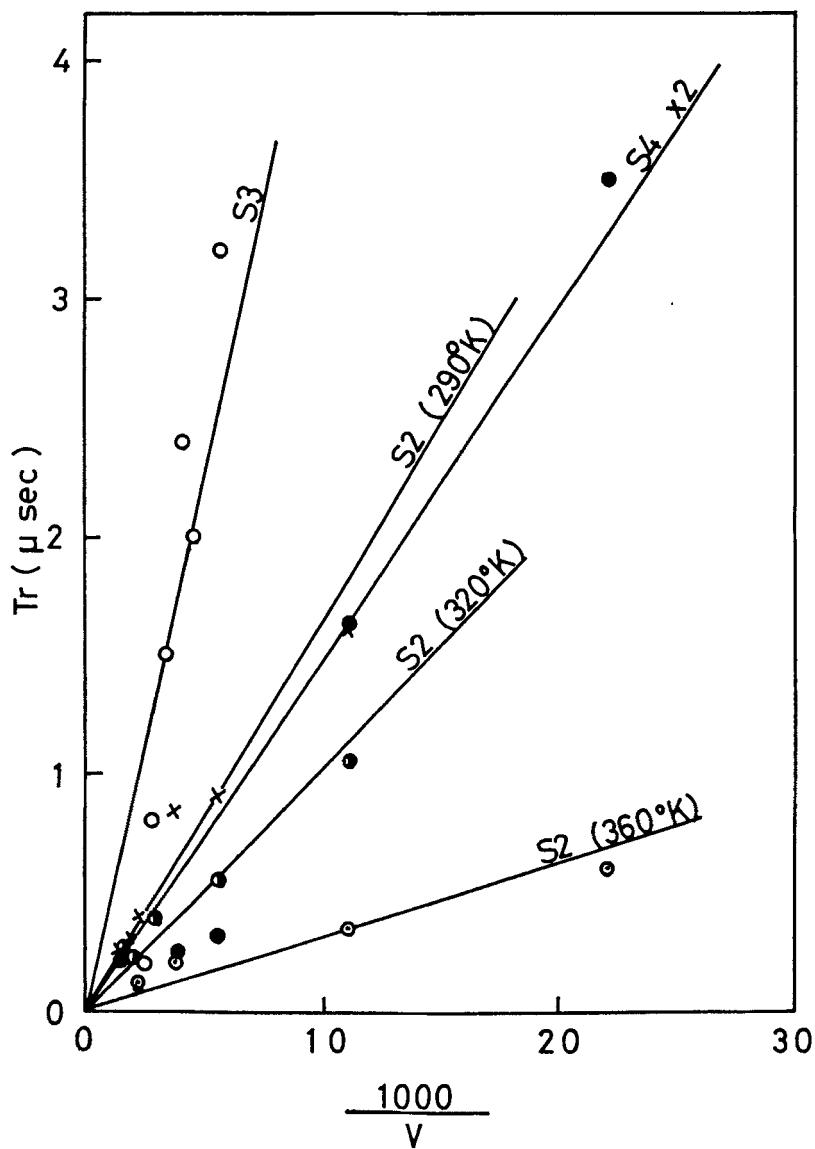


Figure 4. Transit time vs, $1/V$ for several samples.

sample	hole mobility	tem. dep.
S3(70 μ)	0.2 cm ² /V.sec	exp. E=0.10eV
S4(120 μ)	0.5	—

TABLE I. Observed mobilities of holes in copper phthalocyanine.

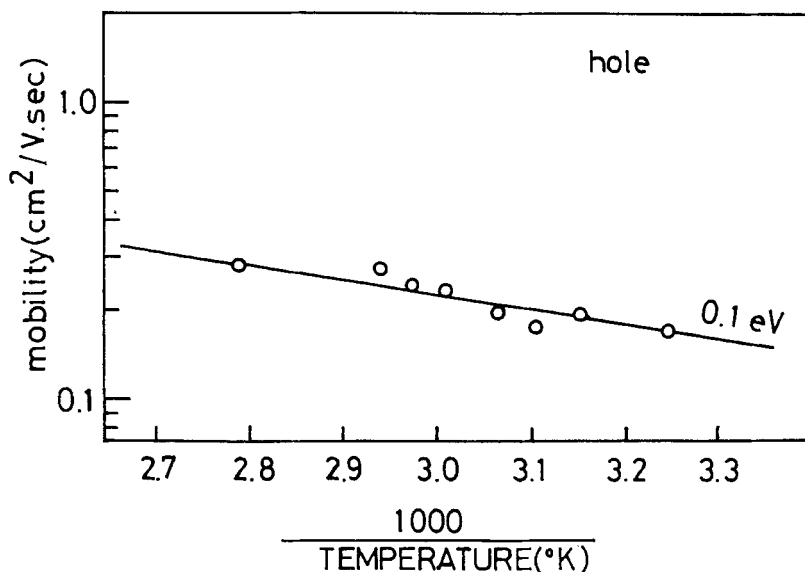


Figure 5. Mobility of holes vs. temperature.

drift mobilities of metal free phthalocyanine. This result suggests that the central metal ion in phthalocyanine enhances the probability of the charge transfer from molecule to molecule.⁽¹⁶⁾

The observed activation energy of the photoconductivity in copper phthalocyanine is 0.31 eV as shown in Fig. 6. This result suggests the following scheme; photocarriers are generated through the thermal activation process with 0.21 eV activation energy from singlet exciton level and move in the crystal with 0.1 eV activation energy.

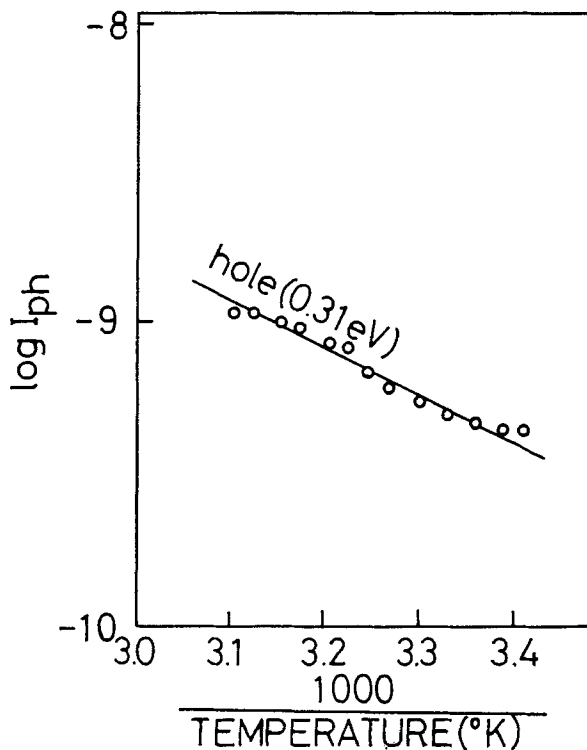


Figure 6. Temperature dependence of the photoconductivity.

4. Conclusion

The drift mobilities of holes in copper phthalocyanine are about $0.2\text{--}0.5\text{ cm}^2/\text{V}\cdot\text{sec}$ at room temperature and carriers move in the crystal with the thermal activation energy of 0.1 eV .

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