

Photoconductivity in thin films of phthalocyanine

FRANCIS P XAVIER* and GEORGE J GOLDSMITH

Physics Department, Boston College, Chestnut Hill, MA 02167, USA

*Present Address: Physics Department, Loyola College, Madras 600034, India

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Abstract. The photocurrent and electrolyte electromodulation (EEM) spectra of thin films of metal-free phthalocyanine (H_2Pc) and of copper phthalocyanine (CuPc) were investigated. The modulation spectra yielded three distinct features around 1.61, 2.30 and 2.93 eV for H_2Pc and around 1.63, 2.04 and 3.20 eV for CuPc. The spectral dependence maxima of photoconductivity correspond to the modulation spectra. These features are interpreted to indicate transitions at critical points, i.e. the existence of transitions between three valence bands, since Pc's are p-type, and the lowest conduction band in Pc's.

Keywords. Organic semiconductors; films; polymer.

1. Introduction

Some organic compounds having single–double bond structure, such as anthracene and phthalocyanine (Pc), were found to possess semiconducting properties (Inokuchi 1989). The Pc's exist in at least three different (polymorphic) modifications (Gutmann and Lyons 1981), the most common of these are designated α -form and β -form (Kanemitsu *et al* 1991; Qian 1989), and differ slightly in structure and electrical properties. The α -form is tetragonal, while the β -form is monoclinic (Schoch *et al* 1988). The α -form has six molecules per unit cell but the β -form has only two molecules per unit cell (Moser and Thomas 1963; Aoyagi *et al* 1971; Robertson 1935, 1936). The α -form, which is the subject of this investigation, occurs as polycrystalline films when sublimed under vacuum onto cool (room temperature) substrates, while the β -form is crystallized into single crystals by vacuum sublimation at a temperature around 460°C.

Modulation technique is used to obtain sharp, well-resolved spectra that can be analysed to yield directly the properties of the material under study (Aspnes 1973), for example the band structure. In electromodulation the applied electric field on the material under study produces changes in the dielectric function associated primarily with interband transitions at the critical points (Bordas 1976). Thus the electromodulation is of greatest importance in studying the band structure of a semiconductor. This technique provides optimum sensitivity for the detection of weak or closely spaced critical points. Electrolyte electromodulation techniques on thin films could be used to gain further insight into details of the band structure of the material under study.

Under the influence of an electric field the energy bands of the semiconductors are tilted and an electron, in order to tunnel from the valence band to the conduction band, meets with a triangular barrier. Further, as the electron tunnels through the barrier, if it interacts with a photon the effective width of the barrier becomes smaller. As a result of this photon-assisted tunnelling the transmission probability becomes exponential. Therefore oscillatory behaviour is seen in the dR/R vs energy data (Pollak *et al* 1993). These are Franz–Keldysh oscillations.

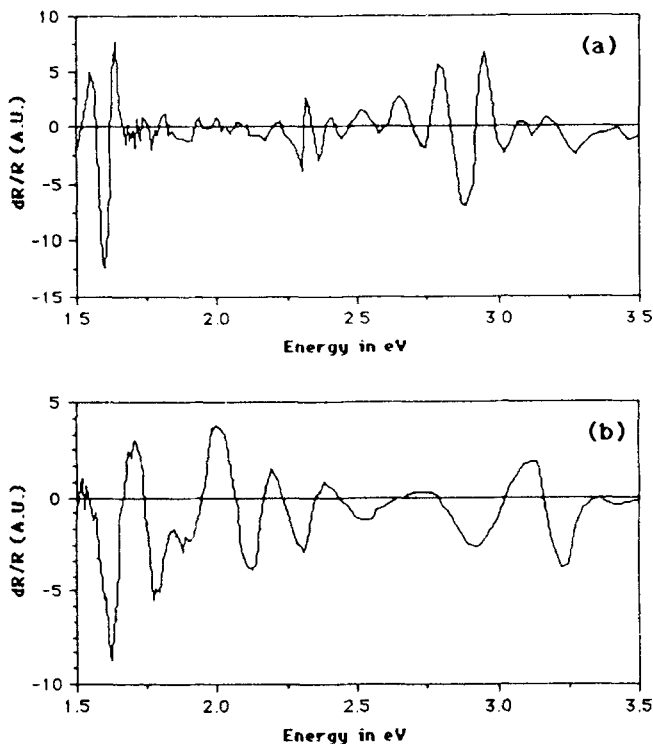


Figure 1. Electromodulation spectrum of (a) H_2Pc film and (b) $CuPc$ film.

2. Experimental

Films of metal-free phthalocyanine (H_2Pc) and of copper phthalocyanine ($CuPc$) were prepared (for room-temperature electrolyte electromodulation studies) by vacuum sublimation (at 10^{-6} torr) atop an aluminium electrode which had been deposited onto pre-cleaned glass microscope slides. Electrical connections were made to the aluminium electrode by means of thin copper wire (0.08 mm) fixed by air-dried silver conducting paint. The electrode was isolated from coming into contact with the electrolyte by spreading a thin layer of paraffin exposing only the Pc thin film to the electrolyte. The sample thus prepared was inserted into an electrolyte consisting of ethylene glycol containing a trace of dry KOH . A platinum electrode was inserted into the solution to complete the electrical circuit.

The electromodulation (EM) measurements were carried out at room temperature using modulation spectroscopy. Modulation spectroscopy involves the application of a periodic perturbation (here electrical field, i.e. square waves of p-p amplitude between 2 and 16 V at a frequency of 235 Hz) to the material under study. By separating the effect of the perturbation from the reflection or absorption background using lock-in phase-sensitive detection, the periodic modulation of the optical properties of the material (Aspnes *et al* 1968) is recorded by scanning over a wavelength range. The measured output was proportional to dR/R , with R , the reflectance.

The EM spectra were characterized by three spectral regions where there were prominent features. In H_2Pc the first extends between 1.5 and 1.7 eV, the second between 2.3 and 2.4 eV and the third between 2.8 and 3 eV as shown in figure 1a. In the case of $CuPc$ the regions were broader, the first extending from 1.5 to 1.7 eV, the second from 1.9 to 2.1 eV and the third from 2.9 to 3.3 eV as shown in figure 1b (Tokura *et al* 1983). The oscillatory structures after the second and third prominent features on the higher energy side are Franz-Keldysh oscillations.

The spectral dependence of the photoconductivity was measured in the range between 1.5 and 3.5 eV at room temperature. The resulting spectra are illustrated in figures 2a and 2b. In both H_2Pc and $CuPc$, the spectra are characterized by an initial peak at about 1.60 eV followed by broad, shallow maxima. The maxima occur around 1.64, 1.84, 2.29 and 2.93 eV for H_2Pc and around 1.59, 1.85, 2.39 and 2.92 eV for $CuPc$.

3. Discussion

The first of the prominent features in the EM spectra (figures 1a and 1b) are third-derivative-like. Features such as these are interpreted to indicate transitions between critical points. On the assumption that electroreflection/absorption spectra in these materials are analogous to those from inorganic semiconductors, the Aspnes three-point method (Aspnes 1973) was applied to compute the transition energies at the critical point. These are at 1.61 eV for H_2Pc and at 1.63 eV for $CuPc$.

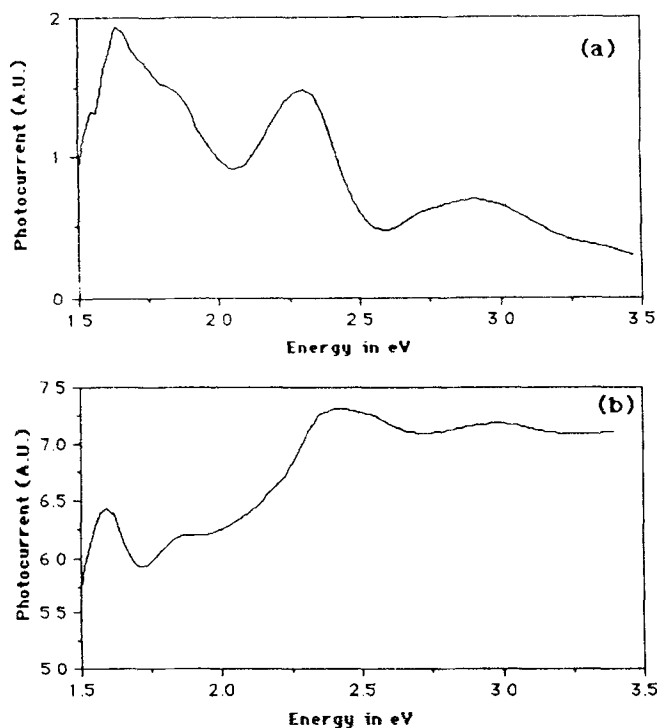


Figure 2. Photoconductivity spectrum of (a) H_2Pc film and (b) $CuPc$ film.

The oscillatory features (the second and third prominent features) in the EM spectra (figures 1a and 1b) are interpreted as photon energies above the absorption edge (Pollak *et al* 1993) corresponding to the transition energies at the critical points. These energies are calculated using the Aspnes three-point method to be 2.30 and 2.93 eV for H₂Pc and 2.04 and 3.20 eV for CuPc.

Even poorly conducting molecular materials exhibit photoconduction (Wright 1989). When the material is subjected to exciting radiation many electron and hole pairs are created. These will drift, under the influence of the applied field, giving rise to photocurrent. The threshold of light absorption normally corresponds to excitation of an electron from the valence band to the conduction band, which in turn corresponds to the maxima in the photoconductivity spectrum.

The photoconductivity maxima of H₂Pc and CuPc are indicated in figures 2a and 2b which correspond to the maxima of EM spectra as shown in table 1. The maxima of the photoconductivity spectra are interpreted as the many possible electronic transitions. These photoactive transitions are assumed to take place within the π -electron system of the phthalocyanine molecule. Since the material under study is p-type (Epstein 1960; Eley 1962; Heilmeyer 1962; Gutmann and Lyons 1981), its transport characteristics involve electron traps. So it is assumed that the net effect of photoconduction is to increase the population of free holes in the valence bands and each of the prominent maxima corresponds to an energy level in the valence band.

Table 1. Comparison of maxima of electromodulation and photoconductivity spectra of H₂Pc and CuPc thin films.

Metal-free phthalocyanine		Copper phthalocyanine	
Electroreflectance	Photoconductivity	Electroreflectance	Photoconductivity
1.5–1.7 eV	1.64 eV 1.84 eV	1.5–1.7 eV	1.59 eV 1.85 eV
2.3–2.4 eV	2.29 eV	1.9–2.1 eV	2.39 eV
2.8–3.0 eV	2.93 eV	2.9–3.3 eV	2.92 eV

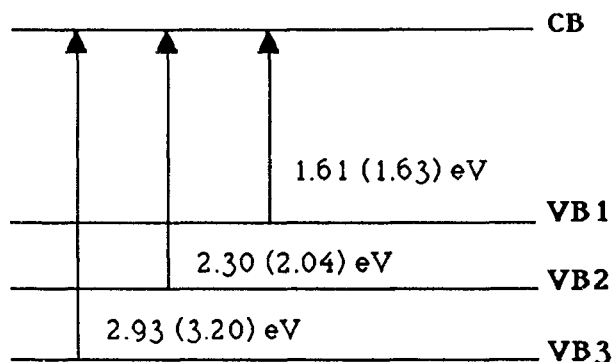


Figure 3. Proposed band diagram of H₂Pc (CuPc) film.

Thus these observations indicate that the maxima in the ER spectra corresponding to those in the photoconductivity spectra are transitions at critical points which most likely occur between three narrow valence bands and the lowest conduction band. Figure 3 illustrates the band structure model for thin films of phthalocyanine where transitions at critical points for H₂Pc (CuPc) are indicated. In the case of H₂Pc there are three distinct third-derivative-like features at 1.61, 2.30 and 2.93 eV which are transition energies at the critical points and in the case of CuPc the transition energies at the critical points are 1.63, 2.04 and 3.20 eV. The maximum seen in the photoconductivity spectrum (figures 2a and b) around 1.84 (1.85) eV for H₂Pc (CuPc) is ascribed to excitonic level.

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