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Spectra and Photoconduction of Phthalocyanine Complexes (I)

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Reflection spectra of Co, Ni, Cu, Zn, and metal-free phthalocyanines have been measured. The Davydov splitting of the main absorption peak in the metal compounds correlates with the relative tendencies of the metals to out-of-plane bonding. Photoconduction response curves have been measured between 1500 and 300 mμ for single crystals of these compounds. Besides a high response following the crystal absorption, metal-free Ni and Cu phthalocyanines also had considerable photosensitivity in the near infrared, peaking at 900–1100 mμ. The effect on the short-wavelength photoconduction of measuring *in vacuo* instead of in air also correlates with the ability of the metals to bond out-of-plane groups.

I. INTRODUCTION

THE problem of photoconduction in organic molecular crystals concerns both the production of charge carriers and their mode of transport. Each of these facets has produced two types of theory. The ionization of excitons, either at surfaces or dislocations[1] and intersystem crossing from singlet to triplet molecular states[2] have both been proposed as the method of carrier formation; carrier migration could occur, either in a series of phonon-assisted jumps, or in a conduction band with phonon scattering. The temperature variation of mobility in anthracene[3,4] agrees well with Leblanc's calculations using the band model.[5] but there have not yet been any decisive experiments on carrier formation.

The present work was designed to investigate the relation between the triplet state and exciton ionization theories by studying the effect of metal substitution on the photoconduction of phthalocyanine crystals. Heavy atoms and paramagnetic ions are known to enhance the probability of singlet–triplet transitions by spin-orbit coupling and charge transfer (see Allison and Becker's work on the luminescent spectra of metal porphyrins[6]), so that if triplet states play an important part in carrier formation, the effect should be clearly seen. The phthalocyanines are particularly suitable, not only because they can be prepared in high purity and sublimed into good single crystals, but also because changing the metal ion has very little effect on the crystal structures, several of which are known with great accuracy.[7] Moreover, we have the metal-free compound, on which work has already been done with sublimed films,[8] as a control. The semiconducting activation energies of the metal phthalocyanines were measured by Fielding and Gutman,[9] the only previous work on single crystals.

II. EXPERIMENTAL

The compounds were prepared by precipitation from lithium phthalocyanine and the anhydrous metal chloride in absolute ethanol[10] and purified by subliming in a tube furnace at 400°C in a stream of dry N_2 at low pressure. By this method, crystals could be grown up to 1.5 cm long.

Because of their very high color, transmission spectra of the crystals could not be measured. Reflection spectra were obtained for powdered samples in a Unicam SP 500 spectrophotometer with diffuse reflectance attachment. In the region of high absorption the phthalocyanines are metallic reflectors, so that maxima of reflection correspond to maxima of crystal absorption. The spectra were therefore plotted as percentage reflection from the powder supported on a piece of black photographic paper, against another piece of the same paper in place of the $MgCO_3$ standard. The two reflection maxima in our spectrum of metal-free phthalocyanine coincide with the two highest absorption maxima in the single-crystal transmission spectrum[11] (Table I). When run against a polished Al plate as standard, the reflection maxima were not shifted significantly, and the Davydov splittings remained unchanged.

For the photoconduction experiments, the needle-shaped crystals were attached by silver paste (Johnson–Matthey silver preparation FSP 3) to thin copper-wire electrodes in turn attached to copper rods passing through a B40 Teflon cone which closed the end of the glass container that could be evacuated through a side arm. For electrical shielding, the glass container was enclosed in a brass tube, screwed on to a Beckman DU monochromator. The current was measured by

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[1] L. E. Lyons, J. Chem. Soc. **1957**, 5001.

[2] B. Rosenberg, J. Chem. Phys. **29**, 1108 (1958).

[3] R. G. Kepler, Phys. Rev. **119**, 1226 (1960).

[4] O. H. Leblanc, J. Chem. Phys. **33**, 626 (1960).

[5] O. H. Leblanc, J. Chem. Phys. **35**, 1275 (1961).

[6] J. B. Allison and R. Becker, J. Chem. Phys. **32**, 1410 (1960).

[7] J. M. Robertson, J. Chem. Soc. **1935**, 615; **1936**, 1195; R. P. Linstead and J. M. Robertson, *ibid.* **1936**, 1736.

[8] For example, A. T. Vartanian and I. A. Karpovitch, Doklady Akad. Nauk S.S.S.R. **111**, 561 (1956).

[9] P. E. Fielding and F. Gutman, J. Chem. Phys. **26**, 411 (1957).

[10] P. A. Barrett, D. A. Frye, and R. P. Linstead, J. Chem. Soc. **1938**, 1157.

[11] L. E. Lyons, J. R. Walsh, and J. W. White, J. Chem. Soc. **1960**, 167.

TABLE I. Crystal spectra and Davydov splittings (cm^{-1}).

	Metal-free						Cobalt		Nickel		Copper		Zinc
	Ref. 11		This work		Ref. 9		This work	9	This work	9	This work	9	This work
	14440	15350	...	...	...	...	14190	14750	14540	14920	13980	14520	13510
	15750	13900	15740	13910	16500	14640	16000	16500	16130	16560	15870	16480	15740
Splitting	1350	1450	...	...	...	...	1810	1760	1590	1640	1890	1960	2230

observing the voltage drop across a standard high resistor (Victoreen Highmeg $10^{10}-10^{12}$ Ω) using E.I L. Ltd. Vibron 33C vibrating-reed electrometer with a time constant of 30 sec at 10^{12} Ω, the potential being obtained from a 90-V H.T. battery.

The shape of the crystals prevented the use of a guard ring to eliminate surface currents. The photocurrent was taken as the difference between the current with light on and light off, read alternately at 3-min intervals. This allows for possible changes in the dark current if the crystal heats by light absorption. However, the dark current did not increase by more than 5% during a run, while the ratio of photocurrent to dark current at the infrared peak is about five. The photocurrent is not expected to be a very steep function of temperature (E_{act} about 0.2 eV[19]).

III. SPECTRA

Table I gives the reflection maxima (i.e., absorption maxima) together with the only single-crystal transmission data[11] and the transmission minima for sublimed films.[9] The latter are almost certainly the α modification, whereas the crystals have the β form. This may account for the systematic difference from our results, though one would not in any case expect transmission and reflection curves to coincide, because of anomalous dispersion.[12]

The solution spectrum of metal-free phthalocyanine has two major bands, and the metal derivatives only one, corresponding to an increase in symmetry from D_{2h} to D_{4h}. On the Davydov theory the bands will split, in the crystal, into as many components as there are nontranslationally equivalent molecules in the unit cell. The β form has two such molecules,[7] and so we expect four major bands in the metal-free, and two in the metal phthalocyanine. The four bands (two oppositely polarized pairs) can be clearly seen in the single-crystal transmission spectrum, but one band of each pair is much weaker, and is not seen in our reflection spectrum or the film-transmission spectrum.

Again according to the Davydov theory,[13] the size of the splitting of an allowed molecular transition is a direct measure of the interaction energy between molecules of differing site symmetries. The splittings tabulated for the metal phthalocyanines, however, show a clear correlation with the known tendencies of the metals to out-of-plane bonding, that is, to interaction with translationally equivalent molecules, for in the β structure there are two nitrogen atoms on adjacent molecules, lying on the perpendicular to the molecular plane passing through the metal atom, and distant 3.05 Å (Fig. 1).

The energy levels of a pure tetragonal system, such as a metal phthalocyanine in a noncoordinating solvent, are given in Fig. 2(a). The crystal interaction will raise the d_{z^2} and lower the d_{xy} relative to d_{yz} and d_{xz} to an unknown extent. Paramagnetic resonance results[14] place the unpaired Cu electron unequivocally in the $d_{x^2-y^2}(\sigma^*)$ orbital, but for Co they are equally consistent with it being in d_{xy} or d_{z^2}. For Cu at least, the hyperfine structure shows that d_{xy} is more stable than $d_{xz,yz}$. A small tetragonal distortion from octahedral symmetry would result in the levels shown in Fig. 2(b).

From Co to Ni the out-of-plane bonding becomes weaker as d_{z^2} is filled, but Ni has the strongest in-plane bonding (maxima in solution spectrum at shorter wavelength) because all the bonding, but none of the antibonding orbitals are occupied. Half-filling the lowest σ^* orbital ($d_{z^2-y^2}$) in Cu, to decrease the in-plane bonding again, means that it might become energetically more profitable to place some electron density in $4p_z$ and coordinate a fifth and sixth group into σ-bonding orbitals. With increasing nuclear charge, $4p_z$ contracts faster than $3d_{z^2}$ and thus takes an increasing part in bonding. Zn, with a filled d shell, has the strongest out-of-plane bonding of all, because the $3d_{z^2}$ has now contracted sufficiently not to repel out-of-plane groups.

It follows from these arguments and the observed Davydov splittings that increasing interaction between equivalent molecules in the crystal increases the interaction between inequivalent stacks of molecules. The splittings in the metal compounds are all greater than in the metal free, for which the ordinary theory is in moderate agreement with observation.

A feature of all the reflection spectra is the sharp rise in reflectivity at longer wavelengths than the lowest Davydov bands. That this cannot be due to metal-

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[12] J. W. Weigl, J. Chem. Phys. **24**, 577 (1956).

[13] D. P. Craig and P. C. Hobbins, J. Chem. Soc. **1955**, 539.

[14] J. F. Gibson, D. J. E. Ingram, and D. Schonland, Discussions Faraday Soc. **26**, 72 (1958); J. S. Griffith, *ibid.* **26**, 81 (1958).

lic reflection accompanying high absorption follows from the height of the peak, which would require a transition even more allowed than those at 600–700 mμ. The single-crystal transmission spectrum shows no trace of a rising background up to 770 mμ and a saturated solution in chloronaphthalene (about $10^{-3}M$) had no absorption between 700 and 1500 mμ in a 2-cm cell. The effect is probably not a crystal absorption but a consequence of the changeover from metallic to nonmetallic reflection, since for the latter, high reflection implies low absorption. Other workers[12,15] have observed, without comment, a similar effect in the reflection spectra of sublimed dye layers when the absorption of the same layers showed no increase.

IV. DARK CURRENT

Accurate values for volume resistivities are difficult to calculate because of the uncertainty in measuring the distance between the irregularly shaped lumps of silver paste forming the electrodes, the irregular shapes of some of the crystals, and possible barrier effects at the electrodes. All samples were tested for ohmicity before carrying out spectral response measurements, and their resistivities were calculated from the slopes of the Ohm's law plots:

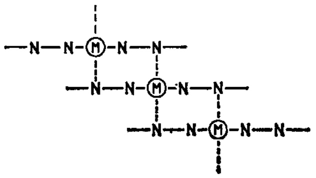


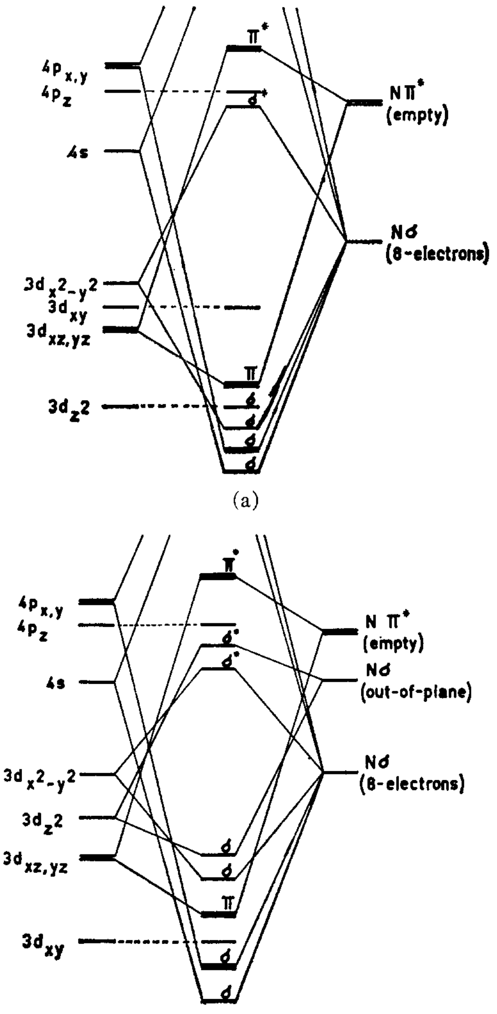
FIG. 1. Molecular interaction in the metal phthalocyanines.

Co	$(9.9\pm7.5)\times10^{9}\ \Omega$ cm	(2 runs),
Ni	$(6.3\pm3.1)\times10^{10}$	(7 runs),
Cu	$(3.0\pm0.1)\times10^{11}$	(4 runs),
Zn	$(2.8\pm1.0)\times10^{9}$	(5 runs).

The dark current in the metal-free compound was very low and subject to hysteresis. Its resistivity is at least $10^{12}\ \Omega$ cm.

The resistivities tabulated do not correlate with paramagnetism, though all the metal compounds have values at least 10 times lower than the metal free. Neither does the atomic number effect on spin-orbit coupling seem to apply, for the phosphorescent intensities of the corresponding meso-porphyrins are in the ratio Zn/Ni=60 and Cu/Zn=5−10^{6}, i.e., though Zn contains a far higher concentration of triplets than Ni, Cu, because of its paramagnetism, is still greater than Zn.

The uncertain contribution of surface currents makes further discussion of the dark resistivities unprofitable.



(a)

(b)

FIG. 2. Metal phthalocyanine energy levels. (a) In solution (no out-of-plane bonding); (b) in the solid ($3d_z{}^2$ alone is engaging in out-of-plane bonding).

Experiments with guard rings are being attempted, and will be reported in later papers.

V. PHOTOCONDUCTION

All the compounds examined except Co, the results for which were in any case unreliable, as the dark cur-

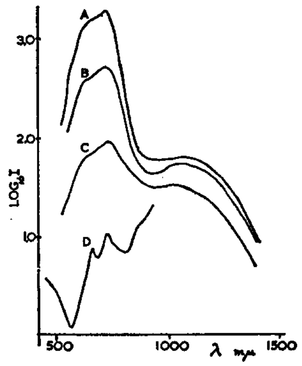


FIG. 3. Wavelength dependence of the photocurrent I in metal-free phthalocyanine, in air, A, in high vacuum, C, and in an atmosphere of nitrogen equilibrated with water in the absence of oxygen, B. D is the reflection spectrum plotted on an arbitrary scale.

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[15] W. West and B. H. Carroll, J. Chem. Phys. **19**, 417 (1951).

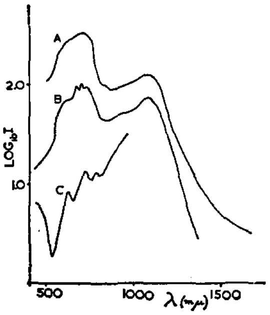

FIG. 4. Wavelength dependence of the photocurrent I in cupric phthalocyanine in air, A, and in high vacuum, B. C is the reflection spectrum.

rent swamped the photocurrent, showed their maximum photosensitivity in the singlet absorption region, in agreement with previous work on layers.[8] However, the metal-free, Ni and Cu compounds also had considerable photosensitivity in the near infrared, detectable up to 1800 mμ. This was not caused by scattered visible light, since it was not affected by placing a filter, transmitting only above 750 mμ, at the monochromator exit. Spectral response curves were plotted for constant frequency bandwidth $\Delta\nu = 750$ cm^{-1} and corrected for the intensity distribution of the lamp to constant incident energy (Figs. 3 and 4).

A novel feature of the results is the different effect of evacuating on the photoresponse from visible and infrared regions. After 24 h at 10^{-5} mm Hg the singlet response of the metal-free compound dropped 25-fold while the broad peak at 1000 mμ only halved. In general, the effect of applying a vacuum on the singlet photoresponse correlates with the ease of coordinating further groups to the metal atom. Thus the Zn compound has a very high response at 600–700 mμ, that in the infrared being undetectable by comparison, and the response falls about 40-fold after 24 h at 10^{-5} mm Hg. The singlet peaks in the Cu curve are about twice as high as the infrared peak in air, but only a third as high *in vacuo*. The curve for Ni has no high singlet peak in air, and is unchanged *in vacuo*.

Where the crystal absorbs strongly, the light only penetrates a few microns and so photoconduction in the singlet region, even if it involves crossing to triplet states, will inevitably be dominated by surface effects. Since there is no appreciable light absorption at 1000 mμ the relative insensitivity of the infrared photoresponse to evacuation suggests that it represents a true bulk conduction.

VI. DISCUSSION

All the work on sublimed layers of the phthalocyanines has concentrated on the singlet region, but if formation of a molecular triplet is a necessary part of the mechanism, irradiation in the region of ground state–triplet absorption will produce a high photocurrent. The lowest phthalocyanine triplet should lie at about 900–1000 mμ. Becker and Kasha[16] found no phosphorescent emission from Zn phthalocyanine up to 900 mμ, the limit of their photographic plates. Rosenberg[2] detected structure in the photoresponse curve of anthracene below the first excited singlet, though several orders of magnitude smaller than in the singlet region, and Schneider's group have reported long wavelength photosensitivity in several hydrocarbons.[17,18] They have also noted that the form of the response curve depends on whether the light is incident on the same side of the crystal as the electrodes in a surface cell arrangement. In our work both electrodes were fully illuminated, but the singlet photocurrent does not have the inverse relation to the absorption spectrum found by Schneider *et al.* They calculate from the long-wavelength tails of the crystal spectra that the quantum efficiencies are many times greater than in the singlet region, and a similar argument will apply to the phthalocyanines, though it is understandable that our thick (about 0.5-mm) needle crystals should show a relatively greater photocurrent in regions of low absorption. The photocurrent in 9:10-dichloroanthracene is about 10^2–10^3 times greater than that observed in anthracene under similar conditions,[19] and chlorine substitution might be expected to enhance the probability of triplet formation. However, the new peak in the response curve[18] is at 22 000 cm^{-1}, whereas the $T \rightarrow S(0,0)$ emission from the compound[20] is near 14 000 cm^{-1}. However, the response curve also has shoulders at 19 000 cm^{-1} and 13–14 000 cm^{-1}. Bree and Schneider maintain that the process of free carrier production is still associated with the short wavelength region, since the long-wavelength current rises and decays, and the curve can only be retraced by previously irradiating in the exciton region. On the other hand, our curves were plotted starting from the long-wavelength end, and high-infrared photocurrents were obtained without any previous visible illumination. These photocurrents were also quite steady, and did not decay after 30 min.

It is possible that the infrared photocurrents may result from the release of thermally produced trapped carriers and not from triplets, but if so, they are trapped at a different depth (1.2 eV) from the optically produced carriers (0.2 eV).[21] Rosenberg attributes the thermal activation energy for photoconduction to the need to populate the vibrational level of the first excited singlet which crosses the first triplet. If photoconduction can occur by direct excitation to the triplet no thermal excitation is required and the photocurrent should be temperature independent. We are now investigating the temperature dependence of the visible and infrared photocurrents.

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[16] R. S. Becker and M. Kasha, J. Am. Chem. Soc. **77**, 3669 (1955).

[17] J. Kommandeur, G. J. Korinek and W. G. Schneider, Can. J. Chem. **36**, 607 (1958).

[18] A. Bree and W. G. Schneider, J. Chem. Phys. **34**, 1453 (1961).

[19] E. Bock, J. Ferguson and W. G. Schneider, Can. J. Chem. **36**, 507 (1958).

[20] M. R. Padhye, S. P. McGlynn, and M. Kasha, J. Chem. Phys. **24**, 588 (1950).

[21] G. Tollin, D. R. Kearns, and M. Calvin, J. Chem. Phys. **32**, 1013 (1960).