

The Photoconductivity of Metal-free and Copper Phthalocyanine Crystals in High and Ultra-high Vacua

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Two-probe d.c. photoconductivity measurements are reported for crystals of metal-free and copper phthalocyanines in the frequency range 5000–20,000 cm.⁻¹. Crystals were prepared by sublimation both in nitrogen and in nitrogen–hydrogen ambients. Experiments were carried out in air, and at pressures of 10⁻⁶ torr and 10⁻⁹ torr, the latter after baking the crystals at 200°C for 12 hr. Evacuation of nitrogen sublimed crystals at 10⁻⁶ torr at room temperature removed most of the photoconductivity associated with the intense visible absorption bands and caused a smaller decrease in the near-infrared photoconductivity. When air was re-admitted the photoconductivity returned. Baking under vacuum reduced the photoconductivity even further, and it did not return on exposure to air. Crystals grown in nitrogen–hydrogen mixtures already had photoconductivity spectra in air resembling nitrogen-sublimed samples which had been evacuated and baked. It is suggested that the photoconductivity in the visible region results from traps formed by the interaction of oxygen with free radical impurities near the surface of the crystals.

Of the available data on photoconductivity in organic molecular crystals, by far the largest proportion concerns anthracene. If the intrinsic band gap of anthracene is indeed in the region of 4.0 eV,¹ then photoconductivity excited by light absorbed in the lowest triplet and singlet transitions is probably extrinsic in origin. Surface states are among the most important contributors to impurity conduction mechanisms, and there is plenty of evidence² about the effect of adsorbed gases on the conductivity characteristics of anthracene. Nevertheless it is doubtful whether any experiments on anthracene have been carried out in the definite absence of surface-adsorbed oxygen, because ultra-high vacuum techniques would be needed, and the low sublimation temperature of anthracene prevents the necessary baking of the vacuum system. From simple kinetic theory, at a pressure of 10⁻⁶ torr a monolayer of gas molecules will form on a clean surface in 1 second, assuming a sticking probability of 1 for molecules colliding with the surface. The only molecular crystal whose photoconductivity has so far been studied under ultra-high vacuum conditions is quaterylene,³ and here an evaporated film was employed. It therefore seemed to us desirable to examine the photoconductivity of a material which could be obtained as single crystals, and whose sublimation temperature was high enough for a bakable ultra-high vacuum system to be used. For this purpose the phthalocyanines are very suitable.

A good deal is known about the effects of gases on the semiconductivity of phthalocyanine crystals. Experiments with guard rings⁴ have demonstrated that the activation energy for both surface and bulk conductivity

of copper phthalocyanine increases when oxygen is removed, though only the surface conductivity of metal-free phthalocyanine is affected.⁵ It was also found⁴ that evacuating to 10⁻⁶ torr at room temperature was not sufficient to remove all the oxygen from copper phthalocyanine crystals, and reproducible semiconductivity plots were only obtained after baking the crystals in a hydrogen atmosphere. Phthalocyanines are known to catalyse the reaction between hydrogen and oxygen.⁶ Another result of oxygen adsorption on to phthalocyanines is the appearance of a narrow e.s.r. signal at $g = 2$, corresponding to an unpaired spin concentration of about 10¹⁷ per cm.³. The intensity of the signal diminishes when the crystals are heated in hydrogen.⁷

Photoconductivity measurements on single crystals of several phthalocyanines have previously been reported.^{8,9} In air, photoconductivity is observed in the region of the first and second π – π^* absorption bands in the visible and near-ultraviolet, and also, in the copper compound, a further photoresponse is observed in the near-infrared,¹⁰ which correlates with some weak absorption bands found¹¹ in the crystal transmission spectrum. Oxygen is known to enhance reversibly the photocurrents in metal-free and copper phthalocyanines,⁸ and to reduce the photocurrents in the manganese compound,¹² but the spectral dependence of the effect has not been studied. There has also been a study of the effects of several gases on a range of metal phthalocyanines,¹³ but these results relate only to thin films and to the temperature-dependence of conductivity in light of a single wavelength. Also, no attempt was made to separate the dark and photoconductivity contributions to the observed current. In this paper we report the photoconductivity charac-

⁷ J. M. Assour and S. E. Harrison, *J. Phys. Chem.*, 1964, **68**, 872.

⁸ P. Day and R. J. P. Williams, *J. Chem. Phys.*, 1962, **37**, 567.

⁹ G. H. Heilmeyer and G. Warfield, *J. Chem. Phys.*, 1963, **38**, 897.

¹⁰ P. Day and R. J. P. Williams, *J. Chem. Phys.*, 1965, **42**, 4049.

¹¹ P. E. Fielding and A. C. Mackay, *Austral. J. Chem.*, 1964, **17**, 750.

¹² P. Day, G. Scragg, and R. J. P. Williams, *Nature*, 1963, **197**, 589.

¹³ J. Kaufhold and K. Hauße, *Ber. Bunsengesellschaft Phys. Chem.*, 1965, **69**, 168.

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¹ R. F. Chaiken and D. C. Kearns, *J. Chem. Phys.*, 1966, **45**, 3966.

² See, e.g., F. Gutmann and L. E. Lyons, 'Organic Semiconductors,' Wiley, New York, 1967.

³ Y. Maruyama and H. Inokuchi, *Bull. Chem. Soc. Japan*, 1966, **39**, 1418.

⁴ G. H. Heilmeyer and S. E. Harrison, *Phys. Rev.*, 1963, **132**, 2010.

⁵ J. M. Assour and S. E. Harrison, *J. Phys. and Chem. Solids*, 1965, **26**, 671.

⁶ M. Calvin, E. G. Cockbain, and M. Polanyi, *Trans. Faraday Soc.*, 1936, **32**, 1436.

teristics of metal-free and copper phthalocyanine crystals prepared by sublimation both in nitrogen and nitrogen-hydrogen mixtures, and measured both in conventional and in ultra-high vacua.

EXPERIMENTAL

Acid purified samples of metal-free and copper phthalocyanines were kindly provided by Dyestuffs Division of I.C.I. Limited. In addition samples of copper phthalocyanine were also prepared by the method of Linstead *et al.*¹⁴. All samples were further purified by entrainer vacuum-sublimation at 450° c under a pressure of 2–6 torr of either

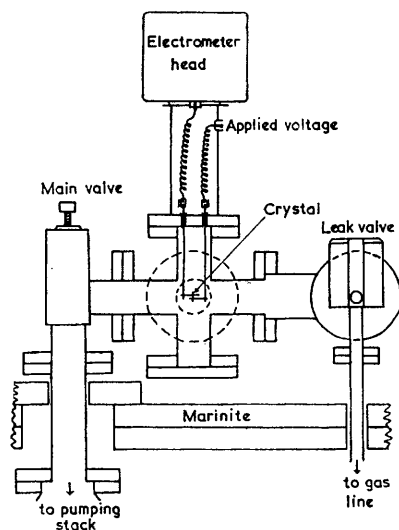


FIGURE 1 Ultra-high vacuum apparatus

oxygen-free ('white spot') nitrogen or a 1:9 hydrogen-nitrogen mixture. During about 6–12 hr. needle-like crystals up to 2 cm. \times 0.5 mm. \times 0.1 mm. were obtained.

Preliminary photoconductivity measurements were made with an apparatus using a conventional glass vacuum system which has been described elsewhere.¹⁵ For the ultra-high vacuum experiments the apparatus shown schematically in Figure 1 was constructed. The vacuum system, designed for rapid pumping, was formed from 1½ in. internal diameter stainless steel components supplied by Vacuum Generators Limited, coupled together *via* flat flanges with gold ring seals. The system was pumped through a bakable valve by a 2 in. oil diffusion pump (Edwards EO 2) fitted with a chevron baffle and bakable liquid-nitrogen trap. The needle-shaped crystals were mounted in a conventional two-probe surface cell arrangement between nickel wires using thermosetting silver paste as the electrode material. The ceramic seals between the nickel wires and the steel flanges of the vacuum line proved to have an insulation resistance greater than 10^{16} ohms, even after repeated baking, provided the ceramic was periodically washed with absolute ethanol. Light from a 100 watt quartz iodine lamp reached the crystal through a monochromator and the kodial glass viewing port of the vacuum chamber, and was monitored on the farther side by a thermopile, whose output was fed to a scalamp galvano-

meter used in conjunction with a galvanometer preamplifier. The monochromator slits were adjusted to give the chosen galvanometer deflection (*i.e.*, constant light energy incident on the crystal) over the frequency range studied. A bakable leak valve permitted controlled amounts of gas to be leaked to the sample from a glass vacuum system. Hydrogen was admitted to the gas line through a heated silver-palladium thimble, reaching the leak valve through a liquid-nitrogen trap. Oxygen was admitted from a bulb of spectroscopically pure gas or, at higher pressures direct from a cylinder, reaching the leak valve through a solid carbon dioxide-acetone trap. The entire metal high-vacuum assembly could be surrounded by a demountable oven so that it could be baked to a maximum temperature of 450° c. When first put into use, the assembly was baked under vacuum for 24 hr. at 400° c and subsequently, with crystals mounted, at 200° c. On cooling to room temperature and degassing the ionization gauge, the indicated pressure was usually in the range $2\text{--}5 \times 10^{-9}$ torr.

A d.c. potential was applied to the crystal from a three-stage Zener stabilised power supply and the current was measured by an Ekco type 616B vibrating-reed electrometer. The measuring unit of the electrometer was positioned above the vacuum system on a Dexion frame which enabled easy removal before the oven was put in place. The metal vacuum system, being efficiently earthed, provided excellent screening against fluctuating external fields, permitting current measurements of 10^{-15} amp. to be readily recorded with a noise level corresponding to 10^{-16} amp.

RESULTS

Current-voltage plots were recorded for all crystals, and only those which were ohmic and non-rectifying over the whole potential range up to 1000 volts/cm. were examined further. Room-temperature resistivities obtained in this way are shown in the Table and compared with literature

Specific resistivities (ohm-cm.)				
	In air initially	<i>In vacuo</i> without baking	In air finally	Literature values
Metal-free	3.0×10^{13}	5.0×10^{14}	1.5×10^{14}	10^{13} ^a 10^{13} ^b 5×10^{12} ^c 3.6×10^{12} ^d
Copper	3.0×10^{12}	2.0×10^{13}	4.0×10^{12}	2×10^{11} ^b $10^{12}\text{--}10^{13}$ ^e

^a G. H. Helmeier, G. Warfield, and S. E. Harrison, *Phys. Rev. Letters*, 1962, **8**, 309. ^b Ref. 12. ^c G. H. Helmeier and G. Warfield, *J. Chem. Phys.*, 1963, **38**, 163. ^d C. Hamann and M. Starke, *Phys. Stat. Solidi*, 1964, **4**, 509. ^e Ref. 4.

values. Evacuation to 10^{-6} torr for 12 hours increases the resistivity by approximately an order of magnitude, while a 12 hour bake at 200° c increases it to an immeasurably high value.

Each crystal was taken round a cycle from air at 1 atmosphere to 10^{-6} torr for 12 hours, followed by 12 hours' baking at 200° c, cooling to room temperature and re-admission of air or oxygen. At each stage the current-voltage characteristics of the photoconductivity, the photoconductivity spectrum, and photocurrent-intensity plots at various wavelengths were recorded. In air, *in vacuo*, and also after baking, the photoconductivity of both metal-free and copper

¹⁴ P. A. Barrett, D. A. Frye, and R. P. Linstead, *J. Chem. Soc.*, 1938, 1157.

¹⁵ C. K. Prout, R. J. P. Williams, and J. D. Wright, *J. Chem. Soc. (A)*, 1966, 747.

phthalocyanines obeyed Ohm's law. On the other hand, the photoconductivity spectrum both initially in air and after evacuation, depended on the ambient in which the sample crystal had been sublimed. We will describe first the characteristics of metal-free and copper phthalocyanine crystals sublimed under nitrogen.

Before evacuation large peaks were observed in the photoconductivity spectra of both compounds in the region

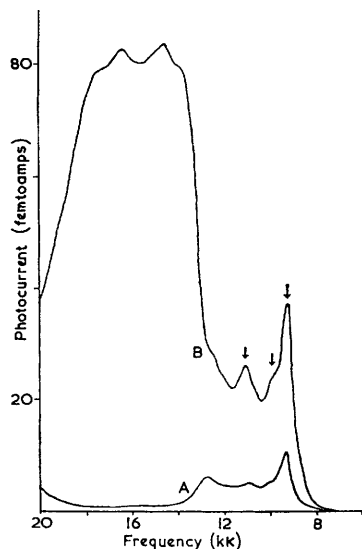


FIGURE 2 Photoresponse of copper phthalocyanine for constant incident light energy: A, *in vacuo* (5×10^{-6} torr); B, after 2 days in oxygen (125 mm.)

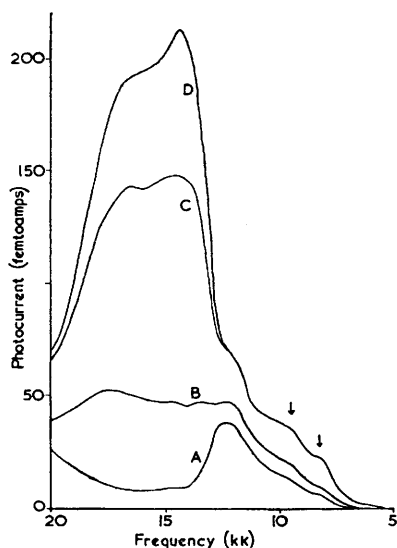


FIGURE 3 Photoresponse of metal-free phthalocyanine: A, *in vacuo* (5×10^{-6} torr); B, after 2 hr. in air (1 atm.); C, after 1 day in air; D, after 3 days in air

from 14,000 to 18,000 cm^{-1} where these phthalocyanines have their lowest-energy allowed transitions, and smaller peaks could be seen in the near-infrared. The correlation between the latter and the weak infrared bands in the single-crystal absorption spectrum of copper phthalocyanine has already been commented on,¹⁰ but we note that there is a similar correlation between the infrared photoconductivity

and the single-crystal absorption spectrum of the metal free compound. In Figures 2 and 3 the vertical arrows indicate the frequencies of the weak absorption bands as determined by Fielding and MacKay.¹¹

After 12 hours' evacuation at 10^{-6} torr, the weak infrared photoconductivity had diminished somewhat, but the large photoconductivity peaks in the visible had vanished completely (see Figures 2 and 3). If air was re-admitted to the crystal at this stage, the visible photoconductivity returned, though the process was very slow (Figure 3) and the initial photoconductivity level was never fully recovered. A feature of the photoconductivity spectra under high vacuum was the appearance, in both compounds, of small peaks in the 12,000–13,000 and 18,000–20,000 cm^{-1} regions, *i.e.*, to higher and lower energies than the main peaks observed in air. It is possible that these peaks may also be present in the spectrum measured in air, though obscured by the much larger peaks at 14,000–18,000 cm^{-1} .

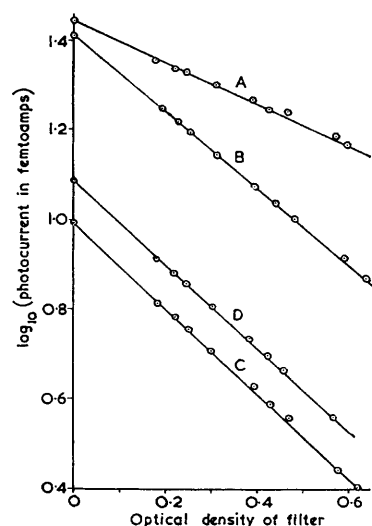


FIGURE 4 Intensity dependence of the photocurrent of copper phthalocyanine at 9150 cm^{-1} : A, in air initially, slope = 0.45; B, *in vacuo* (5×10^{-7} torr), slope = 0.84; C, baked *in vacuo* (5×10^{-9} torr), slope = 0.93; D, in air subsequently, slope = 0.92

Apart from its effect on the wavelength-dependence of the photoconductivity, evacuation also altered the intensity dependence of the photoconductivity. In air, the customary relationship $i_{ph} \propto I^n$ (i_{ph} being the photocurrent and I the light intensity) was obeyed in all spectral regions, with n in the range 0.5–1.0. The value of n was greater in the near-infrared than in the visible, both in air and vacuum, and evacuation to 10^{-6} torr caused an increase in n throughout the spectrum. A typical set of results for a copper phthalocyanine crystal is shown in Figure 4.

Now if the partial pressure of oxygen in the apparatus is reduced to 10^{-9} torr, simple kinetic theory predicts that a monolayer will form in 24 hours, assuming a sticking probability of the order of 0.01, which may be a reasonable value for a molecular crystal. It is therefore reasonable to assume that, under our ultra-high vacuum conditions, the effect of adsorbed oxygen will have been entirely eliminated.

After baking at 200° C for 12 hours (pressure $\sim 5 \times 10^{-9}$ torr), the photocurrents in both the metal-free and copper compounds were reduced to about half the magnitude

found at 10^{-6} torr, but there was no further change in the overall appearance of the photoconductivity spectra. Figure 5 shows such a spectrum. The slope of the photocurrent-intensity plot also increased (Figure 4), approaching 1.0 in some cases. However, the most striking change brought about by baking was in the effect of re-admitting oxygen to the crystal. Whereas crystals which had merely

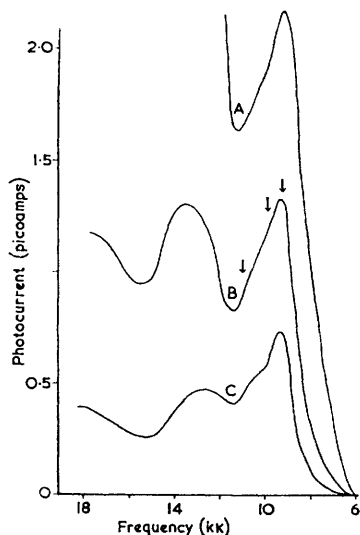


FIGURE 5 Photoresponse of copper phthalocyanine in ultra-high vacuum: A, in air initially; B, in *vacuo* (10^{-6} torr); C, baked in *vacuo* (10^{-8} torr)

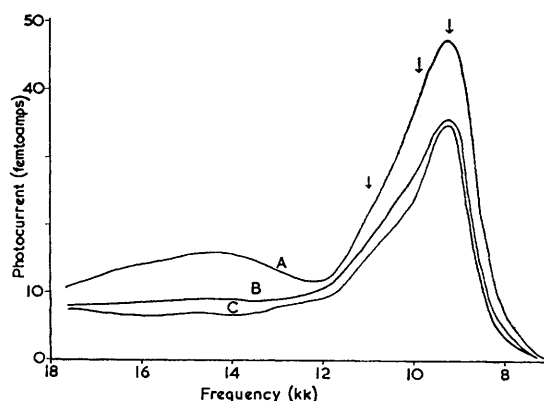


FIGURE 6 Photoresponse of a copper phthalocyanine crystal grown in a hydrogen-nitrogen ambient: A, in air initially; B, in *vacuo* (2×10^{-7} torr); C, baked in *vacuo* (2×10^{-9} torr)

been evacuated to 10^{-6} torr at room temperature recovered their visible photoconductivity, those which has been baked did not, even after 4 days. This was also reflected in the photocurrent-intensity plots (Figure 4).

It is well known that the residual gas in a stainless steel ultra-high vacuum system, after baking under vacuum, consists mainly of hydrogen outgassed from the steel. We therefore thought that the difference in behaviour between baked and unbaked crystals might result from chemical reduction of the paramagnetic defect centres which these phthalocyanines contain. Baking in a hydrogen atmosphere is known⁷ to decrease the intensity of the free-radical e.s.r. signal in phthalocyanines, and we confirmed that baking under vacuum in our stainless steel apparatus had

the same effect. We also prepared crystals of both the metal-free and copper compounds, using the same starting materials but subliming these compounds in a 1:9 hydrogen-nitrogen mixture. In external appearance the crystals were identical to those grown under nitrogen, but the intensity of the free-radical e.s.r. signal was substantially lower. Moreover the photoconductivity characteristics of nitrogen-hydrogen-sublimed crystals were quite different from those of the nitrogen-sublimed materials. Figures 6 and 7 give examples. In air, both compounds showed little photoconductivity in the visible, but instead gave spectra resembling those of the nitrogen-sublimed crystals after evacuation and baking. As can be seen from Figure 6, evacuating and baking such a crystal caused very little change in its photoconductivity, and in addition the slope

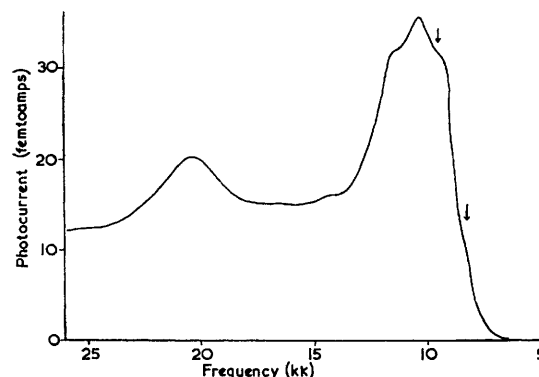


FIGURE 7 Photoresponse in air of a metal-free phthalocyanine crystal grown in a hydrogen-nitrogen ambient

of the log-log photocurrent-intensity plot at 9150 cm^{-1} was now 1.02.

DISCUSSION

First we consider the photoconductivity in the visible, *i.e.*, in the region of the first spin-allowed $\pi-\pi^*$ absorption bands. In air, the photoconductivity spectra of both the metal-free and copper compound usually consist of four bands as do the absorption spectra.^{11,16} However, the variation of both the absorption spectrum and the photoresponse from crystal to crystal makes this correlation tentative. This variation is not surprising since, with strongly absorbed light, surface effects could be very important.

Our measurements in *vacuo* clearly demonstrate that the photoconductivity between $14,000$ and $18,000 \text{ cm}^{-1}$ is extrinsic, since it disappears when oxygen is removed. The experiments with baked crystals further indicate that two requirements must be satisfied before photoconductivity can be observed in this frequency range. Evacuation to 10^{-6} torr without baking produces a decrease in photoconductivity which can be reversed by re-adsorbing oxygen on to the sample. When a crystal is baked in a reducing atmosphere, on the other hand, either in the photoconductivity apparatus or when it is sublimed, its photoconductivity is removed irreversibly. Such baking eliminates many of the paramagnetic

¹⁶ L. E. Lyons, J. R. Walsh, and J. W. White, *J. Chem. Soc.*, 1960, 167.

defects, but no change in the free-radical concentration was detected when metal-free phthalocyanine crystals were evacuated at room temperature,⁷ though under the same conditions the visible photoconductivity is almost entirely removed. Thus the paramagnetic defects alone are not responsible for the photoconductivity. Neither, apparently, is the presence of oxygen necessary to observe the free radical e.s.r. signal. At present the nature of the paramagnetic defect is not known. The absence of hyperfine structure indicates that the unpaired electron spin density on surrounding nuclei is small.⁷

We therefore propose that defect-oxygen complexes act as electron traps, releasing holes, which are known to be the majority carriers in these phthalocyanines.² Since visible light is very strongly absorbed by the crystals, only complexes located on or near the surface will be active in creating carriers, unless exciton diffusion is important. From the extinction coefficient of the lowest-energy phthalocyanine absorption band in solution it can be calculated that 99% of the incident light at that frequency is absorbed within 700 Å of the crystal surface. Most of the adsorbed oxygen being on or close to the surface, carrier formation *via* defect-oxygen complexes will be most efficient when the light is most strongly absorbed. Hence the observed correspondence between photoconductivity and absorption peaks is explained.

When the oxygen has been removed, charge carrier production probably proceeds *via* traps whose origin is in the paramagnetic defects themselves or perhaps the surface. The small photoconductivity peaks which now appear to higher and lower energy of the main peaks in air may be interpreted by assuming that the efficiency of carrier formation at the surface is very much reduced in the absence of oxygen. Hence bimolecular recombination is now the dominant factor determining the spectral dependence of the photoconductivity, and the small peaks occur at the wings of absorption bands, where a smaller fraction of the incident light is absorbed close to the surface.

If the photoconductivity in the visible is extrinsic, and the result of electron trapping by defect-oxygen complexes, the photoconductivity in the near-infrared must likewise be extrinsic. There is an excellent correlation in this spectral region between the photoconductivity and the absorption spectra, but, unlike that in the visible region, the infrared photocurrent is not entirely eliminated by evacuating to 10^{-6} torr, or by subsequent

baking *in vacuo*. Oxygen might well be implicated in carrier formation by this weakly absorbed light, but then molecules far from the surface, and included during crystal growth rather than by adsorption, might be important. This oxygen may be extremely difficult to remove, even by prolonged pumping and baking, and could thus account for the remaining infrared photoconductivity. On the other hand, even crystals grown in a reducing atmosphere, which lack any photoconductivity in the visible, and which are scarcely affected by pumping and baking, retain photoconductivity in the near-infrared.

The weight of evidence indicates that these near-infrared absorption bands arise from π - π^* triplet transitions. Schott's¹⁷ near-infrared crystal absorption spectrum of copper phthalocyanine shows vibrational structure very similar to that of the visible absorption spectrum of copper phthalocyanine in 1-chloronaphthalene. A similar correspondence is apparent between the lowest-energy π - π^* triplet absorption of anthracene crystals¹⁸ and the lowest-energy π - π^* singlet absorption of anthracene in iso-octane.¹⁹ This together with the red shift observed in the copper phthalocyanine solution spectrum in concentrated sulphuric acid indicates we are observing π - π^* triplet rather than n - π^* transitions.¹⁷ It should also be noted that the photoconductivity of anthracene,²⁰ like that of copper phthalocyanine, closely follows the absorption spectrum in the π - π^* triplet region, though no data on gas effects are available for photoconduction in this region. Phthalocyanines however, show no phosphorescence in the near-infrared, even at -175°C .²¹ This plus the strong temperature-dependence of the triplet-state lifetime suggests²¹ that the triplet decays by a very efficient non radiative process.

Conclusions.—The photoconductivity of metal-free and copper phthalocyanines in the region of the lowest-energy intense absorption bands ($14,000$ – $18,000\text{ cm}^{-1}$) is extrinsic. Electron traps formed by the interaction of oxygen with free-radical defects in the crystals release holes to act as charge carriers. Crystals from which free-radical impurities and oxygen have been largely eliminated either by subliming or baking in a reducing atmosphere still photoconduct in the near-infrared at the frequency of the weak crystal absorption bands. The latter probably arise from the lowest π - π^* triplet transitions.^{17*}

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* Note added in proof: Recent work has shown (K. Gano, K. Masuda, and J. Yagamuchi, *J. Phys. Soc. Japan*, 1968, **25**, 431) that the photoconductivity of copper phthalocyanine single-crystals is consistent with the scheme whereby photo-carriers are generated *via* exciton surface interaction and decay *via* bimolecular recombination, as we have suggested.

¹⁷ M. Schott, *J. Chem. Phys.*, 1966, **44**, 429.

¹⁸ P. Avakian, E. Abramson, R. G. Kepler, and J. C. Caris, *J. Chem. Phys.*, 1963, **39**, 1127.

¹⁹ 'Absorption Spectra in the Ultraviolet and Visible Region,' ed. L. Lang, Academic Press, vol. 1, 1961, p. 227.

²⁰ J. H. Sharp and W. G. Schneider, *J. Chem. Phys.*, 1964, **41**, 3657.

²¹ W. F. Kosonocky and S. E. Harrison, *J. Appl. Phys.*, 1966, **37**, 4789.