Electrical Properties of Phthalocyanines

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numerous multi-centered exchange integrals which appear even with the simplest form of eigenfunction in the LCAO scheme. Furthermore, the evaluation of molecular integrals can be exact, while in the LCAO scheme some approximation must be taken.

The present results on the ionization potentials of CH_4 and H_2 are comparable in accuracy to Mulligan's work on CO_2[2].

Apart from the applications to chemically saturated simple molecules such as discussed in the foregoing, the central-field approximation could be applied to radicals such as CH_2, CH_3, and NH_2. In such cases, consideration of the configuration interaction seems to be an absolute necessity, since there are many low excited states which may seriously affect one form of the wave function for the ground state.

Electrical Properties of Phthalocyanines

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The electrical conductivity of single crystals of metal-free, copper, nickel, and cobalt phthalocyanines were measured over temperature ranges extending from 50° to 390°C. The weighted mean values of the activation energies obtained were: 1.71 ev for the metal-free, 1.60 ev for the cobalt, and for the nickel, and 1.64 ev for the copper substituted compounds. No significant difference in the activation energy of the metal-free compound was observed between directions parallel and perpendicular to the (001) face of the crystal. The results were well reproducible and showed no significant variation for different crystals. It is concluded that these compounds are, above room temperature, intrinsic semiconductors and that the introduction of a metal atom into the molecule produces comparatively little change in the activation energy of conduction. A thermoelectric power of $+50$ $\mu v/°C$ was measured for metal-free and for copper phthalocyanine, indicating that the majority carriers are holes. Since the values of the constant σ_0 were found to be in the order of 100 Ω^{-1} cm^{-1} it is concluded that their mobilities are rather low. Optical transmission spectra are reported for these compounds in solution as well as in the form of thin evaporated films. The energy of the first electronic transition evident in the film spectra agrees with the thermal activation energy for electrical conduction. There is little difference in the positions of the absorption maxima observed in evaporated films and in solution, although the intensities are altered. The photoconductive response resembles the spectral transmission characteristics of the compounds. The quantum efficiency is low.

INTRODUCTION

MUCH interest has been taken recently in the electrical properties of organic compounds, considered as semiconductors. Most of this work has been carried out on polycrystalline samples, owing to the difficulties encountered in obtaining single crystals of sufficient size. The interpretation of results thus obtained, however, presents grave difficulties.

We have therefore selected a compound which permits the growing of single crystals of a size sufficiently large to allow sectioning and attachment of electrodes, without having to use micro-manipulatory methods. Phthalocyanines moreover, also permit the coordination of different metal atoms into the organic molecule and are quite stable over wide ranges of temperature. Eley,[1,2] Vartanyan,[3] and others[4] have examined these compounds, but their measurements were obtained on either films deposited from solution or from polycrystalline samples.

EXPERIMENTAL

The materials used were metal-free, nickel, cobalt, and copper phthalocyanines. The manganese and iron phthalocyanines were prepared but only in small quantities which did not suffice for crystallization from the vapor phase. The metal-free and copper phthalocyanines were obtained from Imperial Chemical Industries Ltd; the others were prepared according to Linstead.[5] All were purified by entrainer vacuum sublimation in a horizontal tube furnace. The material to be sublimed was heated to between 415–440°C. The crystals were grown in a region of the tube maintained between 320°–350°C. Purified nitrogen was used as entrainer gas, at 5 to 7 mm pressure.

Many well-developed single crystals were thus obtained, their dimensions ranging up to 3 cm length, 2 mm width, and 1 mm thickness.

A modification of the above method was also used in which a sealed and evacuated tube containing the phthalocyanine was drawn up through a temperature gradient so that the material sublimed from the hot end toward the tapered end of the tube. This method was not used to any great extent since the crystals obtained were not superior to those produced by the previous method, which also gave a greater number of

[1] D. D. Eley, Nature 162, 819 (1948); Eley, Parfitt, Perry, and Taysum, Trans. Faraday Soc. 49, 79 (1953).
[2] D. D. Eley, Trans. Faraday Soc. 51, 1529 (1955).
[3] A. S. Vartanyan, J. Phys. Chem. U.S.S.R. 20, 1065 (1946); Zhur. Fiz. Khim. 24, 1361 (1950).
[4] E.g., H. Meier, Z. Elektrochem. 58, 859 (1954).
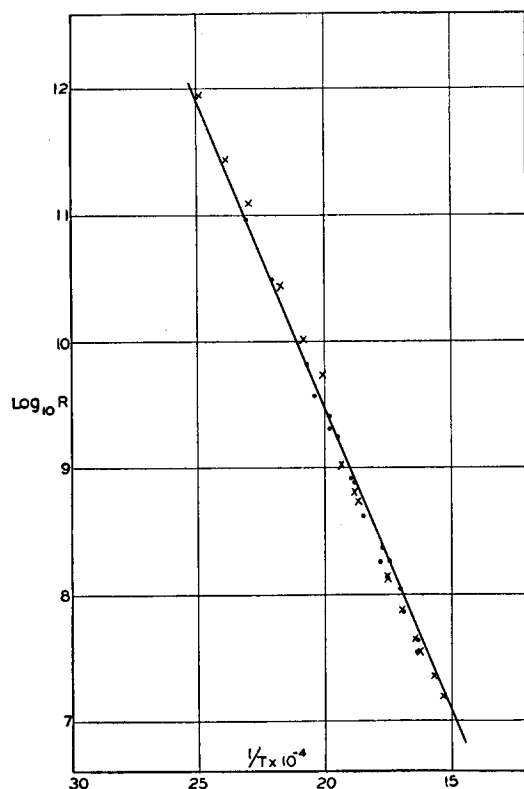[5] R. P. Linstead et al., J. Chem. Soc. 1936, 1721.

FIG. 1. Log plot of resistance R vs $1/T$ of a single crystal of metal-free phthalocyanine; field parallel to the b axis and perpendicular to the (010) face.

FIG. 2. Same as Fig. 1, but different crystal. The dots and crosses refer to two different runs at ascending temperatures.

large crystals. The electrical measurements were carried out on crystals selected for length and/or surface area of the (001) face. The crystal was first embedded in Canada balsam, prior to mounting, and sectioned with a jeweller's saw. The resin was then removed with xylene and the crystal section degreased in a Soxhlet thimble under refluxing carbon tetrachloride. The crystals were attached by means of silver paste to electrodes mounted on silica tubing and held in a jig accommodating 3 specimens. Nichrome-Constantan thermocouples were placed at a distance of 1 to 2 mm from each crystal. The jig was then placed into an electrically heated furnace mounted in a vacuum flask, and dry, oxygen-free nitrogen passed through during the measurements.

The resistance measurements were carried out by means of a "Twentymillion Megohm-Meter" (Electronic Instrument Ltd.), applying a voltage of either 85 v or 500 v dc to the sample under test. Guard rings were employed to avoid errors due to leakage currents.

The furnace was controlled from a Variac and the temperature allowed to come into equilibrium at each value so that it did not change by more than 0.5°C over a period of 15 min. Both temperature and resistance of each sample were measured at the same time. The cross-sectional area and length of some of the crystals were measured by means of a traveling micro-
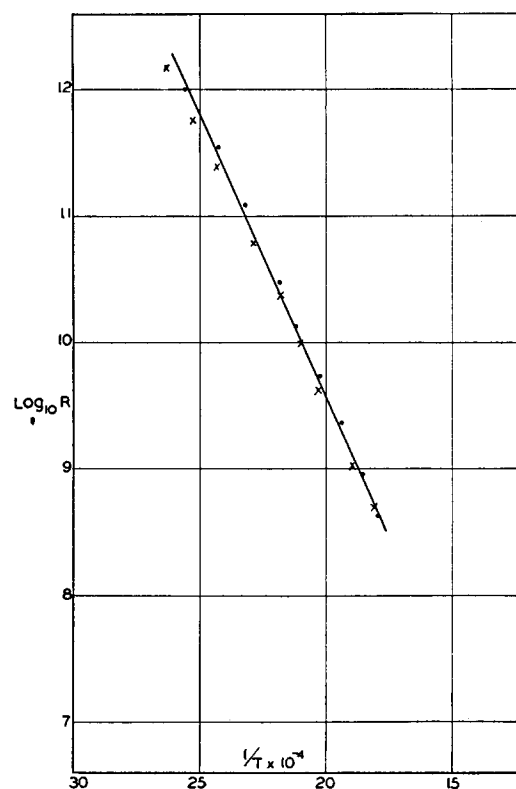
scope to permit the calculation of the absolute conductivity σ.

Thermoelectric emf's of metal-free and of copper-phthalocyanine single crystals were measured at average temperatures ranging from 70° and 130°C: two silver wires 2 mm diameter and 12 mm long were recessed, 3 mm apart, into a Teflon block and the crystal itself mounted between these wires, to which it was attached by means of silver paste. The operating temperatures as well as the temperature gradient were established by means of shielded heating wires situated at both ends of the Teflon block and heated from ac. One of the silver wire electrodes was earthed and the other connected to a Lindemann Electrometer (Cambridge Instruments Ltd.) in such a manner that the whole assembly could be mounted on a microscope stage.

The capacitance against earth of the whole apparatus was about 8 pF. The resistance of the crystals being in the order of $10^{12}\Omega$, time constants of about 50 seconds or less were thus obtained.

The electrometer was first calibrated from a known source; its deflections were observed by means of a microscope eyepice micrometer. Control blanks were run to check for any spurious thermo emf's.

The temperatures were determined by means of Nichrome-Constantan thermocouples mounted on each electrode. These thermocouples were removed during the actual measurement of the thermo emf; this ob-
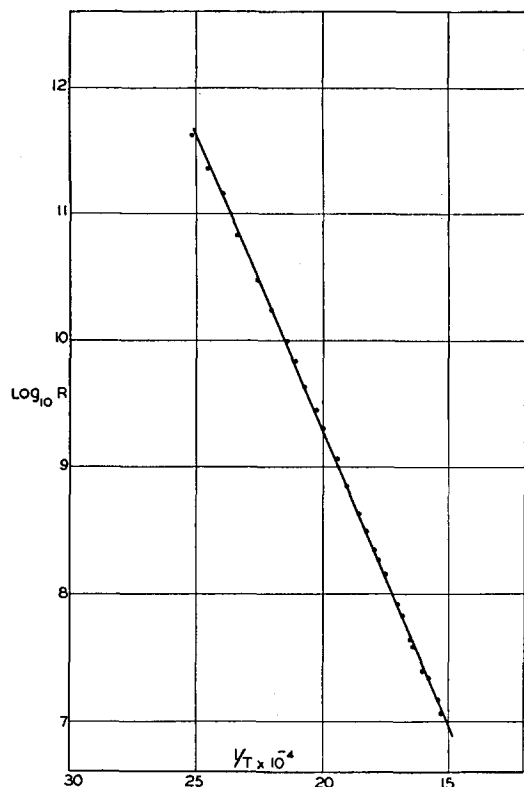
FIG. 3. Log plot of resistance R *vs* $1/T$ for a single crystal of metal free phthalocyanine, field perpendicular to the b axis, perpendicular to the (001) and parallel to the (010) face of the crystal.

FIG. 4. Log plot of resistance R *vs* $1/T$ for a single crystal of copper phthalocyanine, direction of field parallel to the b axis and perpendicular to the (010) face.

viated the need for electrical insulation of one thermocouple from the high-resistance side of the electrometer and yet maintaining good thermal contact.

Spectral transmission curves of solutions of metal-free and of metal substituted phthalocyanines were obtained with the aid of a Cary Recording Spectrometer, using α-chloronaphthalene and benzene as solvents, in order to permit comparison with the spectra obtained from evaporated films. These were prepared by vacuum evaporation onto quartz disks. Examination under a polarizing microscope showed that they were not dichroic. The film spectra at low temperatures were obtained with the normal specimen holders, but the low-temperature transmission curves were determined in a cryostat in which the disks could be cooled by liquid air; the specimens were mounted in an evacuated chamber fitted with quartz windows.

Attempts were made to measure the spectra of single crystals by grinding down a number of suitable specimens. However, most of the crystals broke up before they could be reduced sufficiently in thickness to transmit enough light for the measurements.

The photoconductivity of metal-free phthalocyanine was studied on films evaporated onto clean quartz surfaces. Graphite electrodes 15 mm long and spaced 1 mm apart were sprayed onto the films, the cell then evacuated to 10^{-6} mm Hg and sealed off. Some photo-
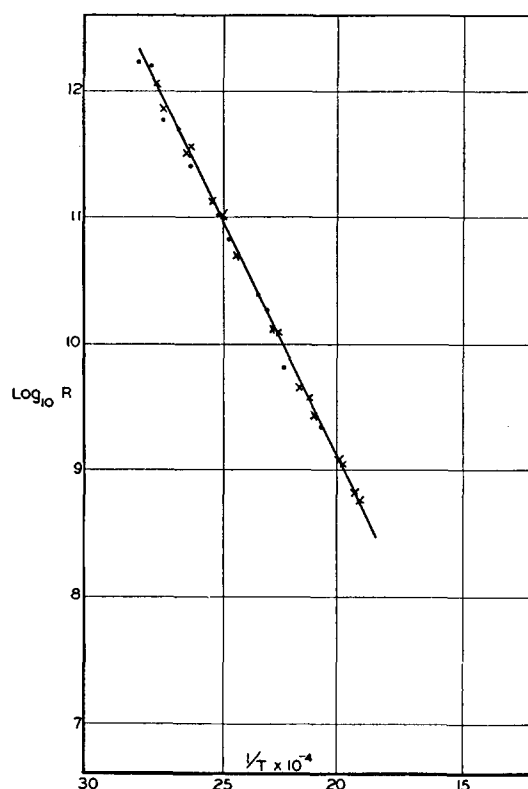
conductivity measurements were also made in the cryostat used for the low temperature spectral transmission determinations; the graphite electrodes were then first sprayed onto quartz disks upon which the phthalocyanine was subsequently evaporated. The separation of the electrodes was again 1 mm. The specimen chamber was evacuated to 10^{-3} mm Hg. The photoconductive current was measured as the potential drop across a 10^{10} ohm resistor in series with the specimen, 470 v dc being applied. For the low temperature measurements a 10^{12} ohm dropping resistor had to be used, the resistance of the films, at room temperature, being in the order of 10^{10} to 10^{11} ohm. A Baldwin-Farmer Electrometer served as indicator. The light source was an Osram High Pressure Mercury Lamp, followed by a condenser. Infrared radiation above 700 mμ was cut off by means of a filter cell 7 cm long and containing a 2.5% solution of cupric chloride. Wratten filters were employed to obtain monochromatic light and the relative energy of each band thus isolated was measured with a Perkin-Elmer thermocouple and galvanometer.

RESULTS

The validity of Ohm's law was verified for these compounds in a number of preliminary measurements; no significant departure was found for voltages up to 500 v, corresponding to fields up to 1000/cm.

TABLE I. The activation energy E [Eq. (1)] and the fit of Eq. (1) for single crystals of phthalocyanines.

No.	Compound	SPE, %	E in ev	σ_0 in Ω^{-1} cm^{-1}	Remarks
1A–B	Metal-free	19	1.73	25	Parallel to b axis and perpendicular to (010)
3A	Metal-free	15	1.93	21	Parallel to b axis and perpendicular to (010)
3B	Metal-free	4	1.63	10	Parallel to b axis and perpendicular to (010)
4A	Metal-free	20	1.78	35	Parallel to b axis and perpendicular to (010)
5/55–1, 2, 3	Metal-free	21	1.84	80	Results of 3 runs on same crystal, perpendicular to b axis and to (001)
5–2	Metal-free	34	1.88	291	Same orientation as No. 1A–B
5–3	Metal-free	25	1.86	49	Same orientation as No. 1A–B
5–54/1	Metal-free	40	1.91	299	Same orientation as No. 1A–B
7–54/1	Metal-free	63	1.98	142	Same orientation as No. 1A–B
4	Cu	12	1.63	343	Same orientation as No. 1A–B
1A	Cu	18	1.50	58	Same orientation as No. 1A–B
1B	Cu	7	1.54	⋯	Same orientation as No. 1A–B
1C	Cu	6	1.77	35	Same orientation as No. 1A–B
2A	Cu	7	1.87	⋯	Same orientation as No. 1A–B
2C	Cu	13	1.67	118	Same orientation as No. 1A–B
1A	Cu	7	1.48	⋯	Same orientation as No. 1A–B
3A	Cu	29	1.52	⋯	Same orientation as No. 1A–B
1B	Cu	10	1.38	⋯	Same orientation as No. 1A–B
7–2/55	Ni	⋯	1.68	⋯	Graphical fit
3–2/55	Ni	⋯	1.50	⋯	Graphical fit
A	Ni	7.7	1.64	⋯	Graphical fit
4	Co	12	1.63	⋯	Graphical fit
1	Co	45	1.52	⋯	Graphical fit
5	Co	27	1.69	⋯	Graphical fit
3	Co	12	1.54	⋯	Graphical fit

Weighted mean Values of E		Probable error
Metal free	1.71 ev	0.05 ev
Cu	1.64	0.03
(Ni	1.60	0.03
Co	1.60	0.025

Weighted mean Values of σ_0	
Metal free	37 Ω^{-1} cm^{-1}
Cu	135

Resistance *vs* temperature measurements were carried out on a number of single crystals of metal-free phthalocyanine with the electric field parallel to the b axis, perpendicular to the (010) face. Three crystals were examined with the field perpendicular to the b axis, the electrodes being placed upon the (001) face.

No evidence of hysteresis effects was observed upon repeated recycling of crystals of the metal-free as well as of the metal substituted compounds throughout a temperature range of 20 to 400°C. This is shown in Figs. 1 and 2 for the metal-free and in Fig. 4 for the Cu substituted compound; the readings obtained in several runs of ascending temperature are seen to fall on one single curve. These figures show plots of log$R$ *vs* $1/T$ for two different samples, the direction of current flow being parallel to the (001) face. Figure 3 shows the results obtained in a direction perpendicular to this. Good straight lines are seen to be obtained from these plots, indicating the applicability of the well-known relationship

$$\sigma = \sigma_0 e^{-E/2kT} \qquad (1)$$

for these compounds; σ being the electrical conductivity

at a temperature T. The experimental results were also subjected to least-square analyses, results whereof are shown in Table I. The statistical fit is expressed by means of a "Standard Percentage Error of Fit" (SPE), defined as

$$SPE = 100 \left[\frac{\Sigma \left(\frac{R_{calc} - R_{obs}}{R_{obs}} \right)^2}{n} \right]^{\frac{1}{2}} \qquad (2)$$

where R_{calc} and R_{obs} represent the resistance values calculated from Eq. (1) and those observed, respectively. No significant difference is found to exist between the values for E measured in the two crystallographic directions *viz.* parallel and perpendicular to the (010) face. There is no evidence for any discontinuity in the slopes of the log$R$ *vs* $1/T$ plots; thus there is no reason to assume the presence of more than one conduction mechanism. The results may be summarized by calculating the weighted mean values of E; these are also listed in Table I. The SPE's are appreciable; even in the cases where the graphical representation yields a
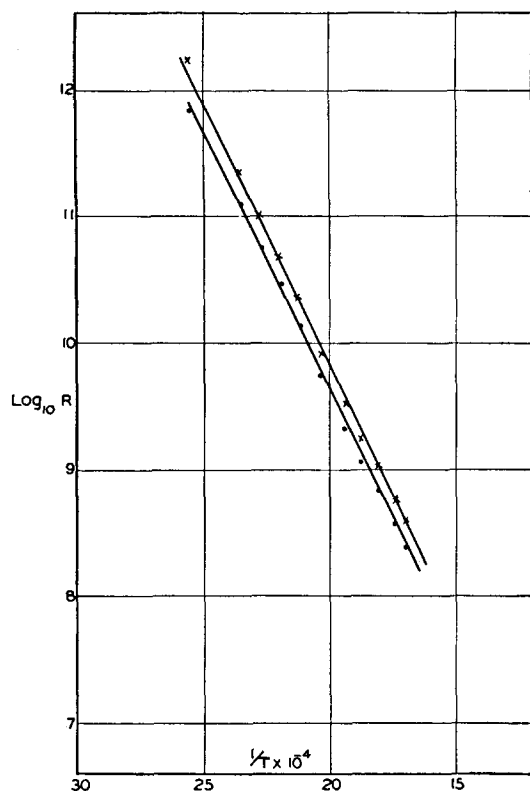
FIG. 5. Same for nickel phthalocyanine (single crystal), 2 runs (ascending temperatures).
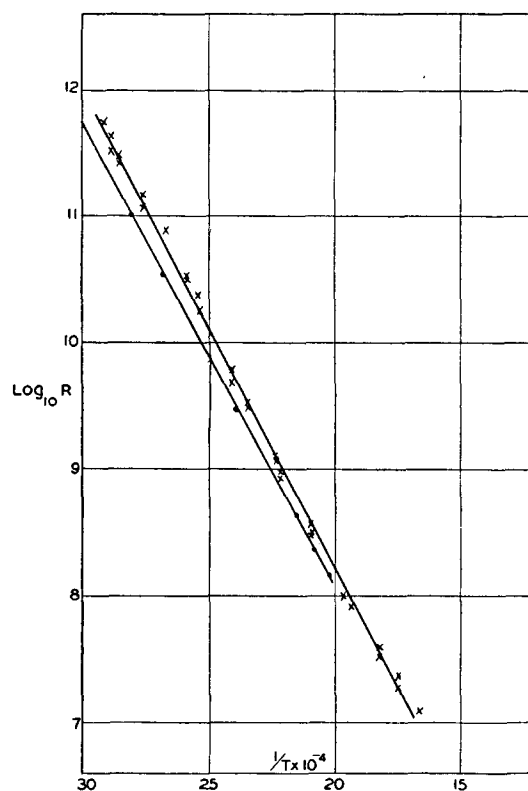

FIG. 6. Same for cobalt phthalocyanine (single crystal).

nearly perfect straight line: the curve shown in Fig. 3 has an SPE of 19%.

Values for σ_0 in Ω^{-1} cm^{-1} are also listed in Table I; this quantity has been determined only for those crystals where values are listed, due to the difficulties in measuring the small cross-sectional areas involved. Values differ rather widely; they are much lower than those to be expected for an intrinsic semiconductor, thus indicating charge carriers of rather low mobility.

However, the values of σ_0 are considerably higher than those obtained by Northrop and Simpson[6] for anthracene, naphthacene, pentacene, and perylene.

The weighted mean values of σ_0 for the metal-free and the copper phthalocyanine are also listed in Table I.

No measurements were carried out on the metal-substituted compounds with the field perpendicular to the needle axis, because these crystal faces were too small for the reliable attachment of electrodes. All data refer to measurements in a direction parallel to the needle axis.

Figure 4 shows the results obtained with single crystals of copper phthalocyanine on two runs of ascending temperatures, and similar curves for single crystals of the Ni and Co compounds are shown in Figs. 5 and 6; again for two runs at ascending temperatures.

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[6] D. C. Northrop and O. Simpson, Proc. Phys. Soc. (London) B57, 892 (1954).

The values of E obtained for the metal substituted compounds are seen (Table I) to differ but slightly from the value obtained for metal-free phthalocyanine. This is evident from the probable errors of the weighted mean values of E, also listed in Table I.

The thermoelectric emf was measured for metal-free and for copper phthalocyanine. The Seebeck coefficient was found to be +50 microvolts/°C for both compounds, the temperature gradient being applied in a direction parallel to the needle axis. The values of the coefficients did not vary significantly for temperature differences between 30 and 10°C.

While our attempts to reduce the thickness of single crystals by grinding on the whole were unsuccessful, one crystal could be thinned down sufficiently to permit at least an approximate measurement of its spectral transmission. This showed a strong absorption in the vicinity of 600 mμ. No evidence of dichroism could be found on examination of this crystal under the polarizing microscope. It is thus likely that the spectral transmission curves obtained from thin, evaporated films would more nearly approximate those which might have been obtained from single crystals, than could be expected from solution spectra. However, the spectral transmissions were determined for the metal free, copper, nickel, and cobalt phthalocyanines, dissolved in α-chloronaphthalene, Figs. 7, 8, 9, 10; Fig. 11 shows the solution spectrum of the metal-free compound
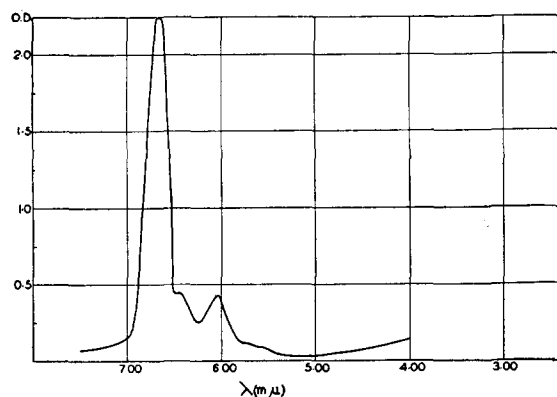
FIG. 7. Solution spectrum of nickel phthalocyanine dissolved in α-chloronaphthalene.

dissolved in benzene. In these figures absorption is plotted as optical density. The main absorption lines are in good agreement with those reported by Anderson, Bradbrook, Cook, and Linstead.[7] The solution spectra are shown mainly for the purpose of permitting comparison with those obtained from thin evaporated films.

Figures 12, 13, 14, and 15 show such transmission spectra of thin evaporated films of metal-free, nickel, cobalt, and copper phthalocyanine at room temperatures; absorption is again plotted as optical density. We cannot report absolute values of absorption coefficients; the absorption was very intense, requiring the use of very thin films. Two main absorption maxima are evident in the visible region: one at an energy of 1.8 ev and the other at 2.0 ev. These are seen to correspond with the absorption maxima observed in solution, although the intensities are altered. The 1.8 ev transition is in excellent agreement with a doubly degenerate $B_{1u}-E_g$ transition theoretically predicted by Basu[8] at a wave number of 14 720 cm^{-1} i.e., 1.82 ev. The double maximum appearing in the solution spectra of the metal-free compound near 680 mμ is replaced by a single rather indistinct maximum, which is more
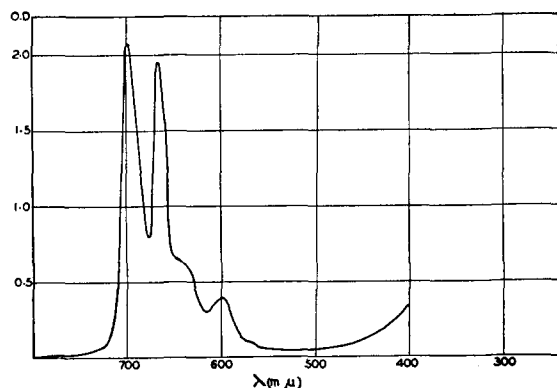

FIG. 8. Same for metal-free phthalocyanine.

[7] Anderson, Bradbrook, Cook, and Linstead, J. Chem. Soc. 1938, 1151.
[8] S. Basu, Indian J. Phys. 37, 511 (1954).

pronounced in the metal substituted compounds; however, only a single maximum appears in the solution spectra of the metal substituted phthalocyanines. It is seen that the general character of the spectra does not alter; there is comparatively little difference in the spectra of the different phthalocyanines which we studied. It can thus be concluded that the metal atom has rather little effect on the energy levels of the compounds within the region of, say, 300 to 800 mμ, this agrees also with our findings on the thermal activation energies of electrical conductivity. Low temperature
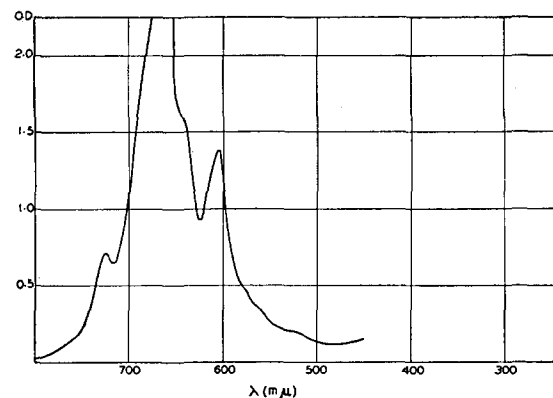

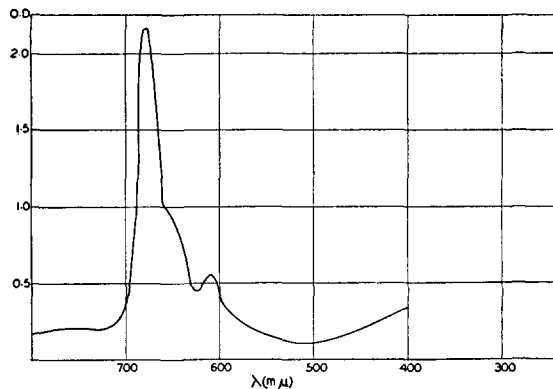FIG. 9. Solution spectrum of cobalt phthalocyanine dissolved in α-chloronaphthalene.

FIG. 10. Same for copper phthalocyanine.

spectra of thin evaporated films are shown in Figs. 16 and 17, at higher resolution, together with the spectra obtained at room temperatures; Fig. 16 referring to the nickel and Fig. 17 to the metal-free compound. While the absorption maximum for nickel phthalocyanine was found to shift slightly with temperature, changing from 6680 A (1.867 ev) at 19°C to 6720 A (1.856 ev) at −180°C, we do not consider this shift as significant. It is quite likely due to a sharpening of the band, which is rather broad at room temperatures. The thickness of the films was in the region of 200 millimicrons.

The photoconductivity of several films of metal-free phthalocyanine was studied at room temperatures. No polarization phenomena or time lags were observed,

apart from the unavoidable capacitive time constant of the whole apparatus. The relative response for light of 20 mμ band with at 3 different wavelength is given in Table II, referred to a constant energy level of the incident light. Measurements were also made at liquid air temperatures, using films evaporated onto quartz blanks and mounted in a cryostat, as well as on films in sealed-off cells. These latter results were, however, only qualititative since noise due to the electrodes interfered with the electrometer readings.
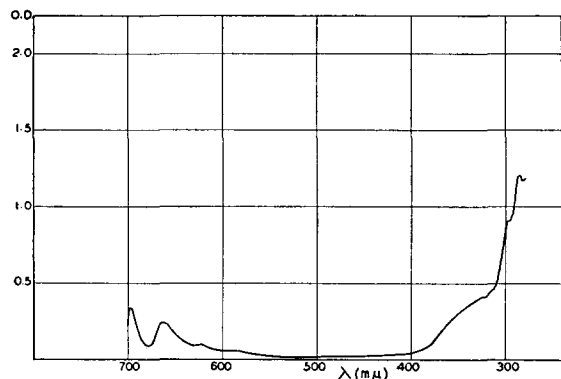
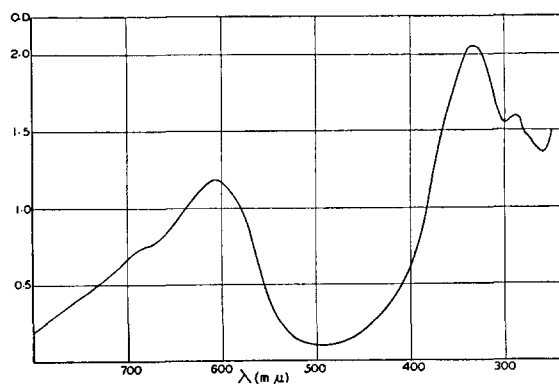FIG. 11. Solution spectrum of metal-free phthalocyanine dissolved in benzene.

FIG. 12. Transmission spectrum of thin evaporated film of metal-free phthalocyanine, at 19°C.

DISCUSSION

Eley,[1] working with compressed powders, reports values for $2E$ [in our notation, Eq. (1)] varying between 16 and 20 kcal/mole, i.e., between 0.7 to 0.87 ev below 310°C and values of 20 to 29 kcal/mole, i.e., 0.87 to 1.26 ev above this temperature for the metal-free compound in powder form; this author also finds Ohm's law to hold only within 5%. As mentioned before, we could not find any evidence of departures from Ohm's law on several single crystals studied, any such departure, if present, being certainly below 1%. We also could not confirm any change in the activation energy between room temperature and 400°C, as may be seen from Figs. 1 and 3. The single crystal measurements
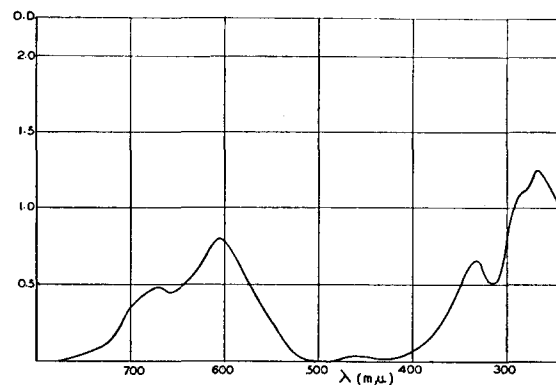
FIG. 13. Same for nickel phthalocyanine.

proved to be quite reproducible throughout the whole temperature range studied.

No hysteresis effects, as found by Eley, were observed in the resistance of copper phthalocyanine single crystals.

We believe that these discrepancies are caused by the fact that Eley worked with polycrystalline specimens, while we studied single crystals.

In a more recent paper, Eley[2] reports a value of 1.5 ev for polycrystalline phthalocyanine and also finds that the transition previously observed at 250°C now takes place at 150°C. His best sample analysis contains a total of approximately 1.7% of impurities, whereas a spectroscopic analysis of our single crystals yields a total impurity content of only 0.02% for metal-free phthalocyanine and 0.1% for nickel phthalocyanine; the results of these analyses are given in Table III.

Phthalocyanine exists in 3 forms,[9] α, β, γ; the α and γ forms are low temperature modifications, while the β form is stable at temperatures above 200°C. Comparing x-ray diffraction patterns obtained from our single crystals with those given by Karasek and Decius,[9] we find that these are identical with the patterns given by these authors for the beta modification. It thus would seem that our results refer to this.
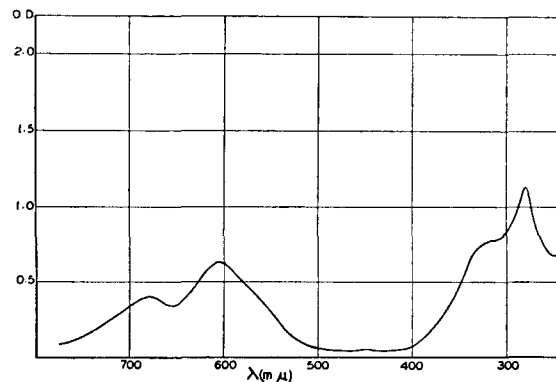
FIG. 14. Same for cobalt phthalocyanine.

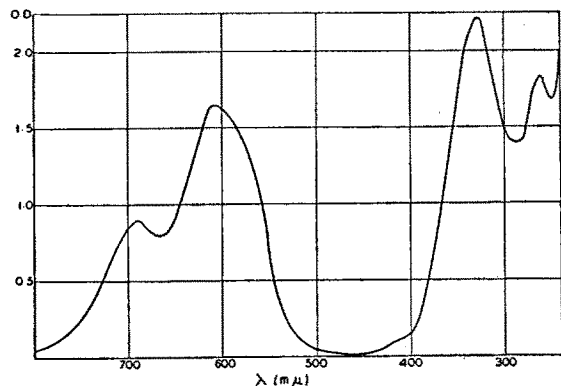[9] F. W. Karasek and J. C. Decius, J. Am. Chem. Soc. 74, 4716 (1952).

FIG. 15. Same for copper phthalocyanine.

Eley associated the activation energies which he observed, with the absorption maxima appearing at 40.4 kcal/mole i.e., 1.75 ev in solution spectra. This lowering in E he attributed to an appreciable interaction between the II electron shells of adjacent molecules. Some doubt was cast upon this by Lions et al.,[10] who pointed out that in the case of anthracene the measured activation energy of 38.03 kcal/mole, i.e., 1.65 ev, corresponded to a singlet-triplet transition at 14 700 cm^{-1}, i.e., at 1.82 ev. Recent work by Davydov[11] and by Craig[12] has shown that such interaction in a molecular crystal would be unlikely to cause such a first-order effect as Eley attributes to a II-electron overlap. Such interactions are responsible for splitting of absorption lines, part of the absorption being shifted, resulting in different intensities. Moreover, the absence of any evidence of phosphorescence up to 9000 A[13] in the metal-free and Mg and Zn substituted phthalocyanine also indicates that single-triplet transitions do not take place in these compounds.

Basu[8] calculated that the extreme values of the II-electron density occur in the vicinity of the nitrogen
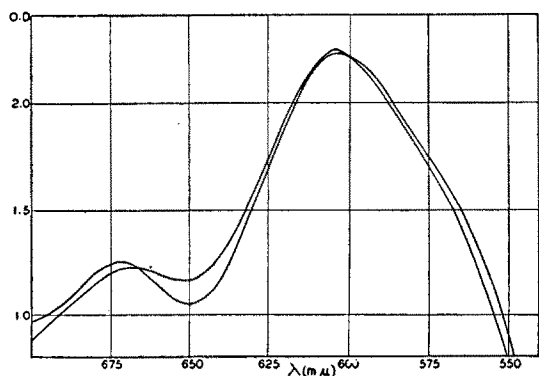

FIG. 16. Same for nickel phthalocyanine at 19°C and at −180°C.

[10] L. E. Lyons et al., Nature 173, 736 (1954).
[11] A. S. Davydov, Izvest. Akad. Nauk. S.S.S.R. Ser. Fiz. 15, 605 (1951).
[12] D. P. Craig and P. C. Hobbins, J. Chem. Soc. 1955, 539.
[13] R. S. Becker and M. Kasha, J. Am. Chem. Soc. 77, 3670 (1955).

atoms, in the central part of the molecule. This would tend to enhance the probability of a II-electron overlap from molecule to molecule. In fact, the first electronic transition is probably due to II electrons and it is this transition which is of importance for the purposes of this paper.

Vartanyan[3] reports a value for $2E$ (in our notation, Eq. (1) of 10.4 kcal/mole, i.e., 0.45 ev, working with powdered films rubbed onto quartz surfaces; this value is even lower than Eley's. This is likely to be caused by large concentrations of crystal imperfections introduced by the rubbing process.

A conduction mechanism involving tunneling of electrons through nontransparent intermolecular bar-
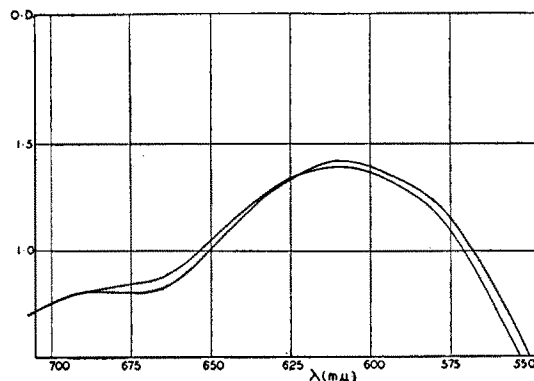

FIG. 17. Same for metal-free phthalocyanine at 19°C and at −180°C.

TABLE II. Photoconductive relative response of thin evaporated films of metal free phthalocyanine, at 20°C.

In mμ	Relative response
450	0.5
610	1.3
620	2.1

riers has been envisaged by Many, Harnik, and Gerlich,[14] also involving II electrons. Such a mechanism would require that activation energy and mobility are roughly proportional. Employing the authors' method for the estimation of the order of magnitude of mobility we find from our measurements values in the order of 10^{-10} cm^2/volt-sec, which would correspond, again from these authors' tables, to an activation energy of the order of 0.5 ev, which contrasts with the values of about 1.7 ev which we obtained experimentally.

Furthermore, taking $N_0 \simeq 10^{21}$, as assumed by these authors,[14] we obtain a value for the concentration of charge carriers in the order of 10^8 at $T = 373°K$. If n were that high one would expect a thermoelectric power in the order of 10^3 μv/°C, using the method given by Lark-Horovitz[15] and J. Tauc[16] for such calculations. However, we find a value of 50 μv/°C.

[14] Many, Harnik, and Gerlich, J. Chem. Phys. 23, 1733 (1955).
[15] K. Lark Horovitz, Phys. Rev. 92, 226 (1953).
[16] J. Tauc, Czechslov. J. Phys. 3, 282 (1952).

TABLE III. Comparison of spectroscopic analyses of single crystals with analyses given by Eley.[a]

	Fe	Cu	Mn	Mg	Si	Co	Ag	Ni	Al	Pb	Bi	Sn	Ti	Co
Eley (metal-free)	···	0.1–0.01	1–0.1	1–0.1	1–0.1	···	···	···	···	0.01–0.001	0.1–0.01	0.1–0.01	···	···
F and G metal-free	≤0.01	≤0.02	0.002	≤0.002	≤0.002	0.002	0.001	0.0007	≤0.0004	···	···	···	···	···
F and G (Ni)	0.02	≤0.0007	0.0002	≤0.001	≤0.01	0.02	0.0004		≤0.01	0.002	0.005	···	≤0.002	≤0.03

[a] See reference 2.

The similarity between the spectral transmission curves in the solid state and in solution, and the agreement found between the thermal and optical activation energies for metal-free as well as for metal substituted phthalocyanines suggests that the primary conduction process involves the production of a metastable excited state, rather independent of the influence of the metal atom. The difference in the relative intensities of the absorption maxima occurring at about 680 and 600 mμ could be explained by a displacement to another part of the spectral region of the 680 mμ maximum, on going from the solution to the solid state; this assumption is supported by the fact that a similar effect is known to take place in anthracene.[17]

While the photoconductivity of phthalocyanine has been studied at 3 wavelengths only, there is evidence for a peak in the vicinity of 620 mμ, similar to the absorption peak observed in the transmission spectrum in this region; the photoconductive response thus seems to run parallel to the optical spectrum, as has been found by Carswell[18] for anthracene. This lends further support to the hypothesis of a metastable excited state.

Davydov[11] has shown that, given such an excited state, the energy migrates in the form of excitons; and in phthalocyanine, particularly at higher temperatures, their number may become quite appreciable. However, the production of excitons does not result in a charge transfer, so that the actual mechanism of electrical conductivity must involve another, secondary, process: it is suggested that the conduction depends on the presence of surface states, crystal imperfections and dislocations. Bree and Lyons[17] as well as Chynoweth and Schneider[19] report that the photoconductivity depends markedly on the surrounding atmosphere, and the remarkably low activation energy found by Vartanyan[3] for rubbed on films of phthalocyanine support our contention; the rubbing process must needs introduce a high concentration of crystal imperfections. This would also explain the considerably lower values for E found by Eley in the polycrystalline form; such specimens are certain to contain a far higher concentration of surface states and crystal imperfections than single crystals.

The excitons thus are thermally dissociated in the vicinity of such defects, the electron is trapped and the hold left free to migrate. Such a hole would have a rather short mean free path, again in agreement with the conclusion of Chynoweth and Schneider[19] from a study of the photoconductivity of anthracene.

Localized phonon-phonon interaction thus creates excitons. These are not thermally dissociated into free charge carriers, otherwise the activation energy would correspond to an ionization energy; rather, as Seitz[20] has discussed, the exciton is trapped at a defect and then thermally dissociated. Since the crystals were grown under conditions of high vapor saturation at a relatively high temperature it is likely that a large concentration of traps, such as we envisage, would be created in the form of Schottky and Frenkel type thermal imperfections.

This hypothesis also explains our findings, from thermoelectric measurements, that the majority carriers are holes; it also agrees with the small value of σ_0 which we found.

The metal atoms are unlikely to greatly alter the trapping, since they are quite firmly bound and placed in the center of the molecular plane; they are probably bonded through the metal d-s-p-orbitals and the σ orbitals of the nitrogen atoms, 37, 38, 39, and 40 (in Basu's notation[8]), thus leaving the II electrons unaffected.

The spectroscopic analyses given in Table III shows that the impurity concentration in the single crystals of Ni phthalocyanine totalled about 0.1%, compared to 0.01% for the metal free compound. As the impurity level is reduced the transition temperature from impurity to intrinsic conduction is also lowered; this would explain the low values of E which we observed in the metal substituted compounds.

[17] A. Bree and L. E. Lyons (private communication, 1955).
[18] D. Carswell, J. Chem. Phys. 21, 1890 (1953).
[19] A. G. Chynoweth and W. G. Schneider, J. Chem. Phys. 22, 1021 (1954).
[20] F. Seitz, Imperfections in Nearly Perfect Crystals (John Wiley and Sons, Inc., New York, 1952).