

Charge Transport in Copper Phthalocyanine Single Crystals

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The conductivity and Hall mobility in single crystals of the organic semiconductor, copper phthalocyanine, were investigated over the temperature range 300–425°K, using a new differential electrometer scheme. A two-carrier Hall mobility of the order of $-75 \text{ cm}^2/\text{V-sec}$ was found at 300°K which decreased with increasing temperature. Conductivity studies as a function of various gaseous ambients indicated that oxygen was an electrically active impurity. It was impossible to determine whether it gave rise to a donor level 0.4 eV above the valence band or an acceptor level 1.6 eV above the valence band. In one sample the Hall mobility changed sign from negative to positive for temperatures above 100°C. This was approximately the same temperature at which the activation energy for conductivity changed from 1.6 to 2 eV. From these data assuming a donor model for the oxygen impurity the ratio of electron to hole mobility was found to be 0.67 at 373°K. Assuming that the temperature dependences of the hole and electron mobility were the same, and that the effective densities of states for electrons and holes were equal, the individual hole and electron mobilities were calculated as a function of temperature. The applicability of a band model to this material was suggested by the fact that the carrier mobility decreased with increasing temperature. The greater mobility of carriers in copper phthalocyanine crystals as compared to the $0.1 \text{ cm}^2/\text{V-sec}$ mobility in metal-free phthalocyanine crystals can be attributed to the mixing of the copper $3d$ orbital with the π orbital system of the phthalocyanine molecule. The copper $3d$ orbital also provides an out-of-plane interaction with an antibonding orbital of a nitrogen atom in molecules above and below it. Since this interaction takes place at a distance of nearest approach of adjacent molecules, charge transport is facilitated.

I. INTRODUCTION

THE understanding of the transport properties of molecular crystals has been severely limited by a lack of galvanomagnetic experiments on such crystals. This is due to the fact that these materials generally behave like insulators having resistivities ranging from $10^{13} \Omega\text{-cm}$ to $10^{19} \Omega\text{-cm}$ at 300°K and, as a consequence, the desired experiments become extremely difficult to instrument. A successful Hall effect experiment has been performed on metal-free phthalocyanine single crystals at 300°K, by integrating the Hall signal out of the noise¹ which emphasizes the difficulties involved in such measurements.

This paper describes the measurement of the Hall effect in copper phthalocyanine single crystals, and attempts to elucidate the nature of charge transport in this material. Copper phthalocyanine is a base-centered monoclinic molecular crystal with two molecules per unit cell possessing semiconductor properties (see Fig. 1). The copper phthalocyanine molecule is shown in Fig. 2. It is structurally similar to the biologically important molecules, chlorophyll and haemoglobin. It differs from the so-called metal-free variety in that a

divalent metal is substituted for two central hydrogen atoms.

II. EXPERIMENTAL TECHNIQUES

The copper phthalocyanine crystals used in these experiments were grown by sublimation techniques based on modifications of Linstead's methods.² The starting material was DuPont pigment grade phthalocyanine which was twice sublimed to improve the purity. An analysis of the crystals yielded the following metallic impurities in parts per million: Fe, 3–30; Si, 0.1–1; Mg, 3–30; and Al, 1. Typical dimensions of the crystals as grown were: length, 2 cm; width, 3 mm; and thickness, 0.2 mm. The crystals were extremely brittle and virtually impossible to work mechanically.

The sample was mounted on a carefully cleaned quartz substrate which was enclosed in a circular copper holder with a thermocouple. An electrical heater was wound on the outside of the sample holder, and the entire apparatus was mounted between the pole pieces of a Varian V2200-A magnet. The magnet pole pieces also served to thermally stabilize the sample. At least three hours were allowed between temperature changes to insure complete thermal equilibrium and minimize drift before measurements were attempted. In addition to the shielding provided by the copper sample holder, Amphenol Nos. 21–537 low-noise cable was used to make all connections to further minimize stray effects.

Hall measurements of insulators have always been extremely difficult due to the aforementioned problems of drift and noise. The effects of these quantities on the measurements were greatly reduced by the use of a differential measurement technique. The circuit is

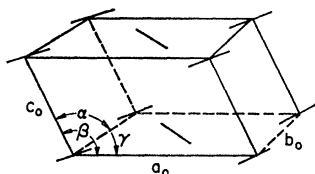


FIG. 1. Positions of the copper phthalocyanine molecules in the monoclinic crystal.

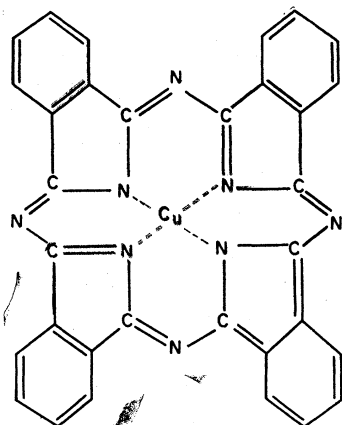
$$\begin{aligned} \alpha &= \gamma = 90^\circ \\ \beta &= 120^\circ 36' \end{aligned}$$

$$\begin{aligned} a_0 &= 19.6 \text{ \AA} \\ b_0 &= 4.79 \text{ \AA} \\ c_0 &= 14.6 \text{ \AA} \end{aligned}$$

¹ G. H. Heilmeier, G. Warfield, and S. E. Harrison, *Phys. Rev. Letters* **8**, 309 (1962).

² R. P. Linstead, P. A. Barrett, and C. E. Dent, *J. Chem. Soc.* **1936**, 1719.

FIG. 2. Structure of the copper phthalocyanine molecule.



shown schematically in Fig. 3. In this scheme the Hall voltage is fed directly to the grids of the electrometer tubes. Since the capacitively coupled drift and noise are fed in phase to the differential electrometer input, they are effectively cancelled in the output. This scheme presents some improvement over single-ended detectors in the measurement of high-resistivity materials. An additional advantage of this differential electrometer method is that in the region where the probe input resistance is much greater than the sample resistance, the main dc supply need not be floated, which also improves the stability and reliability of the measurements. The disadvantage of such a connection is that one-half of the applied sample voltage appears across the grids of the input tubes. This limits the magnitude of the applied voltage in our present system resulting in a limiting mobility sensitivity of

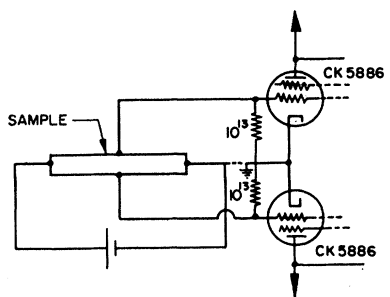
$$\mu_H \min = V_H \min l / B_{\max} V_A \max w \approx 9 \text{ cm}^2/\text{Vsec},$$

where $V_H \min$ = minimum detectable Hall voltage = 0.15 mV, l/w = crystal length to width ratio = 7.5, B_{\max} = maximum magnetic field available = 6.5 kG and $V_A \max$ = maximum permissible applied voltage = 2V. Thus, one is forced to sacrifice sensitivity for stability. The differential measurement technique was checked by measurements on some high-resistivity gallium arsenide crystals whose Hall effect had been measured previously by conventional single-ended methods.³

The care necessary to insure that a true measurement of the Hall effect is obtained cannot be overemphasized. All electrical connectors and sample supports were insulated with degreased Teflon. It was found necessary to select such components for low leakage (i.e., $R \gg 5 \times 10^{14} \Omega$ at 400°K) at all temperatures of interest by measurement of their resistance as a function of temperature. In cases where this was not done, mobilities of the order of a few hundred $\text{cm}^2/\text{V sec}$ were found at temperatures above 400°K. This result was traced to the formation of an effective bridge circuit by the sample

³R. H. Bube and H. E. MacDonald, Phys. Rev. **128**, 2062 (1962).

FIG. 3. Schematic of the differential electrometer Hall effect apparatus.



and associated leakage paths, which became unbalanced evidently due to the sample magnetoresistance. All thermomagnetic effects, except the Ettingshausen effect, were eliminated by reversal of the sample current and applied magnetic field. Thus, the data presented were not corrected for all thermomagnetic effects, but for the sake of simplicity, the subsequent interpretation of the data ignores the Ettingshausen contribution to the Hall voltage.

The contacts to the crystal were made using an air-dried silver paste. This material is known to make Ohmic contact to metal-free phthalocyanine crystals.⁴ Linear I - V characteristics were observed at fields below 10^4 V/cm in copper phthalocyanine crystals, however, this in itself is not sufficient to insure that a contact is Ohmic. Indeed, any exponential dependence of current on voltage will yield "Ohmic" behavior at sufficiently low fields. The field distribution along the b axis of a copper phthalocyanine crystal at a temperature of 135°K is shown in Fig. 4. These probe measurements were made at higher temperatures, using a Cary electrometer to insure that the probe resistance was orders of magnitude higher than that of the sample at all points. These data show that the field distribution along the sample was approximately linear, indicating that the electrodes were indeed either Ohmic or neutral. In electroding the samples, extreme care was taken to align the Hall probes in order to minimize unbalance potentials.

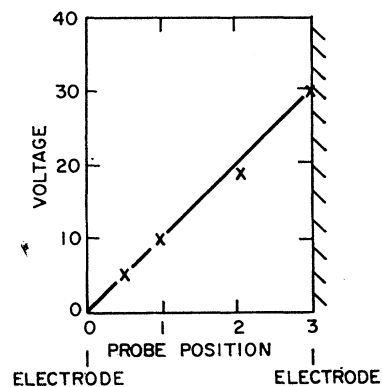


FIG. 4. Field distribution along the b axis of a copper phthalocyanine crystal with silver paste electrodes.

⁴G. H. Heilmeyer and G. Warfield, J. Chem. Phys. **38**, 163 (1963).

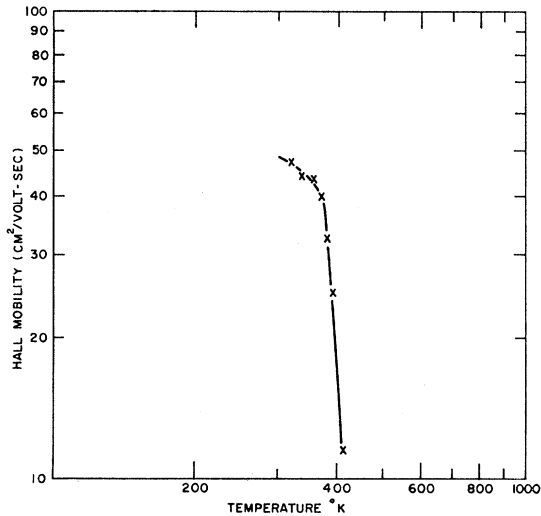


FIG. 5. Hall mobility versus temperature (°K)—sample No. 5.

III. EXPERIMENTAL RESULTS

The measurements were performed on four different crystals over the temperature range 25–150°C. Reliable measurements could not be made at higher temperatures in our apparatus although such measurements have been reported.⁵ The results differed slightly from crystal to crystal, but some general agreement was obtained in certain important aspects. The measurements below approximately 50°C were made using the differential measurement technique with the dc source *floating*. In this temperature range, the measured Hall voltage was corrected for the loading of the sample by the detector in a linear manner. No correction for this effect was necessary above 50°C because the detector input resistance was much greater than that of the sample at the Hall probes. In this case the applied dc source was grounded to the cathodes of the differential electrometer input. All measurements were made with a magnetic field of 6.5 kG. Since higher fields were not available, the variation of the Hall voltage with magnetic field strength could not be measured.

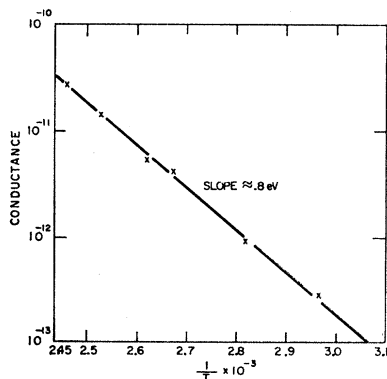


FIG. 6. Conductance versus reciprocal temperature (°K⁻¹)—Hall sample No. 5.

⁵ G. Delacote and M. Schott, Phys. Stat. Solidi 2, 1460 (1962).

A typical result is shown in Fig. 5. The Hall mobility, calculated from the expression

$$\mu_H = V_H l / B V_A W \quad (1)$$

was found to be of the order of 70 cm²/V sec at 300°K. It decreased rapidly with temperature, becoming unmeasurable in our present apparatus below approximately 425°K. In most cases the sign of the Hall coefficient was negative. The temperature dependence of the sample conductivity is shown in Fig. 6. From the slope of this curve, an activation energy of approximately 1.62 eV is found. This approximate value has been found by a number of workers^{5,6} and has been interpreted as being the intrinsic band gap of the material. Some extremely interesting effects were observed in one sample which tended to contradict this hypothesis. The Hall mobility versus temperature of sample No. 4 is shown in Fig. 7. The mobility is seen to decrease

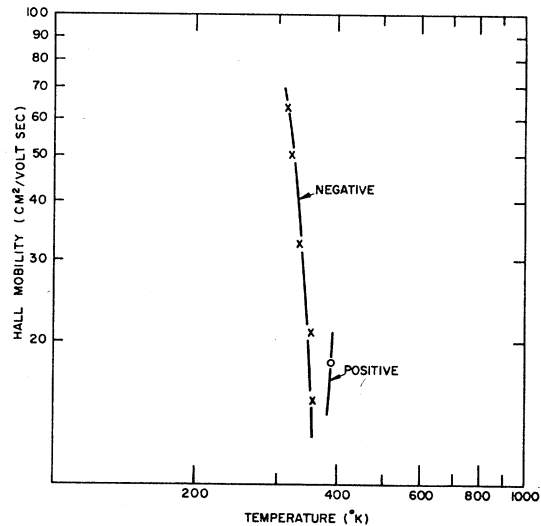


FIG. 7. Hall mobility versus temperature (°K)—sample No. 4.

rapidly with temperature from 300 to 370°K. In this region the sign of the Hall effect was negative. However, above this temperature range the sign of the effect became positive. Corresponding to the change in sign of the Hall effect with temperature, a discontinuity in the slope of the sample conductance was observed as shown in Fig. 8. In the region of the negative Hall constant, the slope of the conductance versus $1/T$ curve indicates an activation energy of approximately 1.66 eV, while above the transition temperature the slope indicated an activation energy of approximately 2 eV. In further experiments on crystals from the same batch, the conductance versus temperature was measured along the c' axis of the crystal using silver paste guard ring electrodes to eliminate surface currents.⁴ These measurements were made as a function of various gaseous ambients over the temperature range 25 to 200°C. The data are shown in

⁶ P. E. Fielding and F. Gutmann, J. Chem. Phys. 26, 411 (1957).

Fig. 9. The discontinuity in activation energy was found in the measurements in air and vacuum. No discontinuity was found in the oxygen ambient, and the slope indicated an activation energy of approximately 1.62 eV. In contrast to this, measurements in a hydrogen atmosphere yielded an activation energy of approximately 2 eV over the range of the measurements. The measurements in all four ambients were repeated several times on the same crystal and were made as a function of both increasing and decreasing temperatures. These data are summarized in Table I.

IV. DISCUSSION OF RESULTS

The observation of a change in sign of the Hall constant as a function of temperature together with the change in activation energy indicates that two carrier effects are playing an important role in the conduction process of our crystals. One also concludes that the previous interpretation that 1.7 ± 0.05 eV represented the intrinsic gap of copper phthalocyanine^{5,6} is incorrect. Our work on the temperature dependence of conductivity as a function of ambient seems to indicate that oxygen absorbed by the crystal is responsible for the

TABLE I. Activation energy as a function of ambient.

Ambient	Slope above 373°K (eV)	Slope below 373°K (eV)
Vacuum	1.03	0.81
Air	1.02	0.72
Oxygen	0.81	0.81
Hydrogen	1.07	1.07

activation energy of 1.7 ± 0.05 eV. This is supported by the fact that hydrogen was able to remove the discontinuity in the activation energy yielding a value of 2 eV, while the oxygen ambient yielded the lower value of approximately 1.62 eV over the entire temperature range. It is not certain at this time just how the oxygen is incorporated into the lattice. Nevertheless, it can be concluded that the oxygen does not merely produce a surface effect since the conductivity measurements were performed using guard ring electrodes. In addition, the experimental evidence strongly suggests that hydrogen is effective in reducing the electrical activity of this lattice oxygen.

There are several schemes of energy levels which could be used to explain our results. Two of the simplest, one involving a donor and the other an acceptor, will be presented in this paper. Noting that the Hall mobility is negative for temperatures less than 375°K the first model assumes that the extrinsic semiconductor is n type. The change in sign of the Hall mobility at higher temperature implies for this model that the hole mobility is greater than the electron mobility. This difference in

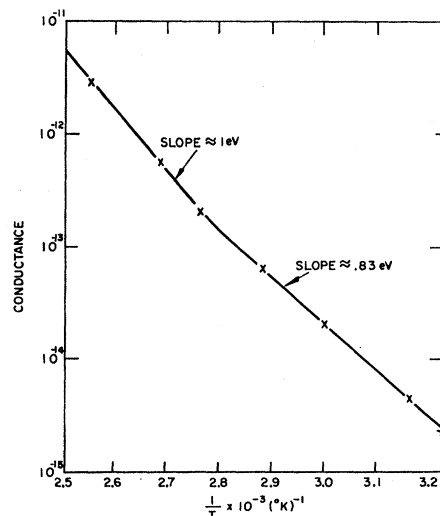


FIG. 8. Conductance versus reciprocal temperature ($^{\circ}\text{K}^{-1}$)—Hall sample No. 4.

the mobility of the two types of carriers has also been suggested by the experiments of Terenin *et al.*⁷ on copper phthalocyanine films. According to this model the density of electrons in the extrinsic region is given by

$$n = (N_D N_C)^{1/2} e^{-E_D/2kT}, \quad (2)$$

where E_D = donor energy, N_D = donor density, and N_C = effective state density. In order to fit our experi-

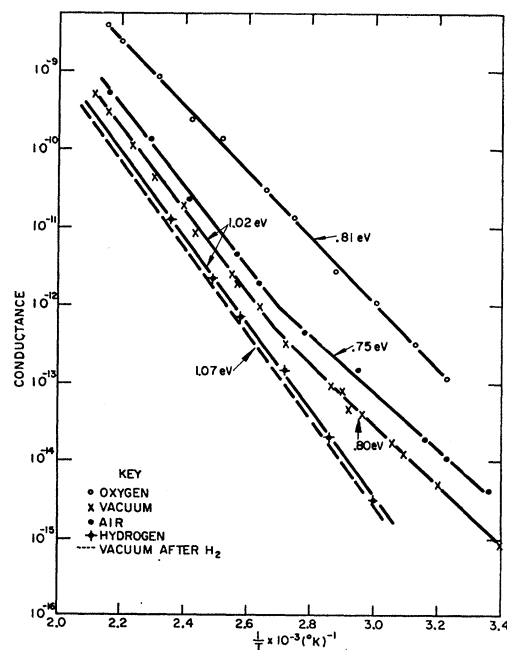


FIG. 9. Conductance versus reciprocal temperature ($^{\circ}\text{K}^{-1}$) for various ambients.

⁷ A. Terenin, E. Putzeiko, and J. Akimov, *Discussions Faraday Soc.* **27** (1959).

mental data, it is required that the donor level be situated at 1.6 eV below the conduction state. For highly compensated donors, the electron density is given by

$$n = [(N_D - N_A)N_C/N_A]e^{-E_D/kT}, \quad (3)$$

where N_A is the density of acceptors and E_D is 0.8 eV below the conduction state. If it is further assumed that the high-temperature activation energy is the intrinsic value, the ratio of the donor density to the effective state density can be computed for the case of no compensation. Equating the electron density for high- and low-temperature Fermi levels at the experimentally determined temperature at which the slope discontinuity in the conductivity activation energy occurred in sample No. 4 (approximately 100°C), one obtains

$$N_C e^{-E_D/2kT_1} = (N_C N_D)^{1/2} e^{-E_D/2kT_1} \quad (4)$$

and

$$N_C/N_D \approx 10^5.$$

Thus, the ratio of the effective density of states to the donor density in this crystal was approximately 10^5 . It is interesting to note that if this ratio were 10^4 , the transition in the activation energy would occur at approximately 250°C. This possibly accounts for the fact that the transition was observed in only one of our Hall samples, since it was not possible to make reliable Hall measurements above 150°C in any of the samples.

The decrease in Hall mobility with temperature would seem to indicate the applicability of the band model to a particular semiconductor if only one sign of carrier were important. However, the strong temperature dependence of this mobility of our samples does not seem to be characteristic of the well-known lattice and impurity scattering mechanisms found in inorganic semiconductors. This evidence together with the activation energy studies seem to indicate that we are dealing with a two-carrier system. The Hall mobility in such a system is given by

$$\mu_H = [(p\mu_p^2 - n\mu_n^2)/(p\mu_p + n\mu_n)]k, \quad (5)$$

where n = density of free electrons, p = density of free holes, μ_n = electron mobility, μ_p = hole mobility, and k = constant characteristic of the scattering processes which we assume ≈ 1 .

The Hall effect data from sample No. 4 indicated that a reversal of sign took place at approximately 100°C. At this temperature the Hall mobility approaches zero. Using the model of a donor level at approximately 0.4 eV above the valence band with $N_c/N_d \approx 10^5$, one can solve Eq. (5) for the ratio of the electron mobility to hole mobility at 100°C. Thus,

$$\frac{\mu_n^2}{\mu_p^2} = \frac{p}{n} = \frac{N_c e^{-E_f/kT}}{N_c e^{-E_c + E_f/kT}} \Big|_{T=373^\circ\text{K}}$$

The model of a donor level at 0.4 eV above the ground

TABLE II. Calculated electron mobility for donor model.*

T (°K)	β	μ_H (exp)	μ_n (calc)	μ_p (calc)
300	-1.17	-75 cm ² /V sec	88 cm ² /V sec	131 cm ² /V sec
322.5	-1.58	-52	82.3	122
337	-2.5	-31	77.5	116
357	-4.25	-16	68	101.5
381	+3.26
396	+1.46	+18	26.2	39

* $\mu_n = \mu_H(p/b + n)/(p/b^2 - n) = \beta\mu_H$, where $b = \mu_n/\mu_p = 0.67$.

state with $N_c/N_d \approx 10^5$ yields a Fermi level given by

$$E_f = \frac{1}{2}kT \ln \left(\frac{N_d}{N_c} e^{-E_d/kT} + e^{E_c/kT} \right) \Big|_{T=373^\circ\text{K}} = 1.01 \text{ eV}.$$

Hence,

$$\frac{\mu_n}{\mu_p} \Big|_{T=373^\circ\text{K}} \approx 0.67.$$

The question of whether a band model is applicable to conduction in copper phthalocyanine still remains to be answered. The observation of a two-carrier Hall mobility which decreases with increasing temperature does not necessarily imply the validity of such a model. Indeed, the temperature dependence of the measured mobility in the two carrier case is a function of the number of holes and electrons in addition to the temperature dependences of the individual carrier mobilities. On the basis of our impurity model, the ratio of electron mobility to hole mobility at 373°K was found to be 0.67 in sample No. 4. If it is assumed that the respective mobilities have the same temperature dependence, this ratio remains constant as a function of temperature. From the measured Hall mobility and calculated carrier concentrations the electron and hole mobility can be obtained from Eq. (5). Table II summarizes these calculations and indicates that these mobilities decrease with increasing temperature. This implies that it is not unreasonable to apply a band model to this material. This conclusion is not unequivocal, because we have again invoked the condition that the effective densities of ground and conduction states are equal for the sake of simplicity. The assumption that the hole and electron mobility have the same temperature dependence does not seem to be too unreasonable in the temperature range of interest. However, it is to be emphasized that due to the nature of the assumptions, the computed temperature dependence of the mobility is not to be taken too literally. Rather at best it suggests that it is reasonable to apply a band model to this material.

A second model for extrinsic semiconduction can be formulated by assuming that the oxygen impurity forms an acceptor level. In this case the acceptor must lie 1.6 eV above the filled band, and an analysis similar to that presented previously for the donor model yields a ratio of acceptor density to the effective state density of

approximately 10^5 . The Hall mobility sign requires that the electron mobility be at least 5 times greater than the hole mobility at 300°K but less than the hole mobility in the intrinsic range. Kepler's⁸ results on the temperature dependence of the drift mobility in anthracene show that such a change in the more mobile carrier can occur in molecular crystals.

The particular kind of center which the absorbed oxygen creates is not clear since electron spin resonance experiments on related crystals yielded only a single sharp resonance which was due to oxygen.⁹ This was established by performing the resonance experiments in various ambients on metal free phthalocyanine. Once again oxygen increased the spin concentration while hydrogen was found to be quite effective in reducing the spin concentration. This behavior was similar to the effects of these ambients on the conductivity. Indeed, the spin concentration (approximately $10^{17}/\text{cm}^3$) corresponded closely to the donor or acceptor density computed for sample No. 4, assuming the effective density of states to be approximately $10^{21}/\text{cm}^3$.

The question of whether the absorbed oxygen behaves as a donor or acceptor cannot be answered on the basis of our experiments since there is no independent measure of the hole and electron mobilities available. The problem of doping organic semiconductors is still unsolved, hence, one cannot study *n*- or *p*-type samples to obtain mobility information as is the case in inorganic semiconductors. Oxygen has been found to form both donor and acceptor states in inorganic semiconductors. Although it most commonly acts as an acceptor impurity,¹⁰ it can behave as a donor when present substitutionally or as part of a complex.¹¹⁻¹³

The reasons for the difference in Hall mobility between metal-free phthalocyanine¹ and copper phthalocyanine can be found in two sources.

- (1) The spatial arrangement of atoms.
- (2) The interaction of the copper $3d$ atomic orbitals and the π molecular orbitals of the organic part of the molecule.

In this discussion we assume, along with the other workers in the field (e.g., Garrett, 1959),¹⁴ that the conduction electrons are π electrons.

Because of point (1) above, in attempting to understand more fully the conductivity of phthalocyanine, it is necessary for us to look further into the molecular

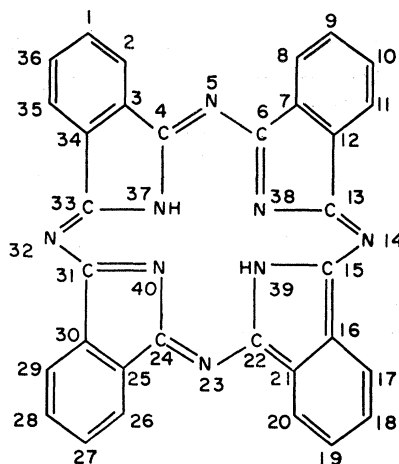
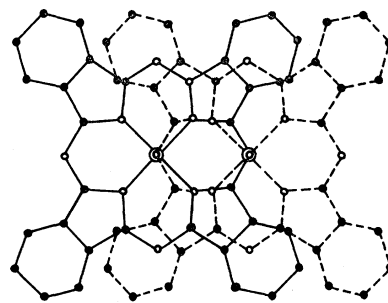


FIG. 10. Structure of metal-free phthalocyanine molecule.

dimensions and arrangements. In both the metal-free and copper phthalocyanine, the molecular planes are inclined at an angle of 44.2° to the *ac* or (010) plane. The molecules are inclined alternately to the left and to the right along the *a* axis (see Fig. 1). A twofold screw rotation transfers one molecule into the second. When a projection is taken normally to the molecular plane, none of the atoms in parallel molecules at either end of the *b* axis come exactly over one another. In Fig. 10 the atoms in the phthalocyanine molecule are numbered for the convenience of this discussion. The distances of nearest approach for parallel molecules are between carbons Nos. 4-35', Nos. 24-29', Nos. 17-22', and Nos. 11-6' where the distances are 3.41 \AA (the primes refer to a second molecule). Nitrogen atoms come almost as close: Nos. 39-40' and Nos. 37'-38 are 3.44 \AA apart. These calculations indicate that the usual order of mini-



- CARBON ATOMS
- NITROGEN ATOMS
- METALLIC CENTER OF THE MOLECULES

FIG. 11. Normal projection of two parallel molecules. Solid lines outline upper molecule; dashed lines are the underlying molecule.

⁸ R. G. Kepler, Phys. Rev. **119**, 1226 (1960).

⁹ J. M. Assour and S. E. Harrison (unpublished work).

¹⁰ R. H. Bube, *Photoconductivity in Solids* (John Wiley & Sons, Inc., New York, 1960), p. 174.

¹¹ M. Gershenzon and R. M. Mikulyak, Solid State Electron. **5**, 313 (1962).

¹² L. R. Weisberg, F. D. Rosi, and P. G. Herkart, *Properties of Elemental and Compound Semiconductors* edited by H. C. Gatos (Interscience Publishers, Inc., New York, 1960).

¹³ W. Kaiser, H. L. Frisch, and H. Reiss, Phys. Rev. **112**, 1546 (1958).

¹⁴ C. B. G. Garrett, in *Semiconductors*, edited by N. B. Hannay (Rheinhold Publishing Corporation, New York, 1959).

mum intermolecular distance, which occurs when only van der Waals forces are operative between the molecules, is maintained in the phthalocyanines.

The fact that none of the atoms in a molecule exactly overlap the corresponding atom in a parallel molecule is illustrated by the projection on a molecular plane shown in Fig. 11. In fact, there is a distinct tendency for the atoms on the underlying molecule to lie in the gaps between the atom of the upper molecule. This staggering of the atoms is probably what governs the orientation of the molecule in the crystal.

The central atom (Cu in our case) lies over a nitrogen which is 3.38-Å distant (see Fig. 10). This is the distance of closest approach for parallel molecules. Incidentally, the interplanar distance of successive overlying molecules is 3.38 Å, almost identical to the 3.40-Å interplanar separation in graphite. For the nonparallel molecules, the nearest distance of approach is 3.35 Å. This is between C-10 on the fiducial molecule and N-32 on the reflected molecule. All other distances are greater than 3.35 Å.

It appears, therefore, from the atomic positioning that the central copper atom adds another path or bridge for intermolecular electron transfer. If a π electron can be shown to spend part of its time on the copper atom, it is highly likely that the copper acts as a bridge to the transfer of π electrons between nitrogens above and below the copper atom. That the π electrons do spend part of their time on the copper atoms is shown by the nitrogen hyperfine structure found in the electron spin resonance spectrum.¹⁵ The copper bridge concept is further supported by the fact that the implicated nitrogens have the lowest π electron density in the phthalocyanine ring. Calculations by Longuet-Higgins *et al.*¹⁶ on the related porphyrin molecule, show that the nitrogens above and below the copper ion (Nos. 5, 14, 23, or 32 in Fig. 10) have the lowest concentration of π electrons. This is purely a geometrical result and one might expect that in phthalocyanine these bridge atoms have the same low electron density. The low electron density suggests that the electron repulsion is lower for the transfer of an electron from a copper atom to this nitrogen of a neighboring molecule. The possibility of the participation of the copper ion in the π electron transfer is enlarged by the probable mixing of the copper atomic and phthalocyanine molecular orbitals which may be shown as follows.

In the copper phthalocyanine the orbital wave functions fall into the A_{1u} , A_{2u} , B_{1u} , B_{2u} , and E_g irreducible representations of the D_{4h} symmetry class. On the other

hand, the copper $3d$ orbitals are the A_{1g} , B_{1g} , B_{2g} , and E_g representations. Therefore, we can expect that there will be a mixing of the E_g orbitals of the organic ring and the copper ion. Evidence is found for the mixing of the E_g orbitals from the inversion of the usual order of the copper B_{2g} and E_g orbitals as determined from electron spin resonance.¹⁵ Though this argument qualitatively indicates that the insertion of a $3d$ transition element core in phthalocyanine may increase the conductivity a quantitative estimate is too difficult to obtain. Several methods are available to check this hypothesis. Other transition-element ion phthalocyanines should also have the higher conductivity and higher carrier mobility *i.e.*, compared to metal-free phthalocyanine. Also, in silver phthalocyanine, where silver has nine $4d$ electrons compared to nine $3d$ electrons in copper, the metal E_g level is expected to lie much deeper and would be expected to have more influence on the conductivity. Therefore, this argument predicts that all $4d$ and $5d$ transition element ions would have higher conductivities than the corresponding $3d$ element phthalocyanine.

The comparatively high mobility of carriers in copper phthalocyanine as compared to that found in metal-free phthalocyanine and other molecular crystals has also been inferred from measurements of space charge limited currents in thin films of copper and metal-free phthalocyanine by Sussman.¹⁷ Thus, an independent confirmation of our measurements is available and is in agreement.

It would seem that with mobilities of the order of 100, one should be able to treat the band structure of this material using techniques applicable to inorganic semiconductors such as the orthogonalized plane wave method. However, a comparison of the optical absorption spectrum of copper phthalocyanine thin films with that obtained on solutions of the same material shows that the molecular properties are still quite evident in the solid. This strongly suggests that the tight binding approach should be applicable. However, calculations by Glarum¹⁸ indicate that this method is not applicable to materials with mobilities above 10–30 cm²/V sec. Thus, further work appears necessary to understand the nature of charge transport in copper phthalocyanine crystals.

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¹⁷ A. Sussman, Post-deadline paper, Electrochemical Society Meeting, Pittsburgh, April 1963 (unpublished).

¹⁸ S. Glarum, in Program Abstracts of the Organic Crystal Symposium, Ottawa, October 1962 (unpublished).

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