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MEASUREMENT OF THE HALL EFFECT IN METAL-FREE PHTHALOCYANINE CRYSTALS

George H. Heilmeier and George Warfield
Princeton University, Princeton, New Jersey

and

Sol E. Harrison
RCA Laboratories, Princeton, New Jersey

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The very low conductivity of organic semiconductors makes it extremely difficult to measure a Hall voltage in these materials. If one uses sensitive ac methods for detection, the signal voltage is usually comparable to the noise voltage. Previous attempts at Hall measurements on organic semiconductor crystals and films[1-3] have succeeded only in establishing an upper limit for carrier concentration and mobility. It is the purpose of this note to describe our techniques and results for Hall measurements on single crystals of metal-free phthalocyanine. This is believed to be the first Hall measurement ever reported on organic semiconductor crystalline solids.

The crystals tend to grow as needles and are extremely brittle, making them difficult to cut and impossible to work mechanically. Likely specimens[4] were selected carefully and had typical dimensions of: length, 5 mm; width, 0.5 mm; thickness, 0.3 mm. They were found to contain the following metallic impurities in parts per million: Cu, 200-2000; Na, 1-10; Ca, 1-10; Fe, 6-60; Si, 0.1-1; Mg, 3-30; Al, <1. No measure of the organic impurities is available at this time. Silver paste was found to make Ohmic contact to this material for fields 15 volts/cm to 10^3 volts/cm.

The schematic diagram of the experimental setup is shown in Fig. 1. The measurement technique consisted of recording the output of the electrometer across the Hall probes as a function of time, with the magnetic field on, off, and reversed. A typical result with field in a specific direction is shown in Fig. 2. The data were integrated using a planimeter to eliminate the effects of noise. The results of measurements on several samples are given in Table I, where it has been assumed in the calculation of the Hall coefficient, mobility, and carrier concentration that only one type of carrier is mobile, a band model is applicable, and the conductivity is isotropic.[5]

Careful thermal-probe measurements confirmed that the sign of the carriers in these crystals was negative.

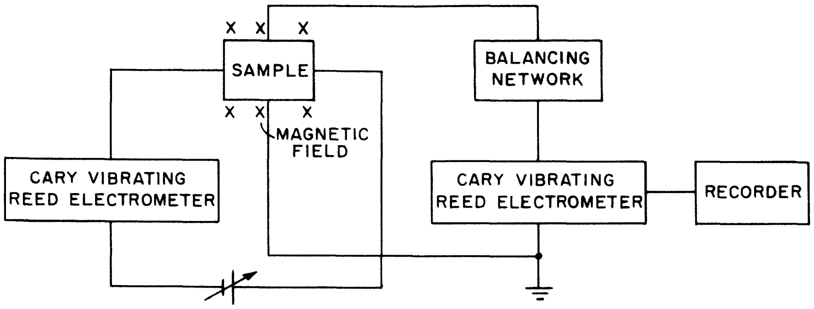

FIG. 1. Schematic diagram of Hall measurement equipment.

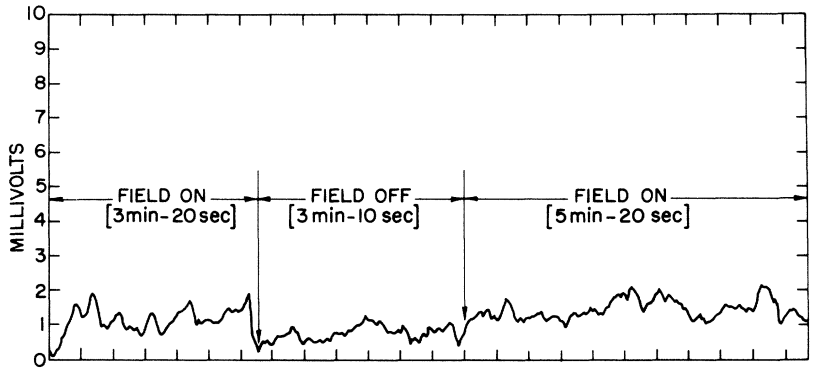

FIG. 2. Hall probe voltage vs time.

Several workers[6] have attempted to determine the sign of the majority carriers in metal-free phthalocyanine films by observing the magnitude of the photocurrent as a function of the polarity of the electrode illuminated with strongly absorbed light. Since the current is higher when the illuminated electrode is positive, they infer that the majority carriers are positively charged. Our Hall and thermal-probe measurements indicate that the dark conductivity in our crystals is due to negatively charged carriers. However, the change in the photocurrent magnitude as a function of the polarity of the illuminated electrode has been observed in our crystals in agreement with the work of Kearns and Calvin.[6]

These results are not inconsistent when interpreted in the following manner:

If one illuminates the negative electrode with strongly absorbed radiation, both holes and electrons are produced. If the contacts are Ohmic to electron flow, as they were in our experiments, no increase in conductivity due to electrons is possible, because there is already an excess of electrons at the Ohmic cathode before illumination. If one illuminates the positive electrode, the photogenerated holes or minority carriers can move to the negative electrode, thus producing enhanced conductivity in the crystal. Thus, the sign of the minority carrier can be inferred from experiments of this type on crystals with Ohmic contacts.

To compare these results with a theory based on a band model, the carrier concentration can be estimated from the effective density of states N_C and the activation energy E_G:

$$n = N_C \exp(-E_G/2kT).$$

From measurements of conductivity as a function of temperature and from the first optical activation energy, E_G is found to be 1.7 ev. Because of the narrow energy bands, N_C is taken to be of the order of the concentration of molecules, $10^{21}/\mathrm{cm}^3$. This yields $n \approx 10^6/\mathrm{cm}^3$. Many et al.[7] take N_C to be the concentration of molecules times the number of π orbitals. If this procedure is followed, n is increased by approximately two orders of magnitude. However, it does not seem appropriate to include all of these π orbitals in the first empty or conduction band, because there are indications from optical-absorption experiments that some of the π orbital levels are well separated above the first absorption band.

The experimental value for the concentration of carriers points out that the metallic impurities have no influence on this concentration. The impurity concentration is so enormous compared to that of the carriers that if the impurities had any influence at all, they would mask 10^6-10^7 carriers/cm^3. Also, the correspondence be-

Table I. Summary of results.

Sign of carriers	negative
Hall voltage, measured	0.3 - 0.5 mv
Hall voltage, corrected for detector loading	42 - 70 mv
Hall coefficient	10^{12}
Carrier concentration	$2 - 12 \times 10^6$ carriers/cm^3
Hall mobility	0.1 -0.4 cm^2/volt sec

tween optical and thermal activation energies suggests intrinsic conduction.[8] It seems likely that the metallic impurities are incorporated in phthalocyanines in such a way that they do not influence the conductivity, i.e., the metal ions substitute for the H_2 core in the metal-free phthalocyanine. It is found from electron spin resonance[8] that the wave functions of the metallic core do not spread over the entire molecule and have little effect on the π orbitals which provide the current carriers.

The sign of the Hall voltage may be explained by using the following molecular model. The conduction process involves an intramolecular excitation and the intermolecular transfer of the carrier. The former process involves an activation energy; the latter is a measure of the mobility. The electron is raised to an excited state where the overlap of the excited-state wave function is greater than the overlap of the lower lying ground-state functions. The hole left behind in the ground state may be considered to be somewhat less mobile.

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CLASSICAL EXPLANATION OF THE ANOMALOUS MAGNETORESISTANCE OF BISMUTH*

J. J. Hopfield
Department of Physics, University of California, Berkeley, California
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Recently, Esaki[1] has reported anomalous breaks in the current-voltage relations for bismuth at high electric fields when a magnetic field is applied perpendicular to the direction of current flow. These breaks occur at an electric field approximately given by $E_{\text{kink}} = Hu/c$, where u is the velocity of a transverse acoustic phonon in bismuth. His qualitative explanation of the phenomena noted that this E_{kink} is the electric field in which the cycloidal transverse drift velocity of electrons and holes (which drift in the same direction) would be equal to the velocity of sound. He attributed the kink to a change in the electron-phonon scattering of quantized orbits when $v_{\text{drift}} = u$. We suggest instead that an additional force is present represented by the possibility of travelling wave amplification, that this force is a collective force involving the drift velocity (rather than the Fermi velocity, which is two orders of magnitude larger), and that the occurrence of the observed megacycle oscillations is a reasonable outcome for such a collective process. The model also gives a good qualitative description of the measured E-I characteristics.

Consider a classical positive charge moving in a magnetic field H_z and an electric field E_y. The existence of a phenomenological damping time τ is assumed. We further assume an additional force F in the x motion. This force is assumed to be directed opposite to v_x, to be zero for $|v_x| < u$, and to increase very rapidly with increasing v_x for $|v_x| > u$. The equations of motion are

$$m\dot{v}_y = e[E_y - (v_x/c)H] - mv_y/\tau, \tag{1a}$$

$$m\dot{v}_x = e(v_y/c)H + F - mv_x/\tau. \tag{1b}$$

The equations for the drift velocity are obtained by setting the left-hand side of (1) equal to zero. If F increases rapidly enough as a function of the drift velocity v_x, when E is greater than some critical electric field, Eq. (1b) will have a drift velocity solution $v_x = u$, and the current density will be given by

$$j = \frac{ne^2\tau}{m} E\left(\frac{1}{1+(\omega_c\tau)^2}\right), \quad E < \frac{Hu}{c}\left(1+\frac{1}{(\omega_c\tau)^2}\right), \tag{2a}$$