

tween optical and thermal activation energies suggests intrinsic conduction.<sup>8</sup> 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<sub>2</sub> core in the metal-free phthalocyanine. It is found from electron spin resonance<sup>8</sup> that the wave functions of the metallic core do not spread over the entire molecule and have little effect on the  $\pi$  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 some-

what less mobile.

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<sup>1</sup>C. G. B. Garrett, in Semiconductors, edited by N. B. Hannay (Reinhold Publishing Company, New York, 1959).

<sup>2</sup>C. G. B. Garrett, Proceedings of the International Conference on Semiconductor Physics, Prague, 1960 (Czechoslovakian Academy of Sciences, Prague, 1961).

<sup>3</sup>J. Kommandeur and I. R. Hall, J. Chem. Phys. **34**, 129 (1961).

<sup>4</sup>The crystals were supplied by G. E. Gottlieb and J. F. Corboy of RCA Laboratories based on preliminary work by J. Assour.

<sup>5</sup>The validity of a band model for metal-free phthalocyanine and the assumption of isotropic conductivity is still under study.

<sup>6</sup>D. R. Kearns and M. Calvin, J. Chem. Phys. **34**, 2022 (1961).

<sup>7</sup>A. Many, E. Harnik, and D. Gerlich, J. Chem. Phys. **23**, 1733 (1955).

<sup>8</sup>S. E. Harrison and J. M. Assour (to be published).

## CLASSICAL EXPLANATION OF THE ANOMALOUS MAGNETORESISTANCE OF BISMUTH\*

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Recently, Esaki<sup>1</sup> 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  $E_{\text{kink}}$  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 traveling 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  $\tau$  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

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

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

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

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

$$j = \frac{ne^2\tau}{m} \left( E - H \frac{u}{c} \right), \quad E > \frac{Hu}{c} \left( 1 + \frac{1}{(\omega\tau)^2} \right), \quad (2b)$$

where  $n$  is the density of charges.

Equations (2) give a qualitative description of Esaki's published curves, including the constant differential conductivity above the critical field, the high-field magnetoresistance below the critical field, and a reason for the critical field to lie above  $Hu/c$ . The zero-field resistivity obtained by extrapolating the high-field magnetoresistance data of Esaki to zero magnetic field in fact agrees fairly well with the above kink differential resistivity, as predicted from (2). (The actual zero-field resistivity is, however, much lower.)

That both holes and electrons are involved is important because their transverse drift produces no Hall field. The model, of course, neglects all quantum effects, effects of mass anisotropies, differences in relaxation times of electrons and holes, etc.

This model is reasonable only if an explanation for a very sharply varying force at  $v_x = u$  can be found. We pose the following question. Why, in bismuth, does not the kind of phonon amplifier described by Hutson, McFee, and White<sup>2</sup> exist when an electric field is applied? The answer seems to be: Because electrons and holes drift in opposite directions in an electric field, the condition of charge neutrality (a strong limitation in a semimetal) precludes driving bunched electrons and holes with an electric field.

Esaki's experiments, however, produce a transverse drift of electrons and holes in the same directions. These can be bunched in a travelling wave without violating charge neutrality.

In a one-dimensional scalar model an analysis, similar to that of reference 2, for the case of deformation potentials and an induced drift velocity  $v$  for electrons and holes yields

$$\frac{\partial n(x, t)}{\partial t} = -v \frac{\partial n(x, t)}{\partial x} - \frac{n(x, t) + V(\partial z / \partial x)N}{\tau_{eh}},$$

$$\rho \frac{\partial^2 z}{\partial t^2} = Y \frac{\partial^2 z}{\partial x^2} + V \frac{\partial n(x, t)}{\partial x}, \quad (3)$$

for the equations of motion of the lattice displacement  $z$  and the deviation of the electron and hole concentration  $n(x, t)$  from its equilibrium value.  $V$  is the difference in the electron and hole deformation potentials,  $N$  is the density of states at the

Fermi surface, and  $\tau_{eh}$  is the electron-hole recombination time. These equations yield the approximate relation for left-running waves:

$$k(\omega) = u\omega + \frac{V^2 N}{2Y\tau_{eh}} \frac{u}{u} \left( \frac{1/\omega\tau_{eh} - i(1+v/u)}{(1+v/u)^2 + (1/\omega\tau_{eh})^2} \right),$$

for the relation between wave vector  $k(\omega)$  and frequency  $\omega$ . As in Hutson's case, for  $v > -u$ , the result is an acoustic loss. For  $v < -u$ , the phonons show a net gain. The maximum gain/unit length attainable is approximately

$$V^2 N \omega / Y u,$$

of the order of  $0.3 \text{ cm}^{-1}$  for 1-Mc/sec sound waves and parameters appropriate to bismuth. The  $\omega$  dependence is weak, so a band of acoustic waves could be amplified.

Gain to the sound waves represents an effective force opposed to the velocity of the electron motion in the  $x$  direction. The magnitude of this force is a complicated function of the acoustic properties of the crystal. When this force increases rapidly enough with velocity, however, the nature of the  $E-I$  curves are independent of the details of the force. This force can become large if the phonon gain becomes sufficient to overcome usual phonon losses, and coherent phonon waves of sufficient amplitude are generated. The observation by Esaki of megacycle oscillations suggests that this coherent travelling-wave amplification occurs.

It thus seems possible to understand the behavior of the additional force due to the onset of travelling-wave amplification, which is possible in bismuth only when the electrons and holes drift in the same direction. It should be emphasized that this energy loss mechanism is a collective effect involving the drift velocity. The model seems therefore to give a plausible description of the dominant effects in the kinks observed in the magnetoresistance of bismuth.

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