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## EXPERIMENTAL EVIDENCE FOR CARRIERS WITH NEGATIVE MASS

G. C. Dousmanis, R. C. Duncan, Jr., J. J. Thomas, and R. C. Williams RCA Laboratories, Radio Corporation of America, Princeton, New Jersey (Received September 30, 1958; revised manuscript received October 29, 1958)

Cyclotron resonance experiments, suggested earlier<sup>1</sup> for the detection of negative-mass carriers, have been carried out with Ge crystals at 4°K. Use of circularly polarized microwaves has revealed a new spectrum of heavy holes which, from the tests tried so far, may be assigned to carriers of negative mass. This spectrum is of the emission type: it appears as a "dip" in the background absorption, rather than as an absorption peak.

It has been pointed out<sup>2</sup> that, because of the re-entrant type of energy contour in Ge and Si, the transverse effective mass of heavy holes close to the [100] axis should be negative. Calculations have shown that the number of negativemass carriers at equilibrium should be substantial and it was suggested that they be detected by cyclotron resonance.<sup>1</sup> This type of negativemass effect is expected to persist at low energies and seemed more promising for experimental detection than the effect expected from carriers in the upper parts of simple band structures.<sup>3, 4</sup>

The negative-mass holes would not yield a simple cyclotron line because of the large spread in mass (from about  $-0.2 m_0$  to  $-\infty$  in Ge). Despite this, one calculates a single but broad and asymmetric line with the half-width on the high-field side larger than that on the lower. If one denotes by  $H_0$  the field value for resonance of the positive-mass holes ( $m^* = 0.28 m_0$ ), the maximum of the negative-mass interaction should occur in the region of  $-0.8H_0$  to  $-2H_0$ . The negative-mass interaction would produce a dip on the background absorption rather than an

absorption peak since the negative-mass carriers are thrown into lower energies. It is, of course, obvious that no net emission will result if strict thermal equilibrium prevails. In the absence of any information the relaxation time for negative masses is assumed to be comparable to that for positive ones. Since the center of the negative-mass cone<sup>1</sup> offers a line of constant  $m^*$  [its value is predicted in the range of (-0.2 to -0.5)  $m_0$ ], with H in the [100] direction, one may expect the observable  $m^*$  to represent roughly that of the cone axis.

The apparatus used in these experiments is similar to that of other workers,<sup>5,6</sup> except that no use is made of phase-sensitive detection. The magnetic field is applied along the [100] axis. In contrast to most earlier work, H is perpendicular to the plane of the samples (disks 0.5 cm in diameter and 0.03 cm thick). It is not clear whether this arrangement is preferable, but surface and plasma (depolarization) effects must be different in the two cases. The carriers are generated by illumination with a tungsten lamp. Illumination provides input energy to the specimen. Majority carriers are preferentially generated with infrared. Very few majority carriers are generated by impact ionization in the applied rf field. The microwave power is less than one milliwatt.

Data taken with a 10-ohm-cm *p*-type Ge sample that yields narrow spectra are shown in Fig. 1. On the side marked +*H*, spectra with positive  $q/m^*$  are detected. On the -*H* side one expects



FIG. 1. Cyclotron resonance spectra of Ge (taken with circularly polarized waves) and the new structure ("dip") on the -H side. A weak absorption peak is also seen near the light holes. H is oriented along the [100] axis. The dip here, seen also in the subsequent figures, is assigned to carriers with negative mass.

electron spectra and evidence for negative-mass heavy holes  $(q/m^*$  negative). Since the circular polarization is not complete, traces of spectra appear even on the "wrong" side of H. In Fig. 1 a new structure is seen where negative-mass holes are expected. The structure consists mainly of a "dip" at  $H \sim -0.7H_0$ . Since the dip occurs between the electrons and the heavy holes it can be easily distorted by the former or the latter depending on the electron concentration and the degree of polarization, respectively. To our knowledge there are no data in the literature for comparison with the -H side or the low-field +H side. In several cases a small peak appears at  $\pm 1.9H_0$  which had been seen earlier.<sup>7</sup>,<sup>8</sup> A new absorption peak appears near the light holes and is more prominent on the +H side. This peak is weak and its exact determination and interpretation will require further work.<sup>9</sup> Structure is also indicated on the low-field side of the heavyhole line (Fig. 1). The data are taken with an undercoupled cavity. That the dip is not simply a continuation of the electron line is shown by the data of Fig. 2, taken with less rf power, much better polarization, and the cavity undercoupled but further from match. It is seen that the dip is separate from both the electrons and the residual heavy-hole resonance. The dip is strong enough to displace to the right the heavy holes on the -H side. The apparent small shifts of the spectra from one run to another are mainly due to the manual setting of the coil current.



FIG. 2. Part of the spectra of Ge showing the region of the new dip. By comparison to Fig. 1, the microwave power here is lower, the polarization more complete, and the cavity coupling further away from match.

The dip may be interpreted as a new resonance for heavy holes. Referring to Fig. 1, reference 1, with H along the  $k_{\chi}$  axis one would expect two resonances from the heavy holes, corresponding respectively to  $m_1$  (usual heavy-hole mass) and  $m_2$  (points along  $k_{\chi}$ , the re-entrant contours).  $m_2$  is negative and is associated with the dip on the -H side. For single mass values,  $m_1$  and  $m_2$ , one calculates, using the constants of earlier work, <sup>5,6</sup> for H along the [100] axis,

$$|m_1/m_2| \sim |A-B-(C^2/2B)| / [A-(B^2+C^2/6)^{1/2}]$$
  
~0.6±0.2 from A, B, C of reference 5  
~1.4±0.4 from A, B, C of reference 6.

The experimental value, an average of several measurements, is  $1.3 \pm 0.3$ . The  $m_2$  interaction is weak since under resonance  $E_{\rm rf}$  may tend to change the carrier mass, more so than in the case of  $m_1$ .

Negative-mass spectra, by comparison to the absorption spectra, are possibly detected over a different range of the instrumental curve of reflected power  $\underline{vs}$  rf conductivity. As one approaches negative-mass resonance the sample conductivity presumably tends to decrease rather than increase as with the absorption spectra of positive-mass carriers. Hence, depending on the linearity of the instrument, negative-mass effects may be somewhat different from that predicted from the usual spectra.

The shape and intensity of the emission-type spectrum are sensitive to microwave power. Figure 3 shows data taken with another sample



FIG. 3. The spectra of Ge taken with another 10ohm-cm p-type sample. Note that as the microwave power is progressively decreased the new spectrum (dip) becomes pronounced. The insert shows a smaller dip observed at higher fields  $(m^{*} \sim -0.48 m_{0})$ .

and with more electrons present. The polarization here is better than in Fig. 1. As the rf power is progressively decreased the "dip" becomes pronounced. No evidence of the heavyhole line is seen on the -H side, presumably as a result of the subtracting new signal. A smaller effect, similar to the main dip, appears on the +H side (Fig. 3). The effect of the rf may be due partly to impact ionization, but a strong rf may also tend to depopulate the negative-mass cone.<sup>1</sup> This would correspond to power saturation in other types of emission spectra.

The new spectrum taken with a 30-ohm-cm sample is shown in Fig. 3, Part A. The higher resistivity does not necessarily imply better crystalline quality and narrower spectra. The "dip" is reduced in intensity if H is misoriented by about 15° from the [100] axis, as expected from the small angle of the negative-mass cone.<sup>1</sup> Such a run, where the new spectrum is not seen, is shown in Fig. 4, part B.

With *H* at values outside the new "dip," the conductivity  $\sigma_{rf}$ , as measured from the reflected rf power, increases monotonically with illumination *I*, starting with I = 0. When -*H* was set at the position of the main dip,  $\sigma_{rf}$  did not change with *I* and in some cases it even decreased with increasing *I*. A similar, but less pronounced, tendency has been found with the dip following the light holes on the +*H* side. This suggests the presence of a negative conductivity component that tends to cancel the increase in  $\sigma_{rf}$  expected from the increased numbers of the usual car-



FIG. 4. Part A: Spectra of Ge and the new structure obtained with a 30-ohm-cm p-type sample. Part B: Spectra of Ge with H misoriented by 18° from [100] axis. The new spectrum is not seen in this case, a behavior to be expected from the small angle of the negative-mass cone.

riers. That the "dip" in Fig. 3 is lower than the high-field absorption limit (on either side of H) may again be indicative of negative conductivity. Further measurements at higher fields are required to establish whether the limits indicated by the data represent truly zero rf conductance.

The lack of correlation between electron intensity and the new "dip" makes it unlikely that this effect is due to electrons. In any case, the electron cyclotron spectra in either the ground or excited states should be of the absorption type. The rf power and the temperature are too high for occurrence of quantum effects.<sup>8-10</sup> Complications from magnetoresistance are unlikely because of the low carrier densities. The small dip on the +H side may be assigned to the extreme low-field end of the negative-mass spectrum detected with small intensity on that side.

The main dip occurs at  $m^* = -(0.22 \pm 0.06)m_0$ . A smaller dip (see insert, Fig. 3) has also been observed at  $m^* \sim -0.48m_0$ .

In summary, a new resonance has been found for the heavy holes in Ge. The new heavy-hole  $effect^{11}$  is more prominent on that side of *H* that is appropriate for detection of negative-mass holes. The direction of the effect (decreased absorption) and its spectral position, approximately, are as expected. The intensity of the effect varies with microwave power. All observations on intensity fall well within an order of magnitude of the earlier prediction,<sup>1</sup> but mainly on the upper magnitude side. The reentrant part of the contours should be given more accurately by detailed analysis of the present data. The sensitivity to rf power suggests that the dependence on temperature and relaxation time should be of much interest. The energy relations and carrier distribution under which this emission-type effect occurs have not as yet been evaluated in detail. The very magnitude of the new effects in Ge offers promise for further band structure studies in this as well as other crystals.

The authors are indebted to Professor Charles Kittel for a helpful discussion, and to many members of the RCA Laboratories for their cooperation.

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<sup>9</sup>Indications of distortion on the hole peak have been obtained by the Lincoln Laboratory group in work with plane waves [Zeiger, Behrndt, and Rauch, Proceedings of the Rochester Conference on Semiconductors, J. Phys. Chem. Solids (to be published)]. Structure on the heavy-hole peak on the +H side had been reported by Dresselhaus, Kip, and Kittel [Phys. Rev. <u>95</u>, 568 (1954)]. The high-resolution spectrum of Fletcher, Yager, and Merritt<sup>8</sup> (circular polarization, +H side) shows no structure on the heavy-hole line at 4° K.

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 $^{11}A$  distortion has been found with plane waves on the low-field side of the heavy-hole line. The absolute value of the mass is about  $0.26m_0$ , which is within the range where the emission-type effect occurs with circular polarization.

## THEORY OF THE MEISSNER EFFECT

D. Pines\* and J. R. Schrieffer†
Ecole d'Eté de Physique Théorique,
Les Houches (Haute Savoie), France (Received November 7, 1958)

In order to obtain an explicitly gauge-invariant description of the Meissner effect in superconductors, Wentzel<sup>1</sup> has recently suggested an approach which differs in several essential respects from that developed by Bardeen, Cooper, and Schrieffer.<sup>2</sup> Wentzel finds in the long-wavelength limit a relation between the current density and the magnetic vector potential which differs from the London value given by the BCS theory. We wish to point out that this discrepancy is due to Wentzel's assumption that corrections to his approach possess a convergent expansion in powers of the phonon-electron coupling constant, g. It is our belief that this expansion does not exist.

Wentzel considers the Hamiltonian

$$H = H_0 + H_g + H_A \equiv H' + H_A, \quad (1)$$

where the three terms describe the free electrons and phonons, the electron-phonon interaction of strength g, and the coupling of the electrons to the vector potential, A. Coulomb interactions between electrons are neglected. By carrying out a perturbation theoretic canonical transformation based on the <u>unperturbed Hamiltonian</u>,  $H_0$ , Wentzel eliminates the coupling of the system to the vector potential through order  $g^2$ . Thus he finds

$$\widetilde{H} = e^{-K} H e^{K} = H_0 + H_g + O(g^3 A), \qquad (2)$$

where

$$K = K_A + K_{gA} + K_{ggA} , \qquad (3)$$

and the generators are defined by

$$[H_0, K_A] = -H_A, \qquad (4)$$

$$[H_0, K_{gA}] = -[H_g, K_A], \qquad (5)$$

$$[H_0, K_{ggA}] = -[H_g, K_{gA}].$$
(6)

To the same order in g, the transformed current density operator is given by

$$\tilde{j}_{\mu}(\mathbf{\dot{q}}) = j_{\mu}(\mathbf{\dot{q}}) + [j_{\mu}(\mathbf{\dot{q}}), K], \qquad (7)$$

where  $j_{\mu}(\mathbf{q})$  is the current density operator in the presence of the vector potential in the original representation. Wentzel then calculates the current density by taking the expectation value of (7) with respect to the Bogoliubov<sup>3</sup>-Valatin<sup>4</sup> representation of the BCS ground state appropriate to  $H' \cong \tilde{H}$ . Since  $H_g$  is not treated as a perturbation in this last step, a Meissner effect is obtained and it is found that

$$\lim_{q^2 \to 0} J_{\perp}(\vec{\mathbf{q}}) = -\frac{\rho}{2} \frac{ne^2}{m} A_{\perp}(\vec{\mathbf{q}}) , \qquad (8)$$

where  $\rho = g^2 N(0) \approx \frac{1}{4}$ , N(0) being the density of states in energy of electrons of one spin at the Fermi surface and  $\perp$  denotes the transverse components.<sup>5</sup>

To understand the difficulties with this approach, we note that the exact expression for the current density including terms linear in A may be written as<sup>6</sup>

$$J_{\mu}(\mathbf{\tilde{q}}) = (\Psi_{0} | j_{\mu}(\mathbf{\tilde{q}}) | \Psi_{0}) + (\Psi_{0} | [j_{\mu}(\mathbf{\tilde{q}}), S_{A}](\Psi_{0})$$
$$\equiv \sum_{\nu} K_{\mu\nu}(\mathbf{\tilde{q}}) A_{\nu}(\mathbf{\tilde{q}}), \qquad (9)$$

where

$$[H', S_A] = -H_A , \qquad (10)$$

and  $\Psi_0$  is the ground-state eigenfunction of H':

$$H'\Psi_{\alpha} = W_{\alpha}\Psi_{\alpha}.$$
 (11)

If  $S_A$  were expanded in powers of g, one would obtain Wentzel's expression for the current den-