Cyclotron Resonance Experiments in Silicon and Germanium\*

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Experimental techniques are described for cyclotron resonance in silicon and germanium at 9000 Mc/sec, 24000 Mc/sec, and higher frequencies. Results are presented for electrons and holes in both germanium and silicon. The parameters for the heavy holes are evaluated, with corrections from an approximate theory of line shape for warped surfaces. Observations of the harmonics of cyclotron resonance of the heavy holes in germanium and silicon are described.

### INTRODUCTION

'N a dc magnetic field, free charges spiral about the  $\blacksquare$  direction of the magnetic field H with angular frequency given by

$$
\omega_c = \pm eH/mc. \tag{1}
$$

 $\omega_c$  is conventionally called the cyclotron frequency, e is the particle's charge and  $m$  is its mass. If an rf electric field of angular frequency  $\omega$  is applied perpendicular to  $H$ , resonant absorption of energy from the electric field may occur when  $\omega = \omega_c$ .

The resonance is not well resolved unless the particle's mean free path is a significant fraction of the circular path it tends to make about the magnetic field. That is, for resonance  $\omega \tau \searrow 1$ , where  $\tau$  is the average time between collisions.

Although this is a familiar classical phenomenon, it was pointed out only recently by Dingle' and Dorfman' that measurement of the effective mass of charge carriers in solids might be accomplished directly by cyclotron resonance experiments. Shockley<sup>3</sup> pointed out that conditions were suitable for resonance experiments in germanium and silicon. All three authors discussed the importance of resonance measurements for obtaining information about the band structure of solids.

The first successful cyclotron resonance experiment in solids was carried out on germanium by Dresselhaus, Kip, and Kittel, $4$  and was followed by more complete experiments on germanium and silicon by present authors<sup> $5-8$ </sup> and the Berkeley group.<sup>9</sup> We will frequently refer to the papers by Dresselhaus, Kip, and Kittel"

and Zeiger, Lax, and Dexter<sup>11</sup> as DKK and ZLD, respectively.

#### I. EXPERIMENTAL PROBLEM

The basic problem of the experiment is to produce a combination of long mean free path and high angular frequency of the electric field,  $\omega$ , such that  $\omega \tau \leq 1$ , where  $\tau$  is the average collision time for the free carriers.<sup>12</sup>  $\tau$  is the average collision time for the free carriers.<sup>12</sup> For microwave frequencies of 24 000 Mc/sec,  $\tau$  must For microwave frequencies of 24 000 Mc/sec,  $\tau$  must<br>be of the order of 10<sup>-11</sup> second. In semiconductors at present, such values occur only at very low temperatures where the lattice scattering frequency is small. Moreover, high crystal purity and perfection is required. By 1953, purification techniques developed for germanium and silicon had produced the perfection required for a successful resonance experiment. This fact was pointed out by Shockley. '

At very low temperatures, germanium and silicon are essentially insulators with the carriers frozen into impurity levels or into the bands and not free to contribute to conduction processes or to resonance. Three methods for producing free carriers have been used in germanium for the resonance experiments, They are: breakdown of the impurity levels by the microwave field (in analogy to microwave breakdown of gases during cyclotron resonance<sup>13</sup>), breakdown of impurity during cyclotron resonance<sup>18</sup>), breakdown of impurit<sub>i</sub><br>levels by an applied dc electric field,<sup>14</sup> and excitation with light. In silicon, only the photoexcitation has been useful since the levels lie lower than in germanium and are dificult to break down.

In the electric breakdown it is possible to give energy to the few carriers remaining in the bands such that some of them are able to ionize a neutral impurity when they collide with it. Such breakdown. phenomena occur in both dc and microwave observations on germanium.

Measurements of the real and imaginary parts of the rf conductivity of the sample,  $\sigma_r$  and  $\sigma_i$ , respectively, in the prebreakdown region (from changes in cavity Q

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t Now at the Department of Physics, University of Wisconsin, Madison, Wisconsin. ' R. B.Dingle, Proc. Roy. Soc. (London) A212, 38 (1952).

<sup>&</sup>lt;sup>2</sup> J. G. Dorfman, Doklady Akad. Nauk U.S.S.R. 81, 765 (1951).<br><sup>3</sup> W. Shockley, Phys. Rev. 90, 491 (1953).<br><sup>4</sup> Dresselhaus, Kip, and Kittel, Phys. Rev. 92, 827 (1953).<br><sup>5</sup> Lax, Zeiger, Dexter, and Rosenblum, Phys. Rev. 93,

<sup>(1954).</sup>

<sup>e</sup> Dexter, Lax, and Zeiger, Phys. Rev. 95, 557 (1954). <sup>r</sup> R. N. Dexter and B. Lax, Phys. Rev. 96, 223 (1954).

<sup>8</sup> Dexter, Lax, Kip, and Dresselhaus, Phys. Rev. 96, 223 (1954).

<sup>s</sup> Dresselhaus, Kip, and Kittel, Phys. Rev. 95, 568 (1954). "Dresselhaus, Kip, and Kittel, Phys. Rev. 98, 368 (1955).

<sup>&</sup>lt;sup>11</sup> Zeiger, Lax, and Dexter (to be published).

<sup>&</sup>lt;sup>12</sup> The complicating effects of high carrier densities have not been found at liquid helium temperatures in germanium and silicon. They are discussed in Dresselhaus, Kip, and Kittel, Phys. Rev. 100, 618 (1955).

<sup>&</sup>lt;sup>13</sup> Lax, Allis, and Brown, J. Appl. Phys. 21, 1297 (1950). <sup>14</sup> Sclar, Burstein, Turner, and Davisson, Phys. Rev. 91, 215 (1953).

and frequency) gave the number of carriers as a function of microwave power. This was done as follows:

$$
\Delta Q = C\sigma_r = C \frac{ne^2 \tau}{m(1 + \omega^2 \tau^2)},
$$
  
\n
$$
\Delta f/f = C\sigma_i = C \frac{ne^2 \omega \tau^2}{m(1 + \omega^2 \tau^2)}.
$$
\n(2)

The ratio  $\Delta Q/(\Delta f/f) = \omega \tau$ . Since the frequency is known, the collision time is then determined. From the known geometry of the cavity and sample, the constant C was calculated. By varying the rf field strength from very low values (where  $n \approx 0$ ) to prebreakdown value,  $n$  was calculated from the measured frequency shift assuming the average value of  $m^*$  from the cyclotron resonance experiments. Approximately  $10^{11}$  electrons could be produced by rf ionization of impurity levels in germanium ( $\rho \approx 1$  ohm-cm at room temperature) at power levels of about 100 milliwatts. The corresponding electric field was 10 volts per cm ( $\tau$  was found to be  $\sim 10^{-11}$  to 10<sup>-12</sup> second).  $\sim$ 10<sup>-11</sup> to 10<sup>-12</sup> second)

Measurement of the real and imaginary parts of rf conductivity has been used by several research groups<sup>15-18</sup> in attempts to determine the effective mass of carriers in germanium with microwaves at temperatures where cyclotron resonance is not resolved.

The advantage of rf or electric breakdown is that it permits only one type of carrier to be excited into a conducting state, and allows some control of carrier density. Disadvantages are:

(1) The effective temperature of the free carriers may be raised well above the lattice temperature into a region of higher scattering frequency.

(2) At high rf levels, carriers may be distributed over a wide energy range. H the energy has a quartic dependence on momentum, the effective mass will depend on the energy. Thus, a distribution in energy might obscure the resonance anisotropy. Moreover, at high powers, the average carrier may move between collisions from its orbit on the constant energy surface to a higher energy surface and an orbit (with the same momentum along the magnetic field direction) which has a different periodicity. These two effects are probably important for holes in germanium.

(3) The numbers of carriers in rf breakdown depends on the magnetic field, making line shape studies impractical. Such effects, called enhancement, arise when the magnetic field is adjusted to resonance, since the carriers in the bands then gain energy and produce ionized carriers most efficiently. Unusually sharpened resonance peaks can occur in this fashion.

Excitation of carriers by light is the most versatile method. Suitable filtering of the light can give excitation







Fro. 1. (a) An experimental arrangement for cyclotron resonance studies at 9000 Mc/sec. (b) An experimental arrangement for cyclotron resonance studies at 24 000 Mc/sec and higher frequencies.

<sup>&</sup>lt;sup>16</sup> T. S. Benedict and W. Shockley, Phys. Rev. 89, 1152 (1953).<br><sup>16</sup> H. Suhl and G. L. Pearson, Phys. Rev. 92, 858 (1953).<br><sup>17</sup> F. A. D'Altroy and H. Y. Fan, Phys. Rev. 94, 1415 (1954).<br><sup>18</sup> J. M. Goldey and S. C. Brown,

only from impurity levels and thus produce only one type of carrier. The number of carriers remains constant as the magnetic field is varied and simplifies line-shape studies. Low rf power levels may be used, thus permitting an approach to equilibrium of carrier and lattice temperatures.

As discussed in ZI.D, the measurement of the resonance line width  $\Delta H$  yields the collision or scattering time  $\tau$ . The relation for spherical or ellipsoidal constant energy surfaces is  $\Delta H/H_0=2/\omega\tau$ , where  $H_0$  is the field for resonance. Typical values of  $\tau$  were found to be for resonance. Typical values of  $\tau$  were found to be about  $6 \times 10^{-11}$  second. Thus, at  $4^{\circ}K$ , carriers with thermal velocity and effective mass  $m^* = 0.3m_0$  (m<sub>0</sub> is the free electron mass) have a mean free path of about 1.5 microns. In a field of 2500 oersteds, the radius of their circular orbit is about 0.3 micron.

#### II. EXPERIMENTAL APPARATUS AND **TECHNIQUES**

Resonance experiments have been carried out by using microwave frequencies of 9000, 23 500, 35 000, and 47 000 Mc/sec. The bulk of the observations were made at 23 500 Mc/sec. The only difference in technique occurred in the manner of producing photoexcitation. At 9000 Mc/sec, as shown in Fig. 1(a), light entered the wave guide above the Dewar through an E-plane bend and illuminated the disk shaped sample through the cavity coupling iris. The cavity was a  $\lambda/2$  rectangular wave-guide resonator with the sample mounted in the geometrical center and the plane of the disk normal to the long axis of the cavity. The sample could be rotated by a gear arrangement connected to the sample by means of a teflon mount which entered the end wall of the cavity through a tapered plug. The static magnetic field (for transverse cyclotron resonance) was perpendicular to both the rf electric field and the axis of rotation.

At the higher frequencies, as shown in Fig. 1(b), light was sent down a quartz rod tapered from  $\frac{5}{16}$  in. to  $\frac{1}{8}$  in. on which the disk-shaped sample was mounted in a hollow Teflon holder. The holder entered a hole in the side of the cavity at the equator of a  $TE_{111}$  cylindrical cavity. The quartz rod behaved like a light pipe and could be rotated from outside the Dewar system by a calibrated gear train. Moreover, by pulling the rod from the Dewar, samples could be efficiently moved or changed during a liquid helium run. Radiation transmitted by the quartz usually gave about equal numbers of holes and electrons. The rf electric field was parallel to the axis of rotation and perpendicular to the static magnetic field. The hole in the side of the cavity (0.22 in. at 23 500 Mc/sec) behaved like a wave guide below cutoff and did not seriously perturb the cavity. At frequencies above 23 500 Mc/sec, we found it useful to Gll the cavity with Polyfoam to avoid the cavity frequency shifts produced by the formation of bubbles of helium gas. At all frequencies, the cavities were immersed in liquid helium and were connected to the



FIG. 2. Block diagram of the experimental system.

microwave setup with thin-walled stainless steel wave guide which had been silver-plated. A double glass Dewar system used liquid nitrogen in the outer Dewar. Temperatures down to 1.3'K could be reached by pumping on the helium vapor.

In the resonance experiments using photoexcitation, the light was totally amplitude modulated at 90 cps. This produced a total amplitude modulation of the number of carriers and of the absorption they pronumber of carriers and of the absorption they pro-<br>duced.<sup>19</sup> The modulated absorption signal was sent through a narrow band amplifier and lock-in detector. The reference signal for the lock-in detector was obtained from a phototube receiving a chopped light beam from a second source. The detector output was a dc signal proportional to the absorption and was recorded as a function of the magnetic field. The field was swept by a slowly varying dc signal fed into the regulation circuit of the Varian 12-in. magnet. Magnetic field measurements were made with a proton resonance magnetometer and with a rotating flip-coil magnetometer calibrated against proton resonance. With the flip-coil system, markers were manually placed on the recorder to produce an absorption trace plotted against magnetic field. A block diagram of the system is shown in Fig. 2.

The microwave circuit was conventional, similar to one used for paramagnetic resonance. The klystron source was normally stabilized to the sample cavity frequency by application of a small frequency modulation with phase detection to produce a stabilizing feedback signal;  $2K25$ ,  $2K50$ ,  $\overline{OK}291$ , and second harmonic generation from  $2K33$  klystrons were used at the different frequencies. The microwave power was fed into a hybrid junction having two of its side arms terminated with the sample cavity and matching sections, respectively. A crystal detector in the fourth arm was connected to the narrow-band amplifier. A very similar arrangement was described by the Berkeley<br>group.<sup>20</sup> group.

For the resonance experiments in germanium and silicon it is essential that oriented single crystal samples

 $19$  Recombination times were usually small compared with  $1/90$ second.<br><sup>20</sup> A. F. Kip, Physica **20**, 813 (1954).

be used, because of the striking anisotropies. A diskshaped sample with dimensions about 4 mm $\times$ 4 mm  $\times\frac{1}{2}$  mm with the disk face being a (110) plane, was found to be most useful. Since the sample was rotated about the normal to the disk,  $[001]$ ,  $[111]$ , and  $[110]$ directions could be made parallel to the magnetic field in this plane. These three orientations provide the most useful anisotropy data. Typically, the samples were etched with a CP-4 solution. The etching influenced only the photoconduction efficiency; we could see no effect of the etching on the measured scattering frequency.

## III. CYCLOTRON RESONANCE OF ELECTRONS IN GERMANIUM

Four separate resonance peaks due to electrons may occur for arbitrary alignment of magnetic field and crystal directions, as initially reported by Lax, Zeiger, Dexter, and Rosenblum.<sup>5</sup> One resonance is seen<sup>4</sup> when the magnetic field is parallel to the [100] axes. The symmetries of the resonances indicate that the electrons move on four or eight equivalent constant energy surfaces which are ellipsoids of revolution along the body diagonals or  $[111]$  axes. If the energy surfaces are at the zone edges, four ellipsoids are involved, otherwise, four pairs occur. There is no apparent way to distinguish the true situation from the resonance results. There is evidence from magnetic susceptibility studies<sup>21</sup> and other data<sup>22</sup> that the minima occur at the zone edges.

Shockley' derived the equation for the resonance effective mass  $m^*$  for ellipsoidal surfaces as follows:

$$
m^* = \left(\frac{m_1 m_2 m_3}{m_1 \alpha^2 + m_2 \beta^2 + m_3 \gamma^2}\right)^{\frac{1}{2}},\tag{3}
$$

where  $m_1$ ,  $m_2$ , and  $m_3$  are the effective masses along the three principal axes of the ellipsoid and  $\alpha$ ,  $\beta$ ,  $\gamma$  are the direction cosines of the angles the magnetic field makes with these axes. From measurements of the anisotropy of the effective mass for resonance, it is simple to evaluate the effective-mass values associated with the constant energy ellipsoids. Resonance effective-mass values are shown in Table I. These resonances were originally recognized as due to electrons by observing resonance of carriers produced by rf breakdown of impurity levels in *n*-germanium. At  $4^\circ K$ , the principal mass values of the constant energy surfaces are

TABLE I. Resonance effective-mass values of electrons in germanium for various directions of the magnetic field.

	F1007	<b>F1117</b>	$\lceil 110 \rceil$
$\it{m}^*$	$0.164 + 0.001$	$0.208 \pm 0.001$ $0.0819 + 0.0003$	$0.368 \pm 0.005$ $0.138 + 0.001$

<sup>&#</sup>x27; Stevens, Cleland, Crawford, and Schweinler, Phys. Rev. 100, 1084 (1955).

 $m_1 = (1.64 \pm 0.03)m_0$  and  $m_2 = m_3 = (0.0819 \pm 0.0003)m_0$ , where  $m_0$  is the mass of the free electron. The errors arise largely through difhculty in correctly orienting the sample in the magnetic field. A small angular error can produce a significant error in the apparent axial ratio of the energy ellipsoids. The error in alignment was responsible for the somewhat smaller axial ratio quoted in our preliminary report.<sup>5</sup> DKK have found by cyclotron resonance measurements that  $m_1 = 1.58m_0$  and  $m_2 = m_3 = 0.082m_0$ , with which our present results are in close agreement.

The constant energy surfaces are prolate or needle shaped ellipsoids of revolution with axial ratio of  $\sim$ 20 pointing along the body diagonals. The interpretation<sup>28</sup> of magnetoresistance measurements on  $n$ -germanium<sup>24</sup> yielded results indicating ellipsoids along the [111] axes with axial ratio of perhaps twenty. Piezoresistance measurements also indicated the  $\lceil 111 \rceil$  ellipsoid model.<sup>25</sup>

When the dc magnetic field is parallel to the rf electric field, longitudinal cyclotron resonance may be studied. In comparison with the transverse cyclotron resonance it is found that for some directions certain resonance peaks disappear. When the magnetic field is perpendicular to a principal plane of a constant energy ellipsoid, longitudinal resonance does not occur for electrons on that ellipsoid. This is a theoretical result checked by experiment. Thus, when the magnetic field and electric field are along a  $[111]$  direction, resonance occurs (with reduced intensity) for the three pairs of ellipsoids lying with their long axis 70' from the magnetic field and does not occur for the pair of ellipsoids lying with their long axis along the magnetic field. Actually, when cyclotron resonance can be resolved, the transverse orientation is much easier to study because the intensities remain substantially constant, and because of the difhculty in closely aligning the electric and magnetic fields in the longitudinal resonance.

### IV. CYCLOTRON RESONANCE OF ELECTRONS IN SILICON

The constant energy surfaces in silicon are three or six equivalent prolate ellipsoids pointing along the cube edges or  $\lceil 100 \rceil$  directions of the Brillouin zone.<sup>8,25,26</sup> Experiments on magnetoresistance of  $n$ -silicon<sup>26</sup> yielded a mass ratio of 5 for the energy ellipsoids and indicated their  $[100]$  orientation as did the piezoresistance meas<br>urements of Smith.<sup>25</sup> urements of Smith.

Cyclotron resonance measurements' showed that for arbitrary orientation three resonance peaks may occur and these peaks merge into one when the magnetic field is parallel to  $\lceil 111 \rceil$  directions. When the magnetic field is in the (110) plane, two ellipsoid pairs present the same aspect to the magnetic field direction and at

<sup>22</sup> B. Lax and J. G. Mavroides, Phys. Rev. 100, 1650 (1955).

<sup>23</sup> S. Meiboom and B. Abeles, Phys. Rev. 93, 1121 (1954); M. Shibuya, Phys. Rev. 95, 1385 (1954).<br>
<sup>24</sup> G. L. Pearson and H. Suhl, Phys. Rev. 83, 768 (1951).<br>
<sup>25</sup> C. S. Smith, Phys. Rev. 94, 42 (1954).

<sup>&</sup>lt;sup>26</sup> G. L. Pearson and C. Herring, Physica 20, 975 (1954).

TABLE II. Effective masses of electrons in silicon for various orientations of the magnetic field.

	1001	F111 T	[110]		<b>「100]</b>	F111 <sup>-</sup>	1107
$m^*$	$0.43 + 0.02$ $0.19 + 0.01$	$0.27 + 0.02$	$0.43 + 0.02$ $0.24 \pm 0.01$	m <sub>L</sub> $m_H$	$0.0438 + 0.003$ $0.284 \pm 0.001$	$0.0426 \pm 0.002$ $0.376 \pm 0.001$	$0.0430 + 0.003$ $0.352 \pm 0.004$

most two electron resonances are observed. Although cyclotron resonance does not distinguish the k value at which the band minima lie, there is reason<sup>27,28</sup> to believe that the minima do not occur at the edge of the Brillouin zone. Thus, there are probably three pairs of constant energy ellipsoids.

In Table II are listed effective masses for resonance for various orientations of the magnetic field. Using Eq.  $(3)$ , we may solve for the mass parameters of the constant energy surfaces. The longitudinal mass is  $m_1 = (0.98 \pm 0.04) m_0$  and the transverse mass is  $m_2 = m_3$  $= (0.19 \pm 0.01) m_0$ , as originally reported<sup>8</sup> and confirmed  $= (0.19 \pm 0.01) m_0$ , as originally reported<sup>8</sup> and confirmed<br>by DKK.<sup>10</sup> It was originally possible to ascertain the ellipsoid model through selective excitation of electrons by the infrared and relative suppression of the hole resonances. The ellipsoids were associated with electrons by assuming the results of the piezoresistance<sup>25</sup> and magnetoresistance<sup>26</sup> experiments.

# V. CYCLOTRON RESONANCE OF HOLES IN GERMANIUM

At the top of the valence band near  $k=0$ , the valence energy band structure of germanium can be described by the two functions $6,9$ 

$$
\epsilon(k) = -\frac{h^2}{2m_0} \{ A k^2 \pm \left[ B^2 k^4 + C^2 (k_x^2 k_y^2 + k_x^2 k_z^2 + k_y^2 k_z^2) \right] \}, \quad (4)
$$

where  $A$ ,  $B$ , and  $C$  are constants. The derivation of this expression is due to Dresselhaus, Kip, and Kittel.<sup>9,10</sup> Holes normally reside in these two bands and possess effective masses of approximately  $m_l \approx 0.043m_0$  and  $m_H=0.34m_0$ . The anisotropy which is introduced by the constant C affects the heavy or slow holes more importantly than the light or fast holes. The experimental anisotropy of cyclotron resonance of holes when the magnetic field is in the (110) plane is indicated in Table III.

A third valence band<sup>29</sup> probably exists with an energy  $\sim$ 0.3 ev below these two valence bands at  $k=0$ . Its energy should be<sup>10</sup>  $\epsilon = -(\hbar^2/2m_0)Ak^2$ . This band is not normally occupied, and no cyclotron resonance has been detected for it.

The experimental data used for determining the parameters  $A$ ,  $B$ , and  $C$  were the magnetic field values for the heavy mass hole peaks with  $H$  along the [001]

TABLE III. Experimental values of effective masses for cyclotron resonance of holes in germanium.

01		F <sub>100</sub>	[111]	[110]
-0.02 -0.01	mг. mн	$0.0438 + 0.003$ $0.284 \pm 0.001$	$0.0426 \pm 0.002$ $0.376 \pm 0.001$	$0.0430 \pm 0.003$ $0.352 \pm 0.004$

and  $\lceil 111 \rceil$  directions; and the field value for the light hole with  $H$  along the [111]. For the two heavy mass hole peaks, corrections must be applied to the experimental peak positions, as discussed in ZLD, to obtain the resonance magnetic field values for the center contour about the constant energy surface. The center contour cyclotron resonance fields are functions of  $A, B$ , and C, which can be obtained as power series expansions from the Shockley integral. The corrected values of A, B, and C obtained by this method are:  $A = -13.1$  $\pm 0.4,$   $|B| = 8.3 \pm 0.6,$   $|C| = 12.5 \pm 0.5.$  The quoted errors include an estimate of the effect of possible misalignment of the crystal. Our preliminary results,  $A = -13.6,$   $|B| = 9.1,$   $|C| = 11.2$ , were in rough agreement with these values, but did not take into account the effects of holes with nonzero wave vector,  $k_H$ , in the magnetic field direction. DKK reported  $A = -13.2$ 0.1,  $|B| = 8.9 \pm 0.05$ , and  $|C| = 10.6 \pm 0.2$ , taking approximate account of the holes with  $k_H \neq 0$ .

The shape of the constant energy curve in the (110) plane through  $k_H=0$  is shown in Fig. 3. The deviation from spherical energy surfaces indicated in Eq. (3) produces the anisotropy of magnetoresistance<sup>24</sup> and<br>piezoresistance.<sup>25</sup> piezoresistance.

The anisotropy of  $\epsilon(k)$  has a strong effect on the resonance line shape and even causes a resonant absorption at harmonics of the fundamental cyclotron frequency of the heavy holes. The fundamental resonance condition for the heavy holes is  $\omega=n(eH/m_h *c)$ , with  $n=1$ . We have also observed the second and third harmonic resonances  $n=2$  and  $n=3$ , respectively, for



FIG. 3. The germanium valence band constant energy contour  $\epsilon(\mathbf{k})$  vs (**k**), through  $k=0$  in the (110) plane.

<sup>&#</sup>x27;r W. Kohn, Phys. Rev. 98, 1561(A) (1955). 2' G. G. MacFarlane and V. Roberts, Phys. Rev. 98, 1865  $(1955)$ .<br><sup>29</sup> R. J. Elliott, Phys. Rev. 96, 266 (1954).



FIG. 4. Copy of cyclotron resonance trace in germanium near xternal magnetic field was about 10°<br>from [100] direction. Orientation was selected to show the eight resonance observ

At most orientations the second harmonic resonance is<br>obscured by the electron shape was distorted by the electron second possured by the resonance of the electrons which are is not shown. The high absorption persisted to obscured by the resonance of the electrons which are also excited by the infrared. The third harmonic is visible in many orientations and its anisotropy has been plotted to confirm its identification. A pronounced difficult to study because of the presence of the strong anisotropy of its intensity has been observed but is

There is some evidence that the third harmonic ds to disappear when the magnetic field parallel to the  $\left[\begin{smallmatrix} 111\end{smallmatrix}\right]$  axes and the second harmonics tend and [110] directions. These results are in agreement with the theoretical results described in ZLD. When the magnetic field is somewhat out of the (110) plane the harmonic resonances change intensity very strongly. In st orientations, the harmonic intensities are small but in some orientations we have observed that the third harmonic intensity becomes as large as that of the fundamental and the second harmonic int tain orientations has been up to one-third as intens sensitive to orientation, are quite surprising and diffi-



of heavy holes in germanium for  $H_0$  parallel to a [100] axis. The dashed line is a mirror image and indicates the asymmetry.

<sup>30</sup> The harmonic resonances were apparently first seen by A. F. Kip (see reference 19) and w<br>Phys. Rev. **98,** 1560(A) (1955).

cult to explain on the basis of the present theory of harmonic intensities, described in ZLD.

A trace of an experimental resonance curve appears in Fig. 4, and shows the eight resonances we have seen in germanium. Four electron resonances, the light-hole resonance and the first, second, and third harmonics o nance, are all apparent for this orientation which was about  $10^{\circ}$  out of the (110) plane.

Since the constant-energy surface has an irregular shape, the slices for various  $k_H$  values all have different average effective masses associated with them as discussed in ZLD and in Sec. 5 of DKK. Thus, the inteabsorption. This effect is indicated in nium near Fig. 5, which shows the experimental line shape of the heavy hole resonance when the magnetic field is along 100] direction. The base line was obtained by g the light pipe and eliminating the photo  $0 \text{ Mc/sec.}^{30}$  conductivity. On the low-field



FIG. 6. Experimental trace of fundamental cyclotron resonance of heavy holes in germanium for  $H_0$  parallel to a [111] axis. The dashed line is a mirror image and indicates the asymmetry.

elds and presents a marked difference from the behavior of a Lorentzian or Gaussian reso mance is indicated in the figure.<br>mined by the distribution of  $k_H$ <br>n effects of scattering; in some<br>30% wider than the scattering metry of the resonance is indicated i e li orientations the line is  $30\%$  wider than the scattering line width. A theoretical resonance line shape for  $H$ along a  $\lceil 100 \rceil$  was derived by ZLD, for a different and compared with the shape o for  $k_H$ =0. The effect of nonzero  $k_H$  was shown to  $\frac{\text{where } \pi R}{\text{increase the absorption on the high-field side of the}}$ peak as well as to shift the peak. When the magnetic field is along [111] directions, the nonzero  $k_H$  contributes to the low-field tail. An experimental trace is shown in Fig. 6. For magnetic field parallel to  $\lceil 110 \rceil$ directions, the effect of nonzero  $k_H$  is to tend to flatten the peak in a rather symmetrical manner. Theoretical FIG. 5. Experimental trace of fundamental cyclotron resonance curves derived by ZLD and the experimental line shapes show similar trends. Theoretically, the resonance s Lorentzian and narrowest when the magnetic field is  $30^{\circ}$  from [100] in the (110) plane. The by R. N. Dexter, then them is 50  $\mu$  from  $\mu$  to  $\mu$  and  $\mu$  the  $\mu$  and  $\mu$  and  $\mu$  experiments are consistent with this but difficult to

study quantitatively because of the presence of the electron resonances. Selective excitation experiments have been started to try to see hole resonances alone.

# VI. CYCLOTRON RESONANCE OF HOLES IN SILICON

The resonance results for holes in silicon initially studied by Dexter and Lax<sup>7</sup> are very similar to those found for holes in germanium. The top of the valence band consists of two surfaces of different curvature centered at  $k=0$  and degenerate there. The average masses of the two kinds of holes are  $m_l \approx 0.17m_0$ , and  $m_H \sim 0.52m_0$ . The energy function is of the form found for germanium  $(Eq. (3))$  as determined by the resonance results. Experimental values of effective masses for resonance are shown in Table IV. The constants were found, by the method described for germanium, to be:  $A = -4.0 \pm 0.1$ ,  $|B| = 1.1 \pm 0.4$ , and  $|C| = 4.1 \pm 0.4$ . In confirmation of the preliminary results obtained by two of us<sup>7</sup> DKK found  $A = -4.0 \pm 0.2$ ,  $|B| = 1.1 \pm 0.5$ ,  $C=4.0\pm0.5$ , taking into account  $k_H\neq0$ . In all these experiments, a major experimental error was due to errors in alignment of the magnetic held which might have been  $\sim 2^{\circ}$  out of the experimental (110) plane. Another difficulty arose from overlap of the electron

TABLE IV. Experimental values of effective masses for cyclotron resonance of holes in silicon.

	F <sub>100</sub>	[111]	<b>F1107</b>
m 1.	$0.171 + 0.006$	$0.157 + 0.005$	$0.163 + 0.005$
$m_H$	$0.46 \pm 0.01$	$0.57 \pm 0.01$	$0.53 \pm 0.01$

and hole resonance. The relatively large error in  $|B|$ arises because of the way the data are combined.

The anisotropy of the mass of the heavy holes is about 20% and that of the light holes  $9\%$  in the (110) plane. Considerations of the line shape asymmetry apply to silicon as well as germanium, but line shape studies have been complicated by the presence of the electron resonances which also tended to obscure the second harmonic. The third harmonic resonance of the heavy holes falls very near to the light-hole resonance and could only be distinguished (even for the highest  $\omega\tau$  values) when the magnetic field was near the [111] directions; an experimental trace is shown in Fig. 7. The trace also shows the electron resonance and the light- and heavy-hole resonances.

Since the theory indicates that the third harmonic resonance should be absent when the magnetic field is parallel to the  $\lceil 111 \rceil$  axes, we attempted to resolve the apparent disagreement. The resonance was reproduced on separate experimental runs and appeared at the expected field for third harmonic resonance within a  $2\%$ experimental error. It is possible that a slight misorientation could be significant, but the lack of agreement of theory and experiment is unclear. There may, perhaps, be some longitudinal rf electric 6eld present



FIG. 7. Copy of cyclotron resonance trace in silicon near 4'K and 23 000 Mc/sec; external magnetic field was nearly parallel to  $\lceil 111 \rceil$  axis.

under the conditions of the experiment, and this would give a third harmonic resonance in the  $\lceil 111 \rceil$  direction, without significant increase of the fundamental resonance intensity.

## VII. MISCELLANEOUS

The scattering times of light and heavy holes is nearly the same experimentally for both Ge and Si. Adams<sup>31</sup> has shown that this may be true if intraband scattering is of major importance for the heavy holes and interband scattering is of major importance for the light holes; in this case the final density of states for the two holes is the same, being that of heavy holes. for the two holes is the same, being that of heavy holes.<br>In the purest samples, typical values of  $\tau$  are  $6-8\times10^{-11}$ second for both germanium and silicon. The highest second for both germanium and silicon. The highest<br>values of  $\tau$  we have found in germanium were  $1.4 \times 10^{-10}$ values of  $\tau$  we have found in germanium were  $1.4 \times 10^{-10}$ <br>second for the holes and  $1.3 \times 10^{-11}$  second for the electrons in the same sample at 4'K. Line widths were measured between points of half power absorption. While a systematic study of scattering has yet to be made, it is clear that neutral impurity scattering can become important in our samples at liquid helium temperatures. Fletcher  $et$   $al.^{32}$  have found that at ultra-low rf power levels  $(10^{-9}$  watt or less) the electron resonance lines narrow by a factor of two in lowering the temperature from  $4.2^{\circ}K$  to  $1.4^{\circ}K$ . Operating at rf power levels above one microwatt, we find in our experiments below 4.2'K that the line widths remain substantially constant. It is probable the electron temperature is raised above the lattice temperature by the rf energy which the carriers absorb. This effect can become very important at low temperatures where few phonons exist to produce equilibrium between electron<br>and lattice.<sup>33</sup> and lattice.

At  $4.2^{\circ}$ K, the ratio of heavy- to light-hole resonance intensity in germanium is about 2.6. The theoretical

<sup>22</sup> Hetcher, Yager, and Merritt, Phys. Rev. 100, 747 (1955).<br><sup>23</sup> We are indebted to Dr. A. Overhauser for a letter discussing the equilibrium problem.

<sup>3&#</sup>x27; E. N. Adams, II, Westinghouse Research Reports 60-94769-2 R1, 1955 (unpublished).

ratio is

$$
\frac{n_{H}\tau_{H}/m_{H}}{n_{L}\tau_{L}/m_{L}} \approx \left(\frac{m_{H}}{m_{L}}\right)^{\frac{1}{2}} \approx 2.7,\tag{5}
$$

assuming that  $n \propto m^{\frac{3}{2}}$  and  $\tau_L = \tau_H$ .

At low power levels and temperatures below  $\sim 2^{\circ}$ K, the intensity ratio gradually changes and the hole resonances tend to disappear as first observed by resonances tend to disappear as first observed b<br>Fletcher, Yager, and Merritt.<sup>32</sup> The onset of quantum effects at low temperatures where small quantum numbers are involved apparently tends to change the resonance behavior of holes, and additional resonances are expected to occur.<sup>34</sup>

With some selectively doped samples, unequal numbers of holes and electrons appear in equilibrium with radiation in the intrinsic range. For example, a galliumdoped sample<sup>35</sup> at  $4.2^{\circ}$ K gave detectable photoconductivity only by electrons, as recognized by the cyclotron resonance spectrum. Such properties were usually a function of time. Cyclotron resonance can yield a measurement of the relative number of carriers of each type, their effective masses, and their respective scattering and recombination times. Such measurements may prove very informative for studying photoconduction and scattering mechanisms, for example.

In pure germanium, the freeze-out temperature for the extrinsic carriers seems to be about 8'K. Above this temperature, high carrier densities usually cause<br>effects which tend to obscure the cyclotron resonance.<sup>12</sup> Since effective mass may change with temperature, we are attempting to raise the freeze-out temperature with selectively doped samples (doped with Au, Mn, etc.) and to extend the resonance measurements to higher temperatures. It appears likely that resonance could be resolved with microwave frequencies at temperatures as high as  $\sim$  20°K, if carrier densities were reduced. In preliminary experiments we have found that by warming the sample to about  $15^{\circ}K$  the anisotropy of the hole resonance in germanium has decreased appreciably. It is not clear whether this is due to a change of band parameters near  $k=0$ , or to the presence of a quartic term of momentum in the energy.

In the microwave breakdown of impurity levels, an oscillation was noted in several cases where the internal electric field following breakdown was reduced by the screening effect of the free charge carriers to a value below the breakdown field. The excitation relaxed until the electric field within the sample again rose to the breakdown value. The typical relaxation frequency was of the order of 20 kc/sec and could be varied with the magnetic Geld and rf power level. The relation between the relaxation frequency and the recombination time was not clear.

We tried briefly, without success, to detect millimeter radiation at harmonics of the heavy hole resonance while driving their fundamental cyclotron resonance at 23 000 Mc/sec.

Efforts to observe resonance of carriers in higher energy bands by using selective excitation have been unsuccessful. The carriers probably did not exist long enough in the excited states.

Cyclotron resonance experiments in new materials have been largely unsuccessful thus far. In semiconductors, such as InSb, AISb, and PbS, the scattering time in our samples has been too small for resolving the resonance.

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<sup>84</sup> J. W. Lnttinger and W. Kohn, Phys. Rev. 97, <sup>869</sup> (1955). <sup>85</sup> Sample provided by Dr. Tyler of General Electric Research Laboratory.