

# Low-Temperature Impurity Conduction and Magnetoresistivity in *n*-Type Germanium

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The resistivity of several lightly doped (Sb) *n*-type germanium samples has been calculated and compared with values measured at 2.5°K. An order of magnitude agreement has been obtained for a span of five orders of magnitude in the resistivities. It has been assumed that the mechanism of conductivity consists of jumping of electrons from occupied to empty donors. The number of charge carriers has been determined by calculating the number of "free" donor ions. The "trapped" donor ions, due to the presence of charged compensating acceptors, have been assumed not to participate in the conduction process. The effect of a constant magnetic field on impurity conduction has also been investigated and a simple theory of magnetoresistivity is presented. The calculated magnetoresistive ratio is in order of magnitude agreement with the measured value.

## I. INTRODUCTION

HUNG and Gliessman<sup>1</sup> were the first to find that the log resistivity versus reciprocal temperature curve of *n*-type germanium exhibits a sudden decrease of slope at low temperatures. The flat part of the resistivity curve is attributed to impurity conduction which is believed to follow different mechanisms<sup>2</sup> depending on the amount of doping. Here we shall only be concerned with lightly doped samples, having a donor concentration  $N_D < 10^{16}/\text{cc}$ , and assume that in this case the interaction among the donors is very weak. The limit set above for light doping is supported by the fact that the ionization energy of donors in germanium is practically constant<sup>3</sup> up to  $N_D \approx 10^{16}/\text{cc}$ . Further support for this limit is furnished by calculations of Baltensperger<sup>4</sup> and Erginsoy,<sup>5</sup> who have studied the conditions of impurity band formation and found that the broadening of the ground-state impurity level becomes significant only if  $N_D > 10^{16}/\text{cc}$ .

According to current views<sup>2</sup> impurity conduction in lightly doped *n*-type germanium is not possible unless compensating acceptors ( $N_A/\text{cc}$ ) are present. As a result positive donor ions and negative acceptor ions appear and the electric conduction is pictured as jumping of electrons from neutral to ionized donors. If this is the mechanism, then the conductivity of weakly compensated *n*-type germanium should initially increase with increasing compensation ( $K = N_A/N_D$ ) since the number of empty donors, to which electrons can jump, increases. This effect has been observed by Fritzsche.<sup>2</sup>

## II. JUMPING MECHANISM

The first step in treating this problem was made by Conwell<sup>6</sup> who assumed a regular distribution of impurities and pictured a neutral donor adjacent to an

ionized donor as a system similar to that of an  $\text{H}_2^+$  molecule ion embedded in a medium of dielectric constant  $\kappa = 16$ . To a certain approximation<sup>7</sup> the electron of the above system can be thought of as "jumping" back and forth between the two donor ions. Relating the jumping to diffusion, Conwell arrives at a conductivity<sup>8</sup> of

$$\sigma = \frac{N_A e^2 (2R_s)^2 \Delta E}{kT h} \quad (1)$$

In Eq. (1)  $2R_s$  is the distance between donors, which, neglecting the small amount of compensating acceptors, is determined from

$$(4\pi/3)R_s^3 = N_D^{-1}. \quad (2)$$

The other quantities in Eq. (1) have their customary meaning, except  $\Delta E$ , which is the difference in the energy between the antisymmetric and symmetric states of the donor-donor ion system. We shall discuss this quantity later.

Equation (1) predicts an incorrect temperature dependence, since it is known from experiments<sup>2</sup> that in the low-temperature region the conductivity follows an expression of the form

$$\sigma = C(T) e^{-\epsilon/kT}, \quad (3)$$

where  $\epsilon$  denotes the activation energy of the conduction process. In what follows we shall show that Conwell's theory coupled with theories of Mott<sup>9</sup> and Price<sup>10,11</sup> can be brought to the form of Eq. (3).

According to Eq. (1) the maximum number of electrons able to jump is equal to the number of acceptor atoms, which, in turn, at low temperatures, is

<sup>7</sup> H. Eyring, J. Walter, and G. E. Kimball, *Quantum Chemistry* (John Wiley & Sons, Inc., New York, 1958), p. 192.

<sup>8</sup> If the quantities in Eq. (1) are expressed in cgs units, the  $\text{ohm}^{-1} \text{cm}^{-1}$  value is obtained by dividing  $\sigma$  by  $9 \times 10^{11}$ .

<sup>9</sup> N. F. Mott, *Can. J. Phys.* **34**, 1356 (1956).

<sup>10</sup> P. J. Price, *IBM J. Research Develop.* **2**, 123 (1958).

<sup>11</sup> For the simplest version of the model, see also the appendix by P. J. Price in a paper by S. H. Koenig and G. R. Gunther-Mohr, *J. Phys. Chem. Solids* **2**, 268 (1957).

<sup>1</sup> C. S. Hung and J. R. Gliessman, *Phys. Rev.* **79**, 726 (1950).

<sup>2</sup> H. Fritzsche, *J. Phys. Chem. Solids* **6**, 69 (1958). This paper also contains references to earlier literature.

<sup>3</sup> P. P. Debye and E. M. Conwell, *Phys. Rev.* **93**, 693 (1954).

<sup>4</sup> W. Baltensperger, *Phil. Mag.* **44**, 1355 (1953).

<sup>5</sup> C. Erginsoy, *Phys. Rev.* **88**, 893 (1952).

<sup>6</sup> E. M. Conwell, *Phys. Rev.* **103**, 51 (1956).

equal to the number of donor ions. Mott, however, has suggested that only a fraction of the donor ions is "free" to participate in conduction while the remaining fraction is "trapped" in the vicinity of acceptor ions. Energetically, the occupancy of trapped donor ions by electrons is unfavorable and, therefore, we shall assume that they do not take part in the conduction process unless they are thermally activated. Mott's idea was quantitatively formulated by Price who has performed a statistical calculation and has shown that for weakly compensated samples the average number of empty donors occupying "free" sites is

$$\bar{n} \approx N_A K^{-1} [(1-rK)K/r]^{\frac{1}{2}} e^{-W/2kT}. \quad (4)$$

Equation (4) is a limiting case of a more general expression<sup>10,11</sup> and valid only if  $e^{-W/kT} \ll K$ . In Eq. (4)  $r$  is that number of donor sites around an acceptor ion which may become trap sites for donor ions. Since we have assumed a regular distribution of impurities in the germanium crystal and subdivided the crystal volume into spheres of radius  $R_s$ , it is evident that at very small degrees of compensation an "acceptor sphere" can be surrounded by 12 nearest "donor spheres." We shall assume that any one of the 12 sites may become a trap site with equal probability and, for this reason, we shall use the  $r=12$  value in the numerical calculation. Here we must add that Eq. (4) is valid only for the case when out of the  $r$  trap sites only one is occupied at a time. According to Price, the quantity  $W$  in Eq. (4) is the binding energy of a trapped donor ion. If in place of  $N_A$  in Eq. (1) one substitutes  $\bar{n}$  from Eq. (4) the resulting expression for the conductivity is that of Conwell's multiplied by a factor of  $K^{-1} [(1-rK)K/r]^{\frac{1}{2}} e^{-W/2kT}$ . Qualitatively, the conductivity is now of the same form as the expression in Eq. (3), as required by experiments. Furthermore, it is seen that the experimental activation energy  $\epsilon$  should equal  $W/2$ . Assuming that the donor ion-acceptor ion distance is approximately equal to the donor-donor distance, one expects  $W = e^2 / [\kappa(2R_s)]$ . This turns out about a factor of  $\frac{1}{2}$  too small to satisfy  $\epsilon = W/2$ .<sup>2</sup> An accurate prediction of  $\epsilon$  would in itself be a complicated problem, mainly because of the long-range nature of the Coulomb forces and because of the deviation from regularity in the impurity distribution. For this reason, although speculations have been made,<sup>2,9</sup> in the following numerical calculations we choose  $W$  exactly equal to  $2\epsilon$  and take  $\epsilon$  from measurements.<sup>2</sup>

### III. CALCULATION

The above considerations enable us now to calculate resistivities and compare them with measured values. Recently, Fritzsche<sup>2</sup> carried out extensive measurements of resistivity on Sb-doped germanium at low temperatures. For samples with  $N_D < 10^{16}/\text{cc}$  the amount of compensating acceptors was calculated<sup>2</sup> to be between  $0.02N_D$  and  $0.06N_D$ . In view of this uncer-

tainty in  $K$ , for the purposes of the present calculation an average value of  $K=0.04$  will be used. It follows from Eq. (4) and (2) that the  $K$  dependence of  $\sigma$  is given by  $N_D [(1-12K)K]^{\frac{1}{2}}$  so that use of  $K=0.02$  or use of  $K=0.06$  would roughly leave unchanged the conductivity value obtained with  $K=0.04$  at a given donor concentration  $N_D$ . This is so because the approximate  $\bar{n}$  has a maximum at  $K=0.04$  if  $r=12$ .

In order to calculate  $\Delta E$ , one has to specify the wave function of the donor electron and the approximation in which the energies of the symmetric and antisymmetric states of the donor-empty donor system are calculated. This quantity has already been given by Conwell<sup>6</sup> but we shall briefly rederive it since many of the expressions will be needed in the discussion of the magnetoresistivity. Instead of using a "pancake-like" wave function, corresponding to the more exact formulation of the effective mass theory,<sup>12</sup> we choose

$$\psi^0 = (\pi a_0^{*3})^{-\frac{1}{2}} \exp(-r/a_0^*), \quad (6)$$

which corresponds to a donor Hamiltonian

$$H_d^0 = -\frac{\hbar^2}{2m^*} \Delta - \frac{e^2}{\kappa r}, \quad (7)$$

with one average effective mass  $m^*$ . In this case the energy spectrum is "hydrogenic" and the ionization energy is given by

$$E_0 = -\frac{1}{2} \frac{e^2}{\kappa a_0^*}, \quad a_0^* = a_0 \frac{\kappa}{(m^*/m_0)}, \quad (8)$$

where  $a_0$  is the first Bohr radius and  $m_0$  is the free electronic mass.

As Kohn<sup>12</sup> suggested, one could choose the average effective mass in Eqs. (7) and (6) so that upon substituting it in Eq. (8) the same energy is obtained as in the more exact theory. This is  $9.2 \times 10^{-3}$  ev,<sup>12</sup> whereas recent optical measurements of Fan and Fisher<sup>13</sup> at liquid He temperatures led to the value of  $9.8 \times 10^{-3}$  ev. To take a rough account of the central cell correction,<sup>12</sup> which is supposed to be mainly responsible for the small discrepancy between the measured and calculated values, we have chosen an effective mass of  $m^* = 0.185m_0$ . This value, when substituted in Eq. (8), yields the experimental value of the ionization energy. In the present model the Hamiltonian of the donor-empty donor system is

$$H = -\frac{\hbar^2}{2m^*} \Delta - \frac{e^2}{\kappa r_a} - \frac{e^2}{\kappa r_b} + \frac{e^2}{\kappa(2R_s)}, \quad (9)$$

where  $a$  and  $b$  refer to the donor ions as "nuclei."

<sup>12</sup> For a review of this problem, see W. Kohn, in *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1957), Vol. 5, p. 258.

<sup>13</sup> H. Y. Fan and P. Fisher, *J. Phys. Chem. Solids* **8**, 270 (1959).

To the approximation that the overlap integral is neglected, a first order perturbation calculation<sup>7</sup> based on the use of

$$\psi = (1/\sqrt{2})(\psi_a^0 \pm \psi_b^0), \quad (10)$$

and  $H$  in Eq. (9) leads to  $\Delta E = 2I_0$ , where

$$I_0 = \frac{e^2}{\kappa} \int \frac{\psi_a^0 \psi_b^0}{r_b} dv = \left[ 1 + 2 \left( \frac{R_s}{a_0^*} \right) \right] e^{-2(R_s/a_0^*)} \frac{1}{\kappa a_0^*}. \quad (11)$$

In Columns 1 and 2 of Table I we have listed the code numbers and donor concentrations of some of the samples investigated by Fritzsche<sup>2</sup> and considered here. Column 3 contains the measured activation energies which can be compared with the values in Column 4, calculated from  $2W = e^2/(\kappa R_s)$ . In Column 5 are the  $R_s$  values, calculated with Eq. (2), and in Column 6 the  $\Delta E$  values, calculated with Eq. (11). The  $\bar{n}$  values, calculated with Eq. (4), are listed in Column 7. The experimental resistivity values at 2.5°K are given in Column 8 and the ratio of the experimental values to the calculated ones for  $T = 2.5^\circ\text{K}$  is shown in Column 9.

#### IV. DISCUSSION

It is seen from Column 9 of Table I that the agreement of theory with experiment is surprisingly good in view of the very simplified model applied. An order of magnitude agreement is obtained for a span of five orders of magnitude in the resistivities. It is interesting that ignoring the randomness in impurity distribution, which one feels should be closer to the actual situation, the assumption of a regular distribution, or as one might say an "impurity sublattice" works so well. It is less surprising that use of a spherically symmetric donor wave function seems to be sufficient. The reason for this is that a superposition of pancake-like wave functions, corresponding to the "multivalley" structure of the conduction band roughly approximates spherical symmetry.<sup>12</sup>

Another interesting feature is the approximate constancy of the number of free empty donors,  $\bar{n}$ , as it is seen from Column 7 of Table I. This suggests that the variation in resistivity does not come from the variation in the number of carriers but from that in the jumping

frequency  $\nu = \Delta E/h$ . If this prediction of the model is correct, then the Hall constant of the samples considered should be nearly equal at  $T = 2.5^\circ\text{K}$ . Unfortunately, measurements of the Hall constant<sup>2</sup> could not be extended into that temperature region. Noting that the activation energy decreases with decreasing impurity content, the constancy of  $\bar{n}$  values can be explained as follows. From Eq. (4) it is seen that  $\bar{n}$  increases with decreasing  $W$ . It is also seen that  $\bar{n}$  decreases with decreasing  $N_D$ . As a result these opposite tendencies compensate one another.<sup>14</sup> Whether it is so in a much lower concentration region than that we have considered is an open question until experiments are conducted in that region. Since it is apparent from Fritzsche's measurements<sup>2</sup> that the temperature at which the change in the resistivity occurs shifts to lower values with decreasing impurity concentration, the measurements must be carried out below  $2.5^\circ\text{K}$ .

#### V. MAGNETORESISTIVITY

In this section we wish to investigate the effect of a constant magnetic field on the jumping mechanism of impurity conduction. It is known from the theory of the Zeeman effect<sup>15</sup> that for strong magnetic fields and large electron orbits the dominating interaction term in the Hamiltonian of a valence electron is quadratic in the magnetic field  $H$ . For the magnetic field along the  $z$  axis, the donor Hamiltonian can be written<sup>15</sup> as

$$H_d = H_d^0 + \eta, \quad (12)$$

where  $H_d^0$  is given in Eq. (7) and

$$\eta = \frac{1}{2} m^* \lambda^2 r^2 \sin^2 \vartheta, \quad \lambda = -eH/2m^*c. \quad (13)$$

We shall consider  $\eta$  as a perturbation and want to find the first-order change in the donor wave function, due to the presence of the magnetic field. According to standard procedure,<sup>16</sup> the perturbed wave function is given by

$$\psi_i = \psi^0 + \sum_i' \frac{\int \psi_i^* \eta \psi^0 dv}{-(E_0 - E_i)}, \quad (14)$$

where  $\psi^0$  and  $-E_0$  are the unperturbed wave function and energy, given by Eqs. (6) and (8), respectively, and the  $\psi_i$ 's are hydrogen-like functions of energy states  $-E_i$ . Retaining only the first term of the series in Eq. (14) and changing to the obvious notation below, one obtains

$$\varphi = \psi_{1s} + \alpha \psi_{2s}, \quad \alpha = \frac{1}{2} m^* \lambda^2 \frac{\int \psi_{2s}(r^2 \sin^2 \vartheta) \psi_{1s} dv}{E_{1s} - E_{2s}}, \quad (15)$$

<sup>14</sup> We have to note here again that Eq. (4) is a limiting case and under other circumstances one has to use another expression to calculate  $\bar{n}$ . In this regard see the appendix by Price mentioned in reference 11.

<sup>15</sup> L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1949), p. 286.

<sup>16</sup> See reference 15, p. 149.

TABLE I. Quantities entering into the calculation of resistivities of *n*-type Ge samples.

Code No.	$N_D$ in cm <sup>-3</sup>	$\epsilon$ in 10 <sup>-3</sup> ev	$2W$ in 10 <sup>-3</sup> ev	$R_s$ in Å	$\Delta E$ in 10 <sup>-3</sup> ev	$\bar{n}$ in cm <sup>-3</sup>	$\rho_{\text{exp}}$ at $T = 2.5^\circ\text{K}$ in ohm-cm	$\rho_{\text{calc}}/\rho_{\text{exp}}$ at $T = 2.5^\circ\text{K}$ in ohm-cm
-2	$9.3 \times 10^{14}$	0.81 <sup>a</sup>	0.71	635	0.000101	$2.9 \times 10^{11}$	$7 \times 10^{11}$	6
-5	$1.6 \times 10^{15}$	0.99	0.84	530	0.00830	$6.8 \times 10^{11}$	$5.8 \times 10^9$	6.6
-7	$2.3 \times 10^{15}$	1.1	0.96	469	0.106	$5.8 \times 10^{11}$	$3.2 \times 10^8$	3.2
-8	$3.0 \times 10^{15}$	1.2	1.0	430	0.543	$4.8 \times 10^{11}$	$5.0 \times 10^7$	1.7
-10	$5.2 \times 10^{15}$	1.5	1.3	358	10.5	$2.1 \times 10^{11}$	$5.6 \times 10^6$	1.1
-12	$8.5 \times 10^{15}$	1.6	1.5	304	95.9	$2.1 \times 10^{11}$	$1.6 \times 10^6$	2.1

<sup>a</sup> Extrapolated from an  $\epsilon$  versus  $N_D$  graph.

where

$$\psi_{2s} = \frac{1}{4}(2\pi a_0^{*3})^{-\frac{1}{2}} e^{-\frac{1}{2}(r/a_0^*)} (2 - r/a_0^*),$$

and

$$E_{2s} = \frac{1}{4}E_{1s}.$$

In order to obtain the conductivity in the magnetic field,  $\sigma_H$ , one has to calculate  $\Delta E_H$ . Corresponding to the approximation used in previous sections

$$\Delta E_H = 2 \frac{e^2}{\kappa} \int \frac{\varphi_a \varphi_b}{r_b} dv, \quad (16)$$

where the  $\varphi$ 's are given in Eq. (15). It is seen that the conductivity

$$\sigma_H = \frac{\bar{n} e^2}{kT} \frac{(2R_s)^2 \Delta E_H}{h} \quad (17)$$

is isotropic in our lowest approximation because the donor wave function in Eq. (15) is spherically symmetric. For this reason, in the present theory the longitudinal and transverse magnetoresistive ratio are equal. This situation is very different from the case of conduction in the conduction band, since there the magnetoresistive ratio very strongly depends on the angle between the current and magnetic field.<sup>17</sup> Assuming that the number of "free" empty donors (e.g., the number of charge carriers  $\bar{n}$ ) is not affected by the magnetic field, the magnetoresistive ratio is given by

$$\zeta = \frac{\rho_H - \rho}{\rho_H} = 1 - \frac{\sigma_H}{\sigma} = 1 - \frac{\Delta E_H}{\Delta E}. \quad (18)$$

Dropping the small term in  $\alpha^2$  in Eq. (16) one can rewrite Eq. (18) as

$$\zeta = -\alpha \frac{I_1 + I_2}{I_0}, \quad (19)$$

where  $I_0$  is defined in Eq. (11) and

$$I_1 = \frac{e^2}{\kappa} \int \frac{\psi_{2s(a)} \psi_{1s(b)}}{r_b} dv, \quad I_2 = \frac{e^2}{\kappa} \int \frac{\psi_{1s(a)} \psi_{2s(b)}}{r_b} dv.$$

Now we want to compare theory with experiment. The only measurement of the magnetoresistive ratio on Sb-doped germanium in the low- $T$  and low- $N_D$  region this author is aware of is that of Fritzsche and Lark-Horowitz.<sup>18,19</sup> They measured the magnetoresistive ratio on a sample, denoted by Sb-15, at  $T = 4.2^\circ\text{K}$  in a magnetic field of  $3.5 \times 10^3$  Gauss. The Hall coefficient of this sample at  $T = 297^\circ\text{K}$  is  $R = 10^3 \text{ cm}^3 \text{ coulomb}^{-1}$ . Using  $R = 1(N_D - N_A)ec$  and assuming a small compensation,

<sup>17</sup> For a review of this problem see H. Brooks, *Advances in Electronics and Electron Physics*, edited by L. Marton (Academic Press, Inc., New York, 1955), Vol. 7, p. 85.

<sup>18</sup> H. Fritzsche and K. Lark-Horowitz, *Physica* **20**, 834 (1954).

<sup>19</sup> See also H. Fritzsche, *Phys. Rev.* **99**, 406 (1955), where a sample, denoted by Sb-15-2, has apparently the same characteristics as Sb-15 of the previous paper. For sample Sb-15-2 the field-current direction is neither longitudinal nor transverse.

$K = N_A/N_D = 0.04$ , one obtains  $N_D = 6.5 \times 10^{15}/\text{cc}$ . On the basis of Eq. (2), at this concentration, the distance between donors is  $2R_s = 664 \text{ \AA}$ . Evaluation of Eq. (19) leads to the value of

$$\zeta_{\text{calc}} = 6 \times 10^{-3},$$

which is to be compared with the measured value of

$$\zeta_{\text{exp}} = 2 \times 10^{-2}.$$

Unfortunately, the field-current direction at which this value was obtained is not given in the paper by Fritzsche and Lark-Horowitz.<sup>18</sup> They remark only that the magnetoresistive ratio showed some directional dependence.<sup>19</sup> If one assumes that the measured value is representative of the order of magnitude of the magnetoresistive ratio, regardless of the field-current direction, then the calculated value seems to be not inconsistent with the experimental results. A more conclusive proof of the theory awaits further measurements, especially at lower temperatures, since the change in the slope of the resistivity curve occurs<sup>18</sup> at about  $5^\circ\text{K}$ , not too far from  $4.2^\circ\text{K}$ , where the magnetoresistive ratio was measured.

We also wish to make a few remarks on what one might expect by including higher order terms in the perturbed wave function. Evidently, as long as only  $s$ -type wave functions are considered in Eq. (14), the longitudinal and transverse magnetoresistive ratio remain equal. To differentiate between them, one must include wave functions with angular dependence in the resistivity calculation.

Finally, we wish to touch upon another point. In the above treatment we have ignored the fact that according to the more exact formulation of the effective mass theory,<sup>12</sup> the donor wave function is essentially a superposition of four "pancake-like" wave functions contributed by the four conduction band minima. Out of the four linearly independent combinations which can be formed only one has nonvanishing amplitude at the donor nucleus. For this reason, if the central cell correction is applied, the ground state splits into a nondegenerate and a triply degenerate level. One assumes<sup>20</sup> that the nondegenerate level corresponds to the empirical ionization energy and the triply degenerate level to the calculated value<sup>12</sup> when only one of the minima is considered. The splitting, usually referred to as the chemical shift, is very small for Sb in germanium, namely  $6 \times 10^{-4} \text{ ev}$ .<sup>21</sup> At very low temperatures, when  $kT$  is much smaller than the chemical shift, only the singlet level will be populated. At higher temperatures transitions to the triplet level will occur. In the present calculation we have considered only the singlet level. For the resistivity calculation it is a good approximation since at  $2.5^\circ\text{K}$  the Boltzmann factor of the

<sup>20</sup> E. M. Conwell, *Phys. Rev.* **99**, 1195 (1955).

<sup>21</sup> At the American Physical Society Meeting in Detroit, H. Fritzsche [*Bull. Am. Phys. Soc.* **5**, 159 (1960)] gave  $5.7 \times 10^{-4} \text{ ev}$ , measured in experiments on strained germanium.

transition from the lower to the upper "ground-state" level is small. In the case of the magnetoresistivity the Boltzmann factor at 4.2°K is not so small and, for this reason, the calculated magnetoresistive ratio should strictly be compared with values measured at lower temperatures where the population of the triplet level is vanishingly small.

*Note added in proof.*—One can expect that (with appropriate rephrasing) the above model can be applied to *p*-type germanium too. This view is supported by measurements<sup>22</sup> which show that the conductivity of a lightly doped and weakly compensated ( $K' = N_D/N_A$ ) *p*-type germanium crystal increases with a small increase in the compensation. This is expected, since the number of acceptor ions to which holes can jump increases. To arrive at numerical results and compare

<sup>22</sup> H. Fritzsche and K. Lark-Horowitz, Phys. Rev. **113**, 999 (1959).

them with measured data on In-doped<sup>23</sup> and Ga-doped<sup>19</sup> samples, we have assumed a hydrogenlike 1s wave function for a hole. This is an admittedly rough choice because it corresponds to only one term of the more exact but complicated hole wave function, derived<sup>23</sup> from the effective mass theory. The effective masses ( $m_{In}^* = 0.214 m_0$  and  $m_{Ga}^* = 0.203 m_0$ ) have been determined from the ionization energy of In and Ga acceptors<sup>24</sup> at liquid He temperatures. Calculated and measured data are shown in Table II, where the number of "free" acceptor ions/cc is denoted by  $\bar{p}$ .

## VI. ACKNOWLEDGMENT

The writer wishes to thank Dr. Evan O. Kane for many valuable discussions during the course of this work.

<sup>23</sup> W. Kohn and D. Schechter, Phys. Rev. **99**, 1903 (1955).

<sup>24</sup> P. Fisher and H. Y. Fan, Phys. Rev. Letters **2**, 456 (1959).

## Adiabatic Demagnetization and Specific Heat in Ferrimagnets

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The specific heat of yttrium iron garnet (YIG) has been measured at 1.45°K as a function of magnetic field from zero to 18 kilo-oersteds. It is found to drop about 30% over this field range as the field is increased. Adiabatic temperature changes,  $\Delta T$ , were observed during magnetic cycles over various field intervals in the range from 3 to 18 kilo-oersteds, and at various temperatures between 1 and 4°K. The experimental values of  $\Delta T$  and the specific heat fit the predictions of spin-wave theory to within experimental error. The data are sufficiently extensive to provide a useful test of spin-wave theory as well as checks on the consistency of the data itself as between the two types of observations. Values of various parameters which characterize the thermal and magnetic properties of YIG are determined from this investigation to have the following values: Landau-Lifshitz exchange constant  $A = 4.3 \times 10^{-7}$  erg/cm; Debye temperature  $\theta = 510^\circ\text{K}$ . The serious effect of magnetic impurities on investigations of this sort is pointed out.

## I. INTRODUCTION

WE have observed the heat capacity as a function of magnetic field and the adiabatic magnetization and demagnetization of yttrium iron garnet (YIG) at temperatures in the liquid helium range. The heat capacity has been observed at only one temperature, namely 1.45°K, and is significantly smaller at zero magnetic field than the earlier results obtained by Edmonds and Peterson<sup>1</sup> and by Meyer and Harris.<sup>2</sup> Our other observations are of the temperature changes in a thermally isolated sample as entropy is transferred back and forth between the magnetic spin system and the crystal lattice by means of adiabatic changes of an applied magnetic field. These experiments require care in isolating the

sample thermally and in measuring sample temperature with thermometry which has a heat capacity small compared to that of the sample. Because of the temperature and field dependence of the population of the energy levels of the magnetic lattice, the density of states of the magnetic lattice can be deduced from these results. When combined with specific heat data they provide a new test of the predictions of spin-wave theory.

Adiabatic demagnetization has found wide use in the study of paramagnetics at liquid helium temperatures. In such materials, the difference in entropy between completely disordered states and essentially ordered ones can be achieved experimentally. The maximum entropy change which can be produced in ferrimagnetics like YIG with Curie points above room temperature is much smaller, since the amount of magnetic disorder and thus the amount of magnetic entropy present at liquid helium temperatures is very small compared to

<sup>1</sup> D. T. Edmonds and R. G. Petersen, Phys. Rev. Letters **2**, 499 (1959); **4**, 92 (1960).

<sup>2</sup> H. Meyer and A. B. Harris (private communication); and *Fifth Conference on Magnetism and Magnetic Materials, Detroit, Michigan, November, 1959* [J. Appl. Phys. **31**, 49S (1960)].