# Magnetic Susceptibility of Germanium

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The magnetic susceptibility of highly doped germanium has been measured between 300°K and 1.3°K. The contribution of the carriers to the susceptibility has been derived from the data. Most of the measurements concern electrons occupying unbound states in the conduction band. The observed conduction-electron susceptibility has been compared with theoretical estimates based on the effective-mass values given by cyclotron-resonance experiments. Our results support a 4-ellipsoid model of *n*-Ge. No appreciable change in the effective masses is observed between room temperature and 1.3°K. We find no evidence for any substantial change in the curvature of the conduction band for energies up to 0.08 ev above the band minimum. This finding contradicts certain conclusions of Stevens *et al.* An explanation for the disagreement is proposed.

Measurements have been made of the spin susceptibility of quasi-bound states of electrons and holes in germanium at a carrier density near $6\times10^{16}$/cc. In each case, the spin susceptibility was found to be almost independent of temperature. We conclude that there is strong exchange coupling between neighboring impurity centers at this concentration.

The susceptibility of high-purity germanium has been measured. It is found to be independent of temperature below 60°K.

## INTRODUCTION

THIS paper describes a study of the contribution of extrinsic charge carriers to the magnetic susceptibility of germanium. The purpose of the work was to examine the validity of the simple theories of carrier susceptibility and also to obtain information concerning the band structure of germanium. Of special interest is the resulting information about effective masses above the bottom of the conduction band. Most of our measurements have been made on *n*-Ge under conditions such that all of the electrons occupy unbound states in the conduction band. We have also obtained some information on the susceptibility of electrons and holes in bound states.

In recent years, several experimental studies of the magnetic susceptibility of germanium have been made.[1–4] At the time we began our work, most of the published measurements of the extrinsic carrier contribution to the susceptibility had been made in the temperature range 300°K to 77°K, and the principal features observed were due to nonlocalized carriers obeying classical statistics. We wished to extend these studies to lower temperatures and also cover a somewhat larger range of electron densities. Since the completion of our work, Hedgcock[2] has published a study of extrinsic carriers down to 4.2°K but the range of carriers studied is not as extensive as in the present work.

There are several reasons why it is desirable to extend the measurements into the low-temperature region. Firstly, for free carriers, any physical quantity derived from the measured susceptibility is always obtained as an average over a range of energy levels of the order of $kT$ in the band; it is possible to keep this range very narrow by working at liquid-helium temperatures. Secondly, the degenerate carrier susceptibility observed at low temperatures is proportional to the cube root of the carrier density, whereas in the nondegenerate case it is proportional to the first power of the carrier density. Hence the results of measurements in the degenerate range are less sensitive to uncertainties in the knowledge of the carrier density. Thirdly, we are able to study the contribution to the susceptibility from electrons and holes in bound impurity states.

The usefulness of susceptibility measurements as a means of studying the electronic structure of semiconductors was first established by Busch and Mooser[5] with their work on grey tin. These authors and also Stevens *et al.*[1] have given a detailed account of the theoretical analysis of susceptibility measurements. We shall restrict ourselves here to a few comments on the interpretation of susceptibility measurements.

The total susceptibility of a semiconductor is the sum of the lattice susceptibility $\chi_L$ and the susceptibility of the charge carriers $\chi_e$. The lattice susceptibility may be determined from measurements on a high-purity crystal. The presence of substitutional impurities affects $\chi_L$ in two ways, directly because of the change of atomic orbitals and indirectly because of the deformation of the lattice. Both of these effects may be neglected in our work. Hence the carrier contribution in a doped crystal may be obtained by subtracting off the measured susceptibility of the pure crystal.

The carrier contribution to the susceptibility consists of two parts, a paramagnetic contribution $\chi_s$ resulting from the spin of the carrier and a diamagnetic contribution $\chi_0$ resulting from the carriers' orbital motion. In

[1] Stevens, Cleland, Crawford, and Schweinler, Phys. Rev. **100**, 1084 (1955).
[2] F. T. Hedgcock, Can. J. Phys. **34**, 43 (1956); J. Electronics **2**, 513 (1957).
[3] A. van Itterbeck and W. Duchateau, Physica **22**, 649 (1956).
[4] G. Busch, *Proceedings of International Conference on Semiconductors, Garmisch, 1956* (to be published).
[5] G. Busch and E. Mooser, Helv. Phys. Acta **26**, 611 (1953).

the case of nonlocalized states, the former can be interpreted with the Pauli theory[6] and the latter by using the Landau-Peierls theory.[7,8] For carriers localized at donor or acceptor sites, the spin and orbital susceptibilities are given by the Langevin relations.[9]

The electronic diamagnetism is of special interest for theoretical purposes. It is instructive to contrast the ease with which we can study conduction-electron diamagnetism in certain semiconductors with the difficulty of making a similar study in simple metals.[10] In a metal, one cannot determine the lattice ("ionic core") susceptibility in the direct manner described above. Furthermore, in most metals, the spin susceptibility and the orbital susceptibility of the carriers are approximately the same size, so it is difficult to separate the two contributions with precision. Further, in a metal the electron gas is always degenerate, so susceptibility measurements at various temperatures yield essentially the same information. On the other hand, in a semiconductor, the Fermi temperature is readily attainable and the susceptibility can be studied in both degenerate and classical conditions. Another advantageous feature of semiconductors is that the number of carriers can be varied over several orders of magnitude.

We shall first discuss the specific case of electrons moving in the conduction band of germanium, i.e., electrons in nonlocalized states. Because the appropriate effective masses in germanium are small, the spin contribution $\chi_s$ to the carrier susceptibility is only 6% of the orbital contribution $\chi_0$. Hence in our work on the conduction band susceptibility, we shall be concerned mainly with $\chi_0$. In the interpretation of the data, the Landau-Peierls formula will be used. While it should be remembered that this is not an exact formula for $\chi_0$,[8,11,12] it is expected to be adequate for our purposes because of the relatively low density of electrons involved in our work.[13]

We have made measurements of the *degenerate* conduction-electron susceptibility over a carrier-density range from $1\times10^{17}$ to $3\times10^{19}$ per cc. The concentration $1\times10^{17}$/cc is approximately that at which the ionization energy falls to zero so that the carriers remain in the conduction band to the lowest temperatures.[14]

We have studied the degenerate susceptibility as a function of carrier density because we wished to observe the manner of growth of the diamagnetism as the Fermi level moves up in conduction band. There are two things that we may hope to study by means of such experiments. One is the applicability of the simple theory of carrier diamagnetism to a solid of known simple band structure. The other is the change of curvature of the energy surfaces as the Fermi level is moved up into the conduction band. Existing measurements by cyclotron resonance experiments give the curvatures only at the bottom of the band. Our measurements give information about the curvature for values of the Fermi energy as much as 0.08 ev above the energy-band minimum. Up to this value of the Fermi energy, we find no evidence for any substantial departure of the energy band from a simple parabolic form.

In some of the samples, the temperature dependence of the susceptibility exhibits the effects of the transition from degenerate to classical statistics. We could observe this effect with useful precision only for samples with a carrier density in excess of $10^{18}$/cc.

The above discussion concerned electrons moving in the conduction band. We have attempted to study electrons and holes under conditions where they are localized at their respective donor and acceptor sites. For this work, samples of both *n*- and *p*-Ge with carrier concentration of $6\times10^{16}$/cc were used. At this concentration, we expect the carriers to be "frozen-out" of the conduction and valence bands, although the carriers cannot be completely localized since impurity-band conduction is observed at this concentration.[15]

Our principal interest in these quasi-localized states concerned the magnitude of the spin susceptibility. In the *n*-Ge, we wished to observe in the spin susceptibility the effects of wave-function overlap between neighboring donors. In the *p*-Ge, we hoped to study a more complicated phenomenon involving an orbital contribution to the paramagnetism.[16]

Our experiments show that the interaction between neighboring impurities is quite strong at the concentrations used, However, they give no information about the magnetic moment of independent impurities. We could not repeat the experiment at lower impurity concentrations because of the sensitivity of the apparatus.

## EXPERIMENTAL METHODS

The magnetic susceptibility has been measured by using the Gouy method.[17] The specimens used had a cross section of $2.5\times2.5$ mm and were between 5 and 6 cm long. The temperature dependence of the susceptibility from room temperature to 1.3°K was measured on one system, while the magnitude of the susceptibility at room temperature was determined on a second system which was specially designed for this purpose; we have found the low-temperature balance somewhat clumsy for measuring susceptibility values at room temperature. The room-temperature system uses a Stanton microbalance MC1A. The low-temperature measurements were made with magnetic fields up to

[6] W. Pauli, Z. Physik **41**, 81 (1927).
[7] L. Landau, Z. Physik **64**, 629 (1930).
[8] R. Peierls, Z. Physik **80**, 763 (1933).
[9] L. F. Bates, *Modern Magnetism* (Cambridge University Press, New York, 1951), pp. 41 and 10.
[10] R. Bowers, Phys. Rev. **100**, 1141 (1955).
[11] E. N. Adams, Phys. Rev. **89**, 633 (1953).
[12] A. H. Wilson, Proc. Cambridge Phil. Soc. **49**, 293 (1953).
[13] T. Kjeldaas and W. Kohn, Phys. Rev. **105**, 806 (1957).
[14] P. Debye and E. M. Conwell, Phys. Rev. **93**, 693 (1954).
[15] H. Fritzsche, Phys. Rev. **99**, 406 (1955).
[16] W. Kohn, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1957), Vol. 5 (to be published).
[17] L. F. Bates, reference 9, p. 115.

4500 gauss and the room-temperature measurements up to 8300 gauss. Relative susceptibilities can be measured with a precision of 1%; the absolute calibration is accurate to 3%.

The Gouy method is somewhat simpler than the Faraday ("Field Gradient")[17] method because one does not have to keep the specimen at a critical position in a field gradient and because absolute calibration is easier. However, with the Gouy method long specimens are required. This is a disadvantage because it is often difficult to get heavily doped specimens whose doping density is sufficiently uniform.

We had no difficulty in getting sufficiently uniform specimens of single-crystal germanium with impurity concentration less than $5\times10^{17}$/cc. In preparing the material for these specimens (Table I), standard pulling or zone-leveling techniques were used and we estimate that the specimens are uniform to better than 10%.

Specimens containing $2\times10^{18}$ and $1\times10^{19}$ donors/cc were made with the Bridgman technique,[18] phosphorus or arsenic being used as a doping agent. In this technique the germanium and dope are sealed in a quartz tube, melted, and then dropped through a temperature gradient. The resulting ingots were not single crystals but contained a few grains. Polycrystalline material is entirely satisfactory for our work because the susceptibility is isotropic. (Nevertheless, we have used material which is as nearly single-crystal as possible so the amount of grain-boundary material is small.)

Our most highly doped material, phosphorus-doped germanium containing $3\times10^{19}$ donors/cc, was prepared by rapid cooling of a molten alloy. This material was highly polycrystalline with an average grain size of a few mm.

Allowing for any lack of uniformity, the doping densities in the three most highly doped specimens (Table I) are estimated to be known to within 20%. An accuracy of 20% is adequate for the degenerate-carrier studies since the susceptibility depends only on the cube root of the carrier density.

Two methods have been used to probe the doping density along the length of the specimens. In one, the local resistivity was measured along the length of the specimen by the well-known potential-probe methods.[19] In the second, three Hall plates have been cut along the length of the specimen from a slice of the ingot adjacent to that from which the specimens were cut. The number of carriers in each plate was determined from measurements of the Hall coefficient.

We have made several attempts to make specimens with $10^{20}$ donors/cc and above without success.

TABLE I. Some electrical properties of the specimens.

| Specimen | Impurity | Hall coeff. at room temp. (cm³/coul) | Resistivity at room temp. (ohm cm) | Carrier density ($cm^{-3}$) |
|---|---|---|---|---|
| *A* *n*-Ge | ··· | $\sim10^5$ | 40 | $<10^{14}$ |
| *B* *n*-Ge | As | 105 | 0.040 | $5.5\times10^{16}$ |
| *C* *n*-Ge | As | 52 | 0.028 | $1.1\times10^{17}$ |
| *D* *n*-Ge | As | 19.5 | 0.014 | $3.0\times10^{17}$ |
| *E* *n*-Ge | As | 2.5 | 0.0036 | $2.0\times10^{18}$ |
| *F* *n*-Ge | P | 0.51 | 0.0013 | $1.0\times10^{19}$ |
| *G* *n*-Ge | P | 0.154 | 0.0006 | $3.2\times10^{19}$ |
| *H* *p*-Ge | Al | 90 | 0.07 | $6.8\times10^{16}$ |
| *I* *n*-Si | As | 109 | 0.17 | $6\times10^{16}$ |

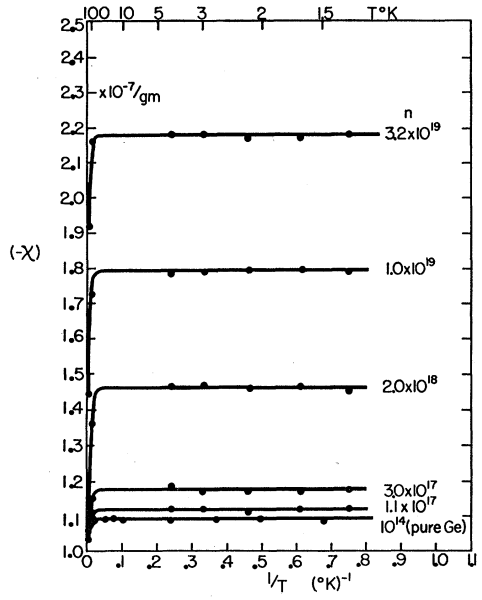


FIG. 1. The magnetic susceptibility of *n*-Ge for various carrier densities plotted against $1/T$.

## EXPERIMENTAL RESULTS

In Fig. 1, we show measurements of the total susceptibility of various specimens of *n*-Ge plotted against $1/T$. The number of carriers quoted were derived from Hall measurements. The susceptibility was found to be independent of magnetic field. The lowest curve ($n<10^{14}$) represents the lattice susceptibility because the number of carriers in this case is below the limit of detection in the susceptibility.

Some care is necessary in deriving $n$, the number of carriers, from the measured Hall coefficients. The measured Hall coefficients as a function of $1/T$ are shown in Fig. 2. The Hall constant $R_H$ and $n$ are related in the following way:

$$R_H=K_1K_2(1/ne).$$

$K_1$ is a coefficient which depends only on the geometry of the energy surfaces and for *n*-Ge is[20] 0.79. $K_2$ is a factor, which, in the nondegenerate case (assuming moderate magnetic fields) depends on the mechanism of scattering. $K_2$ becomes equal to 1 for the degenerate case, irrespective of the scattering mechanism. The

[18] W. Crawford Dunlap, *An Introduction to Semiconductors* (John Wiley and Sons, Inc., New York, 1957), p. 215.

[19] See reference 18, p. 179.

[20] C. Herring, Bell System Tech. J. **34**, 237 (1955).

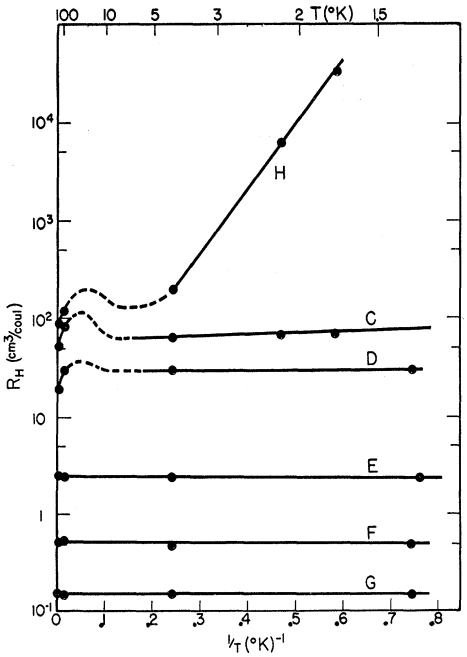


FIG. 2. The Hall coefficient plotted against $1/T$. The letters refer to the list of specimens given in Table I.

magnitude of $K_2$ for the nondegenerate case is the principal uncertainty in the interpretation of Hall data.

We have interpreted our Hall data for $n$-Ge on the following basis:

(1) For concentrations less than $5\times10^{17}$/cc, where lattice scattering is the predominant scattering mechanism at room temperature, and where the electron gas is not degenerate, we have set[21] $K_2=3\pi/8$.

(2) For concentrations of more than $5\times10^{17}$, impurity scattering is important at room temperature. In this case there is considerable uncertainty concerning the value of $K_2$ at room temperature. We have attempted to determine the appropriate value of $K_2$ from a measurement of the temperature dependence of the Hall coefficient. The Hall coefficient was measured at room temperature and at liquid-helium temperatures. Since the electron gas is completely degenerate in the liquid helium range, the *low-temperature* Hall coefficient was interpreted on the assumption that $K_2=1$. We found that for all three specimens, the low-temperature Hall coefficient was equal to the room-temperature value within a few percent. Hence we have found no evidence of a departure of $K_2$ from the value 1. (This was expected for the most highly doped specimen which has a degeneracy temperature of about 800°K.)

In Fig. 3, we present a plot of our experimental low-temperature conduction-electron susceptibility against $n^{\frac{1}{3}}$. The points on this curve were obtained by subtracting the low-temperature lattice susceptibility from the low-temperature susceptibility of the doped crystals.

[21] F. J. Morin, Phys. Rev. **93**, 62 (1954).

In Fig. 3, we have also given a plot of the theoretical conduction-electron susceptibility based on the Landau-Peierls and Pauli formulas for the completely degenerate case. In making these plots, we have used the effective masses given by cyclotron resonance.[22] The two theoretical curves correspond to the two possible numbers of conduction-band energy minima. One line is for 4 ellipsoids and the other assumes 8 ellipsoids.

The curve $\chi_a(n)$, in Fig. 3, gives the *diamagnetism* to be expected[16] if the electrons had remained in atomic states. This susceptibility is proportional to $n$. The calculated curve assumes no overlap of the wave functions. Overlap is certainly large at concentration in excess of $10^{17}$. Accordingly, in discussing our data on degenerate samples, this curve will only be used for the purpose of qualitative discussion.

Figure 4 shows the carrier susceptibility as a function of $1/T$ in the temperature range 300°K to 77°K. The susceptibility exhibits the transition from degenerate to classical statistics. For each specimen, the upper curve is a theoretical plot assuming the cyclotron-resonance masses and 4 ellipsoids, while the lower curve is a theoretical plot with effective masses chosen so as to get the best fit with the experimental values for $\chi_e$. It should be noted that in fitting the data we have adjusted the transverse mass, leaving the longitudinal mass unaltered. The quantity $f^2$ is equal to $(2m_t+m_l)/(3m_t^2m_l)$; it is the combination of effective masses determining the orbital magnetic moment.[1]

In Fig. 5, we present some data referring to quasi-localized states of electrons and holes. In this curve, we give the temperature dependence of the susceptibility

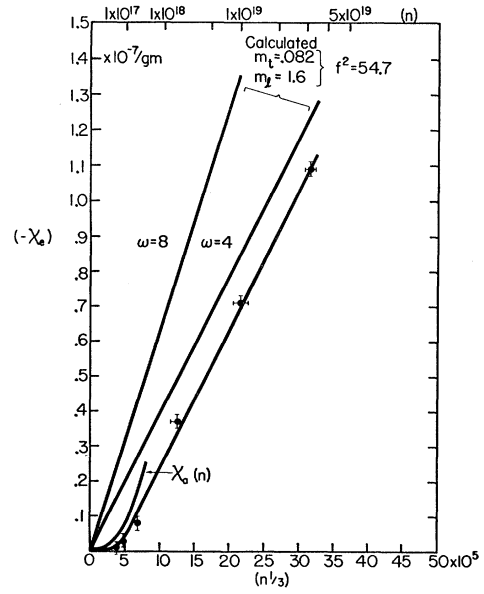


FIG. 3. The degenerate conduction-electron susceptibility plotted against the cube root of the carrier density.

[22] Dresselhaus, Kip, and Kittel, Phys. Rev. **98**, 368 (1955); Lax, Zeiger, Dexter, and Rosenblum, Phys. Rev. **93**, 1418 (1954).

for $n$-Ge, $p$-Ge, and $n$-Si near the concentration density $6\times10^{16}$/cc. The broken lines in this figure give, for each specimen, the slope which would occur if all the spins were independent, with a $g$ value of 2 ($\chi_{fs}=n\mu^2/kT$; $\mu$ is the Bohr magneton). The number of carriers in the $n$-Si and $p$-Ge were derived from the measured Hall coefficient on the assumption that $R_H ne$ was equal to unity. For the $p$-Ge, the resulting value for the carrier density might be too low by as much at 50%.

## DISCUSSION

The lowest curve of Fig. 1, shows the temperature dependence of the host-crystal susceptibility. Near room temperature, the lattice susceptibility has an appreciable temperature dependence. We find that this temperature dependence disappears below about 60°K. Our data for the high-purity material do not exhibit the anomalous temperature dependence found by Hedgcock below 100°K. Hence, we conclude that this behavior is a property of particular specimens and is not a general property of the germanium lattice.

Krumhansl and Brooks[23] have suggested that the explanation for the temperature dependence observed near room temperature is to be sought in a contribution to the filled-band susceptibility arising from a magnetic-field induced admixture of states from the conduction band. The temperature dependence, they suggest, arises from the variation of the energy gap with temperature. Since the temperature dependence of the gap vanishes at low temperatures,[24] our observation is consistent with the explanation of Krumhansl and Brooks.

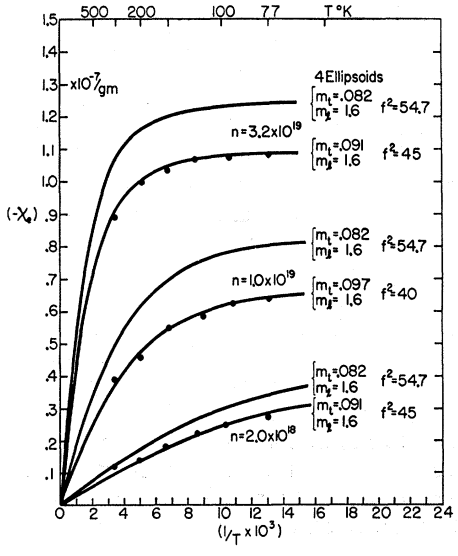


FIG. 4. The conduction-electron susceptibility plotted against $1/T$, exhibiting the transition from classical to degenerate statistics.

[23] J. A. Krumhansl and H. Brooks, Bull. Am. Phys. Soc. Ser. II, 1, 117 (1956).

[24] G. G. MacFarlane and V. Roberts, Phys. Rev. 97, 1714 (1955); 98, 1865 (1955).

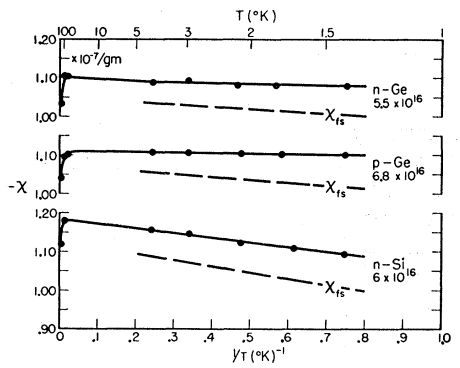


FIG. 5. The susceptibility of $n$-Ge, $p$-Ge and $n$-Si, with carrier densities near $6\times10^{16}$/cc, plotted against $1/T$.

The curves in Fig. 1 give the temperature dependence of the susceptibility for variously doped crystals. In all cases the susceptibility is temperature independent at helium temperatures. This is as expected since the electron gas is degenerate in this range for all the specimens shown in this figure.

It is difficult to compare our low-temperature data on doped crystals with those of Hedgcock[2] because our measurements were made in a somewhat different temperature range. However, it appears that there is no major discrepancy in our respective values at 4.2°K, although the data of Hedgcock exhibit a temperature dependence just above 4.2°K which appears to be inconsistent with our liquid helium data.

Figure 3, shows the observed conduction-electron susceptibility, as deduced from the curves of Fig. 1, when plotted against $n^{\frac{1}{3}}$. It is seen to parallel the 4-ellipsoid line except at small carrier densities. That the curve does not follow an $n^{\frac{1}{3}}$ dependence at the low-concentration end is to be expected, because in this range the electron donor wave functions do not overlap very much, and the free-electron model for the donor electrons is no longer appropriate. Under these conditions we expect an "atomic-like" susceptibility, proportional to the number of carriers. The theoretical curve $\chi_a(n)$ gives a qualitative indication of this atomic-like term. The spin contributions are expected to be very small near $10^{17}$ cm$^{-3}$ because of overlap.

For concentrations above about $5\times10^{17}$, an $n^{\frac{1}{3}}$ dependence predominates. The observed susceptibility runs approximately parallel to the theoretical $\omega=4$ curve. However, it does not merge with the $\omega=4$ line in the range of measurement but stays consistently below it. The observed susceptibility values lie much closer to the theoretical four-ellipsoid line than the theoretical eight-ellipsoid line.[1,4] Because of this, we shall assume henceforth that in the conduction band of Ge, there are 4 energy minima located at the [111] faces of the Brillouin zone.

Our experimental carrier susceptibility for the higher carrier densities are well fitted by the form

$$-\chi_e^{\exp}=an^{\frac{1}{3}}-b.$$

The first term is of the form of the Landau-Peierls susceptibility with a constant effective mass and $b$ is a constant, independent of the carrier density. The part of our measured susceptibility which is proportional to $n^{\frac{1}{3}}$ is accurately given by Landau-Peierls and Pauli formulas with the cyclotron-resonance masses for all carrier densities. The constant $b$ represents a disparity between the experimental curve and the 4-ellipsoid line. This disparity, though small, seems to be real since it exceeds our estimates of possible errors.

We have no explanation for the disparity represented by the constant term. The observed parallelism of the experimental and theoretical curves suggests that we should look to the theory of the susceptibility for the cause rather than to details of the band structure. It is entirely possible that the discrepancy is due to a neglect of the higher order contributions to the orbital susceptibility[13] or even to impurity contributions.

Since the discrepancy between theory and experiment is not large, we shall use the Landau-Peierls and Pauli formulas to compute effective masses from the observed carrier susceptibility of the three most highly doped specimens. This will be done only to get some measure of the discrepancy $b$ in terms of effective masses. The values obtained should not be taken literally as giving the local band curvature. In order to compute the effective masses, we draw a straight line between the origin and each experimental point in Fig. 3, and derive the effective mass for each point from the slope of this line. We find that if we hold the longitudinal mass constant[25] at the value 1.6, the values obtained for the transverse mass $m_t$ are 0.101, 0.094, and 0.090 for the three points in increasing order of carrier density. These values are to be compared with the value 0.082 obtained from cyclotron resonance.

Any reasonable analysis of the data will show that the departure of the computed values from the cyclotron-resonance value of 0.082 is small. Hence, we find no evidence for any substantial change in effective mass with carrier density such as found by Stevens *et al.* in the nondegenerate range.

We have estimated the Fermi level in our degenerate samples by assuming that the density of states in the conduction band is not very much affected by the presence of impurities. We found for the Fermi levels in the three specimens the values 0.01, 0.04, and 0.08 ev, respectively. Thus, it would appear that the parabolic part of the conduction band extends to at least an energy of 0.08 ev.

It would be of interest to extend our measurements to higher carrier densities for it is reasonable to expect that effects of band curvature will be seen at somewhat higher levels. Unfortunately we have not been able to prepare suitable specimens for this work.

We have not attempted to analyze the susceptibility data near an impurity concentration of $10^{17}$/cc in terms of effective masses. For such concentrations, the overlap between neighboring centers is not very great, so it is probable that the simple band theory of carrier diamagnetism fails.

We now wish to discuss Fig. 4, which shows the carrier susceptibility in 3 specimens exhibiting the transition from degenerate to classical statistics. The experimental points fall below the curve computed for cyclotron-resonance masses and four ellipsoids. The effective mass associated with the lower curve for each specimen has been chosen to get the best fit with the experimental data.[26] As is the case for the degenerate data, we find that these computed masses differ only slightly from the cyclotron-resonance values. We disagree on this point with Stevens *et al.*[2] who concluded that in a similar concentration and temperature range, their susceptibility data required effective masses which increase drastically with increasing concentration of carriers. At lower carrier concentrations Stevens *et al.*[1] and also Hedgcock,[2] find a susceptibility whose magnitude is close to that calculated from cyclotron-resonance masses.

We believe that the apparent substantial dependence of effective mass on carrier density is spurious and results from the use of an interpretation of the Hall coefficient which is no longer thought to be correct. There is no major disparity in our respective experimental data.

Stevens *et al.* have not allowed for the anisotropy of the energy surfaces in computing $n$ from the Hall coefficient because the importance of this factor was not realized at the time of their work. An application of the anisotropy correction would reduce[20] all their calculated carrier densities (for $n$ type) by 20%. Furthermore, they have applied, in some cases, large corrections to the measured room-temperature Hall coefficient to allow for ionized-impurity scattering using the theory of Johnson and Lark-Horovitz.[27] Our measurements of the Hall coefficient as a function of temperature indicate that Stevens *et al.* have used too large a correction.

If these factors are taken into account, and their data are interpreted in the same way as ours, the effective masses computed from their measurements fall very close to the cyclotron-resonance values for all of the specimens except one, their most highly doped specimen. A disparity still exists for this specimen. Since Stevens *et al.* chose to compute their effective

[25] The susceptibility data yield only a combination of the effective masses and not the individual values. The combination for the degenerate case is a product of $(m_t^2 m_l)^{\frac{1}{3}}$ from the density of states and $[(2m_t+m_l)/9m_t^2m_l]-1$ from the magnetic moments. We have chosen to reduce the data by keeping $m_l$ constant; this choice is somewhat arbitrary. In making this choice we have been guided by the fact that the susceptibility is less sensitive to a small change in $m_l$ than it is to the same relative change in $m_t$. Furthermore, if any deviation of the bands from parabolic form did occur, we expect $m_l$ to change less rapidly than $m_t$.

[26] The values derived for $m_t$ are more sensitive to the values assumed for $n$ than was the case in the degenerate range. Since $n$ is uncertain to 20% in these samples, no significance should be attributed to the differences between the computed $m_t$ in different samples.

[27] V. A. Johnson and K. Lark-Horovitz, Phys. Rev. **82**, 977 (1951).

masses from the slope of the $\chi_e$ *versus* $1/T$ plot at high temperatures, this disparity may be due to errors in estimating this slope because there are significant departures from the $1/T$ dependence in this highly doped specimen. The reinterpretation of the Hall data of Stevens *et al.* implies that their most heavily doped material contained about $6\times10^{18}$ carriers per cc, which is a factor 5 smaller than the highest density we have studied.

From a comparison of the data in Figs. 3 and 4, we conclude that the effective masses do not change appreciably between room temperature and liquid helium temperatures.

We now discuss Fig. 5, which gives the results of our work on the spin susceptibility of quasi-bound states. First, we consider the situation in *n*-Ge. At the donor density $5.5\times10^{16}$/cc, we expect the electrons to become mainly localized at the donor site on cooling to liquid helium temperatures.[14] If the electron spins were not coupled to each other, we would expect a free-spin susceptibility $\chi_{fs}=n\mu^2/kT$, where we assume a $g$ factor of 2 for the electronic $S$ state. This would produce a *slope* at low temperatures in Fig. 5, shown by the broken line. We actually find that the observed susceptibility is almost independent of temperature in the helium range. We have repeated the measurements in the liquid helium range several times and we consistently find that the observed temperature dependence is smaller than that expected for free spins by at least a factor 3. This implies there is spin coupling, tending to pair the spins antiparallel. Such a coupling of the spins is expected from direct exchange through the overlap of the wave functions of neighboring donor electrons at concentrations of $5.5\times10^{16}$/cc because of the very large radius of the donor electron wave function. Estimates of the exchange energy, using a hydrogenic model of the donor states, indicates that one would expect to see coupled spin susceptibility in *n*-Ge at concentrations in excess of $10^{16}$/cc.

This explanation for the absence of slope is supported by measurements on *n*-Si at a similar density. The donor electron wave functions in *n*-Si have radii about one third of those in *n*-Ge, and crude estimates of exchange in *n*-Si indicate that overlap should not be important in the spin susceptibility below $10^{17}$ donors/cc. We find for *n*-Si, with $6\times10^{16}$ donors/cc, a $1/T$ dependence in the susceptibility which is in reasonable agreement with the free-spin value.

It would be of interest to examine the overlap of donor wave functions by measuring the spin susceptibility as a function of concentration, starting from a concentration low enough for free spins and then reaching concentrations where the spins are coupled. This would be easy in Si because of the relatively high concentrations involved, but it would be very difficult in Ge since one must begin such a study well below $10^{16}$ carriers/cc. At such low concentrations, the carrier contribution to the susceptibility becomes very small compared to that of the host crystal.

The case of the spin susceptibility of localized holes is more complicated than that of electrons. Since the localized hole states are formed from atomic $p$ states, we have to consider orbital contributions to the paramagnetism. This has been done by Kohn[16] who shows that it is quite possible to have a paramagnetic susceptibility different from the $n\mu^2/kT$ characteristic of simple spins. It can be seen from the slopes in Fig. 5, that, just as for *n*-Ge, we find the paramagnetic contribution of localized holes is much less than that of free spins. Just as with the *n*-type material, the possibility of strong exchange between impurity centers prevents us from drawing any conclusion about orbital contributions to the paramagnetic term.

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