may be reduced by suitably annealing the specimen. They have correlated this decrease with a decrease in the dislocation density as determined by etching. These results offer no serious problem to the interpretation of the present data because these effects were found at temperatures below those used in the present work. However, if we are to believe the interpretation based on vacancy pairs advanced above, this means that at sufficiently low temperatures the diffusing species with which they were dealing was a vacancy pair and not a free vacancy as they have supposed. This in turn means that their arguments concerning the effect of a charged dislocation line on the diffusion are inapplicable, and one must look for some interaction of dislocations with vacancy pairs which increases either their number or their mobility. Such an interaction can only depend indirectly on the charge of the dislocation line since the vacancy pair is uncharged. On the other hand these results suggest that the difference in diffusion coefficient between pure and doped crystals reported here may be (at least partially) the result of a difference in the dislocation content between the two types of crystals. Dislocations might be expected to augment the diffusion coefficient by providing easy paths for the diffusing species, and such a process need not result in a deviation from bulk kinetics, as Hart[25] has shown. It is possible that the presence of the calcium ion alters the equilibrium dislocation density, thereby affecting the diffusion coefficient. This field is still in its infancy, and further work, both experimental and theoretical, is needed to understand the effect of dislocations.

ACKNOWLEDGMENTS

It is a pleasure to acknowledge the guidance and assistance of Professor R. J. Maurer throughout the course of this work. I wish to thank Professor J. A. Morrison for stimulating correspondence and for the privilege of reading his manuscript prior to publication. I also wish to thank Professor A. B. Lidiard for his correspondence and for supplying me with the results of his calculations. The support afforded by a National Science Foundation Fellowship held during the course of this investigation is gratefully acknowledged.

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PHYSICAL REVIEW VOLUME 120, NUMBER 1 OCTOBER 1, 1960

Magnetic Susceptibility of *p*-Type Ge

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(Received May 26, 1960)

The magnetic susceptibility of *p*-type Ge has been measured for a range of extrinsic carrier densities extending from 5×10^{17} cm^{-3} to 5×10^{20} cm^{-3}. Measurements were made in the temperature range 300°K to 1.3°K. The degenerate hole susceptibility was determined from the data. At the lower carrier densities, the data depart appreciably from the Landau-Peierls value; above 10^{20} cm^{-3} the data exhibit features due to the population of the split-off band. From the experimental results, it is estimated that the Fermi level touches the minimum of the split-off band at a carrier density of 1.3×10^{20} cm^{-3}. A qualitative discussion is given of the factors determining the susceptibility including band degeneracy and spin-orbit coupling; a detailed quantitative analysis is not attempted.

INTRODUCTION

THIS paper describes an investigation of the static magnetic susceptibility of extrinsic holes in Ge. This investigation is similar to our earlier magnetic studies of electrons in Ge[1] and InSb.[2] The purpose of the work is to compare the experimentally observed carrier susceptibility with theoretical expectations and thereby obtain information concerning the band structure. A study of *p*-type Ge was undertaken because the valence band not only departs from a simple parabolic form in the experimentally attainable range[3,4] but also, at the highest carrier densities, it was expected that carriers would occupy the band "split-off" by spin-orbit coupling.[3,4] Band degeneracy and spin-orbit interactions are expected to be important in determining the susceptibility of the holes. An investigation of carrier susceptibility in this case seemed a worthwhile extension of our previous studies of the susceptibility in a parabolic band (*n*-type Ge[1]) and in a nondegenerate nonparabolic band (*n*-type InSb[2]). Studies of this kind on relatively simple and understood systems are desirable if static susceptibility measurements are to be used for the investigation of materials with poorly known band

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[4] E. O. Kane, J. Chem. Phys. Solids 1, 83 (1956).

structures, e.g., metals. The reader is referred to references 1 and 2 for the details of the analysis of experimental data. As in the earlier work, the carrier susceptibility in p-type Ge is mainly orbital in character.

The measurements to be reported in this paper cover a temperature range of 300°K to 1.3°K and a range of carrier densities from 5×10^{17} to 5×10^{20} cm^{-3}. The range of carrier densities studied is much larger than in any previous susceptibility work on p-type Ge.[5,6] The Fermi level at absolute zero for the highest carrier density studies was estimated to be about 0.6 ev from Kane's results[4]; hence the band was occupied to this level.

The experimental data obtained exhibit two notable features: (a) For carrier densities less than 10^{20}, the carrier susceptibility is appreciably smaller than the Landau-Peierls value even in the region where the bands are parabolic. (b) An increase of the carrier susceptibility is observed at higher carrier densities which we attribute to population of the $J=\frac{1}{2}$ split-off band.

EXPERIMENTAL METHODS

The methods of susceptibility measurement were identical to those used in the work on n-type Ge.[1] The specimen dimensions were approximately $0.2\times0.2\times5$ cm.

The highest purity specimen used for the determination of the lattice susceptibility was obtained from a zone refined ingot. The doped material was prepared by the Bridgman method using Ga or Al as a doping agent; the resulting ingots were polycrystalline with large grains. The number of carriers and the uniformity of doping of the final susceptibility specimens were examined by measuring the room temperature Hall coefficient at 4 places along the length of the specimen. These Hall coefficient measurements were made on the actual susceptibility specimens; this is an improvement over our previous practice[1,2] of making such measurements on a slice of the ingot cut adjacent to the susceptibility specimen. The Hall coefficients were measured in a magnetic field of 12 800 gauss. The specimen current used varied from a fraction of an amp up to one amp depending on the carrier density in the specimen. In the most highly doped specimens, the smallest Hall voltage measured was 6μv. We believe our measuring technique to be reliable to 1μv. All the doped specimens are extrinsic at room temperature.

The hole density p has been calculated from the Hall coefficient R_H using the relation $R_H=\alpha/pe$.[1] The factor α has been taken to be unity. Deviations of α from unity might be expected from two sources: (1) the multiplicity of the bands and (2) the warping of the heavy hole band. Substituting values appropriate for p-type Ge into the two band Hall coefficient formulas[7] and assuming ionized impurity scattering, we do not expect α to depart from unity because of band multiplicity by more than a few percent for our specimens. Neglect of the warping could be more serious. There is no quantitative theory of the effect of warping on α which has been substantiated by experiment. Consequently, we retain the value unity for α. Goldberg, Adams, and Davis[8] estimated that warping causes α to depart from unity by about 20% and we use this as a guide to the uncertainty in our evaluation of the carrier densities.

A total of 32 specimens were studied in this work. The room temperature susceptibility of every specimen was measured. The change in susceptibility between room temperature and liquid helium temperatures was determined as a function of carrier density from measurements made on 10 of the specimens. The resulting curve of temperature dependence versus carrier density was used to reduce the data of all 32 specimens to the lower temperature limit by interpolation. The change in susceptibility between room temperature and 4°K is not large (<11%) in the specimens studied; hence the interpolation method of reducing all data to the low temperature limit is adequate for our purposes.

The lattice parameter of the material in the most highly doped specimen was compared with that of the high purity material. Debye-Scherrer diffraction patterns obtained on a Philips 114.6-mm diameter camera yielded $a=5.6577\pm0.0002$ A for the Ge+(5×10^{20} Ga/cm^3) while the lattice parameter of the high purity material Ge+(10^{14} carriers) was $a=5.6576\pm0.0001$ A.[9] This change in lattice parameter is insignificant in the interpretation of susceptibility data.

EXPERIMENTAL RESULTS

The magnetic susceptibility of all specimens was independent of magnetic field (maximum field 4500 gauss for the low-temperature measurements and 8300 gauss for the room temperature measurements). The change in susceptibility between 300°K and liquid helium temperatures is small (<11%); nearly all of this change occurs between room temperature and 77°K. In Fig. 1 is shown the relative change of the *total* susceptibility between room temperature (χ_{RT}) and helium temperatures (χ_{LT}) plotted against carrier density (p).

Figure 2 is a plot of the low-temperature degenerate carrier susceptibility plotted against $p^{\frac{1}{3}}$. The experimental points on this curve were obtained by subtracting the lattice susceptibility (5.5×10^{-7} per cc determined from the purest material) from the susceptibility of the doped material.[1,2] For $p=10^{18}$ cm^{-3}, the carrier contribution is 4% of the measured total susceptibility; at $p=5\times10^{20}$ cm^{-3} the carrier contribution is 35% of the total susceptibility. The results designated by open circles in Fig. 2 have been obtained from measurements

[5] D. K. Stevens, J. W. Cleland, J. H. Crawford, and H. C. Schweinler, Phys. Rev. **100**, 1084 (1955).
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[9] We are grateful to A. Taylor and B. Kagle of Westinghouse Research Laboratory for determining these lattice parameters.

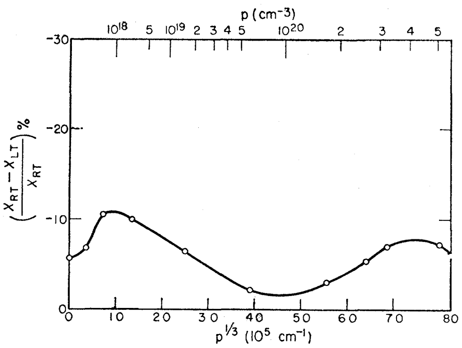

FIG. 1. The relative change of the total susceptibility between room temperature (χ_{RT}) and liquid helium temperatures (χ_{LT}) plotted against the cube root of the carrier density.

on doped specimens which extended down to 1.3°K. The closed circles were obtained from room temperature measurements on other specimens; these measurements were corrected to the low-temperature limit by interpolation in Fig. 1. The data designated by triangles were obtained by extrapolating to low temperatures some data of Stevens *et al.*[5] The straight lines diverging from the origin in Fig. 2 have the following significance: the broken line (ℓ.h.) is the Landau-Peierls value ($-e^2k_0/12\pi^2c^2m^*$ with conventional notation) for carriers in the light hole band, the broken line (h.h.) is a similar value for the heavy holes and the solid line (χ_{LP}) is the sum of these two contributions. The effective masses assumed in this computation are $0.04m$ and $0.3m$,[3] and the values of k_0 for each band are determined by the condition that the Fermi level is common to both bands. For a fixed carrier density, this results in a wave vector ratio equal to the square root of the effective mass ratios and consequently the ratio of susceptibility contributions from the two bands is proportional to the inverse of this square root since $\chi \propto k_0/m^*$. No Pauli paramagnetism term was included in these computations.

Figure 3 is a plot of resistivity versus carrier density p for the material used in this work. The solid line represents data of other workers.[10,11]

From an extrapolation of lower carrier density data,[12] we expected the Hall coefficients of the highly doped specimens to be essentially independent of temperature below room temperature. We made measurements of the Hall coefficient of two specimens ($p=1.6\times10^{19}$ and $p=4.0\times10^{19}$) at 300°K, 77°K, and 4°K. The change in Hall coefficient between 300° and 4°K for these two specimens was 20% and 10%, respectively. We assume that at higher carrier densities, the corresponding change in Hall coefficient would be smaller and hence negligible.

[10] F. A. Trumbore and A. A. Tartaglia, J. Appl. Phys. **29**, 1511 (1958).
[11] W. W. Tyler and T. J. Soltys (unpublished).
[12] H. Fritzsche, Phys. Rev. **99**, 406 (1955). H. Fritzsche and K. Lark-Horovitz, Phys. Rev. **113**, 999 (1959).

DISCUSSION

The experimental results shown in Fig. 2 exhibit two notable general features. At the lower carrier densities, the data are consistently lower than the Landau-Peierls value $-e^2k_0/12\pi^2c^2m^*$. In particular, below $p=10^{19}$ cm^{-3} ($\zeta_0=0.05$ ev) where the occupied bands are still approximately parabolic, the observed susceptibility is 2 or 3 times smaller than the Landau-Peierls value with effective masses appropriate for the band minimum.[3] A second feature is the rise in carrier susceptibility in Fig. 2 for carrier densities above 10^{20}; this rise is attributed to population of the split-off band, carriers in this band giving an additional diamagnetism to the carrier susceptibility.

In order to make a quantitative comparison between the experimental data and the susceptibility expected for holes in Ge, it would be necessary to make a detailed calculation of considerable complexity since many factors preclude any direct application of the Landau-Peierls formula[13] to this problem. We have not made such a calculation and shall limit ourselves to a qualitative discussion of the factors determining the susceptibility, particularly those due to the band degeneracy. The basis for this discussion is the work of Luttinger[14] on the valence band and our previous magnetic susceptibility work.[2]

Three regions of carrier concentrations will be considered[15]; (1) Low carrier concentrations where the carrier susceptibility for degenerate statistics is proportional to $p^{\frac{1}{3}}$; in this region the effective masses are constant. (2) Intermediate carrier concentrations for which the split-off band is not yet populated. (3) High carrier

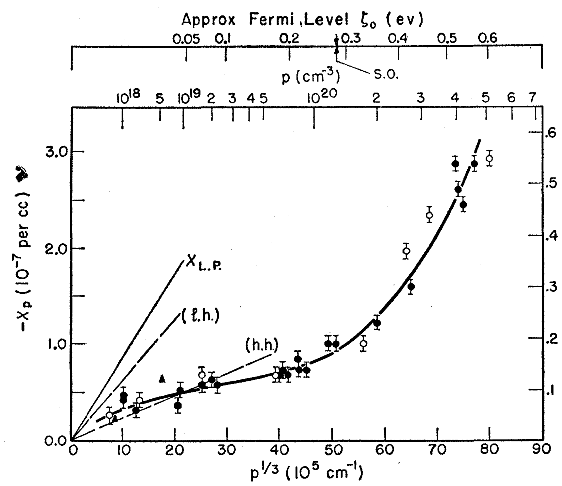

FIG. 2. The magnetic susceptibility of degenerate holes in Ge plotted against $p^{\frac{1}{3}}$. The top abscissa scale gives approximate values for the zero temperature Fermi level estimated from Kane's results (reference 4). This estimate involved taking spherical averages of the anisotropic bands.

[13] See discussion, page 1166 of reference 2.
[14] J. M. Luttinger, Phys. Rev. **102**, 1030 (1956).
[15] We assume that the carrier densities in our work exceed those for which acceptor bound-states are important.

concentrations where the split-off band is occupied and where the dominant contribution to the susceptibility is from holes in this band.

(1) Low Carrier Density: Below 5×10^{18} cm^{-3}

At the lowest carrier concentrations, the susceptibility in a *nondegenerate* band is the sum of two contributions: the Landau diamagnetism with the effective mass, and a Pauli paramagnetism with a g factor determined by the effective mass and the strength of the spin-orbit coupling.[16] In the case of *degenerate* bands three new features arise which we discuss under the designations a, b, c. (a) The strength of the spin-orbit coupling does not appear[14] in the value of the g factor at the bottom of the band; an analogous situation exists for the Landé g factor in free atoms. The g factor is determined by the band shape, i.e., the band to band interactions which determine the effective mass. We have calculated g for the two types of holes in the spherical approximation. In the notation of Dresselhaus, Kip, and Kittel, the following values for the interaction constants were used: $H_2=0$, $3G=2H_1$ (the latter is the requirement of spherical bands) and with $E=(\frac{3}{5})\times(G+H_1)$; the 4×4 secular determinant is solved in the presence of the magnetic field, giving the Zeeman splittings

$$\Delta\epsilon_{\pm}=g\beta HS_Z \quad \text{near } k=0.$$

For the heavy holes we can solve exactly:

$$g=-(4Em/\hbar^2)(4|\cos\theta|-1)-2(2|\cos\theta|-1).$$

For the light holes:

$$g=-\frac{4Fm}{3\hbar^2}-\frac{4Em}{\hbar^2}\left(\frac{8-6\cos^2\theta}{5}\right)-\tfrac{2}{3}(1-2\cos^2\theta)$$

to first order in E/F and $\hbar^2/mF$. Here θ is the angle between the magnetic field H and the $\mathbf{k}$ vector. The limiting values of g as $\mathbf{k}\rightarrow0$ depends on the direction of $\mathbf{k}$; this nonanalytic behavior at the origin is due to the band degeneracy. For the value $F=-14.4\ \hbar^2/m$ and $E=-2.1\ \hbar^2/m$, the g factors are large, varying between 27.2 and -10.2 for the heavy holes and being near 30 for the light holes. The Pauli paramagnetism calculated with these values of g is larger in absolute value than the Landau diamagnetism by a factor of 5 for the heavy hole and 1.3 for the light hole. However, there are two other contributions to χ which we now consider. (b) In the *nondegenerate* case, the level shifts of order H^2 give[2] a contribution to χ which is proportional to the carrier concentration p and is therefore negligible at low carrier concentrations. In *degenerate* bands there is a level shift contribution of order $p^{\frac{1}{3}}$ which can be understood as follows: In a representation by Bloch states, there are matrix elements of the Hamiltonian between the light and heavy hole states which fire first order in H. Since the energy separation is of order k^2, there follows by second order perturbation theory a level shift $\Delta\epsilon=\alpha H^2/k^2$ where α depends on F and E. The contribution to the free energy $\int\Delta\epsilon k^2dk$ and hence proportional to the k vector at the Fermi surface, or to $p^{\frac{1}{3}}$. This is a Van-Vleck type paramagnetism. (c) The quantum effects[14] which are responsible for the nonuniform level spacings at the bottom of the degenerate bands give an additional contribution of order $H^2p^{\frac{1}{3}}$ to the free energy when the latter is computed by expansion of the energy levels in powers of H, i.e., in the limit of large magnetic quantum numbers.[2]

[16] Appendix A in L. M. Roth, B. Lax, and S. Zwerdling, Phys. Rev. 114, 90 (1959).

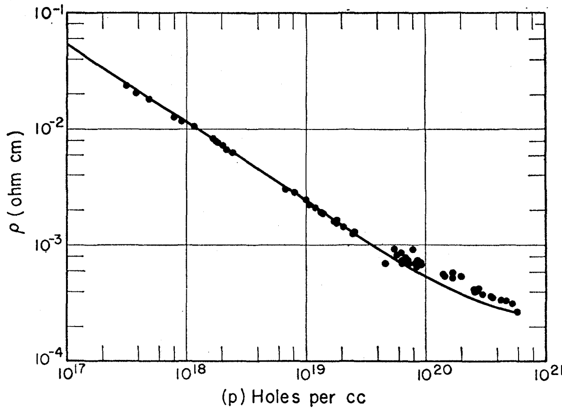

FIG. 3. Plot of resistivity versus carrier density (p) for p-Ge. The points are values obtained in the present work; the solid line represents comparable data of other workers, see references 10 and 11.

The theoretical χ is the sum of all the contributions listed above. It is not surprising that earlier results[5,6] did not agree with simple effective mass theory.

(2) Intermediate Carrier Density: 5×10^{18} to 1.3×10^{20} cm^{-3}

The prescription for calculating χ in this region is similar to that used in our work on InSb with additional complexity introduced by the multiplicity of the bands. The work involved in such a calculation seems excessive for interpreting our experimental results. We note there will be a substantial paramagnetic term in this region due to the large g values.

(3) High Carrier Density: Above 10^{20}

We attribute the steeper rise in χ observed beyond $p=1.3\times10^{20}$ to population of the split-off band. From Kane's results[4] we have estimated that the Fermi level should touch the bottom of the split-off band at a carrier density of about 1.4×10^{20} cm^{-3}; this estimate involves taking spherical averages of the anisotropic bands and is probably uncertain to about $\pm0.3\times10^{20}$.

The effective mass and the g factor at the bottom of the split-off band have been given by Luttinger.[17]

$$(\epsilon_s)_\pm = \hbar^2 k^2/2m + \tfrac{1}{3}(L+2M)k^2 \pm (2mK-1)eH/6mc,$$

where the constants L and M are those of Dresselhaus and the constant K is given by Kohn[18]

$$K = F - G - H_1 + H_2.$$

Using the values for F, G, H_1 given by Dresselhaus, we find

$$K = N - M + 4H_2 = -10.9\hbar^2/m + 4H_2,$$

or a g factor of $-[15.2+(8/3)H_2]$. The value of H_2, which is negative, has been estimated by Kohn to be between 0 and $-(\frac{1}{4})\hbar^2/m$. The effective mass at the bottom of the band is $-1/13.2\ m$; the ratio of spin paramagnetism to orbital diamagnetism assuming $H_2=0$ would be $\frac{3}{4}\times(15.2)^2/(13.2)^2 \simeq 1$. There is therefore a fortuitous cancellation of paramagnetic and diamagnetic effects at the bottom of the band and accurate measurements of the susceptibility might be of use in giving additional information on the 4 band constants F, G, H_1, H_2. Very precise measurements would be needed for this purpose in a limited concentration range near 1.5×10^{20} cm^{-3}; our present experimental methods are not adequate for this.

The number of carriers (p_{so}) in the split-off band is given by:

$$p_{so} = (\text{consts})(p^{\frac{2}{3}} - p_0^{\frac{2}{3}})^{\frac{3}{2}},$$

for constant effective masses, where p_0 is the value of the *total* carrier concentration p at which the Fermi-level touches the bottom of the splitoff band. The susceptibility contribution χ_{so} proportional to $(p_{so})^{\frac{1}{3}}$ will ideally have an infinite slope at $p=p_0$ when plotted in Fig. 2 (abscissa $p^{\frac{1}{3}}$). The χ_{so} contribution proportional to the first power of p_{so} would result in a curve that is concave upwards on the same plot. Because of the cancellation mentioned above, the latter contribution may be dominant. In this case no simple connection is expected between χ_{so} and the effective mass of the bottom of the band.

To complete this section, we discuss the temperature dependence of χ shown in Fig. 1. In this figure is plotted the temperature dependence of the *total* magnetic susceptibility, i.e., lattice plus carrier susceptibility. The temperature dependence (5.5%) at $p=0$ is the anomalous temperature dependence of the lattice alone.[1,19] If we assume that the lattice anomaly is not affected by the doping densities used in this work, the temperature dependence of the carrier susceptibility alone can be obtained by subtracting 5.5% from all the points on the curve in Fig. 1. This will result in a temperature dependence plot of the following characteristics: There is a small negative temperature dependence (i.e., $d|\chi|/dT$ is negative) at the lowest carrier densities, followed by a positive temperature dependence at somewhat higher carrier densities and finally a negative temperature dependence for the highest carrier densities. The two peaks of negative temperature dependence result from the transition from classical to degenerate statistics[20] on cooling when carriers occupy the lower levels of a band. The first peak is caused by holes in the "$J=\frac{3}{2}$" bands and the second peak is caused by holes in the "split-off" band. A positive temperature dependence could result from redistribution of carriers between bands as the temperature is changed and such an effect is expected when the Fermi-level is just below the minimum of the split-off band. However, the positive temperature dependence actually observed begins at lower carrier densities than is expected for the redistribution mechanism and we have no explanation for this.

ACKNOWLEDGMENT

We wish to thank A. J. Cornish for advice and assistance in preparing specimens and D. Watt for his assistance in performing the experiments. We acknowledge the help of M. L. Glasser with preliminary computations.

[17] Reference 14, formula (89) corrected for a numerical error in the g factor.

[18] W. Kohn, *Solid State Physics* (Academic Press, Inc., New York, 1957), Vol. 5, p. 257 and unpublished work; Kohn used both K and κ where $\kappa = -(mK/\hbar^2+1)/3$.

[19] J. A. Krumhansl and H. Brooks, Bull. Am. Phys. Soc. **1**, 117 (1956).

[20] See fig. 4 in reference 1.