For the ground state the integrals are easily evaluated to yield

$$-E'' \approx (\alpha/12)[\beta^2 + \beta^4 + \mathcal{O}(\beta^6)]. \tag{35}$$

The first term is precisely the effective mass correction since $-\beta^2/2 = E_{\text{hydrogen}}$. The second is a Lamb-shift-type correction for the phonon perturbed system. For $\beta < 1$, the "Lamb-shift"-like corrections are small; they are of the order of 10–15% of the hydrogen binding even for α's of the order of unity. We might have expected, from order-of-magnitude arguments, corrections due to

phonon coupling of the order of the hydrogen binding energy itself.

Infrared Absorption in Heavily Doped n-Type Germanium

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Measurements of the infrared absorption spectrum of compensated and uncompensated heavily doped n-type germanium at 80, 200, and 295°K are reported. The edge absorption in the doped samples differs strongly from the edge absorption in pure germanium. Both the indirect and the direct energy gap change with doping. The change depends on the total impurity concentration $N_A + N_D$ approximately as $(N_A + N_D)^{\frac{1}{3}}$. For $N_A + N_D = 4.7 \times 10^{19}$ cm^{-3} the change of the indirect gap is about 0.07 ev, the change of the direct gap about 0.06 ev. The absorption due to indirect transitions rises more rapidly with the photon energy in n-type germanium than in pure germanium. This extra absorption is proportional to the free electron concentration and must be due to virtual electron-electron scattering between the $\langle 000 \rangle$ and $\langle 111 \rangle$ valleys.

It is shown that the effective electron density in heavily doped n-type germanium is larger than in most metals. The properties of the conduction electrons in germanium with $n > 10^{19}$ cm^{-3} correspond to the properties of a dense electron gas ($r_s < 1$).

INTRODUCTION

THE optical properties of very pure germanium have been studied extensively, and a great deal of information on the band structure of this semiconductor has been obtained.[1,2] Extensive studies have also been made of the energy states associated with impurities in not too large concentrations.[3] Recently, the application of tunnel diodes has stimulated interest in the properties of heavily doped semiconductors. A number of optical studies on these "dirty semiconductors" have already been published by Pankove[4,5,6] and by Cardona.[7,8]

In a heavily doped n-type semiconductor the localized impurity states have disappeared, and the conduction electrons may be regarded as a dense degenerate electron gas perturbed by the presence of charged impurities. Electron-electron interaction in such a situation be-

comes important, giving rise to electron correlation and exchange energies just as in metals. As a result, the one-electron approximation will no longer give an adequate description of the properties of the system.

In this paper we report measurements of the absorption spectrum of heavily doped n-type germanium. The results are discussed and some conclusions pertaining to the band structure of heavily doped germanium are drawn.

EXPERIMENTAL PART

Single crystals of n-type germanium doped with various impurities were pulled from a melt containing the required dope. Donor and acceptor concentrations N_D and N_A in these crystals were determined by chemical analysis. The free-carrier concentration n was found from the Hall coefficient R_H and the formula $R_H = (en)^{-1}$. The relation $n = N_D - N_A$ was fulfilled in all cases within the experimental error. We remark that heavily doped crystals may contain precipitates and regions with an inhomogeneous impurity distribution as a result of "constitutional supercooling" during crystal growth.[9] These regions are easily identified by etching. For the optical measurements crystals free from such precipitates were used. The impurity concentration in the crystals used is given in Table I.

[1] T. P. McLean, *Progress in Semiconductors* (John Wiley & Sons, Inc., New York, 1960), Vol. 5, p. 52.
[2] B. Lax and S. Zwerdling, *Progress in Semiconductors* (John Wiley & Sons, Inc., New York, 1960), Vol. 5, p. 221.
[3] W. Kohn, *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 5, p. 258.
[4] J. I. Pankove, Phys. Rev. Letters 4, 20 (1960).
[5] J. I. Pankove, Phys. Rev. Letters 4, 454 (1960).
[6] J. I. Pankove, Ann. phys. 6, 331 (1961).
[7] M. Cardona and W. Paul, Helv. Phys. Acta 33, 329 (1960).
[8] M. Cardona and H. S. Sommers, Jr., Phys. Rev. 122, 1382 (1961).
[9] J. A. M. Dikhoff (private communication).

Table I. The concentration of donors N_D, acceptors N_A, electrons n, and the position of the Fermi-level F relative to the band edge.

Specimen	Type of acceptor	Type of donor	N_A(cm^{-3})	N_D(cm^{-3})	n(cm^{-3})	F(ev) 295°K	F(ev) 200°K	F(ev) 80°K
1	...	...	...	...	...	...	...	...
2	...	P	...	2.4 ×10^{18}	2.4 ×10^{18}	−0.036	−0.012	+0.008
3	...	P	...	4.5 ×10^{18}	4.5 ×10^{18}	−0.018	+0.003	+0.016
4	...	P	...	9.6 ×10^{18}	9.6 ×10^{18}	0.000	+0.021	+0.029
5	...	P	...	1.95×10^{19}	1.95×10^{19}	+0.032	+0.043	+0.047
6	...	P	...	4.3 ×10^{19}	4.3 ×10^{19}	+0.071	+0.080	+0.083
7	...	As	...	2.17×10^{19}	2.17×10^{19}	+0.037	+0.047	+0.051
8	Ga	As	1.8×10^{19}	2.9 ×10^{19}	1.1 ×10^{19}	+0.003	+0.024	+0.032
9	Ga	As	1.5×10^{19}	2.6 ×10^{19}	1.1 ×10^{19}	+0.003	+0.024	+0.032
10	Ga	As	1.0×10^{19}	1.5 ×10^{19}	0.5 ×10^{19}	−0.012	+0.007	+0.020

The crystals were polished in a conventional way. Most measurements were done on crystals about 100 μ thick. In some cases we also measured the absorption in thinner crystals (25 μ), in order to be sure that we were not determining surface but bulk properties.

The transmission of the crystals at 80, 200, and 295°K was determined using a Perkin-Elmer double-beam spectrometer with LiF prism. The spectral slit width at 0.7 ev was better than 0.004 ev.

The absorption coefficient α was calculated from the observed transmission T using the equation

$$T = \frac{(1-R)^2 e^{-\alpha d}}{1 - R^2 e^{-2\alpha d}}. \tag{1}$$

For uncompensated n-type germanium the reflection coefficient R as a function of the carrier concentration has been determined by Cardona and Paul[7]; these data were used to calculate α. For compensated n-type germanium we used the reflection coefficients that Cardona and Paul give for uncompensated material with the same carrier concentration. This procedure gives correct values for R because in the wavelength region of interest the reflection coefficient depends only on the free carrier concentration.

FREE CARRIER ABSORPTION

A typical example of the absorption curves obtained is shown in Fig. 1. At shorter wavelengths there is a strong absorption due to band-band transitions. At longer wavelengths the absorption is due to free carriers. The absorption in this region varies with the wavelength λ approximately as λ^2, and is relatively independent of temperature. Pankove[5] reported a hump in the absorption for germanium with $n = 2.25 \times 10^{19}$ cm^{-3} at about 0.5 ev. In our spectra such a hump was not present.

The wavelength and temperature dependence are in qualitative agreement with what one expects for free carrier absorption in a degenerate semiconductor where impurity scattering probably dominates. A quantitative analysis of the results is very difficult. First of all the absorption was measured at relatively short wavelengths, corresponding to transitions of electrons to levels lying rather high in the conduction band (between 0.2 and

0.6 ev). Therefore transitions to other valleys such as the ⟨000⟩ or ⟨100⟩ valleys (0.14 ev [1] and 0.22 ev [10] above the ⟨111⟩ valley, respectively) will certainly contribute to the absorption. It is difficult to treat the intervalley scattering related to this type of absorption theoretically, because the large change which the momentum of the electron undergoes in the transition implies that the "hard core" of the impurities make an important contribution to the scattering. Moreover the band will not remain parabolic at higher energies, introducing additional uncertainties in the calculations.

Secondly, as we shall see, electron-electron scattering is important in heavily doped n-type germanium. The calculation of the contribution of electron-electron scattering to the free carrier absorption is very difficult.

In view of the difficulties just mentioned, we have not tried to interpret our data on free carrier absorption in terms of these complicated effects.

INDIRECT TRANSITIONS

In order to obtain the absorption due to band-band transitions, the free carrier absorption must be subtracted. This was done by extrapolating the absorption measured at longer wavelength. Although this procedure cannot be very accurate, it will not lead to serious errors (except at very small α's), because the band-edge absorption increases so rapidly. For the presentation of the band-edge absorption due to indirect transitions, the square root of α is plotted as a function of the photon energy $h\nu$. The results for 80°K are shown in Fig. 2. The curves for 200°K and 295°K are similar. The absorption curves exhibit two typical features: (a) the absorption in heavily doped uncompensated n-type germanium rises more steeply than in pure germanium. (b) the absorption in the uncompensated samples begins at approximately the same photon energy, while the curve for compensated germanium is shifted. These results show that the band gap decreases considerably with dope, because one expects the absorption to begin at about $h\nu = E_g + F$, where F is the Fermi

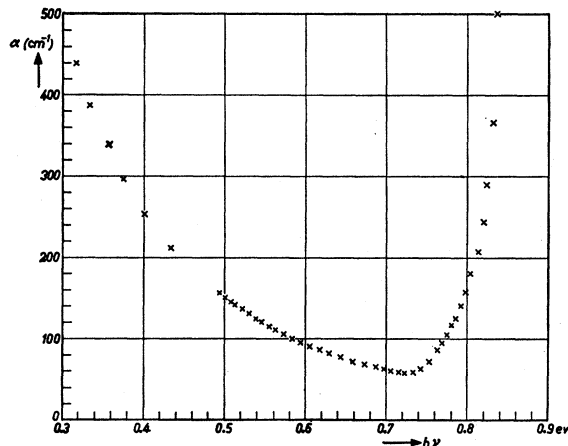[10] R. Braunstein, A. R. Moore, and F. Herman, Phys. Rev. 109, 695 (1958).

FIG. 1. Absorption coefficient at 80°K of germanium doped with 1.95×10^{19} phosphorus atoms per cm³.
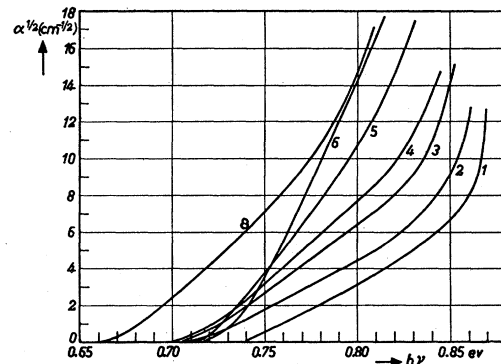

FIG. 2. Square root of the absorption coefficient due to band-band transitions as a function of photon energy $h\nu$ at 80°K. Curves 1 to 6 for uncompensated n-type Ge. Curve 8 for compensated n-type Ge. (For the concentration of impurities see Table I.)

level.[11] In sample 6 with $n=4.3 \times 10^{19}$ cm⁻³, $F=0.083$ ev at 80°K. Therefore the band gap E_g of this crystal will be about 0.08 ev smaller than the band gap of pure germanium.

ANALYSIS OF THE INDIRECT TRANSITION REGION

The rise of the absorption for indirect transitions is related to the density of states in the bands and to the matrix element for the virtual scattering of an electron from the $\langle 000 \rangle$ valley to the $\langle 111 \rangle$ valley.

There is little evidence of any considerable change in the shape of the $\langle 111 \rangle$ valley of the conduction band with dope. Cardona and Paul[7] reported a change of m^* from $0.14m_0$ in pure germanium to $0.24m_0$ in germanium with $n=4.4 \times 10^{19}$ cm⁻³. Such a change is not sufficient to explain the observed increase in the absorption. Moreover, the effective mass m^* measured by Cardona and Paul is an average over the longitudinal and transverse masses m_l and m_t in the $\langle 111 \rangle$ valleys (for parabolic bands $1/m^* = \frac{2}{3}m_t^{-1} + \frac{1}{3}m_l^{-1}$). The density of states effective mass m_{ds}^* involved in the indirect transitions is a different average of m_l and m_t (in the case of 4 parabolic valleys $m_{ds}^* = 4^{\frac{2}{3}}m_t^{\frac{2}{3}}m_l^{\frac{1}{3}}$). Therefore, a change in m^* with dope is not incompatible with a constant m_{ds}^*. A number of experiments have been reported which show that the density-of-states mass is independent of dope in n-type germanium.[12-14] Also Spitzer[15] found that m^* is fairly independent of dope,

contrary to the conclusions of Cardona and Paul. We conclude that the density-of-states effective mass of the $\langle 111 \rangle$ valleys in germanium is independent of the dope, although the anisotropy of the energy surfaces may change. The position of the Fermi level was calculated on this assumption (Table I).

For $n=4.3 \times 10^{19}$ cm⁻³ the Fermi level at 80°K is 0.083 ev. Higher conduction band minima occur at 0.22 ev ($\langle 100 \rangle$ valleys[10]) and at 0.14 ev ($\langle 000 \rangle$ valley[1]). These valleys will not contribute to the density of states at the dopes and temperatures considered.

As a result the enhanced indirect absorption that we found in n-type germanium cannot be due to a change in the density of states, but must be ascribed to some extra scattering mechanism. In pure germanium the virtual scattering of electrons from the $\langle 000 \rangle$ to the $\langle 111 \rangle$ valley is due to phonons.[1] In the impure germanium extra scattering may occur either at impurity atoms or by electron-electron scattering. We shall try to separate the extra scattering mechanism from the normal phonon contribution. The experiments then strongly indicate that in heavily doped n-type germanium electron-electron scattering dominates in the indirect transitions.

The phonon-aided indirect transitions in pure germanium have been studied extensively by Macfarlane al et.[16] These studies show that the absorption is the sum of a number of contributions of different phonon processes. To calculate the phonon contribution, we should in principle use these results and calculate the absorption curve taking into account the change in the band gap and the fact that in n-type germanium part of the conduction band is occupied. This would be a very tedious procedure. Realizing that the phonon contribution in the most heavily doped samples is relatively small, we used a rough approximation to estimate the contribution of phonon scattering. Inspecting the α vs $h\nu$ curves of Macfarlane, it was found

[11] Strictly speaking F used in this paper is a measure of the kinetic energy of the electrons; for complete degeneracy F is equal to the kinetic energy of the most energetic electrons. F defined in this way is not necessarily equal to the Fermi energy. In the one-electron approximation F coincides with the Fermi-level. However, if electron-electron interaction is important, F is no longer equal to the Fermi-level (defined as the thermodynamic potential of the electrons).
[12] R. Bowers, Phys. Rev. 108, 683 (1957).
[13] M. Pollak, Phys. Rev. 111, 798 (1958).
[14] R. Wolfe and R. L. Moore, Bull. Am. Phys. Soc. 6, 155 (1961).
[15] W. G. Spitzer, F. A. Trumbore, and R. A. Logan, Bull. Am. Phys. Soc. 6, 155 (1961).

[16] G. G. Macfarlane, T. P. McLean, J. E. Quarrington, and V. Roberts, Phys. Rev. 108, 1317 (1957).

TABLE II. Parameters A and Δ, used to estimate the phonon scattering in indirect transitions. $E_g{}^0$ is the indirect energy gap in pure germanium.

	A (cm$^{-\frac{1}{2}}$ ev^{-1})	$E_g{}^0$(ev)	Δ(ev)
80°K	45	0.734	0.000
200°K	48	0.700	0.016
295°K	63	0.664	0.016

that the curves may be approximated in the region of interest by

$$\alpha_p = A^2(h\nu - E_g{}^0 + \Delta)^2. \tag{2}$$

In this equation $E_g{}^0$ is the indirect energy gap of pure germanium, and A and Δ are parameters obtained by fitting Macfarlane's result to Eq. (2). The values of A and Δ, found in this way, are given in Table II.

Equation (2) is the theoretical expression for indirect transitions if all phonon processes are added, and complications such as exciton effects are neglected.[17] The energy of the phonons is taken into account in a very approximate way by introducing a shift Δ of the absorption curve.

The influence of the filling of the conduction band can now be introduced, giving for the phonon contribution to the indirect transitions in n-type germanium:

$$\alpha_p = \frac{8A^2}{\pi} \int_0^{h\nu - E_g + \Delta} \frac{x^{\frac{1}{2}}(h\nu - E_g + \Delta - x)^{\frac{1}{2}}dx}{1 + \exp\{(F-x)/kT\}}. \tag{3}$$

The term $1 + \exp\{(F-x)/kT\}$, where F is the position of the Fermi level relative to the band edge, excludes transitions to occupied levels in the conduction band. For pure germanium $\exp\{(F-x)/kT\} \ll 1$, and Eq. (3) reduces to Eq. (2), as required.

A^2 is proportional to the density-of-states effective mass $m_{ds}{}^*$ in the conduction band. $m_{ds}{}^*$ is independent

of the dope, and the other factors occurring in A are probably not very sensitive to the dope. Because the same is true for Δ, we will assume A and Δ to be independent of the dope. For calculating the phonon contribution in doped germanium we therefore use the values of A and Δ for pure germanium (see Table II). The value of the indirect energy gap E_g certainly depends on the dope, and we will use E_g as an adjustable parameter.

The extra scattering mechanism responsible for the enhanced absorption in n-type germanium will be given by an equation of the same type as Eq. (3):

$$\alpha_e = \frac{8B^2}{\pi} \int_0^{h\nu - E_g} \frac{x^{\frac{1}{2}}(h\nu - E_g - x)^{\frac{1}{2}}dx}{1 + \exp\{(F-x)/kT\}}. \tag{4}$$

There is no reason to introduce a shift Δ here, because no phonons are involved. For the two scattering mechanisms proposed for α_e, i.e., impurity or electron-electron scattering, B^2 is expected to be independent of temperature and proportional to the impurity concentration or to the free electron concentration, respectively.

We first analyze the experimental curves taken at 80°K. At this temperature Δ happens to be zero (see Table II).

$$\alpha = \alpha_p + \alpha_e$$
$$= (8/\pi)(A^2 + B^2) \int_0^{h\nu - E_g} \frac{x^{\frac{1}{2}}(h\nu - E_g - x)^{\frac{1}{2}}dx}{1 + \exp\{(F-x)/kT\}}. \tag{5}$$

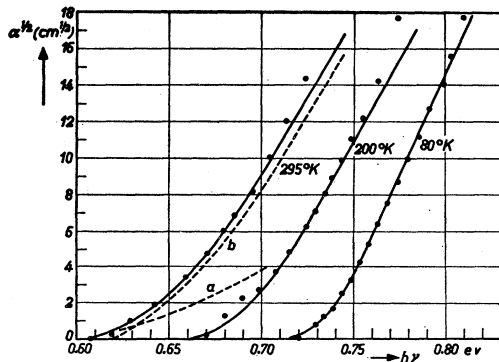The integral was computed numerically for the

FIG. 3. Comparison of calculated absorption curves (drawn lines) and experimental points for specimen 6 ($n = 4.3 \times 10^{19}$ cm^{-3}). At 295°K the two contributions used to find the total calculated absorption curve are shown separately: curve a is the phonon, curve b the electron-electron contribution.

[17] J. Bardeen, F. J. Blatt, and L. H. Hall, *Proceedings of the Conference on Photoconductivity, Atlantic City, November 4-6, 1954* (John Wiley & Sons, Inc., New York, 1956), p. 147.
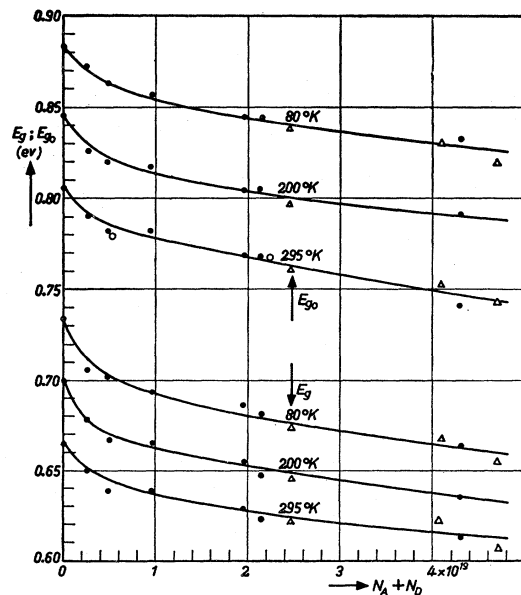

FIG. 4. Direct and indirect energy gap E_{g_0} and E_g as a function of the total impurity concentration $N_A + N_D$. ● : uncompensated n-type Ge, $N_A = 0$ (sample 2 to 7). △ : compensated n-type Ge, $N_A \neq 0$ (sample 8, 9, and 10). ○ : results of Pankove.[5]

TABLE III. Indirect and direct energy gap E_g and E_{g_0} (in ev) in n-type germanium.
B^2 is a measure of the enhancement of the indirect absorption by dope.

Specimen	N_A+N_D (cm^{-3})	n (cm^{-3})	E_{g_0} (295°K)	E_{g_0} (200°K)	E_{g_0} (80°K)	E_g (295°K)	E_g (200°K)	E_g (80°K)	B^2 (cm^{-1} ev^{-2})
1	...	...	0.806	0.845	0.883	0.664	0.700	0.734	...
2	2.4×10^{18}	2.4×10^{18}	0.790	0.826	0.872	0.651	0.679	0.707	0.05×10^4
3	4.5×10^{18}	4.5×10^{18}	0.781	0.820	0.864	0.639	0.667	0.703	0.28
4	9.6×10^{18}	9.6×10^{18}	0.781	0.817	0.858	0.640	0.666	0.694	0.50
5	1.95×10^{19}	1.95×10^{19}	0.769	0.804	0.845	0.629	0.655	0.687	1.37
6	4.3×10^{19}	4.3×10^{19}	0.740	0.792	0.832	0.614	0.635	0.664	2.88
7	2.17×10^{19}	2.17×10^{19}	0.766	0.806	0.844	0.623	0.646	0.680	1.07
8	4.7×10^{19}	1.1×10^{19}	0.744	...	0.820	0.608	...	0.654	0.52
9	4.1×10^{19}	1.1×10^{19}	0.753	...	0.830	0.622	...	0.669	0.65
10	2.5×10^{19}	5×10^{18}	0.764	0.795	0.840	0.624	0.643	0.673	0.28

samples 1 to 10 as a function of $h\nu - E_g$. Thus the shape of the absorption curve is known. B and E_g were adjusted so as to obtain the best fit with the experimental data. In this way it was found possible to represent all experimental curves quite accurately by Eq. (5). The calculated curve and the experimental points for one sample are compared in Fig. 3. At high absorption coefficients, the experimental points deviate from the calculated curve; this deviation is due to the onset of direct transitions just as in pure germanium. The values of E_g and B^2 at 80°K obtained in this way are given in Table III.

It was found that one value of B enables us to represent the $\alpha^{\frac{1}{2}}$ vs $h\nu$ curves for a given sample at 80, 200, and 295°K quite well (Fig. 3). At these temperatures the appropriate values of A and Δ were used, and the absorption coefficient $\alpha = \alpha_p + \alpha_e$ was calculated with the complete Eqs. (3) and (4) because $\Delta \neq 0$. These calculations thus show that the extra scattering parameter B is independent of temperature. The values of E_g consistent with the experimental data are found in Table III.

If we compare the band gap of compensated germanium with the band gap of uncompensated germanium, we find that the decrease of E_g does not depend on the electron concentration. An uncompensated sample (sample 6) and a compensated one (sample 8) with the same total impurity concentration, but with electron concentrations differing by a factor of 4, have the same decrease of E_g. The decrease of E_g depends on the total impurity concentration $N_A + N_D$ approximately as $(N_A + N_D)^{\frac{1}{3}}$. In Fig. 4 E_g is shown as a function of $N_A + N_D$ for 80, 200, and 295°K. The decrease of E_g with dope is rather independent of the temperature.

By comparing compensated and uncompensated germanium we find that B does not depend on the total impurity concentration, but on the electron concentration $n = N_D - N_A$. From Fig. 5, where B^2 is given as a function of n, it can be seen that B^2 is proportional to n.

DIRECT TRANSITIONS

We have already remarked that at higher photon energies some extra absorption over the absorption calculated for indirect transitions occurs which is probably due to direct transitions. The absorption curve for direct transitions is very steep,[1] and its shape is perhaps not strongly influenced by the dope. Assuming the shape to be the same in all specimens, it is possible to make an estimate of the direct energy gap E_{g_0}. The results are given in Table III and Fig. 4.

The value of E_{g_0} in n-type germanium with $n = 2.25 \times 10^{19}$ cm^{-3} was determined from the absorption in thinner samples in a more direct way by Pankove.[5] Our results are in good agreement with Pankove's data (Fig. 4).

Inspection of Fig. 4 shows that the change of the direct and the indirect energy gap with dope is very similar. The change of E_{g_0} with dope is rather independent of temperature and independent of the electron concentration n. E_{g_0} varies with the total impurity concentration approximately as $(N_A + N_D)^{\frac{1}{3}}$. The change of E_{g_0} is perhaps somewhat smaller than the change of E_g, but the difference between the two is hardly significant.
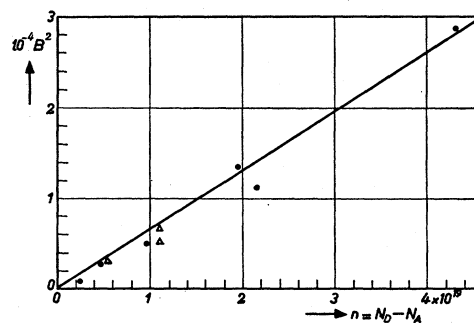

FIG. 5. Scattering parameter B^2 (in cm^{-1} ev^{-2}) as a function of the free electron concentration n. ●: uncompensated n-type Ge (sample 2 to 7). △: compensated n-type Ge (sample 8, 9, and 10).

DISCUSSION

In order to discuss the results obtained for the band gap E_g and E_{g_0} and the extra scattering B^2 in heavily doped n-type germanium, we will first make some general remarks on the properties of heavily doped semiconductors.

In n-type crystals containing only shallow impurities, the electrons may be described by the effective mass theory.[3] The Hamiltonian for electrons in a semiconductor with a single isotropic conduction band is

$$H = -\frac{\hbar^2}{2m^*}\sum_i \nabla_i^2 + \sum_i \sum_{j\neq i}\frac{e^2}{\epsilon|\mathbf{r}_i-\mathbf{r}_j|} - \sum_i\sum_l \frac{Z_l e^2}{\epsilon|\mathbf{R}_l-\mathbf{r}_i|}, \quad (6)$$

where $\mathbf{r}_i$ is the coordinate of electron i, $(\hbar/i)\nabla_i$ the conjugate momentum operator. The second term in (6) represents the electron-electron repulsion, the last term the interaction of the electrons with impurity atoms, charge $Z_l e$, position $\mathbf{R}_l$. The Hamiltonian may be written as

$$H = -\sum_i \nabla_i^2 + \sum_i\sum_{j\neq i}\frac{2}{|\mathbf{r}_i-\mathbf{r}_j|} - \sum_i\sum_l\frac{2Z_l}{|\mathbf{R}_l-\mathbf{r}_i|}, \quad (7)$$

provided we express all coordinates in units of $a = \hbar^2\epsilon(m^*e^2)^{-1}$ (the radius of the first Bohr orbit for an electron with mass m^* in a medium with dielectric constant ϵ), and the energy in units $\mathrm{ry} = m^*e^4(2\hbar^2\epsilon^2)^{-1}$ [rydberg modified for m^* and ϵ]. We remark that m^* and ϵ have disappeared from the Hamiltonian. Equation (7) describes the motion of electrons, their mutual interaction and the interaction with charged impurities in a most general way for any semiconductor provided all parameters are expressed in the appropriate units. The electron concentration should be expressed for example in terms of r_s, defined by $n^{-1} = (4\pi/3)(r_s a)^3$ (r_s is the radius of a sphere with volume equal to the inverse electron concentration), the donor concentration N_D in terms of r_D with $N_D^{-1} = (4\pi/3)(r_D a)^3$.

Equation (7) is the fundamental equation for a large variety of phenomena such as impurity scattering and impurity band conduction. All these phenomena, in the approximation used, must be identical in all semiconductors, if the appropriate dimensionless quantities are used. We remark that anisotropy of the effective mass and multiple valleys give some deviations from this general rule.

If the electron and the impurity concentrations are very low (r_s, r_D, $r_A \gg 1$) the electron-electron interaction is not important, and the lowest states of H will be the well-known bound impurity states described by Kohn.[3] In the ground state each electron is bound to a donor at $E = -1$ (one rydberg below the conduction band). For larger concentrations ($r_D > 1$), the wave functions begin to overlap, giving rise to an impurity band.

At very high electron concentrations ($r_s < 1$) the electron-electron interaction increases, and the impurity and the conduction band are no longer separated. The situation in this region may be described as a dense electron gas ($r_s < 1$) perturbed by charged impurities. The effective electron density in heavily doped germanium ($n = 4\times10^{19}$ cm^{-3}; $r_s = 0.4$) is even larger than in many metals (Na; $r_s = 4$). This comes from the fact that in germanium we have large Bohr orbits (small m^* and large ϵ), giving a strong overlap already at low electron concentrations.

The electron-electron interaction energy for a high-density electron gas (but neglecting the influence of impurities) has been calculated.[18] Several authors have studied the interaction of electrons with charged donor impurities.[19,20] A calculation in which both electron-electron and electron-impurity interaction for a semiconductor with a random distribution of impurities are treated in a rigorous way, has not been given.

The experiments on the edge absorption show that the direct and the indirect energy gap change with the total impurity concentration in the same way. The change does not depend on the electron concentration. Apparently the electron-electron interaction has little influence on the band gap. The conduction band as a whole shifts to lower energies, due to the presence of the charged impurity atoms.

The fact that the electron-electron interaction does not lead to a marked change of the energy gap may be understood from the calculations of the energy of a dense electron gas.[18] The main term in the electron-electron interaction for $r_s < 1$ is the exchange energy per electron, given by $E_x = -0.916/r_s$ (in modified Rydberg units). The corresponding change of the indirect energy gap will be the change of E_x if one electron is added to the gas: $\Delta E_g(\text{exchange}) = E_x + n(\partial E_x/\partial n)$, giving $\Delta E_g(\text{exchange}) = -1.22/r_s$. For a multivalley semiconductor with anisotropic valleys this result should be modified (see Appendix). For germanium with four valleys, and $m_1 = m_2 = 0.082m_0$ and $m_3 = 1.58m_0$ we find for $n = 4.3\times10^{19}$ cm^{-3} ΔE_g (exchange) $= 0.017$ ev. This value is much smaller than the observed change of 0.07 ev. The direct energy gap is not influenced by the exchange energy because the wave functions of the $\langle 000 \rangle$ and the $\langle 111 \rangle$ valleys are sufficiently different. For the same reason the hole created in the absorption process will not contribute to the exchange energy. Therefore, we expect that the exchange energy will give a small difference in change between E_g and E_{g_0}. The observed difference, though small, is consistent with this prediction.

The main effect on E_g and E_{g_0} must be due to the interaction with the impurity atoms. To the author's knowledge, no adequate theory has yet been given for the effect on the band gap of charged impurities (positive and negative) distributed at random through the crystal. Such a theory should take into account the

[18] M. Gell-Mann and K. A. Brueckner, Phys. Rev. 106, 364 (1957).
[19] W. Baltensperger, Phil. Mag. 44, 1355 (1953).
[20] F. Stern and R. M. Talley, Phys. Rev. 100, 1638 (1955).

interaction with the impurities of both the hole and the electron created in the absorption process. Also the fact that the direct and the indirect energy gap show approximately the same change with the impurity concentration should be explained.

Contributions to the virtual scattering of electrons from the $\langle 000 \rangle$ to the $\langle 111 \rangle$ valley may arise either from impurities or from electron-electron interaction. Due to the large change in **k** in this process, the short-range potential of the impurity will be more important than the long-range Coulomb potential. Therefore the contribution of impurities to B will presumably depend on the type of impurity, i.e., one expects different values for P, As, etc. Taking into account these considerations, our data strongly suggest that the main contribution to B comes from electron-electron interaction. In the first place, B has the same value for uncompensated As- and P-doped samples. Secondly, B for an uncompensated As-doped sample with 2.17×10^{19} As per cm^3 is considerably larger than for a compensated sample with 2.6×10^{19} As per cm^3 (compare sample 7 and 9 in Table III).

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APPENDIX

Exchange Energy in a Multivalley Semiconductor

The total exchange energy in a medium with dielectric constant ϵ is given by[21]:

$$W_x = -\tfrac{1}{2} \sum_i \sum_{j \neq i} \frac{e^2}{\epsilon} \int \int \frac{1}{r_{12}} \varphi_i^*(\mathbf{r}_1) \varphi_j(\mathbf{r}_1)$$

$$\times \varphi_j^*(\mathbf{r}_2) \varphi_i(\mathbf{r}_2) d\tau_1 d\tau_2, \quad (A1)$$

where the first summation is carried out over all occupied one-electron states φ_i and the second sum-

[21] F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940).

mation only over those occupied states φ_j with the same spin direction as φ_i.

In a multivalley semiconductor the exchange energy between electrons of different valleys vanishes. In the effective mass approximation, the one-electron wave functions in a particular valley may be written as $V^{-\frac{1}{2}} e^{i\mathbf{k} \cdot \mathbf{r}}$, where V is the volume of the crystal. For a degenerate semiconductor with four equivalent valleys equation (A.1) becomes

$$W_x = -\frac{4e^2}{\epsilon V^2} \int \int \{ \sum_k e^{i\mathbf{k} \cdot (\mathbf{r}_2 - \mathbf{r}_1)} \}$$

$$\times \{ \sum_{k'} e^{i\mathbf{k}' \cdot (\mathbf{r}_1 - \mathbf{r}_2)} \} \frac{d\tau_1 d\tau_2}{r_{12}}. \quad (A2)$$

The sum $\sum_k e^{i\mathbf{k}\mathbf{r}}$ for one anisotropic valley, energy $E = (\hbar^2/2)(m_1^{-1} k_1^2 + m_2^{-1} k_2^2 + m_3^{-1} k_3^2)$, may be evaluated directly. The result is

$$\sum_k e^{i\mathbf{k} \cdot \mathbf{r}} = \frac{V}{2\pi^2} \left(\frac{2F}{\hbar^2} \right)^{\frac{3}{2}} (m_1 m_2 m_3)^{\frac{1}{2}} \left(\frac{\sin\alpha - \alpha \cos\alpha}{\alpha^3} \right), \quad (A3)$$

where F is the kinetic energy of the electrons in the highest occupied state (Fermi-level), and $\alpha = \hbar^{-1}(2F)^{\frac{1}{2}} \times (m_1 r_1^2 + m_2 r_2^2 + m_3 r_3^2)$, and r_1, r_2, and r_3 are the components of **r** along the main axes of the effective mass ellipsoid of the valley under consideration.

Substituting (A.3) in (A.2) and performing the integration (which is elementary), we obtain for the total exchange energy in the case $m_1 = m_2$:

$$W_x = -\frac{4e^2 F^2 m_1 m_3 V}{\epsilon \pi^3 \hbar^4} \left(\frac{m_3 - m_1}{m_1} \right)^{-\frac{1}{2}} \tan^{-1} \left(\frac{m_3 - m_1}{m_1} \right)^{\frac{1}{2}}. \quad (A4)$$

In a degenerate semiconductor with four equivalent valleys in the conduction band the number of electrons is given by

$$N = nV = \frac{4}{3\pi^2} \left(\frac{2F}{\hbar^2} \right)^{\frac{3}{2}} m_1 m_3^{\frac{1}{2}}. \quad (A5)$$

Eliminating F, we find for the total exchange energy per electron $E_x = N^{-1} W_x$

$$E_x = \frac{3e^2}{4\epsilon} \left(\frac{3n}{4\pi} \right)^{\frac{1}{3}} \left(\frac{m_3}{m_1} \right)^{\frac{1}{2}} \left(\frac{m_3 - m_1}{m_1} \right)^{-\frac{1}{2}} \tan^{-1} \left(\frac{m_3 - m_1}{m_1} \right)^{\frac{1}{2}}. \quad (A6)$$