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Interband Scattering in *n*-Type Germanium*

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The pressure dependence of the electrical conductivity of *n*-type germanium has been measured to pressures of 30 000 kg/cm^2 at temperatures between 273° and 350°K. A satisfactory explanation of the results requires the existence of two different types of minima in the conduction band, separated by between 0.15 and 0.21 ev at 350°K with the lower range of values slightly preferred. The higher energy minima lie in the [100] direction in reciprocal space, and are similar in properties to the lowest set of minima in silicon. The changes in position of the two minima with pressure are determined. For the minima that are lowest at atmospheric pressure, $d(E_{111}-E_v)/dP=(4.9\pm0.5)\times10^{-6}$ ev/kg-cm^{-2}, and for the [100] set, $d(E_{100}-E_v)/dP=(0_{-2}^{+1})\times10^{-6}$ ev/kg-cm^{-2}. The change in average electron mobility with pressure is explained in terms of a sharing of electrons between states in the two sets of minima, and an additional relaxation process that scatters carriers from one type of minimum into the other. The effect of pressure on the effective masses, the elastic constants, and the deformation potential is briefly considered.

I. INTRODUCTION

In a semiconductor the transport properties are normally governed by a small number of current carriers at the top of the valence band or at the bottom of the conduction band. Each band edge is located at a set of symmetrically equivalent regions in reduced momentum or **k** space. The possibility exists that a different set of equivalent regions in **k** space from the same or a different energy band will have energy states or extrema close enough in energy to the band edges so that enough carriers occupy them to give a significant contribution to the transport properties.

Furthermore, it is possible that the probability for scattering current carriers between the two nonequivalent sets of extrema will be comparable with the probability of scattering in each extremum itself. We shall call this process interband scattering. Interband scattering becomes particularly interesting when, by varying some parameter of the semiconductor, it is possible to shift the band edge from one set of regions in **k** space to another. It is the purpose of this paper to examine the problem of interband scattering, and to show that the behavior under hydrostatic pressure of *n*-type germanium is well explained by such a mechanism.

We begin our discussion by reviewing briefly the effects of high pressure on the properties of germanium, and then looking qualitatively at these effects with a two-band theory in mind.

Bridgman[1] found a marked difference between the behavior of the electrical conductivity of *p*- and *n*-type germanium as a function of pressure. The conductivity of the former increases by about 6% in 30 000 kg/cm^2, while that of the latter shows a gradual decrease until about 15 000 kg/cm^2, when the rate of decrease becomes much greater. The conductivity at 30 000 kg/cm^2 is about one-fourth of the value at atmospheric pressure. Since the germanium used in these experiments was in the extrinsic range, that is, the number of current carriers was independent of temperature, these changes in conductivity were presumed to be caused by a variation of the mobility of the current carriers. A typical plot of conductivity or mobility as a function of pressure for *n*-type germanium (4 ohm-cm) is shown in Fig. 1.

Bridgman[2] extended the conductivity measurements to 100 000 kg/cm^2. These data show a sharp minimum at about 50 000 kg/cm^2 in *n*-type material. The experiment was complicated by the fact that pressure could not be transmitted hydrostatically. Nevertheless,

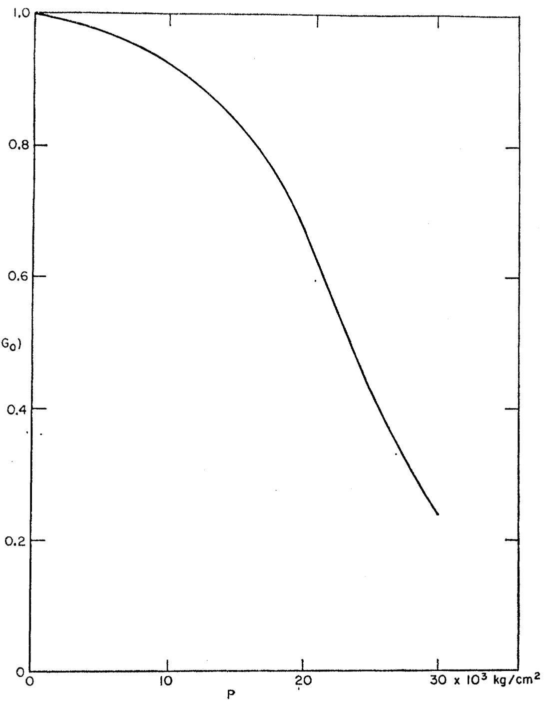

FIG. 1. Conductance, normalized to its atmospheric value, vs pressure for *n*-type germanium at 295°K.

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* Research supported by the Office of Naval Research.

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[1] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **79**, 127 (1951).

[2] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **81**, 221 (1952).

measurements on a number of samples indicated that the minimum is, very probably, a genuine hydrostatic pressure effect.

Measurement of the change of the forbidden energy gap with pressure shows it to be increasing with increasing pressure. The deduction is made from a number of measurements, namely, the change in resistance of a *p-n* junction,[3] the shift of the optical absorption edge,[4] and the change in intrinsic conductivity at elevated temperatures.[5]

Let us discuss this last method. The conductivity of a semiconductor is given[6] by

$$\sigma = ne\mu_n + pe\mu_p, \tag{1}$$

where e is the electronic charge, n is the density of electrons in the conduction band, p is the density of holes in the valence band, and μ_p and μ_n are the mobilities of holes and electrons, respectively. In an intrinsic semiconductor $n=p=n_i$. The intrinsic concentration n_i can be shown to be[7]

$$n_i = A\exp(-E_G/2kT), \tag{2}$$

where A depends upon the effective masses of the electrons and holes at the band extrema and the absolute temperature T, E_G is the forbidden energy gap, and k is Boltzmann's constant. It is seen from Eqs. (1) and (2) that, by applying the appropriate mobility corrections, the energy gap may be obtained as a function of pressure. Paul and Brooks[8] measured the conductivity of intrinsic germanium to 30 000 kg/cm^2 at 349°K. They took into account the variation of the mobilities with pressure by using Bridgman's[9] results on impure samples at room temperature. The validity of this procedure will be discussed later. The results which they obtained for E_G are shown in Fig. 2. At low pressures the rate of change of energy gap with pressure is

$$(dE_G/dP) = 5\times10^{-6}\ \text{ev/kg-cm}^{-2}.$$

Near 30 000 kg/cm^2, the apparent dE_G/dP is about one-half this value. This degree of nonlinearity in the pressure shift is difficult to understand with a simple "one-band" model.

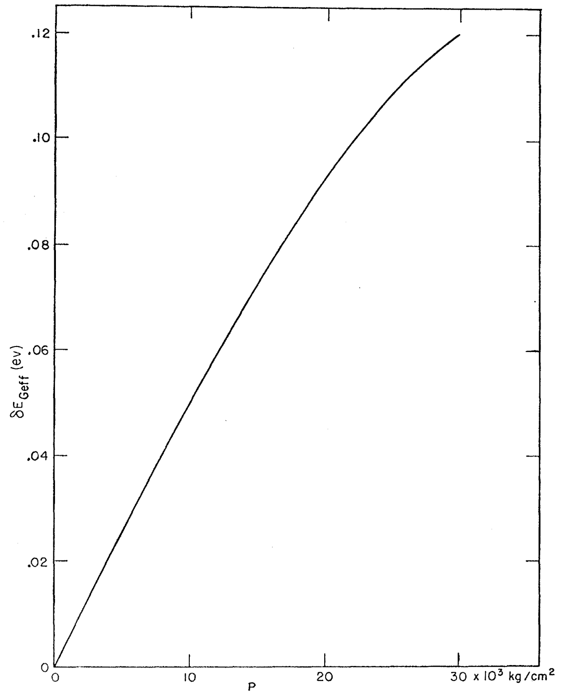

FIG. 2. The change of effective energy gap in germanium vs pressure at 349°K (after Paul and Brooks[8]).

We assume that in addition to the set of minima ($\mathbf{k}_1$) in the conduction band which determines the energy gap at atmospheric pressure, there is a second set of minima ($\mathbf{k}_2$) which becomes important at high pressures. This will occur if the set ($\mathbf{k}_1$) is moving away from the valence band with increasing pressure, and the set ($\mathbf{k}_2$) is approximately stationary relative to the valence band edge. The initial linear increase in E_G is explained by the motion of the ($\mathbf{k}_1$) energy states away from the valence band. The bending over at high pressures is explained by the ($\mathbf{k}_2$) minima becoming important. The mobility variation is explained qualitatively if it is assumed that electrons in the vicinity of the ($\mathbf{k}_2$) minima have a lower mobility than electrons in the vicinity of the ($\mathbf{k}_1$) minima, and if the two sets of minima have approximately the same energy for a pressure between 30 000 kg/cm^2 and 40 000 kg/cm^2. Furthermore, to account for the maximum in the resistance observed by Bridgman, it is necessary to assume that the mobility is further reduced by scattering between the two sets of minima when this is compatible with energy conservation. Then it is seen that the initial change in mobility of n-type material is caused by the increasing importance of the states ($\mathbf{k}_2$). As the pressure is further increased the states ($\mathbf{k}_1$) move away from the valence band, and the mobility becomes characteristic of the states ($\mathbf{k}_2$). In the range of pressure where both sets of states are important the conductivity goes through its minimum, and there is a great deal of interband scattering.

Thus, the effects of high pressure on n-type and intrinsic germanium are qualitatively explained by the assumption of a twofold conduction band. We can identify the two sets of regions in $\mathbf{k}$ space which we have been discussing. Figure 3 shows the band structure

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[3] H. H. Hall, J. Bardeen, and G. L. Pearson, Phys. Rev. **84**, 129 (1951).

[4] W. Paul and D. M. Warschauer, J. Phys. Chem. Solids **5**, 89 (1958).

[5] P. H. Miller and J. Taylor, Phys. Rev. **76**, 179 (1949). W. Paul and H. Brooks, Phys. Rev. **94**, 1128 (1954).

[6] W. Shockley, *Electrons and Holes in Semiconductors* (D. Van Nostrand and Company, Inc., New York, 1950), p. 16.

[7] See reference 6, p. 245.

[8] W. Paul and H. Brooks, Phys. Rev. **94**, 1128 (1954).

[9] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **82**, 71 (1953).

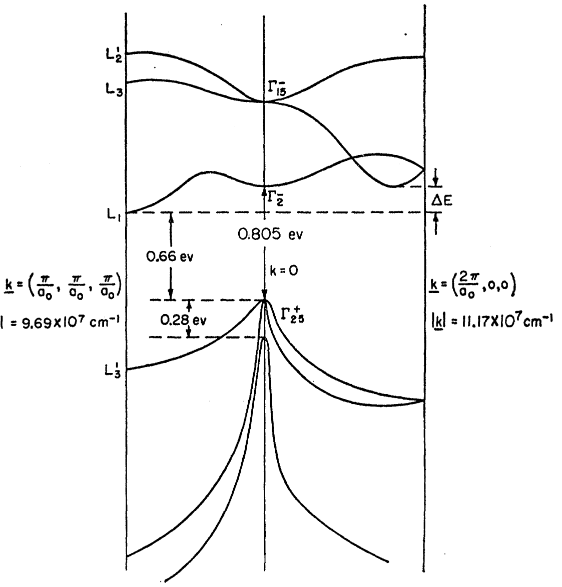

FIG. 3. Band structure of germanium near 300°K.

of germanium as suggested by Herman[10] and the cyclotron resonance experiments of the Lincoln[11] and Berkeley[12] groups. Energy is plotted as a function of **k** for two directions in the first Brillouin zone. The energy differences listed were the accepted values at the time of the Rochester Semiconductor Conference in 1958.[13] The maximum of energy in the valence band is at the **k** = [000] position. The regions of minimum energy in the conduction band, which we have been calling ($\mathbf{k}_1$) are along the [111] directions in **k** space.

Where are the ($\mathbf{k}_2$) states? The states centered around **k** = [000] are excluded because measurement of the shift with pressure of the onset of optical absorption due to transitions between the [000] position in the valence and conduction bands shows that these states move away from the valence band with increasing pressure at a rate two or three times that of the minima in the [111] direction.[14] On the other hand, the minima in the [100] direction at ~0.18 ev above those in the [111] direction are a reasonable choice to explain the experimental data.

The basis for placing these minima at this energy is as follows: The lowest energy states in the conduction band in silicon are in the [100] direction. Johnson and Christian[15] measured the intrinsic optical absorption edge as a function of composition for silicon-germanium alloys. The results of their determination are shown in Fig. 4. We note that the variation of the energy gap is not a linear function of the composition, but is composed of two linear portions with a break at about 15 mol percent silicon in germanium. In interpreting these results, Herman[10] assumes that the linear portion of the curve between 0 and 15 mol percent silicon is caused by a linear change of the energy of the [111] minima with composition. The linear portion between 15 and 100 mol percent silicon is caused by a linear variation of the energy of the [100] minima with composition. The break at about 15% is caused by the two bands crossing. In subsequent work,[16] it was shown that the variation was inadequately represented by two straight lines, although the curve relating the (arbitrarily determined) optical energy gap and composition could still be divided into two parts. The later relation makes it harder to extrapolate the position of minima to concentrations where they are not directly measurable, but has no effect on the validity of establishing the *type* of minimum appropriate for our experiments by this sort of extrapolation.

The identification of the minima was later confirmed by magnetoresistance measurements on the alloys.[17] The position of the [100] minima in germanium is estimated by extrapolating the upper portion of the curve of energy gap versus composition to zero percent silicon content. An estimate of 0.22 ev is obtained for the separation of the [111] and [100] minima, ΔE.[16]

It was suggested independently by Brooks and Paul[18]

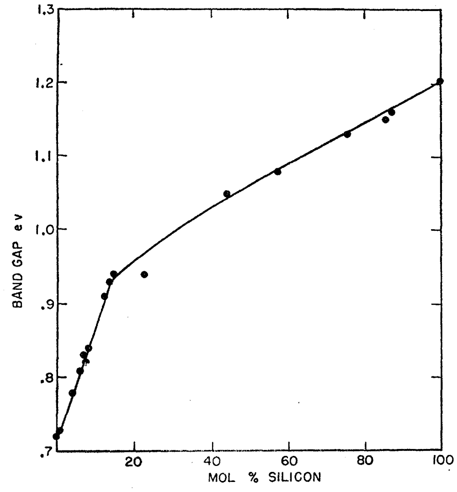

FIG. 4. Variation of energy gap of Ge-Si alloys (after Johnson and Christian[15]).

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[10] F. Herman, Phys. Rev. **95**, 847 (1954).

[11] B. Lax, H. J. Zeiger, R. N. Dexter, and E. S. Rosenblum, Phys. Rev. **93**, 1418 (1954).

[12] G. Dresselhaus, A. F. Kip, and C. Kittel, Phys. Rev. **98**, 368 (1955).

[13] G. G. Macfarlane, T. P. McLean, J. E. Quarrington, and V. Roberts, J. Phys. Chem. Solids **8**, 388 (1958). S. Zwerdling, L. Roth, and B. Lax, *ibid.* **8**, 397 (1958); A. Kahn, Phys. Rev. **97**, 1647 (1955).

[14] H. Y. Fan, M. L. Shepherd, and W. Spitzer, *Proceedings of the Conference on Photoconductivity, Atlantic City, 1955*, edited by R. G. Breckenridge *et al.* (John Wiley & Sons, Inc., New York, 1956), p. 184. W. Paul, J. Phys. Chem. Solids **8**, 196 (1959). M. Cardona and W. Paul, *ibid.* **17**, 138 (1960).

[15] E. R. Johnson and S. M. Christian, Phys. Rev. **95**, 560 (1954).

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

[17] M. Glicksman, Phys. Rev. **100**, 1146 (1955).

[18] H. Brooks and W. Paul, Bull. Am. Phys. Soc. **1**, 48 (1956).

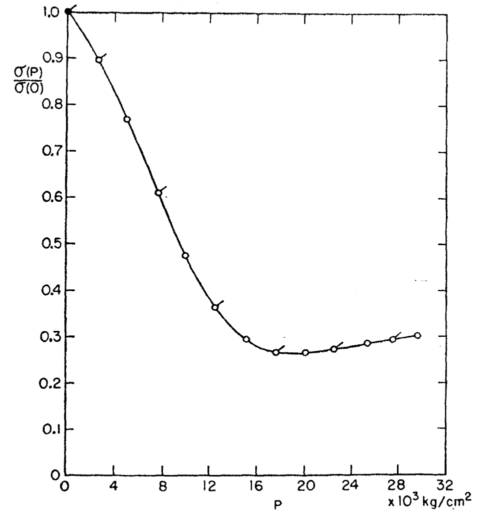

FIG. 5. Normalized conductance vs pressure at room temperature of a sample containing approximately 8% silicon in germanium (after Bridgman and Paul[21]).

and by Herman[10] that it is the [100] minima which become important at high pressures in germanium. The energy gap in silicon decreases as a function of pressure at a rate of approximately 1.5×10^{-6} ev/kg-cm^{-2}. This is deduced from measurement of the change of conductivity of intrinsic silicon at elevated temperatures[19] and the pressure shift of the optical absorption edge.[20] Hence, it seems not unreasonable that the [100] minima remain approximately stationary relative to the valence band in germanium.

If this picture is correct, the two sets of minima are closer in energy in a germanium-silicon alloy, between 0 and 15% silicon concentration, than in pure germanium. Thus, an alloy in this range should behave at atmospheric pressure like pure germanium at an elevated pressure. If the conductivity of an n-type sample of say 8% silicon in germanium is measured, a minimum in the conductivity should be found at much lower pressure than Bridgman observed in his 100 000 kg/cm^2 determination and should thus be accessible to measurement in a pressure range where purely hydrostatic pressures are attainable. This supposition has been confirmed by Bridgman and Paul[21] whose unpublished measurements is reproduced in Fig. 5 by kind permission of the authors.

In view of these results, we shall assume that the two sets of minima which are important in germanium are along the [111] and the [100] directions in **k** space.

In Sec. II, we present an approximate theory of the conductivity of a semiconductor with two conduction bands. The apparent energy gap obtained from measurement of intrinsic conductivity will also be predicted. Section III contains experimental results on the conductivity of n-type germanium as a function of pressure over a range of temperature. Section IV presents the fit of the theory in Sec. II with the data of Sec. III and other data.

II. INTERBAND SCATTERING THEORY

We designate all those quantities which refer to properties of the [111] minima by a subscript (g) and those which refer to properties of the [100] minima by a subscript (s). Our immediate purpose is to calculate the electrical conductivity which we may write as

$$\sigma=e(n_g\mu_g+n_s\mu_s+p\mu_p), \tag{3}$$

where n_x= the density of electrons in the x-conduction band, (the subscript x will be used as a general subscript for quantities referring to more than one band), p= the density of holes in the valence band, and μ_x= the mobility of the carriers in the x band. We assume that Boltzmann statistics hold, i.e., $(E_x-E_F)/kT\gg1$, where E_F is the Fermi energy and E_x is the energy of the band edge. It follows that

$$\begin{aligned} n_g&=C_0C_g\exp(E_F-E_g)/kT,\\ n_s&=C_0C_s\exp(E_F-E_g-\Delta E)/kT,\\ p&=C_0C_v\exp(E_v-E_F)/kT, \end{aligned} \tag{4}$$

where E_g= the energy of the g conduction band edge, E_v= the energy of the valence band edge, ΔE= the energy separation between the two conduction band edges, $C_0=2(2\pi kT/h^2)^{\frac{3}{2}}$, C_x= a density-of-states factor $=m_{dx}{}^{\frac{3}{2}}\nu_x$, m_{dx}= the density of states effective mass for the x band, ν_x= the number of extrema in the x band, and h= Planck's constant.

In writing the third part of Eq. (3) we ignored the existence of more than one kind of hole. This, however, makes no difference to any of the arguments that follow.

For an n-type crystal ($p\ll n$) in the extrinsic temperature range it can easily be shown that

$$n_g+n_s=N_D-N_A=n_0, \tag{5}$$

where N_D= the density of donor impurities and N_A= the density of acceptor impurities.

Thus, we see that measurement of the conductivity of an n-type sample of germanium as a function of pressure will yield the pressure variation of the effective electron mobility

$$\mu_{\text{eff}}=(\mu_gn_g+\mu_sn_s)/n_0. \tag{6}$$

The quantities n_g and n_s can be obtained from Eqs. (4) and (5)

$$\begin{aligned} (n_s/n_g)&=(C_s/C_g)\exp(-\Delta E/kT),\\ n_g&=n_0/[1+(C_s/C_g)\exp(-\Delta E/kT)],\\ n_s&=n_0/[1+(C_g/C_s)\exp(\Delta E/kT)]. \end{aligned} \tag{7}$$

That we are actually measuring a change in the

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[19] W. Paul and G. L. Pearson, Phys. Rev. **98**, 1755 (1955).

[20] W. Paul and D. M. Warschauer, J. Phys. Chem. Solids **5**, 102 (1958).

[21] P. W. Bridgman and W. Paul (unpublished).

average mobility has been verified by Smith.[22] He showed experimentally that the variation with pressure of the conductivity and drift mobility in germanium are the same.

Using Eq. (4) we may write

$$
\begin{aligned}
n_i^2 &\equiv np = C_0^2 C_v C_g \exp(-E_{Gg}/kT) \\
&\qquad \times[1+(C_s/C_g)\exp(-\Delta E/kT)], \\
E_{G\mathrm{eff}} &\equiv -2kT\ln(n_i) = -kT\ln(C_0^2 C_v C_g)+E_{Gg} \\
&\qquad -kT\ln[1+(C_s/C_g)\exp(-\Delta E/kT)],
\end{aligned}
\tag{8}
$$

where

$$E_{Gg}=E_g-E_v,$$

$$n=n_s+n_g.$$

In an intrinsic crystal

$$n=p=n_i.$$

By dividing out the mobility as a function of pressure, we can from measurement of the conductivity of intrinsic material as a function of pressure obtain the variation of $E_{G\mathrm{eff}}$ with pressure, assuming that the effective masses are independent of pressure. In practice it is necessary to correct the conductivity for the density of impurity derived electrons, n_0, which can be determined by measuring the conductivity at low temperatures. The quantity n_i is determined from

$$
\begin{aligned}
&[(n_0/2)^2+n_i^2]^{\frac{1}{2}} \\
&\quad =[(\sigma/e)-(\mu_n-\mu_p)n_0/2]/(\mu_n+\mu_p),
\end{aligned}
\tag{9}
$$

which is obtained from Eq. (1), the charge balance equation, $n-p=n_0$, and $n_i^2=np$.

If we assume that the band edges all move linearly with pressure and that the low pressure increase of $E_{G\mathrm{eff}}$ is due entirely to the change of E_{Gg}, we obtain $(C_s/C_g)\exp(-\Delta E/kT)$ as a function of pressure.

In order to calculate the mobilities of the electrons in the two bands we make the following assumptions:

(1) The scattering time τ is a function of energy, but not of direction in $\mathbf{k}$ space. The results of magnetoresistance measurements on n-type germanium[23] indicate that this is the case for intravalley acoustic mode scattering. For interband scattering, if the range of $\mathbf{k}$ values over an ellipsoid of constant energy, to or from which there is scattering, is small compared to the $\mathbf{k}$ vector of the phonon between the centers of the two minima, then the probability of scattering will be independent of the position of the final state in each valley. Under these conditions it can be shown that τ is independent of the direction of $\mathbf{k}$.[24] Herring has discussed this case in connection with intervalley scattering, where the conditions are quite well fulfilled. For interband scattering, the reasoning for intervalley scattering applies when $\Delta=\Delta E/kT<1$, and therefore all points on the ellipsoids between which interband scattering can occur with the emission or absorption of phonons are well separated in $\mathbf{k}$ space. However, as Δ becomes large the ellipsoids which contribute to interband scattering become larger. The maximum range of the electronic $\mathbf{k}$ vectors in the (111) valleys in germanium at an energy ΔE above the band edge is given by the relation

$$\Delta E=\hbar^2(\Delta k)^2/2m_{lg},$$

$$\Delta k\equiv|\mathbf{k}-\mathbf{k}_g|,$$

where $\hbar=h/2\pi$, $\mathbf{k}_g=$ the center position of the minima (assumed to be on the zone boundary) and m_{lg} is the longitudinal effective mass in the [111] minima. For $\Delta E=0.15$ ev, $\Delta k=2.4\times10^7$ cm^{-1}. The value of $|\mathbf{k}|$ at the boundary$\cong10^8$ cm^{-1}. We take the [100] minima 0.8 of the distance to the zone boundary which is their position in silicon.[25] The absolute magnitude of the $\mathbf{k}$ vector, $\mathbf{k}_{gs}$, between the centers of the two types of minima is

$$|\mathbf{k}_{gs}|=|\pi/a_0(1,1,0.6)|\cong8.5\times10^7\ \mathrm{cm}^{-1}.$$

Therefore, the condition is approximately fulfilled, i.e.,

$$\Delta k/|\mathbf{k}_{gs}|\cong1/3.$$

(2) We assume that the effective mass is constant from the band edge up to an energy greater than ΔE. We may not be justified in making this assumption in view of the work of Bowers[26] and Cardona *et al.*[27] The former finds little dependence of the mass on energy, while the latter workers find quite a considerable increase of the mass with energy. We shall regard the question as open, but shall not include any variation explicitly in our theory.

This assumption will actually affect our fit of theory to experiment very little. The effect on the electron statistics will be buried in the phenomenological constants used to describe state densities. The effect on the mobility of carriers in the g band will be pressure independent, if we assume the mass to be independent of pressure, and further assume that the nonparabolic regions of the s band are inaccessible in our range of

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[22] A. C. Smith, Gordon McKay Laboratory, Harvard University, Technical Report HP-2, 1958 (unpublished).

[23] Magnetoresistance measurements give $K=K_m/K_\tau$, where K_m is the ratio of the two principal components of the effective mass tensor for electrons in a [111] minimum and K_τ is the ratio of the electron scattering probabilities in the corresponding directions. C. Goldberg, Phys. Rev. **109**, 331 (1958) finds K at room temperature close to the cyclotron resonance value for K_m at 4°K, as do R. M. Broudy and J. D. Venables, Phys. Rev. **105**, 1757 (1957). On the other hand, C. Herring, T. H. Geballe, and J. E. Kunzler, Bell System Tech. J. **38**, 657 (1959) find K at room temperature some 15% below K_m at 4°K. Recent precise measurements of magnetoconductivity by Howard (unpublished) at Harvard University, support the conclusion that, provided lattice scattering is dominant, the K for room temperature and below is very close to K_m determined at 4°K, which implies that it is rather probable that K_m is relatively constant with temperature and $K_\tau=1$ for lattice scattering dominant.

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

[25] G. Feher, Phys. Rev. **114**, 1219 (1959). W. P. Dumke, *ibid.* **118**, 938 (1960).

[26] R. Bowers, J. Phys. Chem. Solids **8**, 206 (1959).

[27] M. Cardona, W. Paul, and H. Brooks, Helv. Phys. Acta. **33**, 329 (1960).

pressure; this assumption is probably very well justified. Mass variation with energy in the g band affects the interband scattering probability for electrons in the s band for high values of ΔE, but at pressures high enough that there is appreciable conductivity in the s band, the departure from parabolicity of the g band is negligible.

(3) We neglect all forms of scattering except intravalley acoustic mode scattering and interband scattering. This is tantamount to neglecting the deviation of the temperature dependence of the mobility from a $T^{-1.5}$ law, or to assuming that it is caused by explicit variations of parameters in the intravalley scattering mobility. However, it is not finally established what causes the deviation. Involved may be a temperature dependence of the effective mass[26,27] or deformation potential[28] or a contribution from optical mode scattering.[29] Since the deviation is small (closer[30] to $T^{-1.75}$), we have not considered any other scattering mechanisms in the theory.

(4) The energy of the interacting phonons is neglected. The lowest energy branch of the phonon spectrum is the transverse acoustic one[31]; from Brockhouse and Iyengar's data[31] for the [100] and [111] directions, the phonon energy appears to be = 0.009 ev, so that at room temperature this mode is almost classically excited. If the energy of more energetic vibration modes is comparable with kT, the mode is appreciably excited, but it appears that the contributions of these modes may be lumped in with the classically excited ones, and the total contribution described by a phenomenological constant (the constant B defined below). This situation is analogous to that which occurs in free carrier absorption, where the very large contribution of optical modes does not affect the temperature and wavelength dependence of the absorption even although the phonon energy is comparable with kT. In qualitative fashion, the low excitation of the most energetic modes compensates the errors committed through neglect of their energy in the transition. We have not worked out so far a detailed theory which includes the phonon energies, but it is anticipated that neglect of these energies will involve only small uncertainties of the energy separation of the conduction bands and other parameters in the theory.

(5) No other minima in **k** space besides those along the [100] and [111] directions contain enough electrons to contribute appreciably to the conductivity. The only known possibility for appreciable conductivity is the [000] minimum. As we argued earlier, the contribution of this minimum at atmospheric pressure is negligible because of its energy separation from the [111] minima and its low mass, and this contribution becomes even less important with increasing pressure.

Using these assumptions we can write

$$\begin{aligned} 1/\tau_g(E) &= A_g C_g' E^{\frac{1}{2}} + B_g C_s' (E-\Delta E)^{\frac{1}{2}} \nu_s, && E \geq \Delta E \\ &= A_g C_g' E^{\frac{1}{2}}, && E < \Delta E \qquad (10) \\ 1/\tau_s(E) &= A_s C_s' (E-\Delta E)^{\frac{1}{2}} + B_s C_g' E^{\frac{1}{2}} \nu_g \end{aligned}$$

for $\Delta E \geq 0$. (If $\Delta E < 0$, interchange subscripts g and s throughout.) In Eq. (10), E_g is taken as the zero of energy. A_x = intravalley scattering matrix element squared $\times (2\pi)^2/h$, B_x = interband scattering matrix element squared $\times (2\pi)^2/h$, C_x' = a density of states factor $= m_{lx}^{\frac{1}{2}} m_{tx} 4\pi 2^{\frac{1}{2}}/h^3$, m_{lx} = longitudinal mass in x valley, m_{tx} = transverse mass in x valley, and ν_x = number of equivalent x valleys. From the principle of detailed balance we find $B_g = B_s = B$.

We can calculate the transport properties in terms of the scattering times.[24] The mobility in each band is

$$\begin{aligned} \mu_g &= e\langle \tau_g(E) \rangle [(1/m_{lg}) + (2/m_{tg})]/3, \\ \mu_s &= e\langle \tau_s(E) \rangle [(1/m_{ls}) + (2/m_{ts})]/3, \end{aligned} \qquad (11)$$

where

$$\langle \tau_x^n(E) \rangle = (4/3\pi^{\frac{1}{2}}) \int_0^\infty \tau_x^n(y) y^{\frac{3}{2}} \exp(-y) dy, \qquad y = E/kT. \qquad (12)$$

Calculation[32] of the Hall effect and magnetoresistance for n-type material, which involves $n=2$ and 3 in Eq. (12) is a straightforward extension of the treatment for one set of minima.[33] The Hall constant is

$$\begin{aligned} R_H = -e\{&[(K_g+2)K_g n_g \langle \tau_g^2 \rangle / 3m_{lg}^2] \\ &+ [(K_s+2)K_s n_s \langle \tau_s^2 \rangle / 3m_{ls}^2]\}/c\sigma^2, \end{aligned} \qquad (13)$$

where $K_x = m_{lx}/m_{tx}$, c is the velocity of light, and σ is the conductivity given in Eq. (3) with $p=0$. The longitudinal and transverse magnetoresistance coefficients for the current in the [100] direction are

$$\xi_{100} = 2K_g(K_g-1)^2 n_g \langle \tau_g^3 \rangle / 27(R_H ec)^2 (\sigma m_{lg})^3, \qquad (14)$$

$$\xi_{001}{}^{010} = \frac{[K_g(2K_g+1)(K_g+2) n_g \langle \tau_g^3 \rangle / 3m_{lg}^3] + [K_s(K_s^2+K_s+1) n_s \langle \tau_s^3 \rangle / m_{ls}^3]}{9(R_H ec)^2 \sigma^3} - 1, \qquad (15)$$

where $\xi_{ijk}{}^{lmn} = (\sigma - \sigma_H)/(H^2 R_H^2 \sigma^3)$ and σ_H is the conductivity with the magnetic field applied to the sample. The subscript on ξ refers to the current direction and the superscript to the magnetic field direction. No

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[28] H. Fritsche, Phys. Rev. **115**, 336 (1959).

[29] T. N. Morgan, J. Phys. Chem. Solids **8**, 245 (1959).

[30] T. N. Morgan, Proceedings of the International Conference on Semiconductors, Prague, 1960, p. 151.

[31] B. N. Brockhouse and P. K. Iyengar, Phys. Rev. **111**, 747 (1958).

[32] M. Glicksman, Phys. Rev. **102**, 1496 (1956). M. I. Nathan, Gordon McKay Laboratory, Harvard University, Technical Report HP-1, 1958 (unpublished).

[33] B. Meiboom and S. Abeles, Phys. Rev. **95**, 31 (1955); M. Shibuya, *ibid.* **95**, 1385 (1955).

TABLE I. The values for the analytic approximation to the scattering times. All values are $\Delta \geq 0$. $\mathrm{erf}(x) \equiv (2/\pi^{\frac{1}{2}})\int_0^x \exp(-u^2)du$.

n	$\langle\tau_g^n(\Delta)\rangle/\langle\tau_g^n(\infty)\rangle$	$\langle\tau_s^n(\Delta)\rangle/\langle\tau_s^n(\infty)\rangle$
(1)	$1-\{[S(\Delta+1)/(1+S)]-[S\Delta/2(1+S)^2]\} \exp(-\Delta)$	$[1/(1+S')]-[S'\Delta/2(1+S')^2]$
(2)	$\mathrm{erf}(\Delta^{\frac{1}{2}})-(2/\pi^{\frac{1}{2}})\Delta^{\frac{1}{2}} \exp(-\Delta)+\{[1-\mathrm{erf}(\Delta^{\frac{1}{2}})+(2/\pi^{\frac{1}{2}})\Delta^{\frac{1}{2}} \exp(-\Delta)]/(1+S)^2\}$ $-2\Delta[1-\mathrm{erf}(\Delta^{\frac{1}{2}})]/(1+S)^3$	$1/(1+S')^2$
(3)	$1-[1-1/(1+S)^3]\exp(-\Delta)$	$1/(1+S')^3$

superscript is used for the longitudinal coefficient. It is much easier to treat magnetoconductance[34] theoretically than magnetoresistance. Pressure measurements on magnetoconductance will be reported elsewhere.[35]

The integrals for the average scattering time in Eq. (13) cannot be evaluated analytically. However, we have made analytical approximations to the integrals. The results for $n=1$, 2 and 3 and $\Delta=\Delta E/kT\geq 0$ are shown in Table I. The quantities $S=BC_s'\nu_s/A_gC_g'$ and $S'=BC_g'\nu_g/A_sC_s'$ are parameters which give the strength of interband scattering relative to the strength of intravalley scattering. The values for $\Delta<0$ are given by

$$\langle\tau_g^n(-\Delta, S)\rangle=\langle\tau_s^n(\Delta,S')\rangle \tag{16}$$

for all Δ. The method of obtaining the analytic approximation and its validity are discussed in the Appendix.

III. EXPERIMENTAL

Measurements of conductivity as a function of pressure, to a maximum pressure of 30 000 kg/cm^2 at room temperature and 349°K, were made in apparatus of the type described by Bridgman.[36] The technique used has been discussed in detail elsewhere.[8] Another apparatus capable of a maximum pressure of 18 000 kg/cm^2 was used to measure conductivity at several temperatures between 196° and 355°K. In this apparatus the sample is in a small bomb (3 in. diameter by 8 in. long), which is connected to the rest of the system by $\frac{1}{8}$ in. stainless steel tubing, so that the temperature is easily controlled. Apparatus of this type has been discussed by Bridgman[37] and by Warschauer and Paul.[38]

In order to obtain the pressure dependence of the electron mobility with lattice scattering predominant over a large range of temperature, several samples of extrinsic n-type germanium were measured. The samples for each temperature range were chosen so as to have negligible impurity scattering and constant electron density with pressure. They were cut into the shape of rectangular parallelepipeds, and the resistance measured by a dc potentiometric technique with four tin contacts soldered to the sample. The total change in conductance with pressure in different samples was the same to within 3%. Results at 311°K for those samples having room temperature resistivities of 3, 1, 0.5 ohm-cm are shown in Fig. 6, where conductance normalized to atmospheric pressure is plotted. In order to convert conductance changes to conductivity or mobility changes with pressure it is necessary to make a small correction for dimension changes. The change in length is approximately 1% in 30 000 kg/cm^2.[39]

IV. FIT OF THEORY TO EXPERIMENT

Energy Gap Variation

The pressure dependence of $E_{G\mathrm{eff}}$ [defined in Eq. (8)] determined by Paul and Brooks[8] from measurements of intrinsic resistivity at 349°K, is shown in Fig. 3. They used the room temperature pressure variation of the resistivity of n-type germanium obtained by Bridgman[1] to correct for the electron mobility change. It is obvious that, if the two-band picture is correct, the electron mobility change will be temperature dependent. Figure 7 shows the normalized conductance of an n-type germanium sample of 0.5 ohm-cm room temperature resistivity vs pressure at 349° and 302°K. The density of electrons is constant for both of these temperatures,[40] so

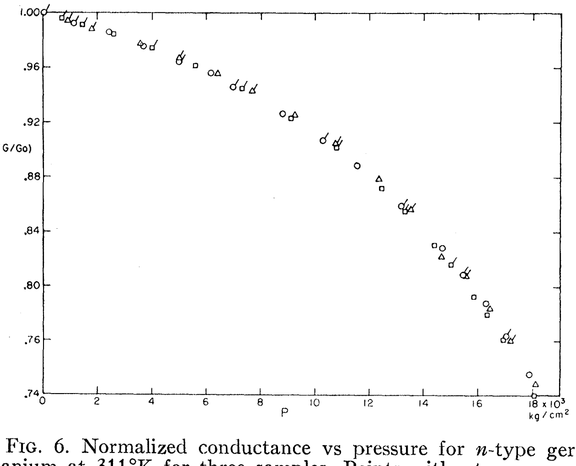

FIG. 6. Normalized conductance vs pressure for n-type germanium at 311°K for three samples. Points without ears were taken on increasing the pressure, those with ears on decreasing the pressure.

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[34] C. Goldberg, Phys. Rev. **109**, 331 (1958).

[35] W. E. Howard and W. Paul (to be published).

[36] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **72**, 157 (1938).

[37] P. W. Bridgman, *The Physics of High Pressures* (G. Bell and Sons, London, 1949).

[38] D. M. Warschauer and W. Paul, Rev. Sci. Instr. **29**, 675 (1958).

[39] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **77**, 187 (1949).

[40] This is a simple extrapolation from the equality of the drift mobility and conductivity variation at room temperature. This conclusion can also be inferred from the fact that the group five donor electrons in silicon and germanium are describable by the effective mass approximation, and the pressure coefficient of the ionization energy of such donors in silicon has been shown experi-

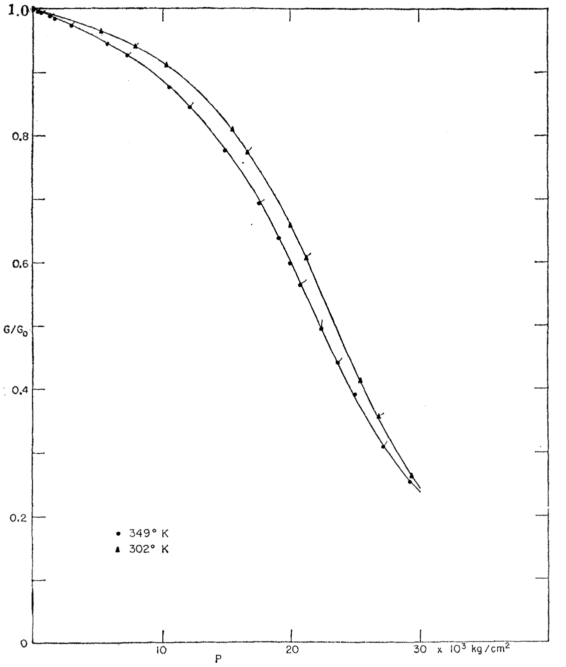

FIG. 7. Normalized conductance vs pressure for n-type germanium at 302° and 349°K. Points without ears were taken on increasing the pressure, those with ears on decreasing the pressure.

that the curves represent the variation of electron mobility provided that a small correction for dimensional changes is made. Neglecting the small variation in the hole mobility,[1] and using Eqs. (9) and (2), we can calculate the correct pressure dependence of $E_{G\mathrm{eff}}$. This is shown in Fig. 8. The total change of $E_{G\mathrm{eff}}$ in 30 000 kg/cm^2 is the same as obtained in Fig. 3. However, Fig. 8 deviates from the initial linear dependence at a lower pressure than the Paul and Brooks[8] determination which means that the (s) band is more important at lower pressures, but $d\Delta E/dP$ is smaller.

If the change in $E_{G\mathrm{eff}}$ below 10 000 kg/cm^2 is interpreted as a linear change in E_{Gg}, we obtain

$$(dE_{Gg}/dP)=4.9\times10^{-6}\ \mathrm{ev}/(\mathrm{kg\text{-}cm}^{-2}). \tag{17}$$

If we assume that the effective masses do not change with pressure and Eq. (17) is valid to 30 000 kg/cm^2, we can compute the quantity $\ln(C_g/C_s)+(\Delta E/kT)$ as a function of pressure, from Eq. (8) and Fig. 8. The results of this calculation are shown by the x's in Fig. 9. Points below 15 000 kg/cm^2 cannot be computed with any accuracy because $(C_s/C_g)\exp[-(\Delta E/kT)]$ is too small to produce an accurately measurable deviation in $E_{G\mathrm{eff}}$ from the initial straight line.

We see that the points in Fig. 9 lie on a straight line. Assuming the C's do not change with pressure we obtain from Fig. 9

$$\begin{aligned}(d\Delta E/dP)&=-5\times10^{-6}\ \mathrm{ev}/(\mathrm{kg\text{-}cm}^{-2}),\\(C_g/C_s)\exp(\Delta E_0/kT)&=69.\end{aligned} \tag{18}$$

The subscript (0) refers to atmospheric pressure. Since $(C_g/C_s)\exp(\Delta E_0/kT)$ is so large, we introduce a negligible error by ascribing all the initial linear change in $E_{G\mathrm{eff}}$ to E_{Gg}.

We must remark at this point that the values obtained in Eq. (18) are extremely sensitive to the exact curve in Fig. 6. Estimates of the errors in the measurement of n_0 lead to an uncertainty in $d\Delta E/dP$ of $\pm1\times10^{-6}$ ev/(kg-cm^{-2}), and in $\Delta E_0+kT\ln(C_g/C_s)$ of ±0.03 ev. Hence, a decreasing energy gap as obtained by Slykhouse and Drickamer[41] at pressures above 50 000 kg/cm^2 is not inconsistent with our experiment although the value they obtain appears to be outside our experimental error. In spite of the uncertainty in $(d\Delta E/dP)$ and $\Delta E_0+kT\ln(C_g/C_s)$ we shall take the values given in Eq. (18) for fitting theory to experiment.

Since the value of ΔE_0 has not been well determined directly by any experiment, we shall take ΔE_0 as an adjustable parameter in the theory, remembering, however, that the value 0.18 ev obtained by Johnson and Christian[15] is probably of the right order of magnitude. More recent optical data on silicon-germanium alloys[16] indicate, with a large uncertainty, that $\Delta E_0=0.22$ ev. We shall now use our data to show that ΔE_0 is very probably ≥0.15 ev.

We notice in Fig. 7 that above 20 000 kg/cm^2 the normalized conductivities or effective electron mobilities

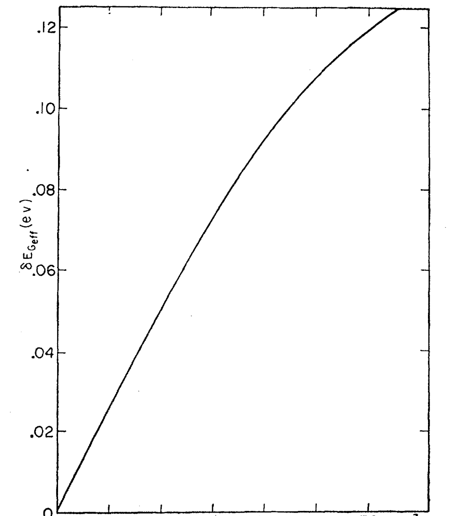

FIG. 8. The change of effective energy gap in germanium vs pressure at 349°K.

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mentally to be negligible by M. G. Holland, Gordon McKay Laboratory, Harvard University, Technical Report HP-4, 1958 (unpublished). Alternatively, it can be argued that the ionization energy change will be given by the fractional changes in effective mass and dielectric constant; the former can be estimated from the changes in energy gaps and the latter has been measured directly by M. Cardona, W. Paul, and H. Brooks, J. Phys. Chem. Solids **8**, 204 (1959).

[41] T. E. Slykhouse and H. G. Drickamer, J. Phys. Chem. Solids **7**, 210 (1958).

at the two temperatures approach one another as the pressure is increased. At 30 000 kg/cm² they are within 2% of each other and it appears likely that the curves will eventually coincide. This is consistent with the simple assumption that the normalized mobility is independent of temperature when $\Delta E=0$.

Consider the conductivity at the crossover point ($\Delta E=0$) using Eq. (3) and Table I.

$$\frac{\sigma}{\sigma_0}=\frac{[\mu_g^*/(1+C_s/C_g)(1+S)]+[\mu_s^*/(1+C_g/C_s)(1+S')]}{(\mu_{g0}n_{g0}+\mu_{s0}n_{s0})/n_0}, \tag{19}$$

where $\mu_x^*=$ mobility without interband scattering. This expression can be simplified since the following conditions hold:

(1) $n_{s0}/n_{g0}=(C_s/C_g)\exp[-(\Delta E_0/kT)]\ll 1$, $n_{g0}\cong n_0$.

(2) $\mu_{s0}n_{s0}$ can be neglected in comparison with $\mu_{g0}n_{g0}$.

(3) $\mu_{g0}^*\cong\mu_{g0}$ for all T of interest.

The experimentally determined value of $(C_s/C_g)\times\exp[-(\Delta E_0/kT)]$ shows that condition (1) is fulfilled. Since μ_{s0} is probably small compared to μ_{g0} because of interband scattering, condition (2) is fulfilled. Condition (1) also helps to ensure condition (2). Condition (3) demands only that ΔE_0 be large enough so that μ_{g0} is not much different from μ_{g0}^*. This is true for $\Delta E_0=0.18$ ev to within 1%. These three conditions are well fulfilled if, as is undoubtedly the case, the conduction in the upper band is negligible at atmospheric pressure and $\Delta E_0/kT\gg 1$.

Equation (19) then becomes

$$(\sigma/\sigma_0)=[\mu_g^*/\mu_{g0}^*(1+C_s/C_g)(1+S)]+[\mu_s^*/\mu_{g0}^*(1+C_g/C_s)(1+S')]. \tag{20}$$

Unless there is an accidental canceling effect, which is unlikely, all the quantities in Eq. (20) must be nearly independent of temperature for σ/σ_0 to remain nearly constant with temperature. We shall examine this hypothesis.

We have little physical basis for the assumption that μ_s^*/μ_{g0}^* is independent of temperature, especially since we might expect $\mu_s^*\sim T^{-2.6}$, the temperature dependence for the silicon mobility.[42] However, from the standpoint of developing the interband scattering theory the simplest procedure is to neglect this indication and to assume that μ_s^* and μ_g^* have the same temperature dependence. There is the possibility that μ_s^*/μ_{g0}^* is small, so that σ/σ_0 is not very sensitive to changes in it. In fact, this is what happens. S and S' are expected to be approximately independent of temperature since the phonons for interband scattering are almost classically excited. (See Sec. II.)

If the normalized mobility is independent of temperature, the curves will coincide exactly at the crossover point ($\Delta E=0$). Since the curves have not yet coalesced at 30 000 kg/cm², this pressure is probably below the crossover point.

Hence, using the value of $d\Delta E/dP$ obtained, we have $\Delta E_0\geq 0.15$ ev. The error in $d\Delta E/dP$ previously quoted, however, weakens this statement to $\Delta E_0\geq 0.12$ ev.

Effective Mobility Variation

The conductivity of extrinsic n-type germanium as a function of pressure may be written

$$(\mu_{\text{eff}}/\mu_{\text{eff}0})=(n_g\mu_g+n_s\mu_s)/n_{g0}\mu_{g0}, \tag{21}$$

where $\sigma=ne\mu_{\text{eff}}$ defines μ_{eff}. We have assumed in writing Eq. (21) that the contribution of the (s) band to the conductivity can be neglected at atmospheric pressure. If we confine our considerations now to 349°K, n_g and n_s, given by Eq. (7), are known as a function of pressure. This is true even though we have not assumed or found a value for ΔE_0, because at 349°K we have the pressure dependence of the quantity $(C_g/C_s)\exp(\Delta E/kT)$.

The conductivity is an experimentally determined function of pressure. At each pressure we have two unknowns μ_s and μ_g, but only one equation, Eq. (21). To overcome this difficulty we attempt a first-fit to the data on the basis that there exists a range of pressure at low pressures where the conduction in the (s) band may be neglected. We shall assume that we can neglect it for

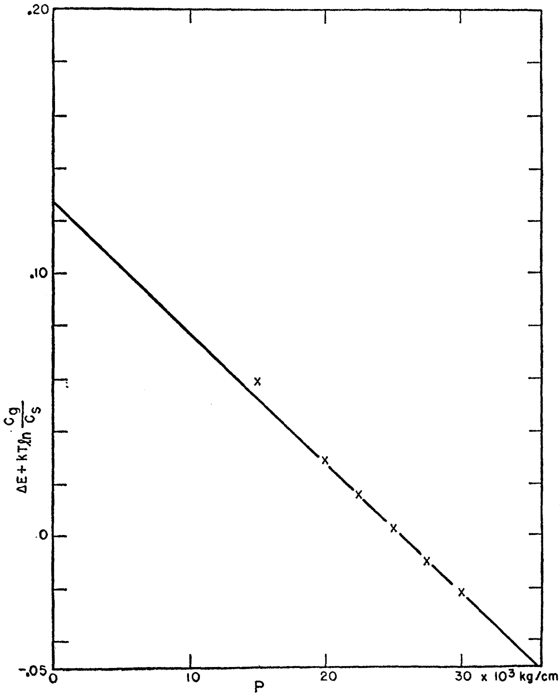

FIG. 9. Energy separation between the [111] and the [100] minima vs pressure.

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[42] M. B. Prince, Phys. Rev. 93, 1204 (1954).

$P \leq 3000$ kg/cm^2. After we have performed our calculations it will be seen that this is fairly well fulfilled for the values of the parameters in the theory. We may write

$$(\mu_{\text{eff}}/\mu_{\text{eff}0}) = (n_g/n_{g0})(\mu_g/\mu_{g0}). \tag{22}$$

From the experimentally determined values of σ/σ_0 and the deduced n_g/n_{g0} at 349°K we can find μ_g/μ_{g0} as a function of pressure. This is shown in Fig. 10. The abscissa for the curve is $\delta\Delta = \Delta_0 - \Delta$ ($\Delta = \Delta E/kT$), where we have used the pressure dependence of μ_{eff} determined from Fig. 7. A value of $\delta\Delta = 0.5$ corresponds to a pressure of approximately 3000 kg/cm^2 at 349°K, since $kT = 0.0301$ ev. The approximate theoretical expression for μ_g/μ_{g0} calculated in Sec. II is

$$\frac{\mu_g}{\mu_{g0}} = \frac{\mu_g^*\{1 - [S(1+\Delta)/(1+S)]\exp(-\Delta) + [S\Delta/2(1+S)^2]\exp(-\Delta)\}}{\mu_{g0}^*\{1 - [S(1+\Delta_0)/(1+S)]\exp(-\Delta_0) + [S\Delta_0/2(1+S)^2]\exp(-\Delta_0)\}}. \tag{23}$$

We next consider whether there is any change in the mobility not due to interband effects. In Fig. 11 the experimentally determined μ_{eff} (2500 kg/cm^2)/$\mu_{\text{eff}0}$ is plotted as a function of temperature. We notice that $\mu_{\text{eff}}/\mu_{\text{eff}0}$ is almost temperature independent for $T < 200$°K and is not equal to unity. As the temperature approaches zero, interband effects become negligible. For 2500 kg/cm^2 pressure this undoubtedly occurs above $T = 77$°K. Therefore, μ_g^* must be changing with pressure. This must be due to a pressure effect on the effective mass, the deformation potential or the elastic constants. The effect of pressure on these quantities is probably temperature independent.

Therefore, we assume from Fig. 11 that there is an explicit dependence of μ_g^* on pressure, which is independent of temperature and can be extrapolated through the whole pressure range to give:

$$(1/\mu_g^*) = (1/\mu_{g0}^*)(1 + 0.004P), \tag{24}$$

where P is in units of 10^3 kg/cm^2.

We defer discussion of the explicit dependence of the mobility on the pressure given by Eq. (24) and proceed with the fit of the experimental data.

We choose $\delta\Delta = \Delta_0 - \Delta = 0.5$, corresponding to $P = 3000$ kg/cm^2 when $k(349°) = 0.0301$ ev. From Eq. (23) we can calculate the change in μ_g due to interband effects, $(\mu_g/\mu_{g0})_{\text{ib}}$, as a function of Δ_0 for several values of S.

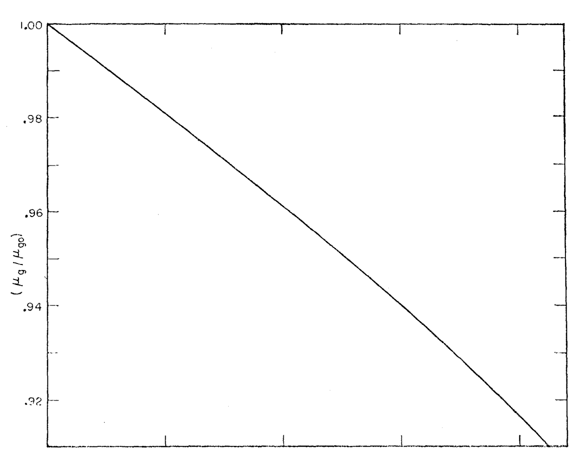

FIG. 10. Experimental (μ_g/μ_{g0}) vs $\delta\Delta$ at 349°K.

The results of this calculation are shown in Fig. 12. Using Eqs. (22) and (24) and the experimental $\mu_{\text{eff}}/\mu_{\text{eff}0}$ we find $(\mu_g/\mu_{g0}) = 0.9927$ for $P = 3000$ kg/cm^2. From Fig. 12 we obtain S as a function Δ_0 as shown in Fig. 13. For $\Delta_0 > 5$ ($\Delta E_0 > 0.15$ ev), we have approximately $S > 1$, and for $\Delta_0 = 6.3$ ($\Delta E_0 = 0.19$ ev), S tends to infinity. If $S = 5$, $B/A_g = 0.22$. This is not an unreasonable value for the ratio of these matrix elements.

Now that we have a reasonable fit to the very low-pressure data, we turn to the conductivity in the higher pressure region. At 349°K the normalized effective mobility may be written, for any pressure,

$$(\mu_{\text{eff}}/\mu_{\text{eff}0}) = (n_g/n_{g0})(\mu_g/\mu_{g0}) + (n_s/n_{g0})(\mu_s/\mu_s^*)(\mu_s^*/\mu_{g0}^*)(\mu_{g0}^*/\mu_{g0}). \tag{25}$$

If we choose a value for S, Δ_0 is fixed from Fig. 13 and thus C_g/C_s from Fig. 9. Since μ_g^*/μ_{g0}^* is given by Eq. (24), the contribution of the first term to the effective mobility is determined. We can use the value of $\mu_{\text{eff}}/\mu_{\text{eff}0}$ at the highest pressure (30 000 kg/cm^2) to find the contribution of the second term. We choose the maximum pressure since the contribution of the second term is the largest there, and our analytic approximation to μ_s/μ_s^* (which is valid for small Δ) is the best.

The normalized number of carriers in the (s) band, n_s/n_{g0}, is known, so that there are only two unknowns left: S' and μ_s^*. We shall assume that μ_s^* is independent of pressure. This is not unreasonable, since μ_g^* has only

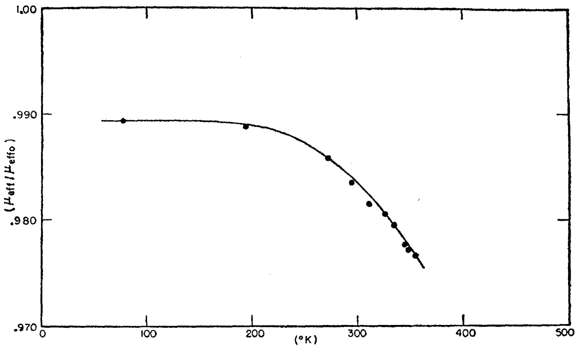

FIG. 11. Normalized effective mobility in n-type germanium at 2500 kg/cm^2 vs temperature. The point at 77°K is from Paul and Brooks.[8]

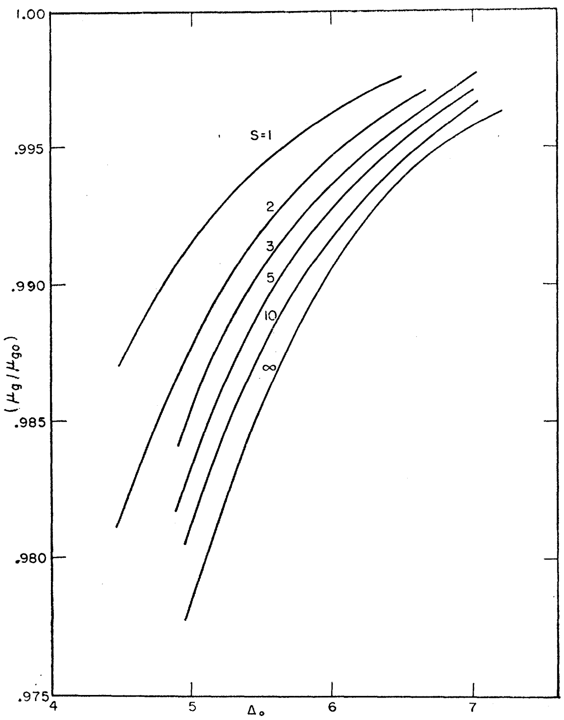

FIG. 12. Calculated (μ_g/μ_{g0}) vs Δ_0 for $\delta\Delta=0.5$ with S as a parameter.

a small pressure coefficient and the electron mobility in silicon is almost pressure independent.[22]

We find a relationship between μ_s^*/μ_{g0}^* and S'/S.

$$(\mu_s^*/\mu_{g0}^*)=A_gC_g(2K_s+1)m_{lg}\nu_s/A_sC_s(2K_g+1)m_{ls}\nu_g, \quad (26)$$

$$(S/S')=C_s^2A_s\nu_g/C_g^2A_g\nu_s. \quad (27)$$

Combining these two equations to eliminate A_s/A_g, we find

$$(\mu_s^*/\mu_{g0}^*)=(S'/S)(C_s/C_g)^{\frac{1}{3}}(K_g\nu_s/K_s\nu_g)^{\frac{2}{3}} \times(2K_s+1)/(2K_g+1). \quad (28)$$

We shall next estimate the quantity

$$V=(K_g\nu_s/K_s\nu_g)^{\frac{2}{3}}(2K_s+1)/(2K_g+1). \quad (29)$$

Cyclotron resonance experiments in germanium[11] at 4.2°K, and atmospheric pressure, have given $K_g=19.8$. It is impossible to estimate K_s by this means in germanium, but similar experiments in silicon[43] give $K=5.2$, and we shall assume this value for K_s as a close approximation. Some justification for this comes from magnetoresistance measurements made by Glicksman[44] on silicon-germanium alloys: he found $K\cong5$ in the silicon-germanium alloys for all compositions where the [100] minima are appreciably below the [111] minima in energy (>20% silicon in germanium). It seems reasonable to extrapolate this to pure germanium.

If we take $\nu_s=6$, $\nu_g=4$, $K_s=5$, $K_g=20$, we find $V=0.9$. However, we have neglected any dependence on pressure of the K's. Benedek *et al.*[45] found that K_g decreases about 10% in 10 000 kg/cm² from magnetoresistance measurements. Although they neglected interband scattering, this does not affect the size of the change much. If we extrapolate this decrease of K_g to 30 000 kg/cm² (a 30% decrease), we obtain $K_g=14$; then $V=1$. However, more recent estimates of K_g from magneto-conductance measurements which are less subject to errors of interpretation show that K_g is almost independent of pressure.[35] There is no experimental evidence concerning the pressure variation of K_s. It appears, however, that $V=1$ to within 10% for any set of reasonable assumptions. It can be shown that the deduced values of the parameters are not very sensitive to V for $S<3$. Moreover, the conductivity, for pressures less than 30 000 kg/cm², is not sensitive to it for any S. In view of these considerations we shall take $V=1$.

Thus, using Eqs. (24) and (28), and Table I, we can calculate S' and μ_s^*/μ_{g0}^* for each S. S' and μ_s^*/μ_{g0}^* are shown as a function of S in Fig. 14. We see that S' and $\mu_s^*/\mu_{g0}^* \sim \infty$ as $S\sim 6$. Bridgman's measurement of the conductivity of n-type germanium to 100 000 kg/cm² indicates that the conductivity in the vicinity of 100 000 kg/cm² is probably smaller than the conductivity at atmospheric pressure, and therefore $\mu_s^*/\mu_{g0}^*<1$. If this requirement is made we must certainly have $S<6$.

With the foregoing discussion we have reduced the many parameter theory to a point where we have only one independent parameter; say S. We have also put

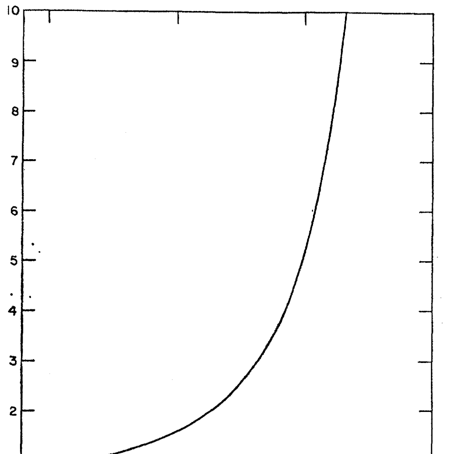

FIG. 13. S vs Δ_0 for $(\mu_g/\mu_{g0})_{\text{ib}}=0.9927$.

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[43] R. W. Dexter, B. Lax, A. F. Kip, and G. Dresselhaus, Phys. Rev. **96**, 222 (1954).

[44] M. Glicksman and S. M. Christian, Phys. Rev. **104**, 1278 (1956).

[45] G. B. Benedek, W. Paul, and H. Brooks, Phys. Rev. **100**, 1129 (1955).

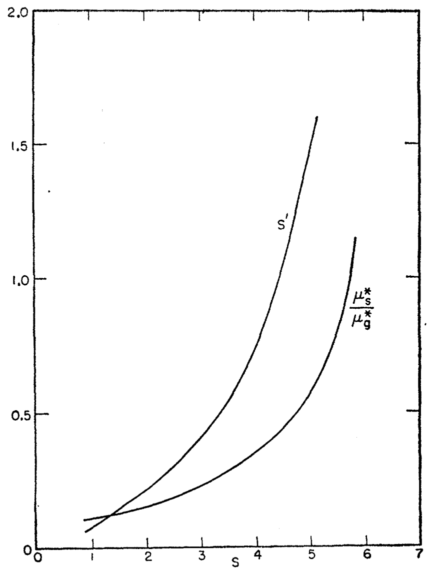

FIG. 14. S' and (μ_s^*/μ_g^*) vs S.

upper and lower limits on the value of this parameter:

$$1<S<6.$$

We might hope, by choosing values for the parameter S and calculating σ/σ_0 between 1 and 30 000 kg/cm², to determine the value for S more closely. The calculation has been performed for $S=1$ and 5. The calculated curves for the normalized effective mobility vs P at 349°K are shown in Fig. 15 along with the experimentally observed curve. There is little to choose between the calculated points for $S=1$ and $S=5$ as compared with experiment, so that we can extract no further information concerning the parametric solution we performed from the conductivity data at 349°K. Thus far, we have restricted the parameters of the theory as follows:

$$1<S<6, \quad 5<\Delta_0<6.1. \tag{30}$$

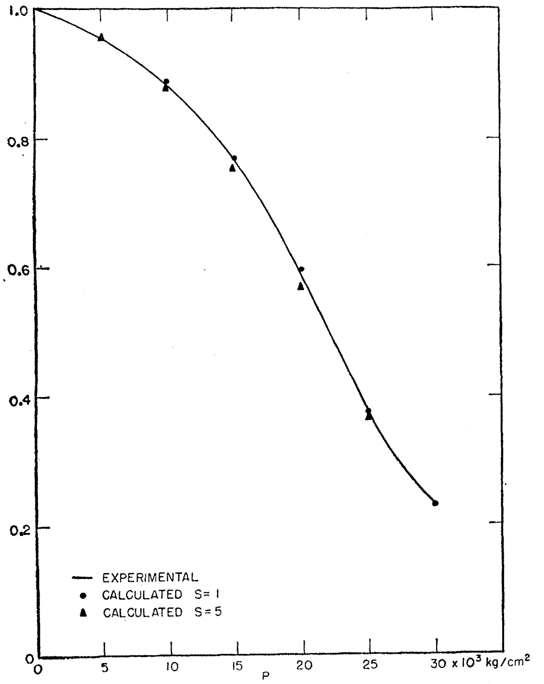

FIG. 15. Normalized effective mobility vs pressure for n-type germanium at 349°K.

We can now examine some of the assumptions made in order to fit the data. First, we neglected the contribution of the (s) band for $\delta\Delta=0.5$. Actually we have:

$$\frac{\mu_{\text{eff}}}{\mu_{\text{eff}0}}=\frac{n_g\mu_g+n_s\mu_s}{n_{g0}\mu_{g0}+n_{s0}\mu_{s0}}=\frac{n_g\mu_g(1+n_s\mu_s/n_g\mu_g)}{n_{g0}\mu_{g0}(1+n_{s0}\mu_{s0}/n_{g0}\mu_{g0})}. \tag{31}$$

Since quantities with subscript (s) are small, we can expand the denominator and neglect products of μ_s and μ_{s0}.

$$(\mu_{\text{eff}}/\mu_{\text{eff}0})=(n_g\mu_g/n_{g0}\mu_{g0})+(n_g\mu_g/n_{g0}\mu_{g0}) \times[(n_s\mu_s/n_g\mu_g)-(n_{s0}\mu_{s0}/n_{g0}\mu_{g0})]. \tag{32}$$

The term in brackets which we neglected is largest for small S. For $S=1$, it equals 0.0007. If we were to correct $(\mu_g/\mu_{g0})_{\text{ib}}$ by this amount from Fig. 12 we would decrease Δ_0 by only 0.11 or ΔE_0 by only 0.003 ev. As S is increased, this correction decreases rapidly. The correction is, therefore, insignificant for all reasonable values of S.

We also assumed that $V=1$. If we take $V=0.9$, as suggested by atmospheric pressure values for the parameters (K_g,K_s,ν_s,ν_g) the calculated values of S' and μ_s^*/μ_{g0}^* will be different. S' and μ_s^*/μ_{g0}^* will be higher for a given S. This effect is not significant until $S=5$ when it increases considerably, making S' and μ_s^*/μ_{g0}^* almost twice as large as they are for $V=1$. Essentially, what happens is that S' and μ_s^*/μ_{g0}^* diverge for a smaller value of S (closer to 5) than before. The only modification which is required by this is that we lower the upper limit to $S\leq 4$. For this change of S, the maximum value of Δ_0 is hardly affected at all.

Summarizing what we have done in this section thus far, first, we use the measured intrinsic resistivity and the mobilities deduced from resistivity experiments on impure samples, to compute $E_{G\text{eff}}$ as a function of pressure. Second, the pressure dependence of $(C_s/C_g) \times\exp[-(\Delta E/kT)]$ is determined from $E_{G\text{eff}}$. Then we obtain an experimental value for (σ/σ_0) from the pressure data at 349°K. With the assumption that the (s) band does not contribute very much to the conductivity in the low-pressure region, we divide out the carrier density change effect and an "explicit effect" on the mobility and determine an experimental $(\mu_g/\mu_{g0})_{\text{ib}}$. From this we deduce S as a function of Δ_0. Then, using the value of σ/σ_0 at 30 000 kg/cm², S' and (μ_s^*/μ_{g0}^*) are determined for each S. Certain criteria are used to determine limiting values of the parameters. These extreme values are then used to predict the normalized effective mobility as a function of pressure. Good agreement is found between theory and experiment over the whole range of the parameters provided the deduced relationship among them is maintained.

A weakness of this procedure lies in the determination of the experimental value of $(\mu_g/\mu_{g0})_{\text{ib}}$. First, we must determine (σ/σ_0) from experiment. Due to a spread in values for the different samples there is at least a 0.15% error in this. In addition there is also an uncertainty in the correct value of (σ/σ_0) due to impurity scattering effects and intrinsic carrier effects. The latter effect might lead to overestimation of (σ/σ_0) by as much as 0.1%. There is also an uncertainty of 0.1% introduced because of the explicit pressure effect on the mobility. The value of $(\mu_g/\mu_{g0})_{\text{ib}}$ used is within the limits of experimental error but these limits should undoubtedly be as large as 0.3%. We might very well ask what will happen to the values of our parameters and our fit to experiment if we change the value of $(\mu_g/\mu_{g0})_{\text{ib}}$. Can we find another set of parameters for a different value of initial slope which will fit the experiment just as well, and is there a much greater uncertainty in our parameters?

We can vary the value of the experimental initial slope put into the theory and see if it affects the over-all fit to experiment. This has been done for two other values of initial slope. We both increased and decreased (μ_g/μ_{g0}) for $\delta\Delta=0.5$ by 0.3%. For each S the deduced values of Δ_0 changed considerably. The curves determined from Fig. 12 are shown in Fig. 16. The remaining parameters can be calculated as before. The normalized mobility can be computed between 1 and 30 000 kg/cm^2 for a typical set of parameters corresponding to either initial slope. The following sets of parameters were chosen.

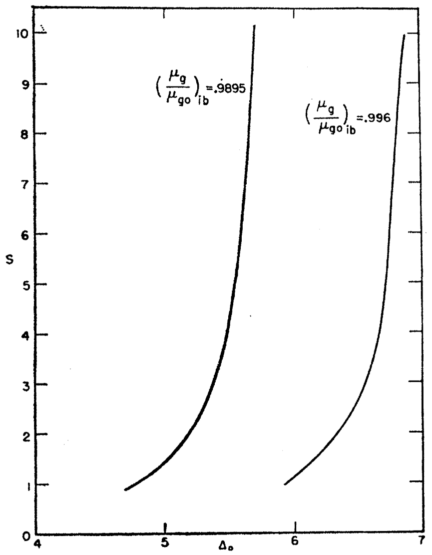

FIG. 16. S vs Δ_0 with $(\mu_g/\mu_{g0})_{\text{ib}}$ as a parameter.

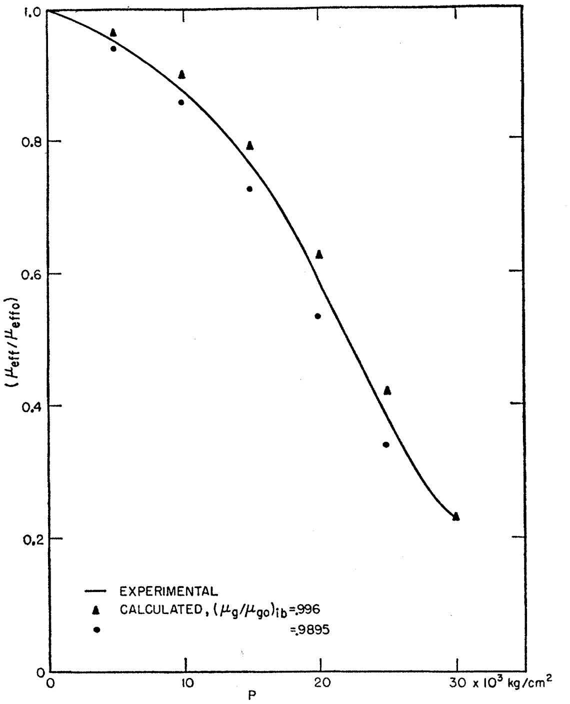

FIG. 17. Normalized effective mobility vs pressure for n-type germanium at 349°K.

For $(\mu_g/\mu_{g0})_{\text{ib}}=0.9895$,

$$S=3,\quad S'=0.896,\quad \Delta_0=5.37,\quad (\mu_s^*/\mu_g^*)=0.41. \tag{33}$$

For $(\mu_g/\mu_{g0})_{\text{ib}}=0.996$,

$$S=5,\quad S'=0.23,\quad \Delta_0=6.7,\quad (\mu_s^*/\mu_g^*)=0.105. \tag{34}$$

These are reasonable values of the parameters in the light of previous considerations. Since the conductivity does not change much as long as we confine ourselves to one S vs Δ_0 curve, these were the only two sets of parameters used.

The results for these calculations along with the experimental curve are shown in Fig. 17. A comparison with Fig. 15 shows that the fit to experiment is much poorer for the new values of initial slope. The deviations from experiment are about four to five times larger than for the first fit.

What we have done is to transfer the basis of the fit of theory to experiment from the rather inaccurately determined initial slope, to the better defined behavior of the conductivity over the whole pressure range to 30 000 kg/cm^2.

We can estimate the sensitivity of the theory with the aid of Figs. 15 and 17. Since the deviations in Fig. 17 are approximately four times those in Fig. 15 we can say that the sensitivity to the change in the set of parameters is about one-fourth of that used in computing Fig. 17. This means that the theory will be insensitive to changes in $(\mu_g/\mu_{g0})_{\text{ib}}$ of 0.08%. The effect this has on Δ_0 as a

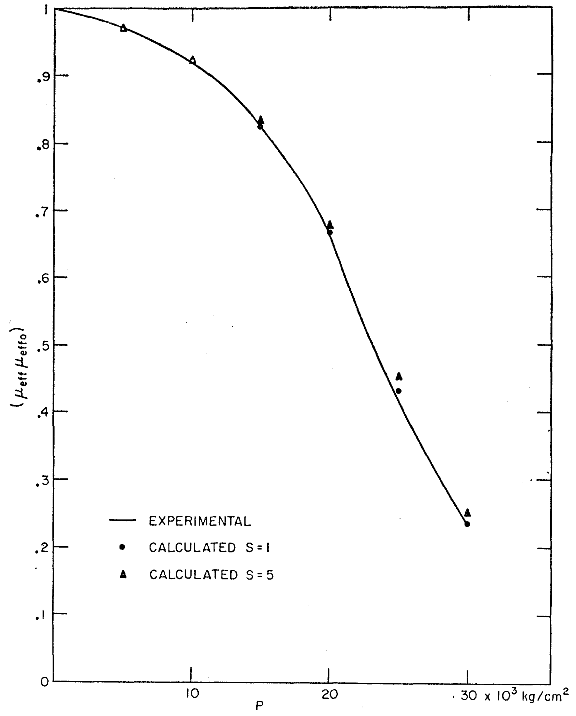

FIG. 18. Normalized effective mobility vs pressure for n-type germanium at 295°K.

function of S can be found easily from Fig. 12. For a fixed S, ΔE_0 will be uncertain by approximately 0.004 ev.

Without any further assumptions or hypotheses we can compute $\mu_{\text{eff}}/\mu_{\text{eff0}}$ at other temperatures. The only temperature dependence is due to change in the quantity $(\Delta E/kT)$. All the parameters have been assumed independent of T.

Figure 18 shows the theoretical and experimental conductivity at 295°K as a junction of pressure for $S=1$ and $S=5$. The agreement with experiment for both values of S is good for $P\leq 20\,000$ kg/cm². However, above this pressure both calculated curves deviate from the experimental curve. The $S=1$ curve agrees somewhat better above 20 000 kg/cm². This is consistent with the fact that the experimental $\mu_{\text{eff}}/\mu_{\text{eff0}}$ shows only a slight temperature dependence in this pressure region; for in this case we must be close to the crossover point, and since $d\Delta/dP$ is determined by experiment, this is more likely if Δ_0 is small, and thus S is small. However, it would be hazardous to assert that $S=1$ is correct on this basis alone, since the difference in the quality of the agreement with the whole experimental curve is small. A comparison of the experimental and theoretical pressure dependence of the normalized mobility at 311° and 273°K is shown in Figs. 19 and 20. The experimental curve for 311°K is for the purest sample measured at that temperature. Again it is seen that the agreement for $S=1$ is somewhat better than for $S=5$, although the agreement is insensitive to the change.

More evidence concerning the values of the parameters comes from Bridgman's measurements[2] to 100 000 kg/cm², which indicate that (μ_s^*/μ_{g0}) is approximately equal to 0.5. This would tend to favor the higher values for S. However, since this is a nonhydrostatic pressure measurement, we should not be too surprised if we do not predict quantitative agreement with it.

We have mentioned previously that the magnetoresistance measurements of Glicksman[44] on silicon-germanium alloys indicate that the mass ratio in the (100) minima, K_s, has the same value in germanium as in silicon. The masses m_{ls} and m_{ts} derive their magnitudes from different energy differences.[46] Glicksman points out that if these masses change in going from silicon to germanium through the alloys it is unlikely that their ratio will remain constant. Therefore, it is probable that neither of them changes very much, and we should expect C_s to have the value characteristic of pure silicon. Using the electron mass values for silicon and germanium, with $\nu_g=4$ and $\nu_s=6$, we have[47] $C_s/C_g=2.8$. This leads us to choose a value $S\cong 1$. However, this indirect argument is not certain enough to allow us to restrict the range of our parameters.

Discussion of the Explicit Effect on the Mobility

We have seen that the pressure dependence of the effective mobility in n-type germanium can be explained in terms of a two-band theory. We have found, however, that it is necessary to postulate an explicit decrease of the mobility, μ_g^*, with applied pressure [see Eq. (24)]. This effect is independent of temperature.

For lattice scattering we have[48]

$$\mu_g^*=2(2\pi)^{\frac{1}{2}}\hbar^4 c_p K_g(2K_g+1)/9(kT)^{\frac{3}{2}}E_{1g}{}^2 m_{lg}{}^{\frac{5}{2}}, \quad (35)$$

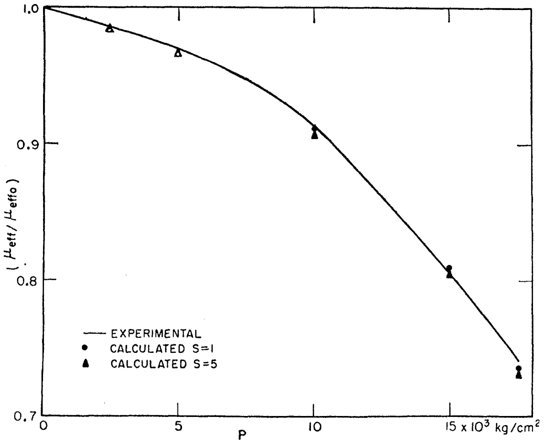

FIG. 19. Normalized effective mobility vs pressure for n-type germanium at 311°K.

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[46] G. Dresselhaus, A. F. Kip, H. Y. Ku, G. Wagoner, and S. M. Christian, Phys. Rev. **100**, 1218 (1955).

[47] H. Brooks, Advances in Electronics and Electron Phys. **7**, 120 (1955).

[48] See reference 47, p. 146.

where c_p is a linear combination of the elastic constants and E_{1g} is the deformation potential. The quantities K_g, c_p, E_{1g}, and m_{lg} in Eq. (35) can be a function of pressure.

The elastic constants have been measured as a function of pressure.[49] It is found that

$$(c_{11})_N = 1.04,$$
$$(c_{12})_N = 1.09,$$
$$(c_{44})_N = 1.02,$$

where $(X)_N = X(10\,000 \text{ kg/cm}^2)/X(1 \text{ kg/cm}^2)$. If we take the average for $(c_p)_N$, we have

$$(c_p)_N = 1.05. \tag{36}$$

The deformation potential E_{1g} is the rate of change of the energy of the conduction band edge with strain (both dilatation and shear strain). The fact that the change of $E_{Gg} = E_g - E_v$ with pressure is linear to 10 000 kg/cm² (see Fig. 8) suggests that the change of the deformation potential with dilatation is small—probably less than 5% in 10 000 kg/cm²—since, unless there is accidental canceling by the valence band, nonlinearity would show up in E_{Gg} if the dilatation contribution to E_{1g} were not constant. We have no information about the pressure coefficient of the shear contribution to E_{1g}.

Assuming that the change of the deformation potential is less than 5% and using Eqs. (35) and (36) we find

$$0.94 < (m^*)_N < 0.98,$$

where $m^* = m_{lg}/[K_g(2K_g+1)/3]^{2/5}$.

V. SUMMARY AND CONCLUSIONS

In this concluding section we shall recapitulate the results and comment on their validity.

The evidence for the existence of three sets of minima in the conduction band of germanium is regarded as conclusive. Cyclotron resonance measurements[11,12] establish that a (111) set is lowest in energy at atmospheric pressure; the present data confirm previous electrical and optical measurements of the pressure dependence of the energy gap between the maximum energy of the valence band at $k = [000]$ and these [111] minima.[3–5] Measurements of the optical absorption spectrum,[50] *inter alia*, establish a second minimum at the center of the Brillouin zone; pressure measurements show that this minimum moves away from the valence band at a rate more than twice as great as the [111] set.[14] The third set of minima required by the data in this paper is almost certainly a [100] set; firstly, because theoretical and experimental results on the group IV and group III–V semiconductors suggest that any third set probably lies in this direction in k space; and secondly, because extrapolation of measurements on Si-Ge alloys[15–17] suggests minima of this symmetry at about the energy value the data in this paper require.

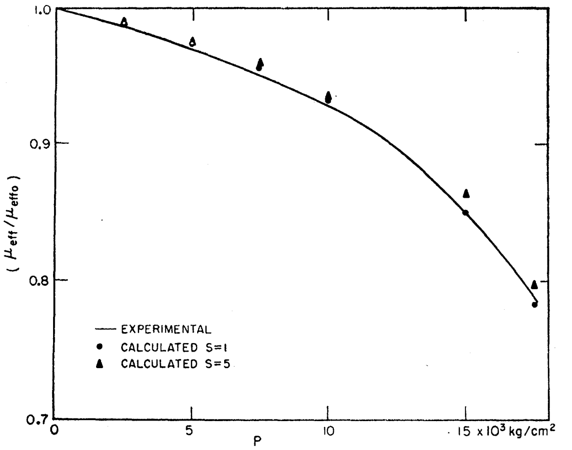

FIG. 20. Normalized effective mobility vs pressure for n-type germanium at 273°K.

Positive identification of the third set as a [100] set could be accomplished by measurement of the magnetoresistance symmetry relations at pressures higher than 20 000 kg/cm², where there is appreciable population of these minima. This has not been accomplished because of experimental difficulties, but it is regarded as advisable for experimental completeness, rather than because there is any reasonable doubt about the result.

The rate of separation of the [111] minima from the valence band, 4.9×10^{-6} ev/(kg-cm²), is in satisfactory agreement with a number of previous determinations.[3–5]

The present data show the [100] minima remaining static with respect to the valence band. On the other hand, optical absorption spectra found by Slykhouse and Drickamer[41] at pressures greater than 40 000 kg/cm² show that the third set of minima approaches the valence band at a rate of about 1.2×10^{-6} ev/(kg-cm^{-2}). Identification of the properties of this third set with those of silicon reminds us that the silicon energy gap decreases at a rate of 1.5×10^{-6} ev/(kg-cm^{-2}).[19] Again, scattered data on the [100] minima in the analogous family of III–V compounds, which will not be reported in detail here, indicate that these minima may approach the valence band. Indeed, if we confine ourselves to germanium, unpublished analysis by Howard of the magnetoconductance of n-type material to pressures of 20 000 kg/cm² requires a coefficient of -1.5×10^{-6} ev/(kg-cm^{-2}) for the third set of minima.

This variety of evidence strongly indicates that the [100] minima approach the valence band with increasing pressure rather than remain stationary; however, let us be reminded that the variety above noted is individually of no greater precision than the data of this paper. Thus, Howard's measurements are confined to pressures less than 20 000 kg/cm², while Drickamer's are uncorrected for changes in compressibility. (We note, in passing, that the compressibility of germanium

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[49] H. J. McSkimin, J. Acoust. Soc. Am. **30**, 314 (1958).

[50] W. C. Dash and R. Newman, Phys. Rev. **99**, 1151 (1955).

will change sufficiently[51] in the range of pressures above 30 000 kg/cm^2 that pressure coefficients measured at high pressures cannot be simply extrapolated to low pressures. Compressibility corrections would, however, worsen the agreement of Drickamer's results with ours.) The errors in analysis of the present data do not allow a pressure coefficient for the [100] set as large as 1.5×10^{-6} ev/(kg-cm^{-2}). We can, however, guess at two possible explanations, the first less likely than the second: (1) Most of the analysis of this paper is for a temperature of 350°K ,whereas the other measurements are for 300°K. However, a significant temperature dependence of the pressure coefficient is regarded by us as highly unlikely. (2) The pressure gauge calibrations at the high pressure and high temperature are less reliable than those at room temperature and high pressure.

We have tried to bypass (2) by measuring nearly intrinsic germanium at room temperature and high pressure, but at the time of writing have been unable to secure material sufficiently pure to give a reliable value for $d\Delta E/dP$ at this temperature.

Therefore, we presently assess the pressure coefficient of the [100] set of minima as $(0_{-2}^{+1})\times10^{-6}$ ev/(kg-cm^{-2}). We have the assurance that it is indeed close to the coefficient for the [100] set in other material, and that the methods outlined in this paper will be adequate to determine the coefficient exactly when superior material is available and more precise determination is desirable.

Just as the existence of a second set of minima is established, while its pressure coefficient is in doubt, so the necessity for interband scattering is established, without an exact evaluation of the parameters. The most convincing single piece of evidence for the presence of interband scattering here is afforded by the maximum in the Bridgman resistance versus pressure curve for germanium[2]: if the carriers changed from one set of minima to the other without interband scattering, only a monatonic change from the conductivity characteristic of one set to that for the other would be observed. The best fit to the data suggests that the matrix element for interband scattering is between 10 and 30% of that for intravalley scattering in the [111] minima. However, the interband scattering frequency, where energetically possible, is greater than or equal to the [111] intravalley scattering frequency because of the higher density of states in the [100] minima.

The similar, but better defined, curve found by Bridgman and Paul[21] foran 8% Si in Ge alloy verifies the over-all picture of the two sets of minima shifting with alloying and with pressure, and of interband scattering which reaches a maximum near the pressure where the two sets of minima are equal in energy. Optical investigations of Si-Ge alloys under pressure help confirm this picture.[52]

The fit to the resistivity pressure data for germanium at the several temperatures is good enough to enable us to assert that only small quantitative errors can remain, and that the general phenomenological theory is established.

We find from the theory that the zero-pressure separation of the [100] and [111] minima is between 0.15 ev and 0.18 ev. If in addition we allow for the uncertainty in $d\Delta E/dp$ previously mentioned in this section we find (using Figs. 7, 11, and 12) that the upper limit must be raised to 0.21 ev.

The low-pressure variation of the electron mobility is temperature independent for temperatures less than 200°K in samples where lattice scattering dominates. The variation is possibly compounded of changes in effective masses, elastic constants and deformation potentials. The various contributions cannot be separated here, but the over-all size and sign of the change are of the right order of magnitude. Changes in mass are expected, but have not been measured in isolation; changes in elastic constants have been determined,[48] and an average change may be inserted with small error; from the constancy of the gap change with pressure,changes in deformation potential are expected to be small, but not negligible compared to the small observed mobility variation.

ACKNOWLEDGMENTS

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APPENDIX

We evaluate $\langle\tau_g{}^n(\Delta)\rangle$ for $\Delta\geq0$. From Eqs. (10) and (12) we have

$$\begin{aligned}\langle\tau_g{}^n(\Delta)\rangle&=(4/3\pi^{\frac{1}{2}})D_g{}^n\int_0^{\Delta}y^{(3/2)-(n/2)}\exp(-y)dy\\&\quad+(4/3\pi^{\frac{1}{2}})D_g{}^n\int_{\Delta}^{\infty}\frac{y^{(3/2)-(n/2)}\exp(-y)dy}{[1+S(1-\Delta/y)^{\frac{1}{2}}]^n}\\&=(4/3\pi^{\frac{1}{2}})D_g{}^n(I_{1n}+I_{2n}),\end{aligned}\qquad\text{(A-1)}$$

where

$$D_g=[A_gC_g'(kT)^{\frac{1}{2}}]^{-1}.$$

$S=BC_s'\nu_s/A_gC_g'=$ interband scattering parameter. I_{1n} can be evaluated easily in terms of tabulated functions for $n\leq4$. For $n>4$, I_{1n} diverges. This does not mean that the transport integrals diverge.[53]

We cannot evaluate I_{2n} analytically for any value of n unless $\Delta=0$ or ∞. However, we can approximate it by

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[51] U. N. Ryabinin (private communication).

[52] W. Paul and D. M. Warschauer, J. Phys. Chem. Solids 6, 6 (1958).

[53] See reference 47, p. 130.

expanding the integrand in a Taylor series about $\Delta=0$ and then integrating term by term between the limits of Δ and ∞.

$$I_{2n}=\sum_{j=0} I_{2nj}(\Delta)\Delta^j. \qquad \text{(A-2)}$$

This is not a convergent process; that is, $I_{2nj}(0)\rightarrow\infty$ for all $n>2$ and $j>1$; and for $n=1$ or 2, $j>2$. The first term in the expansion gives a lower bound on the contribution of I_{2n} to $\langle\tau_g{}^n\rangle$. The term is finite regardless of n. In spite of the divergence involved we proceed to use this approximation, stopping the series expansion before the divergent terms. Table I shows values of $\langle\tau_g{}^n(\Delta,S)\rangle$ computed in this manner for $n=1$, 2, 3.

In spite of the fact that this approximation looks rather poor at first glance, it turns out to be fairly good. In the first place $\langle\tau_g{}^n\rangle$ tends to the correct values for $\Delta\rightarrow\infty$, namely,

$$\Gamma[(5/2)-(n/2)]D_g{}^n,$$

where $\Gamma(x)$ is the gamma function. Secondly, the correct value for $\Delta=0$ is obtained, i.e.,

$$\Gamma[(5/2)-(n/2)]D_g{}^n/(1+S).$$

Finally, Fig. 21 shows plots of $\langle\tau_g(\Delta,S)\rangle$ as a function of Δ for a typical value of S. The lower curve was computed using our approximation. The upper one was calculated directly from the integrals using Simpson's rule. It seems that the maximum difference occurs at approximately $\Delta=2$, when it is about 6%. Thus we see that we are fairly well justified in using the approximations to the integral.

We can also calculate $\langle\tau_s{}^n(\Delta,S')\rangle$ when $\Delta\geq 0$.

$$\langle\tau_s{}^n(\Delta,S')\rangle=(4/3\pi^{\frac{1}{2}})D_s{}^n \times\int_0^\infty \frac{y^{(3/2)-(n/2)}\exp(-y)dy}{[1+S'(1+\Delta/y)^{\frac{1}{2}}]^n}, \qquad \text{(A-3)}$$

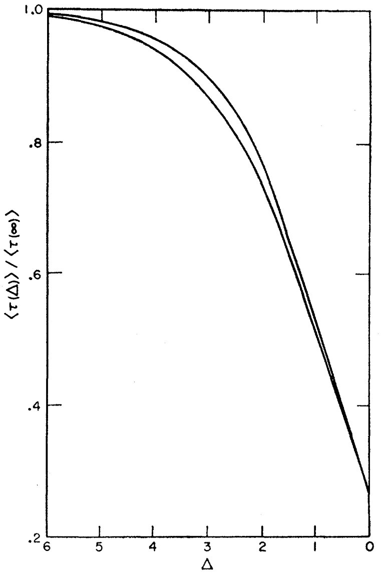

FIG. 21. Normalized scattering time vs Δ for $S=2.8$. The upper curve is the numerical calculation. The lower curve is the analytical approximation.

where $y=(E-\Delta E)/kT$. D_s and S' are defined as D_g and S with an interchange of all subscripts. If we use the same method to evaluate this integral as before, we obtain the values for $\langle\tau_s{}^n(\Delta,S')\rangle$ shown in Table I. This time the approximation is not as good. The wrong value is obtained for

$$\langle\tau_s{}^n(\Delta,S')\rangle=\sum_{j=0} I_{nj}\Delta^j$$

as $\Delta\rightarrow\infty$. Moreover, I_{nj} approaches infinity for all Δ, unless $j=0$, or $j=1$ and $n=1$ or 2. Despite the rather poor approximation to $\langle\tau_s{}^n(\Delta,S')\rangle$ it turns out that our fits to experimental data are little affected. The range of our experimental data extends to 30 000 kg/cm^2 so that $\Delta>0$. Since $(\mu_s{}^*/\mu_g{}^*)<1$, the fit of the mobility is not very sensitive to $\langle\tau_s\rangle$.