observed at room temperature, providing the conditions on $\omega_0\tau$, etc., are satisfied. However, in order to investigate quantum degeneracy effects by cyclotron resonance, it is necessary to go to sufficiently low temperatures so that only the lower l sub-bands are occupied. This has been accomplished thus far only for germanium by Fletcher *et al.*[30] who carried out microwave CR experiments at temperatures below 4°K. It should be possible to use appreciably higher temperature in CR experiments at infrared frequencies. Since the IMO effect does not depend on the distribution of free carriers in the magnetic sub-bands, it can be used to study quantum degeneracy effects without any restrictions on temperature other than those which arise from its effect on $\omega_0\tau$.

Both the IMO effect and CR yield information about the effective masses of the carriers and about quantum effects in degenerate energy bands. The IMO effect also yields information about the g factor for the carriers, and is useful for obtaining a precise value for the optical gap between the energy bands involved.

The IMO effect for transitions between two valence bands or two conduction bands does depend on the presence of carriers. Here, the absorption constants will generally be several orders of magnitude smaller so that it should be possible to use much larger specimen thicknesses.

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[30] Fletcher, Yager, and Merrit, Phys. Rev. 100, 747 (1955).

5. ACKNOWLEDGMENTS

We wish to express our appreciation to E. N. Adams, R. R. Goodman, E. O. Kane, W. Kohn, and J. M. Luttinger for valuable discussion of the physics underlying the interband magneto-optical effect. We also wish to acknowledge our thanks to W. C. Dash for supplying polished thin sections of Ge for the initial experiments, to C. Goldberg for supplying the high-mobility germanium used in the final experiments, to S. Slawson for preparing polished thin sections, to A. Wing for determining the orientation of the thin sections, to M. Hass for designing the Fresnel rhomb of NaCl which was used to produce circularly polarized light, to A. Mister and R. Anonson for operating the Bitter magnet, and to B. W. Henvis for her assistance in preparing the manuscript.

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Specific Heat of Germanium and Silicon at Low Temperatures*

P. H. Keesom and G. Seidel†
Department of Physics, Purdue University, Lafayette, Indiana

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The specific heats of several samples of silicon have been measured between 1.2°K and 4.2°K. The Debye characteristic temperature θ_0 at 0°K is estimated to be 636°K, a value slightly lower than previously reported. Measurements of germanium between 0.5°K and 4.2°K yield $\theta_0=363$°K, in very good agreement with older results.

From knowledge of the electronic specific heat and the carrier concentration of several degenerate samples of germanium and silicon, information is deduced concerning the energy band structure of the crystals. Measurements of n-type germanium indicate that the conduction band of this substance has four minima. Similar measurements of silicon indicate that there are six minima in its conduction band. The density-of-states effective masses of both electrons and holes in germanium, calculated from this work on degenerate samples, are not appreciably different than found from cyclotron resonance experiments on pure crystals. This result is consistent with the assumption, used in the calculations, that the addition of impurities to a crystal does not change the density of states in the vicinity of the band edge. For silicon, however, the specific heat yields somewhat larger effective masses for the electrons and holes than obtained from cyclotron resonance. Thus, the addition of impurities to silicon affects the shape of the bands.

INTRODUCTION

THE specific heats of the semiconductors silicon[1] and germanium[2] have previously been measured in the liquid helium temperature region. The present reinvestigations of these substances were primarily performed to obtain the electronic specific heats of both heavily doped n- and p-type germanium and silicon samples. As is well known,[3] the specific heat of a degenerate electron gas is a direct measure of the density of states at the Fermi level. Then, by determining the specific heat and carrier concentration of a sample, it is possible to obtain information concerning the energy band structure of the crystal. By making certain assumptions regarding the energy dependence of the density of states, the effective masses of the carriers can be calculated for impure crystals. From measurements on n-type samples it is also possible to determine

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* This work was supported by a Signal Corps contract.

† Present address: Kamerlingh Onnes Laboratory, Leiden University, Leiden, The Netherlands.

[1] N. Pearlman and P. H. Keesom, Phys. Rev. 88, 398 (1952).

[2] P. H. Keesom and N. Pearlman, Phys. Rev. 91, 1347 (1953).

[3] F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 151.

whether the conduction band minima lie inside or at the surface of the Brillouin zone.

EXPERIMENTAL

As these measurements were performed over a period of several years, many different techniques were employed in carrying out various parts of the experiments. For instance, the measurements on silicon extended only down to temperatures obtainable by pumping on a bath of He^4, this temperature being sufficiently low for deducing the Debye temperature at 0°K, θ_0, and the electronic specific heat of very impure samples. However, above 1°K the lattice specific heat of germanium overwhelms its electronic specific heat. Thus, the measurements of degenerate samples of this substance were extended below 1°K to improve the estimate of the coefficient of the electronic specific heat. Temperatures below 1°K were obtained using a He^3 cryostat described in a previous paper.[4]

The earliest work reported here, namely, that on pure silicon, was performed in the manner discussed by Pearlman and Keesom[1] using a phosphor-bronze wire as a thermometer. More recently, the measurements were made using a carbon resistance thermometer, the temperature calibration being handled in the same fashion as described in a discussion of the heat capacity measurements of gallium and zinc.[5]

The main difficulties in obtaining reliable measurements of the heat capacity of silicon below 4°K, and of germanium below 1°K, result from the fact that the specific heats of these substances are very small in the specified temperature ranges. Thus, ordinarily negligible effects can become quite important. One such effect on the measured heat capacity is the influence of gas adsorbed on the surface of the sample. However, adsorption could not have affected the measurements of germanium employing the He^3 cryostat, as in this apparatus the samples were cooled using a thermal switch and the heat capacity measured without the samples ever experiencing an environment of exchange gas at low temperatures. The measurements of silicon, on the other hand, using a standard He^4 cryostat, were performed without the aid of such a thermal switch; hence, the samples had to be cooled from room temperature to 4.2°K using exchange gas. And although the vacuum space surrounding the samples was pumped for many hours before the heat capacity measurements were begun, adsorbed gas still appears to have affected the results (see below).

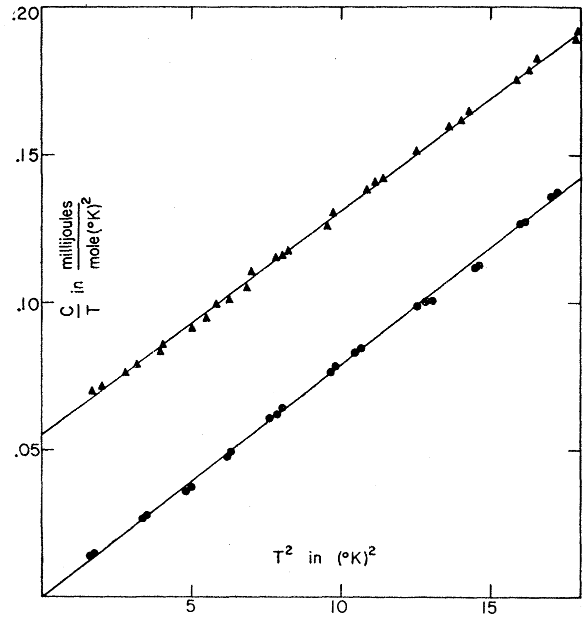

FIG. 1. Specific heat of pure (●) and degenerate (▲) silicon.

An equally important concern is the contribution of the addenda (thermometer, heater wire, and adhesive) to the total measured heat capacity. To determine the heat capacity of the Glyptal, used to attach the thermometer and heater to the sample, a separate experiment was performed. One of the silicon samples, which has previously been measured, was coated with approximately one gram of Glyptal and remeasured. The additional heat capacity was attributed to the Glyptal and could be represented between 1.3°K and 4.2°K by the relation

$$C_{\text{glyptal}}=0.027\ T^3 \text{ millijoule/gram (°K)}, \qquad (1)$$

the precision of the determination being no worse than 20%. Pearlman and Keesom[1] previously measured the heat capacity of Glyptal at 4°K and above 10°K. At 4°K the heat capacity reported here is smaller by a factor of two, a difference which is within the combined error of the experiments.

While the heat capacity of the Glyptal adhesive was never more than 1% of the total heat capacity of the sample being measured (except, of course, in the one measurement to determine the heat capacity of the Glyptal), the heat capacity of the carbon thermometer was more significant. This heat capacity was determined by measuring a 15-gram crystal of high-resistivity silicon. The total measured heat capacity was noticeably larger than that expected for pure silicon, the additional amount assumed to be due to the thermometer. When correction was made for the Glyptal, the heat capacity of the 0.05-gram, 1/10th-watt, nominal 10-ohm, Allen Bradley carbon resistor was found to be

$$C=0.0064\ T+0.0013\ T^3 \text{ millijoule/°K}. \qquad (2)$$

This expression fitted the results with an accuracy of better than 10%.

The heat capacities of the constantan heater wire and the phosphor-bronze thermometer wire, however, could safely be neglected. Even if the Debye tempera-

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[4] G. Seidel and P. H. Keesom, Rev. Sci. Instr. **29**, 606 (1958).

[5] G. Seidel and P. H. Keesom, Phys. Rev. **112**, 1083 (1958).

TABLE I. Specific heat of silicon.

Sample[a]	θ_0 °K	$\gamma\times10^5$ joule/mole(°K)^2
VI	621	...
VI *N*	630	...
VII	628	...
VIII	632	...
IX	630	...
X	625	...
XI	625	5.13
XI *N*	633	0.19
XII	626	6.7
XII *N*	641	0.71
XIV	636	5.54

[a] All the samples, except VIII, were single crystals weighing approximately 100 grams. Sample VIII was high-purity polycrystalline material. *N* indicates that the sample was irradiated with an integrated flux of greater than 5×10^{18} neutrons/cm^2.

ture of these metals were as low as 200°K, the lattice heat capacities of the wires would still have been negligible. Also, the electronic heat capacities of the wires were not significant. Although no correction was made for the wires, the measured heat capacity of pure silicon contained no term varying linearly with temperature (see below).

RESULTS AND DISCUSSION

Lattice Specific Heats

(*a*) *Silicon*

Representative specific heat measurements in the liquid helium temperature region of two silicon samples, one relatively pure and the other highly degenerate, are indicated in Fig. 1 where C/T is plotted against T^2. The specific heats of all the silicon samples measured could be fitted, within the accuracy of the experiment, by an equation of the form

$$C=\gamma T+\alpha T^3, \qquad (3)$$

where γT is an expression for the specific heat of the conduction carriers, and αT^3 is an expression for the lattice specific heat. From the coefficient α, θ_0 can be calculated; the results for the various samples are listed in Table I. As the 99% confidence limit of any one of the determinations of θ_0 is at most 6°K, the scatter of the values is certainly outside the random error of measurement. Such systematic effects as errors in thermometry, temperature scale, and correction for the heat capacity of the addenda are considered unlikely to be responsible for the variations. Also, the variations do not appear to be due to any property of the silicon samples. Two separate measurements of one sample, performed on different days, gave θ_0 values differing by 9°K (the γ did not change). Such an effect has never been observed by us with any other material although many different substances have been measured with the same apparatus. It seems probable to us that adsorption of He^4 gas on the surface of the samples manifests itself as an apparent change in the value of θ_0. Indeed, a rough estimate of the apparent heat capacity involved in desorbing gas during the measurements is of the correct order of magnitude. Although the average of all the tabulated values of θ_0 is 630°K, we feel that this value is too low and that a better estimate is (636 ± 10)°K.

The value we estimate for θ_0 of 636°K is slightly lower than the 658°K quoted by Pearlman and Keesom.[1] However, on recalculation of their data using the 55_E temperature scale and removing inaccuracies in the previous calculations, the result of their work is $\theta_0=642$°K, in reasonable agreement with the present investigation.

Several of the samples studied were irradiated with integrated fluxes of greater than 5×10^{18} neutrons/cm^2 and the specific heat remeasured. The differences of the θ_0 values before and after irradiation appear to be within the accuracy of the experiment; see Table I. This is in contradiction to what has previously been reported.[6]

Samples for which no value of γ is listed in Table I were known to have been reasonably pure ($\rho_{RT}>1$ ohm cm). Indeed, in all such cases a least-squares fit of the results by Eq. (3) gave a value of γ that was smaller in magnitude than the 70% confidence limit. Adsorption of gas apparently does not affect the determination of γ.

(*b*) *Germanium*

The specific heats of the two single-crystal samples of germanium investigated between 0.5°K and 4.2°K could also be fitted by Eq. (3). The results of one of the samples is indicated in Fig. 2 where C/T is plotted

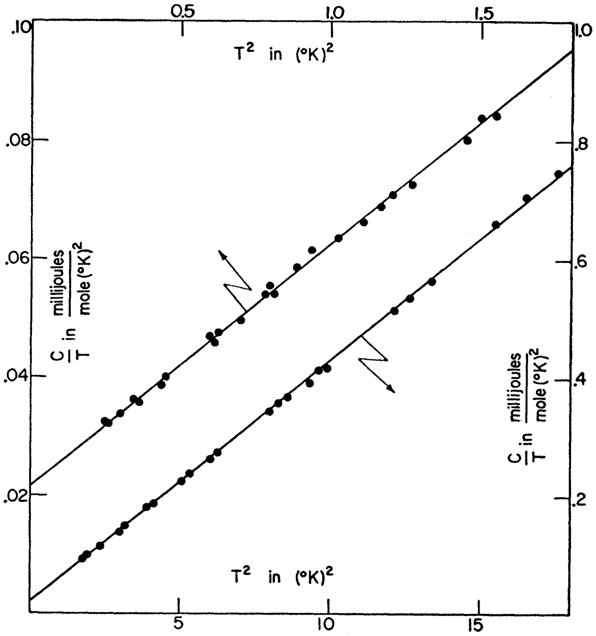

FIG. 2. Specific heat of degenerate germanium.

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[6] Keesom, Lark-Horovitz, and Pearlman, Science **116**, 630 (1952).

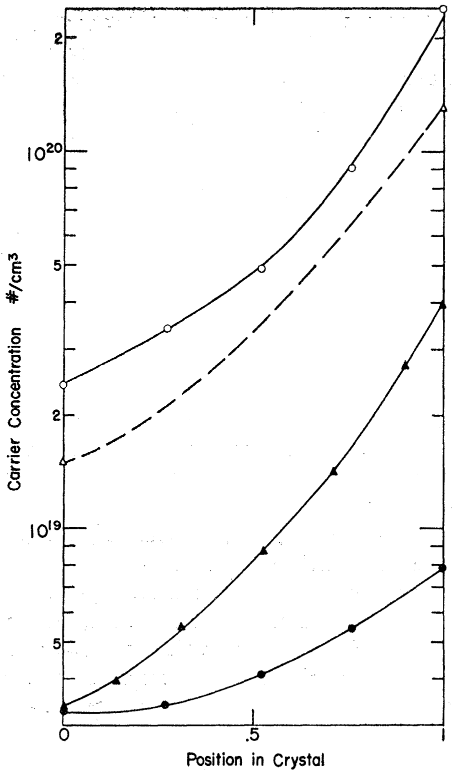

FIG. 3. Variation of the carrier concentration in direction of crystal growth. Horizontal axis is normalized so that total length of each crystal is 1. Samples: ●—n-type Ge, ▲—n-type Si, ○—p-type Ge, △—p-type Si.

against T^2. The lattice specific heat of one sample gave $\theta_0 = (362 \pm 2)$°K, whereas the other gave $\theta_0 = (364 \pm 2)$°K. The limits quoted are for the 99% confidence level and account only for the random error in the experiment. Systematic effects could at most introduce an additional uncertainty of 1°K. The average of the two measurements, $\theta_0 = 363$°K, is in very good agreement with the work of Keesom and Pearlman[2] who obtained 362°K.

Electronic Specific Heats

(a) *n-Type Germanium and Silicon*

Cyclotron resonance experiments[7] have shown that the conduction band of germanium consists of a set of minima located in equivalent positions along the ⟨111⟩ axes of k space, the k coordinate system taken coincident with the cubic axes. There are, then, either four or eight minima, the number depending on whether these minima are located at the surface or inside the Brillouin zone. Also, for pure crystals the surfaces of constant energy in the vicinity of the minima have been found to be ellipsoids of revolution in k space and can be characterized by two effective-mass parameters, m_l and m_t.

The situation is much the same for the conduction band of silicon where the constant-energy surfaces are also ellipsoids of revolution. However, the minima lie along the ⟨100⟩ axes, and consequently the conduction band consists of either three or six minima.

The density of states in the vicinity of the bottom of the conduction band for a pure crystal is expressible as

$$g(\epsilon) = N_c[4\pi(2m_d)^{\frac{3}{2}}/h^3]\epsilon^{\frac{1}{2}}, \tag{4}$$

where N_c is the number of band minima, ϵ is the energy measured from the band edge, and m_d is the density of states effective mass. The relation between m_d and the effective mass parameters m_l and m_t is

$$m_d = (m_l m_t^2)^{\frac{1}{3}}. \tag{5}$$

The coefficient of the electronic specific heat of a degenerate electron gas [γ of Eq. (3)] is related to the density of states at the Fermi surface, $g(\zeta)$, by the expression

$$\gamma = \tfrac{1}{3}\pi^2 k^2 V_m g(\zeta), \tag{6}$$

where ζ is the Fermi energy, k is Boltzmann's constant, and V_m is the molar volume.

In order to calculate the effective masses of carriers from specific heat data, we now *assume* that Eq. (4) accurately represents the density of states in the conduction band of a degenerate crystal up to the position of the Fermi level. This is an assumption that (1) for the pure crystal the band is parabolic up to an energy of a few hundredths of an electron volt, and (2) the added impurities do not appreciably affect this shape.

On the basis of this assumption, the electronic specific heat, effective mass, and the carrier concentration, n, are related as

$$\gamma = aN_c^{\frac{2}{3}}(m_d/m_0)n^{\frac{1}{3}}, \tag{7}$$

where $a = (4\pi^{8/3}k^2 V_m m_0)/(3^{\frac{2}{3}}h^2)$, and m_0 is the free electron mass. Then, by experimentally determining the carrier concentration and the electronic specific heat, the product $N_c^{\frac{2}{3}}(m_d/m_0)$ can be deduced for degenerate n-type germanium and silicon.

The expression for the Fermi level in terms of γ and n is

$$\zeta = bn/\gamma, \tag{8}$$

where $b = \frac{1}{2}\pi^2 k^2 V_m$.

Although relatively large ingots are required for heat capacity measurements, such samples with high uniform impurity concentrations were unfortunately not available to us. All the samples, both n- and p-type germanium and silicon, had concentration gradients in the direction they were pulled from the melt. Thus, the measured electronic specific heat is an average,

$$\langle\gamma\rangle = (\textstyle\int \gamma\, dV)/V, \tag{9}$$

and Eqs. (7) and (8) have to be modified accordingly:

$$\langle\gamma\rangle = aN_c^{\frac{2}{3}}(m_d/m_0)\langle n^{\frac{1}{3}}\rangle, \tag{10}$$

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[7] Dresselhaus, Kip, and Kittel, Phys. Rev. **98**, 368 (1955); Dexter, Zeiger, and Lax, Phys. Rev. **104**, 637 (1956). For other references see these two papers.

and

$$\langle\zeta^{\frac{1}{2}}\rangle^2=b\langle n^{\frac{1}{3}}\rangle^3/\langle\gamma\rangle. \tag{11}$$

To obtain the average carrier concentration, actually $\langle n^{\frac{1}{3}}\rangle^3$, the samples were cut up on completion of the heat capacity measurements and the Hall coefficient determined at 77°K with a field of 3500 gauss at several different places in the sample. For n-type germanium and silicon the relation

$$R_H=K_1K_2/ne \tag{12}$$

was used to calculate n from the Hall coefficient R_H. The coefficient K_1 is dependent only on the shape of the energy surfaces,[8,9] and for n-type Ge, K_1 is 0.79. For n-type Si, K_1 equals 0.87. K_2 is a factor assumed to be 1 for the samples measured here. At 77° this should be a good approximation for Ge when $n>3\times10^{18}$ cm^{-3} and for Si when $n>1\times10^{19}$ cm^{-3}. The fact that K_2 may be somewhat greater than 1 below 10^{19} cm^{-3} for Si should make little difference in these measurements, as the average carrier concentration of the sample measured (see below) is largely determined by the high impurity concentration that occurs at one end.

The variation of the carrier concentration in the direction of crystal growth is indicated in Fig. 3. The concentrations increase approximately exponentially with position, as one would expect for samples grown from the melt, doped with impurities whose segregation coefficients are less than 1. No variation of the concentration was found perpendicular to the pulling direction. $\langle n^{\frac{1}{3}}\rangle$ was determined by numerically averaging $n^{\frac{1}{3}}$ over the sample, taking into account the sample shape.

The accuracy of the determination of the effective mass in the manner described is essentially limited by the error in the average carrier concentration, the error in the electronic specific heat being negligible in comparison. However, since m_d is dependent upon $n^{-\frac{1}{3}}$, the percentage error in m_d is only a third of the error in n.

The results of the measurements on n-type germanium and silicon are listed in Table II. For germanium, the density-of-states effective mass calculated from these measurements with N_c equal to 4 is in close agreement with the cyclotron resonance value, and it appears that the conduction band minima are at the surface of the Brillouin zone. In fact, since the specific heat m_d is the same, within experimental accuracy, as found by cyclotron resonance, the original assumption concerning the density of states is consistent with the results. That N_c equals 4 for Ge is in accord with the prediction of Herman[10] and with the magnetic susceptibility studies of Stevens *et al.*[11] and Bowers.[12] However, employing the same assumption regarding the density of states as used here, Bowers obtains, from susceptibility measurements of samples of comparable carrier concentrations, an effective mass that appears to be somewhat larger than found from this work.

TABLE II. Effective masses of electrons in degenerate germanium and silicon.

Material	Doping agent	$\langle\gamma\rangle\times10^5$ joule/mole (°K)^2	$\langle n^{1/3}\rangle^3$ $\times10^{-19}$ cm^{-3}	$\langle\zeta^{1/2}\rangle^2$ ev	N_c	m_d/m_0	m_d/m_0 from cyclotron resonance
Ge	As	2.15	0.47	0.018	4	0.23	0.22
					8	0.14	
Si	As	5.54	1.0	0.012	3	0.66	0.33
					6	0.42	

The effective mass of electrons in silicon is calculated from the specific heat using the two possibilities for the number of minima in the conduction band. As can be seen in Table II, the specific-heat and cyclotron-resonance values are in closer agreement with N_c equal to 6 rather than 3. The difference between 0.42 m_0 and 0.33 m_0, however, is outside the error of the experiment. The average carrier concentration would have to be in error by a factor of two to account for this difference. Therefore, the addition of impurities to the silicon lattice appears to affect the shape of the conduction band. The result that N_c is equal to 6 for silicon is consistent with the infrared measurements of Macfarlane and Roberts[13] and Haynes, Lax, and Flood.[14] In addition, the effective mass which is calculated here from specific heat appears to agree with the susceptibility studies of Sonder and Stevens.[15]

(*b*) *p-Type Germanium*

The maximum of the valence band of germanium is known from cyclotron resonance to consist of two bands degenerate at $k=0$, the surfaces of constant energy being warped spheres. From measurements on pure crystals the density-of-states effective masses of the holes in these two bands have been calculated to be $m_{d1}=0.33\ m_0$ and $m_{d2}=0.043\ m_0$, where the subscripts 1 and 2 are used to distinguish the two types of holes.

An assumption, similar to that employed before for the conduction band in n-type semiconductors, is now made concerning the valence band. The density of states of each band of a degenerate crystal is assumed to be given by

$$g_i(\epsilon)=[4\pi(2m_{di})^{\frac{3}{2}}/h^3]\epsilon^{\frac{1}{2}}, \tag{13}$$

the subscript i having the values 1 and 2.

Since the total density of states is the sum of the

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[8] B. Abeles and S. Meiboom, Phys. Rev. **95**, 31 (1954).

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

[10] F. Herman, Physica **20**, 801 (1954).

[11] Stevens, Cleland, Crawford, and Schweinler, Phys. Rev. **100**, 1084 (1955).

[12] R. Bowers, Phys. Rev. **108**, 683 (1957).

[13] G. Macfarlane and V. Roberts, Phys. Rev. **97**, 1714 (1955).

[14] Haynes, Lax, and Flood, Bull. Am. Phys. Soc. Ser. II, **3**, 30 (1958).

[15] E. Sonder and D. K. Stevens, Phys. Rev. **110**, 1027 (1958).

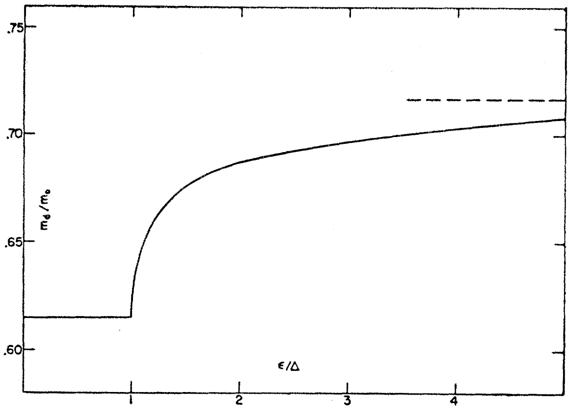

FIG. 4. Variation of the density-of-states effective mass of holes in silicon. Energy is expressed in units of Δ. Dashed line is the value of m_d at $\epsilon = \infty$.

contributions of the two bands, it follows that

$$m_d^{\frac{3}{2}} = m_{d1}^{\frac{3}{2}} + m_{d2}^{\frac{3}{2}}. \tag{14}$$

Thus, by setting N_c equal to 1 and substituting p for n, Eqs. (10) and (11) are applicable to p-type germanium:

$$\langle\gamma\rangle = a(m_d/m_0)\langle p^{\frac{1}{3}}\rangle, \tag{15}$$

and

$$\langle\zeta^{\frac{1}{2}}\rangle^2 = b\langle p^{\frac{1}{3}}\rangle^3/\langle\gamma\rangle. \tag{16}$$

In germanium a third valence band exists approximately 0.3 ev below the other two bands at $k=0$. The presence of this band, however, does not appreciably affect these considerations. Although at the very impure end of the sample (see Fig. 3) the Fermi level may possibly be within this third band, the influence should be so small that it can safely be neglected.

The carrier concentration was calculated from the Hall coefficient according to the equation

$$R_H = (p_1\mu_1^2 + p_2\mu_2^2)/e(p_1\mu_1 + p_2\mu_2)^2, \tag{17}$$

where the μ's are the mobilities of the two types of holes. This equation is an expression for the Hall coefficient of a degenerate electron gas occupying two overlapping bands that have spherical constant-energy surfaces. Unfortunately, the more sophisticated treatments of the Hall effect, e.g., that of Beer and Willardson,[16] taking into account the influence of the shape of the warped surfaces, are applicable only to p-type germanium less impure than measured here.

When the appropriate effective masses are used to obtain the ratios of the concentrations and mobilities, Eq. (17) becomes

$$R_H = 2.0/pe, \tag{18}$$

where $p = p_1 + p_2$.

The results for p-type germanium are listed in Table III. The effective mass calculated from the specific heat is approximately the same as found by cyclotron resonance; the difference in the values may easily be accounted for by an error in the constant appearing in Eq. (18). As was the case for n-type germanium, the results are consistent with the original assumption concerning the density of states.

TABLE III. Effective masses of holes in degenerate germanium and silicon.

Material	Doping agent	$\langle\gamma\rangle\times10^5$ joule-mole (°K)^2	$\langle p^{1/3}\rangle^3$ $\times10^{-19}$ cm^{-3}	$\langle\zeta^{1/2}\rangle^2$ ev	m_d/m_0	m_d/m_0 from cyclotron resonance
Ge	Ga	2.72	5.4	0.16	0.33	0.34
Si	B	5.2	4.0	0.06	0.81	0.69

(c) p-type Silicon

The maximum of the valence band of silicon is similar to that of germanium, consisting of two warped spherical bands degenerate at $k=0$. From cyclotron resonance measurements the best estimates of the density-of-states effective masses of the two types of holes are $m_{d1} = 0.56\ m_0$ and $m_{d2} = 0.16\ m_0$. However, in silicon the third valence band, depressed by spin-orbit coupling, is split from the two upper bands by only 0.035 ev. Therefore, for p-type silicon the calculations are complicated by the necessity of including this third band. Theory predicts that the constant-energy surfaces of the third band are spherical and that the effective mass of holes in this band can be calculated from the shape of the two upper bands. The calculated m_{d3} is $0.25\ m_0$.

As before, the density of states of each band is assumed to be dependent on $\epsilon^{\frac{1}{2}}$. Since the total density of states is the sum of the contributions of the three bands, it follows that

$$g(\epsilon) = (4\pi 2^{\frac{3}{2}}/h^3)\{m_{d1}^{\frac{3}{2}}\epsilon^{\frac{1}{2}} + m_{d2}^{\frac{3}{2}}\epsilon^{\frac{1}{2}} + m_{d3}^{\frac{3}{2}}(\epsilon-\Delta)^{\frac{1}{2}}F(\epsilon,\Delta)\}, \tag{19}$$

where ϵ is the energy measured from the top of the two upper bands, Δ is the magnitude of the band splitting, and $F(\epsilon,\Delta)$ is a step function such that

$$\begin{aligned} F(\epsilon,\Delta) &= 0 \quad \text{for} \quad \epsilon<\Delta \\ &= 1 \quad \text{for} \quad \epsilon>\Delta. \end{aligned}$$

Then, to describe the total density of states as

$$g(\epsilon) = [4\pi(2m_d)^{\frac{3}{2}}/h^3]\epsilon^{\frac{1}{2}}, \tag{20}$$

the total density-of-states effective mass must be a function of energy:

$$m_d(\epsilon)^{\frac{3}{2}} = m_{d1}^{\frac{3}{2}} + m_{d2}^{\frac{3}{2}} + m_{d3}^{\frac{3}{2}}(1-\Delta/\epsilon)^{\frac{1}{2}}F(\epsilon,\Delta). \tag{21}$$

A plot of m_d so defined for silicon is given in Fig. 4. The cyclotron resonance values are used for m_{d1} and m_{d2} while the theoretically predicted value is used for m_{d3}.

The quantities γ, m_d, and p can quite easily be shown

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[16] A. C. Beer and R. K. Willardson, Phys. Rev. 110, 1286 (1958).

to be related by an equation of the form

$$\gamma=a[m_d(\zeta)/m_0]p^{\frac{1}{3}}\{1-[m_{d3}/m_d(\zeta)]^{\frac{3}{2}}\times(1-\Delta/\zeta)^{\frac{1}{2}}(\Delta/\zeta)F(\zeta,\Delta)\}^{-\frac{1}{3}}. \quad (22)$$

However, the accuracy of the experiment, in particular the accuracy of the determination of the carrier concentration, does not warrant such complication. The value of the term in brackets is such that $1.00<\{\ \}^{-\frac{1}{3}}<1.03$ for all values of ζ and hence the curly bracket can be neglected. Furthermore, the variation of $m_d(\zeta)$ is assumed to be small compared to the variation in $p^{\frac{1}{3}}$. Then Eq. (15) can be used to calculate m_d from the electronic specific heat and carrier concentration.

By similar arguments $\langle\zeta^{\frac{1}{2}}\rangle^2$ can be shown to be given approximately by Eq. (16).

The equation for the Hall coefficient in terms of carriers occupying three bands, each assumed to have a spherical energy surface, is

$$R_H=(p_1\mu_1^2+p_2\mu_2^2+p_3\mu_3^2)/e(p_1\mu_1+p_2\mu_2+p_3\mu_3)^2. \quad (23)$$

This expression reduces to $R_H=K/pe$, where K varies only from 1.4 to 1.3 as ζ varies from zero to infinity. Since the error involved in using Eq. (23) as an expression for the Hall coefficient is probably larger than the difference between 1.4 and 1.3, a consideration of the position of the Fermi level with respect to the third band is not necessary in calculating p. The value of 1.3 was used in these calculations.

Because the p-type silicon sample was to be irradiated with neutrons, the ingot could not be cut up on completion of the heat capacity measurements. Consequently, Hall measurements were made only on plates cut from the ends of the sample. However, by noting the concentration distributions of the other samples, the average carrier concentration of the p-type silicon was estimated to be 4×10^{19} cm^{-3}. As listed in Table III, the effective mass resulting from the specific heat is 0.81 m_0, somewhat larger than the 0.69 m_0 estimated from the cyclotron resonance and the theoretical prediction for the third band.

CONCLUSIONS

For germanium the density-of-states effective masses of both electrons and holes calculated from specific heat measurements of degenerate samples are in very good agreement with the masses obtained from cyclotron resonance experiments made on pure crystals. This result is, indeed, surprising in view of the assumption made in the calculations concerning the energy dependence of the density of states. From electrical and optical investigations, the addition of small impurity concentrations to germanium is known to introduce states in the forbidden gap near the edge of the bands (conduction band for donors, valence band for acceptors). As the concentration is increased, the band formed by the impurity states gradually overlaps with the conduction (valence) band. Since the number of impurity states is of the same order of magnitude as the number of free carriers, one would expect the impurities to affect seriously the energy dependence of the density of states and, therefore, the effective masses calculated on the basis of the assumption that $g(\epsilon)\sim\epsilon^{\frac{1}{2}}$.

Essentially, what one determines in measuring the specific heat and Hall coefficient is the value of the density of states at the Fermi level, $g(\zeta)$, and the total number of occupied states in the band, $n(\zeta)$ (=total number of states below the Fermi level for a degenerate gas). Thus, the measurements indicate that if the impurities are influencing the density of states, they must do so in such a way that these two quantities, $g(\zeta)$ and $n(\zeta)$, are related in the same way as for a normal band, namely, $g(\zeta)[n(\zeta)]^{-\frac{1}{3}}=\text{const}$. While it is impossible to conclude that the density of states has been unaltered by the addition of impurities, the agreement of the results for both electrons and holes appears to be more than fortuitous. At large impurity concentrations it seems that the density of states is not significantly changed in the vicinity of the band edge. Perhaps at large concentrations the impurity states are perturbed well into the conduction (valence) band.

For silicon, however, the density-of-states effective mass of electrons, calculated with 6 minima in the conduction band is larger than the value obtained from cyclotron resonance. Similarly, the specific heat m_d of holes in silicon is larger than the cyclotron-resonance value. It appears that the addition of impurities to silicon may seriously influence the energy dependence of the density of states below the Fermi level. And since the original assumption that $g(\epsilon)\sim\epsilon^{\frac{1}{2}}$ for the various bands in silicon may be in error, the calculated effective masses should not be assumed to have further significance than indicating that the bands are disturbed by the impurities.

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