Phonon Scattering by Neutral Donors in Germanium*

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The excess thermal resistivity, w_{ep}, produced in n-type Ge by neutral donors at temperatures below that of the maximum in thermal conductivity, has been measured for samples with P and Bi donor, and with samples with Ga and In acceptor compensation as well. If neutral-donor concentration, n_{ex}, is low enough for the donor levels to be located in the gap, then w_{ep} decreases with increasing chemical shift $4\Delta_c$, as found earlier for As and Sb donors. In contrast to the insensitivity of w_{ep} to Ga or In compensation in Sb-doped n-Ge, Ga compensation strongly enhances w_{ep} in n-Ge doped with As or P. Electrical resistivity measurements agree with the attribution of this effect to modification of the core potential on compensation, the modification being stronger for larger $4\Delta_c$. For $n_{ex}>5\times10^{17}$ cm^{-3}, the donor levels overlap the conduction band, and $w_{ep}\propto n^{1/3}$ and is independent of impurity species or compensation.

I. INTRODUCTION

PHONON scattering by neutral donors in n-type Ge at low temperatures has been discussed recently by Keyes[1] and by Griffin and Carruthers[2] (theory) and by Goff and Pearlman[3] (experiment—this paper will hereafter be referred to as GP). At temperatures below that of the maximum in thermal conductivity k ($T_{max}\sim20$°K), this is the most important scattering mode introduced by donor impurities in nondegenerate material (donor concentration $N_d<10^{17}$ cm^{-3}). Indeed, in material with N_d as low as 10^{15} cm^{-3}, neutral donor scattering around 1°K in samples with smallest dimension of the order of mm can be as strong as the residual scattering in pure material (size-dependent boundary scattering and isotope point-defect scattering). We use the symbol w_{ep} (signifying phonon scattering by interaction with electrons) to denote the extra thermal resistivity observed in material with donors compared with pure Ge.

Phonons are coupled to neutral donors through virtual excitation of electrons from the singlet-donor ground state to the next higher state, a triplet. These states originate in the ground state of the effective-mass approximation, which is fourfold degenerate because of the four equivalent valleys in the conduction band.[4] The valley-orbit splitting removes part of the degeneracy, raising the triplet above the singlet by the "chemical shift"[5] $4\Delta_c$. As reported in GP, w_{ep} was found to be much larger for Sb donors (small chemical shift) than for As donors (large chemical shift) as expected from theory.[1,2]

Phonon scattering due to the mass difference of donor atoms as point defects in the Ge lattice[6] should also be larger for Sb than for As since the difference in molecular weight ΔM between Sb and Ge is much larger than that between As and Ge. We describe below in Sec. III observation of the species effect in w_{ep} and P and Bi donors, which have $4\Delta_c$ values intermediate between those of As and Sb. Since the cross section for mass-difference point-defect scattering is proportional to $(\Delta M)^2$, it is an order of magnitude larger for Bi in Ge than for P in Ge. However, P and Bi produce roughly the same scattering per neutral donor, which indicates that mass-difference point-defect scattering, although it is an important scattering mechanism at higher temperatures, is negligible below T_{max}.

The unimportance of ΔM point-defect scattering has a striking consequence in the effect of compensation on w_{ep}. In nondegenerate crystals grown from pure Ge to which only donor impurity has been added, the neutral-donor concentration N_d^0 is equal to the total concentration of donor atoms N_d at liquid-He temperatures, since the number of electrons excited from the donor levels to the conduction band is essentially zero. Furthermore, if the small amount of compensation due to naturally occurring acceptors is neglected, $N_d=N_I$, the total impurity concentration. If now the acceptor concentration is deliberately increased by adding Group-III impurity to the melt, $N_d^0=N_d-N_a$ decreases while $N_I=N_d+N_a$ increases. Hence w_{ep}, which varies monotonically with N_d^0, will decrease as increasing compensation decreases N_d^0, even though N_I is simultaneously increasing. This effect was observed in Ge doped with Sb donor and compensated with Ga acceptor, as reported in GP, including material for which the compensation ratio $C=N_a/N_d$ was close to unity.

The measurements on (Sb+Ga)-doped Ge displayed a very curious feature, however. Within the accuracy of its determination (estimated to be on the order of 10%), w_{ep} as a function of N_d^0 did not change on compensation. Now the species effect described above shows clearly that the magnitude of phonon scattering depends strongly on the nature of the neutral donor

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involved. Hence insensitivity of w_{ep} to compensation implies that the wave functions of electrons bound to Sb donors in Ge may be essentially unaltered despite the drastic change in their surroundings which accompanies the introduction of large concentrations of ionized acceptors $N_a^- = N_a$ on compensation.

In order to examine whether this apparent insensitivity of donor wave functions to compensation is uniquely associated with Sb in Ge or whether it is displayed by other donors as well, we extended our measurements to (As+Ga)Ge and (P+Ga)Ge. We also measured w_{ep} for (Sb+In)Ge to see whether the peculiar behavior of (Sb+Ga)Ge was related to the specific acceptor involved.

From these measurements we were able to conclude that: (i) The insensitivity of w_{ep} to compensation is a specific property of Sb—the function $w_{ep}(N_d^0)$ is greatly modified on compensation when either As or P is the donor impurity, the general effect being that w_{ep} is increased on compensation; (ii) this property of Sb donors is the same for either Ga or In as acceptor. We discuss in Sec. III below conclusions regarding donor wave functions in Ge and their modification on compensation that can be drawn from these observations. We also discuss some measurements on the electrical resistivity of compensated samples, which are pertinent to the question of the effect of compensation on donor wave function and the difference observed between Sb donor, on the one hand, and As or P donor, on the other.

The discussion so far has been limited to impurity concentrations so low that donor electron levels are in the energy gap. At high enough concentrations ($N_d > 5 \times 10^{17}$ cm^{-3}) a number of effects[7,8] (narrowing of the energy gap; formation of tails of states from valence and conduction bands, in the energy gap) combine to remove the donor levels from the gap, so that $N_d^0 = 0$. Hence neutral donor scattering vanishes, but electrons in the conduction band (concentration n) now scatter phonons. This contribution to w_{ep}, unlike that from neutral donors, shows no species effect. Phonon scattering by conduction electrons is similar to that in metals, with the difference first pointed out by Ziman[9] that momentum and energy conservation restrict the number of electrons which can scatter phonons. We refer to GP for a detailed discussion of the effects of this restriction on the thermal conductivity of degenerate Ge.

In order to be able to use a uniform notation for the entire range of impurity concentrations, we note that $n_{ex} = N_d - N_a$ (excess of donor concentration over acceptor concentration, which also equals carrier concentration, in the exhaustion temperature range) equals N_d^0 for nondegenerate material, and equals n (the electron concentration in the conduction band) for degenerate material, both single-doped and compensated. Hence we can refer to $w_{ep}(n_{ex})$ in all cases.

Measurements on p-type Ge (degenerate and nondegenerate) above 0.2°K have been reported by J. A. Carruthers *et al.*[10,11] and interpreted in terms of scattering by holes in a band[9] rather than by neutral acceptors. Griffin and Carruthers[2] have pointed out, however, that there is some evidence for neutral acceptor scattering, at least in some of the samples measured. The effect of compensation on p-type material has not been reported. Keyes and Sladek[12,13] have described their results on the effect of pressure on thermal conductivity of doped Ge in terms of neutral donor scattering.

Neutral impurity (donor or acceptor) scattering has also been invoked in interpreting measurements on a number of other semiconductors at temperatures below T_{max}—Si (Thompson and Younglove),[14] InSb (Challis *et al.*),[15,16] InSb, GaAs, GaSb, CdTe, CdS (Holland).[17,18] However, in all the cases except Si,[14] much less is known about the electronic structure of the neutral impurity presumably involved, than is the case for donor levels in Ge.[4]

II. APPARATUS AND SAMPLES

A. Apparatus

The thermal conductivity k and electrical resistivity ρ were measured in an apparatus similar to that described in GP. Instead of carbon resistors, germanium thermometers were used to measure the temperature difference ΔT along the sample. These thermometers were L shaped and were mounted by glueing the short leg to the sample with GE 7031 adhesive varnish. The resistance was measured along the long leg, which was parallel to the sample surface and perpendicular to the sample axis. In this way hysteresis effects due to differential thermal contraction in cycling between room temperature and liquid-He temperatures were minimized.

Thermal conductivity was measured by the steady-heat-current method. The heat source was a dc heater

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[14] J. C. Thompson and B. A. Younglove, J. Phys. Chem. Solids **20**, 146 (1961).

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soldered to the lower end of the sample while the other end of the sample was soldered to the bottom of a heavy copper gas thermometer bulb which served as the thermal sink. Electrical resistivity was measured by passing a small current through the sample and measuring the potential difference between two points on the sample with a Rubicon six-dial thermofree potentiometer.

The vapor pressure of the liquid-He bath was used to determine the temperature at the surface of the bath according to the T^{58} scale[19] and also the temperature at the top of the vacuum can. The pressure P_b at the top of the bath was measured with a Hg manometer for pressure in the range 50–760 mm Hg. For lower pressures an Octoil-S manometer was used. Manometer levels were measured with a cathetometer (least count 10^{-3} cm). To determine the vapor pressure at the vacuum can, a correction for the hydrostatic head of He was applied when the temperature was above the λ point.

B. Samples

1. Preparation. Single-crystal ingots of Ge, singly doped and also doubly doped (compensated), were grown by Miss Roth of this laboratory by pulling seeds from starting melts of high-purity Ge to which the specified doping material had been added. The resulting ingots had their growth axes in the [110] direction. The segregation coefficient (ratio of impurity concentration in the crystal to that in the melt) is less than unity for P, As, Sb, Bi, Ga, and In in Ge, so that the concentration of impurity in the melt changes as the crystal is grown and thus an impurity-concentration gradient occurs along the growth axis. Since each impurity has a different segregation coefficient, the degree of compensation will also vary along the growth axis in the double-doped samples. To minimize these effects on our measurements, we used samples (about 4×4×20 mm) that were cut with their long axes transverse to the growth axis. Most of the samples had their surfaces ground with a mixture of 600 mesh carborundum powder with glycerin or water on a glass plate, followed by an etch with CP4 solution and a rinse with distilled water. Electrical contacts were made by Cerroseal solder with stainless steel flux.

The cross-sectional area of the sample was determined by measuring thickness and width with a dial-type probe gauge (least count 1/10 μm). The distance between thermometers (usually about 15 mm) was measured with a traveling microscope.

Companion plates cut from material adjacent to thermal conductivity samples were treated in a similar fashion and used for measurement of Hall coefficient and electrical resistivity between 77 and 400°K. Electrical resistivity at liquid-He temperatures was measured on the thermal conductivity samples themselves.

TABLE I. Noncompensated samples; $k=AT^m$ $(T<T')$.

Sample	n_{ex} (10^{17} cm^{-3})	k_b(1°K) (mW/cm°K)	k(1°K) (mW/cm°K)	m	T' (°K)
P-1	0.13	126	84	2.4	>4.2
P-2	0.263	161	40	3.0	>4.2
P-3	0.3	135	20	3.1	>4.2
P-4	0.63	139	27	2.5	>4.2
P-5	1.2	127	15	2.8	>4.2
P-6	1.7	134	4.6	3.2	2.8
P-7	2.35	134	2.6	3.4	>4.2
P-8	5.6	140	1.5	3.9	>4.2
P-9	11	134	1.6	3.2	>4.2
Bi-1	0.14	138	90	2.0	2.5

2. Parameters. The samples are characterized by their impurity concentrations, N_d (donor impurities) and N_a (acceptors), and excess electron concentration n_{ex}. These parameters were determined in the manner described in GP, using measurements of electrical resistivity ρ and Hall constant R. The electron concentration in the conduction band is

$$n=-rs/eR, \tag{1}$$

where r is the ratio of Hall mobility to conductivity mobility, s is a factor that depends on the shape of the conduction band, and e is the magnitude of the electronic charge. The Hall mobility is given by

$$\mu_H=R/\rho. \tag{2}$$

At temperatures above the exhaustion temperature, $n=n_{ex}$. Since the exhaustion temperature is below room temperature for the noncompensated samples, n_{ex} can be determined from measurements of R at room temperature. For compensated samples exhaustion does not occur at room temperature, so that R is measured between 77 and 400°K and n_{ex} is calculated from R(400°K).

In the compensated samples, ρ is also measured between 77 and 400°K, so that $\mu_H(T)$ can be calculated in this temperature range. Near the lower end of this temperature range, μ_H appears to be proportional to $T^{3/2}$, which is the behavior expected for scattering by ionized impurities. Therefore, the product rs is taken to have the value 1.51,[20] which is appropriate to ionized impurity scattering, and the Brooks-Herring formula[21] is used to derive the total impurity concentration N_I from the Hall mobility μ_H. The second column in Table I lists values of $n_{ex}=N_d=N_I$ for the noncompensated samples. For the compensated samples, the second column in Tables II and III lists n_{ex}, and the next three columns list N_I, N_d, and N_a, respectively, with the latter two quantities calculated from N_d

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[21] H. Brooks, Advan. Electron. Electron Phys. **7**, 85 (1955).

TABLE II. Compensated samples, P+Ga, As+Ga; $k=AT^m$ $(T<T')$.

Sample	n_{ex} (10^{17} cm^{-3})	N_I (10^{17} cm^{-3})	N_a (10^{17} cm^{-3})	N_d (10^{17} cm^{-3})	$C=N_a/N_d$	k_b (mW/cm°K)	$k(1°K)$ (mW/cm°K)	m	T' (°K)
PGa-1	0.116	0.813	0.465	0.348	0.75	147	40	2.24	>4.2
PGa-2	0.241	1.8	1.02	0.78	0.76	122	14	3.00	>4.2
PGa-3	0.628	525	265	260	0.98	131	6.2	3.40	>4.2
PGa-4	2.89	7.12	5.0	2.12	0.42	133	2.0	3.60	>4.2
PGa-5	4.18	10.7	7.5	3.2	0.43	138	1.0	4.10	>4.2
AsGa-1	0.15	~2	~1	~1	~1	149	22.5	2.50	>4.2
AsGa-2	0.26	240	120	120	1.0	147	34.0	1.80	>4.2
AsGa-3	1.1	46.4	23.7	22.7	0.96	135	6.0	3.00	>4.2
AsGa-4	2.0	75.4	38.7	36.7	0.95	152	4.4	2.90	>4.2
AsGa-5	6.42	121	63	63	1.0	155	1.6	3.28	>4.2

$=\frac{1}{2}(n_{ex}+N_I)$ and $N_a=N_I-N_d$. The next column gives C, the compensation ratio defined by $C=N_a/N_d$.

III. RESULTS AND DISCUSSION

Electrical resistivity measurements for most of the noncompensated P-doped samples at 300, 77, and 4.2°K are presented in Table IV. Measurements could not be extended much below this temperature for the purer samples because of the sensitivity limit of our apparatus, which corresponded to ρ about 10^6 Ω cm for samples of the size we used. Figures 1–3 present the electrical resistivity of the compensated samples, in plots of log ρ versus $1/T$ on a scale that emphasizes the region below 4°K. In Fig. 3, samples reported earlier in GP are included for comparison.

For single-doped material in this temperature range and somewhat above, ρ is often observed to have the form[22]

$$\rho(T)=f(T)e^{-\epsilon/k_BT}, \quad (3)$$

where $f(T)$ is a slowly varying function of T (proportional to T^q, with q of order unity), ϵ is an activation energy, and k_B is Boltzmann's constant. Often, different values of ϵ are observed in different temperature regions, so that plots of log ρ versus $1/T$ exhibit successive linear segments with different slopes. In contrast, the curves in Figs. 1–3 (excluding the horizontal lines corresponding to degenerate material) seem to have no straight-line portions, but instead exhibit continuous curvature, with the slope decreasing with decreasing temperature.

Somewhat similar behavior can be seen in some of the measurements reported by Davis and Compton[23] on compensated Ge with Sb donor (particularly at the upper ends of their ranges of compensation ratio, C) and of donor concentration. This is consistent with our results, since their highest donor concentration is lower than that in all but two of our samples, and most of our heavier-doped samples ($N_d>2\times10^{17}$ cm^{-3}) have C near unity.

The thermal conductivity results are plotted in Figs. 4–8: Figure 4 gives the results for some of the purer P-doped samples and for a Bi-doped sample; Fig. 5 gives results for the remaining P-doped samples; Fig. 6 includes the Ga-compensated P-doped samples; Fig. 7 includes the Ga-compensated As-doped samples; Fig. 8 includes the Sb-doped samples, compensated with Ga or In.

The straight lines on the log-log plots of k versus T show that at least in the lower part of the temperature region covered, the thermal conductivity can be described by equations of the form

$$k(T)=AT^m \quad (T<T'), \quad (4)$$

TABLE III. Compensated samples, Sb+Ga, Sb+In; $K=AT^m$ $(T<T')$.

Sample	n_{ex} (10^{17} cm^{-3})	N_I (10^{17} cm^{-3})	N_d (10^{17} cm^{-3})	N_a (10^{17} cm^{-3})	$C\equiv N_a/N_d$	$k_b(1°K)$ (mW/cm°K)	A $[k(1°K)]$	m	T' (°K)
SbIn-1′	0.31	2.91	1.61	1.30	0.81	150	5.6	4.17	2.5
SbIn-2′	0.535	3.62	2.08	1.54	0.74	153	2.9	4.7	>4.2
SbIn-3′	0.696	6.5	3.6	2.9	0.81	148	6.4	2.8	>4.2
SbIn-4′	2.17	287	145	145	1.0	143	1.1	4.6	3.0
SbGa-4	6.43	40.6	23.5	17.1	0.73	106	1.2	3.94	>4.2
[a]SbGa-183	1.5	27.2	14.0	13.0	0.93	126	1.58	4.1	3.3
[a]SbGa-170	0.54	10.8	5.6	5.2	0.93	138	3.2	4.1	3.2
[a]SbGa-204	0.26	20	10	10	1	137	7.1	3.9	3.3

[a] See Ref. 3.

[22] E. A. Davis, Solid-State Electron. **9**, 605 (1966).
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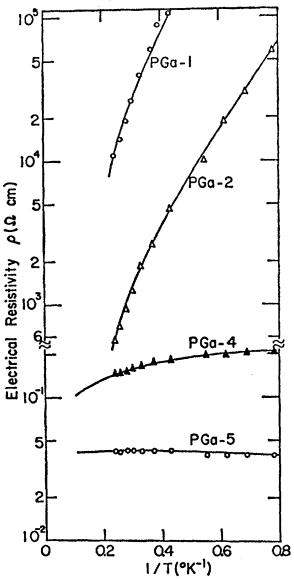

FIG. 1. Electrical resistivity as a function of inverse temperature for P+Ga-compensated samples.

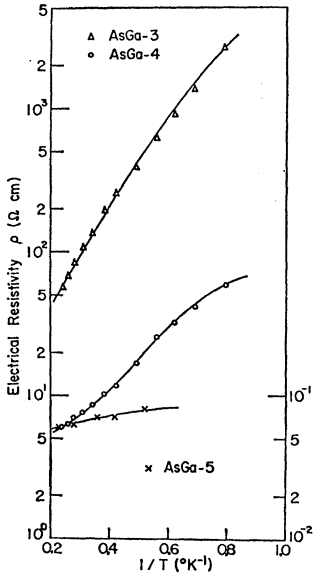

FIG. 2. Electrical resistivity as a function of inverse temperature for As+Ga-compensated samples.

where the coefficient A is numerically equal to $k(1°\text{K})$. In Tables I–III, the values of A and m are listed and also the temperature T', above which appreciable departure from the linear log-log plot is observed.

In Fig. 9, we plot A $[=k(1°\text{K})]$ versus n_{ex} for single-doped and compensated samples, including some Sb-doped material reported in GP. A decreases monotonically as n_{ex} increases, and its magnitude also depends on the impurity species, at least for low enough values of n_{ex} that the material is not degenerate ($n_{ex}<2\times10^{17}$ cm^{-3}). The exponent m, which has the value three for constant mean free path, is between two and three for nondegenerate material and around four and even higher for degenerate samples.

In pure Ge in the neighborhood of 1°K, boundary scattering is the dominant mechanism limiting the phonon mean free path. Therefore, according to the Debye expression for thermal conductivity[24]

$$k=\tfrac{1}{3}C_V v\lambda \qquad (5)$$

(where C_V is the heat capacity per unit volume, which is proportional to T^3,[25] and v is the speed of sound, which is constant), a constant λ of the order of transverse dimensions of the sample gives $m=3$. The column headed $k_b(1°\text{K})$ in Tables I–III gives the value of k calculated from Eq. (5) using Casimir's relation[26] to

TABLE IV. Electrical resistivity of P-doped Ge.

Sample	n_{ex} (10^{16} cm^{-3})	ρ (Ω cm) (300°K)	(77°K)	(4.2°K)
P-2	2.63	6.1×10^{-2}	2.8×10^{-2}	9.9×10^{4}
P-4	6.3	3.03×10^{-2}	2.1×10^{-2}	4.5×10^{3}
P-5	12	5.0×10^{-2}	3.9×10^{-2}	8.0×10^{3}
P-6	17	1.7×10^{-2}	2.0×10^{-2}	0.22
P-7	24	1.7×10^{-2}	2.1×10^{-2}	0.13
P-8	56	7.3×10^{-2}	1.0×10^{-2}	0.013
P-9	110	3.4×10^{-3}	4.9×10^{-3}	0.0037

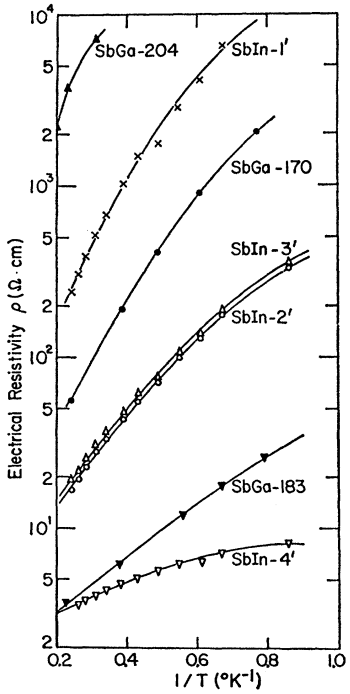

FIG. 3. Electrical resistivity as a function of inverse temperature for Sb+Ga- and Sb+In-compensated samples.

[24] P. Debye, in *Vorträge über die Kinetische Theorie der Materie und der Elektrizität* (B. G. Tuebner, Leipzig, 1914), pp. 17–60.

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

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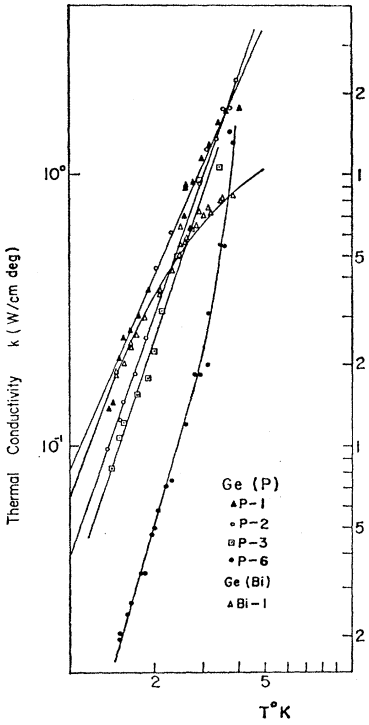

FIG. 4. Thermal conductivity of lightly doped P-doped samples and Bi-doped sample.

find λ from the sample dimensions. This provides an estimate of the conductivity in pure samples with the same dimensions as ours. It appears from Fig. 9 that

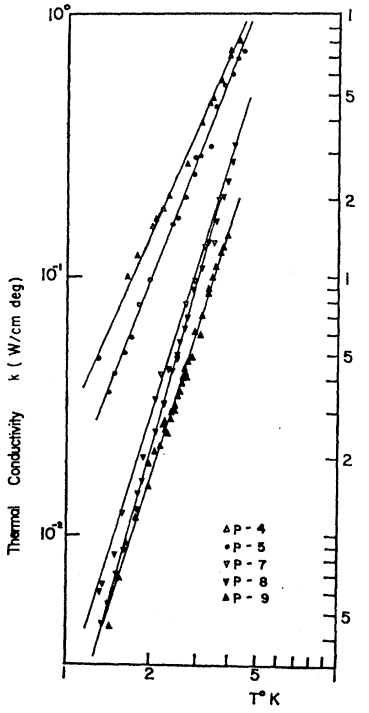

FIG. 5. Thermal conductivity of heavily doped P-doped samples.

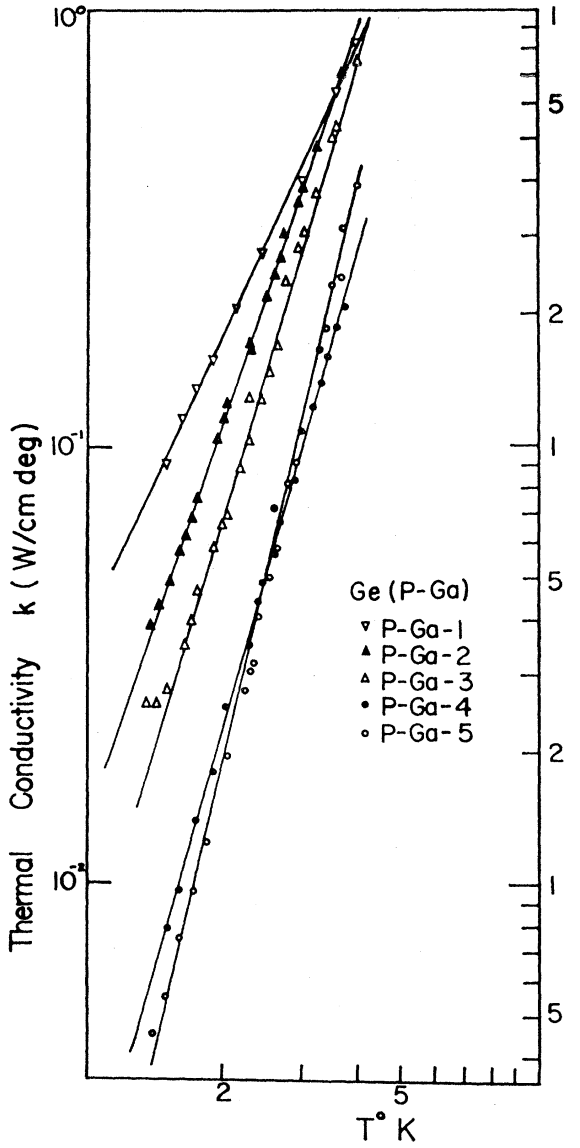

FIG. 6. Thermal conductivity of P+Ga-compensated samples.

phonon scattering, besides that due to the boundaries, has depressed $k(1°\mathrm{K})$ by about 30% in our purest samples, and by as much as two orders of magnitude in the most highly doped samples.

An estimate of the magnitude of the excess scattering can be made, using the procedure adopted in GP, by writing

$$1/k \equiv w = w_b + w_{ep}, \tag{6}$$

with the boundary thermal resistance w_b equal to $1/k_b$. In this expression, w_{ep} is an estimate of the thermal resistance due to phonon scattering by the mechanism associated with the impurities in our samples. Evidence that umklapp scattering and passive-point-defect impurity scattering do not make significant contributions to w was discussed in GP.

TABLE V. Ground-state parameters for shallow donors in Ge($Z=32$) (energies in meV).

Donor	Z	E_0[a] (ionization energy)	$4\Delta_c$[a] (chemical shift)	$\Delta(E_0)-4\Delta_c$ (triplet depression, from effective-mass value, 9.2 meV)	a_0 (Å) (effective Bohr radius)
P	15	12.76	2.83	0.74	35.2
As	33	14.04	4.23	0.63	32.0
Sb	51	10.19	0.32	0.68	44.2
Bi	83	12.68	2.87	0.59	35.5

[a] J. H. Reuszer and P. Fisher, Phys. Rev. 135, A1125 (1964).

The variation of w_{ep} with n_{ex} and its dependence on compensation is shown in Figs. 10 and 11, where $w_{ep}(2°K)$ is plotted against n_{ex}. The w_{ep} is calculated from Eq. (3), with $w_b=\frac{1}{8}k_b(1°K)$; 2°K is chosen for the calculation because it is well below T' for all samples but does not require extrapolation of measured data. In Fig. 10, the upper dashed line represents the data

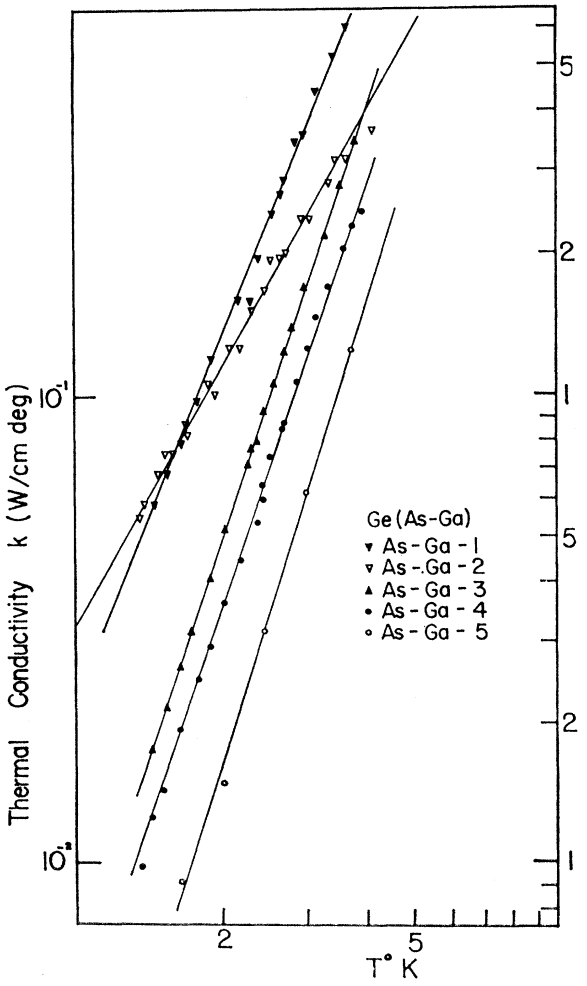

FIG. 7. Thermal conductivity of As+Ga-compensated samples.

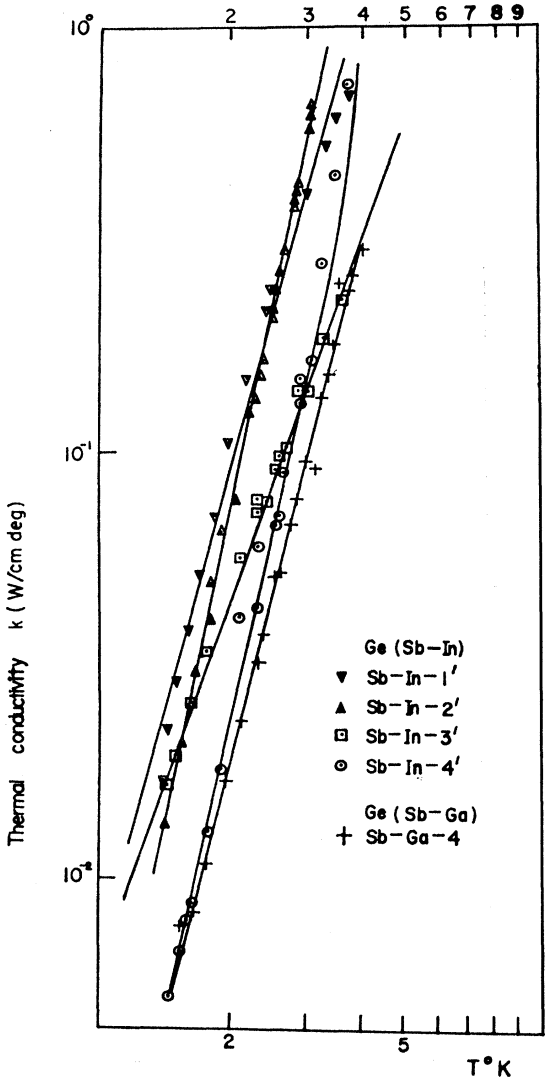

FIG. 8. Thermal conductivity of Sb+In- and Sb+Ga-compensated samples.

reported earlier in GP for single-doped SB(Ge), and the lower dashed line, the data for single-doped As(Ge), also reported in GP. The lower solid line is drawn through the points for the single-doped P(Ge), while the upper solid line fits the Ga-compensated, n-type P(Ge) and As(Ge). For greater clarity, the data for the compensated Sb(Ge) samples, using both Ga and In for compensation are not shown in Fig. 10. These points are plotted in Fig. 11, where they are superimposed on lines drawn through the data points for all the other materials.

As was discussed in GP, thermal resistance w_d due to point-defect scattering can be written[6]

$$w_dT=KS_a^2, \tag{7}$$

where K is a constant and S_a^2 is a dimensionless scattering parameter related to the scattering cross section.

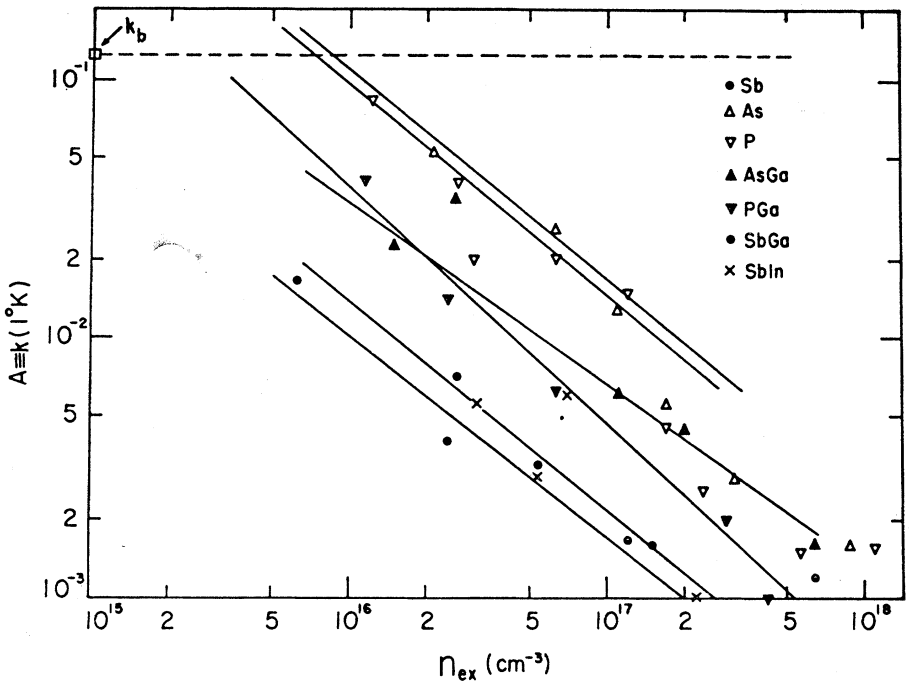

FIG. 9. Thermal conductivity in W/cm deg at 1°K as a function of neutral-donor concentration n_{ex}.

The contribution to S_a primarily responsible for w_{ep} in nondegenerate Ge, according to the analyses of Keyes and of Griffin and Carruthers, is that arising from virtual excitations between the singlet-impurity ground state and the next higher triplet levels, separated by the amount $4\Delta_c$. The values of $4\Delta_c$ for shallow impurities in Ge are listed in Table V, along with other relevant parameters of the ground state. Since this contribution to S_a is proportional to $\Xi_\mu^2/4\Delta_c$, where Ξ_μ is the shear deformation potential,[20] the values of w_{ep} are expected to be larger for Sb impurities than for As impurities, as is observed to be the case for the data plotted in Fig. 10 for single-doped material. Since $4\Delta_c$ for P is much closer to that for As than to its value for Sb, it is to be expected that w_{ep}(P) will be closer to w_{ep}(As) than to w_{ep}(Sb). If Eq. (6) were a precise relation, the values of w_{ep} could be related to those of $4\Delta_c$ for the three-donor impurities. However, Eq. (6) is an oversimplification of the accurate calculation based on solution of the Boltzmann transport equation. As shown by Callaway[27] such a solution can be expressed in terms of an integration

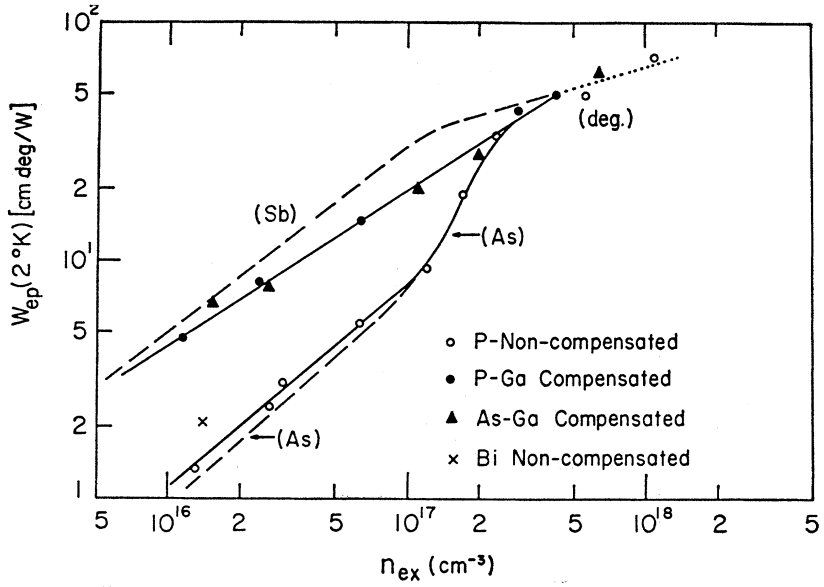

FIG. 10. Excess thermal resistivity w_{ep}(2°K) as a function of neutral-donor concentration n_{ex} for P- and Bi-doped Ge and P+Ga- and As+Ga-compensated samples.

[27] J. Callaway, Phys. Rev. 113, 1046 (1959).

over the phonon spectrum in which the integrand is proportional to a combined relaxation time which is a function of phonon wave number q. The approximation in Eq. (6) amounts essentially to the assumption that all contributions to the combined relaxation time depend on phonon wave number in the same way. Since w_b is independent of phonon wave number, while w_{ep} [see w_d in Eq. (7)] is proportional to q^4, this assumption is not even approximately satisfied in the present case. However, since for the less pure samples w_{ep} is the dominant contribution to the total thermal resistance w, Eq. (6) serves as a useful qualitative approximation.

Figure 10 also includes one point corresponding to a measurement on one sample doped with a relatively low concentration of Bi. Unfortunately, samples with higher concentrations of Bi were inhomogeneous, the Bi tending to segregate rather than form a solid solution. For this sample $w_{ep}(2°K)$ is only about twice as large as $w_b(2°K)$, so that Eq. (4) does not represent an especially good approximation. In view of this, the agreement between $w_{ep}(2°K)$ for Bi and P donors, which have about the same value of $4\Delta_c$, is reasonably good.

Since the relaxation rate responsible for w_d is proportional to q^4, this thermal-resistance contribution is proportional to T, as shown in Eq. (7). On the other hand, w_b, independent of q, should give a contribution proportional to T^{-3}. The values of m in Table I show, however, that k is proportional to a power of T between 2 and 3 for the nondegenerate samples single doped with P or Bi. This was also the behavior observed by GP with As-doped Ge, while Sb-doped Ge gave values of m in the neighborhood of 4.

The analyses of Keyes and of Griffin and Carruthers account for this behavior by pointing out that the relaxation rate for the virtual scattering by electrons in the donor ground state (neutral-donor scattering) contains additional q dependence, in addition to the q^4 dependence mentioned above for ordinary point-defect (Rayleigh) scattering. This extra q dependence comes about from the fact that the effect has a resonance character and therefore depends on the relation of the phonon wavelength λ, $\lambda=2\pi/q$, to the extent of the donor wave function, which is of the order of the effective Bohr radius a_0, tabulated in the last column of Table V. The exact nature of the way in which the relaxation time τ depends on λ/a_0 (or qa_0) is different in Keyes' treatment of the problem from that given by Griffin and Carruthers but the essential result in either case is a very rapid cutoff in τ^{-1} for λ of the order of a_0 and larger. The over-all effect of combining this form for τ^{-1} with that appropriate to boundary scattering is a T variation for k like that observed in Figs. 4–8 and tabulated in Table I.

The three most heavily doped P(Ge) samples, P-7, P-8, and P-9, were degenerate in the liquid-He temperature range, as can be seen from the electrical resistivity data in Table IV.[28] Thus, for these samples the concentration of neutral donors is essentially zero and their w_{ep} cannot be due to the scattering mechanism discussed above for the more pure samples. Indeed, the points for the two most impure samples lie along the same line as was observed by GP for Sb(Ge) samples with similarly high concentrations. Hence the species effect in w_{ep} for nondegenerate material is not present in degenerate samples. The scattering mechanism is one that involves free electrons in the conduction band of the type that has been discussed by Ziman.[9] This scattering is characterized by a generally steeper T dependence than is found for the neutral-donor scattering in As(Ge), as observed by GP. This same feature is observed in P(Ge), as can be seen from Table IV, with one of the degenerate samples exhibiting a value of m near 4.

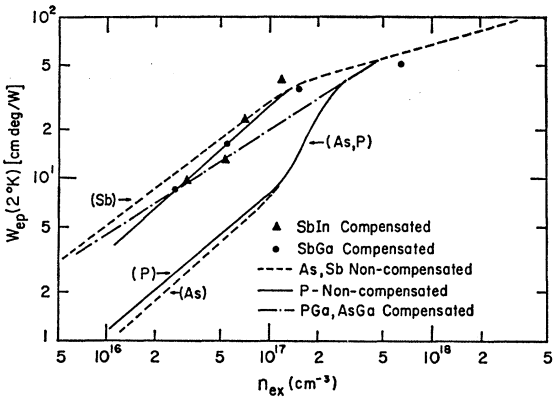

FIG. 11. Excess thermal resistivity $w_{ep}(2°K)$ as a function of neutral-donor concentration n_{ex} for Sb+Ga- and Sb+In-compensated samples and comparison with As-, Sb-, and, P-doped and P+Ga- and As+Ga-compensated samples.

It can be seen from Fig. 10 that neither neutral-donor scattering nor conduction-band scattering leads to $w_{ep}(2°K)$ proportional to n_{ex}, though in each case the relevant interaction rate $(\tau)^{-1}$ will be proportional to n_{ex}. In the case of neutral-donor scattering, the discussion above on the "mixing" of neutral-donor scattering and boundary scattering (which is independent of n_{ex}) leads to a variation of w_{ep} which is slower than simple proportionality with n_{ex}. In the degenerate material, on the other hand, w_{ep} is an order of magnitude larger than w_b, so that this argument should not hold. Here, however, another factor enters besides the proportionality of $(\tau)^{-1}$ to n_{ex}. Since the electrons in the conduction band are degenerate, only those within k_BT of the Fermi level ζ can contribute to the scattering (in fact, not all of these are capable of scattering if momentum and energy are conserved,

[28] The intermediate sample P-6, whose value for w_{ep} fell in the transition region (see Fig. 10), exhibited an anomalous behavior in k as shown in Fig. 4. Hence, although its electrical resistivity data in Table IV indicate that it may have been degenerate, we do not include it in the present discussion.

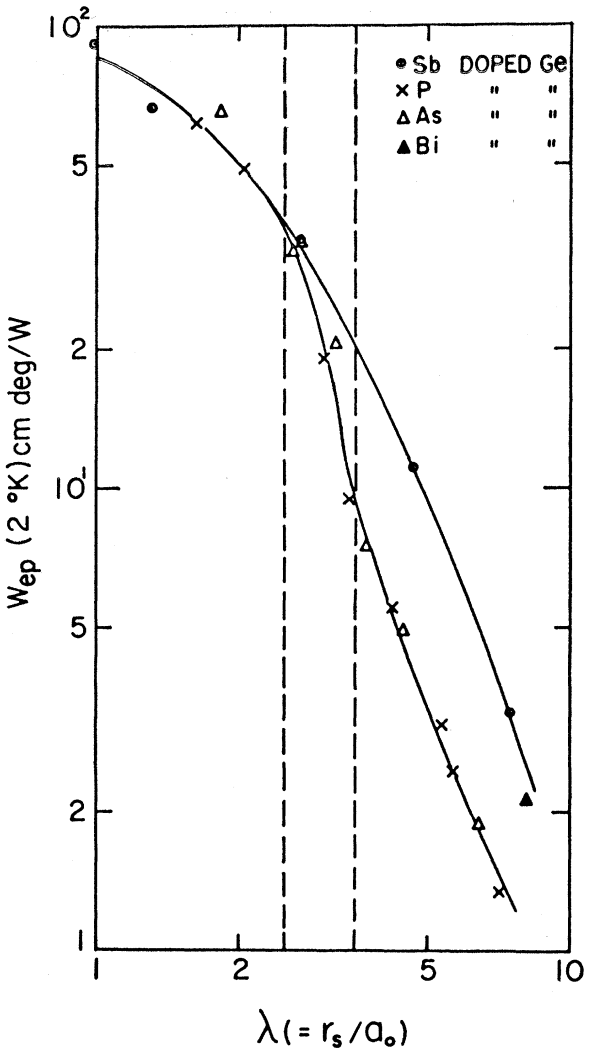

FIG. 12. Excess thermal resistivity $w_{ep}(2°K)$ as a function of λ, the ratio of impurity distance r_s to effective Bohr radius a_0.

as pointed out by Ziman[9], but this extra restriction is irrelevant in the present context). Hence, w_{ep} should be proportional to $n_{ex}(k_BT/\zeta)$ and since ζ is proportional to $n_{ex}^{2/3}$, this leads to an expected variation of the form w_{ep} proportional to $n_{ex}^{1/3}$. In fact, the dotted line at high values of n_{ex} in Fig. 10, which is labeled (Sb) but which also fits the w_{ep} values for As(Ge) and P(Ge) at these high concentrations, has a slope which gives w_{ep} proportional to $n_{ex}^{0.3}$.

The transition region in Fig. 10, observed for As(Ge) and P(Ge) samples [but not for Sb(Ge)] around 2 to 5×10^{17} cm^{-3} values for N_d is reminiscent of similar behavior in the variation of electrical resistivity of n-type Ge with N_d in the liquid-He temperature range.[29] The physical process involved in the latter case is quite different, however, since electrical conduction involves ionization of electrons bound to donor states, while, as we have seen above in the phonon scattering that we have been considering in nondegenerate material, the donor atoms remain neutral. Nevertheless, it will be useful for our discussion of compensated material below to introduce the parameter r_s as an average separation of donor atoms, defined by $r_s^3 = 3/(4\pi)N_d^0$. The dimensionless parameter λ, defined by $\lambda = r_s/a_0$, can then be used to characterize the sample impurity concentration. As has been discussed, e.g., by Mott,[8] values of λ greater than 5 correspond to samples in which electrical conduction in the liquid-He temperature range involves "hopping" of electrons among donor levels. A small degree of compensation by acceptors is necessary so that empty donor levels will be available, and the resistivity as a function of temperature shows exponential activation-energy-type behavior, with a factor of the form $e^{-\epsilon/k_BT}$, where ϵ is related to the ionization energy of donor levels. Degenerate material corresponds to λ of the order of 2 or less. Values of λ between 2 and 5 correspond to a transition region often referred to as the "impurity-band regime."

Despite the fact, mentioned above, that the physical processes are very different in the two cases, the thermal conductivity also exhibits features that correspond to the three sets of values for λ. In Fig. 12 values of $w_{ep}(2°K)$ are plotted as functions of λ for single-doped n-type Ge, using our values for P(Ge) and the one sample of Bi(Ge), and the values from GP for the As(Ge) and Sb(Ge) samples. It can be seen that the points for As(Ge) and P(Ge) show a distinct transition, for values of λ between about 2.5 and 3.5, between the low-λ (degenerate) region and the high-λ (isolated donor) regions. In the case of Sb(Ge), on the other hand, the transition is smooth and no special transition region can be distinguished. We shall refer to these results later on when we discuss the effects of compensation on the effective Bohr radius a_0.

The results we observed on compensating P(Ge) with Ga acceptors were similar to those seen with As(Ge) compensated with Ga but, in either case, the behavior was rather different than that reported by GP for Sb(Ge) compensated with Ga. The upper line in Fig. 10 corresponds to the latter results, and to the accuracy of the measurements reported in GP, it was impossible to distinguish between Sb(Ge) and Sb +Ga(Ge) for a given value of n_{ex}, although the compensated samples had much higher values of N_I. The closed symbols in Fig. 10 give the results for P+Ga(Ge) and As+Ga(Ge) and it is clear that these are very different, for a given value of n_{ex}, than the corresponding values of w_{ep} for the single-doped uncompensated material. However, once again, the samples with the three highest values of n_{ex} had values of w_{ep} that were consistent with the low-slope degenerate line, so that phonon scattering for λ less than about 2 exhibits neither compensation nor impurity-species dependence.

[29] H. Fritzsche, J. Phys. Chem. Solids 6, 69 (1958).

TABLE VI. Resistivity values and ratios.

n_{ex} (10^{16} cm^{-3})	ρ_c (compensated) (Ω cm) 4.0 K	1.5 K	$\rho(1.5°K)/\rho(4.0°K)$	ρ_s (single-doped) (Ω cm) 4.0°K	1.5°K	$\rho(1.5°K)/\rho(4.0°K)$	$(\rho_c/\rho_s)_{4°K}$
			As-doped samples				
20	6.3	38	6	. . .	. . .	. . .	9×10^{-2}
(18.6)[a]	. . .	. . .	. . .	7×10	7×10^{5}	10^{4}	
(13.3)[a]	. . .	. . .	. . .	1×10^{5}	1×10^{9}	10^{4}	
11.0	64	1.28×10^{3}	20	. . .	. . .	. . .	6.4×10^{-4}
(11.0)[b]	. . .	. . .	. . .	5×10^{5}	$>10^{9}$[e]	$>2\times10^{3}$	1.3×10^{-5}
(9.32)[a]	. . .	. . .	. . .	10^{4}	5×10^{7}	5×10^{3}	6.4×10^{-3}
2.6	2.2×10^{5}	. . .	. . .	. . .	. . .	. . .	2.2×10^{-2}
(2.1)[b]	. . .	. . .	. . .	10^{7}	. . .	. . .	
			P-doped samples				
56.0	. . .	. . .	. . .	1.25×10^{-2}	. . .	. . .	~3
41.8	4.2×10^{-2}	4×10^{-2}	1	. . .	. . .	. . .	
28.9	1.5×10^{-1}	2.01×10^{-1}	1.3	. . .	. . .	. . .	~1.9
(28.9)[a]	. . .	. . .	. . .	8×10^{-2}	8×10^{-2}	1	
28.9	1.5×10^{-1}	2.01×10^{-1}	1.3	. . .	. . .	. . .	~1.1
23.5	. . .	. . .	. . .	1.26×10^{-1}	. . .	. . .	
6.3	. . .	. . .	. . .	4.5×10^{3}	. . .	. . .	~10^{-4}
6.28	3.16×10^{-1}	. . .	. . .	. . .	. . .	. . .	
2.41	7×10^{2}	2.6×10^{4}	37	. . .	. . .	. . .	7×10^{-3}
2.63	. . .	. . .	. . .	9.9×10^{4}	. . .	. . .	
			Sb-doped samples				
21.7[c]	3.5	7.2	2	. . .	. . .	. . .	50
(21.07)[a]	. . .	. . .	. . .	7×10^{-2}	7×10^{-2}	1	
(8.76)[a]	. . .	. . .	. . .	1.2	7	5.8	17
6.96[c]	20	180	9	. . .	. . .	. . .	
(15.3)[a]	. . .	. . .	. . .	10^{-1}	10^{-1}	1	40
(15)[b,d]	4	17	4.2	. . .	. . .	. . .	
(2.6)[b,d]	6×10^{3}	1.5×10^{6}[e]	2.5×10^{2}	. . .	. . .	. . .	0.15
(2.4)[b]	. . .	. . .	. . .	4×10^{4}	1.5×10^{7}[e]	3.7×10^{2}	

[a] Fritzsche's data (18a,b). [b] Goff and Pearlman's data (Ref. 5). [c] SbIn → *i*. [d] SbGa → *g*. [e] Extrapolated data.

In order to examine whether the difference in behavior between Sb(Ge), As(Ge), and P(Ge) on compensation was itself dependent on the acceptor species used, samples with a range of concentration of Sb +In(Ge) as well as Sb+Ga(Ge) were measured, with the results plotted in Fig. 11. It appears that the two different acceptors give essentially similar results. Although it now appears to be possible, because of the greater range of concentrations covered, to distinguish between Sb(Ge) and compensated material, the effect on w_{ep} of compensation is very much smaller in this material than in either As(Ge) or P(Ge) and, furthermore, is in the opposite direction. Whereas compensation increases w_{ep} for As(Ge) and P(Ge), it decreases w_{ep} for Sb(Ge).

The correspondence between the behavior of $w_{ep}(\lambda)$ and $\rho(\lambda)$, described above for the single-doped material with As and P as donor, and the lack of correspondence for Sb(Ge), suggested that it might be profitable to examine the behavior of ρ in the compensated material as well, to see if the difference in behavior of w_{ep} on compensation were also reflected in electrical conductivity. The manner in which we made this comparison is indicated in Table VI. The first column in each of the parts of this table lists the value of n_{ex} for the samples considered. In order to have a reasonable range of values, we have included some samples measured by GP and also some samples reported by Fritzsche.[30] Both compensated samples (indicated by subscript *c*) and single-doped samples (denoted by subscript *s*) are included, and the nature of the compensating acceptor (Ga or In) used with Sn(Ge) is also indicated. The body of the table lists resistivity values at 4 and 1.5°K, as well as the ratios of these values. Such resistivity values and their ratios are given separately for compensated and single-doped material in separate sections of the table for As, P, and Sb as donors, and in the last column, the ratio of resistivity at 4°K of compensated to noncompensated samples with comparable values of n_{ex} is listed.

The results are most clear cut for As(Ge), and also rather surprising. Although compensation increases

[30] H. Fritzsche, Phys. Rev. **125**, 1552 (1962); **125**, 1560 (1962).

TABLE VII. Effect of compensation on λ.

Samples	n_{ex} (10^{16} cm^{-3})	w_{ep}(2°K) (cm °K/W)	λ_c	λ	$\lambda/\lambda_c = (a_0)_c/a_0$
		PGa samples			
PGa-1	1.16	4.71	4.4	7.4	1.682
PGa-2	2.41	8.07	3.7	5.8	1.567
PGa-3	6.28	14.05	3.25	4.2	1.292
PGa-4	28.9	42.54	2.55	2.5	0.980
PGa-5	41.8	49.1	2.05	2.2	1.073
		AsGa samples			
AsGa-1	1.5	6.86	3.86	7.12	1.84
AsGa-2	2.6	7.85	3.75	5.92	1.579
AsGa-3	1.1	19.90	3.03	3.7	1.221
AsGa-4	2.0	27.75	2.75	3.0	1.091
AsGa-5	64.2	61.69	1.65	2.02	1.224
		SbGa samples			
SbGa-170	5.4	16.3	3.9	3.57	0.915
SbGa-183	1.5	35.4	2.58	2.55	0.988
SbGa-204	2.6	9.35	5.00	4.50	0.900
SbGa-4	64.2	50.92	1.95	1.65	0.856
		SbIn samples			
SnIn-1′	3.1	9.694	4.90	4.29	0.876
SbIn-2′	5.35	13.07	4.30	3.50	0.814
SnIn-3′	6.96	22.97	3.30	3.28	0.994
SbIn-4′	21.7	40.80	2.35	2.22	0.945

N_I for a given value of n_{ex} and hence increases impurity scattering, the resistivity in compensated As(Ge) is less than that in single-doped material by a factor that is at least 1 order of magnitude, and in the transition region it is about 5 orders of magnitude. Hence, we are observing a change in ρ that is not due to the increase in N_I but depends rather on another process that influences the resistivity much more strongly.

The results for P(Ge) are less clear cut in that compensation increases ρ at high values of n_{ex}, while it decreases ρ for the purer samples, and in the latter case, to an extent comparable to that observed with As(Ge). On the other hand, the Sb(Ge) samples exhibit a much larger increase for all but the most pure sample, and the decrease in ρ on compensation for small n_{ex} is much less striking than is the case for As(Ge) or P(Ge).

The results for the various impurities are not strictly comparable because they have different values of $4\Delta_c$ and hence different values of a_0 (see Table V). In order to remove this effect in discussing the change in w_{ep} on compensation, a value of the ratio $r_s/(a_0)_c$ for compensated samples was read from Fig. 12, and denoted λ_c, as listed in Table VII, for all three-donor species. The last column lists the ratio λ/λ_c, which we take to be equal to $(a_0)_c/a_0$, since r_s is constant for a given n_{ex}, regardless of compensation. We see from Table VII that for Sb(Ge) a_0 is either unchanged on compensation or decreases slightly, while for As(Ge) and P(Ge) it has increased by an amount that averages about 50%. This interpretation of the cause of the observed change in w_{ep} is consistent with the observations on the ratio $(\rho_c/\rho_s)_{4°K}$ discussed above, since electrical resistivity is a sensitive function of the ratio λ. It remains, thus, to discuss the origin of the change in a_0.

Calculations of the ground state of impurity atoms in n Ge have been forced to employ rather drastic simplifying assumptions as to the nature of the wave functions[4] in order to make the problem at all tractable. In most cases a spherically symmetric function is assumed, whereas, in fact, the value a_0 must represent some sort of average over a function which is direction-dependent. This will not make much difference in calculating the energy levels but, as has been pointed out by Keyes,[1] the matrix element for neutral-donor scattering is rather sensitive to the direction dependence of the wave function.

The successful calculation of the deviation of the ground-state energy from the effective-mass value[4] (see Table V) depends on introducing, in addition to the Coulomb potential, a correction potential $U(r)$ that is large only in the vicinity of the lattice cell containing the impurity atom. This correction potential depends mainly on the impurity atom, but since it must match the potential outside the cell at the boundary, it must also depend on the surroundings of the cell containing the impurity atom. Now the neighborhood of any lattice site is changed drastically by the introduction of acceptors which compensate to the high degree that occurs in our samples. In the uncompensated material the potential at the boundary of the impurity cell is, on the average, that of the host Ge lattice. On the other hand, in the compensated lattice, the potential will be, with nonvanishing probability, that of a negative acceptor ion. It is therefore surprising that this difference produces such a small change in w_{ep} (and a_0) in Sb(Ge), and the behavior observed in As(Ge) and P(Ge) is the more expected.

In the absence of explicit calculations of the wave function of the impurity-atom ground state which include a realistic approximation for $U(r)$, it is of course impossible to make any quantitative statements concerning Δa_0 to be expected on compensation. Since the position of the triplet state, that is split from the originally fourfold degenerate ground state, is given fairly accurately by effective-mass theory, the decrease of $4\Delta_c$, which corresponds to the increase in w_{ep}, appears to correspond mostly to a decrease in ionization energy on compensation. This would be a surprising result in view of the introduction of negatively charged acceptor ions in the vicinity of the donor cell. However, the assumption made above that the major change on compensation affects the singlet rather than the triplet need not be correct. The singlet amplitude is much larger within the cell containing the donor than is the triplet, since the latter vanishes at the center of the cell. Since the effective size of the region in which the interaction is important increases on compensation with a_0, it is possible that the triplet wave function, with its amplitude concentrated away from the center of the cell is modified more strongly than the singlet.

The consequent lowering of the triplet energy due to the presence of negative acceptor ions would have the effect mentioned above of decreasing $4\Delta_e$ as required by the observed increase in w_{ep}.

In the limit of large n_{ex} this effect must go over smoothly to the conduction-band scattering observed in degenerate material, so that it would be expected that the over-all effect of negative acceptor ions on the triplet states of the donors must decrease as N_a^- increases. This would occur as increasing acceptor concentration smooths the potential variation observed at any lattice site. Indeed, the results shown in Figs. 10 and 11 do display an effect of this sort. It can be seen that the line $w_{ep}(n_{ex})$ for the compensated As(Ge) and P(Ge) samples is not parallel to the corresponding lines, either for uncompensated Sb(Ge) or uncompensated As(Ge) or P(Ge). The magnitude of Δw_{ep} on compensation is larger at low n_{ex} (values of λ larger than 5) than at higher concentrations. Because w_{ep} itself increases with n_{ex}, the change in the relative magnitude $\Delta w_{ep}/w_{ep}$ is even more striking.

Another consequence of this increase of $\Delta w_{ep}/w_{ep}$ as n_{ex} decreases, is that in the isolated donor-state regime (λ greater than 5) all compensated samples display the same magnitude of w_{ep}. Whether this is an accidental effect, or whether it corresponds in some fundamental way to the as yet poorly understood insensitivity of w_{ep} in Sb(Ge) to compensation is still unclear.

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Pair Spectra Involving Si Donors in GaP

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We discuss the preparation of Si-C- and Si-Zn-doped GaP crystals and present an interpretation of their emission spectra in the light of a recent theory of donor states in GaP. We find that the no-phonon peak is weak or absent in Si-Zn and Si-C pair spectra, and that the multiple peaks observed arise from transitions induced predominantly by phonons from the point X of the Brillouin zone. This interpretation differs from that of a recent paper by Dean *et al.* The energy of the weak no-phonon transition agrees with that calculated from the binding energies and a reasonable Coulomb pair energy, and the phonon energies equal the known values for the TA, LA, and TO phonons at X. We show that the displacement in energy between a pair peak and one of its phonon replicas may under certain conditions differ from the energy of the phonon emitted.

I. INTRODUCTION

THE Group-IV element silicon acts as an amphoteric impurity in GaP. It tends to enter the lattice on Ga sites as a shallow donor,[1] but in n-type material can also occupy a P site as an acceptor.[2] Efficient luminescence from Si-Si (shallow donor-deep acceptor) pairs has been reported by Lorenz and Pilkuhn,[3] and recently Dean *et al.*[4] have identified pair lines and distant pair bands from Si-Zn and Si-C pairs,[5] although the phonon structure of the bands was not understood. The symmetry properties of donor states on Ga sites in GaP have been discussed by Morgan[6] and shown to have a marked influence on the selection rules for radiative transitions, including those of interest in this paper. We report here photoluminescent studies of GaP ingots which were either undoped or doped with combinations of the impurities S, Si, C, and Zn. We show that the energies and phonon structure of the pair bands are explained in detail by the theory developed in Ref. 6. These results are summarized in Table I.

II. EXPERIMENTAL

The GaP was prepared by reacting PH_3 with molten Ga at about 1150°C in a vertical open-tube system. A 30-g charge of Ga was placed in a pyrolytic BN crucible (1.5 cm in diameter and about 8 cm deep) which fitted closely in a quartz tube. A stream of 10% PH_3 in Ar gas was injected with a high velocity onto the surface of the molten Ga.[7] The details of the process are described elsewhere.[8] By maintaining the proper temperature profile along the axis of the crucible, the reactor caused a solid polycrystalline ingot to grow at the bottom at a rate of about 1.8 cm/day.

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[2] M. Rubinstein, J. Electrochem. Soc. **112**, 1010 (1965); F. A. Trumbore, H. G. White, M. Kowalchik, C. L. Luke, and D. L. Nash, *ibid.* **14**, Abstract No. 2 (1965).
[3] M. R. Lorenz and M. H. Pilkuhn, J. Appl. Phys. **38**, 61 (1967).
[4] P. J. Dean, C. J. Frosch, and C. H. Henry, J. Appl. Phys. **39**, 5631 (1968); (private communication).
[5] To avoid confusion in labeling pair species, we list the elements in the order established by the generic name, donor-acceptor.
[6] T. N. Morgan, Phys. Rev. Letters **21**, 819 (1968).
[7] The PH_3-Ar gas mixture was supplied by Precision Gas, Linden, N. J.
[8] T. S. Plaskett, presented at the Electrochemical Society Meeting, Montreal, 1968 (unpublished).