

Thermal Transport Properties of *n*-Type Ge at Low Temperatures*

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The thermal resistivity w contributed to Ge at low temperatures by electrically active impurities has been investigated by measurements on a series of single crystals (*n*-type) between 1.3 and 150°K. By comparing compensated [(Sb+Ga)-doped] with noncompensated (Sb- or As-doped) samples, it is found that at temperatures below its minimum, w may be correlated with the concentration of neutral donors n_{ex} (excess of donor over acceptor concentration). The form of the relation indicates that there must be at least two types of electron-phonon interaction: one for electrons in semi-isolated impurity states ($n_{ex} < 6 \times 10^{17} \text{ cm}^{-3}$) and another for electrons in the well-defined band formed at higher concentrations. In the low concentration range there is an impurity-species effect; the thermal conductivity k in As-doped material is proportional to T^3 and is larger than in Sb-doped material with the same concentration, where it is proportional to T^4 . These results seem qualitatively compatible with the models proposed by Keyes and by Griffin and Carruthers and confirm their main point: This phonon-electron interaction involves occupied semi-isolated states rather than transitions. An attempt to analyze the high concentration range by including in the Callaway model the phonon-electron relaxation time introduced by Ziman suggests that the theory is incomplete. The conservation of crystal momentum in these interactions may require correction terms that have not been considered. The thermoelectric power Q , the electrical resistivity ρ , and the Hall constant (the last for the compensated samples, from 77 to 400°K) were also measured. These data indicate that in *n*-type Ge with total impurity concentration greater than about 10^{18} cm^{-3} , the effect of 80% or more compensation is to re-instate the impurity levels in the energy gap. In addition it is found that Q shows an impurity-species effect at temperatures at which the donor states are neutral, but not at higher temperatures. In the high-concentration material both Q and ρ can be analyzed by semimetal theory.

I. INTRODUCTION

SOME time ago, Fagen, *et al.*¹ reported that the addition of as little as 10^{-4} at. % of Sb to single crystals of Ge resulted in a decrease of the thermal conductivity k by about two orders of magnitude at temperatures below 4°K. The lattice is responsible for heat transport in this material and in pure crystals in this temperature range phonons are scattered predominantly by the sample boundaries.² The phonon mean free path in the impure samples is thus much smaller than sample dimensions, but according to the theory of phonon-impurity scattering³ the thermal resistance contributed by the Sb ions should be negligible at these temperatures. It was conjectured that the valence electrons of the Sb atoms were responsible for the increase in thermal resistance below the maximum in the thermal conductivity, which was observed in these samples between about 15 and 30°K. We therefore denote the increase in thermal resistance observed below the conductivity maximum on the addition of impurities by w_{ep} .⁴ Carruthers *et al.*² came to an analogous conclusion with regard to acceptor atoms from measurements on Ge with *p*-type impurities.

Subsequent work by Goff and Pearlman^{5,6} with compensated (Sb- and Ga-doped, *n*-type) Ge single crystals in the same temperature range has apparently confirmed this hypothesis, at least with regard to donor centers. They showed that the effect of compensation, even with increased total impurity concentration, was to reduce w_{ep} , and that this decrease could be correlated with the decrease in the concentration of electrons bound to donor atoms, n_{ex} . However, it was also found by comparison with the effect on electrical resistivity that w_{ep} was independent of electron transition probabilities between donor impurity states. Also measurements at higher temperatures showed that an increase in thermal conductivity above the temperature of its maximum was also associated with compensation. Further experiments have been carried out on a series of Sb- and As-doped Ge single crystals from 1 to about 150°K in an attempt to clarify the nature of this phonon-electron interaction. It is the purpose of this report to describe the entire series of measurements and the conclusions that can be drawn from them.⁶

Since this interaction can be expected to influence other transport properties besides the thermal conductivity, our apparatus was designed to permit measurement of the electrical resistivity ρ and thermoelectric power Q , as well as k . Also, the Hall coefficient of some of the samples was measured in a separate apparatus so that an analysis of Q could be made in terms of electron concentration.

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¹ E. Fagen, J. F. Goff, and N. Pearlman, *Phys. Rev.* **94**, 1415 (1954).

² J. A. Carruthers, T. H. Geballe, H. M. Rosenberg, and J. M. Ziman, *Proc. Roy. Soc. (London)* **238A**, 502 (1957).

³ P. G. Klemens, in *Advances in Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Vol. 7, pp. 1-99; in *Encyclopedia of Physics*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. 14, pp. 198-281.

⁴ N. Pearlman and J. F. Goff, *Bull. Am. Phys. Soc.* **4**, 410 (1959).

⁵ J. F. Goff and N. Pearlman, in *Proceedings of the 7th International Conference on Low Temperature Physics*, edited by G. M. Graham and A. C. Hollis Hallett (University of Toronto Press, Toronto, 1961), pp. 284-288.

⁶ J. F. Goff, thesis, Purdue University, 1962 (unpublished).

TABLE I. Sample parameters.

Sample	$-R^a$ (cm ³ /C)	ρ^a (Ω cm)	rS	n_{ex} (10 ¹⁷ cm ⁻³)	Sample X-sec. (mm×mm)
Sb 30	2.30	3.14	b	25	3.2×1.5
222		4.951	c	11	4.1×4.1
187		24.4	c	1.2	3.9×4.1
207		94.6	c	0.24	3.9×3.9
172		398.8	b	0.061	3.8×3.7
As 226	5.43	6.584	c	8.8	4.0×3.9
232	18.8	14.71	c	3.1	3.8×4.0
233II	34.1	19.77	c	1.7	3.9×4.1
233I	53.2	31.29	c	1.1	4.1×4.0
223II	92.4	41.78	c	0.63	3.9×4.0
223I		98.47	b	0.21	4.1×4.1
SbGa 183	37.9	61.87	c	1.5	3.7×3.6
170	105	130.4	c	0.54	4.2×3.7
204	219	427.9	c	0.26	3.9×3.9

^a Measured at room temperature for As- and Sb-doped samples; at 400°K for SbGa samples.
^b $rS=1.0$. ^c $rS=0.925$.

A significant conclusion that can be drawn from these additional measurements is confirmation of an effect on the impurity levels due to compensation which was suggested earlier by Fritzsche⁷ for *p*-type Ge. In material with sufficiently high donor concentration the donor states merge with the conduction band and at sufficiently low temperatures the conduction electrons form a degenerate assemblage. Compensation by acceptors will remove electrons from these donor states to the acceptor states at lower energy, but it also appears that with a sufficiently high degree of compensation the donor levels are removed from the conduction band to a position in the energy gap. This conclusion is reinforced by the fact that it plays an essential role in the models which have been proposed^{8,9} to account for w_{ep} .

II. APPARATUS AND SAMPLES

Thermal conductivity was measured by the steady-heat-current method,¹⁰ heat being supplied by a dc heater 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. To minimize strains in the sample due to differential contraction during cooling the Cu-Ge junctions were separated by thin W plates hard soldered to the Cu and tinned with hard solder to facilitate soldering the Ge. The apparatus and procedures were similar to those described by Goff¹¹ except that the temperature difference along the sample, ΔT , was obtained by subtraction using two carbon-composition resistors as thermometers, rather than from a thermocouple.

⁷ H. Fritzsche, Phys. Rev. **113**, 999 (1959).

⁸ R. W. Keyes, Phys. Rev. **122**, 1171 (1961).

⁹ A. Griffin and P. Carruthers, Phys. Rev. **131**, 1976 (1963).

¹⁰ N. Pearlman, in *Methods of Experimental Physics*, edited by K. Lark-Horovitz and V. A. Johnson (Academic Press Inc., New York, 1959), Vol. 6A, pp. 385-406.

¹¹ J. F. Goff, J. Appl. Phys. **35**, 2919 (1964).

The principal errors in the measurements occur in ΔT , which enters into k and Q , in the sample form factor (ratio of distance between thermometers L to cross-sectional area A) which affects k and ρ , and in the emf between probes, ΔV , related to ρ and Q . Since ΔT tends to be smallest near the thermal conductivity maximum its relative error is largest there, about 7%, and it decreases to about 2% at temperatures well below the maximum. Deviations from a perfect prism make the relative error in L/A about 4%. Thus the over-all error in k is between 4 and 8%. That in Q is about 10% because the greater precision in ΔT at low temperatures is offset by the fact that as T decreases so does ΔV (thermal). Since ΔV (Ohmic) depends on the measuring current, its contribution to the error can be kept well below 1% and hence negligible. When ρ is greater than about $10^4 \Omega$ cm its value depends on the nature of the sample surface, being about 10% lower for ground surfaces such as those on our samples than for etched surfaces.¹²

The over-all uncertainty in determinations of the Hall constant R , which involves probe placement and Hall voltage, sample current and magnetic field measurements, is about 5%.

Samples: (1) Preparation. The samples were prepared from plates cut transverse to the growth axis of single-crystal Ge ingots grown by the Czochralski technique; double-doped ingots were used for the compensated samples.¹³ The transverse cuts minimized impurity concentration gradients in the samples, and potential probing along their length showed no inhomogeneities in the single-doped samples and only minor inhomogeneity in those which were double doped, except for SbGa 170. In this sample the observed potential variation corresponded to an uncertainty of about 10% in the assignment of impurity parameters (see Sec. 2 below). The samples were prisms about 25 mm long and about 4 mm by 4 mm in cross section, with ground surfaces. The sample axis was approximately the (100) crystal direction except for Sb 172, in which it was the (111) direction. Individual sample dimensions are given in Table I.

(2) Parameters. The samples are distinguished by their values of donor and acceptor impurity concentrations, denoted n_d and n_a , respectively, total impurity concentration N_I , and excess electron concentration n_{ex} . We define $n_{ex}=n_d=N_I$ for the single-doped samples and $n_{ex}=n_d-n_a$ in the compensated samples, for which $N_I=n_d+n_a$. Values of n_{ex} are listed in Table I, along with the measurements from which they were calculated in the manner described below.

At low temperatures all the donor atoms are neutral in the single-doped samples of low and moderate N_I (about 10^{17} cm⁻³ or lower) since they have a finite

¹² H. Fritzsche, thesis, Purdue University, 1954 (unpublished).

¹³ We are indebted to Louise Roth, Physics Department, Purdue University, for supplying the samples.

TABLE II. Impurity concentrations of compensated samples: measurements at 77°K.

Sample	μ_H (cm ² /V sec)	n (10 ¹⁷ cm ⁻³)	N_I (10 ¹⁷ cm ⁻³)
SbGa 183	305	1.44	27.2
170	464	0.35	10.8
204	198	0.12	20

ionization energy. In the compensated samples n_a of the donors per cm³ are ionized since their electrons have made transitions to the acceptor levels which lie at much lower energy so that $n_d - n_a$ per cm³ remain neutral. At sufficiently high temperature T_e (exhaustion range) all the neutral donor atoms have been ionized by thermal excitation of their electrons to the conduction band. Hence the concentration of conduction electrons in the exhaustion range $n(T_e)$ provides a measure of n_{ex} for both types of material. In the single-doped samples with high N_I the ionization energy is zero and their electron energy levels have merged with those of the conduction band so that n is essentially independent of T and again equal to n_{ex} .

For the three samples which have no entry in the “-R” column in Table I n was determined from Fritzsche’s data¹⁴ relating it to ρ at room temperature. This temperature is in the exhaustion range for Sb 207 while Sb 187 and Sb 222 are examples of the “merged” case described above.

For the other samples the relation

$$n = -rS/eR \tag{1}$$

was used to calculate n . Here r is the ratio of the Hall mobility, $\mu_H = R/\rho$, to the electrical conductivity mobility; S is the band-shape factor (according to Herring¹⁵ $S = 0.784$ for Ge); and e is the magnitude of the electronic charge. In the case of the single-doped samples room temperature is in the exhaustion range, so again $n(290^\circ\text{K}) = n_{ex}$. For the compensated samples room temperature is below T_e so $R(400^\circ\text{K})$ was used to estimate n_{ex} . As noted in Table I, R was measured either on the same sample used for the other measurements (k, Q, ρ) or on samples prepared from the same ingot plate.

These data cannot be used to find N_I for the compensated samples. Their value of μ_H was found to be proportional to $T^{3/2}$ in the neighborhood of 77°K, which implies that ionized impurity scattering (IIS) is the dominant scattering mechanism for electrons. N_I was therefore calculated from the Brooks-Herring mobility formula¹⁶ with the effective mass $m^* = 0.20m_0$ and $n(77^\circ)$ calculated from Eq. (2) with $r = 1.93$, the value appropriate for IIS. These values are listed in Table II.

¹⁴ H. Fritzsche, J. Phys. Chem. Solids **6**, 69 (1958).

¹⁵ C. Herring, Bell System Tech. J. **34**, 237 (1955).

¹⁶ H. Brooks, *Advances in Electronics and Electron Physics* (Academic Press Inc., New York, 1955), Vol. 7, pp. 85-182.

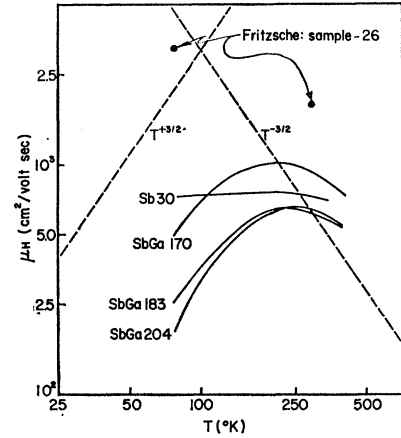


FIG. 1. Hall mobility of compensated samples and of a degenerate Sb-doped sample.

As a check on the applicability of the Brooks-Herring formula to samples with such high values of N_I we plot in Fig. 1 two points which are μ_H values reported by Fritzsche¹⁴ for an Sb-doped sample with $n_{ex} = N_I = 1.3 \times 10^{17}$ cm⁻³. This sample thus has about the same n_{ex} as SbGa 183, but about an order of magnitude smaller N_I . Its Hall mobility according to the Brooks-Herring formula should therefore be about an order of magnitude larger and this is seen to be the case.

III. RESULTS

A. Thermal Conductivity

Thermal conductivity as a function of temperature is shown for the Sb-doped samples in Fig. 2, for the

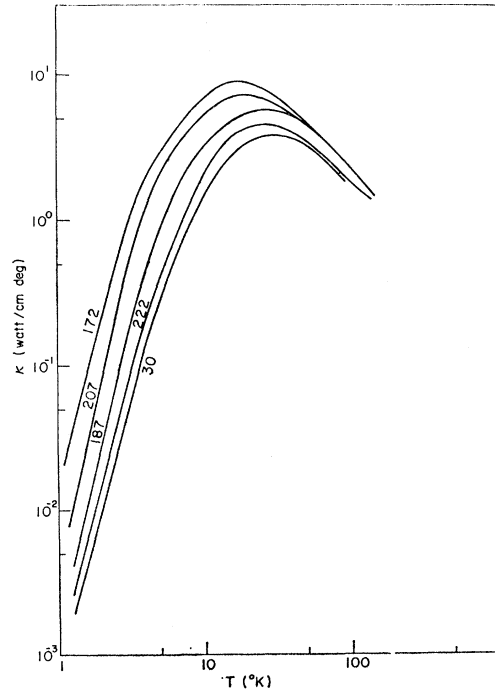


FIG. 2. Thermal conductivity: noncompensated Sb-doped samples.

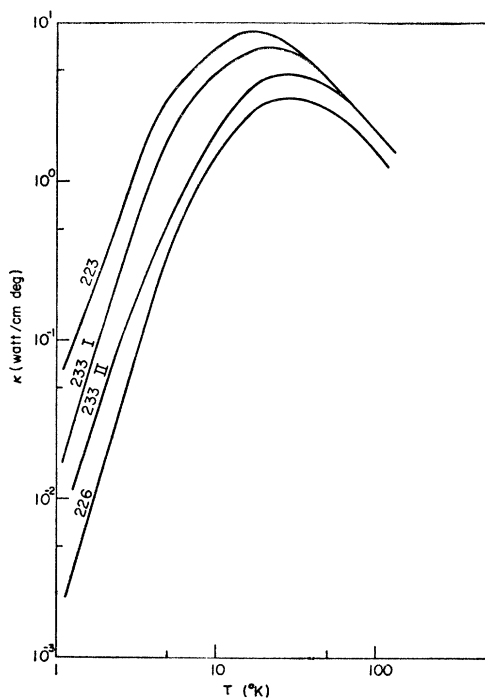


FIG. 3. Thermal conductivity: noncompensated As-doped samples.

As-doped samples in Fig. 3, and for the Sb-Ga-doped (compensated) samples in Fig. 4. Two of the Sb curves are repeated in the last figure for comparison. Measured points are omitted from these curves for clarity. Figure 5, using the data for sample As 226 as a typical case, shows the order of agreement between the curves and measured values of thermal conductivity and of thermoelectric power and electrical resistivity as well.

It can be seen that at the lowest measured temperatures $k(T)$ has the form

$$k = AT^m. \quad (2)$$

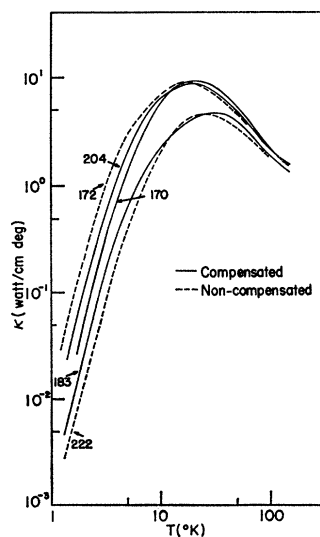


FIG. 4. Thermal conductivity: comparison of compensated and noncompensated Sb-doped samples.

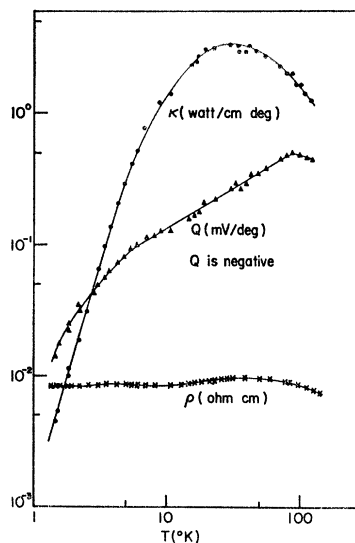


FIG. 5. Data for sample As 226.

Values of A and m for the various samples are listed in Table III. The exponent m is seen to be characteristically larger for the samples containing Sb, both single and double doped, than for these with As impurity—being about 4 for the former and around 3 for the latter.

The table also lists T' , the temperature above which $k(T)$ increases more slowly than Eq. (2), and the conductivity at the maximum, k_M , as well as T_M , the temperature at which the maximum occurs. Finally, the "boundary conductivity" $k_b(1^\circ\text{K})$ is given. This is the conductivity at 1°K calculated for a sample of the same size as that used on the assumption that it is limited only by phonon scattering at the boundaries of the sample.¹⁷ It can be compared with A , which is equal to the observed conductivity extrapolated to 1°K . All the samples have about the same value of k_b since they all have roughly the same transverse dimensions but $A [=k(1^\circ\text{K})]$ has a range of almost two orders of magnitude, its largest value being only about one-third that of k_b for the same sample.

TABLE III. Thermal conductivity at low temperatures $k = AT^m$, $T < T'$.

Sample	n_{ex} (10^{17} cm^{-3})	A $\frac{\text{mW}}{\text{cm}^{-1}} \text{ } ^\circ\text{K}^{-1}$	m	T' ($^\circ\text{K}$)	k_M $\frac{\text{W}}{\text{cm}^{-1}} \text{ } ^\circ\text{K}^{-1}$	T_M ($^\circ\text{K}$)	$k_b(1^\circ\text{K})$ $\frac{\text{mW}}{\text{cm}^{-1}} \text{ } ^\circ\text{K}^{-1}$
Sb 30	25	0.72	3.8	4.8	3.8	30	76
222	11	1.00	3.9	3.9	4.6	25	140
187	1.2	1.65	4.2	3.5	5.8	25	139
207	0.24	4.0	4.5	3.0	7.3	19	134
172	0.061	16.5	3.9	3.0	9.3	16	129
As 226	8.8	1.62	3.4	4.8	2.7	30	137
232	3.1	2.85	3.4	~5	134
233II	1.7	5.43	3.0	3.3	4.8	30	138
233I	1.1	12.4	3.2	4.3	7.0	20	139
223II	0.63	26	2.7	3.3	6.3	25	137
223I	0.21	51	2.8	3.3	8.8	17	140
SbGa 183	1.5 (27)	1.58	4.1	3.3	4.7	29	126
170	0.54 (10.8)	3.2	4.1	3.2	9.7	19	138
204	0.26 (20)	7.1	3.9	3.3	9.0	21	137

¹⁷ H. B. G. Casimir, Physica 5, 495 (1938).

It is apparent that the variation in A from sample to sample within each of the three groups is correlated with that of n_{ex} . This is equal to N_I for the single-doped samples but not for the compensated ones, for which $N_I(>n_{ex})$ is given in parentheses next to n_{ex} . The variation in A for these samples is clearly not related to that of N_I , nor are the absolute values in agreement with those estimated from the Sb-doped samples (uncompensated) with comparable values of N_I . On the other hand, reasonable agreement is found if values of n_{ex} are used in making the comparisons between single- and double-doped samples.

In contrast to the large variation in A , the total range of k_M encompasses only a factor of about 2.5. As would be expected, samples with higher N_I tend to have lower values of k_M and higher T_M . This is true of both the single- and double-doped samples. At temperatures above T_M there is only a relatively small variation in k from sample to sample; at 100°K the values for all thirteen samples measured at that temperature are within about 20% of the average value, $2.0 \text{ W cm}^{-1} \text{ }^\circ\text{K}^{-1}$. There is a tendency for higher N_I to be associated with lower $k(100^\circ\text{K})$ but the most striking feature of the behavior of $k(T)$ above T_M is seen in Fig. 4, where the compensated samples are compared with two of the Sb-doped representing the extremes in N_I . The last two samples in the table, which have high values of $N_I(>10 \times 10^{17} \text{ cm}^{-3})$ but which also have high compensation ratios, $K = n_a/n_d$ over 0.9, are seen to have $k(T)$ greater than that for the Sb-doped sample with lowest N_I . Even for the compensated sample SbGa 183, which has the highest N_I of all, $k(T)$ in this region exceeds that of the relatively impure Sb 222 with N_I only about one-third as large. Thus it is apparent that between T_M and 100°K there is a small but nevertheless clear enhancement of k which is associated with compensation and which begins in the neighborhood of T_M .

B. Thermoelectric Power

The thermoelectric power of the Sb-doped samples is shown in Fig. 6, of the As-doped samples in Fig. 7,

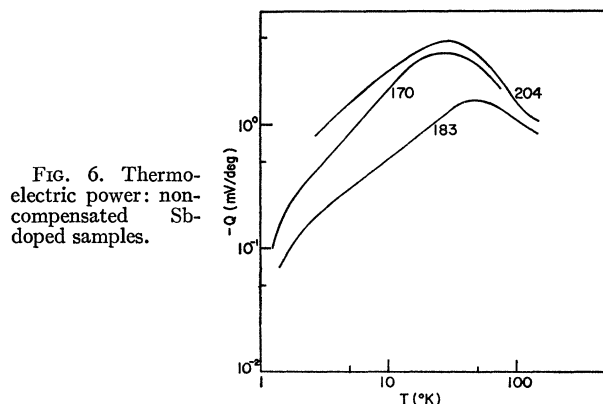


FIG. 6. Thermoelectric power: non-compensated Sb-doped samples.

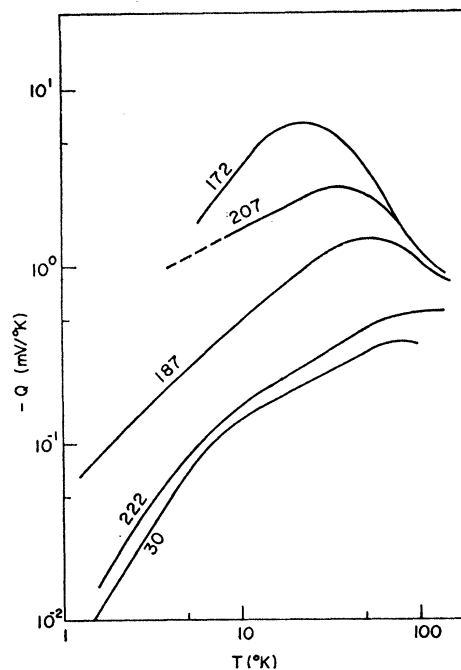


FIG. 7. Thermoelectric power: noncompensated As-doped samples.

and of the Sb+Ga compensated samples in Fig. 8. For all the samples except the very impure Sb 222 and Sb 30 there is a region at the upper end of the temperature range covered in which the magnitude of Q increases with decreasing temperature. The magnitude is rather high in this region, over 1 mV/deg. In all of the remaining samples except the most pure As-doped,

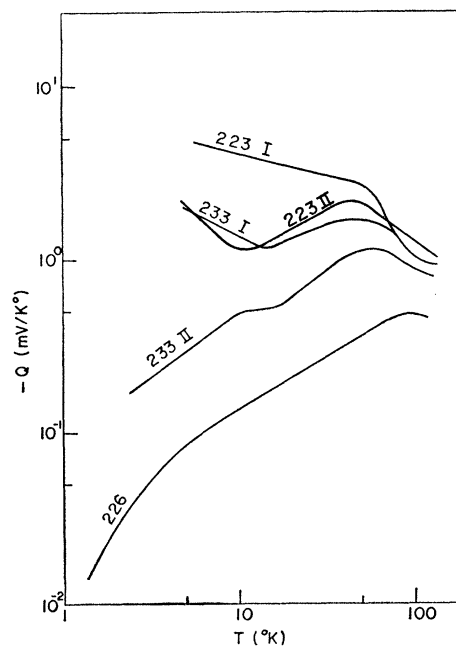


FIG. 8. Thermoelectric power: compensated Sb-doped samples.

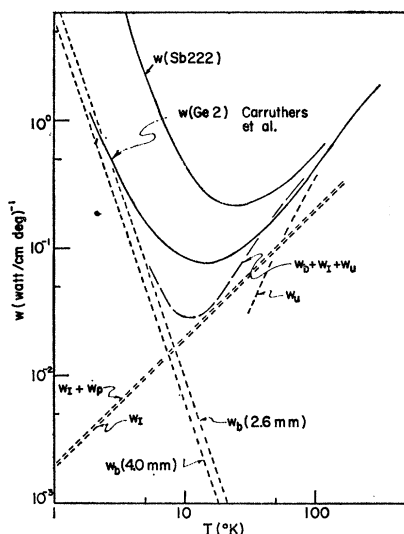


Fig. 9. Comparison of measured and calculated thermal resistance: pure Ge (Ge 2) and $n_{ex} = 10^{18} \text{ cm}^{-3}$.

As 223I, there is at least a local maximum in the neighborhood of 50°K below which the magnitude of Q decreases with decreasing T . For As 223I, instead of a maximum, a decrease in slope is observed at about 50°K , and the magnitude of Q continues to increase down to the lowest temperature at which it could be measured. As the temperature decreases the electrical resistivity increases very rapidly, and when the sample reaches a resistance of the order of $10^6\text{-}\Omega$ loss in galvanometer sensitivity makes it possible to measure the submillivolt thermal emf.

Somewhat similar behavior is also displayed by the other two As-doped samples with N_I about 10^{17} cm^{-3} or lower, As 223II and As 233I. They display a local maximum at about 50°K and also a local minimum near 10°K , below which the magnitude of Q rises. In the other two As-doped samples which were measured at these temperatures the magnitude of Q decreases monotonically below the maximum, but in the purer of these, As 233II, there are two changes of slope near 10°K which may be an indication of an incipient transition to the temperature variation of the purer samples. The Sb-doped and the compensated samples give no indication of this sort of behavior.

IV. DISCUSSION

A. Thermal Conductivity

(1) Phonon-scattering mechanisms. In discussing the thermal conductivity of these samples only phonon transport need be considered, since the electronic contribution is so small it may be neglected. The electronic contribution to k , k_e , is related to ρ by the Lorenz number L according to

$$k_e = L(T/\rho). \quad (3)$$

With ρ given in ohm cm and L in $(\text{V}/\text{deg})^2$, k_e is in $\text{W cm}^{-1} \text{ }^\circ\text{K}^{-1}$. In a degenerate electron gas at temperatures above the Debye temperature and at low temperatures $L = 2.45 \times 10^{-8}$. Its value is smaller at intermediate temperatures in this case, and at all temperatures in a classical electron gas. In the most impure sample, Sb 30, ρ is about $3 \text{ m}\Omega \text{ cm}$ at 1°K so $k_e(1^\circ\text{K})$ is about $10^{-5} \text{ W cm}^{-1} \text{ }^\circ\text{K}^{-1}$. But from Table I we see that $A = k(1^\circ\text{K})$ is over a hundred times larger and since k increases with T^4 while k_e is proportional to T (because ρ is roughly independent of T) the ratio k/k_e becomes much larger at higher temperatures. It is larger yet for the purer samples, for which k is somewhat higher and ρ is much smaller, by many orders of magnitude for those samples with classical electron gas in the conduction band. Hence we need be concerned hereafter exclusively with lattice thermal conduction, as would also be the case for a dielectric solid.

Klemens³ has analyzed the total thermal resistance w in dielectric solids in terms of scattering at the sample boundaries (w_b), by point defects (w_d) and in the "umklapp" process in which the phonon wave vector changes by a reciprocal-lattice vector, so that "crystal momentum" is not conserved (w_u). Below about 100°K these are the only significant contributions to phonon scattering in pure Ge (no free electrons) so that we may write

$$w = w_b + w_d + w_u. \quad (4)$$

The umklapp term has been estimated from the measurements on isotopically enriched Ge by Geballe and Hull.¹⁸ It is proportional to phonon concentration and hence decreases rapidly at temperatures below the Debye temperature, becoming negligible at temperatures somewhat below that of the maximum in k .

The boundary scattering term can be estimated by inserting the appropriate mean free path L_b ($L_b = 1.12$ times the side in a sample of square cross section in which phonons are diffusely scattered at the boundaries)¹⁷ in the Debye expression¹⁹

$$w_b = 3/CvL_b, \quad (5)$$

where C is the lattice heat capacity per unit volume and v is the phonon group velocity. C is proportional to T^3 below about 5°K ,²⁰ so that the Debye model for the lattice, with constant v , is an adequate approximation.

In Fig. 9 are plotted values of w_b for $L_b = 4.6 \text{ mm}$ (Sb 222) and $L_b = 2.9 \text{ mm}$ (sample Ge 2 of Carruthers *et al.*² which has $n_d = N_I = 10^{18} \text{ cm}^{-3}$ and is a "pure" sample with no intentional doping). Also plotted are the measured values of w for both these samples and it appears that below about 5°K w_b accounts rather well for the thermal resistance of the pure sample, except that its slope is somewhat lower than the pre-

¹⁸ T. H. Geballe and G. W. Hull, *Phys. Rev.* **110**, 773 (1958).

¹⁹ P. Debye, in *Vorträge über die Kinetische Theorie der Materie und der Elektrizität* (B. G. Teubner, Leipzig, 1914), pp. 17-60.

²⁰ P. H. Keesom and N. Pearlman, *Phys. Rev.* **91**, 1347 (1953).

diction of Eq. (5), according to which w_b is proportional to T^{-3} . Hence it appears that in pure Ge below about 3°K, w_d does not make an appreciable contribution to w .

Equation (3) can be used to estimate other resistivity contributions as well, if the scattering cross section $\sigma (=1/NL$, where N is the concentration of scattering centers and L is the corresponding mean free path) is known. σ can be calculated if the matrix elements connecting initial and scattered states are known since then the collision rate $\tau^{-1} = Nv\sigma = v/L$ can be determined. Now it would be expected quite generally that the matrix elements would decrease with phonon frequency ω , simply because the phase-space available for scattering decreases. Hence τ^{-1} and also σ should decrease with ω so that L should increase. Since the average phonon frequency decreases with T , this implies that in general L should increase as T decreases, if it varies at all. Then from Eq. (3), since $C \propto T^3$ and v is constant, w should increase with T no faster than T^{-3} . Thus results such as those in Sec. III, where $k(T)$ is proportional to powers of T greater even than 4 in some cases, require a special mechanism which somehow negates the general argument given above.

From Klemen's theory of point-defect scattering,³ according to which w_d is given by

$$w_d/T = 3(2\pi)^2 V_a^2 n_d S_a^2 / 0.90 h v^2 \quad (6)$$

it also follows that w_d is an insignificant component of w , even for a sample as impure as Sb 222. Here V_a is volume per atom, n_d is the number of scattering centers per unit volume, h is Planck's constant, and S_a is a dimensionless scattering parameter related to the scattering cross section which includes terms corresponding to deviations in mass M , force constant F_c , and nearest-neighbor distance R_n . S_a has the form

$$S_a^2 = a(\Delta M/M)^2 + (b\Delta F_c/F_c + c\Delta R_n/R_n)^2, \quad (7)$$

where a , b , and c are numerical constants. Since pure natural Ge has five isotopes with appreciable abundance, it has a relatively large value of S_a , even though ΔF_c and ΔR_n are both zero, since n_d in this case is equal to its maximum value, the total number of atoms per unit volume.²¹ The value of isotope scattering calculated from Eq. (6), which we denote by w_{is} , is $(1.89 \times 10^{-3} \text{ W}^{-1} \text{ cm}) \times T$, which is in good agreement with the value calculated by Klemens²² from the data of Geballe and Hull,¹⁸ $w_{is} = (2.3 \times 10^{-3} \text{ W}^{-1} \text{ cm}) \times T$.

In impure Ge the thermal resistance due to chemical impurities, which we denote w_{ch} must be added. In this case S_a^2 will be larger than for w_{is} , since ΔM is larger and ΔF_c and ΔR_n no longer vanish. However, even for $N_I = 10^{18} \text{ cm}^{-3}$, n_{ch}/n_{is} will be only 2.5×10^{-5} , so that w_{ch} is much smaller than w_{is} . We have estimated

S_a^2 using values of ionic radii compiled by Winkler²³ and neglecting ΔF_c on the basis of Klemens' discussion²⁴ of this quantity for impurities in alkali halide crystals, where he showed that the term $b\Delta F_c/F_c$ was an order of magnitude less than $c\Delta R_n/R_n$ and of opposite sign. Thus our estimate should represent an upper limit to w_{ch}/w_{is} . We find for this ratio, in samples with $N_I = 10^{18} \text{ cm}^{-3}$, 3.1×10^{-2} for Sb atoms, 7.8×10^{-4} for As atoms, and 1.5×10^{-2} for Ga atoms. Thus $w_d \approx w_{is}$, as shown in Fig. 9.

The value of w_u calculated from the data of Geballe and Hull is also plotted in Fig. 9. It is expected to be independent of N_I and of the nature of the impurities, and is seen to become the dominant term in w for temperatures above 100°K. Since it decreases rapidly with T it is not a major contribution to w in the neighborhood of T_M , which is thus seen to be determined mainly by w_b and w_d .

(2) Excess impurity scattering below T_M —bound donor electrons. While the terms so far considered in w seem to represent quite well the observations on pure Ge for $T < T_M$ and on both pure and impure Ge for $T > T_M$, the large excess in w for the latter is in no way accounted for. On the other hand, the figures and table in Sec. III clearly indicate that this excess is associated with impurities, even though w_{ch} is far too small to account for it and has the wrong T dependence as well.

It therefore seems reasonable to examine the relation of the excess conductivity to the electrons introduced into the crystal by donor impurities, rather than the impurity ions. Further, the good agreement seen in Fig. 9 between w and w_b at low temperatures suggests that we can identify this excess resistance, which we denote w_{ep} , simply as

$$w_{ep} = w - w_b \quad (8)$$

for T well below T_M . If it is taken, for $T > T_M$ as $w_{ep} = w - (w_b + w_d + w_u)$ it appears that it is not appreciable in the higher temperature range.

The distinction between the electrons and the impurity ions can be explored by examining the thermal conductivity of compensated samples which are prepared with n_{ex} comparable to that of low-concentration single-doped samples, but with N_I more than an order of magnitude larger. Such comparisons are shown in Fig. 10 for $n_{ex} \approx 1.5 \times 10^{17} \text{ cm}^{-3}$, and Fig. 11, for $n_{ex} \approx 0.2 \times 10^{17} \text{ cm}^{-3}$. Below about 4 or 5°K w_{ep} is the same for the two samples in each pair, so that it is clearly determined by n_{ex} . The relation between n_{ex} and w_{ep} (2°K) for all the Sb-doped samples is shown in Fig. 12. The point for the third compensated sample is seen to agree with the data for the other Sb-doped samples.

An important characteristic of the phonon scattering mechanism involved can be deduced by comparing

²¹ G. A. Slack, Phys. Rev. **105**, 829 (1957).

²² Footnote 3, first entry, p. 63.

²³ H. G. F. Winkler, *Struktur und Eigenschaften der Kristalle* (Springer-Verlag, Berlin, 1955).

²⁴ P. G. Klemens, Proc. Phys. Soc. (London) **A68**, 1113 (1955).

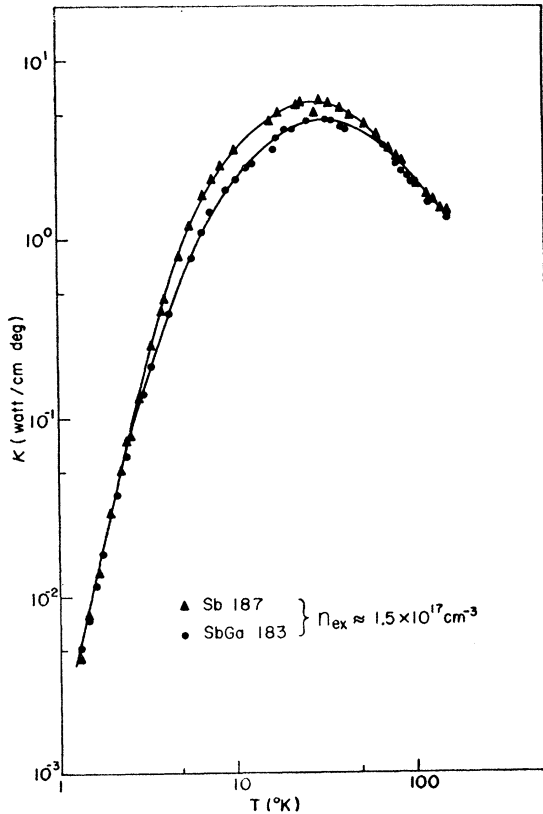


FIG. 10. Thermal conductivity: comparison of compensated and noncompensated Sb-doped samples with $n_{\text{ex}} = 1.5 \times 10^{17} \text{ cm}^{-3}$.

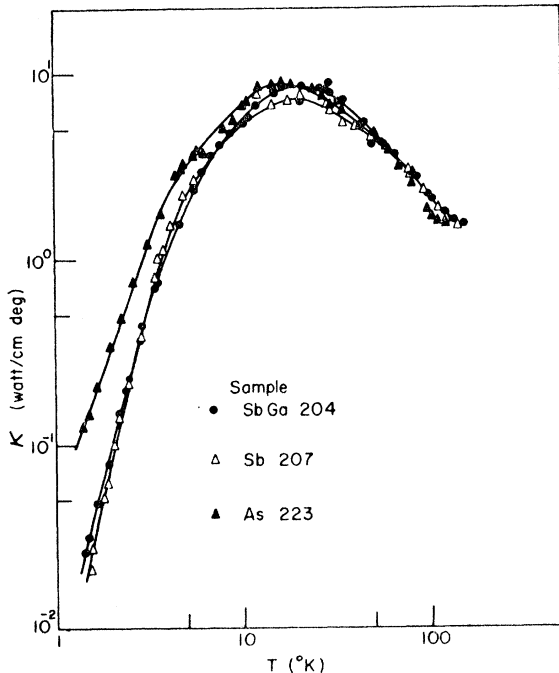


FIG. 11. Thermal conductivity: comparison of noncompensated (Sb- and As-doped) and compensated samples with $n_{\text{ex}} = 2 \times 10^{16} \text{ cm}^{-3}$.

the behavior of the electrical resistivity in the same temperature range, as shown in Fig. 13. The samples in the pairs compared in Figs. 10 and 11 show strikingly different magnitude and T dependence in ρ , in contrast to their identical values of k and hence w_{ep} . Since ρ depends on electron transition probabilities between donor states it appears that w_{ep} must be independent of these transition probabilities and depend only on the states themselves.

While the excited states of donor electrons in Ge agree well with the hydrogenic model and thus are essentially independent of the particular donor species,²⁵ the lower-lying levels reflect differences in donor wavefunction and hence different donors have distinct ionization energies E_1 , and valley-orbit splitting²⁵ E_{13} ($=4\Delta_c$, where Δ_c is the "chemical shift") between the singlet ground state and the first excited (triplet) state. For Sb donors these values are 9.8 meV²⁶ and 0.57 meV,²⁷ respectively, while for As they are 14.5 meV²⁶ and 4.2 meV²⁷ with the values for Bi and²⁸ P lying between these limits. The effect on w_{ep} of these differences in the donor states can be seen in Fig. 11, where k is plotted for an As-doped sample with about the same n_{ex} as the Sb-doped pair, single-doped and compensated, also plotted there. It is also shown, for all the As-doped samples, in Fig. 12, where their values of w_{ep} (2°K) are plotted. It is seen that w_{ep} for a given n_{ex} is significantly smaller in As-doped than in Sb-doped material, for n_{ex} less than a few times 10^{17} cm^{-3} . The difference in the exponent in the temperature dependence of k , about 4 for Sb and about 3 for As, was pointed out earlier in Sec. III.

Keyes⁸ and Griffin and Carruthers⁹ have examined the phonon scattering to be expected from electrons in donor states. Their conclusions are in reasonable agreement with the results we have presented above, and also with each other, although the two approaches to the problem are somewhat different. However, they both consider electrons in bound states, so that their results apply only to w_{ep} for n_{ex} smaller than that corresponding to the merged case, and would be expected to be more accurate in the isolated donor region than in the transition region.

Keyes points out that Price²⁹ has shown that the effect of strain in the lattice is to introduce a term in the electron energy which is proportional to the square of the strain. Such an energy perturbation leads to phonon scattering of the point-defect type³ and thus can be calculated from Eq. (6) using the appropriate value of S_a^2 . The relation between the energy perturbation and strain leads to the factor $\bar{E}_\mu/4\Delta_c$ in S_a , where

²⁵ W. Kohn, in *Advances in Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 5, pp. 258-321.

²⁶ H. Y. Fan and P. Fisher, *J. Phys. Chem. Solids* **8**, 270 (1962).

²⁷ H. Fritzsche, *Phys. Rev.* **120**, 1120 (1960).

²⁸ D. K. Wilson, *Phys. Rev.* **134**, 265 (1964).

²⁹ P. J. Price, *Phys. Rev.* **104**, 1223 (1956).

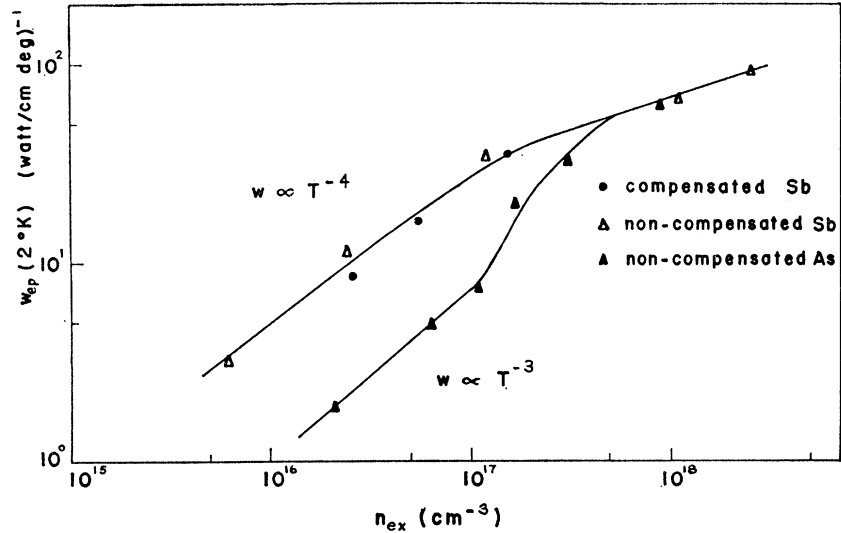


FIG. 12. Thermal resistivity excess over boundary scattering at 2°K as a function of n_{ex} .

$\bar{\epsilon}_\mu$ is the shear deformation potential.^{14,30} Since $4\Delta_c(\text{Sb}) < 4\Delta_c(\text{As})$, the values of S_a should have the inverse relation, and $w_{ep}(\text{Sb})$ should be larger than $w_{ep}(\text{As})$, which we have seen to be the case. Further, while we have seen that S_a^2 for point-defect scattering arising from mass differences is so small that w_d is negligible at low temperatures, Keyes showed that S_a^2 in w_{ep} is large enough to account for the observed magnitudes.

This discussion does not yet account for the temperature dependence, however, since as we have seen, w is proportional to T in scattering of the point-defect type, while w_{ep} is proportional to T^{-3} or T^{-4} in As-doped and Sb-doped material, respectively. It is simplest to follow Keyes' argument in accounting for the observed T dependence of w_{ep} in terms of Klemens' analysis³¹ of w . He shows that if S_a^2 (proportional to $1/L$) is proportional to ω^j , where ω is the phonon frequency, then the corresponding contribution to w is proportional to T^{j-3} . Thus for boundary scattering, where $L=L_b$ so that S_a^2 is independent of ω and $j=0$, $w_b \propto T^{-3}$ and $k_b \propto T^3$; for point-defect scattering, $j=4$ and, as we have seen, $w_d \propto T$. However, a given scatterer will act as a point defect only so long as its size r_s is much less than the phonon wavelength, $\lambda=2\pi v/\omega$, so in the neighborhood of a critical frequency, $\omega_c=2\pi v/r_s$, the quantity S_a^2 must decline rapidly from the large value corresponding to low ω , to a very low value above ω_c . Thus in the neighborhood of ω_c , j has a large negative value and the corresponding contribution to w will be proportional to a high negative power of T . At somewhat lower ω the transition of j from a large negative value to $+4$ will result in a region where $j \approx 0$ and a corresponding w proportional to T^{-3} or T^{-4} may be expected. The temperatures at which these changes in the T dependence may be expected to occur may be estimated at by calculating T_c , the temperature at which the modal fre-

quency $\bar{\omega}$ of the phonon distribution, is equal to ω_c . Using the linear relation between $\bar{\omega}$ and T at low temperatures, we find

$$\frac{T_c}{\Theta_D} \sim \left[\frac{(4\pi/9)^{1/3}}{2.7} \right] \left(\frac{a}{r_s} \right),$$

where Θ_D is the Debye temperature and a is the lattice

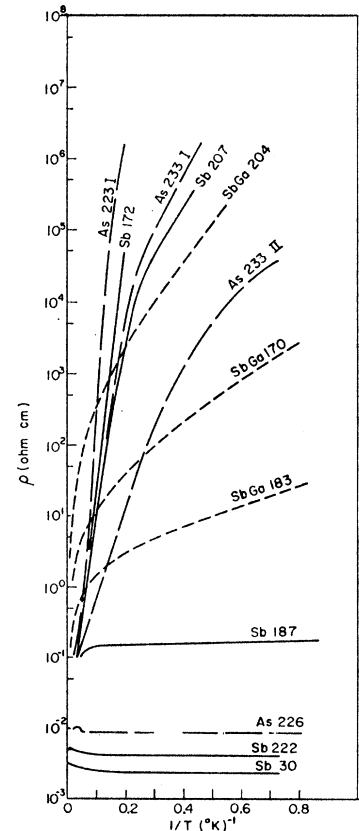


FIG. 13. Electrical resistivity at low temperatures.

³⁰ C. Herring and E. Vogt, Phys. Rev. **101**, 944 (1956).
³¹ P. G. Klemens, J. Phys. Chem. Solids **8**, 345 (1959).

constant. For the scattering under consideration r_s will be of the order of the diameter of the donor electron orbit. This is given in A by $r_s \sim \frac{1}{2}(1/E_1)(1/\epsilon)$ if E_1 is given in rydbergs, ϵ is the dielectric constant. Hence a/r_s is of the order of one-tenth, so T_c is indeed in the neighborhood of T_M (see Table III), as is required to account for the observed behavior of w_{ep} .

Since S_a^2 becomes proportional to ω^4 at low frequencies ($\omega \ll \omega_c$), w_{ep} is proportional to T at very low temperatures and the thermal conductivity diverges. Keyes therefore includes boundary scattering in his calculation in order to avoid the low-temperature divergence. His results display an impurity species effect of the right order of magnitude, as well as values of k which agree reasonably well with our measurements but which do not reproduce the observed temperature dependence below T' (see Table III). No T^m dependence is seen in the calculated curves; they do show the decrease in slope in k , which is expected from the discussion above when j approaches 4, below about 2°K but no such feature is discernible in the measurements.

Impressive confirmation of the influence of strain on w_{ep} as deduced by Keyes is provided by measurements reported by Keyes and Sladek³² in which k was measured at low temperatures as a function of applied tensile stress and crystal direction of the applied stress. In appropriate directions such stress removes the degeneracy of the four valleys in the conduction band of Ge and hence alters the wave function of the singlet-donor ground state. As a result the dependence of the energy of this state on strain is changed and hence the magnitude of w_{ep} . As expected, the changes observed in k were large in Sb-doped Ge, because of the small value of $4\Delta_c$; the larger value of the chemical shift in As-doped Ge made the effect too small to be observed, and no effect was seen in pure Ge, or in Sb-doped Ge when the stress was applied in crystal directions which did not affect the degeneracy of the conduction-band valleys.

Keyes' calculation regards the donor states as static scattering centers, but since the strain is in fact periodic with the phonon frequency, Griffin and Carruthers⁹ point out that this should be an adequate approximation only when the time during which the strain is roughly constant, which is of the order of $1/\omega$, is long compared to the time required for the electron wave function to adjust to the strain. However, because $4\Delta_c$ is so small, the latter time, of the order of $\hbar/4\Delta_c$, is rather long. Again using the relation between $\bar{\omega}$ and T , we find that for Sb in Ge $1/\bar{\omega} = \hbar/4\Delta_c$ at about 2°K, so only for much lower temperatures should the static approximation be applicable.

Griffin and Carruthers⁹ take the dynamic behavior of the electrons into account by exploiting the analogy with resonance fluorescence radiation. In the present case, phonons are scattered as a result of virtual

transitions of electrons between the singlet and triplet states separated by $4\Delta_c$. As in the case of Keyes' treatment the detailed calculations are rather complex, but the following crude argument is intended to indicate how exponents greater than 3 can arise in $k(T)$. In S -wave scattering (no higher order scattering is considered because of the long wavelengths involved) the scattering cross section has the factor $(\sin\delta/q)^2$, where δ is the phase shift of the scattered wave and q is the phonon wave number. Hence the frequency dependence of S_a^2 has $j = -2$ (except in the immediate neighborhood of the resonance, where δ is changing by $\frac{1}{2}\pi$), and the corresponding contribution to w_{ep} will be proportional to T^{-5} . The additional effect of the resonance itself is difficult to detect in $k(T)$ because the contributions w_b and w_{is} of competing processes become important at temperatures where the resonance frequency equals $\bar{\omega}$, and also because the resonance may be very narrow. In addition, of course, the resonance will have no significant effect if its frequency exceeds ω_c .

The calculations based on this analysis⁹ incorporating also boundary and isotope scattering by Callaway's procedure³³ show very good agreement with the results below 5°K, especially in view of the fact that no fitting of adjustable parameters is involved. As would be expected, they agree with Keyes' calculation at low frequencies, $\omega \ll \hbar/4\Delta_c$. Hence here too $k(T)$ is expected to change its slope at very low temperatures, as w_{ep} becomes proportional to T . Measurements at lower temperatures than reported here are in progress to investigate this prediction.

(3) Excess impurity scattering—conduction electrons. It has already been pointed out that for sufficiently high values of n_{ex} (about 10^{17} cm⁻³ for Sb and 4 to 6×10^{17} cm⁻³ for As impurities) the interaction of donor wave functions is strong enough to cause the activation energy E_a to vanish so that the donor-electron energy levels overlap those in the conduction band. Also, at temperatures of the order of T_c and above electrons have been excited from discrete levels in the energy gap to the conduction-band levels. Hence in both these cases (all temperatures in samples with high n_{ex} and $T > T_c$ in those with low n_{ex} , and including all compensated samples measured) we are no longer dealing with electrons bound to donor ions.

The discussion of phonon scattering by electrons in the conduction band requires separate treatment. It is clear that the physical basis of the scattering must be quite different from that described above for bound donor electrons, even though the magnitudes of the two types of scattering are comparable, presumably fortuitously. Indeed for Sb there is only a rather slight change in slope to signal the transition between the two regimes; with As the transition is more distinct, but still smooth. Nevertheless, the impurity species effect,

³² R. W. Keyes and R. J. Sladek, Phys. Rev. **125**, 478 (1962).

³³ J. Callaway, Phys. Rev. **113**, 1046 (1959).

which is of central importance in bound electron scattering, is no longer present in the magnitude of w_{ep} when we are dealing with levels merged with the conduction band, as can be seen from Fig. 12. However, the fact that this figure compares $w_{ep}(2^\circ\text{K})$ for the different samples suppresses the detail of temperature dependence, which can be seen in Fig. 14, where an As- and an Sb-doped sample with about the same concentration (about 10^{18} cm^{-3}) are compared. This concentration is high enough for the donor levels to have merged with the conduction band and for the conduction electrons to be degenerate below about 70°K . Although the $k(T)$ curves are very similar there remains a difference in slope, the Sb sample having a higher exponent of T (3.9) than the As sample (3.4). The latter exponent is somewhat higher than that observed for the four As-doped samples with $n_{ex} < 2 \times 10^{17}\text{ cm}^{-3}$, in which the donor levels are not merged with the conduction band. Hence in As-doped samples the conduction-band scattering has different T dependence as well as different magnitude than the bound donor scattering, but there still appears to be a small species effect remaining.

The increase in electron population in the conduction band that begins in the neighborhood of T_M in the samples with levels in their energy gap leads to the possibility that the conduction electron-phonon interaction may account for the curious behavior of k in the compensated samples in that temperature region. As can be seen from Table III and Fig. 4, k_M for the three compensated samples decreases with increasing N_I , but it is larger for these samples than for the single-doped samples of similar and even much smaller N_I . The comparisons in Figs. 10 and 11 disclose an additional difference among the compensated samples. In Fig. 10 we see that $k(\text{SbGa } 183) < k(\text{Sb } 187)$ for T between 5 and 100°K . Both samples have the same n_{ex} , but SbGa 183 is the most impure of all the samples, and is the compensated sample for which $n(T)$ (concentration of electrons in the conduction band) shows hardly any variation between 77 and 400°K (see Fig. 18). In contrast, $k(\text{SbGa } 204)$ is greater than that of its companion sample between 10 and 80°K . For this compensated sample, Fig. 18 shows $n(T)$ decreasing rapidly with decreasing T .

This evidence speaks for a contribution w_e (related to n) in the neighborhood of T_M and at higher temperatures as well, in addition to w_d and w_u . Such a contribution would account for the comparisons discussed above if n were smaller for the compensated than for the single-doped samples at these temperatures. The evidence for this as seen in Fig. 18 will be discussed in Secs. IVB and IVC.

Ziman³⁴ has calculated the cross section for phonon scattering by electrons in a conduction band. He gives an expression for the collision rate τ_e^{-1} calculated so

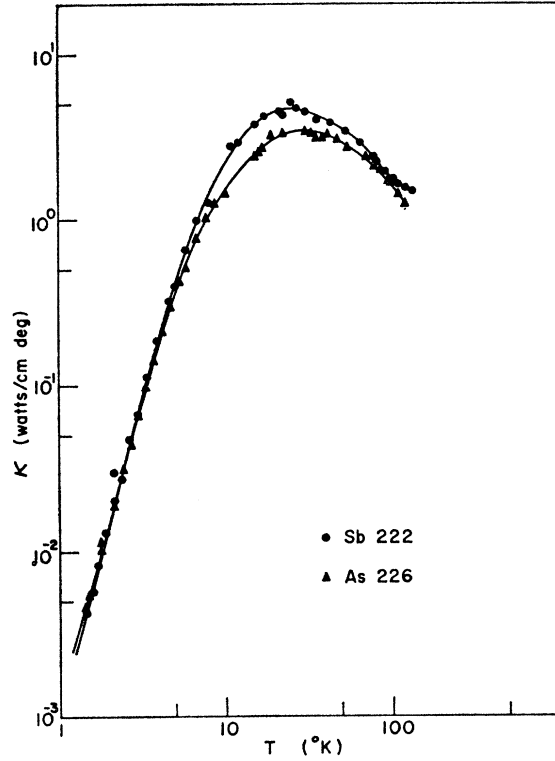


FIG. 14. Thermal conductivity: comparison of degenerate samples, Sb- and As-doped.

as to satisfy the requirement that energy and momentum are conserved in the phonon-electron collisions; i.e., if an electron is scattered from a state with wave vector \mathbf{K} to one with wave vector \mathbf{K}' in a collision in which a phonon q is absorbed, then

$$\mathbf{K}' = \mathbf{K} + \mathbf{q} \tag{9}$$

and also

$$\hbar^2 K'^2 / 2m^* = (\hbar^2 K^2 / 2m^*) + q\hbar v. \tag{10}$$

This requirement restricts collisions to those in which K has at least the minimum value K_0 , given by

$$K_0 = |\frac{1}{2}q - m^*v/\hbar|. \tag{11}$$

As a consequence, as q increases (and hence ω , which equals vq in the Debye approximation) the scattering decreases since the minimum K_0 given by Eq. (11) moves to higher electron energy.

We calculated values of τ_e^{-1} using Ziman's expression, for an artificial case of a Ge sample with $n = 10^{18}\text{ cm}^{-3}$ but $N_I \approx 0$. This case was chosen because as we have seen the corresponding w_{ch} is small, so that we could hope to isolate a possible conduction effect. These values are plotted in Fig. 15 as a function of the dimensionless variable $x = \hbar\omega / K_b T$. The cutoff in τ_e^{-1} arising from Eq. (11) is seen to be sharpest at lowest T .

The notation " $x = \text{Debye cutoff at } (^\circ\text{K})$ " at the top of the figure has the following significance. In the Debye model, the density of lattice modes as a func-

³⁴ J. M. Ziman, Phil. Mag. (8) 1, 191 (1956).

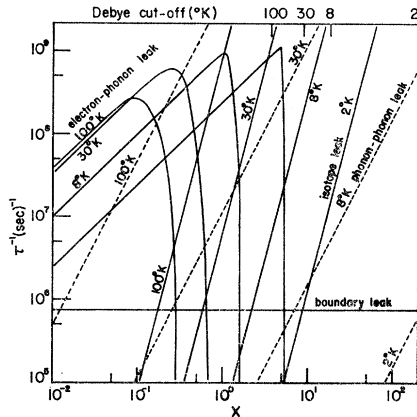


FIG. 15. Phonon collision rates as a function of $x = \hbar\omega/K_bT$.

tion of frequency is proportional to ω^2 up to the maximum frequency ω_M , which is determined by the condition that the total number of modes is $3N_A$ (N_A is Avogadro's number). The Debye temperature Θ_D (365°K in Ge) is related to ω_M by $k\Theta_D = \hbar\omega_M$, so in terms of x , integrations are cut off at $x_M = \Theta_D/T$. The temperatures given at the top of the figure are those at which this cutoff occurs at the value of x where the temperature is shown; e.g., at $T = 100^\circ\text{K}$, $x_M = 3.6$.

Since $\bar{\omega} \propto T$ at low temperatures the value of x corresponding to $\bar{\omega}$ is $\bar{x} = 2.7$. It is clear from the figure that at this value of x boundary scattering (horizontal line near bottom of figure) is negligible. The high exponent of $T (> 3)$ in $k(T)$ arises here from the fact that with decreasing temperature (increasing x at constant ω) the cutoff in τ_e^{-1} moves to higher x more slowly than does the Debye cutoff x_M . Hence the number of effective electron-phonon collisions increases so as to decrease the mean free path as the temperature decreases.

These arguments must be refined considerably, however, before a reasonably good estimate of $k(T)$ can be made. The simple addition of contributions to w , as expressed in Eq. (4) can be expected to be useful only when one scattering mechanism makes a dominant contribution to w . It is not really adequate in a case such as the one we are considering, $k(T)$ near and above T_M , where, as we have seen, there are several important mechanisms to consider, each with a different value of j in the ω dependence of S_a^2 . It should be pointed out that the analog of Eq. (4) as applied to the electrical resistivity of metals, which is known as Matthiessen's rule³⁵ does not suffer this limitation. The reason is that in metals the exclusion principle ensures that the scattered electrons all have the same energy, that of the Fermi surface, to a very good approximation, so to the same approximation the energy dependence of the different scattering mechanisms is irrelevant.

³⁵ C. Kittel, *Introduction to Solid State Physics* (John Wiley & Sons, Inc., New York, 1956), 2nd ed., p. 305.

No such limitation is imposed on the scattering of phonons, however, so that the validity of Eq. (4) is limited as described above. While it is possible to make crude estimates by considering only frequencies in the neighborhood of $\bar{\omega}$, realistic calculations of $k(T)$ must include the entire phonon distribution and combine the different contributions to w in a more refined manner than Eq. (4).

Callaway³³ has described a phenomenological procedure which, subject to certain approximation, achieves this end. In particular, his method attempts to take into account the effects of three-phonon processes (due to lattice anharmonicities) which conserve crystal momentum, the N processes, on the scattering processes we have considered so far, which do not.

As was first pointed out by Peierls³⁶ the N processes cannot by themselves contribute to w ; but by the same token, they do not cause relaxation to the equilibrium phonon distribution $n_{\text{ph}}^{(0)}(\omega)$, but rather to a distribution $n_{\text{ph}}^{(d)}(\omega)$ which is displaced from $n_{\text{ph}}^{(0)}$. In this way they affect the contributions to w of the resistive, nonconserving processes, since these depend on ω and hence on $n_{\text{ph}}(\omega)$.

Callaway has presented the results of a calculation of $k(T)$ for Ge, in which he determined the values of the parameters required for applying his procedure from the measurements of Geballe and Hull⁸ on pure, isotopically enriched Ge and on pure Ge with normal isotopic abundance. These give estimates for the strength of isotope scattering, and of umklapp and N processes combined. The collision rate corresponding to the latter is shown for the same temperatures as τ_e^{-1} in Fig. 15, labeled "phonon-phonon leak." Our calculation used these values, and added to Callaway's expression for the total collision rate $1/\tau$ (τ here corresponds to Callaway's "combined relaxation time") our

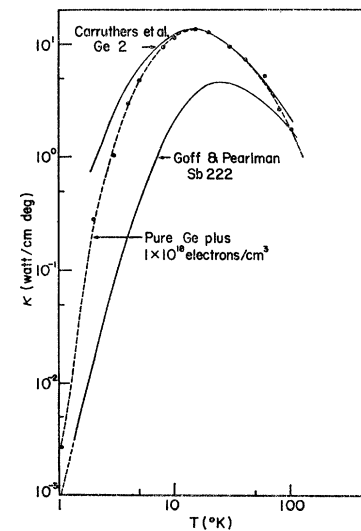


FIG. 16. Thermal conductivity: calculated from Callaway model for pure Ge plus electron-phonon interaction with $n_{\text{ex}} = 10^{18} \text{ cm}^{-3}$.

³⁶ R. E. Peierls, *Ann. Physik* 3, 1055 (1929).

calculated values of τ_c^{-1} which are plotted in Fig. 15. The results of this calculation are shown in Fig. 16, where they are compared with $k(T)$ for a sample of pure Ge² and also our sample Sb 222, which has about the same electron concentration as the artificial case for which our calculation was made. It appears that the observed magnitude of $k(T)$ in the presence of phonon-conduction electron scattering is reproduced only at the lowest temperatures and near 100°K. However, the agreement at the high-temperature end may be fortuitous, since Ziman's calculation³⁴ of τ_c^{-1} is based on a degenerate electron gas, while the degeneracy temperature for Sb 222 is 80°K. In particular the calculation does not provide any indication of a decrease in k in the neighborhood of T_M sufficient to account for the observed enhancement of k in the compensated samples with $n(T)$ less than that of the corresponding (similar n_{ex}) single-doped samples. While this may indicate that the effect is spurious, it is also possible that the approximations inherent in Callaway's method are responsible.

Indeed, the method Callaway uses to incorporate the effects of N processes suggests a refinement that may be required in order for his calculation to be appropriate for free-electron-phonon collisions. His technique is to replace the combined relaxation time, which is similar to a relaxation time that would follow from Eq. (4), by a corrected value τ' given by

$$\tau' = (1 + \beta_1 / \tau_N), \quad (12)$$

where τ_N is the relaxation time (to the displaced distribution $n_{ph}^{(d)}$) due to the N processes and β_1 is a parameter which measures the effect on the resistive process of the displacement of n_{ph} due to the N processes. Now Eq. (9) shows that in the scattering we have attempted to include an additional momentum-conserving condition, namely one for the electron-phonon system jointly. Hence there arises still an additional displacement of n_{ph} , the effect of which might be described by modifying τ still further, to $\tau''(\tau, \beta_1, \tau_N, \beta_2, \tau_c)$, where β_2 measures the effect of the new displacement of n_{ph} , after the fashion of β_1 . The form of τ'' would be considerably more complicated than that of Eq. (12) and we have not pursued this matter further.

It should be pointed out that an argument similar to that just given and relating to the effect of momentum conservation as required by Eq. (9) has been given by Klemens³⁷ in connection with an explanation of the validity of the Bloch theory of electrical resistivity at low temperatures, where electron-phonon umklapp processes do not occur.

B. Effect of Compensation on Donor Levels

(1) Thermal conductivity. Implicit in the phenomenological discussion of w_{ep} in Sec. A.(2) above was the

assumption that the donor states are similar in the compensated and single-doped material. The necessity for this assumption, based on the equality of w_{ep} for equal n_{ex} in the two cases, is reinforced by the observation that w_{ep} is drastically modified by the difference in donor states between Sb and As. As we have seen it is further strengthened by the models of Keyes⁸ and of Griffin and Carruthers,⁹ which invoke electrons bound in donor states in accounting for w_{ep} . Further confirmation of this idea comes from the observation that in single-doped material of sufficiently high N_I , where the ionization energy of the donor states vanishes and the electrons are in the conduction band even at the lowest temperatures, the impurity-species effect disappears and w_{ep} is the same for Sb and As donors.

The presence of semi-isolated donor states in compensated material is somewhat surprising, however, since they all have values of n_d (roughly half N_I —see Table I) so large that before compensation the donor states were unquestionably merged with the conduction band. The addition of acceptors on compensation must therefore do more than merely drain electrons from the conduction band to the lower-lying acceptor states; it must also modify the nature of the remaining donor states. As was pointed out earlier, a similar effect has been reported by Fritzsche⁷ in *p*-type Ge. In either case, the effect may arise from a modification of the effective potential at the majority impurity ion sites resulting from the presence of a large concentration of ionized minority impurity ions.

While the strongest evidence supporting the occurrence of this effect appears to be that discussed above relating w_{ep} to n_{ex} in the compensated samples, there is further confirmation in the behavior of the electrical resistivity and of the Hall constant and the Hall mobility. We discuss this evidence here before going on to consider the thermoelectric power.

(2) Electrical resistivity. Curves of $\rho(1/T)$ have been presented in Fig. 13 with a scale chosen to emphasize the values below 20°K. The slope of the straight-line portion of each curve (low values of $1/T$) is closely related to the donor activation energy E_d for each sample. At low concentrations n_d this approaches E_1 , the impurity ionization energy, since for n_d less than about 10^{16} cm⁻³ the impurity ions are far enough apart that their electric fields do not interact appreciably with one another. At concentrations above this "isolated" range the ion fields begin to interact and E_d drops sharply with increasing n_d (transition range).^{38,39} For n_d greater than about 2×10^{17} cm⁻³ the interaction is strong enough for the impurity levels to overlap the conduction band and E_d drops to zero (merged case). These three ranges are all represented in Fig. 13: Sb 172 (isolated), Sb 207 (transition), and Sb 187,222,30 (merged). The electron concentration in the last three

³⁷ P. G. Klemens, Proc. Phys. Soc. (London) **A64**, 1030 (1951).

³⁸ P. P. Debye and E. M. Conwell, Phys. Rev. **93**, 693 (1954).

³⁹ G. W. Lehman and H. M. James, Phys. Rev. **100**, 1698 (1955).

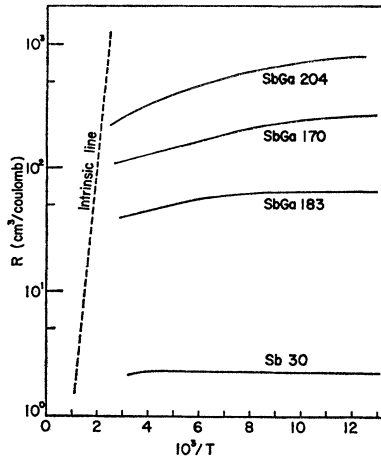


FIG. 17. Hall constant of the compensated Sb-doped samples at high temperatures.

samples is so high that the electron gas in the conduction band is degenerate in the temperature range below 10°K . The degeneracy temperature, which for a four-valley conduction band and $m^* = 0.22m_0$ is given by $T_d = 7.56 \times 10^{-11} \times (n_{\text{ex}})^{2/3} \text{ }^\circ\text{K}$, is above 15°K for all these samples.

For As ions E_d is about 40% higher than for Sb, which has the consequence that the curve for As 223I has a steeper slope than that for Sb 207 although both have about the same impurity concentration. Also, since the Bohr radius of the impurity states, $r_B = e^2/2\epsilon E_d$, where ϵ is the dielectric constant of Ge, is correspondingly smaller for As than for Sb, the effective interaction of the ion fields commences at lower concentrations for Sb than for As. Thus As 233I is still in the transition range, while Sb 187, although its impurity concentration is comparable, has already reached the merged case and at 2°K has a resistivity lower by seven orders of magnitude. If the impurity states in As 233I were in the conduction band this sample would also exhibit degenerate behavior, since T_D for this concentration is about 20°K . Arsenic 226, with impurity concentration about 8 times larger, has apparently reached the merged range and is degenerate as well ($T_D = 70^\circ\text{K}$).

All three of the compensated samples have donor concentrations well within the range corresponding to the merged case for Sb-doped samples and SbGa 183 has n_{ex} in this range as well. In fact, if the impurity levels in these samples were merged with the conduction band all of them would have degenerate conduction electrons for $1/T > 0.2$. Instead, they all have the $\rho(1/T)$ behavior which is typical of the single-doped samples in the transition concentration range, rather than the merged and degenerate case.

However, they do exhibit differences in two important respects from the three single-doped samples in the transition concentration range. Figure 13 shows that for the single-doped samples in the neighborhood of 10°K the slope of $\rho(1/T)$ changes rather sharply from

the higher value related to E_d to a much lower value. This has been interpreted^{40,41} as marking the transition from the higher temperature region in which the current is carried by electrons in the conduction band to a lower temperature region in which it is carried in "hopping" transitions^{42,43} between impurity states. Despite the fact that this latter process has very low mobility it becomes dominant at low enough temperatures because of the exponential depopulation of electrons from the conduction band. The low slope of $\rho(1/T)$ in this "impurity band" conduction range can be described in terms of an energy $E_h (< E_d)$ which is related to the transition probabilities in the hopping process.

The compensated samples show no such sharp transition from a high to a low slope in their $\rho(1/T)$ curves. Instead, these curves have curvature everywhere, with continuously decreasing slope. For this reason it is not really possible to assign an unambiguous value to either E_d or E_h from any portion of these curves. This would indicate that the transition probabilities between donor states in the compensated samples are not identical with those in the single-doped samples, although in both cases the states involved are in the energy gap. A further indication of this difference is seen from the fact that SbGa 204 has significantly lower resistivity below about 10°K than Sb 207 despite the fact that both samples have about the same n_{ex} .

We have seen above, however, that the phonon-electron interaction responsible for w_{ep} must depend on the wave function of the donor states, since w_{ep} is different for As and Sb donors. Hence the donor states present after compensation must be similar to those in the single-doped material of equal n_{ex} , despite the fact that as we have seen the matrix elements governing transitions between them are different. Unfortunately, the calculations of Keyes and of Griffin and Carruthers are too complex to allow an estimate to be made of the degree of difference that could exist and still permit the observed agreement in w_{ep} .

(3) Hall coefficient and Hall mobility. Curves of $\mu_H(T)$ between 77 and 400°K for the compensated samples and for a companion sample to Sb 30 (cut from the same ingot) have been given in Fig. 1; Fig. 17 shows $R(T)$ for the same samples in the same temperature range. For Sb 30, as would be expected from our discussion of the electrical resistivity, R is independent of T , so n is constant and the electrons are in the conduction band; also μ_H is independent of T , corresponding to degenerate electrons.

The $T^{3/2}$ proportionality of μ_H for the compensated samples below the maximum corresponds as discussed above (see Sec. II. D2) to dominant IIS for non-degenerate electrons. The temperature region under

⁴⁰ C. S. Hung and J. R. Gliessman, Phys. Rev. **96**, 1226 (1954).

⁴¹ H. Fritzsche, Phys. Rev. **99**, 406 (1955).

⁴² N. F. Mott, Can. J. Phys. **34**, 1356 (1956).

⁴³ N. F. Mott and W. D. Twose, Advan. Phys. **10**, 107 (1961).

consideration is well above T_D for these samples, so this result would be expected regardless of the location of the energy levels involved. At temperatures above the maximum in μ_H the curves for the compensated sample appear to be approaching proportionality to $T^{-3/2}$, which is characteristic of lattice scattering (LS).

The temperature dependence of R for the compensated sample (Fig. 17) cannot be explained so simply. The ratio $R(77^\circ\text{K})/R(400^\circ\text{K})$ is 0.97 for Sb 30, while it is 1.6 for SbGa 183, 2.3 for SbGa 170, and 3.4 for SbGa 204. According to Eq. (1) these numbers are the ratios $[(n/r)(400^\circ\text{K})]/[(n/r)(77^\circ\text{K})]$. We have seen that the dominant scattering mechanism is LS at the higher temperature and IIS at the lower but the decrease in r expected from admixtures of these types of scattering is somewhat less than a factor of 2.⁴⁴ Hence the change in $R(T)$ in this temperature range cannot be attributed entirely to variations in r .

At sufficiently high temperatures, well above T_e , n will increase due to interband transitions. The corresponding variation in R is shown in Fig. 17 as the dotted line. Since this contribution to n is seen to be negligible for these samples below 400°K the temperature variation in R cannot be accounted for in this way either.

On the basis of our assumption that the impurity states have been removed from the conduction band we can calculate n from the condition for charge neutrality,

$$n = n_a \left\{ 1 - \left[\frac{1}{2} \exp\left(\frac{E_d - \zeta}{K_b T}\right) + 1 \right]^{-1} \right\} - n_a, \quad (13)$$

where ζ is the Fermi energy and K_b is Boltzmann's constant. We use our estimates of n_{ex} and N_I (see Tables I, II) to determine n_d and n_a . We assume that n is approximately equal to $n_d - n_a$ and much smaller than n_a . Since we have concluded that we are dealing with classical statistics we can use the relation

$$n = N_v N_c \exp(\zeta / K_b T), \quad (14)$$

where N_v is the number of valleys in the conduction band (4 for Ge) and $N_c = 2(2\pi m^* K_b T / h^2)^{3/2}$.

$$n = \frac{N_v N_c n_{\text{ex}}}{2n_a} \left[\exp\left(\frac{E_d}{K_b T}\right) + \frac{N_v N_c}{2n_a} \right]. \quad (15)$$

We choose for E_d values reported by Fritzsche¹⁴ for noncompensated samples (Sb doped) with comparable n_{ex} : 6.9 meV for SbGa 204 and 5.9 meV for SbGa 170. For SbGa 183, n_{ex} is close to the concentration at which merging is observed in single-doped samples, so E_d would be too small for a reasonable calculation. These values are used in Eq. (3) to calculate the dotted lines shown in Fig. 18.

⁴⁴ E. M. Conwell, Proc. IRE 40, 1327-37 (1952).

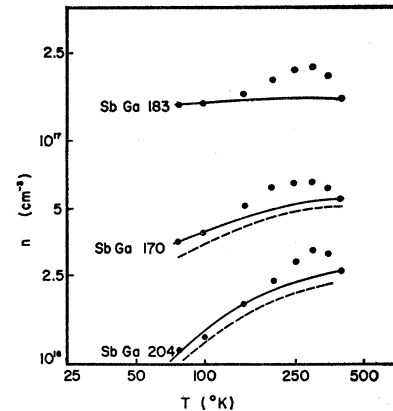


FIG. 18. Electron concentration as a function of temperature for the compensated samples.

The points plotted in the figure were calculated from Eq. (1) assuming $r=1.93$ (the value for IIS) at temperatures below 150°K and $r=1.18$ (the value for LS) at 400°K . The maximum in μ_H shows that both scattering mechanisms are important in the temperature range between these limits, and unfortunately the calculation of r presents difficulties when this is the case, since it amounts to determining the relative importance of their respective contributions to the over-all mobility. Various attempts have been made to improve on the simplest possible assumption, which is that the scattering effects simply add, which amounts to setting $\mu^{-1} = \mu_I^{-1} + \mu_L^{-1}$. We used the results of Conwell⁴⁴ who gives curves from which μ/μ_L can be calculated if μ_I/μ_L is known. Then n can be calculated from Eq. (1) using $r = (\mu_H/\mu_L)/(\mu/\mu_L)$. The points plotted in Fig. 18 were calculated in this way, but there is no physical reason to expect the maxima they exhibit. We therefore regard the maxima as an artifact of the calculation, and consider the smooth lines drawn through the values at the extremes, where r is known with greatest accuracy, as better estimates of $n(T)$. These curves will be used later in the analysis of the electronic component Q_e of the thermoelectric power.

Unfortunately, this discussion provides no unambiguous evidence concerning the location of the electron states in SbGa 183. Also, the smooth transition between w_{ep} values corresponding to bound donor scattering and to conduction-band electron scattering makes it impossible to reach a definite conclusion from the thermal conductivity data either. Thus the $\rho(1/T)$ data remains stronger confirming evidence for the inference that heavy compensation may remove donor states to the energy gap even for n_{ex} so high that in single-doped material the states would be merged with the conduction band.

C. Thermoelectric Power

(1) Isolated levels: phonon drag. Measurements on Sb-doped Ge covering a range of N_I and temperatures between 10 and 300°K have been reported by

Frederikse⁴⁵ and Geballe and Hull⁴⁶ have measured a series of relatively pure As-doped Ge samples between 20 and 300°K, and impure samples between 80 and 300°K. Thus our measurements extend these results to lower temperatures, and also extend them to compensated material. A principal reason for our interest in Q is the information it can provide on the location of electron energy levels and their occupancy as a function of T . As we have seen above in discussing $k(T)$ this information can be of importance in understanding the electron-phonon scattering mechanism, especially in the compensated samples. Because the processes involved in the samples with isolated electron levels, while similar to a certain extent to those in the samples with levels merged with the conduction band, nevertheless require rather different treatment, we consider the former case in this section and then turn briefly to the latter in the next section.

The measurements of Frederikse⁴⁵ and of Geballe and Hull⁴⁶ included the first reported observation of the phonon-drag effect, in thermoelectric power. This effect increases the thermoelectric power because the drift of charge carriers down a temperature gradient ∇T , which is responsible for the normal thermoelectric power, is enhanced by carrier collisions with phonons also drifting down ∇T . It was first suggested by Gurevich⁴⁷ and was used by Frederikse in discussing his results⁴⁵; Herring^{48,49} has since discussed it in detail.

It is clear that phonon drag should enhance Q regardless of the sign of the charge carrier. Since according to the usual convention the sign of Q is the sign of the carrier charge, we are dealing in our n -type samples with negative Q . In order to avoid excessive verbiage, however, we shall use the ellipsis "maximum in Q " for "maximum in the magnitude of Q " and in general avoid the explicit labeling of magnitudes except where confusion may result. Thus we write

$$Q = Q_e + Q_p, \quad (16)$$

where in fact each term is negative. Here Q is the total measured thermoelectric power, Q_e is the normal electronic contribution, and Q_p results from the phonon-drag effect.

Since the equilibrium phonon distribution $n_{ph}^{(0)}$ is isotropic only a displacement from it which increases its value for phonons moving down ∇T with respect to those moving up can account for Q_p . This anisotropy arises from ∇T and the displacement in n_{ph} can be described in terms of an effective relaxation time $\bar{\tau}$ to $n_{ph}^{(0)}$. In this respect it differs from the displacement of n_{ph} which we discussed at the end of the last section

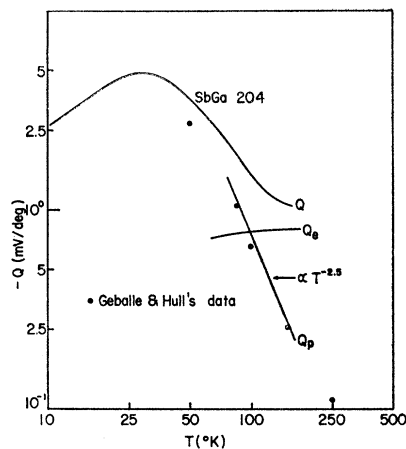


FIG. 19. Thermoelectric power: electron and phonon-drag components for SbGa 204.

in an attempt to include the effect of electron-phonon scattering in $k(T)$. In that case, since momentum-conserving collisions were involved, the resulting relaxation was to a distribution that was itself displaced from $n_{ph}^{(0)}$ so that the effect on $k(T)$ was indirect. In metals or degenerate semiconductors the effective scattering of phonons by electrons should make $\bar{\tau}$ very small, so that Q_p should not be a significant contribution to Q .

The calculation of $\bar{\tau}$ (and Q_p) presents formidable difficulties in even the most tractable cases, and unfortunately the concentrations n_{ex} and N_I in most of our samples is at or beyond the limit of validity of Herring's calculations.^{48,49} Hence we will perforce be limited here to a qualitative examination of our measurements, guided by suggestions from his results.

It might at first glance be expected from the argument given above on the origin of $\bar{\tau}$ that it would be close to the relaxation time governing k . The latter can be found by inverting Eq. (3) and writing it as

$$\tau^{(k)} = 3k/Cv^2. \quad (17)$$

By an ingenious argument Herring shows⁴⁸ that in fact $\bar{\tau}$ is much longer than $\tau^{(k)}$ in semiconductors, and is related to the rate at which low-frequency phonons transfer crystal momentum to high-frequency phonons, which would be appropriate in a momentum-conserving process such as that mentioned above, rather than a resistive process. The separation between low- and high-frequency phonons is made at phonon wave vector $q_0 = K'$, where K' is the wave vector of thermal electrons in the material. The distinction arises because phonons with $q > q_0$ cannot interact with electrons and still satisfy the conservation conditions given by Eqs. (9) and (10), while except at high temperatures electron umklapp collisions are unlikely. The conclusion that $\bar{\tau} > \tau^{(k)}$, based on these considerations, requires that momentum-dissipating collisions are unimportant both in the electron system (negligible IIS) and for the low-

⁴⁵ H. P. R. Frederikse, Phys. Rev. **92**, 248-52 (1954).

⁴⁶ T. H. Geballe and G. W. Hull, Phys. Rev. **94**, 1134 (1954).

⁴⁷ L. Gurevich, J. Phys. (USSR) **9**, 477 (1945); **10**, 67 (1946).

⁴⁸ C. Herring, Phys. Rev. **96**, 1163 (1954).

⁴⁹ C. Herring, in *Semiconductors and Phosphors*, edited by M. Schön and H. Welker (Interscience Publishers, Inc., New York, 1958), pp. 184-235.

frequency phonons. At low temperatures, boundary scattering becomes important and τ approaches $\tau^{(k)}$ which for the cases Herring considers is $\approx \tau_b$. As we have seen, this will not be the case in our samples, where w_{ep} exceeds w_b down to the lowest temperatures measured.

The result of the argument given above is that a maximum is expected in Q_p and hence in Q if Q_p exceeds Q_e , since the latter is much less temperature dependent (see below).

Such a maximum is exhibited in the nondegenerate Sb-doped samples (Fig. 6) and in the compensated samples as well (Fig. 8), with the magnitude decreasing with increasing n_{ex} as expected from Herring's result⁴⁸ that Q_p will saturate at high n . The values agree well with those reported by Frederikse⁴⁵ for similar single-doped samples. In order to calculate Q_p for the compensated samples from Eq. (16) we found Q_e by using the relation⁵⁰

$$Q_e = - (K_b/e)(a-z), \quad (18)$$

where e is the magnitude of the electronic charge, z is the Fermi level, and a is the average energy of conduction electrons measured with respect to the band edge, both z and a being measured in units of K_bT . Values of z were derived from Eq. (14) using $n(T)$ calculated from Eq. (15) and plotted in Fig. 18. Since IIS predominates in these samples below 200°K (see Fig. 1) and $n = N_I$, $a = 4$.⁴⁸ These values of Q_e are plotted in Figs. 19 and 20, respectively, together with Q and Q_p calculated from Eq. (16). The points in the figures were calculated from measurements on single-doped As samples by Geballe and Hull⁴⁶ and the agreement is surprising in view of the fact that Herring's calculation predicts a strong influence on Q_p from IIS. The lack

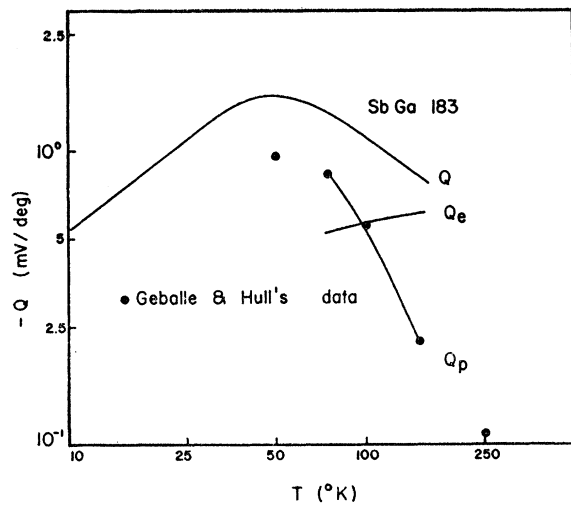


FIG. 20. Thermoelectric power: electron and phonon-drag components for SbGa 183.

⁵⁰ V. A. Johnson and K. Lark-Horovitz, Phys. Rev. 69, 259 (1946).

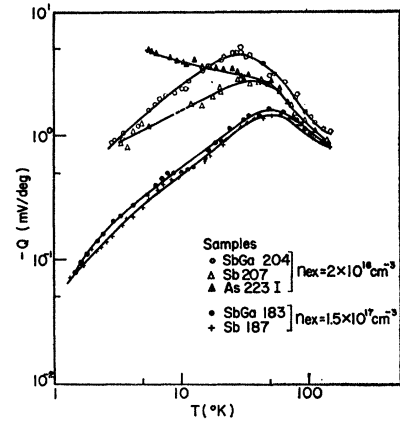


FIG. 21. Thermoelectric power: comparison of noncompensated (Sb and As doped) and compensated samples.

of such an effect is also seen in Fig. 21, where SbGa 183 and Sb 187, differing in N_I by a factor larger than 20, are seen to have essentially the same Q .

This comparison requires that the two samples have similar values of n . We noted above in Sec. IV.B that SbGa 183, the least pure of all the samples, had $n(T)$ almost constant between 77 and 400°K. Since this temperature range is above T_e for Sb 187 and the two samples have similar n_{ex} this condition should be met. In contrast, SbGa 204 was noted to have a strongly decreasing $n(T)$ in the same temperature range. We see in Fig. 21 that Q for this sample exceeds that of its companion (similar n_{ex}) between 100 and about 3°K, where the values become equal although the temperature dependence is not. This can be understood if the insensitivity to N_I in Q_p holds here also, since smaller n , by making z more negative, will increase Q_e and hence Q . Thus the assumption of a smaller n in the compensated samples of higher purity than SbGa 183, by which we sought to account for the enhancement in their $k(T)$ with respect to the similar uncompensated samples between 10 and 80°K, is borne out. The lack of an excess in Q of SbGa 183 compared to its companion sample would thus correspond to the lack of enhancement in k , see Fig. 10.

This argument would suggest an impurity-species effect operating through the influence on Q_e (through z) of differences in activation energies E_a . In fact, the species effect is surprisingly more striking than would be expected from an effect of this sort. As shown in Fig. 21, Q for the purest sample, As 223I, increases with decreasing temperature down to the lowest temperature measured, with only a change of slope in the temperature region where the maximum in Q_p would be expected. The curve drawn in Fig. 22 for a somewhat less pure As-doped sample, which has a similar negative slope in $Q(T)$ at the lowest temperatures but also a region of positive slope between 20 and 50°K, suggests that the expected decrease in Q_p below its maximum is being overcome by some competing process which is stronger in the more pure sample. The

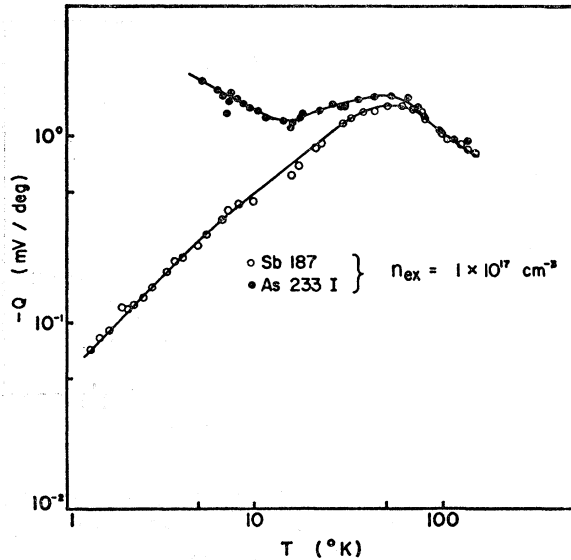


FIG. 22. Thermoelectric power: comparison of Sb- and As-doped noncompensated samples.

fact that this effect seems to be related to impurity species makes it unlikely that it is connected with the onset of conduction in the impurity band. Such an origin is also argued against by the circumstance that impurity band conduction in these samples seems to commence only at rather lower temperatures than the observed increase in Q (see Fig. 13) and also by the very low mobility in the impurity band. Thus the possibility cannot be excluded that the curious behavior exhibited by Q in the purer As-doped samples is in fact related to Q_p .

In this connection it may be worth recalling that an impurity-species effect was also observed in the temperature dependence of $k(T)$, see Table III. The exponent m defined in Eq. (2) was consistently lower for the As-doped samples than for the Sb-doped, except in the very impure samples with merged levels, for which m seemed to be approaching the high value observed for all the Sb-doped samples. Now from Eq. (17) above, the exponent in the T dependence of $\tau^{(k)}$ will be given by $m-3$ in the Debye limit. It is thus higher by about unity for Sb-doped than for As-doped samples. Recalling that Herring's τ approaches $\tau^{(k)}$ in the low-temperature limit, we see that this very crude argument does not disagree with our measurements. It is also possible to see that negative slopes such as are observed are at least not excluded. A simple argument by Herring gives

$$Q_p \approx f v^2 \bar{\tau} / \mu T, \quad (19)$$

where f is the fraction of electron momentum given up to low-frequency phonons and μ is the electron mobility. Now μ should be independent of T in impurity band conduction, although it depends on the impurity species through dependence on orbit size of

the bound donors.⁵¹ The observed negative slopes in Q for the As-doped samples are somewhat smaller than the -1 exponent that would follow from this argument with $m=3$ (-0.3 for As 223I; -0.5 for As 233I) but it is possible that f may be somewhat temperature-dependent. This might arise as a result of the influence of w_{ep} in providing collision processes which compete with those conserving momentum. Since we are dealing with an effect which commences above T_M it must be the conduction electron, not the bound donor process, which determines w_{ep} . Unfortunately, this is the case in which we have been unsuccessful in establishing the contribution to w , so we have no independent confirmation of such an effect on f and can say nothing about the way in which f might be affected.

One further peculiarity may be noted. The (positive) slopes of Q below the maximum also vary from sample to sample in Sb-doped material; here higher values of this slope are associated with lower values of m .

(2) Merged levels: semimetal case. We have just concluded that it is possible that conduction electron-phonon scattering in the neighborhood of and above T_M , the effects of which could be seen in k , could also be associated with the peculiarities observed in Q_p at those temperatures in the purer single-doped samples, and that if this were the case, the effect would be impurity-species-dependent. Now in principle this mode of scattering is effective also in the heavily doped samples, in which the donor electron levels are merged with those of the conduction band. If this is so, this may be the source of the observed depression of k_M and of $k(T)$ in the neighborhood of T_M in these samples, although our attempt to verify this possibility using the Callaway³³ method in a sample with $n=10^{18}$ cm^{-3} did not succeed. Another consequence, in view of the observations discussed in the last section, might be a species effect in the thermoelectric power. In this case, however, n is so large that the saturation effect noted by Herring⁴⁸ will depress Q_p and we are left with $Q \approx Q_e$.

We do not attempt the kind of detailed study which one would expect to be necessary for obtaining an accurate view of the behavior of Q_e . Instead we examine whether a simpler approach based on the theory of Q

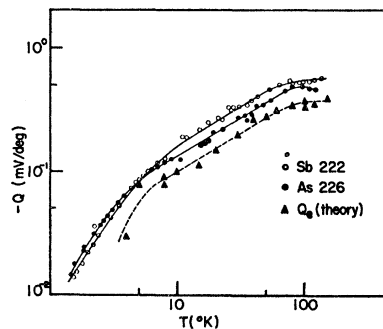


FIG. 23. Thermoelectric power: comparison of degenerate samples, $n_{ex}=10^{18}$ cm^{-3} , Sb and As doped.

⁵¹ R. K. Ray and H. Y. Fan, Phys. Rev. **121**, 768 (1961).

in semimetals⁵² can give any insight at all into the problem. Since T_D is about 75°K for $n=10^{18}$ cm⁻³ our two samples As 226 ($N_I=8.8\times 10^{17}$ cm⁻³) and Sb 222 ($N_I=11\times 10^{17}$ cm⁻³) should be amendable to the semimetal model from about 100°K down to the lowest temperatures measured.

Q for both these samples is plotted in Fig. 23, and it is seen that although $Q(T)$ is very similar for both, there is a much larger difference between them from about 10 to 80°K than at either end of the temperature range plotted. In calculating Q_e we cannot expect to find an effect of this sort directly, since the theory does not contain any explicit species parameters, unlike for instance, bound-donor electron scattering with its parameter $4\Delta_e$. However, we may hope to infer it from indirect effects. The relevant expression for Q_e is that given in Eq. (18), where now z is determined from

$$n = N_v (2m^* K_b T)^{3/2} F_{1/2}(z) / 2\pi^2 h^3, \quad (20)$$

where N_v is the number of valleys in the conduction band (4 for Ge) $m^*=0.22m_0$ and $F_{1/2}(z)$ is a Fermi function of the form

$$F_i(z) = \int_0^\infty \frac{(z')^i dz'}{\exp(z'-z)+1}. \quad (21)$$

Now a is determined from

$$a = (5+2p)F_{p+3/2} / (3+2p)F_{p+1/2}, \quad (22)$$

where p is the exponent in the assumed energy dependence of the electron relaxation time. The limits of p which are relevant in the case we are considering

are $p=\frac{3}{2}$ (IIS) and $p=-\frac{1}{2}$ (LS). Since the precise admixture of the two types of scattering may depend on the details of w_{ep} it is here that its influence in Q_e may occur. To investigate the sensitivity of Q_e to p , we made the calculation with $p=\frac{3}{2}$ for $T<8^\circ\text{K}$ (LS); for $p=\frac{3}{2}$ and $p=1.0$ at 8°K (admixture of IIS and LS); $p=1.0$ from 8 to 80°K; $p=1.0$ and $p=0.0$ (larger admixture of LS) at 100°K; $p=0$ above 100°K.

The tabulation by Beer *et al.*⁵³ was used for the F_i of half-integral value, and of Newman⁵⁴ for F_i of integral order. The double points plotted in Fig. 23 at 8 and 80°K show that the range of variation chosen in p is not sufficient to account for the observed difference in Q . It would not be worthwhile to attempt to refine the calculation by using the nominal values of n for the two samples, rather than the value 10^{18} cm⁻³ for both. In the first place, the difference in nominal values is just at the limit of accuracy in Sec. II. Also, a difference from this source would persist to the lowest temperatures. In any event, such a modification would make the difference in $Q_e(\text{calc})$ have the wrong sign. Below T_D , z is positive so that increasing n , which increases z , will diminish the magnitude of Q_e . Hence a calculation on this basis would give a higher curve for As 226 than for Sb 222, rather than the ordering which is observed. It is thus apparent that a considerably more refined calculation than simple semimetal theory is required to describe the behavior of these degenerate samples.

⁵³ A. C. Beer, M. N. Chase, and P. F. Choquard, *Helv. Phys. Acta* **28**, 529 (1955).

⁵⁴ P. A. Newman, Jr., U. S. Army Signal Research and Development Laboratory USASRD Technical Report No. 2154, 1960 (unpublished).

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