

Low-Temperature Thermal Resistance of *n*-Type Germanium

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It is proposed that the scattering of phonons by donors in germanium at low temperatures results from the large effect of strain on the energy of an electron in a hydrogen-like donor state. A calculation of the thermal conductivity with this scattering mechanism is presented. Reasonable agreement with the following features of the observed thermal conductivity is obtained: the very large scattering power of donors, the difference between the scattering powers of antimony and arsenic, a temperature dependence of thermal conductivity stronger than T^3 , and a dependence of the scattering on number of occupied donors rather than on the total impurity concentration.

I. INTRODUCTION

RECENT measurements of the thermal conductivity of germanium at low temperatures have shown some striking features which are not explained by established theories of phonon scattering.¹⁻³ In particular, (1) the scattering of phonons by small concentrations of donors or acceptors is far too strong to be accounted for by the usual mechanisms of scattering by impurity atoms; (2) at very low temperatures the thermal conductivity of certain specimens increases with the temperature more strongly than T^3 , a result which also is inconsistent with the usual theories of scattering by impurities.

Carruthers *et al.* interpreted these observations as evidence for scattering of the phonons by excess carriers (electrons or holes) introduced by the electrically active impurity.⁴ The model which they used assumed that the excess carriers were in a band of the usual type at very low temperatures. While this model is quite consistent with other evidence for impurity concentrations greater than about $2 \times 10^{17} \text{ cm}^{-3}$, various theoretical and experimental studies of the electrical conductivity at low temperatures show that in the lower part of the concentration range spanned by the thermal conductivity experiments the properties of the "impurity band" are more appropriately regarded as arising from relatively weak interaction between electronic states which are localized on impurity atoms.⁵⁻¹⁰ For example, the electrical conductivity is an activated function of

temperature, is strongly frequency dependent,⁹ and shows a magnetoresistance many orders of magnitude greater than that expected on the basis of a band model.¹⁰ Thus, an explanation of the thermal conductivity based on the localized model would be more satisfying. In this communication we show that a calculation of phonon scattering by donors based on the accepted model of a donor state reproduces, at least semiquantitatively, the unusual features of the thermal resistance of *n*-type germanium.¹¹

Qualitative Discussion

The first effect mentioned above, the great strength of the scattering of phonons by donors, results from the large effect of strain on the energy of an electron bound to a donor.¹² The ground state of a donor in germanium is fourfold degenerate in the effective-mass approximation. Deviations from the effective-mass theory split this set of states into a singlet and a triplet separated by an energy 4Δ , the "chemical shift," in the usual nomenclature.¹² The perturbation of the germanium band structure by a shear strain produces matrix elements of order of magnitude $\Xi_u \epsilon$ between the singlet state and the states of the triplet, where Ξ_u is the shear deformation potential constant and ϵ is the magnitude of the strain in the vicinity of the donor. According to second order perturbation theory, these matrix elements give rise to a term of order $(\Xi_u \epsilon)^2/4\Delta$ in the dependence of the energy of a state on the strain. However, a perturbation of the energy of a lattice by a term proportional to the square of the strain at a point produces scattering of phonons of the point defect type, as considered by Klemens^{13,14} and Pomeranchuk.¹⁵ This is the source of the scattering of phonons by donors.

Carruthers¹⁶ has suggested the possibility of phonon scattering due to the production of virtual electronic

¹ J. A. Carruthers, T. H. Geballe, H. M. Rosenberg, and J. M. Ziman, *Proc. Roy. Soc. (London)* **A238**, 502 (1957).

² E. Fagen, J. F. Goff, and N. Pearlman, *Phys. Rev.* **94**, 1415 (1954); N. Pearlman and J. F. Goff, *Bull. Am. Phys. Soc.* **4**, 410 (1959).

³ J. F. Goff and N. Pearlman, in *Proceedings of the Seventh International Conference on Low-Temperature Physics*, Toronto, 1960 (University of Toronto Press, to be published).

⁴ J. M. Ziman, *Phil. Mag.* **1**, 191 (1956).

⁵ N. F. Mott, *Can. J. Phys.* **34**, 1356 (1956); T. Kasuya and S. Koide, *J. Phys. Soc. Japan* **13**, 1287 (1958); E. M. Conwell, *Phys. Rev.* **103**, 51 (1956); P. J. Price, *IBM J. Research and Develop.* **2**, 123 (1958).

⁶ A. Miller and E. Abrahams, *Phys. Rev.* **120**, 745 (1960).

⁷ H. Fritzsche, *Phys. Rev.* **99**, 406 (1955).

⁸ H. Fritzsche and M. Cuevas, *Phys. Rev.* **119**, 1238 (1960).

⁹ M. Pollak and T. H. Geballe, *Bull. Am. Phys. Soc.* **5**, 159 (1960).

¹⁰ R. W. Keyes and R. J. Sladek, *Bull. Am. Phys. Soc.* **5**, 358 (1960); R. J. Sladek and R. W. Keyes, *Phys. Rev.* **122**, 437 (1961).

¹¹ A report based on preliminary phases of this work has been presented to the Physical Society: R. W. Keyes, *Bull. Am. Phys. Soc.* **5**, 264 (1960).

¹² P. J. Price, *Phys. Rev.* **104**, 1223 (1956).

¹³ P. G. Klemens, *Proc. Phys. Soc. (London)* **A68**, 1113 (1955).

¹⁴ P. G. Klemens, in *Solid State Physics*, edited by F. Seitz and D. Turnbull, (Academic Press, Inc., New York, 1958), Vol. 7.

¹⁵ I. Pomeranchuk, *J. Phys. (U.S.S.R.)* **6**, 237 (1942).

¹⁶ P. Carruthers, *Rev. Modern Phys.* **33**, 92 (1961).

transitions by a phonon. The scattering can be regarded as arising from virtual transitions between the singlet and triplet donor levels.

It is easy to see that the donor scattering is very strong compared to the sources of point-defect scattering usually considered. For example, comparing the perturbation of the lattice energy by a donor with that due to the difference in mass between a substitutional atom and a host lattice atom,^{13,14} we see that the replacement

$$\Delta M v^2 \epsilon^2 \rightarrow (\Xi_u^2/4\Delta)\epsilon^2,$$

has been made, where v is the elastic wave velocity. For an antimony atom in germanium $\Delta M v^2 \approx 10$ ev while $\Xi_u^2/4\Delta \approx 5 \times 10^5$ ev.

The second effect mentioned above, the increase of thermal conductivity with temperature at a rate greater than T^3 , we attribute to the fact that the donor scattering as described above is only effective for phonons with wavelength long compared to the effective Bohr radius of the bound state; for shorter wavelengths the donor state cannot be considered as a point defect. The scattering by the donor becomes very small at short wavelengths because the value of the strain averaged over the electronic wave function decreases very rapidly with decreasing wavelength for wavelengths less than the diameter of the bound state. Thus there is a range of phonon energies in which the phonon relaxation time is a rapidly increasing function of phonon energy. This phenomenon can produce a temperature range in which the average phonon mean free path is an increasing function of temperature and in which the thermal conductivity therefore increases more rapidly than T^3 .

In the next sections we will present a more quantitative version of the arguments of this section.

II. PHONON SCATTERING BY AN ELECTRON IN THE SINGLET STATE

The matrix of the Hamiltonian of the ground states of an electron bound to a donor atom in germanium is

$$H = \begin{vmatrix} u^{(1)} & -\Delta & -\Delta & -\Delta \\ -\Delta & u^{(2)} & -\Delta & -\Delta \\ -\Delta & -\Delta & u^{(3)} & -\Delta \\ -\Delta & -\Delta & -\Delta & u^{(4)} \end{vmatrix}, \quad (2.1)$$

in the formulation of the problem of the effect of strain on the ground states described by Price.¹² Here the zero of energy has been chosen as the energy of a hydrogen-like state¹⁷ derived from a single valley in the "decoupled" approximation and the basis of the representation (2.1) is the set of decoupled wave functions. The quantity $u^{(i)}$ is the displacement of the energy of the "decoupled" state arising from valley (i) by the

strain, and has the value

$$u^{(i)} = \int \Xi^{(i)} : \epsilon(\mathbf{r}) \psi^{(i)2} dV. \quad (2.2)$$

Here $\Xi^{(i)}$ is the deformation potential tensor,¹⁸ $\epsilon(\mathbf{r})$ is the strain tensor, which is a function of position, and $\psi^{(i)}$ is the envelope wave function¹⁷ of the hydrogen-like state associated with valley (i). We treat (2.2) only in the isotropic approximation used by Hasegawa,¹⁹ according to which the effect of the averaging over the electronic wave function in (2.2) is to reduce the deformation potential tensor by a factor $(1 + \frac{1}{4}a^*k^2)^{-2}$ for a phonon with wave vector of magnitude k . Here a^* is an appropriately averaged Bohr radius of the hydrogen-like donor state.

The Δ 's in Eq. (2.1) are matrix elements between the decoupled hydrogen-like wave functions. For further discussion and justification of Eq. (2.1) the reader is referred to the paper of Price¹² and the references therein. The energy levels of the Hamiltonian of Eq. (2.1) in the unstrained state are $E = -3\Delta$ and $E = \Delta$ (triply degenerate). The experiments of Fritzsche²⁰ and others²¹ show that Δ is positive so that the singlet state is lowest in energy for both arsenic and antimony donors. The best demonstration of the adequacy of Eq. (2.1) to describe the effects of strain on the donor states in germanium is furnished by the low-temperature piezoresistance experiments of Fritzsche.²⁰ These experiments can be very accurately fitted by the model defined by Eq. (2.1) and provide a good determination of the parameters of the model.

The strain of interest here is that due to the phonons and we will calculate the phonon scattering for electrons in the lowest, or singlet, state. From the Hamiltonian of Eq. (2.1), the energy of an electron in the lowest state to terms of second order in the $u^{(i)}$ is found to be

$$E = -3\Delta + (1/4)(u^{(1)} + u^{(2)} + u^{(3)} + u^{(4)}) - (1/64\Delta)[4(u^{(1)2} + u^{(2)2} + u^{(3)2} + u^{(4)2}) - (u^{(1)} + u^{(2)} + u^{(3)} + u^{(4)})^2]. \quad (2.3)$$

From this point on, the calculation of the thermal resistance can be continued by following closely the methods of Klemens.^{13,14} The strain, ϵ , in Eq. (2.2) is expanded in terms of phonons and the resultant $u^{(i)}$ are substituted in Eq. (2.3). The phonon scattering comes from the last part of Eq. (2.3), the part which depends quadratically on the $u^{(i)}$ and on ϵ . The details in the present problem are somewhat more tedious than in the problems considered by Klemens because of the

¹⁸ C. Herring and E. Vogt, Phys. Rev. **101**, 944 (1956).

¹⁹ H. Hasegawa, Phys. Rev. **118**, 1523 (1960).

²⁰ H. Fritzsche, Phys. Rev. **115**, 336 (1959); **120**, 1120 (1960).

²¹ G. Weinreich, W. S. Boyle, H. G. White, and K. F. Rodgers, Phys. Rev. Letters **2**, 96 (1959); **3**, 244 (1959); D. K. Wilson and G. Feher, Bull. Am. Phys. Soc. **5**, 60 (1960).

¹⁷ C. Kittel and A. H. Mitchell, Phys. Rev. **96**, 1488 (1954); M. Lampert, Phys. Rev. **97**, 352 (1955); W. Kohn and J. M. Luttinger, Phys. Rev. **97**, 1721 (1955); **98**, 915 (1955).

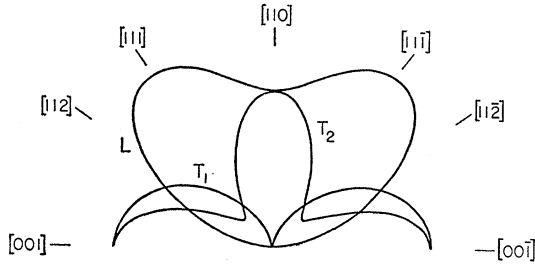


FIG. 1. A polar plot of the anisotropy factor, $\phi(\mathbf{e}, \mathbf{k})$, Eq. (2.5), which appears in the phonon scattering rate, Eq. (2.4). The plot refers to phonons with $\mathbf{k} \perp [110]$. The values for the longitudinal phonon ($\mathbf{e} \parallel \mathbf{k}$) are labelled L and those for the transverse phonons T_1 ($\mathbf{e} \parallel [110]$) and T_2 ($\mathbf{e} \perp [110]$). The resolution of the two transverse branches is arbitrary with the assumption of elastic isotropy used in the text. However, in a cubic crystal the two transverse phonons with $\mathbf{k} \parallel [110]$ are resolved as shown here.

anisotropy in the dependence of E , Eq. (2.3), on the wave vectors and polarization vectors of the phonons. The principal additional complication in the calculation is the necessity for including angular variables in the integration of the phonon transition probabilities over the possible final phonon states. Significant numerical factors which reduce the effective strength of the perturbation of the phonon energies by a factor of about 30 with respect to the order of magnitude estimate given in the previous section are introduced in this process. We assume for simplicity that the crystal is elastically isotropic.

We find for the relaxation time of a phonon of circular frequency ω in a crystal containing N_I donors per unit volume

$$\frac{1}{\tau} = \frac{N_I}{\pi \rho^2} \left(\frac{\Xi_u^2}{\Delta} \right)^2 \frac{\omega^4}{2^3 3^4 5} \left[\frac{2}{3 v_L^7} + \frac{1}{v_T^7} \right] \phi(\mathbf{e}, \mathbf{k}) \chi(\mathbf{k}). \quad (2.4)$$

Here ρ is the density of the crystal, Ξ_u is the shear deformation potential constant,¹⁸ and v_L and v_T are, respectively, the velocities of longitudinal and transverse elastic waves. $\phi(\mathbf{e}, \mathbf{k})$ is a dimensionless anisotropy factor which has the value

$$\phi(\mathbf{e}, \mathbf{k}) = 1 + k^{-2} [(\mathbf{k} \cdot \mathbf{e})^2 - 2(e_x^2 k_x^2 + e_y^2 k_y^2 + e_z^2 k_z^2)]. \quad (2.5)$$

Here \mathbf{e} is the polarization vector of the phonon and the (x, y, z) axes are the fourfold axes of the crystal. The form of ϕ when \mathbf{k} is in a (110) plane is shown in the polar plot of Fig. 1. The factor $\chi(\mathbf{k})$ in Eq. (2.4) represents the effect of the cutoff of the scattering at wavelengths short compared to the extent of the electronic wave function. In accord with the discussion of this effect given in connection with Eq. (2.2), this factor is

$$\chi(\mathbf{k}) = (1 + \frac{1}{4} k^2 a^{*2})^{-8}. \quad (2.6)$$

Note that, apart from the factors $\phi(\mathbf{e}, \mathbf{k})$ and $\chi(\mathbf{k})$, the expression for τ in Eq. (2.4) is a form of the formula for point-defect scattering, since τ is proportional to ω^{-4} .

III. DISCUSSION OF THE THERMAL CONDUCTIVITY

In this section we attempt to evaluate the effect of the phonon scattering described by Eq. (2.4) on the thermal conductivity of germanium in the liquid helium temperature range and we compare the results with the experimental curves given by Goff and Pearlman.³

A. Role of the Triplet Level

Throughout part of the temperature range of interest an appreciable number of electrons are thermally excited from the singlet to the triplet state of the donor; at 4.2°K about $\frac{1}{3}$ of the electrons are in the triplet in the case of antimony donor. We have not worked out the theory of scattering by the triplet in the same detail as that by the singlet. It is to be expected that the scattering by an electron in the triplet will be about the same as that due to an electron in the singlet, however. This follows from the fact that the trace of the Hamiltonian, Eq. (2.1), contains no term quadratic in the strain. Therefore, the net quadratic term in the energies of the triplet levels must be of exactly the same size as the quadratic term in the singlet energy. The scattering by electrons in the triplet states must therefore be roughly the same as that due to electrons in the singlet. We will neglect the difference here and assume that all of the electrons scatter phonons according to Eq. (2.4). This approximation can only have a serious effect on the results near 4.2°K, since in the low-temperature part of the range of interest practically all of the electrons are in the singlet level.

B. Low-Energy Divergence

A straightforward calculation of thermal conductivity with scattering by point defects as the only source of scattering, i.e., with $\tau \sim \omega^{-4}$, leads to a divergence of the heat current due to the contribution of the low-energy phonons to the current integral. This is also true of the τ of Eq. (2.4) which is proportional to ω^{-4} for low-energy phonons. This divergence must be removed by the introduction of some other scattering mechanism which limits τ at low phonon energies into the theory. Klemens¹³ introduced phonon-phonon scattering to cut off τ at low energies and included the effect in the theory by assuming that phonon-phonon " N -processes" transfer momentum from phonons of energy less than kT to higher energy phonons in such a way that the effective τ for momentum loss by phonons of energy less than kT is equal to the τ for phonons with energy equal to kT . Berman *et al.*²² have modified the method of Klemens¹³ by using a variational procedure to determine the point of division between the two regions. Slack,²³ in a study of point-

²² R. Berman, P. T. Nettley, F. W. Sheard, A. N. Spencer, R. W. H. Stevenson, and J. M. Ziman, Proc. Roy. Soc. (London) **A253**, 403 (1959).

²³ G. A. Slack, Phys. Rev. **105**, 832 (1957).

defect scattering, included the effect of boundary scattering, which is sufficient to prevent the divergence of the thermal current, but also included phonon-phonon scattering in the same way as Klemens, namely, by dividing the heat current integral into parts $\hbar\omega > kT$ and $\hbar\omega < kT$. In the present case, in which we are concerned with the temperature range below 4.2°K, it is satisfactory to entirely neglect phonon-phonon scattering and calculate the thermal resistance due to the combination of donor-electron and boundary scattering. For example, using Klemens estimate of the phonon-phonon mean free path [Eq. (6.33) of reference 14],

$$l_{\text{ph-ph}} = \frac{3\pi}{32\gamma^2} \frac{1}{(ak)^5} \frac{a^2 M v}{\hbar} \exp(\hbar\omega/kT),$$

we find that if $T \leq 4.2^\circ\text{K}$ no phonon has an $l_{\text{ph-ph}}$ less than 1 cm. In any case, we have not developed a suitable method for quantitatively including the effects of phonon-phonon scattering in these calculations.

C. Divergence in Special Directions

Another divergence is encountered in the calculation of the thermal conductivity with the τ of Eq. (2.4). It is seen from Fig. 1 that the scattering vanishes for a longitudinal phonon with \mathbf{k} in a [100] direction and for one of the transverse phonons with \mathbf{k} in a [110] direction. The integration over angular variables in the expression for the thermal current diverges logarithmically in the vicinity of these special directions. Thus it is necessary to invoke some additional scattering mechanism to cut off the thermal conductivity integral in these directions. If boundary scattering is again resorted to as a cutoff for the angular integrations our calculation predicts that the measured thermal conductivity should depend on the crystallographic orientation of the specimen length, being greater for

the special directions in which there are phonons of vanishing point defect scattering propagating parallel to the length. We are not aware of any evidence for the existence of this effect, nor are we aware of any record of its having been explicitly sought for. It is worth noting, however, that Goff and Pearlman⁸ used specimens of varying orientations without observing any anomalies worthy of comment.

In any case, we have not found any adequate way of treating the anisotropy factor for our present purpose. To get a rough idea of the scattering strength for comparison with the experiments we have simply replaced, $\phi(\mathbf{e}, \mathbf{k})$ by its average over all orientations, obtaining, for transverse phonons, $\bar{\phi}_T = \frac{2}{3}$ and, for longitudinal phonons, $\bar{\phi}_L = \frac{1}{3}$. This method of handling the anisotropy factor is probably the least satisfactory aspect of the present treatment.

D. High-Frequency Cutoff

Even after using the simple averaging procedure just described for the angular integration, our problem differs from that encountered in point defect scattering through the presence of the factor $\chi(\mathbf{k})$, given in Eq. (2.6). If the τ of Eq. (2.4), combined with a boundary scattering relaxation time corresponding to a length L and with the $\phi(\mathbf{e}, \mathbf{k})$'s replaced by the $\bar{\phi}$'s, is substituted into the integral for the heat current, then it is found that the thermal conductivity is

$$\kappa = \sum_{s=1}^3 \frac{4\pi}{3} v_s L k \left(\frac{kT}{\hbar v_s} \right)^3 I(A, B). \quad (3.1)$$

Here the summation is over the branches of the vibrational spectrum and $I(A, B)$ is the integral

$$I(A, B) = \int_0^\infty \frac{e^x}{(e^x - 1)^2} \frac{x^4 dx}{1 + Ax^4(1 + Bx^2)^{-8}}. \quad (3.2)$$

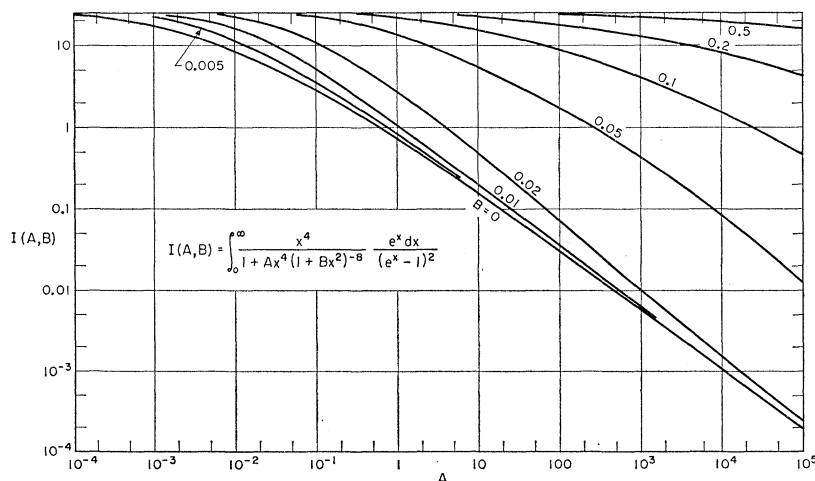


FIG. 2. Values of the integrals defined by Eq. (3.2) (after Keyes and Fein²⁴).

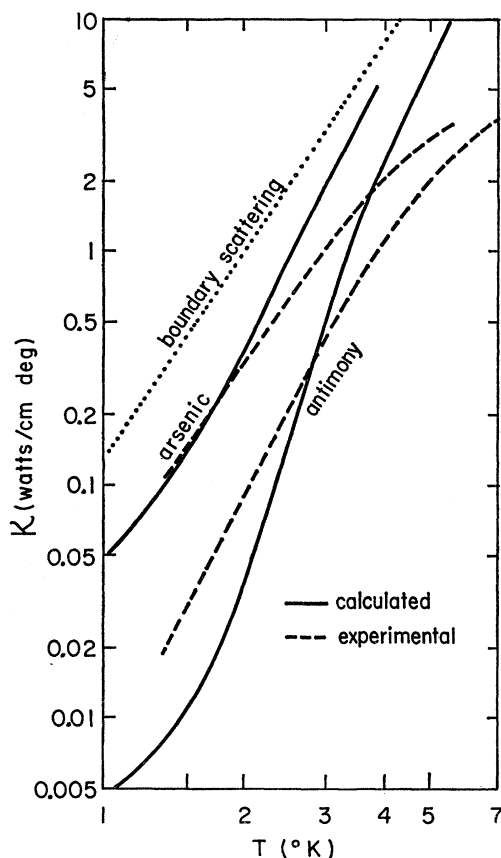


FIG. 3. A comparison of the values of thermal conductivity of *n*-type germanium calculated by the method described in the text with those measured by Goff and Pearlman.³ The antimony-doped samples represented by the experimental curve contain an extrinsic electron concentration of about $2 \times 10^{16} \text{ cm}^{-3}$ and the arsenic-doped sample an extrinsic concentration of $1.6 \times 10^{16} \text{ cm}^{-3}$.

A and B are defined by

$$A = \frac{N_I \bar{\phi}_s \Xi_u^4 (kT)^4 L}{2^3 3^4 5 \pi \rho^2 v_s \Delta^2 \hbar^4} \left(\frac{2}{3v_L^7} + \frac{1}{v_T^7} \right), \quad (3.3)$$

$$B = a^{*2} (kT)^2 / 4 \hbar^2 v_s^2. \quad (3.4)$$

The integrals defined by Eq. (3.2) have been evaluated numerically by Fein and the author, and have the values shown in Fig. 2.²⁴

E. Comparison with the Results of Goff and Pearlman

We have used the approximations and methods described above to calculate values of thermal conductivity for the samples of *n*-type germanium used in the recent work of Goff and Pearlman.³ The comparison of the calculated values with those measured by Goff and Pearlman is given in Figs. 3 and 4. It is seen that the

model accounts for several important features of the data:

(1) The calculated magnitude of the scattering is about right for both arsenic and antimony donors. The difference between these two cases is a result of the fact that Δ for an arsenic donor is about seven times larger than Δ for an antimony donor. This means that the scattering strength given by Eq. (2.4) is only (1/50) as great for the case of arsenic. The factor by which the thermal conductivities differ is, of course, considerably less than this, since part of the scattering is by the boundaries.

(2) The calculated temperature dependence of the thermal conductivity is nearly correct, but slightly stronger than that observed in the range 1.5°K to 4.2°K. According to our model, the scattering strength is greatest for phonons with wavelength about equal to the effective Bohr radius of the hydrogen-like donor wave function. The scattering approaches zero for very high and for very low phonon energies. Consequently, the calculated thermal conductivity must approach the boundary limited value at very high and very low temperatures. On the low-temperature side, the calculated curves show that this phenomenon should become noticeable just at the lower limit of the experimental temperature range. It should be apparent in measurements extending to 1°K. At the high-temperature end of the range of comparison, the calculated scattering rapidly becomes too small as the temperature is increased above 4.2°K. The leveling off of the experimental thermal conductivity with increasing temperature seen here is very probably a manifestation of phonon-phonon scattering. It is seen that, even though the temperature range in which our model predicts that κ varies more rapidly with temperature than T^3 is quite limited, it coincides very well with the range in which the stronger temperature dependence has been observed.

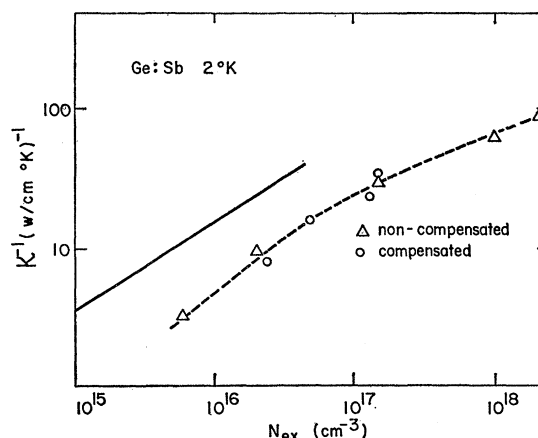


FIG. 4. A comparison of the calculated and observed³ thermal resistance of antimony-doped germanium at 2°K as a function of extrinsic carrier concentration. The solid line represents the calculated values.

²⁴ R. W. Keyes and A. E. Fein, Westinghouse Research Report 6-40602-3-R2, April 25, 1960 (unpublished).

(3) The experimental curve given for antimony-doped germanium in Fig. 3 actually represents results for two samples, each with about the same intrinsic carrier concentration.³ In one of these samples the donor concentration is essentially the total impurity concentration; in the other the donor and acceptor concentrations are nearly equal and the total impurity concentration is about one hundred times larger than the extrinsic electron concentration. The thermal conductivities of these two specimens are about the same throughout the temperature range studied. This is in accord with our model, according to which the scattering strength depends only on the concentration of occupied donors.

(4) The calculated concentration dependence of the thermal resistance at 2°K, shown in Fig. 4, is also close to that observed. The model presented here is expected to be valid up to a concentration such that the resonance integral between donors is about equal to Δ . We estimate this concentration to be $4 \times 10^{16} \text{ cm}^{-3}$ for antimony donors.

F. Conclusions

In conclusion, our model accounts qualitatively for a number of important features of the results of Goff and Pearlman³: the very large phonon scattering strength of donor impurities, the large difference between the scattering powers of antimony and arsenic, the unusually strong temperature dependence of the thermal conductivity between 1.3°K and 4°K, and the fact that the scattering depends on the number of occupied donors rather than the total number of impurities. A quantitative calculation of the thermal conductivity on the basis of this model is hampered by our failure to find satisfactory ways of treating the effect of the anisotropy factor, Eq. (2.5), and the effects of phonon-phonon scattering.

IV. OTHER ASPECTS

There are several other aspects of the thermal conductivity problem which deserve mention. One of these is the possibility of other mechanisms of scattering by the electrons in donor states. Phonons are absorbed in electronic transitions involving the transfer of an elec-

tron from a state localized on one donor to a state localized on another donor.⁶ These are the transitions involved in the phenomenon of impurity conduction.⁶ Transition probabilities for these processes have been given by Miller and Abrahams.⁶ Using their results we estimate that the phonon mean free path due to scattering by this mechanism is never less than 1 cm in the samples of Goff and Pearlman. Thus this "impurity conduction scattering" is probably negligible in these samples and details of the estimate will not be reproduced here. However, this scattering is proportional only to ω for small ω and thus can furnish a means of preventing the divergence of thermal conductivity integrals at low frequencies.

Phonons can also be absorbed by excitation of an electron from the singlet to the triplet state of the donor. In the case of isolated donors only phonons of energy 4Δ are absorbed by this mechanism. Such a monoenergetic absorption mechanism has no effect on the thermal conductivity when phonon-phonon scattering is neglected, however, and for this reason we have not included it here.

Phenomena similar to those reported by Goff and Pearlman have also been observed in *p*-type germanium. The mechanism discussed in this paper as an explanation of the large scattering power of donors is obviously inapplicable to acceptors because the structure of the valence band is entirely different from that of the conduction band. However, the effective Bohr radius of an acceptor wave function is about the same as that of a donor wave function,¹⁷ so that scattering by isolated acceptors might be expected to have about the same dependence on phonon energy as scattering by donors. Further, the effect of strain on several properties of the valence band is quite large.²⁵ Thus it is possible that a detailed theory of the effects of strain on acceptor states could account for phonon scattering effects of the order of magnitude of those reported here for donors.

²⁵ R. Lawrence, Phys. Rev. **89**, 1295 (1953); C. S. Smith, Phys. Rev. **94**, 42 (1954); E. N. Adams, Phys. Rev. **96**, 803 (1954); J. C. Hensel and G. Feher, Phys. Rev. Letters **5**, 307 (1960); G. Feher, J. C. Hensel, and E. A. Gere, Phys. Rev. Letters **5**, 309 (1960).