Thermal Conductivity of Solids IV: Resonance Fluorescence Scattering of Phonons by Donor Electrons in Germanium*

A. Griffin and P. Carruthers

Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York

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The scattering of phonons from donor electrons in germanium is computed and applied to the problem of heat conduction below the low-temperature maximum. The effective-mass approximation is used for the electronic wave function. The calculation is analogous to that of the dispersive scattering of light by atoms. Since the ground state is split into a singlet and a triplet with a separation of energy within the thermal phonon distribution, anomalous effects due to resonance scattering occur. Apart from these, our results are similar to previous work by Keyes. Taking into account the boundary and isotopic scattering as well as the electron-phonon interaction, excellent quantitative agreement with thermal conductivity data is obtained, with no adjustable parameters, for Sb and As donors in Ge. Certain discrepancies at higher temperatures can be traced to the inadequacy of the effective-mass approximation. In addition, anomalies in the "phonon drag" thermoelectric power can be understood on the basis of our theory. A by-product of our calculation is the lifetime broadening of the triplet state. The slightly different case of n-type Si is worked out while a more qualitative treatment of our resonant scattering mechanism is given for p-type semiconductors and samples under uniaxial strain.

I. INTRODUCTION

THE lattice thermal conductivity of doped semiconductors is unusual in several respects.[1-3] First of all, the depression in conductivity below the low-temperature maximum ($\sim 15°K$) is quite substantial for dilute concentrations of impurity atoms. Secondly, the temperature dependence of the thermal conductivity coefficient $K(T)$ in this region is often "anomalous," e.g., $K(T)$ sometimes varies as T^4 down to the lowest temperatures reached (0.3°K for p-type Ge, 1.3°K for n-type Ge). As is well known,[4-6] such a temperature dependence implies that the effective scattering rate *increases* with increasing phonon wavelength. The usual scattering mechanisms do not exhibit such a behavior. Further, the thermal conductivity of doped Ge is unusually sensitive to strains.[7,8] Finally, as a function of temperature, $K(T)$ sometimes exhibits wiggles.[2] In this paper we shall limit ourselves mainly to donor impurities in Ge and their effect in the liquid helium (and slightly above) temperature range.

Substantial progress toward the understanding of these phenomena has been made by Keyes.[9] For impurity concentrations sufficiently low ($\lesssim 10^{17}$ cm^{-3}), the impurity atoms may be regarded as independent scatterers. Keyes calculates the phonon scattering by the bound electron in the following way. The ground state of Ge, fourfold degenerate in the effective-mass theory, is split into a singlet and a triplet by the valley-orbit interaction. These levels are split[10] by a very small amount, the "chemical shift" 4Δ. The energy change of the electron in the presence of strain is, therefore, substantial. The energy due to a *static* strain is proportional to the square of the strain. Thus, if one uses this *static* expression as an interaction Hamiltonian for the phonons, the low-frequency scattering is proportional to ω^4, where ω is the circular frequency of the phonon. There is an additional source of ω dependence in the matrix elements: If the wave vector of the final phonon has a magnitude greater than the reciprocal of the mean radius r_0 of the localized state, the interaction is small. The form of the single-mode relaxation time τ ($1/\tau$ is proportional to the scattering cross section) found by Keyes is

$$\tau^{-1} \propto \omega^4 (1 + \tfrac{1}{4}k^2 r_0^2)^{-8} \tag{1.1}$$

in the usual acoustic approximation $\omega = kc$, c some average velocity of sound. When k increases past $1/r_0$, the scattering dies off very quickly. It is this cutoff which Keyes proposed as an explanation of the steepness of slope of the conductivity curve below the maximum.

Now, one expects the static interaction to provide a good description of the scattering only when the phonon frequency is small compared to the characteristic frequency with which the electron wave function adjusts to the perturbation. In our problem this characteristic frequency is 4Δ. It happens that 4Δ lies within the range of heat conduction, e.g., for Sb in Ge, 4Δ is 6.6°K. Therefore, a more accurate theory is called

* Research supported in part by the U. S. Atomic Energy Commission.

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

[2] J. F. Goff, Ph.D thesis, Purdue University, 1962 (unpublished). An account of some of this work is given by J. F. Goff and N. Pearlman, in *Proceedings of the Seventh International Conference on Low Temperature Physics* (University of Toronto Press, Toronto, Canada, 1960), p. 284.

[3] J. A. Carruthers, J. F. Cochran, and K. Mendelssohn, Cryogenics **2**, 160 (1962).

[4] P. G. Klemens, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Vol. 7, p. 1.

[5] J. M. Ziman, *Electrons and Phonons* (Oxford University Press, New York, 1960).

[6] P. Carruthers, Rev. Mod. Phys. **33**, 92 (1961); referred to as I.

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

[8] R. J. Sladek, in *Proceedings of the International Conference on the Physics of Semiconductors, Exeter* (The Institute of Physics and the Physical Society, London, 1962).

[9] R. W. Keyes, Phys. Rev. **122**, 1171 (1961).

[10] P. J. Price, Phys. Rev. **104**, 1223 (1956).

for to describe properly the *dynamic* response of the electron. In a previous paper,[6] one of the authors compared the scattering of phonons by donor electrons to the well-known problem of the scattering of light from atoms.[11] The electron-phonon interaction induces virtual transitions of the bound electron to higher excited states. This analogy and the fact that 4Δ lies within the energy range of heat conduction makes obvious the fact that resonance scattering of phonons will be significant in the experiments of interest. We have then only to modify the usual theory[11] of resonance fluorescence for the problem at hand. For low frequencies ($\hbar\omega \ll 4\Delta$), our results agree with those of Keyes apart from some inessential angular factors and some different approximations. Besides providing a more accurate description of the scattering process, we believe our description of the mechanism is physically more perspicuous than that of Keyes.[9]

The occurrence of resonances is also significant in understanding the occurrence of the anomalous temperature dependence mentioned in the first paragraph. The idea is based on a very general result, proposed[12] by one of the authors as an explanation for such anomalous slopes in $K(T)$. Crudely speaking, for the long wavelengths of interest, one need consider only S-wave scattering (neglecting complications due to polarization and anisotropy) so that the scattering cross section σ is of the form $4\pi(\sin^2\delta)k^{-2}$, where δ is the phase shift and k the phonon wave number. As k increases through the resonance value, δ goes rapidly through $90°$ and then varies slowly as k is increased further. If δ were a constant, for example, then $\sigma \propto k^{-2}$, giving rise to a characteristic T^5 dependence for $K(T)$. More generally, one can only say that the scattering decreases as k increases above the resonance value, and, hence, the $K(T)$ is steeper than T^3 in the corresponding heat conductivity region. Practically speaking, for the present problem the resonance is numerically important only if it occurs at a frequency around the critical value ($\approx c/r_0$) at which the cutoff discussed by Keyes[9] occurs. It is, therefore, more important for Sb in Ge than for As in Ge. These remarks will become clearer later on.

There are many other scattering mechanisms which compete with the one described. It is essential to include boundary and isotope scattering, of course. At high concentrations ($\sim 10^{18}$ cm^{-3}) where overlap between bound-electron wave functions becomes large, the impurity states probably merge with the conduction band as discussed by Ziman.[1,13] Even at lower concentrations, impurity conduction may occur by the hopping of electrons from occupied to unoccupied localized states. This may occur due to the localized fields produced by nearby ionized impurities or to the "resonance" jumping between two sites sharing one

electron, as in a hydrogen molecule.[14,15] We believe that these involve negligible phonon scattering compared to our single donor electron mechanism. At very low temperatures ($< 1°K$) where our mechanism becomes ineffective, it is possible there is some new scattering process.

The influence of some other quite different processes may be remarked upon here. The strain-field scattering due to the modification of the elastic force constants via the anharmonic forces can be estimated according to the methods of I. One calculates the displacements induced by the polarization due to the extra electron. The result is very similar to Eq. (1.1), but much smaller in magnitude. The scattering due to the mass difference of the impurity is very small in Born approximation.[16] However, when resonances occur in the continuum, as found by Brout and Visscher[17] for a particular case, the scattering is no longer negligible. We would like to call attention to the important work of Lifshitz, reviewed by Lifshitz himself in Ref. 18. This work, which contains implicitly the results of Refs. 16 and 17, has been unaccountably neglected. Another obvious source of scattering is the phonon modulation of the hyperfine coupling of the donor electron to the impurity nucleus. However, calculation shows this scattering to be very much weaker than that due to the electron-phonon interaction considered in Sec. III [see Eq. (3.20)]. Denoting the Fermi contact term by $A\mathbf{I}\cdot\mathbf{s}$, the relative strength of the two processes is $S(EP)/S(HF) = [24/I(I+1)](4\Delta/A)^2$ for $0°K$ (this holds for both Ge and Si). In general, $4\Delta \gg A$ and, thus, the hyperfine interaction may be neglected.

The calculation of the heat flow is subject to well-known complications,[4-6] even when the scattering cross section is known. We use Callaway's semiphenomenological formulation of the problem.[19] We obtain especially good quantitative agreement with no adjustable parameters in the region where our theory should be most reliable, i.e., near the temperature at which electron-phonon mechanism is most effective. The special effects of the true resonances are of particular interest. We find that as the temperature is decreased from $1°K$ to about $0.5°K$, the thermal resistance should decrease abruptly for Sb in Ge. For As in Ge, the data[2] show a dip at about $7°K$, just about where we would expect the true resonance scattering to occur. Unfortunately, other mechanisms (boundary and isotope scattering) dominate at these temperatures due to the rapid cutoff of our mechanism. Thus, the resonance will be extremely narrow and is difficult to detect. This cutoff factor varies extremely rapidly [$\approx \exp(-2k^2r_0^2)$] as can be seen from Eq. (1.1) and so the result is quite

[11] W. Heitler, *Quantum Theory of Radiation* (Oxford University Press, London, 1954), 3rd ed., Chap. 5.

[12] P. Carruthers, Bull. Am. Phys. Soc. **7**, 16 (1962).

[13] J. M. Ziman, Phil. Mag. **1**, 191 (1956). See also Refs. 4 and 5.

[14] I. C. Pyle, Phil. Mag. **6**, 609 (1961).

[15] A. Miller and E. Abrahams, Phys. Rev. **120**, 745 (1960).

[16] P. G. Klemens, Proc. Phys. Soc. (London) **A68**, 1113 (1955).

[17] R. Brout and W. Visscher, Phys. Rev. Letters **9**, 54 (1962).

[18] I. M. Lifshitz, Suppl. Nuovo Cimento **3**, 716 (1956).

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

sensitive to the approximations used for this factor. We believe that the result we obtain, that the resistivity dies off a little too rapidly as the maximum is approached, is partly due to a poor approximation for this factor. One other important source of resistance in this region is the normal three-phonon process.

To summarize, we have found excellent experimental agreement somewhat below the maximum by considering the scattering to be due to three processes: boundary scattering, phonon scattering by bound electrons, and isotopic scattering present in naturally occurring germanium. Near the maximum the resistivity is largely due to the isotopic scattering. We predict that $K(T)$ will be much steeper (T^5, for example) in the corresponding region for an isotopically pure crystal. Such experiments would be very sensitive to deviations from the effective-mass theory wave functions (Sec. IV).

In Sec. II, we briefly review the corrected effective-mass approximation[20] used to describe the shallow impurity states and then, on the basis of the usual adiabatic approximation, discuss the matrix elements for electronic transitions between the singlet and triplet states with absorption or emission of one phonon. We have used Hasegawa's results.[21] Implicit in our whole discussion is that 4Δ is large enough so that the donor electron-phonon interaction may be considered as a small perturbation causing transitions between the singlet and triplet. The matrix elements found are consistent with this assumption. We do not consider in any way the (presumably small) spin-orbit interaction as a correction to the intervalley splitting.

In Sec. III, we calculate the phonon scattering amplitude for virtual electronic transitions, transition probabilities, and, finally, the single-mode relaxation time. Angular averages are used to remove any anisotropic features the latter may have. We have considered the possibility that the electron is originally in the triplet state. Since the scattering is by virtual processes, with the possibility of vanishing energy denominators, the usual second-order perturbation theory in the Born approximation must be generalized to include damping. We have calculated the width of the levels forming the triplet and show explicitly that $\frac{1}{2}\hbar\Gamma \ll 4\Delta$. We have also made a detailed comparison between our relaxation time and that of Keyes.[9]

In Sec. IV, we compute the lattice thermal conductivity assuming the three-phonon scattering mechanisms mentioned previously (bound electron, boundary, and isotope). The integrals are evaluated by numerical integration and compared to the experimental work of Goff[2] and the calculations of Keyes.[9] We discuss the relative importance of other mechanisms, and, in particular, show that the contribution of the true excited states of the shallow impurity is small for several reasons. It is also pointed out that the neglect

of "core" corrections to the donor wave functions results in underestimating the scattering of high-energy phonons.

Some extensions of our work to other kinds of doped semiconductors are considered in the last section. A quantitative analysis is given for n-type Si. A preliminary treatment of p-type material indicates that our electron-phonon mechanism will have the same general features that it had in n-type material. The effect of uniaxial strains on the resonant phonon scattering is touched on. The resonant phonon frequencies may be altered at will by varying the effective "valley-orbit" splitting. Lastly, we indicate briefly how some depressions in the "phonon drag" thermoelectric power of Ge[2] can be explained on the basis of our calculations. We have not discussed the effect of large static magnetic fields. Since the latter effectively "compress" the donor-state wave function, they are of some interest. As Keyes first pointed out, our electron-phonon mechanism has a maximum around $\omega \approx c/r_0$ which depends critically on the size of the localized state. As a result, the temperature at which *this maximum* most strongly depresses the thermal conductivity or phonon drag should increase with the application of a magnetic field.

II. SHALLOW IMPURITIES AS TWO LEVEL SYSTEMS AND MATRIX ELEMENTS FOR DIRECT PHONON PROCESSES

For the nature of shallow impurity states, we refer to the review article of Kohn in which the effective-mass approximation (with corrections) is discussed.[20] As mentioned in the Introduction, we are specifically interested in Sb and As-doped Ge, the concentrations being such that there is little overlap between impurity states. Geometrically, for an effective donor-state radius $r_0 \approx 40$ Å, this condition *should* be met by concentrations $n_{ex} \lesssim 10^{17}$ cm^{-3}. To be more definite about allowed values of n_{ex}, we must, of course, check that the scattering mechanisms involving interaction of donor states[14,15] are negligible compared to that arising from individual donor states. This will be discussed in Sec. IV.

The ground state of a donor in Ge is fourfold degenerate in the effective-mass approximation with energy 9.2×10^{-3} eV below the conduction band. In addition, there is a whole spectrum of hydrogenic excited states (4.5×10^{-3} eV, 2.6×10^{-3} eV, etc., below the conduction band). Due to the intervalley interaction caused by the impurity potential, this ground state is split. Because of the symmetry of the four conduction-band minima in $\mathbf{k}$ space, the degeneracy is only partly removed[10] to a first approximation. The result is two levels. The lowest level is a singlet (S), and the highest a triplet (T), separated by the "valley-orbit" splitting 4Δ.

The valley-orbit splitting 4Δ depends on both the donor and the host semiconductor. The best available determinations are listed in Table I for some relevant

[20] W. Kohn, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 5, p. 258.
[21] H. Hasegawa, Phys. Rev. **118**, 1513 (1960).

TABLE I. Experimental values of valley-orbit splittings 4Δ and equivalent temperatures $\bar{T}_R$ for some donors in Ge.[a]

Donor	4Δ (eV) $(\times 10^{-3})$	$\bar{T}_R$ (°K)
Sb	0.57	6.6
P	2.90	33.6
As	4.15	48.1

[a] See Ref. 22.

donors in Ge.[22] In addition, this table includes the equivalent temperature $\bar{T}_R$, with $k\bar{T}_R \equiv 4\Delta$, k being Boltzmann's constant. The energy difference between the unshifted triplet and the first true excited state is 4.5×10^{-3} eV. Since we are interested in low temperatures $(0 < T \lesssim 5°K)$, we shall neglect all excited states and concentrate on the singlet and triplet states. Before proceeding, we may add two remarks. First, the smallness of 4Δ for Sb raises the question of whether it will be valid later to treat the electron-phonon interaction as a weak perturbation causing electronic transitions between the singlet and triplet state levels. In Sec. III, we shall see that it is. Moreover, our calculation of the resonance scattering explicitly satisfies unitarity (i.e., conservation of probability). The second remark is that for consistency, if we consider the possibility of the electron being originally in the triplet state, we should certainly consider transitions to the first excited state, as well as to the lower singlet state, since the energy differences are of the same order. To consider transitions to true excited states would result in no great difficulty, though the calculations would become tedious. Certainly this extension might be necessary if we wanted to consider the effect of the virtual electronic transitions for temperatures well out of the liquid-helium range. We shall return to this point at the end of Sec. IV.

We now consider the effective-mass wave functions,[20] which to a good approximation are unchanged by impurity potential corrections which lead to the valley-orbit splitting. We have

$$\Psi_d(\mathbf{r}) = \sum_{v=1}^{4} \alpha_d{}^{(v)} \Phi^{(v)}(\mathbf{r}), \qquad (2.1)$$

where $\Psi_0(\mathbf{r})$ is the singlet donor state and $\Psi_d(\mathbf{r})$, with $d = (1, 2, 3)$, are the three degenerate states forming the triplet. The function $\Phi^{(v)}(\mathbf{r})$ can be closely approximated by the product of the Bloch function $\phi_\mathbf{k}(\mathbf{r})$ at the bottom of the vth valley ($\hbar\mathbf{k}$ is the donor electron's momentum at the vth conduction-band minimum) and an envelope function $F_v(\mathbf{r})$. The latter can be approximated by a hydrogen-type function

$$F(\mathbf{r}) = (\pi a^2 b)^{-1/2} \exp\{-[(x^2+y^2)/a^2 + z^2/b^2]^{1/2}\}, \qquad (2.2)$$

where a and b are determined from the relevant effective masses and ionization energy. Finally, the amplitudes

$\alpha_d{}^{(v)}$ are fixed entirely by the symmetry of the true Hamiltonian of the impurity state (the full tetrahedral group). Hasegawa, whose results[21] we wish to use, chose the set (note that $\sum_v \alpha_d{}^{(v)}\alpha_{d'}{}^{(v)} = \delta_{dd'}$),

$$\alpha_0{}^{(v)} = \tfrac{1}{2}(1,1,1,1),$$
$$\alpha_1{}^{(v)} = (1/\sqrt{2})(1,0,0,-1), \qquad (2.3)$$
$$\alpha_2{}^{(v)} = (1/\sqrt{2})(0,1,-1,0),$$
$$\alpha_3{}^{(v)} = \tfrac{1}{2}(1,-1,-1,1).$$

Even expression (2.2) is usually too complicated to use and one approximates it by a valley-independent function

$$F(r) = (\pi r_0{}^3)^{-1/2} e^{-r/r_0}, \qquad (2.4)$$

where r_0 is some "appropriate average" of a and b. It seems appropriate to regard r_0 as a parameter to be fixed by experiment. We shall have a few more remarks on the proper choice of r_0 in Sec. IV, but for the time being we mention that r_0 is of the order of 40 Å.

The notation we shall use for the matrix elements describing electronic transitions between levels given in Eq. (2.1), with the emission or absorption of a phonon, should be clear from an example. As usual, we only refer explicitly to the phonons and electrons which are involved in the interaction. Suppose an electron in the singlet state absorbs a phonon q and as a result is excited to the level T_i (one of three degenerate levels forming the triplet state T). The amplitude for the transition is denoted by

$$\langle T_i | V_{\mathrm{ep}} | q, S \rangle,$$

where V_{ep} is the donor electron-phonon interaction operator. Here the label q represents a phonon of wave vector $\mathbf{q}$ and polarization vector $\mathbf{e}_t(\mathbf{q})$, or more briefly $q \equiv (\mathbf{q}, t)$. The context should always make it clear when q represents $|\mathbf{q}|$.

Since Hasegawa has given a lucid discussion in his paper[21] (see Secs. 1, 2, and 3B, in particular), we simply quote his results for the relevant matrix elements. His calculations were based on the following assumptions and approximations, which are general enough for our purposes as well:

(a) The bound electron-phonon interaction is taken in the deformation-potential approximation suitable for multivalley semiconductors,[23] with both dilation and shearing strain terms included. Thus, we are limited to one-phonon processes. No spin-orbit interaction is considered.

(b) Only the acoustic modes contribute, which is reasonable at the low temperatures and energy differences of interest. For the same reasons, umklapp electronic processes, in general, and intervalley electronic transitions, in particular, were neglected. That is, only the intravalley orbit-lattice coupling is included.

[22] H. Fritzsche, Phys. Rev. 120, 1120 (1960).

[23] C. Herring and E. Vogt, Phys. Rev. 101, 944 (1956).

Under the above conditions, Hasegawa found

$$\langle S | V_{ep} | q, T_r \rangle = i(E_u/3) f(q) q D_r^{(t)} a_{qt},$$
$$\langle q, S | V_{ep} | T_r \rangle = -i(E_u/3) f(q) q D_r^{(t)} a_{qt}^*,$$
$$\langle T_r | V_{ep} | q, S \rangle = \langle S | V_{ep} | q, T_r \rangle,$$
$$\langle q, T_r | V_{ep} | S \rangle = \langle q, S | V_{ep} | T_r \rangle,$$

$$(2.5)$$

where

(a) the cutoff function, defined by

$$f(\mathbf{q}) \equiv \int d\mathbf{r} \, e^{i\mathbf{q}\cdot\mathbf{r}} F^2(\mathbf{r}) \qquad (2.6a)$$

is, in the isotropic approximation using Eq. (2.4),

$$f(q) = [1 + (r_0 q/2)^2]^{-2}. \qquad (2.6b)$$

It is useful to remember that $f(\mathbf{q})$ is the qth Fourier component of the charge distribution of the donor state, i.e., the form factor of the donor atom.

(b) E_u is the deformation potential related to the shearing strain due to the phonons. We shall take[24] $E_u = 19$ eV in numerical calculations.

(c) The coefficients $D_r^{(t)}$ are defined by

$$D_r^{(t)} \equiv \mathbf{e}_t(\mathbf{q}) \cdot D_r \cdot \mathbf{q} / |\mathbf{q}|, \qquad (2.7a)$$

where

$$D_r \equiv 3 \sum_{v=1}^{4} \alpha_0^{(v)} \alpha_r^{(v)} \hat{K}^{(v)} : \hat{K}^{(v)}, \qquad (2.7b)$$

with the unit vector $\hat{K}^{(v)}$ pointing from the origin to the bottom of the vth valley of the conduction band. Hasegawa denotes the dyad $\hat{K}^{(v)} : \hat{K}^{(v)}$ as $U^{(v)}$ in his work.[21]

(d) a_{qt} and a_{qt}^* are the destruction and creation operators of phonon q, and obey the usual commutation rules with the following normalization:

$$[a_{qt}, a_{q't}^*] = \hbar/(2M\omega_{qt})\delta_{qq'}, \delta_{tt'},$$
$$[a_{qt}, a_{q't'}] = [a_{qt}^*, a_{q't'}^*] = 0, \qquad (2.8)$$

where M is the total mass of the semiconductor and $\hbar\omega_{qt}$ is the energy of phonon q.

We note that the D_r matrices depend only on the geometrical structure of the conduction band. The deformation-potential constant E_d related to dilation due to the phonons actually appears in the matrix elements in Eq. (2.5) but with the coefficient $\sum_v \alpha_0^{(v)} \alpha_r^{(v)}$. Since the $\alpha_d^{(v)}$ coefficients are orthogonal, the sum vanishes and the E_d term does not appear in the final result. The electronic transitions are due entirely to the shearing strains produced by the phonons.

An explicit representation of the functions $D_r^{(t)}$ requires the choice of a coordinate system. If the lattice vibrational spectrum can be characterized by pure longitudinal and transverse modes, the three polarization vectors $\mathbf{e}_t(\mathbf{q})$ form a suitable basis, with

$\mathbf{e}_1(\mathbf{q})$ along $\mathbf{q}$. Taking

$$\mathbf{e}_1(\mathbf{q}) = (\sin\theta \cos\phi, \sin\theta \sin\phi, \cos\theta),$$
$$\mathbf{e}_2(\mathbf{q}) = (\cos\theta \cos\phi, \cos\theta \sin\phi, -\sin\theta), \qquad (2.9)$$
$$\mathbf{e}_3(\mathbf{q}) = (-\sin\phi, \cos\phi, 0),$$

with θ and ϕ the usual spherical coordinates, Hasegawa gives, in Table III of his paper, explicit representations of $D_r^{(t)}$. Of course, the frequency spectrum of Ge is not completely isotropic, but if experience is any guide, the above assumption of one purely longitudinal and two transverse modes is good enough at the low temperatures of interest. With these results we can now proceed to find the relaxation time of a phonon due to its interaction with an isolated donor electron via the intravalley orbit-lattice coupling.

III. SCATTERING AMPLITUDES FOR VIRTUAL ELECTRONIC TRANSITIONS AND RESULTING PHONON RELAXATION TIME

It is sometimes stated that the only way in which one can find a nonmonotonic phonon relaxation time (as a function of the phonon's energy) is to consider *inelastic* phonon scattering mechanisms. If one restricts oneself to *real* processes, this is generally true, but *elastic virtual* processes can also lead to resonance type relaxation times.

In our problem, the most important electronic transitions induced by the phonons are second-order *virtual* transitions. By the usual density of final states argument, the first-order *real* transitions $S+q \leftrightarrow T_r$ are easily seen to be negligible in comparison. We should mention here that Orbach[25] has recently calculated resonance scattering by spin systems on the assumption of incoherent real transitions. His calculation as well as earlier ones by other authors, however, involves the tacit assumption that there is some additional perturbation by means of which the excited state can relax— such as, the spin-spin interaction. This additional interaction, besides broadening the energy distribution of the excited states, destroys the coherence of the de-excitation. In the case we are considering, where presumably only one type of interaction with the donor electrons is important, coherence effects are important and Orbach's approach would lead to incorrect results. Of course, for a broad band of phonon frequencies, the resonance fluorescence calculation gives rise to *multiplicative* probabilities of absorption and emission.[11]

The task before us, then, is to enumerate all possible virtual electronic transitions resulting in a phonon q being absorbed and a phonon q' being created. From a formal point of view, the scattering problem for the singlet electron is almost identical to the study of resonance fluorescence caused by the electron-photon

[24] H. Fritzche, Phys. Rev. 115, 336 (1959).

[25] R. Orbach, Phys. Rev. Letters 8, 393 (1962). See also Part V of R. Orbach's thesis, University of California, 1960, and R. Orbach, Proc. Roy. Soc. (London) 264, 458 (1961).

interaction in a two-level electronic system.[11,26] We have, in addition, to consider the nontrivial problem of scattering by the donors in their various excited states, in particular, the triplet. At any finite temperature, the donors are excited and decay by means of the same electron-phonon coupling considered here. For simplicity, we might assume that even in the presence of the heat current the deviation from equilibrium is sufficiently small that the probability of finding an atom in the various states is given by the Boltzmann factor. By this means, one effectively replaces an explicit consideration of the direct inelastic processes $(S+q \leftrightarrow T)$ by assuming a distribution of electrons among the two levels. From a more fundamental point of view the "scattering in the triplet state" is built up of the process (2 phonons+singlet $\rightarrow$ 2 phonons+singlet). It will be noticed that in the two-level atom model (valid so long as the effective-mass excited states are far removed in energy), one should not include the inelastic scattering (phonon+triplet $\rightarrow$ 2 phonons +singlet) because the dominant contribution to this process conserves energy, i.e., breaks up into two real processes, decay of the triplet followed by scattering of the phonon by the singlet state. This latter process is already included.

In Fig. 1, we have drawn perturbation diagrams for the four possible kinds of virtual transitions. We first consider the case in which the electron is initially in the singlet state. The total scattering amplitude for transitions such as $S1$ is, in the Born approximation,

$$M_1(q, S \rightarrow q', S) = \sum_{i=1}^{3} \frac{\langle q',S|V|T_r\rangle\langle T_r|V|q,S\rangle}{E_S+\hbar\omega_q-E_T}, \quad (3.1)$$

where the summation is over the three intermediate states of the triplet, and E_S, E_T are the electronic energies of the singlet and triplet states, respectively. Defining $4\Delta \equiv E_T - E_S$, we see that the energy denominator vanishes for $\hbar\omega_{qt}=4\Delta$. We have resonant scattering for certain phonon energies and, therefore, we must extend our calculation to include the damping effects to get rid of the singularity in Eq. (3.1). We postpone this modification until we have discussed all
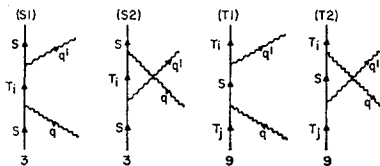

FIG. 1. Diagrams for virtual electronic transition with scattering of phonon $q \rightarrow$ phonon q'. As in the text, S represents the singlet state and T_i represents one of the states of the triplet of the donor electron. The numbers below each graph give the actual number of transitions of a given type.

[26] V. Weisskopf, Ann. Physik 9, 23 (1931). The original work on broadening is to be found in V. Weisskopf and E. Wigner, Z. Physik, 63, 54 (1930); 65, 18 (1930).

the diagrams in Fig. 1; actually this correction is of negligible interest in transport processes such as thermal conduction.

The total scattering amplitude for $S2$ transitions (where in contrast to $S1$, the phonon q' is emitted before phonon q is absorbed) is

$$M_2(q, S \rightarrow q', S)$$

$$= \sum_{i=1}^{3} \frac{\langle q',S|V|q,q',T_r\rangle\langle q,q',T_r|V|q,S\rangle}{(\hbar\omega_q+E_S)-(\hbar\omega_q+\hbar\omega_{q'}+E_T)}$$

$$= \sum_{r=1}^{3} \frac{\langle q',S|V|q,q',T_r\rangle\langle q,q',T_r|V|q,S\rangle}{-(\hbar\omega_{q'}+4\Delta)}. \quad (3.2)$$

Next, we consider the scattering by electron in the triplet state. In contrast to the previously discussed transitions $S1$ and $S2$, all the transitions of type $T1$ are noninterfering since the initial level T_r and the final level T_s are different (though degenerate). Thus, we have nine scattering amplitudes of type $T1$

$$M_1(q, T_r \rightarrow q', T_s) = \frac{\langle q',T_s|V|S\rangle\langle S|V|q,T_r\rangle}{(\hbar\omega_q+4\Delta)}. \quad (3.3)$$

Transitions of type $T2$ are again noninterfering but they are of the resonant type, similar to $S1$. The nine scattering amplitudes are

$$M_2(q, T_r \rightarrow q', T_s)$$

$$= \frac{\langle q',T_s|V|q',q,S\rangle\langle q',q,S|V|q,T_r\rangle}{-(\hbar\omega_{q'}-4\Delta)}. \quad (3.4)$$

We note that $M_1(q,T_r \rightarrow q',T_s)$ and $M_2(q,T_r \rightarrow q',T_s)$ for the same values of r and s are interfering processes.

We must now improve on the Born approximation used up to now and include the effects of damping in order to get rid of the meaningless singularities in Eqs. (3.1) and (3.4). This was first done by Weisskopf[26] on the similar problem of resonance fluorescence. The result of the electron-phonon interaction is to give rise to a shift and breadth to the excited state. Formally, the modification of the Born approximation is to replace the unperturbed energies by complex values $E \rightarrow E' - \frac{1}{2}i\hbar\Gamma$, where E' is the real, renormalized energy and $\hbar\Gamma$ the transition rate for the electron to go to a lower state via phonon emission. The problem may be solved in an economical way by the use of Van Hove's resolvent formalism.[27] As remarked by Van Hove, the two level atom is the unstable analog of the Lee model, solved in Ref. 27. For the scattering of a phonon by a singlet electron the unperturbed denominator (E_0-E) is replaced by $D_0^{-1}(E)=E_0-E-G_0(E+i\epsilon)$, where D_0 is the diagonal part of the resolvent for the triplet state and G_0 is essentially the irreducible self-energy (ϵ is

[27] L. Van Hove, Physica 21, 901 (1955); 22, 343 (1956).

a positive infinitesimal, defining the sign of the imaginary part of G_0). The root of $\mathrm{Re}\{D_0^{-1}(E_r)\}=0$ gives the perturbed energy E_r of the excited state, which is quasistationary with lifetime Γ^{-1}, where

$$\Gamma = 2\ \mathrm{Im}[G_0(E_r)/(1+\partial\ \mathrm{Re}G_0/\partial E_r)] \approx 2\ \mathrm{Im}G_0(E_r).$$

On the other hand, phonon scattering by the triplet electron (or any excited state) is much more involved, as we noted in the third paragraph of this section. We hope to systematically investigate the inelastic scattering elsewhere. We shall not distinguish in our notation between the unperturbed and renormalized energies. Naturally, the experimental values we shall use correspond to the renormalized ones. In summary, then, the damping effects result in an effective change for the $S1$ and $S2$ denominators (E_q^- and $E_{q'}^+$, respectively) given by

$$E_{q''}{}^{\pm} \equiv \hbar\omega_{q''}\pm 4\Delta \rightarrow E_{q''}{}^{\pm}\mp i\gamma_T, \tag{3.5}$$

where $2\gamma_T \equiv \hbar\Gamma_T$ is the "lifetime broadening" of the triplet state. To first order, we have

$$\gamma_T = \lim_{\epsilon\to 0^+}\ \mathrm{Im}\left\{\sum_q \frac{|\langle q,S|V|T\rangle|^2}{\hbar\omega_q - 4\Delta - i\epsilon}\right\}. \tag{3.6}$$

The necessary modification for the energy denominators of the $T1$ and $T2$ processes is not so well discussed in the literature. Formally, however, the processes $S1$ and $T1$ are identical and so are the processes $S2$ and $T2$. Making use of the general formulation of Heitler,[11] we find that to lowest order, at least, the changes in the $T1$ and $T2$ energy denominators (E_q^+ and $E_{q'}^-$, respectively) are given by Eq. (3.5) again. Of course, only $S1$ and $T2$ are resonant processes. The modification of the nonresonant denominators is numerically unimportant and is only included for reasons of symmetry. Although we do not consider it any further, we should also point out that we have neglected to include the imaginary part of the phonon self-energy in modifying the energy denominators.

This completes our enumeration of the possible virtual transitions to first order. The total probability per unit time for the scattering of phonon q to state q' is

$$W(q\rightarrow q')n_q(1+n_{q'})$$

$$= (2\pi/\hbar)\delta(\hbar\omega_q - \hbar\omega_{q'})$$

$$\times [B_S(T)|M_1(q, S\rightarrow q', S) + M_2(q, S\rightarrow q', S)|^2$$

$$+ B_T(T)\sum_{r,s=1}^{3} |M_1(q, T_r\rightarrow q', T_s)$$

$$+ M_2(q, T_r\rightarrow q', T_s)|^2]. \tag{3.7}$$

In Eq. (3.7), $W(q\rightarrow q')$ is a reduced transition probability in that the statistical factors are separated. The $B(T)$'s are the occupation probabilities for the singlet

and triplet state as a function of the temperature T and $n_q = a_q{}^*a_q$ gives the number of phonons in the qth mode. We note that, whether the electrons are in thermal equilibrium or not,

$$B_S(T)+3B_T(T)=1. \tag{3.8}$$

Using Eq. (2.6), we are able to evaluate the various scattering amplitudes given by Eqs. (3.1), (3.4), (3.5), and (3.6) (corrected for damping):

$$M_1(q, S\rightarrow q', S)$$
$$= +B_{qq'}/(E_q^- + i\gamma)\sum_{r=1}^{3} D_r{}^{(t')}D_r{}^{(t)}a_{q'}{}^*a_q,$$

$$M_2(q, S\rightarrow q', S)$$
$$= -B_{qq'}/(E_{q'}{}^+ - i\gamma)\sum_{r=1}^{3} D_r{}^{(t')}D_r{}^{(t)}a_q a_{q'}{}^*, \tag{3.9}$$

$$M_1(q, T_r\rightarrow q', T_s)$$
$$= -B_{qq'}/(E_q^+ - i\gamma)D_s{}^{(t')}D_r{}^{(t)}a_{q'}{}^*a_q,$$

$$M_2(q, T_r\rightarrow q', T_s)$$
$$= +B_{qq'}/(E_{q'}{}^- + i\gamma)D_r{}^{(t')}D_s{}^{(t)}a_q a_{q'}{}^*,$$

where

$$B_{qq'} \equiv (E_u/3)^2 f(q)f(q')qq'. \tag{3.10}$$

Combining Eqs. (3.9) and (3.7) and making use of the phonon "matrix elements,"

$$(a_q a_{q'}{}^*)^2 = (a_{q'}{}^*a_q)^2$$
$$= (\hbar/2M)^2(\omega_q\omega_{q'})^{-1}n_q(1+n_{q'}), \tag{3.11}$$

we find

$$W(q\rightarrow q')$$

$$= \frac{2\pi}{\hbar}\delta(\hbar\omega_q - \hbar\omega_{q'})B_{qq'}{}^2\left(\frac{\hbar}{2M}\right)^2 \frac{1}{\omega_q\omega_{q'}}$$

$$\times \left\{B_S(T)\left(\sum_{r=1}^{3} D_r{}^{(t)}D_r{}^{(t')}\right)^2\left|\frac{1}{E_q^- + i\gamma_T} - \frac{1}{E_{q'}{}^+ - i\gamma_T}\right|^2\right.$$

$$\left.+ B_T(T)\sum_{r,s=1}^{2}\left|\frac{D_s{}^{(t)}D_r{}^{(t')}}{E_{q'}{}^- + i\gamma_T} - \frac{D_r{}^{(t)}D_s{}^{(t')}}{E_q^+ - i\gamma_T}\right|^2\right\}. \tag{3.12}$$

Since the expressions are already quite complicated, we shall simplify the resonance terms immediately by making use of the fact that $\gamma_T \ll 4\Delta$. We can completely omit γ_T even in the resonance denominators since we plan to use our results to compute a single-mode relaxation time τ_{qt} (see below) for use in a heat transport calculation. When $1/\tau_{qt}$ is very large, so little heat flow occurs at that frequency that putting $\gamma_T=0$ has little numerical consequence. Away from the resonance, γ_T has negligible importance. It is a simple matter to keep the damping factor in the expressions if for some reason this is desired. With this simplification and using

the delta function, (3.12) becomes

$$W(q \rightarrow q')$$

$$= \frac{2^2 \pi B_{qq'}{}^2}{(2M\omega_{qt})^2} \delta(\omega_{qt} - \omega_{q't'}) \frac{1}{[(\hbar\omega_{qt})^2 - (4\Delta)^2]^2}$$

$$\times \{B_S(T)D_S{}^{tt'}2(4\Delta)^2 + B_T(T)[\{D_T{}^{tt'} - D_S{}^{tt'}\}$$

$$\times (\hbar\omega_{qt})^2 + \{D_T{}^{tt'} + D_S{}^{tt'}\}(4\Delta)^2]\}, \quad (3.14a)$$

where

$$D_S{}^{tt'} \equiv (\sum_r D_r{}^{(t)}D_r{}^{(t')})^2,$$

$$D_T{}^{tt'} \equiv \sum_{r,s} (D_r{}^{(t)}D_s{}^{(t')})^2. \quad (3.14b)$$

For the application of our results to transport theory, the so-called "single-mode relaxation time" τ_{qt} defined by

$$\frac{1}{\tau_{qt}} = N \sum_{q't'} W(qt \rightarrow q't') \quad (3.15)$$

is of great use. Equation (3.15) gives the rate of decay of a single phonon q into all other modes. We have simply added the effect of the N-uncorrelated impurity donor electrons in the sample of interest, since we have neglected any phonon scattering due to the donor-donor interaction. In general, τ defined by Eq. (3.15) does not coincide with the one appropriate to heat conduction, since the inverse transitions have not been taken into account. By formulating a proper transport equation in terms of (3.15), one finds in simple cases (e.g., isotropic scattering) that the correct τ is just that given in Eq. (3.15), or differs only by a multiplicative constant of order unity.[4-6] We shall adopt (3.15) as the effective relaxation time. The uncertainty thereby introduced is certainly no greater than that due to other rough approximations presently necessary in the calculation of the lattice thermal conductivity.

To use (3.14) to calculate the relaxation time given in Eq. (3.15), we change the sum to an integral in the usual way. For the phonon spectrum, which is assumed to be unchanged by the donor impurities, we make the usual acoustic approximation

$$\omega_{qt} = v_t(\theta, \phi)q; \quad q \equiv |\mathbf{q}|, \quad (3.16)$$

where v_t depends only on the directional coordinates of $\mathbf{q}$. The angular integration over $d\Omega' = \sin\theta' d\theta' d\phi'$ is approximated in the usual crude fashion, where $v_{t'}(\theta', \phi')$ is replaced by its angular average $\bar{v}_{t'} = (1/4\pi)\int d\Omega' \, v_{t'}(\theta', \phi')$ wherever it occurs. For consistency, $v_t(\theta, \phi)$ is also averaged. We find the following relaxation time:

$$\frac{1}{\tau_{qt}} = \frac{E_u{}^4 n_{ex}}{2.3^4 \cdot \rho^2 \cdot \pi} \frac{\omega_{qt}{}^4}{[(\hbar\omega_{qt})^2 - (4\Delta)^2]^2} \sum_{t'} f^2\left(\frac{\omega_{qt}}{\bar{v}_t}\right) f^2\left(\frac{\omega_{qt}}{\bar{v}_{t'}}\right)$$

$$\times \frac{1}{\bar{v}_{t'}{}^5 \bar{v}_t{}^2} \{B_S(T)\langle D_S{}^{tt'}\rangle_{\Omega'} 2(4\Delta)^2$$

$$+ B_T(T)\langle[\cdots]\rangle_{\Omega'}\}, \quad (3.17)$$

where $[\cdots]$ represents the same expression as in Eq. (3.14a), n_{ex} is the number of uncompensated donor electrons per cm^{-3}, and

$$\langle D_x{}^{tt'}\rangle_{\Omega'} \equiv \left(\frac{1}{4\pi}\right)\int d\Omega' \, D_x{}^{tt'}. \quad (3.18a)$$

The evaluation of these angular functions is straightforward using the definition of $D_x{}^{tt'}$ [Eq. (3.14b)] and Hasegawa's representation of $D_r{}^{(t)}$. One may easily verify the following exact results[28]:

$$3\langle D_S{}^{t1'}\rangle_{\Omega'} = \langle D_T{}^{t1'}\rangle_{\Omega'},$$

$$3\langle D_S{}^{t2'} + D_S{}^{t3'}\rangle_{\Omega'} = \langle D_T{}^{t2'} + D_T{}^{t3'}\rangle_{\Omega'}, \quad (3.19)$$

$$3\langle D_S{}^{t1'}\rangle_{\Omega'} = 2\langle D_S{}^{t2'} + D_S{}^{t3'}\rangle_{\Omega'}.$$

Our final expression [using the relations (3.19) in Eq. (3.17)] for the single-mode relaxation time is

$$\frac{1}{\bar{\tau}_{qt}} = \frac{G(4\Delta)^4}{\bar{v}_t{}^2 s_t} \frac{\omega_{qt}{}^4}{[(\hbar\omega_{qt})^2 - (4\Delta)^2]^2} \left(\frac{1}{s_1 \bar{v}_1{}^5} + \frac{3}{2 s_2 \bar{v}_2{}^5}\right) \langle D_S{}^{t1'}\rangle_{\Omega'}$$

$$\times \{B_S(T) + B_T(T)[2 + (\hbar\omega_{qt}/4\Delta)^2]\}, \quad (3.20)$$

where

$$s_t \equiv (1 + [r_0\omega/2\bar{v}_t]^2)^4 = f^{-2}(\omega/\bar{v}_t),$$

$$G \equiv \frac{E_u{}^4 n_{ex}}{3^4 \pi \rho^2 (4\Delta)^2}, \quad (3.21)$$

and

$$\ll D_S{}^{t1'} \gg \equiv \left(\frac{1}{4\pi}\right)\int d\Omega \langle D_S{}^{t1'}\rangle_{\Omega'}$$

$$= 48/225, \quad 32/225, \quad \text{and} \quad 40/225$$

$$\text{for} \quad t = 1, 2, 3. \quad (3.18b)$$

It might be useful to make a few remarks about this relaxation time in Eq. (3.20), in particular, the difference between the singlet and triplet donor electron contributions. Note first of all that, at resonance ($\hbar\omega = 4\Delta$), the factor in the curly bracket reduces to $B_S(T) + 3B_T(T)$, which is 1. That is, at resonance, the relaxation time is temperature-independent and we would have obtained the same result if we had assumed all the electrons were in the singlet state. The second point is that, of course, $B_S(T) \gg B_T(T)$ for the low temperatures of interest. If we assume, for simplicity, that these occupation probabilities are given by the usual Boltzmann factors, then $B_T/B_S = \exp(-\bar{T}_R/T)$, where $\bar{T}_R$ is given in Table I. While we may set $B_T = 0$ for As with little error, $\bar{T}_R$ is small enough for Sb that B_T is appreciable even for T as low as 3 or 4°K. Note also that the triplet contribution increases with the phonon energy. To be more exact, it would seem that

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[28] In Table IV of Ref. 22, the first entry should read $\langle D_S{}^{11'}\rangle_{\Omega'} = (4/15)(\sin^2 2\theta + \sin^4\theta \sin^2 2\phi)$. Note that

$$\langle D_S{}^{t1'}\rangle_{\Omega'} = (\tfrac{2}{3})\langle D_S{}^{t2'} + D_S{}^{t3'}\rangle_{\Omega'}$$

making the second column redundant.

if we simply assumed all the electrons were in the ground singlet state, we would overestimate the scattering strength for $\hbar\omega < 4\Delta$ and underestimate it for $\hbar\omega > 4\Delta$. The last remark we wish to make is that the temperature dependence of τ is closely related to our mechanism of phonon scattering via *virtual* electronic transitions in a two-level system. If we had assumed that the phonons were scattered mainly by *real* electronic transitions, as Orbach[25] did in the spin-phonon problem, we would find that the temperature dependence of τ is quite different to that in Eq. (3.20), namely, $1/\tau \propto [B_S(T) - 3B_T(T)]$.

We now turn our attention to the consistency of the perturbative approach we have used in discussing the donor-electron mechanism. First of all, our expansion requires for its validity

$$|\sum_{i=1}^{N} V_i|^2 \ll (4\Delta)^2, \qquad (3.22)$$

where V_i is the electron-phonon interaction due to the ith donor impurity and we assume a random distribution of donors. This inequality is equivalent to $N\langle V_{ep}\rangle^2 \ll (4\Delta)^2$. If $\langle V_{ep}\rangle$ is assumed to be correctly given by the matrix elements in Eq. (2.5), a simple numerical check will show that this inequality is easily satisfied up to the highest impurity concentrations for Sb as well as As. We note that this also "justifies" our use of the adiabatic or Born-Oppenheimer approximation, even though the usual condition (which, in this problem, would be $\hbar\omega \ll 4\Delta$) may not hold.

The next problem is to estimate γ_T, one-half the lifetime broadening of the triplet-state levels. Our entire approach in this paper is based on treating the electron-phonon interaction as a weak perturbation causing transitions between the singlet and triplet states. A necessary but not sufficient condition is that $\gamma_T \ll 4\Delta$. Using the same sort of approximations as in the derivation of Eq. (3.17), we find from Eqs. (3.6), (2.6a), and (3.10)

$$\gamma_T = \pi \sum_{q,t} \delta(\hbar\omega_{qt} - 4\Delta)|\langle q,S|V|T_r\rangle|^2$$

$$= \left(\frac{\pi E_u^2}{2 \times 3^2 \rho \Omega}\right) \sum_t (D_r^{(t)})^2$$

$$\times \sum_q \delta(\omega_{qt} - 4\Delta/\hbar)\frac{f^2(q)q^2(n_{qt}+1)}{\omega_{qt}} \qquad (3.23)$$

$$\approx \frac{E_u^2(4\Delta)^3}{3^2\hbar^4 4\pi\rho} \sum_t \frac{\langle(D_r^{(t)})^2\rangle_\Omega}{\bar{v}_t^5}\left(\frac{1}{1 - e^{-4\Delta/kT}}\right),$$

where

$$\bar{v}_t = \bar{v}_t[1 + (4\Delta r_0/(2\hbar\bar{v}_t))^2]^{1/5}. \qquad (3.24)$$

Using Table III of Hasegawa,[21] it is fairly easy to prove

TABLE II. The valley-orbit splitting versus the lifetime broadening $2\gamma_T$ of the triplet state.

Impurity in Ge	4Δ (eV) ($\times 10^{-3}$)	$4\Delta/2\gamma_T$[a]	$4\Delta/2\gamma_T$[b]	$4\Delta/2\gamma_T$[c]
As	4.15	5300	70	1400
Sb	0.57	65	5	30

[a] Effective Bohr radius $r_0 = 45$ Å and 0°K.
[b] Effective Bohr radius $r_0 = 23$ Å and 0°K.
[c] Values found by W. D. Twose, as quoted in Ref. 22, at 7°K.

that for $r = 1$, 2, or 3,

$$\sum_{t=1}^{3} \frac{\langle(D_r^{(t)})^2\rangle_\Omega}{g(\bar{v}_t)} = \frac{2}{5}\left(\frac{2}{3g(\bar{v}_1)} + \frac{1}{g(\bar{v}_2)}\right), \qquad (3.25)$$

where $g(\bar{v}_t)$ is any function of $\bar{v}_t$. Thus, the last result of Eq. (3.23) reduces to

$$\gamma_T = \frac{E_u^2(4\Delta)^3}{2\pi 3^2 \times 5\hbar^3\rho}\left(\frac{2}{3\bar{v}_1^5} + \frac{1}{\bar{v}_2^5}\right)\left(\frac{1}{1 - e^{-4\Delta/kT}}\right). \qquad (3.26)$$

In Table II, we have listed some values of γ_T (relative to 4Δ) for Sb and As found from Eq. (3.26). The average velocities used are those computed by Hasegawa[21] from elasticity data, $\bar{v}_1 = 5.37 \times 10^5$ cm sec^{-1} and $\bar{v}_2 = \bar{v}_3 = 3.28 \times 10^5$ cm sec^{-1}, while $\rho = 5.35$ g cm^{-3} and $E_u = 19$ eV. Though γ_T increases very rapidly as r_0 decreases, even for $r_0 = 23$ Å we still have $\gamma_T \ll 4\Delta$.

It might be useful to make some qualitative comments about the frequency dependence of τ_{qt} in Eq. (3.20) and make a detailed comparison to the relaxation time τ_{qt}^K given by Keyes[9] (he simply assumed all electrons were in the singlet state),

$$\frac{1}{\tau_{qt}^K} = G\omega_{qt}^4\frac{2}{5}\left(\frac{2}{3\bar{v}_1^5} + \frac{1}{\bar{v}_2^5}\right)\phi(\mathbf{e}_t,\mathbf{q})f^4(q), \qquad (3.27)$$

where the dimensionless factor $\phi(\mathbf{e}_t,\mathbf{q})$ is defined by

$$\phi(\mathbf{e}_t,\mathbf{q}) \equiv 1 + q^{-2}[(\mathbf{q}\cdot\mathbf{e}_t)^2 - 2\sum_{i=1}^{3}(\mathbf{q})_i^2(\mathbf{e}_t)_i^2] \qquad (3.28)$$

and the function $f(q)$ and constant G are given in Eqs. (2.6b) and (3.21), respectively. In Figs. 2 and 3 we have sketched $1/\tau$ versus ω for longitudinal phonons, using the formula given by Keyes (3.27) and the improved formula derived in this paper (3.20) with $T = 0°K$. In Fig. 2, which is for Sb-doped Ge, we have also sketched what Eq. (3.20) would predict if $r_0 = 0$. We see that we still get a resonance but instead of the scattering vanishing as ω increases, it settles down to a constant, independent of ω. For later use, we have also included in Fig. 3 the value of $1/\tau_B$ for pure boundary scattering with an effective mean-free path $L = 0.45$ cm. Lastly, we may note that longitudinal phonons are scattered much more strongly than transverse phonons are.

A quantitative comparison of Eq. (3.27) and our result is easily done and will show what approximations are made in the former. Our basic result (3.20) may be rewritten as, if $\hbar\omega \ll 4\Delta$,

$$1/\bar{\tau}_{qt} = G\omega_{qt}^4 \sum_{t'} f^2(\omega_{qt}/\bar{v}_t) f^2(\omega_{qt}/\bar{v}_{t'})(\bar{v}_{t'}{}^5\bar{v}_t{}^2)^{-1}$$

$$\times \sum_r (D_r^{(t)})^2 \langle(D_r^{(t')})^2\rangle_{\Omega'}, \quad (3.29)$$

where we have not averaged over (θ,ϕ) and have used the fact that the interference contribution vanishes in $\langle D_s^{tt'}\rangle_{\Omega'}$, leaving only $\sum_r (D_r^{(t)})^2 \langle(D_r^{(t')})^2\rangle_{\Omega'}$. By means of a little algebra we can express Keyes' relaxation time (3.27) in a form similar to (3.29). Keyes' anisotropy factor $\phi(\mathbf{e}_t,\mathbf{q})$ defined in Eq. (3.27) is, in terms of Hasegawa's notation,

$$\phi(\mathbf{e}_t,\mathbf{q}) = \sum_r (\mathbf{e}_t \cdot D_r \cdot \mathbf{q})^2$$

$$= \sum_r (D_r^{(t)})^2. \quad (3.30)$$

In addition, we have from Eq. (3.25),

$$\tfrac{2}{5}(3/(2\bar{v}_1{}^7)+1/\bar{v}_2{}^7) = \tfrac{1}{3}\sum_r \sum_{t'} \langle(D_r^{(t')})^2\rangle \Omega'/\bar{v}_{t'}{}^7. \quad (3.31)$$

Equation (3.27) can be rewritten, using Eqs. (3.30) and (3.31), as

$$1/\tau_{qt}{}^K = G\omega_{qt}^4 f^4(\omega_{qt}/\bar{v}_t) \sum_{t'}\sum_r\sum_s (D_r^{(t)})^2$$

$$\times \langle(D_s^{(t')})^2\rangle_{\Omega'}(1/3\bar{v}_{t'}{}^7). \quad (3.32)$$
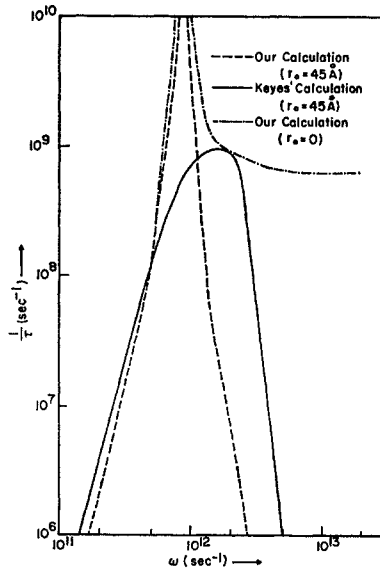

FIG. 2. A plot of the reciprocal single-mode relaxation time versus the frequency for longitudinal modes in Sb-doped Ge with n_{ex} =1.7×10^{16} cm^{-3}. The valley-orbit splitting was taken to be 4Δ = 0.57×10^{-3} eV and the effective radius r_0=45 Å. Our curve is based on Eq. (3.20) of the text for $T=0°$K and Keyes' curve is based on Eq. (3.27). We have also plotted our result for r_0=0 to separate the effect of the true resonance from the cutoff factor $f(q)$.
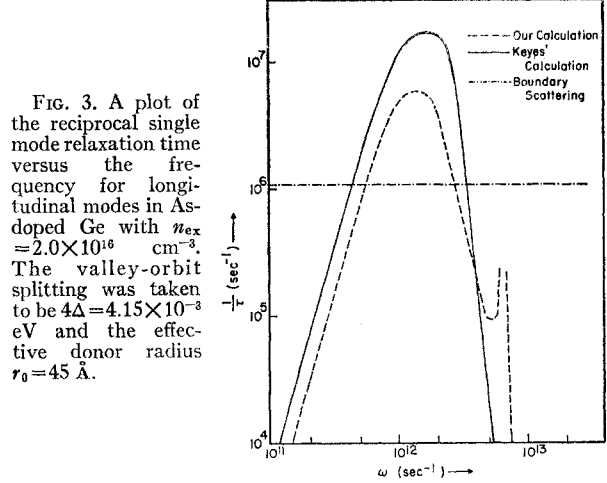

FIG. 3. A plot of the reciprocal single mode relaxation time versus the frequency for longitudinal modes in As-doped Ge with n_{ex} =2.0×10^{16} cm^{-3}. The valley-orbit splitting was taken to be 4Δ=4.15×10^{-3} eV and the effective donor radius r_0=45 Å.

Comparing Eq. (3.32) with the correct expression (3.29), we can see what approximations have been made. First of all, $f^2(\omega/\bar{v}_t)f^2(\omega/\bar{v}_{t'})$ and $\bar{v}_{t'}{}^5\bar{v}_t{}^2$ in Eq. (3.29) have been replaced by $f^4(\omega/\bar{v}_t)$ and $\bar{v}_{t'}{}^7$, respectively. This change results in the scattering of a longitudinal phonon to be overestimated by a factor of 3 or so, while the scattering of a transverse phonon is slightly underestimated. This difference for a longitudinal phonon is clearly shown in Fig. 3 in the case of As.

The second approximation in Eq. (3.32) has to do with the anisotropy factor, where $\langle(D_r^{(t')})^2\rangle_{\Omega'} \rightarrow \tfrac{1}{3}\sum_s \langle(D_s^{(t')})^2\rangle_{\Omega'}$. Since we shall not make any use of it, the correct anisotropy factor in Eq. (3.29) will not be worked out explicitly or investigated. As far as averages go, this change in the anisotropy factor produces little error. In summary, then, the *major* difference between our result for the singlet electron and Keyes' is the presence of our true resonance factor. Note that at a true resonance, one has

$$1/\tau \approx (1/\tau_{\text{Keyes}})(4\Delta/2\gamma_T)^2, \quad (3.33)$$

where τ is the correct relaxation time due to the singlet electrons [Eq. (3.20)]. A glance at Fig. 2 and Table II will show that though the resonance is strong, the general condition $\omega\tau \gg 1$ holds.

The effect of the resonance depends on the value of 4Δ. In the case of Sb, the true resonance frequency ω_0 is slightly to the left of maximum around $\omega_M \approx c/r_0$ due to the finite size of the impurity state. Since it occurs in a frequency range of already high scattering, its effect will not only be undramatic but it will occur at very low temperatures ($\lesssim 1°$K). In addition, it will result in a faster cutoff for high frequencies ($\omega \gg \omega_M \approx \omega_0$) than Keyes predicts. For As, in contrast, the true resonance occurs to the right of ω_M at higher phonon frequencies ($\omega_0 \approx 4\omega_M$). Since boundary and isotope scattering dominate in this region, our results will again be similar to Keyes. A donor with 4Δ somewhere in between that of As and Sb (i.e., around 2×10^{-3} eV;

P would be a possibility) would exhibit the effects of the true resonance at a more convenient temperature. Of course, overlaid on any qualitative effects of the electron-phonon mechanism, the true resonance should still be there as a *very* narrow region of high scattering, at least if it is not damped by the effects of other impurity states.

IV. APPLICATION TO THE LOW-TEMPERATURE THERMAL CONDUCTIVITY OF n-TYPE GERMANIUM

We are now in a position to estimate the influence of our scattering mechanism on the heat conductivity of lightly doped $(n_{ex} \lesssim 10^{17}$ cm$^{-3})$ n-type germanium. Experimentally, most of the interesting effects occur below the low-temperature maximum. In this region the dominant scattering mechanisms are boundary scattering and impurity scattering. We neglect the normal three-phonon processes. (This last approximation is usually well justified in this temperature region, but in the present case, where there is strong scattering at one frequency, the normal processes might have a disproportionate effect by splitting the weakly scattered high-frequency phonons into strongly-scattered lower frequency phonons.) We follow the usual semi-phenomenological method of combining the mechanisms as developed by Klemens[4] and Callaway.[19] Combining reciprocal relaxation times gives for the total relaxation time $\tau_T(q)$,

$$\tau_T^{-1}(q) = \tau_B^{-1}(q) + \tau_I^{-1}(q) + \tau_{ep}^{-1}(q), \qquad (4.1)$$

where τ_{ep} is the relaxation time for the donor electron-phonon scattering, τ_I is for point defect scattering by the ever present isotopes of Ge, and τ_B is for boundary scattering. By following this procedure, we are emphasizing the dependence of $K(T)$ on the scattering cross sections and glossing over the more subtle transport problems involved.

For boundary scattering, we take

$$\tau_{Bt}^{-1} = \bar{v}_t/L, \qquad (4.2)$$

where t denotes the polarization and L is the Casimir length,[29] a measure of the diameter of the specimen. For a sample of square cross section, the theoretical value is $L = 1.12d$, where d is the side dimension. L is generally found from experiment, such values agreeing with the calculated ones to within a factor of 2 or 3. This is satisfactory agreement in view of the crudity of the theory. However, from the low-temperature thermal conductivity of Goff's purest sample,[2] we feel that $L = 1.12d$ (which we have used in our calculations) is an excellent approximation for the experimentally correct value of L.

The theory of phonon scattering by small mass fluctuations randomly distributed in an otherwise pure crystal seems to be on a firm footing. The scattering

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[29] H. B. G. Casimir, Physica **5**, 495 (1938).

due to the mass differences introduced by the presence of impurity atoms is completely negligible for the low concentrations of interest. Since an adequate introduction with references can be found in Sec. V of I, we shall be brief and simply state that the *isotopic* relaxation time τ_I is given by[4]

$$\tau_I^{-1} = A\omega^4, \qquad (4.3)$$

where the polarization averaged factor A depends in a known manner on the crystal's parameters and degree of isotopic disorder. For normal Ge, calculations give $A \simeq 2.40 \times 10^{-44}$ sec^3. As shown by Callaway,[19] this value is in excellent agreement with experimental work and we have used this value in our numerical calculations. Isotope scattering dominates the phonon-phonon processes well up to the maximum in $K(T)$, at least if the latter are incorporated in the manner discussed by Callaway.[19]

Our major interest, of course, is in the resonance electron-phonon relaxation time derived in Sec. III and given in a suitable form by Eq. (3.20). Although we incorporate boundary and isotope scattering, we have used the theoretical values of the constants involved. We have *not* used A and L as unknown parameters to be fitted by experiment.

Starting from Eq. (3.32) of I and transforming to the dimensionless variable $x \equiv \hbar\omega/kT$, one obtains for the thermal conductivity

$$K(T) = \left(\frac{k^4 L T^3}{6\pi^2 \hbar^3}\right) \sum_t (I_t(T)/v_t^2), \qquad (4.4)$$

where the temperature-dependent integrals $I_t(T)$ are defined by

$$I_t(T) \equiv \int_0^\infty \frac{e^x x^4}{(e^x - 1)^2} \frac{dx}{R_t(x,T) + P_t(x,T)}, \qquad (4.5)$$

in which the following dimensionless functions are used:

$$R_t(x,T) \equiv 1 + (AL/v_t)(kT/\hbar)^4 x^4, \qquad (4.6)$$

$$P_t(x,T) \equiv \frac{HT^4 x^4 \langle\langle D_s^{t1'} \rangle\rangle}{[(T^2 x^2 - \bar{T}_R^2)^2 s_t v_t^3]} \times \left(\frac{1}{s_1 \bar{v}_1^5} + \frac{3}{2 s_2 \bar{v}_2^5}\right)$$

$$\times \left(B_s(T) + \left[2 + \left(\frac{T}{\bar{T}_R}\right)^2 x^2\right] B_T(T)\right), \qquad (4.7)$$

with

$$H \equiv \frac{E_u^4 n_{ex}(4\Delta)^2 L}{3^4 \rho^2 \pi \hbar^4}; \quad \bar{T}_R \equiv 4\Delta/k. \qquad (4.8)$$

The cutoff factors s_t and the numerical coefficients $\langle\langle D_s^{t1'}\rangle\rangle$ are given in Eqs. (3.21) and (3.18b), respectively. An obvious simplification is to omit $1/s_1 \bar{v}_1^5$ in Eq. (4.7), though we have kept it.

We have had Eq. (4.4) evaluated by electronic computer for some representative samples used in Goff's experiments.[2] For simplicity, we have taken

$B_S(T)=1$ and $B_T(T)=0$ [see discussion after Eq. (3.20)]. In Figs. 4 and 5 we have plotted the results of our work for Sb 207 and As 223I, respectively. We have used the same values of ρ, E_u, and $\bar{v}_t$ as with Eq. (3.28). For the effective radii, we have somewhat arbitrarily set $r_0=\frac{1}{2}(a+b)$ and made use of data collected in Table I of Ref. 16. This procedure gives $r_0=43$ Å for Sb and $r_0=37$ Å for As. In Fig. 6, we have made a comparison between our results and that of Keyes for Sb 207. Since we were interested in the different way the electron-phonon mechanism shows up in the two calculations, we have left out isotope scattering in Fig. 6. We have not plotted the relevant curves for As since our result is almost identical to Keyes (due to cancelling of effects).

As we have indicated at the end of Sec. III, except for the true resonance our results are not very different from that of Keyes.[9] Quantitatively, though, ours are


FIG. 4. The experimental and theoretical thermal conductivity of Sb-doped Ge is shown. The theoretical curve is based on Eqs. (4.4) and (4.5) which adds our electron-phonon scattering mechanism and the standard expressions for boundary and isotope scattering. We have assumed all electrons are in the singlet state. Goff's sample (Ref. 2) Sb 207 had $n_{ex}=1.7\times10^{16}$ cm^{-3} and a square cross section of side $d=0.4$ cm. We have taken as the effective donor radius, $r_0=43$ Å.
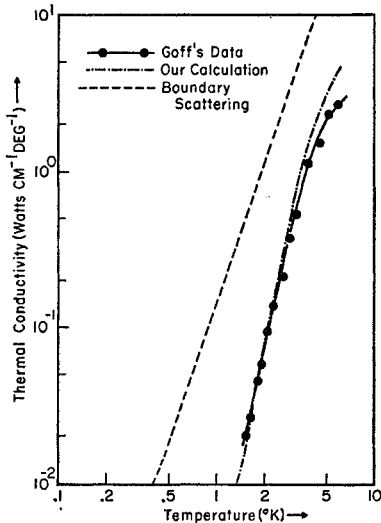
superior. We note the satisfactory feature that our results consistently overestimate the conductivity, with excellent agreement at low temperatures. Keyes overestimates the electron-phonon scattering (see Fig. 6) for lower temperatures and underestimates it for higher temperatures in the case of Sb—a qualitative discrepancy which is quite unsatisfactory. If we included isotope scattering in evaluating Keyes' expression for $K(T)$, his curve would underestimate the conductivity for *both* high and low temperatures. Since it lacks the resonance factor and incorrectly averages a sum involving the velocities $\bar{v}_t$, Keyes' expression leads to slightly more scattering for high-energy phonons, as can be seen in Figs. 2 and 3. As a result, his better fit for Sb at high temperatures (in the absence of isotope scattering) is fortuitous (see Fig. 6).

The thermal-conductivity integral not only smooths out the effect of a region of maximum scattering, but also shifts the effective temperature T_M at which it has

FIG. 5. The experimental and theoretical thermal conductivity of As-doped Ge is shown. Goff's sample As 223I had $n_{ex}=2.0\times10^{16}$ cm^{-3} and $r_0=37$ Å.
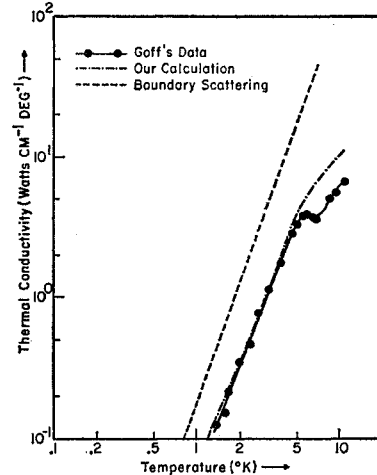
its most noticeable effect. The factor $e^x x^4(e^x-1)^{-2}$ has a maximum for x a little less than 4. One would expect that a resonance (or more generally a maximum) at $\omega_R\approx kT_R/\hbar$ would have its strongest effect at $x_M\approx kT_R/kT_M\approx4$ or $T_M\approx\frac{1}{4}T_R$. It has been found[30] that due to an extra factor such as τ_T in Eq. (4.1), T_R is divided by $a\lesssim6$. Now, in the problem at hand, we have a broad region of maximum scattering centered around $\omega\approx c/r_0$ (as first shown by Keyes) and, in addition, a sharp resonance at $\omega=4\Delta/\hbar$. The first maximum should have its largest effect for all donors around 1.8°K. This is verified by the results in Figs. 4 and 5. The true resonances, on the other hand, should show their effect directly at $T_M(\text{Sb})\approx1$°K and $T_M(\text{As})\approx8$°K. This is,

FIG. 6. A comparison is made between our and Keyes' estimate of the electron-phonon interaction's effect on the thermal conductivity of Sb 207 (the same parameters were used in both cases). We have left out isotope scattering in order to see more clearly the contribution of the electron-phonon interaction.
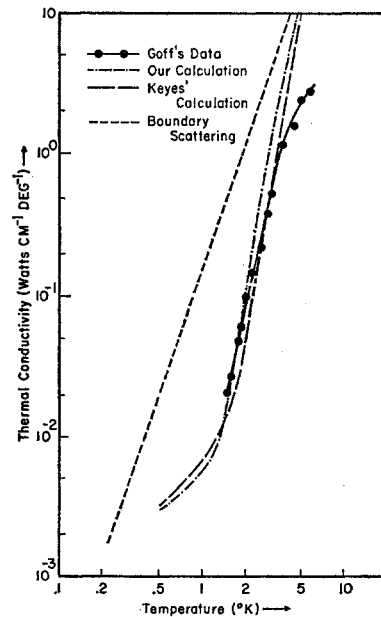
[30] R. O. Pohl, Phys. Rev. Letters, 8, 481 (1962) and private communication. Actually any value between 5 and 6 is reasonable. We have taken the upper limit.

indeed, the case for Sb as shown by Fig. 6. Our calculated curve is depressed relative to that of Keyes around 1°K, and consequently, a sharper change in direction occurs at lower temperatures. This is as expected from the qualitative discussion of the Introduction. Unfortunately, the experimental points do not extend to this region. It will be noted that our theory for Sb agrees best with experiment precisely where it should, i.e., near the temperature at which the effects discussed are maximal.

As shown in Fig. 5, the data[2] for As show a dip near 7°K, just about where we expect the true resonance scattering to be most effective. Goff's data for other samples of As-doped Ge also show this anomalous behavior near 7°K but in not such a striking fashion. To our consternation, our calculation does not easily reproduce this feature which should constitute the most important evidence for the mechanism described in this paper. A glance at Fig. 3 aids in the understanding of this dilemma. For As, the true resonance energy lies at a frequency such that qr_0 is substantially greater than unity. Thus, the cutoff suppresses the effect of the resonance in that when it does occur, our mechanism's strength is well below that of boundary and isotope scattering. The resonance is still there, but has almost zero width. A more detailed experimental investigation of this region would be of great interest.

According to Carruthers et al.,[3] experimental work on p-type material (see part B of Sec. V) at temperatures as low as 0.3°K results in the thermal conductivity continuing downward in a straight line. Our curve predicts this for the different case of Sb in Ge down to about 1°K but not further. As the temperature is lowered below this resonance value, the mechanism we have considered rapidly becomes ineffective. Unless a new process takes over then, we expect a kink in $K(T)$ at temperatures below $T_M \approx 4\Delta/6k$. Experiments on the theoretically tractable case of donors in Ge would be valuable in clarifying the situation. For As, the broad scattering peak first discussed by Keyes dominates at low temperatures since the true resonance can be important only around 8°K. As a result, the electron-phonon mechanism reaches its maximum around 1.5–2°K and becomes ineffective at lower temperatures in a smoother fashion than in the case of Sb. Of course, the major reason for the difference between the slopes of $K(T)$ for Sb and As is due to the simple fact that the electron-phonon mechanism is much more effective in Sb than in As because of the difference in valley-orbit splittings.

In general, we obtain too little resistance above the liquid-helium range. There are several obvious reasons why this is to be expected: (a) We have totally neglected the three-phonon processes, which may be important by themselves and also in connection with our resonant mechanism. (b) We have not considered the effect of the increasing number of ionized donor impurities as the temperature increases (see Goff[2]). (c) We have, for

simplicity, assumed that all the electrons are in the singlet state (this may lead to some non-negligible error for Sb). (d) We have forgotten about the true excited donor states. (e) The "effective-mass" theory breaks down near the impurity core. These last two points are of some theoretical interest and merit a few more words.

As we have seen, the sharpness of the cutoff factor $f(q)$ has rendered our scattering mechanism ineffective at higher temperatures. It is important to realize that we have underestimated to some extent the strength of our electron-phonon mechanism for higher energy phonons simply because we have not taken into account any corrections to the effective-mass wave functions. From Eq. (2.6a), we note $f(\mathbf{q})$ for high $\mathbf{q}$ is closely related to the charge distribution at $\mathbf{r}=0$. Due to this core effect, the corrected wave function has an envelope function $\bar{F}(\mathbf{r})$ which is considerably more concentrated at the origin.[20] This implies that $\bar{F}^2(\mathbf{r})$ will have larger high-frequency Fourier components than $F^2(\mathbf{r})$.

There are many ways of taking the core corrections into account.[20,31] While the symmetric singlet state has a nonzero value at the origin, the three donor functions of the triplet vanish there. As a result, the uncorrected effective mass theory should be quite good for the triplet. To improve on the singlet, the simplest procedure might be to take a smaller value of r_0 in the singlet envelope function.[31] One finds with

$$\bar{F}(\mathbf{r}) = (\pi \bar{r}_0{}^3)^{-1/2} e^{-r/\bar{r}_0} \quad \text{for the singlet},$$
$$F(\mathbf{r}) = (\pi r_0{}^3)^{-1/2} e^{-r/r_0} \quad \text{for the triplet}, \tag{4.9}$$

where $\bar{r}_0$ is somewhat smaller than the effective mass radius r_0, that the new cutoff factor is

$$\bar{f}(q) = \frac{8c^3}{(r_0 \bar{r}_0)^{3/2}} \frac{1}{(1+c^2 q^2)^2}, \tag{4.10}$$

with $1/c = 1/r_0 + 1/\bar{r}_0$. Taking a smaller value for the effective radius, of course, simply raises and shifts to the right the relevant curves in Figs. 2 and 3. The functional form of $f(q)$ is still the same in that the steepness of the cutoff is unchanged. We believe that if the correct wave function were known, $f(q)$ would be sufficiently modified that the resonance would not be suppressed.

While on the subject of corrections to the all important function $f(q)$, we note that we always have worked in the isotropic approximation. The conduction valleys are quite anisotropic and the trial envelope function given by Eq. (2.2) is considerably closer to reality than that given by Eq. (2.1). The changes in $f(q)$ might not be negligible, especially in the critical region of higher phonon energies.

We should like to make a remark on the transport of energy by resonantly scattered phonons. As is well known,[32] the energy is not carried at the group velocity,

[31] H. Fritzsche, Phys. Rev. 125, 1560 (1962).

[32] L. Brillouin, Wave Propagation and Group Velocity (Academic Press Inc., New York, 1958).

as assumed in deriving Eq. (4.4), but at some slower velocity in the resonance region. This effect has been observed for phonons by Shiren.[33] The error suffered by using the wrong velocity is negligible in our problem since those phonons whose group velocity deviates appreciably from the energy velocity are too strongly scattered to contribute very much to the heat current. That the energy velocity decreases, aids in making their contribution negligible.

There is the possibility that phonons are scattered during electronic transitions from one localized state to another localized state.[14,15] According to an estimate by Keyes,[9] the mean-free path of a phonon due to this process is always greater than 1 cm in the liquid-helium temperature range for the samples of Goff and Pearlman[2] and, hence, can be neglected. Pyle[14] notes that the scattering his theory predicts underestimates the thermal resistance by a factor of 10. His scattering also depends critically on the degree of compensation, a feature which does not seem to be compatible with the experimental data of Goff[2] (of course, Pyle's work was for p-type material).

At higher temperatures, the problem also arises as to whether the true excited levels (in the effective-mass approximation) can be neglected. The energies involved in transitions between the low-lying intervalley-excited states are not much smaller than the energies involved in transitions to true excited levels. If δ is the difference between the ground state given by the effective-mass approximation and the first excited state, $\delta/4\Delta$ is 8.2 for Sb but only 1.1 for As in Ge. In the case of Si (see part A of Sec. V), the intervalley correction splits the sixfold degenerate ground state into a singlet, a triplet, and a doublet. If $6\Delta'$ is defined as the difference between the singlet and doublet, then one finds $\delta/6\Delta' \approx O(1.5)$ for As, P, and Sb in Si.

Phonon scattering by transitions to true excited states might be quite important for higher phonon energies if they have a slower cutoff factor. As we saw earlier, the ineffectiveness of the electron-phonon interaction at higher phonon energies was due to the steepness of the factor $(1+[\frac{1}{2}r_0q]^2)^{-2}$ appearing in the matrix element for each electronic transition. Referring to Hasegawa's discussion in Sec. 3B of his paper for details, one finds the matrix element describing the absorption (or emission) of phonon $(\mathbf{q},t)$ with the electron in the ith valley $\Psi^{(i)}(\mathbf{r})$ to be

$$(\Psi^{(i)}(\mathbf{r}), V_{ep}\Psi^{(i)}(\mathbf{r}))_{\mathbf{q},t} = a_{\mathbf{q}t}C(\mathbf{q},t)f^{(i)}(\mathbf{q}) + \text{H.c.}, \quad (4.11)$$

where $C(\mathbf{q},t)$ is some function of $\mathbf{q}$ and t [see Hasegawa's (hereafter referred to as H) Eq. (3.31)] and

$$f^{(i)}(\mathbf{q}) \equiv \int A^{*(i)}(\mathbf{k}+\mathbf{q})A^{(i)}(\mathbf{k})d\mathbf{k}/(2\pi)^3$$

$$= \int [F^{(i)}(\mathbf{r})]^2 e^{i\mathbf{q}\cdot\mathbf{r}}d\mathbf{r}. \quad (4.12)$$

[33] N. Shiren, Phys. Rev. 128, 2103 (1962).

In the effective-mass approach of Kohn and Luttinger,[20] one may also approximate the true excited state $\Psi_n(\mathbf{r})$ as linear combinations of the (4 for Ge, 6 for Si) valley functions $\Psi_n^{(i)}(\mathbf{r})$. The relevant matrix element describing the absorption (or emission) of phonon $(\mathbf{q},t)$ with the electron going from the ith valley of the ground state to the ith valley of the nth state is now

$$(\Psi_n^{(i)}(\mathbf{r}), V_{ep}\Psi^{(i)}(\mathbf{r})) = a_{\mathbf{q}t}C(\mathbf{q},t)f_n^{(i)}(\mathbf{q}) + \text{H.c.}, \quad (4.13)$$

where

$$f_n^{(i)}(\mathbf{q}) \equiv \int A^{*(i)}(\mathbf{k}+\mathbf{q})A_n^{(i)}(\mathbf{k})d\mathbf{k}/(2\pi)^3. \quad (4.14)$$

Since $A^{(i)}(\mathbf{k})$ and $A_n^{(i)}(\mathbf{k})$ are orthogonal to a first approximation, we expect that for $q \to 0$, $f_n^{(i)}(\mathbf{q}) \to 0$ and not 1. As an example, let us consider the transition between the ground state $1S$ (fourfold degenerate), which has

$$F_{1S}(\mathbf{r}) = (\pi r_0^3)^{-1/2}e^{-r/r_0} \quad (4.15)$$

and the $2S$ state, which has

$$F_{2S}(\mathbf{r}) = (32\pi r_0^3)^{-1/2}e^{-r/2r_0}(2-r/r_0). \quad (4.16)$$

The integrals involved in finding $f(q)$ from Eqs. (4.14) and (4.12) are elementary, with the result

$$f_{1S,2S}(q) = (1/\sqrt{2})(2/3)^6(r_0q)^2(1+[\tfrac{2}{3}r_0q]^2)^{-3}. \quad (4.17)$$

In general, one has

$$f(q) \propto (\text{polynomial in } r_0q) \times (1+[r_0q]^2)^{-n}; \quad n \geqslant 3. \quad (4.18)$$

We conclude that if we work out the phonon scattering via virtual electronic excitations between the ground state and the true excited states, it will, relative to that found in this paper for intervalley-excited states,

(a) be smaller due to the increased electronic energy difference δ, since $1/\tau \propto 1/\delta^2$;

(b) have a much faster high-energy phonon cutoff factor, since $1/\tau \propto f^4(q)$;

(c) possibly be larger for high-energy phonons $q > 1/r_0$ due to factors $(r_0q)^m$ in $f(q)$.

Fortunately, the effect of (b) cancels out the effect of (c). Thus, the contribution of the true excited states (as given by the effective-mass approximation) is negligible even without considering the effect of (a). This only refers to the qualitative importance of the true excited states. It still might be that the true resonances arising from certain virtual transitions involving these states might cause observable (though small) dips in $K(T)$. These would occur around $T_M \gtrsim \delta/6k$, where δ is the relevant donor electron energy difference. Needless to say, in looking for such dips in the thermal conductivity, one must have extremely accurate data with little "scatter."

V. SOME GENERALIZATIONS

We have treated in some detail the case of unstrained n-type Ge, concentrating on the thermal conductivity. We should like to indicate, somewhat more briefly, how one extends the treatment to other situations of interest.

A. n-Type Si

In Si, the effective-mass ground state is sixfold degenerate. The intervalley potential splits it into three states, a singlet, a doublet and a triplet.[34] Briefly, the singlet is reduced most (due to its symmetry) in energy, while the doublet and triplet are, to first order, unchanged.[35] Hasegawa's matrix elements[21] [Eq. 2.5)] are valid once more, the constants being now taken for Si. The D_r matrices are changed since they are characteristic of the conduction band edge.

Let us consider various transitions between the low-lying intervalley-excited states. The probability amplitude for the donor electron making a triplet (T)—doublet (D) transition will be proportional to

$$D_{DT} = 3 \sum_{v=1}^{6} \alpha_D{}^{(v)} \alpha_T{}^{(v)} \hat{K}^{(v)} : \hat{K}^{(v)}, \qquad (5.1)$$

where, in Kohn and Luttinger's representation,

$$\alpha_S{}^{(v)} = (1/\sqrt{6})(1,1,1,1,1,1),$$
$$\alpha_{D1}{}^{(v)} = \tfrac{1}{2}(1, 1, -1, -1, 0, 0),$$
$$\alpha_{D2}{}^{(v)} = \tfrac{1}{2}(1, 1, 0, 0, -1, -1),$$
$$\alpha_{T1}{}^{(v)} = (1/\sqrt{2})(1, -1, 0, 0, 0, 0), \qquad (5.2)$$
$$\alpha_{T2}{}^{(v)} = (1/\sqrt{2})(0, 0, 1, -1, 0, 0),$$
$$\alpha_{T3}{}^{(v)} = (1/\sqrt{2})(0, 0, 0, 0, 1, -1),$$

and

$$\hat{K}^{(1)} = (1,0,0); \quad \hat{K}^{(4)} = (-1, 0, 0);$$
$$\hat{K}^{(2)} = (0,1,0); \quad \hat{K}^{(5)} = (0, -1, 0);$$
$$\hat{K}^{(3)} = (0,0,1); \quad \hat{K}^{(6)} = (0, 0, -1).$$

One can easily see that (5.1) will be identically zero and, thus, there are no triplet-doublet transitions. Similarly, one can easily show that D_{ST}, defined by

$$D_{ST} \equiv 3 \sum_{v=1}^{6} \alpha_S{}^{(v)} \alpha_T{}^{(v)} \hat{K}^{(v)} : \hat{K}^{(v)} \qquad (5.3)$$

is also zero and, therefore, there are no singlet-triplet transitions.[21] The intervalley orbit-lattice interaction, however, does couple these states.[35]

In contrast, the singlet-doublet transitions are not negligible. Since the intervalley splitting $6\Delta'$ between these two states is of the order of 10^{-2} eV for P, As, or Sb,[35-37] we can assume that the donor electron is

always initially in the singlet state, and, in addition, completely neglect the true excited states. Once again, the phonon relaxation time for n-type Si is given by Eq. (3.19) with $4\Delta \rightarrow 6\Delta'$. As in the case of Ge, one may verify that $\langle D_S{}^{t1'} \rangle_{\Omega'} = \tfrac{2}{3} \langle D_S{}^{t2'} + D_S{}^{t3'} \rangle_{\Omega'}$ from Hasegawa's Tables III and IV.[28] Averaging over the unit sphere, we find

$$\langle\langle D_S{}^{t1'} \rangle\rangle = 8/25, 7/25, 5/25 \quad \text{for} \quad t = 1, 2, 3. \quad (5.4)$$

On the whole, the donor-electron scattering mechanism in Si is not as important as in Ge.[8] One finds for longitudinal modes, assuming that $6\Delta'$ and $4\Delta \gg \hbar\omega$,

$$\frac{\tau_{Si}}{\tau_{Ge}} \approx \left[43\left(\frac{6\Delta'}{4\Delta}\right)^2\right]\left(\frac{1+6.4\times10^{-27}\omega^2}{1+1.8\times10^{-25}\omega^2}\right)^8. \quad (5.5)$$

We have taken the shear deformation potential $E_u \approx 11$ eV and $r_0 \approx 15$ Å for n-type Si in deriving Eq. (5.5). Since, in general, the valley-orbit splitting for Si (singlet-doublet) is much larger than for Ge (singlet-triplet), we conclude that the phonon scattering due to virtual excitation of donor electrons will be negligible in Si. The cutoff factor for Si, though, is considerably reduced compared to Ge.

The work of Castner[35] seems to indicate that the intervalley umklapp orbit-lattice interaction may play an important role in scattering phonons, especially at higher energies $(qr_0 \gtrsim 1)$ where our intravalley mechanism becomes ineffective.

B. p-Type Semiconductors

The original experimental work of Carruthers et al.,[1] in which the anomalous features of the low-temperature thermal conductivity for $n_{ex} \approx 10^{16}$ cm^{-3} were found, was done with p-type Ge and Si. A more recent paper by Carruthers et al.[3] gives additional data down to around 0.3°K. Since the general effects are similar to those found by Goff and Pearlman[2] at Purdue for n-type material, presumably the same scattering mechanism is at work. We suggest that at the low end of the helium range of temperatures, one should also be able to explain much of the thermal conductivity data for p-type material by means of our resonance phonon scattering. As Keyes pointed out in his paper[9] on Ge, though, the structure of the valence band is quite different from the conduction band and, consequently, the fundamental matrix elements for the electronic transitions [such as in Eq. (2.5)] used for n-type material cannot be generalized in a trivial manner. Still, since the "size" of acceptor states is about the same order of magnitude (≈ 40 Å) as that of donor states and, in addition, the valence band is strongly affected by strains,[36,37] one would expect that the mechanism discussed in this paper will be important. Although we do not plan to give a complete quantitative analysis, we think it might be useful to discuss in a little more detail the theoretical picture of acceptor

[34] W. Kohn and J. M. Luttinger, Phys. Rev. 98, 915 (1955).
[35] T. G. Castner, Jr., Phys. Rev. Letters, 8, 13 (1962).
[36] J. C. Hensel and G. Feher, Phys. Rev. Letters, 5, 307 (1960).
[37] G. Feher, J. C. Hensel, and E. A. Gere, Phys. Rev. Letters, 5, 309 (1960).

states and the effect of strains on the valence band. As in our discussion of donor states, the mixing of acceptor states due to the effect of static strains leads to electronic transitions via direct phonon processes.

The highest point of the valence band of both Ge and Si is at $\mathbf{k}=0$ and is sixfold degenerate, including the double degeneracy due to spin. Because of the strong spin-orbit coupling, the degeneracy is partly removed and we have two levels, a doublet somewhat reduced in energy corresponding to an atomic state of total angular momentum $\hbar\mathbf{J}$, with $J=\frac{1}{2}$, and a fourfold degenerate level at the top of the valence band corresponding to $J=\frac{3}{2}$, all centered at $\mathbf{k}=0$. For Ge, to a good approximation, one need only consider the fourfold degenerate state in treating acceptor states. Kohn and Schecter[38] have found a typical set of envelope functions $F_j(\mathbf{r})$ for the ground state (fourfold degenerate). As far as the present authors know, no one has discussed the lowest order corrections, due to the breakdown of the effective-mass formalism near the acceptor ions, which would lead to the splitting of this state. In comparing experimental values of the ionization energy and the best possible effective-mass ionization energy for the ground state, Kohn finds a difference of around 15%, i.e., an energy difference of around 10^{-3} eV. Presumably the fourfold degenerate state for p-type Ge has split into two doublets, separated by this amount. This splitting is of the same order as that which occurred in n-type material.

As the analysis of p-type Si involves even more complications and poorly known parameters, we shall not discuss it except to remark that for our purposes it should resemble p-type Ge.

In deriving the matrix elements for the electron-phonon interaction in n-type material, Hasegawa used the deformation-potential approximation given in Eq. (1.1) of his paper. For p-type material, the shift in the band edge $(J=\frac{3}{2})$ is from symmetry considerations,[39]

$$\delta\epsilon = \sum_{\alpha,\beta=1}^{3} U_{\alpha\beta}\{E_d{}^v\delta_{\alpha\beta}+\tfrac{2}{3}E_{u1}{}^v(J_\alpha{}^2-\tfrac{1}{3}J^2)\delta_{\alpha\beta}$$
$$+\tfrac{2}{3}E_{u2}{}^v(J_\alpha J_\beta)(1-\delta_{\alpha\beta})\} , \quad (5.6)$$

where $U_{\alpha\beta}$ is the (α,β) component of the strain or deformation tensor, $E_d{}^v$ is the energy shift, per unit dilation, of the band edge; $|2E_{u1}{}^v|$ is the splitting of the band edge, due to uniaxial shear strain, per unit extension along the [001] axis; and $|2E_{u2}{}^v|$ is the analogous splitting for the [111] axis. A recent experimental determination[40] of the shear deformation potentials for the valence band in p-type Ge gives

[38] W. Kohn and D. Schechter, Phys. Rev. **99**, 1903 (1955). A detailed theoretical discussion of acceptor states has recently been given by D. Schechter, J. Phys. Chem. Solids, **23**, 237 (1962).
[39] W. H. Kleiner and L. M. Roth, Phys. Rev. Letters **2**, 334 (1959).
[40] J. J. Hall, Phys. Rev. **128**, 68 (1962).

$E_{u1}{}^v=3.2$ eV and $E_{u2}{}^v=6.1$ eV. The electron-phonon interaction for phonon q is given by the qth Fourier component of the energy shift $\delta\epsilon$ defined in Eq. (5.6), namely,

$$\delta\epsilon_q = D_1(i\mathbf{Q}_q\cdot\mathbf{q})+D_2(i\mathbf{Q}_q\cdot\mathbf{J}:\mathbf{J}\cdot\mathbf{q}), \quad (5.7)$$
$$D_1 \equiv (E_d{}^v+\tfrac{5}{3}E_{u1}{}^v-\tfrac{5}{2}E_{u2}{}^v),$$
$$D_2 \equiv \tfrac{2}{3}E_{u2}{}^v, \quad (5.8)$$

where $\mathbf{Q}_q$ is the qth Fourier component of the displacement operator $Q(\mathbf{r})$, i.e., $\mathbf{Q}_q$ is the displacement of the lattice at position $\mathbf{r}$ due to the strain caused by a phonon q.

In evaluating the electron-phonon matrix elements for p-type material, we cannot disregard the spin as we did in n-type material, for the angular momentum of the hole $\hbar\mathbf{J}=\hbar(\mathbf{L}+\mathbf{S})$, with $L=1$ and $S=\frac{1}{2}$, occurs in the interaction operator of Eq. (5.7). In Sec. 3, part A of his paper, Hasegawa discusses[21] the Zeeman energy of donor electrons in a magnetic field. He finds that for the doubly degenerate Bloch functions

$$(\bar{\psi}_k,(\mathbf{L}+\mathbf{S})\bar{\psi}_{k'})=(\mathbf{l}_k\mathbf{I}+\mathbf{s}_k)(2\pi)^3\delta(\mathbf{k}-\mathbf{k}'), \quad (5.9)$$
$$\bar{\psi}_k(\mathbf{r}) \equiv (\psi_k(\mathbf{r}),\phi_k(\mathbf{r})),$$

where $\mathbf{L}$ and $\mathbf{S}$ are the orbital and spin-angular momentum of the electron, $\mathbf{l}_k$ is the angular momentum vector in momentum space (H3.6), $\mathbf{I}$ is the 2×2 identity matrix and $\mathbf{s}_k$ are 2×2 matrices (H3.3) which, to first order in the spin-orbit interaction, are equivalent to usual Pauli matrices divided by 2.

Now in calculating the analog of (H3.29) for p-type material, the major difference is instead of $(\bar{\psi}_k,\hat{K}^{(v)}:\hat{K}^{(v)}\bar{\psi}_{k'})=(2\pi)^3\delta(\mathbf{k}-\mathbf{k}')\hat{K}^{(v)}:\hat{K}^{(v)}$, we have to evaluate $(\bar{\psi}_k,J_\alpha J_\beta\bar{\psi}_{k'})$; $\alpha,\beta=1,2,3$. These matrix elements are, more explicitly,

$$(\bar{\psi}_k,J_\alpha J_\beta\bar{\psi}_{k'})=\int\frac{d\mathbf{k}''}{(2\pi)^3}(\bar{\psi}_k,J_\alpha\bar{\psi}_{k''})(\bar{\psi}_{k''},J_\beta\bar{\psi}_{k'}). \quad (5.10)$$

To simplify this, we use a little foresight. Eventually we want matrix elements between acceptor states and to a first approximation, we shall use a simple hydrogen-type envelope function $F_j(\mathbf{r})$. Since $F_j(\mathbf{r})$ is real, any matrix element involving the orbital angular momentum (an odd operator) will vanish. We conclude that only the term in $S_\alpha S_\beta$ in Eq. (5.10) need be kept. We need hardly add that the use of a hydrogen-type envelope function is more doubtful for p-type semiconductors than for n-type semiconductors. We use it in order to obtain a rough estimate of the matrix elements. Returning to the basic matrix elements Eq. (5.10), we have then

$$(\bar{\psi}_k,J_\alpha J_\beta\bar{\psi}_{k'})=\int\frac{d\mathbf{k}''}{(2\pi)^3}(\bar{\psi}_k,S_\alpha\bar{\psi}_{k''})(\bar{\psi}_{k''},S_\beta\bar{\psi}_{k'}),$$
$$=(\mathbf{s}_k)_\alpha(\mathbf{s}_k)_\beta(2\pi)^3\delta(\mathbf{k}-\mathbf{k}'),$$
$$=\tfrac{1}{4}\sigma_\alpha\sigma_\beta(2\pi)^3\delta(\mathbf{k}-\mathbf{k}'), \quad (5.11)$$

where σ_α ($\alpha = x, y, z$) are the three Pauli spin matrices.

Combining Eqs. (5.11) and (5.7), we find, in place of (H3.29), the basic result

$$(\bar{\psi}_k, \delta\epsilon_q e^{\pm i\mathbf{q}\cdot\mathbf{r}}\bar{\psi}_{k'})$$

$$= a_q i\{D_1 \sum_\alpha (\mathbf{e}_t)_\alpha q_\alpha + D_2 (\sum_{\alpha,\beta} (\mathbf{e}_t)_\alpha \sigma_\alpha \sigma_\beta q_\beta/4)\}$$

$$\times (2\pi)^3 \delta(\mathbf{k} - \mathbf{k}' - \mathbf{q}) \quad \text{for} \quad +\text{sign.}$$

$$= a_q i^* \text{ (same term as above with } \mathbf{q} \to -\mathbf{q})$$

$$\text{for} \quad -\text{sign.} \quad (5.12)$$

To go any further requires a knowledge of how the fourfold degenerate effective mass ground is split into two doublets (double degeneracy always remains in the absence of a magnetic field) and the appropriate doublet acceptor wave functions in terms of the functions $\bar{\Phi}_j(\mathbf{r}) = F_j(\mathbf{r})\bar{\psi}_0(\mathbf{r})$. Instead of (H3.31) we have, of course,

$$(\bar{\Phi}_j(\mathbf{r}), \delta\epsilon_q e^{i\mathbf{q}\cdot\mathbf{r}}\bar{\Phi}_j(\mathbf{r})) = a_q i\{\cdots\}f(q), \quad (5.13)$$

where $\{\cdots\}$ is identical to the factor enclosed in $\{\cdots\}$ in Eq. (5.12) and $f(q)$ is the usual cutoff factor given in Eq. (2.6b).

One can already see that qualitatively the scattering of phonons via virtual excitation of "holes" in p-type material will be similar to that found in Secs. III and IV of this paper for n-type material. Since the magnitude of D_2 is smaller than E_u, the effect may be smaller. This might be counterbalanced by a possibly smaller energy splitting in p-type material. The fact that $K(T)$ continues to decrease[3] as T^4 down to around $0.3°K$ in "Ge 7" (doped with 2×10^{16} indium atoms cm^{-3}) suggests that indeed the relevant ground-state splitting in indium is closer to 10^{-4} eV than to 10^{-3} eV.

C. Phonon Scattering in Strained n-Type Semiconductors

We will now outline the effect of uniaxial strains on our resonant donor electron-phonon scattering mechanism. A semiquantitative analysis was given by Keyes and Sladek[7] in attempting to explain their data on the piezothermal conductivity of n-type Ge.

This generalization is elementary if we assume that to lowest order the only effect of the uniaxial strain is to modify the relative valley contributions, i.e., to modify the numerical coefficients $\alpha_d^{(v)}$ in Eq. (2.1). A detailed theory of the effect of strain, which takes into account that the envelope functions are not all identical and, in addition, are altered by the strain in different ways, has been given by Fritzsche[31] in a recent paper, extending the original work of Price.[10] Impurity conduction via hopping between donors is very sensitive to these corrections but, for our purposes, *slight* changes in the radius of the shallow impurity states are not important to a first approximation.
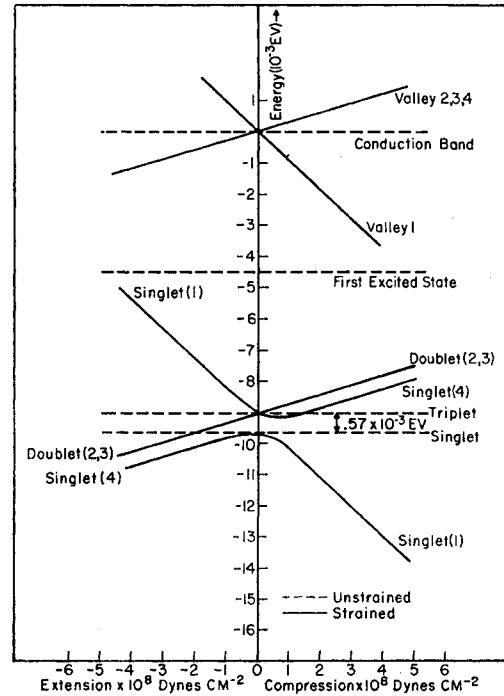

Fig. 7. The effect of uniaxial stress in the [111] direction on the lowest four donor states in Sb-doped Ge. This is based on Refs. 10 and 31. We have also included the first "effective-mass" excited state and the energy shifts of the four conduction valleys.

As Fritzche reviews in Sec. II, part B of his paper,[31] a uniaxial stress along [111] destroys the degeneracy of the four conduction-band valleys.[41] The shift of the first valley along [111] is by deformation potential theory, -3ϵ; similarly the other three valleys along [1 1 -1], [1 -1 1] and [1 -1 -1] are raised by an amount ϵ, with

$$\epsilon = \tfrac{1}{9}E_u S_{44} X$$

$$= 3.11 \times 10^{-4}x \text{ eV}, \quad (5.14)$$

where the stress $X \equiv 10^8 x$ dyn cm^{-2} (positive for compression and negative for extension). In Fig. 7, we have sketched the effect of the stress on the energies of the four donor levels, as first calculated by Price (see Fig. 5 of Ref. 10), for Sb-doped Ge. As-doped Ge would be identical only the energy differences would be about seven times larger. Solving for the $\alpha_d^{(v)}$ coefficients, Fritzche finds

$$\alpha_d^{(v)}: \begin{bmatrix} (1/\sqrt{2})a, & (1/\sqrt{6})b, & (1/\sqrt{6})b, & (1/\sqrt{6})b \\ 0, & 1/\sqrt{2}, & -1/\sqrt{2}, & 0 \\ 0, & 1/\sqrt{6}, & 1/\sqrt{6}, & -2/\sqrt{6} \\ (1/\sqrt{2})b, & -(1/\sqrt{6})a, & -(1/\sqrt{6})a, & -(1\sqrt{6})a \end{bmatrix},$$

$$(5.15)$$

where d represents the donor index (rows), v represents the valley index (columns) and $a \equiv (1 + c(x'))^{1/2}$,

[41] H. Fritzche, Phys. Rev. 119, 1899 (1960).

$b \equiv (1-c(x'))^{1/2}$, with

$$c(x') \equiv \frac{1}{2}(2x'-1)(x'^2-x'+1)^{-1/2}; \quad x' \equiv 4\epsilon/4\Delta. \quad (5.16)$$

Using (5.15) instead of (2.3), it is a straightforward task to repeat the calculations discussed in Secs. II and III of this paper. The thermal conductivity should steadily approach that of pure Ge as a uniaxial compression along the [111] axis is increased. On the other hand, for uniaxial extension, the donor electron-phonon resistance approaches some fixed nonzero value. Plots of $[1 \pm c(x')]^{1/2}$ versus x' are very useful in predicting the effect of uniaxial strains. We may remark that the dilational part of the stress does not enter in the matrix elements. (In Ref. 31, the signs of $\alpha_4^{(v)}$ are wrong.)

Some recent work by Keyes and Sladek[7] on the piezo-thermal conductivity of n-type Ge is of interest. One can obtain considerable insight into the expected differences between the unstrained and strained samples simply by looking at how the valley-orbit energies δ_i change, for one expects the scattering strength to be $1/\delta_i^2$. One Sb-doped sample ($n_{ex} \approx 2 \times 10^{16}$ cm^{-3}) was put under a stress of $\approx -1.2 \times 10^8$ dyn cm^{-2} along the [111] axis. A glance at Fig. 7 will immediately show that the scattering will be decreased only slightly, at least from this rough argument. In contrast, the scattering should be considerably decreased if the same sample was compressed by the same amount. In the latter case, the lowest two energy levels steadily separate as the strain increases. This sort of argument may be refined, of course, but detailed comparison with experiment requires arduous, though straightforward, calculations. For large enough compressions, one may use the fact that all electrons are effectively in one valley to simplify the work.

In the expression one would get for the reciprocal lifetime $1/\tau_q$ of phonon q, the true resonances would occur as before. However, instead of one resonance factor, one would find

$$1/\tau_q = \sum_{i,j=1}^{2} A_{ij}(\omega_q)(\delta_i+\delta_j)^2[(\hbar\omega_q-\delta_i)^{-2}(\hbar\omega_q+\delta_j)^{-2}],$$

where $\delta_1 \equiv E_{2,3}-E_4$ and $\delta_2 \equiv E_1-E_4$. In previous sections we noted that the temperature T_M at which a resonance would be most noticeable is given by $T_M \gtrsim \frac{1}{6}T_R$, where $kT_R \equiv \delta_i$. This implies that we should get some depression in the thermal conductivity of the sample of Keyes and Sladek somewhere around 1°K due to δ_1 transitions and around 3.7°K due to δ_2 transitions. In our discussion so far, we have assumed that the donor electrons are always in the lowest donor level (4). It has appreciable probability of being in the doublet (donor states 2 and 3). As a result, we can have a new resonant transition between the doublet and the upper singlet (level 1), the energy difference being $\delta_3 \equiv E_1-E_{2,3}$. This is $\approx 2(4\Delta)$ or 1.2×10^{-3} eV for the strained sample of interest. The depression arising from this resonance would be expected somewhere around 2°K. It is extremely

tempting to identify these δ_2 and δ_3 resonances with the noticeable depression in the *enhanced* conductivity of Keyes and Sladek's sample around 2.5°K.

D. Phonon-Drag

In Sec. IV, we concentrated on the lattice thermal conductivity of doped semiconductors as a means of studying the effect of our resonant electron-phonon mechanism. In some ways, the lattice contribution to the thermoelectric power Q_p provides a more interesting example. We do not plan to discuss Q_p versus T in any detail in this paper but simply indicate the *extra* features which should arise if our mechanism is at work in n-type Ge.

Physically speaking, Q_p results from the drag on the thermal electrons exerted by the phonons which are traveling under an applied thermal gradient. In the basic papers[42,43] by Herring, the phonon drag in semiconductors is treated both qualitatively and quantitatively and we refer to this lucid work for further information. In a semiquantitative way, he shows that

$$Q_p = \sum_{q,t} v_t^2 F(\mathbf{q},t)\tau_T(\mathbf{q},t)/\mu T, \quad (5.18)$$

where μ is the thermal electron mobility, $\tau_T(q)$ is the total relaxation time of phonon q due to the various scattering processes, and $F(q)$ is the fraction of the total momentum given up by the electrons which is delivered to phonon q. Perhaps the key factor in (5.18) is $F(q)$, which is a strongly peaked function for q of the order of the thermal electron wavevector. This means that only the low-energy phonons are of any importance in phonon drag. As a result, one usually includes normal phonon-phonon and boundary scattering in $\tau_T(q)$; impurity scattering *generally* affects phonons of high q and, hence, is disregarded. However, our resonant bound electron-phonon mechanism is important for low q phonons. While the correct form of $\tau_T(q)$ is quite complicated, the feature we wish to emphasize is that $1/\tau_T(q)$ is strongly peaked for certain values of phonon momentum, which we shall denote by q_R, as a result of the resonant scattering mechanism. We wish to explore some of the qualitative consequences of this on Q_p within the general framework of Herring's formulation of the problem. Our goal is modest—namely, to find the temperature at which our resonant scattering mechanism will have its strongest effect, giving rise to a noticeable depression in Q_p.

We now proceed to study the factor $F(\mathbf{q},t)$ in Eq. (5.18). In terms of the crystal momentum fed into the mode $(\mathbf{q},t)$ per second, denoted by $R(\mathbf{q},t)$, one has

$$F(\mathbf{q},t) = f_t(R(\mathbf{q},t)/\sum_{q'} R(\mathbf{q'},t)), \quad (5.19)$$

[42] C. Herring, Phys. Rev. **96**, 1163 (1954).
[43] For a more extensive review article on phonon drag, see C. Herring, *Halbleiter und Phosphore*, edited by M. Schön and H. Welker (Frederick Vieweg und Sohn, Braunschweig, Germany, 1958), p. 184.

where f_t is the fraction of crystal momentum lost by the thermal electrons and given to the low-energy phonons of polarization t. Herring has evaluated $R(\mathbf{q},l)$, using the thermal electron distribution (given by classical statistics) and an electron relaxation time $\tau_e(K) \propto K^{2r}$. For simplicity, a single-valley semiconductor with a spherical energy surface was assumed, and, thus, only longitudinal phonons interact with the thermal electrons. In Fig. 5 of Ref. 42, the function $R(q,l)$ is drawn as a function of q for several values of r. For pure phonon scattering $(r=-\frac{1}{2})$, $R(q,l)$ is peaked at $q_M(T) = (2mkT/\hbar^2)^{1/2}$, where m is the effective mass of the electron. However, we note that there is more "weight" to the right of q_M than to the left.

We wish to find the temperature T_M at which $\sum_q R(q)\tau_T(q)$ has a minimum. One might think that this would occur when $q_R = q_M(T)$, where q_R and q_M were defined earlier. Because of the extra weight on the right side of $R(q,l)$, though, one expects that q_R is larger, say around $2q_M(T)$. In principle, all one needs to do is to find the minimum value of $\sum_q R(q)\tau_T(q)$ as a function of q_R. Until the arduous calculations are made, we can only say that

$$Q_p \approx f_l \bar{v}_l^2 \tau_T(\bar{q})/\mu T, \qquad (5.20)$$

where

$$\bar{q} = b(2mkT/\hbar^2)^{1/2}; \quad 1 < b \lesssim 2. \qquad (5.21)$$

This, in turn, implies that Q_p should be depressed at a temperature given by

$$T_M = kT_R^2/(b^2 2m\bar{v}_{\text{long}}^2). \qquad (5.22)$$

The constant b can be considered as a sort of asymmetry factor since it depends on the form of $R(q,l)$ around $q_M(T)$.

Now, unfortunately, Ge is a many-valley, highly anisotropic semiconductor, while the preceding analysis assumed a one-valley isotropic model. One must recalculate $R(q,l)$ making use of the longitudinal effective mass $m_l = 1.58m_0$, and the transverse effective mass $m_t = 0.08m_0$, where m_0 is the free electron mass. The calculations are formidable and we shall simply quote Herring's statement that one expects the new R to be some sort of average of the old R curves with different horizontal scales. One certainly expects Eq. (5.22) to hold again but with an "effective mass" m^* replacing m. We do not see any simple way of determining what m^* will be, except that $m_t < m^* < m_l$. In any event, the basic result is that $T_M = \text{const } T_R^2$, where the constant depends only on the semiconductor while T_R depends on the donor as well. If one had several doped samples of one semiconductor, each with a different donor, the above functional relation could be checked. Note that in this more general case, we still only consider longitudinal phonons [and thus use $\bar{v}_l$ in (5.22)] since they are most strongly scattered by our resonance mechanism.

The next task is to estimate the value of T_R. For As-doped Ge (see Fig. 3), we have a broad region of maximum scattering around $\omega \approx \bar{v}_l/r_0$ plus a true resonance at a much higher frequency $\omega = 4\Delta/\hbar$. The former corresponds to a resonance temperature of around $T_R \approx 12°\text{K}$ and the latter to $T_R \approx 48°\text{K}$. We note they are well separated and, in addition, the true resonance occurs in a region of strong phonon-phonon scattering and, hence, will have little effect. In the case of Sb-doped Ge (see Fig. 2), the true resonance occurs at a frequency only slightly less than $\omega \approx \bar{v}_l/r_0$ and, consequently, the two peaks merge. Although there is more weight on the right-hand side of the merged peak at $6.6°\text{K}$, we shall take this value as our effective resonance temperature T_R. From Eq. (5.22), we conclude that the expected depression in Q_p will be at a lower temperature for Sb compared to As, $T_M(\text{As})/T_M(\text{Sb}) \lesssim 3.2$.

We can use Goff's measurements[2,44] of the thermoelectric power to test the above predictions. The essential first step is to identify the expected dips. Taking $b=2$ and $m^* = 0.22m_0$ (the "density of states" effective mass) one finds $T_M(\text{As}) \approx 43°\text{K}$ using Eq. (5.22). Undoubtedly m^* will be larger and, thus, all we can say is that the resonance dips should make their appearance below or around $40°\text{K}$. Now there seems to be striking evidence of a depression in As 233I, As 233II, and As 226 at $15°\text{K}$. All the other samples are consistent with a depression at this temperature, but a general scatter of data or lack of points makes it difficult to say anything more. Using this experimental value of $T_M(\text{As})$, we *predict* that $T_M(\text{Sb}) \gtrsim 4.7°\text{K}$. Experimentally, the only definite dips in Q_p for Sb are at $5°\text{K}$ (especially noticeable in GaSb 168, GaSb 170, GaSb 183, and SbGa 204). Depressions in the region around $10°\text{K}$ are probably due to experimental technique.

To judge the validity of the preceding analysis would require a more detailed investigation. Experimentally, it would of great interest to see if p-doped Ge has a depression at a much higher temperature, as we would predict. A study of strained samples would be useful since the predicted depressions in Q_p should move as the relevant values of T_R (corresponding to the true resonances) change, i.e., as the applied stress changes.

For the sake of a clear exposition of the main ideas involved, we have left two remarks for the end. First of all, Eq. (5.22) was derived mainly on the assumption of the *existence* of a resonant scattering mechanism for the longitudinal phonons. Actually, the particular interaction we are interested in arises from the shearing strains on the bound electrons due to the phonons, and therefore, contrary to what we implied, cannot occur in an *one-valley, single-sheeted* semiconductor. The second point is that we have not considered that part of Q_p due to the transverse phonons, which also interact with the thermal electrons in a many-valley semiconductor such

[44] J. F. Goff and N. Pearlman, Purdue University Quarterly Reports, 1959 and 1960 (unpublished).

as Ge. As we mentioned above, our resonant mechanism scatters longitudinal phonons more strongly than transverse phonons and, hence, the depression in Q_p is smaller for the latter. In addition, the "transverse phonon" depression will occur at a higher temperature than that found for longitudinal phonons [mainly due to the substitution of $\bar{v}_t^2$ for $\bar{v}_l^2$ in (5.22)]. Since phonon-phonon scattering is dominant at these temperatures, the bound electron-transverse phonon interaction is negligible for a second reason.

Theory of Kohn Anomalies in the Phonon Spectra of Metals

P. L. TAYLOR*

Department of Physics, Case Institute of Technology, Cleveland, Ohio

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An expression is derived for the change in frequency of the lattice vibrations in a metal caused by the interaction of the phonons with the conduction electrons. The various factors affecting the magnitude of these Kohn anomalies are considered, and a connection is made with the value of the electrical resistivity of the pure metal. The valence of the metal is found to be the most important factor determining whether such anomalies should be observable. The results of the calculations are applied to Pb, and give good agreement with experiment.

INTRODUCTION

IT has been pointed out by Kohn[1] that the interaction of the conduction electrons in a metal with each other and with the vibrations of the crystal lattice should cause anomalies in the phonon spectra of metals. In particular, it has been suggested that the group velocity of phonons of wave number q will exhibit a logarithmic singularity whenever

$$q = 2k_f + g, \tag{1}$$

where k_f is the wave number of an electron at the Fermi surface, and g is a vector of the reciprocal lattice. There is, at the time of writing of this paper, some controversy as to whether these anomalies should be observable experimentally. While evidence for such behavior has been found by Brockhouse et al.[2] in their investigation of the lattice vibrations of lead, Harrison[3] has suggested that this reflects the form of the electron dispersion relations rather than being directly due to the electron-phonon interaction in the way envisaged by Kohn. It is the purpose of the present work to calculate the expected magnitude of the Kohn anomalies in various metals in a more quantitative way than has hitherto been attempted.

A previous calculation of the magnitude of this effect is due to Woll and Kohn[4] who adopted a semiclassical approach to the problem of calculating the vibration frequencies of a lattice of point charges in a sea of interacting electrons. Their method is a simplification of Nakajima's[5] quantum-mechanical calculation and is essentially a Hartree method which considers only terms of first order in both the electron-electron and electron-lattice interactions. However, while it is very satisfying to be able to calculate the required quantities from first principles, one cannot have complete confidence in a calculation that neglects electron correlation. A more serious criticism arises when it is pointed out that the result given by these authors contains terms that involve the product of parameters describing both electron-electron and electron-lattice interactions. Because the Hamiltonian is diagonalized only to first order in each, the validity of such terms is clearly in doubt, and in fact does, as we shall see, lead to contradictions.

The effect of the interaction of the electrons is to attenuate the Kohn anomalies. In the Hartree approximation, this attenuation is quite large; this is, however, an overestimate of the significance of these interactions, and is considerably reduced by the effect of the lattice potential on the electron wave functions.

We can separate the amplitude of the Kohn anomalies into two parts: The first part is due to the second-order corrections to the phonon energies caused by the electron-phonon interaction; the second part, which we describe by an attenuation coefficient, α, arises from the presence of infinities in the derivative of the matrix element for the interaction itself. No attempt is made in this paper to calculate α, although some of the factors affecting its magnitude will be discussed. The calculation of the direct effects of the interaction is a matter for greater confidence, for here we may have recourse to experiment. The electrical resistivity of pure metals is

* Magnavox Research Fellow.
[1] W. Kohn, Phys. Rev. Letters 2, 393 (1959).
[2] B. N. Brockhouse, K. R. Rao, and A. D. B. Woods, Phys. Rev. Letters 7, 93 (1961); B. N. Brockhouse, T. Arase, G. Caglioti, K. R. Rao, and A. D. B. Woods, Phys. Rev. 128, 1099 (1962).
[3] W. A. Harrison, Phys. Rev. 129, 2512 (1963).
[4] E. J. Woll, Jr., and W. Kohn, Phys. Rev. 126, 1693 (1962).

[5] S. Nakajima, Busseiron Kenkyu, 65, 116 (1953). More accessible are the summaries of his work given by G. V. Chester, Phil. Mag. Suppl. 10, 357 (1961) and in Ref. 10.