

Thermal Conductivity of Solids. III. Modification of Three-Phonon Processes by Isotopic Scattering*

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The experimental observation that the effective strength of the phonon-phonon scattering in Ge-Si mixtures increases with the disorder parameter is explained qualitatively and semi-quantitatively by means of second-order interactions in which the three-phonon processes are modified by isotopic scattering. This effect is large because of the occurrence of small-energy denominators and the increased number of final states resulting from the over-all nonconservation of crystal momentum for such three-phonon processes.

I. INTRODUCTION

IN a previous paper¹ it was suggested that higher-order terms in the perturbation series for phonon interactions² might be observable. In a study³ of phonon-phonon scattering it was found that the possibility of energy, crystal-momentum conserving intermediate states enhanced the process $2 \text{ phonons} \rightarrow 2 \text{ phonons}$ induced by successive interactions via the cubic anharmonic forces. However, the usual three-phonon relaxation time calculated in lowest order is only slightly increased by this process.⁴ The strength of the three-phonon interaction is itself a very elusive quantity to determine theoretically. Therefore, one may hope that combined impurity three-phonon scattering should provide better evidence for higher-order processes. As explained in I, such scatterings lead to over-all three-phonon processes in which crystal momentum is not conserved, even when no Umklapp collision occurs at the three-phonon vertex.

Recently measurements^{5,6} of the thermal conductivity of Ge-Si mixtures have been made over a wide range of temperatures. It is believed that the dominant impurity scattering in these compounds is due to the disruption of periodicity by the mass fluctuations throughout the crystal. This is especially fortunate since the scattering by such "isotopic" mixtures is one of the few problems for which a reliable relaxation time has been computed. The relaxation time τ for such scattering is given by Klemens' formula⁷:

$$1/\tau = A\omega^4, \quad A = \Omega_0\Gamma/4\pi c^3, \quad (1.1)$$

in which ω is the circular frequency of the phonon, Ω_0 is the volume per atom, c is an average velocity of sound,

and the parameter Γ defined by

$$\Gamma = \sum_i f_i (1 - M_i/\bar{M})^2 \quad (1.2)$$

measures the disorder in mass. In (1.2), f_i is the fraction of atoms of mass M_i ; \bar{M} is the average mass. The acoustic relation $\omega = kc$, k being the wave number of the phonon, is assumed in (1.1).

Using Callaway's method⁸ of taking into account the combined effect of the various scattering mechanisms, Toxen found⁵ that he could make a successful fit to his data only if the inverse phonon-phonon relaxation time increased linearly with Γ . A similar effect was observed by Abeles *et al.*⁶ for temperatures greater than 300°K. The latter group proposed that the effect is due to second-order processes composed of an isotope scattering combined with a three-phonon process. To be more explicit, in the above named experiments it was assumed that the phonon-phonon relaxation time is given by $1/\tau_{\text{ph}} = b(T)\omega^2$, where $b(T) \propto 1/T$ at high temperatures. The finding is thus that $b(T) = b_0(T) + b_1(T)\Gamma$, where b_1 has the same temperature dependence as $b_0(T)$. The effect is quite substantial; for large Γ the term $b_1\Gamma$ actually exceeds b_0 . The effect may also be present in the data of Bowers *et al.*⁹ on the thermal conductivity of InAs-P mixtures. This experiment has not yet been analyzed, however.

In this paper we show that the observed behavior may indeed be explained by the combined three-phonon-isotope scattering process. The effect is large because of the occurrence of small energy denominators, and the increased density of final states due to the loss of over-all conservation of crystal momentum. The effect should be qualitatively the same for strain-field scattering by point defects.¹

II. FORMULATION OF THE PROBLEM

The unperturbed system is taken to be a crystal of atoms of mass \bar{M} . As remarked in I, the phonon frequencies are then given correctly up to second order in the perturbation. We follow the notation of I. The unperturbed Hamiltonian H_0 is

$$H_0 = \sum_q \hbar\omega_q (a_q^* a_q + \frac{1}{2}), \quad (2.1)$$

⁸ J. Callaway, Phys. Rev. **113**, 1046 (1959).

⁹ R. Bowers, J. E. Bauerle, and A. J. Cornish, J. Appl. Phys. **30**, 1050 (1959).

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¹ P. Carruthers, Revs. Modern Phys. **33**, 92 (1961), Appendix D. This work will be referred to as I.

² In this paper we consider only lattice conductivity.

³ P. Carruthers, Phys. Rev. **125**, 123 (1962). This work will be referred to as II. The four-phonon process and the three-phonon process to second order were first studied by I. Pomeranchuk, J. Phys. U. S. S. R. **4**, 259 (1941).

⁴ This work will be reported elsewhere.

⁵ A. Toxen, Phys. Rev. **122**, 450 (1961).

⁶ B. Abeles, D. S. Beers, G. D. Cody, and J. P. Dismukes, Phys. Rev. **125**, 44 (1962). The author is grateful to Dr. Abeles for providing a copy of this work before publication.

⁷ P. G. Klemens, Proc. Phys. Soc. (London) **A68**, 1113 (1955).

where q signifies the wave vector \mathbf{q} and polarization index λ ; a_q and a_q^* are, respectively, the destruction and creation operators for the q th mode. The perturbation has the form

$$V = V_i + V_3, \quad (2.2)$$

where V_i is the isotopic perturbation,

$$V_i = \sum_{q,q'} M(q,q') (a_q + a_{-q}^*) (a_{q'} + a_{-q'}^*);$$

$$M(q,q') = (\hbar/4\rho\Omega) \mathbf{e}_q \cdot \mathbf{e}_{q'} (\omega_q \omega_{q'})^{\frac{1}{2}} \sum_{\mathbf{n}} \Delta M_{\mathbf{n}} \exp[i(\mathbf{q} + \mathbf{q}') \cdot \mathbf{n}]. \quad (2.3)$$

In Eq. (2.3) $-q$ means $-\mathbf{q}$, λ ; ρ is the average mass density, Ω is the volume of the crystal, \mathbf{e}_q is the polarization vector of the q th mode. The summation on \mathbf{n} in (2.3) runs over the lattice sites. The cubic anharmonic perturbation V_3 may be written in the form

$$V_3 = \frac{1}{3!} \sum_{q,q',q''} \{ C(q,q',q'') a_q a_{q'} a_{q''} - 3C(-q, q', q'') a_q^* a_{q'} a_{q''} + 3C(-q, -q', q'') a_q^* a_{q'}^* a_{q''} - C(-q, -q', -q'') a_q^* a_{q'}^* a_{q''}^* \}. \quad (2.4)$$

The coefficients $C(q,q',q'')$, defined in Appendix D of I are zero unless $\mathbf{q} + \mathbf{q}' + \mathbf{q}''$ is zero or 2π times a vector in the reciprocal lattice.

To second order in the perturbation the scattering operator is

$$V_i + V_3 + (V_i + V_3)(E - H_0 + i\epsilon)^{-1}(V_i + V_3), \quad (2.5)$$

where ϵ is a positive infinitesimal. The first two members of (2.5) lead to the usual lowest-order isotope scattering and three-phonon interactions. The terms quadratic in V_i represent the second Born approximation for isotope scattering, which we ignore. The terms quadratic in V_3 have already been discussed in II. We have, then, to compute matrix elements of the operator

$$V_i(E - H_0)^{-1}V_3 + V_3(E - H_0)^{-1}V_i, \quad (2.6)$$

where the $i\epsilon$ factor has been left implicit. We are concerned with transitions of the type; one phonon \rightarrow two phonons and two phonons \rightarrow 1 phonon, of which only the former need be considered. Consider the transition $k \rightarrow k', k''$, i.e., the initial state is characterized by the occupation numbers $N_k, N_{k'}, N_{k''}$ and the final state by $N_k - 1, N_{k'} + 1, N_{k''} + 1$. To keep track of the matrix elements of (2.6) we need to specify only those states which change. Thus we use a single-particle notation. The contributions to

$$\langle k'k'' | [V_i(E - H_0)^{-1}V_3 + V_3(E - H_0)^{-1}V_i] | k \rangle \quad (2.7)$$

are shown graphically in Fig. 1. (See I for further explanation.) Actually the sum over intermediate states amounts only to a sum over the polarization index of the virtual phonon. (Also Umklapp terms at the three-phonon vertex have to be allowed for.) Thus we note that the energy denominators can vanish in graphs (a) and (b) when the virtual phonon has the appropriate wave vector and polarization. When this happens the $i\epsilon$ is of no help; one has to account for the instability of the intermediate phonon by including the imaginary

part of its energy as discussed in II. This modification will be made at an appropriate place. The energy denominators corresponding to Figs. 1(c) and (d) are never zero. A typical denominator for Fig. 1(c) or (d) is generally much larger than that for Fig. 1(a) or (b). Correspondingly, the former contribute little to the effect under consideration.

The cumbersome job of summing over intermediate states in Eq. (2.7) can be performed with relative ease by means of the following device. First write (2.3) as

$$V_i = \sum_q M(q,q) (a_q + a_{-q}^*)^2 + V_i'; \quad (2.8)$$

$$V_i' = \sum_{q \neq q'} M(q,q') (a_q + a_{-q}^*) (a_{q'} + a_{-q'}^*). \quad (2.9)$$

The first member of the right-hand side of (2.8) contributes an amount of order $1/N$ relative to V_i' in the total scattering and may be safely omitted in what follows. Now it is easily seen that V_i' can be represented as follows:

$$V_i' = [H_0, S], \quad (2.10)$$

$$\hbar S = \sum_{p,p'} M(p,p') \left(\frac{a_p a_{p'}}{\omega_p + \omega_{p'}} + \frac{2a_{-p}^* a_{p'}}{\omega_{p'} - \omega_p} - \frac{a_{-p}^* a_{-p'}^*}{\omega_p + \omega_{p'}} \right), \quad (2.11)$$

where the prime on the sum excludes the case $p = p'$. The case $\mathbf{p}' = -\mathbf{p}$ is automatically excluded since M is

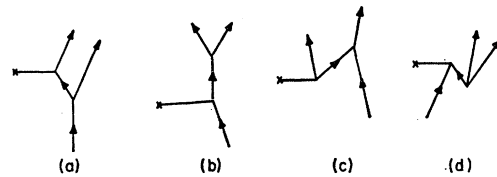


FIG. 1. The second-order contributions to the matrix element of Eq. (2.7) are depicted. The \times marks the action of the isotopic or strain field perturbation.

then zero. Upon utilizing (2.10), it follows readily that (2.7) is reduced to the simple form:

$$\langle k'k'' | [S, V_3] | k \rangle, \quad (2.12)$$

where $[S, V_3]$ is the commutator $SV_3 - V_3S$.

III. MATRIX ELEMENTS

The portion of the commutator $[S, V_3]$ which contributes to (2.12) is

$$-\frac{1}{3! \hbar} \sum_{pp'} \sum_{qq'q''} \left\{ \frac{6C(-q, -q', q'')M(-p, p')}{\omega_{p'} - \omega_p} [a_q^* a_{q'}^* a_{q''}^* a_p^* a_{p'}] \right. \\ \left. + \frac{3C(-q, q', q'')M(-p, -p')}{\omega_p + \omega_{p'}} [a_q^* a_{q'} a_{q''}^* a_p^* a_{p'}] - \frac{C(-q, -q', -q'')M(p, p')}{\omega_p + \omega_{p'}} [a_q^* a_{q'}^* a_{q''}^* a_p a_{p'}] \right\}. \quad (3.1)$$

The commutators in (3.1) are easily worked out; for instance, that in the term expected to be the largest is

$$[a_q^* a_{q'}^* a_{q''}^* a_p^* a_{p'}] = \delta_{pq'} a_q^* a_{q'}^* a_{q''}^* a_p^* - \delta_{qp'} a_p^* a_{q'}^* a_{q''}^* a_q^* - \delta_{p'q''} a_p^* a_{q'}^* a_{q''}^* a_q^*. \quad (3.2)$$

Thus, the first term of (3.1) contributes the following quantity to $\langle k'k'' | [S, V_3] | k \rangle$:

$$-2[N_k(N_{k'}+1)(N_{k''}+1)]^{\frac{1}{2}} \sum_{\lambda(k'+k'')} \left\{ \frac{C(-k', -k'', k'+k'')M[-(k'+k''), k]}{\hbar[\omega(k) - \omega(k'+k'') + \frac{1}{2}i\gamma(k'+k'')]} \right. \\ \left. + \frac{C(k''-k, -k'', k)M(-k', k''-k)}{\hbar[\omega(k) - \omega(k'') - \omega(k'-k) + \frac{1}{2}i\gamma(k''-k)]} + \frac{C(k'-k, -k', k)M(-k'', k'-k)}{\hbar[\omega(k) - \omega(k') - \omega(k'-k) + \frac{1}{2}i\gamma(k'-k)]} \right\}. \quad (3.3)$$

The sum is taken over the polarization index λ ; for each term in curly brackets it is the phonon designated by the sum or difference of wave vectors that has polarization λ . For instance, in the first term $k'+k''$ stands for $\mathbf{k}'+\mathbf{k}''$, λ . We have also inserted the imaginary part of the energy of the intermediate phonon as discussed in II. To lowest order, γ is the rate of scattering of the phonon of specified properties through *both* anharmonic interactions and isotope (or more generally, strain field, etc.) scattering. In principle γ should even include the higher-order effects under consideration. Note the automatic appearance of the occupation numbers referring to the external phonons only; no occupation numbers occur that refer to intermediate states. It is then fairly easy to compare with the corresponding three-phonon scattering matrix element

$$\langle k'k'' | V_3 | k \rangle = [N_k(N_{k'}+1)(N_{k''}+1)]^{\frac{1}{2}} \times C(-k', -k'', k), \quad (3.4)$$

where in the latter $\mathbf{k}=\mathbf{k}'+\mathbf{k}''$ except for Umklapp col-

lisions. Of course there is a difference in that $\mathbf{k} \neq \mathbf{k}'+\mathbf{k}''$ in general for (3.3). However since the linearization of the Peierls' integral equation¹⁰ for three-phonon scattering depends only on $\omega(k)=\omega(k')+\omega(k'')$ which holds for both (3.3) and (3.4), a fairly direct comparison of the processes (3.3) and (3.4) is possible.

Thus, (3.3) and (3.4) differ essentially by the occurrence of the factors M over energy denominators, and also by the necessity of an additional sum on final states in (3.3) as compared with (3.4). However, inspection of Eq. (2.3) shows that M/ω is independent of frequency. The three-phonon contribution to γ varies as $\omega^2/T \sim \omega$. Thus (2.3) depends on temperature and wave vector in the same qualitative way as does (3.4). Moreover the square of the M factors in (3.3) gives rise to the factor Γ for randomly distributed isotopes. Thus all the qualitative features discussed in the introduction are reproduced by the assumed process.

The second term of (3.1) contributes to (2.12) the amount

$$-2[N_k(N_{k'}+1)(N_{k''}+1)]^{\frac{1}{2}} \sum_{\lambda(k'-k)} \left\{ \frac{C(-k', k, k'-k)M(k-k', -k'')}{\hbar[\omega(k'')+\omega(k'-k)]} + (k' \leftrightarrow k'') \right\}. \quad (3.5)$$

The third term of (3.1) likewise contributes

$$2[N_k(N_{k'}+1)(N_{k''}+1)]^{\frac{1}{2}} \sum_{\lambda(k'+k'')} \frac{C(-k', -k'', k'+k'')M[-(k'+k''), k]}{\hbar[\omega(k)+\omega(k'+k'')]} \quad (3.6)$$

¹⁰ R. E. Peierls, *Quantum Theory of Solids* (Oxford University Press, New York, 1955), Chap. 2.

The decay rate γ has been omitted from (3.5) and (3.6) since γ has to be substantially less than ω if the concept of phonon is to be meaningful.

The next task is to square the sum of (3.4)–(3.6). Fortunately, for a random distribution of defects many of the interference terms vanish. Each M contains the factor $\sum_n \Delta M_n \exp(i\mathbf{K} \cdot \mathbf{n})$, where \mathbf{K} is a sum of wave

vectors. For a random distribution the square of the latter is $N\bar{M}^2\Gamma$. A finite interference results from the different matrix elements only if the argument (\mathbf{K}) is the same in the two M 's. Thus, the first member of (3.3) interferes with (3.5) and (3.6). The other contributions add incoherently. The square of the matrix element (2.12) is thus

$$\begin{aligned} \left(\frac{\Gamma}{4N}\right) [N_k(N_{k'}+1)(N_{k''}+1)]^{\frac{1}{2}} & \left\{ \left| \sum_{\lambda(k'+k'')} \frac{C(-k', -k'', k'+k'') \mathbf{e}(k) \cdot \mathbf{e}(k'+k'') [\omega(k)\omega(k'+k'')]^{\frac{1}{2}}}{\omega(k) - \omega(k'+k'') + \frac{1}{2}i\gamma(k'+k'')} \right|^2 \right. \\ & + \sum_{\lambda(k'-k)} \frac{C(-k', k, k'-k) \mathbf{e}(k'-k) \cdot \mathbf{e}(k'') [\omega(k'')\omega(k-k')]^{\frac{1}{2}}}{\omega(k'') + \omega(k'-k)} \\ & + \sum_{\lambda(k''-k)} \frac{C(-k'', k, k''-k) \mathbf{e}(k''-k) \cdot \mathbf{e}(k') [\omega(k')\omega(k-k'')]^{\frac{1}{2}}}{\omega(k') + \omega(k''-k)} \\ & + \sum_{\lambda(k'+k'')} \frac{C(-k', -k'', k'+k'') \mathbf{e}(k) \cdot \mathbf{e}(k'+k'') [\omega(k)\omega(k'+k'')]^{\frac{1}{2}}}{\omega(k) + \omega(k'+k'')} \Big|^2 \\ & + \left| \sum_{\lambda(k''-k)} \frac{C(k''-k, -k'', k) \mathbf{e}(k') \cdot \mathbf{e}(k''-k) [\omega(k')\omega(k''-k)]^{\frac{1}{2}}}{\omega(k) - \omega(k'') - \omega(k''-k) + \frac{1}{2}i\gamma(k''-k)} \right|^2 \\ & \left. + \left| \sum_{\lambda(k'-k)} \frac{C(k'-k, -k', k) \mathbf{e}(k'') \cdot \mathbf{e}(k'-k) [\omega(k'')\omega(k'-k)]^{\frac{1}{2}}}{\omega(k) - \omega(k') - \omega(k'-k) + \frac{1}{2}i\gamma(k'-k)} \right|^2 \right\}. \quad (3.7) \end{aligned}$$

IV. ESTIMATE OF THE MAGNITUDE OF THE EFFECT

Further simplification of (3.7) evidently requires special assumptions. The polarization sums could be performed using the completeness relation if the phonon frequencies were independent of the mode of polarization. Unfortunately the size of those denominators which can become small depends sensitively on the precise form of the dispersion relation. Moreover the interference terms in (3.7), vary in sign and magnitude as k, k' , and k'' are varied. In order to obtain an estimate of the magnitude of the effect we use the following approximations: (1) Neglect interference terms in (3.7); (2) in terms with positive definite denominators ignore the polarization dependence of ω and sum over the polarization index of the intermediate phonon. Then the $C(q, q', q'')$ factors have the same polarization vectors as in (3.4), although, of course, the wave vectors are not quite the same in the two cases. It also seems plausible to neglect interference between transverse and longitudinal intermediate polarizations since we are really interested in the average of (3.7) over all angles. In terms with small denominators we replace $|C(q, q', q'') \mathbf{e} \cdot \mathbf{e}'|^2$ by one-third the same quantity summed on the intermediate polarization vector and retain the sum on λ for the energy denominators.

It is further necessary to consider in detail the conditions for the vanishing of the real part of the denominators. For example, the first term in (3.7) [this corre-

sponds to Fig. 1(a)] can become singular only when the intermediate phonon is longitudinal. For transverse intermediate phonons the real part of denominator can become small, but not vanish. Thus the first term in curly brackets in (3.7) is schematically of the form

$$\frac{1}{3} |\bar{C}|^2 \left[2 \left(\frac{\omega}{\Delta\omega} \right)^2 + \frac{\omega^2}{(\Delta\omega)^2 + \frac{1}{4}\gamma^2} \right], \quad (4.1)$$

where the frequencies have been replaced by some average value and $\Delta\omega$ measures the "lack" of energy conservation by the intermediate phonons. We shall also approximate the last two terms of (3.7) by (4.1), although more careful bookkeeping would change the result slightly.

Now, the net effect results on integrating over the density of states for two of the three phonons. In this respect there are roughly $3N$ times as many final states for (3.7) as (2.12) since in the latter, wave vector conservation reduces the twofold sum to one. For the temperatures of the order of and greater than the Debye temperature we shall make one more approximation, this being no more crude than the preceding simplifications. We replace every wave vector or frequency by a common typical value, except in the small denominators. For the first term of (4.1) we also replace $(\omega/\Delta\omega)^2$ by its average. The second term requires more care. Here there is a *narrow* region in the phase space (of width γ) in which this term is large, of order $(\omega/\gamma)^2$. To

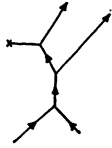


FIG. 2. A third-order scattering is shown.

estimate this contribution we integrate over the phase space of one external wave vector using a Debye spectrum. The other sum gives just $3N$ because of the above averages.

The region outside this peak is expected to contribute a term of the same order as the first term in (4.1), i.e., $(\omega/\Delta\omega)^2$. Thus we can change $2(\omega/\Delta\omega)^2$ to $3(\omega/\Delta\omega)^2$ in (4.1). Comparing Eqs. (3.4), (3.7), and (4.1) we have a primitive approximation for the correction to the three-phonon scattering strength:

$$\frac{\Delta b}{b} \approx -\frac{3\Gamma}{4} \left\{ 3 \left(\frac{\omega}{\Delta\omega} \right)^2 + \frac{3}{4} + \left(\int_0^{\omega_0} \frac{\omega^4 d\omega}{(\Delta\omega)^2 + \frac{1}{4}\Gamma^2} \right) / \left(\int_0^{\omega_0} \omega^2 d\omega \right) \right\}. \quad (4.2)$$

In Eq. (4.2) ω_0 is the Debye frequency. The second term in (4.2) comes from the terms with large denominators. This contribution is seen to be relatively small.

For a plausible value of $\Delta\omega/\omega \approx \frac{1}{2}$, one notes that the first two terms alone give $(\Delta b/b) \approx 10\Gamma$, which is about that observed by Abeles *et al.*^{6,11} The last term in (4.2)

¹¹ The small intrinsic three-phonon scattering observed by Toxen⁶ is probably due to the inhibition of Umklapp collisions at the low temperatures (2°–50°K) in his experiment. For the temperatures of Toxen's experiment the approximation to the density of states leading to (4.2) is invalid. Instead one has to multiply (4.2) by a factor of order $(\omega/\omega_0)^3$, which amounts to $(T/\Theta)^3$, Θ being the Debye temperature. To determine the seriousness of

is not necessarily negligible, despite the small total phase space for which this term is large. To evaluate the integral we note that $\epsilon\pi^{-1}/(x^2 + \epsilon^2)$ acts as a delta function for small ϵ . Thus the last term in (4.2) is roughly $6\pi\bar{\omega}^4/\gamma\omega_0^3$ where γ is the sum of widths for isotope scattering, anharmonic scattering, and also the second-order process of interest. The approximation (4.2) is roughly

$$\frac{\Delta b}{b} \approx -\frac{3\Gamma}{4} \left\{ 3 \left(\frac{\omega}{\Delta\omega} \right)^2 + \frac{3}{4} + \frac{6\pi\bar{\omega}^4}{\gamma\omega_0^3} \right\}. \quad (4.3)$$

Since γ includes a term roughly linear in Γ the last term will cause the last term in (4.3) to decrease with increasing Γ ; i.e., for large Γ , $\Delta b/b$ should increase less rapidly than linearly with Γ . Rough estimates indicate this term to be of order unity. Experimentally the possible importance of this term should be revealed by the mentioned nonlinearity. Present results are not sufficiently accurate to detect this term. Note that since γ includes Δb , (4.3) is really a quadratic equation for Δb which should be solved if the last term were large and if we could actually make a reliable estimate of the quantities involved.

Finally it should be mentioned that there are other higher-order processes with small denominators that contribute to the process under discussion. An example is given in Fig. 2. This type of process does not change any practical conclusions, however. We hope to discuss such terms in another paper.

In conclusion it seems that the main features and magnitude of the effect are adequately described by the preceding calculation. The prospects for an accurate numerical estimate are not bright, however.

this discrepancy seems to require a detailed numerical study. The author is grateful to Dr. P. G. Klemens for emphasizing this difficulty.