PHYSICAL REVIEW VOLUME 95, NUMBER 4 AUGUST 15, 1954

Role of Low-Energy Phonons in Thermal Conduction

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(Received May 13, 1954)

Phonon-phonon collisions in which one of the phonons is of very low frequency have recently become important for the understanding of the thermoelectric powers of semiconductors at low temperatures. Such collisions have also an interest from the standpoint of thermal conduction, since previous theories, which neglect elastic anisotropy, have predicted a very large thermal conductivity for a hypothetical perfect crystal of very large size. It is shown here that elastic anisotropy has a drastic effect on the collision probabilities of modes of very low frequency. A relaxation time τ can be defined, for any mode, which at temperatures T well below the Debye temperature and for wave vectors q well within the acoustic range obeys $\tau(\lambda\mathbf{q},\lambda T)=\lambda^{-5}\tau(\mathbf{q},T)$. As $q\rightarrow 0$, $\tau^{-1}\sim\Lambda_a q^a$, where normally, for modes of the longitudinal branch, $a=2$ for the crystal classes of highest symmetry, 3 and perhaps sometimes 4 for those of lower symmetry. For transverse modes a is normally 1. These asymptotic laws, whose range of validity can be roughly estimated, enable us to calculate the contribution of the low-frequency longitudinal modes to the conductivity. This contribution, though small, may be perceptible at temperatures far above the range where Casimir's formula applies.

THE modern theory of thermal conduction in nonmetals dates from the work of Peierls,[1] who first gave a rigorous formulation to the idea, proposed much earlier by Debye,[2] that thermal resistance is due to the mutual scattering of vibrational waves, a scattering due to the anharmonicity of the interatomic forces. A number of papers have been written since, attempting to develop Peierls' picture in greater detail. As the theory is rather complicated, all these have made the plausible simplification of treating the medium as elastically isotropic. With this assumption it is easily shown that, if terms of higher than the third order are neglected in the elastic potential energy, the expression for the thermal conductivity of an infinite perfect crystal diverges.[3,4] This divergence is due to the fact that the relaxation time τ of a longitudinal mode of wave number q goes as q^{-4} when q is small,[3–5] so that $\int \tau q^2 dq$ diverges at the lower limit.

It has been felt generally that this divergence of the conductivity does not really occur for actual materials, since observations suggest that, except at very low temperatures, the conductivities measured for specimens of usual laboratory size are substantially the same as would be observed for an infinite crystal. To make the conductivity finite, or, more precisely, to avoid predicting that the measured conductivity should depend markedly on the size of the specimen, Pomeranchuk[3] invoked fourth-order terms in the elastic potential energy. This is rather unsatisfactory, as these terms must have an extremely small effect at moderately low temperatures. Herpin,[4] on the other hand, invoked imperfections in the crystal structure. This is also an unsatisfactory escape, since isolated impurities and lattice defects also give $\tau\propto q^{-4}$, while the number of dislocations and stacking faults present in a reasonably good crystal is too small to have an appreciable effect. Klemens,[6] in what is in many ways the most satisfactory treatment of thermal conduction, dismisses the divergence by a remark in a footnote to the effect that it is eliminated by Umklapp collisions. As far as I can see, this statement is not correct, at least for the type of dispersion relation normally expected.

The present study of low-energy phonons was stimulated by their influence on the thermoelectric power of semiconductors.[7–9] The most important object of this paper is therefore to get expressions for the variation of the relaxation time $\tau(\mathbf{q})$ of a phonon of wave number $\mathbf{q}$ with $\mathbf{q}$ and with temperature, for the low-energy acoustic modes which contribute to the scattering of charge carriers in semiconductors at moderately low temperatures. An important by-product, however, is the clarification of the role of these low-energy phonons in thermal conduction. Since the theory of thermoelectric power is itself a complicated subject, the application of the present results to thermoelectricity is given in a separate paper,[9] and we shall confine the present discussion to phonons and thermal conduction.

Briefly put, the thesis which we wish to develop here is that the elastic anisotropy of a crystal can cause the scattering of low energy longitudinal phonons to differ profoundly from the behavior predicted for an isotropic medium. For a great many crystals this difference entirely removes the divergence of the thermal conductivity; for many others it reduces the divergence to a logarithmic one. For these crystals the variation of conductivity with specimen size would be extremely small at temperatures above a few percent of the Debye temperature and over the practical range of

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[1] R. Peierls, Ann. Physik 3, 1055 (1929).

[2] P. Debye, *Vorträge über die kinetische Theorie der Materie und der Elektrizität* (Teubner, Leipzig, 1914).

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[7] H. P. R. Frederikse, Phys. Rev. 91, 491 (1953); 92, 248 (1953).

[8] T. H. Geballe, Phys. Rev. 92, 857 (1953).

[9] C. Herring, Phys. Rev. 92, 857 (1953); full paper to be published.

sizes; however, it might sometimes be measurable. Among the lower symmetry classes it is possible that crystals may exist for which the original divergence applies in full force. Such crystals should show a greater dependence of conductivity on size; however, the dependence would be conspicuous only for rather large single crystals of good quality.

I. THE RELAXATION TIME

Our main concern in this paper will be with temperatures rather smaller than the Debye temperature. In this range, as the calculations of Pomeranchuk[3] show, there are very few collisions involving four or more phonons, i.e., collisions in which the occupation numbers of four or more normal modes are altered. We may therefore restrict attention to three-phonon collisions. These are a consequence of the term U_3 in the elastic potential energy which is of the third order in the relative displacements of the atoms, or equivalently, for modes of long wavelength, of the third order in the strain amplitudes. Detailed expressions for the matrix elements of U_3 have been given by Herpin.[4] For our present purpose, since we are interested in long wavelengths and low temperatures, it will suffice to consider merely the dependence upon the phonon wave numbers when the latter are small. This dependence is determined by the fact that the strain in any normal vibration is proportional to the product of the amplitude by the wave number q, and the fact that the matrix element of the amplitude connecting states of quantum numbers N and $N-1$ is proportional to $(N/\omega)^{\frac{1}{2}}$, where ω is the frequency of the mode. Therefore for any three acoustic modes 0, 1, 2, whose wave vectors satisfy

$$\mathbf{q}_0+\mathbf{q}_1=\mathbf{q}_2, \tag{1}$$

we must have, since $\omega(\mathbf{q})\propto q$,

$$|(N_0, N_1, N_2|U_3|N_0-1, N_1-1, N_2+1)|^2 \propto q_0q_1q_2N_0N_1(N_2+1), \tag{2a}$$

$$|(N_0, N_1, N_2|U_3|N_0+1, N_1+1, N_2-1)|^2 \propto q_0q_1q_2(N_0+1)(N_1+1)N_2. \tag{2b}$$

Here and below the factor implied in each proportionality sign is independent of the N's and the magnitudes of the wave vectors, but depends on the directions of the wave vectors and the polarizations of the three modes. We may note, finally, that even if modes 1 and 2 are high-energy modes to which the acoustic approximation $\omega\propto q$ does not apply, the proportionality of the squared matrix element to q_0N_0 or $q_0(N_0+1)$ will still hold if mode 0 is in the acoustic range.

The transition probability for the process $N_{0,1}\rightarrow N_{0,1}-1$, $N_2\rightarrow N_2+1$, or for the reverse process, is appreciable only in the neighborhood of the surface S_1 in q_1-space where the energy conservation condition

$$\hbar\omega_0+\hbar\omega_1=\hbar\omega_2 \tag{3}$$

is satisfied. The transition probability associated with an element of area dS_1 of this surface is

$$dW(0,1\rightleftarrows 2)\propto |U|^2dS_1|\partial\Delta\omega/\partial q_{1n}|^{-1}, \tag{4}$$

where U is the matrix element, given for the acoustic case by (2a) or (2b), q_{1n} is the component of $\mathbf{q}_1$ normal to dS_1, and

$$\Delta\omega=\omega(\mathbf{q}_0+\mathbf{q}_1)-\omega(\mathbf{q}_0)-\omega(\mathbf{q}_1) \tag{5}$$

measures the departure from energy conservation.

With each mode $\mathbf{q}_0$ we may associate a relaxation time $\tau(\mathbf{q}_0)$ defined by[6]

$$\frac{1}{\tau(\mathbf{q}_0)}=-\lim_{N_0\rightarrow N_0^{(0)}}\frac{(dN_0/dt)_c}{N_0-N_0^{(0)}}, \tag{6}$$

where $N_0^{(0)}$ is the value of the occupation number N_0 in thermal equilibrium and where $(dN_0/dt)_c$ is the total rate of change of N_0 due to phonon-phonon collisions when N_0 departs from equilibrium but all other modes have equilibrium occupation. The relation of this "relaxation time of a single mode" to thermal conduction will be discussed in Sec. IV below; for the present we wish merely to investigate the asymptotic behavior of this quantity for modes of very low frequency. Now $(dN_0/dt)_c$ is a sum of transition probabilities

$$(dN_0/dt)_c=W(2\rightarrow 0, 1)-W(0, 1\rightarrow 2) +W(1, 2\rightarrow 0)-W(0\rightarrow 1, 2), \tag{7}$$

where the first two W's are to be obtained by integrating (4) and the last two W's by evaluating similar expressions with 0 and 2 interchanged. For the contribution of an element dS_1 to the part of (6) arising from the first two W's we have, if (2a) and (2b) are adequate on dS_1,

$$-\lim_{N_0\rightarrow N_0^{(0)}}\frac{dW(2\rightarrow 0, 1)-dW(0, 1\rightarrow 2)}{N_0-N_0^{(0)}}$$

$$=-\frac{\partial}{\partial N_0}[dW(2\rightarrow 0, 1)-dW(0, 1\rightarrow 2)]$$

$$\propto q_0q_1q_2(N_1^{(0)}-N_2^{(0)})dS_1|\partial\Delta\omega/\partial q_{1n}|^{-1}. \tag{8}$$

If any of the q's are too large for (2a) and (2b) to apply, as for Umklapp collisions, only the proportionality to these q's is altered in (8). Consider now the contribution of the last two W's in (7). For these transitions the modes 1 and 2 must have lower frequencies than mode 0, so the area of S_1 is of order q_0^2 as $q_0\rightarrow 0$. The expression analogous to (8) contains $N_1^{(0)}+N_2^{(0)}+1$, a quantity of the order q_0^{-1}, in place of $N_1^{(0)}-N_2^{(0)}$. As the last factor in (8) is finite as $q_0\rightarrow 0$, the total contribution to (6) from the last two W's in (7) is $O(q_0^4)$. Thus $1/\tau(\mathbf{q}_0)$ will be $O(q_0^4)$ as $q_0\rightarrow 0$ if integration of (8) on dS_1 gives $O(q_0^4)$ or smaller, while the value obtained from (8) will predominate if it is larger than $O(q_0^4)$. Thus the problem of determining the asymptotic dependence of $\tau(\mathbf{q}_0)$ on q_0 is reduced to the problem of evaluating the integral of (8).

In the next two sections we shall determine the behavior of the integral of (8) by determining the form of the energy conservation surface S_1 and the magnitude of the normal derivative of $\Delta\omega$ on it. However, one or two scaling laws for $\tau(\mathbf{q}_0)$ can be derived without any detailed information on these topics. Consider a range of temperatures low enough so that all the phonons which take appreciable part in the scattering of phonons of type $\mathbf{q}_0$ are in the acoustic range. In this range let us compare the relaxation time of $\mathbf{q}_0$ at temperature T and that of $\lambda\mathbf{q}_0$ at temperature λT. Since all phonons are in the acoustic range, the conservation surface S_1 for $\lambda\mathbf{q}_0$ differs only by a scale factor λ from that for $\mathbf{q}_0$. Therefore the dS_1 in (4) is $\propto\lambda^2$. Since $N^{(0)}(\lambda\mathbf{q},\lambda T)$ is the same as $N^{(0)}(\mathbf{q},T)$, $|U|^2\propto\lambda^3$, and as the last factor in (4) is independent of scale, every W in (7) is $\propto\lambda^5$. Thus in the low temperature range

$$\tau(\lambda\mathbf{q},\lambda T)\propto\lambda^{-5}. \tag{9}$$

Finally, we may note that for fixed $\mathbf{q}$'s (8) and its counterpart for the last two W's in (7) contain T only through a term linear in the $N^{(0)}$'s. Therefore in the limit of high temperatures, where all modes are highly excited,

$$\tau(\mathbf{q})\propto T^{-1} \tag{10}$$

provided, of course, that higher order processes such as four-phonon collisions are still negligible compared with three-phonon collisions.

II. THE ENERGY CONSERVATION CONDITION

We are interested in the form of the surface S_1 in q_1-space on which the energy conservation Eq. (3) and the wave vector conservation Eq. (1) are simultaneously satisfied, for a given $\mathbf{q}_0$, ω_0. Moreover, our main interest is in very small values of q_0. Consider the two surfaces $\omega(\mathbf{q})=\omega_1$ and $\omega(\mathbf{q})=\omega_1+\omega_0$ in $\mathbf{q}$-space. Let the second of these be displaced rigidly by the vector $-\mathbf{q}_0$, as shown in Fig. 1. The line of intersection (if any) of this displaced surface with the first surface is then a line in q_1-space on which the two conservation conditions (1), (3) are fulfilled, and as ω_1 varies this line generates the desired surface S_1. It is clear from the examples of Fig. 1 that as $q_0\rightarrow 0$ intersections will always occur in the neighborhoods of points such as P, Q, where the frequencies of two branches coincide, but may or may not occur in places far removed from such points. We shall use the term *point of degeneracy* to designate any such point $\mathbf{q}$ where two or more modes of wave vector $\mathbf{q}$ have the same frequency. Degeneracies at certain points of $\mathbf{q}$-space or along certain lines or planes are often necessitated by crystal symmetry.[10,11] Degeneracies may also occur accidentally,[12] although this is not likely to occur for crystals of high symmetry at points of the acoustic branch close to the origin, the region of major interest to us. We have to examine the possibility of satisfying the conservation conditions as $q_0\rightarrow 0$ for fixed direction of $\mathbf{q}_0$, for the following cases:

(i) *At points R of the ω_1-surface not in the neighborhood of any point of degeneracy, when at every such point R the component of group velocity in the direction of $\mathbf{q}_0$ is less than the phase velocity of the mode 0.* This is the case for points such as R in Fig. 1(a). For such points the different branches of the ω_1-surface have a finite separation, so as $q_0\rightarrow 0$ no such point can be a point of intersection of one branch of the ω_1-surface with a different branch of the displaced ω_2-surface. But intersections of a given branch of the former with the same branch of the latter are also impossible for sufficiently small q_0, since when only a single branch is involved (1) and (3) imply

$$\mathbf{q}_0\cdot\partial\omega(\mathbf{q}_1)/\partial\mathbf{q}_1+O(q_0^2)=\omega(\mathbf{q}_0), \tag{11}$$

and this must become impossible as $q_0\rightarrow 0$ if the component of the group velocity $\partial\omega(\mathbf{q}_1)/\partial\mathbf{q}_1$ along $\mathbf{q}_0$ is less than $\omega(\mathbf{q}_0)/q_0$. The latter condition will probably nearly always be fulfilled when mode 0 is a longitudinal mode (i.e., belongs to the highest frequency branch of the acoustic spectrum).

(ii) *At points J not in the neighborhood of any point of degeneracy, when for some such points J the component of group velocity in the direction of $\mathbf{q}_0$ is greater than the phase velocity of mode 0.* Here again intersections of different branches are ruled out, but intersections involving only one branch will occur, since as $q_0\rightarrow 0$ Eq. (11) will always be satisfied somewhere. An example is shown at J in Fig. 1(b). For the present case the intersection line will approach a limiting position on the ω_1-surface as $q_0\rightarrow 0$, and so the area of those parts of the conservation surface S_1 which lie outside the neighborhoods of contact points will approach a finite limit.

It is easy to show that this case must occur for small (but not infinitesimal) values of ω_1, whenever the mode $\mathbf{q}_0$ belongs to one of the transverse branches, i.e., does not belong to the highest frequency branch. For when ω_1 is small enough to be practically uninfluenced by dispersion, the construction of Fig. 1 amounts to finding the intersection of the ω_1-surface with the surface formed from this by a linear projection of each point away from that point F of the ω_1-surface which has $\omega_1,\mathbf{q}_1\propto\omega_0,\mathbf{q}_0$. Such a linear projection is illustrated in Fig. 1(c), which, however, is drawn for a longitudinal mode and a rather large ratio q_0/q_1, instead of the case we wish to consider now. As $q_0\rightarrow 0$, such an intersection will always occur in the neighborhood of any point where the ω_1-surface is tangent to a line through F. Such a tangency will always occur unless (as in the case shown) F lies on the innermost branch of the ω_1-surface, i.e., unless the mode $\mathbf{q}_0$ is longitudinal.

(Although it is legitimate to make a construction

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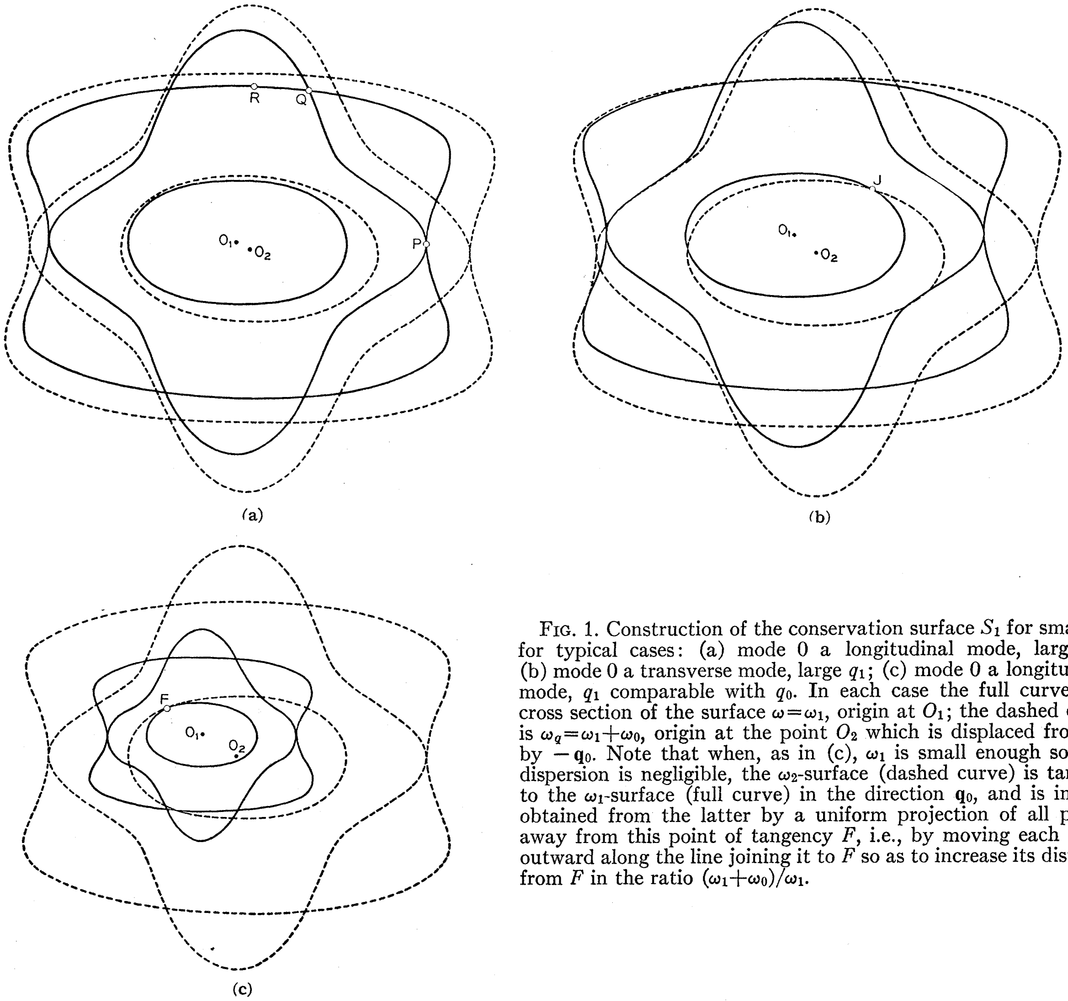
[10] Bouckaert, Smoluchowski, and Wigner, Phys. Rev. **50**, 58 (1936).

[11] C. Herring, Phys. Rev. **52**, 361 (1937).

[12] C. Herring, Phys. Rev. **52**, 365 (1937).



(a) (b) (c)

FIG. 1. Construction of the conservation surface S_1 for small q_0, for typical cases: (a) mode 0 a longitudinal mode, large q_1; (b) mode 0 a transverse mode, large q_1; (c) mode 0 a longitudinal mode, q_1 comparable with q_0. In each case the full curve is a cross section of the surface $\omega=\omega_1$, origin at O_1; the dashed curve is $\omega_q=\omega_1+\omega_0$, origin at the point O_2 which is displaced from O_1 by $-\mathbf{q}_0$. Note that when, as in (c), ω_1 is small enough so that dispersion is negligible, the ω_2-surface (dashed curve) is tangent to the ω_1-surface (full curve) in the direction $\mathbf{q}_0$, and is in fact obtained from the latter by a uniform projection of all points away from this point of tangency F, i.e., by moving each point outward along the line joining it to F so as to increase its distance from F in the ratio $(\omega_1+\omega_0)/\omega_1$.

like that described, based on the conception of a point of tangency F, it should be noted that there will normally be a tiny separation of the two frequency surfaces in the region of their near-tangency, because of dispersion in the velocity of sound. This makes it unnecessary to consider collisions with $q_1\approx F$.)

(iii) *At points in the neighborhood of a point of degeneracy Q, or of a line or plane of degeneracy, where for all directions of approaching Q the frequency separations of the branches which come together at Q are all of the first order in the distance from the degeneracy point, line, or plane.* For this case, illustrated in Fig. 1(a) and (b), the ω_1-surface and the displaced ω_2-surface will always intersect in the neighborhood of Q, regardless of group velocity considerations. Except in the vanishingly improbable case where the intersection occurs exactly at Q, the points of intersection will occur at distances from Q which are $O(q_0)$ as $q_0\rightarrow 0$.

If Q ranges over such a degeneracy line, therefore, this part of S_1 will be a thin cylinder about this line, and the contribution to the area of S_1 will be $O(q_0)$.

Although line degeneracies are the most important type in the present category (iii), degeneracy at all points of a boundary plane of the Brillouin zone is possible for crystals of certain space groups,[11] and will be important for the relaxation times of low-energy longitudinal modes in these cases. The crystals for which this will occur are those with a boundary plane of the Brillouin zone normal to a twofold screw axis. The part of the conservation surface S_1 neighboring such a plane has an area which obviously approaches a finite limit as $q_0\rightarrow 0$.

As we shall see in the next section, the contributions from isolated degenerate points Q are usually unimportant when, as we are assuming under the present heading (iii), the frequency separations of the branches are of the first order in the distance from Q. The principal case where such a point may be important is that of a crystal of such low symmetry that no degeneracies occur except at $q=\omega=0$. For this contact point q_1 and q_2 are both of the same order as q_0. Whether the point is at $\mathbf{q}=0$ or not, the contribution to S_1 from such a point will be $O(q_0^2)$.

(iv) *At points P in the neighborhood of a point or line* *of degeneracy, where for all directions of approaching P the frequency separation of some pair of branches is of the second order in the distance from P.* This case is also illustrated in Fig. 1(a) and (b), and again it is obvious that the ω_1-surface and the displaced ω_2-surface will always intersect in the neighborhood of P. However, the distances of the points of intersection from P will now be of order $q_0^{\frac{1}{2}}$ instead of q_0.

If P ranges over a degeneracy line, therefore, the contribution to the area of S_1 will be $O(q_0^{\frac{1}{2}})$.

If P is an isolated point of degeneracy of the type specified, e.g., the point $\mathbf{q}=0$ in the optical branch of a crystal of high symmetry, the contribution to the area of S_1 will be $O(q_0)$.

Degeneracies of the present type (iv) do not occur over a plane surface in q-space.

We have not enumerated any cases where the variation of energy separation with distance from the degeneracy point or line is linear in some directions, quadratic in others. Such a phenomenon can only occur for degeneracy lines or points on the boundary of the Brillouin zone; the influence of these is usually dwarfed by that of interior contact lines at low temperatures.

III. ASYMPTOTIC BEHAVIOR OF THE RELAXATION TIME

Each of the conservation regions enumerated in the preceding section gives a contribution to the reciprocal relaxation time of the mode $\mathbf{q}_0$ which is proportional to the corresponding contribution to the area ΔS_1 of the conservation surface S_1, but which also involves other factors dependent on $\mathbf{q}_0$. It was shown in Sec. I that $1/\tau(\mathbf{q}_0)$ is proportional to the sum of the integral of (8) and a term of order q_0^4. As $q_0 \to 0$ for a fixed direction the factor $(N_1^{(0)}-N_2^{(0)})$ in (8) is $O(q_0)$, provided ω_1 and ω_2 remain finite, as they will in all cases except that of Fig. 1(c). When this proviso is fulfilled, the integral of (8) over a given part of the S_1-surface gives

$$\text{contrib. to } 1/\tau(\mathbf{q}_0) \propto q_0^2 \Delta S_1 |\partial\Delta\omega/\partial q_{1n}|^{-1}, \qquad (12)$$

provided the factor implied by the proportionality sign in expressions such as (2) for the matrix element remains finite as $q_0 \to 0$.

The assumption of finiteness of the matrix element needs to be examined group-theoretically, of course, since the commonest cause of degeneracy is the occurrence of symmetry operations in the space group of the crystal, and it is conceivable that this same symmetry property may cause the matrix element in question to vanish. The necessary examination is carried out in Appendix A and summarized in Table III there. The result is that, at least for degeneracies on interior lines and boundary planes of the Brillouin zone, symmetry never requires the matrix element to approach zero as $q_0 \to 0$, except for certain special directions and polarizations of the mode $\mathbf{q}_0$. For crystals of the cubic system no mode $\mathbf{q}_0$ is "special" in this sense with respect to all members of an equivalent set of lines of degeneracy, i.e., with respect to all three (100) type axes in $\mathbf{q}_1$-space, or with respect to all four (111) type axes.

The only thing remaining to be done, therefore, in order to evaluate (11) for each of the cases enumerated in the preceding section, is to determine the behavior of $|\partial\Delta\omega/\partial q_{1n}|$ for each case. For all the cases enumerated under (iii) and (iv), the $\omega(\mathbf{q}_0+\mathbf{q}_1)$ and $\omega(\mathbf{q}_1)$ in (5) refer to different branches. Therefore in cases of type (iii) the derivatives of these two frequencies with respect to q_{1n} will approach entirely different limits as $q_0 \to 0$, so that $|\partial\Delta\omega/\partial q_{1n}|$ remains bounded. In cases of type (iv) the latter quantity is $O(q_0^{\frac{1}{2}})$. In case (ii) the frequencies $\omega(\mathbf{q}_0+\mathbf{q}_1)$ and $\omega(\mathbf{q}_1)$ refer to the same branch, so we have on differentiating (5)

$$\partial\Delta\omega/\partial q_{1n} = \mathbf{q}_0 \cdot \partial^2\omega_1/\partial \mathbf{q}_1 \partial q_{1n} + O(q_0^2). \qquad (13)$$

Since the second derivative in (13) in general differs from zero almost everywhere, we may conclude that for points of type (ii) $|\partial\Delta\omega/\partial q_{1n}|$ will be $O(q_0)$ as $q_0 \to 0$.

Inserting into (12) these results and the forms deduced in the preceding section for ΔS_1, we arrive at the exponents shown in Table I for the contributions to $1/\tau(\mathbf{q}_0)$ from the different possible parts of the conservation surface. Also included in the table, on the last line, is the contribution arising from the last two W's of (7). The rows have been arranged in order of increasing powers of q_0. Thus the asymptotic behavior of $1/\tau(\mathbf{q}_0)$ will be determined by the first of these contributions which is present for the given crystal and the given direction and polarization of the mode $\mathbf{q}_0$. The entries are valid at any temperature for which higher-order collisions are negligible, subject only to the possible freezing-out of some of the processes at low temperature, as noted in the last column.

It is now a straightforward matter to compute, for any space group, which of the rows of Table I are required by crystal symmetry to be present. Such a calculation will give an upper limit to the exponent of $\mathbf{q}_0$ in the asymptotic behavior of $1/\tau(\mathbf{q}_0)$. We can of course not predict with certainty that this upper limit

TABLE I. Contributions to the asymptotic behavior of $1/\tau(\mathbf{q}_0)$ as $q_0 \to 0$.

Type of phonon collision		Illustration in Fig. 1	Behavior of $1/\tau(\mathbf{q}_0)$ for most modes	Remarks
$2 \rightleftarrows 0, 1,$ $q_1 \gg q_0$	(ii)	J in (b)	q_0	Valid for any T
	(iii) plane	Q in (a)	q_0^2	High T only
	(iv) line	P in (a)	q_0^2	Valid for any T if interior line
	(iv) point	P in (a)	$q_0^{5/2}$	High T only
	(iii) line	Q in (a)	q_0^3	Valid for any T if interior line
	(iii) point	Q in (a)	q_0^4	Valid for any T
$2 \rightleftarrows 0, 1, q_1 \sim q_0$		G in (c)	q_0^4	Valid for any T
$0 \rightleftarrows 1, 2$			q_0^4	Valid for any T

Except for cubic crystals, there will usually exist special combinations of direction and polarization with longer relaxation times (higher exponents) than shown in the second to fifth rows.

will be realized for any given crystal, unless we know the complete elastic spectrum of this crystal, for two reasons: one has to do with the group velocity inequalities involved in deciding whether case (ii) applies; the other is that accidental degeneracy may cause a higher row to apply than symmetry degeneracy. However, it is likely that the upper limit to the exponent will be realized for longitudinal modes (i.e., modes of the highest frequency branch) in many cases. For transverse modes, or course, the argument given under (ii) of the preceding section shows that the first line of Table I always applies.

It would of course be very laborious to construct a table giving the group-theoretical upper limit to the exponent for each of the 230 space groups. However, if we consider only the contributions to $1/\tau(\mathbf{q}_0)$ which arise from acoustic modes $\mathbf{q}_1$ inside the Brillouin zone, as distinguished from modes on the boundary and modes belonging to optical branches, the problem simplifies greatly, since one need consider only lines of degeneracy lying inside the Brillouin zone. The enumeration of these line degeneracies and the decision as to whether case (iii) or case (iv) applies can be made from a knowledge merely of the point group of the crystal. The procedure for a given point group G is as follows.[13] Determine those subgroups of G whose unit representations are contained in the polar vector representation of G once and once only.[14] Each such subgroup G^i will be the "group of the wave vector"[10] for a line of points $\mathbf{q}_i$ in $\mathbf{q}$-space, i.e., G^i will comprise those operations which take a mode of wave vector $\mathbf{q}_i$ into the same or another mode of the same wave vector. Select those representations of the various G^i which are contained in the polar vector representation of G and which are two-dimensional (higher dimensionalities will not occur) or which, though one-dimensional, are required by the time-reversal symmetry of the problem[11] to coincide in frequency with another one-dimensional representation. These will be the representations to which the various line degeneracies belong. Coincidence in frequency of two modes belonging to one-dimensional representations of a G^i will occur only for the cases listed in Table II of reference 11. For each such representation or pair of representations of a G^i, determine whether a vector operator with the transformation properties of a vector normal to $\mathbf{q}_i$ can split the degeneracy in first order. If it can, the frequency separation in the neighborhood of the line will be linear in the distance from the line, so that case (iii) will apply.[12] If it cannot, the frequency separation will be quadratic and case (iv) will apply.

TABLE II. Asymptotic values of the exponent a in $1/\tau(\mathbf{q}_0)\propto q_0{}^a$, for longitudinal acoustic modes in various crystal classes.

System	Class	G^i for lines of degeneracy	Type of frequency variation near line, for acoustic branch	Dominant value of a for most directions	
				With dispersion[a]	Without dispersion[b]
Cubic	O_h	C_{4v}, C_{3v}	(iv), (iii)	2	2
	O	no degen. lines		4	2
	T_d	C_{2v},[c] C_{3v}	(iv), (iii)	2	2
	T_h	C_{3v}	(iii)	3	2
	T	no degen. lines		4	2
Hexagonal	D_{6h}	C_{6v}	(iv)	2	2
	D_6	no degen. lines		4	2
	C_{6v}	C_{6v}	(iv)	2	2
	C_{6h}	C_6[c]	(iv)	2	2
	C_6	no degen. lines		4	2
Trigonal	D_{3h}	C_{3v}	(iii)	3	3
	C_{3h}	no degen. lines		4	3
	D_{3d}	C_{3v}	(iii)	3	3
	D_3	no degen. lines		4	3
	C_{3v}	C_{3v}	(iii)	3	3
	C_{3i}	C_3[c]	(iii)	3	3
	C_3	no degen. lines		4	3
Tetragonal	D_{4h}	C_{4v}	(iv)	2	2
	D_4	no degen. lines		4	2
	C_{4v}	C_{4v}	(iv)	2	2
	C_{4h}	C_4[c]	(iv)	2	2
	C_4	no degen. lines		4	2
	V_d	C_{2v}[c]	(iv)	2	2
	S_4	C_2[c]	(iv)	2	2
Orthorhombic, monoclinic, and triclinic		no degen. lines		4	3 or 4

[a] Tabulated a is $\lim_{q\to 0}[-d\ln\tau(\mathbf{q},T)/d\ln q]$.

[b] Tabulated a is $\lim_{q\to 0}\lim_{\lambda\to 0}[-d\ln\tau(\lambda\mathbf{q},\lambda T)/d\ln(\lambda q)]$.

[c] Cases where two one-dimensional representations of G^i are required by time-reversal symmetry to have the same frequency.

Except for the cubic classes and for the cases where $a=4$, there will usually be special combinations of direction and polarization of the mode q_0 with longer relaxation times (higher a than those shown). However, a will never exceed 4.

For any direction of q_0 which is not "special" in the sense mentioned above, an entry 2 in the table will be the true value of a, rather than merely an upper limit, except when the group velocity condition (ii) of Sec. II is fulfilled. Similarly an entry 3 will be the true value when (ii) does not apply and when the temperature is sufficiently low. For an entry 4 to be the true value, it suffices that these two conditions be satisfied and that there be no accidental degeneracy.

Table II summarizes in the next to the last column the results obtained for the various point groups by the procedure just outlined. However, these results must be used with caution, as they may be quite misleading in a certain class of cases. For example, consider the scattering of a low-frequency longitudinal mode $\mathbf{q}_0$ by modes $\mathbf{q}_1$ in the neighborhood of the line $q_y=q_z=0$ in the Brillouin zone of a cubic crystal. If the crystal is of class O_h, the transverse modes are degenerate all along this line, and there will be a scattering contribution from a surface in $\mathbf{q}_1$-space closely surrounding this line. If the crystal is of class O, on the other hand, the procedure outlined above predicts no degeneracy along this line, hence no contribution to the scattering, if q_0 is small enough. But in the acoustic approximation, i.e., with neglect of the dispersion of the sound waves, the frequencies along this line are given by a secular equation involving the

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[13] For a fuller exposition of the theory underlying this procedure see references 10, 11, and 12.

[14] For tables of characters of the point groups see E. Wigner, Nachr. Akad. Wiss. Göttingen, Math-physik. Kl., p. 133 (1930).

elastic constants c_{11}, c_{12}, and c_{44} in just the same way as for class O_h, and so in this approximation there is degeneracy on this line. The truth is, therefore, that the frequencies of the two transverse modes going with a $\mathbf{q}_1$ in the x direction are always different, but that as $q_1 \rightarrow 0$ their difference becomes a smaller and smaller fraction of the frequency of either. If the temperature is low, the modes $\mathbf{q}_1$ which are most important in the scattering of $\mathbf{q}_0$ will be modes which come very close to being degenerate along the coordinate axes, and for any given ratio of $\hbar\omega_0$ to kT the scattering processes will become, as $T \rightarrow 0$, qualitatively the same as for class O_h. Thus to assess the significance of the entries in the next to the last column of Table II one should have, for comparison, values of the exponent computed with neglect of dispersion. These can easily be obtained by analyzing the consequences of crystal symmetry for the solution of the 3×3 secular equation for acoustic waves without dispersion. The results are given in the last column of Table II.

At temperatures sufficiently low for (9) to apply, the temperature variation of $1/\tau(\mathbf{q}_0)$ is given by

$$1/\tau(\mathbf{q}_0) \propto q_0{}^a T^{5-a}, \tag{14}$$

where a is the exponent given in Table II.

Finally, a word or two should be said about how small q_0 must be in order for the asymptotic behavior of Table II to be approximately realized. Consider, for example, the intersections near the points P and Q in Fig. 1(a). For the conditions shown, the linear behavior of ω_1 near Q is approximately valid out to the intersection, but the quadratic behavior near P has become more nearly a linear one before the intersection has occurred. Thus the contribution to $1/\tau(\mathbf{q}_0)$ from the neighborhood of P already departs considerably from the asymptotic behavior. The departure is less pronounced at the point diametrically opposite P. Still, it is clear that for these two types of points the contribution to $1/\tau(\mathbf{q}_0)$ from any given ω_1-surface will not have the asymptotic form until ω_0 is a small fraction of ω_1.

A sample plot of the type of Fig. 1 was made for the low energy acoustic spectrum of germanium, using the known elastic constants.[15] A study of this suggested that the contribution from a given scattering phonon frequency ω_1 to the $1/\tau(\mathbf{q}_0)$ of a longitudinal mode should be fairly well proportional to $q_0{}^2$ for $\omega_0 < 0.05\omega_1$, but not at all for $\omega_0 = 0.10\omega_1$. Now because of the way the various factors in (8) depend on $\mathbf{q}_1$ or ω_1, the phonons which contribute most to the scattering at low temperatures are those with energies $\hbar\omega_1$ rather larger than kT. For sufficiently small q_0, the median $\hbar\omega_1$ of all the contributions to $1/\tau(\mathbf{q}_0)$ can in fact be shown to be close to $3kT$ for a crystal of the type giving $1/\tau(\mathbf{q}_0) \propto q_0{}^2$ at low T. For such a crystal, therefore, we might expect the asymptotic behavior to be approximated for longitudinal modes with $\hbar\omega_0$ below something like $0.15kT$.

For a crystal giving $1/\tau(\mathbf{q}_0) \propto q_0{}^3$, with an over-all degree of elastic anisotropy similar to that found for germanium, one might expect asymptotic behavior to be approximated out to a slightly larger value of ω_0/ω_1 than that mentioned in the preceding paragraph. On the other hand, the median ω_1 would be lower. So the critical $\hbar\omega_0/kT$ for asymptotic behavior might well be about the same.

For crystals which give $1/\tau(\mathbf{q}_0) \propto q_0{}^4$ the asymptotic behavior should be realized when q_0 is small enough so that the conservation condition can only be satisfied by modes $\mathbf{q}_1$ with frequencies in the equipartition range. The limiting q_0 for this will depend on the minimum separation in sound velocity between the transverse branches. If this separation is of the order of 10 percent, for example, absence of an energy-conserving collision in Fig. 1(c) requires that the radii of the dashed curves, measured from F, be no more than, say, 7 percent greater than those of the corresponding full curves, so that $\omega_0/\omega_1 \lesssim 0.07$. If this is to hold for values of $\hbar\omega_1$ as small as $\frac{1}{2}kT$ or less, we must have, as the condition for asymptotic behavior to be realized, something like $\hbar\omega_0 < 0.03kT$.

For longitudinal modes $\mathbf{q}_0$ of an elastically isotropic continuum, only the last two lines of Table I apply; this is the result of Landau and Rumer,[5] Pomeranchuk,[3] and Herpin.[4] It is interesting to consider the behavior of $\tau(\mathbf{q}_0)$ with decreasing q_0 for longitudinal waves in a crystal which is almost elastically isotropic, but not quite. For such a crystal, at low T, $\tau(\mathbf{q}_0)$ will behave as for an isotropic body until q_0 gets small enough for intersections of types (iii) or (iv) to occur. The critical q_0 below which such intersections will occur will be one for which ω_0 is of the order of the frequency difference between the two transverse branches, for the modes most important in scattering. Thus this critical q_0 will become smaller and smaller the more nearly the crystal approximates elastic isotropy. When $q_0 \ll$ this critical value, the relaxation time will usually be determined by one of the upper rows of Table I.

IV. THERMAL CONDUCTION AT LOW TEMPERATURES

We wish now to see if the long relaxation times which the theory predicts for longitudinal acoustic phonons of long wavelength can have a significant effect on the thermal conductivity. To this end we shall use the standard formula[6] for the thermal conductivity, which is based on the assumption that the recovery of the phonons from the perturbing influence of the temperature gradient is describable by a relaxation time $\tau(\mathbf{q})$. According to this formula each mode of a unit volume of the crystal contributes an amount $v_\mu v_\nu \tau C_q$ to the thermal conductivity tensor $\kappa_{\mu\nu}$, where $\mathbf{v}(\mathbf{q})$ is the group velocity of the mode $\mathbf{q}$ and C_q is its heat capacity. We shall first undertake to show that for the calculation

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[15] Bond, Mason, McSkimin, Olsen, and Teal, Phys. Rev. **78**, 176 (1950).

of the contribution of the modes of very low frequency it is indeed legitimate to use this formula, with $\tau(\mathbf{q})$ interpreted as the relaxation time of a single mode, defined by (6). Then we shall derive expressions for the contribution of these low frequency modes to the conductivity. These expressions will depend on the size of the specimen, since as $q \rightarrow 0$ phonon-phonon scattering will eventually become less important in determining $\tau(\mathbf{q})$ than scattering from the boundaries of the specimen. The result will therefore be a predicted dependence of thermal conductivity on size, valid at temperatures where the great majority of the phonons are limited by phonon-phonon scattering and only the lowest frequency longitudinal modes are dominated by boundary scattering. It will thus give information on how the size effect diminishes as the temperature is raised from the range where all modes are dominated by boundary scattering[16] to the range where boundary scattering is completely negligible.

We have first, then, to justify the use of the relaxation times of single modes, i.e., of (6) combined with boundary scattering, to calculate the contribution of low frequency modes to the thermal conductivity. This procedure could fail if, and only if, the rate of randomization of the energy flux associated with a particular mode in thermal conduction were significantly different from what it would be if all the other modes were in equilibrium. These two rates of randomization may differ considerably for modes of thermal energy and above, but for the low-energy longitudinal modes they cannot differ very much under most circumstances. The reason is that in a thermal gradient the latter modes, because of their long relaxation times, are much more "off balance" than the modes with which they have most of their collisions.[17] An exception may occur at very low temperatures, when the Umklapp collisions which the phonons require in order to get rid of their heat current may become rare enough to give a relaxation time comparable with the $\tau(\mathbf{q}_0)$'s we have been discussing. Also, at lowest temperatures all modes become limited by boundary scattering, so all have the same unbalance. In this condition (6) will not correctly describe the phonon-phonon scattering rate, but this will not matter much because boundary scattering predominates.

Having accepted the use of (6), let us consider explicitly the contribution of the low-frequency longitudinal modes to the thermal conductivity κ in a given direction x, i.e., to $\sum v_x^2 \tau C_q$. For the low-energy modes of interest to us, C_q is very close to the Boltzmann constant k, so if c is an average longitudinal sound velocity we can write

$$\kappa \approx \text{constant} + (c^2 k / 8\pi^3) \int \tau(q) q^2 dq \cos^2\theta d\Omega, \qquad (15)$$

where θ is the angle between the group velocity of mode $\mathbf{q}$ and the direction in which κ is measured and where the integration is over longitudinal modes with q's in some neighborhood of the origin. Variations in the dimensions or crystal grain size of the specimen, and sometimes also variations in its dislocation content, can affect the value of the integral in (15). However, in the case of interest to us these factors will have much less effect on the contributions from modes with shorter τ's, and so we have lumped these together in the "constant" term. This will clearly be justified if $\tau(\mathbf{q})$ increases sufficiently rapidly with decreasing q; a simple calculation, which need not be given in detail, shows that the size-dependence of the integral in (15) outweighs that of the "constant," in the limit of large specimens or high temperatures, whenever $\tau(q) \propto q^{-a}$ with $a > 3/2$. This is fulfilled for all the cases listed in Table II.

For a crystal sufficiently free of dislocations, then, we can calculate the size-dependence of the conductivity, in the range of sizes and temperatures where this dependence is very small, by evaluating the integral in (15) with a $\tau(\mathbf{q})$ which follows one of the laws given in Table II until $c\tau(\mathbf{q})$ becomes comparable with the diameter L of the crystal, and which for smaller q departs from its behavior in an infinite crystal and approaches a constant limit $\tau_b \approx L/c$. The usual procedure in cases of this sort is to assume τ^{-1} to be compounded additively out of τ_b^{-1} and the phonon-phonon scattering probability, i.e., the value $\Lambda_a q^a$ given by Table II. This procedure is correct if the boundary scattering can be regarded as occurring uniformly throughout the volume of the specimen, a condition which might be approximated in a polycrystalline specimen with only a small acoustic mismatch from one grain to the next. For a single crystal specimen, however, the boundary scattering occurs nowhere except at the edges of the specimen, and to make an accurate calculation it is necessary to take account of the distribution of the energy flux over the cross section of the specimen.[9] This refinement amounts to using in the usual theory a τ_b which varies with $\mathbf{q}$; the effective τ_b turns out to be twice as large for large q as for small, "large" and "small" referring to whether the phonon-phonon $\tau(\mathbf{q})$ is $\ll$ or $\gg$ τ_b. However, we shall not attempt to introduce this refinement here, as it does not modify the computed conductivity contributions in any major way. In fact, for an order-of-magnitude calculation it is accurate enough simply to assume $\tau = (\Lambda_a q^a)^{-1}$ when this quantity is $< \tau_b$, and $= 0$ when it is $> \tau_b$. Equations (16) to (18), which have been computed in Appendix B using the assumption of additivity of reciprocal relaxation times, can in fact be obtained from this simpler assumption, to within a small error in each numerical coefficient. If angular brackets are used to denote averages over solid angle,

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[16] H. B. G. Casimir, Physica **5**, 495 (1938); Berman, Simon, and Ziman, Proc. Roy. Soc. (London) **220**, 171 (1953).

[17] See also reference 6, p. 115.

these equations are

$$\kappa\approx\text{constant}-\frac{c^2k}{4\pi}\left\langle\frac{\cos^2\theta}{\tau_b^{\frac{1}{2}}\Lambda_2^{\frac{3}{2}}}\right\rangle,\qquad(a=2)\qquad(16)$$

$$\kappa\approx\text{constant}+\frac{c^2k}{6\pi^2}\left\langle\frac{\cos^2\theta\ln\tau_b}{\Lambda_3}\right\rangle,\qquad(a=3)\qquad(17)$$

$$\kappa\approx\text{constant}+\frac{2^{\frac{1}{2}}c^2k}{8\pi}\left\langle\frac{\cos^2\theta\tau_b^{\frac{1}{4}}}{\Lambda_4^{\frac{3}{4}}}\right\rangle,\qquad(a=4).\qquad(18)$$

A ticklish question has to do with whether the neighborhoods of the "special directions" of $\mathbf{q}_0$, for which the entries in Tables I and II are invalid, can contribute significantly to the conductivity. If there are only isolated directions which are "special," we may assume that near any such direction the matrix element in (2) is of the first order in the angle ψ between q_0 and this direction. Then the Λ_a of (16) or (17) will be of order ψ^2, and the average over directions will in general diverge. Divergence of this calculation of course merely means that one should have used a higher value of a than that given in Table II, probably usually 4. The situation is even worse when there is a plane or cone of special directions. However, if the direction in which κ is measured is perpendicular to the group velocity of all the special modes, the $\cos^2\theta$ factor in (16) or (17) will be of order ψ^2, and the average over directions will converge. Thus we may conclude that use of (16) to (18) with the a values of Table II is often, perhaps usually, not legitimate for noncubic crystals when Table II gives $a<4$, except when the axis of measurement is perpendicular to the special directions of group velocity. The latter condition may frequently be fulfilled for a direction of measurement normal to the axis of a uniaxial crystal.

Equations (16) to (18) are of course only valid at temperatures sufficiently high so that boundary scattering is negligible for all modes except the low-frequency longitudinal ones. At temperatures low enough for all modes to be dominated by boundary scattering the theory of Casimir[16] must be used.

It remains to make some rough quantitative estimates of the values to be expected for the coefficients Λ_a occurring in Eqs. (16) to (18), and hence of the magnitudes of the size-dependent terms in the conductivity. Reasonably reliable estimates of Λ_2 can be made for semiconducting crystals for which the phonon effect on the thermoelectric power[7,8] has been measured. For example, from a comparison of theory[9] and observation for germanium one can deduce $\Lambda_2\approx3\times10^{-6}$ cm^2 sec^{-1} at 80°K, and proportional, of course, to T^3 at other temperatures. The uncertainty in this value arises from uncertainties in the nature of the processes by which phonons scatter the charge carriers; it is such that the value quoted might be in error by a factor two. Insertion of this into (16) gives, with the known conductivity[18]

$$\kappa\approx\kappa_\infty(1-0.017L^{-\frac{1}{2}})\qquad(19)$$

at 80°, where $\kappa_\infty=2.7$ watts/cm deg is the conductivity of an infinite specimen, and $L=c\tau_b$ is the boundary scattering length in millimeters, roughly equal to the diameter of the specimen if the latter is a single crystal, or to a few times the grain diameter, if a polycrystal. The coefficient 0.017 in (19) varies roughly as T^{-3}, since in this region κ goes about as $T^{-1.5}$. However, it would not be safe to extrapolate this coefficient to say 20° by this law, since a simple calculation shows that below about 50° the values of q for which the asymptotic expression for $\tau(\mathbf{q})$ is of the order of τ_b fail to satisfy the inequality $\hbar cq\lesssim0.15kT$ derived in the preceding section as necessary if the asymptotic expression for $\tau(\mathbf{q})$ is to be trusted. If the behavior of germanium is at all typical, we may conclude that for crystals with $a=2$, very accurate measurements would be required to establish the $L^{-\frac{1}{2}}$ dependence of the size-dependent term in the temperature range where this exponent can safely be predicted. At lower temperatures (but still far above the range where Casimir's formula applies) the size effect should be more easily detectable, but less simply interpretable.

Similar conclusions can be drawn, with a little more uncertainty, for crystals with $a=3$. Such crystals might be expected to behave as germanium would if scattering of the low-energy longitudinal phonons by modes with $\mathbf{q}_1$ near a cube edge direction were suppressed. The dominant modes for scattering would then be those with $\mathbf{q}_1$ near a cube diagonal direction. If the matrix element for scattering by such modes is roughly the same as for those with $\mathbf{q}_1$ near a cube edge direction, the ratio of the Λ_3 for the hypothetical case to Λ_2 for the actual case would be determined by the relative areas of the conservation surfaces S_1 for the two cases and the relative values of the density of states. These can be estimated from the known elastic spectrum. The result is $\Lambda_3\approx4\times10^{-13}$ cm^3 sec^{-1} at 80°, and of course proportional to T^2 at other temperatures. From this and (17) and the conductivity of germanium we get, for the hypothetical substance,

$$\Delta\kappa/\kappa\approx0.021\ln(L_1/L_2)\qquad(20)$$

at 80°K, where $\Delta\kappa$ is the difference in the conductivities of two specimens with diameters (or grain sizes) L_1 and L_2, respectively. The coefficient in (20) should be roughly proportional to $T^{-\frac{1}{2}}$, but here again both this proportionality and the logarithmic dependence would probably break down below say 60°.

A rather larger effect will occur for a crystal with $a=4$, if such exists. As an estimate of the probable size of the Λ_4 of such a crystal would be difficult to make and doubtless very unreliable, we shall be content

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[18] J. F. Goff, thesis, Purdue, 1953 (unpublished); T. H. Geballe (unpublished).

merely to set a rough upper limit to the size-dependent term in (18). The latter formula is applicable only when the maximum q_0 for the validity of the asymptotic formula $\tau \propto q_0^{-4}$, estimated in the preceding section as about $0.03kT/\hbar c$, is one for which $\tau(\mathbf{q}_0) < \tau_b$. If this condition is not fulfilled, the dependence of κ on τ_b will presumably be more gradual than that given in (18). With $\tau_b = L/c$ we find, therefore, that in the range where (18) is valid its size-dependent term $\Delta\kappa$ must satisfy

$$\Delta\kappa < 5\times 10^{-6}(kT/\hbar c)^3 cLk. \tag{21}$$

If $L=1$ mm, $T=300$°K, $c=5\times 10^5$ cm/sec, this is 0.17 watt/cm deg. Thus even for crystals with $a=4$ it is likely that the divergence of the conductivity contribution from low frequency longitudinal modes will have only a small to moderate effect on the conductivities of specimens with diameters or grain sizes of the order of a millimeter or less. For large single crystals, the limitation (21) becomes unimportant, and an easily measurable size effect, with $\Delta\kappa \propto L^{\frac{1}{2}}$, is conceivable.

V. CONCLUDING REMARKS

What we have calculated in the preceding section is only the high-temperature tail of the curve giving the influence of specimen size L on conductivity as a function of temperature. This curve, shown schematically in Fig. 2, approaches the Casimir limit $L\kappa^{-1}\partial\kappa/\partial L = 1$ as $T \rightarrow 0$. Near this point the ordinate falls below unity by an amount determined by the magnitude of the Umklapp and impurity scattering of modes with $\hbar\omega \sim kT$. This part of the curve can be described, at least roughly, by the equations given by Klemens.[6] At high temperatures, on the other hand, the ordinate of the curve is determined almost entirely by the behavior of longitudinal modes with $\hbar\omega \ll kT$; it is calculable from the equations of the preceding section. In the intermediate region of temperatures the detailed behavior is harder to predict, but might be very roughly estimated by interpolation between the two extremes. To show more clearly the difference between these extremes, let τ_b be the relaxation time for boundary scattering, τ_c a mean relaxation time, due to other processes, for all modes of thermal energy, and C a constant proportional to the specific heat. Then the procedure used by Klemens is roughly equivalent to writing

$$\kappa = \frac{C}{\tau_b^{-1}+\tau_c^{-1}} \sim C\tau_b\left(1-\frac{\tau_c}{\tau_b}\right) \quad \text{if} \quad \tau_c \ll \tau_b. \tag{22}$$

The formula (16) of the preceding section, on the other hand, gives, for a cubic crystal,

$$\kappa \sim C\tau_c\left(1-\frac{D}{T^{9/2}C\tau_c\tau_b^{\frac{1}{2}}}\right), \tag{23}$$

where D is a constant. From these equations it is clear,

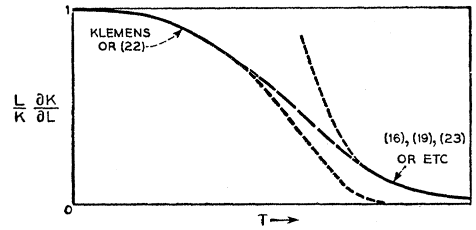

FIG. 2. Schematic temperature-dependence of the sensitivity of the effective thermal conductivity of a rod-like specimen to changes in its diameter L.

for example, that increasing the amount of impurity scattering decreases the ordinate of Fig. 2 at the left-hand end, but increases the ordinate at the right-hand end.

Although the high-temperature tail in Fig. 2 is not of very great interest for its own sake, the theory underlying it turns out[9] to be of considerable importance for the understanding of the thermoelectric powers of semiconductors at low temperatures. The interpretation of data in this field is greatly simplified if one can safely assume that the relaxation times of the longitudinal phonons which the charge carriers emit and absorb are long compared with those of the corresponding transverse phonons, and that the dependence of these times on q and T is substantially the same as the asymptotic form deduced in Sec. III. The range of validity of these asymptotic forms might conceivably be indicated by experimental studies of the size effect in thermal conduction at temperatures corresponding to the right of Fig. 2. Moreover, such studies might give rough values for the Λ coefficients occurring in (16) to (18), which enter importantly into the thermoelectric effect.

I am indebted to Dr. B. Goodman for a number of helpful comments, to Dr. T. H. Geballe for discussions of experimental data, and to the staff of the Institute for Advanced Study for their hospitality during the year 1952–1953.

APPENDIX A. SYMMETRY RESTRICTIONS ON THE MATRIX ELEMENTS OF U_3

As $\mathbf{q}_0 \rightarrow 0$ in a fixed direction the strain tensor due to the mode 0 approaches some limiting form $N_0^{\frac{1}{2}} q_0 u_{0\mu\nu}$ times a sinusoidal function of long wavelength. The strain amplitude tensor $\mathbf{u}_0$ depends only on the direction of $\mathbf{q}_0$ and on the branch of the acoustic spectrum to which mode 0 belongs. The matrix elements (2) of the anharmonic potential U_3 become asymptotically matrix elements of the change $U'(u_0)$ in elastic energy due to a homogeneous strain of the form u_0. In this Appendix we are interested in the behavior of the proportionality constant in (2) at points of the conservation surface S_1 in the neighborhood of a line or plane of degeneracy in q_1-space. As $q_0 \rightarrow 0$, a part of the conservation surface will shrink down onto the line or plane of degeneracy. Let us consider, for definiteness, the behavior of the constant of proportionality in (2) at the sequence of points in $\mathbf{q}_1$-space formed by the intersection of the shrinking S_1-surface with an arbitrarily chosen straight line normal to the line or plane of degeneracy. For this sequence of points the proportionality constant in (2) is asymptotically proportional to

$$|[N_{10}=1, N_{20}=0|U'(\mathbf{u}_0)|N_{10}=0, N_{20}=1]|^2, \quad \text{(A1)}$$

where the modes 10, 20 are the modes in the degeneracy line or plane which are approached by 1 and 2, respectively ($\mathbf{q}_2 \equiv \mathbf{q}_1 + \mathbf{q}_0$). Thus, 10 and 20 have the same wave vector $\mathbf{q}_{10}$ and the same frequency, but are not the same. The task of this Appendix will be to determine under what conditions symmetry considerations require (A1) to vanish.

Since U' is linear in the components of the symmetrical part of the strain tensor $\mathbf{u}_0$, its transformation properties under the operations of the space group of the crystal will be those of a symmetrical second rank tensor. It will thus consist of an invariant part, arising from the dilatation of $\mathbf{u}_0$, and a part transforming according to the representation D_2 of a spherical harmonic with $l=2$. Of course, D_2 is in general reducible into a sum of representations Δ_i when considered as a representation of a crystallographic point group. For certain directions and polarizations of mode 0 the part of U' going with one or more of these representations Δ_i may vanish. Now the initial and final states in (A1) may or may not be orthogonal. If $\mathbf{q}_1$ and $\mathbf{q}_2$ approach $\mathbf{q}_{10}$ from the same direction, modes 10 and 20 will be orthogonal and the initial and final states will be orthogonal. In such case the part of U' transforming according to the unit representation can make no contribution to (A1). But if $\mathbf{q}_{10}$ lies on a line of symmetry near which the frequency separation of two branches varies linearly with distance from the line in any direction, the directions of $\mathbf{q}_1$ and $\mathbf{q}_2$ from $\mathbf{q}_{10}$ will in general be different, and so it may happen that mode 10 represents the limiting mode of the lower branch as $\mathbf{q}_{10}$ is approached from one direction, while mode 20 represents the limiting mode of the upper branch as $\mathbf{q}_{10}$ is approached from a different direction. In such case modes 10 and 20 need not be orthogonal, and the part of U' belonging to the unit representation will in general give a nonvanishing contribution to (A1). Since the latter contribution is not related by any symmetry operation to that of the D_2 part of U', and since it vanishes only for special choices of the direction of $\mathbf{q}_0$ and the orientation of the line along which $\mathbf{q}_1 \rightarrow \mathbf{q}_{10}$, we may state the partial result: *When the frequency separations of two branches vary linearly with distance in any direction from a line of degeneracy, symmetry does not require the constant of proportionality in (2) to vanish, as* $q_0 \rightarrow 0$, *at a general point of the conservation surface near this line, except possibly when* $\mathbf{q}_0$ *is parallel to the line.*

For cases where the initial and final states in (A1) are orthogonal, we may put for U' its part transforming as D_2. When, as is usually the case, the modes 10 and 20 belong to the same irreducible representation Δ_{10} of the group of the wave vector of a line of symmetry on which q_{10} lies, the obvious thing to do first is to see whether, for each Δ_i in D_2, $\Delta_i \times \Delta_{10}$ contains Δ_{10}. This will always happen for at least one of the Δ_i, since for any direction of the line of symmetry there will always be at least one of the Δ_i which is the unit representation Δ_1 of the group of the wave vector. The part of U' belonging to this unit representation can never give any contribution to the off-diagonal matrix element (A1), so we may restrict consideration to the other Δ_i. If any of these $\Delta_{i\neq 1}$ has a cross product with Δ_{10} containing Δ_{10}, the contribution of the corresponding part U_i' of U' to (A1) will be in general nonvanishing unless either $U_i'=0$ or the choice of basis 10, 20 in Δ_{10} is just that which diagonalizes U_i'. If the modes 10, 20 vary with the direction from which the symmetry line is approached, the latter condition can be satisfied only for particular directions. The proviso of the last sentence is always fulfilled when Δ_{10} is a two-dimensional representation on a line of degeneracy in the interior of the Brillouin zone, since if 10 were the same from all directions, it would be taken into a multiple of itself by all operations of the group of the wave vector, so Δ_{10} would have to be one-dimensional. Therefore we can state the result: *Let* Δ_{10} *be a two-dimensional representation of the group of the wave vector*[19] *for a line of symmetry inside the Brillouin zone, and let* Δ_i *be an irreducible representation of this group, other than the unit representation, contained in* D_2. *Then if* $\Delta_i \times \Delta_{10}$ *contains* Δ_{10}, *symmetry does not require the constant of proportionality in (2) to vanish at a general point of the conservation surface near this line, as* $q_0 \rightarrow 0$, *except when the direction and polarization of the mode 0 are such as to make* $U_i' \equiv 0$.

Except for special directions and polarizations of the mode 0, to which we shall return later, we have now answered the question before us for interior lines of the Brillouin zone on which there is a group-theoretical degeneracy. However, even though we have chosen to omit a general discussion of lines of symmetry lying in the boundary of the Brillouin zone, there are two types of cases still to be covered. These are interior lines and boundary planes, respectively, on which the degeneracy is due only to time-reversal symmetry.[11] Now interior lines of this type—enumerated in Table II of reference 11—are all derivable from cases covered in the italicized statements above, by lowering of the symmetry of the crystal. Therefore if the matrix of any U_i' in the subspace spanned by 10 and 20 does not have to be a mere multiple of the unit matrix for the more symmetrical case, it does not have to be so for the present case either. It is easily shown, as before, that as the symmetry line is approached from different directions, the limiting form of mode 10 is not always the same, and so we can extend the conclusions of the

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[19] Defined in Sec. III, or more fully in reference 10.

preceding paragraph to degeneracy lines of the present type.

For boundary planes of degeneracy—those perpendicular to a screw axis[11]—the situation is most conveniently appraised by considering the matrix of any U_i' in the subspace spanned by the four modes going with a given frequency and having wave vectors q_{10} and $-q_{10}$. In this subspace a real basis can be chosen, and if $\bar{G}$ is the group of space group operations taking this subspace into itself, the general form for the matrix of any U_i' in this subspace can easily be written down, this matrix vanishing if and only if $\Delta_i \times \Delta_{10}$ does not contain Δ_{10}, all representations being now real representations of $\bar{G}$. When the matrix of U' does not vanish, we wish to know whether it is diagonalized simultaneously with the matrix of the operator F which determines the form and frequencies of the modes 1, 2, at points just off the plane, in terms of the subspace spanned by 10, 20. This F is an operator of zero wave vector with the transformation properties of the component of a polar vector normal to the plane. It is easily proved that F and U' can be simultaneously diagonal if and only if they belong to the same representation of $\bar{G}$, or if one of them (U') belongs to the unit representation. This type of argument can be extended to provide an alternative proof of the results derived above for symmetry lines.

Table III summarizes the conditions which the mode 0 must satisfy in order that the constant of proportionality in (2) be required to vanish, as $q_0 \rightarrow 0$, everywhere on the part of the conservation surface neighboring a degeneracy line or plane of the type we have been discussing. A straightforward application of the criteria enunciated above shows that there is no case in which vanishing is required for all modes 0, so the results are given in the form of properties which the special modes 0 must have in order that vanishing be required. When the first of the italicized criteria above is used, the requirement is that $\mathbf{q}_0$ be parallel to the line; this is stated in the last column. When the second italicized criterion is used, the requirement is that the strain $\mathbf{u}_0$ in the mode 0 be of one or more specific forms; these are listed in the next to the last column.

TABLE III. Conditions on the mode 0 under which symmetry requires the constant of proportionality in (2) to approach zero at a general point of the conservation surface near a boundary plane or interior line of degeneracy. The Z axis is taken along the symmetry line, or normal to the boundary plane. When there are just two twofold axes normal to the Z axis, the X and Y axes are to be taken along these.

Type of degeneracy	G^{10}	Strain tensor type for special modes (second criterion)	Direction of $\mathbf{q}_0$ for special modes (first criterion)
Boundary plane	C_s or C_1	$x^2+y^2-2z^2$, x^2-y^2, xy	
Interior line,	C_{6v}	$x^2+y^2-2z^2$, xz, yz	
degeneracy due	C_{4v}	$x^2+y^2-2z^2$, xz, yz	
to symmetry only	C_{3v}	$x^2+y^2-2z^2$	Z
Interior line,	C_6	$x^2+y^2-2z^2$, xz, yz	
degeneracy due	C_4	$x^2+y^2-2z^2$, xz, yz	
to time-reversal	C_3	$x^2+y^2-2z^2$	Z
(conditions for	C_{2v}	$x^2+y^2-2z^2$, xz, yz	
degeneracy listed	C_2	$x^2+y^2-2z^2$, xz, yz	
in reference 11)			

It is clear from inspection that no mode 0 can be special with respect to all threefold axes in a cubic crystal, or with respect to all fourfold axes. For uniaxial crystals, on the other hand, a longitudinal mode with $\mathbf{q}_0$ parallel to the axis will always be special.

APPENDIX B. DERIVATION OF (16) TO (18)

We wish to evaluate

$$I \equiv \int_0^{q'} \tau(q) q^2 dq, \tag{B1}$$

where

$$\tau(q) = [\tau_b^{-1} + \Lambda_a q^a]^{-1}, \tag{B2}$$

and q' is a value of q small enough for the asymptotic expression for the phonon-phonon scattering to be valid for $q < q'$, yet large enough so that increasing q' would not appreciably change the dependence of I on τ_b. If $a \leq 3$ the integral (B1) does not converge as $q' \rightarrow \infty$. However,

$$\frac{\partial I}{\partial \tau_b^{-1}} = -\tau_b^2 \int_0^{q'} \frac{q^2 dq}{(1+\tau_b \Lambda_a q^a)^2} \tag{B3}$$

converges if $a > \frac{3}{2}$. Now[20]

$$\int_0^{\infty} \frac{x^2 dx}{(1+x^a)^2} = \frac{(3-a)\pi}{a^2} \csc \frac{(3-a)\pi}{a}. \tag{B3}$$

Inserting this in (B3) and integrating on τ_b^{-1}, we obtain for large q',

$$I \sim \text{constant} - \frac{\tau_b}{(3-a)(\Lambda \tau_b)^{3/a}} \cdot \frac{p\pi}{a} \csc \frac{p\pi}{a}. \tag{B4}$$

Equations (16) to (18) are special cases of this.

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[20] D. Bierens de Haan, *Nouvelles tables d'integrales definis* (Royal Academy of Sciences, Amsterdam, 1867), Table 17, No. 18.