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REVIEWS OF MODERN PHYSICS VOLUME 33, NUMBER 1 JANUARY, 1961

Theory of Thermal Conductivity of Solids at Low Temperatures

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CONTENTS

INTRODUCTION

THIS review provides an introduction to the present theoretical understanding of certain aspects of the lattice thermal conductivity of solids at low temperatures. An attempt is made to collect the various methods used in the analysis of experiments. The adequacy and range of validity of these methods are evaluated, and suggestions are made concerning possible theoretical and experimental investigations which seem desirable.

A few selected topics are discussed thoroughly, instead of attempting a complete survey. This restriction forces the omission of a detailed discussion of some interesting topics, such as the interactions of lattice vibrations with spin waves, excitons, and electrons, but the author feels that in order to understand these latter phenomena it is first necessary to be able to evaluate with confidence the effect of certain defects that are nearly always present in a crystal. (Detailed comparison with experiment is not made here.)

Therefore most of this paper is devoted to a discussion of strain-field scattering, mass-difference scattering, and boundary effects. In order to understand the influence of these scattering mechanisms on the thermal conductivity of a perfect crystal, it is necessary to give a discussion of the three-phonon processes which arise from the anharmonic forces. Much of the discussion is

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applicable to scattering mechanisms not considered here, however, with little or no modification of the basic equations.

First, a review is made of the interatomic potential energy and lattice vibrations. Certain aspects of three-phonon processes are then discussed. Next the heat current is calculated in the presence of scattering processes which can be described by a "relaxation" time. Following this, a general theory of strain-field scattering is presented, including a derivation of an integral equation for the distribution function. The relation of these considerations to the relaxation time approximation, and Boltzmann's equation is given. Application is made to the important cases of strain-field scattering by dislocations and point defects. An important difference between the thermal resistivity due to mass-difference scattering and point defect strain-field scattering is clarified. The relaxation time for scattering by mass deviations (isotopes, in particular) is derived. Special consideration is given to boundary scattering and the associated size effects. A section is devoted to calculation of the heat current when many scattering processes are occurring. A critical examination is made of the common practice of adding thermal resistivities, and a resolution to some current confusion is pointed out. Finally, some other mechanisms of heat transport are mentioned briefly together with miscellaneous scattering mechanisms which may prove of interest in future investigations. The relevance of recent progress in phonon drag and radiation damage experiments is assessed in regard to the understanding of thermal conductivity.

We have not considered the change in the vibration spectrum accompanying the introduction of lattice defects. This is in general a difficult problem; in certain cases there may be low-lying localized modes of vibration, which could provide an important source of scattering.

It may be helpful to classify the various types of processes of interest in the study of thermal conductivity. These processes concern the propagation of energy by the possible unbound elementary excitations, and the interactions of these excitations among themselves and with static structures. (The latter may possess internal structures, e.g., impurity states in semiconductors.) Most of the excitations or processes considered are characterized by one of the following properties: (1) a low-lying continuum of states: acoustical phonons, conduction electrons, spin waves, photons, for example; (2) an excitation energy is required: optical phonons, ionization of an impurity atom, Umklapp processes, plasmons, and excitons. The latter processes usually display an exponential activation-energy type factor in the probability of their occurrence. An example of a process which does not fit neatly into either category is the dispersive scattering of a phonon by virtual excitation of an electron bound to a donor atom in a semiconductor.

An excellent presentation of the thermal conductivity of a perfect lattice is given in Chaps. 1 and 2 of a book by Peierls.[1] Because of the thoroughness of that treatment we try to avoid duplication of the material covered there. Additional material, including many references and a discussion of experimental results, may be found in two review articles by Klemens.[2,3] Of considerable interest is a contribution by Leibfried,[4] who gives a thorough discussion of lattice dynamics. The basic paper in this field was written in 1929 by Peierls.[5] An informative review article on phonon processes has been written by Herring.[6] An older review by Berman[7] is still valuable.

I. LATTICE VIBRATIONS

Perhaps one of the most essential features in the understanding of the solid state is the presence of translational symmetry. This regularity of the lattice imposes definite restrictions on any excitation which may be present in the crystal. In this section we are concerned with a particular kind of excitation, namely, the collective vibrational motions of the atoms composing the lattice.

The potential energy of the lattice may be considered to be a function of the positions of all of the nuclei of the atoms composing the solid. Physically, the more appropriate variables are the relative distances of all the atoms from each other; however, either set of variables follow from the other. At absolute zero the lattice may be considered to be in equilibrium. This implies that the potential energy is a minimum. The increase in energy due to arbitrary small displacements from these equilibrium positions is found by making a Taylor series expansion of the energy function in terms of the displacements (or relative displacements); the first term, aside from the equilibrium value Φ_0 of the potential, is quadratic in the displacements, by the equilibrium condition. It is an experimental fact that this "harmonic" potential is the dominant term in this expansion.

Thus as a first approximation one may regard an ideal crystal as composed of atoms bound together with Hooke's law forces. This problem can be solved exactly. The effects of the smaller (but very important!) terms in the series (cubic, quartic, etc., in the displacements) are then treated as a perturbation on this ideal harmonic crystal. These terms lead to interactions between

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[1] R. E. Peierls, *Quantum Theory of Solids* (Oxford University Press, New York, 1955).

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

[3] P. G. Klemens, *Handbuch der Physik* (Springer-Verlag, Berlin, 1956), 2nd ed., Vol. 14-1, p. 198.

[4] G. Leibfried, *Handbuch der Physik* (Springer-Verlag, Berlin, 1955), 2nd ed., Vol. 7-1, especially p. 290 ff.

[5] R. E. Peierls, Ann. Physik **3**, 1055 (1929).

[6] C. Herring, in *Halbleiter und Phosphore*, edited by M. Schön and H. Welker (F. Vieweg and Sohn, Braunschweig, Germany, 1958).

[7] R. Berman, Advances in Phys. **2**, 103 (1953).

the harmonic vibrational modes, essential for the understanding of thermal resistance, thermal expansion, etc.

Since nearly every textbook on solid-state physics includes a derivation of the vibrational normal modes of a crystal, we only summarize the results here, mainly to introduce the notation used.

We usually consider only the special case in which there is one atom per basic cell of the crystal. Since we are primarily interested in low-temperature phenomena, in which the acoustic branch of the vibration spectrum is of primary interest, the generalization to more complicated crystals is (for the most part) trivial. The burden of carrying the extra superscripts necessary for the description of a general crystal is not compensated in any way in low-temperature thermal conductivity problems.

The energy of the crystal in the harmonic approximation is

$$H_0=\tfrac{1}{2}\sum_{\mathbf{m}} M\dot{\mathbf{u}}_{\mathbf{m}}{}^2+\tfrac{1}{2}\sum_{\substack{\mathbf{m},\mathbf{n}\\ ij}} A_{\mathbf{mn}}{}^{ij}u_{\mathbf{m}}{}^{i}u_{\mathbf{n}}{}^{j}. \tag{1.1a}$$

The first term is the kinetic energy; M is the atomic mass, $\mathbf{u}_{\mathbf{m}}$ the displacement of the atom at the (equilibrium) lattice site $\mathbf{m}$; i, j are Cartesian components of the displacement vectors $\mathbf{u}_{\mathbf{m}}$ and take on the values x, y, z, for example. The constant A is the appropriate second derivative of the potential energy, evaluated at equilibrium. It is related in a well-known way to the elastic constants[1,4]; further, according to translational invariance it can only depend on the relative distance $\mathbf{m}-\mathbf{n}$ of the two lattice sites. Further conditions follow from inversion symmetry (when such exists) and consideration of the point group of the crystal.[4]

The equations of motion follow immediately from Eq. (1.1a). They are

$$M\ddot{u}_{\mathbf{m}}{}^{i}=-\sum_{\mathbf{n},j} A_{\mathbf{mn}}{}^{ij}u_{\mathbf{n}}{}^{j}. \tag{1.2}$$

This equation evidently has as a solution the running wave (i.e., one is to take the real part of this expression)

$$u_{\mathbf{m}}{}^{i}=e_i\exp[i(\mathbf{q}\cdot\mathbf{m}-\omega t)],$$

which yields the secular equation for the frequency ω as a function of the wave vector $\mathbf{q}$:

$$|M\omega^2\mathbf{1}-\sum A_{\mathbf{mn}}{}^{ij}\exp[i\mathbf{q}\cdot(\mathbf{n}-\mathbf{m})]|=0. \tag{1.3}$$

In this equation $\mathbf{1}$ denotes a unit matrix in the indices i, j. There are, in the case of one atom per unit cell, three eigenvalues of this equation for ω^2. For these we introduce the index λ, which takes on the values 1, 2, 3. The three eigenvectors $\mathbf{e}_\lambda(\mathbf{q})$ correspond to the polarization vectors of the plane wave solution. These eigenvectors are real if the lattice possesses inversion symmetry. We suppose this to be the case; otherwise the reader may supply the necessary complex conjugate signs. The eigenvalues of a Hermitian matrix are real; stability further restricts the solutions for ω^2 to be positive. (In certain directions of special symmetry two of these solutions may become degenerate.) The solution with the greatest frequency is called the longitudinal mode; the other two solutions are "transverse." These designations have the usual meaning in the long-wavelength limit. (The different branches usually do not cross.) The problem of the solution of Eq. (1.3) forms a separate field of physics in itself. We do not discuss such solutions, but assume in any given problem that $\omega(\mathbf{q})$ is known. For practical applications most of the calculations assume that the acoustic approximation $\omega_\lambda=c_\lambda q$ ($c=$velocity of sound) holds. To get an idea of some models currently employed, and for references to earlier literature, the recent work of Cochran[8] on the vibrational spectrum of germanium is useful. Further discussion may be found, for example, in works by Leibfried,[4] Born and Huang,[9] and Blackman.[10]

The displacement operator, when expressed in terms of running waves, takes the form (standard periodic boundary conditions are imposed)

$$\mathbf{u}_{\mathbf{m}}=\sum_{\mathbf{q},\lambda}\left(\frac{\hbar}{2\rho\Omega\omega_{\mathbf{q},\lambda}}\right)\times[a_{\mathbf{q}\lambda}\exp(i\mathbf{q}\cdot\mathbf{m})+a_{\mathbf{q}\lambda}{}^*\exp(-i\mathbf{q}\cdot\mathbf{m})]e_{\mathbf{q},\lambda}, \tag{1.4}$$

where the sum on $\mathbf{q}$ goes over the first Brillouin zone.[11]

The dimensionless variables $a_{\mathbf{q}\lambda}$, $a_{\mathbf{q}\lambda}{}^*$ operate on the harmonic oscillator coordinates; they are related to the usual dynamical variables of a harmonic oscillator by a simple transformation.[12] They obey the normal mode equation $i\hbar\dot{a}_q=[a_q,H_0]=\omega_q a_q$. (Hereafter we often write q for the pair of variables $\mathbf{q}$, λ.) In (1.4) ρ is the density of the crystal, Ω the total volume, ω_q the frequency of the qth vibrational mode, $\mathbf{q}$ the wave vector, $\mathbf{e}_q$ the polarization vector. With the normalization indicated in (1.4) the commutation relation for the a_q's becomes simply

$$[a_q,a_{q'}{}^*]=\delta_{qq'};\quad [a_q,a_{q'}]=0. \tag{1.5}$$

Explicitly, $\delta_{qq'}\equiv\delta_{\mathbf{qq}'}\delta_{\lambda\lambda'}$. The energy expression (1.1a) becomes

$$H_0=\sum\hbar\omega_q(a_q{}^*a_q+\tfrac{1}{2}). \tag{1.1b}$$

The term $\frac{1}{2}\hbar\omega_q$ is the familiar zero-point energy. The number operator $n_q\equiv a_q{}^*a_q$ has the significance of the number of quanta of energy $\hbar\omega$, these quanta being called phonons. From (1.5) it is evident that phonons are also bosons. The eigenstates of (1.1a) or (1.1b) are

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[8] W. Cochran, Phys. Rev. Letters 2, 495 (1959).

[9] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, New York, 1954).

[10] M. Blackman, *Handbuch der Physik* (Springer-Verlag, Berlin, 1955), Vol. 7-1, p. 341.

[11] A. H. Wilson, *Theory of Metals* (Cambridge University Press, New York, 1954), p. 251; G. Leibfried, footnote 4, p. 174; L. Van Hove, Mass. Inst. Technol. Solid-State and Molecular Theory Group Tech. Rept. No. 11 (March 15, 1959).

[12] See P. A. M. Dirac, *Quantum Mechanics* (Oxford University Press, New York, 1947), 3rd ed., p. 136.

products of harmonic oscillator states specified by the set of quantum numbers n_q. The simplicity of this so-called number representation lies in the following obtained from Eqs. (1.5):

$$\begin{aligned} a_q\Psi(n_{q1},\cdots,n_q,\cdots)&=(n_q)^{\frac{1}{2}}\Psi(n_{q1},\cdots,n_q-1,\cdots),\\ a_q{}^*\Psi(n_{q1},\cdots,n_q,\cdots)&\\ &=(n_q+1)^{\frac{1}{2}}\Psi(n_{q1},\cdots,n_q+1,\cdots). \end{aligned} \tag{1.6}$$

a_q decreases the number of quanta in state q by one, and hence is called an annihilation operator. Similarly, $a_q{}^*$ is a creation operator. The properties that we need are summarized in Eqs. (1.5) and (1.6).

In Eq. (1.4) the operators a_q are time independent, since we are working in the Schrödinger representation. To achieve correspondence with the classical result, the time dependence is made explicit by going over to the Heisenberg representation. This is easily accomplished by noting that $a_q(t)=a_qe^{-i\omega t}$, since $i\dot{a}_q=\omega_qa_q$, etc. On transforming (1.4) accordingly, the running wave character of the expansion is made explicit.

The connection with thermodynamics is made by recalling that in thermal equilibrium the average occupation of harmonic oscillator states is given by the Planck distribution law $N_q{}^0=(e^{\hbar\omega/kT}-1)^{-1}$.

Now let us consider the consequences of introducing a displacement field into the lattice.

In order to maintain this displacement one must introduce into the Hamiltonian the driving term that represents the stress field; this additional term is linear in the displacements (the proportionality constant is essentially just the stress tensor). Let us write the total displacement as $\mathbf{u}_\mathbf{m}+\mathbf{V}_\mathbf{m}$, where $\mathbf{V}_\mathbf{m}$ is the displacement of the atom at the lattice site $\mathbf{m}$ due to the applied stress (which may be external, or result from a lattice defect). $\mathbf{u}_\mathbf{m}$ is now the displacement from the new equilibrium position $\mathbf{m}+\mathbf{V}_\mathbf{m}$. Since by hypothesis the lattice is still in equilibrium, the effect of the term linear in the stress and in $\mathbf{u}_\mathbf{m}$ must be just to cancel the linear term in $u_\mathbf{m}{}^iV_\mathbf{m}{}^i$ arising from substituting $\mathbf{u}_\mathbf{m}+\mathbf{V}_\mathbf{m}$ for $\mathbf{u}_\mathbf{m}$ in the harmonic Hamiltonian (1.1a). The resultant Hamiltonian is again quadratic in the new displacements; in addition, one has a term representing the strain energy. The new Hamiltonian is diagonal, so that there is no scattering of phonons by a strain field in the harmonic approximation. If, however, one considers the anharmonic terms (of which we discuss only the potential cubic in the displacements, which is sufficient at low temperatures) a strain results effectively in a change in the harmonic force constants. (In this regard recall the standard Grüneisen model.) This change is linear in the displacement field, and hence destroys the translational invariance of the harmonic constants if the strain is nonuniform. This nonuniformity leads to scattering, as discussed in Sec. IV. To understand physically the nature of the scattering one may suppose the strain field to be localized in some region. An incident phonon wave entering this region experiences a change in the force constants, which modulation causes scattering. In the harmonic approximation, the lack of scattering of phonons by a strain field may be compared with the analogous case of passing photons through an electric field. In the latter case photons are not scattered unless an additional interaction (with the electron-positron field) is introduced. For lattice vibrations the supplementary field is the anharmonic part of the potential energy. Indeed, we later see that the matrix elements for strain-field scattering bear a strong formal resemblance to the analogous quantities for the scattering of charged particles by an external electromagnetic field.

If the total displacement $\mathbf{V}_\mathbf{m}$ is large (as is the case for dislocations) doubt concerning the validity of the series expansions made may arise. This question is dealt with by the remark that the appropriate expansion variables are actually relative displacements, although this is somewhat concealed in the forms used thus far. In order to emphasize this feature we often choose the anharmonic potential to be

$$V_3=\frac{1}{3!}\sum_{\substack{\mathbf{mn}\\ ijk}}B_{\mathbf{mn}}{}^{ijk}(u_\mathbf{m}{}^i-u_\mathbf{n}{}^i)(u_\mathbf{m}{}^j-u_\mathbf{n}{}^j)(u_\mathbf{m}{}^k-u_\mathbf{n}{}^k), \tag{1.7}$$

where the sum is taken over all pairs in the crystal. Equation (1.7) is certainly not the most general form for the cubic term; we have selected only that part acting directly between individual pairs $(\mathbf{m},\mathbf{n})$, on the supposition that this is in fact the major part of the contribution. More general anharmonic potential forms can be assumed, but at present the poor theoretical and experimental knowledge of the anharmonic coupling constants does not justify carrying any more subscripts than are already present in (1.7). Actually, one can proceed quite far in a formal calculation of anharmonic processes, even with a quite general interaction. Compromises become necessary when one desires to get numerical results.

Physically, the constants $A_\mathbf{mn}$ and $B_\mathbf{mn}$ are expected to be negligible when $|\mathbf{m}-\mathbf{n}|$ is greater than a few lattice constants. This should be especially true of $B_\mathbf{mn}$. Although the formalism developed later is adequate to cope with long range forces, we usually suppose that only near-neighbor interactions are appreciable. This model should be adequate to understand all the qualitative features of the problem at low temperatures. To estimate the anharmonicities it is always necessary to consider the detailed structure of the crystal of interest.[4]

A detailed consideration of the influence of distant-neighbor interactions or specific symmetries of crystals would obscure the understanding of the physics involved. Hence we must be content with a semiquantitative theory when considering scattering caused by the anharmonic forces.

To summarize, the eigenstates of the harmonic problem are phonons which propagate freely through the crystal without interaction. Now the anharmonic term V_3 is treated as a perturbation; we see that V_3 allows one phonon to turn into two and vice versa.

Standard perturbation theory is not obviously valid, not due to the magnitude of V_3 but rather because the perturbation extends over the whole crystal. Compare the present case with the standard scattering problem, in which the interaction is appreciable only in a finite region, so that the initial and final states are indeed eigenstates of H_0.

In fact, Van Hove[13] has emphasized that the fundamental difference between ordinary scattering problems and many-body systems (the latter including field theory) is just this, that in the latter the potential extends over the entire volume of the system being considered, so that conventional perturbation theory is invalid. In field theory this is spectacularly manifested by the divergence difficulties.

Clearly, a detailed investigation of this point is in order. Although Van Hove has justified the use of the transport equation as obtained with ordinary perturbation theory[11] [see Eq. (3.30)] for similar systems, a detailed investigation of the "persistent" effects due to the anharmonic interaction does not seem to have been made for the steady-state (nonequilibrium) situation. (The equilibrium properties of the anharmonic crystal have been discussed thoroughly in the article by Van Hove.[11]) Since this has not yet been carried out, in the next section we sketch the standard treatment[1] of the problem. For ordinary impurities and scattering centers, perturbation theory should be adequate, however.

II. THREE-PHONON PROCESSES

The perturbation treatment of the anharmonic interaction V_3 is now discussed. This subject is discussed thoroughly in footnotes 1 and 4. Furthermore, in order to understand the effect of impurities and imperfections on the conductivity, it is essential to consider the processes occurring in the "pure" anharmonic crystal as well, and the mutual influence of the different kinds of processes.

In order to examine the matrix elements of V_3, we substitute the expression (1.4) for $\mathbf{u}_\mathbf{m}$ in Eq. (1.7) for V_3. For the energy conserving part we have

$$V_3=\frac{1}{2}\left(\frac{\hbar}{2\rho\Omega}\right)^{\frac{3}{2}}\sum_{qq'q''}(\omega_q\omega_{q'}\omega_{q''})^{-\frac{1}{2}} \times(C_{qq'q''}a_q^*a_{q'}a_{q''}+\text{H.c.}). \tag{2.1}$$

In this equation $C_{qq'q''}$ is given by

$$C_{qq'q''}=\sum_{ijk} e_q{}^i e_{q'}{}^j e_{q''}{}^k b_{ijk}(\mathbf{q},\mathbf{q}',\mathbf{q}''), \tag{2.2}$$

where

$$b_{ijk}(\mathbf{q},\mathbf{q}',\mathbf{q}'')=\sum_{\mathbf{mn}} B_{\mathbf{mn}}{}^{ijk}F_q{}^*F_{q'}F_{q''}. \tag{2.3}$$

In Eq. (2.3) the sum in restricted (each pair counted once) and the F_q's are just phase factors:

$$F_q\equiv\exp(i\mathbf{q}\cdot\mathbf{m})-\exp(i\mathbf{q}\cdot\mathbf{n}). \tag{2.4}$$

For more general anharmonic forces just replace $B_{\mathbf{mn}}$ in Eq. (2.3) by the appropriate force constant and sum over any extra indices introduced thereby.

In Eq. (2.1) terms are omitted which create and destroy three phonons, namely, $a_qa_{q'}a_{q''}$ and $a_q{}^*a_{q'}{}^*a_{q''}{}^*$, since they cannot conserve energy. We usually need only to consider lowest-order perturbation theory. For a general discussion of the anharmonic effects one must keep these other terms to allow for the effect of virtual processes (Appendix D). We use the basic formula of time-dependent perturbation theory: the probability for a transition from state a to state b is[14]

$$w_{ba}=(2\pi/\hbar)|H_{ba}'|^2\delta(E_b-E_a), \tag{2.5}$$

where one must integrate over a range of final states. The delta function expresses conservation of energy. $H_{ba}'=\langle\Psi_b|H'|\Psi_a\rangle$ is the matrix element of the perturbation H'.

The complexity of Eqs. (2.2) and (2.3) ought not to obscure the basic simplicity of the scattering mechanism described by Eq. (2.1). All the complicated effects are due to the structure of the lattice and the polarization of the phonons, and are contained in the "structure factor" $C_{qq'q''}$.

Equation (2.1) shows that V_3 allows for two processes: either two phonons collide, turning into one (factor $a_q{}^*a_{q'}a_{q''}$), or the inverse process: one phonon breaks up into two (factor $a_qa_{q'}{}^*a_{q''}{}^*$). The sum over $qq'q''$ allows for all possibilities, with the relative amplitude $(\omega_q\omega_{q'}\omega_{q''})^{-\frac{1}{2}}C_{qq'q''}$.

It is extremely convenient, and physical, to represent the various processes by means of graphs. Every occurrence of a factor $C_{qq'q''}$ is represented by a vertex; the phonons by lines. (See Fig. 1 for an example.[15])

Now we can extract a very important result from the requirement of translational invariance, namely, the (seemingly) trivial statement that the potential energy of the crystal is unchanged under the substitution $\mathbf{m}\rightarrow\mathbf{m}+n\mathbf{a}$, where n is an integer and $\mathbf{a}$ is any lattice vector.

Equation (1.7) for V_3 is obviously unchanged by this transformation. [Periodic boundary conditions are implicit in the expression (1.4) for $\mathbf{u}_\mathbf{m}$.]

All the information concerning the lattice sites of the crystal is contained in the factor b_{ijk}, Eq. (2.3). Since

$$F_\mathbf{q}(\mathbf{m}+\mathbf{a},\,\mathbf{n}+\mathbf{a})=\exp(i\mathbf{q}\cdot\mathbf{a})F_\mathbf{q}(\mathbf{m},\mathbf{n}), \tag{2.6}$$

invariance under the translation operation requires that

$$b_{ijk}(\mathbf{q},\mathbf{q}',\mathbf{q}'')=\exp[i\mathbf{a}(\mathbf{q}'+\mathbf{q}''-\mathbf{q})]b_{ijk}(\mathbf{q},\mathbf{q}',\mathbf{q}''). \tag{2.7}$$

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[13] L. Van Hove, Physica **21**, 517, 901 (1955); **23**, 441 (1957).

[14] L. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1955), 2nd ed., p. 199.

[15] A good introduction to general scattering theory is contained in an article by G. C. Wick, Revs. Modern Phys. **27**, 339 (1955).

Thus b_{ijk} is zero unless

$$\exp[i\mathbf{a}\cdot(\mathbf{q}'+\mathbf{q}''-\mathbf{q})]=1, \tag{2.8}$$

which is true only if

$$\mathbf{q}'+\mathbf{q}''-\mathbf{q}=\mathbf{G}, \tag{2.9}$$

where $\mathbf{G}$ is 2π times a vector in the reciprocal lattice.[16]

Condition (2.9) is analogous to the conservation of momentum. The latter, however, is a consequence of invariance of the Hamiltonian under arbitrary *infinitesimal* displacements.

As preparation for the complicated transport problems to come, the following simple discussion of the influence of the anharmonic potential on the propagation of a phonon may be instructive. First we note the relation of the entity called a phonon to the so-called displacement operator $\mathbf{U_m}$. The phonon itself is just a plane wave and as such is a certain matrix element of this operator; if $|0\rangle$ denotes the vacuum state and $|k\rangle$ that state with one excitation of type k, then the phonon is described by the wave φ_k:

$$\varphi_k\equiv\langle 0|\mathbf{u_m}|k\rangle=C_k\mathbf{e}_k\exp[i(\mathbf{k}\cdot\mathbf{m}-\omega_k t)];$$

$$C_k\equiv\left(\frac{\hbar}{2\rho\omega_k\Omega}\right)^{\frac{1}{2}}. \tag{2.10}$$

In obtaining this result $\mathbf{U_m}$ has been transformed to the Heisenberg picture. The constant C_k is clearly irrelevant to our considerations. If $\mathbf{m}$ is regarded as a continuous variable $\mathbf{x}$, then $\varphi_k(\mathbf{x})$ obeys the wave equation with phase velocity ω/k. Actually in thermal conductivity problems one must use localized wave packets, which travel with a group velocity $\mathbf{C}=\partial\omega/\partial\mathbf{k}$. We nevertheless calculate our matrix elements using plane-wave states such as (2.10), and use the group velocity whenever a propagation velocity is called for. This is a delicate point, but is common to all transport problems, so the reader is referred to footnotes 1 and 17 for further discussion. (Readers familiar with field theory will note that the displacement operator $\mathbf{u_m}$ is related to the phonon wave in precisely the same way that the electron-field operator is related to the Schrödinger wave function. The analogy with photons is even closer. Some simple field-theoretical properties of the displacement field are described in Appendix D.)

Let us examine the hypothetical case in which a single phonon propagates in an infinite crystal at absolute zero. As a result of the anharmonic potential, this phonon does not travel undisturbed but undergoes two related processes. As already discussed, V_3 forces the phonon to split up into two phonons. The graphical representation for this process is given in Fig. 1(a). Further, in second order the energy can be modified through the virtual splitting up described by Fig. 1(b). As is well known, the finite lifetime is associated with an uncertainty in the phonon frequency. Formally this is connected with the imaginary part of the self-energy. Thus we expect a *real* phonon to be described by

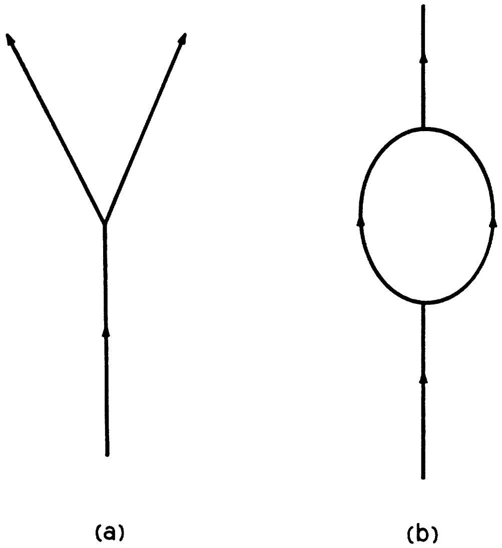

FIG. 1. These diagrams represent the effect of the anharmonic potential V_3 on the propagation of a phonon. (a) shows how the anharmonic forces can split a phonon into two others. (b) shows the second-order perturbation theory contribution to the energy shift of the incident phonon (an eigenstate of H_0) caused by V_3. The lines entering at the bottom label the initial state, those leaving at the top denote the final state, as suggested by the arrows. (A simple explanation of the use of such graphs in the analysis of perturbation series is given in footnote 15.)

$$\exp[i(\mathbf{k}\cdot\mathbf{x}-\omega_0 t)-\Gamma t/2], \tag{2.11}$$

where we have written ω as $\omega_0-i\Gamma/2$. Then the wave dies off as $\exp(-\Gamma t)$. We show explicitly that the imaginary part of the second-order self-energy yields a value of Γ identical with the transition rate calculated in lowest-order perturbation theory, and moreover that there is a real contribution to the harmonic $\omega(k)$, whose effect is to renormalize the phonon frequency. Then it is also obvious by a simple Fourier analysis of (2.11) that Γ is the width associated with the phonon wave (2.11). We use the language of continuous spectra. Let $\epsilon(k)=\hbar\omega(\mathbf{k})$ denote the initial phonon energy, and $\epsilon(p,k)=\hbar\omega(\mathbf{p})+\hbar\omega(\mathbf{k}-\mathbf{p})$ denote the energy of the two-phonon state. Then the second-order self-energy is (η is a positive infinitesimal to define the pole in the usual way)

$$\Delta E_2=\sum_p\frac{|\langle\mathbf{k}|V_3|\mathbf{p},\mathbf{k}-\mathbf{p}\rangle|^2}{\epsilon(\mathbf{k})-\epsilon(\mathbf{p},\mathbf{k})+i\eta}. \tag{2.12}$$

Now use the identity

$$(x+i\eta)^{-1}\equiv P(1/x)-i\pi\delta(x), \tag{2.13}$$

where P denotes principal value and $\delta(x)$ is the Dirac

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[16] For a discussion of the reciprocal lattice see, e.g., G. H. Wannier, *Elements of Solid-State Theory* (Cambridge University Press, New York, 1959).

[17] Progress has been made on this matter recently by E. C. McIrvine and A. W. Overhauser, Phys. Rev. **115**, 1531 (1959).

delta function, to obtain

$$\mathrm{Re}\Delta E_2(k)=P\sum_p \frac{|\langle \mathbf{k}|V_3|\mathbf{p},\mathbf{k}-\mathbf{p}\rangle|^2}{\epsilon(\mathbf{k})-\epsilon(\mathbf{p},\mathbf{k})}. \tag{2.14}$$

The observed phonon frequency is, to second order, just the harmonic value plus $\mathrm{Re}\Delta E_2(k)/\hbar$. By definition of Γ, $[\hbar\Gamma=-2\,\mathrm{Im}\Delta E_2(k)]$, one finds likewise

$$\Gamma=\frac{2\pi}{\hbar}\sum_p |\langle\mathbf{k}|V_3|\mathbf{p},\mathbf{k}-\mathbf{p}\rangle|^2\delta[\epsilon(\mathbf{k})-\epsilon(\mathbf{p},\mathbf{k})] \tag{2.5a}$$

which is just the total transition probability as computed from (2.5). As might be expected, these considerations extend much further than second-order perturbation theory. For this analysis the reader is referred to the work of Van Hove.[13]

Three-phonon processes in which the total wave vector is conserved ($\mathbf{G}=0$) are called *normal processes.* Collisions for which $\mathbf{G}\neq 0$ are called *Umklapp processes.* It is seen that the latter are impossible in a continuous medium. We find that in a "perfect" crystal Umklapp processes are necessary for a finite conductivity. Thus *both* anharmonic forces and a discrete lattice structure are essential for a noninfinite thermal conductivity, a point first appreciated by Peierls.[1,5] This is only true for the model of the lattice here contemplated. For instance in a fluid, intermolecular forces and the randomness of the molecular distribution gives rise to thermal resistance. On the other hand, the essence of the crystalline problem is that of order, and slight departures therefrom. Hence the often mentioned analogy of the phonon "gas" is somewhat misleading.

The main quantity of interest, the rate of change of the number N_q of phonons in the state $\mathbf{q}$, λ due to collisions induced by V_3, is given in footnote 1 (see also Leibfried,[4] p. 306). The classification of the types of processes allowed by the conservation laws mentioned in the last paragraph is extremely important in the understanding of thermal resistance. The normal processes, in which the wave vector is conserved in each collision, are incapable of producing resistance.[1] In fact, for normal processes the "crystal momentum"

$$\mathbf{P}=\textstyle\sum_q \hbar\mathbf{q}N_q$$

is a constant of the motion[1] if Umklapp processes are not considered. Thus if $\mathbf{P}$ were ever made nonzero (e.g., by subjecting the crystal to a temperature gradient for a moment) phonons would propagate without resistance in the absence of Umklapp or other resistance causing mechanisms. In fact, since $\Sigma\mathbf{k}$ and $\Sigma\omega$ are separately conserved in this case, one can show that the distribution function towards which the normal processes tend is not the equilibrium (Planck) distribution but instead[2]

$$N_q(\boldsymbol{\lambda})=\{\exp[(\hbar\omega+\boldsymbol{\lambda}\cdot\mathbf{q})/kT]-1\}^{-1}, \tag{2.15}$$

which is characteristic of a drifting gas.[18] ($\boldsymbol{\lambda}$ is an arbitrary constant vector with the dimension of a velocity times $\hbar$.)

It does not follow, however, that normal processes can be ignored in calculating the thermal resistance (Appendix B). This is because the normal processes can change the distribution of phonons among the various states, even though they "by themselves" cause no resistance. For example, consider a frequency-dependent scattering mechanism: it tends to deplete the population of phonons in certain states more than others. The normal processes in a sense "fight back" to refill these states. In the general case, one must explicitly take all the scattering mechanisms into account to obtain an accurate description of the final steady state. Much work remains to be done on this problem.

Further restrictions on the possible transitions between various polarization modes follow from the requirements of simultaneous conservation of energy and momentum, from an examination of the qualitative features of the vibration spectrum.[19] However, these restrictions are intimately connected with details of the anisotropy of actual crystals.[20] A clear discussion of these questions has been given by Herring.[20]

We return to a discussion of the coefficients b_{ijk}. On introducing a generalized Kroneker delta function $\Delta(\mathbf{q})$,

$$\begin{aligned}\Delta(\mathbf{q})&=0 \quad \mathbf{q}\neq\mathbf{G}\\ &=1 \quad \mathbf{q}=\mathbf{G} \quad (\text{includes } \mathbf{G}=0),\end{aligned} \tag{2.16}$$

Eq. (2.7) can be written as

$$b_{ijk}(\mathbf{q},\mathbf{q}',\mathbf{q}'')=\Delta(\mathbf{q}-\mathbf{q}'-\mathbf{q}'')b_{ijk}(\mathbf{q},\,\mathbf{q}',\,\mathbf{q}-\mathbf{q}'). \tag{2.17}$$

[In deriving (2.17) one notes that b_{ijk} is independent of $\mathbf{G}$; cf. Eq. (2.3).]

The Umklapp processes resemble the more familiar phenomenon of Bragg reflection, which also requires a certain minimum value of q for its occurrence. By utilizing the Δ function, the sum over $\mathbf{q}''$ may be performed (leaving however, the important sum over $\mathbf{G}$, but one expects only the smallest values of $\mathbf{G}$ to be important).

By means of simple trigonometry one may evaluate (2.3), finding

$$\begin{aligned}b_{ijk}(\mathbf{q},\,\mathbf{q}',\,\mathbf{q}-\mathbf{q}')=2i\sum_{\mathbf{mn}} B_{\mathbf{mn}}{}^{ijk}\{&\sin[\mathbf{q}'\cdot(\mathbf{m}-\mathbf{n})]\\ &-\sin[\mathbf{q}\cdot(\mathbf{m}-\mathbf{n})]-\sin[(\mathbf{q}'-\mathbf{q})\cdot(\mathbf{m}-\mathbf{n})]\}.\end{aligned} \tag{2.18}$$

To a good approximation, for low temperature $qa\ll 1$; since $B_{\mathbf{mn}}$ is small for $|\mathbf{m}-\mathbf{n}|\gg a$, it is a good approximation to expand the sines. Then the terms

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[18] D. ter Haar, *Statistical Mechanics* (Rinehart and Company, Inc., New York, 1954), Chap 1. $\boldsymbol{\lambda}$ is the Lagrangian multiplier resulting from the extra constraint $\Sigma\mathbf{q}=$constant. The reader will recognize the close resemblance of the argument $\hbar\omega+\boldsymbol{\lambda}\cdot\mathbf{q}$ to the change in $\hbar\omega$ under a Galilean transformation.

[19] A. Herpin, Ann. Phys. **7**, 91 (1952).

[20] C. Herring, Phys. Rev. **95**, 954 (1954).

linear in **q** cancel, leaving

$$b_{ijk}(\mathbf{q},\mathbf{q}',\mathbf{q}-\mathbf{q}')=i\sum_{\mathbf{mn}}B_{\mathbf{mn}}{}^{ijk}[\mathbf{q}\cdot(\mathbf{m}-\mathbf{n})]$$
$$\times[\mathbf{q}'\cdot(\mathbf{m}-\mathbf{n})][\mathbf{q}'-\mathbf{q})\cdot(\mathbf{m}-\mathbf{n})]. \quad (2.19)$$

The **q** dependence of b_{ijk} as obtained in (2.19) does not depend on the special assumption of forces made. It follows from the observation that for long wavelengths, the relative displacements are proportional to strains; differentiation of Eq. (1.4) for $\mathbf{u}_\mathbf{m}$ brings down the desired factor q.

An idea of the structure of b_{ijk} and $C_{qq'q''}$ is obtained by considering the special case of nearest-neighbor central forces.[4] For the potential $\varphi(|\mathbf{r}|)$ between nearest neighbors (use the chain rule)

$$B^{ijk}=\partial^3\varphi/\partial r_i\partial r_j\partial r_k,\quad g'\equiv\varphi'''(a),\quad f\equiv\varphi''(a); \quad (2.20)$$

$$B^{ijk}=\left(g'-\frac{3f}{a}\right)\frac{a_ia_ja_k}{a^3}+\frac{f}{a^2}(\delta_{ij}a_k+\delta_{ik}a_j+\delta_{jk}a_i). \quad (2.21)$$

The first term is substantially larger than the second, so put

$$B^{ijk}\cong g(a_ia_ja_k/a^3),\quad g\equiv g'=(3f/a). \quad (2.22)$$

(See Appendix A.) Then

$$C_{qq'q''}=\left(\frac{Nig}{2a^3}\right)\sum_{\mathbf{a}}(\mathbf{e}_q\cdot\mathbf{a})(\mathbf{e}_{q'}\cdot\mathbf{a})(\mathbf{e}_{q''}\cdot\mathbf{a})$$
$$\times(\mathbf{q}\cdot\mathbf{a})(\mathbf{q}'\cdot\mathbf{a})(\mathbf{q}'-\mathbf{q})\cdot\mathbf{a}. \quad (2.23)$$

In this sum one fixes on one atom and sums over the **a**'s connecting it to its nearest neighbors.

Equation (2.23) is unchanged if any of the q's are changed by a reciprocal lattice vector, as is evident from inspection of (2.2) and (2.3).

Even this simple case leads to very complicated expressions. A truly accurate treatment can be achieved only at the expense of great computational labor. For the present, the proper attitude might be to consider coefficients such g' and f as parameters to be fitted to the data (or related to macroscopic parameters of elasticity, Grüneisen's γ, etc.[2]) subject to the requirement of order of magnitude agreement with the force constants derived from other experiments or theoretical calculations. Certainly a computer program for more accurate coefficients is not justified until certain matters of principle are cleared up in the calculation of the thermal conductivity (e.g., the applicability of a Boltzmann equation, the effect of normal processes, etc.).

A simple argument due to Peierls yields the temperature dependence of the thermal resistivity due to Umklapp processes for $T\ll\Theta$, where Θ is the Debye temperature.

Consider the process in which two phonons $\mathbf{q}_1$ and $\mathbf{q}_2$ collide to produce a third, **q**. In order that an Umklapp process should occur, the sum of the two colliding phonons must lie outside the Brillouin zone boundary. Thus one of the phonons must have had a wave vector of at least a quarter of the minimum total width of the Brillouin zone.

The position $\mathbf{q}-\mathbf{G}$ near the left-hand edge, say, is completely equivalent to $\mathbf{q}_1+\mathbf{q}_2=\mathbf{q}$ lying outside the right-hand side of the zone. Thus the wave vector essentially flips over in an Umklapp process.

As $T\rightarrow 0$ the number of phonons with this minimum wave vector is

$$N_q{}^0=[e^{\hbar\omega(q)/kT}-1]^{-1}\rightarrow e^{-\hbar\omega(q)/kT} \quad (2.24)$$

since we are keeping $\omega(q)$ fixed above some finite limit. The Debye temperature is $\Theta=\hbar\omega_0/k$ and we define $\alpha\equiv\omega_0/\omega(q)\approx 2$, so

$$N_q{}^0\rightarrow e^{-\Theta/\alpha T}. \quad (2.24a)$$

Since in the absence of such phonons there is no resistivity, the latter must be proportional to this:

$$W\equiv 1/K\approx e^{-(\Theta/\alpha T)}\times\text{const.} \quad (2.25)$$

In a more careful analysis[4] the "constant" varies with T. At sufficiently low temperatures the exponential factor dominates. (This analysis is a bit oversimplified, but the conclusions hold. See Leibfried[4] p. 310.)

The Debye cutoff is $\omega_0=Cq_0$, where $q_0=(6\pi^2/\Omega_0)^{\frac{1}{3}}$; Ω_0 is the volume per atom, C is some average velocity of sound. On assuming that the acoustic approximation $\omega=Cq$ is reasonably valid for phonons with $q\sim\frac{1}{2}q_0$ (see the following), then $\alpha=2q_0/q_m$, where q_m is the distance from the center of the Brillouin zone to the nearest surface. q_m evidently depends on the translation group of the lattice. Because of dispersion, and the approximations made in obtaining (2.25) one cannot really take this definition of α seriously; however, one finds for a simple cubic structure $\alpha\cong 2$; bcc, $\alpha\cong 2.2$; fcc, $\alpha\cong 2.3$. Some experimental values are $\alpha=2.6$ for diamond, $\alpha=2.3$ for solid He, $\alpha=2.1$ for sapphire.[21] This rough agreement is probably better than one should expect from these crude arguments. This exponential behavior of the conductivity is only observed in a narrow range, in isotopically and chemically pure crystals.[22] This observation of the exponential "dying-out" of Umklapp processes at very low temperatures is an extremely important verification of the theoretical foundations of thermal conductivity.

The fact that $K\propto e^{\Theta/2T}$ implies that substances with a high Debye temperature have a correspondingly large conductivity in the exponential range.[2]

These conclusions have to be altered when the details of the vibration spectrum invalidate the assumptions used. Such is the case for Ge, where the determination of $\omega_\lambda(\mathbf{q})$ from neutron scattering experiments by

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[21] R. Berman, F. Simon, and J. Wilks, Nature **168**, 277 (1951).

[22] G. Slack, Phys. Rev. **105**, 829, 832, (1957). The isotopic resistivity was first reported experimentally by R. Berman, E. L. Foster, and J. M. Ziman, Proc. Roy. Soc. (London) **A237**, 344 (1956).

Brockhouse and Iyengar[23] have shown that the transverse acoustical branch in the [111] direction crosses the Brillouin zone boundary at an energy of only 0.007 ev$\sim\frac{1}{4}\Theta$. Thus Umklapp scattering may persist down to temperatures of the order of $(\frac{1}{10})\Theta$ instead of $\sim\frac{1}{2}\Theta$ as quoted previously. Geballe and Hull[24] discuss this point.

In the preceding sections we have used unlocalized (plane wave) phonons with a precisely defined wave vector. In order to describe thermal conductivity, where the state of the crystal varies in space, it is necessary to use localized wave packets. Hence there is a spread in the wave vector δq_x of magnitude

$$\delta q_x \delta x \sim 1, \tag{2.26}$$

if δx is the length of the wave packet. Now if all the quantities in the matrix elements vary slowly with q, then the substitution of wave packets for plane waves causes no change. In particular, consider the factors N_q. Let us write

$$N_q = N_q^0 + n_q, \tag{2.27}$$

where n_q is the deviation from the equilibrium distribution N_q^0. $N_q^0 = (e^{E_q/kT} - 1)^{-1}$ varies slowly as long as

$$\delta E_q = \hbar\delta\omega_q \cong \hbar C\delta q < kT,$$

or, using Eq. (2.22),

$$\delta x > (\hbar C/ka)(a/T) = (\Theta/T)a, \tag{2.28}$$

where a is the lattice constant. The relation (2.25) is usually satisfied.

Consider n_q. Later we find that in certain situations n_q is given approximately by

$$n_q \propto \tau(\omega) dN_q^0/dT,$$

where $\tau(\omega)$ is a "relaxation time." Evidently if $\tau(\omega)$ is a rapidly varying function of ω, then one must handle the problem with more care. Physically, some of the components of the wave packet may be preferentially scattered so that the wave packet cannot be considered as a single unit.

Such a case arises in the case of point defects, where $\tau(\omega) \propto \omega^{-4}$ (see later sections). The uncertainty in the relaxation time $\Delta\tau$ is

$$\frac{\Delta\tau}{\tau} \equiv \frac{\tau(\omega) - \tau(\omega + \delta\omega)}{\tau(\omega)} \cong \frac{\delta q\, d \log\tau}{dq} = \frac{4\delta q}{q}, \tag{2.29}$$

where $\delta q \lesssim T/a\Theta$. Now it is necessary to estimate some mean value of q. We choose that value which maximizes the energy "density" $E(\omega)$ in the Debye theory of specific heats: omitting the zero-point energy, the total energy of the crystal is[1]

$$E = 9RT\left(\frac{T}{\Theta}\right)^3 \int_0^{\Theta/T} \frac{x^3}{e^x - 1} dx.$$

Set $(d/dx)[x^3/(e^x - 1)] = 0$ which gives the transcendental equation

$$e^x - 1 = \tfrac{1}{3} x e^x.$$

The solution is roughly $x = 2.8$ or with $q_0 = (6\pi^2)^{\frac{1}{3}}/a$, $a = (\Omega/N)^{\frac{1}{3}}$, $\Theta = \hbar C q_0/k$, $\bar{q}/q_0 = 2.8T/\Theta$.

Most of the contribution to the integral in Eq. (4.4) comes from the frequency range $\bar{\omega} = C\bar{q}$. The corresponding "effective" wavelength $\bar{\lambda} = 2\pi/\bar{q}$ is

$$\bar{\lambda} \cong 0.6a(\Theta/T). \tag{2.30}$$

Later we see that most scattering processes are most effective for high frequencies, so that in the calculation of thermal conductivity the effective wavelength is generally somewhat greater than (2.30) indicates. Equation (2.30) is still a useful indication of the order of magnitude of the most important wavelengths at a given temperature, however. On using (2.30) we see that (2.29) becomes

$$\Delta\tau/\tau \leqq \tfrac{4}{3} \sim 1, \tag{2.31}$$

so that for point defect scattering it may be necessary to take wave packets into account explicitly. The frequency spread imposed by the requirements of localization can be of the same order as the mean frequency, for this case. Then the relaxation time is not well defined.[25] In a more satisfactory treatment of thermal conductivity one might start from an expansion of the displacement operator $\mathbf{u}_m$ in terms of localized wave packets.

In scattering theory it is well known that one gets the same answers to all important physical questions with or without using wave packets; however, this is not the case in transport problems involving many scatterers and a nonhomogeneous environment. Apparently no one has yet presented an adequate solution of this very difficult problem.[17]

III. PHENOMENOLOGICAL THEORY

Relaxation Time of a Single Mode

Much of the complexity of the three-phonon problem (and indeed of most transport problems) lies in the dependence of the distribution function N_q on the occupation of all the other states as well, as is evident from inspection of Peierls integral equation.[1] Hence, in general, the relaxation of a system to equilibrium does not occur in the same time as would, say, a situation in which all modes except one (or a small number) are in equilibrium. (The latter situation might be realizable experimentally by neutron bombardment.) However,

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[23] B. N. Brockhouse and P. K. Iyengar, Phys. Rev. **108**, 894 (1957).

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

[25] Even though τ fluctuates considerably the distribution function may be well defined.

there are certain situations in which the "relaxation time of a single mode" is the correct τ to use for the calculation of the thermal conductivity. This remarkable result is valid essentially because of the restrictions imposed on the possible phonon collisions by the conservation laws, coupled with a qualitative knowledge of the dispersion curves $\omega(q)$. For these considerations it is essential to examine the anisotropy of real crystals; the profound effect of anisotropy on the qualitative features of phonon-phonon scattering was demonstrated clearly by Herring.[20] Details of this analysis are straightforward but require a reasonably lengthy discussion, and are not reproduced here. The principles involved have been discussed thoroughly by Herring in footnotes 6 and 20 (the former contains a more elementary treatment). Here we are content to indicate the physical reasons for the validity of using the single mode τ.

As $q \rightarrow 0$, the longitudinal modes have much longer relaxation times than do the transverse modes. Therefore, in a reasonably pure crystal, the longitudinal phonons, being much more out of balance than the transverse phonons at very low temperatures, are most important in the conduction of heat. Further, because of the operation of the conservation laws, these longitudinal phonons of small q are only allowed to interact with phonons of rather larger q, which modes are nearly in equilibrium. This last result makes the single mode τ for longitudinal modes essentially the same as the "true" τ which takes into account the behavior of all the modes. At very low temperatures, when the Umklapp processes necessary to obliterate the heat current of the high q modes become rare, the above result is no longer true; but then boundary scattering, or defect scattering, dominates anyway. Hence the results may be expected to be applicable to those longitudinal phonons of small q (more specifically with energy much less than kT) in the temperature range above the peak in $K(T)$. Although these modes constitute a rather small fraction of the total, their effect is significant. Moreover, consistent results are obtained if one assumes the same single-mode relaxation time for all the modes,[26,27] though the correctness of this procedure is questionable.

The basic problem is to calculate the heat current $\mathbf{Q}$. Experimentally one finds that

$$\mathbf{Q} = -K\nabla T, \tag{3.1}$$

where K is the thermal conductivity coefficient and ∇ signifies the gradient operator $\nabla_x = \partial/\partial x$, etc. In anisotropic media one has more generally

$$Q_\alpha = -\sum_{\beta=1}^{3} K_{\alpha\beta}\frac{\partial T}{\partial x_\beta}. \tag{3.2}$$

Cases also arise in which the heat current is not linear in the temperature gradient, but these are not considered here.

The theorist, besides reproducing the factor ∇T, must then calculate the magnitude and temperature dependence of K.

The "standard" diffusion equation does not hold, because $K(T)$ depends on position. The correct equation is obtained by recalling that the basic quantity for energy flow is the divergence of $\mathbf{Q}$.

In this section we review a method of analysis very similar to the calculation of the thermal conductivity of a classical gas. Although many of the difficulties mentioned in the preceding paragraph are glossed over, this treatment is to some extent justified by the reasonable agreement with experiment that can be obtained with it.

The heat current is

$$\begin{aligned}\mathbf{Q} &= \textstyle\sum_q N_q \hbar\omega_q \mathbf{C}_q \\ &= \textstyle\sum_q (\text{energy in state } q) \\ &\qquad \times (\text{group velocity of phonon } q).\end{aligned} \tag{3.3}$$

The group velocity $\mathbf{C}_q$ is defined by $\mathbf{C}_q = \partial\omega_q/\partial\mathbf{q}$. In the acoustic range $\mathbf{C}_q = C_\lambda\hat{q}$, where C_λ is the velocity of sound for a wave of polarization λ; C_λ in general depends on the direction of $\hat{q}$. Besides a knowledge of the dispersion relation $\omega_\lambda(\mathbf{q})$ [which we often approximate by $\omega_\lambda(\mathbf{q}) = C_\lambda|\mathbf{q}|$], we need to know the distribution function N_q, which in turn is the solution of a complicated integral equation. The virtue (and defect!) of the present method is that the direct solution of this integral equation is avoided.

The relation of $\mathbf{Q}$ to the "crystal momentum" $\mathbf{P}$ of the phonon system that is valid when the temperature is sufficiently low that the linear approximation $\omega_\lambda = C_\lambda q$ is valid, and $\mathbf{C}_q = C_\lambda\mathbf{q}/q$, C_λ independent of direction is

$$\mathbf{Q} = \sum_{\mathbf{q},\lambda} N_{\mathbf{q},\lambda}(\hbar\mathbf{q})C_\lambda^2 = C_l^2\mathbf{P}_l + C_t^2\mathbf{P}_t, \tag{3.4}$$

$$\mathbf{P}_\lambda = \sum_{\mathbf{q}} N_{\mathbf{q}\lambda}\hbar\mathbf{q}. \tag{3.5}$$

$\mathbf{P}_t$ is supposed to represent the total contribution of the transverse modes; $\mathbf{P}_l$ that of the longitudinal modes. Thus the heat current is given by the sum of the crystal momenta of the various polarization modes, weighted with the squared velocities of sound of those modes. [In a cubic crystal one can write $\mathbf{Q} = \bar{C}^2(\mathbf{P}_l + \mathbf{P}_t)$ where $\bar{C}$ is an appropriate average velocity.] This point of view is especially useful when considering also the interaction of phonons with charge carriers,[28] since in this case the total crystal momentum of both systems is conserved in their mutual (non-Umklapp) interactions.

We consider the flow of phonons of polarization λ and mean wave vector $\mathbf{q}$ through the walls of an imaginary small volume. In the steady state the total rate of change must be zero. The number changes for two

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[26] This treatment of normal processes is due to J. Callaway, Phys. Rev. **113**, 1046 (1959). An earlier discussion of the combined effect of normal, Umklapp, and defect scattering was given by Klemens.[39,39a]

[27] V. Ambegaokar, Phys. Rev. **114**, 488 (1959).

[28] C. Herring, Phys. Rev. **96**, 1163 (1954).

reasons: (1) collisions of phonons with each other and impurities, (2) transport of phonons due to the presence of a temperature gradient. Contribution (1) we write as $(\partial N_q/\partial t)_c$ and must be calculated according to the detailed scattering mechanism involved. Contribution (2) is easily seen to be $-\mathbf{C}_\lambda\cdot\nabla N_q$. On using $\nabla N_q[T(x)]=\nabla T(dN_q/dT)$, we have the Boltzmann equation for the phonon distribution:

$$(\partial N_q/\partial t)_c=\mathbf{C}_\lambda\cdot\nabla T(dN_q/dT). \tag{3.6}$$

This result is only valid when the distribution function N depends on the position only through the temperature $T(\mathbf{x})$: $N=N(\mathbf{q},T)$. Later we have to take into account the fact that boundary scattering occurs only at the surface of a crystal, which situation leads to an explicit spatial dependence of the distribution function. In that case a more complete Boltzmann equation must be used.

Relaxation-Time Approximation

As we see in the next section, Eq. (3.6) is a complicated integral equation. Often, however, a good approximation to $(\partial N_q/\partial t)_c$ is given by

$$(\partial N_q/\partial t)_c=(N_q{}^0-N_q)/\tau(q). \tag{3.7}$$

Equation (3.7) says that in the absence of a temperature gradient any deviation from equilibrium in the mode q damps out exponentially, in a time $\tau(q)$.

In the present section we explore the consequences of Eqs. (3.7) and (3.8). Questions of validity are discussed later.

From our previous discussion it is evident that the normal processes must be given special consideration. The distribution function which is stationary for normal processes is not $N_q{}^0$ but rather $N_q(\boldsymbol{\lambda})$,[1,2] Eq. (2.8). $\boldsymbol{\lambda}$ is no longer arbitrary, and will be determined by the resistance-causing collisions. Thus instead of Eq. (3.7) we write[26]

$$\left(\frac{\partial N_q}{\partial t}\right)_c=\frac{N(\boldsymbol{\lambda})-N_q}{\tau_N}+\frac{N_q{}^0-N_q}{\tau_r}, \tag{3.8}$$

where τ_N is the relaxation time for normal processes. τ_r describes all processes which change the total wave vector in the phonon system. To first order in $\boldsymbol{\lambda}$,

$$N(\boldsymbol{\lambda})\cong N(0)+\boldsymbol{\lambda}\cdot(\partial N/\partial\boldsymbol{\lambda})_0,$$

$$N(\boldsymbol{\lambda})\cong N^0+\frac{\boldsymbol{\lambda}\cdot\mathbf{q}}{kT}\frac{e^{\hbar\omega/kT}}{(e^{\hbar\omega/kT}-1)^2}. \tag{3.9}$$

Equations (3.6), (3.8), and (3.9) give

$$\left[-\frac{\hbar\omega}{kT^2}\mathbf{C}\cdot\nabla T+\frac{\boldsymbol{\lambda}\cdot\mathbf{q}}{\tau_N kT}\right]\frac{e^x}{(e^x-1)^2}-\left(\frac{1}{\tau_N}+\frac{1}{\tau}\right)n_q=0, \tag{3.10}$$

with

$$x=\hbar\omega/kT.$$

Here the additional approximation has been made that $dN/dT=dN^0/dT$, i.e., it is assumed that the deviation from equilibrium is small.

Callaway[26] defines a "combined" relaxation time τ_C by

$$1/\tau_C=(1/\tau_N)+(1/\tau_r), \tag{3.11}$$

and a "total" relaxation time τ by writing n_q as

$$n_q=-\tau\mathbf{C}\cdot\nabla T(\hbar\omega/kT^2)\cdot[e^x/(e^x-1)^2]. \tag{3.12}$$

The reason for defining τ by Eq. (3.12) is that Eq. (3.8) reduces to

$$[-1+(\tau/\tau_C)](\hbar\omega/T)\mathbf{C}\cdot\nabla T+(\boldsymbol{\lambda}\cdot\mathbf{q}/\tau_N)=0. \tag{3.13}$$

By symmetry considerations, in an isotropic medium $\boldsymbol{\lambda}\propto\nabla T$ so it is convenient to define still another parameter β, which has the dimension of a relaxation time:

$$\boldsymbol{\lambda}=-\hbar\beta C^2[(\nabla T)/T]. \tag{3.14}$$

On using $\mathbf{q}=\mathbf{C}\omega/C^2$ this gives

$$\boldsymbol{\lambda}\cdot\mathbf{q}=-\hbar\omega\beta\mathbf{C}\cdot(\nabla T/T). \tag{3.15}$$

Therefore Eq. (3.13) gives

$$(\tau/\tau_C)-(\beta/\tau_N)=1;\quad \tau=\tau_C[1+(\beta/\tau_N)]. \tag{3.16}$$

Happily the constant β can be eliminated!

The deviation from equilibrium n_q becomes, with expression (3.16),

$$n_q=-\tau_C[1+(\beta/\tau_N)]\mathbf{C}\cdot\nabla T[e^x/(e^x-1)^2]. \tag{3.17}$$

Although we have had to start with the complicated equation (3.8), in the region of applicability of the approximation (3.9) the net result is the simpler equation (3.7). The effect of the normal processes is thus contained in the total relaxation time as indicated in (3.16).

For simplicity we have suppressed the polarization index in the foregoing equations. Each of the relaxation times τ, τ_N, τ_C, τ_r, and β depends on the polarization of the phonon involved. It is evident that Eq. (3.17) is valid for all polarization modes (of course, $\mathbf{C}=\mathbf{C}_\lambda$).

Whatever trepidations the reader may have experienced on seeing Eqs. (3.7) and (3.8) should be diminished somewhat by the physical reasonableness of Eq. (3.12) or (3.17). It is true that τ is a complicated quantity, depending on τ_N, τ_r, and β; this mess is unfortunately necessary because of the N processes which shuffle crystal momentum back and forth between the normal modes.

We are interested in τ only as a way to calculate the distribution function N_q. It seems possible that the problem be formulated in a way avoiding the use of a transport equation, in a form analogous to the recent expressions[29] for the *electrical* conductivity tensor given

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[29] R. Kubo, Can. J. Phys. **34**, 1274 (1956); J. Phys. Soc. Japan **12**, 570 (1957); M. Lax, Phys. Rev. **109**, 1921 (1958); see also F. Englert, J. Phys. Chem. Solids **11**, 78 (1959).

by Kubo and Lax, for example. We do not investigate this possibility here.

The constant β is determined by recalling that the normal processes cannot change the total phonon wave vector.

This condition is

$$\int \left(\frac{\partial N_q}{\partial t}\right)_N \mathbf{q}\,d^3q \equiv \int \left(\frac{N(\boldsymbol{\lambda})-N_q}{\tau_N}\right)\mathbf{q}\,d^3q=0;\ \text{all } \lambda. \quad (3.18)$$

The effect of the wave vector destroying processes (represented by τ_r, due to Umklapp processes, scattering by imperfections, etc.) is contained in N_q.

In detail, Eq. (3.18) can be written as

$$\int \frac{e^{\hbar\omega/kT}}{(e^{\hbar\omega/kT}-1)^2}\left[\frac{\hbar\omega}{kT^2}\tau\mathbf{C}\cdot\nabla T+\frac{\boldsymbol{\lambda}\cdot\mathbf{q}}{kT}\right]\frac{\mathbf{q}}{\tau_N}d^3q=0. \quad (3.19)$$

On inserting Eq. (3.15) for $\boldsymbol{\lambda}\cdot\mathbf{q}$, Eq. (3.19) becomes

$$\int \frac{e^x}{(e^x-1)^2}\left[x\mathbf{C}\cdot\left(\frac{\nabla T}{T}\right)(\tau-\beta)\right]\frac{\mathbf{C}\omega}{\tau_N C^2}d^3q=0, \quad (3.20)$$

where $x=\hbar\omega/kT$ as usual. On extracting constants, (3.20) becomes

$$\int_0^{\Theta/T} \frac{x^4e^x}{(e^x-1)^2}\left(\frac{\tau-\beta}{\tau_N}\right)dx=0. \quad (3.21)$$

On using Eq. (3.16) and solving for the constant β,

$$\beta=\int_0^{\Theta/T} dx\frac{x^4e^x}{(e^x-1)^2}\frac{\tau_C}{\tau^N}\Bigg/ \int_0^{\Theta/T} \frac{x^4e^x}{(e^x-1)^2}\frac{1}{\tau_N}\left(1-\frac{\tau_C}{\tau_N}\right)dx. \quad (3.22)$$

As $\tau_r \rightarrow \infty$ (only normal processes), $\beta\rightarrow\infty$. However, in this case, Eq. (3.22) is no longer valid, since $|\boldsymbol{\lambda}| \propto \beta$ is not small, so that the expansion equation (3.9) is inadequate. The conclusion that infinite conductivity occurs in this limit is still valid since $\boldsymbol{\lambda}$ may be arbitrary, while $\nabla T\rightarrow 0$ (see the following).

The expansion (3.9) for $N(\boldsymbol{\lambda})$ is certainly only valid if the "correction" is smaller than $N_q(0)$; on using the definition (3.14) this condition becomes

$$\beta C<(T/|\nabla T|)x^{-1}(1-e^x), \quad x=\hbar\omega/kT. \quad (3.23)$$

The function $f(x)=x^{-1}(1-e^x)$ has its maximum $f(0)=1$ at $x=0$. Hence the most lenient condition for the validity of the preceding development is

$$\beta C<T/|\nabla T|. \quad (3.24)$$

βC has the dimensions of a length. At low temperatures $T/|\nabla T|$ is of the order of a few centimeters in a typical experiment.

Conductivity

As remarked previously, the knowledge of $N_q=N_q^0+n_q$ is sufficient to give the conductivity. In Eq. (6.2) we have reduced this to a determination of $\tau=\tau_C(1+\beta/\tau_N)$. On examining Eq. (3.3) it is evident that N_q^0 gives no contribution to $\mathbf{Q}$ since $\partial/\partial\mathbf{q}$ is odd in $\mathbf{q}$: all other factors are even. On setting $(\partial/\partial\mathbf{q})\omega_\lambda(\mathbf{q})\equiv\mathbf{C}_\lambda(\mathbf{q})$, Eqs. (3.3) and (3.17) yield (λ is here the polarization index)

$$\mathbf{Q}=-\sum_{\mathbf{q},\lambda}\tau_\lambda(q)\mathbf{C}_\lambda\cdot\nabla T\frac{(\hbar\omega)^2}{kT^2}\frac{e^{\hbar\omega/kT}}{(e^{\hbar\omega/kT}-1)^2}\mathbf{C}_\lambda. \quad (3.25)$$

Equation (3.2) then gives for unit volume

$$K_{\alpha\beta}=\sum_{\mathbf{q},\lambda}\tau_\lambda(q)\frac{(\hbar\omega)^2}{kT^2}\frac{e^{\hbar\omega/kT}}{(e^{\hbar\omega/kT}-1)^2}(C_\lambda)_\alpha(C_\lambda)_\beta. \quad (3.26)$$

On introducing the heat capacity per normal mode

$$C_{\mathrm{ph}}(\omega)=\frac{d}{dT}(\hbar\omega_q N_q^0)=\frac{(\hbar\omega)^2}{kT^2}\frac{e^{\hbar\omega/kT}}{(e^{\hbar\omega/kT}-1)^2}, \quad (3.27)$$

and specializing to the isotropic case, Eq. (3.26) becomes

$$K=\sum_{\mathbf{q},\lambda}\tau_\lambda(q)C_{\mathrm{ph}}(\omega_q)C_\lambda^2\cos^2\theta; \quad (3.28)$$

$\cos\theta$ is the angle between $\mathbf{C}_\lambda$ and ∇T.

The density of states in $\mathbf{q}$ space is sufficiently great that the sum in Eq. (3.28) may be replaced by an integral according to the standard relation

$$\sum_{\mathbf{q}}\rightarrow\frac{\Omega}{(2\pi)^3}\int d^3\mathbf{q}. \quad (3.29)$$

The integral is to be taken over the first Brillouin zone. The thermal conductivity per unit volume is then

$$K=\frac{1}{(2\pi)^3}\sum_\lambda\int d^3\mathbf{q}\,\tau_\lambda(q)C_{\mathrm{ph}}(\omega_q)C_\lambda^2\cos^2\theta. \quad (3.30)$$

This integral is in general quite difficult to evaluate analytically, even when drastic assumptions are made. First, $\tau(q)$ can assume a very awkward form; see, for example, Eq. (6.2). Second, $\omega(\mathbf{q})$ is usually a complicated function of $\mathbf{q}$ and is in turn buried in the inconvenient functional form $C_{\mathrm{ph}}(x)$, Eq. (3.27). This latter difficulty can be shifted somewhat to another problem: that of calculating the density of states per unit frequency range, $n(\omega)$.[30] Unfortunately, this procedure is not convenient for the problem at hand as it is (for example) in the evaluation of the specific heat, because it develops presently that q, rather than ω, is often the natural variable upon which τ depends.

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[30] For a clear discussion of the principles involved in such a calculation see G. H. Wannier, footnote 15.

We are generally resigned to using the acoustic approximation, $\omega = Cq$, subject to reexamination on application to a given crystal (e.g., for $q \gtrsim \frac{1}{2} q_{\max}$ the transverse acoustic mode in Ge has $\omega \approx \text{const}$[22]).

Since in the Debye model one cuts off the integral at some maximum frequency ω_0 instead of a definite q_0, it is often convenient to use the transformation $\omega_\lambda(q) = C_\lambda(\theta, \varphi) q$ to obtain

$$d^3q = \omega_\lambda{}^2 d\omega_\lambda d\Omega_q / C_\lambda{}^3.$$

Equation (3.30) then becomes

$$K = \frac{4\pi}{3} \frac{1}{(2\pi)^3} \sum_\lambda \int_0^{\omega_0(\lambda)} \omega^2 C_{\text{ph}}(\omega) \left\langle \frac{\tau(\omega)}{C_\lambda} \right\rangle d\omega, \tag{3.31}$$

where

$$\frac{4\pi}{3} \langle f(\mathbf{q}) \rangle \equiv \int d\Omega_q \cos^2\theta f(\mathbf{q}).$$

In the special case where τ is adequately represented by a power law such as Eq. (3.35) following, Eq. (3.31) breaks up into an average of some power of C_λ [10] and an integral over ω. In the (fictitious) isotropic case, since $\int \cos^2\theta d\Omega = 4\pi/3$, we have for Eq. (3.30)

$$K = \frac{4\pi}{3} \frac{1}{(2\pi)^3} \sum_\lambda \int q^2 dq C_\lambda{}^2(q) \tau_\lambda(q) C_{\text{ph}}(\omega_q). \tag{3.32}$$

Equation (3.32) is similar to the expression for a classical gas with a constant mean-free path $\bar{l}$, heat capacity C_v, velocity v,

$$K = \tfrac{1}{3} C_v v \bar{l}, \tag{3.33}$$

which might be considered to be a definition of $\bar{l}$. Equation (3.33) is often used in the analysis of experiments. While such a procedure generally gives an order of magnitude understanding of the effect of various scatterers, it must be used with extreme caution; when comparing different scattering processes, whose relaxation times in general have rather different frequency dependence, the addition of $1/\bar{l}$'s (for example) has *at best* only qualitative significance. For small $\mathbf{q}$ (most important at low T), C_λ is essentially constant in most materials. For further discussion we often drop the polarization dependence and put $\sum_\lambda \to 3$. Further put $\omega = Cq$. It is convenient to change to the dimensionless variable $x = \hbar\omega/kT$ to examine the temperature dependence of K. Equation (3.32) is then

$$K = \frac{C^2}{2\pi^2} \left(\frac{kT}{\hbar C} \right)^3 \int_0^{\Theta/T} x^2 \tau[q(x)] C_{\text{ph}}(x) dx. \tag{3.34}$$

For $T \ll \Theta$ the exponential dependence of C_{ph} on x allows one to set the upper limit equal to ∞.

Consider the idealized case in which

$$\tau(q) = A q^{-n} = A(kT/\hbar C)^{-n} x^{-n}. \tag{3.35}$$

Then

$$K \propto T^{3-n} \int_0^\infty \frac{x^{4-n} e^x}{(e^x - 1)^2} dx. \tag{3.36}$$

This result is a useful rule to remember the temperature dependence of K due to a scattering process for which $\tau_n \propto q^{-n}$. This is reliable if $\tau_N \gg \tau_n$ [see Eq. (6.1) for τ]:

$$K \propto T^{3-n} \quad \text{if} \quad \tau \propto q^{-n} \quad \text{and} \quad T \ll \Theta. \tag{3.37}$$

The general case is more complicated since there are several scattering processes which must be considered simultaneously. A table of $\tau(\omega)$ and $K(T)$ for various processes is given by Klemens.[2] Equation (3.37) is a useful "rule of thumb"; the actual temperature is some compromise between the various processes, as discussed later.

The law (3.37) has only asymptotic validity, since it has been derived with the acoustic approximation. Already at temperatures below T_m of the maximum K, the Debye theory is known to fail. (Blackman's article[10] shows how markedly real spectra deviate from the Debye assumption.) When temperatures are sufficiently high that an appreciable fraction of phonons have non-infinitesimal wave numbers q, the simpler T^{3-n} law may fail. Thus even to have a qualitative understanding of the temperature dependence of $K(T)$ one must consider the actual distribution of normal modes. Since the latter is very complicated and varies from crystal to crystal, it is still useful (as in the theory of specific heats) to consider an "ideal" crystal, having the simple Debye distribution. This simplifies the task of announcing general results such as (3.37) and considerably shortens later discussion.

Now that a detailed knowledge of $\omega(\mathbf{q})$ is becoming available for some materials, another method for the evaluation of integrals such as (3.30) becomes available. It is not necessary to know the density of states as a function of ω; the states are distributed uniformly within the first Brillouin zone so that a knowledge of $\omega(\mathbf{q})$ enables one to evaluate (3.30), if $\tau(q)$ is known. In fact, for strain-field scattering q is the more appropriate variable than ω [isotope scattering is actually a function of ω; three-phonon processes involve both q and $\omega(q)$] so that if this is the most important process one would do well to avoid solving for $q(\omega)$ even if $\omega(q)$ is available. As another example consider again the transverse acoustic branch of Ge, which is nearly flat in the [111] direction for $q \gtrsim \frac{1}{2} q_{\max}$. For this particular part of the contribution to K one could just put $\omega = \text{constant}$. The general case, in which many scattering processes occur, is truly formidable from any point of view. The labor involved in making a realistic evaluation of (3.30) would probably be better spent investigating the validity of the various relaxation time assumptions that have gone into that equation.

The integral in Eq. (3.36) diverges if $n > 2$. This is no difficulty in practice; the presence of competing processes always introduces a cutoff. The net result is a size effect.[20,28] Herring[20] has shown that for normal processes $\tau_N^{-1}\propto q^sT^{5-s}$, where s depends on the crystal symmetry. For a longitudinal acoustic mode in cubic crystal $s=2$. Then for $\tau\propto q^{-n}$, $n>2$, $\tau_C\rightarrow\tau_N$ as $q\rightarrow 0$ and $\tau=\tau_C(1+\beta/\tau_N)\rightarrow\tau_N\sim q^{-2}$ so that the right-hand side of (3.36) converges. For lower symmetries $s>2$ and a size dependence follows.[20,28]

In a crystal of sufficient symmetry the normal processes determine the deviation from equilibrium in the limit of small q, if the relaxation time for the "resistive" processes $\tau_r\propto q^{-n}$, $n>2$. Thus there would occur no "infrared" divergence in a cubic crystal of infinite size in which there were, say, only isotopic scatterers, contrary to what would follow if one naively took $\tau\propto q^{-4}$ in Eq. (3.36). Actually, however, one rarely observes the temperature dependence corresponding to τ_N because of boundary scattering, which in real life dominates the conductivity before the temperature is lowered so far that defect scattering is negligible.

For the reader interested in performing calculations we note a way to take care of the fact that the upper limits of integrals such as (3.34) are actually finite. We still suppose that $x_0=\Theta/T$ is rather greater than unity, so that the exponential character of $C_{\text{ph}}(x)$ can be utilized with advantage. These integrals are generally of the form

$$I(x_0)=\int_0^{x_0}f(x)\xi(x)e^{-x}dx,$$

where

$$\begin{aligned}\xi(x)&\equiv(1-e^{-x})^{-2}\\&=1+2e^{-x}+3e^{-2x}+\cdots\end{aligned}$$

is a rapidly converging series, $x\gg 1$. Now

$$\int_0^{x_0}=\int_0^{\infty}-\int_{x_0}^{\infty},$$

so that the correction to $I(\infty)$ is

$$-\Delta I=\int^{\infty}f(x)e^{-x}\xi(x)dx. \qquad (3.38)$$

Under the states assumptions $1\leq\xi(x)\leq\xi(x_0)\cong 1$. Thus one may set $\xi=1$ inside the integral (3.38). Further progress may be made by integrating by parts if $|f'(x)/f(x)|<1$, $x>x_0$, as is very often the case. (The differentiated function is then f.)

As a simple example with a slightly different function, namely, the familiar $E(x)$ defined by Eq. (2.28), the preceding method gives

$$\int_0^{x_0}\frac{x^3}{e^x-1}dx=\frac{\pi^4}{15}-x_0^3e^{-x_0}\left[1+O\left(\frac{1}{x_0}\right)\right],$$

where $\int_0^\infty$ is $\pi^4/15$ and $O(1/x_0)$ denotes a (small) quantity of the order of $1/x_0$.

Here we are ignoring the subtle questions that arise in the statistical mechanics of irreversible processes. For the specific problem of thermal conductivity recent progress has been made by Brout and Prigogine,[31] also Peierls,[5] and Van Hove.[13]

IV. STRAIN-FIELD SCATTERING

In Sec. II we examined the consequences of the (assumed) existence of a relaxation time for the various scattering processes. This section presents a unified exposition of the scattering due to the static strain fields of crystalline imperfections. The formal theory is quite simple. As in the case of three-phonon processes, one can proceed quite far in a formal way if one is content to suppress all ignorance into a single term (similar to $C_{qq'q''}$ in the three-phonon interaction). It is essential to have an understanding of strain-field scattering in order to interpret other effects, for often one cannot work with materials free of strains. For example, the experimental results of Sproull, Moss, and Weinstock[32] show that the thermal resistance of dislocations can be quite large, a result not expected from the original calculations of dislocation scattering by Klemens.[33] Thus if the dislocation content and distribution of a specimen are not known in a given experiment, care must be taken to avoid strain.

In this section the elastic scattering of phonons by static strain fields is examined.

The merits of the formulation presented in the following are that one proceeds directly from the atomic coupling constants; the scattering probabilities can be expressed in a compact form by a method similar to that used previously for the three-phonon case. The approximations presently necessary to obtain numerical results are still crippling; however, these approximations are deferred to the end of the calculation, where their effect may be clearly assessed. Further, by using the atomic approach we can examine structures of the anharmonic constants (4.11) and (2.2), which may be useful in planning future evaluations of these quantities. This subject is especially important for understanding the effect of point defects, dislocations, and grain boundaries on the crystal conductivity. It is necessary to make a remark on the prescription given in the preceding paragraph. The processes of *elastic* scattering of phonons by different static structures are indistinguishable from each other. Therefore, one must first add the matrix elements for the various processes before squaring. Formally, we find this corresponds to a very simple result:

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[31] R. Brout and I. Prigogine, Physica **22**, 263 (1956). Also of interest is an analysis of a one-dimensional system by D. K. C. MacDonald in *Transport Processes in Statistical Mechanics*, edited by I. Prigogine (Interscience Publishers Inc., New York, 1958), p. 63. A simple discussion of the use of detailed balance for transport problems is given by C. Kittel, *Elementary Statistical Physics* (John Wiley & Sons, Inc., New York, 1959), p. 186.

[32] R. Sproull, M. Moss, and H. Weinstock, J. Appl. Phys. **30**, 334 (1959).

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

the quantity "responsible" for the scattering is the Fourier component of the *total* displacement field, the argument of this being $\mathbf{q}'-\mathbf{q}$, expressing conservation of wave vector.[34]

In elastic scattering the number of phonons is conserved (but the wave vector of the phonon is not). Elastic processes cannot interfere with inelastic processes because the final states are different (hence orthogonal). Likewise elastic scattering cannot interfere with three-phonon processes because the number of phonons involved is different, so that one cannot have $\omega(\mathbf{q})=\omega(\mathbf{q}')$.

The interference between elastic processes is conveniently separated as follows: interference between (1) scatterers of the same kind (e.g., an array of dislocations), (2) scatters of different kinds. Such effects can be taken into account by introducing appropriate form factors in the matrix elements. Specific assumptions must then be made to evaluate the scattering, so that it is important to know (at least qualitatively) the arrangement of defects in a given experimental situation.

Before proceeding to the details it seems advisable to discuss a typical curve of the variation of K with temperature. The main features are as follows: at $T=0$, $K=0$; the conductivity rises rapidly to a peak $K(T_m)$ for T_m in the vicinity of 10–30° (the greater Θ, the greater T_m), after which K drops off again, approaching a $1/T$ dependence at high temperatures.

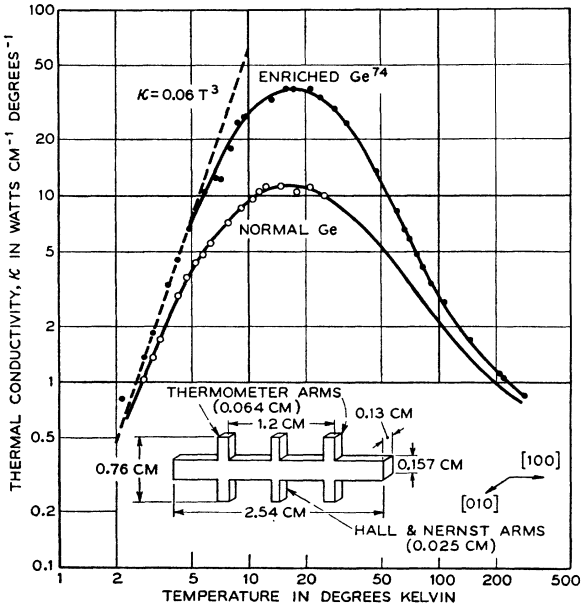

FIG. 2. Isotope effect on thermal conduction in germanium (Geballe and Hull[24]). Note how much higher the peak conductivity is in the isotopically pure (96% Ge^{73}) sample. The boundary scattering ($K\propto T^3$) is in good agreement with the Casimir theory (Sec. VII) for the pure sample, but does not approach T^3 variation in the normal sample even at the lowest temperatures attained.

Above the peak Umklapp resistivity is responsible for most of the resistance. For $T\ll\Theta$ we have seen that the resistivity decreases as T is decreased despite the decrease of the heat capacity as T^3. As the Umklapp resistivity becomes negligible, scattering by defects, boundary scattering, etc., determine the resistance. Thus the temperature range around and below the peak is of primary interest for investigating the effect of various structural and chemical impurities, which depress and shift the peak in a way characteristic of the imperfection. At high temperatures $T\gg\Theta$, the resistivity due to strains is independent of temperature since the distribution of phonons among the various modes does not change with temperature, and the scattering probability is independent of temperature.[1] It is possible that the excitation of the vibrational modes of dislocations would provide a strong resistance at high temperatures.[35]

Figure 2, taken from the work of Geballe and Hall[24] on pure Ge, displays many of these features. (At such low temperatures, the number of conduction electrons becomes negligible in pure Ge.) The upper curve represents the behavior of an isotopically pure sample; the lower, a sample of normal isotopic constitution. (The scattering by isotopes is discussed in a later section.) The thermal conductivity of insulators is often rather large at these low temperatures, being sometimes greater than that of good electrical (hence good thermal) conductors.

The problem of scattering by an arbitrary strain field involves consideration of the change in the potential energy due to a displacement field $\mathbf{V}_m$, supposed known from a calculation in classical elastic theory. The theory is not restricted to the use of displacements calculated from elastic theory, but only such results are readily available. The results of atomic calculations of the displacements due to various defects in any event agree at large distances from the region of disorder responsible for the strain. For strain fields whose range is rather short compared to the extent of the disorder, one cannot expect the results of elastic theory to be sufficient. In particular, the concept of displacement loses meaning in a disordered region. Thus the present development is inadequate for this situation. One should be able to estimate the scattering from such a region by considering most of the scattering to occur at the surface of the disordered region (i.e., impose an appropriate boundary condition). We do not consider the difficult problem posed by such disordered regions, for the details of the strain-field scattering are already rather complicated.

The harmonic potential gives no contribution to the scattering except possibly through the virtual excitation of some internal (nonphonon) degree of freedom, such as the oscillations of a dislocation, which must be investigated separately. For this reason we examine V_3.

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[34] P. Carruthers, Phys. Rev. **114**, 995 (1959).

[35] A. Granato, Phys. Rev. **111**, 740 (1958). At present there is no evidence that these vibrational modes are important in nonmetals at low temperatures. The situation could be quite different for metals.

The expansion of V_3 contains four types of contributions which we write schematically as

ΣBV^3: constant energy shift (4.1)

ΣBV^2U: gives no contribution (4.2)

ΣBVU^2: scatters phonons (4.3)

ΣBU^3: ordinary three-phonon processes. (4.4)

Equation (4.1) represents a constant energy shift, the "anharmonic" strain energy, which we can safely ignore for the consideration of scattering processes. Then there is a term linear in phonon operators (4.2). If we treat this term in perturbation theory we see that the first order gives zero, because of energy conservation. In second order there are two contributions corresponding to the order of emission and absorption of the phonons; these contributions in fact cancel exactly. A more fundamental way is to observe that if it had been included in the Hamiltonian from the beginning, the driving term representing the stress field would have canceled it off by the equilibrium condition, as occurred in the discussion of the harmonic approximation.

The perturbation of interest in Eq. (4.3) (the energy conserving part) is

$$V_3=\frac{\hbar}{4\rho\Omega}\sum_{\substack{\mathrm{qq}'\\ \mathrm{ijk}}}(\omega_q\omega_{q'})^{-\frac{1}{2}}e_q{}^je_{q'}{}^k \times\{a_qa_{q'}{}^*V_{\mathbf{q}'-\mathbf{q}}{}^ib_{ijk}(\mathbf{q},\mathbf{q}',\mathbf{q}-\mathbf{q}')+\mathrm{H.c.}\}. \tag{4.5}$$

In obtaining (4.5) we have expanded $\mathbf{V}_\mathbf{m}$ in a Fourier series:

$$\mathbf{V}_\mathbf{m}=\sum\mathbf{V}_\mathbf{q}\exp(i\mathbf{q}\cdot\mathbf{m}), \tag{4.6}$$

$$\mathbf{V}_\mathbf{q}=\Omega^{-1}\int d^3\mathbf{m}\exp(-i\mathbf{q}\cdot\mathbf{m})\mathbf{V}_\mathbf{m}. \tag{4.7}$$

In obtaining Eq. (4.5) we have used $\mathbf{V}_{-\mathbf{q}}=\mathbf{V}_\mathbf{q}{}^*$ (since $\mathbf{V}_\mathbf{m}=\mathbf{V}_\mathbf{m}{}^*$ is real).

The term b_{ijk} is again given by Eq. (2.3). Wave vector "conservation" follows essentially as in Eq. (2.7). This conservation law is strictly true only in an infinite lattice, for if one moves the defect by some number of lattice constants, the interaction of the defect with the surface is different. The energy is unchanged by such a displacement for the following cases: (a) infinite lattice; (b) short-range strain fields; (c) a sufficiently homogeneous distribution of defects. These situations cover all the cases of practical interest; in fact, we have already implicitly ignored surface effects by using periodic boundary conditions.

Since $\mathbf{V}_\mathbf{m}$ is a function defined on the (unstrained lattice) points $\mathbf{m}$ (even though we are using elastic continuum theory to obtain $\mathbf{V}$) the sum on $\mathbf{q}$ in (4.7) extends only over the first Brillouin zone.

Equation (4.5) shows that the lattice absorbs the amount of wave vector lost by the scattered phonon. Wave vector conservation is in general not the same as momentum conservation, even for long-wavelength phonons, which interact with the lattice as an elastic continuum. The running waves carry no momentum; $\dot{\mathbf{u}}$ is linear in the phonon operators so that $\langle\dot{\mathbf{u}}\rangle=0$. This point, and the transition to the limit of classical elastic theory, are discussed by Leibfried[4] (p. 304).

It is convenient to rewrite Eq. (4.5) in a form similar to Eq. (2.1) by summing over the Cartesian components (ijk). Further, by using simple symmetry properties[36] one may show that the H.c. term is identical to the first term $(q\neq q')$:

$$\Delta V_3=\frac{\hbar}{2\rho\Omega}\sum_{qq'}(\omega_q\omega_{q'})^{-\frac{1}{2}}C_{qq'}a_qa_{q'}{}^*, \tag{4.8}$$

where

$$C_{qq'}=\sum_{ijk}V_{\mathbf{q}'-\mathbf{q}}{}^ie_q{}^je_{q'}{}^kb_{ijk}(\mathbf{q},\mathbf{q}',\mathbf{q}'-\mathbf{q}). \tag{4.9}$$

The consideration of matrix elements of ΔV_3 between specific states selects just one term out of the sum over q, q'. The appropriate matrix elements are, using (1.6),

$$M_{q'\to q}=\frac{\hbar}{2\rho\Omega}C_{qq'}\left(\frac{(N_q+1)N_{q'}}{\omega_q\omega_{q'}}\right)^{\frac{1}{2}}; \tag{4.10}$$

$$M_{q\to q'}=\frac{\hbar}{2\rho\Omega}C_{qq'}{}^*\left(\frac{N_q(N_{q'}+1)}{\omega_q\omega_{q'}}\right)^{\frac{1}{2}}. \tag{4.11}$$

On using Eq. (2.5) for the transition probability, the rate of change of the number of phonons in state $\mathbf{q}$, λ is [cf. the remarks following Eq. (3.4)]

$$\left(\frac{\partial N_q}{\partial t}\right)_c=\sum_{q'}[\mathrm{Prob}(q'\to q)-\mathrm{Prob}(q\to q')] \tag{4.12}$$

or

$$\left(\frac{\partial N_q}{\partial t}\right)_c=\frac{2\pi}{\hbar^2}\sum_{q'}\{|M_{q'\to q}|^2-|M_{q\to q'}|^2\} \times\delta(\omega_q-\omega_{q'}) \tag{4.13}$$

or

$$\left(\frac{\partial N_q}{\partial t}\right)_c=\frac{1}{16\pi^2\rho^2\Omega} \times\int d^3\mathbf{q}'\sum_{\lambda'}\frac{\delta(\omega_q-\omega_{q'})}{\omega_q\omega_{q'}}|C_{qq'}|^2(N_{q'}-N_q). \tag{4.14}$$

We note that $\hbar$ has canceled out in the final equation (4.14). The result is essentially classical, but we believe the quantum-mechanical treatment is far preferable for physical understanding. The natural next step, namely, to represent the strain field as a superposition

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[36] Note that $C_{\mathrm{qq}'}=0$ when $\mathbf{q}=\mathbf{q}'$, as follows from (2.3) and (2.4). Now using the definition (2.5), one can see that $C_{\mathrm{qq}'}{}^*=C_{\mathrm{q}'\mathrm{q}}$, which proves the assertion. [The necessary relations are that $\mathbf{V}_\mathbf{q}{}^*=\mathbf{V}_{-\mathbf{q}}$ and $b_{jik}(-\mathbf{q}',\mathbf{q},\mathbf{q}'-\mathbf{q})=b_{ijk}(\mathbf{q},-\mathbf{q}',\mathbf{q}'-\mathbf{q})$]. (These results hold true for more general potentials.)

of virtual phonons, is probably not worthwhile at the present time. In such a formulation one must retain the quantum-mechanical treatment.

If we compare this result with Eq. (2.4), where dN_q/dT may be approximated by dN_q^0/dT, we obtain a linear integral equation for the distribution function N_q:

$$\mathbf{C}_q\cdot\nabla T\frac{dN_q^0}{dT}=\frac{1}{16\pi^2\rho^2\Omega}\times\int d^3\mathbf{q}'\sum_{\lambda'}\frac{\delta(\omega-\omega')}{\omega\omega'}|C_{qq'}|^2(N_{q'}-N_q). \tag{4.15}$$

It is convenient to rewrite this as follows: simple algebra yields

$$dN^0/dT=N^0(N^0+1)(\hbar\omega/kT^2). \tag{4.16}$$

Define $g_\lambda(q)$ by

$$n_q=N_q^0(N_q^0+1)g_\lambda(q). \tag{4.17}$$

Since $N_q^0=N_{q'}^0$ Eq. (9.9) assumes the form (taking $\hat{x}\|\nabla T$)

$$\frac{\hbar\omega}{kT^2}\frac{\partial\omega_\lambda}{\partial q_x}\frac{\partial T}{\partial x}=\frac{1}{16\pi^2\rho^2\Omega}\times\int d^3\mathbf{q}'\sum_{\lambda'}\frac{\delta(\omega_q-\omega_{q'})}{\omega_q\omega_{q'}}|C_{qq'}|^2[g_{\lambda'}(\mathbf{q})-g_\lambda(\mathbf{q})]. \tag{4.18}$$

The presence of the δ function in Eq. (4.18) restricts the contributions to the integral from states q' on the energy surface. It is often useful to examine the allowed transitions for possible energy surfaces. This is easily done by making the replacement

$$d^3\mathbf{q}'\delta(\omega_q-\omega_{q'})\rightarrow dS'|\partial\Delta\omega/\partial q_n'|^{-1}, \tag{4.19}$$

where $\Delta\omega\equiv\omega_q-\omega_{q'}$ measures the departure from energy conservation and q_n' is the component of $\mathbf{q}'$ in the direction of the normal to the surface S'. This result follows from

$$\delta[f(x)]=[1/|f'(x_0)|]\delta(x-x_0)\quad\text{if}\quad f(x_0)=0, \tag{4.20}$$

by integrating over q_n'.

Equation (4.18) cannot be solved for two reasons. First (4.18) is not complete since the three-phonon collisions have been neglected (and generally one has to add terms corresponding to boundary and "isotope" scattering). Even if one adds only the three-phonon term [see footnote 1, p. 49, Eq. (2.76)] the resulting equation is truly formidable. A solution of this equation, even for a simplified model, is essential for further progress. Until some such solution is accomplished, the following method, which treats some scattering processes exactly, and others according to a relaxation time approximation, may be useful.

Write the net rate of change of phonons in the state $q=(\mathbf{q},\lambda)$ due to elastic scattering as

$$\left(\frac{\partial n_q}{\partial t}\right)_c=\int d^3\mathbf{q}'\sum_{\lambda'}\delta(\omega_q-\omega_{q'})P_{qq'}(n_{q'}-n_q). \tag{4.21}$$

The Boltzmann equation is obtained by setting the right-side side equal to $-R(q)$, where $R(q)=-\mathbf{C}\cdot\nabla T(dN/dT)$ is the rate at which the heat current delivers phonons to the mode q. Further define the single-mode relaxation time (i.e., $n_{q'}=0$) by

$$\frac{1}{\tau_0(q)}=\int d^3\mathbf{q}'\sum_{\lambda'}\delta(\omega_q-\omega_{q'})P_{qq'}; \tag{4.22}$$

$$\frac{1}{\tau_0(q)}=-\frac{1}{n_q}\left(\frac{\partial n_q}{\partial t}\right),\quad n_{q'}=0. \tag{4.23}$$

Then (4.21) can be rewritten in the following convenient form:

$$n_q=\tau_0R(q)+\frac{\int d^3q'\sum_{\lambda'}\delta(\omega_q-\omega_{q'})P_{qq'}n_{q'}}{\int d^3q'\sum_{\lambda'}\delta(\omega_q-\omega_{q'})P_{qq'}}; \tag{4.24}$$

$$n_q\equiv\tau_0R(q)+\langle n_q\rangle. \tag{4.25}$$

The average indicated in (4.25) is clearly over the energy surfaces $\omega=\omega'$, weighted with the transition "probability" $P_{qq'}$. [For dislocations, however, the separation in (4.24) is inconvenient since $1/\tau_0$ diverges.] The form (4.24) is reasonably convenient for solution; in certain situations it may be solved by iteration, in this case we write the solution symbolically as

$$n_q=\tau_0R+\langle\tau_0R\rangle+\langle\langle\tau_0R\rangle\rangle+\cdots. \tag{4.26}$$

The validity of this expansion depends specifically on the problem; tests for convergence may be found in standard references. If (4.26) converges then the relaxation time, defined by $n_q\equiv\tau R(q)$, is given rigorously by

$$\tau(q)=\tau_0(q)+\frac{\langle\tau_0R\rangle}{R}+\frac{\langle\langle\tau_0R\rangle\rangle}{R}+\cdots. \tag{4.27}$$

Since R is essentially $C_\lambda\cos\theta f(\omega)$, $f(\omega)$ cancels out of (4.27) by virtue of the energy-conserving delta function, and the averages are taken essentially over τ_0 weighted by angular factors.

A slight modification covers the case in which there are additional processes described by a relaxation time. Let us add to the right-hand side of (4.21) a term $-n_q/\tau_1$. On defining $\bar{\tau}^{-1}=\tau_0^{-1}+\tau_1^{-1}$, the appropriate generalization of (4.24) is

$$n_q=\bar{\tau}R(q)+\bar{\tau}\int d^3q'\sum_{\lambda'}\delta(\omega_q-\omega_{q'})P_{qq'}n_{q'}. \tag{4.28}$$

Van Hove[13] gives a general argument for the justification of the intuitive relation Eq. (4.12).

Specific Cases: Point Defects and Dislocations

In order to apply Eq. (4.22) it is necessary to evaluate $\mathbf{V}_{\mathbf{q}}$ for the given problem. For our purposes the evaluation of b_{ijk} given by Eq. (2.15) is sufficiently complicated. Recall the definition of the quantity of interest here [see Eqs. (4.9), (2.19), and (2.23)]:

$$C_{qq'}=\left(\frac{Nig}{2a^3}\right)\sum_{\mathbf{a}}(\mathbf{v}_{\mathbf{q}'-\mathbf{q}}\cdot\mathbf{a})(\mathbf{e}_{\mathbf{q}'}\cdot\mathbf{a})(\mathbf{e}_{\mathbf{q}}\cdot\mathbf{a})\times(\mathbf{q}\cdot\mathbf{a})(\mathbf{q}'\cdot\mathbf{a})(\mathbf{q}'-\mathbf{q})\cdot\mathbf{a}, \quad (4.29)$$

where the sum is taken over the nearest neighbors of one atom.

From Eq. (4.29) it is easy to extract the temperature dependence of K from a knowledge of the q dependence of $\mathbf{V}_{\mathbf{q}}$. Assume for simplicity

$$V_q\propto q^{-m/2}. \quad (4.30)$$

Then from Eq. (4.29)

$$|C_{qq'}|^2=\text{const}\times q^{6-m}. \quad (4.31)$$

Consider Eq. (4.22) for τ:

$$\tau^{-1}\propto\int d^3q'\frac{\delta(\omega-\omega')}{\omega\omega'}q^{6-m}, \quad (4.32)$$

or

$$\tau^{-1}\propto q^{6-m};\quad K\propto T^{m-3}. \quad (4.33)$$

In obtaining (4.33) from (4.32) the $\delta(\omega-\omega')$ restricts the integration to the energy surface, of two dimensions in q. Note the T^{m-3} law, obtained from the T^{3-n} law [Eq. (3.37)].

This dimensional argument is only true for "three-dimensional" scatterers and not for two-dimensional objects with translational symmetry, such as dislocations. The reason for this is that when V_3 has translational symmetry (as is the case for a straight dislocation) there is an additional constant of the motion. As an example consider a dislocation whose axis we call z. Invariance under displacements in the z direction gives $q_z=q_z'$ for all collisions besides the condition $|\mathbf{q}|=|\mathbf{q}'|$.

In passing to the continuum this expresses itself as a factor $\delta(q_z-q_z')$ in the integral Eq. (4.32); in other words, the density of states is decreased by one dimension.

Another conceivable complication is that the simple power law such as Eq. (4.30) may not be valid, so that a careful examination of Eq. (4.22) is necessary to extract the temperature dependence of the conductivity; however, one can usually speak of an "effective" m in Eq. (4.30), in certain limiting situations.

For imperfections for which Eq. (4.30) is adequate, we may rewrite Eq. (4.33) as

$$1/\tau\propto q^{6-m-\sigma};\quad K\propto T^{m-3+\sigma},$$

where σ is the number of independent directions in which V_3 is invariant under translation. For example, for scattering by the *strain field* (not "contact" reflection) of a platelike object $\sigma=2$; also, if the plate lies in the xy plane, $q_x=q_x'$, $q_y=q_y'$, $q_z'=-q_z$.

Equation (4.33) is useful for estimating $K(T)$ for strain fields of different ranges and symmetries, since most of the required Fourier transforms are easily estimated.

Point Defects

For an outside sphere embedded in an isotropic elastic medium the displacement field is given by[37]

$$\begin{aligned}\mathbf{V}(\mathbf{r})&=A(\mathbf{r}/r^3)=A\hat{r}/r^2 \quad && r>r_0\\ &=0 && r<r_0,\end{aligned} \quad (4.34)$$

where r_0 is the radius of the impurity ($r_0\approx a$) and A is a constant.

The solution, Eq. (4.34), is characterized by zero divergence, $r>r_0$ (cf. the electric field of a point charge):

$$\nabla\cdot\mathbf{V}(\mathbf{r})=\sum_{i=1}^{3}\frac{\partial}{\partial x_i}\left(\frac{x_i}{r^3}\right)=\frac{3}{r^3}-\sum_i\frac{3}{r^4}\frac{x_i^2}{r}=0. \quad (4.35)$$

Similarly, the *rotation* $\nabla\times\mathbf{V}=0$. In his original formulation[33] of strain-field scattering, Klemens simplified the interaction potential in such a way that the dilatation and rotation appeared, rather than the displacements. This point of view led to the conclusion that a displacement field such as (4.34) produces no scattering. The situation is sufficiently delicate to merit further discussion. First one notes that Eq. (4.35) cannot be valid everywhere; that is, the displacement field must have a source. Previously this source was characterized as an outsized sphere, although a similar model may be used to describe a vacancy. We may incorporate this source into a generalization of (4.35) by using the restrictions (4.34), but first it may be helpful to call attention to the analogous case in electrostatics. The electric field of a point charge is proportional to $\mathbf{E}=-\nabla(1/r)$. Obviously one has $\nabla\cdot\mathbf{E}=\nabla\times\mathbf{E}=0$ if $r\neq0$; however, by including the source (the point $r=0$) one has $\nabla\cdot\mathbf{E}=-\nabla^2(1/r)=4\pi\delta(\mathbf{r})$, where $\delta(\mathbf{r})$ is the usual Dirac delta function.

Hence for the Fourier components of E, one has $\mathbf{E}_q=i\mathbf{q}(1/r)_{\mathbf{q}}=4\pi i\mathbf{q}/q^2$ and not zero, as would be the case if the source were neglected. Evidently the displacement (4.34) can be written as $\mathbf{V}=-A\nabla(1/r)$ so that the present problem is directly analogous to the preceding example, for $r>r_0$. We want to keep r_0 finite, however, as it turns out that this has important consequences. In the following the language used is ap-

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[37] J. D. Eshelby, *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1955), Vol. 3.

propriate to vacancies. Suitable modifications may then be made for other cases of interest. First let us justify the choice $v(r)=0$ inside the vacancy $(r<r_0)$. This is reasonable upon recalling the form of the scattering potential, which is linear in the displacement field; for the case of a vacancy (an inward negative radial displacement) this can be considered as an attractive potential well. Evidently there is no contribution to the strain-field scattering from regions with $r<r_0$, so that even though the concept of a displacement has no meaning in this region, the choice (4.34) is correct. The potential-well analogy is useful; for the vacancy the potential is short range and attractive up to the "radius" of the vacancy, where the potential rises rapidly to zero. This latter feature is discussed in more detail later.

Consider a sphere of radius r and outward surface element $d\mathbf{S}$; Eq. (4.34) shows that

$$\begin{aligned}\int \mathbf{v}(\mathbf{r})\cdot d\mathbf{S} &= 4\pi A \qquad r>r_0,\\ &=0 \qquad r<r_0.\end{aligned} \tag{4.36}$$

If we use Gauss' theorem to rewrite the left-hand side of (4.36) as $\int\nabla\cdot\mathbf{v}d^3x$, then the necessary generalization of (4.35) is

$$\nabla\cdot\mathbf{v}(\mathbf{r})=A\,\delta(r-r_0)/r_0^2. \tag{4.37}$$

If one takes the limit $r_0\rightarrow 0$, the right-hand side of (4.36) approaches $4\pi A\,\delta(\mathbf{r})$ as required. In a theory in which $\nabla\cdot\mathbf{v}$ is the central quantity the interpretation and use of (4.37) could be troublesome; however, our need for it is only to compute $\mathbf{v}_\mathbf{q}$, whose physical significance has been previously considered. For this purpose we use the relation $(\nabla\cdot\mathbf{v})=-i\mathbf{q}\mathbf{v}_\mathbf{q}$, since $(\nabla\times\mathbf{v})_\mathbf{q}=-\mathbf{q}\times\mathbf{v}_q=0$; $\mathbf{v}$ is parallel to q, so $\mathbf{v}_q=i\mathbf{q}(\nabla\cdot\mathbf{v})_\mathbf{q}/q^2$. The discussion of the role of surface terms in these relations is standard. Equation (4.37) is used to derive easily

$$\mathbf{v}_\mathbf{q}=\frac{4\pi iA\hat{q}}{\Omega q}\left(\frac{\sin qr_0}{qr_0}\right). \tag{4.38}$$

The particular form of the factor $\sin(qr_0)/(qr_0)$ depends on the abrupt cutoff used at r_0. For long-wavelength phonons (thus for temperatures below the low-temperature peak) with $\lambda\gg a$ this factor is just unity; that is, the waves cannot feel the structure of the core. At temperatures above the peak there are many phonons for which this is not true. There the scattering is considerably reduced; the potential-well analogy used before guarantees that this result is not due to sharp cutoff. In retaining finite Ω in (4.38) periodic boundary conditions are assumed; the precise method used cannot affect the final results. [Incidentally, if one needed $v(r)=v_0$ for $r<r_0$, say, then one should add to the right-hand side of (4.37) $2v_0/r$ for $r<r_0$ and zero for $r>r_0$. None of the essential conclusions following would be altered.]

First let us consider the behavior for long wavelengths. Then Eq. (4.38) gives $v_\mathbf{q}\propto 1/q$. From Eqs. (4.30), (4.33), and (4.42) one concludes that

$$1/\tau\propto q^4\propto\omega^4;\quad \text{small } q. \tag{4.39}$$

This result might have been anticipated (falsely!) from experience with Rayleigh scattering, which varies with frequency as (4.39). However, it is essentially an accident that the result (4.39) was obtained, for the strain-field scattering depends very definitely on the spatial variation of $\mathbf{v}(\mathbf{r})$. Hence the statement that point defects obey (4.39) because the scattering is essentially Rayleigh scattering must be regarded as incorrect for strain fields. (The point is that the strain field is *not* localized.) In fact, we find that the strain-field scattering arising from (4.38) is in general larger than the Rayleigh scattering.

From (4.39) one might conclude that $K(T)\propto T^{-1}$ for point defect scattering at low frequencies; however, for $\lambda\rightarrow 0$, $\tau\propto\lambda^{-4}$ is so large that other processes determine the scattering in these low frequency modes. This problem is discussed in Sec. VI.

Before calculating $1/\tau$ for the displacement field (4.34) let us estimate the constant A measuring the strength of the distortion. If at r_0 the relative atomic misfit is ϵr_0 (r_0 is of the order of interatomic distances for the problems contemplated here), more precisely $v(r_0)\equiv\epsilon r_0$, one has from (4.34)

$$A=\epsilon r_0^3. \tag{4.40}$$

A typical value of ϵ is, say, $\frac{1}{10}$.[38]

Now we take up the evaluation of $|C_{qq'}|^2$. As mentioned before, Eq. (4.29) is appropriate for nearest-neighbor central force interactions in a simple cubic lattice. We further suppose that the energy surfaces of the polarization branches coincide, that $\omega=cq$, $c=$ constant. These simplifications permit the sum over λ' to be performed using the completeness relation

$$\sum_{\lambda=1}^{3} e_\lambda^{(r)}(q)e_\lambda^{(s)}(q)=\delta_{rs}, \tag{4.41}$$

where r, s specify the Cartesian components of the polarization vector $\mathbf{e}_\lambda$. δ_{rs} is zero for $r\neq s$, unity for $r=s$. If further we define $1/\tau=\frac{1}{3}\sum_\lambda 1/\tau_\lambda$, then (4.41) can be used again to remove all of the polarization vectors from the right-hand side of Eq. (4.22) defining $1/\tau$. This shifts the difficulty of handling the polarization vectors to the problem of determining the meaning of the mean relaxation time defined previously.

For simplicity we set r_0 equal to zero in (4.38) and calculate the scattering of a truly "point" defect. The changes brought about by a finite r_0 is then considered. With these simplifying assumptions the mean single-

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[38] Klemens has compiled a table of various parameters such as ϵ, in footnote 33.

mode relaxation time [see Eqs. (4.22) and (4.23)] is

$$\frac{1}{\tau_0}=\frac{1}{\Omega}\frac{g^2A^2q^4}{3\rho^2c^3}\int d\Omega' f(\hat{q},\hat{q}'); \qquad f(\hat{q},\hat{q}')\equiv\frac{\sum_i \hat{q}_i{}^2\hat{q}_i{}'^2(q_i-q_i{}')^4}{|\mathbf{q}-\mathbf{q}'|^4}. \tag{4.42}$$

In the sum i takes on the values x, y, z (taking the coordinate axes along the cube axes). The differential cross section for scattering is proportional to the function $f(\hat{q},\hat{q}')$. $\tau_0{}^{-1}$ reduces to an integral (over the solid angle) of a rather complicated expression. Ω^{-1} may be identified as the density of scatterers, so that if there are σ random scatterers per cc, then (see the following) just replace Ω^{-1} by σ. Because of the considerable uncertainty in the constants g and A, we evaluate (4.42) for the special case of a phonon traveling down one of the cube axes. Then the angular integral is $8\pi/15$ and τ_0 is given by

$$\frac{1}{\tau_0}\approx\frac{8\pi}{45}\sigma\left(\frac{g\epsilon r_0{}^3}{\rho}\right)^2\frac{q^4}{c^3}. \tag{4.43}$$

Whenever possible g should be calculated from an explicit potential, and care must be taken to evaluate the importance of next-nearest neighbors and the particular lattice structure; however, to get an order of magnitude estimate of (4.43) (see Appendix A), one can set $g\approx 24\gamma\rho c^2$ [γ is Grüneisen's constant (roughly equal to 2)] so that (4.43) is

$$1/\tau_0\approx 3\times 10^2\sigma(\gamma A)^2cq^4.$$

The inclusion of γ as a distinct variable is rather superfluous, since other factors whose variation has been neglected vary much more than γ when different materials are compared. It is instructive to compare the present scattering with the "Rayleigh" scattering by a sphere of radius r_0. (Clearly τ_0 is the appropriate relaxation time to use for the calculation of a scattering cross section.) This comparison is made below, where it is concluded that as long as the relative misfit ϵ is appreciably greater than $\frac{1}{10}$, the strain-field scattering is much greater than the "Rayleigh" scattering.

(Now τ_0 is not the appropriate τ to be used in calculating the thermal conductivity, as discussed before. We note in passing the result obtained if the usual assumption is made[2] that the only important term in the expansion of n_q in terms of Legendre polynomials is just $P_1=\cos\theta$ (here θ is the angle between $\mathbf{q}$ and ∇T.) For $\mathbf{q}$ parallel to ∇T, τ is calculated to be 4/7 of τ_0 given by (4.43.)

From his analysis of the resistivity of the associated calcium ion-potassium ion vacancy complex in KCl, Slack[22] deduced the strength of the ω^4 scattering. Klemens[2] pointed out that this value was about seven times as large as expected from his earlier calculation.[33]

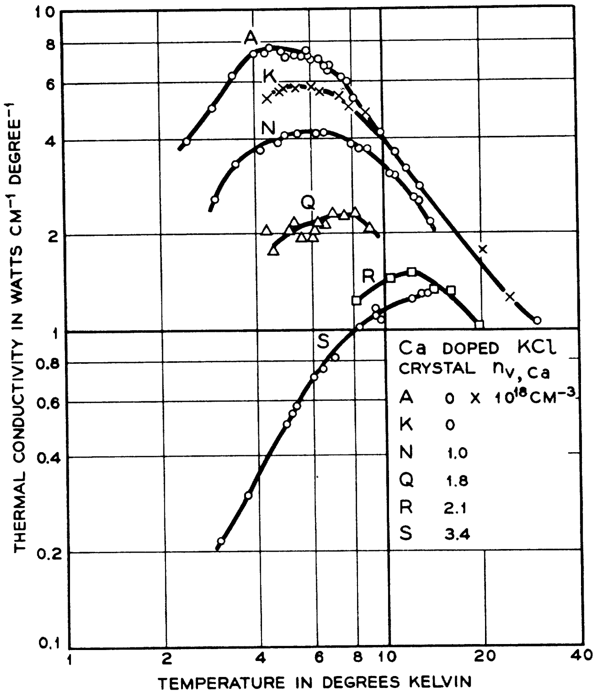

FIG. 3. Thermal conductivity of six KCl crystals containing various concentrations n_v of Ca, as measured by Slack.[22]

It seems that the strain-field scattering calculated here can explain this discrepancy with a modest misfit parameter ϵ of about $\frac{1}{5}$, or if g is twice as large as $24\gamma\rho c^2$, $\frac{1}{10}$. Before this conclusion should be accepted, however, it is necessary to make certain that Slack's method of taking the three-phonon processes into account (taking τ constant[2,39] below $\omega=kT/\hbar$) does not vitiate the result.

Slack's experimental results are shown in Fig. 3. [The curves are much smoother on a linear plot (see footnote 22) but the log-log plot is best for comparison with the other figures herein.] While the depression at temperatures above the maximum is appreciable, the low-temperature depression is enormous, though the data are somewhat incomplete in this region. This behavior is not that expected from pure ω^4 scattering, for which the deprsesions above and below the peak are comparable. (See Fig. 2; actually the most striking illustrations of this latter fact are given in measurements

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[39] In his important paper[39a] of 1951 Klemens noted that for sufficiently low frequencies the three-phonon processes dominate in certain cases. The exact solution was then approximated by considering the contribution of each process separately, but regarding the relaxation times as constant below a certain frequency, chosen as $kT/\hbar$. According to this procedure one can separate the various contributions to the resistivity. It is now clear that this approximation is often very poor, especially for relaxation times which vary strongly with frequency (isotopes, e.g.). Although a much better description of the three-phonon process was made available by the work of Herring[20] in 1954, most published work has continued to use the older approximation. These experiments should be reanalyzed. (a) P. G. Klemens, Proc. Roy. Soc. (London) **A208**, 108 (1951).

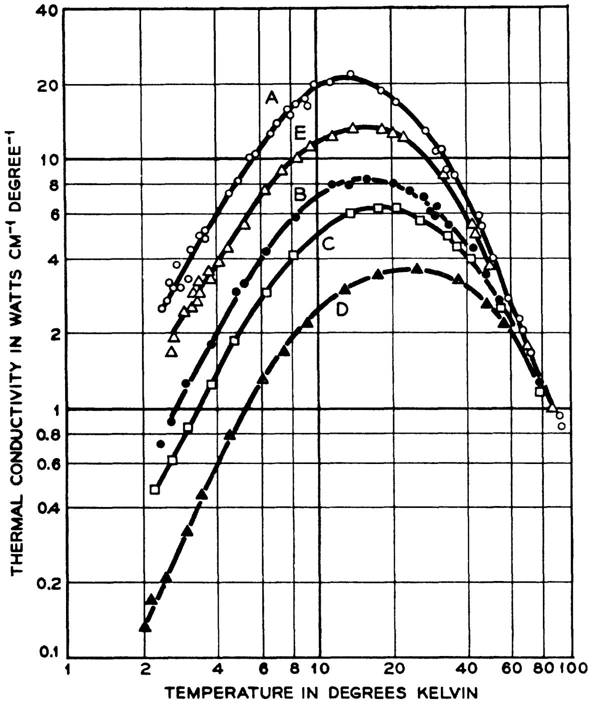

FIG. 4. Thermal conductivity of one crystal of LiF as affected by successive irradiations at room temperature (Pohl[42]). The treatment for each curve is: A, cleaved and annealed (the dimensions are 6.7×7.3×40 mm); B, x rays, $n_F=4.2\times10^{17}$ cm^{-3}; C, x rays, $n_F=7.1\times10^{17}$ cm^{-3}; D, x rays plus 1.5-Mev γ rays, $n_F=2\times10^{18}$ cm^{-3}; E, partly bleached.

of Williams[40] and Toxen.[41]) Although the finite size of the defect causes the reduction of the scattering of high-frequency phonons, this does not occur at temperature below about $\Theta/5$, which is about 50°K in this case. Slack showed that the low-temperature depression was consistent with other evidence that colloidal particles were formed. While further work is needed to make this conclusion firm, the power of thermal conductivity measurements as a tool for exploring lattice defects should be clear from this example. It is the author's opinion that thermal conductivity experiments will reveal many interesting new aspects of defect physics. The reason for this optimism is that in low-temperature thermal conductivity measurements one can measure the scattering of phonons of different frequency merely by varying the temperature. Figure 6 is an especially good example of the sensitivity of the method, as discussed in more detail in the following.

Some interesting features are present in recent experiments by Pohl.[42] F centers were introduced by x-ray and γ-ray irradiation. The results (Fig. 4) are not what one would expect from random point-defect scattering according to $\tau^{-1}\propto\omega^4$, since there is almost no depression on the high-temperature side, but an enormous reduction on the low-temperature side. According to both theory and experiment, the scattering leads to comparable depressions on both sides of the peak. Further, at sufficiently low temperatures the ω^4 scattering decreases so that the various curves become asymptotically tangent. There seems to be no possibility that the curves of Fig. 4 can approach each other.

One can derive qualitative information about the frequency dependence of the scattering from Fig. 6, which compares the F-center data[42] (curves B, C) with the dislocation data of Sproull, Moss, and Weinstock[31] (curves D, E). We anticipate somewhat by asserting that for the dislocations $\tau^{-1}\propto\omega$. Then it is evident that, since the maxima are about the same for the pairs (B, D) and (C, E), the F centers scatter more strongly than dislocations above the peak, and less strongly below. Thus it appears that the relaxation time obeys $\tau^{-1}\propto\omega^2$ or perhaps ω^3. Now how could this happen? One possibility is that irradiation produces the defects in groups having essentially cylindrical geometry. As is evident from Eqs. (4.48)–(4.50), this has the effect of reducing τ^{-1} from ω^4 to ω^3, and also by another factor depending on the precise distribution. If the F centers (interstitials are probably present, too) are indeed randomly distributed, then Pohl's experiments provide evidence that the displacement field has a longer range than (4.36) gives $(1/r^2)$. Now if for some reason

$$\mathbf{v}(\mathbf{r})=A'\mathbf{r}/r^2;\quad A'=\epsilon r_0^2, \tag{4.44}$$

then one finds $\tau^{-1}\propto\omega^2$. A simple calculation almost exactly like that leading to (4.43) shows that for (4.44)

$$1/\tau\approx\tfrac{1}{4}\sigma(gA'/\rho)^2(q^2/c^3), \tag{4.45}$$

where the meaning of the symbols is the same as before. (We have assumed $n_q\propto\cos\theta$ in obtaining this result.) The ratio of (4.45) to 4/7 of (4.43) is roughly $1/(qr_0)^2$ (assuming the same misfit) so that the $1/r$ scattering is appreciably larger than that arising from $v(r)\propto1/r^2$, as expected on physical grounds. Further experiments and calculations are in progress to see which, if any, of these ideas are correct.[43] Another curve obtained by Pohl[42] on the effect of F centers introduced by additive coloration in KCl may be of interest (Fig. 5). (It has not proved possible to color LiF in this way.) Essentially the same behavior is observed as in the irradiation experiments. If precisely the same behavior is observed in more

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[40] W. S. Williams, thesis, Cornell University (unpublished); Phys. Rev. **119**, 1201 (1960).

[41] A. M. Toxen, thesis, Cornell University (unpublished).

[42] R. Pohl (private communication); Phys. Rev. **118**, 1499 (1960). This effect seems to be present also in the work of A. F. Cohen, *Proceedings of the Fifth International Conference on Low Temperature Physics and Chemistry* (University of Wisconsin Press, Madison, Wisconsin, 1958), p. 385. See also footnotes 21 and 40.

[43] By calculations similar to those described following Eq. (6.5), R. Pohl (private communication) has found that curve β of Fig. 8 can be explained by $1/\tau=A\omega^2$, if curve α (the pure crystal) is fit to the proper boundary, three-phonon, and residual ω^4 scattering. The numerical constant A agrees with that indicated in (4.45) with a reasonable misfit $\epsilon=\frac{1}{5}$. This agreement seems to call for a careful study of the displacement field of F centers to see whether the agreement is fortuitous. [Previous calculations have given $v(r)\propto1/r^2$, instead of the $1/r$ implied by (4.45).]

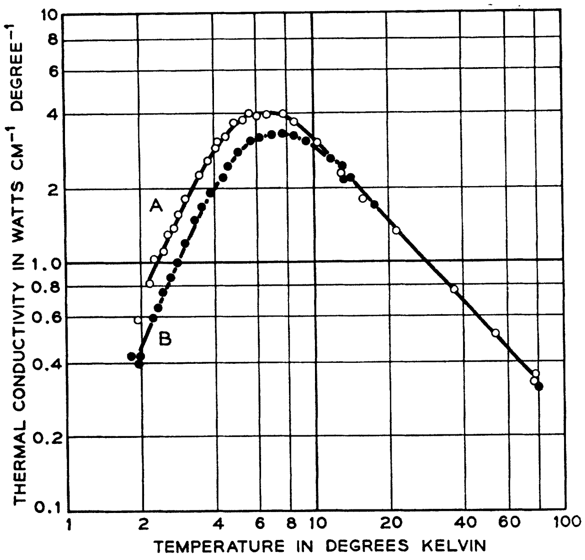

FIG. 5. Thermal conductivity of Harshaw KCl, 4×4.5×40 mm (Pohl[42]). A, cleaved and annealed; B, after additive coloration, F-center density, $n_F = 8\times10^{17}$ cm^{-3}. Since the surface was damaged during the coloration it is not known how much of the low-temperature depression is caused by the change in specular reflection. Since the crystal is rather large, we expect this influence to be small.

complete photochemical and additive coloration experiments, then it seems unlikely that one can invoke arguments such as special characteristics of radiation damage, such as cylindrical distributions. (One must rule out migration to dislocations during additive coloration, however.) In that case one can deduce scattering laws such as (4.45) and then try to understand how they might arise. (Incidentally, the mass-difference effect associated with the F centers is negligible.)

There is evidence against the formation of large clusters in the LiF F-center experiments.[42] Large clusters would be expected to have a frequency-independent cross section. The top curves of Figs. 4 and 6 are not really typical of boundary scattering. There is much specular reflection (the temperature dependence is not T^3), and secondly, the presence of background impurities prevents the maximum from reaching a high sharp peak (see the top curve in Fig. 8). Thus the resemblance of the F-center data to the annealed crystal data is not significant. (In fact, if $1/\tau \propto \omega^3$, then a boundary cutoff is necessary for the low-frequency phonons, so that there is a size dependence.)

For completeness we include the results for screened displacement fields:

$$\mathbf{v}(\mathbf{r}) = (e^{-r/r_1}/r^2)\hat{r}; \tag{4.46a}$$

$$\mathbf{v}(\mathbf{r}) = (e^{-r/r_1}/r)\hat{r}. \tag{4.46b}$$

For (4.46a) the Fourier coefficient is

$$\mathbf{v}_{\mathbf{q}} = 4\pi i\hat{q}(1 - x^{-1}\tan^{-1}x)/q, \tag{4.47a}$$

where x is qr_1; (4.46b) gives likewise

$$\mathbf{v}_{\mathbf{q}} = 4\pi i\hat{q}[\tan^{-1}x - x(1+x^2)^{-1}]/q^2. \tag{4.47b}$$

In the limit $r_1 \to \infty$ the previous results are recovered.

It is simple in principle to consider interference effects of nonrandomly distributed defects.[31] The total displacement at point $\mathbf{m}$ due to defects at positions $\mathbf{n}_\alpha$ is

$$\mathbf{V}_{\mathbf{m}} = \sum_{\mathbf{n}_\alpha} \mathbf{V}(\mathbf{m} - \mathbf{n}_\alpha). \tag{4.48}$$

This supposes that the displacement field is purely a superposition of the displacements of the individual defects. Actually there is a change due to the mutual interactions, so that (4.48) is reliable only if the distance between the various defects is not too small.[37] For a short-range displacement field we can change the coordinates to prove that

$$\mathbf{V}_{\mathbf{q}} = \mathbf{V}_{\mathbf{q}}^{0} \sum_{\mathbf{n}_\alpha} \exp(i\mathbf{q}\cdot\mathbf{n}_\alpha), \tag{4.49}$$

where $\mathbf{V}_{\mathbf{q}}^{0}$ is, as before, the Fourier component of the displacement of a single scatterer. Equation (4.49) is correct if $\mathbf{V}_{\mathbf{m}}^{0}$ does not depend on the orientation of the defect. [For the case of dislocations Eq. (4.49) must be modified.[31]] Thus one must insert under the integral sign of Eq. (4.22) (which determines τ) the form factor

$$F(\mathbf{q} - \mathbf{q}') = \left|\sum_{\mathbf{n}_\alpha} \exp[i(\mathbf{q}' - \mathbf{q})\cdot\mathbf{n}_\alpha]\right|^2. \tag{4.50}$$

For a random array, the interference terms cancel, leaving $F = n$, where n is the number of scatterers.

This correction does not take into account multiple-scattering corrections since we have assumed that the wave approaching each scatterer is just the incident plane wave. This ignores the fact that the waves from the other scatterers are also incident on the chosen defect. In such a case the effective wavelength is changed in a way that often can be described by an index of refraction. The present calculation assumes effectively that for the phonons the index of refraction of the medium is unity. For large concentration of defects this approximation is poor. The uncertainty arising from this is in general much less than that arising from the approximations made in deriving a result such as (4.43), for example. An estimate of such corrections is given in Appendix C, where it is shown that in most experimental situations their importance is probably small.

The form factor $F(\mathbf{q} - \mathbf{q}')$ can be expected to be important when point defects are allowed to migrate in the strain fields of dislocations. The following "ideal" experiment could examine this effect. Suppose one had a number of identical crystals. Deform each under the same conditions; then introduce the same number of point defects in each.

Then the crystals are to be aged for different lengths of time at some temperature which permits substantial diffusion of the introduced point defects. First the strain around the dislocation is somewhat relaxed (but not completely) so that the dislocation scattering is reduced; however, it is possible to have a dislocation density which is both sufficiently low that dislocation scattering is negligible and yet sufficiently high to modify visibly a concentration of point defects large enough to depress the conductivity. We suppose that this is the case, and imagine what might happen as we measure the thermal conductivity of crystals of successively longer aging time. First there would be some constructive interference as the defects became closer, but not so close that their displacement fields are substantially altered. In this case one would expect the conductivity to decrease; however, if the specimen is aged a long time, some precipitation would be expected, so that this "Rayleigh" scattering (smaller than the $1/r^2$ type strain-field scattering) would give less resistance; the conductivity might approach that of a pure crystal if all the defects could be accommodated in the dislocation core. Thus one expects K, as a function of aging time, first to decrease and then to rise to a high asymptotic value.[44]

To understand the tendency of point defects to cluster around dislocations, we quote the elastic energy due to the interaction of a spherical point defect with the dislocation stress field[45] (for an edge dislocation) in an isotropic elastic medium:

$$E=A\sin(\theta)/r, \tag{4.51}$$

where r is the distance of the defect from the center of the dislocation, and A is a constant ($\approx 10^{-20}$ erg cm).

$$\begin{aligned} &A<0 \text{ for a vacancy or undersized atom,}\\ &A>0 \text{ for an oversized atom.}\end{aligned} \tag{4.52}$$

Equations (4.58) say that vacancies move to the region of higher compression.

The Boltzmann factor is

$$n(r,\theta,T)=n_0\exp\left(-\frac{A\sin\theta}{rkT}\right). \tag{4.53}$$

It has recently been shown[46] that Fermi statistics are more appropriate for this problem.

Equations of the type of (4.57) and (4.59) are extremely useful in understanding the migration of point defects in the stress field of an edge dislocation.[47]

Another effect is the clumping together of some of the defects.[22] For example, a vacancy and interstitial generally attract each other, reducing the scattering.

At this point we examine the possible consequences of the fact that for the strain-field scattering of point defects the relaxation time is not pure ω^{-4} [cf. Eq. (4.39)]. In particular, it is instructive to compare this with isotope scattering, which as we see later, should be purely $\tau\propto\omega^{-4}$.

There are essentially two reasons why the scattering of high-frequency phonons is less than estimated by equations such as (4.43). The finite size of any defect has the effect of eliminating the large q components from V_q [e.g., the factor $\sin(qr_0)/(qr_0)$ in Eq. (4.40)] calculated for a point source. The precise way in which this occurs depends upon the detailed structure of the core of the defect, a problem[48] we wish to avoid; however, one can say generally that this detail becomes noticeable when $qa\approx 1$, where a is the range of disorder in which elastic theory is invalid. Secondly, if $qa\approx 1$ (a is a length of the order of a lattice constant), then the expansion of the trigonometric functions [see Eq. (2.14)] which led to (4.29) is no longer valid.

Therefore, at some temperature of about $T\approx\Theta/5$ [cf. Eq. (2.30)] one may expect the strain-field scattering probability to be diminished somewhat. The exact amount of reduction would require a careful investigation. Fortunately, in many cases of interest for thermal conductivity, only the Umklapp scattering is important at such temperatures.

When should one *not* use the theory of strain-field scattering? It was indicated at the beginning of this section that when the displacement field has too short a range, the scattering by the disordered region responsible for the displacements is more important. Now the scattering of long-wavelength waves (i.e., long compared to the dimensions of the disordered region) from such a disordered region is described by the so-called Rayleigh cross section. Hence the magnitude of the strain-field cross section σ_{SF} relative to the Rayleigh cross section σ_R settles this question. To get a rough estimate of σ_{SF} we suppose that the mean-free path l is given by $C\tau_{SF}$; then $\sigma_{SF}=(n\tau c)^{-1}$, where n is the density of point defects. The cross section for the scattering of sound from a sphere of radius r_0 is, when $\lambda\gg r_0$,

$$\sigma_R=(16\pi/9)(\omega^4 r_0^6/C^4).$$

Thus from Eq. (4.45) we have

$$\sigma_{SF}/\sigma_R\approx 150\epsilon^2.$$

So if $\epsilon\gtrsim\frac{1}{10}$, $\sigma_{SF}/\sigma_R>1$. Although there is some uncertainty about the estimate of the anharmonicities it seems that in general one may expect the conclusion to stand. Interstitials may usually be expected to have larger misfits than substitutional atoms. Also, the importance of strain-field scattering is diminished from

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[44] A preliminary experiment of this type has been performed by Miles Klein at Cornell (private communication). A Mn-doped NaCl crystal showed a substantially lower conductivity than the pure crystal (on the low-temperature side of the maximum). After annealing, the conductivity increased to essentially that of the pure crystal.

[45] A. Cottrell, *Dislocation and Plastic Flow in Crystals* (Oxford University Press, New York, 1953), p. 56.

[46] D. N. Beshers, Acta Met. **6**, 521 (1958).

[47] A. H. Cottrell and B. A. Bilby, Proc. Phys. Soc. (London) **A62**, 49 (1949); F. S. Ham, J. Appl. Phys. **30**, 915 (1959).

[48] L. Tewordt, Phys. Rev. **109**, 61 (1958).

that described before if the defects occur as, e.g., an associated vacancy-interstitial (or substitutional atom) pair, as in the experiments of Slack.[22] However, these pairs often have a net ϵ not equal to zero. (The analogous situation in electrostatics is the field of a monopole plus dipole.)

When $\sigma_{SF} \approx \sigma_R$ these two cross sections cannot just be added. When σ_R is dominant the scattering is poorly known, for in addition to the "geometrical" Rayleigh scattering there is scattering due to changes in force constants, etc., near the defect. The very difficult problem of calculating such scattering has been begun by Klemens.[33] He finds that scattering is of the same order as σ_R, as might be expected.

The conclusion is that, when the strain-field scattering dominates, the only major barrier to the calculation of τ is ignorance of the anharmonic force constants, a situation which probably is alleviated in the future by both experimental and theoretical progress.

Dislocations

In this section we treat the scattering of phonons by straight dislocations. Even this idealized case is rather complicated because of the anisotropic nature of the displacement field. Because of this anisotropy the relaxation time is not independent of angle, if only a single dislocation is present in the crystal. However, for an experimentally obtainable situation, there are almost always a sufficient number of dislocations, oriented at sufficiently random angles, that the effective relaxation time is independent of angle.

The first quantitative measurements of the reduction of K due to the introduction of dislocations were made by Sproull, Moss, and Weinstock.[32] (They obtained a reliable estimate of the density of dislocations by using etching techniques developed by Gilman and Johnston.[49]) The results are shown in Fig. 6; the depression is very great on the low-temperature side of the peak.

Since dislocations in crystals generally are in the form of closed loops, it would be interesting to calculate the scattering by a circular loop, which contains all possible ratios of edge and screw components. The displacement field for such loops has been given by Nabarro.[50] In this case the translational symmetry of the straight dislocation is absent, allowing more varied collisions. Such a computation has not yet been performed. For a loop of arbitrary shape the displacement field $\mathbf{V}(\mathbf{r})$ is quite complicated. One expects, however, that the precise shape of the loop is important only when the phonon wavelength becomes as large as the width of the loop. In the case of plastic deformation, this is not generally a problem. In quenched crystals, however, there is evidence that the dislocations are present in small independent loops.[49]

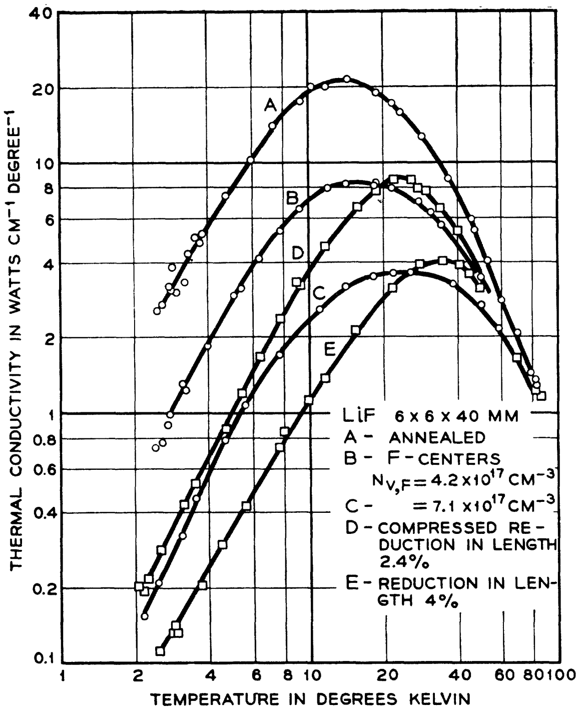

FIG. 6. Comparison of the effect of F centers and dislocations on the thermal conductivity of LiF. Curves A, B, and C are the same as curves A, B, and D of Fig. 4. (The n_v for curve C of Fig. 6 is incorrect.) Curves D and E were obtained by Sproull, Moss, and Weinstock,[32] who compressed LiF crystals. The dislocation densities for curves D and E are $1.8 \times 10^7/\text{cm}^2$ and $4.6 \times 10^7/\text{cm}^2$, respectively, as measured by etch pit counting.[49]

The specific scattering by the core (where the elastic theory expressions are invalid) is in general small. To estimate this scattering we can imagine the core to be a row of vacancies lined up in a row. For an isolated vacancy we expect $\tau^{-1} \propto \omega^4$; however, as mentioned earlier, the lining up introduces translational symmetry, which cuts down the density of states by one factor of ω. Then

$$1/\tau \propto \omega^3 \text{ core scattering.}^{51} \qquad (4.54)$$

The constants could be put in from Eq. (4.47). In the following we find that for dislocations $1/\tau \propto \omega$, so for low temperatures where the phonon wavelength $\lambda \gg a$, the ω^3 dependence and the short-range nature of the strain of the core makes Eq. (4.56) negligible.

The "Rayleigh" scattering cross section (per unit length) of a cylindrical rod is

$$\sigma = (3\pi^2/4)(\omega^3 a^4/C^3). \qquad (4.55)$$

The scattering per atom differs from the point defects case by the factor (ignoring numbers of order unity)

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[49] J. J. Gilman and W. C. Johnston in *Dislocations and Mechanical Properties of Crystals* (John Wiley & Sons, Inc., New York, 1957), p. 116.

[50] F. R. N. Nabarro, Advances in Phys. **1**, 271 (1952).

[51] In footnote 2, Klemens calculates $\tau(\omega)$ by considering the scattering of the core as due to the mass difference of the "vacant" core.

$(C/a\omega)$. For an edge dislocation the displacement field is[52]

$$V_x=\frac{b}{2\pi}\left[\theta+\frac{\sin 2\theta}{4(1-\nu)}\right] \tag{4.56}$$

$$V_y=-\frac{b}{2\pi}\left[\frac{1-2\nu}{2(1-\nu)}\log\left(\frac{r}{r_0}\right)+\frac{\cos 2\theta}{4(1-\nu)}\right] \tag{4.57}$$

$$V_z=0, \tag{4.58}$$

while for a screw dislocation it is

$$V_z=(b/2\pi)\theta \tag{4.59}$$

$$V_x=V_y=0. \tag{4.60}$$

r_0 is the core radius $(r_0\approx a)$, $b(b\approx a)$ is the Burgers vector of the dislocation, ν is Poisson's ratio (a typical value is $\frac{1}{3}$). r, θ are polar coordinates in the xy plane perpendicular to the dislocation axis, chosen to lie in the z direction. For $\theta=\pi/2$, $\mathbf{r}$ lies in the "extra" plane of the edge dislocation. The terms $\sin 2\theta$ and $\cos 2\theta$ arise from satisfying the boundary condition of zero stress on the boundary of a cylinder containing the dislocation.[52]

These equations show that the displacement field has a very long range; indeed, for an edge dislocation v_y increases logarithmically with distance. This peculiarity gives rise to difficulties in the calculation of dislocation scattering; besides the difficulty that the perturbation is not localized, one can expect the net scattering to depend in a critical way on the arrangement of the dislocations. Equally useful for understanding the nature of the strains caused by dislocations are the dilatation $\Delta(\mathbf{x})=\nabla\cdot\mathbf{v}$ and the rotation $\mathbf{R}=\nabla\times\mathbf{v}$. These quantities display the basic difference between edge and screw dislocations:

$$\Delta(\mathbf{x})=-\frac{b}{2\pi}\left(\frac{1-2\nu}{1-\nu}\right)\frac{\sin\theta}{r};\quad R(\mathbf{x})=0;$$

$$\text{for edge dislocations,} \tag{4.61}$$

and

$$\Delta(\mathbf{x})=0;\quad R_x=\frac{b}{2\pi}\frac{\cos\theta}{r};\quad R_y=\frac{b}{2\pi}\frac{\sin\theta}{r};\quad R_z=0;$$

$$\text{for screw dislocations.} \tag{4.62}$$

First we discuss the scattering by a single straight-edge dislocation, using the Born approximation. Even though the long-range nature of the strain may invalidate this approximation, it seems desirable to give a careful discussion of this method, in order to understand the results of any more sophisticated calculation.[53] In order to make the analysis consistent we supply (implicitly) a damping factor $e^{-\mu r}$ to the strain field in order to remove any ambiguity in the handling of surface integrals. Then the limit $\mu\rightarrow 0$ is taken. This procedure accounts crudely for the fact that finite crystals have zero net surface strain; a phonon created at the surface is influenced by the strain field only gradually. This, however, does not guarantee the validity of the simple theory. We return to this point again.

With the foregoing prescription for ignoring surface integrals, one can use (4.61) to find the fundamental quantity $\mathbf{v}_q$. First of all $\mathbf{R}(\mathbf{x})=0$ implies that $\mathbf{v}_q$ is parallel to $\mathbf{q}$.

Define A by the equation $\Delta(\mathbf{x})=A\sin\theta/r$. The Fourier transform of $\sin\theta/r=y/(y^2+x^2)$ is easily performed using Cauchy's theorem. For convenience the volume Ω is considered finite although the domain of integration is all of two-dimensional space; this affords an easy way to keep the dimension straight. At the end the extension $\Omega\rightarrow\infty$ is trivial. On integrating first over x, one obtains

$$\int_{-\infty}^{\infty}dy\int_{-\infty}^{\infty}dx\,e^{ixq_x+iyq_y}\left(\frac{y}{y^2+x^2}\right)$$

$$=\pi\int_{-\infty}^{\infty}dy\frac{y}{|y|}e^{iyq_y-|yq_x|}. \tag{4.63}$$

Thus

$$\left(\frac{\sin\theta}{r}\right)_q=\frac{2\pi i q_y}{(q_x^2+q_y^2)}=\frac{2\pi i\sin\varphi}{q}. \tag{4.64}$$

In (4.64) we have defined φ by $q_y=q\sin\varphi$; here q is actually the two-dimensional "transverse" q. In using this result we must supply $\mathbf{v}_\mathbf{q}$ with a factor $\Delta(q_z)$ resulting from integrating in the z direction; also a factor $\Omega^{-\frac{2}{3}}$ is needed. On recalling our previous assumptions about the surface terms, one may use $\Delta_\mathbf{q}=-iqv_\mathbf{q}$ to obtain

$$\mathbf{v}_\mathbf{q}=-(2\pi A\sin\varphi\mathbf{q}/\Omega^{\frac{2}{3}}q^3)\Delta(q_z)\ \text{(edge dislocation)}. \tag{4.65}$$

Since in using (4.65) we need $\mathbf{v}_{\mathbf{q}'-\mathbf{q}}$, the conservation of q_z permits the q and q^2 to be interpreted as the difference of the *three*-dimensional vectors $(\mathbf{q}'-\mathbf{q})$, etc. For the screw dislocation only the transform of $\cos\theta/r$ is needed. This is easily obtained from (4.64) by the substitution $\sin\varphi\rightarrow\cos\varphi$. Since $\cos\theta/r=x/(x^2+y^2)$, a change of (dummy) variables $x\leftrightarrow y$ leaves (4.63) unchanged if $q_x\leftrightarrow q_y$. Examination of (4.64) gives the quoted result.

To evaluate $1/\tau=\frac{1}{3}\sum 1/\tau_\lambda$, we use the assumptions used in the discussion of point defects. By symmetry we expect the dislocation to lie along a crystallographic axis (called z) and so that again the 2 vectors point in the xyz directions. Making the transition to the continuum

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[52] W. T. Read, Jr., *Dislocations in Crystals* (McGraw-Hill Book Company, Inc., New York, 1953), Chap. 8.

[53] A similar situation occurs in ordinary Coulomb scattering. Fortunately in this case the Born approximation gives the same result as the more careful analysis.

using $[\Delta(q_z)]^2 \rightarrow 2\pi\delta(q_z)/L$, where $L=\Omega^{\frac{1}{3}}$, noting that

$$\sum_{\lambda,\lambda'} |C_{qq'}|^2 = B^2 \frac{(q_y'-q_y)^2}{|\mathbf{q}'-\mathbf{q}|^8} \times [q_x^2 q_x'^2 (q_x'-q_x)^4 + q_y^2 q_y'^2 (q_y'-q_y)^4], \quad (4.66)$$

$$B \equiv \Omega g b a; \quad \alpha \equiv (1-2\nu)/(1-\nu), \quad (4.67)$$

one finds after some straightforward but tedious manipulations the Boltzmann equation

$$\mathbf{C}\cdot\nabla T \frac{dN^0}{dT} = \frac{1}{\Omega^{\frac{2}{3}}} \left(\frac{gb\alpha}{\rho}\right)^2 \frac{q(1-q_z^2/q^2)}{24\pi c^3} \times \int d\varphi' F(\varphi,\varphi')(n_q'-n_q). \quad (4.68)$$

The polarization dependence of n_q' has been ignored; further, $\mathbf{C}$ represents an average sound velocity. $F(\varphi,\varphi')$ is defined by

$$F(\varphi,\varphi') = \tfrac{1}{16}\cos^2\varphi I_1 + \tfrac{1}{16}\sin^2\varphi I_2,$$

$$I_1 = \left[\frac{1+\cos(\varphi+\varphi')}{1-\cos(\varphi'-\varphi)}\right] \times \cos^2\varphi' [1-\cos(\varphi'+\varphi)]^2, \quad (4.69)$$

$$I_2 = \left[\frac{1+\cos(\varphi+\varphi')}{1-\cos(\varphi'-\varphi)}\right] \sin^2\varphi' [1+\cos(\varphi'+\varphi)]^2.$$

$F(\varphi,\varphi')$ has a pole of the second order at $\varphi=\varphi'$ which is a direct consequence of the long range of the dislocation strain field, reflected in the q dependence of the Fourier coefficients. As in the case of Coulomb scattering this implies a large forward scattering; in fact, perturbation theory is invalid for $\varphi \approx \varphi'$. These processes do not contribute appreciably to the resistivity, however [cf. the factor $n_q'-n_q$ in (4.68)] so that as long as higher-order processes are small one may expect the solution of (4.68) to be a reasonable approximation to reality. (It would be of interest to do the problem without using plane waves as the zeroth-order eigenfunctions.)

The complicated angular dependence of the kernel $F(\varphi,\varphi')$ makes the solution of (4.68) formidable and we do not attempt it. If one defines a relaxation time as minus (4.68) divided by n_q, then one finds that, because of the strong forward scattering, the "standard assumption"

$$n_q'-n_q \propto \boldsymbol{\lambda}\cdot(\hat{q}'-\hat{q}) = \lambda_x(\cos\varphi'-\cos\varphi) + \lambda_y(\sin\varphi'-\sin\varphi)$$

cannot be valid, because $\tau(q)$ becomes *negative* at certain angles. (Moreover, the integral converges only upon taking the principal value; such a definition is called for in this case but the result then depends rather critically on the particular assumption about the form of n_q. The author has evaluated these integrals but they are not reproduced, since they are probably not significant.) The effect of the long range of the strain is to peak n_q more strongly about the forward direction than is allowed for in the standard assumption.

As we see later, the introduction of arrays of dislocations does not eliminate the pole in $F(\varphi,\varphi')$. A possible procedure is to average over φ (roughly equivalent to a random array of dislocations with total Burgers vector equal to zero) but then one has to deal with the quantity $\langle Fn \rangle$, where n is still unknown. [Note that the standard assumption would give zero average, since the integral (4.68) would be odd on interchange of φ, φ'.]

We meet this situation with the tentative arbitrary assumption with regard to the factor $1-n_q'/n_q$; this choice is motivated by two essential qualitative features: the net scattering probability $1/\tau$ must be positive definite, and there should be no unphysical contribution from the forward scattering pole. The simplest choice with these properties is clearly

$$(1-n_q'/n_q) = 1-\cos(\varphi'-\varphi).$$

This is no acceptable substitute for a rigorous solution of (4.68) (suitably modified to account for other processes), nevertheless, if the basic equation (4.68) is adequate then the result obtained should be at least semiquantitative. With this arbitrary assumption the details of the angular (φ) dependence of $1/\tau$ are no longer significant so that we average over φ in (4.68) after performing the φ' integration.

This average is easily performed and gives for minus the integral in (4.68) over n_q the result $25\pi/128$. Assuming for the moment that the dislocations are randomly arranged with $\sigma=N/\Omega^{\frac{2}{3}}$ per unit area, one has for the average relaxation time[54] (this average hides a multitude of sins!)

$$1/\tau \cong (\sigma/128C^3)(gb\alpha/\rho)^2 q(1-q_z^2/q^2). \quad (4.70)$$

The q dependence of τ is $\tau^{-1} \propto q$ so that when dislocation scattering dominates all other processes one expects the temperature dependence

$$K \propto T^2. \quad (4.71)$$

Experimentally, this behavior is observed below the low-temperature peak in crystals containing a sufficient number of dislocations.[32,55] Although the scattering is quite strong in this region, (4.70) is negligible above the peak in comparison with other processes, which increase more rapidly with frequency (or with temperature). When dislocation scattering is the only important

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[54] The reader should be warned against the conclusions reached in Sec. II of footnote 34. The method used there violates periodic boundary conditions and so introduces a singularity into the strain field, resulting in a large cross section. Dr. H. Bross, Dr. C. Herring, and Dr. J. Ziman are thanked for enlightening conversions on this problem.

[55] J. N. Lomer and H. M. Rosenberg, Phil. Mag. 4, 467 (1959); W. Kemp, P. G. Klemens, and R. Tainsh, *ibid.* 4, 845 (1959).

resistive mechanism one has with $1/\tau = Dq$ (average first over q_z so that $\langle q_z^2\rangle/q^2=\frac{1}{3}$), where D is given by (4.70) from Eq. (3.32):

$$K_D=[3k^3\zeta(3)/\pi^2\hbar^2D]T^2, \tag{4.72}$$

where we have used the result (safely putting the upper limit equal to infinity)

$$\int_0^\infty \frac{x^3e^x}{(e^x-1)^2}dx=6\zeta(3).$$

$\zeta(3)$ is the Riemann zeta function of argument 3. It is equal to 1.202. In the general case, (4.72) is not valid and one must proceed as described in Sec. VI.

For screw dislocations $1/\tau$ is not very different from (4.70).

In trying to compare (4.72) with experiment, we are crippled by lack of accurate knowledge of the anharmonic coupling characterized by the constant g. For the simple Grüneisen model described in Appendix A, with $g\approx 24\gamma\rho C^2$ and $\alpha=\frac{1}{2}(\nu=\frac{1}{3})$, one has

$$1/\tau\approx\sigma\gamma^2b^2\omega \tag{4.73}$$

This agrees with the earlier calculation of Klemens[33] (with a revised value of the couplings[2]), who used a Grüneisen-type model for the anharmonic coupling. However, in making this approximation we have lost the advantage of working directly with the atomic force constants. In fact, the experiments of Sproull, Moss, and Weinstock[32] on the resistivity of dislocations in LiF show (4.73) to be too small by roughly the factor 100. Experimental results for other substances[2,55] do not show such a large discrepancy; usually (4.73) is too small by a factor of 4 to 6. As shown by the present calculation, consideration of more distant couplings and differences in lattice structure might account for this latter factor. If the large resistivity of dislocations in LiF is due to stronger anharmonicities, then the effective g in LiF is roughly four times as great as in other substances.[56] Dislocation experiments in other alkali halides would be useful for settling this point.

The large thermal resistivity of dislocations in LiF is not understood at the present time.

Two other points must not be forgotten. These are that the validity of the Born approximation is somewhat uncertain because of the long range of the dislocation strain field (although this difficulty is somewhat obviated in calculating the *net* scattering probability) and secondly, that dislocations tend to be arranged in definite arrays in crystals. Further work needs to be done on both of these problems; we discuss both and give a few useful formulas.

As to the convergence of the perturbation series, the second-order correction to the scattering matrix element is obtained by replacing $C_{qq'}$ by ($iC_{qq'}$ is real)

$$C_{qq'}+\frac{1}{2\rho\Omega}\sum_{q''}\frac{C_{qq'}C_{q''q'}(N_q''+1)}{\omega_q''(\omega_q-\omega_q'')}. \tag{4.74}$$

This is used in Eq. (4.18) which supplies an automatic cutoff for forward scattering. Since $C_{qq'}$ is of the form $f(q,q')(|\mathbf{q}-\mathbf{q}'|)^{-1}$, where $f(q,q')$ is regular, the singularities of the integrand have the form

$$[(|\mathbf{q}''-\mathbf{q}|)(|\mathbf{q}''-\mathbf{q}'|)(\omega_q-\omega_{q''})]^{-1}. \tag{4.75}$$

The term in the sum $q''=q$ is to be omitted; the zero of the energy denominator is handled in the standard way. (The poles in general do not coincide when q and q'' belong to different polarization branches.) When q and q'' belong to the same branch the integral still converges by use of the principal value for the angular part ($|\mathbf{q}''-\mathbf{q}|=2q\sin\frac{1}{2}(\varphi''-\varphi)$ in this case when $|\mathbf{q}|=|\mathbf{q}''|$, e.g.). When $\mathbf{q}$ is near $\mathbf{q}'$ (forward scattering) the problem requires special study; we suppose that the factor $n_{q'}-n_q$ in (4.18) cancels any such singularities. The structure of the general term is similar to the simple example just discussed. Thus while there are probably no infinities in the expansion, the contributions from the various poles (due to the long range strain) are larger than one might expect.

On examining the effect of lining up dislocations in arrays, we consider only parallel edge dislocations to simplify the discussion. Suppose the dislocations are at positions $\boldsymbol{\varrho}_i$ and have orientation φ_i with respect to the x axis (the angle between the x axis and the Burgers vector is φ_i). Then if θ_i is the angle between $\mathbf{r}-\boldsymbol{\varrho}_i$ and the x axis, the total dilatation at the position $\mathbf{r}$ is

$$\Delta(\mathbf{r})=A\sum_i\frac{\sin(\theta_i-\varphi_i)}{|\mathbf{r}-\boldsymbol{\varrho}_i|};\quad A=-(b\alpha/2\pi). \tag{4.76}$$

We consider only the case where $\varphi_i=0$. This corresponds roughly to the situation in plastically deformed crystals, e.g., but not in quenched crystals, where the dislocations seem to be randomly distributed. With this assumption we can write (4.76) as

$$\Delta_{\text{total}}(\mathbf{r})=\sum_i\Delta_i(\mathbf{r}-\mathbf{r}_i). \tag{4.77}$$

Hence the Fourier coefficient of Δ_{total} is

$$\Delta_{\text{total}}(\mathbf{q})=\Delta_{\mathbf{q}}\sum_i e^{i\mathbf{q}\cdot\mathbf{r}_i}. \tag{4.78}$$

Hence $\mathbf{v}_\mathbf{q}$ is modified by the form factor, which factors out of the quantity $C_{qq'}$. If the positions $\mathbf{r}_i$ are random then the square of the form factor is just equal to the number of dislocations, a result previously used in writing Eq. (4.70).

If we have $2N'+1$ parallel equidistant dislocations (an idealized model of a slip plane) at positions $x_n=nd$;

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[56] The details of the LiF structure are such that it is essential to take into account next-nearest neighbors. This can account for as much as an order of magnitude in the scattering power. A study of deformation vs quenching could reveal the influence of the distribution of dislocations in a crystal.

$-N'\leq n\leq N'$, then one finds easily

$$\Delta_{\mathrm{total}}(\mathbf{q})=-\Delta_{\mathbf{q}}\frac{\sin[(N'+\frac{1}{2})qd\cos\varphi]}{\sin[\frac{1}{2}qd\cos\varphi]}e^{-\frac{1}{2}iqd\cos\varphi}. \tag{4.79}$$

The phase factor may be neglected. The form factor in (4.79) is familiar from the study of diffraction gratings. However, we are here interested in the case in which the wavelength is much less than the spacing d. Let us call the total number of dislocations $N=2N'+1$. Then we must examine the behavior of the function

$$F(y)=\sin^2(Ny)/\sin^2 y;\quad y=\tfrac{1}{2}qd\cos\varphi. \tag{4.80}$$

$F(x)$ has sharply peaked maxima at $x=m\pi$, m an integer. These peaks are of height N^2, and have width of order $1/N$. The area under each is roughly $N\pi$, so that the total scattering by the array is proportional to N (only a finite number of peaks contributes). For large N we may simplify by using the relation

$$\lim_{N\to\infty}\frac{1}{\pi N}\frac{\sin^2 Nx}{x^2}=\delta(x), \tag{4.81}$$

so, approximately,

$$|\Delta_{\mathrm{total}}(\mathbf{q})|^2=\frac{2\pi N}{d}|\Delta_{\mathbf{q}}|^2\sum_{n=-\infty}^{\infty}\delta\left(q_x-\frac{2n\pi}{d}\right). \tag{4.82}$$

In actual problems $\lambda<d$ so that $|n|<d/\lambda$ in the use of the summation (4.82). Thus if $F(\varphi,\varphi')$ is slowly varying, (4.82) is very roughly d/λ times the contribution of one delta function. If we use $q=2\pi/\lambda$ and extract $q_x=qx$ (angular factor) from the remaining δ function, we have to order of magnitude

$$|\Delta_{\mathrm{total}}(q)|^2\sim\frac{2\pi N}{d}|\Delta_d|^2\cdot\frac{d}{\lambda}\cdot\frac{1}{q}\sim N|\Delta_q|^2. \tag{4.83}$$

Thus the scattering is again approximately equal to that of N independent scatterers. If we define $G(\varphi,\varphi')=F(\varphi,\varphi')(1-n_{q'}/n_q)$, then [Eq. (4.68)] a more exact expression is, putting $\mathbf{q}'-\mathbf{q}$ into the result (4.82),

$$\left(\frac{1}{\tau_N}\right)=\left(\frac{2\pi N}{q_1 d}\right)\frac{\sum_n G(\varphi,\varphi_n)|\sin\varphi_n|^{-1}}{\int G(\varphi,\varphi')d\varphi'}\left(\frac{1}{\tau_1}\right). \tag{4.84}$$

τ_N denotes the relaxation time for N dislocations, τ_1, for one. The quantity φ_n is given by

$$\varphi_n=\cos^{-1}[\cos\varphi-(2n\pi/q_1 d)], \tag{4.85}$$

and q_1 is the magnitude of the transverse part of q.

We do not discuss (4.84) further, but regard (4.83) as adequate for present purposes.

The scattering of N parallel equidistant dislocations arranged in a slip plane, even for large N, is quite different from that of an *infinite* number of them. The physical reason is that an (unlocalized) plane wave spends most of its time, as it were, at distances far from the dislocation array, at which position the strain looks more or less like that of N dislocations at the origin. On the other hand, if there are truly an infinite number of dislocations, then the lattice is perfect above and below the array, though with different densities. We prove the following remarkable result: the scattering by an infinite array is exactly equal to that of a single dislocation (except for the density variation, Appendix E). Although this is rather a useless result it illustrates the care that must be used in such problems. The dislocations are located at the positions $y=0$, $x=nd$. From (4.76) we have

$$\Delta_{\mathrm{total}}(x,y)=Ay\sum_{-\infty}^{\infty}\frac{1}{y^2+(x-nd)^2}. \tag{4.86}$$

The sum is easily evaluated using complex variable theory. The sum is equal to

$$\frac{\pi}{2iyd}\left\{\cot\left[\frac{\pi(x-iy)}{d}\right]-\cot\left[\frac{\pi(x+iy)}{d}\right]\right\}. \tag{4.87}$$

Simplification then gives

$$\Delta_{\mathrm{total}}(x,y)=\frac{\pi A}{d}\frac{\sinh(2\pi y/d)}{\cosh(2\pi y/d)-\cos(2\pi x/d)};\quad\text{infinite array.} \tag{4.88}$$

As y becomes as large as the spacing between dislocations, the dilatation becomes constant:

$$\begin{aligned}\Delta_{\mathrm{total}}&\to\pi A/d & y>d,\ & y>0\\ &-(\pi A/d) & y<d,\ & y<0.\end{aligned} \tag{4.89}$$

This constant dilatation means that there is little or no scattering from regions for which $|y|>d$. For constant y, Δ varies periodically with x. The minimum occurs when $x=(n+\frac{1}{2})d$, the maximum for $x=nd$. In fact, we note the curious result

$$\Delta_{\max}\cdot\Delta_{\min}=A^2=\text{const (fixed } y). \tag{4.90}$$

Let us introduce the variables $u=2\pi x/d$, $v=2\pi y/d$, $k_x=dq_x/2\pi$, $k_y=dq_y/2\pi$. Then the transform of (4.88) is

$$\begin{aligned}\Delta_{\mathrm{total}}(\mathbf{q})&=\frac{Ad}{4\pi}\int_{-\infty}^{\infty}dve^{ivk_y}\sinh v\\ &\quad\times\int_{\infty}^{\infty}due^{iuk_x}\left(\frac{1}{\cosh v-\cos u}\right)\\ &=\frac{Ad}{2}\int_{-\infty}^{\infty}dve^{ivk_y-|vk_x|}\epsilon(v);\end{aligned} \tag{4.91}$$

$$\begin{aligned}\epsilon(v)&=1, & v>0\\ &=-1, & v<0.\end{aligned}$$

$$\Delta_{\mathrm{total}}(\mathbf{q})=A\cdot(2\pi iq_y/q^2).$$

From (4.64) we see that the statement is proved.

Next we consider the scattering by a small-angle grain boundary, using the usual model of an infinite array of equidistant edge dislocations.[45,52] This arrangement is obtained by rotating each dislocation of the preceding problem in the same direction by 90°. Then one has

$$\Delta(x,y)=A\sum_{-\infty}\frac{(y-nd)}{x^2+(y-nd)^2};\quad \text{grain boundary.} \tag{4.92}$$

The sum in (4.92) is

$$\frac{\pi}{d}\left\{\cot\left[\frac{\pi(y-ix)}{d}\right]+\cot\left[\frac{\pi(y+ix)}{d}\right]\right\}, \tag{4.93}$$

which can be rearranged to yield

$$\Delta(x,y)=\frac{\pi A}{d}\frac{\sin(2\pi y/d)}{\cosh(2\pi x/d)-\cos(2\pi y/d)}. \tag{4.94}$$

The important feature of (4.94) is that

$$\Delta(x,y)\propto e^{-2\pi x/d};\quad x>d, \tag{4.95}$$

so that the strain has a very short range. It is obvious that the dislocations should saturate each other's strain fields. From (4.94) Δ_q is equal to that of a single-edge dislocation; thus the scattering by small-angle grain boundaries is generally negligible. This explains why annealing crystals that contain large numbers of dislocations can restore the conductivity to that of the original undeformed crystal.[32] So far we have ignored the fact that the lattice has a different orientation on the two sides of the grain boundary. This results in a rotation of the lattice, and if the angle of the grain boundary is sufficiently small, one can proceed as before (i.e., if the rotation is too abrupt, perturbation theory fails). The scattering is still small. The first calculation of scattering by grain boundaries was made by Klemens.[33] In approximating the sum (4.92) by an integral he obtained $\Delta=0$, however.

Some results for other arrays of interest are now given. For an infinite array of screw dislocations (parallel, lying in the same plane a distance d from each other) one finds

$$R_x(x,y)=\frac{b}{2d}\frac{\sin(2\pi x/d)}{\cosh(2\pi y/d)-\cos(2\pi x/d)}\longrightarrow e^{-2\pi y/d},\quad y>d; \tag{4.96}$$

$$R_y(x,y)=\frac{b}{2d}\frac{\sinh(2\pi y/d)}{\cosh(2\pi y/d)-\cos(2\pi x/d)}\longrightarrow\frac{b}{2d},\quad y\longrightarrow\infty. \tag{4.97}$$

The dislocations from a Frank-Read source[46] have opposite signs on opposite sides of the source. Thus one might desire Δq for an array of parallel edge dislocations, positive at $x=nd$, $n=1, 2, \cdots, N$ and negative at $x=-nd$, $n=1, 2, \cdots, -N$ (none at the origin). This is given by

$$\Delta_{\text{total}}(q)=\Delta_q\left\{\frac{\cos[(N+\frac{1}{2})qd\cos\varphi]-\cos[\frac{1}{2}qd\cos\varphi]}{\sin[\frac{1}{2}qd\cos\varphi]}\right\}. \tag{4.98}$$

Much remains to be done on determining $\mathbf{v}_q$ (or Δ_q) for more realistic arrays (and shapes) of dislocations.

Finally, consider dislocations piled up at an obstacle (Cottrell[42]). As an example, we take parallel edge dislocations located at positions $x_n=n^2d$, $n=0, 1, 2, \cdots$, and arbitrarily give the dislocation at $x_n=0$ half-strength (this may be trivially modified). On measuring all lengths in terms of the parameter d, one finds

$$\Delta(x,y)=\frac{Ay}{2r\pi}\left[\frac{\sinh(2\beta)/2\beta}{\cosh 2\alpha-\cos 2\beta}-\frac{\sin(2\alpha)/2\alpha}{\cosh 2\beta-\cos 2\alpha}\right] \tag{4.99}$$

with

$$\alpha\equiv[(r+x)/2]^{\frac{1}{2}},\quad \beta=[(r-x)/2]^{\frac{1}{2}},\quad r=(x^2+y^2)^{\frac{1}{2}}. \tag{4.100}$$

Figure 6 demonstrates clearly the power of thermal conductivity measurements as a tool for exploring the defect structure of insulating crystals. With some further refinements of both theory and experiment, such measurements contribute greatly to the understanding of the nature, distribution, and structure of lattice defects.

V. MASS-DIFFERENCE SCATTERING (ISOTOPE EFFECT)

That fluctuations in the mass distribution throughout a crystal cause thermal resistance was first pointed out by Pomeranchuk[57] who quoted the correct mass and frequency dependence of $\tau(\omega)$. The formula was derived later by Klemens,[33] who also gave the correct numerical factors. This mass difference can arise from the presence of isotopes, vacancies, and interstitials, among other imperfections. Typical experimental evidence for these effects is given in footnotes 22 and 24.

It is convenient to separate the Hamiltonian as follows:

$$H=\sum_{\mathbf{n}}\tfrac{1}{2}M_n\dot{\mathbf{U}}_{\mathbf{n}}^2+V_2 \tag{5.1}$$

$$H\equiv H_0+H'. \tag{5.2}$$

The harmonic potential V_2 is assumed to be unchanged (valid for isotopes):

$$H_0\equiv\sum_{\mathbf{n}}\tfrac{1}{2}\bar{M}\dot{\mathbf{U}}_{\mathbf{n}}^2+V_2; \tag{5.3}$$

$$H'\equiv\sum_{\mathbf{n}}\tfrac{1}{2}(M_{\mathbf{n}}-\bar{M})\dot{\mathbf{U}}_{\mathbf{n}}^2. \tag{5.4}$$

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[57] I. Pomeranchuk, J. Phys. U.S.S.R. **5**, 237 (1942).

$\bar{M}$ is the average mass

$$M \equiv \sum_i f_i M_i = \frac{1}{N} \sum_{\mathbf{n}} M_{\mathbf{n}}, \tag{5.5}$$

where f_i is the fraction of unit cells having mass M_i. N is the number of unit cells in the crystal. We now discuss the physical meaning of this separation. The lowest-order energy shift due to H' is zero, so that to this order the phonon frequencies are correctly chosen. The use of $\bar{M}$ in the unperturbed problem corresponds to the fact that in the range of most interest (long wavelengths) the phonons do "see" only the average mass. This seems to be the best one can do without giving a detailed solution of the vibrational problem.[58] A similar procedure due to Nordheim has been used in calculating the electrical resistivity of alloys.[59] In this case one uses the average potential.

On introducing the expansion (1.4) for $\mathbf{U}_n$,

$$\dot{\mathbf{U}}_{\mathbf{n}} = -i \sum_q \left(\frac{\hbar\omega_q}{2\rho\Omega}\right)^{\frac{1}{2}} \times [a_q \exp(i\mathbf{q}\cdot\mathbf{n}) - a_q^* \exp(-i\mathbf{q}\cdot\mathbf{n})]\mathbf{e}_q, \tag{5.6}$$

the energy conserving part of H' is then

$$H' = \frac{\hbar}{4\rho\Omega} \sum_{qq'} (\omega_q\omega_{q'})^{\frac{1}{2}} a_q a_{q'}^* \times \{\sum_{\mathbf{n}} \Delta M_{\mathbf{n}} \exp[i(\mathbf{q}-\mathbf{q}')\cdot\mathbf{n}]\}\mathbf{e}_q\cdot\mathbf{e}_{q'} + \text{H.c.}; \tag{5.7}$$

$$\Delta M_{\mathbf{n}} \equiv M_{\mathbf{n}} - \bar{M}. \tag{5.8}$$

Thus the scattering of a phonon from state q to q' is described by the matrix element (here we set $\omega_q = \omega_{q'}$)

$$M'_{q\to q'} = \frac{\hbar\omega_q}{2\rho\Omega} m_{\mathbf{q}-\mathbf{q}'} \mathbf{e}_q\cdot\mathbf{e}_{q'} [N_q(N_{q'}+1)]^{\frac{1}{2}}, \tag{5.9}$$

with

$$m_{\mathbf{q}-\mathbf{q}'} \equiv \sum_{\mathbf{n}} \Delta M_{\mathbf{n}} \exp[i(\mathbf{q}-\mathbf{q}')\cdot\mathbf{n}]; \tag{5.10}$$

$$\left(\frac{\partial N_q}{\partial t}\right) = \frac{\omega_q^2}{16\pi^2\rho^2\Omega} \int d^3\mathbf{q}' \sum_{\lambda'} \delta(\omega_q - \omega_{q'}) |m_{\mathbf{q}-\mathbf{q}'}|^2 \times (\mathbf{e}_q\cdot\mathbf{e}_{q'})^2 (n_{q'} - n_q). \tag{5.11}$$

The beauty of (5.11) lies in the fact that there are few of the unknown quantities that make the calculation of strain field scattering so difficult. For low frequencies, however, the scattering indicated by (5.11) is in general less than for other processes. The completeness relation (4.41) permits a great simplification of (5.11) if the relatively modest assumption is made that the energy surfaces of the different polarization branches coincide, and further that $n_{q'}$ is independent of polarization. In general the energy surface has a rather different shape for longitudinal and transverse phonons.[20] To do better than the preceding average one must examine specific crystal structures. The fit made by Callaway[28] to the isotope scattering data of Geballe and Hull[23] suggests that for germanium, at least, this average is a good approximation.

The completeness relation gives

$$\sum_\lambda (\mathbf{e}_q\cdot\mathbf{e}_{q'})^2 = 1.$$

Hence the single-mode relaxation time (set $n_{q'}$ equal to zero) is

$$\frac{1}{\tau_0} = \frac{\omega^2}{16\pi^2\rho^2\Omega} \int d^3\mathbf{q}' \delta(\omega - \omega') |m_{\mathbf{q}-\mathbf{q}'}|^2. \tag{5.12}$$

In order to calculate $|m_{\mathbf{q}-\mathbf{q}'}|^2$ it is necessary to specify the array of scatterers. We evaluate this factor for randomly distributed defects; such an approximation may be expected to be better for isotopes than for vacancies, for example. Separating the terms for which $\mathbf{n} = \mathbf{n}'$, one has the equation

$$|m_{\mathbf{q}-\mathbf{q}'}|^2 = \sum_{\mathbf{n}} (\Delta M_{\mathbf{n}})^2 + \sum_{\mathbf{n}'\neq\mathbf{n}} \Delta M_{\mathbf{n}'} \Delta M_{\mathbf{n}} \exp[i(\mathbf{q}-\mathbf{q}')\cdot(\mathbf{n}-\mathbf{n}')].$$

The second term vanishes for a random distribution;

$$\sum_{\mathbf{n}} (\Delta M_{\mathbf{n}})^2 = N \sum_i f_i (\Delta M_i)^2,$$

where we repeat that the deviation ΔM_i is measured with respect to the *mean* mass $\bar{M}$.

Therefore Eq. (5.12) reduces to[59]

$$\frac{1}{\tau_0} = \frac{\omega^2\Omega_0\Gamma}{16\pi^2} \int d^3\mathbf{q}' \delta(\omega_q - \omega_{q'}); \qquad \Gamma = \sum_i f_i \left(1 - \frac{M_i}{\bar{M}}\right)^2. \tag{5.13}$$

The integral in (5.13) is essentially the density of states $n(\omega)$ in ω space:

$$\int d^3\mathbf{q}' \delta(\omega_q - \omega_{q'}) = \int dS' \left|\frac{\partial\Delta\omega}{\partial q_n'}\right|^{-1} = 4\pi n(\omega) \qquad \frac{1}{\tau_0} = \frac{\omega^2 n(\omega)\Omega_0\Gamma}{4\pi}. \tag{5.14}$$

The result (5.14) is more general than previous derivations. In particular we show that τ_0 as given by (5.14) is the true relaxation time. In the usual acoustic approximation $\omega = cq$ (c constant) since $\int d^3q' \delta(\omega - \omega')$

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[58] For a discussion of such solutions and further references, see A. A. Maradudin, P. Mazur, E. W. Montroll, and G. H. Weiss, Revs. Modern Phys. **30**, 175 (1958); especially Appendix A.

[59] See, e.g., N. F. Mott and H. Jones, *Theory of Metals and Alloys* (Dover Publications, New York, 1958), p. 296.

$=4\pi q^2/c$, one has $n(\omega)=\omega^2/c^2$ and (5.14) reduces to the result (5.17). However, in general $n(\omega)$ exhibits quite bizarre behavior, varying from substance to substance. It would be interesting to make an experimental test of this feature of (5.14).

In the present case (4.25) is

$$n_q=\tau_0 R+\frac{\int dS' n_{q'}|\partial\Delta\omega/\partial q_n'|^{-1}}{\int dS'|\partial\Delta\omega/\partial_n'|^{-1}}. \tag{5.15}$$

Without more knowledge about $\omega(q)$, it is difficult to make much progress.

In the acoustic approximation $\omega=cq$ this reduces to the following simple equation ($\mu=\cos\theta$, $R'=-c|\nabla T|dN/dT$):

$$n(\mu)=a\mu+\tfrac{1}{2}\int_{-1}^{1} n(\mu')d\mu', \tag{5.16}$$

where $a=-\tau_0 R'$. The solution of (5.16) satisfying $n(\mu)=0$ when $\partial T/\partial x=0$ is found by inspection to be merely $n(\mu)=a\mu$. Thus

$$n_q=\tau_0 R(q);\quad \tau^{-1}=\Omega_0\Gamma\omega^4/(4\pi C^3). \tag{5.17}$$

This simple result does not hold for more general dispersion curves. Nor in this case is the relaxation time appropriate for thermal conductivity the single mode τ_0, Eq. (5.14), since the integral on the right-hand side of Eq. (5.16) contrives to remove singularities of n_q introduced by $n(\omega)$. However, in some materials the ω^4 scattering law fails. One could check on this point by examining some known $n(\omega)$ curves, and measuring K in the appropriate temperature range.

The expression for τ_0 could be verified by observing the decay of some phonons introduced into a given mode $\mathbf{q}$, λ in a crystal otherwise at equilibrium. In fact, retaining complete information about the polarization branches [Eq. (5.11)] one could use this method to measure the density of states after account was taken of the easily calculable weighting factor $(\mathbf{e}\cdot\mathbf{e}')^2$.

When boundary scattering is included, using a constant τ_b, then for $\omega=cq$ (spherical energy surfaces) Eq. (4.25) has the solution $n_q=\bar{\tau}R$, so that the simple relaxation time picture is again suitable. These approximations give only an approximate picture of reality only well below the low-temperature maximum, where three-phonon interaction may be ignored; however, it is unlikely that a more careful calculation requires any drastic changes in the picture developed here. If the array is not random, then one might have some idea of what the correct probability distribution $P(\mathbf{x})$ might be. For example, in the case of one type of defect,

$$m_{\mathbf{q}-\mathbf{q}'}=\Delta M\int P(\mathbf{x})e^{i(\mathbf{q}-\mathbf{q}')\cdot\mathbf{x}}d^3\mathbf{x}, \tag{5.18}$$

where

$$\int P(\mathbf{x})d^3\mathbf{x}=N.$$

[In the case of diffusion into the strain field of a dislocation the appropriate probability distribution would be given by something such as Eq. (4.53).]

The average mass $\bar{M}$ has been carefully retained in defining the unperturbed problem. This is because the concentrations may be quite large. For instance Williams has measured the thermal conductivity of various mixtures of KCl and KBr up to concentration of 50% KBr, at which there is a 25-fold reduction in the peak conductivity as compared to the natural KCl crystal.[40] Presumably, as one further increased the concentration of KBr, the conductivity would increase again. Such would not be the case theoretically if one had insisted on using the pure KCl crystal as the unperturbed system, for $(\Delta M)^2$ would then be a maximum for the pure KBr crystal, in the lowest order of perturbation theory. This poor choice of H_0 would then require going to higher orders in the perturbation series to recover the simple result (5.17), obtained by the choice of H_0 as in Eq. (5.3). Toxen[41] has measured the thermal conductivity of various mixtures of Ge and Si, containing up to 8% Si. Further experimental data and references for point-defect scattering may be found in Slack's article.[22] A theoretical analysis of isotope scattering in Ge has been given by Callaway[25] and Herring.[60] Further discussion and references may be found in Klemens' review articles.[2,3] The high-temperature resistivity of isotopes has been calculated by Ambegaokar.[27]

At sufficiently high temperatures the heat capacity per normal model assumes the classical value, k. If the difference between the polarization modes is ignored, Eq. (3.32) has the simple form

$$K=\frac{k}{2\pi^2 C}\int_0^{k\Theta/\hbar}\omega^2\tau(\omega)d\omega. \tag{5.19}$$

A reasonable form for the three-phonon relaxation time in cubic crystals is $\tau_{\mathrm{ph}}^{-1}=b(T)\omega^2$, where $b(T)$ is some function of the temperature (the angular dependence of τ_{ph} is ignored). When $\hbar\omega\ll kT$, $b(T)$ is proportional to T^3, but this cannot be expected to be true at high temperatures, where $K\propto T^{-1}$. According to the results of this discussion, the relaxation time may be taken to be

$$\tau^{-1}=b(T)\omega^2+I\omega^4. \tag{5.20}$$

This case leads to a simple integral. Equation (5.19) becomes

$$K=(k/2\pi^2 C)(Ib)^{-\frac{1}{2}}\tan^{-1}[k\Theta/\hbar(b/I)^{\frac{1}{2}}]. \tag{5.21}$$

This result may be simplified in the common situation

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[60] C. Herring (private communication). This calculation obtains agreement with experiment using no adjustable parameters. Similar calculations have also been performed by R. Brout (private communication).

where the Umklapp scattering dominates over the entire frequency range (see Fig. 4, e.g.). In this case the argument of the arctangent is small, so that this function may be expanded. Then if K is the conductivity of the pure crystal ($I=0$), the *resistivity* is

$$W\equiv(1/K)-(1/K_0)\cong\Delta K/K_0^2 = (2\pi^2/3)(C\Theta I/\hbar). \quad (5.22)$$

More explicitly, using (5.17) for the constant I, this becomes

$$W=(\pi/6)(\Omega_0\Gamma/C^2)(\Theta/\hbar), \quad (5.23)$$

which is Ambegaokar's result. An important feature is that the temperature dependence of the three-phonon relaxation time cancels out for small depressions. [When the conductivity is greatly reduced one must use the more exact Eq. (5.21).] The result, however, is sensitive to the power of ω assumed in τ_{ph}. For instance, if $\tau_{\text{ph}}\propto\omega^{-1}$ instead of ω^{-2}, the $\pi/6$ in (5.23) should be replaced by $2\pi/5$. In fact, Eq. (5.23) agrees rather well (as it stands) with the results of Geballe and Hull on isotope scattering in germanium. Experiment gives $W=0.15$ cm deg/w as compared with $W=0.19$ cm deg/w calculated from (5.23). On the other hand, $\tau_{\text{ph}}\propto\omega^{-1}$ gives $W=0.46$. This may be taken as evidence that the heat-carrying phonons in germanium are roughly described by the $\tau_{\text{ph}}\propto\omega^{-2}$ law.

In less symmetric crystals than germanium, τ_{ph}^{-1} may vary as some higher power of ω for low frequency ($\omega\ll kT/\hbar$) phonons. In this case the integral (5.19) does not converge at the lower limit. This circumstance leads to a size dependence of the conductivity, as is discussed in Sec. VII, since the phonons of lowest frequency are boundary scattered with a constant relaxation time τ_b. For our purposes we may cut off the integral at ω_1, where ω_1 is the frequency at which τ_{ph} is equal to τ_b. For $\tau_{\text{ph}}^{-1}=b(T)\omega^3$, ω_1 is

$$\omega_1=(b\tau_b)^{-\frac{1}{3}}. \quad (5.24)$$

In this case (5.19) becomes ($\omega_0=k\Theta/\hbar$)

$$K=\frac{k}{2\pi^2Cb}\log\left[\frac{\omega_0(b+I\omega_1)}{\omega_1(b+I\omega_0)}\right]. \quad (5.25)$$

In most cases of physical interest $\omega_0\gg\omega_1$; the resistivity is

$$W=(\pi/2)(\Omega_0\Gamma\Theta/C^2\hbar)[\log(k\Theta/\hbar\omega_1)]^{-2}. \quad (5.26)$$

The dependence on the size of the crystal is contained in ω_1 via (5.24). In conclusion one can expect to learn about the frequency dependence of τ_{ph} by studying the magnitude and size dependence (if any) of the high-temperature resistivity. When the isotopic scattering is not purely ω^4 the preceding equations are to be modified in an obvious way.

VI. ADDITIVITY OF RECIPROCAL RELAXATION TIMES

From the defining equation for $1/\tau$ it is evident that when a relaxation time is well defined for all of the scattering processes under consideration, the total relaxation time (with the qualifications states in the following) is given by

$$\frac{1}{\tau}=\sum_i\frac{1}{\tau_i}. \quad (6.1)$$

This is because in calculating $\dot{n}$ one adds up the probabilities for noninterfering processes, and matrix elements for interfering processes. Thus, in using Eq. (1) we must be careful to investigate interference between all elastic processes (e.g., strain-field scattering interferes with mass-difference scattering and specular reflection). In many cases of interest the elastic $1/\tau$'s are additive owing the random distribution of scatterers.

For illustration we write $1/\tau_c$ for a number of common scatterers; the coefficients identify the scatterers, the different types of which are considered not to interfere with each other. C/L denotes $1/\tau$ for boundary scattering discussed in the next section.

$$1/\tau_c(q)=(C/L)+I\omega^4+Pq^4+Dq +[N_s+U_s(T)]q^sT^{5-s}. \quad (6.2)$$

L is the Casimir length, roughly a typical dimension of the crystal; I is the coefficient of the isotope or mass-difference scattering given by Eq. (5.17); P represents point-defect strain-field scattering, Eq. (4.43); D is for dislocation scattering, Eq. (4.70) or (4.84); N is for normal processes, $U(T)$ for Umklapp processes ($U\propto e^{-\theta/\alpha T}$); s depends on the crystal symmetry and the phonon polarization.[20] A typical value is $s=2$. Most of these τ's are accurate only in the acoustic range where $\omega=Cq$. [Except for the "isotope" contribution, at larger ω, q is the more appropriate variable, which is the reason for writing $1/\tau_C(q)$ in terms of q instead of ω.] Nevertheless this result should give at least semi-quantitative explanation of experimental data up to temperatures well above the peak in $K(T)$. Equation (6.2) for $1/\tau_c(q)$ should be used in conjunction with Eq. (3.30) for $K(T)$.

Figure 7 illustrates the variation of some typical relaxation times with frequency.[61]

Equation (6.1) does *not* mean that resistivities are additive; indeed it is in general a poor approximation to add resistivities. This is because the frequency dependence of the different scattering mechanisms is quite different.

The thermal resistivity W is defined by $W\sim1/K$. The correct resistivity is given by

$$W=\frac{1}{K}\propto\left[\int\left(\sum_i\frac{1}{\tau_i}\right)^{-1}C_{\text{ph}}(\omega)\omega^2d\omega\right]^{-1}, \quad (6.3)$$

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[61] Some of these data are taken from T. H. Geballe.[96]

while the sum of the resistivities due to the various processes is

$$\sum_i W_i=\sum_i \frac{1}{K_i}\propto\sum_i\left[\int \tau_i(\omega)C_{\mathrm{ph}}(\omega)\omega^2d\omega\right]^{-1}. \quad (6.4)$$

Hence for thermal conductivity measurements the usefulness of the concept of individual thermal resistivities seems rather limited. Both the measured and calculated quantities are the same: $K(T)$.

The argument that resistivities are not additive does not depend on the validity of the relaxation time assumption. The physical reason is that the predominant scattering mechanisms are in general different for phonons of different wavelengths. Addition of individual resistivities leads to an embarrassing divergence[62] when applied to point-defect scattering, as mentioned earlier. A natural cutoff for the long-wavelength phonons is provided by boundary scattering, discussed in the next section. Although point defects "by themselves" do not give a finite thermal resistivity, they nevertheless cause a depression of the boundary (or dislocation, e.g.) limited conductivity. (See, however, the discussion at the end of Sec. III.)

A similar "divergence" occurs if one has only three-phonon processes. Herring[20] has found that in many crystals the elastic anisotropy effectively removes this sensitive size dependence. The remaining small size dependence due to boundary scattering had been observed.[63] A careful analysis of these questions has been given by Herring.[20,28]

To illustrate further the failure of the additivity of thermal resistivities we review a typical example: depression of $K(T)$ due to strong mass-difference scattering in the region above the peak.[26] This also serves to clarify some current confusion in the literature. We retain the boundary scattering, which gives rise to a small size effect. We omit the proof that the term proportional to β in τ is negligible,[26] so that $\tau\cong\tau_c$. Then from Eqs. (3.35) and (6.2)[64]

$$K=\frac{C^2}{2\pi^2}\left(\frac{kT}{\hbar C}\right)^3\int_0^{\Theta/T}\frac{x^4}{(fx^4+gx^2+C/L)}\frac{e^x}{(e^x-1)^2}dx. \quad (6.5)$$

Figure 8 shows some values of this integral computed by Pohl[42] for different values of f; g and L were chosen to fit the data given by the annealed crystal. In this equation $f=I(kT/\hbar)$, $g=[N+U(T)]T^3(kT/\hbar)^2$. Set the upper limit equal to ∞, although we are in a range where $\Theta/T\sim10$. If the isotope scattering is large, then the factor $1/f$ makes the high-frequency contribution to Eq. (6.5) small. Thus it is a reasonable approximation to evaluate Eq. (6.5) by replacing $x^2e^x/(e^x-1)^2$ by unity. Then the integrand is a simple algebraic function:

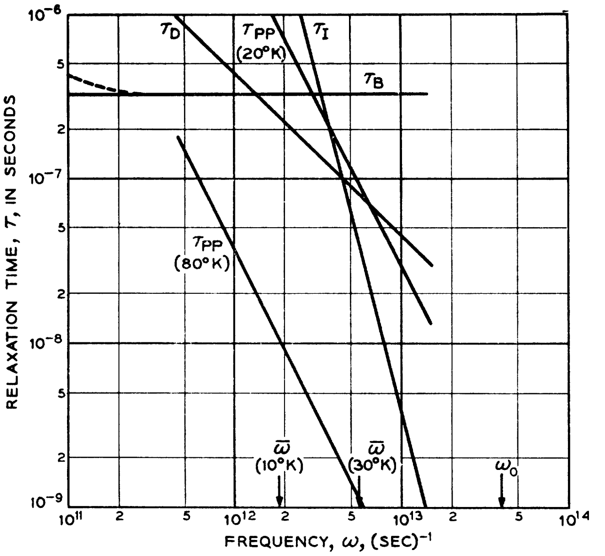

FIG. 7. Some typical relaxation times. Such plots are useful in determining the relative importance of various processes. These curves may be moved up and down to account for varying strengths of the scattering processes by using the formulas in the text and the following data from which the above graph was prepared. For boundary scattering the relation $\tau_B=L/c$ was used, with $L=1$ mm and $c=3\times10^5$ cm/sec. The dashed line shows qualitatively how specular reflection may increase the relaxation time for long wavelengths. The isotope relaxation time τ_I was calculated using $\tau_I^{-1}=A\omega^4$ with $A=2.40\times10^{-44}$ sec^3, appropriate for Ge.[24] The dislocation curve is given by $\tau_D^{-1}=D\omega$ with $D=2.2\times10^{-6}$, for edge dislocations; $\sigma=3\times10^7$ cm^{-2}, $g\approx240\gamma\rho c^2$, $r_0=4$ A, $b=r_0/2^{\frac{1}{2}}$, $\gamma=1.6$. Because of dispersion, this curve may bend downward at the highest frequencies by approximately the factor qc/ω. The phonon-phonon τ_{pp} is appropriate for longitudinal phonons in Ge($\tau_{pp}\propto T^3q^2$), as deduced from thermoelectric power measurements (see Geballe).[96] The Debye frequency ω_0 was arbitrarily chosen as $\omega_0=4\times10^{13}$ sec^{-1}; this corresponds to $\Theta=\hbar\omega_0/k\cong300$°K. The frequencies $\bar{\omega}$ which maximize the Debye distribution $E(\omega)$ at 10° and 30°K are given to show how the dominant scattering mechanisms may be expected to change as the temperature is lowered. The phonon-phonon curves may be scaled (approximately) for the different materials by the appropriate use of the Debye temperature Θ.[2,4]

$$\begin{aligned}K&\cong\frac{k}{4\pi C}\left(\frac{kT}{\hbar}\right)^3\frac{1}{(fg)^{\frac{1}{2}}}\cdot\left[1+\frac{2}{g}\left(\frac{Cf}{L}\right)^{\frac{1}{2}}\right]^{-\frac{1}{2}}\\&\cong\frac{k}{4\pi C}\frac{1}{[I(N+U)]^{\frac{1}{2}}T^{\frac{3}{2}}}\left[1-\frac{2(CI/L)^{\frac{1}{2}}}{(N+U)T^3}\right].\end{aligned} \quad (6.6)$$

In the last equation the boundary scattering has been considered small. We note a few interesting features of this result. First, the conductivity is inversely proportional to the square root of I, which is proportional to the concentration of isotopes. The temperature dependence of $K(T)$ is essentially $T^{-\frac{3}{2}}$; there is a size dependent correction proportional to $T^{-9/2}$.[20] In order to calculate the depression ΔK one must also calculate K

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[62] Strictly one does not have a divergence but rather a striking dependence on the size of the specimen. More precisely

$$\int_{\omega_0}^{\infty}\frac{\omega^2d\omega}{\omega^4}\sim\frac{1}{\omega_0}\propto L,$$

where $L\sim\Omega^{\frac{1}{3}}$. (For a finite crystal the smallest wave vector transporting heat is $q_0\sim1/L$.)

[63] T. H. Geballe and G. W. Hull, "Conférence de Physique de Basses Temperatures," (1956), p. 460.

[64] We take $s=2$, appropriate for longitudinal phonons in cubic crystals.[20]

when the isotope scattering is small; however, Eq. (6.6) could not be obtained by considering the resistivities as additive, for in this case

$$W \propto IT, \tag{6.7}$$

if one could cut off the divergence in K in a convincing manner.[39] Thus both the temperature and concentration dependence are incorrectly given by adding resistivities. Klemens,[65] adding resistivities, tried to explain apparent discrepancies between theory and experiment by invoking higher terms in the perturbation series; however, this explanation requires different coefficients for different experiments, for no apparent reason. By comparing the numbers in the numerical example of footnote 65 one sees that the square-root relationship is well satisfied, so that there is no discrepancy in the concentration dependence given by lowest-order perturbation theory for that case. Klemens also comments on the apparent discrepancy for point defects, which give a resistivity consistently greater than computed from Eq. (6.7). This discrepancy has possibly two origins: (1) resistivities should not be added (2) the strain-field scattering of point defects has not been considered by Klemens. Because of the complicated behavior of the latter in the region above the peak discussed earlier, a detailed comparison with experimental data is necessary to prove or disapprove the second alternative.[66]

Toxen[71] noted experimentally that the slope of $\log W$ vs log(concentration) for the region above the peak is not unity as in Eq. (6.7). The slope is very nearly $\frac{1}{2}$. Toxen's plot includes the result of many experiments. (That the temperature dependence is more nearly $T^{\frac{3}{2}}$ than T should not matter much since the plotted data had roughly comparable temperature and since the plot was log-log.)

To analyze experimental data given as a plot of $W_s = W - W_0$, where ΔK is the depression of K due to some added scatterer s, the following approximate procedure may be used if $\Delta K/K$ is small. The initial resistivity is $W_0 \equiv 1/K$. With the scatterer present, $W \equiv W_0 + W_s$ defines W_s. Also we have $W = 1/(K - \Delta K) \cong 1/K + \Delta K/K^2 = W_0 + \Delta K/K^2$ showing that the appropriate quantity to be calculated is $\Delta K/K^2 = W_s$. The preceding example shows that care must be used in finding ΔK. This W_s is not equal to $1/K_s$, where K_s is the conductivity with only scatterer s acting, so that the use of the expression $W = \Sigma W_i$ is misleading. Since the additional resistivity caused by a defect is not easily separated from the other scattering processes in the "pure" crystal, it seems that at least for large depressions ΔK, it would be more appropriate to analyze the

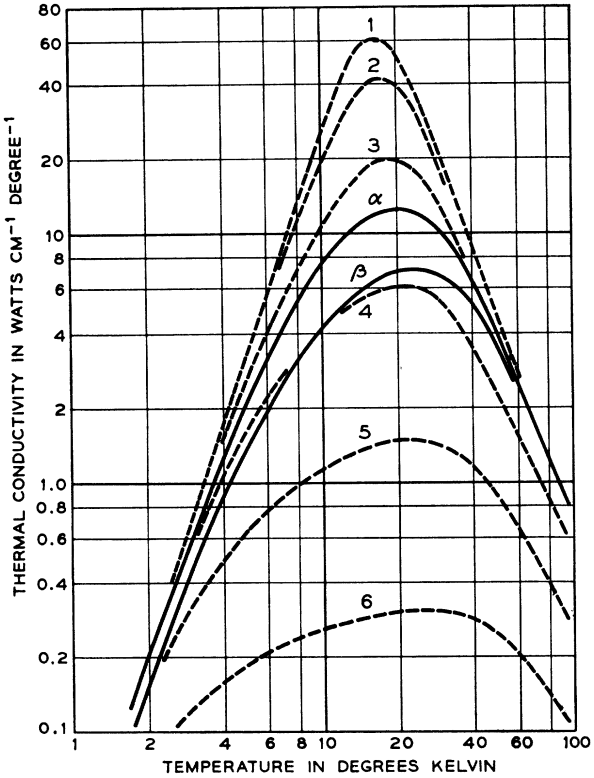

FIG. 8. The family of dashed lines, which shows the effect of scattering according to the law $\tau^{-1} = I\omega^4$, was calculated[42] from the expression (6.5), where the parameters L and g' were adjusted to agree with curve α at very high and very low temperatures, at which the three-phonon and boundary scattering, respectively, are supposed to dominate. (Θ/T) has been set equal to infinity. Curve α is an experimental curve for a "pure" LiF crystal with the dimensions 0.74×0.79×40 mm, which has been sand blasted and annealed.[42] The exponential dependence of the Umklapp term $U(T)$ has been ignored (set equal to unity); the sum of $N+U$ in Eq. (6.2) is then equal to 1.35×10^{-22} sec deg^{-3} c^{-2}, where $c = 5\times10^5$ cm/sec is the sound velocity in LiF. The parameter s in (6.2) has been chosen to be two, appropriate for cubic crystals. The Casimir length L is found experimentally to be 1.55 mm, as compared with the theoretical value of about 1.33 mm (see Sec. VII). This agreement must be considered to be excellent. The different curves of the theoretical family correspond to the following values of the parameter I (in sec^{-3}) in Eq. (6.2): curve 1, $I=0$; curve 2, $I=5\times10^{-46}$; curve 3, $I=5\times10^{-45}$; curve 4, $I=5\times10^{-44}$; curve 5, $I=5\times10^{-43}$; curve 6, $I=5\times10^{-42}$. It is evident that the curve α belongs to the family of calculated curves with a value of I of about 10^{-44} sec^{-3}. This is about 10 times the value corresponding to the natural isotopic consitution of LiF. (This large ω^4 scattering is probably due to the strains of residual point defects, as was described in Sec. IV.) On the other hand, the curve β, in which 2.2×10^{17}/cm^3 F centers have been introduced by x-ray bombardment, does not belong to the family of theoretical curves.

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[65] P. G. Klemens, Proc. Phys. Soc. (London) **A70**, 833 (1957); J. Phys. Chem. Solids **8**, 345 (1959).

[66] Nor should the expression derived by Ziman[67–69] from a variational principle be used as a quantitative formula for the thermal conductivity; however, in a recent paper by Ziman and collaborators[70] this approach has been refined considerably, and applied successfully to a very detailed experimental investigation of the isotope effect in LiF. The theoretical results are in essential agreement with the previous discussion of the isotope effect using the relaxation time method.

[67] J. M. Ziman, Phil. Mag. **1**, 191 (1956); **2**, 292 (1957).

[68] J. M. Ziman, Can. J. Phys. **34**, 1256 (1956).

[69] This expression was also tested in a paper by R. Berman, E. Foster, and J. Ziman, Proc. Roy. Soc. (London) **A237**, 344 (1956), who note the lack of agreement with experiment.

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

[71] A. M. Toxen, Phys. Rev. **110**, 585 (1958).

data in terms of ΔK, or K itself, in the sensitive vicinity of the peak in $K(T)$.

VII. BOUNDARY SCATTERING; SIZE EFFECTS

Since nature does not provide crystals of infinite size, it is necessary to consider in some detail an essentially nonintrinsic effect, that of the geometrical shape and size on the magnitude of the heat current (Fig. 9).

The necessity for such considerations arises from the fact that most of the scattering processes have negligible strength for phonons of sufficiently long wavelength. If the temperature is so low that $C\tau$ is as large as the crystal dimension, then boundary effects are important. This exercise is not altogether unrewarding, however, for one can learn something about the nature of phonon-phonon scattering from the size effect. Since the boundary scattering τ varies rather slowly with frequency, the combined effect of boundary and defect scattering (the latter usually more sensitive to ω) can be analyzed to give some information on the type of defect present.

The most salient feature of boundary scattering is that (in a single crystal) it does not occur uniformly throughout the crystal. This makes the distribution function depend on position, e.g., the phonons at the boundary may be in thermal equilibrium with the boundary. Hence the simple Boltzmann equation (3.6) is no longer adequate. In particular, one cannot simply add reciprocal relaxation times as for other scattering mechanisms; however, one can reinterpret the new term in the more complete Boltzmann equation in terms of an equivalent relaxation time, i.e., if one uses this effective τ in the standard way the correct heat current is obtained. Before entering into these complications, however, we sketch the classical Casimir theory of boundary scattering.[72] This analysis provides a reference point for more sophisticated calculations. We see that the "naive" result $C_\lambda\tau_b=L$, where L is some average dimension of the sample, is valid when the boundary scattering is not specular.

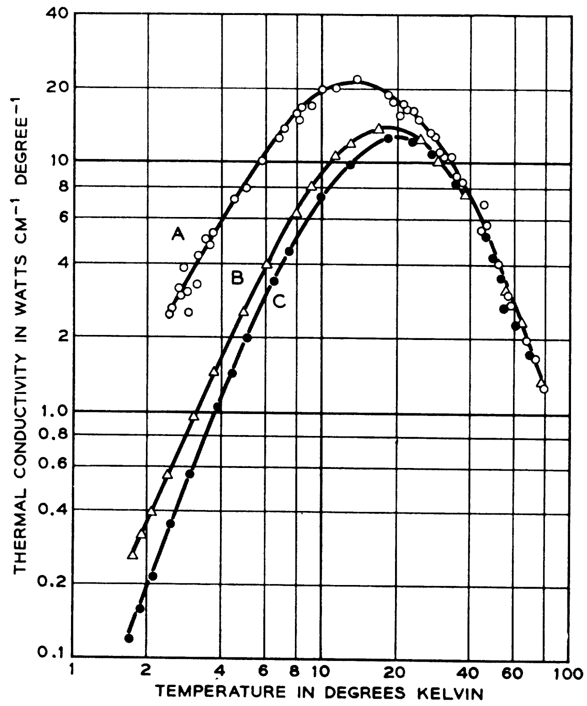

FIG. 9. The boundary effect in LiF.[42] The crystal of curve A is about 10 times as thick as the crystal of curve B. Considerable specular reflection occurs in both of these crystals however. After sand blasting and annealing crystal B displays the conductivity given by curve C. The effect of thus roughening the surface is seen to both reduce the conductivity and change its temperature dependence to a T^3 variation, consistent with diffuse reflection. The experimental L (Eq. 6.5) is about 15% greater than the theoretical value. The exact dimensions are: crystals A, 6.7×7.3×40 mm; crystals B and C, 0.74×0.79×40 mm.

Casimir's theory is completely analogous to the standard theory of blackbody radiation. (The essential difference between the phonon gas and the photon gas is that there is an upper cutoff to the phonon frequency; however, this is of no consequence at the temperatures of interest here.)

The temperature is assumed to be so low that the only collisions made by the phonons are with the boundary. Casimir further supposes that the scattering is completely diffuse, the incident phonons being absorbed, and then reemitted with the equilibrium distribution corresponding to the local temperature. The specimen is taken to be a long cylindrical rod, whose axis is in the x direction.

The energy per unit volume with $\mathbf{q}$ pointing in the solid angle $d\Omega$ with frequency ω in the interval ω, $\omega+d\omega$, and polarization λ is, using $\omega_\lambda=C_\lambda q$,

$$E_\lambda(\omega)d\omega d\Omega=\frac{\omega^2 d\omega d\Omega}{(2\pi)^3 C_\lambda^3}\left(\frac{\hbar\omega}{e^{\hbar\omega/kT}-1}\right). \tag{7.1}$$

(C_λ depends on the direction specified by $d\Omega$.) The phonons contributing to (7.1) can be considered to be traveling waves of velocity $\partial\omega_\lambda/\partial q\rightarrow C_\lambda$ in the low-frequency limit. Thus if θ_1 is the angle made by the axis of the (infinitesimal) solid angle $d\Omega$ with the normal to the element of surface dS_1, the total energy of all modes incident on dS_1 is

$$\begin{aligned} dF(\omega)&=\sum_\lambda E_\lambda(\omega)C_\lambda \cos\theta_1 dS_1 d\omega d\Omega \\ &=\sum_\lambda \frac{\omega^2 d\omega}{(2\pi)^3 C_\lambda^2}\left(\frac{\hbar\omega}{e^{\hbar\omega/kT}-1}\right)\cos\theta_1 dS_1 d\Omega. \end{aligned} \tag{7.2}$$

On integrating this over all frequencies to obtain the total incident energy at the specified angles, and putting

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[72] H. B. G. Casimir, Physica 5, 495 (1938). See also R. E. B. Makinson, Proc. Cambridge Phil. Soc. 34, 474 (1938).

$\Theta/T=\infty$, one obtains, in the usual way,

$$dF\equiv\int^{\infty}\frac{dF}{d\omega}d\omega=\sum_{\lambda}\frac{1}{C_{\lambda}^{2}}\frac{\pi^{4}k^{4}T^{4}}{15h^{3}}\cos\theta_{1}dS_{1}d\Omega. \quad (7.3)$$

In (7.3) T depends on the temperature of the surface dS_1. In the steady state (7.3) is also the rate emitted from dS_1. Consider the transfer of energy between dS_1 and dS_2, where dS_2 subtends the solid angle $d\Omega=dS_2\times\cos\theta_2/r_{12}^2$, r_{12} is the distance between the surface elements dS_1 and dS_2, and θ_2 is the angle between r_{12} and the normal to dS_2. T_2 is different from T_1, in general. Let us write $T^4(x)=T^4(0)+4T^3(0)(dT/dx)\cdot(x)$, where $x=0$ lies in the center of the crystal. This approximation is good for small constant-temperature gradients. Then the net heat flow down the crystal is

$$Q=\frac{4\pi^{4}k^{4}T^{3}}{15h^{3}}\left(\frac{dT}{dZ}\right)\int\int\frac{x_{12}\cos\theta_{1}\cos\theta_{2}}{r_{12}^{2}}\times\sum_{\lambda}\frac{1}{C_{\lambda}^{2}}dS_{1}dS_{2}. \quad (7.4)$$

This is proportional to the heat capacity. If one makes the approximation that the C_λ are essentially independent of angle, or defines a suitable angular average, then (7.4) becomes

$$Q=\left(\frac{dT}{dZ}\right)\frac{\bar{v}C_{v}}{4\pi}\int\int\frac{x_{12}\cos\theta_{1}\cos\theta_{2}}{r_{12}^{2}}dS_{1}dS_{2}, \quad (7.5)$$

with the relations

$$C_{v}=\left(\frac{4\pi^{4}k^{4}}{15h^{3}}\right)\left(4\pi\sum_{\lambda}\frac{1}{C_{\lambda}^{3}}\right)T^{3}, \quad (7.6)$$

$$\bar{v}\equiv\left(\sum_{\lambda}C_{\lambda}^{-2}\right)/\left(\sum_{\lambda}C_{\lambda}^{-3}\right). \quad (7.7)$$

Equation (7.5) gives the conductivity in the form $K=\frac{1}{3}C_v\bar{v}l$ where the mean-free path l is a constant given by $3/4\pi$ times the integral in (7.5). [One has to divide (7.5) by the cross-sectional area to get K.] For a cylinder of circular cross section one finds in this way $l=2R$, where R is the radius. Hence the effective mean-free path is just the diameter of the cylinder. [One must remember the peculiar definition of $\bar{v}$ given by Eq. (7.7) however.] For a square cross section of side d the effective mean-free path is $l=1.1d$.

Now let us see what may be done to relax the assumptions made in the Casimir theory. First, note that the phonons are scattered by other defects, and by each other. We have seen in Sec. III that if the relaxation time approximation is valid, then the total rate of change of n_q can be described by a single "total" τ, which includes the effect of the normal processes. This is incorporated in the Boltzmann equation written in the following. Secondly, it is necessary to consider the effect of specular reflection of the phonons. At present no detailed microscopic theory of specular reflection seems to exist. Nevertheless, it is possible to make certain qualitative statements, and phenomenologically to modify the equations accordingly. For instance, it is plausible that long-wavelength phonons tend to be scattered specularly more often than short-wavelength phonons. By "long" and "short" one refers to some dimension corresponding to the size of the irregularities characterizing a surface. As an illustration of the reality of this effect, an etched surface offers less boundary resistance than does a sand-blasted surface. Further, the crystallographic orientation of the surface is important.[73] Berman, Simon, and Ziman find that in diamond the specularity of boundary scattering exceeds 50%.[74] They have generalized Casimir's theory to account for multiple reflection and end effects, by assuming that a constant fraction of the phonons are specularly reflected. While it should be relatively easy to generalize their approach to include the variation of specularity with wave vector, it is not clear how one would account for phonon collisions within the sample. For this reason we proceed directly from the Boltzmann equation.[75]

The thermal gradient supplies phonons to every element of the cross section at a rate assumed to be independent of location in the cross section. In the body of the sample these phonons lose their crystal momentum at a rate described by the total relaxation time τ. In addition the phonons near the boundary tend to be absorbed, giving rise to a dependence of the flux on the distance from the boundary. We consider the following simplified geometry: a plane parallel slab of thickness d, with a temperature gradient in the x direction. The y direction is perpendicular to the faces of the slab. The distribution function has an explicit y dependence in addition to the implicit dependence on x through $T(x)$. (Strictly T depends on y in this general situation, but to a first approximation the results are correct for small deviations from equilibrium.) The corresponding Boltzmann equation is [cf. Eq. (3.6)], for each polarization mode,

$$C_{x}\frac{\partial T}{\partial x}\cdot\frac{dN_{q}^{0}}{dT}+C_{y}\frac{\partial n_{q}}{\partial y}+\frac{n_{q}}{\tau(q)}=0. \quad (7.8)$$

As usual, n_q is the deviation from the equilibrium, $\tau(q)$ is the total relaxation time defined by Eq. (3.16) C_x and C_y are the x, y components of the group velocity (here given adequately by $C_x=Cq_x/q$, etc.). In the first term we have set dN_q/dT equal to dN_q^0/dT; in the second we have neglected the dependence of N_q^0 on y, which is certainly permissible. The first term is minus the rate at

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[73] T. H. Geballe (private communication).

[74] R. Berman, F. Simon and J. Ziman, Proc. Roy. Soc. (London) **A220**, 171 (1953); R. Berman, E. Foster, and J. Ziman, Proc. Roy. Soc. (London) **A231**, 130 (1955).

[75] The essential features of this approach are given by C. Herring,[28] Sec. VI and Appendix B.

which phonons are delivered to a unit volume of phase space. Let us emphasize this by giving this term a special name, $R(q)$:

$$R(q)\equiv -C_x(\partial T/\partial x)(dN_q{}^0/dT). \qquad (7.9)$$

$R(q)$ is known function of x and q, independent of y. Thus (7.8) is a simple first-order differential equation in the variable y. The effect of the boundary is incorporated into the boundary conditions to be imposed on (7.8). In Eq. (7.8) let us fix on some phonons of a particular wave vector q (and some unspecified polarization). Consider one of the surfaces ($y=0$) and call the positive y direction that of the inward normal, so that a phonon with $q_y>0$ is leaving the surface ($y=0$). It is easy to see what boundary condition is equivalent to the Casimir theory (but now including the effect of processes other than boundary scattering). This condition is that at the back surface (for the phonons having $q_y>0$) the deviation from the equilibrium distribution [appropriate for $T(x)$] be zero, i.e., $n_q(x,0)=0$. All the phonons with $q_y>0$ at position $y=d$ are absorbed (and eventually re-emitted with $q_y<0$ and the distribution $N_q{}^0$). In the more general case thermal equilibrium is not established, so that $n_q(x,0)\equiv\delta_q(x)\neq 0$. $\delta_q(x)$ may be expected to be largest for small q. The x dependence of $\delta_q(x)$ arises from the temperature gradient, e.g., one may expect surface vibrational modes[76] (whose mean excitation depends on T) to affect δ. The explicit calculation of δ_q is the task of a detailed microscopic theory. The solution of (7.8) with the general boundary condition

$$n_q(x,0)\equiv\delta_q(x) \qquad (7.10)$$

is found to be, for $C_y>0$,

$$n_q(x,y)=\tau(q)R(q)[1-\exp(-y/\tau C_y)] + \delta_q\exp(-y/\tau C_y). \qquad (7.11)$$

(See Fig. 10.) In (7.11) the x dependence is contained in $R(q)$ and δ_q.

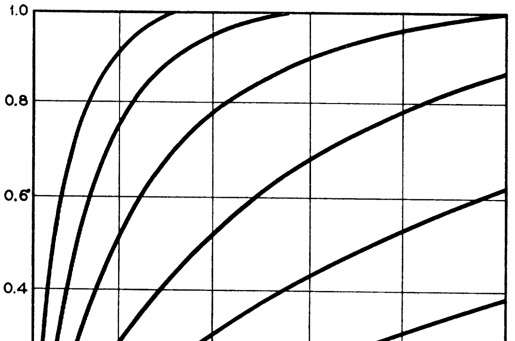

FIG. 10. These curves show how the distribution of phonons varies across a slab with faces at $y=0$ and $y=d$, for phonons traveling away from $y=0$, at which surface the boundary condition $n_q=0$ (diffuse reflection with the equilibrium distribution) has been imposed. n_q is measured in terms of the deviation τR of an infinite crystal (τ is the relaxation time for scattering within the sample). The number attached to each curve is $\tau c_y/d=\tau c\sin\theta/d$ [cf. Eq. (7.11)].

Let us consider the generalization of (7.8); for the second term write $\mathbf{C}_\perp\cdot\nabla_\perp n_q$, where $\perp$ refers to the transverse (y and z) components of $\mathbf{C}$ and ∇. Then we can rearrange (7.8) using (7.9) to obtain, after integrating over the cross section,

$$R(q)=-\left(\frac{1}{\tau}+\frac{1}{\tau_b}\right)\langle n_q\rangle, \qquad (7.12)$$

where $\langle n_q\rangle$ is defined by

$$\langle n_q\rangle=\int n_q dydz/S \qquad (7.13)$$

and

$$\frac{1}{\tau_b}\equiv\frac{\int[C_y(\partial n_q/\partial y)+C_z(\partial n_q/\partial z)]dydz}{\int n_q dydz}. \qquad (7.14)$$

$S=\int dydz$ is the area of the cross section. Thus by a formal rearrangement of the Boltzmann equation we find an equivalent relaxation time, i.e., for a uniform distribution $\langle n_q\rangle$ the relaxation time defined $\tau^{-1}+\tau_q{}^{-1}$ with τ_q given by (7.14) yields the correct thermal conductivity. Equation (7.14) can then be evaluated from explicit solutions such as (7.11). Now τ_b depends on both q and T, although from our experience with the Casimir theory we can expect this dependence to be mild.

The numerator in (7.14) can be subjected to one integration, or rewritten in terms of an integral along the path defined by the intersection of the yz plane with the surface of the cylinder. Then the definition (7.14) displays how the phonons at the boundary are absorbed. From the explicit form of $n_q(x,y)$ it is evident that always $\delta_q\leq\tau R$ [note that $n_q(x,\infty)=R\tau$]. The equality holds for completely specular reflection; then (7.11) reduces to $n_q=\tau R$ which is the same as without boundary scattering. If the internal scattering processes are strong so that $\tau C_y\ll d$, then n_q rises quickly from the value δ_q at the boundary to the asymptotic value τR. (This is always the case at high temperatures.) For long-wavelength phonons at low temperatures the opposite limit obtains and n_q increases linearly across the sample. Thus when $\delta_q=0$ (diffuse boundary scattering) the rate of removal of the total crystal momentum or of $\langle n_q\rangle$ [Eq. (7.13)] is twice as great for large τ as for

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[76] The theory of surface vibrational modes has recently been studied by R. F. Wallis, Phys. Rev. **116**, 302 (1959).

small τ, for a given total crystal momentum (or $\langle n_q \rangle$). Thus for the special geometry considered the total variation of τ_b can be no more than a factor of two.

The explicit formulas for the special case of the slab contain the essential features with a minimum of geometrical complications. (For the evaluation of τ_b in the case $\delta=0$ for some other geometries see Herring.[75] On inserting Eq. (7.11) for n_q in Eq. (7.14), and dropping all the z dependence, one finds

$$\frac{1}{\tau_b}=\frac{C_y}{d}\cdot\frac{[1-(\delta/R\tau)]\{1-\exp[-(d/\tau C_y)]\}}{1-(\tau C_y/d)[1-(\delta/R\tau)]\{1-\exp[-(d/\tau C_y)]\}}, \tag{7.15}$$

where d is the diameter of the slab; the coefficient C_y/d was to be expected from our previous work. Note that $\tau_b \rightarrow \infty$ as $\tau R \rightarrow \infty$, as required. Consider first the special case $\delta_q=0$; and the limits of interest:

$$\frac{1}{\tau_b}=\frac{C_y}{d}\,\frac{1-\exp[-(d/\tau C_y)]}{1-(\tau C_y/d)\{1-\exp[-(d/\tau C_y)]\}};\quad (\delta=0) \tag{7.16}$$

$$\rightarrow C_y/d \quad \text{as} \quad \tau \rightarrow 0; \qquad (\delta=0) \tag{7.17}$$

$$\rightarrow 2C_y/d \quad \text{as} \quad \tau \rightarrow \infty; \qquad (\delta=0). \tag{7.18}$$

The statements made above about the relative magnitude of τ_b in the two limits are explicitly verified in Eqs. (7.17) and (7.18). The most important part of the directional dependence of τ_b is given by the factor $C_y=C\sin\theta$, where θ is the angle between $\hat{q}$ and ∇T. This factor must be included in compounding reciprocal relaxation times. Consider temperatures so low that $\tau \rightarrow \infty$ [this limit is usually a better approximation than (7.17) for temperatures of interest here]. If only boundary scattering occurs then one may define an (isotropic) equivalent boundary scattering time $\bar{\tau}_b$ and mean-free path L by the equation

$$\bar{\tau}_b \equiv \frac{L}{C} \equiv \frac{\int \tau_b \cos^2\theta d\Omega}{\int \cos^2\theta d\Omega}. \tag{7.19}$$

From this definition one finds in the limit (7.18)

$$L=(3\pi/8)d \cong 1.18d; \quad \tau \rightarrow \infty. \tag{7.20}$$

The weight factor $\cos^2\theta$ occurs in order that the thermal conductivity obtained from either τ_b is the same. When τ is finite this approach loses significance, however.

Now let us reduce (7.15) to meaningful form when some specular reflection occurs; $\delta_q \neq 0$. In order to do this we require the behavior of the $\delta/R\tau$ appearing in (7.15). We call that $\delta \rightarrow 0$ as $\omega \rightarrow \infty$ and probably approaches a finite limit for $\omega \rightarrow 0$. Further, for all the scattering processes considered here $\tau \rightarrow \infty$ as $\omega \rightarrow 0$, more rapidly than ω^{-1} (e.g., dislocations and transverse modes have $\tau^{-1} \propto \omega$, longitudinal modes $\tau^{-1} \propto \omega^n$ with $n \geq 2$). From the definition of $R(q)$, Eq. (7.9), we find easily

$$R(q) \rightarrow C_x(k/\hbar\omega)\cdot(\partial T/\partial x) \qquad \omega \rightarrow 0 \tag{7.21}$$

$$R(q) \rightarrow C_x(\hbar\omega/kT^2)e^{-\hbar\omega/kT}\cdot(\partial T/\partial x) \quad \omega \rightarrow \infty. \tag{7.22}$$

The limits 0 and ∞ mean precisely that $\hbar\omega/kT \ll 1$ or $\gg 1$, respectively. Now one always must satisfy $\delta/R\tau \leq 1$. If we set $\tau^{-1}=\omega^n$ ($n \geq 1$, usually), then since δ is roughly constant as $\omega \rightarrow 0$, this inequality becomes $\omega^{n+1} \leq$ constant which can always be satisfied for sufficiently small ω. In this limit $\delta_q/R\tau$ is rather less than $C_y\delta/R\tau \propto \omega$ if $\sin\theta \neq 0$. Thus we conclude that

$$\frac{1}{\tau_b} \rightarrow \frac{2C_y}{d}\cdot\frac{1}{1+(2\delta C_y/dR)}; \quad \tau \rightarrow \infty,\ \omega \rightarrow 0,\ \delta \neq 0. \tag{7.23}$$

The effect of δ is to increase the relaxation time. In the extreme limit $\omega \rightarrow 0$ $1/\tau_b \approx 2C_y/d$; however, in many situations of experimental interest the term $2\delta C_y/dR$ in the denominator may not be negligible, even though $\delta/\tau R \ll 1$.

For large $\omega (\tau \rightarrow 0)$ we have already noted that $\delta_q \rightarrow 0$. In fact from Eq. (7.22) we see that an upper bound to this decrease is given by $\delta < \tau R \propto \omega^{1-n} e^{-\hbar\omega/kT}$. Thus for sufficiently small ω one can ignore $\delta/\tau R$. Again retaining $\delta C_y/dR$ we find

$$\frac{1}{\tau_b} \rightarrow \frac{C_y}{d}\cdot\frac{1}{1+\left(\delta\dfrac{C_y}{dR}\right)}; \quad \tau \rightarrow 0,\ \omega \rightarrow \infty,\ \delta \neq 0. \tag{7.24}$$

It would be of some interest to try to fit experimental results for boundary scattering in very pure crystals with reasonable assumptions about the form of δ. The effect of surface treatment and crystallographic orientation would presumably be fitted with two phenomenological parameters δ_q (i.e., for each q one has both longitudinal and transverse modes). At very low temperatures in pure crystals of reasonably large size (7.23) should be adequate. The form of δ would have to satisfy the qualitative requirements mentioned above. Without a detailed study of the scattering mechanism one can only guess at the form of δ_q; however, from classical wave theory, for general angles of incidence, an appreciable fraction of longitudinal waves leaves the surface as transverse waves, and vice versa. Since longitudinal waves of small q have rather long relaxation times in comparison with transverse phonons, there should be a finite range of temperature in which boundary scattering is negligible for transverse phonons, though important for longitudinal phonons. Many of the longitudinal phonons are reflected as transverse phonons which in

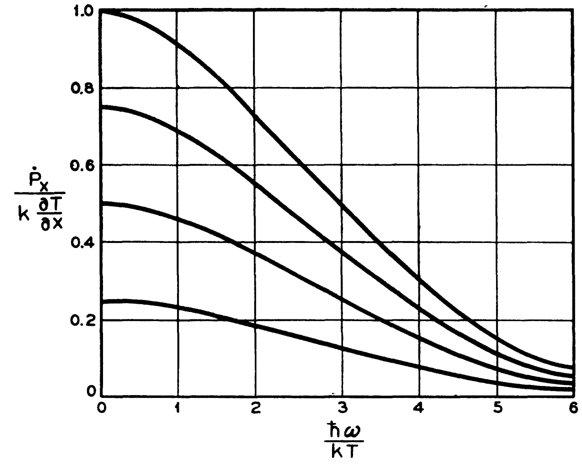

FIG. 11. The rate at which crystal momentum is pumped into a given volume element at an angle θ with respect to the heat current, is shown as a function of $\hbar\omega/kT$ and θ. This crystal momentum is dissipated by the various scattering processes in the steady state. The rate of energy input is just $ck\dot{P}_x$, for small q's. From top to bottom, the curves are for $\theta=0°$, 30°, 45°, and 60°.

turn are rapidly brought to thermal equilibrium. It seems that in this case δ_q cannot be greater than about one-half because of this interpolarization scattering. At very low temperature, however, all modes are equally out of balance with $\tau=\tau_b$ so that the phonon distribution cannot relax by interpolarization-mode scattering. [Perhaps a more fundamental phenomenological approach (or the goal of a detailed theory) would be to express the scattering interaction as a surface density of the form $\sum_{qq'} b(q,q')a_{q'}{}^*a_q$, where the a operators have already been defined. $|b(q,q')|^2$ is zero except on the surface (it would contain as a factor $\delta(\mathbf{x}-\mathbf{x}_s)$, where $\mathbf{x}_s$ is a surface coordinate). Also $b(q,q')$ is zero unless the phonons have the proper directions. Lack of correlation of q and q' would be expressed as a factorization property: $b(q,q')=b_1(q)b_2(q')$; however, this factorization would not occur for the polarization indices as mentioned before.]

An interesting property from Eqs. (7.21) and (7.22) concerns the rate at which crystal momentum P_x is pumped into the various normal modes by the temperature gradient. On using the definition $\dot{P}_x=\hbar q_x R(q)$, one finds

$$\dot{P}_x(q)=k\cos^2\theta(\partial T/\partial x),\quad \hbar\omega/kT\ll 1 \tag{7.25}$$

and

$$\dot{P}_x(q)=k\cos^2\theta(\hbar\omega/kT)^2e^{-\hbar\omega/kT}\cdot\partial T/\partial x,\quad \hbar\omega/kT\gg 1. \tag{7.26}$$

These equations show that for phonons with energies rather less than kT the crystal momentum supplied to each mode by the thermal gradient is constant. Less is supplied to the high energy modes. It is instructive to make a graph of $\dot{P}_x/(\partial T/\partial x)$ vs the variable $\hbar\omega/kT$ (Fig. 11).

Size Effect

In obtaining Eq. (6.6) we found that there was a size-dependent correction to the conductivity, namely, a reduction proportional to $L^{-1/2}T^{-9/2}$ for crystals for cubic symmetry, where L is the Casimir scattering length. This result may be obtained in a more transparent way, using the original formulation given by Herring,[6,20] who predicted this size effect. (Discussion of the experimental verification may be found in footnote 6.)

Except for very low temperatures $T<T_0$ below the peak T_0, where modes of all frequencies are limited by boundary scattering, it is only the long-wavelength phonons which are influenced by the presence of the boundary. Further since τ increases more strongly with q for longitudinal than for transverse modes, one may anticipate that it is the longitudinal phonons which are scattered by the boundary at temperatures $T>T_0$. Although the importance of such low-frequency phonons is relatively small at high temperatures there is a small but measurable contribution to K by the low-frequency longitudinal modes. For these modes $\hbar\omega\ll kT$ so that their heat capacity is k:

$$K=K_h+\frac{kc^2}{8\pi^3}\int_0^{q'}\tau_t(q)q^2dq\cos^2\theta d\Omega. \tag{7.27}$$

Here K_h is the contribution of the high-frequency modes $q>q'$, essentially independent of the boundary. The desired result is obtained by using the "crude" approximation $\tau_b^{-1}=c/L$ and setting $\tau_t^{-1}=\tau^{-1}+\tau_b^{-1}$, where τ on the right-hand side refers to all scattering processes except boundary scattering. (τ_b^{-1} is negligible in the evaluation of K_h.) The same results are obtained if one sets $\tau_t=0$ for $\tau>\tau_b$ and $\tau_t=\tau$ for $\tau<\tau_b$, except for a small numerical error, not of significance in comparison with the approximations already made.[6] This approximation says that the phonons with $\tau>\tau_b$ do not contribute to K. To find the lower cutoff in terms of q we set $\tau=\tau_b$, where for longitudinal phonons in cubic crystals $\tau^{-1}=Aq^2T^3$ is the single-mode relaxation time. This gives $q_0{}^{-1}=(A\tau_b)^{\frac{1}{2}}T^{\frac{3}{2}}$. Assuming the constant A to be independent of angle (not really true!) the conductivity is

$$K\cong\text{const}-\frac{kc^2}{6\pi^2A^{3/2}\tau_b{}^{1/2}T^{9/2}}. \tag{7.28}$$

More precise expressions, and results for crystals of lower symmetry, may be found in Herring's paper.[20]

VIII. SURVEY OF UNSOLVED PROBLEMS

The characteristic feature of the calculations presented in the previous sections is that they all need to be improved. The calculation of scattering matrix elements usually was found to be simple, at least in principle; however, in order to obtain reliable numbers for these quantities detailed account must be taken of lattice structure and the (essentially unknown) anharmonic force constants, except in the case of isotopic scattering. Although such detailed considerations do not in themselves contribute to our understanding of thermal conduction phenomena, they are necessary for a truly quantitative test of the theory. In using these matrix elements to calculate $\dot{n}_q$ one needs further a detailed knowledge of the energy surfaces, or $\omega(q)$, for the substance of interest.

The next step is to solve the integral (Boltzmann) equation for the distribution function. As mentioned before, it is essential to include in this equation the three-phonon processes. Before quantitative success may be expected in calculating the magnitudes of K it is necessary to solve the Peierls integral equation, which contains in its kernel the anharmonic coefficients. The possibility of making a fairly realistic model for the anharmonic couplings is not so remote as it once was. Recent measurements of 6-sec order elastic constants in Ge by McSkimin and Bateman,[77] using calculations by Mason,[78] impose some useful constraints on the anharmonic coefficients. Still, however, it is necessary to use a model. Invention of such a model must be guided by the symmetry of the lattice; considerations of group theory reduce the number of *a priori* force constants, but nevertheless the number of independent anharmonic constants is not small. (It would be interesting to see whether the "shell model" of Dick and Overhauser,[79] which was applied to the vibration spectrum of Ge with rather good success by Cochran,[8] could be used to calculate the anharmonic forces.) Further constraints may be obtained from thermal expansion and specific heat data.

If one could construct plausible couplings, it would be of extreme interest to see whether the solutions resemble those obtained using the single-mode relaxation time, and to ascertain the frequency and temperature range of the correspondence, and the sensitivity of the results to the nature of the couplings. With such knowledge, one could attack the problem of defect scattering with more confidence. In the meantime we can do order of magnitude physics (it is difficult to see how the τ approach could give answers off by an order of magnitude) by assuming that a relaxation time makes sense (as used in Sec. III) and fitting the unknown constants to the experimental data.

There exists independent evidence for the phonon-phonon scattering laws. This arises from the circumstance that in thermoelectric and thermomagnetic phenomena[6] essentially the only unknown is the phonon-phonon relaxation time. For our purposes it is only important to know that the important phonons involved in the phonon-drag effect have energies appreciably smaller than kT, and this is precisely the range in which the single-mode relaxation times should be applicable. In fact, it is found that a quantitative fit, to some very detailed experimental data, is possible by using a relaxation time[80,81]; however, the necessary q dependence departs somewhat from the ideal laws appropriate for Ge. In any event it seems risky to extend the ideal laws to the frequency range important for thermal conductivity ($\sim kT$); even the extrapolation of the experimental results for τ may be unreliable. The use of these "ideal" laws leads to results consistent with experiment.[26,27]

The nature of our problem is such that a quantitative test of the theory requires a close examination of the structural details of the chosen solid. Germanium, which occupies a place in solid-state physics comparable to that of the hydrogen atom in atomic physics as a testing ground for theories, offers the best chances for rewarding a concentrated effort. Its vibration spectrum is being unraveled both theoretically and experimentally, and the information on anharmonic forces is rather greater for Ge than other substances. The possibility of obtaining high-purity samples allows clean experiments to be made. The electrical properties are extensively studied; in particular, the phonon-drag experiments are very sensitive to the behavior of the low-frequency modes. Finally, more bizarre experiments are possible on the effect of addition of controlled impurities on the thermal conductivity (e.g., the scattering of phonons by impurity band electrons seems to be rather strong.[82,83]

This paper is concerned with steady-state situations. A study of the approach to steady state, or the response of the conductivity as a function of the frequency of some applied variable heat source, might yield interesting information, if experimentally possible at low temperatures.

Recently some intriguing work has been done on the thermal conductivity of some antiferromagnets[84,85] and ferrites.[86] These experiments deserve a thorough theorectical investigation. Figure 12 shows curves obtained by Slack and Newman for the antiferromagnets MnO, CoO, and NiO. Not only is there a dramatic dip in K at the Neel temperature but the low-temperature conductivity is rather low. Further, this dip is not characteristic of all antiferromagnets, for in a curve of K for MnF_2 supplied to the author by G. Slack there is no discernable anomalous behavior at the Neel temperature. This difference probably may be attributed to the

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[77] H. J. McSkimin and T. B. Bateman, Bell Telephone Laboratories preprint (unpublished).

[78] W. P. Mason, Bell Telephone Laboratories preprint.

[79] B. G. Dick and A. W. Overhauser, Phys. Rev. **112**, 90 (1958).

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[84] G. Slack and R. Newman, Phys. Rev. Letters **1**, 359 (1958).

[85] G. Slack (private communication).

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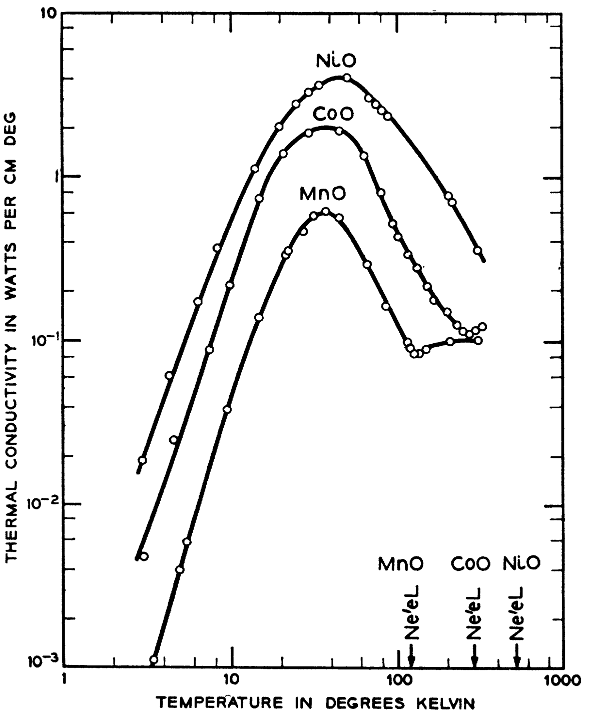

FIG. 12. These measurements of the thermal conductivity of the antiferromagnets MnO, CoO, and NiO were obtained by Slack and Newman.[84, 85] Note the sharp depression at the Neel temperature.

different structures of MnF_2 as compared with MnO, (or CoO and NiO).

The ferrites examined by Douthett and Friedberg[86] also show that different materials exhibit different qualitative behavior. The conductivity is rather low, of the order of mw/cm deg. The interesting fact is that a magnetic field increases the conductivity in two of three specimens examined. These authors have given a theoretical analysis of their results, and conclude that the phonons carry most of the heat current; however, much work remains to be done before this conclusion is accepted. Two recent papers dealing with spin-wave phonon interactions have been published by Kaganov and Tsukernik[87] and Kittel.[88] References to the older literature may be found in a review article by Van Kranendonk and Van Vleck.[89]

These examples serve to illustrate the variety of interesting results that may be expected in magnetic materials.

Graphite presents some special problems because of its cylindrical geometry. In particular, the formulas of this paper need to be used with some care. Experimental and theoretical investigations of the thermal conductivity of graphite are reported in papers by Smith and Rasor[90] and by Hove and Smith.[91]

Very recently Walker and Fairbank[92] have measured the thermal conductivity of solid He^4 containing 0, 0.56, 1.38, and 2.8% He^3 in the temperature range from 1.1 to 2.1 deg K. They find a substantial resistivity which does not vary perceptibly with temperature, and conclude tentatively that the He^3 atoms are aligned along dislocations. However, in discarding the isotope scattering of random He^3 atoms as the source of the resistivity, Walker and Fairbank rely on the theory of Klemens, which predicts that the isotope resistivity is proportional to the temperature. We have already discussed the inadequacy of this approach; in fact, the results of Ambegaokar[27] indicate that the resistivity of isotopes is indeed constant appreciably above the low-temperature maximum. (And remarkably enough, the very low temperatures of the present experiment are above this maximum!) Further, the magnitude of the calculated theoretical resistivity was seen to be in rather good agreement with the experiment of Geballe and Hull. If one uses the numbers given by Walker and Fairbank, the Ambegaokar formula Eq. (5.23) for the resistivity is about an order of magnitude too small. (Actually the temperature is too low to use this formula.) But the dislocation absorption hypothesis requires a dislocation density of $3\times 10^{12}/\mathrm{cm}^2$. This enormous number would probably produce a large strain-field resistivity, which does not seem to be the case in view of the fact that the resistivity is proportional to the He^3 density. Actually Eq. (5.26) is probably more appropriate for solid He^4, which has the close-packed hexagonal structure. Before any definite statement can be made, (5.26) must be revised, allowing $C_{\mathrm{ph}}(\omega)$ to depend on temperature.

There are numerous mechanisms of heat transfer, or scattering mechanisms, which have not been mentioned here. Radiative transfer is discussed briefly by Krumhansl.[93] Exciton mean-free paths have been estimated by Ansel'm and Firsov.[94] In general excitons are not thermally excited at low temperatures (nor is there an observable excitation of electron-hole pairs). It is easy to see that the $1/\tau$ for the scattering of phonons by the creation of these last two excitations contains an exponential activation energy (as was the case for Umklapp processes). The virtual excitation of impurity state electrons is not so restricted, however; the calculation proceeds exactly as in the case of light scattering by an atom except that one uses the electron-phonon interaction Hamiltonian.

We have already expressed the need for a detailed theory of boundary scattering.

Polarons may be expected to scatter phonons by virtue of the distortion of the lattice associated with

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them. We may estimate the importance of such scattering by comparing the Fourier coefficient of the displacement field of the polaron with that of a spherical defect with $v \propto 1/r^2$. This estimate is essentially independent of the anharmonic coupling constants. The distortion is described as a superposition of virtual optical phonons. These phonons, having frequencies much greater than the longitudinal phonons of interest in thermal conduction, can follow the electron adiabatically during the passage of the incident thermal phonon. The theory of Lee, Low, and Pines[95] considers only longitudinal optical phonons. Thus one may extract V_q from their expression for the charge density $\rho = e\,\mathrm{div}\mathbf{v}/\Omega_0$. For a polaron at rest in the limit of small q one obtains

$$V_q \cong \frac{i\Omega_0}{2q\Omega}\left(\frac{1}{n^2}-\frac{1}{\epsilon_1}\right); \quad q \to 0, \tag{8.1}$$

where n is the index of refraction and ϵ_1 the dielectric constant. (In an ionic crystal $\mathbf{v}$ is the relative displacement of positive and negative ions; Ω_0 is the volume per call $\Omega_0 = a^3/4 = 2r_0^3$ in NaCl type crystals, where a is the lattice constant and r_0 the nearest-neighbor distance.) On using Eq. (4.42) we find, dropping the factor i,

$$(V_q)_{\mathrm{pol}}/(V_q)_{\mathrm{pt}} = (2\pi^2\epsilon)^{-1}\cdot\left(\frac{1}{n^2}-\frac{1}{\epsilon_1}\right). \tag{8.2}$$

The square of (8.2) gives the relative strength of the two scattering processes, independent of q and the anharmonic coupling, in the limit of small q. Since typical values of ϵ are $\epsilon > \frac{1}{10}$ the specific polaron scattering can be expected to be at least order of magnitude less than typical point-defect scattering, per scatterer. (For LiF $n^2 = 1.9$, $\epsilon_1 = 9.3$.) (In the limit $q \to 0$ the electron-phonon coupling $\propto q^{\frac{1}{2}}$ becomes small.)

A useful way to obtain information on the influence of crystal structure is to perform experiments on closely related substances. The results for alkali halides have been discussed by Leibfried[4] and Klemens.[2] As suggested by our discussion of the behavior of antiferromagnets, anomalous thermal conductivities may be expected in the vicinity of phase transitions. Some time ago it was observed (Berman[7]) that in certain dielectrics (HBr, CH_4, NH_4Cl) K increases in the region of a specific heat anomally.

The role of thermal conduction (and thermoelectric measurements) in analyzing radiation damage experiments has recently been discussed by Geballe.[96] The influence of irradiation on $K(T)$ can be very useful semiquantitative tool for deciding upon the nature of the damage (just the temperature dependence is very revealing). Conversely new demands made on the theory of thermal conductivity in the analysis of radiation damage experiments should lead to progress in both fields.

ACKNOWLEDGMENTS

Much of this work was done while the author was a summer guest at the Bell Telephone Laboratories. I would like to take this opportunity to thank the staff there for a pleasant and stimulating time. I would like to thank Dr. C. Herring and Professor R. Brout for some very helpful comments on the first draft of this paper, and for a number of enlightening discussions. Dr. J. Hopfield and Dr. M. Lax are to be thanked for several helpful discussions. The author's contact with reality was considerably increased by conversations with his experimental colleagues, especially Dr. T. H. Geballe, Dr. R. Pohl, M. V. Klein, and M. Moss. Dr. R. Pohl and Dr. G. Slack kindly provided some unpublished data. Professor G. Dresselhaus and M. Klein deserve thanks for their patience during the formative period of some of the ideas presented here. I would like to thank the National Science Foundation for fellowship support 1957–60.

APPENDIX A. ESTIMATE OF ANHARMONICITIES

Here we indicate some ways in which one may obtain order of magnitude estimates of the anharmonicity coefficient $g = \varphi'''(a)$. Ideally the quantity required is $C_{qq'}$ (or $C_{qq'q''}$), but it seems very difficult to extract these coefficients from experiment, especially their fluctuations in sign [in terms of a Grüneisen $\gamma(q)$ one would say that the γ's fluctuate considerably, even in sign].[97] In principle there is no real difficulty in evaluating the C's theoretically; one just proceeds as in the text, only with more general forces and considerable patience. Some special cases have been evaluated recently by Stern.[98] The result of the simple model used in the text was that all results should be correlated with a single parameter, $g = \varphi'''(a)$. [More precisely, one also needs $f \equiv \varphi''(a)$.]

First consider an ionic crystal according to the classical model,[99] in which short-range repulsive forces are represented by a power law. The repulsive force varies rapidly with distance so that we expect that it contributes most of the anharmonic force, contrary to the situation in lattice energy calculations. The interatomic potential is taken to be

$$\varphi = (\lambda/r^n \pm (e^2/r). \tag{A1}$$

In the usual theory the lattice energy is obtained by summing (A1) over all distinct pairs in the crystal, which results in two constants: $\Phi = \Sigma\varphi = \lambda A_n R^{-n} - \alpha e^2 R^{-1}$, where R is the equilibrium nearest-neighbor distance, α is Madelung's constant (~ 1.7), and λA_n is determined by the equilibrium condition to be $\lambda A_n \equiv \alpha e^2/nR^{n-1}$. n is found from compressibility data to vary roughly between 6 and 10. Hence the bulk of the contribution to

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[96] T. H. Geballe, J. Appl. Phys. **30**, 1153 (1959).

[97] See e.g., T. H. K. Barron, Ann. Phys. **1**, 77 (1957).

[98] E. Stern, Phys. Rev. **111**, 786 (1958).

[99] See e.g., C. Kittel, *Introduction to Solid-State Physics* (John Wiley & Sons, Inc., New York, 1956), 2nd ed., Chap. 3.

λA_n comes from nearest neighbors and we may eliminate A_n by dividing λA_n by z, the number of nearest neighbors. Thus

$$\lambda \cong \alpha e^2/znR^{n-1}. \tag{A2}$$

Hence (A1) gives the relation

$$R^3\varphi'''(R) = [6-(n+1)(n+2)\alpha z^{-1}]e^2/R. \tag{A3}$$

This result is sensitive to n; for LiF with $n=6$, putting $R=a$ one obtains $ga^3 \cong -10e^2/a$; for $n=8$ one obtains $ga^3 \cong -20e^2/a$; $n=10$ yields $ga^3 \cong -32e^2/a$. This shows that the anharmonicities are more sensitive to n than to γ, which does not differ so greatly as do the preceding g's.

For NaCl, with two ions of comparable size, this estimate may be realistic. NaCl has $n \cong 9$ and $ga^3 \cong -26e^2/a$. For illustration let us compare this with the value quoted in the text, found by a different method, namely, $|g| = \beta\rho\gamma c^2$, where $\beta \cong 24$. For the NaCl structure $\rho = M/2a^3$, where M is the total mass of the two ions, and a is the interionic distance. For NaCl with $M=58.5$ amu, $a=2.75$ A, $\gamma=1.6$, and $c \cong 3\times 10^5$ cm/sec, ga^3 is the same computed by both methods for $\beta \cong 30$. For LiF, with $a=2.01$ A and $c \cong 5\times 10^5$ cm/sec, we find a rather low $\beta \cong 5$. This smallness is to be attributed to the rather large sound velocity. As mentioned previously, LiF is a special case; the NaCl value is probably more typical. In any event it seems that the answers obtained by the present method are more reliable than those from the relation $g = \beta\gamma\rho c^2$, which requires a difficult estimate of a complicated sum over angles; nevertheless, it is reassuring that the two methods give comparable results.

We illustrate the second method by a one-dimensional model of a diatomic lattice with nearest-neighbor interactions. The physical principles involved are more transparent for this case than in the three-dimensional situation. The necessary equations are lifted bodily from p. 55 ff of Born and Huang's book.[9] The distance between the atoms of masses m_1 and m_2 is $s/2$; s is the lattice constant. The interatomic potential is $\varphi(s/2)$. In the long-wavelength limit the velocity c of the acoustic waves is given by

$$c^2 = s^2\varphi''(s/2)/2M, \tag{A4}$$

where $M = m_1 + m_2$ and primes indicate differentiation with respect to the argument. A measure of the change in the force constant when the string is stretched is Grüneisen's γ, defined by $\gamma = d\ \ln\omega/d\ \ln s$. This definition gives

$$\gamma = s\varphi'''(s/2)/4\varphi''(s/2). \tag{A5}$$

Elimination φ'' from (A4) and (A5) gives

$$\varphi'''(s/2) = 8\gamma Mc^2/s^3, \tag{A6}$$

which is of the same form and order of magnitude of the previously quoted result. The three-dimensional problem differs essentially by having different geometry (the density and the number of neighbors are different) and the presence of an angular factor multiplying the equation corresponding to (A5). [See Eq. (2.23), for example.] A rough evaluation by the author gave the result $g = 24\gamma\rho c^2$, but this should not be believed except to order of magnitude. (See also Klemens' article, footnote 2.) As mentioned before in the discussion of ionic crystals, it is preferable to have an explicit potential from which one may compute the quantity $\varphi'''(a)$ (or better yet, B^{ijk}). [For central forces B^{ijk} is just given by (2.21).] Since the anharmonic coefficient is a rather more sensitive test of the assumed repulsive potential, the reader may prefer to replace the power law by an exponential[9]: $Be^{-r/\rho}$. In this case one finds $gR^3 \approx -(\alpha e^2/zR)\cdot(r_0/\rho)^2$ using the preceding argument. Thus the ratio of the power law coupling constant to the exponential law constant is roughly $(r_0/\rho)^2/n^2$. Tables of (r_0/ρ) may be found in the book by Born and Huang; most values lie between 8 and 11. Thus both methods give roughly the same value for g. Note, however, that the variation of g in different materials is rather less for the exponential force; in particular LiF and NaCl have about the same g.

APPENDIX B. ROLE OF NORMAL PROCESSES IN ESTABLISHING EQUILIBRIUM

As indicated in the text, in the absence of Umklapp collisions, in a perfect crystal the total crystal momentum $\mathbf{P}$ would be unchanged by the normal three-phonon processes. However, before one could conclude that the conductivity were infinite ($\mathbf{Q}\neq 0$ when $\nabla T=0$) one must establish that a finite $\mathbf{P}$ implies a nonzero heat flux $\mathbf{Q}$.

This result is very different from the usual situation in the kinetic theory of gases, where the heat current and momentum flux are independent quantities (in this case one usually sets $\mathbf{P}$ equal to zero). The fundamental reason for this possibility is that gas molecules are not destroyed or created, while phonons (bosons) are not conserved, but are absorbed, e.g., at the cold end of the specimen. This latter distinction gives rise to the impossibility of maintaining $\mathbf{P}=0$ in the presence of a temperature gradient.

From Eq. (3.4) one sees that $\mathbf{Q}\rightarrow 0$ if $\mathbf{P}\rightarrow 0$.

This linear relation between $\mathbf{P}$ and $\mathbf{Q}$ is essentially an *accident*, due to the fact that $\omega \rightarrow cq$ for small q. At low temperatures one is then guaranteed that the usual viewpoint is correct, since only small q excitations are important, but the foundation of the standard viewpoint on *general* arguments is somewhat illusory. For example, if $\omega = Aq^2$ instead (e.g., spin waves), then $\mathbf{P}$ and $\mathbf{Q}$ can be independent, for $\mathbf{P} \propto \sum_q N_q\mathbf{q}$ and $\mathbf{Q} \propto \sum N_q q\mathbf{q}$. In this latter example one must prove that such independent solutions satisfy the basic transport equation (else they would not be solutions); however, the author is unaware that anyone has proved that such solutions *do not* exist for the homogeneous (i.e., $\partial T/\partial x = 0$) Peierls integral equation. Such solutions might exist for higher q's, where $\omega(q)$ generally deviates significantly from the linear relation $\omega = cq$. When the branch is flat (cf. especially the transverse acoustic branch of germanium) one has $\partial\omega/\partial q = 0$ so that $\mathbf{Q} = 0$ while $\mathbf{P}$ may be finite. This simple example contradicts the usual step from $\mathbf{P} \neq 0$ to $\mathbf{Q} \neq 0$. At low temperatures this is the case only for a small fraction of the phonons, but it is an important matter of principle that there is no heat transport in these high frequency modes even when the normal process fails to restore equilibrium. If one separates the contributions to K according to frequency, then in the preceding situation K is not infinite for these modes. Some further clarification of these points seems desirable.

The considerations of this appendix were developed in conversations between Professor R. Brout, M. Klein, and the author.

APPENDIX C. MULTIPLE SCATTERING CORRECTIONS

The perturbation treatment given in the text supposes that the wave incident on a scatterer is the unperturbed plane wave, unmodified by the presence of the other scatterers. This assumption may be expected to fail when the density of scatters is sufficiently high, which critical density is less for a large scattering cross section σ. In order to get some idea of the conditions under which such effects are appreciable, we consider the scatterers to be distributed at random. Then one requires that the index of refraction k^1/k be nearly unity where k^1 is the wave number in the medium and k is the vacuum (i.e., perfect crystal) wave number. The necessary information is contained in the equation[100]

$$k'^2 = k^2 + 4\pi n f(0), \tag{C1}$$

where n is the density of scatterers and $f(0)$ is the forward scattering amplitude $f(q \to q)$. (There is an additional factor of order unity in the second term of the right-hand side of (C1) which is of no consequence here.) In order for there to be no correction it is necessary that

$$2\pi n f / k^2 \ll 1. \tag{C2}$$

For an order of magnitude calculation, we take $\sigma \sim 4\pi |f(0)|^2$ as an approximation to $d\sigma/d\Omega = |f(\theta)|^2$.

[Some care is needed when considering strain-field scattering. This is because in the quantity $C_{qq'}$, the factor b_{ijk} is zero for $\mathbf{q} = \mathbf{q}'$, while $\mathbf{V}_{\mathbf{q}'-\mathbf{q}}$ is usually singular in this case. Therefore the considerations of this appendix are somewhat formal, pending more careful investigations. For the case of $v(r) \propto 1/r^2$, however, the limit $C_{qq'}$ is well defined as $\mathbf{q}' \to \mathbf{q}$ so that Eq. (C5) is valid.] For a crude estimate of σ we take $c\tau$ to be a mean-free path (q is larger than this since τ^{-1} is a difference of scattering probabilities). Then if we call $\tau_s \equiv \tau n$ (the τ for $n = 1$) we have $1/\tau_s \sim \sigma c \sim 4\pi c |f(0)|^2$, or

$$f(0) \sim (4\pi c \tau_s)^{-\frac{1}{2}}. \tag{C3}$$

On using (C3), (C2) becomes (with $\lambdabar = k^{-1}$)

$$\lambdabar^2 \ll l_s^{\frac{1}{2}}/n = (l/n)^{\frac{1}{2}}, \tag{C4}$$

when $l_s = c\tau_s$ and $l = c\tau$. Since $l = l(\lambdabar)$ Eq. (4) requires further rearrangement for specific applications. For instance, for ω^4 scattering characteristic of isotopes or simple point defects at low frequencies the condition (C4) is independent of wavelength. In this case if we write $1/\tau = A\omega^4 = Ac^4/\lambdabar^4$, (C4) becomes

$$(nAc^3)^{\frac{1}{2}} \ll 1; \quad 1/\tau = A\omega^4. \tag{C5}$$

For the isotope experiments of Geballe and Hull[23] this inequality is well satisfied. For take $A \approx 2 \times 10^{-44}$ appropriate to Ge,[22] $n \approx 10^{22}/\text{cm}^3$,[23] $c \approx 3 \times 10^5$ cm/sec; the left-hand side is less than 10^{-2} which is clearly less than unity. Although the strain-field scattering cross section is rather larger, per scatterer, than the isotope cross section, the density is however, usually lower. From (4.45) it is evident that in most reasonable situations Eq. (C4) or (C5) is satisfied for strain-field scattering. With $\Omega_0 \sim 10^{-23}$ cm^2, $\epsilon \sim 10^{-1}$, and $\gamma \sim 2$, we find that one must have $n \ll 10^{21}/\text{cm}^3$. Although these conditions are quite lenient, σ is underestimated somewhat by using $1/\tau \sim n\sigma c$. On the other hand, we have overestimated C_{qq} (as mentioned before) in the case of strain scattering. We conclude that for point defects of the usual sort multiple scattering effects can be ignored in most experimental situations. For scatterers of other shapes (such as dislocations) Eq. (C1) will probably have to be modified somewhat.

APPENDIX D. GENERAL ANALYSIS OF THE PERTURBATION SERIES

Future developments in both theory and experiment probably will require a more detailed study of higher terms in the perturbation series for the scattering matrix. The wide variety of properties available in solids should provide an opportunity for testing such higher order effects. An approach to scattering problems is obtained here which is more general than was required in the main body of the paper. For our "low-brow" field theory a general formal analysis is undesirable and unnecessary (except for a study of many-body properties[13]) for the following practical reasons. There are actually two expansions in our problem: the expansion of the potential energy into a power series (although some other form of this nonlinear response may eventually turn out to be appropriate), and the perturbation series itself. There is no guarantee, for example, that a fourth-order perturbation term in the cubic interaction V_3 is as important as a second-order term in the quartic potential V_4. Therefore the discussion is confined to the lower orders in the three-phonon and strain-field interactions. (The perturbation for isotopic scattering has

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[100] For a thorough treatment of multiple scattering theory see M. Lax, Revs. Modern Phys. 23, 287 (1951).

the same formal structure as V_s.) For clarity the various terms are represented by graphs; these graphs are similar to ordinary Feynman diagrams[101] except that the time ordering of the vertices is important.

A slightly more general and more symmetric notation is used here than in the text. On omitting constants, the perturbation considered is (V_s=strain-field perturbation)

$$V=V_3+V_s=\frac{1}{3!}\sum_{\mathbf{mno}} A_{\mathbf{mno}}{}^{ijk}u_{\mathbf{m}}{}^{i}u_{\mathbf{n}}{}^{j}u_{\mathbf{o}}{}^{k} +\tfrac{1}{2}\sum_{\mathbf{mn}}\Big(\sum_{\mathbf{o}} A_{\mathbf{mno}}{}^{ijk}v_{\mathbf{o}}{}^{k}\Big)u_{\mathbf{m}}{}^{i}u_{\mathbf{n}}{}^{j}. \tag{D1}$$

(Summation on the indices i, j, k is implied.) The $A_{\mathbf{mno}}$ coefficients replace the previous constants $B_{\mathbf{mn}}$ of Eq. (1.7). Since the polarization vectors are odd functions of the wave vector $\mathbf{q}$, substitution of (1.4) gives the results

$$V_3=\frac{1}{3!}\left(\frac{\hbar}{2\rho\Omega}\right)^{\frac{3}{2}}\sum_{qq'q''}\frac{C(q,q',q'')}{(\omega_q\omega_{q'}\omega_{q''})^{\frac{1}{2}}} \times(a_q-a_{-q}{}^{*})(a_{q'}-a_{-q'}{}^{*})(a_{q''}-a_{-q''}{}^{*}), \tag{D2}$$

$$V_s=\frac{\hbar}{4\rho\Omega}\sum_{qq'}\frac{C(q,q')}{(\omega_q\omega_{q'})^{\frac{1}{2}}}(a_q-a_{-q}{}^{*})(a_{q'}-a_{-q'}{}^{*}), \tag{D3}$$

in which the quantities $C(q,q',q'')$ and $C(q,q')$ are defined by

$$C(q,q',q'')\equiv\Delta(\mathbf{q}+\mathbf{q}'+\mathbf{q}'') \times\sum_{ijk} b_{ijk}(\mathbf{q},\mathbf{q}',\mathbf{q}'')e_q{}^{i}e_{q'}{}^{j}e_{q''}{}^{k}, \tag{D4}$$

$$C(q,q')\equiv\sum_{q''}\Delta(\mathbf{q}+\mathbf{q}'+\mathbf{q}'') \times\sum_{ijk} b_{ijk}(\mathbf{q},\mathbf{q}',\mathbf{q}'')e_q{}^{i}e_{q'}{}^{j}v_{q''}{}^{k}, \tag{D5}$$

$$b_{ijk}(\mathbf{q},\mathbf{q}',\mathbf{q}'')\equiv\sum_{\mathbf{mno}} A_{\mathbf{mno}}{}^{ijk} \times\exp[i(\mathbf{q}\cdot\mathbf{m}+\mathbf{q}'\cdot\mathbf{n}+\mathbf{q}''\cdot\mathbf{o})]. \tag{D6}$$

The notation $(-q)$ means that the vector q is changed in sign, leaving the polarization index unchanged. Equation (D5) displays the possibility of Umklapp-type scattering by the strain field. For normal zone structures and at low temperatures (where only small q's are important) such scatterings are improbable, because $\mathbf{v}_{\mathbf{q}}$ generally is a decreasing function of q. At short wavelengths, there are some scatterings for which $\mathbf{q}+\mathbf{q}'+\mathbf{G}$ is very small, leading to a large cross section. For the present discussion we ignore the Umklapp collisions.

The fundamental vertex corresponding to V_3 was shown in Fig. 1(a). In addition to this process, and the second-order process of Fig. 1(b) there is the "vacuum" fluctuation Fig. 13(a) in which three-phonons are virtually created and then annihilated. This latter process is of interest in the study of the ground state but not in scattering problems. The basic strain-field scattering process is displayed in Fig. 13(b). An incident phonon q absorbs a virtual phonon $\mathbf{q}'-\mathbf{q}$ from the strain field and is scattered to the state q'. The action of the strain field is indicated by a cross.

The general expression for the transition rate between two states q, q' of the harmonic Hamiltonian H is given by

$$w_{q\to q'}=\frac{2\pi}{\hbar}|\langle q'|\mathbf{T}|q\rangle|^2\delta(E_q-E_{q'}), \tag{D7}$$

where the "transition operator" $\mathbf{T}$ obeys the equation[15]

$$\mathbf{T}=V+V(E-H_0+i\eta)^{-1}\mathbf{T};\quad \eta\to 0. \tag{D8}$$

The interaction V is given by (D1) and contains two parts. If (D8) is iterated, the standard perturbation series is generated. This equation shows clearly how the three-phonon processes modify the propagation of a phonon in a strained lattice.

First consider the Born series for the scattering of "bare" phonons (i.e., ignore V_3). The $\mathbf{T}$ matrix is then an expansion in powers of the strain-field potential V_s. The first three terms are illustrated in Figs. 13(b)–13(d).

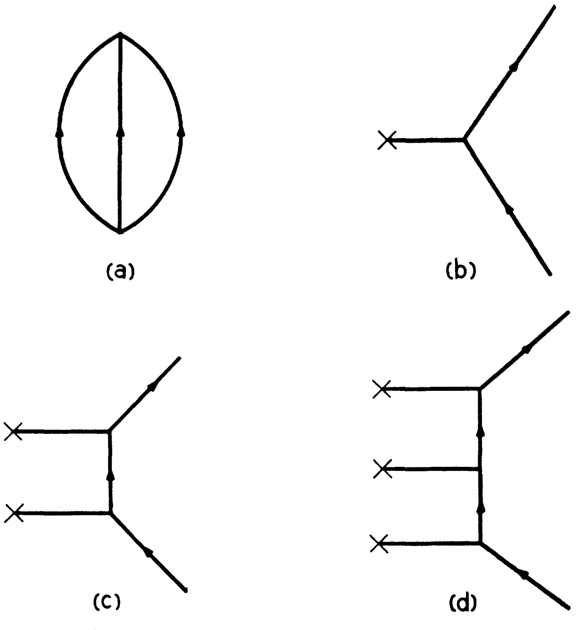

FIG. 13. (a) shows a fluctuation in the ground state caused by the virtual creation of three-phonons by the anharmonic forces. This graph is of interest for a study of the ground state energy but is not involved in scattering problems. (b) represents the basic strain field scattering interaction (or scattering by any static perturbation) in which the incident phonon absorbs a virtual phonon from the strain field, being thereby scattered to another state. (c) and (d) represent successive scatterings, corresponding to higher-order terms in the Born series.

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[101] R. P. Feynman, Phys. Rev. 76, 749 (1949).

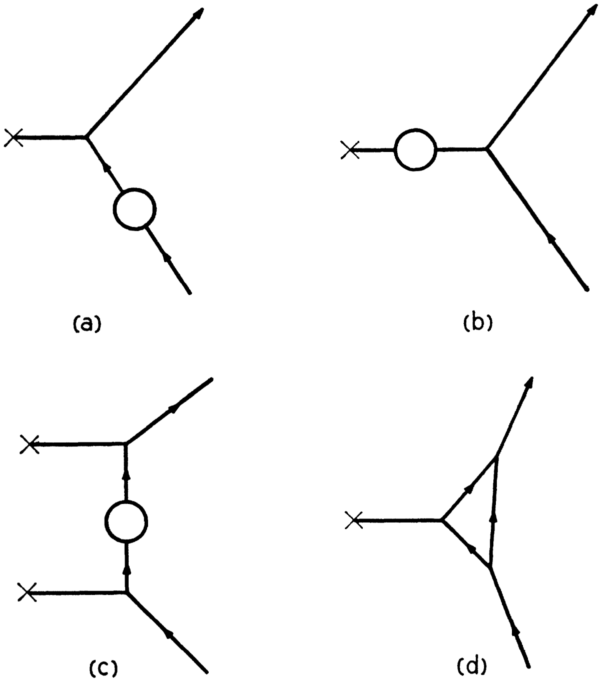

FIG. 14. These diagrams show some typical examples of the modification of the strain-field scattering by the three-phonon interaction. (a) and (c) are typical self-energy modifications (b) shows how the anharmonic interaction can screen the strain field. (d) is a "radiative" correction; or else one can say that one of the virtual phonons in a self-energy bubble has scattered off the strain field.

The influence of the three-phonon processes (in addition to their effect in a "perfect" crystal) may be found by constructing three-phonon vertices (in all possible ways) in these diagrams. We discuss three interesting examples. First, any line may be modified by the insertion of a self-energy "bubble" [Fig. 1(b)] as shown in Figs. 14(a)-14(c). All such graphs are taken into account[102] by renormalizing the phonon energy [just use the experimental $\omega(q)$]; however, the process described by Fig. 14(d) is an observable process (theoretically observable, at least!). It is analogous to the radiative corrections in quantum electrodynamics.[101] In the earlier part of this paper considerable attention was given to the fact that the "normal" three-phonon processes conserve the total wave vector. It is now clear that the strain field can modify the three-phonon processes so that wave vector is not conserved, as shown in Fig. 15(a), if one of the phonons is scattered by the strain field. Closely related are the processes displayed in Fig. 15(b) in which a virtual pair of phonons is created in the strain field, one of which is scattered by an incoming phonon; and Fig. 15(c) which shows how one of the three-phonons created in a vacuum fluctuation may be absorbed (along the incident phonon) by the strain field. It is not obvious that these processes are negligible in comparison with the elementary scattering process Fig. 13(b), because the effect of the three-phonon process is artificially suppressed, as far as the thermal resistivity is concerned, by the conservation law, at temperatures so low that Umklapp scattering is negligible. Until a quantitative estimate is made, the best evidence that these terms are indeed negligible will probably be the reasonable theoretical success in explaining the experimental results without taking such processes into account.

The form of the perturbations (D2) and (D4) makes it possible to write down the relevant matrix elements directly.

Finally, consider some properties of the displacement field operator. The commutator of $u_k(x)$ and $u_l(x')$ at two different positions and times are closely related to the propagation of disturbances in the lattice. [The operators have been transformed to the interaction representation, and so have the explicit time dependence of Eq. (2.10).] The commutation laws (1.5) lead directly to the result (x stands for both $\mathbf{x}$ and t)

$$[u_k(x),u_l(x^1)]=i\hbar\rho^{-1}D_{kl}(x-x'), \qquad \text{(D9)}$$

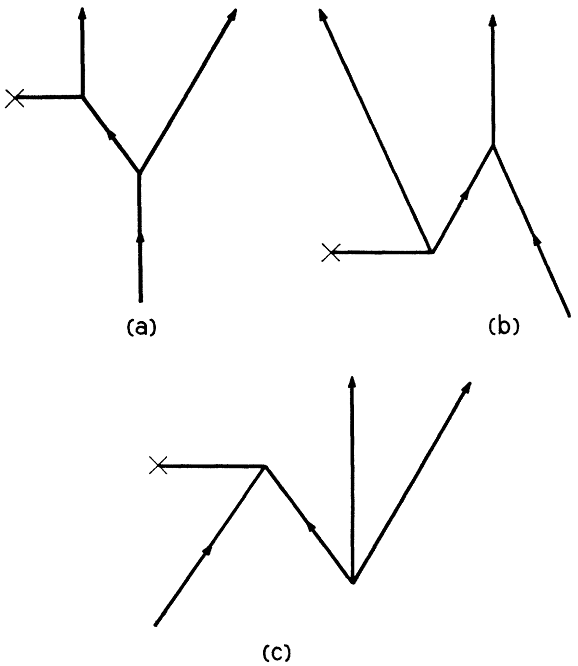

FIG. 15. These diagrams display some ways in which the strain field modifies the three-phonon processes. In (a) one of the final phonons scatters off the strain field. In (b) one of two phonons virtually created by the strain field absorbs an incident phonon. (c) shows how a "vacuum fluctuation" and the strain field can collaborate to produce an ordinary three-phonon scattering process. By including one higher order in the strain field, the non-Umklapp three-phonon processes do not conserve wave vector.

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[102] This is not true for graphs such as Fig. 14(b). The process shown in Fig. 14(b) illustrates how the anharmonic forces can screen the strain field, thereby reducing its strength. This process is similar to the vacuum polarization in quantum electrodynamics.

where

$$D_{kl}(x-x')=\frac{1}{\Omega}\sum_{\mathbf{q},\lambda} e_k^{\lambda}(\mathbf{q})e_l^{\lambda}(\mathbf{q}) \times\left\{\frac{\sin[\mathbf{q}\cdot(\mathbf{x}-\mathbf{x}')-\omega(q)(t-t')]}{\omega_\lambda(\mathbf{q})}\right\}. \quad \text{(D10)}$$

If $\mathbf{x}$ and $\mathbf{x}'$ are taken to be two lattice points $\mathbf{m}$ and $\mathbf{n}$, then the completeness relation for the polarization vectors enables one to prove

$$[\partial D_{kl}(\mathbf{m}-\mathbf{n})/\partial t']|_{t'=t}=\frac{N}{\Omega}\delta_{kl}\delta_{\mathbf{mn}}. \quad \text{(D11)}$$

Now consider the Green's function

$$G_{kl}(x-x')\equiv\langle 0|T[u_k(x)u_l(x')]|0\rangle. \quad \text{(D12)}$$

T is the time-ordering operator and $|0\rangle$ denotes the vacuum state. We now ignore the lattice and assume a continuous unbounded spectrum. One can easily show that G_{kl} obeys the equation $[\delta^{(4)}(x)\equiv\delta(\mathbf{x})\delta(t)]$

$$[\omega^2(-i\nabla)+\partial^2/\partial t^2]G_{kl}(x)=\delta_{kl}\delta^{(4)}(x). \quad \text{(D13)}$$

In (D13) the wave vector $\mathbf{k}$ has been replaced by $-i\nabla$. This approach enables one to formulate the theory in an elegant way by focusing attention on the time development of the displacement operator. For instance, we can write the general solution as

$$u_k(x)=u_k^{in}(x)+\sum_l\int d^4x'G_{kl}(x-x')j_l(x'). \quad \text{(D14)}$$

$\mathbf{j}(x)$ is the source function of the field, and contains the strain field and anharmonic effects. The boundary condition is made explicit by $\mathbf{u}^{in}$. [For instance, the incoming wave could be of the form (2.10).]

APPENDIX E. SCATTERING BY DENSITY VARIATIONS

Another source of scattering in strained lattices besides the modification of the force constants by the intervention of the anharmonic potential is the density change associated with the strain. In this appendix we show that this latter effect is much smaller than the anharmonic scattering described in Sec. IV, at least for localized scattering centers. Consider the wave equation for a wave $\psi(\mathbf{x},t)=\psi(\mathbf{x})e^{-i\omega t}$ of constant frequency ω:

$$[\nabla^2+(\omega^2/c^2)]\psi=0. \quad \text{(E1)}$$

The sound velocity c is given by an expression of the form $c^2=B/\rho$, where B is some elastic constant and ρ is the density. Thus c is not constant in a strained lattice; both B and ρ can vary. We have already discussed the effect on "B" of the anharmonic forces (Sec. IV); now we consider B constant and discuss the effect of density variations. Evidently $\rho=\rho_0(1+\Delta)$, where $\Delta(\mathbf{x})$ is the dilatation, and ρ_0 the normal density. Thus we can write $c^2=c_0^2(1+\Delta)^{-1}$. The index of refraction $n=c_0/c$ is $(1+\Delta)^{\frac{1}{2}}$. On setting $k=\omega/c$, Eq. (E1) may be written as

$$(\nabla^2+k^2)\psi=-k^2\Delta\psi. \quad \text{(E2)}$$

For an incident plane wave e^{ikz}, the solution to this equation for the scattered wave is, in the Born approximation

$$\psi_{\text{sc}}=-[\Delta(\mathbf{k}'-\mathbf{k})k^2/4\pi](e^{i\mathbf{k}'\cdot\mathbf{r}}/r); \quad \text{(E3)}$$

$$\Delta(\mathbf{q})=\int e^{i\mathbf{q}\cdot\mathbf{x}}\Delta(\mathbf{x})d^3x. \quad \text{(E4)}$$

The scattering amplitude $f_1(\theta)$ is $(\cos\theta=\hat{k}\cdot\hat{k}')$

$$f_1(\theta)=-k^2\Delta(\mathbf{q})/4\pi, \quad \mathbf{q}=\mathbf{k}'-\mathbf{k}. \quad \text{(E5)}$$

The differential cross section is related to f_1 by $d\sigma/d\Omega=|f_1|^2$. From the matrix elements (4.12) and (4.13) for strain-field scattering, one finds that (dropping signs)

$$f_s(\theta)=|C_{kk'}|/4\pi\rho c^2. \quad \text{(E6)}$$

From Eq. (4.31), we can obtain an estimate of $C_{kk'}$. For a simple cubic lattice there are six terms in the sum; replacing the angular factors by $\frac{1}{3}$ and setting $Na^3=\Omega$, $|\mathbf{k}|=|\mathbf{k}'|$,

$$C_{kk'}\approx gk^2(qV_q). \quad \text{(E7)}$$

The $\Delta_{\mathbf{q}}$ defined by (E4) is related to V_q in (E7) by

$$|\Delta_{\mathbf{q}}|=\Omega\mathbf{q}\cdot\mathbf{V}_{\mathbf{q}}. \quad \text{(E8)}$$

[Recall the Ω in Eq. (4.8)]. Therefore (E7) and (E6) give

$$f_1/f_s\approx c^2\rho/g\approx 1/40, \quad \text{(E9)}$$

using $g\approx 40\rho c^2$ (Appendix A). Thus one may generally ignore the scattering caused by the density variation, in comparison with that caused by the anharmonic forces.