Thermal Conductivity and Lattice Vibrational Modes

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I. Introduction

1. INTRODUCTION

The heat transport by lattice waves in solids is governed by the anharmonicities of the lattice forces (which are also responsible for ther-

mal expansion), by the various imperfections of the crystal lattice, and by the external boundaries. Moreover, in the case of metallic and semimetallic solids, the lattice component of thermal conduction is also governed by the free electrons. Not only may many different factors influence the thermal conductivity, but the processes which provide the principal sources of thermal resistance may vary from one material to another. In fact they may vary in different temperature regions in any one material. Thus the phenomenon of thermal conduction by lattice waves offers great diversity and provides an interesting field of study, both from a fundamental point of view, in which one desires to attain agreement between observation and the theoretical concepts, and from the more applied viewpoint in which one desires to use thermal conductivity as a tool in the study of lattice imperfections.

Early investigations by Eucken[1] showed that the thermal conductivity of dielectric solids is usually inversely proportional to the absolute temperature T from liquid air temperatures to higher values. This was explained by Debye[2] in the following way. The lattice vibrations can be resolved into traveling waves which carry heat. The thermal conductivity is

$$\kappa \sim Svl, \tag{1.1}$$

where S is the specific heat per unit volume, v the sound velocity, and l an attenuation length of the lattice waves. Because of the anharmonicities, the thermal fluctuations in density of a solid lead to local fluctuations in the velocity of the lattice waves, which are therefore scattered. Debye showed that l, and therefore κ, vary as $1/T$, provided the temperature is not too low (S constant).

While the basis of this approach is sound, at least at high temperatures where individual atoms vibrate as if independent, Debye's treatment is not rigorous. A rigorous formulation of the problem was given by Peierls,[3] who treated the effect of terms anharmonic in the interchange of energy between lattice waves, and who, by quantizing the lattice waves, extended the theory to low temperatures. He investigated the manner in which the crystal attains thermal equilibrium and distinguished between two types of interaction processes: those which conserve quasi-momentum of the lattice waves and those which do not. Without the latter processes, equilibrium could not be attained and the thermal resistance would vanish. Processes arising from the anhar-

[1] A. Eucken, *Ann. Physik* **34**, 185 (1911); *Verhandl. Deut. Phys. Ges.* **13**, 829 (1911); *Physik. Z.* **12**, 1005 (1911).

[2] P. Debye, *in* "Vorträge über die kinetische Theorie der Materie und Elektrizität." Teubner, Berlin, 1914.

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

monicity and not conserving quasi-momentum, namely the "umklapp" processes, contribute a term to the thermal resistance which is proportional to T at high temperatures, but which decreases exponentially at low temperatures. Peierls also pointed out that lattice imperfections and external boundaries increase the resistance.

In order to test the low-temperature predictions of the theory, de Haas and Biermasz[4–6] measured the thermal conductivity of quartz, diamond, and some alkali halides at liquid helium and liquid hydrogen temperatures. At liquid hydrogen temperatures, the resistance decreased with decreasing temperature, but not as fast as predicted by Peierls because, as we now know, point defects made a large contribution to the thermal resistance in these cases. At liquid helium temperatures, the resistance increased again with decreasing temperature and was found to depend upon the diameter of the single crystal rods employed, because the external boundaries limit the mean free path of the lattice waves, as was explained by Casimir.[7]

The theory was extended by Pomeranchuk, who pointed out new restrictions on the anharmonic interactions and showed that the expressions for the thermal conductivity diverge at low frequencies for longitudinal waves, unless one considers higher-order interactions at high temperatures[8] and the external boundary at low temperatures.[9] Herring[10] showed that these divergence difficulties are at least partly removed if one considers the anisotropy of real crystals.

After the war, work on thermal conductivity at low temperature was renewed on a larger scale, particularly at Oxford. Berman[11,12] measured the conductivity of a number of dielectric solids in the form of good single crystals, polycrystalline substances, and glasses over a wide range of temperatures, and studied the effect of neutron irradiation damage.[13] Webb *et al.*[14] made measurements on solid helium.

To account for the various types of behavior thus observed, Klemens[15]

[4] W. J. de Haas and T. Biermasz, *Physica* **2**, 673 (1935).
[5] W. J. de Haas and T. Biermasz, *Physica* **4**, 752 (1937).
[6] W. J. de Haas and T. Biermasz, *Physica* **5**, 47, 320, 619 (1938).
[7] H. B. G. Casimir, *Physica* **5**, 495 (1938).
[8] I. Pomeranchuk, *J. Phys.* (*USSR*) **4**, 259 (1941).
[9] I. Pomeranchuk, *J. Phys.* (*USSR*) **6**, 237 (1942).
[10] C. Herring, *Phys. Rev.* **95**, 954 (1954).
[11] R. Berman, *Proc. Roy. Soc.* (*London*) **A208**, 90 (1951).
[12] R. Berman, *Proc. Phys. Soc.* (*London*) **A65**, 1029 (1952).
[13] R. Berman, F. E. Simon, P. G. Klemens, and T. M. Fry, *Nature* **166**, 277 (1950).
[14] F. J. Webb, K. R. Wilkinson, and J. Wilks, *Proc. Roy. Soc.* (*London*) **A214**, 546 (1952).
[15] P. G. Klemens, *Proc. Roy. Soc.* (*London*) **A208**, 108 (1951).

extended the theory. Processes which conserve quasi-momentum were shown to be relatively unimportant, except at low frequencies. Only scattering by imperfections and umklapp processes produce thermal resistance. Expression (1.1) for the thermal conductivity can be generalized to the form

$$\kappa = \tfrac{1}{3}\int S(\omega)vl(\omega)\,d\omega \tag{1.2}$$

where $S(\omega)$ is the contribution to the specific heat per frequency interval from lattice waves of frequency ω. It follows that the temperature dependence of κ is governed by the frequency dependence and by any intrinsic

TABLE I. FREQUENCY VARIATION OF SCATTERING PROBABILITY AND TEMPERATURE VARIATION OF THERMAL RESISTANCE FOR VARIOUS INTERACTION MECHANISMS

Scattering mechanism	$1/l(\omega)$	$1/\kappa(T)$
(a) Low temperatures $T < \theta$		
External boundaries	ω^0	T^3
Grain boundaries	ω^0	T^3
Thin sheets embedded in crystal of continuous orientation	ω^2	T^1
Stacking faults	ω^2	T^1
Conduction electrons in metals	ω^1	T^2
Dislocations (strain field)	ω^1	T^2
Dislocations (core)	ω^3	T^0
Long cylinders	ω^3	T^0
Point defects	ω^4	T^1
Umklapp processes	ω	$T^3e^{-\theta/\alpha T}$
(b) High temperatures $T > \theta$		
Umklapp processes	...	T^1
All imperfections	...	T^0

temperature dependence of $l(\omega)$. At low temperatures, in particular, where $\int S(\omega)\,d\omega \propto T^3$, $\kappa \propto T^{3-n}$ if $l(\omega) \propto \omega^{-n}$. Since different types of imperfections lead to different forms for the frequency dependence of $l(\omega)$, one can draw conclusions about the nature of lattice imperfections from the thermal resistance which they cause. Both the frequency variation and an estimate of the magnitude of $l(\omega)$ have been obtained for a number of imperfections;[16] these are listed in Table I, together with the corresponding temperature variations of the thermal conductivities at low temperature. If more than one process is operative, the effective value of $1/l$ is found by adding $1/l(\omega)$ for each process; this corresponds very roughly to additivity of the corresponding thermal resistances.

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

The theory of Klemens differs from that of Pomeranchuk mainly in the treatment of the low-frequency longitudinal waves. Pomeranchuk thought that they provide the major part of the heat flow, whereas Klemens thought they are unimportant in good crystals, but important in glasses. It now appears that, while they do not carry the bulk of the heat current, there are cases in which they cannot be neglected.

Leibfried and Schloemann[17] developed a treatment of the thermal resistance due to anharmonic terms which, at high temperatures, gives the magnitude as well as the temperature dependence of the resistivity. At low temperatures, however, where the intrinsic resistance varies very rapidly with temperature, they could obtain only a rough estimate of the resistivity.

The Oxford workers found a number of cases in which the thermal resistance varied exponentially, as predicted by Peierls, notably quartz and sapphire,[11] solid helium,[14] and lithium fluoride.[18] In fact White and Woods[19] found evidence for the umklapp contribution to the resistance even in bismuth. It was therefore considered strange that the umklapp resistance of many materials always seemed to be overshadowed by a large point-defect resistance, even in good crystals. The most notable examples were germanium,[19,20] silicon,[20] and potassium chloride.[5,21] It was finally realized,[18,22] however, that the naturally occurring isotopes can produce a significant point-defect resistance in many cases.

Until the isotope effect was discovered, it was not possible to test the quantitative predictions of the theory concerning imperfection resistance, except in the simple case of boundary resistance,[23] because not enough was known in an accurate way about the concentration and detailed structure of other imperfections. Actually some quantitative work was carried out by Slack[21] on divalent impurities in potassium chloride. In contrast, the concentration and the masses of the isotopes are known so that one may hope to treat the isotope effect accurately. It is therefore significant that the observed point-defect resistances are always larger than those predicted by the theory of the isotope effect. The physically

[17] G. Leibfried and E. Schloemann, *Nachr. Akad. Wiss. Göttingen, Math.-physik. Kl. IIa*, No. 4, 71 (195)4.

[18] R. Berman, E. L. Foster, and J. M. Ziman, *Proc. Roy. Soc.* (*London*) **A237,** 344 (1956).

[19] G. K. White and S. B. Woods, *Can. J. Phys.* **33,** 58 (1955).

[20] H. M. Rosenberg, *Proc. Phys. Soc.* (*London*) **A67,** 837 (1954).

[21] G. A. Slack, *Phys. Rev.* **105,** 832 (1957).

[22] G. A. Slack, *Phys. Rev.* **105,** 829 (1957).

[23] R. Berman, F. E. Simon, and J. M. Ziman, *Proc. Roy. Soc.* (*London*) **A220,** 171 (1953).

equivalent case in which the effect of gold on the lattice thermal conductivity[24] of copper was measured forms an exception.

There are also some fundamental difficulties in the treatment of boundary effects. These will be discussed in Section 7. It seems, in general, that, although the processes leading to thermal resistance are understood in a qualitative manner, there is, as yet, no reliable quantitative theory.

Thermal conduction by lattice waves also occurs in metallic solids, but here the lattice conductivity is small, as a consequence of the scattering of lattice waves by conduction electrons, so that it is often overshadowed by the electronic thermal conductivity. However, in favorable cases, particularly in alloys, it is possible to deduce the lattice conductivity, although not with the accuracy with which one can measure the thermal conductivity of dielectric solids. After a number of isolated estimates of lattice conductivities, measurements over a wide range of temperatures were made on alloys by Hulm,[25] Berman,[26] and Estermann and Zimmerman.[27] Since then, many systematic investigations have been undertaken, particularly at Sydney.[28]

The main interest in this work is to study the thermal resistance arising from the interaction of the lattice waves with the free electrons, so as to obtain information about the interaction processes by comparing the lattice thermal conductivity with electronic conduction properties.[29,30]

Some information about the lattice imperfections can also be obtained from the lattice thermal conductivity, as in the case of dielectric solids. Here, however, the method is less sensitive, because the electron resistance is already present, and only larger additional resistances can be observed. On the other hand, the quantity or nature of the imperfections in metallic solids may be different from those in nonmetals; in particular, dislocations are observed commonly. Thus in spite of difficulties and disadvantages there is some interest in using the lattice thermal conductivities of alloys to study the lattice imperfections. Here again our understanding is qualitative; the quantitative aspects of this work are still unsatisfactory.

The thermal conductivity of dielectric solids has been reviewed previ-

[24] P. G. Klemens, *Proc. Phys. Soc.* (*London*) **A70**, 833 (1957).
[25] J. K. Hulm, *Proc. Phys. Soc.* (*London*) **A64**, 207 (1951).
[26] R. Berman, *Phil. Mag.* [7] **42**, 642 (1951).
[27] I. Estermann and J. E. Zimmerman, *J. Appl. Phys.* **23**, 578 (1952).
[28] W. R. G. Kemp, P. G. Klemens, A. K. Sreedhar, and G. K. White, *Proc. Roy. Soc.* (*London*) **A233**, 480 (1956).
[29] P. G. Klemens, *Australian J. Phys.* **7**, 57 (1954).
[30] P. G. Klemens, *in* "Handbuch der Physik," Vol. 14 (2nd ed.), p. 198. Springer, Berlin, 1956.

ously by Berman,[31] that of metals and alloys by Olsen and Rosenberg.[32] The low-temperature thermal conductivity has been surveyed in general by Klemens.[30]

II. Theory of Heat Transport by Lattice Vibrations

2. Normal Modes of a Lattice (Résumé)

The atoms in a crystal vibrate about equilibrium positions which are arranged in a regular lattice. However, the atoms are not bound to their equilibrium sites, but to the neighboring atoms. Consequently, individual atoms do not vibrate independently, but their vibrations are strongly coupled. The formulation and solution of this dynamical problem has been fully reviewed elsewhere (see, for example, Born and Goeppert-Mayer,[33] Born and Huang,[34] Blackman,[35] or de Launay[36]). A solution can be found in terms of traveling waves, which are the normal modes of vibration of a crystal lattice, provided the lattice is perfect and provided the forces are harmonic, that is, provided the forces acting between pairs of atoms are proportional to their relative displacement. Real crystals are not perfect; the deviations from perfection give rise to thermal resistivity. If these deviations are small, they can be treated by perturbation theory. There exists, as yet, no full treatment of highly imperfect lattices. (See, however, Dyson[37] and Schmidt[38] for a treatment of a disordered linear chain.)

The normal coordinates are found as follows. For simplicity, consider a crystal lattice having one atom per unit cell. Let $\mathbf{x}$ be the equilibrium site of an atom, and let $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ be the three periodicity vectors of the lattice. Thus $\mathbf{x}$ has only discrete values, which are integral combinations of the $\mathbf{a}$'s. Let the linear dimensions of the crystal be $G_1\mathbf{a}$, etc., so that $G = G_1G_2G_3$ is the number of unit cells of the crystal. Let $\mathbf{u}(\mathbf{x})$ be the displacement of the $\mathbf{x}$th atom from its equilibrium site. In an harmonic crystal, where the forces on each atom $\mathbf{x}$ are proportional to the relative

[31] R. Berman, *Advances in Physics* (Phil. Mag. Suppl.) **2**, 103 (1953).
[32] J. L. Olsen and H. M. Rosenberg, *Advances in Physics* (Phil. Mag. Suppl.) **2**, 28 (1953).
[33] M. Born and M. Goeppert-Mayer, *in* "Handbuch der Physik," Vol. 24/2, p. 623. Springer, Berlin, 1933.
[34] M. Born and K. Huang, "Dynamical Theory of Lattices." Oxford Univ. Press, London and New York, 1955.
[35] M. Blackman, *in* "Handbuch der Physik," Vol. 7/1 (2nd ed.), p. 325. Springer, Berlin, 1955.
[36] J. de Launay, *Solid State Phys.* **2**, 219 (1956).
[37] F. J. Dyson, *Phys. Rev.* **92**, 1331 (1953).
[38] H. Schmidt, *Phys. Rev.* **105**, 425 (1957).

displacements between $\mathbf{x}$ and its neighbors $\mathbf{x} - \mathbf{m}$, the equation of motion of the atom $\mathbf{x}$ is of the form

$$M\ddot{u}_i(\mathbf{x}) = \sum_{\mathbf{m},j} A_{ij}(\mathbf{m})[u_j(\mathbf{x} - \mathbf{m}) - u_j(\mathbf{x})]. \tag{2.1}$$

Here M is the atomic mass and the A's are constants describing the interatomic forces. This set of equations contains the coordinates $\mathbf{u}(\mathbf{x})$ in a mixed form. A separation of coordinates can be effected by means of the Fourier transformation

$$\mathbf{u}(\mathbf{x}) = \frac{1}{\sqrt{G}} \sum_{\mathbf{k}} \xi(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{x}} \tag{2.2}$$

where the $\mathbf{k}$'s are integral combinations of three vectors $\mathbf{b}_i/G_i$, and the $\mathbf{b}$'s are the inverse lattice vectors defined by

$$(\mathbf{a}_i \cdot \mathbf{b}_j) = 2\pi\delta_{ij}. \tag{2.3}$$

Since $\mathbf{u}(\mathbf{x})$ is defined only for a discrete set of $\mathbf{x}$ values, the lattice points, a transformation $\mathbf{k} \rightarrow \mathbf{k} + \mathbf{b}_i$ leaves $e^{i\mathbf{k}\cdot\mathbf{x}}$, and hence $\mathbf{u}(\mathbf{x})$, invariant. There are thus only G physically different $\mathbf{k}$ values, which are contained in the first Brillouin zone.

The equations of motion in terms of the new coordinates are

$$\ddot{\xi}_i(\mathbf{k}) = -\sum_j \omega_{ij}^2(\mathbf{k})\xi_j(\mathbf{k}) \tag{2.4}$$

where

$$\omega_{ij}^2(\mathbf{k}) = \frac{1}{M} \sum_{\mathbf{m}} A_{ij}(\mathbf{m})[1 - \cos(\mathbf{k} \cdot \mathbf{m})]. \tag{2.5}$$

To each value of $\mathbf{k}$ correspond three equations (2.4) describing a three-dimensional harmonic oscillator. It is possible to choose three mutually perpendicular directions $\boldsymbol{\varepsilon}_j(\mathbf{k})$ so that this oscillator is resolved into three independent one-dimensional oscillators of the form

$$\ddot{\xi}_j(\mathbf{k}) = -\omega_j^2(\mathbf{k})\xi_j(\mathbf{k}). \tag{2.6}$$

The solution of (2.6) is of the form

$$\xi_j(\mathbf{k}) = b_j(\mathbf{k}) \exp[i\omega_j(\mathbf{k})t] + b_{-j}(\mathbf{k}) \exp[-i\omega_j(\mathbf{k})t] \tag{2.7}$$

where b_j and b_{-j} are two arbitrary constants. The displacements $\mathbf{u}(\mathbf{x})$ thus have been resolved into a set of traveling waves

$$\mathbf{u}(\mathbf{x}) = \frac{1}{\sqrt{G}} \sum_{\mathbf{k},j} \boldsymbol{\varepsilon}_j b_j(\mathbf{k}) \exp[i\mathbf{k} \cdot \mathbf{x} + i\omega_j(\mathbf{k})t] \tag{2.8}$$

where $j = \pm 1, 2, 3$. Since the $\mathbf{u}$'s are real

$$\xi(-\mathbf{k}) = \xi^*(\mathbf{k}) \tag{2.9a}$$

and a convenient notation, implied in (2.8), requires

$$b_{-j}(-\mathbf{k}) = b_j^*(\mathbf{k}) \tag{2.9b}$$

$$\omega_j(\mathbf{k}) = \omega_j(-\mathbf{k}) = -\omega_{-j}(\mathbf{k}) = -\omega_{-j}(-\mathbf{k}). \tag{2.9c}$$

There are $3G$ degrees of freedom: G displacements of 3 components each. These have now been transferred into $3G$ independent normal coordinates, specified by G values of $\mathbf{k}$ and 6 values of j, but with $(\mathbf{k},j)$ and $(-\mathbf{k},-j)$ denoting the same mode, being complex conjugates of each other.

The energy of the crystal is composed additively of the energies of the individual oscillators (2.6), so that

$$\begin{aligned} E = \sum_{\mathbf{k},j} E_j(\mathbf{k}) &= \frac{M}{2} \sum_{\mathbf{k},j} \{\dot{\xi}_j(\mathbf{k})\dot{\xi}_j(-\mathbf{k}) + \omega_j^2(\mathbf{k})\xi_j(\mathbf{k})\xi_j(-\mathbf{k})\} \\ &= M \sum_{\mathbf{k},j} b_j(\mathbf{k})b_{-j}(-\mathbf{k})\omega_j^2(\mathbf{k}) \end{aligned} \tag{2.10}$$

where $j = 1, 2, 3$. The heat flow associated with a normal mode can be shown to be

$$\mathbf{S}_j(\mathbf{k}) = \frac{1}{V} E_j(\mathbf{k})\mathbf{v}_G(\mathbf{k},j) \tag{2.11}$$

where V is the volume of the crystal and

$$\mathbf{v}_G(\mathbf{k},j) = \frac{\partial \omega_j(\mathbf{k})}{\partial \mathbf{k}} \tag{2.12}$$

is the group velocity of the wave $(\mathbf{k},j)$.

Thus the vibrations of the crystal lattice have been resolved into a set of traveling waves, of wave-vector $\mathbf{k}$, frequency ω, and polarization $\boldsymbol{\varepsilon}$. To each wave-vector $\mathbf{k}$ correspond three waves, with mutually perpendicular directions of polarization $\boldsymbol{\varepsilon}$, and three frequencies ω_j. In general, the three directions $\boldsymbol{\varepsilon}$ bear no simple relation to the direction of $\mathbf{k}$. In an elastic continuum one polarization direction is parallel to $\mathbf{k}$ (longitudinal wave) while the other two directions are arbitrary, but lie in a plane perpendicular to $\mathbf{k}$ (transverse waves). The longitudinal wave has a higher frequency than the two transverse waves, the latter having equal frequencies. All these simplifications are lost in the discrete lattice—there is, in general, no longitudinal polarization in the exact sense (except for propagation in certain directions). Nevertheless, it will be convenient to speak of "longi-

tudinal" waves; these are simply waves having the highest value of ω for each value of $\mathbf{k}$. It is this property, rather than the direction of $\boldsymbol{\varepsilon}$, which gives them a distinct role in the subsequent treatment. The other waves are then the "transverse" waves.

In the case of waves of low frequency, ω is a linear function of the components of $\mathbf{k}$, as is apparent from (2.5). Thus the phase-velocity $\omega/\mathbf{k}$ equals the group velocity $\partial\omega/\partial\mathbf{k}$ and the low-frequency waves can be

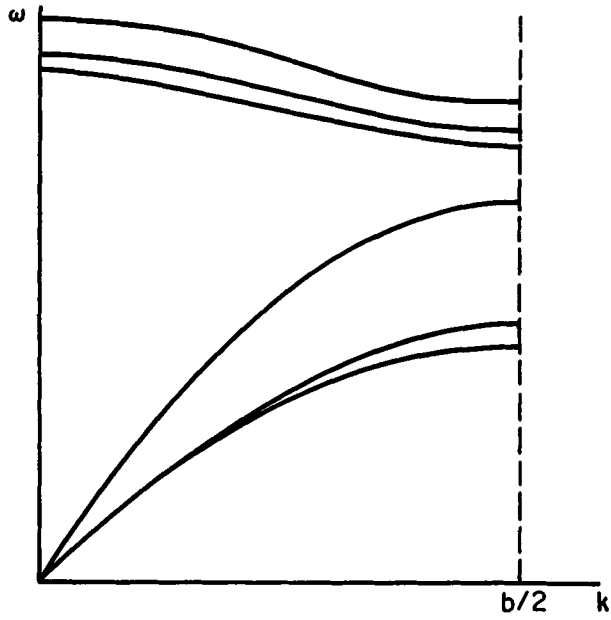

FIG. 1. Schematic plot of the frequency of lattice waves as a function of wave number for a given direction of k for a crystal of two atoms per unit cell.

described in terms of an anisotropic elastic continuum. At higher frequencies, dispersion becomes apparent and the group velocity decreases. Since $\omega(\mathbf{k}) = \omega(\mathbf{k} - \mathbf{b}_i)$ at the zone boundary, and since $\omega(\mathbf{k})$ has the directional symmetry of the crystal lattice, $\partial\omega/\partial\mathbf{k}_n = 0$, where $\mathbf{k}_n$ is normal to the zone boundary.

So far we have considered only lattices with one atom per unit cell. If there are g atoms per unit cell, there are $3g$ modes for every value of $\mathbf{k}$. Three modes describe the motion of the unit cell (in the limit of long waves), and form the three acoustical branches. The other $3(g - 1)$ modes describe the relative motions of atoms in a unit cell (in the limit of long waves). In general the latter branches have a small group velocity. In Fig. 1 the frequencies of the $3g$ modes are drawn schematically as a

function of wave vector for a particular direction of $\mathbf{k}$ in the case of $g = 2$. The upper branches are called "optical" because they correspond to periodic polarization in an ionic lattice even in the limit of long waves, and thus interact strongly with electromagnetic radiation.

3. Quantized Lattice Waves

Each normal mode of vibration obeys the classical equation of motion (2.6) of an harmonic oscillator. Its amplitude and energy are continuously variable. According to quantum-mechanical considerations, however, the energy values of an oscillator are not continuously variable, but form a discrete set of values, increasing in steps of $\hbar\omega$, where ω is the angular frequency of the oscillator. Analogous considerations apply to the normal modes of a crystal lattice.

In place of the amplitude $b(\mathbf{k})$, consider the variable[38a]

$$a(\mathbf{k}) = b(\mathbf{k})e^{i\omega t}. \tag{3.1}$$

The contribution of the mode $\mathbf{k}$ to the Hamiltonian (2.10) is, in symmetrical form,

$$H(\mathbf{k}) = \tfrac{1}{2}M\omega^2[a(\mathbf{k})a(-\mathbf{k}) + a(-\mathbf{k})a(\mathbf{k})]. \tag{3.2}$$

The momentum conjugate to $a(\mathbf{k})$ is given by $\dot{p}(\mathbf{k}) = -\partial H/\partial a(\mathbf{k})$, so that

$$p(\mathbf{k}) = -i\omega M a(-\mathbf{k}). \tag{3.3}$$

In the quantum-mechanical description the variables $a(\mathbf{k})$ and $p(\mathbf{k})$ are replaced by matrices obeying the commutation relations $a(\mathbf{k})p(\mathbf{k}) - p(\mathbf{k})a(\mathbf{k}) = i\hbar$, so that

$$a(\mathbf{k})a(-\mathbf{k}) - a(-\mathbf{k})a(\mathbf{k}) = \frac{-\hbar}{M\omega(\mathbf{k})} \tag{3.4}$$

and other pairs of a's commute. The following matrices satisfy (3.4) and make (3.2) diagonal:

$$a(\mathbf{k})_{N,N-1} = \left[\frac{\hbar}{M\omega(\mathbf{k})}N\right]^{\frac{1}{2}} \tag{3.5a}$$

$$a(-\mathbf{k})_{N,N+1} = \left[\frac{\hbar}{M\omega(\mathbf{k})}(N+1)\right]^{\frac{1}{2}}. \tag{3.5b}$$

All other elements of these matrices vanish. The N's are integers which can be used to label the states of the oscillator and the matrix elements.

[38a] Henceforth the index j will not be written explicitly unless particular reference is made to the nature of the polarization. Thus $\mathbf{k}$ denotes the mode $(\mathbf{k},j)$, while $-\mathbf{k}$ denotes its conjugate $(-\mathbf{k},-j)$.

The nonvanishing elements of (3.2) are

$$H(\mathbf{k})_{N,N} = E(\mathbf{k}) = \hbar\omega(N + \tfrac{1}{2}). \tag{3.6}$$

Thus the energy of the oscillator is quantized; in the state N it consists of the zero-point energy $\frac{1}{2}\hbar\omega$ and N quanta of energy $\hbar\omega$. The vibrational state of the crystal can be specified by means of the set of quantum numbers $N(\mathbf{k})$ of all the modes $(\mathbf{k},j)$. A useful notation, consistent with (2.9), is,

$$N(-\mathbf{k}) = -[N(\mathbf{k}) + 1] \tag{3.7}$$

since $(\mathbf{k},j)$ and $(-\mathbf{k},-j)$ refer to the same wave. Positive values of N are associated with positive values of ω, and vice versa. Note that $a(\mathbf{k})$ is an annihilation operator, for it links a state containing N quanta to one containing $N - 1$; similarly $a(-\mathbf{k})$ is a creation operator. By making use of the convention (3.7) and (2.9), it is not necessary to distinguish between these two operators in the formal theory.

While the N's are constants of the motion in the ideal crystal considered so far, so that a given set of N's are preserved, the N's do not remain constant in a real crystal, where the lattice waves are not the true normal coordinates. As energy is interchanged slowly between the lattice waves, the N's tend to an equilibrium distribution, and then fluctuate about their respective equilibrium values.

There is no limit to the number of quanta in a normal mode. The probability of a mode $\mathbf{k}$ being in an energy state E is proportional to $\exp[-E/KT]$, where K is the Boltzmann constant. Since the energy states are evenly spaced with intervals $\hbar\omega$, the average value of $N(\mathbf{k})$ in thermal equilibrium is

$$\mathfrak{N}(\mathbf{k}) = [e^{\hbar\omega/kT} - 1]^{-1}. \tag{3.8}$$

There is a close analogy between the quantized lattice vibrations and quantized electromagnetic waves in an enclosure, the main difference being the dispersion of the lattice waves (ω/k not constant), the presence of a third polarization branch (longitudinal waves), the anisotropy of the medium, and the finite value of the number of possible waves. These differences already exist in the classical treatment; no further differences are introduced by quantization. In analogy to the quanta of electromagnetic radiation (photons) we have quanta of lattice vibration, called phonons. In treating the thermal properties of a lattice, it is legitimate to speak of a gas of phonons: particles of energy $\hbar\omega$, quasi-momentum[38b] $\hbar\mathbf{k}$, velocity $\partial\omega/\partial\mathbf{k}$, and obeying Bose-Einstein statistics.

[38b] The quantity $\hbar\mathbf{k}$ is not a true momentum, for the wave-vector $\mathbf{k}$ can be changed by the addition of multiples of $\mathbf{b}_i$ without changing the atomic displacements. While the momentum of the crystal is related to the invariance of the dynamical system

4. Formal Theory of Thermal Conductivity

The phonons carry a heat current which is the sum of the heat current carried by all normal modes:

$$\mathbf{Q} = \sum_{\mathbf{k}} N(\mathbf{k})\, \hbar\omega\, \frac{\partial \omega}{\partial \mathbf{k}}. \tag{4.1}$$

Since the modes are distributed symmetrically in $\mathbf{k}$ space, that is to every $(\mathbf{k},j)$ there corresponds a mode $(-\mathbf{k},j)$ with equal frequency, the zero-point energy carries no net heat current, nor is there any heat current if the distribution of phonons is isotropic. In particular, $\mathbf{Q} = 0$ is $N = \mathfrak{N}$. Net heat flow arises from an anisotropy of the phonon distribution.

In the absence of processes tending to restore equilibrium, a small asymmetry in the distribution and the associated thermal current persists indefinitely, even in the absence of a temperature gradient. This leads to infinite thermal conductivity. In real crystals, any deviation of N from its equilibrium value $\mathfrak{N}$ disappears in the absence of a temperature gradient. Assuming that the return to equilibrium follows an exponential law, one can write

$$\left.\frac{\partial N}{\partial t}\right] = \frac{\mathfrak{N} - N}{\tau} = -\frac{n}{\tau}. \tag{4.2}$$

The left-hand side denotes the average rate of change due to interactions, and n is the deviation from equilibrium. Thus (4.2) defines a relaxation time τ.

We have not considered the phonons to be localized so far. By a superposition of states, it is possible to define wave packets of wave-vector range Δk, localized to within a region $\Delta x \sim 1/\Delta k$. This procedure has been outlined by Peierls (1929).[3] These wave packets can now be treated as localized particles. We shall disregard here the wave character of the phonons[40a] and treat the wave packets as particles moving with velocity

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under small translations of the crystal in space, the quasi-momentum is related to the invariance when the pattern of atomic displacements is shifted relative to the crystal lattice by multiples of the lattice vectors $\mathbf{a}_i$. The relation between this quasi-momentum and the true momentum of the crystal lattice is discussed by Suessmann.[39] In an elastic continuum the displacement pattern can be shifted through small distances, and there is associated with the elastic waves a momentum of the solid, as discussed by Brenig.[40]

[39] G. Suessmann, *Z. Naturforsch.* **11a**, 1 (1956); *ibid.* **13a**, 1 (1958).

[40] W. Brenig, *Z. Physik* **143**, 168 (1955).

[40a] This is justified provided the temperature gradient is sufficiently small that the relative change in temperature over a distance of one wavelength is small. This is so in all practical cases.

$\mathbf{v} = \partial\omega/\partial\mathbf{k}$. A Boltzmann equation can now be set up for the steady state in the presence of a temperature gradient:

$$\frac{\partial N}{\partial t}\Big] + (\mathbf{v} \cdot \text{grad } T)\frac{dN}{dT} = 0. \tag{4.3}$$

The second term denotes the rate of change of N arising from the drift motion of the phonons in the temperature gradient. To a first approximation N can be replaced by $\mathfrak{N}$ of (3.8) in this term, so that from (4.2)

$$n = -(\mathbf{v} \cdot \text{grad } T)\tau S(\mathbf{k})/\hbar\omega \tag{4.4}$$

where

$$S_j(\mathbf{k}) = \frac{(\hbar\omega)^2}{KT^2}\frac{e^{\hbar\omega/KT}}{(e^{\hbar\omega/KT} - 1)^2} \tag{4.5}$$

is the contribution of the mode $(\mathbf{k},j)$ to the specific heat. Substituting into (4.1)

$$\mathbf{Q} = \sum_{\mathbf{k},j} (\mathbf{v} \cdot \text{grad } T)\mathbf{v}\tau S(\mathbf{k}) \tag{4.6}$$

where $\mathbf{v}$ and τ are functions of $\mathbf{k}$.

The thermal conductivity tensor is defined as

$$Q_l = -\kappa_{lm}(\text{grad } T)_m \tag{4.7}$$

where the indices l,m denote components of vectors. Hence

$$\kappa_{lm} = \sum_{\mathbf{k},j} v_l v_m \tau S(\mathbf{k}) \tag{4.8}$$

which satisfies the Onsager relation $\kappa_{lm} = \kappa_{ml}$.

In the isotropic case in which $\omega(\mathbf{k})$ and $\tau(\mathbf{k})$ are functions of k only, so that $\mathbf{v}(\mathbf{k}) = \mathbf{k}k^{-1}v$, the summation over $\mathbf{k}$ for each polarization branch can be split into an integration over all k and an integration over all directions of $\mathbf{k}$. Since the average value of $v_l v_m$ over all directions is $\delta_{lm}v^2/3$, (4.8) becomes

$$\kappa = \delta_{lm}\kappa_{lm} = \tfrac{1}{3}\sum_j \int dk\, v_j^2(k)\, \tau_j(k)\, S_j(k) \tag{4.9}$$

where $S_j(k)\,dk$ is the contribution to the specific heat arising from modes of the polarization branch j and lying in the wave-number interval k,dk.

In the case of anisotropic crystals having cubic symmetry, it is seen easily that the thermal conductivity is also isotropic; however, the integrand of (4.9) is not independent of direction in $\mathbf{k}$ space; a suitable average over one octant in $\mathbf{k}$ space must be taken.

In the subsequent theoretical discussions it will be assumed that the crystal is isotropic and that the thermal conductivity is given by (4.9). The complexities arising from anisotropy do not, in general, affect the principles involved in these discussions.

One can use (4.9) to discuss the temperature dependence of the thermal conductivity. In general $v(k)$ does not depend strongly on k, but $\tau(k)$ does, and, depending on which is the major cause of phonon interactions, $\tau(k)$ may show different types of variation with k. In consequence one may find different types of temperature dependence of thermal conductivity.

In particular, in the limit of low temperatures, where $\int S(k)\, dk \propto T^3$, and where dispersion can be neglected, it is easily seen that $\kappa(T) \propto T^{3-n}$ if $\tau(k) \propto k^{-n}$. If, in addition, $\tau(k)$ has an intrinsic dependence on temperature, this will also be reflected in $\kappa(T)$.

The frequency and temperature dependence of $\tau(\mathbf{k})$ will be discussed in Sections 5 to 7. This dependence is summarized in Table I for the various interaction processes. The temperature dependence of the resulting thermal resistances are shown.

5. The Interaction Processes

The thermal resistance is the result of processes that allow the interchange of energy between the lattice waves, which are almost normal modes. In Section 2 three simplifications have been made which have the consequence that the lattice waves become true normal modes: (a) the crystal was assumed to be perfectly periodic; (b) the restoring forces were assumed to be harmonic; and (c) the displacements at the boundaries were restricted by a boundary condition of the type $u(\mathbf{x}) = u(\mathbf{x} + G_i\mathbf{a}_i)$, so that (2.1) also applied at lattice points near the boundary. None of these conditions apply exactly in real crystals, and the interchange of energy between lattice waves resulting from the relaxation of these restrictions will be discussed in this section. The role of these interactions in thermal conduction will be discussed in Sections 6 and 7.

a. Scattering by Static Imperfections

All real crystals contain irregularities of the lattice, such as impurities, vacancies, interstitials, dislocations, and more complex imperfections, which can scatter lattice waves. These scattering processes and their effect on the thermal conductivity have been discussed by Klemens[16] along the following lines.

In a regular lattice, the energy is a quadratic function of the displacements $u(\mathbf{x})$ and their time derivative $\dot{u}(\mathbf{x})$, summed over all lattice points $\mathbf{x}$. Thus the functional form of the Hamiltonian H^0 is invariant under a transformation $\mathbf{x} \rightarrow \mathbf{x} + \mathbf{m}$. This invariance is destroyed by the presence

of imperfections. The Hamiltonian can then be expressed in the form $H = H^0 + H'$, where H^0 is invariant, and H' is a function of $u(\mathbf{r})$ and $\dot{u}(\mathbf{r})$, where $\mathbf{r}$ is a lattice point in the vicinity of the imperfection. H' is not invariant under displacement.

When u and $\dot{u}$ are expressed in terms of the variables $a(\mathbf{k})$ of (3.1), H^0 is given by (3.2). Mixed terms of the form $a(-\mathbf{k}')a(\mathbf{k})$ disappeared on summation over $\mathbf{x}$. The perturbation Hamiltonian can be expressed likewise in terms of the a's. If the perturbation is quadratic in the $u(\mathbf{r})$'s and $\dot{u}(\mathbf{r})$'s, it has the form

$$H' = \sum_{\mathbf{k},\mathbf{k}'} c(\mathbf{k},\mathbf{k}')a(\mathbf{k})a(-\mathbf{k}'). \tag{5.1}$$

Since only a restricted number of lattice points $\mathbf{r}$ contribute to H', mixed terms appear in (5.1).

In the quantum-mechanical treatment, the a's are the annihilation and creation operators (3.5). A term $a(\mathbf{k})a(-\mathbf{k}')$ in H' corresponds to the removal of a phonon from mode $\mathbf{k}$ and its creation in mode $\mathbf{k}'$, and thereby to a transfer of energy. On the other hand, there are diagonal terms of the form $a(\mathbf{k})a(-\mathbf{k})$; they correspond to a change of the energy eigenvalue $E(\mathbf{k})$ as a result of the perturbation, that is, of a change in the frequency of mode $\mathbf{k}$.

Consider the state of the lattice, specified by the set of quantum numbers $N(\mathbf{k})$. If the system is initially in a state i, the probability of finding it in a state j after a time t is given by

$$W_j(t) = 2H_{ij}'^2 \frac{1 - \cos (E_i - E_j)t/\hbar}{(E_i - E_j)^2} \tag{5.2}$$

according to second-order perturbation theory.[41] Here E_i is the energy of state i, and H_{ij}' is the perturbation energy matrix element linking states i and j. Let i, j, and k be states for which $N(\mathbf{k})$ and $N(\mathbf{k}')$ have values N and N', $N - 1$ and $N' + 1$, and $N + 1$ and $N' - 1$, respectively, all other modes having unaltered occupation. Thus

$$E_i - E_j = \hbar(\omega - \omega') = E_k - E_i$$

and the average rate of change of $N(\mathbf{k})$ is

$$t\frac{dN}{dt}\Big] = 2[H_{ik}'^2 - H_{ij}'^2] \frac{1 - \cos (\omega - \omega')t}{\hbar^2(\omega - \omega')^2}. \tag{5.3}$$

Making use of (5.1) and the explicit form (3.5) of the matrix elements $a(\mathbf{k})$, the rate of change due to processes in which a phonon is taken from

[41] P. A. M. Dirac, *Proc. Roy. Soc.* (*London*) **A112**, 661 (1926).

mode $\mathbf{k}'$ to $\mathbf{k}$, or vice versa, is

$$t\frac{dN}{dt}\Big]=2c^2(\mathbf{k},\mathbf{k}')\frac{\hbar^2}{M^2\omega\omega'}\frac{1-\cos(\omega-\omega')t}{\hbar^2(\omega-\omega')^2}[(N+1)N'-(N'+1)N]. \tag{5.4}$$

To get the total rate of change, this must be summed over all interacting modes $\mathbf{k}'$. This summation may be regarded as an integration in $\mathbf{k}'$ space, whence

$$\sum_{\mathbf{k}'}=\frac{V}{(2\pi)^3}d\mathbf{k}'=\frac{V}{(2\pi)^3}\iint\frac{1}{v}\,dS'\,d\omega' \tag{5.5}$$

where V is the volume of the crystal, v is the group velocity, and dS' is an element of the surface $\omega'=$ constant. The resonance factor in (5.4) selects contributions from states $\mathbf{k}'$ in the immediate vicinity of the surface $\omega'=\omega$, and ensures conservation of energy. Thus

$$\frac{dN}{dt}\Big]=\frac{V}{M^2(2\pi)^2}\sum_{j'}\int dS'\,\frac{c^2(\mathbf{k},\mathbf{k}')}{v\omega^2}[N'-N] \tag{5.6}$$

where the integration is over the three contours $\omega'=\omega$ in $\mathbf{k}'$ space corresponding to the three modes of polarization of $\mathbf{k}'$.

While the present derivation uses quantum-mechanical language, an analogous calculation can be made classically, in which $a(\mathbf{k})$ would be a classical variable, and $N(\mathbf{k})$ would be replaced by $E(\mathbf{k})$, now continuously variable. Since $(N+1)N'-(N'+1)N=N'-N$, classical and quantum-mechanical calculations yield the same results. In either case a perturbation method is used to calculate the scattering of a wave; it is assumed that the incident wave is not modified by the perturbation.

A static imperfection can contribute to the perturbation Hamiltonian (5.1) in the following way: (a) a small region (or single atom) has a mass which differs from the normal mass; (b) the elastic constants (restoring force per unit relative displacement) of some interatomic linkages differ from the normal value; (c) as a special case of the previous one, a strain field causes changes in the elastic constants of linkages as a result of the anharmonic parts of the lattice forces.

For illustration, consider the case of a difference in mass, which is the simplest to treat. Let the rth atom have a mass $M+\Delta M$, instead of M. Then $H'=\frac{1}{2}\Delta M\dot{u}(\mathbf{r})^2$. Expressing $\dot{u}(\mathbf{r})$ in terms of lattice waves

$$c(\mathbf{k},\mathbf{k}')=-\frac{\Delta M}{2G}\omega\omega'(\boldsymbol{\varepsilon}\cdot\boldsymbol{\varepsilon}')e^{i\mathbf{r}\cdot(\mathbf{k}-\mathbf{k}')}. \tag{5.7}$$

In the case of an isolated impurity, or when impurities are distributed at random, the factor $e^{ir\cdot(k-k')}$ in the square of the matrix element disappears; substituting (5.7) into (5.6) and integrating over dS', we find

$$\frac{dN}{dt}\Big]_{} = -\frac{a^3}{G}\left(\frac{\Delta M}{M}\right)^2 \frac{\omega^4}{4\pi v^3}(N - \bar{N}') \tag{5.8}$$

where $a^3 = V/G$, and $\bar{N}'$ is a suitable average of N' over the states $\mathbf{k}'$ in the integral (5.6). In (5.8), dispersion and anisotropy have been neglected, and $(\boldsymbol{\varepsilon}\cdot\boldsymbol{\varepsilon}')$, the cosine of the angle between the polarization directions, has been taken as $1/\sqrt{3}$, the root-mean-square value for an angle between two random directions.

Now we see from (4.4) that N is of the form $\mathfrak{N} + a(v\cdot \operatorname{grad} T)$, and $\mathfrak{N} = \mathfrak{N}'$ since $\omega = \omega'$. Hence $\bar{N}' = \mathfrak{N}$. Thus

$$\frac{1}{\tau} = -\frac{1}{n}\frac{dN}{dt}\Big]_{} = \frac{a^3}{G}\left(\frac{\Delta M}{M}\right)^2 \frac{\omega^4}{4\pi v^3}. \tag{5.8'}$$

If $c(\mathbf{k},\mathbf{k}')$ consists of contributions from more than one lattice site, expressions of the form (5.7) must be summed. The phase factors $e^{ir\cdot(k-k')}$ are then significant. If a number of defect lattice sites are arranged at random, interference terms cancel in the average, and the scattering, given by (5.8), is proportional to the number of defect sites. On the other hand, if the defects cluster in a region which is small when compared with the phonon wavelength, there is reinforcement of the scattering matrix, and the scattering probability varies as the square of the number of defects in the cluster, but still varies as ω^4. In intermediate cases, reinforcement is not complete, and the scattering probability varies more slowly with frequency. It is also of interest to consider an infinite row and an infinite sheet of defect sites; these have a scattering probability proportional to ω^3 and ω^2, respectively, and the components of $\mathbf{k}$ and $\mathbf{k}'$ in the direction of the cylinder (or in the plane of the sheet) are equal. This is to be expected, for H is invariant under displacements in those directions, so that these components of the $\mathbf{k}$ vector must be conserved.

Similar considerations apply to the perturbation arising from differences in the force constants of linkages near an imperfection, such as the linkages between an impurity atom and its neighbors. The corresponding perturbation in the potential energy again can be expressed in the form (5.1), where $c(\mathbf{k},\mathbf{k}') \propto kk'$. In practice the calculations are more complicated, for the perturbation arising from a single linkage depends upon the directions of $\mathbf{k}$ and $\mathbf{k}'$. On the other hand, a certain smoothing arises from the fact that perturbed linkages do not occur in isolation, but in groups of

different direction. The grouping of the linkages, on the other hand, enhances deviations from the 4th power law.

If an impurity or other point defect is introduced, it does not alter the nearest linkages alone, but also affects linkages a few atoms removed. The lattice about an imperfection is distorted, and the force constants of linkages consequently are altered in virtue of the anharmonic component of the interatomic forces. A very approximate treatment of the effects of perturbations in the linkages about point imperfections has been given by Klemens.[16] In practice such calculations gain added difficulty from the fact that reliable information about the perturbed force constants and the anharmonicities is usually lacking. Thus one can calculate with some degree of confidence the scattering arising from mass differences (isotopes, very heavy impurities) and with somewhat less confidence the effect of missing linkages (vacancies). However, distortion effects (impurities with small mass difference) are difficult to estimate.

Estimates of the scattering arising from point imperfections in cubic lattices have been given[16] for the limit of long waves. The result is

$$\frac{dN}{dt}\Big]_{} = -\frac{3a^3}{G}\frac{\omega^4}{\pi v^2}S^2(N-\bar{N}') \tag{5.9}$$

in which S^2 is a constant of order unity. Approximately

$$S^2 = S_1^2 + (S_2 + S_3)^2 \tag{5.10}$$

where $S_1^2 = (\Delta M/M)^2/12$, in accordance with (5.8), $S_2 = \Delta f/\sqrt{6}\,f$, and $S_3 \sim -6\sqrt{\frac{2}{3}}\,\Delta R/R$. Here f is the force constant of a linkage, R is the distance to the nearest neighbors, and Δf, ΔR are the changes in them.

Extended imperfections, which can be described in terms of their elastic strain field, scatter because the anharmonic terms produce changes in the linkages. The potential energy is not a quadratic function of the displacements, but contains higher terms; in particular, cubic terms of the form

$$\sum_{\mathbf{x}}\sum_{\mathbf{m}}\sum_{\mathbf{m}'} A_{ijk}(\mathbf{m},\mathbf{m}')u_i(\mathbf{x})u_j(\mathbf{x}+\mathbf{m})u_k(\mathbf{x}+\mathbf{m}'). \tag{5.11}$$

Substituting (2.8) and (3.1) into the expression for the energy and summing over all $\mathbf{x}$, one gets

$$E = M\sum_{\mathbf{k}}\omega^2(\mathbf{k})a(\mathbf{k})a(-\mathbf{k}) + \sum_{\mathbf{k},\mathbf{k}',\mathbf{k}''} c(\mathbf{k},\mathbf{k}',\mathbf{k}'')a(\mathbf{k})a(\mathbf{k}')a(\mathbf{k}'') \tag{5.12}$$

instead of (2.10). The coefficients $c(\mathbf{k},\mathbf{k}',\mathbf{k}'')$ contain the factor

$$\Sigma_{\mathbf{x}} e^{i\mathbf{x}\cdot(\mathbf{k}+\mathbf{k}'+\mathbf{k}'')}$$

so that they vanish unless

$$\mathbf{k} + \mathbf{k}' + \mathbf{k}'' = 0 \tag{5.13a}$$

or

$$\mathbf{k} + \mathbf{k}' + \mathbf{k}'' = \mathbf{b} \tag{5.13b}$$

where $\mathbf{b}$ is an integral combination of the three inverse lattice vectors defined by (2.3). The c's can be calculated in terms of the anharmonic coefficients (5.11); in general, the resulting expressions are complicated —see, for example, Leibfried.[42] Since the cubic anharmonicities are also responsible for thermal expansion, however, their magnitude may be estimated as follows.

An elastic strain alters the force constants and hence the frequencies of the lattice waves; in particular, a uniform dilatation Δ alters the frequencies in such a way that

$$\omega(\mathbf{k}) = \omega_0(\mathbf{k})[1 - \gamma(\mathbf{k})\Delta] \tag{5.14}$$

where $\gamma(\mathbf{k})$ represents a set of parameters. The coefficient of thermal expansion can then be shown to be

$$\frac{d\Delta}{dT} = \frac{1}{\lambda} \sum_{\mathbf{k}} \gamma(\mathbf{k}) S(\mathbf{k}) \tag{5.15}$$

where λ is the compressibility, and $S(\mathbf{k})$, given by (4.5), is the specific heat of mode $\mathbf{k}$. Grüneisen[43] has assumed, as a simplification, that all the parameters $\gamma(\mathbf{k})$ are the same and equal to γ, a constant determined from the relation between $d\Delta/dT$ and $\Sigma_{\mathbf{k}} S(\mathbf{k})$. Thus if γ is determined from the thermal expansion at high temperatures, at which $S(\mathbf{k}) = K$, it is the average over all values of $\gamma(\mathbf{k})$.

Consider now a static strain field and let $\mathbf{v}(\mathbf{x})$ represent the static atomic displacement. The displacement can be resolved into Fourier components in the manner

$$\mathbf{v}(\mathbf{x}) = \frac{1}{\sqrt{G}} \sum_{\mathbf{q}} \mathbf{n}(\mathbf{q}) e^{i\mathbf{q}\cdot\mathbf{x}}. \tag{5.16}$$

The dilatation is given by

$$\Delta(\mathbf{x}) = \operatorname{div} \mathbf{v} = \frac{i}{\sqrt{G}} \sum_{\mathbf{q}} (\mathbf{q} \cdot \mathbf{n}(\mathbf{q})) e^{i\mathbf{q}\cdot\mathbf{x}}. \tag{5.17}$$

A uniform strain corresponds to $i/\sqrt{G}\ (\mathbf{q} \cdot \mathbf{n}(\mathbf{q}))$ in the limit $q \to 0$. The energy change arising from a strain component $\eta(\mathbf{q})$ is obtained by sub-

[42] G. Leibfried, *in* "Handbuch der Physik," Vol. 7/1 (2nd ed.), p. 104. Springer, Berlin, 1955.

[43] E. Grüneisen, *in* "Handbuch der Physik," Vol. 10, p. 1. Springer, Berlin, 1926.

stituting $\eta(\mathbf{q})$ into the second term of (5.12) whenever $a(\mathbf{q})$ occurs. A typical term is

$$c(\mathbf{k}, -\mathbf{k} - \mathbf{q}, \mathbf{q})a(\mathbf{k})a(-\mathbf{k} - \mathbf{q})\eta(\mathbf{q}) \tag{5.18}$$

because of (5.13a). Substituting (5.14) into the first term of (5.12), a typical term in the energy change associated with the dilatation is

$$-2\gamma M\Delta\ \omega^2(\mathbf{k})a(\mathbf{k})a(-\mathbf{k}). \tag{5.19}$$

Replacing Δ by $i/\sqrt{G}\ (\mathbf{q} \cdot \mathbf{n})$ and equating (5.19) in the limit $\mathbf{q} \to 0$, we find

$$\lim_{q \to 0} c(\mathbf{k}, -\mathbf{k} - \mathbf{q}, \mathbf{q}) = -\frac{i}{\sqrt{G}} 2M\gamma\omega^2(k)q \tag{5.20}$$

provided $\mathbf{n}(\mathbf{q})$ is a longitudinal displacement and $\mathbf{k}$ and $(\mathbf{k} + \mathbf{q})$ belong to the same polarization branch.

While (5.20) holds only under the restrictions described above, one may generalize the relation and assume that

$$c(\mathbf{k},\mathbf{k}',\mathbf{k}'') = -\frac{i}{\sqrt{G}} \frac{2M}{\sqrt{3}\,v} \gamma\omega\omega'\omega'' \tag{5.21}$$

irrespective of the magnitude of the k's and the polarizations of the three waves, provided (5.13) is satisfied. While (5.21) should give the order of magnitude of these coefficients, one cannot place great quantitative reliance on it. A reliable estimate can be obtained only in terms of the coefficients A of (5.11). These, in turn, can be derived only from a knowledge of the interatomic forces. So far, theoretical work[44] has been confined to the calculation of the $\gamma(\mathbf{k})$'s, which, as we have seen, are related to $q^{-1}c(\mathbf{k}, -\mathbf{k} - \mathbf{q}, \mathbf{q})$ in the limit of small q. It has been found that $\gamma(\mathbf{k})$ varies with frequency. Since the coefficients $c(\mathbf{k},\mathbf{k}',\mathbf{k}'')$ are generalizations of $\gamma(\mathbf{k})$, they are even more likely to vary and deviate from (5.21). We adopt (5.21) merely because a better estimate is lacking.

The scattering by a static strain field (5.16) can now be estimated from (5.18), again replacing in turn each $a(\mathbf{q})$ occurring in the perturbation term of (5.12) by the corresponding component of $\mathbf{n}(\mathbf{q})$. If the strain field is expressed in terms of dilatations $\Delta(\mathbf{x}) = \text{div } \mathbf{v}(\mathbf{x})$ and rotations $\mathbf{\Pi}(\mathbf{x}) = \text{curl } \mathbf{v}(\mathbf{x})$, and if their Fourier inversions are defined as

$$D(\mathbf{q}) = \int \Delta(x) e^{-i\mathbf{q}\cdot\mathbf{x}}\, d\mathbf{x} = ia^3 \sqrt{G}\ (\mathbf{q} \cdot \mathbf{n}(\mathbf{q})) \tag{5.22a}$$

$$\mathbf{P}(\mathbf{q}) = \int \mathbf{\Pi}(\mathbf{x}) e^{-i\mathbf{q}\cdot\mathbf{x}}\, d\mathbf{x} = ia^3 \sqrt{G}\ [\mathbf{q} \times \mathbf{n}(\mathbf{q})] \tag{5.22b}$$

[44] T. H. K. Barron, *Phil. Mag.* [7] **46**, 720 (1955).

a typical perturbation term is of the form

$$c(\mathbf{k}, -\mathbf{k}-\mathbf{q}, \mathbf{q})a(\mathbf{k})a(-\mathbf{k}-\mathbf{q})\eta_j(\mathbf{q}) = \frac{1}{Ga^3}\frac{2M\gamma}{\sqrt{3}}\omega(\mathbf{k})\omega(\mathbf{k}+\mathbf{q})[D(\mathbf{q}), \text{ or } P(\mathbf{q})]a(\mathbf{k})a(-\mathbf{k}-\mathbf{q}). \quad (5.23)$$

This term can be regarded, however, as a quadratic perturbation term of the form (5.1), leading to a scattering of a lattice wave by the static strain field. The perturbation coefficient is

$$c(\mathbf{k},\mathbf{k}') = \frac{2M\gamma}{\sqrt{3}\,Ga^3}\omega\omega'[D(\mathbf{k}'-\mathbf{k}), \text{ or } P(\mathbf{k}'-\mathbf{k})] \quad (5.24)$$

and the scattering probability is obtained from (5.6).

An analogous expression was obtained by Klemens[16] from a model of anharmonic linkages in a cubic crystal. Although this model was adjusted to lead to a Grüneisen law of thermal expansion as well, his coefficients $c(\mathbf{k},\mathbf{k}')$ are about four times smaller than (5.24). This reflects the arbitrary nature of the approximations underlying either of these expressions. We shall base subsequent discussions on the earlier expression, rather than on (5.24), so as to conform to other published presentations, but shall keep in mind the fact that it could easily underestimate the scattering due to strain fields by a factor of the order of 10.

These considerations can be applied to the scattering of lattice waves by dislocations. The strain field of a dislocation falls off inversely as the distance from the dislocation line. While one might, at first sight, think of a dislocation as a cylindrical imperfection, with most of the scattering arising from the dislocation core, so that $dN/dt] \propto \omega^3$, in actual fact the scattering by the long-range strain field outweighs the scattering by the core. Most of the scattering arises at regions about one wavelength λ from the dislocation line. Dimensional considerations lead to a variation $dN/dt] \propto \lambda^2\omega^3 \propto \omega$, as was pointed out by Nabarro.[45] Substituting the Fourier inversion of the dislocation strain field into the expression corresponding to (5.24), Klemens[16] obtained for the scattering by screw dislocations perpendicular to the temperature gradient

$$\frac{1}{\tau} = 6 \times 10^{-2} N_d\, b^2\gamma^2\omega. \quad (5.25)$$

Here b is the magnitude of the Burgers vector and N_d the number of dislocation lines per unit area. A similar expression was obtained for edge dislocations. If the dislocations are arranged at random, $1/\tau$ is reduced by a factor $\sim$0.55.

[45] F. R. N. Nabarro, *Proc. Roy. Soc.* (*London*) **A109**, 278 (1951).

It is instructive to compare (5.25) with the scattering from the dislocation core. If we consider the effect of the core to be equivalent to the deficit of two mass points per atomic plane along the dislocation line, in accordance with the density change due to dislocations,[46,47] then, in analogy to (5.8), the scattering is found to be

$$\frac{1}{\tau} = N_d \frac{a^4}{v^2} \omega^3 \tag{5.26}$$

if the dislocations are perpendicular to the temperature gradient. Comparing (5.26) with (5.25), the scattering from the core is seen to be smaller than that from the long-range strain field, except for the highest frequencies, where the two effects are comparable.

If a number of parallel dislocations are grouped together in a region small compared with the wavelength, their scattering is reinforced, and they can be treated as a single dislocation having a Burgers vector given by the sum over the individual dislocations. Since the scattering varies as b^2, there is some enhancement as a result of the scattering by dislocations which are piled up against an obstacle.

In face-centered cubic lattices a dislocation may split into two partial dislocations, leaving a connecting sheet across which the sequence of close-packed layers is disturbed. The scattering by such a stacking fault has been estimated in the limit of large separation of the partial dislocations[48] as follows. A stacking fault can also be regarded as a plane separating two halves of the crystal which have been mutually displaced by sliding, so that there is a thin but highly sheared region between them. Thus the scattering can be obtained in terms of the present formalism. The effective value of $1/\tau$ is

$$\frac{1}{\tau} = 0.7 \frac{a^2}{v} \gamma^2 \omega^2 N_s \tag{5.27}$$

where N_s is the number of stacking faults crossing a line of unit length. In each scattering process, the quasi-momentum in the plane of the stacking fault is conserved, so that the scattering process is one of specular reflection.

A grain boundary separates two regions of the crystal rotated relative to each other. If the internal structure of the grain boundary is disregarded, the strain field is simply one of rotation: $\Pi = \pm\frac{1}{2}\alpha$ on either side of the boundary, where α is the angle of tilt. It is then easily seen[16] that

[46] H. Stehle and A. Seeger, *Z. Physik* **146**, 217 (1956).
[47] L. M. Clarebrough, M. E. Hargreaves, and G. W. West, *Phil. Mag.* [8] **1**, 528 (1956).
[48] P. G. Klemens, *Can. J. Phys.* **35**, 441 (1957).

the present theory leads to an effective inverse relaxation time

$$\frac{1}{\tau} = 3 \times 10^{-2}\gamma^2\alpha^2 v N_g \tag{5.28}$$

where N_g is the number of grain boundaries crossing a line of unit length. One should consider, however, a grain boundary to be an array of dislocations lying in the plane of the boundary, the spacing between dislocations being d. The angle of tilt, in the case of a simple tilt boundary, is $\alpha = b/d$, where b is the Burgers vector. The dislocations produce a variable strain field, in addition to the simple rotation, with a range of the order of d. If d is much less than the phonon wavelength, its effect is the same as that of a sheet-like imperfection, $dN/dt] \propto \omega^2$, and arguments similar to those leading to (5.26) show that this source of scattering is relatively unimportant. If, however, the spacing of the dislocations is larger than the phonon wavelength, the dislocations scatter independently (H. Montgomery, private communication), and we find from (5.25)

$$\frac{1}{\tau} = 6 \times 10^{-2}\gamma^2\alpha^2 d\,\omega N_g \tag{5.29}$$

which is larger than (5.28), provided $\lambda < \sim 10d$. Thus in general one can expect the scattering to be intermediate between (5.28) and (5.29) for $\lambda \sim d$.

b. Interactions due to Anharmonicities

Since the potential energy associated with displacements is not a quadratic function of the displacements $\mathbf{u}$, but also contains cubic terms (5.11), there is an interchange of energy between the lattice waves. One can express the perturbation energy in terms of the amplitudes $a(\mathbf{k})$, as in (5.12), so that

$$E' = \sum_{\mathbf{k},\mathbf{k}',\mathbf{k}''} c(\mathbf{k},\mathbf{k}',\mathbf{k}'')a(\mathbf{k})a(\mathbf{k}')a(\mathbf{k}''). \tag{5.30}$$

The quantity $c(\mathbf{k},\mathbf{k}',\mathbf{k}'')$ vanishes unless either of the interference conditions (5.13) is satisfied. In the quantum-mechanical treatment, the $a(\mathbf{k})$ are the creation or annihilation operators (3.5), so that (5.30) corresponds to processes in which three phonons are created or destroyed, each term in (5.30) being a matrix element linking two states of the crystal in which the occupation numbers of three modes differ by unity. Substituting these

matrix elements and their conjugates into (5.2), one obtains in analogy to (5.4),

$$t\frac{dN}{dt}\Big] = \frac{2\hbar}{M^3}\sum_{\mathbf{k}',\mathbf{k}''}\frac{c^2(\mathbf{k},\mathbf{k}',\mathbf{k}'')}{\omega\omega'\omega''}\frac{1-\cos(\omega+\omega'+\omega'')t}{(\omega+\omega'+\omega'')^2}\times$$
$$[(N+1)(N'+1)(N''+1)-NN'N''] \quad (5.31)$$

having used the explicit form (3.5) for $a(\mathbf{k})$.

To enumerate the triplets of modes which contribute to (5.31) for a

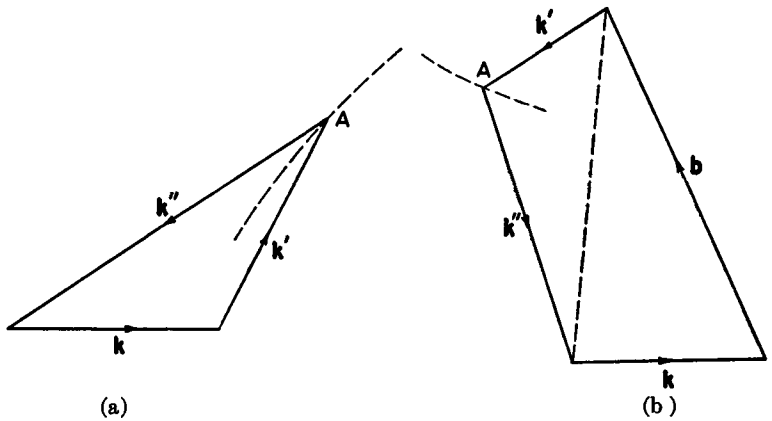

FIG. 2. The triplet of modes participating in a three-phonon interaction: (a) N process; (b) U process. For a fixed $\mathbf{k}$ each triplet is specified by a vertex A; the locus of all possible vertices is a surface of revolution about the axis (a) $\mathbf{k}$ or (b) $\mathbf{k}+\mathbf{b}$.

given mode $\mathbf{k}$, one can choose a mode $\mathbf{k}'$: the mode $\mathbf{k}''$ is then determined by (5.13). This is equivalent to choosing a point A in the vector diagram of Fig. 2. However, the resonance factor

$$[1-\cos(\omega+\omega'+\omega'')t]/(\omega+\omega'+\omega'')^2$$

in (5.31) ensures that the only significant contribution comes from those triplets for which

$$\Delta\omega = \omega+\omega'+\omega'' = 0 \quad (5.32)$$

that is, from triplets such that A lies on a surface of revolution about $\mathbf{k}$ (or $\mathbf{k}+\mathbf{b}$) generated by the curve determined by (5.32). In the absence of dispersion, these curves are hyperbolas or ellipses. Equation (5.32) implies conservation of energy in individual interaction processes.

Replacing the summation over $\mathbf{k}$ by an integration, (5.31) can be expressed as

$$\left.\frac{dN}{dt}\right] = \frac{2\hbar V}{M^3} \sum_{j',j''} \int dS' \frac{c^2(\mathbf{k},\mathbf{k}',\mathbf{k}'')}{\omega\omega'\omega''} \frac{\pi}{(2\pi)^3} \times$$
$$(|\mathrm{grad}_{\mathbf{k}}\, \Delta\omega|)^{-1}[(N+1)(N'+1)(N''+1) - NN'N''] \quad (5.33)$$

where dS' is an element of the surface $\Delta\omega = 0$, and the summation is taken over all polarizations of $\mathbf{k}'$ and $\mathbf{k}''$.

Note that one or two of the frequencies in (5.32) must be negative. Thus the corresponding annihilation operator in (5.30) is really a creation operator and the corresponding factor N in (5.31) and (5.33) should be replaced by $N + 1$, and vice versa, in conformity with the convention (2.9) and (3.7). Thus (5.31) includes terms such that $|\omega| = |\omega'| + |\omega''|$, corresponding to processes in which a phonon $\mathbf{k}$ splits into two phonons $\mathbf{k}'$ and $\mathbf{k}''$ or vice versa. In addition, there are terms such that

$$|\omega| + |\omega'| = |\omega''|$$

corresponding to processes in which a phonon $\mathbf{k}$ combines with a phonon $\mathbf{k}'$ to form $\mathbf{k}''$, or vice versa.

It is convenient to classify interaction processes into two types: "normal" processes which satisfy the interference condition (5.13a), and "umklapp" processes[48a] satisfying (5.13b). There is no difference between them in principle, since a wave $\mathbf{k}$ produces the same lattice displacements as a wave $\mathbf{k} + \mathbf{b}$. Hence an N process can be turned into a U process by changing the zone in which one of the waves is specified. If, however, we agree to specify all waves by wave vectors in the fundamental zone, there is a unique distinction between N processes and U processes. Moreover, it is seen that the N processes do not exhaust all possible processes, and that U processes must be taken into account. The distinction which we have drawn between the two types of process is admittedly somewhat arbitrary, but it happens to be a convenient one: we shall see later that the two types of process play a different role in the establishment of thermal equilibrium.

The simultaneous requirements (5.13) and (5.32) restrict the possible types of three-phonon processes. Consider N processes: the three wave vectors must form a closed triangle, as in Fig. 2a, but (5.32) gives the following relation between the magnitudes of the wave vectors:

$$vk + v'k' = v''k'' \quad (5.34)$$

[48a] While in normal processes the total wave vector of the interacting phonons is conserved, it "flips over" into approximately the opposite direction by the addition of the vector $\mathbf{b}$ in "umklapp" processes.

where the v's are now the phase velocities. Consider the case of an isotropic solid without dispersion. If $v = v' = v''$, it clearly is impossible to construct such a closed triangle, except for the trivial case when A lies on $\mathbf{k}''$. Thus, as pointed out by Peierls,[3] the three interacting modes cannot all belong to the same polarization branch. It is also seen easily that the triangle can be closed only if v'' is greater than either v, or v', or both. Thus the only types of processes which are allowed by (5.13a) and (5.32) are the following:

$$\text{transverse} + \text{transverse} \rightleftharpoons \text{longitudinal} \tag{5.35a}$$

$$\text{transverse} + \text{longitudinal} \rightleftharpoons \text{longitudinal}. \tag{5.35b}$$

This restriction was first stated by Herpin.[49] Use has been made of the property that the longitudinal branch has the highest phase velocity; in fact we shall adopt this as definition of the longitudinal branch for purposes of the present theory. The direction of polarization, which in general is neither longitudinal nor transverse, is unimportant.

As will be seen later, an important class of process is such that $|\omega| \ll |\omega'| \sim |\omega''|$. This implies $k \ll k' \sim k''$, therefore, $\mathbf{k}'$ and $\mathbf{k}''$ must belong to the same polarization branch. The only possible process is (5.35b), with $\mathbf{k}$ a transverse wave. Hence a longitudinal wave cannot interact with waves of frequency much higher than its own, a result first stated by Pomeranchuk.[8]

When we consider the effects of dispersion, we find that these results hold *a fortiori*, for in general dispersion will decrease the phase velocity of the high-frequency waves more than that of the waves of lower frequency. The effect of anisotropy may be to relax these rules, since a longitudinal wave in one direction may now have a lower phase velocity than a transverse wave in another direction. Three-phonon interactions in anisotropic media were discussed by Herring.[10]

At first sight it would appear that these restrictions applied only to N processes, not to U processes, since there are more degrees of freedom in constructing the quadrilateral of Fig. 2b than the triangle of Fig. 2a. There is, however, a restriction on the magnitude of the interacting wave vectors, since they must lie in the fundamental zone. Consequently the restrictions (5.35), and thus also Pomeranchuk's restriction apply for U processes as well. (This was pointed out by S. Simon in a private communication.) This is seen best by adding the inverse lattice vector $\mathbf{b}$ to the wave of highest frequency and treating the process as an N process. The phase velocity of that wave is now decreased and the restrictions again hold *a fortiori*.

[49] A. Herpin, *Ann. phys.* [12] **7**, 91 (1952).

c. Boundary Scattering

In the theory of Section 2, implicit use was made of the "cyclic" boundary condition

$$\mathbf{u}(\mathbf{x}) = u(\mathbf{x} + G_i\mathbf{a}_i) \tag{5.36}$$

so that the equation of motion (2.1) of a lattice element, when expressed in terms of the displacements of its neighbors, should hold not only in the interior but also at the boundary. Such a fictitious crystal has effectively no boundaries. For real crystals the movement of atoms at opposite faces is uncorrelated. Such a pair of boundaries can be introduced into a cyclic crystal by removing a sheet of linkages. The atoms on either side of this sheet will now obey the equation of motion of atoms at two opposite external boundaries.

While perturbation theory can deal with the removal of a small number of linkages, it cannot deal with an impenetrable obstacle, such as that associated with the removal of a complete sheet of linkages. However, qualitative results of the perturbation theory can still be used. If the linkages are harmonic, the perturbation is of the form (5.1), and results in the scattering of phonons from a mode $\mathbf{k}$ to a mode $\mathbf{k}'$ in such a way that energy is conserved. The component of the wave vector in the plane of boundary is also conserved, because the system is invariant under displacements in the plane of the boundary. Thus the lattice waves are reflected specularly at the boundary. Since the linkages which were removed are not perfectly harmonic, however, there are also higher order perturbation terms; in particular, cubic terms of the form (5.12), which lead to three-phonon interactions. Although energy is conserved in these interactions, as well as the wave vector in the plane of the boundary, the normal component of the wave vector is not conserved, so that many more types of three-phonon interactions can take place at the boundary than in the interior of the crystal.

If the boundary is not perfectly plane, but irregular on a microscopic scale, so that the system is not invariant under displacements in the plane of the boundary, the tangential component of the wave vector is no longer conserved. Although a perfectly plane boundary cannot be treated by perturbation theory, it may be possible to treat these microscopic irregularities as a perturbation. They will give rise to two-phonon processes in which the wave vector is not conserved, that is, to diffuse reflection. Their contribution to three-phonon processes which do not conserve the tangential wave vector will be relatively weak. The magnitude of the coefficient of diffuse reflectivity will be frequency-dependent: irregularities which are small compared with the phonon wavelength scatter as ω^4, thin scratches as ω^3, growth steps as ω^2, etc.

Thus an external boundary has a total reflection coefficient of unity, additively composed of a coefficient of diffuse reflection, which can be calculated from perturbation theory, and a coefficient of specular reflection, which is composed of two-phonon processes (simple specular reflection) and three-phonon processes that conserve the tangential wave vector (combined specular reflection and three-phonon process).

6. Approximate Solution of the Transport Equation

In Section 4, the Boltzmann equation governing the distribution of phonons was set up and solved on the assumption that a relaxation time τ can be defined, that is, provided

$$\frac{dN(\mathbf{k})}{dt}\Big]_{} = \frac{\mathfrak{N}(\mathbf{k}) - N(\mathbf{k})}{\tau(\mathbf{k})} = -\frac{n(\mathbf{k})}{\tau(\mathbf{k})} \tag{6.1}$$

in which $\tau(\mathbf{k})$ is a function of $\mathbf{k}$, but is independent of $n(\mathbf{k})$ and of the quantities $N(\mathbf{k}')$, or $n(\mathbf{k}')$, of all the other modes $\mathbf{k}'$.

In a wider sense, however, one can always define a quantity $\tau(\mathbf{k})$ appropriate to a particular circumstance simply as the ratio of two quantities, $n(\mathbf{k})$ and $dN(\mathbf{k})/dt]$. The $\tau(\mathbf{k})$ thus defined must be used in the formal theory of Section 4. In general, however, this relaxation time will depend upon all the $n(\mathbf{k}')$ through the dependence of $dN(\mathbf{k})/dt]$ on them. The appropriate values to use for the purposes of calculating the thermal conductivity are the values of $n(\mathbf{k}')$ corresponding to a steady state in the presence of a temperature gradient.[49a] If the temperature gradient is suddenly removed, $\tau(\mathbf{k})$ characterizes the *initial* rate of return of $N(\mathbf{k})$ to equilibrium.

Confining ourselves to small temperature gradients and small deviations from equilibrium, so that only terms linear in the n's need be considered, (6.1) is of the form

$$\frac{dn(\mathbf{k})}{dt}\Big]_{} = -\frac{n(\mathbf{k})}{\sigma(\mathbf{k})} + \sum_{\mathbf{k}' \neq \mathbf{k}} W(\mathbf{k},\mathbf{k}')n(\mathbf{k}'). \tag{6.2}$$

Since the temperature gradient appears as a factor in the second term of (4.3), it is a factor common to all $n(\mathbf{k}')$'s.

If all $n(\mathbf{k}')$'s were to vanish except the $n(\mathbf{k})$ of a single mode $\mathbf{k}$, $n(\mathbf{k})$ would return to equilibrium with a relaxation time $\sigma(\mathbf{k})$. This concept of the relaxation time of a single mode will be useful in later discussion.

[49a] In other situations the appropriate values of $\tau(\mathbf{k})$ change; see for example a discussion by Klemens[50] of the case where the phonon distribution is disturbed not by a temperature gradient, but by a current of electrons which interact with the phonons.

[50] P. G. Klemens, *Proc. Phys. Soc.* (*London*) **A64**, 1030 (1951).

Substituting (4.4) into (6.2),

$$\tau(\mathbf{k}) - \sigma(\mathbf{k}) = \sum_{\mathbf{k}' \neq \mathbf{k}} W(\mathbf{k},\mathbf{k}')\sigma(\mathbf{k})\tau(\mathbf{k}') \frac{\mu'}{\mu} \tag{6.3}$$

where μ is the direction cosine between $\mathbf{v}(\mathbf{k})$ and grad T. This relation illustrates the difference between σ and τ in the case of a temperature gradient.

Consider the deviation from $\mathfrak{N}(\mathbf{k})$ produced by a small increase in temperature of the system, so that $n = \delta T(d\mathfrak{N}/dT)$. Then $dn/dt] = 0$, for this is still an equilibrium situation. We get the following relation between $W(\mathbf{k},\mathbf{k}')$ and $\sigma(\mathbf{k})$ from (6.2):

$$\sum_{\mathbf{k}' \neq \mathbf{k}} W(\mathbf{k},\mathbf{k}') \frac{d\mathfrak{N}(\mathbf{k}')}{dT} = \frac{1}{\sigma(\mathbf{k})} \frac{d\mathfrak{N}(\mathbf{k})}{dT}. \tag{6.4}$$

As a simple example, consider elastic scattering in an isotropic medium. Here $\omega = \omega'$ and, since τ is a function of ω only, (6.3) with (6.4) become

$$\frac{1}{\tau} = \frac{1}{\sigma}(1 - \bar{\mu}) \tag{6.5}$$

where $\bar{\mu}$ is the average value of μ'/μ taken over all scattering processes. In the case of scattering with spherical symmetry, $\bar{\mu}$ is the average of the cosine of the scattering angle. In the case of isotropic scattering $\bar{\mu} = 0$. This definition of τ was used in deriving (5.8′), (5.25), (5.27), (5.28), and (5.29).

One can regard the establishment of equilibrium as a balance between two processes. As a result of the drift of phonons in the temperature gradient, the "momentum" of the phonon gas $\Sigma\hbar\mathbf{k}N(\mathbf{k})$ in the direction of heat flow is continuously increased, because of the directional dependence of the second term in (4.3). The interaction processes, which attempt to restore equilibrium, tend to obliterate the excess momentum; the steady state is one of excess momentum and therefore net heat flow. The effectiveness of individual interaction processes depends upon their power to obliterate excess momentum. Thus we may regard σ in (6.5) as a mean free time between processes. However, $(1 - \bar{\mu})$ is a factor describing their effectiveness in destroying momentum. $(1 - \bar{\mu})$ is small for small angle scattering processes so that such processes are relatively ineffective.

It is clear that N-processes, that is three-phonon processes conserving quasi-momentum, must play a special role in the establishment of equilibrium, for they do not affect the over-all momentum of the phonon gas

at all, but merely redistribute the momentum among the modes of different frequency. The rate of change of $N(\mathbf{k})$ for three-phonon interactions is of the form (5.33):

$$\frac{dN}{dt}\Big] = \sum_{\mathbf{k}',\mathbf{k}''} A_{\mathbf{k},\mathbf{k}',\mathbf{k}''}[(N+1)(N'+1)(N''+1) - NN'N''']. \quad (6.6)$$

If now these interactions satisfy a conservation condition

$$x + x' + x'' = 0 \quad (6.7)$$

a distribution of the form $\mathfrak{N} = (e^x - 1)^{-1}$ is stationary, for the term in the square bracket vanishes for each triplet separately, so that $dN/dt] = 0$. This is verified easily by substitution. Since energy is conserved in each interaction (5.32), we can identify x with $\hbar\omega/KT$. Thus the Planck distribution (3.8) is stationary for three-phonon processes, as one would expect. Since $\mathbf{k}$ also is conserved in the case of N processes (5.13a), the distribution

$$\mathfrak{N}_\lambda(\mathbf{k}) = \frac{1}{e^{(\hbar\omega+\lambda\cdot\mathbf{k})/KT} - 1} \quad (6.8)$$

is stationary for N processes for any value of λ. Hence these processes would tend to restore a given nonequilibrium distribution $N(\mathbf{k})$ not to the equilibrium distribution (3.8), i.e., (6.8) with $\lambda = 0$, but toward a distribution of the form (6.8), with the value of λ given by

$$\Sigma\mathbf{k}N(\mathbf{k}) = \Sigma\mathbf{k}\mathfrak{N}_\lambda(\mathbf{k}). \quad (6.9)$$

However, a distribution of the form (6.8) carries a heat current, so that N processes, acting by themselves, cannot obliterate a heat current which, once established, would be maintained without a temperature gradient; thus N processes cannot produce thermal resistance.

It was thus pointed out by Peierls[3] that thermal resistance arising from anharmonic forces cannot be treated by means of an elastic continuum model, for the anharmonicities in a continuum would give rise to N processes only, while U processes, which produce thermal resistance, arise only as a result of the discreteness of the lattice. In calculating the thermal resistance arising from lattice imperfection, on the other hand, the discreteness of the lattice need not necessarily be considered explicitly.

Even though N processes do not contribute to the thermal resistance directly, they must be considered in the establishment of thermal equilibrium. Consider a situation in which the steady state in the presence of a temperature gradient is maintained by the combined effect of elastic

scattering processes[50a] and N processes. Let the elastic scattering processes have a relaxation time $\tau'(\omega)$, which is a function of frequency. In the absence of N processes the effective relaxation time τ is simply equal to τ'. The N processes tend to produce a quasi-equilibrium distribution (6.8), which for small values of $\mathfrak{A}$ is equivalent to

$$n = -\frac{\mathfrak{A} \cdot \mathbf{k}}{KT} \frac{e^{\hbar\omega/KT}}{(e^{\hbar\omega/KT} - 1)^2}. \tag{6.10}$$

This is a deviation from true equilibrium which is of the same form as (4.4) if we equate

$$\mathfrak{A} = \frac{\text{grad } T}{T} \hbar v^2 \tau \tag{6.11}$$

in the case of an isotropic medium. A similar but more complicated relation is valid if the medium is anisotropic. However, the effect of N processes is to produce a distribution of the form (6.10) with $\mathfrak{A}$ independent of frequency. Hence they tend to turn the distribution into the form (4.4) with τ arbitrary but independent of frequency. If τ' is frequency independent, N processes have no effect and $\tau = \tau'$. If, however, $\tau'(\omega)$ decreases with increasing frequency, as is often the case, the N processes affect the steady-state distribution, for they tend to make $\tau(\omega)$ independent of frequency. Hence, in combination with elastic scattering, they make $\tau(\omega)$ vary more slowly with frequency than $\tau'(\omega)$. This, in turn, affects the heat current in the steady state, and thus the thermal conductivity. The effect of N processes is the more important, the stronger the variation of $\tau'(\omega)$ with frequency.

In the absence of N processes, the thermal conductivity (4.9) is simply

$$\kappa = \tfrac{1}{3} \sum_j \int d\omega \, S_j(\omega) v_j^2 \tau'(\omega) \tag{6.12}$$

where $S_j(\omega)d\omega$ is the contribution to the specific heat from modes of polarization j and from the frequency interval $\omega, d\omega$. In the limit of very strong N processes, however, we can take τ to be independent of frequency and determine its magnitude from the condition that the rate of gain of quasi-momentum of the system as a result of the temperature gradient is equal to the rate of loss resulting from elastic scattering processes. Of

[50a] Elastic scattering processes cannot always establish thermal equilibrium by themselves, for although they can alter the total quasi-momentum of the system, they cannot interchange energy between normal modes of different frequency. Therefore, they could not restore equilibrium if the distribution of energy among the frequencies is disturbed. Elastic scattering and N processes in combination can deal with any type of nonequilibrium distribution.

course the N processes do not contribute to the over-all momentum balance. Taking $n \propto \tau$, multiplying each term in (4.3) by $\mathbf{k}$, summing over all $\mathbf{k}$, and using (4.4), the condition of momentum balance becomes

$$\tau \sum_j \int d\omega \, (S_j(\omega)/\tau'(\omega)) = \sum_j \int d\omega \, S_j(\omega) \tag{6.13}$$

and thus from (4.9)

$$\kappa = \tfrac{1}{3} \Big(\sum_j S_j v_j \Big)^2 \Big/ \Big[\sum_j \int d\omega \, (S_j(\omega)/\tau'(\omega)) \Big]. \tag{6.14}$$

This result was first derived by Ziman.[51] Since $\tau'(\omega)$ generally decreases with increasing ω, (6.14) leads to smaller values of the conductivity than (6.12), although in general the N processes are less effective, and the conductivity is intermediate between (6.12) and (6.14). N processes reduce the conductivity below (6.12), even though they do not obliterate momentum, for they transport excess momentum from the low to the high frequencies, where the elastic scattering processes are more effective.

For example, if $\tau'(\omega) \propto \omega^{-2}$, (6.14) leads to a value of the conductivity less than (6.12) by a factor of about 3.6, when the Debye continuum model is taken for the specific heat. However, (6.12) diverges at low frequencies if $\tau'(\omega)$ varies as ω^{-3} or faster, so that it becomes essential to take account of N processes. In this case (6.14) becomes a lower limit of the conductivity and could, of course, be substantially lower than the true conductivity.

To find $dN/dt]$ for N processes with the use of values of n, or τ, given by the combined effect of N processes and scattering by imperfections, an integral equation of the form (6.2) must be set up. This equation can then be solved by a variational method, as was done first by Leibfried and Schloemann[17] in a study of the combined effect of N processes and U processes,[51a] and later by Ziman.[51] This procedure yields a value of the conductivity less than the true conductivity. Moreover, if the trial function deviates from the correct solution, the error in the conductivity is only of second order. Nevertheless, the success of the variational method depends upon a reasonable choice of the trial function. If the trial function is badly chosen, even a second-order error can be comparable to the true conductivity. Both Leibfried and Schloemann and Ziman have chosen their trial function in the form (6.10) with λ constant; that is, they chose τ to be independent of frequency. They then adjusted the magnitude of τ by means of the normalizing condition, the only adjustment possible if

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

[51a] As will be seen later, U processes can for the present purposes be treated as scattering processes with a relaxation time $\tau'(\omega) \propto \omega^{-1}$.

the trial function has only one parameter. For this particular trial function, the normalizing condition is equivalent to (6.13), the condition for over-all momentum balance. This trial function has the unique advantage that the rate of change resulting from N processes vanishes at all frequencies, so that N processes need not be considered explicitly. On the other hand, this trial function is not always a good one, and the conductivities thus deduced, although they are lower limits, may be seriously in error. The error introduced is unlikely to be serious in the case of U processes where $\tau'(\omega)$ does not vary strongly with ω. (With $\tau'(\omega) \propto \omega^{-1}$, (6.12) and (6.14) differ only by a factor 1.3.) However, if this method is applied to scattering processes with a strong frequency variation, such as scattering by point imperfections, the error can be quite large.

It would be desirable to use the variational method with a different trial function; the operator describing N processes would then have to be considered explicitly, and the calculations would become complex. Such calculations have not yet been carried out.

A partial, though approximate, solution of the problem can be given,[15] using the following arguments.

Three-phonon processes involving a mode $\mathbf{k}$ can be divided into three groups:

$$\begin{aligned} &\text{(a)}\ |\omega| \sim |\omega''| \gg |\omega'| \\ &\text{(b)}\ |\omega| \sim |\omega'| \sim |\omega''| \\ &\text{(c)}\ |\omega| \ll |\omega'| \sim |\omega''|. \end{aligned}$$

To first order in the n's, the rate of change (6.6) of N is

$$\left[\frac{dN}{dt}\right]_c = \sum_{\mathbf{k}',\mathbf{k}''} A_{\mathbf{k},\mathbf{k}',\mathbf{k}''}[n(\mathfrak{N}' + \mathfrak{N}'' + 1) + n'(\mathfrak{N}'' + \mathfrak{N} + 1) + n''(\mathfrak{N} + \mathfrak{N}' + 1)] \quad (6.15)$$

where, according to (5.21) and (5.33), $A \propto \omega\omega'\omega''$. The processes contributing to (6.15) are enumerated by those vertices A in the vector diagram of Fig. 2a, which lie on the surface of revolution of points satisfying (5.13a) and (5.32). The number of solutions for which k lies in the range k', dk' is roughly proportional to $k'\,dk'$.

In the case of processes (a), $\mathbf{k}$ and $-\mathbf{k}''$ are nearly in the same direction, the angle between them being of order k'/k, and $\omega \simeq -\omega''$, so that $\mathfrak{N} + \mathfrak{N}'' + 1 \ll 1$. Furthermore n and n'' are of the opposite sign, but nearly equal, and $n + n'' \simeq (k'/k)n$. Still further, for almost every process with a positive value of ω' there corresponds a process with a negative value of ω'. Since n' is an odd function of ω' amd $\mathfrak{N} + \mathfrak{N}'' + 1 \ll 1$, the

sum of the terms in n' vanishes. Thus

$$\left.\frac{dN}{dt}\right]_{(a)} \propto n \int x' \left[2\mathfrak{N} \pm 0\left(\frac{k'}{k}\right)\mathfrak{N}'\right] x'\,dx' \tag{6.16}$$

where $x = \hbar\omega/KT$, etc. The greatest contribution to (6.16) comes from the largest values of ω', that is, from processes other than those of type (a), so that the latter are relatively unimportant for the equilibrium of mode $\mathbf{k}$.

To consider processes (b) and (c), let us first assume that $n' = n'' = 0$, that is, let us study their influence on the relaxation of a single mode. The term in n of (6.15) is

$$\left.\frac{dN}{dt}\right\} \propto n \int x'x'' \left[\frac{\mathfrak{N}'\mathfrak{N}''}{\mathfrak{N}}\, e^{-x}\right] x'\,dx'. \tag{6.17}$$

If $\hbar\omega \sim KT$ or if $\hbar\omega > KT$, the greatest contribution to (6.17) comes from processes such that $x' \sim x'' \sim 1$ or $x' \sim x'' \sim x$, that is, from processes of type (b). However, if $\hbar\omega \ll KT$, the greatest contribution to $dN/dt]$ also originates in processes for which $x' \simeq x'' \sim 1$, that is, from interactions with modes whose frequency is of the order $\omega_1 = KT/\hbar$. Hence processes of type (c) are important only for waves of low frequency ($x \ll 1$).

Consider (c) processes if n' and n'' do not vanish. We have seen that $dN/dt] = 0$ for N processes if τ is constant. Since (c) processes link the mode $\mathbf{k}$ mainly with modes of frequency ω_1, $dN/dt]_{(c)} = 0$ if $\tau(\omega) = \tau(\omega_1)$; more generally

$$\left.\frac{dN}{dt}\right]_{(c)} = \left.\frac{dN}{dt}\right\}_{(c)} \left(1 - \frac{\tau(\omega_1)}{\tau(\omega)}\right). \tag{6.18}$$

Thus, if $\omega \ll \omega_1 = KT/\hbar$

$$\frac{1}{\tau(\omega)} = \frac{1}{\tau'(\omega)} + \frac{1}{\sigma(\omega)}\left(1 - \frac{\tau(\omega_1)}{\tau(\omega)}\right) \tag{6.19}$$

where

$$\frac{1}{\sigma(\omega)} = -\sum_{\mathbf{k}',\mathbf{k}''} A_{\mathbf{k},\mathbf{k}',\mathbf{k}''}(\mathfrak{N}' + \mathfrak{N}'' + 1). \tag{6.20}$$

If $\omega > \omega_1$, the important processes are of type (b). While the relaxation time of a single mode can be obtained from (6.20), the effective relaxation time must be much longer, for if ω' is the frequency of those

waves whose contribution to N processes is most important,

$$\left.\frac{dN}{dt}\right]_{(b)} \sim \left.\frac{dN}{dt}\right\}_{(b)} \left(1 - \frac{\tau(\omega')}{\tau(\omega)}\right). \tag{6.21}$$

However $\omega' \sim \omega$, so that $\tau(\omega') \sim \tau(\omega)$, and

$$\frac{1}{\tau(\omega)} - \frac{1}{\tau'(\omega)} = -\frac{1}{n}\left.\frac{dN}{dt}\right]_{(b)} \ll \frac{1}{\sigma(\omega)} \tag{6.22}$$

if $\omega > \omega_1$. Klemens[16] has simply assumed

$$\frac{1}{\tau(\omega)} - \frac{1}{\tau'(\omega)} = 0 \qquad \text{if } \omega > \omega_1 \tag{6.23}$$

although this definitely underestimates the effect of N processes, particularly if $\sigma(\omega) < \tau'(\omega)$. From (6.19) and (6.23)

$$\tau(\omega) = \frac{\tau'(\omega)[\sigma(\omega) + \tau(\omega_1)]}{\tau'(\omega) + \sigma(\omega)} \qquad \omega < \omega_1 \tag{6.24a}$$

$$= \tau'(\omega) \qquad \omega \gtrsim \omega_1. \tag{6.24b}$$

However, (6.23) is merely an approximation which can be justified only if $\sigma(\omega) > \tau'(\omega)$. Thus (6.24) is justified provided

$$\sigma(\omega_1) > \tau'(\omega_1). \tag{6.25}$$

In the derivation of (6.19) it was assumed that any mode of frequency $\omega < \omega_1$ can interact with modes of higher frequency by processes of type (c). We have seen, however, that only transverse modes can interact with two modes of much higher frequency (5.35b), so that (6.24) can apply only to transverse modes.

Longitudinal modes can interact only with modes of about the same frequency; that is, they can undergo (b) processes, but not (c) processes. If $\omega \geq \omega_1$, the important N processes are (b) processes, so that $\sigma(\omega)$ is about the same for modes of all polarization, and the effect of N processes on them is also about the same. If $\omega < \omega_1$, however, the effect of N processes is different for longitudinal waves. Since (c) processes are forbidden, the major contribution to N processes are from (b) processes, which are now less effective, so that $\sigma(\omega)$ is greater for longitudinal than for transverse waves. Furthermore, since longitudinal waves are coupled to transverse waves of the same frequency, we have in place of (6.18)

$$\left.\frac{dN}{dt}\right]_{(b)} = \left.\frac{dN}{dt}\right\}_{(b)} \left(1 - \frac{v_{II}^2\tau_{II}(\omega)}{v_I^2\tau_I(\omega)}\right) \tag{6.26}$$

where the suffices I and II refer to longitudinal and transverse modes, respectively. The factor on the right-hand side has been introduced in such a way as to be unity if the transverse waves do not depart from equilibrium, and to be zero if both groups of waves have the same value of λ, that is, in view of (6.11), have the same value of $v^2\tau$. Expressing (6.26) in terms of $\tau_I(\omega)$ and $\sigma_I(\omega)$, we obtain by means analogous to those leading to (6.24a)

$$\tau_I(\omega) = \frac{\tau_I'(\omega)[\sigma_I(\omega) + \tau_{II}(\omega)/c^2]}{\tau_I'(\omega) + \sigma_I(\omega)} \tag{6.27}$$

where $c = v_I/v_{II}$, and τ_{II} is given by (6.24).

Substituting these relaxation times into (4.9), the thermal conductivity becomes

$$\kappa = \kappa_I + \kappa_{II} \tag{6.28a}$$

$$\kappa_I = \tfrac{1}{3}\int_0^\infty S_I(\omega) v_I \frac{l_I' l_I}{l_I' + l_I}\, d\omega \tag{6.28b}$$

$$\kappa_{II} = \tfrac{1}{3}\int_0^\infty S^*(\omega) l_{II} v_{II}\, d\omega. \tag{6.28c}$$

Here

$$S^*(\omega) = S_{II}(\omega) + S_I(\omega)\frac{l_I'}{l_I' + l_I} \tag{6.29a}$$

and

$$l_{II}(\omega) = l_{II}'(\omega) \qquad \text{if } \omega \geq \omega_1 \tag{6.29b}$$

$$= \frac{l_{II}'(\omega)[l_2(\omega) + l_{II}'(\omega_1)]}{l_{II}'(\omega) + l_2(\omega)} \qquad \text{if } \omega < \omega_1. \tag{6.29c}$$

Moreover, $S_I(\omega)$, $S_{II}(\omega)$ are the specific heats per unit frequency interval arising from longitudinal and transverse modes, $l_2 = v_{II}\sigma_{II}$, $l_1 = v_I\sigma_I$, $l_I' = v_I\tau_I'$, and $l_{II}' = v_{II}\tau_{II}'$.

The relaxation times σ_I and σ_{II} can be estimated from (6.20), by using (5.33) and (5.21) and integrating over all admissible values of $\mathbf{k}'$. An estimate of σ_{II} was first made in this way by Landau and Rumer,[52] and an estimate of σ_I was made by Pomeranchuk.[8] Thus

$$\left.-\frac{1}{n}\frac{dN}{dt}\right\} = \frac{4}{3(2\pi)^2}\gamma^2\frac{V}{G}\frac{\hbar}{Mv^2}\sum_{j',j''}\int dS'\,\omega\omega'\omega''[\operatorname{grad}\Delta\omega]^{-1}\times \frac{e^x - 1}{(e^{x'} - 1)(e^x - e^{-x'})}. \tag{6.30}$$

If $\mathbf{k}$ is a low-frequency ($\omega \ll KT/\hbar$) longitudinal wave, it can interact with two transverse waves (5.35a) or with a longitudinal and a transverse wave (5.35b). Thus $\Sigma_{j',j''} = 6$, and $\int dS' \simeq 4\pi k^2$. Moreover, $\operatorname{grad}_{\mathbf{k}}\Delta\omega \simeq v$,

[52] L. Landau and G. Rumer, *Physik. Z. Sowjetunion* **11**, 18 (1937).

$\omega'\omega'' \simeq \omega^2/4$, and, since $x \ll 1$,

$$\frac{1}{\sigma_{\mathrm{I}}} \simeq \frac{16}{3\pi}\gamma^2 (ak)^4 \frac{v}{a}\frac{KT}{Mv^2}. \tag{6.31}$$

If $\mathbf{k}$ is a low-frequency transverse wave, it will interact mainly with two longitudinal waves (5.35b), both of frequency $\sim KT/\hbar$. Thus $\Sigma_{j',j''} = 1$, $dS' \simeq 2\pi k'\,dk'$, $\mathrm{grad}_{\mathbf{k}}\,\Delta\omega \simeq vk/k'$, and

$$\frac{1}{\sigma_{\mathrm{II}}} \simeq \frac{100}{6\pi}\gamma^2 \frac{KT}{Mv^2}\frac{v}{a}(ak)\left(\frac{aKT}{\hbar v}\right)^3. \tag{6.32}$$

Still further, $\sigma_{\mathrm{I}} \sim \sigma_{\mathrm{II}}$ if $\omega \sim KT/\hbar$, as would be expected.

If $\mathbf{k}$ is a wave of high frequency ($\omega > KT/\hbar$), the important contributions to (6.30) are such that $x' \sim x'' \sim x$. The integration is analogous to that leading to (6.31), except that the factor $(e^x - 1)/(e^{x'} - 1)(e^x - e^{-x'})$ is now approximately e^{-x}, instead of $1/2x$ as previously. Thus if $\omega > KT/\hbar$

$$\frac{1}{\sigma} \simeq \frac{32\gamma^2}{3\pi}(ak)^5 \frac{\hbar}{a^2 M} e^{-\hbar\omega/KT} \tag{6.33}$$

so that $1/\sigma$ increases with frequency, reaches a maximum value at $\omega = 5KT/\hbar$ and then decreases exponentially.

Klemens[15] has simplified (6.28) in the case of good crystals by neglecting all terms containing l_1 or l_2 in the numerator. He has based this procedure on the argument that, when l_{I}' and l_{II}' are large, l_1 and l_2 are negligible in comparison. Thus the following approximation was obtained

$$\kappa = \kappa_{\mathrm{II}} = \tfrac{1}{3}\int_0^{\omega_1} S(\omega) v_{\mathrm{II}} l_{\mathrm{II}}'(\omega_1)\,d\omega + \tfrac{1}{3}\int_{\omega_1}^{\infty} S(\omega) v_{\mathrm{II}} l_{\mathrm{II}}'(\omega)\,d\omega. \tag{6.34}$$

However, this approximation is inconsistent with (6.25), the criterion for the validity of (6.23), which was assumed in the derivation of (6.28). Thus if $l_2 < l_{\mathrm{II}}'$, (6.34) probably over-estimates κ_{II}. More seriously still, the expression for κ_{I} when $l_1 \ll l_{\mathrm{I}}'$, namely

$$\kappa_{\mathrm{I}} = \tfrac{1}{3}\int S_{\mathrm{I}}(\omega) v_{\mathrm{I}} l_1\,d\omega \tag{6.35}$$

diverges at low values of ω, for

$$S_{\mathrm{I}}(\omega) \propto T^3 \frac{x^4 e^x}{(e^x - 1)^2} \text{ and } l_1 \propto T^{-5}x^{-4}.$$

Thus it is essential to consider scattering processes in which l_{I}' varies more slowly than ω^{-3} in order that the divergence be removed. Nevertheless, if the absolute magnitude of l_1 is sufficiently small, and if the crystal contains a sufficient number of dislocations, stacking faults, and grain boundaries, or has sufficiently small external dimensions, κ_{I} may be

negligible compared with κ_{II}. In this case, however, (6.34) is no longer a good approximation for κ_{II}. Nevertheless, it is possible that (6.34) may still be a reasonable approximation for κ, for the two errors are of opposing sense.

It is also very probable that in real crystals, which are elastically anisotropic, l_1 does not increase with decreasing frequency as fast as ω^{-4} (6.31), for elastic anisotropy increases the number of simultaneous solutions of (5.13a) and (5.32), as discussed by Herring[10] and Schloemann.[53] If, in particular, the waves of the two transverse polarization branches have equal frequencies along lines of degeneracy in $\mathbf{k}$ space, but differ elsewhere, $\sigma_I \propto \omega^{-2}$ in the limit of low frequencies at high temperatures, but varies as ω^{-2} or ω^{-3} at low temperatures, depending on the nature of the degeneracy.

So far we have considered the combined effect of N processes and scattering by imperfections. U processes must be considered if scattering by imperfections is sufficiently weak. The relaxation time for U processes is always long compared with $\sigma_{II}(\omega)$, except at temperatures at or above the Debye temperature θ, for at least two of the interacting waves have frequencies of the order of $K\theta/\hbar$. We therefore have to consider the combined effect of N processes and U processes.

Consider U processes acting by themselves. The rate of change of $N(\mathbf{k})$ is given by (6.15), with n, n', and n'' of the form (6.10), so that, in view of (5.13b),

$$\left.\frac{dN}{dt}\right]_U = \frac{1}{KT}\sum_{\mathbf{k}',\mathbf{k}''} A_{\mathbf{k},\mathbf{k}',\mathbf{k}''}\left[\boldsymbol{\lambda}\cdot\mathbf{k}\,\frac{d\mathfrak{N}}{dx}(\mathfrak{N}'+\mathfrak{N}''+1)+\right.$$

$$\left.\boldsymbol{\lambda}\cdot\mathbf{k}'\,\frac{d\mathfrak{N}'}{dx'}(\mathfrak{N}''+\mathfrak{N}+1)+\boldsymbol{\lambda}\cdot(\mathbf{b}-\mathbf{k}-\mathbf{k}')\,\frac{d\mathfrak{N}''}{dx''}(\mathfrak{N}+\mathfrak{N}'+1)\right]. \quad (6.36)$$

Now it is easily seen that $(d\mathfrak{N}/dx)(\mathfrak{N}'+\mathfrak{N}''+1) = -\mathfrak{N}\mathfrak{N}'\mathfrak{N}''$, whence the terms in $\boldsymbol{\lambda}\cdot\mathbf{k}$ and $\boldsymbol{\lambda}\cdot\mathbf{k}'$ cancel, leaving

$$\left.\frac{dN}{dt}\right]_U = -\frac{1}{KT}\sum_{\mathbf{k}',\mathbf{k}''} A_{\mathbf{k},\mathbf{k}',\mathbf{k}''}(\boldsymbol{\lambda}\cdot\mathbf{b})\mathfrak{N}\mathfrak{N}'\mathfrak{N}'' \quad (6.37)$$

where the summation is over all U processes involving $\mathbf{k}$. Thus the relaxation time becomes

$$\frac{1}{\tau_U} = -\frac{1}{n}\left.\frac{dN}{dT}\right]_U = -\sum_{\mathbf{k}',\mathbf{k}''} A_{\mathbf{k},\mathbf{k}',\mathbf{k}''}\frac{\boldsymbol{\lambda}\cdot\mathbf{b}}{\boldsymbol{\lambda}\cdot\mathbf{k}}(\mathfrak{N}'+\mathfrak{N}''+1) \quad (6.38)$$

where $\boldsymbol{\lambda}$ is in the direction of the temperature gradient.

[53] E. Schloemann, Thesis, Göttingen, 1953.

Six different vectors $\mathbf{b}$ must be considered in the sum over all U processes; however, if we require that $\mathbf{k}'$ and $\mathbf{k}''$ lie in the fundamental zone, the only possible $\mathbf{b}$'s are the three inverse lattice vectors for which $(\mathbf{b} \cdot \mathbf{k})$ is negative. This is illustrated in Fig. 3 for a two-dimensional square lattice. Although there are directions of the temperature gradient for which $(\lambda \cdot \mathbf{b})/(\lambda \cdot \mathbf{k})$ is positive for a particular $\mathbf{b}_i$, even though $(\mathbf{k} \cdot \mathbf{b})$ is negative, it can be shown that $\Sigma_i(\lambda \cdot \mathbf{b}_i)/(\lambda \cdot \mathbf{k})$ is negative when this expression is summed over the three possible values of $\mathbf{b}_i$; therefore, $1/\tau_U$ is positive.

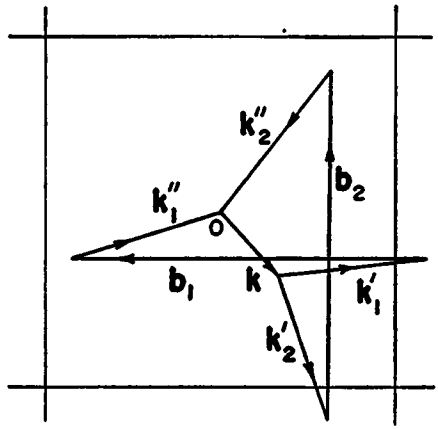

FIG. 3. U processes in a two-dimensional square lattice. Note that $\mathbf{k} \cdot \mathbf{b}$ is negative.

Now $A \propto \omega$ and $(\mathfrak{N}' + \mathfrak{N}'' + 1) = \mathfrak{N}'\mathfrak{N}''(e^{-x} - 1)$. There will also be a further dependence on ω through the summation over all admissible states $\mathbf{k}',\mathbf{k}''$, however, this dependence is weak if $k \ll b$. Thus for low frequencies ($x < 1$), $\tau_U \propto \omega^{-1}$. (An error was incurred by Klemens,[15] who omitted the factor $(\lambda \cdot \mathbf{k})/(\lambda \cdot \mathbf{b})$, and thus obtained $\tau_U \propto \omega^{-2}$.) If we now consider the combined effect of N processes and U processes, the N processes tend to make τ independent of frequency. The conductivity is intermediate between (6.12) and (6.14) if we substitute τ_U of (6.38) in place of $\tau'(\omega)$. That is, we can treat U processes as if they were elastic scattering processes with a relaxation time τ_U.

It should be noted, however, that if $k \ll b$ and if $\mathbf{k}$ is a longitudinal wave, (5.13b) and (5.32) cannot be satisfied together, so that a low-frequency longitudinal wave cannot participate in U processes. Thus, for purposes of (6.28), l_{II}' can be identified with $v_{II}\tau_U$—or rather

$$\frac{1}{l_{II}'} = \frac{1}{v_{II}\tau_U} + \frac{1}{l_{\text{imperf.}}}$$

—but l_I' is determined solely by imperfections. Hence κ_I has to be considered explicitly. It is limited by stacking faults, dislocations, grain boundaries, etc., or by external boundaries, as well as by N processes, as discussed above.

7. Boundary Resistance

We have seen in Section 5(c) that the external boundaries of a crystal give rise to scattering of lattice waves similar in character to the scattering by imperfections, so that one would expect the boundaries to contribute to $1/\tau'$ by an amount of order v/L, where L is the shortest linear dimension

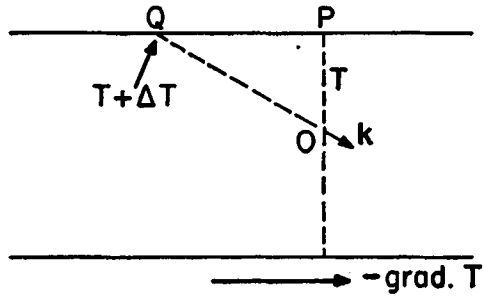

Fig. 4. The phonon distribution at O is governed by the emission of phonons from the boundaries. At O, the number of phonons in mode $\mathbf{k}$ is appropriate to $T + \Delta T$, the temperature at Q, rather than to T, the temperature at P.

of the specimen, and to contribute correspondingly to the thermal resistivity. One would also expect the boundary scattering to be substantially independent of frequency, so that the thermal conductivity at the lowest temperatures, where $1/\tau'$ is limited by the boundaries, should be proportional to LT^3.

While the importance of boundary scattering at lowest temperatures had already been pointed out by Peierls,[3] the first quantitative treatment was given by Casimir.[7] Casimir considered a crystal at such a low temperature that l_1, l_2, l_I', and l_{II}' all exceed the linear dimensions, whence interaction and scattering processes within the crystal can be neglected. The lattice waves run from one boundary to the opposite boundary, where they are scattered isotropically.[53a] The scattered radiation issuing from a point Q (see Fig. 4) has the equilibrium distribution appropriate to the temperature at Q. The distribution at O is determined by the various points of emission of the lattice waves passing through O. If there

[53a] For the present argument it does not matter whether the scattering is elastic or whether there are also three-phonon processes at the boundary, as long as the tangential momentum is not conserved.

is a temperature gradient along the crystal, so that the temperature is T at P and $T + \Delta T$ at Q, the density of phonons of wave-vector $\mathbf{k}$ at O is $\mathfrak{N}(\mathbf{k},T + \Delta T)$ instead of the equilibrium distribution $\mathfrak{N}(\mathbf{k},T)$. Moreover, $\Delta T = q \text{ grad } T$, where q is the length of PQ. Thus it is possible to find the deviation of the mode $\mathbf{k}$ at O, namely, $\mathfrak{N}(\mathbf{k}, T + q \text{ grad } T) - \mathfrak{N}(\mathbf{k},T)$, from geometrical considerations. In this way the density of energy flow at O can be deduced. Hence by integrating over the cross section, one can find the heat flow per unit temperature gradient.

Casimir found in this way that

$$\kappa = \tfrac{1}{3} \sum_j S_j v_j L \tag{7.1}$$

where L is an effective mean free path, independent of phonon frequency and polarization, since it depends only on the geometry of the crystal. He considered the case of long cylinders and, in the case of cylinders of circular cross section of radius R, obtained

$$L = 2R \tag{7.2}$$

In the case of a square cross section, each side of the square being D, he obtained $L = 1.12D$.

Berman *et al.*[23] have extended this theory to include cylinders of finite length (the effect of the terminal surfaces is to reduce L) and partly specular reflection (this tends to increase L), still using purely geometrical arguments. They also pointed out that if boundary scattering is partly specular, one would expect the fraction of phonons reflected specularly to vary with frequency. Thus the effective value of L would be frequency-dependent and would decrease with increasing frequency; correspondingly, κ would vary more slowly than the specific heat.

If we describe the deviation from equilibrium in terms of an anisotropy parameter $\boldsymbol{\lambda}$ and (6.10)

$$n = -\frac{\boldsymbol{\lambda} \cdot \mathbf{k}}{KT} \frac{e^{\hbar\omega/KT}}{(e^{\hbar\omega/KT} - 1)^2} \tag{7.3}$$

$\boldsymbol{\lambda}$, according to the Casimir theory, is independent of frequency, but depends on the direction of $\mathbf{k}$ and on the position within the crystal. The phonons are localized. If scattering is partly specular, $\boldsymbol{\lambda}$ varies with frequency as well.

The theory becomes quite complicated as soon as we consider other processes occurring at the same time as boundary scattering. Consider, for example, boundary scattering together with scattering by static imperfections, distributed uniformly throughout the crystal. A naive approach

would be to add the inverse mean free paths

$$\frac{1}{l} = \frac{1}{l'} + \frac{1}{L} \tag{7.4}$$

where l is the effective mean free path determining the thermal conductivity, l' the mean free path arising from imperfections, and L the geometrical (Casimir) mean free path. This, however, neglects the fact that boundary scattering is not distributed uniformly throughout the crystal. More properly, if λ_B is the value of λ (a function of position and direction) calculated from boundary scattering in the absence of imperfections, and if λ' is the value calculated from imperfection scattering alone, then

$$\frac{1}{\lambda} = \frac{1}{\lambda'} + \frac{1}{\lambda_B}. \tag{7.5}$$

The heat flow is obtained by integration over direction and position. Herring[54] has shown that if $l' \ll L$, the effective value of $1/L$ for substitution into (7.4) is approximately twice the geometrical (Casimir) value.

Consider now three-phonon N processes. So far we have assumed that $L \ll l_1 \sim l_2$ for the important frequencies. If now $l_1 \sim l_2 \ll l'$, which should be the case at all but the lowest temperatures, it is possible to have a situation such that L is not small compared with l_1 or l_2 even though $L \ll l'$. Since N processes tend to make λ the same for all frequencies and directions, and since λ_B, the value of λ in the absence of N processes, is dependent on direction, N processes should modify the boundary resistance.

This conclusion is particularly valid if the cross section is irregular, with one diameter (L_1) much larger than the other (L_2). Thus most waves should have small values of λ, appropriate to L_2. However, waves whose direction is nearly in the plane of the long axis should have large values of λ, appropriate to L_1, in the absence of N processes. If N processes are present, and if $L_2 \sim l_1 \sim l_2 < L_1$, the λ values of all directions are equalized, and the effective value of L is reduced to about L_2.[55] Thus, since $l_1 \sim l_2 \propto T^{-5}$, L is larger at sufficiently low temperatures, where $l_1 \sim l_2 > L_2$, than at higher temperatures.

Finally, a situation may arise in which $l_2 \ll L \ll l'$, if $l_2 \ll l'$. The assumptions of Casimir's theory would then break down, for a phonon could not travel across the width of the crystal without undergoing N processes, even though it would not be scattered by imperfections. There is, as yet, no satisfactory treatment of the combined effect of boundaries

[54] C. Herring, *Phys. Rev.* **96**, 1163 (1954).
[55] P. G. Klemens, *Australian J. Phys.* **6**, 405 (1953).

and N processes in such a case; however, one may consider the following argument.

The N processes tend to give the phonons of all frequencies and directions a distribution $\mathfrak{N}_\lambda(\mathbf{k})$ of the form (6.8) with a common value of λ. This value of λ, and the consequent thermal current, can be obtained by balancing the gain of quasi-momentum of the system resulting from the temperature gradient against the momentum carried to the external boundaries. The rate of gain of momentum in an element of volume δV through the temperature gradient is, from (4.3),

$$\frac{dP}{dt}\Big]_{\nabla T} = \delta V \sum_{\mathbf{k}} (\mathbf{v} \cdot \operatorname{grad} T)\hbar\mathbf{k} \frac{d\mathfrak{N}}{dT}. \tag{7.6}$$

The number of phonons emitted per unit time from an element δA of the boundary surface into the crystal is

$$\delta A \sum_{k_n>0} \mathfrak{N}(\mathbf{k})(\mathbf{v} \cdot \mathbf{n}). \tag{7.7}$$

Here $\mathbf{n}$ is a unit vector normal to δA and the summation extends over all values of $\mathbf{k}$ for which the wave travels from the surface into the crystal. Thus, from symmetry, no net momentum is emitted. However, the phonons absorbed by the surface have a distribution $\mathfrak{N}_\lambda(\mathbf{k})$, whence the momentum absorbed by the boundary element is

$$\begin{aligned} \frac{dP}{dt}\Big]_B &= \delta A \sum_{k_n<0} \hbar\mathbf{k}\mathfrak{N}_\lambda(\mathbf{k})(\mathbf{v} \cdot \mathbf{n}) \\ &= \delta A \sum_{k_n<0} (\lambda \cdot \mathbf{k})(\mathbf{v} \cdot \mathbf{n})\mathbf{k} \frac{T}{\omega} \frac{d\mathfrak{N}}{dT}. \end{aligned} \tag{7.8}$$

We have expanded $\mathfrak{N}_\lambda(\mathbf{k})$ according to (6.10). Equating (7.6) and (7.8), and noting that $\delta V/\delta A \sim L$ for a section across the cylinder, if L is the shortest external dimension, we find

$$\lambda \sim \frac{\operatorname{grad} T}{T} \hbar v L. \tag{7.9}$$

In view of (6.11), this implies an effective mean free path of the order of L. Thus the N processes do not change the magnitude of the boundary resistance greatly from the Casimir value.

This argument is based on the assumption that λ is independent of position. It is, however, also possible to take the following point of view, admitting a possible variation of λ with position.

There is an analogy between the quantized lattice waves and a gas. The anisotropy parameter λ is proportional to the macroscopic velocity of the phonon gas, for it is proportional to the momentum density. If the parameter λ varies with position, it is possible to define a viscosity, proportional to $\int S(\omega)l(\omega)\,d\omega$, where l is the mean free path of a single mode arising from N processes, and determining the rate of momentum transfer between neighboring regions with different λ. One can then balance the momentum increase in a small region produced by the temperature gradient against the net momentum transferred laterally as a result of the variation of λ. Thus λ is determined as a function of position by a macroscopic equation, with the condition that $\lambda = 0$ at the external boundaries, analogous to the Poiseuille equation of viscous flow. The average value of λ would be given by an expression analogous to (7.9)

$$\lambda \sim \frac{\text{grad } T}{T} \hbar v \frac{L^2}{l(\omega_1)}. \tag{7.10}$$

That is, L has been replaced by $L^2/l(\omega_1)$, and the boundary resistance has been reduced by a factor l/L, because the viscosity of the phonon gas, rather than the conditions at the boundary, governs the rate of transfer of momentum to the boundary. Thus in the temperature range for which $l(\omega_1) < L < l'(\omega_1)$, the thermal conductivity would be higher than predicted by Casimir's theory by a factor $L/l(\omega_1)$, and would vary as L^2T^8.

We shall see in Section 10 that such behavior has not been observed and that $\kappa \propto LT^3$, except where the imperfection resistance is important, when κ increases more slowly with temperature. Therefore it seems that it is not permissible to regard λ as a function of position, although it is not clear why this should not be allowed. Apparently it would be necessary to reformulate the theory, paying some attention to a more rigorous treatment of the localization of the lattice waves.

III. Thermal Conductivity of Nonmetals

8. Thermal Conductivity at High Temperatures

At high temperatures ($T > \theta$), where the specific heat per normal mode is K, the thermal conductivity of good crystals should vary inversely as the absolute temperature, for in the expression for the thermal conductivity,

$$\kappa = \tfrac{1}{3} \sum_j \int d\omega\, S(\omega) v^2 \tau' \tag{8.1}$$

the temperature dependence of κ is governed only by the temperature dependence of τ'. If U processes are the only resistive processes, τ' is given

by (6.38) as

$$\frac{1}{\tau_U} = \sum_{\mathbf{k}',\mathbf{k}''} A_{\mathbf{k},\mathbf{k}',\mathbf{k}''} \frac{\boldsymbol{\lambda}\cdot\mathbf{b}}{\boldsymbol{\lambda}\cdot\mathbf{k}} (\mathfrak{N}' + \mathfrak{N}'' + 1). \tag{8.2}$$

The only factor depending on temperature is $(\mathfrak{N}' + \mathfrak{N}'' + 1)$, which is proportional to T.

In principle the magnitude of τ_U can be found in terms of the magnitude of $A_{\mathbf{k},\mathbf{k}',\mathbf{k}''}$, given by (5.31) and (5.21), and in terms of the summation over $\mathbf{k}'$ (8.2). The summation is somewhat difficult to carry out, but an estimate has been given by Leibfried and Schloemann.[17] They obtained for the thermal conductivity

$$\kappa \sim \frac{24}{10} \frac{(4)^{\frac{1}{2}}}{\gamma^2} \left(\frac{K}{h}\right)^3 Ma\theta^2 \frac{\theta}{T} \tag{8.3}$$

where a^3 is the volume and M the mass per atom. It should be noted that their estimate of $A_{\mathbf{k},\mathbf{k}',\mathbf{k}''}$ is smaller by a factor $\sim$4 than the one given by (5.31). Thus the numerical factors in (8.3) may be regarded with some doubt, but (8.3) does indicate the way in which κ depends on other physical quantities. A similar expression, equivalent except for numerical factors, was also given by Dugdale and MacDonald.[56]

It is an obvious consequence of relating the frequency of U processes to the cubic anharmonicities, which are also responsible for thermal expansion, that the thermal resistivity should vary as γ^2. More important than the dependence on γ^2 is the variation with θ^3, for most substances have similar values of γ, but differ widely in their Debye temperature. The factor θ^3 arises as follows: a factor θ^2 originates in the factor v^2 in (8.1), while in (8.2) $(\mathfrak{N}' + \mathfrak{N}'' + 1) \propto T/\theta$. The factor A is independent of θ. The factor a arises from a factor a^{-3} in $S(\omega)$, a factor $a^2 \propto v^2/\theta^2$ and a factor $\Sigma_{\mathbf{k}',\mathbf{k}''} \propto a^{-2}$.

It was already noted by Eucken[1] that $\kappa \propto T^{-1}$ for most good crystals at all but the low temperatures. This was explained by Debye[2] and Peierls.[3] It is now also possible to check whether the theory gives the correct order of magnitude of κ. Leibfried and Schloemann showed that the agreement with (8.3) is as good as can be expected in view of the approximations made in deriving this relation. Observed values of κT are compared with values derived from (8.3) in Table II; it will be seen that (8.3) generally overestimates κT. The pronounced increase of κT with θ predicted by (8.3) is generally observed. The various substances in Table II have θ values ranging over a factor larger than 10. Thus the dependence on θ^3 is quite well established. This is borne out particularly

[56] J. S. Dugdale and D. K. C. MacDonald, *Phys. Rev.* **98**, 1751 (1955).

TABLE II. THEORETICAL AND OBSERVED VALUES OF κT FOR VARIOUS DIELECTRIC SOLIDS AT ORDINARY TEMPERATURES

Substance	γ	M	a 10^{-8} cm	θ °K	κT in watt-cm^{-1} from (8.3)	obs.	Ratio	Remarks
Diamond	1.1	12	1.78	1840	6400	1750	3.7	Eucken[a]
Al_2O_3	3	20.4	2.06	980	2500	1100	2.3	Berman[b]
Beryllia	2(?)	25	3.0	855	660	450	1.5	Ditmars *et al.*[c]
CaF_2	1.7	26	2.4	470	105	30	3.5	Eucken[a]
Quartz	0.7	20	3.3	290	200	45	4.5	Eucken[a]
Si	2(?)	28	5.9	660	680	440	1.5	Carruthers *et al.*[d]
Ge	2(?)	72.6	5.9	370	310	150	2.1	Carruthers *et al.*[d]
Te	2(?)	127.6	7.0	150	43	10	4.3	Fischer *et al.*[e]
								$m_1:m_2$ =
LiF	1.8(?)	13	4.3	620	240	50	4.8	= 7:19
NaF	1.7(?)	21	4.9	300(?)	55	29	1.9	= 23:19
NaCl	1.63	29	6.1	280	84	27	3.1	= 23:35
NaBr	1.56	50	6.3	250(?)	115	6.6	17.4	= 23:80
KF	1.6(?)	29	5.8	260(?)	66	19	3.5	= 39:19
KCl	1.6	37	6.8	230	68	28	2.4	= 39.35
KBr	1.68	59	6.7	170	39	10	3.9	= 39:80
KI	1.6(?)	83	7.6	150(?)	50	8.2	6.1	= 39:123
RbCl	1.3(?)	60	7.1	140(?)	40	5.4	7.4	= 85:35
RbBr	1.37	83	7.4	130	41	10.3	4.0	= 85:80
RbI	1.41	106	7.9	120	42	8.8	4.8	= 85:123

Remarks: Some of the data in this table are not reliable; in particular, quantities marked (?) are often only a rough guess. The γ values were obtained from Grüneisen,[f] the Debye temperatures from various sources. The values of κ for alkali halides were obtained from Eucken and Kuhn[g] with the exception of LiF, which was extrapolated from the results of Berman *et al.*[h] For the alkali halides the ratio of the masses of the two ions is given: it will be noted that the discrepancy is larger the more $m_1:m_2$ departs from unity.

[a] A. Eucken, *Ann. Physik* **34**, 185 (1911); *Verhandl. Deut. Phys. Ges.* **13**, 829 (1911); *Physik. Z.* **12**, 1005 (1911).

[b] R. Berman, *Proc. Phys. Soc.* (*London*) **A65**, 1029 (1952).

[c] D. A. Ditmars and D. C. Ginnings, *J. Research NBS* **59**, 93 (1957).

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

[e] G. Fischer, G. K. White, and S. B. Woods, *Phys. Rev.* **106**, 480 (1957).

[f] E. Grüneisen, *in* "Handbuch der Physik," Vol. 10, p. 1. Springer, Berlin, 1926.

[g] A. Eucken and G. Kuhn, *Z. physik. Chem.* **134**, 193 (1928).

[h] R. Berman, E. L. Foster, and J. M. Ziman, *Proc. Roy. Soc.* (*London*) **A237**, 344 (1956).

in the case of solid helium, measured by Webb *et al.*,[14] where by varying the density it is possible to vary θ, keeping the same crystal structure.

The dependence on γ^2 cannot be regarded as definitely established from the data of Table II. It should be noted, however, that the discrepancy is always large when the values of γ are unusually low. The values of γ derived from the coefficient of expansion at high temperatures are the average of $\gamma_k = d \log \omega_k / d \log V$. Low values of γ do not necessarily imply low values of the individual γ_k's, and thus, even more, they do not imply low values of the coefficients $c(\mathbf{k},\mathbf{k}',\mathbf{k}'')$ of (5.21). This has been discussed by Barron.[57]

The case of the alkali halides is of some interest, for κT is largest and the discrepancy from (8.3) least for those solids which have alkali and halogen ions of nearly equal masses. Such crystals can be regarded as monatomic. The decrease in conductivity with increasingly different masses, which had already been noted by Eucken and Kuhn,[58] was ascribed by Blackman[59] to an increase in the number of simultaneous solutions of (5.13) and (5.32) as a result of the enhanced dispersion of the lattice waves, whereas Leibfried[42] ascribed it to the decrease of the group velocity because of enhanced dispersion. However, the increase in resistance is probably the result of the additional U processes arising from the extra zone boundaries associated with the mass difference;[59a] the change in the group velocity would also contribute to this increase.

In some cases κT decreases with increasing temperature. These cases can be grouped into two classes: (a) the variation of κT becomes more pronounced as the temperature is lowered. This is the normal behavior of all good crystals, as will be discussed in Section 9, but would be noticed even at room temperatures for crystals with high Debye temperature. (b) The variation becomes more pronounced as the temperature is increased. This is a result of the additional resistance arising from higher order anharmonicities. If terms of the fourth power in the relative displacements had been considered in the potential energy, as well as the cubic anharmonicities (5.11), there would have been additional terms in

[57] T. H. K. Barron, *Nature* **178**, 871 (1956); *Ann. phys.* **1**, 77 (1957).

[58] A. Eucken and G. Kuhn, *Z. physik. Chem.* **134**, 193 (1928).

[59] M. Blackman, *Phil. Mag.* [7] **19**, 989 (1935).

[59a] This causes one to ask why one does not observe new U processes with a reduced inverse lattice vector if one doubles the unit cell of a monatomic crystal. It should be remembered that, even if the interference condition (5.13b) is satisfied, the matrix element of the perturbation Hamiltonian (5.21) may still vanish. We have only proved that it is certain to vanish if (5.13) is not satisfied. It is easily seen that the additional spurious U processes indeed have vanishing matrix elements if the unit cell is twice the usual size. However, these matrix elements become finite if the masses of the two subcells are made to differ.

(8.2) quadratic in the $\mathfrak{N}$'s. These would lead to an additional component of thermal resistivity proportional to T^2 at high temperatures, which would become increasingly important as the temperature is increased. Such a T^2 component of thermal resistivity seems to have been found in indium antimonide.[60]

So far we have disregarded the term κ_I (6.28), which arises from the fact that the low-frequency longitudinal phonons have a very long mean free path for three-phonon interactions in an elastic continuum. Pomeranchuk[8] has discussed the way in which the fourth-order interactions could remove the divergence of κ_I at low frequency. The mean free path for phonons of low frequency arising from four-phonon processes varies as $T^{-2}\omega^{-2}$. Substituting this in place of l_I' into κ_I of (6.28b), we find $\kappa_I \propto T^3$, the greatest contribution to the integral coming from frequencies such that $l_I' \sim l_I$.

However, since the low-frequency divergence of κ_I is much decreased, if not altogether removed,[23,53] in real lattices, which are discrete and anisotropic, it is doubtful whether κ_I is appreciable at higher temperatures,[60a] and whether a decrease of κT with increasing T originates in κ_I, or rather in the direct effect of fourth-order processes on κ_{II}, as mentioned above. It does not seem possible to discriminate with confidence between these two possibilities in an experimental way, for the measurements can be made only over a range of temperatures with a restricted fractional change of temperature. Moreover, the accuracy of measurements decreases at higher temperatures.

All imperfections contribute to $1/\tau'$ in an additive manner. Since $(1/\tau')_{imp}$ is independent of temperature, and a function only of frequency, their contribution to the thermal resistance is independent of temperature. Thus it is not possible to deduce the frequency dependence of $1/\tau'$ and the nature of the imperfections from the observed thermal resistance at high temperatures, as one can do from observations at low temperatures (see Section 11).

Since the intrinsic resistance increases with temperature, whereas the imperfection determined resistance is independent of temperature, the effect of crystal imperfections on the thermal conductivity is not as significant as at lower temperatures; however, a sufficient concentration of imperfections will reduce the conductivity appreciably. Eucken and Kuhn[58] observed the thermal resistance in mixed crystals of KCl – KBr

[60] A. D. Stuckes, *Phys. Rev.* **107**, 427 (1957).

[60a] In addition, the mean free path of the phonons of thermal frequency is not large, so that the low-frequency phonons have a wavelength at least comparable to that mean free path. The momentum conservation conditions (5.13) are then relaxed and the mean free path of the low-frequency phonons is reduced.

as a function of concentration and temperature, and noted that the additional impurity-determined resistance was roughly independent of temperature between liquid oxygen and room temperatures, whereas Devyatkova and Stilbans[61] observed that F centers in KCl also produced a temperature-independent resistance in that temperature range.

9. Intrinsic Thermal Resistance at Low Temperatures

The thermal resistance at low temperatures arising from umklapp processes can also be derived from (6.38). Now, however, the important modes $\mathbf{k}$ are of low frequency, so that $k \ll b$. In order that a U process can occur, both $\mathbf{k}'$ and $\mathbf{k}''$ must lie in the vicinity of opposite zone boundaries, and $\omega' \sim \omega'' \gg \omega$. Thus

$$\mathfrak{N}' + \mathfrak{N}'' + 1 \simeq -x\frac{d\mathfrak{N}'}{dx'} \simeq xe^{-x'} \tag{9.1}$$

where $x = \hbar\omega/KT$, etc. Since

$$A_{\mathbf{k},\mathbf{k}',\mathbf{k}''} = \tfrac{8}{3}\gamma^2\frac{\hbar}{Mv^2G}\omega\omega'\omega''\frac{1-\cos\Delta\omega t}{\Delta\omega^2} \tag{9.2}$$

according to (5.31) and (5.21), and since very approximately

$$\sum_{\mathbf{k}',\mathbf{k}''} \sim \left(\frac{a}{2\pi}\right)^3 G4\pi k_0^2\frac{1}{v}\int d\,\Delta\omega \tag{9.3}$$

where $k_0 = K\theta/\hbar v$ is the Debye limiting wave number, we obtain from (6.38) that

$$\frac{1}{\tau_U} \sim 8\gamma^2\frac{K\theta}{Mv}bxe^{-\theta/\alpha T} \tag{9.4}$$

if $\hbar\omega \sim KT \ll K\theta$. Here the factor $e^{-\theta/\alpha T}$ arises from the factor $e^{-x'}$ in (9.1), so that α is a numerical constant of order unity and depends upon the details of the zone structure and the dispersion of the lattice waves near the zone boundaries. Substituting (9.4) into (6.34), the thermal conductivity as limited by U processes becomes

$$\kappa \sim \frac{7.05}{4\gamma^2}\left(\frac{K}{\hbar}\right)^3 aM\frac{T^3}{\theta}e^{\theta/\alpha T} \qquad T \ll \theta. \tag{9.5}$$

This may be compared with the thermal conductivity at high temperatures (8.3), so that

$$\kappa(T) = A\kappa_0\left(\frac{T}{\theta}\right)^3 e^{\theta/\alpha T} \qquad T \ll \theta \tag{9.6}$$

where $\kappa_0 = \kappa(T')T'/\theta$, $T' > \theta$. There is, of course, considerable uncer-

[61] E. D. Devyatkova and L. S. Stilbans, *J. Tech. Phys. (USSR)* **22**, 968 (1952).

tainty in the numerical factor A in (9.6). A literal application of (9.5) would yield $A = 0.5$. Equation (9.6) was derived, apart from numerical constants, by Leibfried and Schloemann[17] in a slightly different manner; however, the occurrence of the exponential factor in (9.6), which is the major coefficient governing the temperature dependence of $\kappa(T)$ at low temperatures, had already been pointed out by Peierls.[3]

Since the temperature dependence of $\kappa(T)$, as well as its magnitude, is governed mainly by the magnitude of θ/α, which must be regarded as an arbitrary parameter at the present stage of development of the theory, it is not possible to decide whether the presence of the other factors in (9.5) or (9.6) agrees with the observed variation of $\kappa(T)$. One would expect, however, from (9.5) that substances with a high value of θ should show high intrinsic thermal conductivities at low temperatures, as well as at high temperatures.

Substances having the same value of α should have reduced thermal conductivities $\kappa(T)/\kappa_0$ which, when plotted as functions of T/θ, should lie on one curve. Since substances of different crystal structure have different values of α, one cannot expect such a similarity relation to hold, except among substances having the same crystal structure and type of binding.

Since the umklapp-determined resistance decreases rapidly with temperature, the resistance arising from external boundaries is appreciable at lowest temperatures. Each resistive process contributes additively to $1/l_{II}'$ in (6.34). This is approximately equivalent to having the total thermal resistance composed additively of the resistivity arising from each process, so that

$$W(T) = AT^{-3} + F(T) + BT^{-3}e^{-\theta/\alpha T} \tag{9.7}$$

in which the first term arises from the boundary, the second term from the static imperfections, and the third term is the umklapp resistance (9.6). The imperfection-determined resistance $F(T)$ does not increase more rapidly than linearly with temperature. In the case of point imperfections $F(T) \propto T$, whereas it increases more slowly, or even decreases, with increasing temperature (see Table I) for other imperfections. Thus if $W(T)$ varies faster than linearly with T at low temperatures, an appreciable fraction of the resistance must be caused by U processes. At sufficiently low temperatures, the boundary resistance predominates and $W(T)$ increases with decreasing temperature. The umklapp resistance is discernible at low temperatures only if $F(T)$ is sufficiently small, that is, if the specimen is sufficiently free from imperfections, and is a single crystal of reasonable size, so that the boundary resistance is sufficiently low.

Apart from some indications of a variation of $W(T)$ faster than linear in the case of quartz, as observed initially by de Haas and Biermasz[4,5] and later confirmed by Berman,[11] the predicted exponential variation of $W(T)$ was first found by Berman[11,62,63] in the case of aluminum oxide

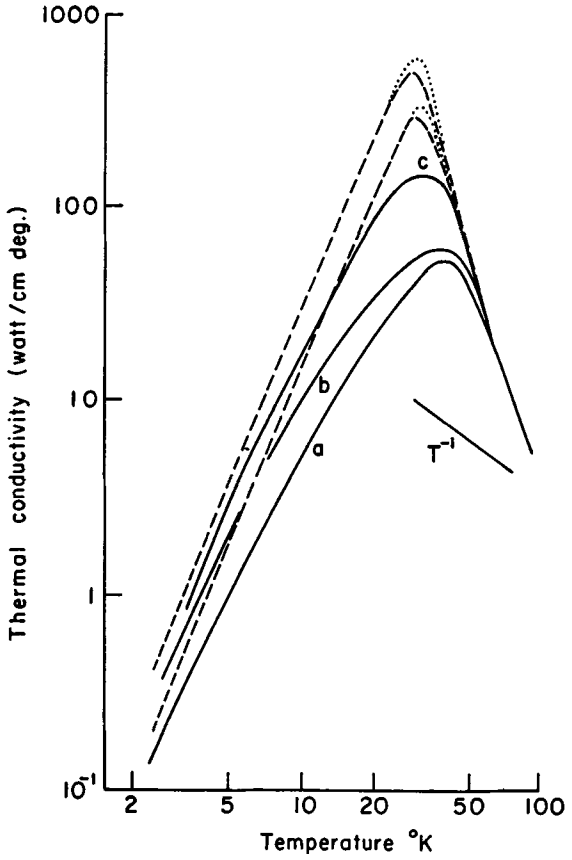

FIG. 5. The thermal conductivity of some artificial sapphire crystals according to Berman.[11,63] Curve a, 1.5-mm diameter; curve b, 3-mm diameter; curve c, crystal from a different source, 2.5-mm diameter. The broken lines give the conductivity of a and b expected if only boundary and umklapp processes contributed to the resistance.

(artificial sapphire). The thermal conductivity is shown in Fig. 5. Taking $\theta = 980°K$, the variation of $W(T)$ between 50 and 100°K could be expressed in terms of an exponential factor $e^{\theta/\alpha T}$ with $\alpha = 2.1$. At the

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

[63] R. Berman, E. L. Foster, and J. M. Ziman, *Proc. Roy. Soc.* (*London*) **A231**, 130 (1955).

lowest temperatures, $\kappa(T)$ is limited by the boundary resistance; however, it is clear that some imperfection-determined resistance limits the observed conductivity near the maximum, for umklapp resistance and boundary resistance alone would have led to a peak in the conductivity much higher than the observed peak,[63a] as is indicated in Fig. 5.

Exponential variations have been observed subsequently in solid helium, with $\alpha = 2.3$, by Wilks, Wilkinson, and Webb,[64,14,65] in lithium fluoride and titanium oxide (rutile) by Berman and Foster,[18] and by White and Woods[19] in bismuth.[65a] The thermal conductivity of bismuth behaves like that of a nonmetal at low temperatures. However, in diamond,[23] germanium and silicon,[20,67] potassium chloride,[21] and tellurium,[68] $W(T)$ was found to increase little, if at all, faster than linearly with T. This indicates a strong resistance originating in point imperfections. The importance of the isotopic constitution in producing such a resistive component, swamping the umklapp resistance in the exponential region, has been pointed out by Slack[22] and by Berman *et al.*[18] This topic will be discussed in Section 11. Recently Berman and Tirmizi[69] have found a rapid variation of $W(T)$ in crystals of caesium iodide and Cohen[70] has found the same in sodium fluoride. Neither substance possesses significant isotopic mass variation.

The measurements on solid helium are of particular interest, for the density can be varied by a factor 2 and the Debye temperature correspondingly by a factor 4. For densities extending from 0.19 to 0.28 g-cm^{-3}, the values of θ could be estimated from measurements of specific heat (θ ranged from about 25°K to 55°K). In the intrinsic region, the conductivity increases with increasing θ, but at the lowest temperatures, where

[63a] Recently Berman (private communication) has indeed found a maximum conductivity of ~200 w-cm^{-1}-deg^{-1} for another sapphire crystal, which evidently contains fewer imperfections.

[64] K. R. Wilkinson and J. Wilks, *Proc. Phys. Soc.* (*London*) **A64**, 89 (1951).

[65] F. J. Webb and J. Wilks, *Phil. Mag.* [7] **44**, 664 (1953).

[65a] The exponential variation is apparent if their measurements above helium temperatures are combined with Shalyt's[66] measurements at helium temperatures on a crystal with lower boundary resistance. This is confirmed by further measurements on a specimen of larger grain size, reported by G. K. White and S. B. Woods, *Phil. Mag.* [8] **3**, 342 (1958). The boundary resistance has been reduced and the exponential variation has become more pronounced.

[66] S. Shalyt, *J. Phys.* (*USSR*) **8**, 315 (1944).

[67] G. K. White and S. B. Woods, *Phys. Rev.* **103**, 569 (1956).

[68] G. Fischer, G. K. White, and S. B. Woods, *Phys. Rev.* **106**, 480 (1957).

[69] R. Berman and S. M. A. Tirmizi, *Proc. 5th Intern. Conf. Low Temperature Phys., Madison* No. 42-5 (1957).

[70] A. F. Cohen, *Proc. 5th Intern. Conf. Low Temperature Phys., Madison* No. 11-1 (1957).

the thermal resistance originates in the boundaries, and $\kappa \propto \theta^{-2}T^3$, the conductivity decreases as θ is increased. Thus the effect of increasing θ is a shift of the maximum to higher temperatures, and an increase in the conductivity at the maximum and at higher temperatures (see Fig. 6).

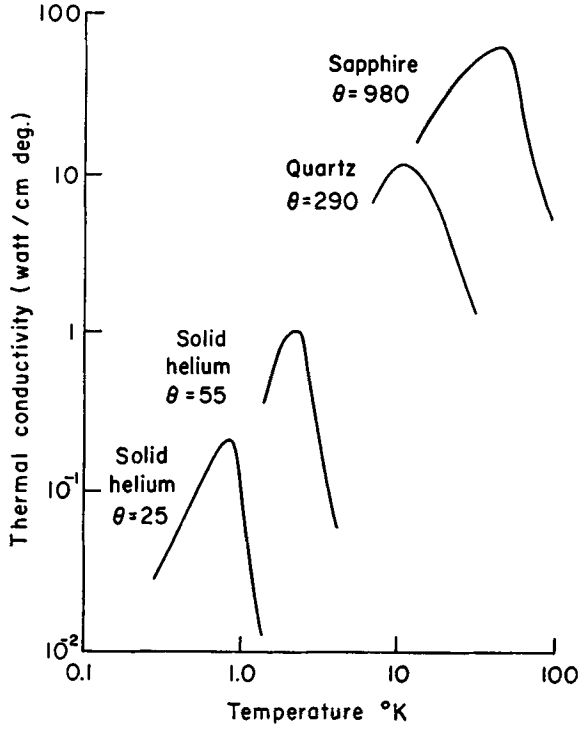

FIG. 6. The thermal conductivities of some dielectric solids of different Debye temperature, according to Wilks,[65] showing the profound influence of the Debye temperature on the conductivity.

Webb *et al.*[14] showed that the average phonon mean free path $3\kappa/Sv$ appears to be a unique function of T/θ, whereas $3\kappa/Sv \propto \theta e^{\theta/\alpha T}$ according to (9.5). In view of the relative insensitivity of the mean free path to the factor θ, in comparison with the rapidly varying exponential factor, it is hard to decide from their data whether $3\kappa/Sv$ or $3\kappa/Sv\theta$ is a unique function of T/θ.

At higher densities (from 0.28 to 0.35 g-cm^{-3}), the θ values are not well known. This makes comparison with (9.5) very difficult. In addition, it appears from the measurements of Webb and Wilks[65] that the helium crystals having high density were not perfect but contained imperfections which caused the thermal conductivity to behave irregularly. Neverthe-

less, one can infer from these measurements that the intrinsic thermal conductivity continues to increase with increasing θ.

Although the similarity condition derivable from (9.6) is thus fulfilled, as far as one can see, for solid helium of different densities, it holds only to within an order of magnitude when substances of different crystal structure and type of binding are compared. This was attempted, for example, by Berman[31] and by Leibfried and Schloemann.[17] The variation is attributable to different values of α, of course, and is in accordance with our previous discussion.

The rapid variation of the intrinsic thermal conductivity, which was predicted in essence by Peierls,[3] can be regarded as a direct confirmation of his conception that umklapp processes are the source of the intrinsic resistance. It can now be regarded as established that this rapid variation will always be found at low temperatures unless the intrinsic resistance is overshadowed by the resistance associated with boundaries, imperfections, or interaction with electrons. With the validity of this theoretical concept thus established, one can have confidence in the analogous concept in the theory of electron-phonon interactions.[71] Although there was an early tendency to disregard umklapp processes between electrons and phonons—see, however, Bardeen[72]—it has become clear recently that the behavior of the conduction properties of even the monovalent metals cannot be understood without reference to them (see, for example, Klemens[30]).

10. The Size Effect

We have seen in Section 7 that the mean free path of the important phonons is limited by the external boundary at sufficiently low temperatures, so that the thermal conductivity becomes size-dependent and decreases with decreasing temperature. The same effect is, of course, even more pronounced in polycrystalline solids, to be discussed in Section 12; however, the first observations of the size effect for large crystals were made by de Haas and Biermasz[6] on quartz, diamond, and potassium chloride. Subsequently boundary resistance has been observed in almost all dielectric solids measured at helium temperatures.[72a]

If boundary scattering is the only resistive process, and if complications arising from N processes are disregarded, the conductivity should

[71] R. Peierls, *Ann. phys.* **4**, 121 (1930); **5**, 244 (1930); **12**, 154 (1932).

[72] J. Bardeen, *Phys. Rev.* **52**, 688 (1937).

[72a] For some materials of low Debye temperature, such as solid helium, the region of boundary resistance lies below 1°K; conversely this region extends into the hydrogen range in materials of high Debye temperature (e.g., diamond, artificial sapphire).

be (a) proportional to the specific heat, that is, usually proportional to T^3, (b) proportional to the size of the specimen, and (c) of such magnitude that the average mean free path

$$L = \frac{3\kappa}{Sv} \tag{10.1}$$

has the magnitude of the shortest linear dimension of the crystal.

The observations of de Haas and Biermasz[6] on quartz and potassium chloride at helium temperature gave a conductivity which varied more slowly than T^3 except at the lowest temperatures studied, and a dependence on the external specimen diameter less than linear, except for the thinnest rods used. This indicates that even at such temperatures the phonons are scattered by imperfections as well as by the boundary. In the case of quartz, the imperfections presumably are the same as those which prevent the thermal conductivity near the maximum from attaining a value as high as one would have expected from boundary and umklapp resistance alone. However, it is not possible to deduce the frequency variation of the scattering cross section unambiguously from the data, so that one cannot identify the imperfections. In the case of potassium chloride, however, the thermal resistance at higher temperatures (in the liquid hydrogen range) is mainly the result of point imperfections, and it is natural to conclude that such imperfections are also responsible for the deviations from Casimir's value (7.1) of the conductivity.[15]

If the thermal resistance associated with boundary and point defect scattering were composed additively of the individual resistances in a simple way, i.e.,

$$W(T) = AT^{-3} + BT \tag{10.2}$$

the point defect resistance BT would rapidly become negligible below T_m, the temperature at which $W(T)$ is a minimum, and could not account for the observed deviations from (7.1). However, the mean free path for point scattering and that for boundary scattering have strongly different frequency dependence, varying as ω^{-4} and ω^0, respectively. Since the two processes contribute additively to $1/l'$ for each group of phonons separately, the thermal conductivity for combined boundary and point defect scattering is, according to (6.34), given by an expression of the form

$$\kappa(T) \propto T^3 \int_0^1 \frac{x^4 e^x}{(e^x - 1)^2} [a + bT^4]^{-1}\, dx + T^3 \int_1^\infty \frac{x^4 e^x}{(e^x - 1)^2} [a + bT^4 x^4]^{-1}\, dx. \tag{10.3}$$

This expression is cumbersome and can only be treated numerically;

however, it was shown[15] that the deviations from (7.1) observed by de Haas and Biermasz could be accounted for in terms of (10.3) using the value of the coefficient b that had to be assumed to account for the point defect resistance at liquid hydrogen temperatures.

The expression (10.3) has been evaluated numerically by Slack,[21] who tabulated $\kappa(T)/\kappa(T_m)$ as a function of T/T_m for the combined scattering;

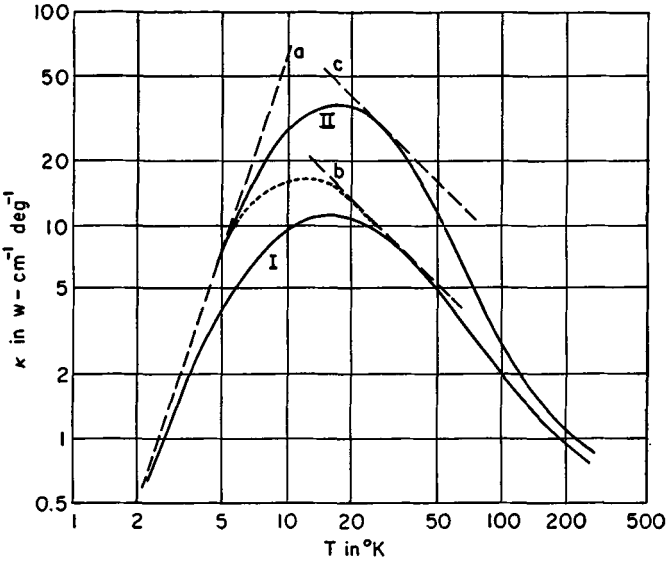

FIG. 7. Thermal conductivity of germanium according to Geballe and Hull.[73] Curve I, a specimen of natural isotopic constitution; curve II, similar specimen, but isotopically enriched; curve a, conductivity according to (7.1), governed by boundaries alone; curve b and c, lines $\kappa \propto T^{-1}$ tangential to I and II, giving the conductivity governed by point imperfections alone. Broken line: conductivity of I if compounded from boundary and point imperfection resistances according to (10.2).

he found that $\kappa(T)$ deviates from a T^3 behavior above $T_m/10$. The circumstance that the effect of the point imperfections extends surprisingly far below T_m is a consequence of the important contributions of phonons of high frequency ($x > 4$) to the specific heat and to $\kappa(T)$ of (7.1); since the scattering of point defects varies as ω^4, these high frequencies are affected strongly by point defects.

This point is also borne out by recent measurements made by Geballe and Hull[73] on the thermal conductivity of two germanium crystals identical in all respects but in isotopic composition and thus differing only in the point defect scattering. The dotted line in Fig. 7 denotes the ther-

[73] T. H. Geballe and G. W. Hull, *Proc. 5th Intern. Conf. Low Temperature Phys. Madison* No. 42-6 (1957).

mal conductivity of I according to (10.2). The conductivity of I actually is considerably lower even well below T_m, and is in agreement with (10.3).

A detailed study of the boundary resistance is carried out best on materials of high Debye temperature and thus of high T_m. Berman, Simon, and Ziman[23] have made an extensive study of the boundary resistance of diamond. The available crystals were not in the shape of long rods. Since the finite length of the specimens reduced L, a comparison with Casimir's theory proved difficult, even though the authors attempted to correct for the finite length. They observed that κ varies more slowly with T than T^3. Thus L effectively increased with decreasing T, indicating that the scattering of phonons at the boundaries was not completely diffuse, but partly specular, the fraction of specular reflection increasing with decreasing frequency.

Substantially the same conclusion was drawn by Berman, Foster, and Ziman[63] from a study of synthetic sapphire crystals. These were available as long rods, so that the end effect was less important. The conductivity was found to vary with specimen diameter, which shows that the boundary was the only resistive process. In the case of smooth-faced crystals, L was larger than expected from the specimen size and increased with decreasing temperature; here again scattering was partly specular, becoming more so at lower frequency. If the sides were ground rough, L decreased and became temperature-independent, so that scattering became diffuse. All this is in accordance with expectation; however, they did find anomalous behavior with a less perfect crystal. This crystal had a higher resistance than expected from the Casimir theory. Thus although there was an additional resistance, the conductivity was still proportional to the diameter when the crystal was reduced in size by grinding. It is possible that the grinding process introduced imperfections, or that the boundary favored back-reflection, possibly as a result of serration of the boundary.

Evidence for partially specular reflection of phonons was also obtained by Slack[21] with potassium chloride crystals having cleaved faces.

Except for the influence of specular reflection, which can be recognized by an increase of L with decreasing temperature at the lowest temperatures, the observed values of L do not exceed Casimir's value, nor does κ vary faster than as T^3. However, according to the arguments of Section 7 based on the analogy of the heat transport with the viscous Poiseuille flow of the phonon gas, one would have expected L to increase with increasing temperature above a critical temperature at which $l_2 = L$. Such behavior has not been observed. One may argue that this is a consequence of the fact that $l_2 > L$ below T_m in all these cases. However, this explanation is unlikely in the case of the sapphires, for which $l_u \sim L$ near T_m, since $l_2 \ll l_u$ at low temperatures, so that $l_2 \ll L$. The conductivity below

T_m should exceed Casimir's value in this case. As mentioned in Section 7, one must regard the fact that N processes do not seem to invalidate the simple Casimir theory as an anomaly.

So far, we have disregarded the term κ_I (6.28). However, $l_1(\omega)$ increases strongly with decreasing frequency. If $l_1(\omega)$ varies faster than ω^{-2}, and if there are insufficient dislocations and two-dimensional imperfections in the crystal, κ_I would diverge except for the scattering of low-frequency phonons by the external boundary. Thus κ_I would be weakly dependent on size even at higher temperatures ($T > T_m$), and, provided κ_I was not too small compared with κ_{II}, there would be a weak dependence of the thermal conductivity on size. Such an effect was predicted by Pomeranchuk,[9] who believed that κ_I was the dominant component of κ. For example, if $l_1 \propto \omega^{-4}T^{-1}$, $\kappa_I \propto L^{\frac{1}{2}}T^{-\frac{1}{2}}$, whereas if $l_1 \propto \omega^{-3}T^{-2}$,

$$\kappa_1 \propto T^{-2}(\text{const} + \log LT^5).$$

The major contribution to κ_I comes from low frequencies such that $l_1 = L$.

In the absence of reliable information about the magnitude and frequency variation of l_1, it is difficult to estimate κ_I. Herring[10] thought that κ_I would not provide the major contribution to κ in general. In the case of germanium it is possible to estimate l_1 from the lattice contribution to the thermoelectric power. Herring concluded that the thermal conductivity should exhibit a weak dependence on size at temperatures well above T_m, where κ_{II} definitely would show a very much smaller dependence on size.

Normal methods would not be sufficiently sensitive to reveal such a weak size dependence, but Geballe and Hull,[74] using an ingenious comparison method, did establish a small dependence on size for two germanium crystals, which were identical except for diameter. This result is consistent with Herring's theory.

11. Thermal Resistance due to Imperfections

As seen in Section 5, all lattice imperfections scatter lattice waves to some degree, and contribute correspondingly to the thermal resistance. Substituting the various values of the relaxation time into (6.34), the following results are obtained for the thermal resistivity.

For *point imperfections*, where it is essential to use (6.34) to avoid divergence at low frequencies, one obtains from (5.9)

$$\frac{W}{T} = \frac{3(2\pi)^2a^3}{hv^2 0.90}\frac{S^2}{G} \tag{11.1}$$

if one takes the Debye model for the specific heat. Here G is the number of unit cells in a volume containing one imperfection, so that $(a^3G)^{-1}$ is the

[74] T. H. Geballe and G. W. Hull, *Conf. phys. Basses Temperatures, Paris*, p. 460 (1955).

number of imperfections per unit volume, and S^2 is a parameter describing the magnitude of the scattering cross section (5.10). In the special case in which an imperfection scatters only because of a mass difference ΔM,

$$S^2 = \frac{1}{12}\left(\frac{\Delta M}{M}\right)^2 \tag{11.2}$$

where M is the average mass of a unit cell. Note that the factor $a^3S^2G^{-1}$ in (11.1) can be replaced by $(12)^{-1}n(\Delta M)^2\rho^{-2}$, where n is the number of defects per unit volume and ρ is the density of the material. We see that (11.1) is then independent of the choice of the unit cell.

The resistance arising from *dislocations* which are arranged at random is obtained by substituting (5.25) into (6.34), and including a factor 0.55 for randomness. Thus when there are N dislocation lines intersecting unit area, each having Burger's vector of magnitude b,

$$WT^2 \simeq \frac{h^2v\gamma^2}{60K^3 \times 7.05} Nb^2. \tag{11.3}$$

It should be noted that the magnitude of this resistance could easily be larger by a factor 10 to 20, as discussed in Section 5.

All materials measured to date have a thermal resistance governed by imperfections at least in a narrow temperature range around T_m, the temperature of the resistance minimum. Many materials exhibit an imperfection-determined resistance over a wide range of temperature which permits the dominant imperfections to be identified into the groups listed in Table I.

Thus, if point imperfections are sufficiently numerous, $\kappa \propto 1/T$ over a wide range of temperatures above T_m, and the exponential variation arising from U processes is not observed. Such point imperfection resistance was first observed at low temperatures in potassium chloride and potassium bromide by de Haas and Biermasz,[4,5] and has since become apparent in other cases.

Klemens[15] suggested that this resistance is the result of point imperfections, in particular of vacancies, which occur in alkali halides along with divalent impurities to form electrically neutral systems. Using reasonable values of S^2, it was estimated[16] from (11.1) that the concentration of divalent impurities in the specimen of potassium chloride employed was somewhat less than 10^{-4}.

This interpretation was not confirmed by the extensive measurements made by Slack[21] on the thermal conductivity of potassium chloride crystals, both in a very pure state and when known amounts of divalent calcium ions were incorporated substitutionally. While the additional resistance arising from the impurity was in rough agreement with theory,

the pure crystals (divalent impurities stated to be less than 2×10^{-5}) showed a resistance comparable to that of the specimen used by de Haas and Biermasz. Thus it is most probable that the bulk of that residual resistance arising from point imperfections originates in some other cause. Slack suggested that it is the result of the various isotopes of the two constituent elements.

Slack found that the effective value of S^2 for a calcium ion in KCl was 1.4, whereas Klemens[16] estimated $S^2 > 0.4$ for the calcium ion, $S^2 = 0.8$ for the vacancy. These results make the effective value of $S^2 \sim 1.2$ for the two imperfections if dissociated. In contrast an associated vacancy and calcium ion complex would give a much smaller value of S^2 (probably less than 0.2) because of interference. This would indicate that the divalent ion and the vacancy are largely dissociated. Yet other evidence, discussed by Slack, suggests that the majority of vacancies are associated. It must be emphasized, however, that the estimates of S^2 are very uncertain since the effect of lattice distortion and foreign bonds are difficult to estimate.

Slack not only noted a point defect resistance ($W \propto T$), but also found a component of resistance, roughly proportional to T^{-2}, which varied roughly as the square of the calcium concentration. He ascribes this resistance to colloidal particles of calcium chloride.

An appreciable resistance arising from point defects which swamps the umklapp resistance in the interesting exponential region, and thus prevents it from being observed, was found not only in potassium chloride but in a number of other materials as well, even though measurements were made on apparently pure crystals. The most notable of these materials is germanium, since most impurities, as well as vacancies, in it can be detected in very small concentrations by their effect on the electrical properties. A number of investigators[19,20,67,75] have measured germanium. Above T_m all their results were in substantial agreement and similar to curve I of Fig. 7. The resistance of germanium arising from point imperfections (curve b) corresponds to a value of S^2/G of about 1.3×10^{-4}.

Slack[22] and Berman *et al.*[18] considered an old suggestion of Pomeranchuk[9] and suggested that the variation of isotopic mass is responsible for the point imperfection resistance of those solids which have persistently defied all the attempts to eliminate it. Isotopes scatter because of their variation in mass. The resistance is given by (11.1) with S^2/G replaced by

$$\frac{\epsilon}{12} = \frac{1}{12} \sum_a f_a \left(\frac{M_a - M}{M} \right)^2. \tag{11.4}$$

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

Here the sum extends over all isotopic species, f_a is the relative concentration of each isotope, and M is the average mass. In the case of compounds, the summation must be taken over all combinations of isotopes.

In most cases $(M_a - M)^2/M^2$ is quite small; however, since the concentration of isotopes is often of order unity, the isotope resistance may be comparable to the resistance of defects which scatter strongly, but which are present only in small concentrations.

It was shown by Berman *et al.*[18] and by Slack[22] that there is indeed a correlation between a large variation in isotopic mass and the absence of observable umklapp resistance. The rapid temperature variation of $W(T)$, which indicates that the resistance is intrinsic, has only been observed in substances having a value of ϵ less than 10^{-4}. However, the observed resistances did not agree quantitatively with the isotope resistances calculated from (11.1) and (11.4). Thus Slack found the calculated resistances too small by factors ranging from about 3 upwards. In the case of germanium (Fig. 7, curve I), for example, the apparent point imperfection resistance (obtained from the tangential curve b) corresponds to $S^2/G = 1.3 \times 10^{-4}$, whereas $\epsilon/12$, calculated from (11.4), is only 4.8×10^{-5}. A slightly smaller discrepancy holds for lithium fluoride,[75a] measured by Berman *et al.*[18] In other cases the discrepancy is larger. For example it is 4 in potassium chloride, nearly 5 in silicon,[19,20,75] and is almost 10 in tellurium.[68]

The discrepancy between the calculated isotope resistances and the observed resistances can arise from three causes: (a) the scattering cross section (5.9) is in error, (b) expression (6.34) for the thermal conductivity is in error because of an inadequate treatment of N processes, or (c) other imperfections, in some cases (e.g., tellurium) not necessarily point imperfections, contribute to the thermal resistance.

It is unlikely that (5.9) is seriously in error, for the mass differences are known, and the perturbation arising from mass differences is simple to calculate. The only approximation which could falsify the magnitude is the replacement of $(\boldsymbol{\epsilon} \cdot \boldsymbol{\epsilon}')^2$ by an average value of $\frac{1}{3}$, which cannot cause a large error in the required sense.

We have seen that (6.34) is an approximation which would, in view of (6.14), underestimate the resistance if N processes were very strong. It is significant that in the case of the copper-gold alloys of Kemp and

[75a] R. Berman, E. L. Foster, and J. M. Ziman calculated the isotope resistance not from (11.1), but from (5.9) and (6.14). The resistances thus estimated exceed those calculated from (11.1) by a factor ~55. They found the calculated isotope resistances to be larger than the observed resistances, so that (6.14), which is only a theoretical upper limit of the resistances, substantially overestimates the isotope resistances. The present comparison, as that of Slack, is based on (11.1).

Tainsh[76] (see Section 18), for which the "isotope" resistance is very high and the N processes relatively unimportant, there is fair agreement with (11.1), so that (5.9) seems to be substantially correct.[24] If the discrepancies are the result of a failure of (6.34), we may expect them to be larger the weaker the isotope scattering. It should be remembered, however, that other imperfections are more likely to be important whenever the isotope scattering is weak. In the opinion of the present author,[24] they are probably the major cause of those discrepancies.

Recently, Geballe and Hull[73] verified the isotope resistance directly. They measured two specimens of germanium; one (curve I of Fig. 7) was a single crystal of natural germanium, whereas the other (curve II) was enriched isotopically to contain about 96% of Ge^{74}, but was prepared in an identical manner otherwise. While the removal of the isotopic resistance did indeed enhance the conductivity substantially (by a factor ~ 3 from 15 to 45°K), the increase was not as large as one might have expected from complete removal of all imperfection resistance. Whereas the resistance of II varies noticeably faster than linearly, it still appears to be limited by point imperfections whose resistance (from curve c) would be about half the resistance associated with the isotopes. The nature of these residual point imperfections, which apparently are present in all specimens of germanium measured until now, has still to be clarified. They seem to be inactive electrically. Since germanium is in frequent contact with graphite, they may be substitutional carbon atoms. The concentration required to account for the resistance is about 4×10^{-4}.

The isotope resistance is the difference between the resistances arising from point imperfection of specimens I and II. These resistances are given by curves b and c, so that the observed isotope resistance is

$$\frac{W}{T} = 2.1 \times 10^{-3} \text{ cm-w}^{-1}.$$

The isotope resistance calculated from (11.1) with $\epsilon = 5.7 \times 10^{-4}$ and $v = 3.50 \times 10^{5}$ is $W/T = 1.74 \times 10^{-3}$ cm-w^{-1}. Thus the observed isotope resistance exceeds the theoretical value by a factor of about 1.2. This agreement is as good as one can expect in view of the various approximations made in the derivation of (11.1).

Although the bulk of the previously observed discrepancy can be ascribed to the presence of other imperfections in the case of germanium, it does not necessarily follow that this is the explanation of similar discrepancies in all materials. Further investigations on isotopically enriched materials would be extremely valuable, as would measurements on

[76] W. R. G. Kemp, P. G. Klemens, and R. J. Tainsh, *Australian J. Phys.* **10**, 454 (1957).

materials containing impurities which scatter principally because of their mass difference, and which thus have scattering cross section that can be estimated with confidence.

A. M. Toxen, *Phys. Rev.* **110,** 585 (1958) reports that the point defect resistance of germanium—0.5% silicon agrees with that calculated from (11.1), if the scattering cross-section is obtained from the mass difference alone, but that the resistances of alloys containing 3%, 6% and 7% silicon are *lower* than the calculated resistances by factors of up to about 2.

Dislocation resistance, which varies as T^{-2} (11.3), makes its appearance below T_m. It has been observed frequently in metallic materials (see Section 18), but has also been observed in solid argon,[77] tellurium,[68] and artificial sapphire.[69] In the case of solid argon and tellurium the dislocations apparently were formed during growth; in tellurium they could be removed by annealing. White and Woods estimated the dislocation density in tellurium to be 5×10^9 per cm^2 from (11.3). In the case of the artificial sapphire, the dislocations were introduced by a 15% elongation at 1400°C. Their density is estimated by Berman and Tirmizi to be about 10^{10} per cm^2 from (11.3). In both cases, the real density easily could be substantially lower because of the uncertainty in the scattering cross section. Unfortunately there is no other evidence available concerning the likely dislocation density in these cases. The same situation prevails in the case of metals, as discussed in Section 18, although the usual dislocation densities are considerably higher in these materials.

Dislocations also can be introduced into germanium, but it appears that in this case the phonons are scattered primarily by electrons associated with the dislocations rather than by the dislocations themselves (see Section 19).

12. Polycrystalline and Highly Disordered Materials

In Sections 9–11 we have considered the thermal conductivity of large and almost perfect crystals. Materials whose lattice is far from perfect have, of course, a much lower conductivity, because—as already pointed out by Debye[2]—the average mean free path of their lattice waves is limited and does not vary strongly with temperature, especially at low temperatures, where the intrinsic mean free path is long. Therefore, such materials have a thermal conductivity which, below room temperature, varies with temperature in a manner similar to the specific heat. In other words, their conductivity increases with temperature at all but the highest temperatures.

[77] G. K. White and S. B. Woods, *Nature* **177,** 851 (1956).

a. Polycrystalline Solids[31]

The thermal conductivity of polycrystalline solids is reduced both by the porosity of the material, which changes the conductivity by a temperature independent factor p, and by the reduction in the conductivity of each individual grain resulting from the enhanced boundary scattering. If the mean free path of phonons in each grain is L, then in analogy with (7.1)

$$\kappa = \tfrac{1}{3}pSvL \qquad l_u > L \tag{12.1}$$

$$\kappa = p\kappa_0 \qquad l_u < L \tag{12.2}$$

where κ_0 is the conductivity of a large crystal, l_u is the intrinsic mean free path (8.2), and L is of the order of the grain size.

A T^3 variation of κ of iron ammonium alum had been observed by van Dijk and Keesom[78] between 0.04 and 0.3°K. Kurti *et al.*[79] had measured the same material both as a powder and a coherent crystal, whereas Hudson[80] measured a powder of known grain size between 0.10 and 0.22°K. These measurements have been discussed by Berman.[31] The difference between the crystal and the powder is not as large as one would have expected from the ratio of the external diameter of the former to the grain size of the latter, but the average mean free path deduced from the conductivity of the powder agrees roughly with the stated grain size, while the phonon mean free path of the crystal was apparently limited by internal boundaries.

Berman[12] measured the thermal conductivity of polycrystalline alumina, beryllia, and graphite. The results for the first two substances generally confirm (12.1) and (12.2). The results for alumina are of particular interest since they may be compared with the conductivity of the corresponding single crystal—sapphire (see Fig. 8). The measured grain sizes ranged from 5 to 30 $\times$ 10^{-4} cm, and values of L deduced from (12.1) fall within that range. However, these values of L increase with decreasing temperature (i.e., the conductivity varies more slowly than T^3). This indicates that grain boundary scattering is not quite independent of frequency. Scattering by a single grain boundary should be substantially independent of frequency (5.28), the contribution to the scattering Hamiltonian being mainly from regions of the order of a phonon wavelength from the boundary.[16] The contribution from the disordered boundary region should be smaller. In the compressed powders, however, there

[78] H. van Dijk and W. H. Keesom, *Physica* **7**, 970 (1940).
[79] N. Kurti, B. V. Rollin, and F. Simon, *Physica* **3**, 266 (1936).
[80] R. P. Hudson, Thesis, Oxford, 1949.

probably is a disordered or heavily deformed region at the junction of two grains whose thickness is not negligible compared to the grain size. Since the wavelength of the phonons important at low temperatures is not very much smaller than the grain size for these materials of high Debye temperature, it is not surprising that the boundary scattering should show some frequency dependence.

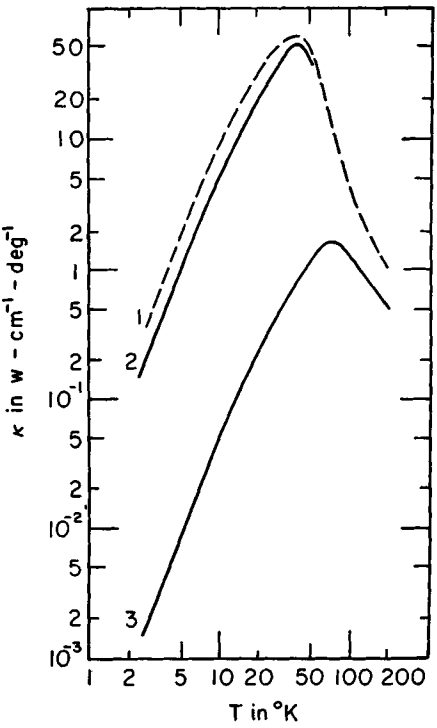

FIG. 8. Thermal conductivity of single crystal and polycrystalline aluminum oxide, according to Berman.[12] Curve 1, single sapphire crystal, 3-mm diameter; curve 2, single crystal, 1.5-mm diameter; curve 3, polycrystalline (sintered) alumina.

The case of graphite is complicated because it is highly anisotropic and the grains are in the shape of flakes or plates. In consequence of the structural anisotropy, the variation of specific heat is closer to T^2 (two-dimensional Debye model) over a fair range of temperatures than T^3, although it does approach a T^3 variation at sufficiently low temperatures.[81] Berman found the thermal conductivity of some of his specimens to vary faster than the specific heat ($T^{2.6}$ from 5 to 20°K compared to $T^{2.2}$).

[81] P. H. Keesom and N. Pearlman, *in* "Handbuch der Physik," Vol. 14 (2nd ed.), p. 282. Springer, Berlin, 1956.

Since the scattering cross section for imperfections should never decrease with increasing frequency, this seemed anomalous (but scattering by electrons can lead to a conductivity varying faster than the specific heat—see Section 19). Klemens[55] attempted to explain this as follows. The longitudinal waves, whose specific heat varies faster than that of the transverse waves, have a longer effective mean free path, so that they contribute relatively more to the conductivity (7.1) than to the specific heat. The reason their mean free path is longer originates in the plate-like shape of the crystallites. L is determined by the long dimension in the absence of N processes, and by the short dimension if N processes are strong; however $l_2 < l_1$, so that transverse waves have a shorter mean free path. A different explanation, which apparently is supported better by recent observations,[82] has been given by Hove and Smith.[83] The thermal conductivity of pure graphite is proportional to the specific heat, but in some cases (where the anomalous temperature variation was observed) the resistance does not originate in the graphite crystallites, but arises from a bonding material (amorphous carbon) between them. The bonding material has a specific heat which varies as T^3. Its contribution to the over-all specific heat is very small, but it determines the temperature variation of the over-all conductivity.

b. Glasses

Since the lattice structure of glass lacks both symmetry and periodicity, the normal modes of vibration differ substantially from the plane waves of Section 2. The instantaneous atomic displacements can still be resolved in terms of waves of the form (2.2). There is a strong interchange of energy between them, however, since they are not the normal modes, whence their mean free path l' is short. It was suggested by Kittel[84] that except for long waves, l' is constant and of order of the distance of coherence (or short-range order), that is of the order of a few lattice spacings. This explains why the conductivity is roughly proportional to the specific heat from liquid oxygen temperatures upwards. At lower temperatures, however, the conductivity decreases more slowly than the specific heat, that is the mean free path of the low-frequency waves increases with decreasing frequency. This is to be expected, for glass is macroscopically homogeneous, and the longer the waves, the less important is the microscopic disorder.

Berman[11] measured the conductivity of fused silica (see Fig. 9) and found that $\kappa \propto T$ at liquid helium temperatures, which indicates that

[82] A. W. Smith and N. S. Rasor, *Phys. Rev.* **104**, 885 (1956).
[83] J. E. Hove and A. W. Smith, *Phys. Rev.* **104**, 892 (1956).
[84] C. Kittel, *Phys. Rev.* **75**, 972 (1949).

$l'(\omega) \propto \omega^{-2}$ at low frequencies. Klemens[15] showed that such a variation is in accordance with theory.[84a] However, the presence of a "knee" in the curve of κ against T at about 10°K makes it impossible to fit the conductivity with a single mean free path which varies steadily with frequency.

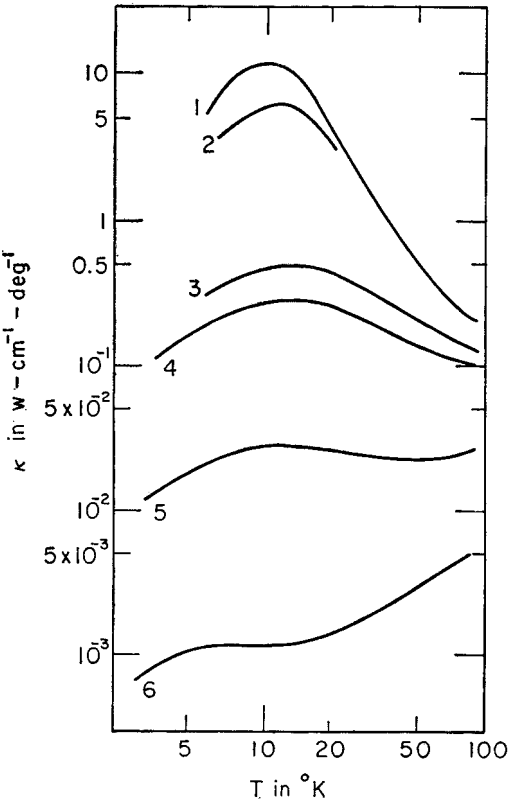

FIG. 9. Thermal conductivity of quartz, neutron-irradiated quartz, and quartz glass, according to Berman.[11,31] Curve 1, quartz crystal; curve 2, neutron-irradiated, 0.03 unit; curve 3, irradiated, 1 unit; curve 4, irradiated, 2.4 units; curve 5, irradiated, 19 units; curve 6, quartz glass. 1 unit of irradiation is about 1.8×10^{18} neutrons/cm^2.

Klemens assumed that the mean free path of longitudinal waves l_{I}' is greater (by a factor $\sim$50) than l_{II}', which is intuitively plausible. He also considered explicitly the term κ_{I} of (6.28), which is appreciable if $l_{\mathrm{II}}' < l_1$ and $l_{\mathrm{II}}' < l_{\mathrm{I}}'$. By choosing the magnitudes of l_{I}', l_{II}', and l_1 he found that

[84a] A large number of small-angle grain boundaries spaced more closely together than a phonon wavelength λ would scatter not as (5.28), but more weakly by a factor of order $(d/\lambda)^2$, in which d is the spacing, for the scattering Hamiltonian would arise only from a region of depth $\sim d$ instead of one of depth $\sim\lambda$.

the observed conductivity curve could be fitted quite well at all temperatures. The value of l_1 chosen to give a fit was smaller, by a factor of about 10, than the value estimated[30] from (6.31). While this semiempirical theory can be made to fit Berman's observations without too great a strain on one's credulity, this is, perhaps, not the only way of accounting for the observations.

The matter is complicated by the fact that there does not seem to be a unique vitreous state. Berman had already found small differences from specimen to specimen, but his results agreed roughly with earlier measurements of Bijl,[85] Wilkinson and Wilks,[86] and Stephens.[87] However, Cohen[87a] found a conductivity which was higher than Berman's by a factor ~ 4 at 10°K, and which varied considerably faster than linearly at helium temperatures. It appears that the chemical composition is not the dominant factor in the thermal conductivity of silica-based glasses. The difference is perhaps associated with a possible crystallinity of some of the specimens. It is possible that the thermal conductivity is one of the most sensitive indicators of the degree of crystallinity of glasses and polymers.

c. Effects of Radiation Damage

Berman[11,13] measured the thermal conductivity of crystalline quartz after various doses of neutron irradiation and noted a profound effect on the thermal conductivity at low temperature (see Fig. 9). He also found that subsequent annealing increased the conductivity, but not in a completely reversible way. An attempt to interpret these results in terms of the theory of radiation damage[88] and the present theory of thermal conductivity was made by Klemens.[15] The additional thermal resistance appears to consist of two components. One increases with temperature, and is ascribed to single defects (or possibly to small groups of defects); the other increases with decreasing temperature and is a result of large clusters of defects. It was suggested that the large clusters are produced by knocked-on atoms at the end of their range, whereas isolated defects or small clusters are produced in the early part of the range of a displaced atom. The large clusters do not disperse or anneal out at room temperature but form metastable vitreous regions, since quartz can exist in the vitreous state.

This description of the effect of radiation damage is probably not complete. There is, for example, more recent evidence (R. Berman, pri-

[85] D. Bijl, *Physica* **14**, 684 (1949).
[86] K. R. Wilkinson and J. Wilks, *J. Sci. Instr.* **26**, 19 (1949).
[87] R. W. R. Stephens, *Phil. Mag.* [7] **14**, 897 (1932).
[87a] A. F. Cohen, *J. Appl. Phys.* **29**, 591 (1958).
[88] F. Seitz, *Discussions Faraday Soc.* **5**, 271 (1949).

vate communication) that at least part of the resistance at low temperature may be caused by the scattering of phonons by electrons. Moreover, an attempt to explain the changes in density of neutron-irradiated quartz in terms of the model of vitreous inclusions[89] failed to provide a full description of the observed structural changes.[90] Nevertheless it is well known that quartz becomes amorphous after strong neutron irradiation. This vitreous state cannot be the same as that of fused silica, for its density is higher.[91] This fact suggests that it has a higher degree of short-range order than fused silica. Indeed Cohen[87a] has observed a substantial increase of the thermal conductivity of fused silica after neutron irradiation.

Berman, Foster, and Rosenberg[92] have measured the thermal conductivity of neutron-irradiated sapphire and diamond. In the case of sapphire a similar analysis was carried out. Here too large clusters of defects seem to be responsible for the low-temperature thermal resistance; yet alumina does not occur as a glass. They also found a change as a consequence of gamma radiation. It occurred only below T_m, was smaller than that due to neutrons, and saturated. It is probably a result of a change in the electronic structure associated with previously existing impurities.

Cohen[70] found changes in the thermal conductivity of potassium chloride after both gamma and neutron irradiation. The former seems to introduce both point defects (single displacements) as well as electronic changes; the effect of the latter is not clear; however, it does not seem to produce single defects.

The effects of radiation damage on the thermal conductivity are complicated and not yet fully understood, as is the case with other irradiation phenomena. However, they represent a potential source of information and may play a part in the elucidation of these complex phenomena.

IV. Thermal Conductivity of Metals, Alloys, and Semiconductors

13. Electronic Thermal Conductivity (Résumé)

The wave function of an electron moving in the periodic potential $V(\mathbf{r})$ of a crystal lattice has the form

$$\psi_{\mathbf{k}}(\mathbf{r}) = \phi_{\mathbf{k}}(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}} \tag{13.1}$$

in which the modulating function $\phi_{\mathbf{k}}(\mathbf{r})$ is periodic in $\mathbf{x}$ with the lattice

[89] P. G. Klemens, *Phil. Mag.* [8] **1**, 938 (1956).
[90] M. Wittels, *Phil. Mag.* [8] **2**, 1445 (1957).
[91] M. Wittels and F. A. Sherrill, *Phys. Rev.* **93**, 1117 (1954).
[92] R. Berman, E. L. Foster, and H. M. Rosenberg, *Rept. Bristol Conf. Defects in Crystalline Solids (Phys. Soc., London)*, p. 321 (1955).

period $\mathbf{a}_i$. The wave-vector $\mathbf{k}$ specifies the orbital electron state, but a complete specification of the electron state also requires specification of one component of spin, so that there are two states to every value of $\mathbf{k}$. The energy $E(\mathbf{k})$ of the electron is a function of $\mathbf{k}$, however, the form of the function depends upon the details of the lattice potential $V(\mathbf{r})$ in a unit cell, as does the form of $\phi_{\mathbf{k}}(\mathbf{r})$. If $V(\mathbf{r})$ is constant, $\phi_{\mathbf{k}}(\mathbf{r}) = 1$ and $E(\mathbf{k}) = \hbar^2k^2/2m$; in general, however, $E(\mathbf{k})$ departs progressively from the free-electron value, the more $V(\mathbf{r})$ deviates from constancy.

The wave vector of an electron, as that of a lattice wave, is not defined uniquely. It is always possible to change $\mathbf{k}$ by an inverse lattice vector $\mathbf{b}_i$ defined in (2.3), or any integral combination of lattice vectors, and still leave $\psi_{\mathbf{k}}(\mathbf{r})$ unaltered, for a factor $e^{i\mathbf{b}\cdot\mathbf{r}}$ can be incorporated into $\phi_{\mathbf{k}}(\mathbf{r})$ and still leave the modulating function with the required periodicity.

As in the case of lattice waves, it is possible to divide the $\mathbf{k}$ space into Brillouin zones, the zone boundaries being planes satisfying the condition of Bragg reflection

$$(\mathbf{k} + \mathbf{b}/2) \cdot \mathbf{b} = 0 \tag{13.2}$$

where $\mathbf{b}$ is an integral combination of the $\mathbf{b}_i$'s. The values of $E(\mathbf{k})$ are continuous functions of $\mathbf{k}$, except that they are discontinuous across a zone boundary. If we describe all states by wave vectors in the fundamental zone, a set of energy values corresponds to each value of $\mathbf{k}$. Each such value of $E(\mathbf{k})$ traces out a continuum or "band" of energy values as $\mathbf{k}$ is moved over all points of the zone. The bands of low energy are narrow, and separated by forbidden energy values; the higher bands are wider and overlap.

According to the Pauli principle, the maximum occupation of each state is one. The number of $\mathbf{k}$ values in each zone is G, the number of unit cells in the crystal, so that there are $2G$ states in each band. If the number of electrons per unit cell is odd, at least one zone is only partly filled at absolute zero, and the solid is a metal. If the number of electrons per unit cell is even, it may be an insulator or a metal, depending on whether there is a gap between the highest filled band and the next band, or whether there is an overlap between these bands.

The equilibrium occupation probability of a state of energy E is

$$f^0(E) = [e^{(E-\zeta)/KT} + 1]^{-1} = (e^{\epsilon} + 1)^{-1} \tag{13.3}$$

where the parameter ζ is the Fermi energy, given by the condition

$$\int f^0(E,\zeta)n(E)\,dE = N. \tag{13.4}$$

Here $n(E)\,dE$ is the number of states in the energy interval E,dE, and N is the number of electrons. This makes ζ temperature dependent, although

this temperature dependence is small in most metals, since $KT \ll \zeta$ and $n(\zeta)$ is both comparable to N/ζ and slowly varying.

The modulated plane waves are eigenstates only if the potential $V(\mathbf{r})$ is perfectly periodic. In real crystals there are transitions of electrons between these states because of the deviations of the potential from perfect periodicity, which originate partly in the thermal vibrations and partly in the static imperfections. These processes tend to maintain equilibrium. On the other hand, an electric field $\mathbf{F}$ or a temperature gradient tend to disturb the equilibrium. The actual probability of occupation $f(\mathbf{k})$ in the steady state when an electric field and a temperature gradient are present is governed by the Boltzmann equation

$$\frac{e}{\hbar}\mathbf{F}\cdot\frac{\partial f}{\partial \mathbf{k}} + \frac{1}{\hbar}\frac{\partial E}{\partial \mathbf{k}}\cdot \operatorname{grad} T\,\frac{df}{dT} = \left.\frac{df}{dt}\right]. \tag{13.5}$$

Here $\mathbf{v} = \hbar^{-1}\partial E/\partial \mathbf{k}$ is the velocity of the electron in state $\mathbf{k}$ and the right-hand side denotes the rate of change of $f(\mathbf{k})$ arising from the interaction processes.

A formal solution of (13.5) can be obtained by replacing $f(\mathbf{k})$ by $f^0(\mathbf{k})$ on the left-hand side, and writing

$$\left.\frac{df}{dt}\right] = \frac{f^0 - f}{\tau(\mathbf{k})} = -\frac{g(\mathbf{k})}{\tau(\mathbf{k})}. \tag{13.6}$$

In this way the deviation from equilibrium $g(\mathbf{k})$ can be obtained in terms of $\tau(\mathbf{k})$. Consider the case of an isotropic medium in which $E(\mathbf{k})$ is a function of k only (spherical energy contours in $\mathbf{k}$ space), and in which $\mathbf{F}$ and grad T are in the same direction. We may then write

$$g(\mathbf{k}) = -\mu\tau(\mathbf{k})\frac{df^0}{dE}\frac{1}{\hbar}\frac{dE}{dk}\left[eF - \operatorname{grad} T\left(\frac{E}{T} + \frac{d\zeta}{dT}\right)\right] \tag{13.7}$$

where μ is the direction cosine of $\mathbf{k}$ relative to $\mathbf{F}$, and grad T is positive in the same direction as F.

The electric current density is

$$\mathbf{j} = \int e\,\frac{1}{\hbar}\frac{\partial E}{\partial \mathbf{k}}\,g(\mathbf{k})\,\frac{2}{(2\pi)^3}\,d\mathbf{k} \tag{13.8a}$$

and the heat current is

$$Q = \int E\,\frac{1}{\hbar}\frac{\partial E}{\partial \mathbf{k}}\,g(\mathbf{k})\,\frac{2}{(2\pi)^3}\,d\mathbf{k}. \tag{13.8b}$$

The electrical conductivity is defined as $\sigma = \mathbf{j}/\mathbf{F}$ when grad $T = 0$.

Substituting (13.7) into (13.8a), we obtain

$$\sigma = \frac{e^2}{12\pi^3} \int \frac{\tau v^2}{|\text{grad}_{\mathbf{k}}\, E|}\, dS \tag{13.9}$$

in which the integration extends over the surface $E = \zeta$ in $\mathbf{k}$ space, and dS is an element of that surface.

The thermal conductivity is defined as $\kappa = -Q/\text{grad } T$, with the condition $j = 0$. Substituting (13.7) into (13.8a) and equating the result to zero, we find a relation between eF and grad $T(E/T + d\zeta/dT)$. If this is substituted into (13.8b), the following expression for the thermal conductivity is obtained after some reduction:

$$\kappa = \frac{K^2 T}{36\pi} \int \frac{\tau v^2}{|\text{grad}_{\mathbf{k}}\, E|}\, dS. \tag{13.10}$$

Hence we obtain the Wiedemann-Franz law

$$\frac{\kappa}{\sigma T} = \frac{\pi^2}{3}\left(\frac{K}{e}\right)^2 = L. \tag{13.11}$$

Use has been made of the following expansion, applicable for a degenerate assembly of Fermi particles:

$$\int F(E)\frac{df^0}{dE}\, dE = -F(\zeta) - \frac{\pi^2}{6}(KT)^2\left(\frac{d^2F}{dE^2}\right)_\zeta. \tag{13.12}$$

It has been assumed in this treatment that $\tau(\mathbf{k})$ is independent of $g(\mathbf{k}')$, the deviation of the states $\mathbf{k}'$ which interact with $\mathbf{k}$. This is analogous to a similar assumption underlying the definition of a relaxation time in Section 4. However, a proper treatment of the scattering of electrons by static imperfections and by lattice waves shows that $\tau(\mathbf{k})$ generally is a functional of $g(\mathbf{k}')$. Now the formal theory leads to the following expressions for g, correct to lowest order in KT/ζ:

$$g(\mathbf{k}) \propto \mathbf{k}\cdot\mathbf{F}\, df^0/d\epsilon \qquad \text{(electrical conduction)} \tag{13.13a}$$

$$g(\mathbf{k}) \propto \mathbf{k}\cdot\nabla T\epsilon\, df^0/d\epsilon \qquad \text{(thermal conduction).} \tag{13.13b}$$

Since the functional form of $g(\mathbf{k})$ is different in these two cases, one may, likewise, expect the effective $\tau(\mathbf{k})$ to be different in these two cases, and hence expect a breakdown of the Wiedemann-Franz law (13.11).

There are two sources of electron scattering and hence of resistance, namely, static imperfections and lattice vibrations. To a first approximation, their contributions to the scattering of electrons is additive. Thus they contribute additively to $1/\tau(\mathbf{k})$, and hence to the electrical and

thermal resistivities (Matthiessen's rule). It follows that

$$\frac{1}{\sigma} = \rho = \rho_0 + \rho_i \tag{13.14a}$$

and

$$\frac{1}{\kappa} = W = W_0 + W_i \tag{13.14b}$$

in which the subscript i denotes the ideal (or intrinsic) resistivities, and the subscript 0 the imperfection induced (or residual) resistivities.

The scattering by static imperfections is elastic, that is, electrons are scattered from a state $\mathbf{k}$ to a state $\mathbf{k}'$ having the same energy. In general $\tau(\mathbf{k})$ is a functional of $g(\mathbf{k})$. Since the only interacting states have the same energy, however, $\tau(\mathbf{k})$ is a functional only of those $g(\mathbf{k}')$ for which $E' = E$. While in general $g(\mathbf{k}')$ is different for thermal and electrical conduction (13.13), the ratio $g(\mathbf{k}')/g(\mathbf{k})$ is the same in both cases, depending only on the angle between $\mathbf{k}$ and $\mathbf{k}'$. Thus in the case of elastic scattering, $\tau(\mathbf{k})$ is the same for electrical and thermal conduction and the two residual resistivities ρ_0 and W_0 are related by the Wiedemann-Franz law (13.11)

$$\rho_0 = LW_0T. \tag{13.15}$$

It can be shown that at high temperatures ($T > \theta$) the scattering by lattice waves is essentially an elastic process ($|E - E'| < KT$), so that a similar relation holds for ρ_i and W_i at high temperatures. In general, however, it can be shown that the Wiedemann-Franz law breaks down for the ideal resistivities at low temperatures, and that

$$\rho_i < LW_iT. \tag{13.16}$$

The electronic thermal conductivity of metals has been discussed fully elsewhere by Olsen and Rosenberg,[92] Wilson,[93] Jones,[94] and Klemens.[30]

14. Scattering of Lattice Waves by Conduction Electrons

In the previous section we have considered the eigenstates of electrons in the periodic potential of the crystal lattice, assuming the atoms are at their equilibrium sites. The displacements $\mathbf{u}(\mathbf{x})$ of the atoms (2.8) cause the effective potential to change from $V(\mathbf{r})$ to $V(\mathbf{r}) + U(\mathbf{r})$. To a first approximation, $U(\mathbf{r})$ can be regarded as a linear function of the displacements, so that the effect of each lattice wave $(\mathbf{q}, j)$ may be considered

[93] A. H. Wilson, "Theory of Metals," 2nd ed. Cambridge Univ. Press, London and New York, 1953.

[94] H. Jones, *in* "Handbuch der Physik," Vol. 19 (2nd ed.), p. 227. Springer, Berlin, 1956.

separately. Thus $U(\mathbf{r})$ is of the form

$$U(\mathbf{r}) = \frac{1}{\sqrt{G}} w(\mathbf{r}) a_j(\mathbf{q}) e^{i\mathbf{q}\cdot\mathbf{x}} \tag{14.1}$$

in which $w(\mathbf{r})$ may depend on $\mathbf{q}$ and j, and is determined by $V(\mathbf{r})$ and the redistribution of electrons, particularly conduction electrons, when the atoms are displaced. $w(\mathbf{r})$ is difficult to calculate from first principles, because of this redistribution, as has been discussed, for example, by Bardeen.[95]

A model which probably typifies the behavior of $w(\mathbf{r})$ is the rigid ion model

$$w(\mathbf{r}) = (\boldsymbol{\varepsilon} \cdot \operatorname{grad} V). \tag{14.2}$$

The matrix element of the perturbation Hamiltonian which links two states of the crystal for which electrons are in states $\mathbf{k}$ and $\mathbf{k}'$, respectively, and in which all other electrons are equally distributed, is

$$\begin{aligned} U_{\mathbf{k},\mathbf{k}'} &= e \int U(\mathbf{r}) \Psi_{\mathbf{k}'}^* \Psi_{\mathbf{k}} \, d\mathbf{r} \\ &= \frac{e}{\sqrt{G}} a(\mathbf{q}) \sum_{\mathbf{x}} e^{i\mathbf{x}\cdot(\mathbf{k}+\mathbf{q}-\mathbf{k}')} \int w(\mathbf{r}) e^{i\mathbf{r}\cdot(\mathbf{k}-\mathbf{k}')} \phi_{\mathbf{k}'}^* \phi_{\mathbf{k}} \, d\tau. \end{aligned} \tag{14.3}$$

The integration is now over a unit cell. Since $U_{\mathbf{k},\mathbf{k}'}$ contains the operator $a(\mathbf{q})$, it describes the scattering of an electron from $\mathbf{k}$ to $\mathbf{k}'$, and the simultaneous absorption of a phonon $\mathbf{q}$. On summing over all $\mathbf{x}$, $U_{\mathbf{k},\mathbf{k}'}$ vanishes unless the following interference conditions are satisfied:

$$\mathbf{k} + \mathbf{q} - \mathbf{k}' = 0 \qquad (N \text{ process}) \tag{14.4a}$$

or

$$\mathbf{k} + \mathbf{q} - \mathbf{k}' = \mathbf{b} \qquad (U \text{ process}). \tag{14.4b}$$

Thus the total wave vector of the electron-phonon system is conserved in N processes.

Let us consider N processes, so that $\mathbf{k} - \mathbf{k}' = -\mathbf{q}$ in (14.3). We note that $w(\mathbf{r})$ has the periodicity of the crystal and $w(\mathbf{r})$ is an odd function of $\mathbf{r}$ in each unit cell, if $\mathbf{r}$ is measured from the center of the cell. In particular this is so for (14.2), since V is even. Likewise, the electron density $\phi_{\mathbf{k}}^* \phi_{\mathbf{k}}$ is an even function of $\mathbf{r}$. It is possible therefore to expand (14.3) to first

[95] J. Bardeen, *Can. J. Phys.* **34**, 1171 (1956).

order in $\mathbf{q}$, provided q is small, and obtain the form

$$\int w(\mathbf{r})\phi_{\mathbf{k}+\mathbf{q}}{}^*\phi_{\mathbf{k}}\, e^{-i\mathbf{q}\cdot\mathbf{r}}\, d\tau = \int w(\mathbf{r})\phi_{\mathbf{k}}{}^*\phi_{\mathbf{k}}\, d\tau - i\mathbf{q}\cdot\int \mathbf{r}w(\mathbf{r})\phi_{\mathbf{k}}{}^*\phi_{\mathbf{k}}\, d\mathbf{r} + \int w(\mathbf{r})\left(\frac{\partial\phi_{\mathbf{k}}{}^*}{\partial\mathbf{k}}\cdot\mathbf{q}\right)\phi_{\mathbf{k}}\, d\tau. \quad (14.5$$

The first term vanishes from symmetry. Thus we may write

$$U_{\mathbf{k},\mathbf{k}'} = \frac{i\sqrt{2}}{3}\frac{1}{\sqrt{G}}\, qa(\mathbf{q})C(\mathbf{k},\mathbf{q},j) \quad (14.6)$$

where, for small q, C depends on the direction, but not the magnitude, of $\mathbf{q}$. The numerical factors are chosen to agree with the notation of Sommerfeld and Bethe,[96] taking note of the fact that they use a different notation for $a(\mathbf{q})$.

The calculation of C would be difficult even if $w(\mathbf{r})$ were known, for it involves a knowledge of the modulating functions $\phi_{\mathbf{k}}$. Clearly C would vanish if the electrons were free, and in general $C \sim [E(\mathbf{k}) - \hbar^2k^2/2m]$. It can be shown,[97] however, that, if the energy contours are spherical and if $\phi_{\mathbf{k}}(\mathbf{r})$ has spherical symmetry, C is proportional to $(\mathbf{q}\cdot\boldsymbol{\varepsilon})$ and thus vanishes for waves having truly transverse polarization, but not necessarily for waves which are "transverse" in the sense used in Section 6.

If the system is initially in a state with $\mathbf{k}$ occupied, the probability of finding the system in a state in which $\mathbf{k}'$ is occupied and $\mathbf{k}$ empty after a time t is

$$2U_{\mathbf{k},\mathbf{k}'}{}^2\frac{1 - \cos(\Delta E\, t/\hbar)}{\Delta E^2} \quad (14.7)$$

where $\Delta E = E(\mathbf{k}') - E(\mathbf{k}) - \hbar\omega$. In general, the probability of a transition from $\mathbf{k}$ to $\mathbf{k}'$ is proportional to $f(\mathbf{k})[1 - f(\mathbf{k}')]$, for $\mathbf{k}$ must be occupied and $\mathbf{k}'$ empty initially. Since such a transition reduces the occupation of $\mathbf{k}$ by unity, and since the inverse process must also be considered, the rate of change of $f(\mathbf{k})$ is given by

$$t\left.\frac{df}{dt}\right]_p = \frac{4\hbar}{9GM}\sum_{\mathbf{q},j} C_j{}^2\frac{q^2}{\omega}\{f(\mathbf{k}')[1 - f(\mathbf{k})][N(\mathbf{q}) + 1] - f(\mathbf{k})[1 - f(\mathbf{k}')]N(\mathbf{q})\}\frac{1 - \cos(\Delta E\, t/\hbar)}{\Delta E^2} \quad (14.8)$$

if we make use of (14.6), (14.7), and the explicit form (3.5) for $a(q)$. The

[96] A. Sommerfeld and H. Bethe, *in* "Handbuch der Physik," Vol. 24/2, p. 333. Springer, Berlin, 1933.

[97] F. Bloch, *Z. Physik* **52**, 555 (1928).

summation extends over all $(\mathbf{q},j)$, and $\mathbf{q}$ specifies $\mathbf{k}'$. Although (14.8) considers only processes $\mathbf{k} + \mathbf{q} = \mathbf{k}'$, it can also account for processes $\mathbf{k} - \mathbf{q} = \mathbf{k}'$ if we admit negative values of ω and use the convention (3.7). The resonance factor ensures that the major contribution comes from processes which conserve energy:

$$E(\mathbf{k}) + \hbar\omega = E(\mathbf{k}'). \tag{14.9}$$

In a degenerate electron assembly, $\hbar\omega \sim KT \ll E(\mathbf{k}) \simeq E(\mathbf{k}')$, so that the states $\mathbf{k}$ and $\mathbf{k}'$ are both near the Fermi surface and $\mathbf{q}$ is almost tangential to the Fermi surface at $\mathbf{k}$.

Each process $\mathbf{k} + \mathbf{q} = \mathbf{k}'$ increases (or decreases) the occupation of $\mathbf{k}$ by unity. At the same time, however, it also changes $N(\mathbf{q})$ by the same amount, so that the rate of change of $N(\mathbf{q})$ as a result of the electron-phonon interaction processes becomes

$$t\left.\frac{dN}{dt}\right]_e = \frac{4\hbar}{9GM} C_j^2 \frac{q^2}{\omega} \sum_{\mathbf{k}} \{f(\mathbf{k}')[1 - f(\mathbf{k})][N(\mathbf{q}) + 1] - f(\mathbf{k})[1 - f(\mathbf{k}')]N(\mathbf{q})\} \frac{1 - \cos(\Delta E\, t/\hbar)}{\Delta E^2}. \tag{14.10}$$

However $\mathbf{q}$ is now kept fixed. The summation extends over all states $\mathbf{k}$ and both states of spin.

If it is assumed that the electrons are at equilibrium, the expression in the curly bracket of (14.10) becomes simply

$$n(\mathbf{q})[f^0(\mathbf{k}') - f^0(\mathbf{k})] = n(\mathbf{q})\left[\frac{1}{e^{\epsilon+x}+1} - \frac{1}{e^{\epsilon}+1}\right] \tag{14.11}$$

and $dN/dt]$ can be described in terms of a relaxation time. Bethe[96] has carried out the summation for the case of spherical energy contours, and has obtained

$$\frac{1}{\tau_{pe}} = -\frac{1}{n}\left.\frac{dN}{dt}\right]_e = \frac{2C^2\hbar V}{9\pi GM} q\, k_f^2 \left(\frac{dE}{dk}\right)_f^{-2}. \tag{14.12}$$

In general, one cannot assume that the electrons are in equilibrium so that terms in $g(\mathbf{k})$, $g(\mathbf{k}')$ must be considered. Although full consideration of the mutual equilibrium of electrons and phonons is necessary if one desires to understand electrical conduction and thermoelectricity—see, for example, discussions by Hanna and Sondheimer[98] and by Klemens[50,99] —it has been shown[100,30] in the case of thermal conduction that the terms

[98] I. I. Hanna and E. H. Sondheimer, *Proc. Roy. Soc.* (*London*) **A239**, 247 (1957).
[99] P. G. Klemens, *Australian J. Phys.* **7**, 520 (1954).
[100] R. E. B. Makinson, *Proc. Cambridge Phil. Soc.* **34**, 474 (1938).

in $g(\mathbf{k})$ in (14.10) practically cancel when one sums over $\mathbf{k}$ because of the symmetry (13.13b) of $g(\mathbf{k})$ in the absence of an electric current.

The electronic conduction properties can be deduced by substituting (14.8) into (13.5) and solving the transport equation, which is an integral equation. All intrinsic resistivities (ρ_i and W_i) are proportional to

$$C^2 = \Sigma_j C_j^2. \tag{14.13}$$

Explicit solutions have been derived only for spherically symmetric Fermi surfaces, a model which applies at best only to monovalent metals. Small deviations from spherical form affect ρ_i much more than W_i at low temperatures,[101,30] whereas U processes, which the present theory cannot as yet treat adequately become important at high temperatures. Thus while C^2 can be estimated from observed electronic conduction properties in principle, reasonably reliable estimates can be made only from the intrinsic electronic thermal resistivity W_i at low temperatures and only for monovalent metals.

15. Lattice Component of Thermal Conductivity

The lattice component of thermal conduction in metals and alloys is governed by the same resistive processes as that of nonmetals;[101a] however, the scattering of phonons by conduction electrons is an additional resistive process. This scattering can be described by a relaxation time (14.12), so that one can use the theory of Section 6, in a form in which $1/\tau_{pe}$ contributes additively to $1/\tau'$. In general, $1/\tau_{pe}$ is large compared with values of $1/\tau'$ prevalent in good dielectric solids, particularly at low temperatures. Thus the lattice component of thermal conduction in metals and alloys is smaller than the thermal conductivity of dielectric solids.

Since $1/\tau_{pe} \propto \omega$, there are no difficulties of divergence at low frequencies. Moreover, provided τ_{pe} does not vary between the polarization branches, N processes do not affect the thermal resistance significantly. If τ_{pe} differs markedly for transverse and for longitudinal waves, however, N processes play an important role.

If we neglect N processes completely and substitute (14.12) for τ' into (6.12), the thermal conductivity becomes

$$\kappa_g = (W_E)^{-1} = \sum_j C_j^{-2} T^2 \frac{6\pi^2 K^3 MG}{h^3 V} \left(\frac{1}{k}\frac{dE}{dk}\right)_\zeta^2 \int_0^{\theta/T} \frac{x^3 e^x}{(e^x - 1)^2}\, dx. \tag{15.1}$$

[101] P. G. Klemens, *Australian J. Phys.* **7**, 70 (1954).

[101a] Of course, the dominant imperfections usually are of a different nature, in keeping with the difference in the mechanical properties between metals and nonmetals.

Thus $\kappa_g \propto T^2$ at low temperatures ($T \ll \theta$). At high temperatures, κ_g would tend to a constant value if it were limited only by the electrons. However, other scattering processes must also be considered at high temperatures. Thus $\kappa_g \propto T^{-1}$ as a result of three-phonon U processes and, in the case of some alloys, point imperfections, as discussed by Makinson.[100]

Since the coefficients C_j cannot be obtained from first principles at present, but are related to the electronic conduction properties, it is advantageous to express κ_g in terms of κ_i, the intrinsic electronic component of thermal conductivity. Makinson has expressed κ_g in terms of $\kappa_i(\infty)$, the (constant) value toward which κ_i tends at high temperatures. However, the neglect of electron-phonon U processes (14.4b) and the dispersion of the high-frequency lattice waves in Bloch's theory almost certainly lead to overestimates of $\kappa_i(\infty)$. As pointed out by Klemens,[29] it is better to compare κ_g with the values of $\kappa_i(T)$ for the range $T \ll \theta$, where $\kappa_i \propto T^{-2}$. Thus[30]

$$\kappa_i = \frac{1}{C^2}\left(k\frac{dE}{dk}\right)_f^2 N_a^{\frac{2}{3}} \frac{\theta v M K^2}{6\pi\hbar^2} \frac{1}{64.0}\left(\frac{\theta}{T}\right)^2 \tag{15.2}$$

in which $C^2 = \Sigma_j C_j^2$ and N_a is the number of conduction electrons per atom.

The relationship between κ_g and κ_i depends upon the nature of the interaction of electrons with lattice waves in the different branches of polarization, for this determines the relation between $\Sigma_j C_j^2$ and $\Sigma_j C_j^{-2}$. Makinson has assumed equal interaction between the electrons and all branches of polarization:

$$C_{\mathrm{I}}^2 = C_{\mathrm{II}}^2 = \tfrac{1}{3}C^2 \tag{15.3}$$

so that $[\Sigma_j C_j^2]^{-1} = [\Sigma_j C_j^{-2}]/9$. Substituting (15.2) into (15.1), we get

$$(W_E)^{-1} = \kappa_g = 313\kappa_i(T)\left(\frac{T}{\theta}\right)^4 N_a^{-\frac{4}{3}} \tag{15.4}$$

in the limit of low temperatures.

Note that κ_g of (15.1) is independent of θ; the factor θ^{-4} occurs only in (15.4) because $\kappa_i \propto \theta^4$. Similarly, the factor $N_a^{-\frac{4}{3}}$ does not represent the variation of κ_g with electron concentration; this variation is also governed by (15.1), with the provision that the coefficients C_j probably increase with increasing electron concentration.

In its simplest form the Bloch theory requires that

$$C_{\mathrm{II}}^2 = 0,\ C^2 = C_{\mathrm{I}}^2 \tag{15.5}$$

for complete spherical symmetry. While it is unlikely that C_{II}^2 vanishes

in real materials, we could expect that $C_{II}^2 < C_I^2$ in many cases. If $C_{II}^2 = 0$, W_E would vanish in the absence of N processes, and κ_g would be comparable to the thermal conductivity of a dielectric solid.

If $C_{II}^2 < C_I^2$, the N processes tend to make the effective relaxation times of the two branches equal. Their effect will be analogous to that of the interaction between the polarization branches discussed in Section 6, with the difference that now $\tau_{II}' > \tau_I'$, so that the interaction tends to reduce τ_{II}. When $\omega < \omega_1$, transverse waves interact with longitudinal waves of frequency around ω_1 whereas they interact with waves of frequency ω if $\omega > \omega_1$. Thus in analogy to (6.27)

$$\tau_{II}(\omega) = \frac{\tau_{II}'(\omega)[\sigma_{II}(\omega) + c^2\tau_I(\omega_1)]}{\tau_{II}'(\omega) + \sigma_{II}(\omega)} \qquad \text{if } \omega < \omega_1 \tag{15.6a}$$

$$= \frac{\tau_{II}'[\sigma_{II} + c^2\tau_I(\omega)]}{\tau_{II}' + \sigma_{II}} \qquad \text{if } \omega > \omega_1 \tag{15.6b}$$

where $c = v_I/v_{II}$. If $\omega < \omega_1$, so that $\sigma_I > \sigma_{II}$, it is possible for τ_I to exceed τ_{II}, even though $\tau_{II}' > \tau_I'$, for a mode (ω,II) can interact with (ω_1,I), whereas (ω,I) cannot. Thus

$$\tau_I = \frac{\tau_I'[\sigma_I + \tau_{II}(\omega)/c^2]}{\tau_I' + \sigma_I} \qquad \text{if } \omega < \omega_1. \tag{15.6c}$$

If $\omega > \omega_1$ however, so that $\sigma_I \sim \sigma_{II} = \sigma$, we find

$$\tau_I \simeq \tau_I' \tag{15.6d}$$

on substituting (15.6c) into (15.6b). Moreover, if we use (16.6d) also for low frequencies, the resulting error will never be serious. Thus the thermal conductivity is given by

$$\kappa = \kappa_I + \kappa_{II} \tag{15.7}$$

where

$$\kappa_I = \tfrac{1}{3}\int S^*(\omega) v_I^2 \tau_I'(\omega)\, d\omega \tag{15.8a}$$

$$S^*(\omega) = S_I(\omega) + \frac{\tau_{II}'}{\tau_{II}' + \sigma_{II}} S_{II}(\omega) \tag{15.8b}$$

and

$$\kappa_{II} = \tfrac{1}{3}\int S_{II}(\omega) v_{II}^2 \frac{\tau_{II}'\sigma_{II}}{\tau_{II}' + \sigma_{II}}\, d\omega. \tag{15.8c}$$

There are no convergence difficulties at low frequencies, for $\sigma_{II} \propto \omega^{-1}$ and τ_I' and τ_{II}' do not vary faster than ω^{-1}.

In the case of the Makinson coupling scheme (15.3), $\tau_I = \tau_{II}$. Hence κ is independent of the magnitude of σ, and N processes may be disregarded. However, if $\tau_{II}' > \tau_I'$, κ_{II} is appreciable unless $\sigma \ll \tau_I'$ (tight coupling). In the opposite case of loose coupling ($\sigma \gg \tau_I'$)

$$\kappa = \tfrac{1}{3}\Sigma_j \int S_j(\omega) v^2 \tau_j'(\omega)\, d\omega \tag{15.9}$$

which is equivalent to (15.1).

If the coupling is tight and if $C_{II}^2 = 0$ (Bloch scheme), it follows, on substituting (14.12) into (15.8a) and comparing with (15.2), that

$$(W_E)^{-1} = \kappa_g = \frac{313}{3}\kappa_i(T)\left(\frac{T}{\theta}\right)^4 N_a^{-\frac{4}{3}} \tag{15.10}$$

instead of (15.4). This relation differs from (15.4) by a factor 3, which arises because effectively $[\Sigma_j C_j^{-2}]^{-1} = C_I^2/3 = C^2/3$, for $C_j = C_I$ in (15.1) for all polarizations. Moreover, in the case of Bloch coupling, the value of θ in (15.10) is θ_I, the Debye frequency of the longitudinal branch, whereas the value of θ in (15.4) is given by

$$\frac{3}{\theta^4} = \frac{1}{\theta_I^4} + \frac{2}{\theta_{II}^4} \tag{15.11}$$

and is thus close to the Debye temperature determined from the low-temperature specific heat. Hence the ratio κ_g/κ_i is about 15 to 20 times as large in the case in which there is equal interaction with all polarizations (Makinson scheme) as it is in the case in which there is no interaction with transverse waves (Bloch scheme) and there is tight coupling between the polarization branches.

Since $\sigma_{II}(\omega_1) \propto T^{-5}$, the assumption of tight coupling must break down at low temperatures. Although theoretical estimates of σ_{II} are unreliable, one may expect τ_{pe} to equal σ_{II} at some temperature near 10°K. At that temperature the coupling between the polarization branches changes rapidly from a loose to a tight case as the temperature is increased. Thus κ_g/T^2, while being almost constant elsewhere, decreases rapidly in this temperature region. Thus the magnitude and behavior of κ_g can yield information concerning the nature of the electron-phonon interaction.

So far we have considered only scattering of phonons by electrons. Imperfections also contribute to $W_g = 1/\kappa_g$ in an approximately additive way. At low temperatures the most important imperfections in metals and alloys usually are dislocations. Their scattering cross section varies with frequency in the same way as the probability of scattering by electrons. Both mechanisms lead to a thermal resistance which varies as T^{-2}.

It is therefore difficult to distinguish between electron scattering and dislocation scattering. Other imperfections can be identified through the temperature dependence of their thermal resistance, as in the case of dielectric solids.

16. Separation of Observed Thermal Conductivity into Electronic and Lattice Components

In metals and alloys the observed thermal conductivity is composed additively of an electronic component κ_e and a lattice component κ_g. Thus

$$\kappa = \kappa_e + \kappa_g \tag{16.1}$$

where κ_e is given by (13.14b). We have

$$\frac{1}{\kappa_e} = W_e = W_i + W_0 \tag{16.2}$$

in which W_i is the ideal and W_0 the residual thermal resistivity. The electrical resistivity ρ is given in a similar fashion (13.14a); ρ_0 and W_0 are related by the Wiedemann-Franz law (13.15). Since ρ_0 is independent of temperature, $W_0 \propto T^{-1}$.

Measurements of the lattice component κ_g involve a measurement of the total thermal conductivity κ, and a calculation of κ_e from other data (usually from measured values of ρ); κ_g is then deduced by subtraction. This can be done only if κ_e is not too large compared with κ_g, for present measurements of κ have only limited accuracy, and only if it is possible to calculate κ_e.

Since $\kappa_g \ll \kappa_i = W_i^{-1}$, as seen from (15.4), κ_g cannot be deduced from measurements of pure metals, where W_0 is not large. Therefore it is necessary to reduce κ_e substantially, so that it becomes comparable to κ_g. Three methods of doing this are known.

(a) Reduction of κ_e through the application of a magnetic field. This method has not yet been used with real success, because the variation of κ_e with magnetic field is not well understood. Furthermore, with the fields at present available, it is not possible to achieve a sufficient reduction of κ_e in those metals which have a simple band structure, and which are, as a result, the most interesting for purposes of studying W_E, the component of W_g which arises from electron scattering.

(b) Reduction of κ_e in the superconducting state. This effect is accompanied by a decrease of W_E, so that well below the transition temperature κ_e is negligible, and κ_g is enhanced by the elimination of W_E. This method does not, of course, permit a study of W_E, but is eminently suitable for studying those imperfections whose effect is important at lowest temperatures (dislocations, grain boundaries, etc.). Such investigations

will be reviewed separately in this series,[101b] and will not be dealt with here.

(c) Reduction of κ_e through alloying. If imperfections which scatter electrons without scattering phonons can be introduced, κ_e can be reduced without affecting κ_g. This is achieved best by alloying with suitable elements, ideally with those having different valence but very similar atomic mass and radius. In practice it is not possible to leave κ_g completely unaffected. Although the direct impurity scattering easily can be made negligible at low temperatures, it appears that the introduction of impurities is associated with the creation of other imperfections, notably dislocations, which decrease κ_g at low temperatures. Nevertheless, this method has been used successfully by various investigators. Much of our present knowledge of the lattice conductivity of metals has been derived in this way.

Increasing W_e by alloying has an additional advantage. Not only is κ_e reduced to a value comparable to κ_g, but W_e is determined mainly by W_0 and can be calculated, for W_0 can be deduced from measured values of ρ_0. On the other hand, W_i is not well known. In the case of dilute alloys it is possible to adopt values for W_i determined from measurements of the thermal conductivity of the parent metal. However, changes in the band structure on alloying may change W_i. A check on whether such changes are likely to be important can be made by comparing values of ρ_i for the alloy and the parent metal. Fortunately W_i is only a small correction to W_e, although it becomes increasingly important the higher the temperature and the more dilute the alloy. At the same time, κ_g/κ_e decreases as T is increased or the impurity concentration is decreased. Moreover, the accuracy with which the over-all thermal conductivity is measured decreases rapidly above liquid oxygen temperatures. All these factors combine to make determinations of κ_g possible only to temperatures as high as that of liquid oxygen and for alloys having sufficiently high residual resistance. While no rigid rule can be given, since these limitations depend upon the material studied, it has been the experience of the group at Sydney that κ_g cannot be determined above 90°K, and cannot be determined on alloys more dilute than one containing 2% per atom of a divalent addition in a monovalent metal, or a solution having a similar residual resistance.

[101b] By K. Mendelssohn and H. M. Rosenberg. The thermal conductivity of superconductors has been reviewed recently by Serin,[102] Klemens,[30] and Mendelssohn.[103] Recent Oxford work was summarized by Mendelssohn.[104]

[102] B. Serin, *in* "Handbuch der Physik," Vol. 15 (2nd ed.), p. 210. Springer, Berlin, 1956.

[103] K. Mendelssohn, *Progr. in Low Temp. Phys.* **1**, 184 (1955).

[104] K. Mendelssohn, *Can. J. Phys.* **34**, 1315 (1956).

The main disadvantage of this method is that one is prevented from working with pure metals. For this reason it would be very useful if the magnetic field method could be developed into a practicable form for more dilute alloys, if not for pure metals.

In view of (16.1), (16.2), (13.14a), (13.15), and (13.16), a lower limit to κ_g is given by

$$\kappa_g > \kappa - \frac{LT}{\rho}. \tag{16.3}$$

At low temperatures and for good conductors this inequality is not very illuminating, since this lower limit turns out to be negative. In some cases, for example those of bismuth at low temperatures[19] and chromium above room temperatures,[105] κ_e is either negligible or can be calculated and the lattice conductivity can be deduced readily.

Since the residual resistance is not a reproducible quantity, it need hardly be emphasized that it is necessary to measure electrical and thermal conductivities on the same specimen in order to deduce the lattice conductivity.

17. The Intrinsic Lattice Thermal Conductivity (Observations)

The lattice thermal conductivities of various alloys have been deduced —see, for example, the review by Klemens.[30] At the present state of the theory, however, the main interest in the study of intrinsic effects centers on alloys of the monovalent metals. Hulm,[25] Berman,[26] and Estermann and Zimmerman[27] each measured copper-nickel alloys containing 20%, 40%, and 10% of nickel content, respectively. They found that $\kappa_g \propto T^2$ at low temperatures, as expected if phonons are scattered by electrons. Estermann and Zimmerman also noted that while still proportional to T^2 in a cold-worked specimen, κ_g was smaller. This effect has since been explained in terms of dislocation scattering.[16] Since both dislocations and free electrons produce a thermal resistivity W_g which varies at T^{-2}, it is necessary to use well-annealed specimens if conclusions concerning the magnitude of W_E are to be drawn.

In general, alloying changes the electron concentration and thus may also change W_E. In order to deduce W_E for pure monovalent metals, it was suggested[29] that a range of alloys with electron concentrations both above and below that of the monovalent metal be measured. W_E could then be obtained by interpolation. A series of silver-palladium and silver-cadmium alloys were measured by Kemp *et al.*,[106,28] giving some attention

[105] R. W. Powell and R. P. Tye, *J. Inst. Metals* **85**, 185 (1956).

[106] W. R. G. Kemp, P. G. Klemens, A. K. Sreedhar, and G. K. White, *Proc. Phys. Soc. (London)* **A67**, 728 (1954).

to the effects of annealing. The lowest concentration of Pd or Cd for which κ_g could be deduced was about 2%. Some typical lattice conductivities are shown as functions of temperature in Fig. 10.

It will be seen that $\kappa_g \propto T^2$ only at the lowest temperatures, and that it increases more slowly at higher temperatures, no doubt because of the

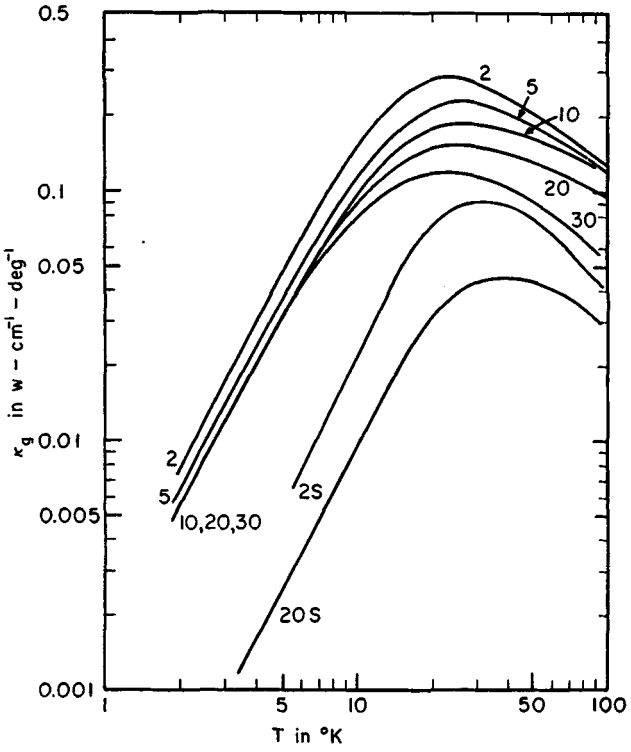

FIG. 10. Lattice component of thermal conductivity of some silver-cadmium alloys, according to Kemp *et al.*[28] Numbers denote percentage cadmium content, 2*S* and 20*S* are strained specimens.

scattering of phonons by imperfections. Finally it passes through a maximum and decreases again with increasing temperature. This indicates that κ_g is limited either by umklapp processes or by point defects. Since the solute atoms provide a large number of point defects, one would expect some resistance; however, the relative insensitivity of κ_g to composition in the low concentration alloys at these temperatures suggests that κ_g is mainly limited by U processes at least in the alloys of low solute content. In other cases there is a contribution to the resistance arising from the solute atoms. This will be discussed in Section 18.

Similar investigations have been made on copper alloys. White and Woods[107,19] found that very low concentrations of iron in copper reduce κ_e sufficiently to permit the evaluation of κ_g. Kemp *et al.*[108] studied a series of copper-zinc alloys; Zimmerman[109] studied some additional copper-nickel and copper-zinc alloys. Recently a sequence of gold alloys were measured by Birch *et al.*[110]

Some of the values of $W_g T^2$ obtained by these various authors for annealed alloys at the lowest temperatures (where $\kappa_g \propto T^2$) have been

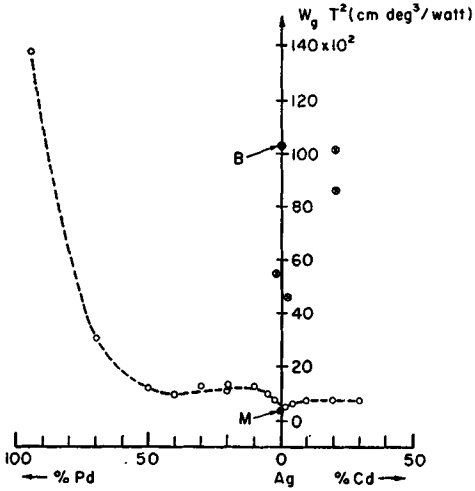

FIG. 11. Values of $W_g T^2$ at helium temperatures for silver alloys as a function of electron concentration or solute content, according to Kemp *et al.*[28] Annealed specimens ○, strained specimens ⊗.

plotted as functions of electron concentration in Fig. 11 (silver alloys) and in Fig. 12 (copper alloys). The theoretical values of $W_E T^2$ for the pure metals are also marked. Here B denotes the value given by (15.10), that is, the Bloch coupling scheme, whereas M is given according to (15.4), the Makinson coupling scheme. Both were derived on the assumption that the polarization branches are closely coupled through N processes.

It is seen from these values that W_E lies closer to (15.4) than (15.10). This indicates that the interaction of the conduction electrons with transverse waves is not very much weaker, if at all, than with longitudinal

[107] G. K. White and S. B. Woods, *Phil. Mag.* [7] **45**, 1343 (1954).

[108] W. R. G. Kemp, P. G. Klemens, R. J. Tainsh, and G. K. White, *Acta Metallurgica* **5**, 303 (1957).

[109] J. E. Zimmerman, *Bull. Am. Phys. Soc.* [2] **2**, 58 (1957); *Proc. 5th Intern. Conf. Low Temperature Phys., Madison* No. 7-2 (1957).

[110] J. A. Birch, W. R. G. Kemp, and R. J. Tainsh, private communication.

waves. The same conclusion can also be drawn for gold from its alloys.[110] This result is also in accord with an analysis of the electronic conduction data[101,30] for these metals. Unfortunately it has not been found possible to deduce W_E for alkali metals with confidence so far, partly because of the difficulty of making suitable solid solutions with high electrical resistance.[111]

Although these results indicate that electrons interact equally strongly with all polarizations, it is also possible to assume that $C_{\mathrm{I}}^2 > C_{\mathrm{II}}^2$, and

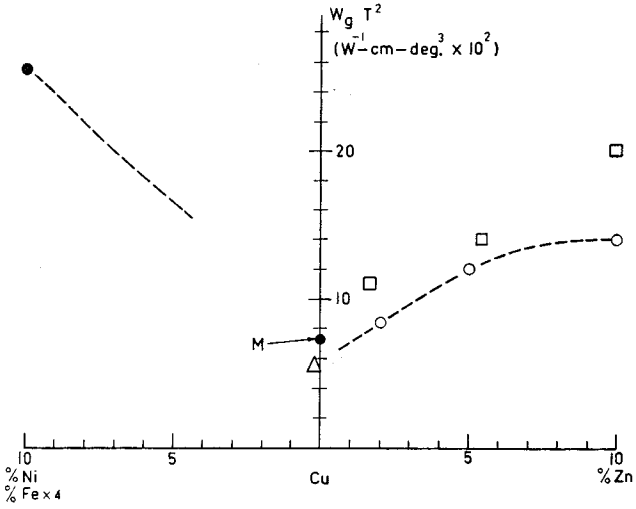

FIG. 12. Values of $W_g T^2$ at helium temperatures of some copper alloys as function of electron concentration or solute content, according to Kemp *et al.*[76] Copper-zinc alloys[108] annealed at 500°C, □; copper-zinc alloys[76] annealed at 850°C, ○; copper-nickel,[27] ●; copper-iron,[19] △.

that the coupling of polarization branches through N processes is weak. In that case, however, one would expect to find a rapid variation of $W_g T^2$ at the temperature where $\sigma = \tau_{pe}$. Such variation is not found, except for the slow increase of $W_g T^2$ arising from other scattering processes. Although this variation is in the right sense, it is too slow, since $\sigma/\tau_{pe} \propto T^{-4}$.

It is interesting to note, however, that Chari[112] found such a variation at about 2°K in silver alloys. He ascribed it to the uncoupling of the branches of polarization below that temperature. If these observations are confirmed in a wide range of silver alloys, and if the interpretation is correct, it will follow that C_{I}^2 is somewhat, but not very much, larger

[111] G. K. White, *Can. J. Phys.* **34,** 1328 (1956).

[112] M. S. R. Chari, Thesis, Leiden, 1956; see also C. J. Gorter, *Can. J. Phys.* **34,** 1332 (1956).

than C_{11}^2, and the tight-coupling assumption will be justified above the transition temperature. However, the values of σ required to fit his observations are smaller than those predicted by (6.32).

Since the low-temperature values of W_0T^2 seem to vary with alloy composition (see Figs. 11 and 12), there is some uncertainty in the interpolated value of W_BT^2 for the pure metals. The cause of this variation is not known. It is, of course, quite possible for W_BT^2 to vary with electron concentration, and even to show a minimum, although no certain predictions can be made from the theory as developed at present. It is an unlikely coincidence, however, that a cusp-like minimum located at a concentration of one electron per atom should be a consequence of the band structure of these metals, even though it is believed that at some neighboring electron concentration the Fermi surface just touches the zone boundary.[101] No doubt investigations of the magnetic susceptibility and the electronic specific heat of these alloys will throw light on this point. Another possible explanation, however, is that impurity atoms, irrespective of their valency, are associated with dislocations which cannot be removed by ordinary annealing just above the recrystallization temperature. This model, if confirmed, would imply a locking of dislocations by impurities. With increasing solute content, the number of such dislocations would increase. However, in order to account for the variation of W_0T^2 in this way, the number of locked dislocations would have to be quite large—of the order of 10% of the number introduced by heavy deformation.

In order to test this hypothesis, Kemp and Tainsh[76] measured κ_0 for some copper-gold alloys (7.5 and 16.5% Au). It was found that W_0T^2 was about 2×10^3 in both cases and thus was significantly higher than for dilute alloys, even though the electron concentration, and hence W_BT^2, should not have altered much. This seems to confirm the dislocation model. Attempts were then made to reduce W_0T^2 by annealing at higher temperatures. Whereas Kemp *et al.*[108] had annealed copper-zinc at 500°C, Kemp and Tainsh[76] now annealed a sequence of copper-zinc specimens at 850°C. They did observe a decrease of W_0T^2, but it seemed that W_0T^2 was still larger than expected, even after that anneal and increased with zinc content (see Fig. 12). Birch *et al.*[113] found no significant change in W_0T^2 with an alloy containing 2% of platinum in gold when they increased the annealing temperature from 750°C to 900°C. However they found a decrease of about 20% after annealing at 1070°C. Thus the dislocations are in extremely stable configurations.

Kemp *et al.*[28] observed the lattice conductivity of silver-palladium over

[113] J. A. Birch, W. R. G. Kemp, and P. G. Klemens, *Proc. Phys. Soc.* (*London*) **71**, 843 (1958).

the complete range of alloy compositions (see Fig. 11). The high values of $W_g T^2$ for the palladium-rich alloys are most probably the result of an enhancement of $W_E T^2$ because of the scattering of phonons by holes in the d band, which are thought to make their appearance at these higher palladium concentrations.

These investigators also found a discrepancy between the values of κ/T, extrapolated to zero temperature, and the values of κ_e/T deduced from the electrical resistance (13.15), in the case of some of the alloys of high electrical resistance. They thought that this discrepancy was a result of experimental errors; however, Zimmerman[109] found a similar discrepancy in copper-nickel alloys of high nickel content. Since he used carbon resistance thermometers, and thus enhanced his accuracy at the lowest temperatures, he was able to show that the discrepancy arose because $\kappa_g \propto T$ at lowest temperatures. He also showed that the anomaly disappeared in cold-worked alloys, where dislocations reduced the lattice conductivity and $\kappa_g \propto T^2$. Pippard explained the anomaly as follows. In the alloys having a high electrical resistance the electron mean free path is shorter than the wavelengths of the dominant lattice waves. Under those conditions the theory of electron-phonon interactions discussed in Section 14 breaks down and the resistance associated with scattering of phonons by electrons is no longer given by (15.1). Pippard[114] had shown that in the opposite extreme case, where the lattice waves are long compared with the electron mean free path, the electron gas must be treated macroscopically. The absorption of sound waves is then proportional to ω^2 and to the mean free path of the electrons. Thus κ_g/T tends to a finite value at the lowest temperatures, and κ_g is inversely proportional to κ_e.

It is also of interest to compare the high-temperature values of κ_g, for which $\kappa_g \propto T^{-1}$, with Leibfried and Schloemann's[17] theoretical value (8.3) of the lattice thermal conductivity at high temperatures as limited by U processes. In some cases it is probable that κ_g is limited only by U processes, either because the solute atoms are unlikely to produce a sufficiently high point defect resistance, or because κ_g is found to be insensitive to variations in solute content in this temperature range. Such cases are provided by the dilute copper-iron alloy of White and Woods,[107,19] the dilute silver-palladium alloys and the most dilute silver-cadmium alloy used by Kemp *et al.*[28] and by a dilute gold-chromium alloy.[110] These values of κT are compared with the theoretical values (8.3) in Table III. Although the observed resistances are somewhat higher than the calculated ones, the agreement in order of magnitude is similar to that for dielectric solids (see Section 8).

[114] A. B. Pippard, *Phil. Mag.* [7] **46**, 1104 (1955).

TABLE III. THEORETICAL AND OBSERVED VALUES OF $\kappa_g T$ FOR SOME METALS AT LIQUID OXYGEN TEMPERATURES, AS LIMITED BY ANHARMONICITIES

Alloy group	γ	M[a] (atomic)	a 10^{-8} cm	θ °K	$\kappa_g T$ in watt-cm^{-1} from (8.3)	$\kappa_g T$ in watt-cm^{-1} obs.
Ag-Pd, Ag-Cd[b]	2	108	2.58	225	45	15
Cu-Fe[c]	2	64	2.22	340	80	30
Au-Cr[d]	2	197	2.58	165	35	5
Chromium[e]	2	52	2.31	500(?)	200	150

[a] M in atomic units (1.67×10^{-24} g).

[b] W. R. G. Kemp, P. G. Klemens, A. K. Sreedhar, and G. K. White, *Proc. Roy. Soc. (London)* **A233,** 480 (1956).

[c] G. K. White and S. B. Woods, *Can. J. Phys.* **33,** 58 (1955).

[d] J. A. Birch, W. R. G. Kemp, and R. J. Tainsh, private communication.

[e] High-temperature values of κ_g estimated from measurements of Powell and Tye[f] on pure chromium by using the lower limit (16.3). There is considerable doubt as to the appropriate values of θ, and no special significance should be attached to the apparently better agreement between the calculated and observed values of $\kappa_g T$.

[f] R. W. Powell and R. P. Tye, *J. Inst. Metals* **85,** 185 (1956).

18. THE EFFECT OF CRYSTAL IMPERFECTIONS

The effect of imperfections on the lattice thermal conductivity of alloys can be studied by noting the changes in the same specimen when introducing the imperfections or removing them by annealing, or by observing changes with alloy composition, regarding the solute atoms themselves as the imperfections. The former method permits more confident interpretation, especially as simultaneous changes in the electrical resistance can also be studied.

While, in principle, one can study the effects of quenching and irradiation in this way, the only studies carried out to date have been on the effect of cold work. Even these effects have, in the main, been observed on specimens cold-worked during fashioning, and have been followed by observations on the same specimen after annealing. While such work is carried out better on a more controlled basis, these primitive investigations are not quite without value, for the effects of cold work usually show some saturation. It is believed that this saturation has been approached in the manufacture of the specimens.

The major effect of cold work is usually a substantial decrease of κ_g at the lowest temperature. κ_g still varies as T^2, so that the additional resistance is the result of dislocations. Such dislocation-induced resistance was first observed by Estermann and Zimmerman[27] in the case of Cu-10%

Ni, and later by Kemp *et al.*[28] for Ag-2% Pd, Ag-2% Cd, and Ag-20% Cd. Further investigations were made on a number of copper-zinc alloys,[108] on a specimen of arsenical copper, and on Au-7% Cr.[110] The energy stored in the arsenical copper on deformation was studied by Clarebrough *et al.*[115] The increases in W_0T^2 and the corresponding densities of dislocations deduced from (5.25) and (11.3) are given in Table IV.

TABLE IV. ESTIMATES OF DISLOCATION DENSITIES OF DEFORMED ALLOYS FROM THEIR LATTICE THERMAL CONDUCTIVITY

Alloy	W_0T^2 Before annealing	W_0T^2 After annealing	ΔW_0T^2	N_d (a)	N_d (b)
Ag-20 % Cd	86×10^2	8×10^2	78×10^2	8×10^{12}	5×10^{11}
Ag- 2 % Cd	46×10^2	5×10^2	41×10^2	20×10^{12}	13×10^{11}
Ag- 2 % Pd	55×10^2	8×10^2	43×10^2	6×10^{12}	4×10^{11}
Cu- 2 % Zn	20×10^2	11×10^2	9×10^2	1.5×10^{12}	1.0×10^{11}
Cu- 5 % Zn	30×10^2	14×10^2	16×10^2	2.7×10^{12}	1.8×10^{11}
Cu-30 % Zn	140×10^2	20×10^2	120×10^2	20×10^{12}	13×10^{11}
Cu- 0.4% As	60×10^2	15×10^2	45×10^2	7.5×10^{12}	5×10^{11}
Au- 7 % Cr	94×10^2	45×10^2	49×10^2	11×10^{12}	7.4×10^{11}
Au- 0.7% Cr	22×10^2	9×10^2	13×10^2	2.7×10^{12}	1.8×10^{11}

Remarks: Values of W_0T^2 (in w^{-1}-cm-deg^2) are derived from liquid helium temperatures, where $\kappa_g \propto T^2$. Estimates of the dislocation density (lines per cm^2) are obtained (a) from (11.3) and (b) from an analogous expression derived from (5.23).

It appears that the density of dislocations produced on deformation increases with solute content, although we do not know whether all the deformations are equivalent. Although the thermal resistance gives a good relative measure of dislocation densities, an absolute calibration has not yet been carried out because of the difficulty of measuring densities of dislocations by other methods. The absolute values of estimates from (11.3) cannot be regarded as convincing. Actually, it does seem that estimates of dislocation densities from (11.3) are too high. Thus Williamson and Smallman[116] estimated the density of dislocations in heavily deformed brass filings (Cu-30% Zn) from x-ray data and found it to be about 3×10^{12} cm^{-2}. The value of the density in Cu-30% Zn estimated from (11.3) is 2×10^{13}, a discrepancy of about 7. (The discrepancy is probably even larger, for the rod was probably less heavily deformed than the filings.) Again, in the case of arsenical copper, the density of dis-

[115] L. M. Clarebrough, M. E. Hargreaves, and G. W. West, *Proc. Roy. Soc.* (*London*) **A232**, 252 (1955).

[116] G. K. Williamson and R. E. Smallman, *Phil. Mag.* [8] **1**, 34 (1956).

locations estimated from the stored energy is only 1×10^{11}, which is almost a factor 100 lower[116a] than the estimate from (5.25).

In order to explain discrepancies such as these, it was suggested[16] that the dislocations have a tendency to cluster in groups of the same sign. As long as they are contained in a region whose dimensions are of the order of a phonon wavelength (say 100 A) or less, their scattering is proportional to the square of the combined Burgers vector. However, no mechanism is known which would produce an average cluster size leading to an enhancement of say 10. Polygonization walls would behave as grain boundaries, unless they were very short. While there is probably some piling of dislocations against obstacles, the over-all enhancement of scattering is probably no more than a factor of 2 or 3, for the dislocations are widely spaced except close to the obstacle. To generate the stress necessary to keep a few dislocations together, so that their scattering may be reinforced, one would require a larger number of widely spaced dislocations, which would reduce the over-all enhancement. (The author is indebted to Dr. F. C. Frank for this argument.)

Thus it is more probable that the discrepancy arises because (5.25) underestimates the scattering by a factor of at least 10. This is quite plausible for we have seen that (5.23) leads to a scattering of lattice waves by strain fields which is about 15 times higher than the corresponding expression on which (5.25) was based. Hence it is reasonable to decrease the estimates of dislocation densities by a factor 15, as was done in the last column of Table IV.

In addition to the changes in κ_g observed at the lowest (liquid helium) temperatures, there are cases in which changes are observed at higher (liquid oxygen) temperatures, where $\kappa_g \propto T^{-1}$. The results indicate that point defects are introduced by cold work. Such changes were observed by Kemp, Sreedhar, and White[28] in the three silver alloys which were measured both before and after annealing. They were also observed by Kemp, Tainsh, and White[108] in two copper-zinc alloys, although Kemp and Tainsh[110] failed to find significant changes in the point-defect resistance on annealing arsenical copper and gold-chromium. (In both of these materials ρ_0 increased on annealing.) However, there was a decrease in dislocation density. The changes in W_g/T at high temperatures are given in Table V, together with the corresponding values of nS^2. Here S^2 is defined by (5.9) and (5.10), and n is the concentration of point defects per atom.

[116a] This probably underestimates the dislocation density by a factor of about 2 or 3, for the stored energy depends logarithmically on the size of the crystal. It may be argued that the effective size of the crystals should be of the order of the mean distance between dislocations, rather than the external size.

In order to identify the point defects, Kemp *et al.*[108] compared changes in W_g/T with simultaneous changes in ρ_0, assuming provisionally that the changes in ρ_0 are entirely the result of point defects. If the defects are vacancies, one can calculate their concentration n_v from Jongenburger's estimate[117] of the scattering of electrons by vacancies and compare this concentration with the value of n calculated from W_g/T, under the assumption that there is no distortion around the vacancy, so that from (5.10) $S^2 = \frac{1}{4}$. These values are given in Table V for the copper-zinc alloys, as well as the silver alloys. It is seen that there is a discrepancy

TABLE V. CHANGES IN THE LATTICE THERMAL RESISTANCE W_g/T AT LIQUID OXYGEN TEMPERATURES, AND IN THE RESIDUAL RESISTANCE ρ_0, OF SOME ALLOYS, ASCRIBED TO VACANCIES

Alloy	$\Delta W_g/T$ watt^{-1}-cm	S^2n	n_v ($S^2 = \frac{1}{4}$)	$\Delta\rho_0$ $\mu\Omega$-cm	n_v (from $\Delta\rho_0$)
Cu- 2% Zn	4×10^{-2}(?)	1×10^{-3}(?)	4×10^{-3}(?)	4.5×10^{-2}	3.5×10^{-4}
Cu- 5% Zn	4×10^{-2}	1×10^{-3}	4×10^{-3}	9×10^{-2}	7×10^{-4}
Cu-30% Zn	15×10^{-2}	4×10^{-3}	15×10^{-3}	71×10^{-2}	6×10^{-3}
Ag- 2% Pd	4×10^{-2}	6×10^{-4}	2.5×10^{-3}	5×10^{-2}	3×10^{-4}
Ag- 2% Cd	20×10^{-2}	3×10^{-3}	12×10^{-3}	7×10^{-2}(?)	5×10^{-4}(?)
Ag-20% Cd	23×10^{-2}	3.4×10^{-3}	14×10^{-3}	40×10^{-2}	2.5×10^{-3}

between the estimates of concentration. Apart from the case of Ag-2% Cd, which seems particularly anomalous, $\Delta W_g/T$ is too high relative to $\Delta\rho_0$ by factors ranging from 3 to 6. The discrepancy would be even more serious if the defects were interstitials or if there was distortion around the vacancies, for this would increase $\Delta\rho_0/n_v$ more than it would S^2. Furthermore, if part of $\Delta\rho_0$ originated in other imperfections (stacking faults, changes in short-range order), the discrepancy would also be increased. It was suggested that the defects are small groups of vacancies, so that $\Delta W_g/T$ is enhanced by reinforcement of the scattered lattice waves. The shorter electron waves would not be subject to such reinforcement.

The interpretation of the thermal resistance of annealed alloys in terms of imperfections associated with the solute atoms is even less certain, for $W_E T^2$ is not well known at low temperatures and W_U/T is not known at higher temperatures. If the increase of W_g/T^2 with solute content at helium temperatures is indeed caused by dislocations, as was suggested in Section 17, the residual dislocation density of Cu-2% Zn after annealing at 850°C is of the order of 6×10^{11} cm^{-1}, if we use (5.25) and (11.3), or 4×10^{10}, if we use the modified scattering formula based on

[117] P. Jongenburger, *Appl. Sci. Research* **B3**, 237 (1953).

(5.23). These densities are increased by a factor of 10 for alloys containing 10% or more of solute atoms.

The increase of W_0/T with solute content at high temperatures observed in the case of Ag-Cd and Cu-Zn is most probably the result of the scattering of phonons by the solute atoms. Since the differences in mass are too small to produce an appreciable resistance, the scattering probably arises from differences in the forces binding a solute atom to its neighbors in the lattice and from distortions of the lattice around the solute atom. One must also consider the possibility of clustering. However, it does not seem possible, at the present stage, to draw any definite conclusions from the observed resistance.

The point-defect resistance of copper-gold alloys[76] is of some interest, however, since gold atoms are much heavier than copper atoms and scatter phonons mainly in virtue of the difference in mass. Therefore the scattering probability can be calculated with confidence from (5.8), and the thermal resistivity can be deduced from (6.34). Since the relative mean square deviation $\epsilon = \Sigma f_a(\Delta M_a/M)^2$ of (11.4) is not small in this case however, first-order perturbation theory probably is insufficient. The thermal resistance may be expected not to vary linearly with ϵ, but to show saturation for high values of ϵ. Such a tendency towards saturation actually was observed. It was shown[24] that the coefficient of the linear term did agree with the theoretical value if an empirical relation

$$W_0/T = a\epsilon - b\epsilon^2 \tag{18.1}$$

was fitted to the observed values of W_0/T. This agreement between the observed and calculated thermal resistance originating in variation of the mass is in contrast to the discrepancies observed for the isotope effect in dielectrics (see Section 11) and lends support to the suggestion that in that case the discrepancy originates in other imperfections or in an enhancement of the resistance by N processes, as discussed in Section 6. In the present case, N processes would be relatively less important, for the other resistive processes (point defects, electron interaction) are much stronger.

It would be interesting to extend the study of this quasi-isotope effect to lower values of ϵ. This probably could be done conveniently with Cu-Pt alloys.

19. Semiconductors: Resistance due to Free Electrons

The thermal conductivity of germanium was first measured by Estermann and Zimmerman,[118] who noted a substantial difference between a

[118] I. Estermann and J. E. Zimmerman, *O.N.R. Tech. Rept.* (*Carnegie Inst. Technol.*) No. 6 (1951).

pure specimen and one heavily doped (6×10^{-5} per atom) with aluminum. The additional resistance increased with decreasing temperature, and therefore could not be ascribed to the scattering of lattice waves by the impurity atoms themselves. The resistance was also surprisingly large. It was suggested that this resistance arose from the scattering of phonons by the carriers associated with the impurities. Such scattering cannot arise if the electrons (or holes) are bound to impurity sites, but only if the impurity concentration is sufficiently high so as to form an impurity band. (See, for example, Conwell[119] and Mott[120] for a discussion of impurity bands.) The fact that an impurity band was formed in this case, and that the electrons in it formed a degenerate gas at low temperatures, was borne out by the metallic behavior of the specific heat of the same material at low temperatures, measured by Estermann and Friedberg.[121] The observed thermal conductivity was not inconsistent with the theory of Section 15, which predicts that $\kappa \propto T^2$ at lowest temperatures, the electronic thermal conductivity being quite negligible. Not enough is known about the properties of impurity bands to know the magnitude of the conductivity to be expected.

Rosenberg[122] found a thermal resistivity in p-type germanium which apparently was caused by scattering by free carriers, whereas Berman and co-workers[92,123] found indications that a relatively small number of electrons or holes could increase the resistance in various irradiated solids significantly. The resistance found by Rosenberg was remarkable because it increased faster than T^{-3} with decreasing temperature, so that the corresponding mean free path decreased with decreasing temperature, which is at variance with what may be expected from scattering by any static imperfection. A similar behavior of the thermal resistance of impure germanium had previously been reported by Fagen *et al.*[124]

The scattering of phonons by the electrons in a simple band containing a small number of quasi-free electrons was investigated by Ziman.[125] This treatment is an extension of the theory of Section 14 for the case when the electron gas is nondegenerate. Again the starting point of the calculations is the expression (14.10) for $dN/dt]$, together with the simplification (14.11). There are, however, two features which make the

[119] E. M. Conwell, *Phys. Rev.* **103**, 51 (1956).
[120] N. F. Mott, *Can. J. Phys.* **34**, 1356 (1956).
[121] I. Estermann and S. A. Friedberg, *Compt. rend. 2e Reunion chim. phys., Paris* p. 312 (1952).
[122] H. M. Rosenberg, *Conf. phys. Basses Temperatures, Paris* p. 464 (1955).
[123] R. Berman, B. Schneidmesser, and S. M. A. Tirmizi, *Conf. phys. Basses Temperatures, Paris* p. 456 (1955).
[124] E. Fagen, J. Goff, and N. Pearlman, *Phys. Rev.* **94**, 1415 (1954).
[125] J. M. Ziman, *Phil. Mag.* [8] **1**, 191 (1956); **2**, 292 (1957).

calculations different. The Fermi energy ζ is strongly dependent on temperature and the requirement of simultaneous conservation of energy (14.9) and wave vector (14.4a) restrict the possible electron states in the summation of (14.10) over $\mathbf{k}$.

If $E = \hbar^2k^2/2m$, in which m is an effective mass, and $\omega = vq$, the values of $\mathbf{k}$ which satisfy both (14.4a) and (14.9) for a given value of $\mathbf{q}$ lie on the following surface of revolution in $\mathbf{k}$ space:

$$q - q_0 = 2k \cos \alpha \tag{19.1}$$

in which α is the angle between $\mathbf{q}$ and $\mathbf{k}$ and $q_0 = 2mv/\hbar$. Since $|\cos \alpha|$ cannot exceed unity, the smallest admissible value of k is given by

$$k_0 = \tfrac{1}{2}|q - q_0| \tag{19.2}$$

that is, a wave q cannot interact with electrons of wave number less than k_0 or energy less than

$$E_0 = \frac{\hbar^2\omega^2}{8mv^2} + \tfrac{1}{2}mv^2 - \tfrac{1}{2}\hbar\omega. \tag{19.3}$$

It is convenient to define a characteristic temperature

$$T_s = \frac{mv^2}{2K} \tag{19.4}$$

which would be about 0.3°K if $v = 3 \times 10^5$ cm/sec and m is the equal to the mass of a free electron.

After integration over the resonance factor, (14.10) and (14.11) become

$$\frac{1}{\tau_{pe}} = \frac{4C^2mV}{18\pi MGv\hbar^2} \int_{k_0}^{\infty} \left(\frac{1}{e^{\epsilon} + 1} - \frac{1}{e^{\epsilon+x} + 1} \right) k \, dk \tag{19.5}$$

where $\epsilon = (E - \zeta)/KT$ and $x = \hbar\omega/KT$. This becomes

$$\frac{1}{\tau_{pe}} = \frac{4C^2m^2V}{18\pi MGv\hbar^4} KT \log \left\{ \frac{e^x(e^{\epsilon_0} + 1)}{e^{\epsilon_0+x} + 1} \right\}. \tag{19.6}$$

If ϵ_0 is large and negative (that is, if $\zeta > E_0$ and $\zeta - E_0 \gg KT$), the factor $\log [e^x(e^{\epsilon} + 1)(e^{\epsilon_0+x} + 1)^{-1}]$ simply becomes x, and we revert to the case of a metal (14.12). In other cases, however, (19.6) must be evaluated differently, and one must consider the fact that ζ is a function of temperature and E_0 is a function of the phonon frequency. The important phonon frequencies also depend upon temperature. In general (19.6) can only be evaluated numerically. Ziman has performed such calculations and gives curves of $<\tau_{pe}(T)>$, the value of τ_{pe} averaged over all

phonon frequencies by means of the variational expression (6.14). He finds that $<\tau_{pe}>$ increases with increasing T if $T > T_s$, has a minimum about T_s, and increases again with decreasing T if $T < T_s$. If $T < T_s$, there are two cases: either $T_s < \zeta_0/K$, where ζ_0 is the Fermi energy at absolute zero, and τ_{pe} is given again by (14.12), or $T_s > \zeta_0/K$. In the latter case only the high-energy tail of the electron distribution contributes to the scattering by phonons, and τ_{pe} is increased by a factor of order $\exp[(KT_s - \zeta_0)/KT]$.

Thus the case of particular interest is $T > T_s$, for in that case τ_{pe} increases with T. The reason for this increase is twofold: ζ is negative and decreases with increasing T; E_0 increases with T (as T^2, if $T \gg T_s$). Consider the extreme case in which Boltzmann statistics apply (ζ negative and $|\zeta/KT| \gg 1$), so that $e^{\zeta/KT} \propto (KT)^{-\frac{3}{2}}$, and in which the phonons have the frequency $2KT/\hbar$. From (19.3)

$$\epsilon_0 = \frac{T}{4T_s} + \frac{T_s}{T} - 1 - \frac{\zeta}{KT} \tag{19.7}$$

while

$$\log\left\{\frac{e^x(e^{\epsilon_0}+1)}{e^{\epsilon_0+x}+1}\right\} \simeq e^{-\epsilon_0} \propto (KT)^{-\frac{3}{2}} e^{-T/4T_s} e^{-T_s/T} \tag{19.8}$$

so that

$$\tau_{pe} \propto T^{\frac{1}{2}} e^{T/4T_s} \tag{19.9}$$

if $T \gg T_s$ and increases as T is increased. If $T > \theta$, however, the phonons have frequency $K\theta/\hbar$,

$$\epsilon_0 = \frac{\theta^2}{16T_sT} + \frac{T_s}{T} - \frac{\theta}{T} - \frac{\zeta}{KT} \tag{19.10}$$

as pointed out by Stratton,[126] and $\tau_{pe} \propto e^{\theta^2/16T_sT}$. At high temperatures the scattering by electrons is negligible compared with other scattering mechanisms.

Since the scattering by electrons in the impurity band can account in principle for an increase of the average mean free path $\kappa/3Sv$ with temperature, Carruthers *et al.*[75] interpreted the observed T^4 dependence of the conductivity of one of their specimens (2.3×10^{18} carriers per cm^3 at room temperatures) in terms of this mechanism. In this case one would expect $\kappa/3Sv$ to increase again as T is lowered below T_s. No sign of such a reversal of the behavior at low temperatures was found down to 0.3°K. Instead κ varied as $T^{3.8}$ over a range from 0.3°K upward.[127] Thus it would appear that the effective electron mass m for that impurity

[126] R. Stratton, *Phil. Mag.* [8] **2**, 422 (1957).

[127] J. A. Carruthers and J. F. Cochran, *Proc. 5th Intern. Conf. Low Temperature Phys., Madison* No. 7-3 (1957).

band is not much larger than the free electron mass. This may be considered surprising; however, not enough is known about the structure of impurity bands to make a detailed comparison with Ziman's theory possible. It would appear, however, that the scattering of phonons by the electrons of the impurity band is an important resistive mechanism in the case of heavily doped, deformed, and irradiated semiconductors, as well as in other irradiated dielectric solids. The possibility of such a scattering mechanism, which can produce a thermal resistance having various temperature dependences, makes it imperative to use caution when attempting to interpret the thermal resistance in terms of various imperfections according to the scheme of Table I.