

# Theory of Lattice Thermal Conductivity: Role of Low-Frequency Phonons

P. G. Klemens<sup>1</sup>

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The lattice thermal conductivity arises from contributions by phonons of all frequencies. The mean free path  $l(\omega)$  is limited mainly by three-phonon interactions, and  $l(\omega) \propto \omega^{-2}T^{-1}$ , where  $\omega$  is the phonon frequency, and  $T$  is the absolute temperature. Since the spectral specific heat varies as  $\omega^2$ , the spectral thermal conductivity is independent of frequency, and low frequencies play a larger role than they do in the heat content. The effect of additional scattering processes due to defects must be compared to intrinsic scattering, not just at the highest frequency, but over the full spectral range. This enhances the resistance due to grain boundaries and large obstacles, and reduces the effect of point defects. Some typical examples are discussed. The role of low-frequency phonons may be even further enhanced if longitudinal low-frequency phonons have their interaction with other phonons reduced by wave vector conservation. Such modes would then contribute substantially to the overall thermal conductivity, and this contribution would be sensitive to grain size and to large-scale defects. However, the mean free path must be consistent with ultrasonic attenuation data. This enhanced sensitivity may be observable.

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## 1. INTRODUCTION

The vibrations of the atoms in a crystal can be described by a superposition of plane wave normal modes, ranging in frequency from the ultrasonic to the infrared regime. At high temperatures, the thermal equilibrium vibrational properties are dominated by the modes of highest frequency, but the lattice thermal conductivity depends on the behavior of waves at all frequencies,

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<sup>1</sup>Department of Physics and Institute of Materials Science, University of Connecticut, Storrs, Connecticut 06268, USA.

since the low-frequency modes, though few in number, have a larger mean free path.

It is the purpose of this paper to discuss the consequences of the enhanced role of the low-frequency modes. These include a smaller sensitivity of the thermal conductivity to point defects than would have been expected if most of the heat had been carried by the highest-frequency modes, and a larger effect due to extended defects and free electrons, which scatter lattice waves of low frequency. Finally, the conductivity may be sensitive to the behavior of a small group of low-frequency longitudinal modes of very large mean free path, thus causing an even greater sensitivity to grain size in polycrystalline materials, and to extended defects.

## 2. HEAT CONDUCTION BY LATTICE WAVES

The lattice waves that transport heat are characterized by their polarization  $j$  and their wave vector  $\mathbf{q}$ . The frequency of each wave is a function of  $\mathbf{q}$  and  $j$ , and  $\omega_j(\mathbf{q})$  depends on the nature of the crystal structure, the interatomic forces, and the atomic masses. For small values of  $q$  or  $\omega$ , the lattice waves become elastic waves in the corresponding continuum, and  $\omega$  is proportional to  $q$  for fixed direction and given polarization. In this limit, the number of normal modes in the frequency interval  $\omega, d\omega$ , is proportional to  $\omega^2$ . In the Debye approximation, this density of modes is assumed to hold at all frequencies up to a cutoff frequency  $\omega_D$  (Debye frequency), dropping abruptly to zero for  $\omega \geq \omega_D$ . The specific heat per unit volume of the solid can be written

$$C = \int_0^{\omega_D} C(\omega) d\omega = \frac{9}{a^3} k \int_0^{\omega_D} (\omega^2/\omega_D^3) d\omega \quad (1)$$

where  $a^3$  is the atomic volume, and  $k$  is the Boltzmann constant.

If we associate with each normal mode a mean free path or attenuation length  $l(\omega)$ , assumed to be a function of frequency  $\omega$ , then the lattice thermal conductivity can be written as

$$\lambda = \int K(\omega) d\omega = \frac{1}{3} \int C(\omega) v l(\omega) d\omega \quad (2)$$

where  $v$  is the average velocity of lattice waves, assumed for simplicity to be the same for all modes [1].

## 3. INTRINSIC THERMAL CONDUCTIVITY

The mean free path is limited by anharmonic processes (leading to an intrinsic mean free path  $l_i$ ) and by defects and boundaries, which also scatter

lattice waves. Anharmonic processes arise from terms in the potential energy as a function of strain which are higher than quadratic. The most important such terms are cubic; in the lowest order of perturbation theory, they lead to interactions amongst groups of three lattice modes (three-phonon interactions). The intrinsic mean free path can be shown [1] to be of the form

$$1/l_i(\omega, T) = 2\gamma^2(T/T_0)(\omega^2/\nu\omega_D) \quad (3)$$

Here  $\gamma$  is the Grüneisen constant, and  $T_0 = \mu a^3/k$ , where  $\mu$  is the shear modulus.

Substituting Eq. (3) into Eq. (2) and noting that  $a^3\omega_D^3 = 6\pi^2\nu^3$ , we obtain for the intrinsic thermal conductivity  $\lambda_i$ ,

$$K_i(\omega) = (2\pi\gamma)^{-2}(kT_0/\nu T)\omega_D \quad (4)$$

which is independent of  $\omega$ , and

$$\begin{aligned} \lambda_i &= \int K_i(\omega) d\omega = K_i\omega_D \\ &= (2\pi\gamma)^{-2}(kT_0/\nu T)\omega_D^2 \end{aligned} \quad (5)$$

Except for a numerical coefficient, which arises from the numerical coefficient in Eq. (3), Eq. (5) is equivalent to the well-known formula of Leibfried and Schlömann [2]. Equation (5) can be put into the form

$$\lambda_i = \frac{1.61}{\gamma^2} \left(\frac{k}{h}\right)^3 \frac{Ma\theta^3}{T} \quad (6)$$

where  $h$  is the Planck constant, and  $M$  is the atomic mass. The Debye temperature  $\theta$  is defined by  $h\omega_D/2\pi k$ . In the Leibfried-Schlömann formula, the factor 1.61 is replaced by 3.81. We used the identity  $kT_0 = M\nu^2$ . The Leibfried-Schlömann theory has been carefully compared to thermal conductivity data in a recent review by Slack [3]. For the present discussion, Eq. (6) can be regarded as a reasonable fit for simple structures.

The fact that  $K_i(\omega)$  is independent of  $\omega$  implies that all frequency intervals (but not all normal modes) contribute equally to the intrinsic conductivity  $\lambda_i$ , in contrast to the energy content, to which all modes make equal contributions, so that the energy content is dominated by the highest frequencies or shortest waves. In the lattice thermal conductivity, the entire spectral range is important.

The greater weight given to low-frequency modes is fortunate for theoreticians, since most of the scattering rates are calculated at low frequencies and then extrapolated to high frequencies. Since low and intermediate

frequencies matter most in the conductivity integral, Eq. (5), this procedure has some validity.

At high temperature  $l_i(\omega, T)$  becomes so short that one has to question the adequacy of perturbation theory and to doubt the  $T^{-1}$  dependence of the mean free path. Thus in a typical case when  $T_0 = 50,000$  K,  $\gamma = 2$ ,  $\omega_D = 4 \times 10^{13} \text{ s}^{-1}$ , and  $v = 3 \times 10^5 \text{ cm/s}$ , one finds  $l_i(\omega_D) = 3 \times 10^{-8} \text{ cm}$  at  $T = 1500$  K. The theory must therefore fail for modes of the highest frequency just below the melting point of most solids. Even the average mean free path

$$\bar{l} = 3\lambda/Cv = 3l_i(\omega_D) \quad (7)$$

is only about  $10 \text{ \AA}$ . But since  $l_i \propto \omega^{-2}$ ,  $l_i$  is less than  $10 \text{ \AA}$  only if  $\omega > 0.6\omega_D$ , and these modes contribute only 40% to the conductivity. If  $10 \text{ \AA}$  were a minimum mean free path, the mean free path of the high-frequency modes would no longer scale as  $T^{-1}$  but would remain constant, and  $\lambda_i$  would vary not as  $T^{-1}$  but as  $T^{-0.6}$  above 1500 K. However,  $\lambda_i$  would not be independent of temperature, as one would have expected from similar considerations based on the average mean free path  $l$ .

Although the theory predicts both  $K(\omega)$  and therefore  $\lambda_i$  to vary as  $T^{-1}$ , this assumes the solid to remain at constant volume. Since solids expand with increasing temperature, and since the thermal conductivity decreases with increasing volume (or increases with pressure),

$$(T/\lambda) d\lambda/dT = -(1 + n) \quad (8)$$

where

$$n = - \frac{d \ln \lambda}{d \ln V} \cdot \frac{d \ln V}{d \ln T} \quad (9)$$

and where  $V$  is the volume. Typically  $d \ln \lambda/d \ln V \simeq -7$  to  $-8$  [4], and  $d \ln V/d \ln T = 0.03$  at 1000 K, so that  $n = 0.2$  and increases roughly linearly with  $T$ , owing to the variation of the second factor. Another contribution to  $n$  may come from quartic anharmonicities, but since one would expect these processes to be weaker than cubic anharmonicities by a factor of order  $T/T_0$ , their contribution to  $n$  is expected to be an order of magnitude smaller [5].

#### 4. EFFECT OF IMPERFECTIONS

Lattice waves are also scattered by crystal defects with a mean free path  $l_D(\omega)$ , and to a first approximation,

$$1/l(\omega, T) = 1/l_i(\omega, T) + 1/l_D(\omega) \quad (10)$$

The second term is itself additively composed of contributions from various defects. The additivity holds for each frequency separately, and since the various scattering probabilities in Eq. (10) have different frequency dependences, this does not imply an additivity of the corresponding thermal resistivities. Point defects have a scattering cross-section that varies as  $\omega^4$  at low frequencies, while extended defects, such as colloid inclusions and grain boundaries, scatter independently of frequency. Other defects, such as dislocations or thin laminar defects, fall between these two extremes.

Consider the case when there are point defects as well as large obstacles, as in the case of some oxides following intense neutron irradiation [6]. Point defects reduce  $K(\omega, T)$  mainly at the highest frequencies, extended defects mainly at the lowest frequencies, while  $K(\omega, T)$  is virtually unaffected over a wide range of intermediate frequencies. Each defect causes a decrease in the thermal conductivity  $\lambda$ ,

$$\lambda = \lambda_i - \delta\lambda_p - \delta\lambda_{EX} \quad (11)$$

and  $\delta\lambda_p$ , the decrease due to point defects, and  $\delta\lambda_{EX}$ , due to extended defects, are independent of each other. Equation (11) also differs from the additive resistance approximation.

Neutron irradiated alumina [7] has large defects, seen under the electron microscope, of 50 Å diameter, in a concentration of  $3 \times 10^{17} \text{ cm}^{-3}$ , so that  $(l_{EX})^{-1} = 5.9 \times 10^4 \text{ cm}^{-1}$ . Defining a dimensionless parameter  $X_0$  by

$$X_0^2 = l_i(\omega_D, T)/l_{EX} \quad (12)$$

so that  $l_i$  and  $l_{EX}$  are equal at a frequency  $X_0\omega_D$ , one can show that

$$\frac{\delta\lambda_{EX}}{\lambda_i} = X_0 \tan^{-1} \left( \frac{1}{X_0} \right) \simeq \frac{\pi}{2} X_0 \quad (13)$$

since  $X_0$  is usually small. In the present case of alumina at 1000 K, using an empirical value for  $l_i$ ,  $X_0 = 0.077$  and  $\delta\lambda_{EX}/\lambda_i = 0.12$ . Since observed reductions on strong neutron irradiation are around 50%, the excess reduction is probably due to point defects.

Let us assume a vacancy concentration  $c = 0.02$ , which makes the volume occupied by the vacancies equal to that of the large obstacles. Using an expression due to Ratsifaritana [8] for the vacancy cross-section, i.e.,

$$1/l_p = 9c \frac{a^3 \omega^4}{4\pi v^4} \quad (14)$$

one finds

$$\delta\lambda_p/\lambda_i = 1 - \frac{\omega_0}{\omega_D} \tan^{-1} \frac{\omega_D}{\omega_0} \quad (15)$$

where  $\omega_0$  is defined by  $l_p(\omega_0) = l_i(\omega_0, T)$ , so that

$$\omega_0^2 = \frac{4\gamma^2}{3\pi} \frac{T}{T_0 c} \omega_D^2 \quad (16)$$

With  $c = 0.01$ ,  $T_0 = 100,000$  K, and  $T = 1000$  K, we find  $\omega_0 = 0.92 \omega_D$  and  $\delta\lambda_p/\lambda_i = 0.24$ . If we had included "normal" (wave-vector conserving) three-phonon processes, the reduction would have been about 60% larger. The simplified theory predicts  $\delta\lambda/\lambda_i = 36\%$  at 1000 K, somewhat less than the observed reduction of 50%.

Another case of interest is the reduction in  $\lambda$  in a fine-grained material due to grain-boundary scattering. If the mean free path in alumina is thus limited to  $5 \times 10^{-4}$  cm,  $X_0$  of Eq. (12) becomes 0.014 at 1000 K, and  $\delta\lambda/\lambda_i = 0.022$ . Similarly, at 300 K,  $X_0 = 0.026$  and  $\delta\lambda/\lambda_i = 0.041$ . These are then the fractional changes in lattice thermal conductivity between a fairly fine-grained and a coarse-grained polycrystalline material. It is doubtful whether this small effect can be observed, particularly as there may be a small radiative component which would also increase with grain size. However, the effect of grain size is considerably larger than one would have expected by comparing  $l_{EX}$  with  $l_i(\omega_D, T)$ , for at this highest frequency, the change is only  $X_0^2$ , and thus an order of magnitude smaller.

## 5. LONGITUDINAL PHONONS

The preceding discussion was based on Eq. (3), which in turn is based on the assumption that all modes interact mainly with modes of the highest frequency  $\omega_D$ . This is correct for transverse modes, but may not be correct for longitudinal modes. Longitudinal low-frequency modes cannot interact with high-frequency modes and still conserve both frequency and wave vector (i.e., phonon energy and phonon momentum) in a three-phonon process. This was already pointed out by Pomeranchuk [9]. If the conservation conditions are satisfied, longitudinal phonons have a longer mean free path, given by [10],

$$1/l_i(L, \omega, T) = 6\pi^2\gamma^2 \frac{T}{T_0} \left(\frac{\omega}{\omega_D}\right)^2 \frac{\omega^2}{\omega_D v} \quad (17)$$

unless limited by defects or four-phonon processes. This would have two consequences: the additional heat transported by the longitudinal modes

would modify the temperature dependence of  $\lambda_i(T)$ , and the thermal conductivity would be more sensitive to other scattering mechanisms which are important at low frequencies, particularly grain boundaries and large defects.

Comparing this with Eq. (3), we find that longitudinal modes would make an additional contribution to  $K_i(\omega)$  and thus to  $\lambda$  in the frequency range  $\omega < \omega_D/5$ . Also,  $K_i(L, \omega)$  would diverge at low frequencies as  $\omega^{-2}$ , so that  $\lambda$  would be sensitive to the relatively weak processes that are needed to remove the divergence, such as four-phonon interactions, extended defects or grain boundaries, or perhaps even free electrons.

Whether this sensitivity to grain boundaries, etc., is real depends on whether three-phonon interactions are indeed restricted by wave-vector conservation, or whether the finite mean free path of the high-frequency modes relaxes this restriction and allows forbidden interactions to occur. At very low (ultrasonic) frequencies the latter is true, and longitudinal ultrasonic waves are attenuated by interacting with high-frequency modes almost as strongly as transverse waves. Under these conditions, the attenuation is given by the Akhieser theory [11], (see also [10]),

$$1/l_{AK}(\omega) = \frac{1}{10} \frac{\omega^2}{\omega_D v} \quad (18)$$

independently of temperature. Thus longitudinal waves are attenuated not very differently from Eq. (3) at  $T/T_0 \sim 10^{-2}$ , i.e. around 500 to 1000 K.

However, Eq. (18) applies only if  $\omega l_i(\omega_D)/v \gtrsim 1$ . Using Eq. (3) again, we find that Eq. (18) ceases to hold and must be replaced by Eq. (17) at higher frequencies, i.e., if

$$\omega > \omega_D 2\gamma^2 \frac{T}{T_0} \quad (19)$$

At 300 K, with  $\gamma = 2$ , this critical frequency is  $\omega_D/20$ . Above that frequency, the mean free path of longitudinal modes is given by Eq. (17); hence it exceeds that of Eq. (3) in the range 0.05–0.2  $\omega_D$ . If these estimates are correct, the longitudinal modes have a long mean free path (up to  $10^{-3}$  cm), and their contribution to  $\lambda$  is both appreciable and sensitive to grain boundary scattering. However, this argument depends on the choice of the multiplicative constant in Eq. (17). Whether longitudinal modes of low frequency (say around  $\omega_D/20$ ) play indeed a significant role in heat transport at room temperature is still an open question, requiring both theoretical and experimental investigation. At high temperatures (say 1000 K), their role is probably small; below room temperature, it is undoubtedly significant.

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