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# Heat conduction in solids by phonons

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## ABSTRACT

The theory of heat conduction by phonons is reviewed, with emphasis on ordinary and high temperatures. The spectral contribution to the conductivity is discussed for various resistive processes. These include anharmonic interactions, scattering by point defects, by extended defects, by grain boundaries and by inclusions. Phonons are also absorbed and reemitted by two-level systems such as spins and mechanically bistable centers.

## INTRODUCTION

Heat in solids can be regarded as the energy due to an assembly of excitations, and heat transport is due to those excitations which are mobile, principally electrons and phonons. As in the kinetic theory of gases, the thermal conductivity can be expressed in the form

$$\lambda = \sum_i C_i \, v_i \, \ell_i / 3 \tag{1}$$

where $C_i$ is the specific heat per unit volume due to excitations of type i, $v_i$ is their velocity (or group velocity in the case of waves) and $\ell_i$ the mean free path or attenuation length.

Phonons are quanta of energy of the various vibrational modes of the solid. Some of these modes are localised, some are not. For purposes of heat transport one needs only to consider the latter modes, which are progressive waves (elastic or lattice waves). Each such mode is specified by its angular frequency $\omega$, its wave-vector $\underline{q}$ and by an index j which denotes polarisation and branch (optic or acoustic). The thermal energy of each mode consists of an integral number of phonons, behaving like particles, each of energy $\hbar\omega$, quasi-momentum $\hbar\underline{q}$, and moving with the group velocity $\underline{v} = \partial\omega/\partial\underline{q}$. In principle all branches contribute to the energy transport, but frquently the major contribution comes from the three acoustic branches.

One can set up a Boltzmann equation for the phonons, as in

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the kinetic theory of gases, and obtain for the lattice thermal conductivity (e.g. Klemens 1959)

$$\lambda = (1/3) \sum_j \int C_j(\omega)\ v_j(\omega)\ \ell_j(\omega)\ d\omega \tag{2}$$

where $C_j(\omega)d\omega$ is the contribution to the specific heat per unit volume from modes of frequency $\omega, d\omega$ and the j'th polarisation branch. The mean free path $\ell(\omega)$ is generally a function of frequency as well as temperature T.

In an ideal crystal, i.e. one which has perfectly regular structure, which has no external boundaries, and which has harmonic interatomic forces, the lattice waves are normal modes. The energy content of each lattice waves, or the number of phonons in it, are a constant of motion, and the mean free path is infinite. A finite thermal conductivity is the result of energy interchange between the waves, which are now normal modes only approximately, owing to the departures from this ideal. External boundaries scatter phonons from one mode into another, as do structural imperfections of the crystal lattice. Even in a perfect crystal there are anharmonicities: terms in the potential energy as function of displacement of higher power than quadratic. All these effects cause energy to be interchanged between lattice waves, limiting their mean free path. A mean free path which is limited only by anharmonicities is the intrinsic mean free path $\ell_i(\omega, T)$.

## INTERACTION PROCESSES

The potential energy of a solid contains not only harmonic terms (bilinear in the strains or relative displacements of the atoms) but also terms of higher order. Except possibly near the melting point, the major contribution comes from cubic terms. Including these in the equation of motion as a perturbation, there results an exchange of energy, always between three normal modes. In the quantum-mechanical treatment, these become three-phonon interactions: a phonon each from two modes combine (are annihilated) to form or create a phonon in a third mode, or vice versa. Symbolically

$$(\underline{q}, j) + (\underline{q}', j') \longleftrightarrow (\underline{q}'', j'') \tag{3}$$

where $(\underline{q}, j)$ denote the wave-vector and polarisation index of one of the modes. As for any non-linear process involving three oscilators, these interactions must satisfy the frequency condition

$$\omega + \omega' = \omega'' \tag{4}$$

as well as a wave-vector interference condition (phase matching in space)

$$\underline{q} + \underline{q}' = \underline{q}'' \pm \underline{b} \tag{5}$$

In a uniform continuous medium, $\underline{b}=0$, but in a discrete crystal lattice, where the anharmonicity resides in discrete linkages, there are also processes for which $\underline{b}$ is a reciprocal lattice vector, leading to combined three-phonon Bragg scattering interactions. The former are termed normal or N-processes, the latter are Umklapp or U-processes (German: umklappen, to flip over).

The intrinsic thermal reistance is due to the U-processes only, because a temperature gradient increases continuously the net momentum of the phonon gas, so that a steady state can be attained only by processes which change the net momentum. Nevertheless, the N-processes do play an indirect role: they can transfer momentum between groups of modes which differ in the rate at which momentum is obliterated by other, resistive processes, i.e. by U-processes but also by defect scattering. It is the role of the N-processes, acting in conjunction with the resistive processes, which makes the solution of the phonon Boltzmann equation difficult, particularly at low temperatures.

If this complication is disregarded, one can derive by perturbation theory (Klemens 1969) the reciprocal mean free path for the three-phonon processes. At temperatures comparable to or higher than the Debye temperature $\Theta$

$$1/\ell_i(\omega,T) = 2\gamma^2\,(kT/\mu a^3)\,\omega^2/v\,\omega_D \qquad (6)$$

where $\mu$ is the shear modulus, $a^3$ the atomic volume, $\omega_D=k\Theta/\hbar$ and $\gamma$ is a parameter describing the strength of the anharmonicity (Grüneisen constant); also k and $\hbar$ are the Boltzmann constant and the reduced Planck constant.

At temperatures well below the Debye frequency, the theory is more complicated and

$$1/\ell_i(\omega,T) = \phi(\omega,T)\,\exp(-T_0/T) \qquad (7)$$

where $\phi$ is a slowly-varying function of $\omega$ and T, while $kT_0=\hbar\Delta\omega_Z$, where $\Delta\omega_Z$ is the difference in frequency between the lowest and the next-to-lowest modes of different polarization at the zone boundary: $\underline{\Theta}/T_0$ usuallyranges between 2 and 3. In this review the emphasis will be on ordinary and high temperatures, so that (6) will be used for $\ell_i$.

Scattering by external boundaries in single crystals, and by grain boundaries in polycrystalline solids, limit the mean free path to a value $\ell_B$, either close to the shortest linear dimension of the specimen, or near the average grain diameter.

Of the various defects which scatter phonons, point defects are the strongest at high frequencies, while extended defects are more important at low frequencies, as are boundaries. Writing for defects

$$1/\ell_d \propto \omega^n \qquad (8)$$

then n=4 for point defects, n=3 for cylindrical defects, n=2 for sheets, and n=0 for boundaries and for inclusions which are larger than the phonon wave-length and thus present a geometrical shadow.

Dislocations, in virtue of their long-range strain field, cannot be considered to be cylinders, except at the highest phonon frequencies. For sessile dislocations n=1, for fluttering dislocations low frequency phonon scattering is considerably enhanced (Anderson 1983).

If we regard point defects as regions of volume $a^3$ in which the density and the elastic moduli are changed, so that locally the phonon velocity v is changed by $\Delta v$,

$$1/\ell_p(\omega) = c(a^3/\pi v^4)\,(\Delta v/v)^2\,\omega^4 \qquad (9)$$

where c is the fractional concentration of point defects (Klemens 1955). If there is some correlation in the position of point defects, this must be multiplied by a factor proportional to the Fourier inversion of the correlation function. In the case of substitutional impurities and mass difference $\Delta M$, $\Delta v/v = -\Delta M/2M$. Distortion makes a contribution which either reinforces or reduces the scattering. Since distortions limit the solid solubility, there is an upper limit to their effect (Klemens 1986). For vacancies, $\Delta v/v = -3/2$.

## INTRINSIC CONDUCTIVITY

One can now substitute the expressions for the mean free path into (2). In view of the major role played by the mean free path and the uncertainties in its estimate, one is usually justified in using a simple Debye model for the specific heat, particularly as this model is a good representation of the low-frequency part of the spectrum, and as the low frequencies play a relatively large role in the phonon thermal conductivity, as will be seen below.

According to the Debye theory, after summing over the three polarisation branches,

$$C(\omega) = 9k\,a^{-3}\,(\omega^2/\omega_D^{\,3})\,x^2\,e^x\,(e^x-1)^{-2} \qquad (10)$$

where $x=\hbar\omega/kT$. At high temperatures $C(\omega)\propto\omega^2$ (classical limit) up to the highest frequency $\omega_D$. At low temperatures $C(\omega)$ falls rapidly below the classical limit at frequencies above $2kT/\hbar$.

At ordinary temperatures and above, where the classical limit can be used, $C(\omega)\,\ell_i(\omega)$ is independent of frequency, because $\ell_i(\omega)\propto\omega^{-2}$. Thus while the highest frequencies make the major contribution to the specific heat and to the thermal energy, equal frequency intervals make equal contributions to the intrinsic thermal conductivity

$$\lambda_i = (1/3)\int_0^{\omega_D} C_i(\omega)\,\ell_i(\omega)\,v\,d\omega = (3/2\gamma^2)(v^2/\omega_D)(\mu/T) \qquad (11)$$

Since $v\propto a\omega_D$, the intrinsic thermal conductivity, which varies as 1/T, is higher the higher the Debye temperature or Debye frequency, but also depends on the shear modulus, which is less variable than the Debye temperature. Tightly bound crystals of low atomic mass have the highest intrinsic thermal conductivity.

## EFFECT OF IMPERFECTIONS

To first order, the various imperfection reduce the mean free path, making additive contributions to the interaction probability per unit path length. Thus

$$1/\ell(\omega) = 1/\ell_i(\omega,T) + 1/\ell_p(\omega) + 1/L + \dots \qquad (12)$$

where the terms are due to intrinsic scattering, point defects, boundary scattering, and there may be terms due to other defects, spins and other two-level systems and interaction with free electrons and holes.

Because contributions to the thermal conductivity come from a wide spectral range, and because of the wide difference of the frequency dependence of the contributions to $1/\ell(\omega)$, one cannot treat the thermal resistivity as being additively composed of the intrinsic, point defect and boundary resistivities. It is sometimes a better approximation to treat the reduction in conductivity due to point defects and grain boundaries as independent of each other, since point defects are most important at high frequencies, grain boundaries at low frequencies.

### *Point Defects*

Since $\ell_p(\omega) \propto \omega^{-4}$ and $\ell_i(\omega) \propto \omega^{-2}T^{-1}$, point defects are more important at frequencies $\omega > \omega_p$, where $\omega_p$ is the frequency at which $\ell_p = \ell_i$. Using (6) and (9)

$$\omega_p^2 = (kT/\mu a^3 c)\,(\Delta v/v)^{-2}\,(2\pi\gamma^2 v^3/a^3\omega_D) \qquad (13)$$

With $\ell(\omega) = (1/\ell_i + 1/\ell_p)^{-1}$, one readily sees that $\lambda_p$, the conductivity in the presence of point defects, is given by

$$\lambda_p/\lambda_i = (\omega_p/\omega_D)\,\arctan(\omega_D/\omega_p) \qquad (14)$$

The stronger the point defect scattering, the lower is $\omega_p$, and the lower is the thermal conductivity.

Since $\omega_p \propto T^{\frac{1}{2}}$, and $\lambda_i \propto T^{-1}$, the thermal conductivity varies as $(cT)^{-\frac{1}{2}}$ in the limit of strong point defect scattering. Equation (14) holds for all concentrations, even when $\omega_p > \omega_D$. In that case the intrinsic and the point defect resistivities combine additively, but in general this is not true.

### *Grain Boundaries*

The limit placed on the phonon mean free path by the specimen dimensions is important only at low temperatures. The thermal conductivity of crystals with 2 to 5 mm diameter typically reaches a maximum between 15 and 30K (for diamond this is 70K), and is size dependent at lower temperature. In thin films and polycrystalline solids the term 1/L is important at lowest phonon frequencies even at ordinary and elevated temperatures. One can define a frequency

$\omega_B$ such that $\ell_i(\omega_B,T)=L$, i.e. from (6)

$$\omega_B^2 = (\mu a^3/2\gamma^2 kT)\ v\omega_D/L \tag{15}$$

so that $\omega_B \propto (TL)^{-\frac{1}{2}}$. Roughly speaking, this frequency-independent scattering removes phonons of frequency below $\omega_B$ from the conduction process. The conductivity is reduced by an amount $\Delta\lambda_B$, where

$$\Delta\lambda_B/\lambda_i \simeq \tfrac{1}{2}\pi\,\omega_B/\omega_D \tag{16}$$

Now $\omega_B \propto T^{-\frac{1}{2}}$, whereas from equation (13) $\omega_p \propto T^{\frac{1}{2}}$. Comparing typical magnitudes for grain boundary scattering with $L=5\mu m$, with $\mu a^3/k=50{,}000K$, $\gamma=2$, $v=4\times10^5 cm/s$ and $\omega_D=4\times10^{13}s^{-1}$, $\omega_B/\omega_D=0.02$ at 300K and 0.01 at 1,200 K.

If there is point defect scattering as well as grain boundary scattering, as in random solid solution polycrystalline ceramics, then at ordinary temperatures $\omega_p$ is well above $\omega_B$. For example, with the same material constants and 20% solutes of $\Delta v/v=1$, and if $a^3=1\times10^{-23}cm^{-3}$, equation (13) yields $\omega_p/\omega_D=0.17$ at 300K and 0.3 at 1,200K. Thus at ordinary and high temperatures $\omega_B$ lies well below $\omega_p$. In such cases the reduction due to grain boundaries $\Delta\lambda_B$ and the reduction due to point defects $\Delta\lambda_p=(\lambda_i-\lambda_p)$ are independent of each other, and

$$\lambda = \lambda_i - \Delta\lambda_p - \Delta\lambda_B \tag{17}$$

However, at lower temperatures, say at 70K, $\omega_B/\omega_D=0.04$ while $\omega_p/\omega_D=0.08$. In this case there is a frequency range where all three scattering processes are important and the reductions in conductivity are no longer additive. If $\omega_B$ and $\omega_p$ are comparable, the thermal conductivity is almost independent of temperature. This may be the case in fine-grained materials or in thin films with strong point defect scattering.

### *Inclusions and Radiation Damage*

Small inclusions, which are however larger than or comparable to the phonon wave-length, scatter idependently of frequency with a mean free path L' given by their geometrical cross-section, i.e.

$$1/L' = N/\pi r^2 \tag{18}$$

where N is the number of inclusions per unit volume, and r is their radius. Since the fractional volume occupied by the inclusions is $4\pi r^3N/3$, smaller inclusions are more effective for the same fractional volume. The inclusions may be colloidal particles, small foreign crystallites, or damage clusters in the case of radiation damage. It is assumed that these inclusions are randomly distributed throughout each crystal or grain; inclusions concentrated at the grain boundaries would merely affect grain boundary scattering just slightly. Also phonons of very low frequency, such that $\omega < v/r$, have a much lower scattering cross-section than that given by (18).

Radiation damage produces vacancies and interstitials in equal number. These tend to recombine, but if there is a sink for one species, e.g. at grain boundaries, the other species will tend to cluster into small colloids (or cavities respectively), while some will remain atomically dispersed. The effect of radiation damage on thermal conductivity can be modelled in terms of inclusions and point defects. The inclusions can be related to macroscopic volume increases (Klemens 1984, Rohde and Schulz 1990).

## OTHER PROCESSES

This simplified overview, even though it excludes low temperatures, does by no means exhaust the factors to be considered in a quantitative analysis.

For example, the effects of normal or momentum-conserving processes were disregarded. These processes move phonon-momentum from the low frequencies, where scattering is weak, to high frequencies, where scattering is stronger. They thus reduce the mean free path of low frequency phonons and are the more important the stronger the frequency dependence of $\ell(\omega)$. However, since they themselves affect $\ell(\omega)$, the problem of determining $\ell(\omega)$ or solving the phonon Boltzmann equation is equivalent to solving an integral equation. The approximation of Callaway (1959) is widely used . It is based on the principle that normal processes do not change the total momentum of the phonon gas. The stronger the point defect scattering, or any other process which is very frequency dependent, the more important do the normal processes become.

At high temperatures, when there are only point defects and the intrinsic interaction, and if $\omega_p/\omega_D < \frac{1}{2}$, one can account for N-processes roughly by halving $\lambda_i^{P}$(Klemens, White and Tainsh 1962).

Sometimes one must consider a scattering center which can be in one of two distinct energy levels, with energy seperation $\hbar\omega_o$, and which can make a transition from one level to the other with the emission or absorption of a phonon of frequency $\omega_o$. These levels may be spin states, or they may correspond to two distinct configurations of a molecular group in the crystal lattice, such as Si-O-Si in silica. If all centers have the same splitting $\hbar\omega_o$, the only phonons affected will be those in a narrow frequency band about the resonance frequency. Even though the interaction is much stronger than point defect scattering, since the perturbation is linear in the stain of the lattice modes rather than bilinear, the effect on the thermal conductivity is small and proportional to the line width $\Delta\omega$ : the fractional reduction in thermal conductivity is of order $\Delta\omega/\omega_D$. This model applies to spins , where $\Delta\omega_o$ is increased in the paramagnetic state because of the random influence of neighboring spins, and it describes the reduction in thermal conductivity of crystals with magnetic ions at the Curie or Néel temperature (Klemens 1989).

Amorphous solids also contain two-level centers with a wide distribution of resonance frequencies, in fact so wide that over the important frequency range the number of two-level centers in the resonance frequency range $\omega_0 d\omega_0$ is independent of $\omega_0$. This results in a phonon mean free path proportional to $\omega^{-1}$ and a thermal conductivity proportional to $T^2$ (Zeller and Pohl 1971) The other scattering mechanism important in glasses is a very strong point defect scattering (Anderson 1981). Since each microscopic element of volume $a^3$ is randomly oriented, and since the phonon velocity in the corresponding crystalline form depends on orientation, one can estimate $(\Delta v/v)^2$ in equation (9). However, the effective value of $a^3$ is larger than an atomic volume, because there are structural correlations (Klemens 1985).

That the two-level mechanism persists even at high temperatures can be seen by comparing the thermal conductivity at 500K of vitreous silica (1.6 $W\text{-}m^{-1}\text{-}K^{-1}$) with that of a 50:50 Ge-Si alloy (6 $W\text{-}m^{-1}\text{-}K^{-1}$). The point defect scattering should be the same to within a factor 2: both systems have the same average value of $(\Delta v/v)^2$ of about 0.15 (Klemens 1985). The difference is that in the case of Ge-Si phonons with $\omega < \omega_p$ are limited only by intrinsic interactions (equation 6) while in vitreous silica the mean free path is much shorter due to the two-level interactions.. The nature of the two-level center is probably a double-well potential of the oxygen atom in some of the Si-O-Si links, randomised by the strains of the irregular structure of the surroundings. Bistable centers also affect other properties at low temperatures, such as specific heat, dielectric loss, ultrasonic attenuation and thermal expansion (Phillips 1981), and are frequently met with not only in amorphous solids, but also in crystals with radiation damage and molecular impurities, and even in alloys with size misfit. However, the exact nature of these centers and their resonance frequency distribution has yet to be elucidated in the majority of case.

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