Thermal conductivity of thermoelectrics

Andrei Novitskii, Academic Research Center for Energy Efficiency, NUST MISIS
Email: novitskiy@misis.ru
@anovitzkij

Let's recall what is the thermal conductivity?

$$\kappa = -\frac{\vec{Q}}{\vec{\nabla}T}$$

where $\vec{Q}$ is the heat flow rate (or heat flux) vector across a unit cross section perpendicular to $\vec{Q}$ and T is the absolute temperature. In solids the thermal conductivity for various excitations (electrons, phonons, photons, etc.) can be generalized to

$$\kappa = \frac{1}{3}\sum_{\alpha} C_\alpha v_\alpha \Lambda_\alpha$$

where the summation is over all excitations, denoted by α. In general, this equation gives a good phenomenological description of the thermal conductivity, and it is practically very useful for order of magnitude estimates.[1]

In general, total thermal conductivity κ_{tot} is equal to

$$\kappa_{tot} = \kappa_{lat} + \kappa_{el}$$

where κ_{lat} is the lattice contribution, and κ_{el} is the electronic contribution.

In general, the electronic component of the thermal conductivity has contributions from electrons, holes, and the bipolar conductivity κ_b, which arises at high temperatures when both holes and electrons are present and contributing to the electrical conductivity and is largest when the conductivity of minority and majority carriers is equal. Considering the Wiedemann-Franz law $\kappa_{el}/\sigma = LT$ (where σ is the electrical conductivity, and L is the Lorenz number) and the Lorenz number for the intrinsic region, the electronic of κ_{tot} can be written as:

$$\kappa_{el} = \kappa_{el,n} + \kappa_{el,p} + \kappa_b = \kappa_{el,n} + \kappa_{el,p} + \left(\alpha_p - \alpha_n\right)^2 \frac{\sigma_n \sigma_p}{\sigma} T$$

In the intrinsic regime, the quantity $\alpha_p - \alpha_n$ is proportional to $E_g/k_B T$ and thus κ_b can be large.

$$\kappa_{lat} = -\frac{\vec{Q}}{\vec{\nabla}T} = \frac{1}{3}\sum_{\vec{q}}\hbar\omega_{\vec{q}}v_g^2\tau_c\frac{\partial N_{\vec{q}}^0}{\partial T}$$

where $\vec{q}$ is the wave vector, $\omega_{\vec{q}}$ is the phonon frequency, v_g is the phonon group velocity, τ_c is the phonon scattering relaxation time and $N_{\vec{q}}^0$ the equilibrium phonon distribution function:

$$N_{\vec{q}}^0 = \frac{1}{e^{\frac{\hbar\omega_{\vec{q}}}{k_B T}} - 1}$$

At this point approximations need to be made and Debye theory should be used: an average phonon velocity v (approximately equal to the velocity of sound in solids) is used to replace for all the phonon branches, and the phonon velocities are the same for all polarizations. Thus, summation can be replaced by the integral.[1]

Lattice thermal conductivity

$$\kappa_{lat} = \frac{k_B}{2\pi^2 v_m} \left(\frac{k_B T}{\hbar}\right)^3 \int\limits_0^{\theta_D/T} \tau_c(x) \frac{x^4 e^x}{(e^x - 1)^2} dx$$

where $x = \hbar\omega/k_B T$, θ_D is the Debye temperature equals to $\hbar\omega_D/k_B$ with ω_D is the Debye frequency (maximum frequency of atoms in solids):[1]

$$3N = \int\limits_0^{\omega_D} f(\omega)d\omega = \int\limits_0^{\omega_D} \frac{3\omega^2}{2\pi^2 v_m^2} d\omega$$

Average sound velocity:

$$v_m = \left[\frac{1}{3}\left(\frac{1}{v_l^3} + \frac{2}{v_t^3}\right)\right]^{-1/3}$$

with the longitudinal v_l and transverse v_t velocities expressed as

$$v_l = \sqrt{\left(K + \frac{4}{3}G\right)\Big/ d} \text{ and } v_t = \sqrt{\frac{G}{d}}$$

where K is the bulk modulus, G is the shear modulus and d is the density.

Assuming material as amorphous one, the minimum lattice thermal conductivity can be estimated as:[2]

$$\kappa_{lat,\min} = \left(\frac{\pi}{6}\right)^{1/3} k_B V_{at}^{-2/3} (2v_t + v_l) \left(\frac{T}{\theta_D}\right)^2 \int\limits_0^{\theta_D/T} \frac{x^3 e^x}{(e^x - 1)^2} dx$$

At high temperatures, this expression simplifies to:

$$\kappa_{lat,\min} = \frac{1}{2}\left(\frac{\pi}{6}\right)^{1/3} k_B V_{at}^{-2/3} (2v_t + v_l) = 1.21 k_B \frac{v_m}{V_{at}^{2/3}}$$

here $v_m \approx \frac{1}{3}(2v_t + v_l)$ and V_{at} is the average volume per atom.

$V_{at} = \frac{1}{n_{at}}$, where $n_{at} = \frac{\#atoms}{unit\ cell}\frac{1}{V_{unit\ cell}}$.

On the other hand, the minimum thermal conductivity can be estimated assuming $\kappa_{lat,\min} = k_B v_m \Lambda_{\min}$ when $\Lambda_{\min}$ (mean phonon free path) close to the lattice parameter and considering that the speed of sound is directly related to the elastic properties of material:

$$\frac{1}{3}(2v_t + v_l) \approx A\sqrt{\frac{E}{d}}$$

$$\kappa_{lat,\min} = 0.87 k_B V_{at}^{-2/3}\sqrt{\frac{E}{d}} \approx 0.93 k_B V_{at}^{-2/3}\frac{1}{3}(2v_t + v_l) \approx 0.93 k_B \frac{v_m}{V_{at}^{2/3}}$$

where d is the density and E is the Young's modulus. A constant has a value of $0.80 - 0.94$.[3]

In the extreme scattering limit where the vibrational modes no longer transport heat like propagating waves (propagons or classical phonons) but diffusively and are called diffusons. The minimum thermal conductivity from such heat diffusion can be estimated to be:[4]

$$\kappa_{lat,\min} \approx \frac{k_B}{2\pi^3 v_m^3 V_{at}^{2/3}} \left(\frac{k_B T}{\hbar}\right)^4 \int\limits_0^{0.95\theta_D/T} \frac{x^5 e^x}{(e^x - 1)^2} dx$$

At high temperatures:

$$\kappa_{lat,\min} \approx 0.76 k_B V_{at}^{-2/3} \frac{1}{3}(2v_t + v_l) = 0.76 k_B \frac{v_m}{V_{at}^{2/3}}$$
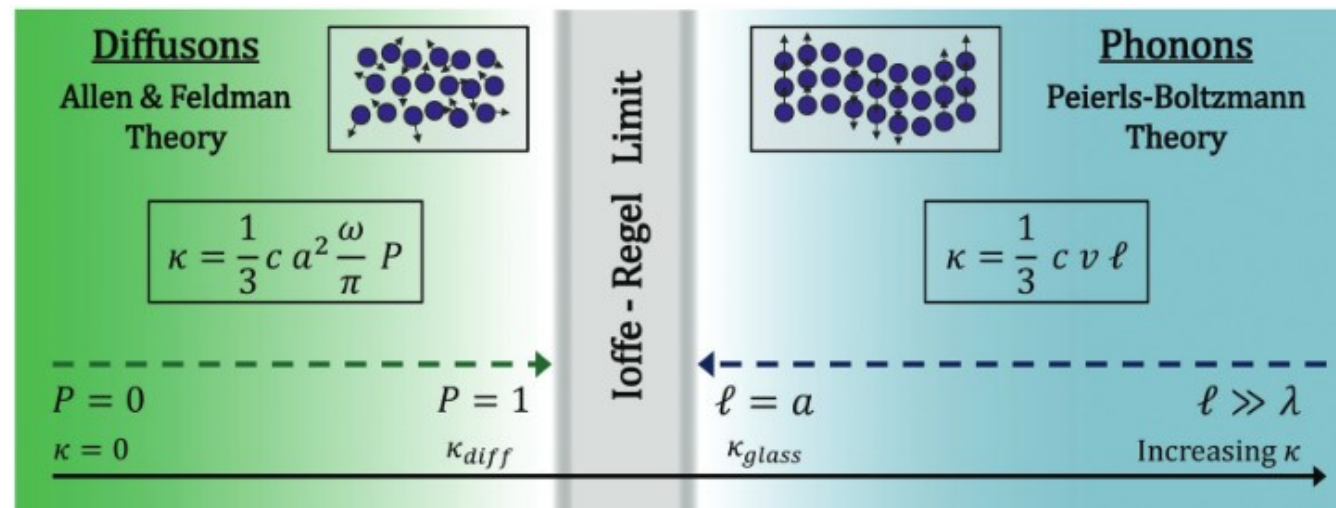
Assuming perfect crystal and only Umklapp processes limit the thermal conductivity Leibfried and Schlömann (1954) suggested:

$$\kappa_{lat} = \kappa_0 f\left(\frac{\theta_D}{T}\right)$$

where κ_0 is the thermal conductivity at θ_D and thus, $f\left(\frac{\theta_D}{T}\right) = 1$ when $\theta_D = T$ and:

$$f\left(\frac{\theta_D}{T}\right) \approx \frac{\theta_D}{T} \text{ at } T > \theta_D$$

$$f\left(\frac{\theta_D}{T}\right) \approx \left(\frac{\theta_D}{T}\right)^3 e^{\theta_D/bT} \text{ at } T \ll \theta_D$$

where b is a numerical parameter, not given accurately by the theory (an estimate of the factor b in the equation as being of the order of 2). b value is determined by the details of the energy spectrum and the structure of Brillouin zone.[5]

$$\kappa_0 = \frac{12}{5} 4^{\frac{1}{3}} \left(\frac{k_B}{h}\right)^3 \frac{\bar{M} \delta \theta_D^2}{\gamma^2}$$

here $\delta^3 = V_{at}$, γ is the acoustic-phonon Grüneisen parameter, which contains the effect of the anharmonic forces, $\bar{M}$ is the average atomic weight of atoms in the unit cell, θ_D is the Debye temperature:[5]

$$\theta_D = v_m \frac{h}{k_B} \left(\frac{3}{4\pi V_{at}}\right)^{1/3}$$

Grüneisen parameter can be calculated as follows:

$$\gamma = \frac{3}{2}\left(\frac{1 + v_p}{2 - 3v_p}\right)$$

where v_p is the Poisson's ratio:

$$v_p = \frac{1 - 2\left(v_t/v_l\right)^2}{2 - 2\left(v_t/v_l\right)^2}$$
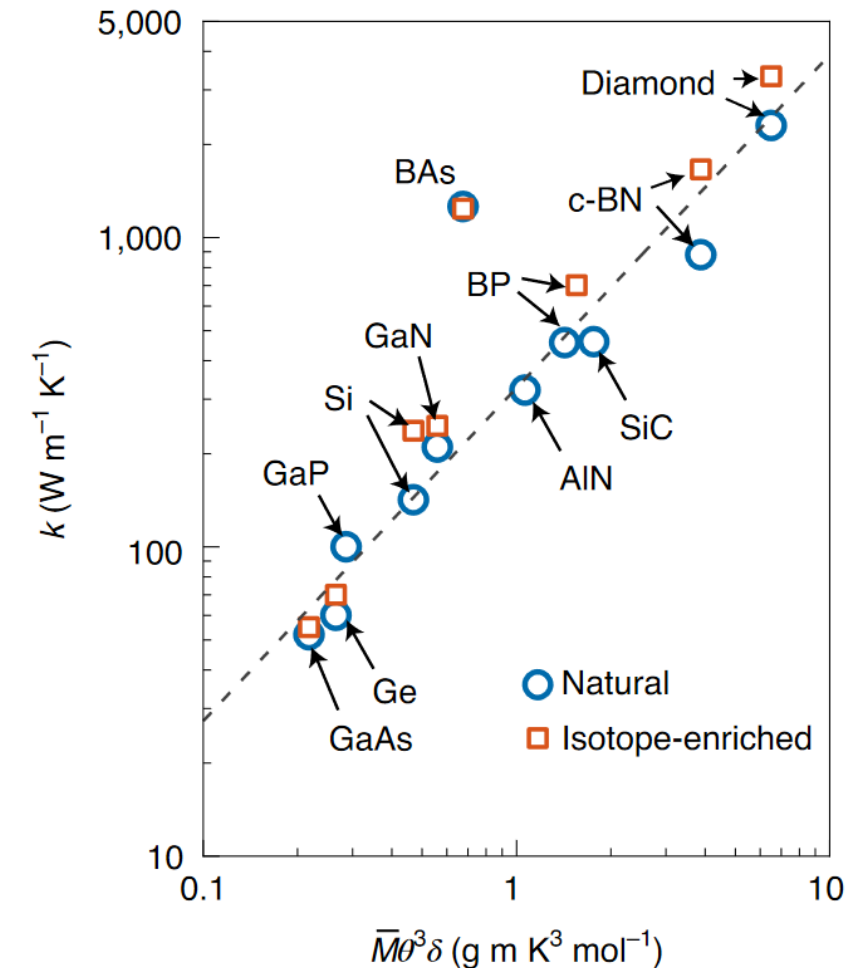
Fig. from X. Qian, J. Zhou, G. Chen, Nat. Mater. (2021)

Although Leibfried and Schlömann model was qualitatively correct, quantitatively it gave incorrect results. Around 1973 Slack proposed a correction for Leibfried and Schlömann model:[5–7]

$$\kappa_{lat} = A \left(\frac{k_B \theta_D}{\hbar}\right)^3 \frac{\overline{M}\delta}{\gamma^2 N_{Av} n^{5/3} T}$$

where N_{Av} is the Avogadro constant, n is the number of atoms in the unit cell (molecule). Here

$$A = \frac{0.849 \cdot 3\sqrt[3]{4}}{20\pi^3(1 - 0.514\gamma^{-1} + 0.228\gamma^{-2})}$$

Moreover, based on Leibfried and Schlömann model Slack also formulated a several rules for low thermal conductivity:[5–7]

(1) high mass of constituent atoms ($\overline{M}\delta\theta_D^3$ is maximized for light mass);

(2) weak interatomic bonding;

(3) complex crystal structure;

(4) high anharmonicity.

Conditions (1) and (2) means a low θ_D, condition (3) means high n, and condition (4) means high γ.

However, in complex materials optical branches and grain boundary scattering may also contributed to the lattice thermal conductivity, thus:[8]
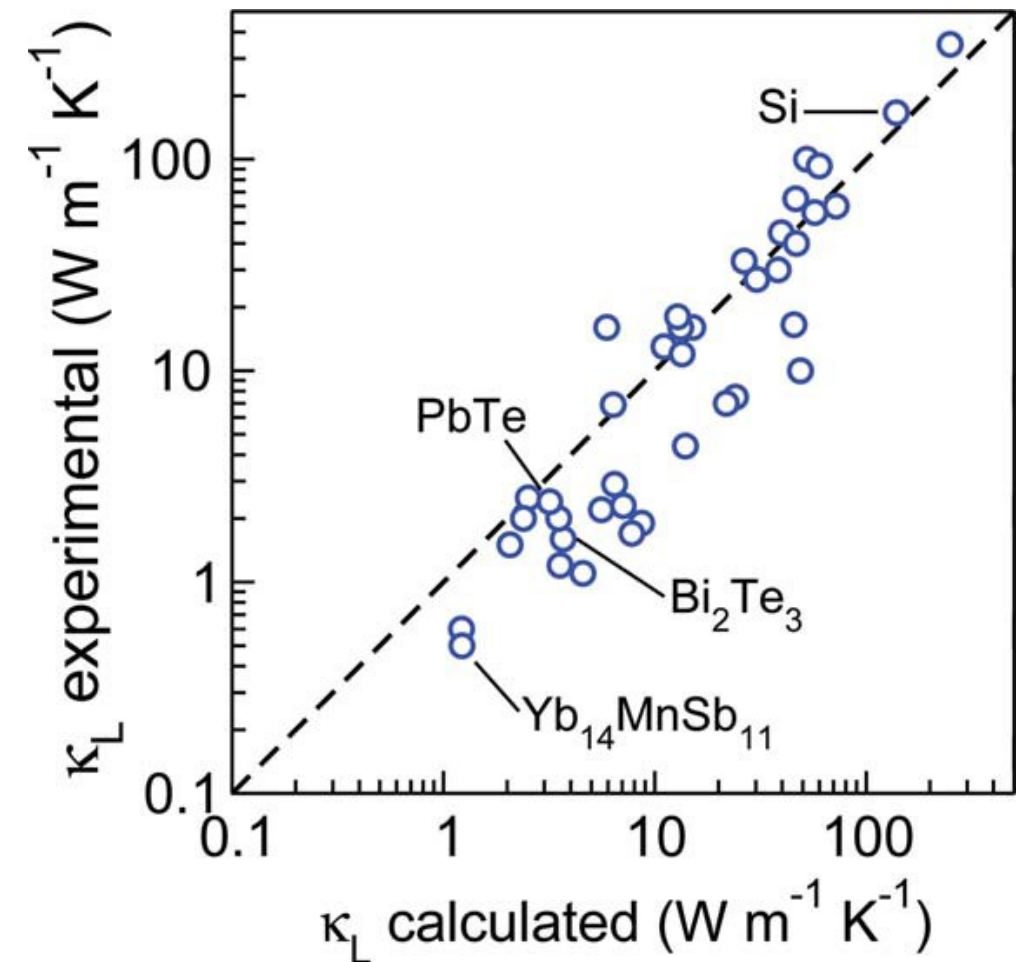
$$\kappa_{lat} = \kappa_U + \kappa_b + \kappa_o$$

where

$$\kappa_U = \frac{(6\pi^2)^{2/3}}{4\pi^2} \frac{\overline{M}v_m^3}{V_{at}^{2/3}\gamma^2 n^{1/3}T}$$

$$\kappa_b = k_B \frac{v_m L_g}{V_{at} n}$$

with L_g as grain size

$$\kappa_o = \frac{3k_B v_m}{2V_{at}^{2/3}} \left(\frac{\pi}{6}\right)^{1/3} \left(1 - \frac{1}{n^{2/3}}\right)$$
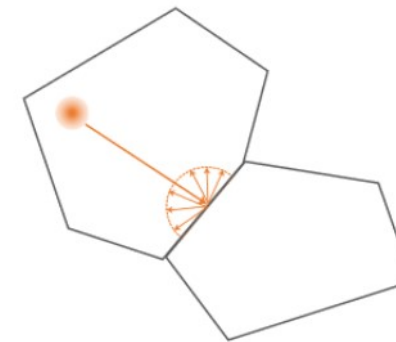
Lattice thermal conductivity. Debye model

$$\kappa_{lat} = \frac{k_B}{2\pi^2 v_m}\left(\frac{k_B T}{\hbar}\right)^3 \int\limits_0^{\theta_D/T} \tau_c(x)\frac{x^4 e^x}{(e^x - 1)^2}\,dx$$

Assuming scattering channels are independent of each other, κ_{lat} can be evaluated by Matthiessen's rule:

$$\frac{1}{\tau_c(x)} = \sum_i \frac{1}{\tau_i(x)}$$

The phonon scattering processes included in the Debye model are Umklapp processes. There exist, however, other non-resistive and total crystal-momentum-conserving processes that do not contribute to the thermal resistance but may still have profound influence on the lattice thermal conductivity of solids – Normal processes (N-processes).[1]
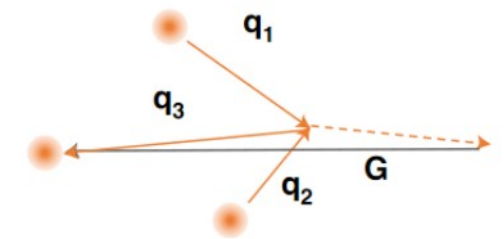

Boundary/interface scattering
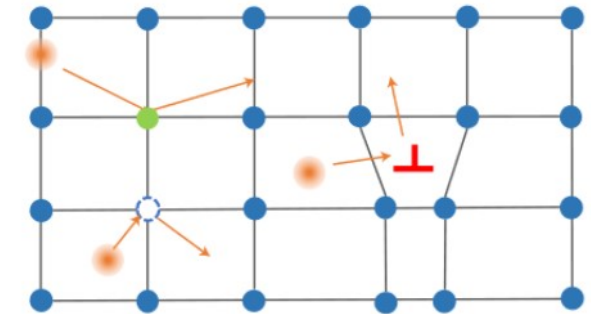
Defect, dislocation scattering
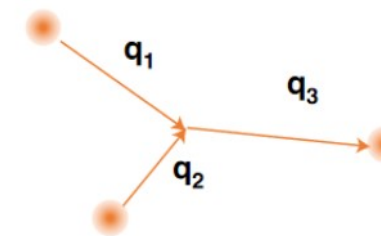
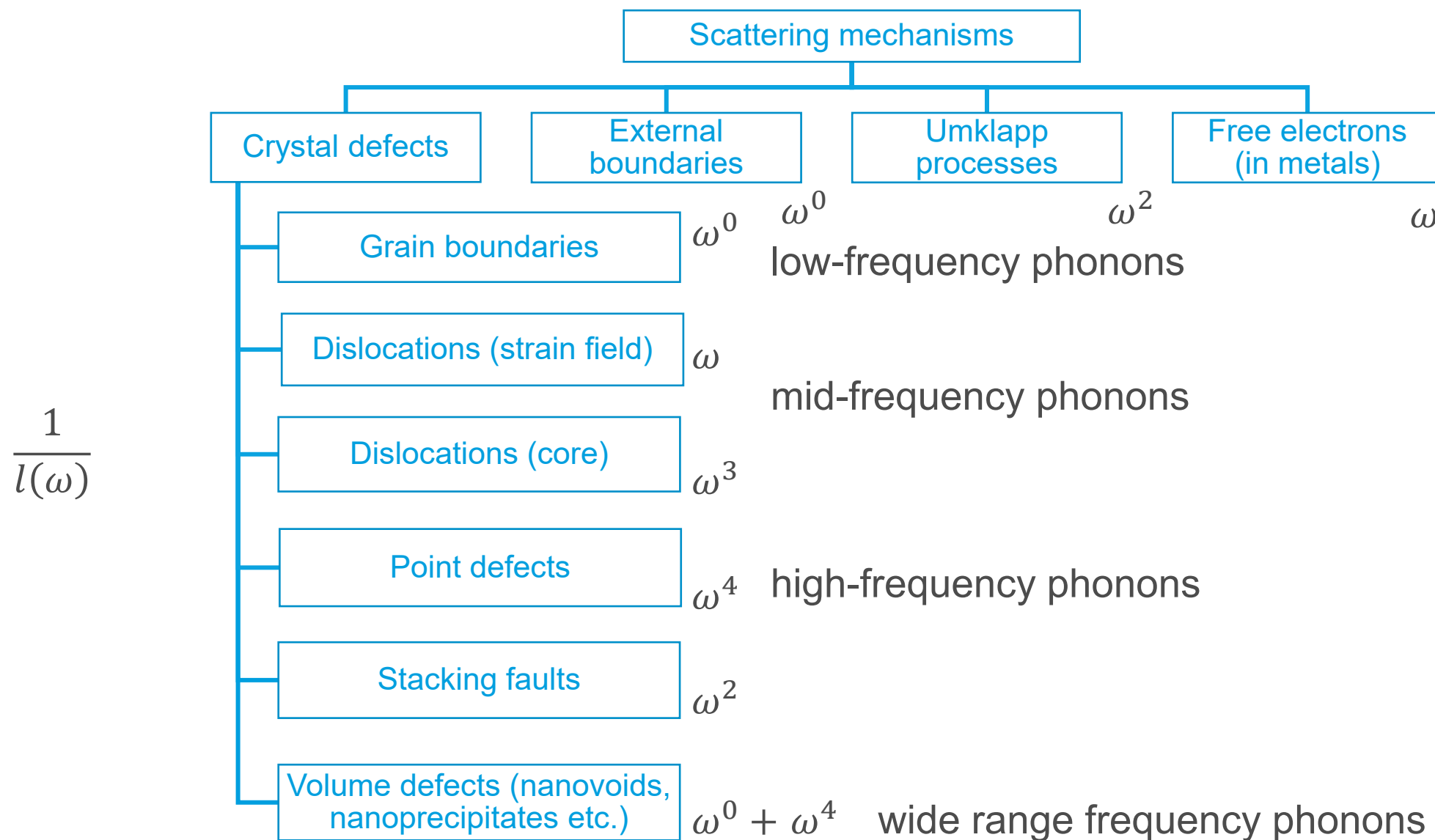Normal scattering

Umklapp scattering

Debye model considers only thermal resistance from Umklapp processes and thus is accurate for simulating the lattice thermal conductivity of materials with relatively low θ_D and simple crystal structures. Based on this model and relaxation time approximation, Callaway developed a phenomenological mathematical model,[1,9] which divided the effect of phonon scattering into several parts and can be written as $\kappa_{lat} = \kappa_1 + \kappa_2$. Here,

$$\kappa_1 = \frac{k_B}{2\pi^2 v_m}\left(\frac{k_B T}{\hbar}\right)^3 \int\limits_0^{\theta_D/T} \tau_c(x)\frac{x^4 e^x}{(e^x-1)^2}dx$$

$$\kappa_2 = \frac{k_B}{2\pi^2 v_m}\left(\frac{k_B T}{\hbar}\right)^3 \frac{\left(\int_0^{\theta_D/T}\frac{\tau_c(x)}{\tau_N(x)}\frac{x^4 e^x}{(e^x-1)^2}dx\right)^2}{\int_0^{\theta_D/T}\frac{\tau_c(x)}{\tau_N(x)\tau_{ph}(x)}\frac{x^4 e^x}{(e^x-1)^2}dx}$$

In this case $\tau_c^{-1}(x) = \tau_{ph}^{-1}(x) + \tau_N^{-1}(x)$, where τ_{ph} is the relaxation time for U-processes, $\tau_{ph}^{-1}(x) = \sum_i \tau_i^{-1}(x)$, and τ_N is the relaxation time for N-process.
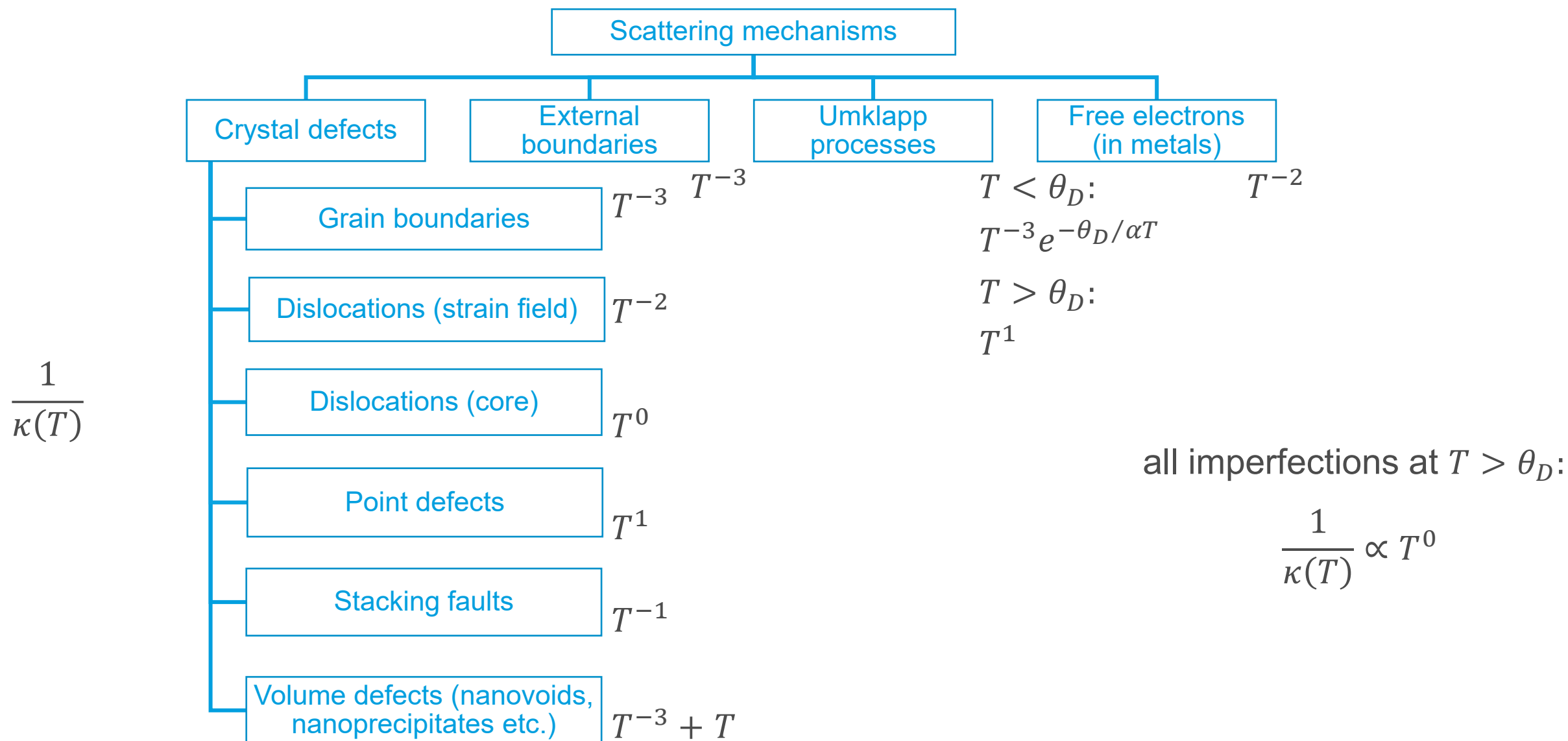
Lattice thermal conductivity. Scattering

Scattering mechanisms

Crystal defects

External boundaries ω^0

Umklapp processes ω^2

Free electrons (in metals) ω

$\dfrac{1}{l(\omega)}$

Grain boundaries ω^0 $\qquad$ low-frequency phonons

Dislocations (strain field) ω

$\qquad$ mid-frequency phonons

Dislocations (core) ω^3

Point defects ω^4 $\qquad$ high-frequency phonons

Stacking faults ω^2

Volume defects (nanovoids, nanoprecipitates etc.) $\omega^0 + \omega^4$ $\qquad$ wide range frequency phonons

For more details see Ref. [10,11].

Scattering mechanisms

Crystal defects | External boundaries | Umklapp processes | Free electrons (in metals)

$\dfrac{1}{\kappa(T)}$

Grain boundaries $\quad T^{-3} \quad T^{-3}$

Dislocations (strain field) $\quad T^{-2}$

Dislocations (core) $\quad T^0$

Point defects $\quad T^1$

Stacking faults $\quad T^{-1}$

Volume defects (nanovoids, nanoprecipitates etc.) $\quad T^{-3} + T$

$T < \theta_D:$ $\qquad\qquad T^{-2}$
$T^{-3} e^{-\theta_D / \alpha T}$

$T > \theta_D:$
T^1

all imperfections at $T > \theta_D$:

$$\dfrac{1}{\kappa(T)} \propto T^0$$

For more details see Ref. [10,11].

In summary,

$$\kappa_{lat} = \frac{k_B}{2\pi^2 v_m}\left(\frac{k_B T}{\hbar}\right)^3 \left(\int_0^{\theta_D/T} \tau_c(x)\frac{x^4 e^x}{(e^x-1)^2}dx + \frac{\left(\int_0^{\theta_D/T}\frac{\tau_c(x)}{\tau_N(x)}\frac{x^4 e^x}{(e^x-1)^2}dx\right)^2}{\int_0^{\theta_D/T}\frac{\tau_c(x)}{\tau_N(x)\tau_{ph}(x)}\frac{x^4 e^x}{(e^x-1)^2}dx}\right)$$

with $x = \hbar\omega/k_B T$ and $\tau_c^{-1}(x) = \tau_{ph}^{-1}(x) + \tau_N^{-1}(x)$.

In turn $\tau_{ph}^{-1}(x) = \sum_i \tau_i^{-1}(x) = \tau_U^{-1}(x) + \tau_{pd}^{-1}(x) + \tau_{gb}^{-1}(x) + \tau_{pe}^{-1}(x) + \tau_{dissl,strain}^{-1}(x) + \tau_{dissl,core}^{-1}(x) + \tau_{sp}^{-1}(x) + \cdots$.[1,11]

Important note: When the impurity level is significant and all phonon modes are strongly scattered by the resistive processes in a solid, then $\tau_N \gg \tau_{ph}$ and τ_c almost equal to τ_{ph}. Under this circumstance $\kappa_1 \gg \kappa_2$ and κ_{lat} is given by κ_1 since the *N*-processes are negligeable (Debye model). In the opposite extreme, when *N*-processes are the only phonon scattering processes, $\tau_N \ll \tau_{ph}$ and τ_c almost equal τ_N. The denominator of κ_2 then approaches 0, leading to infinite lattice thermal conductivity as expected because the *N*-processes do not give rise to thermal resistance.[1]

General form suggested for phonon-phonon normal scattering relaxation rate is given by

$$\tau_N^{-1} = A\omega^a T^b$$

where A is a constant independent of ω and T, $(a, b) = (1, 3)$ was recommended for materials with diamond structure, and $(a, b) = (1, 4)$ or $(2, 3)$ can be suggested for some group IV and III-V semiconductors.[1]

In 1929, Peierls suggested an exponential behavior of the Umklapp relaxation time

$$\tau_U^{-1} \propto T^n e^{\frac{\theta_D}{mT}}$$

with constants n and m on the order of 1. Based on the Leibfried and Schlömann model, Slack proposed the following form for Umklapp relaxation time considering the Grüneisen constant γ and the average atomic mass M in the crystal:

$$\tau_U^{-1} \approx B\omega^\alpha T^\beta e^{-\frac{\theta_D}{mT}}$$

where α, β and m are constants. Typically, α = 2, β can be 1 or 3 and m = 2 – 3. Other empirical values can also be used in order to obtain best fit to experimental data. Parameter B is related to the crystal properties:

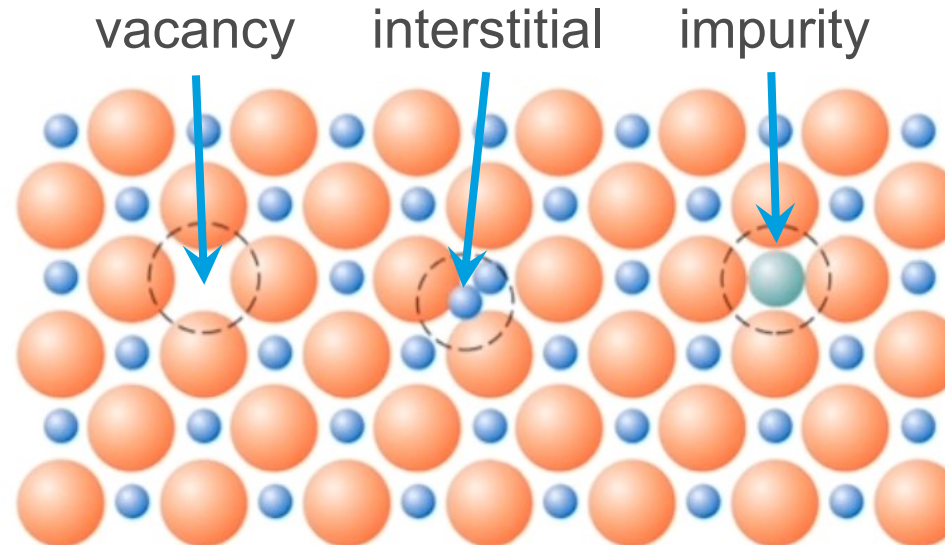$$B = \frac{\hbar \gamma^2}{\overline{M} v_m^2 \theta_D}$$

Klemens was the first to calculate the relaxation rate for phonon point-defect scattering where the linear dimensions of the defects are much smaller than the phonon wavelength.[12,13] Impurities and point defect scatter phonons with wavelengths similar in size to the defect due to strain (radius) and mass fluctuation as ω^4:

$$\tau_{pd}^{-1} = \frac{V_{at}}{4\pi v_m^3} \Gamma \omega^4$$

where Γ is the disorder scattering parameter:

$$\Gamma = \Gamma_M + \Gamma_S$$

A strain field modification has been described by Abeles as discussed later.[14,15]

vacancy   interstitial   impurity

The values of Γ_M and Γ_S can be calculated using the model from Abeles and Slack:[14,15]

$$\Gamma_M = \frac{\sum_{i=1}^n c_i \left(\frac{\overline{M_i}}{\overline{\overline{M}}}\right)^2 f_i^1 f_i^2 \left(\frac{M_i^1 - M_i^2}{\overline{M_i}}\right)^2}{\sum_{i=1}^n c_i}$$

$$\Gamma_S = \frac{\sum_{i=1}^n c_i \left(\frac{\overline{M_i}}{\overline{\overline{M}}}\right)^2 f_i^1 f_i^2 \varepsilon_i \left(\frac{r_i^1 - r_i^2}{\overline{r_i}}\right)^2}{\sum_{i=1}^n c_i}$$

$$\Delta M \qquad \Delta R$$
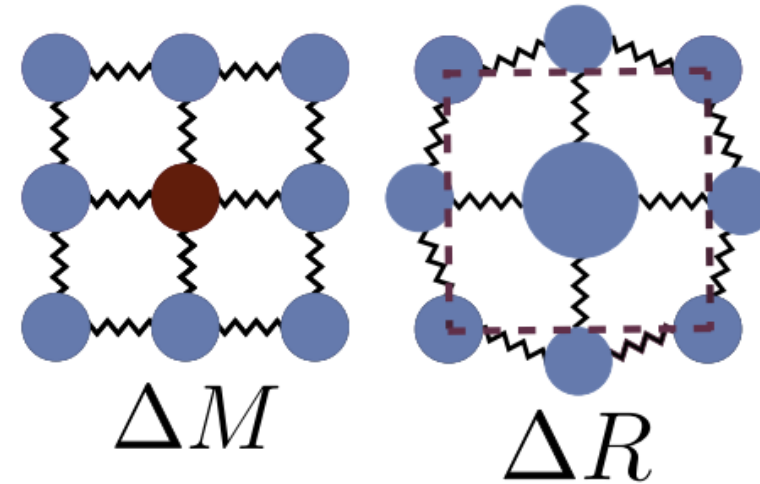
where n is the number of different crystallographic sublattice types in the lattice, c_i are the relative degeneracies of the respective sites, $\overline{\overline{M}}$ is the average atomic mass, f_i^k is the fractional occupation of the k-th atom on the i-th site, M_i^k and r_i^k are the atomic mass and radius of the k-th atom, ε_i is a function of the Grüneisen parameter.[14,15]

$$\varepsilon = \frac{2}{9}\left[(G + 6.4\gamma)\frac{1 + v_p}{1 - v_p}\right]^2$$

with G as a ratio between the contrast in bulk modulus and that in the local bonding length, for cubic crystals with covalent bonding (IV elements, III-V compounds) $G = 4$ and with ionic bonding (II-VI, I-VII compounds) $G = 3$.

$\overline{M_i}$ and $\overline{r_i}$ are the average atomic mass and radius on the i-th site, respectively:

$$\overline{M_i} = \sum_k f_i^k M_i^k$$

$$\overline{r_i} = \sum_k f_i^k r_i^k$$

Thus,

$$\tau_{pd}^{-1} = \frac{V_{at}}{4\pi v_m^3}\Gamma\omega^4 = \frac{V_{at}}{4\pi v_m^3}\left(\sum f_i\left(\frac{\Delta M_i}{M}\right)^2 + \varepsilon\sum f_i\left(\frac{\Delta r_i}{r}\right)^2\right)\omega^4$$

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The Klemens model predicts the ratio of the defective solid's lattice thermal conductivity to that of a reference pure solid ($\kappa_{lat}/\kappa_{lat}^0$), where the disorder scaling parameter u is related to the pure-lattice thermal-conductivity reference κ_{lat}^0, elastic properties of the host lattice through its speed of sound, the volume per atom, and a scattering parameter, which captures the lattice-energy perturbation at the defect site:[16,17]

$$\frac{\kappa_{lat}}{\kappa_{lat}^0} = \frac{\tan^{-1} u}{u} \qquad u^2 = \frac{\pi^2 \theta_D V_{at}}{h v_m^2} \kappa_{lat}^0 \Gamma$$

$(PbTe)_{1-x}(PbSe)_x$

$$B \propto \frac{\mu_w}{\kappa_{lat}}$$

$$\mu_H \propto \frac{N_0}{z(1-z)U^2}$$
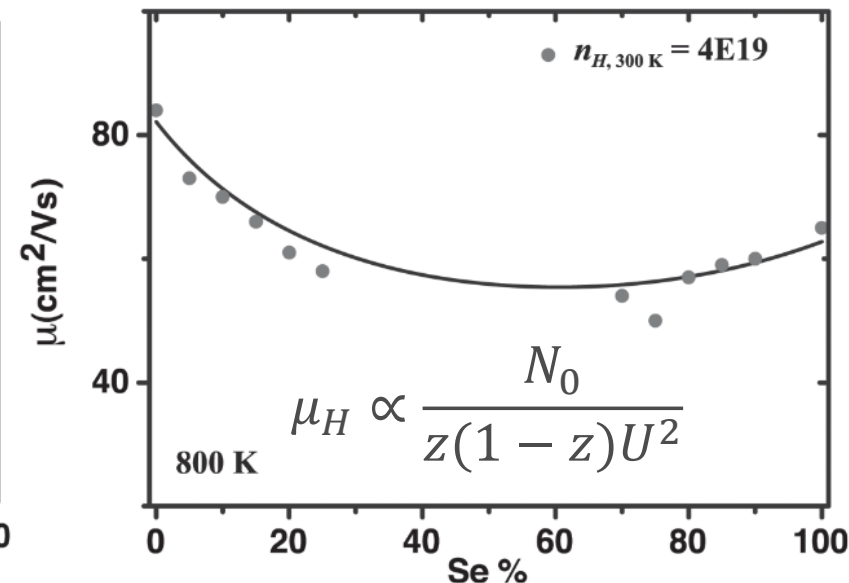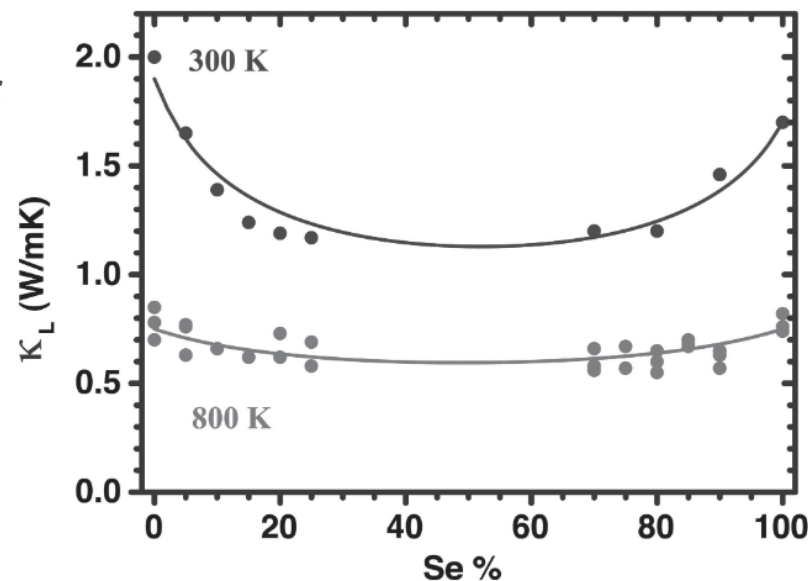
Vacancy or interstitial defects are extremely effective scatters not only because the mass difference is entire mass of the atom involved, but also because the bonds to neighboring atoms are either completely removed or formed. Thus, $\Delta M_i = M_i + 2M$ and $\Gamma = \Gamma_M + \Gamma_S + \Phi$. Φ is the vacancies scattering parameter, which can be calculated using similar to Γ_M expression including broken-bond term, as was proposed by R. Gurunathan *et al.*[15,17]
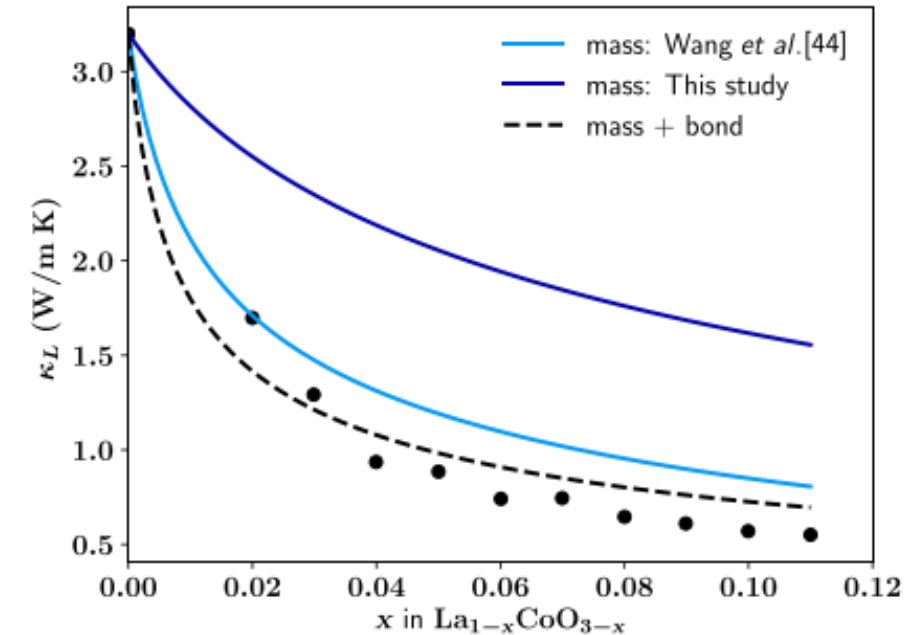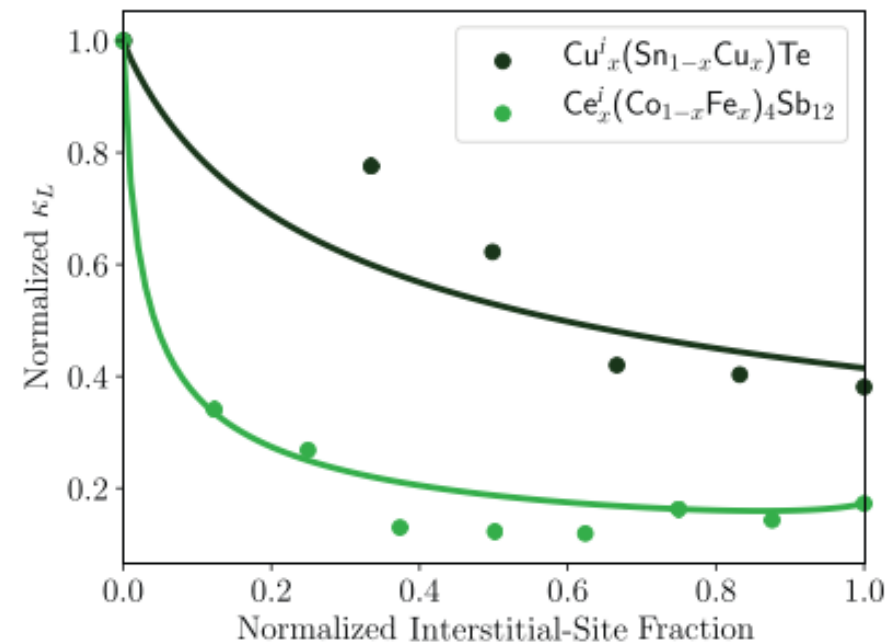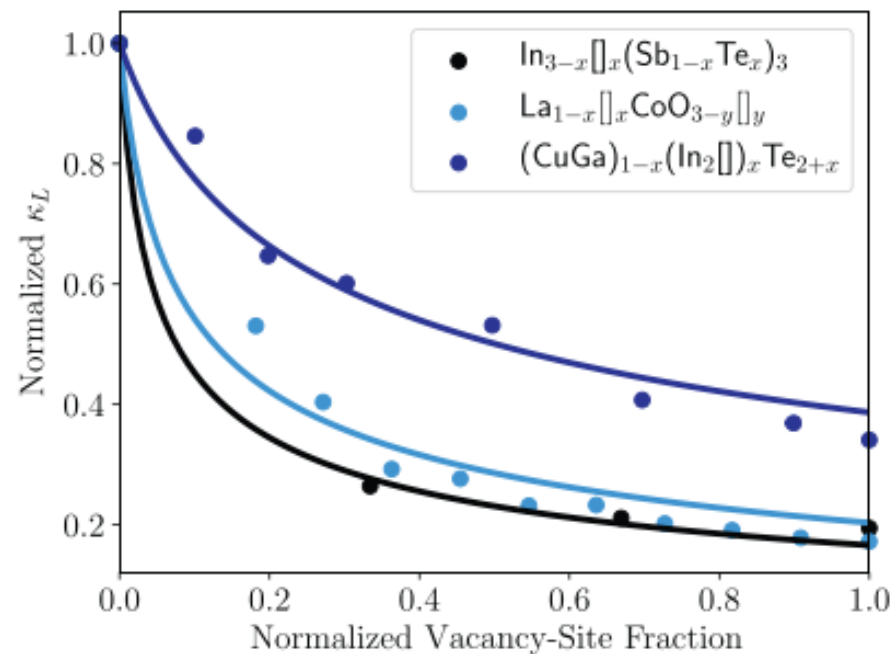
Phonon-boundary scattering

The phonon boundary scattering rate is independent of phonon frequency and temperature and with an assumption of purely diffuse scattering can be written as[1]

$$\tau_{gb}^{-1} = \frac{v_m}{L_g}$$

where L_g is the sample size for a single crystal or the grain size for a polycrystalline sample.

Phonon transporting heat

Diffuse Scattering at Interfaces

Phonon-dislocation scattering

For phonon-dislocation scattering, the effects of the core and from the surrounding strain field are separated:[1]

$$\tau_{dissl,core}^{-1} \propto N_D \frac{r^4}{v_m^2} \omega^3$$

and

$$\tau_{dissl,strain}^{-1} \propto N_D \frac{\gamma^2 B_D^2}{2\pi} \omega$$

where N_D is the number of dislocation lines per unit area, r is the core radius, and B_D is the Burgers vector of the dislocation.

strain field (compression)

dislocation

strain field (tension)

phonon wave
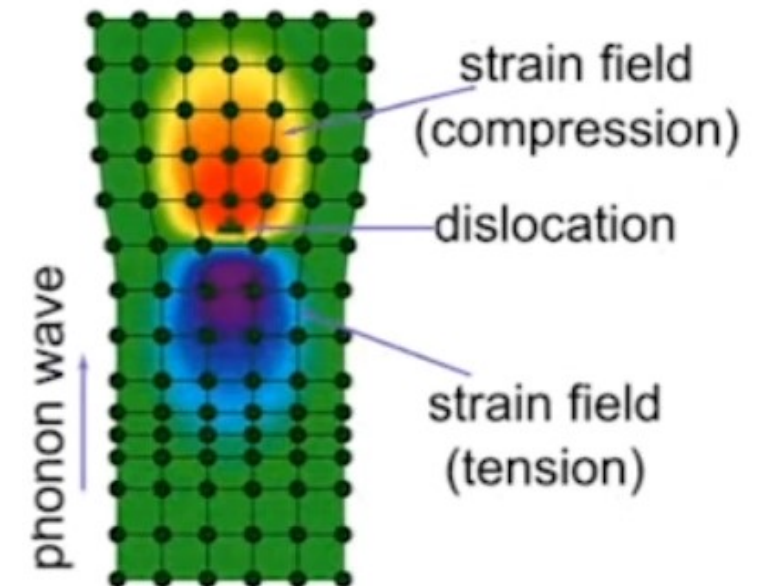
Other possible scattering mechanisms

- nonmagnetic phonon-resonance scattering $\tau_{res}^{-1} = \frac{C_{def}\omega^2}{\left(\omega^2 - \omega_0^2\right)^2}$, where C_{def} is a constant proportional to the concentration of the resonant defects and ω_0 is the resonance frequency. This formula accounted well for the observed low temperature dip in the thermal conductivity of clathrates and skutterudites;

- phonons-electrons scattering $\tau_{pe}^{-1} = D\omega T$;

- scattering of phonons on secondary phases $\tau_{sp}^{-1} = v_m\left(\chi_s^{-1} + \chi_{sp}^{-1}\right)^{-1}V_{sp}$, where χ_s represents the effects of intrinsic superficial area, χ_{sp} is the effect of introduced second phase and V_{sp} is the number density of second phase.

For even more complex structures with many elements producing scattering centers at a various scales, other scattering mechanisms should be considered and estimated.[1]
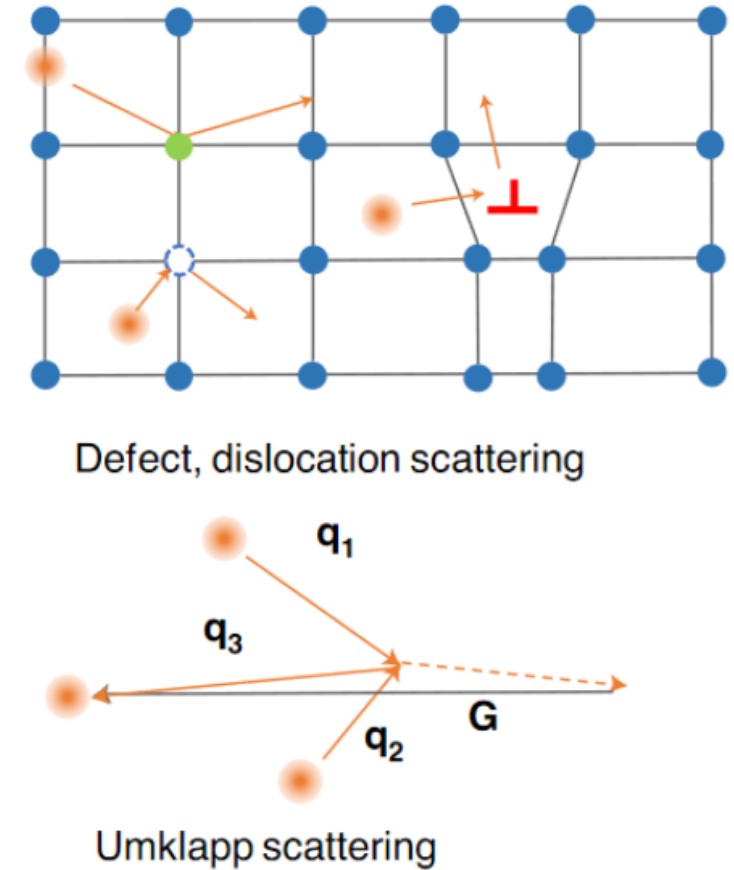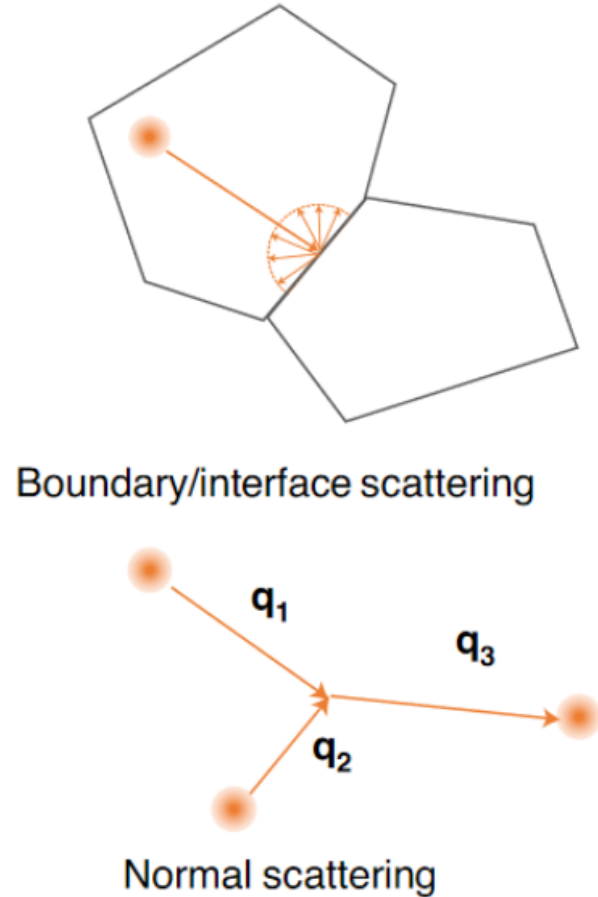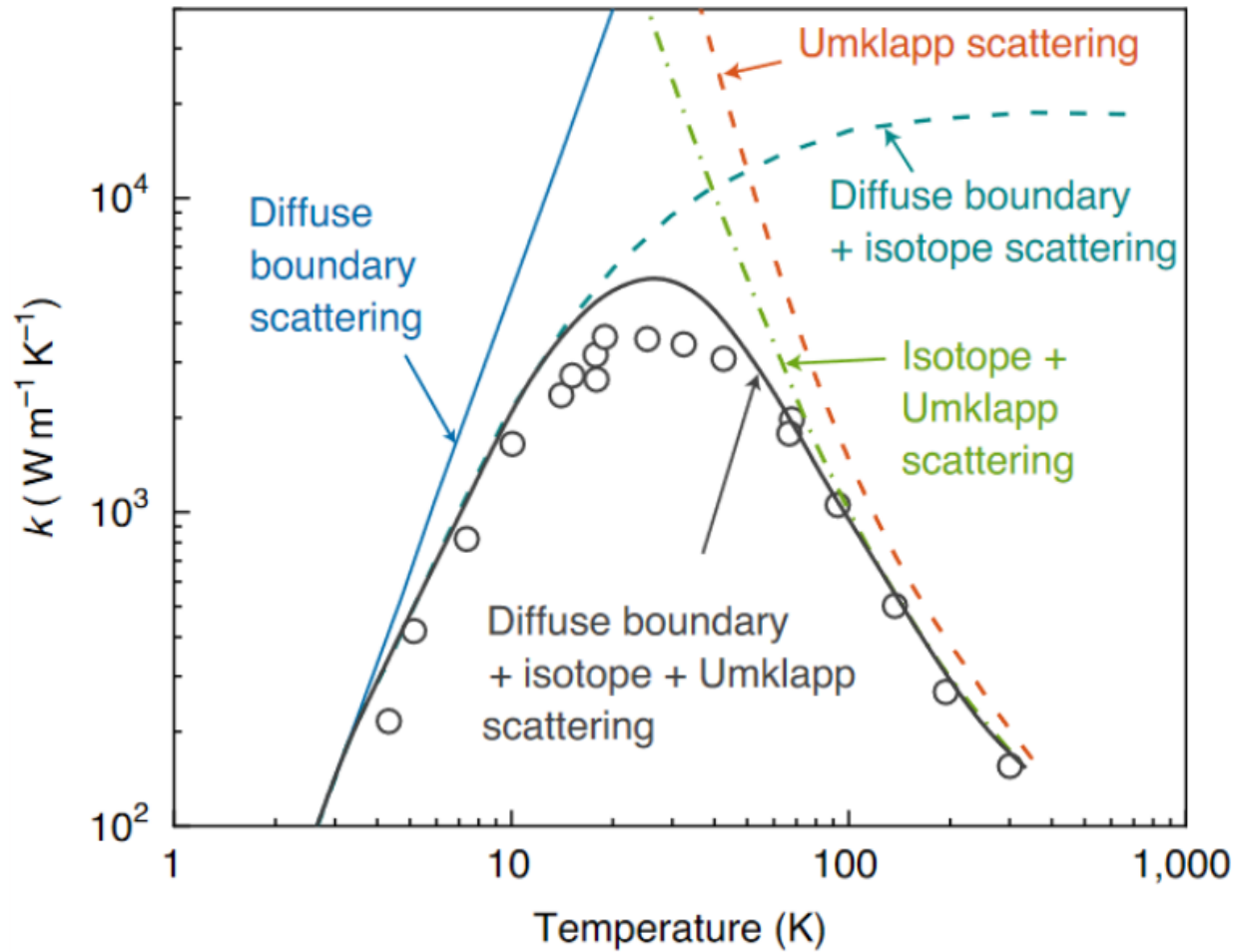
Allen pointed out that the original Callaway's equation has an extra factor of τ_N^{-1}.[18] Allen assumed a quadratic ω dependence for the N-process, following Herring and the newly corrected form of the normal process is given by

$$\kappa_{lat} = \kappa_1 + \kappa_2 = \frac{k_B}{2\pi^2 v_m}\left(\frac{k_B T}{\hbar}\right)^3 \int\limits_0^{\theta_D/T} \tau_c(x)\frac{x^4 e^x}{(e^x-1)^2}dx\left(1 + \frac{\int_0^{\theta_D/T}\frac{\tau_c(x)}{\tau_N(x)}\frac{x^4 e^x}{(e^x-1)^2}dx}{\int_0^{\theta_D/T}\frac{\tau_c(x)}{\tau_N(x)\tau_{ph}(x)}\frac{x^4 e^x}{(e^x-1)^2}dx}\right)$$

In some cases, where the original Debye model without the N-process and Debye-Callaway model fail to fit experimental data (especially at high temperatures) Allen model gives better result.

For high-temperature regions, where $T \gg \theta_D$, the Debye-Callaway model is insufficient at predicting the lattice thermal conductivity. Glassbrenner and Slack proposed a modified model as shown as follows:[19]

$$\kappa_{lat} = \frac{k_B}{2\pi^2 v_m}\left(\frac{k_B T}{\hbar}\right)^3 \int_0^{\theta_D/T} \tau_c(x)x^2 dx$$

here

$$\tau_c^{-1} = (B_U T + B_H T^2)\omega^2 + C\omega^4$$

where C is the constant for point defect scattering, B_U and B_H are coefficients for Umklapp scattering representing the exponential terms $e^{-\theta_D/mT}$.

Original Debye model	Normal scattering process ignored
Debye-Callaway model	Callaway's normal process included
Modified Callaway's model	T-dependence of Umklapp term altered by Slack
Allen model	Corrected normal process by Allen
High-temperature Callaway model	Modified model by Glassbrenner and Slack
…	

Thermal conductivity is extraordinary property and have been treated by numerous scientists:
Ioffe, Abeles, Slack, Klemens, Peierls, Liebfried, Schlömann, Julian, Morelli, Glassbrenner, Eucken, Clarke, Cahill, Snyder with his group (Toberer, Agne, Gurunathan and Hanus) and many more.

References

1. *Thermal Conductivity: Theory, Properties, and Applications*; Tritt, T.M., Ed.; Physics of Solids and Liquids; Springer US: New York, 2004.
2. Cahill, D.G.; Watson, S.K.; Pohl, R.O. Lower Limit to the Thermal Conductivity of Disordered Crystals. *Phys. Rev. B* 1992, 46 (10), 6131–6140.
3. Clarke, D.R. Materials Selection Guidelines for Low Thermal Conductivity Thermal Barrier Coatings. *Surf. Coatings Technol.* 2003, 163–164, 67–74.
4. Agne, M.T.; Hanus, R.; Snyder, G.J. Minimum Thermal Conductivity in the Context of Diffuson - Mediated Thermal Transport. *Energy Environ. Sci.* 2018, 11 (3), 609–616.
5. Drabble, J.R.; Goldsmid, H.J. *Thermal Conduction in Semiconductors*; Pergamon Press, 1961.
6. Slack, G.A. Nonmetallic Crystals with High Thermal Conductivity. *J. Phys. Chem. Solids* 1973, 34 (2), 321–335.
7. Morelli, D.T.; Slack, G.A. High Lattice Thermal Conductivity Solids. In *High Thermal Conductivity Materials*; Shindé, S. L., Goela, J. S., Eds.; Springer: New York, 2006; pp 37–68.
8. Toberer, E.S.; Zevalkink, A.; Snyder, G.J. Phonon Engineering through Crystal Chemistry. *J. Mater. Chem.* 2011, 21 (40), 15843.

References

9. Callaway, J. Model for Lattice Thermal Conductivity at Low Temperatures. *Phys. Rev.* 1959, 113 (4), 1046–1051.

10. Klemens, P.G. Thermal Conductivity and Lattice Vibrational Modes; 1958; pp 1–98.

11. Reissland, J.A. *The Physics of Phonons*; John Wiley & Sons, 1973.

12. Klemens, P.G. Thermal Resistance Due to Point Defects at High Temperatures. *Phys. Rev.* 1960, 119 (2), 507–509.

13. Klemens, P.G. The Scattering of Low-Frequency Lattice Waves by Static Imperfections. *Proc. Phys. Soc. Sect. A* 1955, 68 (12), 1113–1128.

14. Abeles, B. Lattice Thermal Conductivity of Disordered Semiconductor Alloys at High Temperatures. *Phys. Rev.* 1963, 131 (5), 1906–1911.

15. Gurunathan, R.; Hanus, R.; Snyder, G.J. Alloy Scattering of Phonons. *Mater. Horizons* 2020, 7 (6), 1452–1456.

16. Wang, H.; LaLonde, A.D.; Pei, Y.; Snyder, G.J. The Criteria for Beneficial Disorder in Thermoelectric Solid Solutions. *Adv. Funct. Mater.* 2013, 23 (12), 1586–1596.

17. Gurunathan, R.; Hanus, R.; Dylla, M.; Katre, A.; Snyder, G.J. Analytical Models of Phonon–Point-Defect Scattering. *Phys. Rev. Appl.* 2020, 13 (3), 034011.

References

18. Allen, P.B. Improved Callaway Model for Lattice Thermal Conductivity. *Phys. Rev. B* 2013, 88 (14), 144302.
19. Glassbrenner, C.J.; Slack, G.A. Thermal Conductivity of Silicon and Germanium from 3°K to the Melting Point. *Phys. Rev.* 1964, 134 (4A), A1058–A1069.

Further reading:
- Gorbachev, V.V; Spitsyna, L.G. *Physics of Semiconductors and Metals*; Metallurgia, Moscow (in Russian), 1982.
- *Introduction to Solid State Physics*, 8th ed.; Kittel, C., Ed.; John Wiley & Sons, Inc, 2005.
- Kittel, C.; Kroemer, H. *Thermal Physics*; Wiley New York, 1970.
- Peierls, R.; Peierls, R.E. *Quantum Theory of Solids*; Oxford University Press, 1955.
- Ziman, J.M. *Electrons and Phonons*; Oxford University Press, 2001.

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