Tuning phonon transport spectrum for better thermoelectric materials

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The figure of merit of thermoelectric materials can be increased by suppressing the lattice thermal conductivity without degrading electrical properties. Phonons are the carriers for lattice thermal conduction, and their transport can be impeded by nanostructuring, owing to the recent progress in nanotechnology. The key question for further improvement of thermoelectric materials is how to realize ultimate structure with minimum lattice thermal conductivity. From spectral viewpoint, this means to impede transport of phonons in the entire spectral domain with noticeable contribution to lattice thermal conductivity that ranges in general from sub-terahertz to tens of terahertz in frequency. To this end, it is essential to know how the phonon transport varies with the length scale, morphology, and composition of nanostructures, and how effects of different nanostructures can be mutually adopted in view of the spectral domain. Here we review recent advances in analyzing such spectral impedance of phonon transport on the basis of various effects including alloy scattering, boundary scattering, and particle resonance.

Keywords: Thermoelectric material; phonon transport; lattice thermal conductivity; alloy scattering, sintered nanostructure; particle resonance;
1. Introduction

Thermoelectrics has attracted a great attention as a way for energy harvesting or waste heat recovery. The conversion efficiency of thermoelectric materials is governed by the dimensionless parameter, \( ZT = S^2 \sigma T / (\kappa_p + \kappa_e) \)[1], where \( S \) is the Seebeck coefficient, \( \sigma \) is the electrical conductivity, \( T \) is the absolute temperature, and \( \kappa_p \) and \( \kappa_e \) are the lattice and electrical thermal conductivities. Therefore, the challenge for achieving high \( ZT \) is to enhance electrical properties and reduce lattice thermal conductivity simultaneously. The ideal thermoelectric materials is often referred to as phonon-glass electron-crystal[2], which is in general hard to achieve[3]. Great efforts have been made to enhance electrical properties by for instance convergence of electronic bands[4], energy filtering[5,6], and resonance doping[7,8]. On the other hand, the reduction of the lattice thermal conductivity has been realized by controlling the properties of phonons. Phonons are the carriers for lattice thermal conduction[9], and the thermal conductivity in crystals can be characterized as the diffusion of phonons.

Phonons are the lattice vibration modes, and their states are described with wave vector \( \mathbf{q} \) in reciprocal space and branch \( s \) the representing polarization. The frequency of phonon is uniquely determined as a function of the wave vector and branch, namely the phonon dispersion relations, which can be obtained by crystal structure and interatomic
potential. A well-known theoretical model of the phonon dispersion relations is the Debye model, which can successfully reproduce the temperature dependence of specific heat at low temperatures observed in experiments by incorporating the spectral feature of phonon states[10]. The spectral feature of phonon must be also taken into account to accurately describe thermal conduction. From the Boltzmann transport equation, the lattice thermal conductivity can be expressed as follows:

$$\kappa = \frac{1}{3} \sum_{q,s} C_{q,s} v_{q,s}^2 \tau_{q,s} = \frac{1}{3} \sum_{q,s} C_{q,s} v_{q,s} \Lambda_{q,s},$$  \hspace{1cm} (1)$$

where $C$ is heat capacity per phonon mode, $v$ is phonon group velocity, $\tau$ is relaxation time, and $\Lambda=v\tau$ is mean free path (MFP)[9]. These properties strongly depend on the mode of phonons; for instance, MFP is longer for lower frequency. The resulting mode-dependent contribution to lattice thermal conductivity is often quantified by the cumulative lattice thermal conductivity $\kappa_c$ defined in Eq. (2) [11,12],

$$\kappa_c(\Lambda_0) = \frac{1}{3} \sum_{q,s}^{\Lambda_{q,s} \leq \Lambda_0} C_{q,s} v_{q,s} \Lambda_{q,s},$$  \hspace{1cm} (2)$$

where $\Lambda_0$ is the threshold MFP. The cumulative lattice thermal conductivity is the summation of the lattice thermal conductivities by the phonons with MFPs shorter than $\Lambda_0$. The examples of the cumulative lattice thermal conductivity of various materials, normalized by the bulk lattice thermal conductivity $\kappa$, is shown in Fig. 1[13]. For instance,
in silicon, $\kappa_c / \kappa$ is approximately 10% at $\Lambda_0 = 50$ nm, and 90% at $\Lambda_0 = 10$ μm at room temperature. As seen here, phonons with a wide range of MFPs noticeably contribute to lattice thermal conductivity, and this is why evaluation of the modal phonon properties is important, in particular for nanostructures whose length scale lies in the middle of the MFP range. Compared with specific heat and group velocity, evaluation of relaxation time is relatively challenging since the relaxation originates from anharmonic lattice dynamics. However, the recent progress in numerical simulation techniques, such as anharmonic lattice dynamics (ALD) method with first-principles interatomic force constants [14-18], has enabled us to access these anharmonic phonon transport properties. In addition to the numerical methods, experimental methods, such as inelastic neutron scattering [19,20], inelastic x-ray scattering [21,22], and thermoreflectance [23-26] methods have been also developed to probe the modal phonon transport properties.
Fig. 1. Dependence of cumulative lattice thermal conductivity $\kappa_c$ on MFP for various crystals calculated by ALD with first-principles force constants. The values are normalized by the bulk lattice thermal conductivity $\kappa$[13]. Reproduced with permission from Aketo et al., Appl. Phys. Lett., 105 (2014). Copyright 2015 AIP Publishing.

As stated above, for better performance of thermoelectrics, it is necessary to reduce the lattice thermal conductivity without degrading the electrical properties. Alloyping is the traditional approach to realize this difficult balance. In a substitutive alloy or a solid solution, atoms or compounds are mixed in a single homogeneous phase keeping the original crystal structures. This approach mainly aims to facilitate phonon scattering by disordering vibration modes which reduces the relaxation time $\tau$. The alloying has been extensively demonstrated and studied for many thermoelectric materials such as Si$_x$Ge$_{1-x}$[27-29], Bi$_x$Sb$_{2-x}$Te$_3$[30-33], Mg$_2$Si$_x$Sn$_{1-x}$[34-37], Bi$_x$Sb$_{1-x}$[38], PbTe$_x$Se$_{1-x}$[39,40], half-Heusler compounds[41-46], since half a century ago.

As for more recent approach, development in nanotechnology has realized fabrication of nanostructured materials for better thermoelectric performance[47]. Initially, nanostructuring was mainly carried out aiming to increase Seebeck coefficient by quantum confinement[48-50]. Recently the main objective of nanostructuring has shifted to lowering the lattice thermal conductivity. The mechanism of the lattice-thermal-
conductivity reduction by nanostructuring can be explained in the view of phonon transport; phonons experience boundary scattering at vast number of interfaces existing in nanostructures, which corresponds to shortening of MFP[51]. Among the early works on nanostructured thermoelectric materials, ones on super-lattice structures are notable because of the record ZT at that time[52,53]. Although reproducibility has been later questioned[54], it is true that the works have greatly stimulated the research field. Various nanostructures such as nanowires[55,56], sintered nano-polycrystals[57,58], nanoporous materials [59,60], and embedded nanoparticles[61-63] have been fabricated and demonstrated to exhibit high thermoelectric efficiency. Recently, the nanostructuring effect on the conversion efficiency has also been investigated in spin Seebeck thermoelectric materials [64].

The combination of alloying and nanostructuring is beneficial to further reduce lattice thermal conductivity. For example, an experimental work utilizing the combination of the embedded nanoparticles, impurities and sintered interfaces has achieved high performance in a thermoelectric material, which was attributed to the low lattice thermal conductivity[63]. It was suggested that these multiscale structures hierarchically scatter phonons of a wide range of modes. Figure 2 shows that the schematic diagram in the frequency domain. As we will introduce in this review, the alloy and interfaces effectively
scatter phonons with high frequency (short MFP) and low frequency (long MFP), respectively. Meanwhile, it is challenging to suppress the lattice thermal conductivity of phonons with extremely low frequencies in bulk materials. In addition, some higher frequency modes do remain to have noticeable contribution to thermal conductivity even after alloying and nanostructuring. Theoretical calculations show that such phonon modes can be additionally diminished via resonance effect by embedded nanoparticles, where in ideal case, the transport of specific phonon modes are selectively terminated.

Fig. 2. A schematic of frequency dependence of lattice thermal conductivity and the frequency range where different structures are effective in scattering phonons. Phonons with low, medium and high frequency can be scattered by particle resonance, boundary scattering, and alloy scattering effects, respectively.
The key point in designing material with low lattice thermal conductivity reduction is to quantitatively understand transport of which phonon modes can be impeded by alloy scattering, boundary scattering, and particle resonance. This is especially important when it comes to the combination of different mechanisms to impede the transport of a broad range of phonon modes. While there have been many reviews on the related topics[65-83], this review particularly focuses on the lattice thermal conductivity reduction through alloy scattering, boundary scattering, and particle resonance in light of phonon spectral properties. In Section 2, recent analytical works on alloy effect on the lattice thermal conductivity and phonon transport are introduced. Section 3 reviews works on phonons transport in nanocrystals, including detailed description of how to analyze the phonon transport across the interfaces and in complex nanostructures. Section 4 focuses on the particle resonance effect that can impede the phonon transport of targeted modes. In what follows, we simply address “lattice thermal conductivity” as “thermal conductivity” since the focus here is on phonon transport.

2. Phonon-impurity scattering due to alloying

The mechanism of the lattice thermal conductivity reduction by alloying has been
understood as phonon-impurity scattering. Once the phonon-impurity scattering rate $\tau_{\text{imp}}$ is obtained, the effective relaxation time $\tau_{a-i}$ can be calculated with intrinsic relaxation time $\tau_{\text{anh}}$ by utilizing the Matthiessen’s rule[84].

$$\tau_{a-i}^{-1}(q,s) = \tau_{a\text{nh}}^{-1}(q,s) + \tau_{\text{imp}}^{-1}(q,s).$$

Therefore, the challenge to evaluate spectral thermal conductivity of alloys lies in obtaining the mode-dependent scattering rates induced by different atomic species composing the alloys. A widely-used model of the scattering rate, known as the Klemens model[85], estimates that the phonon impurity scattering rate is proportional to the fourth power of its frequency. Here the Klemens model assumes the linearized phonon dispersion relation (Debye approximation). Tamura model[86] based on perturbation theory was later derived, where the scattering rate is expressed by Eq. (4) incorporating realistic phonon dispersion relation.

$$\tau_{\text{imr}}^{-1}(q,s) = \frac{\pi}{2N} \omega^2(q,s) \sum_{q',s'} \delta[\omega(q,s) - \omega(q',s')] \sum_{\alpha} g_2(\alpha) |e(\alpha, q, s) \cdot e(\alpha, q', s')|^2,$$

$$g_2(\alpha) = \sum_i f_i(\alpha) [1 - \frac{m_i(\alpha)}{m_i(\alpha)}]^2.$$  

Here, $f_i(\alpha)$ and $m_i(\alpha)$ are the mole fraction and relative atomic mass of the $i$th isotope of the $\alpha$ atom in unit cells, respectively. Eq. (4) indicates that the scattering rates of high
frequency modes are moderate compared with Klemens model but they are still much higher than those of lower frequency modes. This model is widely used to predict the thermal conductivity of alloys, such as Si$_x$Ge$_{1-x}$[87], PbTe$_{1-x}$Se$_x$[88], Bi$_x$Sb$_{1-x}$[89], Mg$_2$Si$_x$Sn$_{1-x}$[90], half-Heusler[91], Pb$_x$M$_{1-x}$Te (M =Mg, Ca, Sr, Ba)[92] and even a phase transition material Pb$_x$Ge$_{1-x}$Te[93] combining phonon transport properties of the bulk crystals obtained by ALD calculation with first-principles interatomic force constants. In these works, virtual crystal approximation[94] is employed to evaluate intrinsic phonon properties such as $\tau_{anh}$, where the mass and force field of the crystal are kept homogeneous but modulated to be the weighted average between the values of host and guest atoms or compounds. Note that this “ALD + Tamura” model is rigorous for quantifying the effect of isotopes on the thermal conductivity[95,96].

As introduced above, it is possible to incorporate the alloying effect into the evaluation of phonon transport properties using the Tamura model. However, the force-field difference originated from heterogeneity of the atoms in an alloy crystal is not commonly taken into account in the model. A model utilizing sound speed to incorporate force-field difference has been reported[85] but it lacks in the realistic complexity. Thus the previous studies utilizing ALD have approximated alloys as mass difference system[87-89] even in the case with strong force-field contrast. This is probably the
reason why the model fails to reproduce the thermal conductivity of PbTe$_x$Se$_{1-x}$[88], while it works for Si$_x$Ge$_{1-x}$[87] where the interatomic force constants of Si and Ge single crystals are transferable[97]. Another issue is that the validity of the perturbation theory for mass difference is limited to a small mass contrast and low concentration. As the alternative way to overcome these limitations, T-matrix method based on Green’s function method is gaining attention [98-101]. In this method, molecular positions are explicitly taken into account and the effect of higher order scattering due to mass difference can be incorporated, unlike the perturbation model in Eq. (4). Figure 3 shows the work by Kundu et al.[99] on the scattering rate due to Si or Ge nanoparticles in Si$_{0.5}$Ge$_{0.5}$ crystals calculated by the T-matrix method. It clearly indicates that the scattering rates caused by heavier and lighter particles are different while they are identical in Tamura model, in other words, the Born approximation (“Born” in Fig. 3). The study only considered mass difference, but force-field difference can be also incorporated in the T-matrix method. Katre et al. evaluated the effect of B substitution in SiC crystals incorporating local changes in both the masses and interatomic force constants [101]. The study revealed that the scattering rate is 3 orders of magnitude larger than that calculated accounting for only the mass difference.
Fig. 3. Scattering rate $\tau_{np}^{-1}$ due to Si or Ge nanoparticles embedded in Si$_{0.5}$Ge$_{0.5}$ crystals calculated by the T-matrix method. The rate is normalized by nanoparticle volume fraction $f_p$[99]. Copyright 2011 The American Physical Society.

Another approach to overcome the above limitations of the theoretical models is molecular dynamics (MD) simulation, which solves Newton’s equations of motion with a given intermolecular potential function to obtain the time evolution of the positions and velocities. The method is capable of directly incorporating mass and force-field differences in alloys. In addition, the exact spatial distribution of the atom species in alloys can be incorporated since MD solves the trajectories in real space. Therefore, owing also to its simplicity, MD is widely utilized to evaluate thermal conductivity of alloys[16,102-108]. One of the previous studies[107] performed MD simulations with a potential function obtained from first-principles to investigate the effect of force-field
difference on the thermal conductivity of PbTe\textsubscript{x}Se\textsubscript{1-x}. The results have shown that the mass difference alone cannot reproduce the thermal conductivity reduction observed in experiments\cite{109} and the inclusion of the local force field is essential for the reproduction, as shown in Fig. 4.

The phonon properties of each mode in alloy can be evaluated by MD using the normal mode decomposition (NMD) method\cite{110-112}. In this method, the time correlations of the decomposed normal modes are recorded. In particular, much attention has been paid to the effect of alloying on relaxation time \cite{113-119}. For example, Baker and Norris reported the influence of long- and short-range order of composition of Si\textsubscript{x}Ge\textsubscript{1-x} alloy on the relaxation time, and found that the latter one is dominant \cite{116}. Feng et al. validated the Matthiessen’s rule in Eq. (3)\cite{117} by exploiting the method. It was found that Eq. (3) overestimates the phonon relaxation time and thus thermal conductivity because it does not take into account the coupling between phonon-phonon and phonon-impurity scattering. In this way, MD has been successfully used to investigate not only the total thermal conductivity, but also its spectral properties. Note that, while the relaxation time with alloying effect has been gradually unveiled, the variation of group velocity due to alloying has not yet been fully understood\cite{114}. 
Fig. 4. Thermal conductivities of PbTe\(_{1-x}\)Se\(_x\) with and without force-field difference, normalized by those of pure PbTe crystal. The results are compared with the experiment[109]. Reproduced with permission from Murakami et al., EPL, 102, 46002 (2013). Copyright 2013 IOP publishing.

Experiments have also contributed to understanding of alloy effects on phonon transport. Much of it has been realized by the recent development of nanotechnology to fabricate and characterize nanostructures. For instance, strong size effect on the thermal conductivity of Si\(_x\)Ge\(_{1-x}\) alloy films was found by time-domain thermoreflectance measurement[120]. Huberman et al. performed transient thermal grating measurements[121] to study the size effect on thermal transport of Si\(_x\)Ge\(_{1-x}\) alloy[122]. The strong size dependence on thermal conductivity indicates that the phonons of long MFP, namely low frequency modes, remains to largely contribute to the thermal...
conductivity of alloy crystals, which is consistent with the numerical calculations. In addition to the thermal conductivity measurement, the direct probing of phonon dispersion relations and relaxation times of alloys has also been performed by using inelastic x-ray scattering[123]. The observed phonon dispersion relations of PbTe$_x$Se$_{1-x}$ alloys have shown good agreement with the results of the calculations under a virtual crystal approximation, which suggests that the approximation is a reasonable to predict the phonon dispersion of the PbTe$_x$Se$_{1-x}$ alloys. These experimental approaches are expected to be utilized in various materials and conditions in conjunction with the numerical approaches to further understand the phonon transport of alloys.

3. Phonon-boundary scattering in sintered nanocrystals

As introduced in Sec. 1, various kinds of nanostructured thermoelectric materials have been fabricated in recent years. Among the nanostructures, sintered nanocrystal structures have been shown to be one of the most promising approaches owing to its high performance, relatively low fabrication cost, and high scalability compared with the structures that requires precise fabrication such as superlattices. As for power factor $S^2\sigma$, it can remain almost unchanged after the sintering[57]. The method is applicable to various materials, not only simple crystals such as Si[124-127], but also the complex
alloys and compounds such as Si$_x$Ge$_{1-x}$[128-130], Bi$_x$Sb$_{2-x}$Te$_3$,[57,131,132], and half-Heusler [133,134]. The thermal conductivity reduction in the nanostructures originates from phonon scattering at grain boundaries, which reduces the effective MFPs of phonons. Owing to the scattering, effective MFPs of the nanostructured become shorter. Therefore, phonon transmission probabilities (PTPs) at the interfaces are the key properties to understand the thermal conduction in nano-crystals. Here we note that PTP is known to strongly depend on phonon modes. In addition, the geometries of the nanostructures such as the crystal-size distribution affect the thermal conduction. Although the analytical solutions of the effective MFP of phonons in simple structures such as thin films[135-137] or nanowires[138,139] are already well known, they cannot be easily extended to nanocrystals that is much more complex with broad grain size distribution and spatial inhomogeneity. Therefore, to unveil how phonon transport depends on the mode and complex geometry, numerical approaches are beneficial and have been widely utilized.

The empirical models of frequency dependent PTP that are widely known and used are the acoustic mismatch model[140] and diffusive mismatch model[141]. However, it is also widely known that these models derived under bold assumptions cannot reproduce thermal boundary resistance observed in experiments. Meanwhile, the numerical approaches such as MD (phonon wave packet simulation)[142], lattice
dynamics[143], atomistic Green’s function[144] have been developed to evaluate the PTP. In particular, atomistic Green’s function approach has become popular and has been applied to analyze various interfaces between heterogeneous structures[144-149] because the frequency-dependent PTP can be obtained with relatively low computational cost. However, these numerical calculations are limited to the case of the simple interfaces, mainly attributed the difficulty in modelling realistic interfaces, namely their geometries and interatomic force-fields, rather than the limitation in the computational technique.

As for the experimental approaches, the PTP can be investigated but still requires inputs from corresponding numerical calculations or theoretical assumptions. For example, PTP at sintered silicon interfaces was investigated based on the thermal boundary conductance obtained by the time-domain thermoreflectance[150]. In the study, the function of PTP $t$ is assumed by a simplified equation,

$$
t(\omega) = \frac{1}{\gamma \omega / \omega_{\text{max}} + 1}.
$$

(6)

which was suggested from the experimentally measured temperature dependence of thermal conductivity of sintered silicon nanocrystals[151]. In Eq. (6), $\omega_{\text{max}}$ and $\gamma$ represent the maximum frequency of materials and a fitting parameter. This equation reproduces the frequency dependence of PTP obtained by the previous models and calculations, where it decreases with increasing phonon frequency. Indeed, although the decaying
curve in Eq. (6) is simplified, a previous study using atomistic Green’s function showed that it agrees with the PTP of silicon interfaces consisting of monolayer amorphous SiO$_2$, as shown in Fig. 5[152]. A framework to extract PTP at solid interfaces is also recently reported, where phonon transport properties obtained by ALD with first-principles calculation[14] and time-domain thermoreflectance are utilized[153]. These measurement methods would make contributions to the understanding of the phonon transmission phenomenon at the sintered interface in future.

Fig. 5. (a) Structure of amorphous SiO$_2$ at the interface between crystalline Si layers for the atomistic Green’s function simulations. SiO$_2$ layer thicknesses are 0.72 and 0.36 nm. (b) Phonon transmission probabilities (PTPs) across the interfaces. Dashed line represents the fitting curve of Eq. (6) [152]. Reproduced with permission from Oyake et al., Phys. Rev. Lett., 120, 045901 (2018). Copyright 2018 The American Physical
Several works employed MD simulations to analyze heat transfer phenomenon in sintered nanocrystals[154-158]. However, the size and number of the nanocrystals are limited due to the computational cost. Therefore, coarse-grained model is needed to analyze thermal conduction in the sintered nanocrystals. A promising way is to solve the Boltzmann transport equation under relaxation time approximations[8],

$$\frac{\partial f_s(\omega, \mathbf{r})}{\partial t} + v_s(\omega) \mathbf{e} \cdot \frac{\partial f_s(\omega, \mathbf{r})}{\partial \mathbf{r}} = -\frac{f_s(\omega, \mathbf{r}; t) - f_0(\omega, T(\mathbf{r}))}{\tau_s(\omega, T(\mathbf{r}))},$$

(7)

which describes phonon transport in terms of non-equilibrium distribution function. Here, $f, f_0, \mathbf{r},$ and $T$ are the phonon distribution function, Bose-Einstein distribution, position, and temperature, respectively. Equation (7) indicates that time evolution of the distribution of phonons with $\omega, s$ at $\mathbf{r}$ is described by the advection and scattering terms.

Phonon transport in nanostructures can be characterized by adopting complicated geometries. Monte Carlo(MC) simulation is a good way to resolve such situations. In the method phonons are treated as particles and their time evolutions of advection and scattering by other phonons and interfaces are explicitly simulated. The frequency dependent phonon properties such as relaxation time and group velocity are required as
input parameters. Following long history of the MC method for Boltzmann transport equation to solve rarefied gas dynamics[159], in recent years, there is a growing number of studies applying the method to phonon transport problems[160-173]. The most notable development of the simulation technique is the variance-reduced MC simulation[165,168,171], which can realize drastically low computational cost by simulating only the deviational particles from a reference distribution.

Other simplified calculation methods have also been developed[174-178]. For example, the test particle method developed in the field of rarefied gas dynamics[179-181] has been applied to the phonon transport[176-178], which is also called the ray-tracing simulation by an analogy with photon. In this method, the transmission probability of particles from one side of an entire structure to the opposite side is calculated. Then the transmission probability gives the effective MFP. The method has been used to investigate the effective MFP of sintered nanocrystals[176]. The nanocrystal geometries were prepared by tuned Voronoi diagrams, where the crystal size $x$ with log-normal distribution $P$ [Eq.(8)] as in realistic polycrystalline materials were numerically generated [151].

$$P(x) = \frac{1}{\sqrt{2\pi}\sigma x} \exp \left(-\frac{(\ln x)^2}{2\sigma^2}\right).$$  \hfill (8)
The descriptor of crystal size distribution $\sigma$ is varied in the range of the experimental results[151] to evaluate its effect on the effective MFP. The constructed crystal structure and the crystal size distribution are shown in Fig. 6(a). By performing the simulations, the effective MFP is evaluated as a function of $t$ and compared with the simple model that combines MFPs of a superlattice and a square nanowire using the Matthiessen’s rule expressed by Eq. (9),

$$\frac{\Lambda_{\text{bdy}}}{D_{\text{ave}}} = \left[\left(\frac{3}{4} \frac{t}{1 - t}\right)^{-1} + (1.12)^{-1}\right]^{-1},$$

where $\Lambda_{\text{bdy}}$ is effective MFP when intrinsic MFP is infinity, $D_{\text{ave}}$ is average crystal size. The comparison shown in Fig. 6 (b) indicates that Eq. (9) can mostly predict the calculated results. Here we note that the simulation and theory assume the fully diffusive scattering of phonons at the interfaces; thus the effective MFP of high $t$ region, or low frequency as seen in Eq. (6), can be underestimated. Phonons of extremely long MFP have low frequency and thus are less affected by the interfaces as in Eq. (6). Once effective MFP is obtained thermal conductivity can be accessed by utilizing bulk properties of phonons such as group velocity, as in the MC method.
While it is clear from above that impedance of phonon transport is stronger for smaller grains, an important question now is; what is the limit to suppression of phonon relaxation or mean free path? A widely accepted reference so far is the minimum thermal conductivity scenario, i.e. mean free path of phonon becomes equal to half its wavelength. Aiming to gain further insight into this aspect, measurements have been performed for nanocrystal grains with diameters of 3 nm, 5 nm, and 40 nm[182]. The samples are epitaxial silicon nanocrystalline (SiNC) structures composed of grains separated by ultra-
thin silicon-oxide films. The ultra-thin silicon-oxide films have nanowindows that connect the nanograins preserving the crystal orientation, and thus, allowing electrons to travel with coherent wavefunctions. Thermal conductivities of SiNC structures are significantly below the values of bulk amorphous Si and SiO$_2$. To identify the mechanism of the low thermal conductivity, its temperature dependent was measured. Figure 7(a) summarizes the temperature dependence of the thermal conductivity of SiNC structures compared with those of amorphous Si and amorphous SiO$_2$[183-185]. The temperature dependence was successfully reproduced by a phonon gas kinetics model with intrinsic (bulk) transport properties obtained by first-principle-based anharmonic lattice and phonon transmittance across silicon-oxide films obtained by atomistic Green’s function. Consequently, as shown in Fig. 7(b), the analysis revealed that relaxation time of acoustic phonons in the case of 3-nm SiNC structures are suppressed below the minimum thermal conductivity scenario.

When applying the above MC simulations, ray-tracing calculations, or theoretical model on the basis of phonon gas kinetics, a relevant question is the applicability to utilize the bulk properties to predict thermal conduction in nanostructures, where the phonon modes can be altered by confinement effect. This validity is not rigorously supported yet by any theory and should depend on materials and temperature. However, in addition to
the successful reproduction of SiNC thermal conductivity with the phonon gas kinetics model using bulk phonon properties, molecular dynamics simulations have shown that the partial density of states of Si nanocrystals with a diameter of 3 nm is similar to that of bulk Si, [152]. Therefore, reported studies suggest that the phonon kinetic model with bulk phonon transport inside the grain and PTP at the interference is relevant for nanostructures of broad length scales, and thus, the multiscale phonon approach introduced here is useful for simulating complex geometries in practical materials such as sintered nanocrystals.

Fig. 7. (a) Temperature-dependent thermal conductivity of silicon nanocrystalline (SiNC) structures compared with amorphous Si (asterisks)[183,184] and SiO$_2$
4. Resonance effect by embedded nanoparticles

Embedded nanoparticles, as well as the sintered nanocrystals, have been shown to enhance performance thermoelectric materials. The merits of the structures are that coherent interfaces and small band offsets between host and embedded materials can be realized by suitable selection of nanoparticle. Such interfaces allow carrier transmission [186], unlike the sintered interfaces that inevitably result in degraded electrical conductivity. Yet, thermal conductivity can be significantly decreased as the phonons are scattered by the particles. The scattering is often described by the combination of impurity and geometrical scattering[187,188]. Previous works have identified the correlation between the size distribution of the nanoparticles and thermal conductivity, and investigated the optimized distribution that can effectively scatter phonons with a broad
range of MFPs[189]. An experimental study has also shown that the combination of the nanoparticles, impurities and boundary scattering of phonons is effective in reducing thermal conductivity because the multiscale structures hierarchically scatter phonons with a range of MFPs[63].

Molecular dynamics simulations have also been conducted to understand the phonon scattering with nanoparticles[190-192]. It was shown that these nanoparticles can act as resonators that impedes phonon transport[192]. Note that the phonon resonance effect and its influence on thermal conductivity has been investigated in substructures such as thin films with surface pillars[193-198]. Figure 8 shows that a schematic of wave packet simulation in silicon matrix with embedded germanium nanoparticles, and the PTP through the system. As can be seen in Fig. 8, sharp and significant transmission probability dips are observed at resonant frequencies. The study also revealed that the dips can be made more pronounced by arraying multiple nanoparticles. In addition, the frequency of the dips can be tuned through the distance between arraying particles. A similar result was reported in a previous work where the influence of the distance between two impurity atoms on the phonon scattering rate was investigated by the T-matrix method[100].
Fig. 8. (a) Schematic diagram of the system where the Ge nanoparticles are embedded in a Si matrix. (b) Frequency-dependent transmission probability $\alpha(\omega)$ of longitudinal acoustic phonon calculated by MD simulations. Inset diagram shows the motion of the particle in the rattling mode\cite{192}. Reproduced with permission from Feng, et al., Phys. Rev. B., 96, 220301 (2017). Copyright 2017 The American Physical Society.

Detail discussion of the mechanism of various resonance effects can be learned also from the series of modelling works on atomistically controlled structures [199-201].
Han et al. employed MD wave packet simulations and revealed that a single crystal plane of heterogeneous atom arrays embedded in a host crystal can strongly impede phonons of a specific frequency\cite{199}. The mechanism originates from a wave interference, namely anti-resonance\cite{202}, where the phonons coming by the paths through the impurity atom bonds and host atom bonds interfere destructively.

Blocking the phonon transport through resonance effect originated from the nanoparticles is beneficial for suppressing the thermal conductivity of specific phonon modes. For example, when some of the phonon modes still significantly contribute to thermal conductivity even after alloying and nanostructuring, the tuned resonance effect leads to a further reduction of thermal conductivity. More importantly, it can significantly block the lower frequency range of phonon transport, which is hardly terminated by other nanostructures. Here the problem is how to realize the optimized arrangement of nanoparticles in actual materials. However, when the technical problem is resolved in near future, ultimately low thermal conductivity materials may be realized by the phonon engineering.
5. Summary and perspectives

We reviewed the recent theoretical, numerical, and experimental works on effects of nanostructure on phonon transport spectrum, whose progress can lead to design of superior thermoelectric materials. There has been a strong progress in theoretical and numerical methods to analyze alloy scattering, boundary scattering, and structure-induced interference and resonance of phonon transport. Together with mesoscopic approach that lumps multiple effects and quantifies the overall impact on thermal conductivity, it has become possible to design a structure that impedes phonon transport in the entire spectral domain with noticeable contribution to thermal conductivity, ranging in general from sub-terahertz to tens of terahertz. As many interesting structures have been already fabricated experimentally and have been shown to enhance $ZT$ by reducing thermal conductivity, such designability provided by theoretical and numerical calculations is expected to contribute to further enhancement in terms of controlling spectral (mode-dependent) thermal conductivity. There, machine learning can be a useful tool to realize optimal design [203-205].

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