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Cite as: Appl. Phys. Lett. **91**, 231922 (2007); <https://doi.org/10.1063/1.2822891>

Submitted: 30 October 2007 . Accepted: 19 November 2007 . Published Online: 07 December 2007

D. A. Broido, M. Malorny, G. Birner, Natalio Mingo, and D. A. Stewart



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# Intrinsic lattice thermal conductivity of semiconductors from first principles

D. A. Broido<sup>a)</sup>

Department of Physics, Boston College, Chestnut Hill, Massachusetts 02467, USA

M. Malorny and G. Birner

Department of Physics, University of Regensburg, D-93040 Regensburg, Germany

Natalio Mingo

CEA-Grenoble, 17 Rue des Martyrs, Grenoble 38054, France

and Department of Electrical Engineering, University of California, Santa Cruz, California 95064, USA

D. A. Stewart

Cornell Nanoscale Facility, Cornell University, Ithaca, New York, 14853, USA

(Received 30 October 2007; accepted 19 November 2007; published online 7 December 2007)

We present an *ab initio* theoretical approach to accurately describe phonon thermal transport in semiconductors and insulators free of adjustable parameters. This technique combines a Boltzmann formalism with density functional calculations of harmonic and anharmonic interatomic force constants. Without any fitting parameters, we obtain excellent agreement (<5% difference at room temperature) between the calculated and measured intrinsic lattice thermal conductivities of silicon and germanium. As such, this method may provide predictive theoretical guidance to experimental thermal transport studies of bulk and nanomaterials as well as facilitating the design of new materials. © 2007 American Institute of Physics. [DOI: 10.1063/1.2822891]

Thermal conductivity is a fundamental transport parameter that is commonly used to characterize a broad range of materials and systems. In semiconductors and insulators, heat is carried by the vibrating lattice. A predictive theoretical approach to calculate the lattice thermal conductivity in these materials is of tremendous importance for modern science and technology. It would facilitate understanding of heat dissipation in microelectronics and nanoelectronics<sup>1</sup> as well as assist in material design for efficient thermoelectric refrigeration and power generation.<sup>2</sup>

Above a few tens of Kelvin the behavior of the lattice thermal conductivity of semiconductors is usually dominated by phonon-phonon scattering, which arises because of the anharmonicity of the interatomic potential. Unlike phonon scattering by defects, impurities or boundaries, phonon-phonon scattering is an *intrinsic resistive process*. A microscopic description of the intrinsic lattice thermal conductivity  $\kappa^{(i)}$  of semiconductors and insulators was first formulated theoretically by Peierls<sup>3</sup> in 1929 through what has become known as the phonon Boltzmann equation (PBE).

While the general framework to describe thermal conductivity is well known, the development of a predictive theoretical approach to calculate  $\kappa^{(i)}$  has been hindered by the significant complexity inherent in describing (i) interatomic forces between atoms, and (ii) the inelastic phonon-phonon scattering processes. This is true even for common materials such as silicon and germanium.<sup>1</sup> A tremendous simplification is achieved in the calculation of  $\kappa^{(i)}$  in bulk semiconductors<sup>4,5</sup> and nanomaterials<sup>6</sup> by using the relaxation time approximation to solve the PBE. However, the relaxation time approximation is derived under the assumption of elastic scattering, but the anharmonic phonon-phonon scattering is an inelastic scattering process.<sup>4</sup> Furthermore, be-

cause the relaxation time approximation introduces adjustable parameters that are fit to existing experimental data, it has limited predictive power. In recent years, molecular dynamics approaches to calculate the lattice thermal conductivity of materials<sup>7,8</sup> have been introduced. These approaches have the advantage that they treat anharmonicity to all orders. However, they typically rely on empirical interatomic potentials (EIPs) that are fit to experimental properties of materials (i.e., crystal structure, elastic constants, point defects, etc.). Also, the atomic motion is treated classically so molecular dynamics approaches are most appropriate for temperatures typically much higher than 300 K.

In this letter, we present a predictive theoretical approach to calculate  $\kappa^{(i)}$  that invokes *no adjustable parameters* and is valid over a wide temperature range around room temperature. This approach implements an exact iterative solution of the PBE for phonon transport,<sup>9,10</sup> which explicitly incorporates the quantum mechanical phonon-phonon scattering processes and solves self-consistently for the phonon distribution function. The only inputs required for the exact solution of the PBE are the harmonic and anharmonic interatomic force constants (IFCs), and these are determined from first principles using density functional perturbation theory.<sup>11,12</sup> A key initial test of the predictive capability of this approach is how the calculated  $\kappa^{(i)}$ 's compare to the corresponding measured lattice thermal conductivity in commonly studied materials such as silicon and germanium. We find that our calculated  $\kappa^{(i)}$ 's show excellent agreement with the experimentally determined  $\kappa^{(i)}$  for isotopically enriched Si<sup>13</sup> and Ge.<sup>14</sup>

We begin by considering a perfect bulk crystal free of defects or impurities and take silicon or germanium atoms to reside on a diamond lattice. The lowest order scattering processes are between three phonons.<sup>4,15</sup> These processes are constrained to satisfy conservation of energy,  $\omega_j(\mathbf{q}) \pm \omega_{j'}(\mathbf{q}') = \omega_{j''}(\mathbf{q}'')$ , and quasimomentum,

<sup>a)</sup> Author to whom correspondence should be addressed. Electronic mail: broido@bc.edu.

$\mathbf{q} \pm \mathbf{q}' = \mathbf{q}'' + \mathbf{K}$ , where  $\mathbf{q}$ ,  $j$ , and  $\omega_j(\mathbf{q})$  are the phonon momentum, branch index, and frequency, and  $\mathbf{K}$  is a reciprocal lattice vector that is zero for normal processes and nonzero for umklapp processes. A small temperature gradient  $\nabla T$  is taken to perturb the phonon distribution function  $n_\lambda = n_{0\lambda} + n_{1\lambda}$ , where  $\lambda$  is a short hand for  $(\mathbf{q}, j)$ ,  $n_{0\lambda} \equiv n_0(\omega_\lambda)$  is the equilibrium (Bose) phonon distribution function, and the non-equilibrium part  $n_{1\lambda}$  produces the thermal current. The PBE is<sup>4,9,10</sup>

$$\mathbf{v}_\lambda \cdot \nabla T \frac{\partial n_{0\lambda}}{\partial T} = \sum_{\lambda', \lambda''} \left[ W_{\lambda\lambda'\lambda''}^+ (\Psi_{\lambda''} - \Psi_{\lambda'} - \Psi_\lambda) + \frac{1}{2} W_{\lambda\lambda'\lambda''}^- (\Psi_{\lambda''} + \Psi_{\lambda'} - \Psi_\lambda) \right], \quad (1)$$

where the left hand side of Eq. (1) represents phonon diffusion induced by the thermal gradient and the right hand side represents the collision term for three phonon interactions. In Eq. (1),  $\mathbf{v}_\lambda$  is the phonon velocity in mode,  $\lambda$ ,  $W_{\lambda\lambda'\lambda''}^\pm$  are the three-phonon scattering rates,  $\Psi_\lambda = n_{1\lambda} / [n_{0\lambda}(n_{0\lambda} + 1)]$ , and the sums on the right-hand side of Eq. (1) are over the phase space of energy and momentum conserving normal and umklapp three-phonon processes. The presence of  $\Psi_{\lambda'}$  and  $\Psi_{\lambda''}$  conveys the inelastic nature of the phonon-phonon scattering. Replacement of collision integral by  $-n_{1\lambda} / \tau_\lambda$  gives the commonly used relaxation time approximation.<sup>4,5</sup> For phonon-phonon umklapp scattering, the relaxation time is typically taken<sup>4-6</sup> to depend on frequency and temperature as  $\tau_\lambda \sim \omega^{-2} T^{-3}$  although this form was derived assuming low frequency and low temperature<sup>16</sup> where umklapp scattering is typically weak.

The three-phonon scattering rates  $W_{\lambda\lambda'\lambda''}^\pm$  determined from Fermi's golden rule are<sup>9,10</sup>

$$W_{\lambda\lambda'\lambda''}^\pm = \frac{\hbar \pi (n_{0\lambda} + 1)(n_{0\lambda'} + 1/2 \pm 1/2)n_{0\lambda''}}{4N \omega_\lambda \omega_{\lambda'} \omega_{\lambda''}} |V_\pm(\lambda, \lambda', \lambda'')|^2 \times \delta(\omega_\lambda \pm \omega_{\lambda'} - \omega_{\lambda''}). \quad (2)$$

Here,  $N$  is the number of unit cells and the delta function ensures energy conservation. The phonon frequencies  $\{\omega_\lambda\}$  and eigenmodes are determined by diagonalizing the dynamical matrix, which depends on the harmonic IFCs,  $\Phi_{\alpha\beta}(0\kappa; \ell' \kappa')$ , that connect pairs of atoms  $0\kappa$  and  $\ell' \kappa'$ . The notation  $\ell \kappa$  specifies the  $\kappa$ th atom in the  $\ell$ th unit cell, and  $\alpha$  and  $\beta$  are Cartesian components. The three-phonon scattering matrix elements,  $V_\pm(\lambda, \lambda', \lambda'') = V(j, -\mathbf{q}, j'; \mp \mathbf{q}'; j'', \mathbf{q}'')$  measure the strength of the scattering events and are given by

$$V(j, \mathbf{q}, j'; \mathbf{q}'; j'', \mathbf{q}'') = \sum_{\kappa} \sum_{\ell' \kappa'} \sum_{\ell'' \kappa''} \sum_{\alpha \beta \gamma} \Phi_{\alpha \beta \gamma}(0\kappa, \ell' \kappa', \ell'' \kappa'') e^{i\mathbf{q}' \cdot \mathbf{R}_{\ell'}} e^{i\mathbf{q}'' \cdot \mathbf{R}_{\ell''}} \times \frac{e_{\alpha \kappa}^j(\mathbf{q}) e_{\beta \kappa'}^{j'}(\mathbf{q}') e_{\gamma \kappa''}^{j''}(\mathbf{q}'')}{\sqrt{M_\kappa M_{\kappa'} M_{\kappa''}}} \quad (3)$$

where  $\mathbf{R}_\ell$  is a lattice vector and  $M_\kappa$  is the mass of the  $\kappa$ th atom. The  $\Phi_{\alpha \beta \gamma}(0\kappa, \ell' \kappa', \ell'' \kappa'')$  are third order anharmonic IFCs for the indicated triplets of atoms, and the  $e$ 's are phonon eigenvectors.

Equation (1) is solved using an iterative approach<sup>9,10</sup> to obtain the nonequilibrium distribution functions,  $\Psi_\lambda$ . These are used to calculate the phonon thermal conductivity tensor  $\kappa_{\alpha\beta}^{(i)}$ , which relates an applied temperature gradient in the  $\beta$  direction to the resulting heat current per unit area in the  $\alpha$  direction through Fourier's law,  $J_\alpha = -\sum_\beta \kappa_{\alpha\beta} \partial T / \partial x_\beta$ . Here,  $\kappa_{\alpha\beta}^{(i)}$  can be expressed as<sup>4</sup>

$$\kappa_{\alpha\beta}^{(i)} = \sum_{\lambda} C_\lambda v_{\lambda\alpha} v_{\lambda\beta} \tau_{\lambda}, \quad (4)$$

where  $C_\lambda = k_B (\hbar \omega_\lambda / k_B T)^2 n_{0\lambda} (n_{0\lambda} + 1)$  is the contribution per mode ( $j$ ,  $\mathbf{q}$ ) to the specific heat, and the scattering times  $\tau_{\lambda\alpha}$  are directly proportional to the  $\Psi_\lambda$ .<sup>10</sup>

The only inputs required to solve the PBE are the harmonic and the anharmonic IFCs,  $\Phi_{\alpha\beta}(0\kappa; \ell' \kappa')$  and  $\Phi_{\alpha\beta\gamma}(0\kappa, \ell' \kappa', \ell'' \kappa'')$ . In a previous study,<sup>10</sup> we calculated the lattice thermal conductivity of bulk silicon combining a full iterative solution of the PBE with harmonic and anharmonic IFCs obtained from three commonly used EIPs.<sup>17</sup> However, the resulting values of  $\kappa^{(i)}$  were several times higher than the measured values.<sup>10</sup> This large disagreement can be traced to inaccurate representation of both harmonic and anharmonic IFCs obtained from the EIPs.

Since accurate harmonic and anharmonic IFCs are crucial elements required to calculate  $\kappa^{(i)}$ , in this work we employ a first principles approach using density functional perturbation theory. Density functional perturbation theory approaches have demonstrated good predictive ability for phonon dispersions<sup>11</sup> and phonon lifetimes,<sup>18</sup> and we use them here to calculate the harmonic IFCs,  $[\Phi_{\alpha\beta}(0\kappa; \ell' \kappa')]$ . The third order anharmonic IFCs,  $[\Phi_{\alpha\beta\gamma}(0\kappa, \ell' \kappa', \ell'' \kappa'')]$ , are determined using the  $2n+1$  theorem.<sup>19</sup> This theorem states that if the derivatives of the wave function up to order  $n$  are known, then it is possible to calculate the energy derivatives for the system up to order  $2n+1$ . We first use the Fourier transform expression

$$\Phi_{\alpha\beta\gamma}^{\kappa\kappa'\kappa''}(\mathbf{q}, \mathbf{q}', \mathbf{q}'') = \delta_{\mathbf{q} \pm \mathbf{q}', \mathbf{q}'' + \mathbf{K}} \sum_{\ell', \ell''} \Phi_{\alpha\beta\gamma}(0\kappa, \ell' \kappa', \ell'' \kappa'') e^{\pm i\mathbf{q}' \cdot \mathbf{R}_{\ell'}} e^{i\mathbf{q}'' \cdot \mathbf{R}_{\ell''}} \quad (5)$$

and the  $\Phi_{\alpha\beta\gamma}^{\kappa\kappa'\kappa''}(\mathbf{q}, \mathbf{q}', \mathbf{q}'')$  are calculated as described in Ref. 12. Previous calculations of the anharmonic IFCs focused on decay of longitudinal optic and transverse optic phonons at the  $\Gamma$  point where  $\mathbf{q} = 0$  and  $\mathbf{q}' = -\mathbf{q}''$ .<sup>18</sup> For calculation of the thermal conductivity, this is insufficient. In our solution of the PBE, hundreds of thousands of energy and momentum conserving three-phonon scattering events throughout the Brillouin zone are required. To our knowledge, Ref. 12 is the first to calculate the  $\Phi_{\alpha\beta\gamma}^{\kappa\kappa'\kappa''}(\mathbf{q}, \mathbf{q}', \mathbf{q}'')$  for general  $(\mathbf{q}, \mathbf{q}', \mathbf{q}'')$ , and we apply this approach here for Si and Ge. The  $\Phi_{\alpha\beta\gamma}^{\kappa\kappa'\kappa''}(\mathbf{q}, \mathbf{q}', \mathbf{q}'')$  are evaluated directly on a  $4 \times 4 \times 4$  mesh for pairs of vectors  $\{\mathbf{q}, \mathbf{q}'\}$  with  $\mathbf{q}''$  fixed by the translational symmetry condition  $\mathbf{q}'' = \mathbf{q} \pm \mathbf{q}' - \mathbf{K}$ . Crystal symmetry reduces the total number of  $\mathbf{q}''$  that need to be evaluated to 42. The linear equations, Eq. (5), are then solved for the  $\Phi_{\alpha\beta\gamma}(0\kappa, \ell' \kappa', \ell'' \kappa'')$ , with triplet interactions computed out to seventh nearest neighbors. For all density functional calculations, an  $8 \times 8 \times 8$  Monkhorst-Pack mesh was used in the Brillouin Zone.<sup>20</sup> An energy cutoff of 24 Ry was used for the plane wave expansion. The pseudopotentials were generated based on the approach of von Barth and Car.<sup>21</sup>



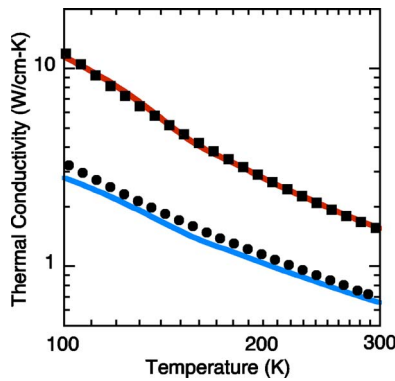


FIG. 1. (Color online) Lattice thermal conductivity  $\kappa^{(i)}$  as a function of temperature. The red line and solid squares are the calculated and measured thermal conductivities of silicon, respectively, while the blue line and the solid circles are the corresponding quantities for germanium.

We calculate the thermal conductivity,  $\kappa^{(i)} = \kappa_{zz}^{(i)}$ , of Si and Ge for heat current parallel to the direction of the temperature gradient, which is taken to lie along the [001] ( $z$ ) direction of the diamond lattice. The cubic symmetry is verified numerically by assuring that  $\kappa_{zz}^{(i)} = \kappa_{xx}^{(i)} = \kappa_{yy}^{(i)}$  and that  $\kappa_{xy}^{(i)} = \kappa_{yz}^{(i)} = \kappa_{xz}^{(i)} = 0$ . Contributions to the intrinsic lattice thermal conductivity for different phonon branches are obtained by summing the integrand in Eq. (4) over all wave vectors. We find that the contribution is dominated by the acoustic branches. Specifically, at room temperature, the acoustic branches provide 95% of the contribution to the thermal conductivity for Si and 92% for Ge. This, however, does not mean that the optic phonons are unimportant. In fact, to the contrary, they provide a dominant scattering channel for the heat-carrying acoustic phonons which, if removed would precipitate a dramatic increase in the thermal conductivity.<sup>9,10</sup>

The calculated intrinsic lattice thermal conductivities for silicon and germanium between 100 and 300 K are compared with measured values<sup>13,14</sup> in Fig. 1. The high isotopic purity (99.9% <sup>28</sup>Si and 99.9% <sup>70</sup>Ge) and quality of these samples ensure that the dominant mechanism that limits the thermal conductivity is phonon-phonon scattering. The agreement between theory and experiment seen in Fig. 1 is exceptionally good. For example, at room temperature the calculated value for Si (Ge) is only 2% (5%) different than the corresponding measured value. This is particularly notable given the poor agreement obtained by us using the EIP models for the IFCs.<sup>10</sup> Previous molecular dynamics calculations of  $\kappa^{(i)}$  using different EIPs for Si obtained room temperature values of about 2.4 (Ref. 7) and 1.4 W/cm K,<sup>8</sup> about 60% higher and 10% lower, respectively, than the measured value.<sup>13</sup> This wide variation could be due to the sensitivity of the result to the EIP used in each calculation and that molecular dynamics approaches are expected to be more accurate at high temperatures.

The computational rigor of the present approach currently precludes consideration of bulk materials with very large unit cells.<sup>22</sup> However, in some nanosystems this is not the case. For example, single-walled carbon nanotubes whose unit cells may contain several tens of atoms could nevertheless be treated using the present theory because the phonon wave vectors are only one dimensional so that the phase space for phonon-phonon scattering is dramatically reducing compared to a bulk system with similar sized unit cell.

To our knowledge, the theoretical results presented here are the only ones to date to provide excellent agreement with measured lattice thermal conductivities of any material over a substantial temperature range using a first-principles-based adjustable-parameter-free approach. The demonstrated accuracy of our theory applied to silicon and germanium suggests its predictive potential for calculating the  $\kappa^{(i)}$  of many other bulk and nanostructured materials of scientific and technological interest. Calculations of  $\kappa^{(i)}$  for other bulk materials are currently underway to further verify the predictive capability of the theory.

Part of this work was done on the Intel Computing Cluster at the Cornell Nanoscale Facility, part of the National Nanotechnology Infrastructure Network supported by the National Science Foundation. Acknowledgment is also made to the Donors of the American Chemical Society Petroleum Research Fund and to the National Science Foundation for support of this research. We thank A. Inyushkin for kindly providing us with his measured lattice thermal conductivity data for silicon and germanium and A. Mayer, G. Deinzer, and D. Strauch for useful communications on this topic.

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- <sup>22</sup>Calculation of the phase space of energy and momentum-conserving three-phonon processes provides both time and memory bottlenecks. The size of the phase space search increases dramatically with the number phonon branches  $3m$ , where  $m$  is the number of atoms in the unit cell.