Lattice thermal conductivity of silicon from empirical interatomic potentials

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We present calculations of the lattice thermal conductivity of silicon that incorporate several commonly used empirical models of the interatomic potential. Second- and third-order force constants obtained from these potentials are used as inputs to an exact iterative solution of the inelastic phonon Boltzmann equation, which includes the anharmonic three-phonon scattering as well as isotopic defect and boundary scattering. Comparison of the calculated lattice thermal conductivity with the experiment shows that none of these potentials provides satisfactory agreement. Calculations of the mode Grüneisen parameters and the linear thermal expansion coefficient help elucidate the reasons for this. We also examine a set of parameters for one of these empirical potentials that produces improved agreement with both the measured lattice thermal conductivity and the thermal expansion data.

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I. INTRODUCTION

In recent years there has been intense interest in developing accurate microscopic descriptions of the properties of materials. Toward this end, numerous empirical interatomic potentials have been developed and studied extensively. Silicon is an ideal test material for the development of these potentials because of the considerable amount of experimental data available, and because of its inherent scientific and technological importance. Empirical interatomic potentials have been used to study a host of physical properties, including liquid and amorphous phases,^{1–5} point defects,^{5–10} and lattice dynamics^{11–13} of bulk Si.

An important test of empirical interatomic potentials is how well they can capture the physics of structures far from the fitting data used to construct them. Recent work^{13,14} highlighted the relevance of the Grüneisen parameters in developing interatomic potentials. These parameters probe both the harmonic and the anharmonic forces and their interrelationship in a material and so go beyond the second-order elastic constants and phonon dispersions commonly extracted from empirical interatomic potentials.

The lattice thermal conductivity κ provides another important and more complex probe of the harmonic and anharmonic forces in crystalline materials. The anharmonicity of the interatomic potential in solids causes scattering between lattice vibrational waves, as was noted some time ago by Peierls.¹⁵ He introduced the concept of "umklapp" processes,¹⁶ in which the phonon momentum in a scattering process is changed by a reciprocal lattice vector.

Anharmonic umklapp scattering is an intrinsic resistive process that typically dominates the room temperature lattice thermal conductivity in crystalline materials above a few tens of degrees.¹⁶ The strength of this anharmonic scattering depends on the phase space available for a phonon to scatter with two others, and on the phonon-phonon scattering matrix elements. Both of these in turn depend on the phonon frequencies and eigenmodes determined from the second-order interatomic potential force constants, and the scattering matrix elements also depend on the third-order force constants.

The standard approach to describing phonon thermal transport in solids is through the Boltzmann equation.^{16–20} We are interested in treating realistic systems where normal and umklapp scattering processes involving phonons throughout the Brillouin zone are accurately represented. A proper treatment of the umklapp processes is essential to any complete theory of thermal transport since these processes provide the thermal resistance. In particular, the commonly invoked elastic continuum approximation for the lattice¹⁸ is inadequate since umklapp processes are fundamentally inconsistent with the basic long-phonon-wavelength assumption of this approximation and since the important nonlinearities in the phonon dispersions cannot be accurately represented. Similarly, the relaxation time approximation^{17,18} is not justified because the inelastic nature of the dominant phonon-phonon scattering precludes the definition of a relaxation time.

Significant progress was made in solving exactly the linearized phonon Boltzmann equation using an iterative scheme.¹⁹ This work addressed the thermal conductivity of rare-gas solids where the interatomic forces can be represented by pairwise central potentials depending only on the distance between any two atoms. Subsequent work applied this central-potential theory to silicon and germanium.²⁰ Covalently bonded semiconductors such as silicon and germanium are characterized by central and noncentral forces, as is reflected in the forms of the numerous empirical interatomic potentials proposed. One paper²¹ included the noncentral forces in an approximate way to calculate the lattice thermal conductivity of bulk Si. More recently, an iterative approach was used²² to solve the phonon Boltzmann equation for the lattice thermal conductivity of Si/Ge based superlattices, incorporating both central and noncentral forces fully within the context of a Keating model.²³ Here, the Keating parameters were fit to the bulk phonon dispersions and bulk thermal conductivity. The Keating model was designed to describe small distortions of the lattice atoms from their equilibrium positions, but it does not describe well other physical features such as defects or amorphous phases. It is therefore of interest to determine whether empirical interatomic potentials, which have demonstrated success in this latter regime, can accurately describe the lattice thermal conductivity of silicon.

In this paper, we present a full inelastic phonon Boltzmann equation approach for the lattice thermal conductivity of silicon. Second- and third-order force constants obtained from several empirical interatomic potentials^{1,5,10} are used as inputs to an iterative solution of the inelastic phonon Boltzmann equation that incorporates three-phonon scattering processes, as well as isotopic defect and boundary scattering. Section II develops the theory used to calculate the thermal conductivity. Section III presents the forms of the interatomic potentials used. In Sec. IV, the calculated thermal conductivity from each model potential is presented and compared to the experiment.

II. THEORY

We consider a bulk crystal consisting of silicon atoms on a diamond lattice and treat transport along a cubic axis direction. The lowest-order anharmonic scattering process involves three phonons.¹⁶ Conservation of energy and quasimomentum require

$$\omega_j(\mathbf{q}) \pm \omega_{j'}(\mathbf{q}') = \omega_{j''}(\mathbf{q}''), \quad \mathbf{q} \pm \mathbf{q}' = \mathbf{q}'' + \mathbf{K}, \tag{1}$$

where \mathbf{q} , *j*, and $\omega_j(\mathbf{q})$ are the phonon momentum, branch index, and frequency, and **K** is a reciprocal lattice vector that is zero for normal processes and nonzero for umklapp processes.

The phonon frequencies and eigenmodes can be found by diagonalizing the dynamical matrix

$$D_{\alpha\beta}^{\kappa\kappa'}(\mathbf{q}) = \frac{1}{\sqrt{M_{\kappa}M_{\kappa'}}} \sum_{\ell'} \Phi_{\alpha\beta}(0\kappa, \ell'\kappa') e^{i\mathbf{q}\cdot\mathbf{R}_{\ell'}}.$$
 (2)

Here, the $\Phi_{\alpha\beta}(0\kappa, \ell'\kappa')$ are the second-order force constants, \mathbf{R}_{ℓ} is a lattice vector in the ℓ th unit cell, κ specifies an atom in this cell whose mass is M_{κ} , and α and β are Cartesian components.

We take a small temperature gradient, ∇T , to perturb the phonon distribution function $n_{\lambda} = n_{\lambda}^{0} + n_{\lambda}^{1}$ with $n_{\lambda}^{1} = -(\partial n_{\lambda}^{0}/\partial \omega_{\lambda})\Psi_{\lambda}$, where ω_{λ} is the phonon energy, $n_{\lambda}^{0} \equiv n^{0}(\omega_{\lambda})$ is the equilibrium phonon-distribution function, and Ψ_{λ} measures its deviation from equilibrium. Here, we have used the shorthand λ in place of (j, \mathbf{q}) . The linearized phonon Boltzmann equation is^{16,20}

$$k_{B}T\mathbf{v}_{\lambda} \cdot \nabla T \frac{\partial n_{\lambda}^{0}}{\partial T} = \sum_{\lambda'\lambda''} \left[W^{+}_{\lambda\lambda'\lambda''}(\Psi_{\lambda''} - \Psi_{\lambda'} - \Psi_{\lambda}) + \frac{1}{2}W^{-}_{\lambda\lambda'\lambda''}(\Psi_{\lambda''} + \Psi_{\lambda'} - \Psi_{\lambda}) \right] + \sum_{\lambda'} W^{imp}_{\lambda\lambda'}(\Psi_{\lambda'} - \Psi_{\lambda}) - n_{\lambda}^{0}(n_{\lambda}^{0} + 1)\Psi_{\lambda}\frac{1}{\tau^{bs}}$$

Here, \mathbf{v}_{λ} is the velocity of the phonon in mode λ . Momentum conservation requires that $\mathbf{q}'' = \mathbf{q} \pm \mathbf{q}' + \mathbf{K}$ so that the sum over λ'' becomes a sum over the phonon branch index, j''. The three-phonon scattering rates are

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

N is the number of unit cells, and the δ function ensures energy conservation. The three-phonon scattering matrix elements, $\Phi_{\pm}(\lambda, \lambda', \lambda'') = \Phi(j, -\mathbf{q}; j', \mp \mathbf{q}'; j'', \mathbf{q}'')$, measure the strength of the scattering events and are given by

$$\Phi(j,\mathbf{q};j',\mathbf{q}';j'',\mathbf{q}'') = \sum_{\kappa} \sum_{\ell'\kappa'} \sum_{\ell''\kappa''} \sum_{\alpha\beta\gamma} \Phi_{\alpha\beta\gamma}(0\kappa,\ell'\kappa',\ell''\kappa'')$$
$$\times e^{i\mathbf{q}'\cdot\mathbf{R}_{\ell'}} e^{i\mathbf{q}''\cdot\mathbf{R}_{\ell''}} \frac{e^{j}_{\alpha\kappa}(\mathbf{q})e^{j'}_{\beta\kappa'}(\mathbf{q}')e^{j''}_{\gamma\kappa''}(\mathbf{q}'')}{\sqrt{M_{\kappa}M_{\kappa'}M_{\kappa''}}}.$$
(5)

 $\Phi_{\alpha\beta\gamma}(0\kappa, \ell'\kappa', \ell''\kappa'')$ is the third-order force constant, and the *e*'s are phonon eigenvectors. The scattering rate from isotopic impurities is^{18,20}

$$W_{\lambda\lambda'}^{imp} = \frac{\pi}{2} g_2 \omega_\lambda \omega_{\lambda'} n_\lambda^0 (n_{\lambda'}^0 + 1) \sum_{\kappa} |\hat{e}_{\kappa\lambda}^* \cdot \hat{e}_{\kappa\lambda'}|^2 \delta(\omega_{\lambda'} - \omega_\lambda),$$
(6)

where g_2 is the mass-variance parameter.^{24–26} The final term in Eq. (3) accounts for phonon scattering from the sample boundary through a relaxation time,

$$\tau^{bs} = \frac{L_{eff}}{v_{ave}},\tag{7}$$

where L_{eff} is an effective phonon mean free path,^{25,27} and

$$v_{ave} = \left[\frac{1}{3}\left(\frac{2}{v_T} + \frac{1}{v_L}\right)\right]^{-1} \tag{8}$$

is an average of the transverse acoustic (TA) and longitudinal acoustic (LA) phonon velocities.

The phonon Boltzmann equation is solved here with an iterative procedure similar to that used previously.^{19,20} We define $\Psi_{\lambda} = \sum_{\alpha} F_{\lambda\alpha} (\partial T / \partial x_{\alpha})$; putting it into Eq. (3) and rearranging, we obtain the three equations

$$F_{\lambda\alpha} = F_{\lambda\alpha}^{0} + \frac{1}{Q_{\lambda}} \Biggl\{ \sum_{\lambda'\lambda''} \Biggl[W_{\lambda\lambda'\lambda''}^{+} (F_{\lambda''\alpha} - F_{\lambda'\alpha}) + \frac{1}{2} W_{\lambda\lambda'\lambda''}^{-} (F_{\lambda''\alpha} + F_{\lambda'\alpha}) \Biggr] + \sum_{\lambda'} W_{\lambda\lambda'}^{imp} F_{\lambda'\alpha} \Biggr\}$$
(9)

(3) for $\alpha = x, y, z$, where

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$$Q_{\lambda} = \sum_{\lambda'\lambda''} \left(W^{\dagger}_{\lambda\lambda'\lambda''} + \frac{1}{2} W^{-}_{\lambda\lambda'\lambda''} \right) + \sum_{\lambda'} W^{imp}_{\lambda\lambda'} + \frac{n^{0}_{\lambda}(n^{0}_{\lambda} + 1)}{\tau^{bs}},$$
(10)

and

$$F^{0}_{\lambda\alpha} = \frac{\omega_{\lambda}n_{0}(n_{0}+1)v_{\lambda\alpha}}{TQ_{\lambda}}.$$
(11)

To initiate the iterative procedure, the second term on the right-hand side of Eq. (9) is set to zero. For a given mode, (j,\mathbf{q}) , and the other two phonon branches, j' and j'' fixed, there is a six-dimensional space of q' and q'' that can form a scattering event. Momentum and energy conservation in Eq. (1) give four constraint equations that leave a twodimensional surface in the Brillouin zone of allowed q'. For each (j, \mathbf{q}, j', j'') , we select q'_x and q'_y from the quadrature grid needed to evaluate Q_{λ} and determine the q'_{z} that satisfies conservation equations. the The resulting set $\{j, \mathbf{q}; j', \mathbf{q}'; j'', \mathbf{q}''\}$ is used in the summation to evaluate Q_{λ} . Thus, $F_{\lambda\alpha}^0$ is the zeroth-order solution of the Boltzmann equation. Plugging this into the right-hand side of Eq. (9) yields the first-order solution, $F_{\lambda,\alpha}^1$. Since \mathbf{q}' and \mathbf{q}'' are off the quadrature grid, the values of $F_{\lambda',\alpha}^n$ and $F_{\lambda'',\alpha}^n$ are obtained by interpolation of F values taken from surrounding on-grid points. The sequence is taken to converge when for largeenough $n, F_{\lambda\alpha}^{n+1} \approx F_{\lambda\alpha}^n$. We typically find that ~50 iterations is sufficient.

The heat current in the α th direction from a temperature gradient along β , $J_{\alpha} = \sum_{\beta} \kappa^{\alpha\beta} (\partial T / \partial x_{\beta})$, defines the phonon thermal conductivity tensor

$$\kappa^{\alpha\beta} = \frac{1}{(2\pi)^3} \sum_{j} \int d\mathbf{q} C_j(\mathbf{q}) v_{j\alpha}(\mathbf{q}) v_{j\beta}(\mathbf{q}) \tau_{j\beta}(\mathbf{q}), \quad (12)$$

where $C_j(\mathbf{q}) = \{ [\omega_j(\mathbf{q})]^2 / k_B T^2 \} n_{0j}(\mathbf{q}) [n_{0j}(\mathbf{q}) + 1]$ is the contribution per mode (j, \mathbf{q}) to the specific heat, and $\tau_{j\beta}(\mathbf{q}) = TF_{j\beta}(\mathbf{q}) / [\omega_j(\mathbf{q})v_{j\beta}(\mathbf{q})]$. The cubic symmetry is verified numerically by assuring that $\kappa^{zz} = \kappa^{xx} = \kappa^{yy}$ and that $\kappa^{xy} = \kappa^{yz} = \kappa^{xx} = 0$.

III. EMPIRICAL INTERATOMIC POTENTIALS

We consider three commonly used empirical interatomic potentials: the Stillinger-Weber (SW) potential,¹ the Tersoff potential,⁵ and the environment-dependent (ED) interatomic potential.^{9,10} These potentials give the total energy of a group of atoms as a function of their coordinates. The SW and ED potentials for the total configuration energy $E = \sum_i E_i$ consist of sums of two-body and three-body terms^{1,10,28}

$$E_i = \sum_{\substack{i,j \\ i < j}} V_2(r_{ij}) + \sum_{\substack{i,j,k \\ i < j < k}} V_3(\mathbf{r}_{ij}, \mathbf{r}_{ik}),$$
(13)

with r_{ij} and r_{ik} the distance between atoms *i* and *j*, and *i* and *k*, respectively.

Here, the two-body term has the form $V_2(r)=A(Br^{-p}-\xi)\exp[\sigma/(r-a_c)]$. The SW potential scales the energy and

length to the observed atomization energy and lattice spacing for Si in the diamond structure; it also takes the parameters ξ and σ to be unity. The parameter a_c gives a cutoff that causes the potential to go to zero smoothly between the first- and second-nearest neighbors.

The three-body term is a product of three terms

$$V_3(\mathbf{r}_{ij}, \mathbf{r}_{ik}) = h(r_{ij})h(r_{ik})g(\theta_{ijk}), \qquad (14)$$

with

$$h(r) = \exp\left(\frac{\gamma}{r - a_c}\right),\tag{15}$$

and

$$g(\theta) = \lambda [\varsigma(1 - e^{-Q(\cos \theta + 1/3)^2}) + \eta Q(\cos \theta + 1/3)^2],$$
(16)

and θ_{ijk} being the angle between \mathbf{r}_{ij} and \mathbf{r}_{ik} . For the SW potential, $\varsigma=0$, and $\eta=Q=1$. For the ED potential, $\varsigma=1$. The SW potential is specified by the six parameters $\{A, B, p, a_c, \gamma, \lambda\}$ ¹ and the ED potential is specified by the nine parameters $\{A, B, p, \xi, a_c, \gamma, \lambda, \eta, Q\}$.¹⁰

The Tersoff potential is modeled by two-body repulsive and attractive terms $^{\rm 5}$

$$E_{i} = \sum_{j \neq i} f_{c}(r_{ij}) [f_{R}(r_{ij}) + b_{ij}f_{A}(r_{ij})].$$
(17)

Here, $f_R(r) = A \exp(-\lambda_1 r)$ and $f_A(r) = -B \exp(-\lambda_2 r)$. The coefficient of the attractive term describing many-body interactions is

$$b_{ij} = (1 + \beta^{n} \varsigma_{ij}^{n})^{-1/2n},$$

$$\varsigma_{ij} = \sum_{k(\neq i,j)} f_{c}(r_{ik})g(\theta_{ijk})\exp[\lambda_{3}^{3}(r_{ij} - r_{ik})^{3}],$$

$$g(\theta) = 1 + \frac{c^{2}}{d^{2}} - \frac{c^{2}}{d^{2} + (h - \cos \theta)^{2}},$$
(18)

and the sum in Eq. (18) is over the remaining three nearestneighbor atoms to atom *i*. $f_c(r)$ is a cutoff function that is one at the equilibrium configuration but becomes zero at a point between the first- and second-nearest neighbors. The Tersoff potential is specified by the 10 parameters $\{A, B, \lambda_1, \lambda_2, \lambda_3, \beta, c, d, h, n\}$. The nonzero force constants obtained from these three potentials extend out to the second-nearest neighbors.

secondthird-order force constants The and $\Phi_{\alpha\beta}(0\kappa,\ell'\kappa')$ and $\Phi_{\alpha\beta\gamma}(0\kappa,\ell'\kappa',\ell''\kappa'')$ are obtained by symbolic differentiation of the interatomic potentials and evaluation of these at the equilibrium configuration for the diamond lattice with Si lattice parameter a=5.43 Å. The 4 nearest-neighbor atoms and 12 second-nearest-neighbor atoms give 16 3×3 second-order force-constant matrices with a total of $16 \times 3^2 = 144$ elements. Only six of these elements are independent.¹¹ The third-order force constants involve three atoms and total $16^2 \times 3^3 = 6912$ elements for first- and second-nearest-neighbor contributions. For the SW and ED models there are 18 independent third-order force-constant

elements, while the Tersoff potential yields 26.

The second- and third-order force constants obtained from these potentials satisfy the translational invariance constraints 29

$$\sum_{\ell'\kappa'} \Phi_{\alpha\beta}(\ell\kappa,\ell'\kappa') = 0 \quad \sum_{\ell''\kappa''} \Phi_{\alpha\beta\gamma}(\ell\kappa,\ell'\kappa',\ell''\kappa'') = 0,$$

along with cyclic permutations of the indices. In addition, rotational invariance requires that

$$\sum_{\mathcal{I}'\kappa''} \Phi_{\alpha\beta\gamma}(\ell\kappa,\ell'\kappa',\ell''\kappa'')X_{\eta}(\ell''\kappa'') + \Phi_{\gamma\beta}(\ell'\kappa')\delta_{\alpha\eta} + \Phi_{\alpha\gamma}(\ell'\kappa')\delta_{\beta\alpha}$$

is equal to its permutation in γ and η . Here, is the η th component of the vector locating the κ th atom in the ℓ th unit cell.

Using the second-order force constants, the phonon dispersion and eigenmodes are calculated by diagonalizing the dynamical matrix, Eq. (2). From these the isotopic impurity scattering rates and the boundary-scattering relaxation time are obtained from Eqs. (6)–(8). The third-order force constants are then used to calculate the three-phonon scattering strengths and corresponding scattering rates, from Eqs. (4) and (5).

IV. RESULTS AND DISCUSSION

For each empircal interatomic potential (EIP) the phonon Boltzmann equation was solved iteratively.^{19,20} On each iteration the nonequilibrium distribution function was determined, and the thermal conductivity was calculated from Eq. (12). The iterative procedure was terminated when successive iterations yielded no change in the thermal conductivity. The number of discrete wave-vector points $\{q\}$ used to sample the Brillouin zone was varied to assure convergence. This convergence procedure is illustrated in Fig. 1 for the case of isotopically enriched Si using the Tersoff EIP. This figure shows the calculated thermal conductivity at room temperature versus the number of iterations for several different numbers of sampling points N. In each case the thermal conductivity approaches a fixed value with increasing number of iterations. As the number of sampling points increases, this value decreases until it converges for sufficiently large N, as demonstrated for the largest two values, N=3856 and N=6912, which have almost identical curves.

The lattice thermal conductivity is calculated as a function of temperature for naturally occurring Si and for isotopically enriched Si and compared to the data in Ref. 24. The mass variance values²⁴ $g_2=2.01 \times 10^{-4}$ and $g_2=2.33 \times 10^{-6}$ were used for these two cases, respectively. The boundary scattering length, L_{eff} , is determined only roughly from the sample length. Qualitative corrections due to the finite length to thickness ratio and sample smoothness are typically made to fit the low-temperature data.²⁷ We find values of L_{eff} =0.3 cm and L_{eff} =1 cm give a decent fit and are comparable with those used previously.^{24,26,27}

Figure 2 shows the calculated lattice thermal conductivity using the SW interatomic potential as a function of tempera-



FIG. 1. Calculated room-temperature lattice thermal conductivity for isotopically enriched Si using the Tersoff EIP as a function of iteration number for different numbers of sampling points in the Brillouin zone, N. The line symbols correspond to the following number of sampling points: N=256 (\blacklozenge); N=2048 (\blacktriangle); N=3856(\bigcirc); N=6912 (\Box).

ture compared with the data from Ref. 24. The filled circles and triangles represent data for isotopically enriched Si, while the plus signs and open circles represent data for naturally occurring Si. The solid (dotted) lines provide the calculated results for isotopically enriched (naturally occurring) Si. At the lowest temperatures the thermal conductivity is dominated by boundary scattering. With increasing temperature, isotopic impurity scattering becomes significant. In the vicinity of the peak (~ 20 K), the impurity scattering and phonon-phonon scattering dominate and are of comparable strength, and for temperatures above 20 K the thermal conductivity is dominated by the phonon-phonon scattering process.

At low temperatures the calculated and measured lattice thermal conductivities are in good agreement. For tempera-



FIG. 2. Calculated lattice thermal conductivity of silicon using the *SW* potential as a function of temperature compared to measured values taken from Ref. 24 as described in the text. Solid line represents isotopically enriched Si; dotted line represents naturally occurring Si.



FIG. 3. Same as Fig. 2, but calculated results are obtained using the Tersoff potential.

tures above the peak, the calculated thermal conductivity becomes significantly larger than the measured value. At 300 K, the measured values²⁴ are 2.37 W/cm K and 1.5 W/cm K for isotopically enriched Si and naturally occurring Si, respectively. In contrast, the corresponding calculated results using the SW potential are 9.00 W/cm K and 7.10 W/cm K. Figures 3 and 4 present results obtained using the Tersoff and ED interatomic potentials. Similar behavior is seen in both figures with reasonably good fits to the data for low temperatures and calculated thermal conductivity too large at temperatures above the peak. The calculated thermal conductivity at 300 K using the Tersoff and ED potentials are, respectively, 4.27 W/cm K and 4.09 W/cm K for the isotopic case, and 3.57 W/cm K and 3.53 W/cm K for the case of naturally occurring Si.

The discrepancy between calculated and experimental values at high temperature is highlighted in Figs. 5 and 6 for isotopically enriched Si and naturally occurring Si, respectively. These figures show results obtained using the SW (dashed line), Tersoff (dashed-dotted line), and ED (solid line) interatomic potentials plotted against the measured val-



FIG. 5. Calculated lattice thermal conductivity for isotopically enriched Si using SW (dashed line), Tersoff (dashed-dotted line) and ED (solid line) models in the temperature range between 100 K and 300 K compared to measured values.

ues. It is evident that in this temperature range the SW results are roughly four times larger than the measured thermal conductivity, while the Tersoff and ED results are roughly two times larger than the measured values.

A precise representation of the full phonon dispersions and modes and of the anharmonic forces is required to calculate accurately the intrinsic lattice thermal conductivity. This is true for the following reasons: (i) Around room temperature and below, the majority of the heat is carried by the dispersive acoustic phonons. The acoustic-phonon frequencies and group velocities enter explicitly in the calculation of the thermal conductivity and so must be described precisely over the entire Brillouin zone. (ii) Large-q acoustic phonons are involved in the three-phonon umklapp scattering processes that limit the thermal conductivity, so the acousticphonon dispersions near the Brillouin-zone boundary must be accurately determined. (iii) The higher-lying optic modes have very low average group velocities and so carry little heat. Nevertheless, these optic branches contribute significantly to the thermal resistance because they provide scatter-



FIG. 4. Same as Fig. 2, but calculated results are obtained using the ED potential.



FIG. 6. Same as Fig. 5, but for naturally occurring Si.

ing channels to heat-carrying acoustic phonons. (iv) Finally, the anharmonic forces must be properly described since they enter explicitly in the determination of the strength of the three-phonon scattering rates.

The poor high-temperature results obtained from these models reflects inaccurate descriptions of the phonon dispersions and the anharmonicity. The Tersoff model provides an excellent description of the LA mode and a reasonably good description of the optic modes. The SW and ED models give reasonably good descriptions of the LA phonon branch, but the optic branches are too high. At the zone center, the SW and ED models give optic-phonon energies too large by 15% and 21%, respectively, compared to the measured values.³⁰ In all three models, the TA phonon frequencies are too high near the zone boundaries. It is well known that the short-range ion-ion interactions in these models cannot reproduce the flatness of the TA modes for large \mathbf{q} .³¹

The overestimated TA phonon frequencies and corresponding group velocities for all three models produce an increase in the lattice thermal conductivity, as seen in Figs. 5 and 6, through its explicit evaluation in Eq. (12). The SW model as well underestimates the phase space for threephonon scattering, which decreases the scattering rates and so further increases the thermal conductivity. For the Tersoff model, the anharmonic forces are stronger, leading to increased scattering rates and a corresponding decrease in the thermal conductivity relative to that for the SW model. For the ED model, the anharmonic forces are weaker than for the Tersoff model but the phase space available for three-phonon scattering is increased. As a result the scattering rates for the two models are quite similar and result in the near overlap of the thermal conductivities.

It is interesting to note that these empirical interatomic potentials have also shown discrepancies with the experiment in the context of the mode Grüneisen parameters and the linear thermal expansion coefficient.^{13,14} The mode Grüneisen parameters are defined through the change in phononmode frequency with crystal volume

$$\gamma_j(\mathbf{q}) = -\frac{V}{\omega_j(\mathbf{q})} \frac{\partial \omega_j(\mathbf{q})}{\partial V}$$

This can be expressed in terms of the phonon dispersions and modes, and the third-order force $constants^{32}$

$$\gamma_{j}(\mathbf{q}) = -\frac{1}{6\omega_{j}^{2}(\mathbf{q})} \sum_{\kappa} \sum_{\ell'\kappa'} \sum_{\ell''\kappa''} \sum_{\alpha\beta\gamma} \Phi_{\alpha\beta\gamma}(0\kappa, \ell'\kappa', \ell''\kappa'')$$
$$\times \frac{e_{\alpha\kappa}^{j^{*}}(\mathbf{q})e_{\beta\kappa'}^{j}(\mathbf{q})}{\sqrt{M_{\kappa}M_{\kappa'}}} e^{i\mathbf{q}\cdot\mathbf{R}_{\ell'}}r_{\ell''\kappa''\gamma}$$
(19)

Here, $r_{\ell\kappa\gamma}$ is the γ th component of the vector locating the κ th lattice atom in the ℓ th unit cell. In previous theoretical treatments of the lattice thermal conductivity, a mode-averaged Grüneisen parameter was connected to the three-phonon scattering rates.³³ These calculations were based on a multitude of approximations and so were meant to be only qualitative in nature. The mode Grüneisen parameters in fact vary over a wide range of values, and they depend on the harmonic and anharmonic parameters in a different fashion than

do the three-phonon scattering strengths, as is evident by comparing Eq. (19) and (5). The $\gamma_j(\mathbf{q})$ also provide a more direct measure of the anharmoncity. They are considerably easier to calculate than the thermal conductivity since they do not involve the phonon-phonon scattering rates and they can be determined without solving the phonon Boltzmann equation. Upon calculating the phonon dispersions and thirdorder force constants, the $\gamma_j(\mathbf{q})$ can be obtained directly using Eq. (19). Alternatively, a simpler evaluation comes from using the formula preceding Eq. (19); here the difference in phonon frequencies calculated for slightly different lattice constants gives $\gamma_j(\mathbf{q})$ immediately.^{13,14}

The linear thermal expansion coefficient, α , is obtained by a sum of the $\gamma_i(\mathbf{q})$ over all modes, weighted by the modespecific heat:^{13,14,32}

$$\alpha = \frac{\kappa_T}{(2\pi)^3} \sum_j \int d\mathbf{q} C_j(\mathbf{q}) \gamma_j(\mathbf{q}), \qquad (20)$$

where κ_T is the isothermal compressibility. It has been shown that above 100 K, the linear thermal expansion coefficient calculated for the Tersoff model is higher than the experiment, while that from the ED model is lower than the experiment.¹³ These results reflect stronger anharmonic forces for the Tersoff model and weaker anharmonic forces for the ED model, consistent with our conclusions about the lattice thermal conductivity obtained from these models, as described earlier.

The unsatisfactory results obtained from the EIPs considered raises the question of whether a set of parameters for one of these EIPs can be found that provides a good fit to both the thermal conductivity and thermal expansion data. To investigate this, we focus on the Tersoff potential. Two parameter sets have been introduced previously for this potential; the set used here already in the thermal conductivity calculations,⁵ which we refer to as set C, and an earlier version,⁶ which we call set B. The most important feature of the set-B parameters is that they give TA phonon branches that are much flatter and lie below the measured TA phonon frequencies. The resulting group velocities of the heatcarrying TA phonons are much lower, causing a significant reduction in the lattice thermal conductivity. In addition, the reduction in TA phonon frequencies produces a pronounced decrease in the TA mode Grüneisen parameters. As a consequence of this, the linear thermal expansion coefficient calculated for set B lies far below the measured values.

As sets C and B sandwich both the measured thermal conductivity and linear expansion coefficient one might hope that a mixture of these parameter sets could be found that produces good agreement with the relevant data. We have found several such sets. The simplest of these that also gives the best results is obtained by using all of the set B parameters⁶ except one; the parameter h=0.0 in set B is changed to its value in the C parameter set: h=-0.60. Such a modification has been shown to produce good agreement with the measured linear thermal expansion coefficient.¹⁴ We refer to this new parameter set as set B^{*}. This change increases the strength of the bond-bending forces, which pro-



FIG. 7. Calculated lattice thermal conductivity of isotopically enriched silicon using the Tersoff EIP for three parameter sets, as described in the text. Set B (dashed line); set C (dashed-dotted line); set B^* (solid line); experimental data from Ref. 24.

duces an increase in the TA phonon frequencies^{14,34} compared to those obtained from Set B.

Figures 7 and 8 present the lattice thermal conductivity for isotopically enriched Si and the linear thermal expansion coefficient as a function of temperature calculated for sets B, C, and B^{*} compared to the experimental data of Refs. 24 and 35, respectively. It is evident from the figures that the parameter set B (dashed lines) lies far below both the measured lattice thermal conductivity and the linear thermal expansion coefficient, while set C (dashed-dotted lines) lies above them. Set B^{*} (solid lines) provides a much better fit to both sets of data.

Table I gives some calculated mode Grüneisen parameters at high-symmetry points for the three parameter sets compared to the measured values from Ref. 36. Note that the TA mode Grüneisen parameters for set B^* at the X and L points are considerably closer to the experimental values than those for sets B and C.



FIG. 8. Calculated linear thermal expansion coefficient for silicon using the Tersoff EIP for three parameter sets, as described in the text. Set B (dashed line); set C (dashed-dotted line); set B^* (solid line); experimental data from Ref. 35.

TABLE I. Mode Grüneisen parameters for the Tersoff EIP calculated using three different parameter sets as described in the text and compared to experimental values from Ref. 36.

	Set B	Set C	Set B*	Experiment
$\gamma_{LTO}(\Gamma)$	1.33	1.32	1.39	0.98 ± 0.06
$\gamma_{TA}(X)$	-6.46	-0.20	-0.91	-1.4 ± 0.3
$\gamma_{TO}(X)$	1.66	1.60	1.71	1.5 ± 0.1
$\gamma_{TA}(L)$	-3.13	-0.31	-1.24	-1.3 ± 0.3
$\gamma_{TO}(L)$	1.48	1.45	1.55	1.3 ± 0.2

While the parameter set B^* gives very good agreement with the lattice thermal conductivity and thermal expansion data, it does not give the correct bond length or cohesive energy. Specifically, we find a decrease in the bond length (and the lattice constant) of Si of about 0.5%, leading to an increase in the cohesive energy per atom of about 4%. All other parameter sets we investigated that produced relatively good agreement with the thermal conductivity and thermal expansion data suffered from the same deficiency. Presumably, calculations of other materials properties such as defect energies fit well by the set B and set C data^{5,6} will also not be fit as well be set B^{*}. Such an investigation is beyond the scope of this work.

In conclusion, we have calculated the lattice thermal conductivity of silicon using second- and third-order force constants obtained from Stillinger-Weber, Tersoff, and ED empirical interatomic potentials.^{1,5,10} We solve the full inelasticphonon Boltzmann equation, including anharmonic phononphonon, isotopic impurity, and boundary scattering using an iterative approach. We find that at low temperatures where boundary scattering and scattering by isotopic impurities dominate, the thermal conductivity is well described by all three models. However, at higher temperatures where phonon-phonon scattering dominates, the three models give thermal conductivities that are significantly larger than the measured ones.

The failure of these models is in part a consequence of their overestimate of the TA phonon frequencies and the corresponding group velocities away from the zone center. The strong anharmonicity of the Tersoff model and the increase in the phase space for three-phonon scattering that occurs for the ED model cause these two EIPs to give better results for the thermal conductivity than those obtained from the SW potential.

For the Tersoff model, we are able to obtain significantly improved agreement with the measured thermal conductivity by considering a modified parameter set. This parameter set provides a better overall fit to the TA phonon frequencies throughout the Brillouin zone than the two parameter sets considered previously.^{5,6} We show that this set also provides improved agreement with the mode Grüneisen parameters and the linear thermal expansion coefficient.

We note that lattice thermal conductivity is significantly more complex to describe theoretically than are the mode Grüneisen parameters and the linear thermal expansion coefficient. This is because the thermal conductivity depends on the phase space for three-phonon scattering and on a solution of the phonon Boltzmann equation. The fact that the Tersoff and ED models give almost identical thermal conductivities (see Figs. 5 and 6) but vastly different thermal expansion coefficients¹³ reflects the fact that the dependence of these quantities on the harmonic and anharmonic forces is differ-

ent. It is a stringent test of any theory to provide good agreement with both. Finally, it is worth noting that the contribution from higher-order phonon-phonon processes should be negligible in the temperature range considered in this work.³⁷

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