

Theoretical Study of the Lattice Thermal Conductivity in Ge Framework Semiconductors

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The lattice thermal conductivity of Ge clathrates is investigated by evaluating the linear response theory heat current correlation functions using molecular dynamics. Clathrate crystals with and without guest atoms in their *fullerane* cages are studied. In comparison with that of diamond-phase Ge, the clathrate conductivity is reduced by approximately 1 order of magnitude due to the open framework itself. The addition of an encapsulated (rattling) Sr guest atom produces a further order of magnitude reduction in the conductivity, making it comparable to that of amorphous Ge. Our results are consistent with experiments, and have impact on the search for improved thermoelectric materials.

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The electrical and thermal transport properties of solids are correlated through phonon scattering processes. Usually, electrical transport also has a strong dependence on carrier concentration. For example, the electrical conductivity (σ) in semiconductors can be altered by several orders of magnitude by doping. In contrast, the lattice thermal conductivity (κ) of a material is difficult to control experimentally except by changing the temperature and pressure. A simple expression for κ in the kinetic relaxation time approximation [1] is

$$\kappa = \frac{1}{3} C \bar{v}^2 \tau = \frac{1}{3} C \bar{v} \lambda, \quad (1)$$

where C is the lattice specific heat per unit volume, \bar{v} is the average phonon speed, τ is the phonon scattering (relaxation) time, and λ is the phonon mean free path. For crystals, τ and λ are determined by the anharmonicity of the interatomic chemical bonding.

In thermoelectric applications, one wishes to maximize the figure of merit, $ZT = S^2 \sigma T / \kappa$, where T is the temperature and S is the Seebeck coefficient. A desired high ZT requires a low κ (which is normally a characteristic of an amorphous material) and a high S and σ (which are characteristics of a crystal). Slack [2] has introduced the phonon glass/electron crystal (PGEC) concept to partially decouple κ from σ and S . In a PGEC material, the electrons move through crystalline energy bands, while the crystalline phonons are scattered by a set of loosely bound scatterers called "rattlers" to produce a short phonon mean free path which mimics an amorphous material.

A physical realization of a PGEC is provided by framework semiconductor clathrates. Such materials, based on Si, Ge, or Sn, have small *fullerane* cages in which encapsulated guest atom rattlers scatter the phonons of the crystalline framework. A recent set of experiments by Nolas *et al.* [3] has demonstrated the basic validity of the rattler concept. These researchers find that type-I Ge clathrates with encapsulated guests have a greatly reduced κ compared to that of diamond structure Ge. Their measured

temperature dependence of κ does not follow the high temperature $1/T^x$ law as in a crystal, but instead has a T dependence similar to that of an amorphous material such as *a*-Ge. The results depend on the guest species, with κ for Sr and Eu guests having an "amorphouslike" T dependence, that for Cs having a $1/T$ crystallinelike dependence, and that for Ba having a T dependence intermediate between these two. In all cases, the room temperature κ is 1 to 2 orders of magnitude smaller than that for crystalline Ge. More recently, the thermal diffusivity of metallic Na doped Si clathrates has been investigated [4], and the results also suggest an amorphouslike low κ .

To theoretically test the rattler concept in the clathrates, we have computed the room temperature lattice thermal conductivities κ of both pure and guest-containing type-I Ge clathrates, and those for both diamond-phase and amorphous Ge. These are the first such calculations in a framework semiconductor. We have assumed that phonon-phonon scattering is the only mechanism limiting the heat current. Neglected are contributions to κ due to charge carriers, surface or boundary effects, impurity or defect scattering, and isotope effects. The calculations were performed using a Kubo linear response theory formulation of κ [5]. For the cubic (or isotropic) systems of interest here, κ can be treated as a scalar, and is

$$\kappa = \int_0^\infty G(t) dt = \frac{\Omega}{3k_B T^2} \int_0^\infty \sum_{i=x,y,z} \langle J_i(t) J_i(0) \rangle dt. \quad (2)$$

Here $\langle J_i(t) J_i(0) \rangle$ is the heat current autocorrelation function, Ω is the volume, T is the temperature, and $\langle \dots \rangle$ denotes an ensemble average. Defining a normalized correlation function $g(t)$, $g(t) = G(t)/G(0)$, then $\kappa = G(0)\tau_I$, where τ_I is the time integral of $g(t)$. In a single relaxation-time approximation, $g(t) = e^{-t/\tau}$, and one has $\tau_I = \tau$.

We begin with a quantum mechanically derived expression for the heat current \vec{J} developed by Hardy [6]. In the

classical limit, this reduces to

$$\vec{J} = \frac{1}{\Omega} \left[\sum_i \vec{v}_i (E_i - \langle E_i \rangle) + \sum_{ij} \vec{r}_{ij} \left(\vec{v}_j \cdot \frac{\partial V_i}{\partial \vec{r}_j} \right) \right], \quad (3)$$

where \vec{r}_i , \vec{v}_i , and E_i are the positions, velocities, and energies of particle i . The two terms correspond to convection and conduction currents. The derivation of Eq. (3) assumes that the Hamiltonian can be partitioned into identifiable contributions for each atom; that is, $H = \sum_i H_i$, with $H_i = \frac{1}{2} m_i v_i^2 + V_i$.

We have evaluated the time-dependent heat current correlation functions in Eq. (2) using molecular dynamics (MD) simulations. The dynamics of the atoms is determined by forces obtained from an empirical interatomic Tersoff potential [7]. Since this potential contains three-body terms, which are necessary for correctly modeling the covalent bonding of Ge, further approximations must be implemented with care. For example, the evaluation of forces must be done only after symmetrizing pairlike potentials so that the assumptions made in the derivation of Eq. (3) are valid. Similar numerical techniques have been implemented by Li *et al.* [8] to study κ in β -SiC, and discussions on many technical issues can be found in that reference.

We have computed κ at room temperature ($T = 300$ K) for four different sp^3 -bonded phases of Ge: (i) diamond-phase Ge (d -Ge), (ii) tetrahedrally bonded amorphous Ge (a -Ge), (iii) pure type-I clathrate Ge (Ge_{46}), and (iv) filled type-I clathrate Ge ($\text{Sr}_6\text{Ge}_{46}$). In the MD simulations we have used a 1 fs time step, and the simulations have each been run for 1.5×10^6 steps (for a total time of 1500 ps). To obtain $G(t)$, the heat current was Fourier-transformed [8], the convolution was formed, and an inverse Fourier transformation was made. Each system was equilibrated for 100 ps with a constant temperature Gaussian thermostat before initiating each microcanonical MD simulation. The results have been averaged with multiple starting configurations to minimize statistical errors.

For d -Ge, 512 atoms in a $4 \times 4 \times 4$ supercell of the fundamental eight-atom cube is used. Previous work has studied the dependence of κ on supercell size [8,9] in Si and SiC. From this we believe that our supercell size is adequate. Our model of a -Ge is taken from Djordjevic, Thorpe, and Wooten [10]. This consists of an amorphous cell of 512 atoms with periodic boundary conditions. This amorphous network is fully fourfold coordinated with no floating or dangling bonds. The type-I clathrate phase of Ge contains 46 atoms in the unit cell, and the cell contains Ge_{20} and Ge_{24} fulleranelike cages in a 1:3 ratio. Each of these cages contains 12 pentagons, but the cages are linked together so that there are no threefold coordinated atoms. As synthesized, the cages of clathrates are generally occupied by guest atoms. The filled clathrate $\text{Sr}_6\text{Ge}_{46}$ contains one guest (Sr) in each of the six tetrakaidecahedron Ge_{24} cages. In our clathrate MD simulations, we have used

$4 \times 4 \times 4$ supercells; the pure and filled clathrate samples contain 2944 and 3328 atoms, respectively.

We have previously studied the guest atom interaction potential in the large tetrakaidecahedron Ge_{24} cages in type-I Ge clathrates using *ab initio* density functional theory (DFT) [11]. We found this interaction to be very sensitive to the size of the rattling atom. This is of practical importance, since it gives experimentalists and engineers an additional “knob” which allows the rattling frequency to be tuned to an optimal value. In order to simulate the guest-host interaction in a manner consistent with the Tersoff potential for the framework, each guest atom has been assumed to interact with the 24-Ge atoms in its cage through a Lennard-Jones (LJ) potential. We have chosen the guest to be Sr, and have obtained the LJ parameters from potential energy surfaces computed from accurate *ab initio* calculations of $\text{Rb}_2\text{Sr}_6\text{Ga}_{14}\text{Ge}_{32}$ [11].

The phonon dispersion curves for the three crystalline-phase Ge solids, computed with the empirical potentials mentioned above, are shown in Fig. 1. Experimentally, the highest frequency mode for d -Ge is 304 cm^{-1} , which compares well with the computed highest frequency mode [Fig. 1(a)] of 329 cm^{-1} . The dispersion curves of the pure type-I clathrate Ge_{46} [Fig. 1(b)] show different behavior than those of d -Ge. Most of these phonon modes are much “flatter” than those of d -Ge. On the basis of this, the clathrate lattice *topology* might be expected to reduce the average phonon speed in Eq. (1); hence κ should be reduced below that for d -Ge by the framework alone. As is discussed below, this is consistent with our MD simulation results.

In Fig. 1(c), we show the phonon dispersion curves of the rattler system $\text{Sr}_6\text{Ge}_{46}$. It is clearly seen that Sr-derived rattler modes cut through (near 30 cm^{-1}) the acoustic phonon branches of the type-I clathrate system. It is precisely these modes that will scatter the heat-carrying acoustic modes of the framework and reduce the heat current. The overall characteristics of the phonon spectra computed

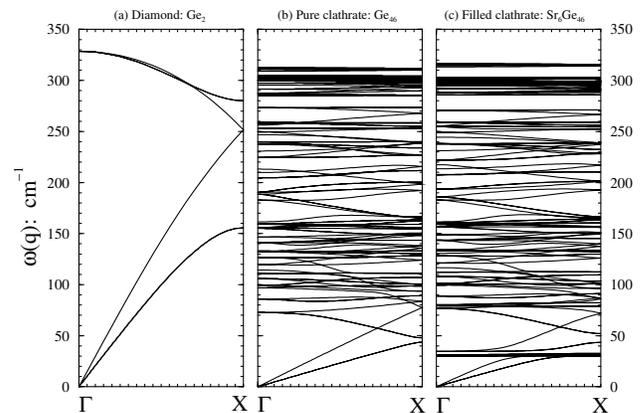


FIG. 1. The phonon dispersion curves of (a) diamond structure Ge, (b) guest-free clathrate Ge_{46} , and (c) guest-containing clathrate $\text{Sr}_6\text{Ge}_{46}$. In (c), Sr occupies the six large cages.

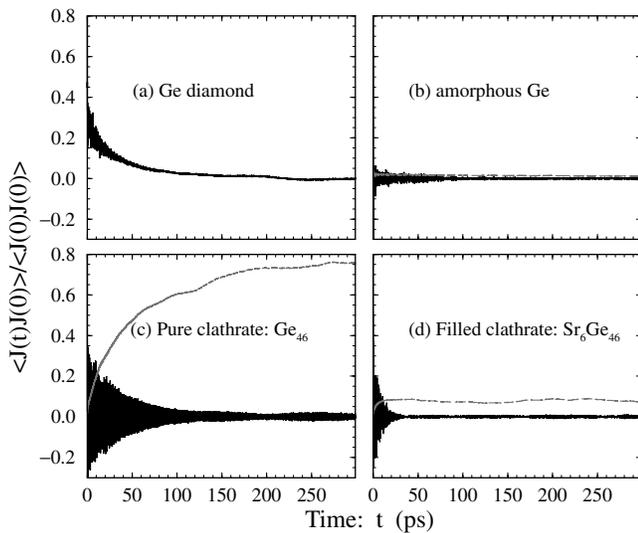


FIG. 2. The normalized time-dependent correlation function $g(t)$ at room temperature for (a) d -Ge, (b) a -Ge, (c) the guest-free clathrate framework Ge_{46} , and (d) the guest-containing clathrate $\text{Sr}_6\text{Ge}_{46}$. The time integration of $g(t)$ is also shown as a dashed curve in (b)–(d).

with the empirical potentials used here are consistent with previous results obtained using *ab initio* theory [11,12].

Our most significant results are shown in Fig. 2, where we show our computed normalized current correlation function $g(t)$ for the four tetrahedrally bonded Ge solids all at room temperature. All $g(t)$ start at $t = 0$ with a value of unity. Data extracted from these functions, including κ , are given in Table I, along with comparisons with experiment.

We first discuss $g(t)$ for d -Ge, which is shown in Fig. 2(a). Within the first ~ 0.1 ps or less, $g(t)$ rapidly drops from unity to a value near 0.3. This is due to a dephasing of the current from multiple vibrational modes. For later times, the decay is similar to an exponential, although there are small amplitude oscillating terms. A model expression for $g(t)$ is

$$g(t) = A_0 e^{-t/\tau_0} + \sum_j B_j e^{-t/\tau_j} \cos(\omega_j t). \quad (4)$$

In this model, the area under $g(t)$, τ_I , is approximately $A_0 \tau_0$. For d -Ge, the B_j are small, and the system behaves much like a single relaxation-time system with $\tau_I \approx A_0 \tau_0 = 10.82$ ps. The computed κ is 114 ± 3 W/K m

(room T). A rough estimate using Eq. (1) of the phonon mean free path can be obtained by averaging the acoustic transverse and longitudinal velocities (≈ 4000 m/s) and by using $\frac{3k_B}{\Omega_{\text{atom}}}$ for the specific heat to give $\lambda^{\text{theory}} = 482$ Å. The comparison of the theoretical value of κ with the experimental value (62 W/K m [13,14]) is not quantitatively accurate. However, we feel that a factor of 2 agreement with experiment is acceptable when it is noted that the fitting process for the Tersoff potentials neglected anharmonic processes which is a key ingredient for the thermal conductivity. Additional errors from neglect of quantum effects should be small since the Ge Debye temperature is 374 K. However, our lattice is isotopically pure (an average mass of 72.6 amu was used), while experimental samples are not, and this is one source of error. Experiments on near-isotopically pure d -Si [15] and d -Ge [14] show an enhancement of the room-temperature κ of 60% (for Si) and 30% (Ge). This is qualitatively consistent with our computed higher value.

Amorphous Ge, Fig. 2(b), has a very different $g(t)$ from that of d -Ge. It rapidly drops from unity to near zero and then oscillates around zero with a decaying envelope. The integrated relaxation time τ_I is approximately 1/100 that of d -Ge, which results in a corresponding reduction of κ . It has been shown that amorphous materials have finite thermal conductivities even for a harmonic lattice [16]. The computed κ is 0.62 ± 0.15 W/K m. An estimate of λ obtained from $g(t)$ using Eq. (1) is 2.5 Å, or only a nearest-neighbor distance. This very short mean free path is consistent with the theory of the minimum thermal conductivity (κ_{min}) of an amorphous adamantane-based solid [17,18]. In the classical (high temperature) limit, this theory gives $\kappa_{\text{min}} = \frac{1}{\nu_A} \times 3k_B \bar{v}^2 / (8\Omega_{\text{atom}})$, where Ω_{atom} is the atomic volume, and ν_A is the maximum acoustic frequency. This model assumes that the scattering in an amorphous material is so large that the mean free path is equal to its wavelength. In this κ_{min} theory, only the acoustic modes are considered. Choosing $\nu_A \approx 200$ cm^{-1} from Fig. 1, and using the estimate $\bar{v} \approx 4000$ m/s given earlier, we obtain $\kappa_{\text{min}} = 0.62$ W/K m, which is in remarkably good agreement with the present results and with the experimental [18] value of 0.50 W/K m. The mean free path in the minimum thermal conductivity model is approximately $\bar{v}/\nu_A = 6.7$ Å, which is larger than the 2.5 Å deduced for λ above.

TABLE I. Results of the MD simulations for the four different Ge materials. The final column is experiment, where available. All results are at 300 K.

Material (No. atoms)	τ_I (ps)	$G(0)$ (W/K m ps)	κ —Theory (W/K m)	κ —Expt. (W/K m)
d -Ge (512)	10.82 ± 0.27	10.5	114 ± 3	62. [13,14]
a -Ge (512)	0.013 ± 0.003	48.8	0.63 ± 0.15	0.50 [18]
Ge_{46} (2944)	0.745 ± 0.015	16.4	12.2 ± 0.25	...
$\text{Sr}_6\text{Ge}_{46}$ (3328)	0.078 ± 0.011	21.0	1.64 ± 0.24	0.89* [3]

*($\text{Sr}_8\text{Ga}_{16}\text{Ge}_{30}$)

The function $g(t)$ for the empty clathrate-I framework Ge_{46} is shown in Fig. 2(c). This function has rapidly oscillating terms with an exponential envelope. Its Fourier transform shows that the static term [A_0 in Eq. (4)] is about 10% of the oscillating terms. This leads to a large reduction of τ_I compared to that of d -Ge. The frequencies ω_j in Eq. (4) which appear with significant weight are above 90 cm^{-1} (see Fig. 1). They are thus derived from the optic modes of the framework. We note that the exponential envelope of $g(t)$ is very similar to the exponential-like decay of $g(t)$ for d -Ge. We conclude that phonon lifetimes are not appreciably different for d -Ge and Ge_{46} , even though τ_I (which is $\approx A_0\tau_0$) differs in the two cases by about an order of magnitude. The computed κ is $12.2 \pm 0.25 \text{ W/K m}$. We note from Table I that $\kappa_{\text{Ge}_{46}}/\kappa_{d\text{-Ge}} = 12.6/118 \approx 0.11$. The origin of this large decrease in κ is found in the arguments of Slack [17] and Roufosse *et al.* [19] on the scaling of κ with the number of atoms in the unit cell. The assumptions are that only acoustic phonons matter, and that κ scales as $\Omega_{\text{cell}}^{1/3}\theta_D^3$, where Ω_{cell} is the cell volume and θ_D the acoustic Debye frequency. This scaling follows from the high temperature thermal conductivity obtained by Leibfried *et al.* [20] and Julian [21]. The scaling with the number of atoms n in the unit cell follows as $\kappa_n = \kappa_1/n^{2/3}$. For the clathrate-diamond ratio, this yields $\kappa_{\text{Ge}_{46}}/\kappa_{d\text{-Ge}} = 0.12$, in remarkable agreement with the result obtained from our MD simulations. We know of no other example where this scaling has been so clearly demonstrated in such a complex system.

The correlation function $g(t)$ for $\text{Sr}_8\text{Ge}_{46}$ is shown in Fig. 2(d). As for Ge_{46} , $g(t)$ has rapidly oscillating terms with an exponential envelope. The decay of this envelope is clearly much more rapid than that for Ge_{46} [Fig. 2(c)]. Thus the τ_I for $\text{Sr}_8\text{Ge}_{46}$ is reduced to 0.078 ps compared to 0.75 ps for Ge_{46} . This clearly demonstrates the strong effect of the Sr rattler on κ ; numerically it reduces κ of the clathrate by approximately 1 order of magnitude. The computed κ is $1.64 \pm 0.24 \text{ W/K m}$, which compares favorably with the experimental value of 0.89 W/K m . The coupling between the resonant Sr rattler modes and the acoustic modes produces enhanced scattering, thus reducing τ_I and κ .

In summary, we have examined the lattice thermal conductivity of Ge in four distinct sp^3 -bonded solids; d -Ge, a -Ge, the guest-free type-I clathrate framework Ge_{46} , and the rattler-containing type-I clathrate $\text{Sr}_8\text{Ge}_{46}$. Our results show that the clathrate framework reduces κ by roughly an order of magnitude compared to that for the diamond phase. We further find that the presence of guest rattlers in the cages of the clathrate framework produces acoustic band local modes which reduce κ by yet another order of magnitude. The theory is able to separate the individ-

ual contributions of each of these effects. Further, we find that κ in the filled clathrate system is comparable to that in a -Ge, which confirms the ideas of Slack and others. Our results are in reasonable agreement with experiment. We hope they will help in the future selection of materials as candidates for optimized thermoelectric materials.

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