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Diameter-dependent thermal conductivity of ultrathin GaP nanowires: A molecular dynamics study

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The diameter dependence of the thermal conductivity of nanowires is usually modeled using Matthiessen's rule, by putting the mean free path of phonons equal to the diameter d of the nanowire. This results in a thermal conductivity κ that decreases with decreasing d , due to the increase in boundary scattering. Recent molecular dynamics studies of heat transport in thin silicon nanowires have shown a nonmonotonic diameter dependence of κ , where a decrease with decreasing d is followed by an increase to a value of κ exceeding the bulk thermal conductivity. This increase of κ was explained by an increase of the importance of hydrodynamic transport effects in the thinner wires, where the normal scattering by phonon-phonon interaction increases, but the Umklapp scattering decreases [Y. Zhou, X. Zhang, and M. Hu, *Nano Lett.* **17**, 1269 (2017)]. Here, we study heat transport in thin nanowires of the compound semiconductor gallium-phosphide in the wurtzite crystal structure, using molecular dynamics simulations. A similar nonmonotonic d dependence of κ is found as in silicon nanowires, but with a minimum in κ occurring at a much larger diameter of $d \approx 8$ nm instead of 2–3 nm.

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I. INTRODUCTION

Semiconductor nanowires (NWs) have been widely recognized as ideal systems for energy conversion [1–3]. Various studies have shown the potential of NWs as highly efficient thermoelectric materials [4–6], with a thermoelectric efficiency higher than that of the bulk material. This increase in the thermoelectric efficiency results mainly from the reduction in the thermal conductivity κ of NWs as compared to the bulk material. Owing to the increase in scattering at the NW boundary, a reduction in κ can be effected by reducing the diameter d of the nanowire [7–9], thereby reducing the phonon mean free path.

Assuming diffuse scattering at the boundary, the phonon mean free path is limited by the thickness of the wire, which limits the thermal conductivity. The reduction in κ with decreasing d is usually modeled using Matthiessen's rule by putting the mean free path of phonon-boundary scattering equal to d [10]. However, a few modeling studies using molecular dynamics (MD) have shown that at extremely small diameters (a couple of nanometers), κ of Si NWs increases with decreasing d [11–13]. Ponomareva *et al.* [11] studied the thermal conductivity of Si NWs using direct (nonequilibrium) MD. They showed that κ increases below a diameter $d = 1.5$ nm and attributed this to a phonon confinement effect [11]. Donadio and Galli [12] showed, using equilibrium MD based on the Green-Kubo formalism, that κ of Si NWs with $d = 1.1$ nm is higher than that of NWs with $d = 2$ and 3 nm. Zhou *et al.* [13] studied the thermal conductivity of Si NWs using equilibrium MD with d ranging from 1 to 4 nm. They also found a nonmonotonic dependence of κ on d with a higher value of κ for very thin wires. They attributed this to

the increased importance of hydrodynamic effects in phonon transport [14–17], where for the low-frequency phonons that are mostly responsible for the heat transport the three-phonon scattering rate of total phonon momentum-conserving normal scattering increases with decreasing d , but that of momentum-destroying Umklapp scattering decreases.

The above MD studies focused on Si NWs, which are one of the most widely studied systems. It is still unknown whether other systems, for example, compound semiconductor NWs, would also show such nonmonotonic behavior. Multiatom systems like compound semiconductors have a phononic bandgap resulting from the difference in masses of the atoms, which could influence phonon-phonon scattering. Also, the effect of crystal structure is unknown. In this work, we study the diameter dependence of the thermal conductivity of wurtzite gallium-phosphide (GaP) NWs using equilibrium MD simulations to investigate whether a similar nonmonotonic dependence of the thermal conductivity on diameter can be found.

The paper is organized as follows. In Sec. II, we discuss the NW structure (Sec. II A), the used interatomic potential (Sec. II B), and the computational methodologies to calculate the thermal conductivity (Sec. II C), the three-phonon scattering rates (Sec. II D), and the phonon band structure (Sec. II E). Section III contains our main results and a discussion. In Sec. IV we present a summary with the main conclusions and an outlook.

II. NANOWIRE STRUCTURE, INTERATOMIC POTENTIAL, AND COMPUTATIONAL METHODOLOGIES

A. Nanowire structure

We study GaP NWs, which have a wurtzite (WZ) crystal structure [18], resulting in a hexagonal cross section [19] (see inset of Fig. 1). The growth (c) axis is along the (0001) direction. As initial lattice parameters for the WZ unit cell before

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FIG. 1. Main panel: Room-temperature (300 K) thermal conductivity κ of WZ GaP NWs as a function of diameter d , as calculated from equilibrium MD. The results are averages over $N = 20$ MD runs for $d \leq 4.99$ nm and $N = 10$ runs for $d > 4.99$ nm, from which also the error bars were estimated. The dashed line indicates κ of bulk WZ GaP obtained using the same method. Inset: top and side view of a NW with $d = 4.99$ nm. Red (blue) spheres correspond to Ga (P) atoms.

relaxation we take $a = 0.3842$ nm [18] and $c = \sqrt{8/3}a = 0.6274$ nm. The diameter of the NW is d . The thermal conductivity κ is calculated for NWs with d ranging from 3 to 41 unit cells, corresponding to the range 1.15–15.75 nm. The latter values are approximate, because of the relaxation of the atoms from their initial positions.

B. Interatomic potential

The atomic interactions are modeled using an optimized Tersoff potential, a preferred choice for modeling atomic interactions of group III-V semiconductors [20]. We use the Tersoff parameters for GaP obtained by Powell and coworkers [20] from a fit to cohesive and elastic properties calculated from first principles. We point out that these parameters were obtained for the bulk zinc blende structure of GaP. Here, we use the same potential with these parameters for a WZ structure. This could possibly somewhat affect the absolute values of κ , but we do not expect a significant effect on the diameter dependence of κ .

C. Calculation of the thermal conductivity

We calculate the thermal conductivity κ of GaP NWs using equilibrium MD. In this method, the thermal conductivity tensor $\kappa_{\alpha\beta}$ ($\alpha, \beta = x, y, z$) is calculated from the integral of the average heat current autocorrelation function (HCACF) using the linear response Green-Kubo formula [21–24]

$$\kappa_{\alpha\beta} = \frac{1}{k_B T^2 V} \int_0^\infty \langle J_\alpha(t_0) J_\beta(t_0 + t) \rangle dt, \quad (1)$$

where V is the system volume, k_B is the Boltzmann constant, and T is the temperature of the system. $J_\alpha(t_0)$ and $J_\beta(t_0 + t)$ are the heat current vector components along direction α and β at time t_0 and time $t_0 + t$. The HCACF $\langle J_\alpha(t_0) J_\beta(t_0 + t) \rangle$ is the ensemble average of their product. We calculate the

TABLE I. Effect of total simulation time t_{total} on the calculated thermal conductivity κ of a GaP NW with diameter $d = 1.15$ nm. Averages were taken over $N = 10$ MD runs for each value of t_{total} , from which also the error bars were estimated. To reduce the required computation time to study this effect, a correlation time $t_{\text{corre}} = 500$ ps was used and a length $L = 4.95$ nm, which are smaller than the values $t_{\text{corre}} = 4000$ ps and $L = 12.55$ nm used in Fig. 1.

Total simulation time t_{total} (ns)	Thermal conductivity κ (W/m K)
40	283 ± 20
60	294 ± 11
80	303 ± 17
120	292 ± 7

HCACF as an average over time, as explained below, combined with an average over N MD simulations with different initial conditions.

The heat current is calculated using the formula (valid for three-body potentials) [25]

$$\mathbf{J} = \sum_i^N E_i \mathbf{v}_i + \frac{1}{2} \sum_{i,j;i \neq j}^N (\mathbf{F}_{ij} \cdot \mathbf{v}_i) \mathbf{r}_{ij} + \frac{1}{6} \sum_{i,j,k;i \neq j \neq k}^N (\mathbf{F}_{ijk} \cdot \mathbf{v}_i) (\mathbf{r}_{ij} + \mathbf{r}_{ik}), \quad (2)$$

where E_i and $\mathbf{v}_i$ are the total energy (kinetic and potential) and velocity of atom i , $\mathbf{F}$ are the interatomic forces, and $\mathbf{r}$ the interatomic distances.

The open-source MD package LAMMPS [26] is used for all the simulations. The MD time step is fixed at 0.5 fs. Periodic boundary conditions with a period L are applied along the z direction of the NW, which is the direction of heat propagation. Free boundary conditions are applied along the other directions. At the beginning of each simulation, the NW structure is relaxed, also along its length, and the NW is equilibrated to room temperature (300 K) using the isobaric-isothermal (NPT) ensemble for 2 ns and the canonical ensemble (NVT) for 0.5 ns. Following the relaxation and equilibration, the HCACF is calculated in the microcanonical ensemble (NVE). For this, the heat current vector $\mathbf{J}(t)$ is sampled every five time steps. The thermal conductivity $\kappa = \kappa_{zz}$ is then obtained by numerical integration of the HCACF $\langle J_z(t_0) J_z(t_0 + t) \rangle$.

Following the nomenclature of Wang *et al.* [27], in Eq. (1) the HCACF is integrated up to a finite correlation time t_{corre} smaller than the total simulation time t_{total} , while a time average is performed over t_0 in the interval $0 \leq t_0 \leq t_{\text{total}} - t_{\text{corre}}$. Finally, an average over N independent simulations is taken. For the thinnest wire ($d = 1.15$ nm) we take $t_{\text{corre}} = 4000$ ps and $N = 20$, for the intermediate-thickness wires ($1.92 \text{ nm} \leq d \leq 4.99$ nm) we take $t_{\text{corre}} = 2000$ ps and $N = 20$, and for the thick wires ($d > 4.99$ nm) we take $t_{\text{corre}} = 500$ ps and $N = 10$. For these values, sufficiently accurate results are obtained. In all results presented below, $t_{\text{total}} = 40$ ns is taken. Table I shows that taking longer values of t_{total} than 40 ns does not significantly change the final result for the thinnest

TABLE II. Effect of finite length L of the NW on the calculated κ of a GaP NW with diameter $d = 1.15$ nm. A correlation time $t_{\text{corre}} = 4000$ ps was used and a total simulation time $t_{\text{total}} = 40$ ns. Averages were taken over $N = 20$ MD runs for each value of L , from which also the error bars were estimated.

NW length L (nm)	Thermal conductivity κ (W/m K)
1.25	53 ± 3
2.51	186 ± 23
5.02	290 ± 29
7.53	379 ± 57
10.04	423 ± 66
12.55	525 ± 50
15.06	663 ± 79
20.08	505 ± 88
25.10	500 ± 65

considered wire with $d = 1.15$ nm, which is the most critical case. Table II shows that a wire length $L = 12.55$ nm yields sufficiently converged results for this most critical case. For the other wire length, taking $L = 4.95$ nm is sufficient.

D. Calculation of the three-phonon scattering rates

In order to interpret the thermal conductivity results, three-phonon scattering rates are calculated using the Tersoff potential for the thinnest considered NWs with $d = 1.15$ and 1.92 nm, and for bulk WZ GaP. These calculations are done using a combination of LAMMPS and PHONO3PY [28]. The third order interatomic force constants (IFCs) are used to compute the imaginary part of the phonon self-energy, from which the phonon lifetimes are obtained [28,29]. For the calculation of the third order IFCs an atomic displacement of 0.03 Å and a pair distance cutoff of 3.9 Å is taken. For the NWs a $1 \times 1 \times 4$ supercell and a $1 \times 1 \times 160$ q -point grid for sampling the first Brillouin zone (1BZ) are used, and for bulk WZ GaP a $3 \times 3 \times 2$ supercell and a $37 \times 37 \times 33$ q -point grid. The summations over the 1BZ are done using the linear tetrahedron method [8]. This approach provides sufficiently accurate three-phonon scattering rates.

E. Calculation of the phonon band structure

We calculate the phonon band structure of the thinnest considered NWs with $d = 1.15$, 1.92 , and 2.69 nm using the Tersoff potential. These calculations are done using a combination of LAMMPS and PHONOPY [29], employing an interface between the two packages [30]. For the calculation of the second order IFCs an atomic displacement of 0.01 Å and a pair distance cutoff of 3.9 Å are taken. The second order IFCs are then used to create the dynamical matrix, from which the phonon frequencies as a function of wave vector q along the NW are obtained. A $1 \times 1 \times 4$ supercell and a $1 \times 1 \times 20$ q -point grid for sampling the 1BZ are used, providing a sufficiently accurate band structure.

III. RESULTS AND DISCUSSION

The thermal conductivity κ as a function of diameter d , which is our main result, is shown in the main panel of Fig. 1. As in the work on Si NWs [11–13] we observe a nonmonotonic dependence of κ on d , with a thermal conductivity $\kappa = 525 \pm 50$ W/m K for the thinnest considered NW ($d = 1.15$ nm). This is about five to six times larger than the calculated bulk thermal conductivity $\kappa_{\text{bulk}} = 92 \pm 5$ W/m K of WZ GaP. No experimental results are yet available for thermal conductivities of WZ GaP nanowires. For bulk GaP, experimental thermal conductivities are only available for the equilibrium zinc blende structure, with a room-temperature value of 75.2 W/m K [31]. Interestingly, the minimum in κ in Fig. 1 appears at a diameter $d \approx 8$ nm that is considerably larger than in Si NWs ($d \approx 2$ – 3 nm [13]). In the remainder of this section we discuss these results and the various steps that lead to them.

In Fig. 2 we show examples of the HCACF for GaP NWs with different diameters d and the HCACF of bulk WZ GaP. The HCACF does not decay monotonically, but shows an oscillation with a period of about 0.1 ps, as indicated in Fig. 2(a). This oscillation is caused by the excitation of optical phonons related to the relative motion of the Ga and P atoms, which have different masses [32]. Such oscillation does not occur for monoatomic materials like Si [27]. Apart from this high-frequency oscillation, a beating with a period of about 2 ps is visible for the thinnest NWs. We suggest that superpositions of the above high-frequency optical phonons with slightly different frequencies lead to this beating. This beating has damped out for the various values of the correlation times t_{corre} we use.

Figure 3 shows the results for κ when integrating the HCACF up to t_{corre} . For the thinnest wire with $d = 1.15$ nm we need a very large value $t_{\text{corre}} = 4000$ ps to obtain a reasonably converged result, while for intermediate-thickness wires of $1.92 \text{ nm} \leq d \leq 4.99$ nm taking $t_{\text{corre}} = 2000$ ps suffices, as mentioned in Sec. II C. For thick wires with $d > 4.99$ nm and for bulk WZ GaP $t_{\text{corre}} = 500$ ps is sufficient. The reason for taking these different values of t_{corre} is that the HCACF for thin wires decays slower than for thicker wires (see Fig. 2), which is related to the larger κ of thin wires (see Fig. 1). For comparison, the result for bulk WZ GaP is shown in Fig. 3(c). The bulk result was obtained from an equilibrium MD simulation for a $8 \times 8 \times 8$ supercell and an average over 10 runs. The averages over the last 50 ps of the curves in Fig. 3 yield the values for κ given in Fig. 1.

The increase in κ with decreasing diameter d in Si NWs was explained by Zhou *et al.* [13] by a decrease of the Umklapp (U) three-phonon scattering rate for low-frequency phonons with decreasing d , accompanied by an increase of the normal (N) scattering rate. To check if the same holds for our GaP NWs, we plot in Figs. 4(a) and 4(b) the U and N scattering rates as a function of frequency f of phonon modes in thin wires with $d = 1.15$ and 1.92 nm. For comparison, we show results for bulk WZ GaP in Fig. 4(c). We observe that also in the case of GaP NWs the U scattering rate for low-frequency phonons decreases while the N scattering rate increases with decreasing d , as indicated by the arrows in Figs. 4(a) and 4(b). These trends lead to a more pronounced

FIG. 2. Normalized HCACF $\langle J_z(t_0)J_z(t_0 + t) \rangle$ as a function of time t , obtained from single MD runs for (a)–(e) GaP NWs with different diameters d and (f) bulk WZ GaP. The oscillation with a period of about 0.1 ps indicated in (a) is related to the excitation of diatomic optical phonons.

hydrodynamic character of the heat flow in thinner NWs and hence to a higher thermal conductivity [13]. Hydrodynamic phonon transport results from the dominance of total phonon momentum-conserving N scattering over resistive U scattering processes [14–17]. U scattering leads to relaxation of the phonon distribution to the equilibrium Bose-Einstein distribution, which has zero total phonon momentum. N scattering conserves total phonon momentum and leads to relaxation to an intermediate drift distribution where the phonons drift as a group with a nonzero average velocity. When U scattering decreases and N scattering increases, the thermal conductivity will therefore increase.

Zhou *et al.* [13] attributed the decrease in U scattering in Si NWs to changes in the phonon band structure of the NWs when their thickness changes. Figure 5 shows the calculated one-dimensional phonon band structure of GaP NWs with diameters $d = 1.15$, 1.92, and 2.69 nm. We observe the expected four gapless modes, consisting of two degenerate

flexural modes, a torsional mode, and a compressional mode, as indicated in Fig. 5(a). Because of the confinement of the phonon modes in the lateral directions, phonon subbands form. The second-lowest subband, which is twofold degenerate, is indicated by arrows in Fig. 5. It corresponds at the Γ point to a standing transversal acoustical wave in the radial direction with one nodal plane. As expected for subband formation, its frequency at the Γ point shifts up with decreasing d . Similar to Zhou *et al.* [13] we argue that U scattering is suppressed for low-frequency phonons in thin NWs for the following reason. The effect of U scattering on the thermal conductivity is dominated by a three-phonon absorption process where two low-frequency phonons from the gapless bands convert into a higher-frequency phonon. The higher-frequency phonon should be in a higher-lying band because of the addition of a nonzero reciprocal lattice vector to the total momentum, which characterizes U scattering. Because of the upward shift of the second-lowest subband in thinner NWs,

FIG. 3. (a) and (b) Thermal conductivity κ of GaP NWs with different diameters d obtained by integration of Eq. (1) up to a correlation time t_{corre} , with an average over $N = 20$ MD runs for $d \leq 4.99$ nm and $N = 10$ runs for $d > 4.99$ nm. Note the different scales of the x and y axes in (a) and (b). Note also that in (a) the longest value of t_{corre} is 4000 ps for the thinnest wire with $d = 1.15$ nm and 2000 ps for the other wires. (c) Result for bulk WZ GaP.

FIG. 4. Calculated three-phonon scattering rates as a function of phonon frequency f for normal and Umklapp processes in GaP NWs with diameters d of (a) 1.15 nm and (b) 1.92 nm. (c) Results for bulk WZ GaP. The phonon band gap occurs around $f = 10$ THz.

the availability of modes for the higher-frequency phonon decreases and thus the U scattering rate decreases. On the other hand, N scattering occurs within the low-lying gapless bands and is thus not suppressed with decreasing d . Hence, we confirm for GaP NWs the mechanism proposed by Zhou *et al.* for Si NWs, with the difference that in Si NWs a surface optical phonon branch lies below the second-lowest subband [13]. We do not have a simple explanation for the observed increase of the N scattering of low-frequency phonons with decreasing d , but this increase should be related to the subtle diameter-dependent changes in the dispersion of the low-frequency bands observed in Fig. 5.

Figures 4(a) and 4(b) show an interesting grouping of both U and N scattering rates of low-frequency phonons in GaP NWs that was not observed for Si NWs [13]. We traced this back to the different scattering rates of phonons in the different gapless bands indicated in Fig. 5(a). The torsional mode in the NWs is observed to have a significantly lower scattering rate than the flexural and compressional modes (by an order of magnitude or even more at low frequency). We also observe, by comparing our Fig. 5 with Fig. 5 in Ref. [13], that the velocity of the torsional mode in our GaP NWs is comparatively smaller than the velocity of this mode in Si NWs. We attribute both observations to the different crystal structures of GaP and Si NWs. The torsional mode in the WZ GaP NWs corresponds to the mutual rotation of planes of Ga and P atoms (see inset of Fig. 1). A relatively small restoring force will be present for the mutual rotation of planes of Ga and P atoms for which the Ga-P bonds are oriented along the wire axis. By contrast, in Si NWs there are no Si-Si bonds that are oriented along the wire axis, leading to a relatively large

restoring force and a comparatively higher velocity. We note that torsional modes cannot exist in the bulk, so there is no equivalent grouping of scattering rates in Fig. 4(c).

All the above results have been obtained for isotopically pure GaP, with 100% ^{69}Ga . The natural abundances of ^{69}Ga and ^{71}Ga are 60% and 40%, respectively, leading to isotope scattering. Table III shows the effect of isotope scattering in calculations of κ for the thinnest and second-thinnest nanowires ($d = 1.15$ and 1.92 nm) and for bulk WZ GaP, where the Ga atoms in our MD simulations were randomly chosen to be ^{69}Ga or ^{71}Ga according to the natural abundances. We note that, in order to reduce the simulation times, the calculations in Table III are for the thinnest wire done for a shorter length $L = 4.95$ nm than the $L = 12.55$ nm in Fig. 1, leading to reduced values of κ . Nevertheless, a clear trend is visible. The relative reduction of κ by isotope scattering increases with decreasing wire thickness, showing that isotope scattering becomes, relatively, increasingly important. However, κ still increases considerably with decreasing wire thickness.

IV. SUMMARY, CONCLUSIONS, AND OUTLOOK

From equilibrium molecular dynamics simulations of ultrathin wurtzite GaP nanowires with thicknesses in the range $d = 1.15$ – 15.75 nm we found a nonmonotonic dependence of the room-temperature thermal conductivity κ , where κ first decreases with decreasing d and then increases to a value much larger than the bulk thermal conductivity. Such nonmonotonic dependence was previously found in Si nanowires [11–13]. Like in the Si nanowires, we attribute the increase in

FIG. 5. Phonon dispersion curves up to a frequency $f = 3$ THz for GaP NWs with diameters d of (a) 1.15 nm, (b) 1.92 nm, and (c) 2.69 nm. In (a) the different types of gapless phonon branches are indicated. The arrow indicates the bottom of the second-lowest phonon subband.

TABLE III. Effect of isotope scattering on the calculated thermal conductivity κ of GaP NWs with diameters $d = 1.15$ and 1.92 nm, and bulk WZ GaP. Results are given for isotopically pure GaP (100% ^{69}Ga) and GaP with the natural abundances of 60% ^{69}Ga and 40% ^{71}Ga . The results for $d = 1.15$ nm, $d = 1.92$ nm, and bulk were obtained with $t_{\text{corre}} = 4000, 2000$, and 500 ps, respectively. The length of the wires is $L = 4.95$ nm. Averages were taken over $N = 10$ MD runs for all cases, from which also the error bars were estimated.

System	Isotopically pure GaP	GaP with 60% ^{69}Ga and 40% ^{71}Ga
Nanowire ($d = 1.15$ nm)	306 ± 30	190 ± 50
Nanowire ($d = 1.92$ nm)	142 ± 16	105 ± 13
Bulk	92 ± 5	78 ± 4

κ with decreasing d to an increased hydrodynamic character of the heat flow in the thinner nanowires. Here, the rates for total phonon momentum-destroying Umklapp three-phonon scattering of low-frequency phonons decrease while the rates for total phonon momentum-conserving normal scattering increase. We found interesting differences as compared to the scattering rates in Si nanowires that are related to a torsional mode with a low velocity and a low scattering rate. These results were obtained for isotopically pure GaP. For GaP with the natural abundances of the two Ga isotopes, we found that isotope scattering reduces κ relatively stronger for thinner wires, but that the increase in κ with decreasing d is still present.

Although the qualitative aspects of the nonmonotonic dependence of κ on diameter d in GaP and Si nanowires are comparable, important quantitative differences exist. For example, the minimum in κ occurs at a much larger value of $d \approx 8$ nm than in Si nanowires ($d = 2\text{--}3$ nm [13]). This means that this monotonic dependence can be much more easily experimentally observed in GaP nanowires than in Si nanowires. Although we do not know the cause of this difference, it suggests that the details of the nonmonotonic behavior depend on the specific semiconductor and/or on the specific crystal structure of the wire. It is likely that the nonmonotonic behavior is more pronounced or that the minimum in κ

occurs at even larger diameters for other semiconductors or crystal structures, and it would be of interest to systematically investigate this. It would also be of interest to investigate the temperature dependence, which was not addressed in the present work. The scattering at the nanowire surface caused by roughness or an oxide layer, which are inevitably present in experiment, should also be investigated [22]. The finding that thermal conductivities of ultrathin nanowires can be much larger than bulk conductivities can have important applications in rapid heat transfer at the nanoscale, possibly leading to cooling solutions in microelectronics.

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- [1] A. I. Hochbaum and P. Yang, *Chem. Rev.* **110**, 527 (2010).
- [2] N. P. Dasgupta, J. Sun, C. Liu, S. Brittan, S. C. Andrews, J. Lim, H. Gao, R. Yan, and P. Yang, *Adv. Mater.* **26**, 2137 (2014).
- [3] M. Y. Swinkels and I. Zardo, *J. Phys. D* **51**, 353001 (2018).
- [4] A. I. Hochbaum, R. Chen, R. D. Delgado, W. Liang, E. C. Garnett, M. Najarian, A. Majumdar, and P. Yang, *Nature* **451**, 163 (2008).
- [5] A. I. Boukai, Y. Bunimovich, J. Tahir-Kheli, J.-K. Yu, W. A. Goddard III, and J. R. Heath, *Nature (London)* **451**, 168 (2008).
- [6] R. Chen, J. Lee, W. Lee, and D. Li, *Chem. Rev.* **119**, 9260 (2019).
- [7] D. Li, Y. Wu, P. Kim, L. Shi, P. Yang, and A. Majumdar, *Appl. Phys. Lett.* **83**, 2934 (2003).
- [8] J. Lim, K. Hippalgaonkar, S.C. Andrews, A. Majumdar, and P. Yang, *Nano Lett.* **12**, 2475 (2012).
- [9] M. M. Rojo, B. Abad, C. V. Manzano, P. Torres, X. Cartoixa, F. X. Alvarez, and M. M. Gonzalez, *Nanoscale* **9**, 6741 (2017).
- [10] N. Mingo, *Phys. Rev. B* **68**, 113308 (2003).
- [11] I. Ponomareva, D. Srivastava, and M. Menon, *Nano Lett.* **7**, 1155 (2007).
- [12] D. Donadio and G. Galli, *Nano Lett.* **10**, 847 (2010).
- [13] Y. Zhou, X. Zhang, and M. Hu, *Nano Lett.* **17**, 1269 (2017).
- [14] S. Lee, D. Broido, K. Esfarjani, and G. Chen, *Nat. Commun.* **6**, 6290 (2015).
- [15] A. Cepellotti, G. Fugallo, L. Paulatto, M. Lazzeri, F. Mauri, and N. Marzari, *Nat. Commun.* **6**, 6400 (2015).
- [16] Y. Guo and M. Wang, *Phys. Rep.* **595**, 1 (2015).
- [17] P. Torres, A. Ziabari, A. Torelló, J. Bafaluy, J. Camacho, X. Cartoixa, A. Shakouri, and F. X. Alvarez, *Phys. Rev. Mater.* **2**, 76001 (2018).
- [18] S. Assali, I. Zardo, S. Plissard, D. Kriegner, M. A. Verheijen, G. Bauer, A. Meijerink, A. Belabbes, F. Bechstedt, J. E. M. Haverkort *et al.*, *Nano Lett.* **13**, 1559 (2013).
- [19] H. I. T. Hauge, M. A. Verheijen, S. Conesa-Boj, T. Etzelstorfer, M. Watzinger, D. Kriegner, I. Zardo, C. Fasolato, F. Capitani, P. Postorino *et al.*, *Nano Lett.* **15**, 5855 (2015).
- [20] D. Powell, M. A. Migliorato, and A. G. Cullis, *Phys. Rev. B* **75**, 115202 (2007).
- [21] S. G. Volz and G. Chen, *Appl. Phys. Lett.* **75**, 2056 (1999).

- [22] D. Donadio and G. Galli, [Phys. Rev. Lett. **102**, 195901 \(2009\)](#).
- [23] D. P. Sellan, E. S. Landry, J. E. Turney, A. J. H. McGaughey, and C. H. Amon, [Phys. Rev. B **81**, 214305 \(2010\)](#).
- [24] B. Qiu, H. Bao, G. Zhang, Y. Wu, and X. Ruan, [Comput. Mater. Sci. **53**, 278 \(2012\)](#).
- [25] Y. He and G. Galli, [Phys. Rev. Lett. **108**, 215901 \(2012\)](#).
- [26] S. Plimpton, [J. Comput. Phys. **117**, 1 \(1995\)](#).
- [27] Z. Wang, S. Safarkhani, G. Lin, and X. Ruan, [Int. J. Heat Mass Transf. **112**, 267 \(2017\)](#).
- [28] A. Togo, L. Chaput, and I. Tanaka, [Phys. Rev. B **91**, 094306 \(2015\)](#).
- [29] A. Togo and I. Tanaka, [Scr. Mater. **108**, 1 \(2015\)](#).
- [30] P. T. Alvarez, *Thermal Transport in Semiconductors: First Principles and Phonon Hydrodynamics* (Springer, New York, 2018).
- [31] W. M. Haynes, *CRC Handbook of Chemistry and Physics* (CRC Press, Boca Raton, FL, 2014).
- [32] A. J. H. McGaughey and M. Kaviany, [Int. J. Heat Mass Transf. **47**, 1799 \(2004\)](#).