Lattice Thermal Conductivity Crossovers in Semiconductor Nanowires

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For binary compound semiconductor nanowires, we find a striking relationship between the nanowire's thermal conductivity κ_{nwire}, the bulk material's thermal conductivity κ_{bulk}, and the mass ratio of the material's constituent atoms, r, as $\kappa_{\mathrm{bulk}}/\kappa_{\mathrm{nwire}} \propto (1 + 1/r)^{-3/2}$. A significant consequence is the presence of crossovers in which a material with higher bulk thermal conductivity than the rest is no longer the best nanowire thermal conductor. We show that this behavior stems from a change in the dominant phonon scattering mechanism with decreasing nanowire size. The results have important implications for nanoscale heat dissipation, thermoelectricity, and thermal conductivity of nanocomposites.

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Considerable progress has recently been made in the synthesis and characterization of semiconducting nanowires [1]. The interest in these systems stems from their great potential for nanoelectronic [2] and thermoelectric [3] applications, and also as fillers for nanocomposite materials [4]. Consequently, it is especially important to know how these nanowires conduct heat. It has been shown that nanowire thermal conductivity may be considerably lower than that of the bulk material [5]. This could have dramatic implications for heat dissipation in nanodevices [6], where a high thermal conductivity might be desirable, or for thermoelectrics, where the goal is to minimize the lattice thermal conductivity [3,7]. Several experiments have measured thermal conductivity of suspended structures: GaAs suspended microstructures [8], individual carbon nanotubes [9], Si nanowires [5], and $\mathrm{SnO_2}$ nanobelts [10]. Some of these experiments have been theoretically addressed [10–15].

One important question to ask is: to what extent does the bulk thermal conductivity of a material determine the thermal conductivity of a nanowire made of that material? One might trivially assume that the higher the bulk material's thermal conductivity, the higher the nanowire's thermal conductivity. Here we show that this is not the case. We prove that the ratio of bulk to nanowire thermal conductivity is directly related to the mass ratio of the constituent atoms in a nontrivial way. Hence, the fact that a bulk material "A" has a higher lattice thermal conductivity than another bulk material "B" does not imply that the same will hold true for nanowires made of these materials. In some cases, a nanowire of material B can have a higher conductivity than a nanowire of material A of the same thickness. We explicitly show this by theoretical calculation of ten different compound semiconductors of the zinc blende structure. The specific dependence of the conductivities on the mass ratio is theoretically derived and computationally verified. Implications for different fields are also discussed.

To describe the harmonic properties of the atomic lattice we employ the potential proposed by Harrison [16], equivalent to a Stillinger-Weber type potential [17,18] in the harmonic limit. The harmonic part of the Hamiltonian has the form

$$\hat{H}^{(h)} = \sum_i \frac{\hat{\mathbf{p}}_i^2}{2m_i} + \frac{1}{2}\sum_{ij} \hat{\mathbf{u}}_i \mathbf{K}_{ij} \hat{\mathbf{u}}_j,\ \mathbf{K}_{ij} = \frac{\partial^2 \mathcal{V}}{\partial \mathbf{u}_i \partial \mathbf{u}_j}, \quad (1)$$

$$\mathcal{V} = \sum_{i,j \in n.n.} \frac{1}{2} C_0 \frac{(d_{ij} - d_0)^2}{d_0^2} + \sum_{i,j,k \in n.n.} \frac{1}{2} C_1 \delta\Theta_{ijk}^2, \quad (2)$$

where the $\mathbf{u}$'s are the displacement vectors with respect to the equilibrium positions, d_{ij} is the distance between nearest neighbor atoms i and j, and $\delta\Theta_{ijk}$ is the change in angle between the i, j and j, k bonds. The sums are extended to all the neighbor pairs and triplets in the system. We take the nanowire direction to be along [111], which we define as the z direction. The nanowire unit cell consists of two adjacent cross-sectional atomic layers and the atoms at the boundary of the wire are taken to be frozen [19]. The potential derivatives defining K_{ij} are obtained analytically and used to calculate the nanowire phonon dispersions, $\omega_\alpha(k_z)$. Here, α is the nanowire phonon branch index and k_z the wave number along the wire.

The two force constants C_0 and C_1 correspond to the two-body stretching and three-body bending terms, respectively. For each material, we computed the bulk phonon dispersion relations, adjusting these constants to exactly match the experimental frequency values [20–23] of the zone center longitudinal optical mode, $\omega_{LO}(\Gamma)$, and the zone edge transverse acoustic mode, $\omega_{TA}(X)$ (Table I.)

The next task is to solve for the phonon transport through the wire, for any arbitrary diameter. The solution of the linearized Boltzmann transport equation in the relaxation time approximation yields the following ex-

TABLE I. Force constants, average speed of sound in the (111) direction, and mass ratio, for each of the materials. The force constants were adjusted by fitting the $TA(X)$ and $LO(\Gamma)$ frequencies to experimental values[20].

	C_0 (eV)	C_1 (eV)	$v_{111}(10^3$ m/s)	r
CdTe	34.57	0.357	2.08	1.14
ZnTe	30.47	0.604	2.97	1.95
ZnSe	32.98	0.690	3.18	1.21
ZnS	35.90	0.704	4.39	2.04
InSb	46.72	0.400	2.3	1.06
InAs	42.13	0.650	2.6	1.53
GaSb	39.20	0.658	2.8	1.75
GaAs	42.04	0.826	3.3	1.07
AlSb	42.02	0.774	3.4	4.51
InP	47.38	0.715	3.04	3.71

pression for the thermal conductivity [15]:

$$\kappa(T) = \frac{1}{s}\sum_{\alpha} \int_0^{\pi/a_z} \lambda_\alpha(k_z) \frac{\hbar\omega_\alpha(k_z)}{2\pi} \frac{df_B}{dT} v_z(\alpha, k_z) dk_z, \quad (3)$$

where s is the wire cross section, v_z is the phonon velocity in the axial direction, $\lambda_\alpha(k_z)$ is the phonon relaxation length, and $f_B \equiv \frac{1}{e^{\hbar\omega/k_B T} - 1}$. Here it is essential to use the complete dispersion relations of the system [15]. The problem of how to properly include the boundary scattering was exactly solved by Dingle [24], actually in connection with the theory of electron transport. The application of Dingle's approach to phonon transport has been discussed in Refs. [25,26]. Dingle's solution assumes that the bulk material's dispersions are isotropic, which is reasonable for the materials considered [25]. For the cylindrical wires treated here, with diffuse boundary scattering, it is not difficult to prove that Dingle's exact solution yields almost identical results as if one uses Eq. (3) with a Mathiessen rule for the phonon relaxation length, $\lambda^{-1} = \lambda_i^{-1} + 1/D$. Here $\lambda(\omega)$ is the total relaxation length, $\lambda_i(\omega)$ is the intrinsic relaxation length in bulk due to anharmonic and impurity scattering, and D is the wire's diameter. A very good approximation for the intrinsic relaxation length is [27] $\lambda_i^{-1} v \equiv \tau_i^{-1} = BT\omega^2 e^{-C/T} + A\omega^4$, where v is an averaged isotropic acoustic phonon group velocity, while B, C, and A are constants that are fit using experimental measurements of the bulk thermal conductivity for the particular material. Results using Mathiessen's rule only deviate from the full Dingle type calculation by at most a few percent.

The procedure is then as follows: we compute the thermal conductivity as a function of temperature for the bulk material, adjusting the two anharmonic parameters B and C in order to obtain a best fit of the experimental bulk thermal conductivity, as described in Ref. [15]. The experimental curves of Refs. [28,29] were used for this. Once this has been done, the thermal conductivity is calculated for wires of any diameter. This approach has proven to yield very good results for Si nanowires [15] and SnO_2 nanobelts [10], in agreement with experimental results.

The results of the thermal conductivity calculation as a function of wire diameter are shown in Fig. 1 for the ten materials at 300 K. Each curve tends to its constant bulk value when D is large, and it approaches linear behavior in D at small diameter values. All curves present a monotonic decrease upon diameter reduction. However, the amount of decrease is by no means uniform throughout the ten materials. Several facts are apparent from the graph:

(1) Some curves run almost perfectly proportional to each other: the curves for CdTe and ZnSe run equidistant to each other in the log-log plot, with the conductivity changing by about 0.9 orders of magnitude between the bulk and 30 nm wire cases; the curves for ZnTe and ZnS are also nearly proportional, but now the conductivity change is nearly 1.1 orders of magnitude.

(2) The decreases are generally larger in the III-V group than in the II-VI group.

(3) There are line crossovers: we can see a crossover between the GaAs and InP curves; also, the curve for ZnSe is very close to that for ZnTe in the bulk, but it splits off for smaller diameters, and it approaches the ZnS curve when $D \sim 30$ nm.

To understand the above facts we must answer the three following questions: (1) What physical reason determines whether two materials have proportional curves or not? (2) From where does the smaller decrease in the II-VI group originate? (3) When can we expect two materials to show a crossover?

The answers stem from the change in the dominant scattering mechanism in going from bulk to nanowire. In the thin nanowire limit, or Casimir limit, phonon scattering is dominated by the boundary, and the relaxation time is $\tau \sim D/v$. For ease of reasoning, let us make the standard high temperature approximation $\frac{1}{1 - e^{\hbar\omega/k_B T}} \simeq \frac{k_B T}{\hbar\omega}$.

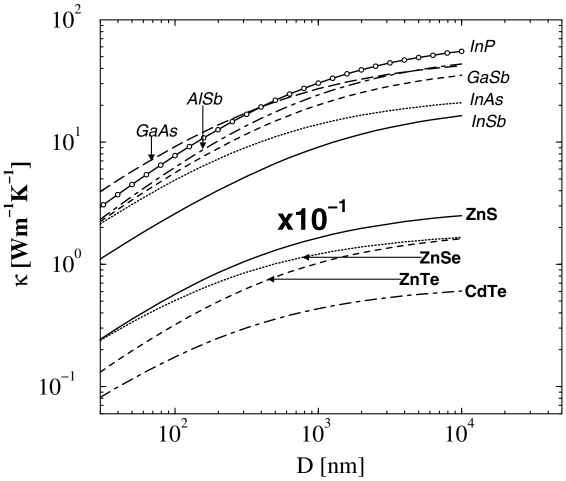

FIG. 1. Lattice thermal conductivity as a function of diameter for III-V (italics) and II-VI (bold) groups, at 300 °K.

Neglecting the small contribution of optical phonons, and approximating the dispersion branches by constant velocity hypercones, the thermal conductivity is roughly proportional to [15]

$$\kappa_{\rm nwire} \propto \frac{2}{v_{TA}^2}\int_0^{\omega_{TA}} \omega^2 d\omega + \frac{1}{v_{LA}^2}\int_0^{\omega_{LA}} \omega^2 d\omega$$
$$\propto 2\omega_{TA}^3/v_{TA}^2 + \omega_{LA}^3/v_{LA}^2. \qquad (4)$$

Let M_l and M_h be the masses of the lighter and heavier atom, respectively, in the material's unit cell. The upper limit of the longitudinal acoustic branch, ω_{LA}, depends on the mass of the heavier component atom only, as $\omega_{LA} \propto 1/\sqrt{M_h}$. This can be verified directly on Eq. 9-5 in Harrison [16]. Although it is not possible to give an analytical expression for the transverse acoustic frequency ω_{TA}, numerical calculation shows that it is nearly proportional to ω_{LA} upon mass variations, and its dependence on M_l is very weak. The speeds of sound depend on the masses as $v \propto 1/\sqrt{M_l + M_h}$, which can be verified by direct differentiation of Eq. 9-5 in Ref. [16]. Therefore, we can approximately write

$$\kappa_{\rm nwire} \propto \omega_{LA}^3/v^2, \qquad (5)$$

which depends on the masses as $\kappa_{\rm nwire} \propto (M_l + M_h)/M_h^{3/2}$. ($v$ is the average speed of sound.) On the other hand, the bulk thermal conductivity can be roughly approximated by [7,29]

$$\kappa_{\rm bulk} \sim c(M_l + M_h)\theta_D^3/T, \qquad (6)$$

where θ_D is the value of the material's experimental Debye temperature. [Constant $c \equiv 3.5(k_B/h)^3 V^{1/3}/\gamma^2$ is nearly equal for all the materials. $V =$ volume per atom, $\gamma =$ Grüneisen constant.]

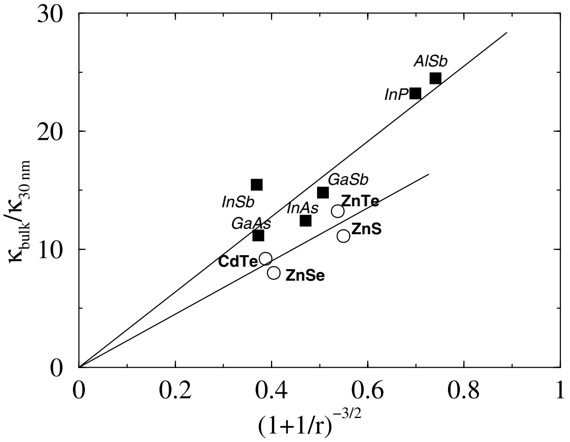

FIG. 2. Ratio of bulk to nanowire (30 nm) thermal conductivities, as a function of $(1 + 1/r)^{-3/2}$. r is the mass ratio of the binary material. The decrease in thermal conductivity with respect to its bulk value is larger for materials with mass ratios very different than 1. Squares: III-V materials. Circles: II-VI materials.

θ_D depends on the masses as $(M_l + M_h)^{-1/2}$, so $\kappa_{\rm bulk} \propto (M_l + M_h)^{-1/2}$. Consequently, the mass dependence of the ratio between the bulk and nanowire thermal conductivities takes place *only* through the mass ratio $r \equiv \frac{M_h}{M_l} \geq 1$, as

$$\kappa_{\rm bulk}/\kappa_{\rm nwire} \propto (1/r + 1)^{-3/2}. \qquad (7)$$

Obviously, this relation is based on very rough assumptions, and it should be understood to be only qualitative. Its meaning is that materials with r significantly higher than 1 will display a larger decrease in thermal conductivity upon diameter reduction than materials with $r \simeq 1$. To verify whether this is true, we have plotted the ratio $\kappa_{\rm bulk}/\kappa_{\rm 30\ nm}$ against $(1/r + 1)^{-3/2}$ for the III-V and II-VI materials in Fig. 2. Within each series, the values approximately lie along a straight line, proving the validity of the qualitative dependence, Eq. (7).

The III-V and II-VI zinc blende groups differ in that the former are stiffer than the latter, when compared side by side. This means that if one compares two materials, $X_m^{\rm III}Y_n^{\rm V}$ and $X_m^{\rm II}Y_n^{\rm VI}$, where their first and second elements, respectively, belong to the mth and nth rows of the periodic table, the III-V material is always stiffer. For example, the ratios between the bulk moduli of InSb/CdTe, GaSb/ZnTe, GaAs/ZnSe, and GaP/ZnS are 1.1, 1.1, 1.27, and 1.13 respectively [30]. This has implications in the line slope for each group, in Fig. 2. Since ω_{LA}, v, and θ_D all increase with stiffness, its effect does not cancel out in the ratio $\kappa_{\rm bulk}/\kappa_{\rm nwire}$ [Eqs. (5) and (6)]. The smaller stiffness of the II-VI group therefore results in a smaller slope of the II-VI line in Fig. 2. This is a qualitative argument, intended only to explain the different slope between the groups, and one should not attempt to use it in any quantitative manner. The effect of stiffness on the $\kappa_{\rm bulk}/\kappa_{\rm nwire}$ ratio results from a complicated interplay throughout all frequencies in the phonon dispersions, and it cannot be just described in terms of zero frequency properties like the bulk modulus. Therefore, only the full calculation, shown in Fig. 1, should be considered reliable in estimating the bulk to nanowire ratio of the thermal conductivities.

Thus we have the answer to the first and second questions posed earlier: (1) materials with similar mass ratios have proportional curves, and they exhibit similar decrease of thermal conductivity, with the dependence shown by Eq. (7). (2) Smaller stiffness of the II-VI materials results in overall smaller ratios of bulk to nanowire thermal conductivity, as compared to III-V materials. The answer to the third question, namely, "when can we expect a crossover?" is also provided by the mass ratio dependence. A crossover will most likely take place between two materials of the same group if the following conditions apply: (a) the components of material "*A*" with higher $\kappa_{\rm bulk}$ are in different rows of the periodic table and have considerably different masses, (b) those of material "*B*" with lower $\kappa_{\rm bulk}$ belong to the same row, and (c) the ratio of the two materials' bulk thermal conductivities is $\kappa^A_{\mathrm{bulk}}/\kappa^B_{\mathrm{bulk}} \lesssim 1.5$. The last condition comes from Eq. (7) and the fact that $r_A \gtrsim 2$ and $r_B \sim 1$. A clear case is that of InP, which crosses below GaAs already at $D \sim 0.1$ μ. In the case of ZnS and ZnSe, the bulk values' ratio is too large, and a crossover does not occur until $D \sim 10^1$ nm.

The results obtained have important implications. One of them concerns the suitability of these nanowires for thermoelectric devices, which is measured by the thermoelectric figure of merit, Z. Z is inversely proportional to the material's thermal conductivity. Although II-VI bulk materials have lower thermal conductivities than III-V, the gain in Z due to thermal conductivity reduction is not as large in II-VI as in III-V nanowires. The electronic properties of III-V nanowires are overall better than those of II-VI nanowires towards achieving a high Z. This, combined with the higher gain due to κ reduction, makes III-V nanowires more favorable than II-VI for thermoelectric applications [31].

Another important implication concerns heat dissipation. If one's goal were to drive heat quickly through a semiconducting nanowire of definite thickness, the best choice would not be InP, despite its high thermal conductivity in bulk. Instead, GaAs might be used with about 50% better conduction.

Finally, a third implication concerns the thermal conductivity of nanocomposites. Novel composite materials consisting of aggregates of nanowhiskers into a ceramic matrix have shown great promise in terms of their improved mechanical properties [4]. The thermal conductivity of these new materials is affected by the ability of the filler nanowhiskers to conduct heat. As we have seen, one cannot use the comparison between bulk conductivities of different materials as a guide towards what to expect for nanowhiskers. When the thermal conductivity is an issue, the choice of nanowhisker material cannot be based on the same considerations used for regular (macro) composites, but must account for the different ratios and possible crossovers that take place between the thermal conductivities of the nanoscale wires.

In conclusion, due to the change in dominant scattering mechanism when going from bulk to nanowire, the best *bulk* thermal conductor is not necessarily the best *nanowire* thermal conductor. In other words, the decrease in thermal conductivity upon wire thickness reduction varies considerably from one material to another. Within binary semiconductors of the III-Vor the II-VI group, this decrease is largely determined by the constituents' mass ratio, and roughly follows the approximate rule $\kappa_b/\kappa_w \propto (1 + M_{\mathrm{lighter}}/M_{\mathrm{heavier}})^{-3/2}$. The very different thermal conductivity reduction for different materials has important implications for nanowire based thermoelectrics, nanodevice heat dissipation, and in the thermal conductivity of nanocomposites.

[1] Y. N. Xia and P. D. Yang, Adv. Mater. **15**, 351 (2003).

[2] C. M. Lieber, MRS Bull. **28**, 486 (2003).

[3] G. Mahan, B. Sales, and J. Sharp, Phys. Today **50** No. 3, 42 (1997).

[4] J. Li, in *Handbook of Nanophase and Nanostructured Materials*, edited by Z. L. Wang, Y. Liu, and Z. Zhang (Kluwer Academic, New York 2003), p. 69.

[5] D. Li, Y. Wu, P. Kim, L. Shi, P. Yang, and A. Majumdar, Appl. Phys. Lett. **83**, 2934 (2003).

[6] M. Forshaw, R. Stadler, D. Crawley, and K. Nikolić, Nanotechnology **15**, s220 (2004).

[7] G. S. Nolas, J. Sharp, and H. J. Goldsmid, *Thermoelectrics* (Springer, New York, 2001).

[8] K. Schwab, E. A. Henriksen, J. M. Worlock, and M. L. Roukes, Nature (London) **404**, 974 (2000).

[9] P. Kim, L. Shi, A. Majumdar, and P. L. McEuen, Phys. Rev. Lett. **87**, 215502 (2001).

[10] L. Shi, Q. Hao, Ch. Yu, N. Mingo, X. Kong, and Z. L. Wang, Appl. Phys. Lett. **84**, 2638 (2004).

[11] D. H. Santamore and M. C. Cross, Phys. Rev. B **63**, 184306 (2001); **66**, 144302 (2002); Phys. Rev. Lett. **87**, 115502 (2001).

[12] M. A. Osman and D. Srivastava, Nanotechnology **12**, 21 (2001).

[13] T. Yamamoto, S. Watanabe, and K. Watanabe, Phys. Rev. Lett. **92**, 075502 (2004).

[14] S. Berber, Y-K. Kwon, and D. Tománek, Phys. Rev. Lett. **84**, 4613 (2000).

[15] N. Mingo, Phys. Rev. B **68**, 113308 (2003).

[16] W. A. Harrison, *Electronic Structure and the Properties of Solids* (Dover, New York, 1989).

[17] E. R. Cowley, Phys. Rev. Lett. **60**, 2379 (1988).

[18] F. H. Stillinger and T. A. Weber, Phys. Rev. B **31**, 5262 (1985).

[19] We have found that our results are relatively insensitive to different boundary conditions provided that the wire thickness in greater than ~20 nm.

[20] We use the frequency of the longitudinal rather than transverse optical mode. This gives an overall better agreement over the Brillouin zone. The results only change by less than a few percent if the TO frequency is used instead.

[21] http://www.ioffe.rssi.ru/SVA/NSM/Semicond/

[22] A. Dal Corso, S. Baroni, R. Resta, and S. de Gironcoli, Phys. Rev. B **47**, 3588 (1993), and references therein.

[23] Landolt and Börnstein, *Numerical Data and Functional Relationships in Science and Technology* (Springer, Berlin, 1982).

[24] R. B. Dingle, Proc. R. Soc. London A **201**, 545 (1950).

[25] S. G. Walkauskas, D. A. Broido, K. Kempa, and T. L. Reinecke, J. Appl. Phys. **85**, 2579 (1999).

[26] J. M. Ziman, *Electrons and Phonons* (Oxford University Press, Oxford, 1960).

[27] J. E. Parrott and A. D. Stuckes, *Thermal Conductivity of Solids* (Pion Ltd., London, 1975).

[28] M. G. Holland, Phys. Rev. B **134**, A471 (1964).

[29] G. A. Slack, Phys. Rev. B **6**, 3791 (1972).

[30] T. Soma, J. Phys. C **11**, 2669 (1978).

[31] N. Mingo, Appl. Phys. Lett. (to be published).