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Nanoscale mechanisms for the reduction of heat transport in bismuth

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Hand-on routes to reduce lattice thermal conductivity (LTC) in bismuth have been explored by employing a combination of Boltzmann’s transport equation and ab initio calculations of phonon-phonon interaction within the density functional perturbation theory. We have first obtained the temperature dependence of the bulk LTC in excellent agreement with available experiments. A very accurate microscopic description of heat transport has been achieved and the electronic contribution to thermal conductivity has been determined. By controlling the interplay between phonon-phonon interaction and phonon scattering by sample boundaries, we predict the effect of size reduction for various temperatures and nanostructure shapes. The largest heat transport reduction is obtained in polycrystals with grain sizes smaller than 100 nm.

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I. INTRODUCTION

Bismuth is an important semimetallic material for applications of the thermoelectric effect because of the low thermal conductivity (TC) [1]. Indeed, the thermoelectric efficiency is inversely proportional to the thermal conductivity. It is however also proportional to the power factor $\sigma S^2$, with $\sigma$ the electrical conductivity and $S$ the Seebeck coefficient. The Seebeck effect ($S$) is large in bismuth, but the presence of two types of carriers, electrons and holes, at the same time and in low concentrations, is not favorable [2] for $\sigma$.

Several experimental routes have been proposed to obtain one single type of carrier in bismuth, like doping the bulk material with a few percents of antimony to favor electron conduction with respect to hole transport [3,4]; or applying a magnetic field to promote field-induced hole Landau states at the Fermi level [5]. Alternatively, nanostructuring on the scale of a few tens of nanometers, with the aim of opening a confinement-induced energy gap [6–8], allows one to break the electron-hole symmetry around the Fermi level [2]. This has led to an increase of $S$ by several orders of magnitude in nanowires [8,9]. The latter route is a very appealing concept for a bismuth-based thermoelectric device because it enables either n- or p-type doping, allowing one to use the same material in the two legs of the thermocouple [10].

In contrast to Si [11–16] and SiGe alloys [12,17], systematic studies of the nanostructuring effect on the thermal conductivity are scarce in bismuth. A quasisuppression of the thermal conductivity has been found in bismuth nanowires, but its origin is still debated [2]. Measurements made on thin films [18–20] and nanowires [2,21–25], most of which are semiconducting, have yielded widely scattered values, preventing a deep understanding of the mechanisms at play in nanostructures [2]. A theoretical determination of the nanostructuring effect on the lattice thermal conductivity (LTC) of bismuth has thus become mandatory.

In bulk crystal, because of the uniaxial symmetry, the transport is anisotropic and is completely determined only by measuring the LTC in two directions, along the trigonal axis and perpendicular to it—either the binary or the bisection directions. Data are missing even in bulk bismuth: in the trigonal direction, the lattice conductivity has not been determined; in the binary direction, Uher et al. [26] were able to measure both total and electron and hole contributions solely up to the temperature $T \approx 150$ K. Estimations of the lattice part of the thermal conductivity given in experimental works [26,27] do not agree with each other, nor with the theoretical work of Ref. [28]. At ambient temperature, Gallo et al. (indirectly) measured 1.7 and 0.9 W/K m$^{-1}$ in the binary and trigonal directions, respectively [27], while the theoretical values produced by recent ab initio calculations [28] were 4.4 and 3.9 W/K m$^{-1}$. Thus large uncertainties also exist on the absolute value of the LTC in bulk Bi.

In this work, we show that ab initio calculations of the phonon-phonon interaction [29] and of phonon scattering by sample boundaries, combined to a transport equation for the phonon system, namely the Boltzmann transport equation (BTE) linearized to first order in the phonon distribution [30] $N$, reliably predicts the LTC for bulk bismuth down to temperatures as low as 30 K. In particular, ab initio calculations allow a direct insight into the microscopic mechanisms determining the transport, and the acoustic-optical phonon interaction turns out to determine the magnitude of the lattice thermal conductivity in bismuth, thus allowing us to explain the discrepancies between previous theoretical work [28] and experiments [26]. Moreover, we show that the available experimental data for the LTC for polycrystalline thin films are remarkably explained by our calculations, which enables us to predict the effect of LTC size reduction for various temperatures and nanostructure shapes and sizes.

More precisely, we have first validated our formalism for the calculation of bulk bismuth in the binary direction by comparing with available experiments (Sec. III A). In a second step, we have validated our theoretical values with available experimental data for polycrystalline thin films (Sec. IV A).
These validation steps have enabled us to predict in bulk bismuth both the lattice and electronic contributions in the trigonal direction. In the binary direction, they are predicted at temperatures at which only total conductivity measurements are available (Sec. III B). Then the heat transport reduction factor has been performed by taking into account the scattering by sample boundaries and by spherical grains inside the sample as two main ingredients are the third-order anharmonic constants and the joint density of states (JDOS). For an initial incoming phonon |ν⟩ = |q, λ⟩ of wave vector q and mode index λ, JDOS reads

\[ J_{q,\lambda} = \sum_{q',\lambda'} \delta(\omega_{q_0} + \omega_{q_0} - \omega_{q_{0}'}) + \delta(\omega_{q_0} - \omega_{q_0}' - \omega_{q_{0}''}). \]  

Here, the first δ function corresponds to a coalescence process, in which |q, λ⟩ and |q', λ'⟩ phonons interact to create a final |q'', λ''⟩ phonon, and the second δ function describes the decay of a |q, λ⟩ phonon, accompanied by the creation of two phonons |q', λ'⟩ and |q'', λ''⟩. One can then introduce a JDOS which depends on the frequency of the initial phonon, or \( \omega \)-dependent JDOS:

\[ J(\omega) = \sum_{q,\lambda} J_{q,\lambda} \delta(\omega_{q,\lambda} - \omega). \]  

In our work, phonon frequencies and group velocities have been computed within the density functional perturbation theory (DFPT) [36] on a \( 6 \times 6 \times 6 \) \( q \)-point grid in the Brillouin zone (BZ) centered at \( \Gamma \). The frequency gap between the highest acoustic branch and the lowest optical branch turns out to be of crucial importance in the calculation of the lattice conductivity (see Sec. III A), and an (upward) rigid shift of 12.5 cm\(^{-1}\) has been imposed on the frequencies of the optical phonon branches. State-of-the-art calculations of the third-order anharmonic constants have been performed on a \( 4 \times 4 \times 4 \) \( q \)-point grid in the BZ and interpolated on denser grids [38]. In BTE, the LTC was accurately converged on a \( 28 \times 28 \times 28 \) \( q \)-point grid in the BZ with a Gaussian broadening of the detailed balance condition [30] taken to be \( \sigma = 1 \) cm\(^{-1}\). Other technical details are reported in Appendix B.

III. THERMAL TRANSPORT IN BULK Bi

A. Lattice thermal conductivity

The magnitude of the LTC in bismuth [Fig. 1, panel (a)] turns out to be controlled by the phonon joint density of states [JDOS, Eq. (4) and Eq. (5)] available for the coalescence of two acoustic phonons into an optical one (Fig. 2, arrow in the right panel). In turn, the JDOS around 40 cm\(^{-1}\) is extremely sensitive to the frequency of the lowest optical phonon branch near zone center. When the latter corresponds to the experimental one at \( \Gamma \), i.e., 73 cm\(^{-1}\) at \( \Gamma \) (Fig. 2, left panel, solid line and green circles), the JDOS is much smaller and, consequently, the calculated lattice thermal conductivity is higher and agrees with the available experimental values for the LTC [26] [Fig. 1, panel (a), solid line and green symbols]. When the average optical frequency is lower with respect to experiment as in the \textit{ab initio} calculation (Fig. 2,
The total thermal conductivity (TTC) of semimetallic Bi contains both lattice and electronic contributions. As already explained above, experimental data for the lattice thermal conductivity of Bi are quite scarce. On the contrary, experimental data for the total thermal conductivity are available in

B. Electronic contribution

The total thermal conductivity (TTC) of semimetallic Bi contains both lattice and electronic contributions. As already explained above, experimental data for the lattice thermal conductivity of Bi are quite scarce. On the contrary, experimental data for the total thermal conductivity are available in
a wealth of experimental works [1,26,27,34,35]. We can use our calculated LTC to extract the electronic contribution from the TTC measurements [26,35].

In panel (c) of Fig. 1, the available experimental data for the electronic part of the TC of Bi are shown by green symbols. In order to compare the results of our calculations with the data shown in panel (c) of Fig. 1, we have used the experimental data of Ref. [26] for the TC, from which we have extracted our calculated LTC with experimentally observed AOPI. As one can see, the agreement between our results and available experimental data shown in panel (c) of Fig. 1 is very good, as a constant value of 6 W(K m)$^{-1}$ for the electronic contribution to the TC is obtained in both theory and experiment in the binary direction of Bi. Moreover, our calculations predict that the electronic contribution will stay constant and equal to 6.0 W(K m)$^{-1}$ over the whole 30–300 K temperature range. The constant behavior of the electronic contribution to TC as a function of temperature has been also observed experimentally; however, the reasons for this behavior, discussed for example in Ref. [26], are not trivial.

In the trigonal direction, the experimental results for the electronic contribution to the TC are not available. Our theoretical result shown in panel (d) of Fig. 1 has been obtained from the result for TTC of Ref. [35] and our calculated LTC with experimentally observed AOPI. As one can see, we predict a value of 3.0 W(K m)$^{-1}$ for the electronic contribution to the TC in the trigonal direction of Bi.

For the sake of comparison, the electronic contributions obtained from measured TTC [26,35] and ab initio LTC without shift of optical phonon branches are also shown in panels (c) and (d) of Fig. 1. For these results shown in dashed lines, not only the predicted value for the electronic contribution to the TC differs from the experiments in the binary direction, but, much more importantly, the experimentally observed constant behavior of the electronic contribution to the TC as a function of temperature is not reproduced in the case of overestimated AOPI.

In conclusion of this paragraph, our calculations predict constant values of 6.0 W(K m)$^{-1}$ and 3.0 W(K m)$^{-1}$ for the electronic contribution to the TC in Bi, in binary and trigonal directions, in the 30–300 K temperature range. This prediction is supported by the available experimental data, and thus can be further used to supplement the lack of experimental data, and to test future future approaches to compute the electronic contribution. In the present work, we will use it to predict the reduction in the total thermal conductivity in metallic nanostructures (see Sec. IV C3).

IV. THERMAL TRANSPORT IN NANOSTRUCTURED BI

It is important to stress that the nanostructures whose size is a few tens of nanometers are on the verge of the confinement-induced semimetal-to-semiconductor transition [41]. Data about this transition are still scarce and depend on the nanostructure shape [42] and sample preparation conditions. This is the reason why, in the following, we study both poly- and monocrystalline nanostructures, as well as semiconducting and conducting films.

Before discussing the nanostructures, we note that describing the sample boundaries though Casimir’s scattering rate, as we have done here, yields very different results with respect to the effect of size reduction on the LTC, compared to the accumulated approach, which is a typical approach used in the literature [43,44]. The comparison between the two approaches is shown in Appendix C.

A. Polycrystalline samples

Turning to the comparison of our calculated LTC with available experiments for Bi polycrystalline thin films [18], we note that, in polycrystalline samples, the nanostructuring effect is determined both by the film thickness, and by the average grain size [18]. In the work of Ref. [18], the average grain size was measured for every thin film investigated. While for very thin films, the average grain size was found to be larger than the film thickness, for films thicknesses larger than 200 nm, the average grain size was inferior to the film thickness (Fig. 3 in Ref. [18]). In our calculation, we took into account both scattering processes through Eq. (2), using the experimental grain sizes of Ref. [18] (Fig. 3, solid lines). As one can see in Fig. 3, we find a remarkable agreement with the results of Ref. [18] (red diamonds). The fact that the theoretical LTCs are close to the experimental total thermal conductivities is consistent with the marked semiconducting temperature-dependent behavior seen in the film electrical resistivity [18].

In Fig. 3, the available experimental data of Ref. [19] is also shown (empty squares). In Ref. [19], the average grain size was found to be approximately equal to the film thickness, i.e., it was found to be larger than that of Ref. [18] for
NANOSCALE MECHANISMS FOR THE REDUCTION OF . . . PHYSICAL REVIEW B 93, 064301 (2016)

FIG. 4. Lattice thermal conductivity (LTC) for different geometries of bismuth nanostructures. Solid lines: LTC in the binary direction for monocrystalline thin films as a function of the film thickness. Dotted lines: LTC along the binary axis of monocrystalline nanowires. Dashed lines: spherical grain.

most samples. Although our calculated LTC lies between the two experimental data sets for 200 K and 300 K, the best agreement is clearly found for the more recent work [18]. The most probable cause of discrepancy between the results of Refs. [18] and [19] is the effect of the film substrate in the latter work, as pointed out in Ref. [18].

B. Monocrystalline samples

The effect of size reduction on the LTC for monocrystalline samples of different geometries is shown in Fig. 4. For Bi nanowires, our theory shows, in agreement with experiments, a monotonical decrease of the LTC when the diameter decreases. But in contrast to polycrystalline thin films, the experimental data for Bi nanowires available in literature are extremely scattered [2,21–25], suggesting the presence of unidentified sample-dependent scattering mechanisms in Bi [2] as well as in Si [14–16]. Available theoretical studies suggest a profound modification of the nanowire atomic structure such as surface oxidation, roughness, and core defects [14–16], which are beyond the scope of this work.

C. Heat transport reduction

1. Semiconducting nanostructures

Having shown the predictive capability of our method for polycrystalline films, we discuss the reduction of thermal transport, which has been rationalized with the concept of the reduction factor which we define as $R(T) = \frac{\kappa_{\text{bulk}}(T)}{\kappa_{\text{nano}}(T)}$. For semiconducting nanostructures (Fig. 5). As already demonstrated in Fig. 4, spherical shape (dashed line) turns out to yield a calculated reduction factor higher than the geometry of a single-crystalline film (solid lines) or a single-crystalline wire. Spherical grains are most commonly found in polycrystalline samples and here we assume, in contrast to Fig. 3, that the sample size is significantly larger than the grain size. In fact, in cases where only thermal properties matter and electronic conductivity is not so important, the control of grain sizes in polycrystalline films turns out to provide the best strategy for the control of heat transport reduction in bismuth. For instance, for a target reduction factor equal to two, the grain size should be smaller than 62 nm at 300 K, 95 nm at 200 K, and 188 nm at 100 K (dashed lines). Figure 5 thus provides an abacus for the thermal management that can be employed to deduce the reduction factor for a given nanostructure size or, alternatively, to choose the nanostructure size to obtain a desired reduction of the heat transport.

2. Semiconducting nanofilms

But in applications for thermoelectricity, it is important to keep the electrical conductivity as high as possible. In this case, the use of polycrystalline samples is precluded because the electronic scattering by grain boundaries lowers the electrical conductivity, for instance by a factor of five at ambient temperature in polycrystalline thin films with respect to monocrystalline ones [18]. Electrical contacts are also very important, and the fabrication of contacts is facilitated in the thin-film geometry. Therefore, we show the reduction factor for single-crystalline thin films (Fig. 5, solid lines). The reduction factor turns out to be lower than for spherical grains, which can be compensated by decreasing the film thickness by about a factor of three. For a target reduction factor of two, the film
thickness should be smaller than 19 nm at 300 K, 27 nm at 200 K, and 60 nm at 100 K (solid lines).

3. Conducting nanofilms

Recently, fabrication of very high quality Bi films became possible [41] in which the electrical conductivity is kept to the semimetallic bulk value even for a thickness as small as 76 nm. The reduction factor of the total thermal conductivity of semimetallic thin films has been estimated as a function of nanostructure size and temperature (dashed dotted curves) (Fig. 6). To this end, we have redefined the reduction factor as $\tilde{\kappa}(T) = \frac{\kappa_{\text{nano}}}{\kappa_{\text{bulk}}}$, and set the electronic contribution $\kappa_E$ to zero for a semiconducting nanostructure, while approximating it in the semimetallic nanostructure by the value for the bulk calculated in Sec. III B, $\kappa_E^{\text{bulk}} = 6 \text{ W} (\text{K} \text{ m})^{-1}$ in the binary direction. This is reasonable for films in which the electrical conductivity is close to the bulk one [41].

The reduction of the total thermal conductivity is smaller in the case of metallic thin films (dashed dotted curves) than in the case of semiconducting ones (solid lines). Nonetheless, for a thickness of 76 nm, the reduction factor amounts to 1.2 at 300 K, 1.3 at 200 K, and 1.6 at 100 K. Thus an experimental investigation of $ZT$ in semimetallic single-crystalline thin films would be of some interest for thermoelectric applications.

V. ANALYSIS OF HEAT TRANSPORT MECHANISMS

In this section, we analyze the contributions to the LTC of bulk and nanostructured bismuth from different phonon modes, as well as the distribution over the Brillouin zone.

A. Roles of different phonons

In Fig. 7 we show relative contributions to the vibrational part of the thermal conductivity of bulk bismuth (thin lines), due to different acoustic phonon modes, as well as the one from the optical modes, as functions of temperature.

As one can see in Fig. 7, at ambient temperature, the major contributions to the LTC come from energetic longitudinal acoustic (LA) and fast transverse acoustic (TAf) phonons. While the relative importance of the highest acoustic modes stays almost unchanged in the 30–300 K temperature range, the contribution of optical modes, which represents 16.5% at ambient temperature, decreases rapidly with temperature and becomes zero at 20 K. The decrease of the role of optical phonons is accompanied by the increase of the role of the lowest acoustic (TAs) mode. As the temperature becomes lower than 30 K, the relative contribution of the most energetic acoustic modes starts to decrease also, due to the decreasing population of phonon states, while the role of TAs increases even faster. At low temperatures, the two lowest acoustic branches carry about 90% of heat, and the dominant contribution comes from the lowest transverse acoustic branch TAs (55%). The behavior of the relative contributions of the acoustic phonons in the trigonal direction as a function of temperature (not shown) was found very similar to that in the binary direction.

Turning to the relative roles of different phonons in the LTC of nanostructured Bi (results for 100 nm spherical grains shown in Fig. 7 in thick lines), the most significant effect with respect to bulk is the reduction of the role of LA phonon in nanostructures (dash-dotted lines). This is not surprising, as LA phonons have the highest group velocities and the longest mean free paths, which are expected to be the most affected by the nanostructure boundaries.

B. Distribution over the Brillouin zone

In Fig. 8, we have analyzed our calculated LTC $\kappa_L$ of Eq. (3) as a function of the modulus of the wave vector of the initial phonon $|\mathbf{q}|$, for bulk Bi and several nanostructure sizes in

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FIG. 6. Nanostructuring-reduced total thermal conductivity in the binary direction of single-crystalline thin films. Solid lines: semiconducting thin films (same as Fig. 5). Dash-dotted lines: conducting thin films. Same color legend as in Fig. 5.

FIG. 7. Bulk (thin lines) and nanostructured (thick lines) Bi: relative contributions of different phonon modes to the lattice thermal conductivity in the binary direction. Nanostructured Bi with 100 nm grain geometry. Solid lines: TAs phonons. Dashed lines: TAf phonons. Dash-dotted lines: LA phonons. Dotted lines: optical phonons. We define TAf phonons, where “f” stands for fast, as those having a larger sound velocity than the one of TAs phonons, where “s” stands for slow.
Brillouin zone distribution of the LTC as a function of $|q|$ of the initial phonon, in the binary direction and at 300 K. Nanostructured bismuth in the grain geometry of diameter 100 nm (dashed line), 50 nm (dash-dotted line), and 10 nm (dotted line). Inset panel: the density of $q$-phonon states.

FIG. 8. Bulk (thick line) and nanostructured bismuth (thin lines): Brillouin zone distribution of the LTC as a function of $|q|$ of the initial phonon, in the binary direction and at 300 K. Nanostructured bismuth in the grain geometry of diameter 100 nm (dashed line), 50 nm (dash-dotted line), and 10 nm (dotted line). Inset panel: the density of $q$-phonon states.

The peak contribution of the LA phonons with large mean free paths is rapidly killed by boundary scattering (already at 100 nm), while other contributions over the BZ are almost uniformly reduced with the reduced nanostructure size.

VI. CONCLUSION

In conclusion, in this work, we have calculated the lattice thermal conductivity of bismuth in a large temperature range for bulk and for nanostructures, finding results in excellent agreement with available experiments. Acoustic-optical phonon interaction turns out to have a preeminent role in the magnitude of the LTC. Finally, we predict the effect of size reduction for various temperatures and nanostructure shapes, and show that the largest heat transport reduction is obtained in polycrystals with grain sizes smaller than 100 nm. The reduction factor is also predicted for semimetallic single-crystalline thin films. We analyze the contribution from the different heat-carrying phonons and their distribution in the Brillouin zone, as a function of the temperature, showing that the contribution of LA phonons to LTC is the most affected by temperature and size reduction.

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APPENDIX A: SAMPLE GEOMETRY DESCRIPTION

In bulk bismuth, because of the uniaxial symmetry, the transport properties are determined by measuring LTC along the trigonal axis (trigonal direction denoted $||$) and perpendicular to it (binary direction denoted $\perp$). The third axis which defines the plane perpendicular to the trigonal axis, additional to the binary direction, is called the bisectrix direction. In bulk bismuth, the binary and bisectrix directions are equivalent by symmetry, and the LTC values are the same in these two directions.

For the samples of finite size, the different sample geometries can be thin films, wires, and spherical nanoparticles (Fig. 9). For the sake of generality, in Fig. 9, we use Cartesian coordinates, and the heat flux is measured in the $y$ direction. If, for example, the heat flux is measured in the binary direction, then the $z$ axis will be the one which corresponds to the trigonal direction, and $x$ axis will denote the bisectrix direction.

In Eq. (1) of the main text, $|c^0_i|$ is the phonon group velocity $c_i$ in the direction in which the phonon transport is limited by the sample boundaries. It is thus different for different sample geometries and depends on the sample orientation in space with respect to the direction in which heat flux is measured.

For instance, in the case of configurations shown in Fig. 9, we have $|c^0_i| = |c^0_i| = \sqrt{(c_{x_i}^0)^2 + (c_{y_i}^0)^2}$ for the thin film geometry, $|c^0_i| = \sqrt{(c_{z_i}^0)^2}$ for the nanowire geometry, and $|c^0_i| = \sqrt{(c_{x_i}^0)^2 + (c_{y_i}^0)^2 + (c_{z_i}^0)^2}$ for the spherical-grain geometry. Here, $c_{x_i}^0$, $c_{y_i}^0$, $c_{z_i}^0$ are Cartesian components of the phonon group velocity $c_i$. 

064301-7
APPENDIX B: TECHNICAL DETAILS

A fully relativistic norm-conserving pseudopotential with 5d electrons frozen in the atomic core and including nonlinear core correction has been designed in this work. Calculations were performed with a plane-wave energy cutoff of 90 Ry and the local density approximation (LDA). Spin-orbit coupling (SOC) was accounted for in the calculation of the electronic structure and vibrational properties.

At theoretical equilibrium, the calculated lattice parameters are \(a_0 = 4.667\text{ Å}, \alpha = 57.99^\circ\), and \(u = 0.236\) (in units of \(a_0\)), which are very close to the experimental values \(a_0 = 4.724\text{ Å}, \alpha = 57.35^\circ\), and \(u = 0.234\) [46]. A \(20 \times 20 \times 20\) Monkhorst-Pack \(k\)-points grid has been used to sample the Brillouin zone and a band structure in extremely satisfactory agreement with the DFT-LDA calculations of Ref. [47]—where the 5d electrons were considered as semicore states and treated with the valence electrons—has been obtained.

APPENDIX C: ACCUMULATED VS CASIMIR APPROACH

As mentioned in the main text, in our work the change in the phonon distribution \(\Delta N_\nu\) has been varied in the presence of the sample boundaries, and/or in the presence of the grains inside the polycrystalline sample, through Casimir’s scattering rate. At variance, the typical approach used in the literature to study the effect of size reduction, the accumulated approach [43,44], is an \emph{a posteriori} analysis of the results obtained for the bulk material. This consists in keeping the \(\Delta N_\nu\) constant in Eq. (3), and in canceling the phonon contribution into the LTC when the phonon mean-free path is larger than the nanostructure size [43,44].

As shown in Table I, for the prediction of the nanostructure size that would yield a 50% reduction of the LTC, our results of the accumulated approach are found in close agreement with those of Ref. [28]. In contrast, we find that nanostructure sizes obtained with the accumulated approach are about three times smaller than those predicted using Casimir’s scattering rate (see Table I), at all temperatures.

APPENDIX D: DISTRIBUTION OVER THE BRILLOUIN ZONE

We have analyzed our calculated LTC \(\kappa_L\) of Eq. (3) as a function of the modulus of the wave vector of the initial phonon \(|q|\) (see main text). It is presented in Fig. 10 for \(T = 300\text{ K}\) (top panels) and for \(T = 5\text{ K}\) (bottom panels) in the binary (left panels) and trigonal (right panels) directions. We have also extracted the contributions of the three acoustic branches (thin lines).

The behavior of the LTC (thick solid lines) at 300 K was discussed in the main text in the binary direction. Results in the trigonal direction are very similar.

**Table I.** Bi: maximum value of the heat carrier mean-free path \(\Lambda\) (nm) which provides a contribution of 50% to the bulk lattice thermal conductivity in the binary direction.

<table>
<thead>
<tr>
<th>Method</th>
<th>Accumulated approach</th>
<th>Casimir’s scattering</th>
</tr>
</thead>
<tbody>
<tr>
<td>(T) (K)</td>
<td>Previous work(^a^)</td>
<td>This work</td>
</tr>
<tr>
<td>10</td>
<td>3380</td>
<td>10400</td>
</tr>
<tr>
<td>20</td>
<td>526</td>
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<td>34</td>
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<td>300</td>
<td>17</td>
<td>22</td>
</tr>
</tbody>
</table>

\(^a^\)Lee \emph{et al.} from Ref. [28].
Coming to the contributions from separate phonon modes, as one can see in Fig. 10, at $|\mathbf{q}|$ smaller than 0.25 $2\pi/\alpha_0$, the main contribution is due to the highest acoustic branch which has the highest group velocity and the smallest phonon-phonon linewidth. However, at $\mathbf{q}$ vectors larger than 0.25 $2\pi/\alpha_0$ the phonon-phonon linewidth of the highest acoustic branch rapidly increases, and, in consequence, the contribution of this branch decreases. The contributions of the lowest acoustic branches, at 300 K, show the behavior similar to that of the $|\mathbf{q}|$-dependent phonon DOS (inset panel of Fig. 8).

Contrastingly, at $T < 20$ K the major contribution to $\kappa_L(|\mathbf{q}|)$ starts to drift towards the small $|\mathbf{q}|$ since most of the high-energy phonon states are not populated due to the small thermal energy $kBT$ at $T$. The only active states are thus located near $1\pi$. In the bottom panels of Fig. 10 we see the LTC $\kappa_L(|\mathbf{q}|)$ at 5 K which has a pronounced peak at $|\mathbf{q}| \approx 0.15 2\pi/\alpha_0$ for both directions.

By comparing right and left panels of Fig. 10, one can see that the contributions of all three phonon modes show anisotropy, at all values of $|\mathbf{q}|$, and at all temperatures. The anisotropy of the lattice thermal conductivity of bismuth, mentioned in the main text, is due at the same time to phonon group velocities, which differ in different directions, and to phonon lifetimes.

[37] Spin-orbit coupling (SOC) was neglected in the calculation of the third-order anharmonic constants. Comparison with Ref. [28] shows that the effect of SOC is weak.
[38] The $4 \times 4 \times 4$ grid amounts to 95 irreducible ($\mathbf{q}$, $\mathbf{q}$, $\mathbf{q}$) phonon triplets [29], where $\mathbf{q}_i = 1, 3$ are phonon wave vectors, and with $\mathbf{q}_i = \mathbf{q}_i \pm \mathbf{q}_i + \mathbf{G}$. $\mathbf{G}$ is a vector of the reciprocal lattice, and both normal and Umklapp processes have been taken into account exactly in the Boltzmann equation. The third-order anharmonic constants were Fourier-interpolated on the $28 \times 28 \times 28$ denser grid necessary for converged integrations in Eq. (3). The convergence has been checked at $T = 5$ K and $T = 300$ K.
[42] A transition from a metallic to a semiconducting state has been found for diameters smaller than about $d = 50$ nm in Bi nanowires [48,49] and of less than about $d = 40$ nm for bismuth.
nanotubes [50]. For films, a semiconducting (111) film with a metallic surface has been reported for a thickness of 90 nm. A semimetallic Bi film has been synthesized [41] with a thickness as small as 76 nm.


