Semiconductor thermal conductivity for wurtzite and zinc-blende polytypes: the role of anharmonicity and phase space

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We calculate the lattice thermal conductivity ($\kappa$) for cubic (zinc-blende) and hexagonal (wurtzite) phases for 8 semiconductors using $ab$ initio calculations and iteratively solving the Phonon Boltzmann Transport Equation, explaining the different behavior of the ratio $\kappa_{\text{hex}}/\kappa_{\text{cub}}$ between the two phases. We show that this behavior depends on the relative importance of two antagonistic factors: anharmonicity, which we find to be always higher in the cubic phase; and the accessible phase space, which is higher for the less symmetric hexagonal phase. Based on that, we develop a method that predicts the most conducting phase—cubic or hexagonal—where other more heuristic approaches fail. We also present results for nanowires made of the same materials, showing the possibility to tune $\kappa_{\text{hex}}/\kappa_{\text{cub}}$ over a wide range by modifying their diameter, thus making them attractive materials for complex phononic and thermoelectric applications/systems.

I. INTRODUCTION

Heat management stands out as one of the key problems for several technologies. The reduction in size [1] and the required increment in operating speeds of devices in electronics, or the necessity to enhance energy conversion ratio for thermoelectrics have increased the importance of phonon engineering or phononics [2]. For instance, for thermoelectric applications a material with low thermal conductivity and high electrical conductivity, the so called “phonon-glass and electron-crystal”, is desired in order to have a good efficiency [3]. Historically, one of the preferred approaches to thermoelectric materials was alloying, as it introduces point-mass defects that strongly scatter phonons, significantly reducing lattice thermal conductivity [4]. A more recent approach to solve this problem is the nanostructuration as an effective way of reducing the lattice thermal conductivity [5] (hereafter just referred to as thermal conductivity, $\kappa$), or a combination of both [4].

At the same time, recent advances in semiconductor synthesis at the nanoscale have granted access to different phases that, in bulk, are only observed under extreme conditions. Namely, the wurtzite phase has theoretically been proved to be the most stable for several bulk-cubic [6] semiconductors when grown as nanowires (NWs) [7]. Indeed, the wurtzite phase in NWs has been reported for a great range of bulk-cubic semiconductors: InP [8, 9], Si [10–12], InAs [13, 14], GaAs [15, 16] or GaP [17, 18] to name but a few.

It is in that context were these new semiconductor phases can become a cornerstone for thermoelectricity and phononics in general, as they normally show a lower thermal conductivity than their more stable counterparts while maintaining similar electronic properties. For example, Togo et al. calculated thermal conductivity of wurtzite and zinc-blende phases for 33 different materials [19], Lindsay et al. [20] studied the zinc-blende/wurtzite thermal conductivity of GaN, and Li et al. addressed the thermal conductivity of bulk and nanowire InAs, AlN, and BeO polymorphs [21]. However, none of these works explained in detail the origin of the reduction in the thermal conductivity. In a more recent example, we have reported and discussed a reduction of 40% in the thermal conductivity between the more stable cubic-Si and hexagonal-Si [22].

With regard to the qualitative behavior of the thermal conductivity of materials, Mukhopadhyay et al. [23], building on earlier work by Slack [24] and Lindsay et al. [25], have provided seven criteria to interpret the relative magnitude of the thermal conductivity between different materials.

In this work we study the thermal conductivity ($\kappa$) of several bulk and nanowire semiconductors for their cubic (zinc-blende) and the hexagonal (wurtzite) phases from first-principles. After seeing that the seven criteria provided in Ref. [23] are unsuitable for rationalizing the $\kappa_{\text{hex}}/\kappa_{\text{cub}}$ value for the different materials, we propose an approach that successfully addresses this issue, providing insight into the factors determining the thermal conductivity of the materials we have studied.

The paper is structured as follows: after discussing the applied methodology for the thermal conductivity calculation in Sec. II we present the results in Sec. III. Results are provided for bulk systems (Sec. IIIA) and nanowires (Sec. IIIB). Summary and conclusions are given in Sec. IV.

II. METHODOLOGY

Harmonic and anharmonic interatomic force constants (IFCs), needed to calculate the thermal conductivity, were obtained using the supercell method, as implemented in Phonopy [26] for the harmonic IFCs and third-order.py [27] for anharmonic IFCs. They were calcu-
lateral in cubic polytypes in a 5x5x5 supercell for harmonic IFCs and 4x4x4 for the anharmonic IFCs. For hexagonal polytypes, the used supercell was 4x4x3 for both types of IFC. The unit cells used to span the supercells were optimized until strict limits for stress (3 \times 10^{-3} \text{GPa}) and forces (5 \times 10^{-4} \text{eV/Å}) were attained. These optimizations were conducted within density-functional theory (DFT), using the VASP [28, 31] code with projector augmented-wave (PAW) potentials [32, 33]. Local density approximation (LDA) for the exchange-correlation was parametrized by Perdew and Zunger [34] to Ceperley-Alder [35] data was used. For each system, the k-point mesh size had been previously optimized, taking into account that the supercell used to calculate 3rd-order IFCs should be commensurate with the mesh in order not to introduce spurious forces. Therefore, the selected k mesh for cubic materials was a 16x16x16 shifted mesh, and a 16x16x12 Γ-centered mesh for hexagonal polytypes, which are converged meshes for all systems. After optimization, a density functional perturbation theory (DFPT) run using VASP, with a doubled k-mesh was performed to obtain the Born charges (Z^*) and dielectric constant at high frequency (ε^∞), needed to calculate the non-analytic term correction for the dynamical matrix near Γ.

After obtaining the IFCs, we solved the full linearized Boltzmann Transport Equation (LBTE) iteratively, as implemented in ShengBTE code [27]. Consequently, the thermal conductivity tensor (κ_{αβ}) is obtained as:

\[
κ_{αβ} = \frac{1}{N k_B Ω T^2} \sum_λ n_0(n_0 + 1)(hω_λ)^2 v_α^2 F_β, \tag{1}
\]

where α and β label the cartesian axes x, y and z; N, k_B, Ω, T are the number of q-points, the Boltzmann constant, the cell volume and the temperature, respectively. The summation is done over all phonon modes λ, which are characterized by the band label n and their q-vector. n_0 is the equilibrium Bose-Einstein distribution function, h is the reduced Planck constant, ω_λ is the phonon mode frequency and v_α^2 is the group velocity of phonon mode α along the α direction. F_β is the generalized mean free path of the phonon mode along the β direction, and it is calculated as τ_λ(ω_λ/(F_β + Δ_λ^β)). τ_λ is the lifetime of the phonon in the relaxation time approximation (RTA) and Δ_λ^β is a measure of how much the population of a specific phonon mode and its associated heat current deviates from the RTA prediction [27]. This correction is obtained iteratively starting from the RTA (Δ_λ^β = 0). In addition to anharmonic three-phonon scattering processes, mass-disorder scattering coming from isotope presence is treated using the Tamura model [36]. Boundary scattering, whose effect is negligible in the temperature range considered (T>100 K), is not explicitly accounted for in the bulk systems (see Sec. III C for a short description on the implementation of boundary scattering in NWs).

III. RESULTS

A. Interatomic Force Constants test

Owing to the computational cost required to obtain the anharmonic IFCs (168 and 208 DFT runs for cubic and hexagonal polytypes, respectively), prior to their calculation an accuracy test to harmonic IFCs was done using Phonopy [19, 20, 37], by checking the optical phonon frequencies at the Γ point. These results, comparing calculated and experimental values, are shown in the phonon dispersion relations (see Figs. [18] in the Appendix), exhibiting, despite small differences, a good agreement between our calculations and the experimental values for the TO modes. The non-analytical correction (NAC), needed in polar materials to get the LO-TO splitting, is underestimated because of it being inversely proportional to ε^∞ [38], which is also overestimated this time due to LDA inability to take into account the polarization dependence on the exchange-correlation functional under a field [39]. This leads to an underestimation of the LO frequency with respect to the experiments. It should be noted, nonetheless, that the effect of LDA and GGA shortcomings have been proven to have a smaller effect in the anaharmonic properties than in the harmonic ones [40, 41].

B. Bulk

In this section we study the thermal conductivities of cubic (ZB) and hexagonal (WZ) phases for different compound semiconductors, using the methodology discussed in Sec. [II]. These two phases have the same coordination (4-fold, tetrahedral) and very similar first neighbor distances, the main difference being the stacking of atomic layers.

We further validate our results by comparing our calculated thermal conductivity to available experimental values (see Table I). It is reasonable to expect that, for some materials, our results overestimate the experimental values, because samples used in such experiments might contain defects (impurities, vacancies, dislocations, etc), which can strongly suppress thermal conductivity, and they have not been considered in our simulations. We note that our values are in excellent agreement with experimental results for GaAs and AlAs, while keeping a good agreement for InP, InAs, ZnSe and GaP. In the nitrides, BN and GaN, we obtain values within the dispersion of the experimentally reported magnitudes.

We found that most of materials under study (GaAs, GaP, InP, InAs, ZnSe and AlAs) follow the silicon behavior of reducing their κ with symmetry [22]. However, we observe that is possible for some materials (GaN) to have the opposite behavior, namely κ increases when symmetry is reduced. Moreover, as previously observed in other materials [21], BN can show these two opposite behaviors
TABLE I: Calculated κ and κ_{hex}/κ_{cub} ratios at room temperature (300 K, unless indicated). The experimental κ at room temperature is also presented at normal conditions.

| Material | κ_{cub}^{calc} (W/mK) | κ_{hex}^{calc} (W/mK) | κ_{hex}/κ_{cub} | κ_{exp}^{\dagger} (W/mK) |
|----------|------------------------|------------------------|-----------------|--------------------------|
| BN       | 1051.10                | 889.903                | 0.847           | 760^{a} (cub)            |
|          | (888.100/893.510)      |                        |                 | 1200^{b} (cub)           |
| AlAs     | 97.485                 | 65.848                 | 0.675           | 98^{a} (cub)             |
|          | (64.861/67.823)        |                        |                 |                          |
| GaN      | 275.550                | 303.823                | 1.103           | 253^{c} (hex)            |
|          | (287.790/335.890)      |                        |                 | 294^{c} (hex)            |
|          |                        |                        |                 | 280^{c} (hex)            |
|          |                        |                        |                 | 300^{c} (hex)            |
|          |                        |                        |                 | 330^{c} (hex)            |
|          |                        |                        |                 | 380^{c} (hex)            |
| GaP      | 146.530                | 143.703                | 0.981           | 100^{a} (cub)            |
|          | (145.710/139.690)      |                        |                 | 110^{a} (cub)            |
| GaAs     | 45.862                 | 38.887                 | 0.848           | 46^{b} (cub)             |
|          | (37.898/40.866)        |                        |                 |                          |
| InP      | 99.907                 | 87.466                 | 0.875           | 93^{a} (cub)             |
|          | (84.726/92.947)        |                        |                 |                          |
| InAs     | 34.835                 | 33.251                 | 0.955           | 30^{a} (cub)             |
|          | (32.418/34.917)        |                        |                 |                          |
| ZnSe     | 25.618                 | 22.727                 | 0.887           | 19^{a} (cub)             |
|          | (21.423/25.337)        |                        |                 | 33^{b} (cub)             |

† Mean of κ trace (in-plane κ / out-of-plane κ, along c-crystallographic axis).
‡ The material phase of the experimental measurement is indicated between brackets.

1 Ref. 42
2 Refs. 43, 44
3 Ref. 45
4 Ref. 46
5 Ref. 47
6 Ref. 48
7 Measurements are done at 298.15 K.
8 Ref. 49
9 Ref. 50
10 Ref. 51

FIG. 1: Hexagonal(black) and cubic(red) BN thermal conductivity κ trace mean as a function of temperature. Experimental results for cubic phase are from Ref. 42 (circle) and Ref. 51 (triangle). Inset: ratio between hexagonal and cubic thermal conductivity as a function of the Temperature.

FIG. 2: Hexagonal(black) and cubic(red) AlAs thermal conductivity κ trace mean as a function of temperature. Experimental results for cubic phase are from Ref. 42.
Inset: ratio between hexagonal and cubic thermal conductivity as a function of the Temperature.

1. Standard analysis of κ_{hex}/κ_{cub}

Four conditions that a crystal must fulfill to have a high κ have been long established [24]: (I) to be structurally simple, (II) to be composed of light elements, (III) to have strong covalent bonds—represented normally by a high Debye temperature/frequency (f_D)—and (IV) to be harmonic, which is normally associated to a low Grüneisen parameter (γ).

Recently, three additional conditions for a high κ have
been introduced by Lindsay et al. [25] and Mukhopadhyay et al. [23]. They demonstrated that, in addition to the four previous conditions, a higher $\kappa$ is obtained if the material also has (V) high “acoustic-optic” gap, (VI) a high “acoustic bunching” and (VII) low optical bandwidth.

We have collected those seven conditions for all materials under study in Table I. Interestingly, by observing those conditions together with the $\kappa$ values, we see that they do not clarify which of the phases—cubic or hexagonal—is the most conductive: for instance, if one looks at GaN four out of seven criteria suggest that zinc-blende phase should be the most conductive one, while one of them is neutral and only two of them predict a larger $\kappa$ for the wurtzite. Yet, the calculations predict the latter to be more conductive. Additionally, those conditions cannot either explain the reason for some materials, like BN, to change their $\kappa_{\text{hex}}/\kappa_{\text{cub}}$ ratio behavior with temperature. Such a shortcoming is due to being based on arguments of a qualitative character that do
TABLE II: Seven standard conditions of high $\kappa$ for all materials in both phases. The winning phase for each condition is in bold. $M_{avg}$ stands for the average atomic mass of the unit cell, $f_D$ for the Debye frequency and $\gamma_{300K}$ for the Grüneisen parameter at room temperature.

| material | (I) | (II) | (III) | (IV) | (V) | (VI) | (VII) |
|----------|-----|------|-------|------|-----|------|-------|
| crystal  | M$_{avg}$ | $f_D$ | $\gamma_{300K}$ | “a-o” gap | “acoustic” bunching | optical bandwidth |
| structure | (amu) | (THz) | (THz) | (THz) | (THz) | (THz) |
| BN       | 12.41 | 39.15 | 0.67 | 0.00 | 30.11 | 11.41 |
| zB       | 12.41 | 39.15 | 0.73 | 0.00 | 15.55 | 9.37  |
| AlAs     | 50.95 | 5.44  | 0.26 | 3.54 | 6.32  | 1.93  |
| zB       | 50.95 | 5.41  | 0.40 | 3.55 | 3.56  | 1.93  |
| GaN      | 41.86 | 9.75  | 0.64 | 6.18 | 10.27 | 5.87  |
| zB       | 41.86 | 9.71  | 0.70 | 6.50 | 6.43  | 5.36  |
| GaP      | 50.35 | 6.66  | 0.51 | 2.67 | 7.01  | 2.10  |
| zB       | 50.35 | 5.57  | 0.57 | 2.49 | 4.53  | 1.99  |
| GaAs     | 72.32 | 4.53  | 0.55 | 0.00 | 6.21  | 2.89  |
| zB       | 72.32 | 4.67  | 0.60 | 0.00 | 4.35  | 2.53  |
| InP      | 72.90 | 3.51  | 0.38 | 3.88 | 4.92  | 1.42  |
| zB       | 72.90 | 3.48  | 0.48 | 3.69 | 3.41  | 1.35  |
| InAs     | 94.87 | 2.92  | 0.35 | 0.82 | 4.56  | 1.55  |
| zB       | 94.87 | 3.07  | 0.38 | 0.51 | 3.62  | 1.39  |
| ZnSe     | 72.17 | 4.70  | 0.67 | 0.00 | 5.29  | 2.03  |
| zB       | 72.17 | 4.47  | 0.70 | 0.00 | 4.00  | 2.06  |

FIG. 7: Hexagonal(black) and cubic(red) InAs thermal conductivity $\kappa$ trace mean as a function of temperature. Experimental results for cubic phase are from Ref. [42]. Inset: ratio between hexagonal and cubic thermal conductivity as a function of the Temperature.

FIG. 8: Hexagonal(black) and cubic(red) ZnSe thermal conductivity $\kappa$ trace mean as a function of temperature. Experimental results for cubic phase are from Ref. [42] (circle) and Refs. [43, 44] (triangle). Inset: ratio between hexagonal and cubic thermal conductivity as a function of the Temperature.
not quantify the relative importance of each condition, thus the necessity of a more quantitative viewpoint to predict/understand which phase is the most conductive at a given temperature.

2. Effective anharmonicity and scattering space

To gain insight on the $\kappa_{\text{hex}}/\kappa_{\text{cub}}$ ratio at different temperatures, we focus our analysis on two quantities that together contain all conditions: the three-phonon scattering matrix elements or anharmonicity (high-$\kappa$ conditions I,II, III and IV) and phase space, i.e. all the energy conserving three-phonon combinations (high-$\kappa$ conditions I,II, III and IV). In fact, these two quantities directly contribute to $\kappa$ via the three-phonon scattering rate ($\Gamma_{\lambda\lambda'\lambda''}^{\pm}$) [27]:

$$\Gamma_{\lambda\lambda'\lambda''}^{\pm} = \frac{n_s}{4\omega_{\lambda}n_{\lambda'\lambda''}} \left\{ n_0 - n_0'' \right\} \delta(\omega_\lambda \pm \omega_{\lambda'} - \omega_{\lambda''}),$$

where $V_{\lambda\lambda'\lambda''}^{\pm}$ stands for the three-phonon scattering matrix element (+ for absorption processes and - for emission) and $n_0$ is a shorthand for $n_0(\omega_{\lambda'})$ and similarly for $n_0''$. As it can be seen from Eq. (2) an increment in anharmonicity ($V_{\lambda\lambda'\lambda''}^{\pm}$) produces an increment in the scattering rate, therefore a reduction in $\kappa$. In the same way, an increment in phase space, represented in Eq. (2) by the energy conservation delta $\delta(\omega_\lambda \pm \omega_{\lambda'} - \omega_{\lambda''})$, also reduces $\kappa$.

Comparing the phonon dispersion of both phases for all materials (see Figs. [18-20] in the Appendix) it becomes obvious that symmetry reduction, which causes the appearance of new low/medium optical eigenmodes with non-vanishing scattering matrix elements, also increases the phase space for transitions at a given temperature. In order to obtain an actual measurement of available phase space while taking into account the effect of temperature, we calculate the scattering space ($\delta_{\lambda\lambda'\lambda''}^{\pm,\text{occ,T}}$) defined as follows:

$$\delta_{\lambda\lambda'\lambda''}^{\pm,\text{occ,T}} = \left( \frac{V_{\text{BZ}}}{2\pi} \right) \int_{BZ} \int_{BZ} \int_{BZ} \delta(\omega_\lambda + \omega_{\lambda'} - \omega_{\lambda''}) n_0 n_0' n_0'' (1 + n_0''') d^3q d^3q' d^3q'' d^3q'',$n

$$\delta_{\lambda\lambda'\lambda''}^{-,\text{occ,T}} = \left( \frac{V_{\text{BZ}}}{2\pi} \right) \int_{BZ} \int_{BZ} \int_{BZ} \delta(\omega_\lambda - \omega_{\lambda'} - \omega_{\lambda''}) n_0 (1 + n_0''') n_0'' d^3q d^3q' d^3q'',$

which gives an idea for a given temperature of the accessible part of the available phase space. Certainly, the attainable phase space for the different materials (see Figs. [9-11]) confirms that, as inferred from dispersion relations, the hexagonal phase has a greater accessible phase space which contributes to reducing the $\kappa_{\text{hex}}/\kappa_{\text{cub}}$ ratio. This is a general feature of all the studied materials. On the other hand, from the scattering matrix elements ($|V_{\lambda\lambda'\lambda''}^{\pm}|^2$) of energy-conserving three-phonon processes one obtains direct information of the material anharmonicity. Notwithstanding that this bare anharmonicity is an interesting quantity by itself, it is not useful for us because it gives the same importance to processes in which the involved modes are occupied to those in which they are not. Therefore, we define an effective anharmonicity that depends on temperature ($|V_{\lambda\lambda'\lambda''}^{\pm}|^2_{\text{occ,T}}$) as:

$$|V_{\lambda\lambda'\lambda''}^{\pm,\text{occ,T}}|^2 = |V_{\lambda\lambda'\lambda''}^{\pm}|^2 n_0 n_0' (1 + n_0''),$$

$$|V_{\lambda\lambda'\lambda''}^{-,\text{occ,T}}|^2 = |V_{\lambda\lambda'\lambda''}^{-}|^2 n_0 (1 + n_0') (1 + n_0''),$$

From the mean effective anharmonicity as a function of first-phonon frequency, it can be seen that, for all materials under study, the cubic phase is more anharmonic than the hexagonal phase both at 77 K (a representative value of the low temperature regime) and at 300 K (see Figs. [12-14]).

Therefore, we have two antagonistic processes occurring when reducing the symmetry from cubic to hexagonal: an increment in the available phase space for phonon-phonon scattering events and a lowering of the anharmonicity, which makes those events weaker when compared to the cubic ones, with no indication of their relative importance as regards to $\kappa$.

As we already mentioned, despite being widely used to predict the relationship between thermal conductivity for different materials [23], the criteria listed in Sec. II B lack the capacity to discern this relative importance of opposed processes. To overcome such limitation and owing to the fact that scattering rates are a product of the anharmonicity with phase space [see Eq. (2)], one can plot $\kappa_{\text{hex}}/\kappa_{\text{cub}}$ versus the hexagonal-cubic ratio of the effective anharmonicity mean and the scattering space product (REAMSPP) at 77K and 300K (see Fig. [15]).

By this analysis of the relative importance of the accessible phase space and effective anharmonicity at a given temperature, we can see that the $\kappa_{\text{hex}}/\kappa_{\text{cub}}$ ratio is greater than one when REAMSPP are lower than 1.37-1.40, indicating that on those cases the effective anharmonicity increment in the cubic phase overwhelm the hexagonal accessible phase space increment, thus giving a higher conductivity in hexagonal phase. For higher values of REAMSPP, the dominant factor is the increment in the accessible phase space of the hexagonal phase, hence the higher conductivity of the cubic phase.

Furthermore, it is remarkable that using such analysis one can explain specific behaviors such as BN, which at 77K has $\kappa_{\text{hex}} > \kappa_{\text{cub}}$ because at low temperatures the dominant factor for determining $\kappa$ is the effective anharmonicity (REAMSPP<1.37-1.40), while at higher temperatures (300K) the most important factor determining $\kappa$ is the accessible phase space (REAMSPP>1.37-1.40), thus giving $\kappa_{\text{hex}} < \kappa_{\text{cub}}$ as a result. Additionally, our
analysis also confirms that the behavior of GaN is due to the fact that even at higher temperatures the dominant factor is anharmonicity, so that the cubic phase has always lower $\kappa$ in agreement with previous works by Lindsay et al. [20], but in opposition to the results by Togo et al. [19], which are obtained by a different approach to the LBTE. These two methods are known to provide different values for the thermal conductivity in some materials [52].

C. Nanowires

As previously mentioned, phases that are not thermodynamically stable at room temperature and atmospheric pressure in bulk form can naturally occur when the materials are grown as nanowires and thus it is in nanowires that the zinc-blende and wurtzite phase can be both easily accepted. Therefore, in this section we discuss the conductivity along the stacking direction ([111] for cubic and [0001] for hexagonal) for nanowires of different materials and diameters.

Despite being one dimensional structures, nanowire phonon dispersions can be approximated to the bulk ones for nanowires with diameters $\gtrsim 60 - 70$ nm. However, the reduction in the symmetry caused by the nanowire boundaries make it unrealistic to use bulk-like scattering rates, as they become position dependent in the direction perpendicular to the nanowire. To solve this problem, an iterative solution under the diffusive regime as proposed by Li et al. [53] is used as implemented in ShengBTE [27].

$\kappa$ along [111] (cubic) and [0001] (hexagonal) is plotted as function of the nanowire diameter for 77K and 300K in Fig. 16. As expected, the bulk $\kappa_{\text{hex}}/\kappa_{\text{cub}}$ ratio behavior is recovered at large diameters. On the contrary, for thin NWs we observe a larger departure (e.g. BN 300K-GaN

\[ \delta_{\lambda' \lambda''}^{\pm \text{occ}, T} \]

\[ f_s(\text{THz}) \]

\[ \text{BN} \]

\[ \text{GaN} \]

\[ \text{FIG. 9: Contribution to the scattering space} \ (\delta_{\lambda' \lambda''}^{\pm \text{occ}, T}) \ \text{as a function of first phonon frequency for BN and GaN. Left images correspond to emission processes and right images to absorption processes.} \]
FIG. 10: Contribution to the scattering space ($\delta_{\lambda\lambda',\lambda''}$) as a function of first phonon frequency for AlAs, GaP and GaAs. Left images correspond to emission processes and right images to absorption processes.
FIG. 11: Contribution to the scattering space \( \delta_{\lambda,\lambda'}^{\text{occ},T} \) as a function of first phonon frequency for InP, InAs and ZnSe. Left images correspond to emission processes and right images to absorption processes.
or GaAs) or even an inversion of the behavior of the bulk (e.g., 77K-GaN or InAs). Moreover, we can observe that BN and GaN show higher $\kappa$ at 300K than at 77K; the $\kappa$ peak being displaced to higher temperatures when compared with their bulk counterparts (see Fig. 17). Such results are coherent with experimental observations for silicon NWs [54], and they are associated to the domination of boundary scatter over the Umklapp scattering in the NW geometry when compared to the bulk one. This explanation is further validated by looking at the 77K-BN $\kappa$ dependence with the NW diameter for both phases, which for thinner NWs are quasi-identical owing to the fact that, to a first approximation, boundary scattering does not discriminate between wurtzite and zinc-blende. Despite these changes with respect to bulk ratio, the available wide range of $\kappa$ ratios by modifying their diameter makes these NWs interesting blockpieces for complex thermoelectric and/or phononic systems.

**IV. SUMMARY AND CONCLUSIONS**

In this work we have presented *ab initio* calculations of the lattice thermal conductivity for the cubic and hexagonal phases of GaAs, GaN, GaP, InAs, InP, AlAs, BN and ZnSe using density functional theory and iteratively solving the Phonon Boltzmann Transport Equation. We find that which phase is the most conductive one depends on the relative strength between effective anharmonicity and accessible phase space. Such factors are shown to be antagonistic for all materials due to the higher effective anharmonicity of the cubic phase when compared to the
(a) Mean of effective anharmonicity as a function of first phonon frequency for AlAs, GaP and GaN. Left images correspond to emission processes and right images to absorption processes.
FIG. 14: Mean of effective anharmonicity as a function of first phonon frequency for InP, InAs and ZnSe. Left images correspond to emission processes and right images to absorption processes.
FIG. 15: $\kappa_{\text{hex}}/\kappa_{\text{cub}}$ ratio as function of the ratio hexagonal-cubic ratio of the effective anharmonicity mean and the scattering space the product at 77K (left) and 300K (right) for different materials. Empty (filled) markers correspond to absorption (emission) processes. The factor that controls the ratio $\kappa_{\text{hex}}/\kappa_{\text{cub}}$ (anharmonicity or phase space) for a given REAMSP is indicated together with which phase is the most conducting for that values. The grey filled region corresponds to a region in which the relative importance of both factors is similar so that such simple analysis does not hold.

hexagonal one, which, on the other hand, has a higher accessible phase space. Furthermore, we carry out an analysis of which factor is dominant in each material at 77 and 300K, showing that, when anharmonicity (phase space) dominates, it leads to a higher (lower) conductivity in the hexagonal phase compared to the cubic one. Moreover, we have observed that when the hexagonal-cubic ratio of temperature-weighted anharmonicity and accessible phase space product is less than 1.37-1.40, the dominating factor determining $\kappa$ is the anharmonicity ($\kappa_{\text{hex}} > \kappa_{\text{cub}}$). On the contrary, when that product is higher than 1.37-1.40, the dominating factor determining the $\kappa$ is the accessible phase space($\kappa_{\text{hex}} < \kappa_{\text{cub}}$), thereby making such quantity an excellent tool to predict which is the most conductive phase at a given temperature where other more qualitative analysis fail. We also present results for NWs showing their ability to have their $\kappa$ ratio tuned with diameter over a wide range, hence making them appealing materials for phononic and thermoelectric applications.

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FIG. 16: Thermal lattice conductivity of nanowires along [111] for cubic (red) and [0001] for hexagonal (black) at 77K (triangles) and 300K (squares) as function of the nanowire diameter. Inset: hexagonal-cubic ratio for 77K and 300K.
Appendix: Phonon dispersions

We provide for completeness the computed phonon dispersion relations for the treated materials in Figs. 18-20 indicating as well the experimentally measured values of the zone-center phonon frequencies.
FIG. 18: Dispersion relation for BN (top) and AlAs (bottom) in the cubic (left) and hexagonal (right) phases. Experimental results for BN are from Ref. 55 (diamonds); and results for AlAs are from Ref. 56 (squares) and Ref. 57 (diamonds).

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FIG. 19: Dispersion relation for GaN (top), GaP (middle) and GaAs (bottom) in the cubic (left) and hexagonal (right) phases. Experimental results for GaN are from Ref. 58 (diamonds); results for GaP are from Ref. 18 (squares) and Ref. 59 (diamonds), and results for GaAs are from Ref. 16 (squares) and Ref. 60 (diamonds).
FIG. 20: Dispersion relation for InP (top), InAs (middle) and ZnSe (bottom) in the cubic (left) and hexagonal (right) phases. Experimental results for InP are from Ref. 61 (squares) and Ref. 62 (diamonds); results for InAs are from Ref. 63 (squares) and Ref. 64 (diamonds), and results for GaAs are from Ref. 65 (squares) and Ref. 66 (diamonds).
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