



Dissertation

Predictive calculation of point-defect phonon scattering in semiconductors

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I confirm, that going to press of this thesis needs the confirmation of the examination committee.

Affidavit

I declare in lieu of oath, that I wrote this thesis and performed the associated research myself, using only literature cited in this volume. If text passages from sources are used literally, they are marked as such. I confirm that this work is original and has not been submitted elsewhere for any examination, nor is it currently under consideration for a thesis elsewhere.

Vienna, December, 2018

Signature

Preface

The work presented in this thesis was accomplished initially between 12/2015 to 12/2016 at the Interdisciplinary Centre for Advanced Materials Simulation, Ruhr-Universität Bochum, Germany and afterwords between 01/2017 to 12/2018 at the Institute of Materials Chemistry, TU Wien, Austria.

This PhD thesis has been composed in a cumulative form, consisting of an introductory chapter followed by five published journal articles, and complies with the guidelines as set out under

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Abstract

Semiconductors are an indispensable part of the tools and machines used by mankind today. While the intrinsic (pure) semiconductors have limited utility on their own, most of the enhanced functional properties of the semiconductors are achieved through extrinsically doping them. When seen from the perspective of enhancing the electrical properties of the system, dopants are named according to whether they donate (donors) or accept (acceptors) electrons from the system. However, the same dopants also act as a hindrance to the flow of heat in the system and are referred to as point defects. Therefore, it has become imperative for device design that equal attention is paid to the effect of the dopants on both the electrical and the thermal properties of the system. This is because, a dopant which behaves as an excellent donor or acceptor might severely impede the heat flow in the system thereby affecting the device performance. While, in certain applications like thermoelectrics this is beneficial, for others like optoelectronics this is a limiting factor.

In the present thesis, we investigate in detail the effect of dopants on the charge carrier concentrations as well as their phonon scattering characteristics. We calculate the *ab initio* defect formation energies and carrier concentrations of various intrinsic and extrinsic defects in the TiNiSn and TiCoSb half-Heusler compounds (HHCs), and cubic SiC (3C-SiC). We also calculate the *ab initio* point-defect phonon scattering rates using the atomistic Green's function approach. The main thrust of this work revolves around elucidating in detail the exact mechanism and factors causing enhanced point-defect phonon scattering in semiconductors.

For the TiNiSn and TiCoSb HHCs, we provide an in-depth understanding of the defect thermochemistry and explore various dopants like Cu, Sb, and V for the

TiNiSn system and Sc, Y, La, Fe, Ge, and Sn for the TiCoSb system. We find that the positively charged Ni and Ti interstitials dominate the intrinsic defects in TiNiSn, whereas, only Sb_{Sn} extrinsic defect is suitable for n-doping. In contrast, TiCoSb is not intrinsically n-dopable, where Sc_{Ti} , Fe_{Co} , and Sn_{Sb} were found as possible p-type dopants. We also investigate the B- and N-doped 3C-SiC and find that both the neutral and charged states of the dopants are stable in the band gap. The neutral B_C defect $(B_C^{(0)})$ produces resonant phonon scattering in 3C-SiC drastically reducing its thermal conductivity, even at small concentrations. This is caused by a small asymmetrical relaxation of the $B_C^{(0)}$ defect in 3C-SiC. Such a relaxation is then shown to produce a large interatomic force constant (IFC) perturbation which is an essential ingredient of resonant phonon scattering. However, a similarly small relaxation of the $B_{\rm C}^{(0)}$ defect in diamond fails to produce any enhanced scattering, and this is found to be related to smaller density of states of diamond as compared to 3C-SiC. We explain this complex phenomenon with the help of a simple monoatomic 1D chain. A defect is introduced in the chain by modifying the interactions of three contiguous atoms with the help of a Tersoff-like potential, resulting in a double well potential. We show that, when the bond order parameter of the potential is progressively increased, the potential energy barrier of the double well potential becomes smaller and smaller. This decrease in the potential barrier results in the two minima moving closer to each other and a subsequent increase in the IFC perturbation. At sufficiently large IFC perturbation a resonant phonon scattering is observed.

Further, we calculate the lattice thermal conductivities (κ_{ℓ}) of bulk and vacancy Si using the Green-Kubo (GK) and homogeneous non-equilibrium molecular dynamics (HNEMD) techniques. We find that the relatively newly-developed HNEMD technique is better suited to calculate κ_{ℓ} of the defected structures as κ_{ℓ} decreases with increasing vacancy concentration and HNEMD becomes computationally cheaper for lower κ_{ℓ} values. Furthermore, in order to overcome the limitations of the parameterized empirical interatomic potentials used in molecular dynamics (MD) techniques, we also calculate the *ab initio* κ_{ℓ} of bulk and thin-film α -Al₂O₃ using both the local density approximation (LDA) and the generalized gradient approximation (GGA) to the exchange and correlation. LDA reproduces the thermal conductivity of bulk α -Al₂O₃ better than the GGA. This is related to the increased phonon group velocities in the LDA calculations as compared to GGA.

We expect that the insights developed by the study of points defects will help the device design in terms of choosing the right dopants by effectively quantifying their doping properties and phonon scattering characteristics. Furthermore, we expect that the parameter-free *ab initio* approach to the κ_{ℓ} calculations of bulk and thin-film compounds will help overcome the limitations of the MD techniques and become an integral part of understanding the experimental observations.

Kurzfassung

Halbleiter sind ein unverzichtbarer Bestandteil der Werkzeuge und Maschinen, die heutzutage von Menschen verwendet werden. Während intrinsische (reine) Halbleiter bereits begrenzt einsetzbar sind, werden die meisten verbesserten funktionalen Eigenschaften von Halbleitern durch extrinsische Dotierung erreicht. Hinsichtlich der Verbessung der elektrischen Eigenschaften des Systems werden Dotierstoffe danach benannt, ob sie Elektronen abgeben (Donoren) oder aus dem System annehmen (Akzeptoren). Diese Dotierstoffe behindern jedoch auch den Wärmefluß im System und werden als Punktdefekte bezeichnet. Daher ist es für das Design von Geräten unabdingbar geworden, dass dem Effekt der Dotierstoffe sowohl auf die elektrische als auch auf die Wärmeleitfähigkeit des Systems gleichermaßen Beachtung geschenkt wird. Dies liegt daran, dass ein Dotierstoff, der sich als ausgezeichneter Donor oder Akzeptor verhält, den Wärmefluss im System erheblich beeinträchtigen kann, wodurch die Leistung des Geräts beeinträchtigt wird. Während dies bei bestimmten Anwendungen wie der Thermoelektrik von Vorteil ist, ist es für andere Anwendungen wie die Optoelektronik ein limitierender Faktor.

In dieser Arbeit untersuchen wir den Effekt von Dotierstoffen auf die Ladungsträgerkonzentration sowie deren Phononenstreuungseigenschaften detailliert. Wir berechnen die *ab initio* Defektbildungsenergien und Ladungsträgerkonzentrationen verschiedener intrinsischer und extrinsischer Defekte in den Halb-Heusler-Verbindungen (HHCs) TiNiSn- und TiCoSb und kubischem SiC (3C-SiC). Weiters berechnen wir die *ab initio* Phononenstreuungsraten von Punktdefekten unter Verwendung eines atomistischen Ansatzes mit Green'schen Funktionen. Der Schwerpunkt dieser Arbeit besteht darin, den genauen Mechanismus und die Faktoren, die zu einer verstärkten Punktdefekt-Phononenstreuung in Halbleitern führen, im Detail aufzuklären.

Für die TiNiSn- und TiCoSb-HHCs bieten wir ein detailliertes Verständnis der Defektthermochemie und untersuchen verschiedene Dotierstoffe wie Cu, Sb, V für das TiNiSn-System beziehungsweise Sc, Y, Fe, La, Ge und Sn für das TiCoSb-System. Es zeigt sich, dass die positiv geladenen Ni- und Ti-Interstitials die intrinsischen Defekte in TiNiSn dominieren, wohingegen nur der extrinsische Sb_{Sn} -Defekt für n-Dotierung geeignet ist. Im Gegensatz dazu kann TiCoSb nicht intrinsisch dotiert werden, wobei Sc_{Ti}, Fe_{Co} und Sn_{Sb} als mögliche p-Dotierstoffe gefunden wurden. Außerdem untersuchen wir B- und N-dotiertes 3C-SiC und finden heraus, dass sowohl der neutrale als auch der geladene Zustand der Dotierstoffe in der Bandlücke stabil sind. Wir beobachten, dass der neutrale $B_{\rm C}$ -Defekt $(B_{\rm C}^{(0)})$ zu resonanter Phononenstreuung in 3C-SiC führt, was die Wärmeleitfähigkeit bereits bei geringen Konzentrationen drastisch reduziert. Dies wird durch eine kleine asymmetrische Relaxation des $B_{C}^{(0)}$ -Defekts in 3C-SiC verursacht. Wir zeigen, dass eine solche Relaxation eine große interatomare Kraftkonstante (IFC) erzeugt, die ein wesentlicher Bestandteil der resonanten Phononenstreuung ist. Eine ähnlich kleine Relaxation durch den $B_{C}^{(0)}$ -Defekt in Diamant erzeugt jedoch keine verstärkte Streuung, und wir stellen fest, dass sie mit der geringeren Zustandsdichte von Diamant im Vergleich zu 3C-SiC zusammenhängt. Wir erklären dieses komplexe Phänomen mit Hilfe einer einfachen monoatomaren eindimensionalen Kette. Ein Defekt wird in die Kette eingeführt, indem die Wechselwirkungen dreier benachbarter Atome mit Hilfe eines Tersoff-ähnlichen Potentials modifiziert werden, was zu einem Potential mit zwei Minima führt. Wir zeigen, dass bei einer schrittweisen Erhöhung des Bond-Order-Parameters des Potentials die potentielle Energiebarriere zwischen den Potentialminima immer kleiner wird. Diese Abnahme der Potentialbarriere führt dazu, dass sich die beiden Minima einadner annähern und die IFC-Störung zunimmt. Bei ausreichend großer IFC-Störung wird resonante Phononenstreuung beobachtet.

Des Weiteren berechnen wir die Wärmeleitfähigkeiten (κ_{ℓ}) von Bulk-Si und Si mit Leerstellen unter Verwendung der Green-Kubo-Methode (GK) und der homogenen Nichtgleichgewichts-Molekulardynamik (HNEMD). Wir finden, dass die relativ neu entwickelte HNEMD-Technik besser geeignet ist, um κ_{ℓ} der Defektstrukturen zu berechnen, da κ_{ℓ} mit zunehmender Leerstellenkonzentration abnimmt und außerdem HNEMD geringere Rechenleistung für niedrigere κ_{ℓ} -Werte benötigt. Um jedoch die Einschränkungen der parametrisierten empirischen interatomaren Potentiale zu überwinden, die in Molekulardynamik-Techniken (MD) verwendet werden, berechnen wir auch den *ab initio* Wert für κ_{ℓ} von Bulk- und Dünnschicht- α -Al₂O₃, wobei wir sowohl die lokale Dichteabschätzung (LDA) als auch die generalisierte Gradientenannäherung (GGA) für den Austausch und die Korrelation verwenden. Wir finden, dass LDA die Wärmeleitfähigkeit von Bulk- α -Al₂O₃ besser als GGA reproduziert. Dies steht im Zusammenhang mit den erhöhten Gruppengeschwindigkeiten der Phononen in LDA-Berechnungen verglichen mit GGA.

Wir erwarten, dass die Erkenntnisse dieser Untersuchung von Punktdefekten dem Design von Geräten helfen werden, die richtigen Dotierstoffe auszuwählen, indem sie ihre Dotierungseigenschaften und Phononstreuungseigenschaften effektiv quantifizieren. Außerdem erwarten wir, dass die parameterfreie *ab initio* Methode für die κ_{ℓ} -Berechnungen von Bulk- und Dünnschichtverbindungen dazu beitragen wird, die Einschränkungen der MD-Techniken zu überwinden, und ein wesentlicher Bestandteil des Verständnisses der experimentellen Beobachtungen werden wird.

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1 Introduction

1.1 Aim of the work

In the present thesis, we start with the investigation of the effect of different dopants on the electronic properties of TiNiSn and TiCoSb half-Heusler compounds (HHCs) by carefully analyzing their defect formation energies, chemical potentials, and carrier concentrations, using state-of-the-art computational methodologies. Next we study in detail, the phenomena of dopant-induced phonon scattering and its effect on the thermal conductivity of cubic SiC with the help atomistic Green's functions (AGF) technique. The primary consideration of the AGF technique is to evaluate the phonon scattering rates based on the transformation matrix which itself requires the computation of the perturbation matrix and the Green's functions matrix of the unperturbed host lattice. The main thrust of the this work deals with the computation of the aforementioned quantities as well as elucidating the effect of each of them on point-defect phonon scattering. Next, the thermal conductivity of bulk and thin-film α -Al₂O₃ is calculated from first principles by solving the Boltzmann transport equation (BTE). We also carry out classical molecular dynamics (MD) simulations to understand the effect of intrinsic point defects like vacancies on the the thermal conductivity (κ) of Si using Stillinger-Weber potential.

1.2 State of the art and methodology

From the first documented observation of the semiconducting effect by Michael Faraday in 1883, through the development of first devices like rectifiers and transistors, all the way to modern day electronic devices, semiconductors have revolutionized almost every sphere of human activity today [2]. The two primary reasons for various semiconductor technologies to flourish are the availability of the substrates and the ease of altering the functional properties of semiconductors by doping. This renders simple semiconducting devices like diodes and transistors as the building blocks of more sophisticated devices like microprocessors, metal-oxidesemiconductor field-effect transistors (MOSFETs), rectifiers, amplifiers, solar cells, and light-emitting diode (LED) displays. Germanium was used to make the first transistor which was a point-contact transistor and shortly thereafter Schockley invented the junction transistor by adding small amount of impurities. Silicon quickly replaced germanium as the material of choice for making transistors because of its ability to form a dioxide, crucial for today's integrated circuits. Since then, compound semiconductors like GaAs, GaN, SiC, InP, and PbSe have also found widespread usage in optoelectronic and thermoelectric applications.

Most of the intrinsic semiconductors, however, have limited utility on their own, and at the heart of modulating the electrical, optical, and magnetic properties of a semiconductor, lie dopants. Electron donating or electron accepting atoms make the semiconductors n- or p-type, respectively, which then become the basic units of devices like diodes, transistors, etc.. Traditionally, the properties of a semiconductor were altered by using an ensemble of dopants, however, over the last couple of decades a large progress has been made in identifying the effects of a single dopant on the fundamental properties of semiconductors, to the extent of opening a new field of "solotronics" [3,4]. Nanoscale technologies such as single-dopant transistors or single-spin devices for quantum information have also been realized by carefully controlling the doping with only one dopant [3]. These dopants inherently act as a hindrance to the flow of heat in semiconductor devices. More precisely, the dopants can be considered as point defects that induce mass and force-constant disorder in the system and consequently lead to elastic scattering of the phonons. This results in a reduction in the thermal conductivity of the material and inefficient diffusion of heat away from the source [5]. Thermal conductivity is an important metric for applications like thermoelectrics which require low κ , as well as devices such as transistors, LEDs, and lasers which require high κ for efficient cooling of the device. Therefore, it becomes imperative to do a comprehensive study of the effect of the

dopants not only on the electrical properties but also the thermal conductivity of the semiconductors. Over the last couple of decades, this has been facilitated by the advent of modern computers and ever more predictive simulation tools, where a range of properties including the electronic structure, lattice relaxation, force constants, etc. associated with a particular dopant can be routinely calculated in a predictive manner. Also, finding the best dopants to attain a given set of properties is not always straightforward and it is experimentally cumbersome to study each and every dopant. In this regard, simulations have become a key tool for not only achieving the aforementioned tasks, but also interpreting the experimental results and helping the device design.

In this thesis, we have carried out simulations to study the extrinsic doping of half-Heusler compounds which is discussed in Sec. 1.2.1, calculating thermal conductivity within the Boltzmann transport equation formalism (Sec. 1.2.2.1) with a special emphasis on the point-defect phonon scattering (Sec. 1.2.2.2) explained with the help of a simple 1D monoatomic chain (Sec 1.2.2.3). Calculation of the thermal conductivity using molecular dynamics methods like Green-Kubo and homogeneous non-equilibrium molecular dynamics is discussed in Sec. 1.2.3.

1.2.1 Extrinsic doping of half-Heuslers

In order to reduce the worldwide carbon footprint and counter the drastic changes in the climate, various international agreements like the Kyoto protocol [6] and the Paris agreement [7] have laid a tremendous emphasis on the reduction of the use of fossil fuels and increasing the utilization of renewable energy sources. Globally, heat is the most abundant energy form used and waste heat accounts for nearly two-thirds of the overall energy production [8,9]. Therefore, finding methods for waste heat recovery is an area of paramount importance in the scientific pursuits today. To this end, thermoelectric technology has emerged as one of the most promising techniques for waste heat recovery, as it directly converts thermal energy to electrical energy [9].

Thermoelectric devices are commonly made up of heavily doped n- and p-type semiconductor pairs which are connected thermally in parallel and electrically in



Figure 1.1: Schematic of a thermoelectric device. The n and p correspond to the n- and p-type semiconductors.

series, as shown in Fig.1.1 [10]. The efficiency of a TE material to convert heat energy to electrical energy or vice-versa, is measured by its dimensionless figure of merit $zT = \frac{S^2 \sigma T}{\kappa_e + \kappa_\ell}$, where S is the Seebeck coefficient, σ the electrical conductivity, T the temperature, κ_e and κ_ℓ the electronic and the lattice contribution to the thermal conductivity, respectively. Although, the TE modules offer a cost efficient, noise-free, and green technology to produce electricity without the hazards related to moving parts, the main challenge associated with the TE technology is the low value of zT of materials used in making the TE devices. This is because, a good thermoelectric material should have a large S, high σ , and low κ , achieving which simultaneously is non-trivial [11]. Depending on the operational temperature various semiconductor materials like Bi₂Te₃, Sb₂Se₃, PbSe, CoSb₃, SiGe, and Zn₄Sb₃ are being used in the thermoelectric modules [9].

Half-Heusler compounds have shown a great potential as thermoelectric materials for the moderate temperature (T = 500 - 800 °C) applications such as, recovering automobile exhaust, and industrial waste heat [1]. HHCs owe their usability to their non-toxicity, high thermal stability, mechanical strength, and moderate zT compared to their counterparts like PbTe, and skutterudites [12]. HHCs with formula ABX have the cubic MgAgAs type structure (space group $F\bar{4}3m$), which is formed by three interpenetrating face-centered-cubic (fcc) sublattices of A (occupying Wycoff position 4b (1/2, 1/2, 1/2)), B (every alternate 4c (1/4, 1/4, 1/4)), and X (4a (0, 0, 0)), as shown in Fig.1.2 [1]. Is has been shown earlier that HHCs with the valence electron count (VEC) of 18 per unit cell are stable and have a band gap of 0 - 1.1 eV [1]. The most extensively studied half-Heuslers are MNiSn and MCoSb, where M is Ti, Zr, and Hf, whereas new HHCs like (Nb/V)FeSb [12], NbCoSn [13], and even 19 VEC systems like NbCoSb [14] are currently being studied.



Figure 1.2: Crystal structure of a half-Heusler compound. A can be a transition metal, a nobel metal, or a rare-earth element, B can also be a transition or noble metal, and X is a main group element [1].

The two main strategies to improve the zT values of the HHCs are, improving the power factor $(S^2\sigma)$, and reducing the lattice thermal conductivity (κ_{ℓ}) . The high

thermal conductivity (6.7–20 W m⁻¹ K⁻¹at 300 K) of the HHCs has been identified as one of the main bottlenecks for their thermoelectric applications [1]. Much effort has gone into solving this and more than 50% reduction in κ_{ℓ} has been reported by the generation of point defects during the binary and ternary isoelectronic doping of *n*-type MNiSn and *p*-type MCoSb, where M = Ti, Zr, and Hf [15–28]. A high $zT \sim 1$ was also achieved for the ternary isoelectronic doping with less Hf amounts in both p- and n-type half-Heuslers [29–31]. Enhancing grain boundary scattering by reducing the grain size in polycrystalline samples has also been shown to greatly reduce the thermal conductivity in HHCs [32–34]. Furthermore, the addition of high melting point oxides like Al₂O₃ [35] and ZrO₂ [36,37], metallic phase nanoinclusions like InSb [38,39], and full-Heuslers [40,41] have been reported to act as phonon scattering centers and reduce κ_{ℓ} .

Power factor can be improved by enhancing the Seebeck coefficient and the electrical conductivity. Increasing the carrier concentration and carrier mobility are the two handles to enhance the electrical conductivity. It should again be noted that all the factors influencing the zT, viz., S, σ , and κ are interdependent, and often, a change in one leads to a change in the other. For example, the aforementioned use of the InSb nanoparticles in Ti(Co, Fe)Sb not only reduces κ_{ℓ} , but also leads to an increase in σ [39]. Similarly, the *in situ* formation of InSb [38] or full-Heusler phase [40–42] nanoprecipitates employed to increase the carrier concentration also leads to an increase in the Seebeck coefficient by scattering low energy charge carriers. Dopants have been more extensively used to enhance the carrier concentration, as they generally increase or decrease the VEC making the HHC n- or p-type, respectively. In half-Heuslers all three lattice sites, viz., A, B, and X can be doped independently to vary the VEC, adding to the chemical versatility of the HHCs. *n*-type type doping has been effectively done on the MNiSn (M = Ti, Zr, Hf) systems with V, Nb, and Ta at the M site [16, 20], Cu at Ni site [43], and Sb, and Bi at the Sn site [16, 20]. Such systems being inherently *n*-type, it is difficult to *p*-dope them [1]. On the contrary, MCoSb compounds are not intrinsically *n*-dopable due to a relatively larger bandgap. However, they can be effectively p-doped by partially replacing M with Sc, and Ta [44, 45], Co with Fe [46, 47], and Sb with Sn, and Ge [18, 22, 30, 33, 48-51]. Furthermore, intrinsic defects formed under

certain growth conditions are also known to enhance the carrier concentrations in HHCs [52–56].

It is thus evident that finding the right dopants to achieve optimal carrier concentration in HHCs is not trivial, as it an interplay between the intrinsic and extrinsic defects, and the growth conditions. It is also possible that the extrinsic doping has not been fully explored in HHCs due to their chemical versatility and possibility to substitute each lattice stie independently. Moreover, considering each and every case experimentally is not easy. It further demands a comprehensive knowledge of the underlying parameters to study the dopability of such materials. To this end, density functional theory (DFT) has emerged as a powerful tool to calculate the properties of the defects in the the host material from first principles. The most widely used approach to calculate the formation energies of the defects is the supercell approach [57]; Green's function approach [58], and cluster approach [59, 60] being among others. The supercell approach overcomes the limitations of the cluster approach which suffer from quantum confinement effects in delocalized wave functions and the Green's function technique which doesn't treat the electrostatic and elastic response accurately [61]. In the following, we present the methodology to calculate the defect formation energies within the supercell approach, the chemical potentials, and the carrier and defect concentrations of the point defects in semiconductors. We also emphasize the importance of the use of on-line repositories like AFLOWlib [62], and the Materials Project [63] which adhere to the REST architectural constraints, in speeding up the calculations.

1.2.1.1 Defect formation energy

Several studies have established the use of DFT within the supercell approach to calculate the defect formation energies (DFE), where the defect is located in a supercell which is made of several repeating unit cells [61, 64–66]. The defect is surrounded by a finite number of atoms of the supercell and periodic boundary conditions are imposed. In order to avoid the defect-defect interactions in the periodic images, the supercell should be large enough to reach the dilute limit and mimic isolated defects. The defect formation energy for a defect D in charge state

q, as a function of the electron chemical potential μ_e can be calculated as [67, 68]:

$$E_{D^{(q)}}^0(\mu_e) = E_{f,D^{(q)}} - \sum_{\alpha} n_{\alpha} \Delta \mu_{\alpha} + q\mu_e, \qquad (1)$$

where,

$$E_{f,D^{(q)}} = E_{D^{(q)}} - E_{\text{bulk}} - \sum n_{\alpha} E_{\alpha}^{\text{ref}}.$$
(2)

The quantities $E_{D^{(q)}}$ and E_{bulk} correspond to the ground state energies calculated using DFT for the defected and bulk supercells, respectively. n_{α} is the number of atoms of species α that are exchanged with the reservoir, with (n > 0) if the atoms are added to the crystal and (n < 0) if the atoms are removed from the crystal. E_{α}^{ref} is the reference energy or in other words ground state total energy of the species α . $\Delta \mu_{\alpha}$ is the change in chemical potential of species α and accounts for the energy needed to exchange it with the reservoir. For neutral defects (q = 0), the DFE is independent of the electron chemical potential, meaning to say that since no electrons are exchanged with an external electron reservoir, it does not effect the DFE. μ_e is referenced with respect to the valence band maximum (VBM) of the bulk system.

The DFE is assumed to be independent of the temperature. Temperature largely plays a role in determining the defect concentrations in thermodynamic equilibrium through the configurational entropy, as we will see later. For defect concentrations below 10^{-4} the configurational entropy per defect is larger than $10k_B$, rendering the additional contributions like vibrational, electronic, and magnetic contributions negligibly small [61]. These contributions also significantly add to the computational costs and therefore are not considered in the present study.

For the charged supercells, say q = -1, one has to consider that, since one electron is being added to the system, the charge neutrality condition is no more satisfied. Also, the periodic repetition of such a system would lead to the divergence of the electrostatic potential. To compensate for this, a jellium background charge is applied by setting the average electrostatic potential to zero during the DFT calculations. The periodic images also cause artificial Coulomb interaction between the defect arrays, which only decays as 1/r, and cannot be simply overcome by increasing the supercell size due to computational limitations. Therefore, for reasonable supercell sizes these interactions cannot be neglected. Furthermore, the Kohn-Sham eigenvalues and therefore the VBM calculated within DFT depend on the average electronic potential in the bulk. The DFE for the charged systems is also dependent on the value of the VBM through μ_e , see Eq. 1. Since the absolute reference of the average electrostatic potential is not defined, the average electrostatic potential in defect supercell has to be aligned with that in the bulk. In the present study we apply the corrections mentioned above *a posteriori* in the form of Markov and Payne multipole correction ($\Delta E_{\rm MP}$) [69] and potential alignment correction ($\Delta E_{\rm pa}$) [66]:

$$\Delta E_{\rm MP}(D^{(q)}) = \frac{q^2 \alpha_M}{2\varepsilon_0 L} + \frac{2\pi q Q}{3\varepsilon_0 L^3} + \mathcal{O}(L^{-5}), \tag{3}$$

and

$$\Delta E_{\rm pa}(D^{(q)}) = q[V_R(D^{(q)}) - V_R^{\rm bulk}] + \Delta \epsilon_{\rm VBM},\tag{4}$$

respectively. In Eq. 3, α_M is the Madelung constant which is a geometrical factor and depends on the lattice type. ε_0 is the dielectric constant of the host material which screens the Coulomb interaction between the defect arrays, and Q is the quadrupole moment. The two terms correspond to the monopole and quadrupole corrections, respectively, and in the present study only monopole correction is considered. In Eq. 4, V_R are the potential energies at given reference points far from the defect and $\Delta \epsilon_{\rm VBM}$ aligns the valence band maximum of the defected and non-defected cells. Finally, after considering the corrections, the DFE takes the form:

$$E_{D^{(q)}}(\mu_e) = E_{D^{(q)}}^0(\mu_e) + \Delta E_{\rm pa}(D^{(q)}) + \Delta E_{\rm MP}(D^{(q)}).$$
(5)

1.2.1.2 Chemical potentials

The chemical potentials that enter Eq. 1 are of the atoms forming the defect in the host material. They represent the energies of the reservoirs with which they are exchanged and are uniquely defined by the experimental conditions. In other words, we can explore different experimental conditions by varying the chemical potentials in the calculations. The chemical potentials always depend on temperature, pressure, and their implicit reference. In the present calculations, they are referenced to the total energy of the elementary phases at T = 0 K, and it is crucial that a consistent choice is made for all chemical potentials. Although, the chemical potentials are treated as variables in the general formalism, they are subject to specific bounds set by the secondary phases. For example, if we consider a compound XY, since the chemical potentials are referenced with the elementary phases, upper bounds are set on the chemical potentials of X and Y so that they do not precipitate into their reference states as:

$$\mu_X \le E_X^{\text{ref}} \tag{6}$$

$$\mu_Y \le E_Y^{\text{ref}}.\tag{7}$$

The chemical potential of the compound XY is fixed as:

$$\mu_X + \mu_Y = \mu_{XY}.\tag{8}$$

Subtracting the reference energies on both side further yields:

$$\Delta \mu_X + \Delta \mu_Y = 2\Delta H(XY),\tag{9}$$

where $\Delta \mu_i = \mu_i - E_i^{\text{ref}}$. Now, if there are any competing phases of X and Y, like $X_a Y_b$, then the chemical potentials of X and Y are further limited, such that they do not form this phase as:

$$a\Delta\mu_X + b\Delta\mu_Y \le (a+b)\Delta H(X_a Y_b). \tag{10}$$

Therefore, in order to get the actual chemical potential stability domain of the desired compound, the list of the conditions imposed by the competing phases has to be complete. The formation energies of such competing phases can be directly obtained from the online repositories like, AFLOWlib, and Materials Project. If doping is done, additional conditions are imposed by the phases formed by the dopant and the elements of the host structure. For example, if we consider the simple case of Si doped with P, the following conditions have to be satisfied. First of all, without any dopants, the chemical potential of Si is limited only by the condition:

$$\mu_{\rm Si} \le E_{\rm Si}^{\rm ref}, or \tag{11}$$

$$\Delta \mu_{\rm Si} \le 0. \tag{12}$$

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Now, when the P is introduced, all the phases formed between Si and P have to be considered. Such a list of competing stable phases can be easily obtained on-line using the aforementioned materials repositories. So for P-doped Si, the competing phases obtained form Materials Project [63] are SiP and SiP₂. Therefore, the bounds placed on the chemical potentials are:

$$\Delta \mu_{\rm Si} + \Delta \mu_{\rm P} \le 2\Delta H({\rm SiP}),\tag{13}$$

$$\Delta \mu_{\rm Si} + 2\Delta \mu_{\rm P} \le 3\Delta H({\rm SiP}_2). \tag{14}$$

Figure 1.3 shows the competing phases when Si is doped with P. The upper bounds placed on the chemical potential of P in order to avoid the formation of competing phases, i.e $\Delta \mu_{\rm P} < 0.31$ (red point Fig. 1.3).



Figure 1.3: Competing phases in P-doped Si. The red point corresponds to the maximum value of the chemical potential of P, before the competing phase SiP is formed. Green line is the allowed chemical potentials of P.

Further, if we consider the binary system of cubic SiC (3C-SiC), similar conditions for the individual chemical potentials are placed:

$$\mu_{\rm Si} \le E_{\rm Si}^{\rm ref},\tag{15}$$

$$\mu_{\rm C} \le E_{\rm C}^{\rm ref}.\tag{16}$$

11

In addition to this, now the chemical potentials of Si and C are bound only by twice the formation energy of 3C-SiC, as there are no competing phases:

$$\Delta \mu_{\rm Si} + \Delta \mu_{\rm C} = 2\Delta H({\rm SiC}). \tag{17}$$

If SiC is doped with nitrogen, the competing phases which can be formed are shown in the ternary phase diagram (Fig.1.4). These compounds pose the following bounds on the chemical potentials:

$$3\Delta\mu_{\rm Si} + 4\Delta\mu_{\rm N} \le 7\Delta H({\rm Si}_3{\rm N}_4),\tag{18}$$

$$2\Delta\mu_{\rm Si} + \Delta\mu_{\rm C} + 4\Delta\mu_{\rm N} \le 7\Delta H({\rm Si}_2{\rm CN}_4),\tag{19}$$

limiting the maximum allowed chemical potential of N such that all the three conditions, viz., Eq. 17, Eq. 18, and Eq. 19 are satisfied.



Figure 1.4: Ternary phase diagram of N-doped SiC consisting of the most stable respective binary and ternary phases.

1.2.1.3 Defect concentrations and electron chemical potential

Various kinds of point defects like vacancies, interstitials, antisites, and substitutional atoms are present in a material because of thermodynamic considerations and fabrication limitations. These defects break the order of the otherwise perfectly ordered crystal structure. The defects are considered to occur in the dilute limit, meaning that the defect-defect interactions can be ignored. This assumption is justified as the number of available lattice sites N is much larger than the number of defects in the lattice.

The defect formation energies are always positive, as negative energies would mean that the host lattice is unstable. However, temperature effects largely in the form of configurational entropy compensate for the energy cost per point defect. In thermodynamic equilibrium, Gibbs free energy determines the equilibrium concentration of the defects, and for n_D point defects it is given as:

$$G = n_D E_D - T S_{\rm conf},\tag{20}$$

where E_D is formation energy of a single point defect, T the temperature, and S_{conf} the configurational entropy. For the N lattice sites available, if there are n_D point defects that occupy them, then the configurational entropy can be calculated as:

$$S_{\rm conf} = k_B \ln\left(\frac{N!}{(N-n_D)!n_D!}\right).$$
(21)

Applying Stirling's approximation, $\ln(x!) = x \ln(x)$, since the number of atoms is of the order of Avogadro's constant N_A , yields:

$$S_{\rm conf} = k_B (N \ln(N) - (N - n_D) \ln(N - n_D) - n_D \ln(n_D).$$
(22)

Using concentration instead of number of the defects, $c_D = n_D/N$, gives:

$$S_{\rm conf} = -k_B N((1-c_D)\ln(1-c_D) + c_D\ln(c_D).$$
(23)

Substituting Eq. 23 in Eq. 20, we get:

$$\frac{G}{N} = c_D E_D + k_B T((1 - c_D) \ln(1 - c_D) + c_D \ln(c_D).$$
(24)

Under thermodynamic equilibrium, the Gibbs free energy has to be minimized with respect to the defect concentration, such that:

$$\frac{\partial G}{\partial c_D} = 0 \tag{25}$$

$$E_D + k_B T \frac{\partial}{\partial c_D} ((1 - c_D) \ln(1 - c_D) + c_D \ln(c_D)) = 0.$$
 (26)

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Differentiating and rearranging gives:

$$E_D + k_B T \ln\left(\frac{c_D}{1 - c_D}\right) = 0 \tag{27}$$

$$\frac{c_D}{1-c_D} = \exp\left(-\frac{E_D}{k_B T}\right).$$
(28)

In dilute limit, $c_D \ll 1$, therefore,

$$c_D = \exp\left(-\frac{E_D}{k_B T}\right). \tag{29}$$

Eq. 29 suggests that for T > 0 K, there is a finite concentration of point defects of a certain kind with formation energy E_D . At a particular temperature, the higher the DFE the smaller the concentration, and vice-versa.

Further, in semiconductors, unlike metals, the point defects commonly occur in charged states. Considering the dependence of E_D on the electronic and defect chemical potentials for charged defects, Eq. 29 can be rewritten as:

$$c_{D^{(q)}}(\mu_e, T; \Delta\mu_\alpha) = \exp\left(-\frac{E_{D^{(q)}}(\Delta\mu_\alpha, \mu_e)}{k_B T}\right).$$
(30)

A particular defect can be present in different charge states in the system as shown in Fig. 1.5. Each defect is independent and has its own formation energy which varies linearly with μ_e , the respective charge being the slope. As can be seen in the figure that, at certain values of μ_e (red points), two differently charged defects have the same energy and a transition between them takes place. At such points both the defects will have the same concentration. Such transitions make different defects energetically more stable than others at particular range of values of μ_e , depicted as solid black line in Fig 1.5. In can be interpreted that, it is energetically less costly to make positively charged (electron donating) defects near the VBM and negatively charged (electron accepting) defects near the CBM.

Taking all the defects into account, charge neutrality has to be maintained in the system such that:

$$n_h(\mu_e, T) - n_e(\mu_e, T) + \sum_{D^{(q)}} c_{D^{(q)}}(\mu_e, T; \Delta \mu_\alpha) = 0.$$
(31)

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Figure 1.5: Schematic illustration of the defect formation energies of a particular defect in its different charge states, ranging from +2 to -1. The most stable charge state at a particular value of the chemical potential is given by the thick black line, whereas the red points denote the transition between two different charge states. The two shaded regions VB and CB correspond to the valence and conduction band regions, respectively.

The sum is taken over all the intrinsic and extrinsic defects of interest. In the dilute limit, it can be assumed that the bandstructure is approximately the same as that of the pure host material. In that case, the number of holes is given by:

$$n_h = \int_{-\infty}^{\epsilon_{\rm VBM}} D(\epsilon) (1 - f(\epsilon, \mu_e)) d\epsilon, \qquad (32)$$

and the number of electrons:

$$n_e = \int_{\epsilon_{\rm CBM}}^{\infty} D(\epsilon) f(\epsilon, \mu_e) d\epsilon, \qquad (33)$$

where $D(\epsilon)$ is the density of states and $f(\epsilon) = \left(\exp\left(\frac{\epsilon-\mu_e}{k_BT}\right) + 1\right)^{-1}$ the Fermi-Dirac distribution. Since the concentration is dependent on the temperature and the $E_{D(q)}$ is dependent on the electronic chemical potential, the charge neutrality condition has to be solved self-consistently, as shown in Fig. 1.6. This can be done using standard root-finding algorithms.



Figure 1.6: Self-consistent cycle for calculating μ_e in order to maintain charge neutrality.

Finally, it should be noted that, the Kohn-Sham DFT (KS-DFT) based supercell approach suffers from a prominent problem knows as the *band gap problem*, which has its origin in the choice of exchange-correlation functionals [61]. The most commonly used functionals are the local-density approximation (LDA) [70] and the generalized gradient approximation (GGA) by Perdew, Bruke, and Ernzerhof (PBE) [71], which contain a spurious self-interaction in DFT. While these functionals are parameter-free and give reasonable lattice constants for many materials, the underestimation in the band gap by a factor of up to two has been seen in case of LDA [72]. A correct band gap is necessary for the calculation of the number of holes and electrons, Eqs. 32 and 33, which are required in the self-consistent calculation of the electron chemical potential in the charge neutrality condition, Eq. 31. Moreover, a smaller band gap can also lead to a wrong prediction of the relative stability of different defects. This can be seen in Fig. 1.5, where the -1 charged defect is not stable in the first-half of the band gap at all.

1.2.2 Predictive *ab initio* lattice thermal conductivity and point defect phonon scattering

Over the last few decades, semiconductor devices have experienced a continuous miniaturization and increasing operating speeds and frequencies, which has put tremendous thermal loads on them. Heat dissipation or thermal transport at the nanoscale has been identified as the bottleneck in producing smaller and faster transistors, consequently pointing to the end of Moore's Law's [73-75]. Various other applications such as thermal barrier coatings, thermoelectric energy conversion, phase change memory devices, heat-assisted magnetic recording, heated nanoparticles in medical therapy, and micro-electrochemical systems are also functionally dependent on nanoscale heat transfer [74, 76]. In order to tackle the problem of nanoscale thermal transport, materials like high-thermal-conductivity cubic crystals, two-dimensional layered materials, and low-dimensional systems like nanowires, nanotubes, or nanoribbons have been employed as heat-spreading layers and substrates in electronic devices [77]. In contrast, nanostructuring using superlattices has also been employed to reduce thermal conductivity in thermoelectric devices [1, 9, 12, 78]. However, modeling thermal transport in these structures is much more complex than for macroscopic systems. This is because, the macroscale continuum approach based on the classical heat transfer is no longer valid for the nanoscale devices where the mean free paths (MFPs) of the heat-carrying phonons become comparable to the characteristic length of the device [74, 79]. Moreover, various defects like vacancies, dislocations, interfaces, grain boundaries, or nanoinclusions present in the system scatter the phonons, where the scattering rate for each defect has to be considered explicitly.

Phonons are the main heat carriers in semiconductors and insulators [80]. In such materials, the phonon-contributed thermal conductivity, also called the lattice thermal conductivity (κ_{ℓ}), largely outweighs the electronic part (κ_{e}) in the total thermal conductivity, $\kappa = \kappa_{\ell} + \kappa_{e}$. Recent advances on the theoretical and computational fronts have facilitated understanding and dealing with heat transport at the nanoscale. In this regard, the Boltzmann transport equation (BTE) combined with DFT has emerged as a powerful tool to study phonon transport from first principles [81,82]. Owing to its various advantages like parameter-free computation

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of the relevant quantities, predictive ability, and a quantum-mechanical treatment of phonons, it has been used on a wide variety of materials, in understanding certain physical phenomena, as well as critically analyzing experimental data [83]. In the DFT-BTE approach the calculation of the transport properties is based on the *ab initio* computation of the interatomic force constants and the numerical solution of the phonon Boltzmann transport equation.

In the previous section, we discussed the importance of dopants or point defects for tuning the properties of semiconductors and the associated thermochemistry. It was shown in case of HHCs, how certain dopants are effective in reducing the lattice thermal conductivity, thereby increasing zT. However, in other technologies that are also heavily dependent on doping, such as power electronics, optoelectronics, photovoltaics, efficient heat removal from the active region is critical to the device performance. In such cases, the dopants can severely hinder the flow of heat-carrying phonons, specially in highly-doped systems or at low temperatures [84]. Thus, accurately describing defect-phonon scattering is critical for the above-mentioned parameter-free DFT-BTE formalism to not only function predictively in case of intrinsic κ_{ℓ} calculations but also for *real* materials containing defects.

The development of atomistic Green's function (AGF) methodology utilizing the T matrix [85] and coupled with the BTE, during the last decade or so, has made it possible to treat the defect-phonon scattering in the crystal from first principles. AGF has been successfully applied to study point defects like vacancies [86–91], as well as external dopants [90–92] in semiconductors. It has also been applied to nanoparticles [93] and very recently to random semiconductor alloys [94] and dislocations [95]. Enhanced scattering caused by certain dopants has also been analyzed by carefully studying the role of the underlying parameters of the AGF approach [92, 96]. AGF takes into account the perturbation to all orders and overcomes the limitations of earlier models that rely only on mass perturbations due to the defects [84, 97, 98], or fitting parameters to match experimental data [84, 99–103].

In the following, we present the theory behind the thermal conductivity calculations with the BTE, and the atomistic Green's function method to treat the defect-phonon scattering.
1.2.2.1 Thermal conductivity using the Boltzmann transport equation

At thermal equilibrium, phonons are distributed according to Bose–Einstein statistics as:

$$n^{0}(\omega_{\lambda}) = \frac{1}{\exp\left(\frac{\hbar\omega_{\lambda}}{k_{B}T}\right) - 1},\tag{34}$$

where ω_{λ} is the angular frequency of the mode $\lambda \equiv (\mathbf{q}, p)$, which is the short hand notation for the phonon mode with wave vector \mathbf{q} and branch or polarization index p. A temperature gradient ∇T perturbs n^0 , which causes the diffusion of phonons and their scattering arising from the allowed processes, resulting in a non-equilibrium phonon distribution n_{λ} . This deviation can be captured by the BTE which gives the time evolution of the phonon populations as [80]:

$$\frac{\partial n_{\lambda}}{\partial t} = \frac{\partial n_{\lambda}}{\partial t} \left|_{\text{diffusion}} + \frac{\partial n_{\lambda}}{\partial t} \right|_{\text{scattering}}.$$
(35)

In the steady state the rate of change in the distribution must go to zero, $\partial n_{\lambda}/\partial t = 0$, such that:

$$-\frac{\partial n_{\lambda}}{\partial t}\bigg|_{\text{diffusion}} = \frac{\partial n_{\lambda}}{\partial t}\bigg|_{\text{scattering}}.$$
(36)

The diffusion term can be written as:

$$\left. \frac{\partial n_{\lambda}}{\partial t} \right|_{\text{diffusion}} = -\nabla T \cdot \mathbf{v}_{\lambda} \frac{\partial n_{\lambda}}{\partial T},\tag{37}$$

where \mathbf{v}_{λ} is the phonon group velocity of the mode λ . The scattering term in Eq. 36 is determined by the allowed scattering events occurring in the system. These events comprise of the temperature-dependent anharmonic scattering due to phonon-phonon interactions and the temperature-independent harmonic scattering caused by the impurities and defects in the system. Considering a small temperature gradient ∇T , the non-equilibrium phonon distribution can be expanded up to the first order in ∇T as [104]:

$$n_{\lambda} = n_{\lambda}^{0} + \mathbf{F}_{\lambda} \cdot \nabla T \left(-\frac{\partial n_{\lambda}^{0}}{\partial T} \right).$$
(38)

In this treatment, the linearized BTE is represented by \mathbf{F}_{λ} as:

$$\mathbf{F}_{\lambda} = \tau_{\lambda}^{0} \left(\mathbf{v}_{\lambda} + \boldsymbol{\Delta}_{\lambda} \right). \tag{39}$$

 τ_{λ}^{0} is the total relaxation time of mode λ whose inverse is the total scattering rate, $\frac{1}{\tau_{\lambda}^{0}}$, which can be obtained according to the Matthiessen's rule as [80]:

$$\frac{1}{\tau_{\lambda}^{0}} = \sum_{\lambda'\lambda''}^{+} \Gamma_{\lambda\lambda'\lambda''}^{+} + \sum_{\lambda'\lambda''}^{-} \frac{1}{2} \Gamma_{\lambda\lambda'\lambda''}^{-} + \sum_{\lambda'} \Gamma_{\lambda\lambda'}^{\rm iso} + \sum_{\lambda'} \Gamma_{\lambda\lambda'}^{\rm pd}.$$
(40)

 Δ_{λ} couples the phonon populations of the mode λ with the other modes through the anharmonic and elastic scattering as [104]:

$$\boldsymbol{\Delta}_{\lambda} = \sum_{\lambda'\lambda''}^{+} \Gamma_{\lambda\lambda'\lambda''}^{+} \left(\frac{\omega_{\lambda''}}{\omega_{\lambda}} \mathbf{F}_{\lambda''} - \frac{\omega_{\lambda'}}{\omega_{\lambda}} \mathbf{F}_{\lambda'} \right) + \sum_{\lambda'\lambda''}^{-} \frac{1}{2} \Gamma_{\lambda\lambda'\lambda''}^{-} \left(\frac{\omega_{\lambda''}}{\omega_{\lambda}} \mathbf{F}_{\lambda''} + \frac{\omega_{\lambda'}}{\omega_{\lambda}} \mathbf{F}_{\lambda'} \right) + \sum_{\lambda'} \Gamma_{\lambda\lambda'}^{\mathrm{iso}} \frac{\omega_{\lambda'}}{\omega_{\lambda}} \mathbf{F}_{\lambda'} + \sum_{\lambda'} \Gamma_{\lambda\lambda'}^{\mathrm{pd}} \frac{\omega_{\lambda'}}{\omega_{\lambda}} \mathbf{F}_{\lambda'}, \qquad (41)$$

where $\Gamma^{\pm}_{\lambda\lambda'\lambda''}$ are the three-phonon transition probability rates, and $\Gamma^{\text{iso,pd}}_{\lambda\lambda'}$ are the two-phonon transition probability rates of isotopes and point defects, respectively. The methodology to calculate these quantities is shown below. First of all, in the present work we consider the anharmonicity only up to the third order in Taylor expansion of the potential energy E as:

$$E \approx E_{0} + \sum_{lk\alpha} \frac{\partial E}{\partial u_{lk}^{\alpha}} \bigg|_{0} u_{lk}^{\alpha} + \frac{1}{2} \sum_{\substack{lk\alpha\\l'k'\beta}} \frac{\partial^{2} E}{\partial u_{lk}^{\alpha} \partial u_{l'k'}^{\beta}} \bigg|_{0} u_{lk}^{\alpha} u_{l'k'}^{\beta} + \frac{1}{6} \sum_{\substack{lk\alpha\\l'k'\beta\\l''k''\gamma}} \frac{\partial^{3} E}{\partial u_{lk}^{\alpha} \partial u_{l'k'}^{\beta} \partial u_{l''k''}^{\gamma}} \bigg|_{0} u_{lk}^{\alpha} u_{l'k'}^{\beta} u_{l''k''}^{\gamma} + \mathcal{O}(u^{4}),$$

$$(42)$$

where α , β , and γ run over the Cartesian axes, l refers to the unit cell, and k locates the atom within the motif. The u describe the atomic deviations from their equilibrium positions. The first term of Eq. 42 is a constant that can be ignored and the second term describes the force exerted on a particular atom by all other

atoms. At equilibrium, where the crystal potential (E) has its minimum, this force must be equal to zero and therefore this term can also be ignored. The secondand third-order derivatives of E are the interatomic force constants (IFCs) of the system which are abbreviated as:

$$\frac{\partial^2 E}{\partial u_{lk}^{\alpha} \partial u_{l'k'}^{\beta}} \bigg|_0 = K_{lk,l'k'}^{\alpha\beta}$$
(43)

$$\frac{\partial^3 E}{\partial u_{lk}^{\alpha} \partial u_{l'k'}^{\beta} \partial u_{l''k''}^{\gamma}} \bigg|_0 = \Phi_{lk,l'k',l''k''}^{\alpha\beta\gamma}$$
(44)

These IFCs can be obtained from first principles using either the linear-response approach within the density-functional perturbation theory [105-107], or the finitedisplacement method [108, 109]. In the present study we have used the finitedisplacement method as it is straightforward and conceptually simpler to implement. In this method the IFCs are calculated in the direct space, usually on a supercell expansion of the unit cell, from the forces induced on the atoms of the supercell when displacing other ions from their equilibrium positions. This can be done utilizing the space-group symmetries of the concerned system and then either displacing atoms by a finite amount sequentially, as done in Phonopy [110] and thirdorder.py [104], or displacing all the atoms in random directions at once, as done in the newly developed technique [111]. In this study, we use the former.

The total anharmonic crystal hamiltonian is then given as:

$$\mathbf{H} \approx \mathbf{H}_2 + \mathbf{H}_3 + \mathcal{O}(u^4), \tag{45}$$

where the first term is the harmonic part given as:

$$\mathbf{H}_{2} = \sum_{lk} \frac{\mathbf{p}_{lk} \cdot \mathbf{p}_{lk}}{2M_{lk}} + \frac{1}{2} \sum_{\substack{lk\alpha\\l'k'\beta}} K^{\alpha\beta}_{lk,l'k'} u^{\alpha}_{lk} u^{\beta}_{l'k'}.$$
 (46)

For this system, the equation of motion for the k-th atom in the l-th unit cell, having mass M, can be written as [112]:

$$M_{lk}\ddot{u}^{\alpha}_{lk} = \frac{\partial E}{\partial u^{\alpha}_{lk}} = -\sum_{l'k'\beta} K^{\alpha\beta}_{lk,l'k'} u^{\beta}_{l'k'}.$$
(47)

Taking

$$u_{lk}^{\alpha} = \frac{1}{\sqrt{M_{lk}}} A_k^{\alpha}(\mathbf{q}) \exp\left(i\mathbf{q}\mathbf{r}_{lk} - \omega t\right)$$
(48)

as a solution to Eq. 47, we obtain the phonon frequencies as

$$\omega^2 \tilde{u}_{lk}^{\alpha} = \sum_{l'k'\beta} \frac{K_{lk,l'k'}^{\alpha\beta}}{\sqrt{M_{lk}M_{l'k'}}} \tilde{u}_{l'k'}^{\beta}, \tag{49}$$

where A_k^{α} is the amplitude, \mathbf{r}_{lk} the position vector of atom k in unit cell l, and $\tilde{u}^{\alpha} = \sqrt{M}u^{\alpha}$. Writing Eq. 49 to obtain the polarization and wave-vector dependent frequencies, we get

$$\omega_{\lambda}^2 e_{\lambda}^{\alpha}(k) = \sum_{k'\beta} D_{kk'}^{\alpha\beta}(\mathbf{q}) e_{\lambda}^{\beta}(k'), \qquad (50)$$

where the dynamical matrix \mathbf{D} is given as:

$$D_{kk'}^{\alpha\beta}(\mathbf{q}) = \sum_{l'} \frac{K_{lk,l'k'}^{\alpha\beta}}{\sqrt{M_{lk}M_{l'k'}}} \exp\left(i\mathbf{q}(\mathbf{r}_{l'k'} - \mathbf{r}_{lk})\right),\tag{51}$$

where e_{λ}^{α} is the normalized eigenvector of the dynamical matrix. The sum on the right-hand side of the equation is independent of l, as l can be set to 0 owing to the property that $K_{lk,l'k'}^{\alpha\beta} = K_{0k,(l-l')k'}^{\alpha\beta}$.

The second term on the right-hand side of Eq. 45, \mathbf{H}_3 , is the anharmonic contribution which can be seen as a perturbation to the harmonic part of the hamiltonian. Therefore, within the perturbation theory, the transition probability rates Γ^{\pm} for such a perturbation can be obtained by using Fermi's golden rule. Fermi's golden rule relates the perturbation \mathbf{H}_3 with the transition of the system from the initial state $|i\rangle$ to a final state $\langle f|$ to yield the transition rate to the first order as:

$$\Gamma_i^f = \frac{2\pi}{\hbar} |\langle f | \mathbf{H}_3 | i \rangle|^2 \delta(E_f - E_i)$$
(52)

Using Eq. 52, the transition probability rate Γ^+ can be calculated for a coalescence transition from $|n_{\lambda}n_{\lambda'}n_{\lambda''}\rangle$ to $|(n_{\lambda}-1)(n_{\lambda'}-1)(n_{\lambda''}+1)\rangle$ as:

$$\Gamma^{+}_{\lambda\lambda'\lambda''} = \frac{\hbar\pi}{4} \frac{n^{0}_{\lambda'} - n^{0}_{\lambda''}}{\omega_{\lambda}\omega_{\lambda'}\omega_{\lambda''}} \left|\Psi^{+}_{\lambda\lambda'\lambda''}\right|^{2} \delta(\omega_{\lambda} + \omega_{\lambda'} - \omega_{\lambda''}), \tag{53}$$

and for a decay transition from $|n_{\lambda}n_{\lambda'}n_{\lambda''}\rangle$ to $|(n_{\lambda}-1)(n_{\lambda'}+1)(n_{\lambda''}+1)\rangle$ as:

$$\Gamma_{\lambda\lambda'\lambda''}^{-} = \frac{\hbar\pi}{4} \frac{n_{\lambda'}^{0} + n_{\lambda''}^{0} + 1}{\omega_{\lambda}\omega_{\lambda'}\omega_{\lambda''}} \left| \Psi_{\lambda\lambda'\lambda''}^{-} \right|^{2} \delta(\omega_{\lambda} - \omega_{\lambda'} - \omega_{\lambda''}), \tag{54}$$

where n_{λ} is the occupancy number of phonons with wave vector **q** in branch *p*. $\Psi^{\pm}_{\lambda\lambda'\lambda''}$ is the scattering matrix element given by:

$$\Psi_{\lambda'\lambda'\lambda''}^{\pm} = \sum_{k \in \text{u.c.}} \sum_{k',k''} \sum_{\alpha\beta\gamma} \Phi_{kk'k''}^{\alpha\beta\gamma} \frac{e_{\lambda}^{\alpha}(k)e_{p',\pm\mathbf{q}'}^{\beta}(k')e_{p'',-\mathbf{q}''}^{\gamma}(k'')}{\sqrt{M_a M_b M_c}},$$
(55)

where $e_{\lambda}^{\alpha}(k)$ is the α component of the normalized eigenfunction of mode λ at the atom k. The summations run over the atom indices k, k', and k'' and the Cartesian coordinates. The sum k runs over only atoms in the central unit cell, whereas k' and k'' cover the whole system [104].

Considering that naturally occurring materials consist of significant concentrations of isotopic and other point-defect impurities, in the Eq. 40, apart from the three-phonon scattering rates, the scattering rates due to isotopic disorder $(\frac{1}{\tau_{\lambda}^{\text{iso}}} = \sum_{\lambda'} \Gamma_{\lambda\lambda'}^{\text{iso}})$ and point defects $(\frac{1}{\tau_{\lambda}^{\text{pd}}} = \sum_{\lambda'} \Gamma_{\lambda\lambda'}^{\text{pd}})$ are also calculated.

The transition probability rate due to the isotopic defects is given as [93, 97]:

$$\Gamma_{\lambda\lambda'}^{\rm iso} = \frac{\pi\omega^2}{2} \sum_{k\in \text{u.c.}} g(k) \left| \mathbf{e}_{\lambda}^{\dagger}(k) \mathbf{e}_{\lambda'}(k) \right|^2 \delta(\omega_{\lambda} - \omega_{\lambda'})$$
(56)

where $g(k) = \sum_{s} f_{s}(k) [1 - M_{s}(k)/\overline{M}(k)]^{2}$ represents the Pearson deviation coefficient of the masses $M_{s}(k)$ of isotopes s of atom k, which are found with a relative frequency $0 < f_{s} \leq 1$, and $\overline{M}(k) = \sum_{s} f_{s}(k)M_{s}(k)$ is their average. The methodology to calculate the third term in Eq. 40, which is the scattering rates due to the point defects $\left(\frac{1}{\tau_{\lambda}^{\text{pd}}}\right)$, is the central topic of this thesis and is presented separately in Sec. 1.2.2.2.

Once all the quantities are calculated in Eqs. 39, 40, and 41, κ_{ℓ} can be computed in terms of \mathbf{F}_{λ} as:

$$\kappa_{\ell}^{\alpha\beta} = \frac{1}{k_{\rm B}T^2 V_{\rm u.c.}N} \sum_{\lambda} n_0 (n_0 + 1) (\hbar\omega)^2 v_{\lambda}^{\alpha} F_{\lambda}^{\alpha\beta}$$
(57)

where, $V_{u.c.}$ is the volume of the unit cell. The zeroth-order approximation to the Eq. 39, i.e. setting $\Delta_{\lambda} = 0$, yields the relaxation time approximation (RTA) contribution to the thermal conductivity. RTA assumes that the relaxation time of each phonon from its non-equilibrium distribution function to its equilibrium function is independent of perturbations of other phonons. In contrast to Eqs. 39 and 41 which couple the scattering events to the phonon populations, this assumption decouples the non-equilibrium phonon distributions of different modes caused by the allowed scattering events. The RTA works well for lower κ_{ℓ} materials [113– 115], however, in certain high-thermal conductivity systems like diamond, it can underestimate the room temperature κ_{ℓ} up to 48% [116]. This is because, RTA treats all the three-phonon scattering processes as resistive. Furthermore, the three-phonon scattering phase space for resistve processes in diamond is smaller as compared to say, Si or Ge. This is caused by high phonon group velocities in diamond owing to its stiff bonds and small mass of carbon. Therefore, an iterative procedure is required to attain a steady-state where the resistive and non-resistive processes balance each other [117]. The iterative solution to the BTE can be obtained by starting with the zeroth-order approximation, $\mathbf{F}_{\lambda}^{0} = \tau_{\lambda}^{0} \mathbf{v}_{\lambda}$, and checking for the convergence in the thermal conductivity tensor, as shown in Fig. 1.7.



Figure 1.7: Solving Eq. 39 iteratively to obtain the fully converged thermal conductivity tensor, Eq. 57. The zero-th iteration value where $\Delta_{\lambda} = 0$, corresponds to the RTA thermal conductivity.

In a more direct approach, utilizing the symmetries of the system, the exact solution

to the linearized BTE can also be obtained by solving the linear system of equations, Eqs. 39 and 41, that take the form [83]:

$$\mathbf{XF} = \mathbf{Y}.\tag{58}$$

The solution of Eq. 58 is returned in the form of a Cartesian vector $\mathbf{F}_{\lambda} = (F_{\lambda}^{\alpha}, F_{\lambda}^{\beta}, F_{\lambda}^{\gamma})$ which can be directly fed into Eq. 57 to obtain the full-BTE thermal conductivity.

1.2.2.2 Ab initio point-defect phonon scattering

In the previous section, we discussed how the anharmonicity of the crystal Hamiltonian establishes a temperature gradient in the system giving rise to inelastic phonon scattering events and subsequently causing thermal resistance. Similarly, there can also be temperature independent perturbation to the harmonic equations of motion in the form of mass $(\mathbf{V}_{\rm M})$ and second-order interatomic force constant $(\mathbf{V}_{\rm K})$ perturbations caused by point defects. Point defects like vacancies, interstitials, and substitutional atoms not only effect the system in terms of a mass perturbation but also locally alter the bonding in their vicinity resulting in force-constant perturbation, as shown in Fig 1.8. As evident from Eq. 40, the scattering caused by point defects directly adds up to the scattering caused by the three-phonon processes and isotopes, thereby effecting the thermal conductivity of the system. This necessitates an *ab initio* treatment of the point-defect phonon scattering to all orders. Such a problem can be dealt with the help of atomistic Green's function (AGF) approach, where the central idea is to obtain $\frac{1}{\tau_{\lambda}^{\text{pd}}}$ in terms of the easily accessible Green's function of the host lattice (\mathbf{g}^+) and the total perturbation $\mathbf{V} = \mathbf{V}_{\mathrm{M}} + \mathbf{V}_{\mathrm{K}}.$

To begin with, Eq. 49 can be written more compactly in the matrix form as:

$$\left(\omega^{2}\mathbf{M}_{0} - \mathbf{K}_{0}\right)\mathbf{u} = 0, \text{ or}$$

$$\left(\omega^{2}\mathbf{I} - \mathbf{M}_{0}^{-\frac{1}{2}}\mathbf{K}_{0}\mathbf{M}_{0}^{-\frac{1}{2}}\right)\mathbf{\tilde{u}} = \left(\omega^{2}\mathbf{I} - \mathbf{H}_{0}\right)\mathbf{\tilde{u}} = 0$$
(59)

where the \mathbf{K}_0 and \mathbf{M}_0 are $3aN_{uc} \times 3aN_{uc}$ matrices, *a* being the total number of atoms in the primitive unit cell and N_{uc} the number of such unit cells that make

1. INTRODUCTION



Figure 1.8: Schematic representation of the perturbation caused by different point defects in the system and resulting phonon scattering.

up the crystal.

$$\mathbf{K}_{0} = \begin{bmatrix} K_{0,0}^{\alpha\alpha} & K_{0,0}^{\alpha\beta} & K_{0,0}^{\alpha\gamma} & \cdots & \cdots & K_{0,3aN_{uc}}^{\alpha\gamma} \\ K_{0,0}^{\beta\alpha} & K_{0,0}^{\beta\beta} & K_{0,0}^{\beta\gamma} & & & \\ K_{0,0}^{\gamma\alpha} & K_{0,0}^{\gamma\beta} & K_{0,0}^{\gamma\gamma} & & & \\ \vdots & & & \ddots & \\ \vdots & & & \ddots & \\ K_{3aN_{uc},0}^{\gamma\alpha} & & & K_{3aN_{uc},3aN_{uc}}^{\gamma\gamma} \end{bmatrix}$$
(60)

$$\mathbf{M}_{0} = \begin{bmatrix} M_{0} & 0 & 0 & \cdots & \cdots & 0 \\ 0 & M_{0} & 0 & & & \\ 0 & 0 & M_{0} & & & \\ \vdots & & & M_{1} & & \\ \vdots & & & & \ddots & \\ 0 & & & & & M_{3aN_{uc}} \end{bmatrix}$$
(61)

Ideally, $N_{\rm uc} \rightarrow \infty$, which makes it difficult to solve this set linear equations in direct space basis. This problem can be circumvented by finding the eigenvalue equation in the reciprocal space basis, which is obtained by back-folding \mathbf{H}_0 into the unit cell, such that Eq. 50 can be written in the matrix form as:

$$\mathbf{D}_0(\mathbf{q})\mathbf{e}_\lambda = \omega_\lambda^2 \mathbf{e}_\lambda,\tag{62}$$

where $\mathbf{D}_0(\mathbf{q})$ is the dynamical matrix of dimension $3a \times 3a$ for a given \mathbf{q} . The above treatment makes use of the periodicity of the system and reduces the problem of solving Eq 59 in the real space with $3aN_{uc}$ degrees of freedom to considering only 3a degrees of freedom in the unit cell for each \mathbf{q} point of the Brillouin zone. We then define the Green's function for Eq. 59, consisting of the mass-normalized harmonic force-constant matrix \mathbf{H}_0 , as [118]:

$$\mathbf{g}(\omega^2) = \left(\omega^2 \mathbf{I} - \mathbf{H}_0\right)^{-1} \tag{63}$$

More generally, when ω^2 approaches the eigenvalues of \mathbf{H}_0 , which are also the eigenvalues of \mathbf{D}_0 , \mathbf{g} diverges and can only be defined in a limiting case to obtain the retarded spectral Green's function of the host lattice, $\mathbf{g}^+(\omega^2)$, as [118]:

$$\mathbf{g}^{+}(\omega^{2}) = \lim_{\epsilon \to 0^{+}} \frac{1}{\omega^{2} + i\epsilon - \mathbf{H}_{0}}$$
(64)

$$= \lim_{\epsilon \to 0^+} \sum_{\lambda} \frac{\tilde{\mathbf{e}}_{\lambda} \tilde{\mathbf{e}}_{\lambda}'}{\omega^2 + i\epsilon - \omega_{\lambda}^2}, \tag{65}$$

where, $\tilde{\mathbf{e}}_{\lambda}$ is the segment of \mathbf{e}_{λ} extended to the whole crystal. The Green's function matrix projected on the atom pairs lk and l'k' is then given as:

$$\mathbf{g}^{+}_{lk,l'k'}(\omega^{2}) = \lim_{\epsilon \to 0^{+}} \sum_{\lambda} \frac{\tilde{\mathbf{e}}_{\lambda}(lk)\tilde{\mathbf{e}}_{\lambda}^{\dagger}(l'k')}{\omega^{2} + i\epsilon - \omega_{\lambda}^{2}},\tag{66}$$

where, $\tilde{\mathbf{e}}_{\lambda}(lk)$ is the eigenvector of the mode λ at the k-th atom in the l-th unit cell.

Next, we consider the doping of the host crystal which leads to the introduction of substitutional defects on different lattice sites. As mentioned earlier, doping will cause both mass and force-constant perturbations in the system. For the defect-laden system, the equations of motion can be written analogous to Eq. 59, where the mass of the atom k in the unit cell l, $M_0(kl)$, is replaced by the mass of the incoming dopant M', such that M(kl) = M'. Similarly, the presence of these defects will alter the harmonic force constants of the system which leads to the modification of the host IFC matrix \mathbf{K}_0 resulting in a new IFC matrix of the defected system \mathbf{K}' . The equation of motion for the defected system can then be written as:

$$\left(\omega^2 \mathbf{M}' - \mathbf{K}'\right) \mathbf{u} = 0, \tag{67}$$

Normalizing Eq. 67 by the masses of the host lattice, we get:

$$\left(\omega^{2}\mathbf{M}_{0}^{-\frac{1}{2}}\mathbf{M}'\mathbf{M}_{0}^{-\frac{1}{2}} - \mathbf{M}_{0}^{-\frac{1}{2}}\mathbf{K}'\mathbf{M}_{0}^{-\frac{1}{2}}\right)\tilde{\mathbf{u}} = 0.$$
 (68)

Adding and subtracting Eq. 59 from Eq. 68:

$$0 = \left[\omega^{2} \mathbf{I} - \mathbf{M}_{0}^{-\frac{1}{2}} \mathbf{K}_{0} \mathbf{M}_{0}^{-\frac{1}{2}} + \omega^{2} \mathbf{M}_{0}^{-\frac{1}{2}} \mathbf{M}' \mathbf{M}_{0}^{-\frac{1}{2}} - \mathbf{M}_{0}^{-\frac{1}{2}} \mathbf{K}' \mathbf{M}_{0}^{-\frac{1}{2}} - \left(\omega^{2} \mathbf{I} - \mathbf{M}_{0}^{-\frac{1}{2}} \mathbf{K}_{0} \mathbf{M}_{0}^{-\frac{1}{2}} \right) \right] \mathbf{\tilde{u}}$$

$$= \left[\omega^{2} \mathbf{I} - \mathbf{H}_{0} + \underbrace{\omega^{2} (\mathbf{M}_{0}^{-\frac{1}{2}} \mathbf{M}' \mathbf{M}_{0}^{-\frac{1}{2}} - \mathbf{I})}_{= \mathbf{V}_{M}} - \underbrace{\mathbf{M}_{0}^{-\frac{1}{2}} (\mathbf{K}' - \mathbf{K}_{0}) \mathbf{M}_{0}^{-\frac{1}{2}}}_{= \mathbf{V}_{K}} \right] \mathbf{\tilde{u}}$$

$$= \left[\omega^{2} \mathbf{I} - \mathbf{H}_{0} + \mathbf{V}_{M} + \mathbf{V}_{K} \right] \mathbf{\tilde{u}}$$

$$= \left[\omega^{2} \mathbf{I} - \mathbf{H}_{0} + \mathbf{V}_{M} + \mathbf{V}_{K} \right] \mathbf{\tilde{u}}, \tag{69}$$

where the elements of the mass perturbation and the force constant matrices are

given as:

$$V_{\mathrm{M};lk} = \frac{M'_{lk} - M_{0;lk}}{M_{0;lk}} \omega^2, \text{and}$$
$$V_{\mathrm{K};lk,l'k'}^{\alpha\beta} = -\frac{K'^{\alpha\beta}_{lk,l'k'} - K^{\alpha\beta}_{0;lk,l'k'}}{\sqrt{M_{lk}M_{l'k'}}},$$
(70)

respectively. Eq. 69 denotes the influence of the substitutional impurities on the ideal(host) crystal equations of motion in terms of the perturbation $\mathbf{V} = \mathbf{V}_{\mathrm{M}} + \mathbf{V}_{\mathrm{K}}$.

Similar to Eq. 63, we can write the retarded spectral Green's function for the perturbed system, $\mathbf{G}^+(\omega^2)$, as:

$$\mathbf{G}^{+}(\omega^{2}) = \left(\omega^{2} + i\epsilon - \mathbf{H}'\right)^{-1},\tag{71}$$

where $\mathbf{H}' = \mathbf{H}_0 + \mathbf{V}$. Substituting this value and using Eq. 64 in Eq. 71, we get [118]:

$$\mathbf{G}^{+}(\omega^{2}) = \left[\omega^{2} + i\epsilon - (\mathbf{H}_{0} + \mathbf{V})\right]^{-1}$$
$$= \left\{ (\omega^{2} + i\epsilon - \mathbf{H}_{0}) \left[1 - \mathbf{V}(\omega^{2} + i\epsilon - \mathbf{H}_{0})^{-1}\right] \right\}^{-1}$$
$$= \mathbf{g}^{+}(\omega^{2})[1 - \mathbf{V}\mathbf{g}^{+}(\omega^{2})]^{-1}.$$
(72)

Expanding the operator $[1 - \mathbf{g}^+(\omega^2)\mathbf{V}]^{-1}$ in Eq. 72 in power series and then writing the equation in a compact form, we obtain:

$$\mathbf{G}^{+} = \mathbf{g}^{+} + \mathbf{g}^{+} \mathbf{V} \mathbf{g}^{+} + \mathbf{g}^{+} \mathbf{V} \mathbf{g}^{+} \mathbf{V} \mathbf{g}^{+} + \cdots$$
$$= \mathbf{g}^{+} + \mathbf{g}^{+} \mathbf{V} (\mathbf{g}^{+} + \mathbf{g}^{+} \mathbf{V} \mathbf{g}^{+} + \cdots)$$
$$= \mathbf{g}^{+} + \mathbf{g}^{+} \mathbf{V} \mathbf{G}^{+}.$$
(73)

Eq. 73 is the Dyson equation, which enables the computation of the Green's function of the perturbed system purely in terms of the perturbation and Green's function of the host system [118].

Central to the scattering theory is the so-called T-matrix which can be defined as:

$$\mathbf{T}^{+} = (1 - \mathbf{V}\mathbf{g}^{+})^{-1}\mathbf{V}.$$
(74)

Eq. 73 can be easily written in terms of \mathbf{T}^+ as:

$$\mathbf{G}^{+} = \mathbf{g}^{+} + \mathbf{g}^{+} \mathbf{T}^{+} \mathbf{g}^{+}.$$
(75)

The practical implication of working with the *T*-matrix, as opposed to just \mathbf{V} is that in Eq. 74 the perturbation caused by \mathbf{V} is treated in all orders. This becomes evident if we expand \mathbf{T}^+ in a Born series as:

$$\mathbf{T}^+ = \mathbf{V} + \mathbf{V}\mathbf{g}^+\mathbf{V} + \mathbf{V}\mathbf{g}^+\mathbf{V}\mathbf{g}^+\mathbf{V} + \cdots$$

Terminating the above series to just first order in \mathbf{V} , is equivalent to staying within the well-known *Born approximation*. However, solving the scattering problem with \mathbf{T}^+ helps us consider the perturbation to all orders in \mathbf{V} . This can be understood in terms of Eq. 52 which treats the perturbation caused by \mathbf{H}_3 only to first order in the evaluation of the three-phonon scattering rates. In contrast, the two-phonon scattering rates can be obtained using the equivalent of Fermi's golden rule in exact time-independent perturbation theory, by considering the perturbation as \mathbf{T} , such that \mathbf{V} is treated in all orders as [82, 92]:

$$\frac{1}{\tau_{\lambda}} = \pi n_{\rm def} V_{\rm uc} \frac{1}{\omega_{\lambda}} \sum_{\lambda'} \left| \tilde{\mathbf{e}}_{\lambda'}^{\dagger} \mathbf{T} \tilde{\mathbf{e}}_{\lambda} \right|^2 \delta \left(\omega_{\lambda'}^2 - \omega_{\lambda}^2 \right), \tag{76}$$

where n_{def} is the volumetric concentration of the point defects, V_{uc} the volume of the unit cell, and ω the angular frequency of phonons. It can be seen that the scattering rate for a particular phonon with wave-vector \mathbf{q} and polarization p is obtained by summing up all the elastic scattering processes which involve the transition from an incoming phonon $\tilde{\mathbf{e}}_{\lambda}$ to an outgoing phonon $\tilde{\mathbf{e}}_{\lambda'}$. However, simultaneously carrying out the sum and satisfying the energy conservation imposed by the Dirac delta function in Eq. 76 can be avoided with the help of the *optical theorem* as [85]:

$$\frac{1}{\tau_{\lambda}} = -n_{\rm def} V_{\rm uc} \frac{1}{\omega_{\lambda}} \Im \left\{ \tilde{\mathbf{e}}_{\lambda}^{\dagger} \mathbf{T} \tilde{\mathbf{e}}_{\lambda} \right\}.$$
(77)

1.2.2.3 1D chain



Figure 1.9: A one dimensional chain model where the equilibrium lattice spacing is a and the displacement of the *n*-th atom is shown as u_n .

A monoatomic 1D chain presents the most simple yet physically insightful treatment of the phonons. In this section, we consider the study of phonon transport using such an infinite chain with one degree of freedom per atom, where the atoms of mass M, are bonded through nearest-neighbor harmonic interactions of magnitude K, and separated by lattice constant a, as shown in Fig. 1.9. Considering only first nearest neighbor interactions, the equation of motion for an atom at position ncan be obtained from Eq. 47 as:

$$M\ddot{u}_n = -K[(u_n - u_{n+1}) + (u_n - u_{n-1})]$$
(78)

The displacements in Eq. 48 is written as:

$$u_n = \frac{1}{\sqrt{M}} A(q) \exp\left[i(qna - \omega t)\right] \tag{79}$$

Substituting this value in Eq. 78, we get the one-dimensional equivalent of Eqs. 49 and 50 as:

$$\omega^2 A = \frac{2K}{M} (1 - \cos qa) A \equiv D(q) A.$$
(80)

Comparing Eq. 80 with equation Eq. 62, we see that for a 1D chain with only one degree of freedom per unit cell, the dynamical matrix is reduced to just one number, for a given q. The analytic expression (Eq. 80) gives the phonon dispersion the 1D chain.

Such a problem can also be studied with the help of atomistic Green's function method which does not require *a priori* knowledge of the phonon dispersion curves or density of states [119]. Rather, the local density of states on each atom can be obtained using this method. Moreover, the methodology discussed in the previous section to calculate the point-defect phonon scattering rates can be better illustrated with the help of a 1D chain where a perturbation in the chain can be easily introduced by altering the interaction of a particular atom with its left and right neighbors, as we will see later. Under the AGF method, the atoms in the 1D chain in Fig. 1.10 can be described as a device region connected to two semi-infinite contacts [119], as shown in Fig. 1.10(top). The idea is to calculate the Green's function for the device region, then obtain the **T** matrix given a perturbation **V**, and finally calculate the scattering rates using Eq. 77.



Figure 1.10: (Top) A one dimensional chain model with three device atoms connected to semi-infinite contacts on either side. The atoms are indexed with respective numbers below them. (Bottom) Force-constant perturbation V_K introduced in the chain by modifying the interaction of 0-th atom with its left (-1) and right (1) neighbors.

We first define the total harmonic matrix H_{tot} of whole system when the contacts left (l) and right (r) are coupled with the device (d) as [120]:

$$H_{\text{tot}} = \begin{bmatrix} H_l & \tau_l^{\dagger} & 0\\ \tau_l & H_d & \tau_r\\ 0 & \tau_r^{\dagger} & H_r \end{bmatrix}$$
(81)

where, H_l , H_r , and H_d are the mass-normalized harmonic force constant matrices for the left contact, right contact, and the device, respectively. τ_l and τ_r are the hopping matrices whose nonzero elements are the force constants for the bonds between the atoms of the device and the contacts. In the present case, since the chain is homogeneous, the harmonic matrices of the contacts and the device are given as:

$$H_{l} = \begin{bmatrix} & \ddots & & \\ [0] & -\frac{K}{m} & \frac{2K}{m} & -\frac{K}{m} & 0 \\ & [0] & -\frac{K}{m} & \frac{2K}{m} & -\frac{K}{m} \\ & & [0] & -\frac{K}{m} & \frac{2K}{m} \end{bmatrix}$$
(82)

$$H_{r} = \begin{bmatrix} \frac{2K}{m} & -\frac{K}{m} & [0] \\ -\frac{K}{m} & \frac{2K}{m} & -\frac{K}{m} & [0] \\ 0 & \frac{2K}{m} & -\frac{K}{m} & [0] \\ & & \ddots \end{bmatrix}$$
(83)

$$H_{d} = \begin{bmatrix} \frac{2K}{m} & -\frac{K}{m} & 0\\ -\frac{K}{m} & \frac{2K}{m} & -\frac{K}{m}\\ 0 & -\frac{K}{m} & \frac{2K}{m} \end{bmatrix}$$
(84)

The hopping matrices are given as:

$$\tau_{l} = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ -\frac{K}{m} & 0 & 0 \end{bmatrix}$$
(85)
$$\tau_{r} = \begin{bmatrix} 0 & 0 & -\frac{K}{m} \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}.$$
(86)

Similar to Eq. 59, we can write the equations of motion for the isolated contacts as [119]:

$$[\omega^2 I - H_l]\Phi_l^c = 0 \tag{87}$$

$$[\omega^2 I - H_r]\Phi_r^c = 0, (88)$$

and their greens functions as:

$$g_l = [(\omega^2 + i\epsilon^+)I - H_l]^{-1}$$
(89)

$$g_r = [(\omega^2 + i\epsilon^+)I - H_r]^{-1}$$
(90)

The dynamical equation for the connected system can be written making use of Eqs. 81, 87, and 88 as [119]:

$$\begin{bmatrix} \omega^2 I - H_l & \tau_1^{\dagger} & 0\\ \tau_1 & \omega^2 I - H_d & \tau_2\\ 0 & \tau_2^{\dagger} & \omega^2 I - H_r \end{bmatrix} \begin{bmatrix} \Phi_l^c + \chi_l\\ \Psi\\ \Phi_r^c + \chi_r \end{bmatrix} = \begin{bmatrix} 0\\ 0\\ 0 \end{bmatrix}.$$
(91)

where, Φ_l^c and Φ_r^c are the eigenvectors of the isolated contacts and χ account for the change in the atomic displacements of the contact after they are connected to the device. Ψ is the excitation of the atoms in the device due to phonon waves from the contacts. Using Eqs. 91, 89, and 90 we can derive the following relations:

$$\chi_l = [(\omega^2 + i\epsilon^+)I - H_l]^{-1}\tau_l^{\dagger}\Psi$$
$$= g_l\tau_l^{\dagger}\Psi$$
(92)

$$\chi_r = g_r \tau_r^{\dagger} \Psi \tag{93}$$

$$\Psi = [\omega^2 I - H_d + \Sigma_l - \Sigma_r]^{-1} S \tag{94}$$

where,

$$[\omega^2 I - H_d + \Sigma_l - \Sigma_r]^{-1} = G_d \tag{95}$$

represents the Green's function of the device, which is a subset of the overall Green's function of the coupled system. $\Sigma_l = \tau_l g_l \tau_l^{\dagger}$ and $\Sigma_r = \tau_r g_r \tau_r^{\dagger}$ are the self-energy matrices associated with the left and right contacts, respectively.

$$S = \tau_l \Phi_l^c + \tau_r \Phi_r^c \tag{96}$$

physically represents the excitation of the device caused by the phonon waves from the contacts [120].

From Eq. 95 we can see that the computation of G_d requires the evaluation of the self-energies which in turn depend on the Green's functions of the contacts, g_l and g_r . The Green's functions of the contacts can be evaluated using a technique called the *decimation technique* [121]. The central idea of this technique is to obtain a converged value of the last block of g_l and g_r . This is done by building a sequence of finite clusters that approximate the infinite contacts, with each successive cluster containing twice the number of layers as its predecessor. The advantages of the decimation method are that the size of the matrices required for the calculation stays constant throughout the iteration, and that it converges geometrically. Once the contact Green's functions are available the Green's functions of the device can be computed which are then used to calculate the **T** matrix. Next, we introduce the force-constant perturbation in the device by modifying the force constants of the atom labelled 0 with its left and right neighbours, from K to K'. The perturbed harmonic matrix for the defect device is given as:

$$H'_{d} = \begin{bmatrix} \frac{K' + K}{m} & -\frac{K'}{m} & 0\\ -\frac{K'}{m} & \frac{2K'}{m} & -\frac{K'}{m}\\ 0 & -\frac{K}{m} & \frac{K + K'}{m} \end{bmatrix}.$$
 (97)

We obtain the force-constant perturbation matrix as:

$$V_{K} = -(H'_{d} - H_{d})$$

$$= -\begin{bmatrix} \frac{K' + K}{m} & -\frac{K'}{m} & 0\\ -\frac{K'}{m} & \frac{2K'}{m} & -\frac{K'}{m}\\ 0 & -\frac{K}{m} & \frac{K + K'}{m} \end{bmatrix} + \begin{bmatrix} \frac{2K}{m} & -\frac{K}{m} & 0\\ -\frac{K}{m} & \frac{2K}{m} & -\frac{K}{m}\\ 0 & -\frac{K}{m} & \frac{2K}{m} \end{bmatrix}$$

$$= -\begin{bmatrix} \frac{K' - K}{m} & -\frac{K' - K}{m} & 0\\ -\frac{K' - K}{m} & \frac{2(K' - K)}{m} & -\frac{K' - K}{m}\\ 0 & -\frac{K' - K}{m} & \frac{K' - K}{m} \end{bmatrix}$$
(98)

Using G_d which is also a 3×3 matrix in the present case, and V_K , the *T* matrix can be computed according to Eq. 74. Finally, using the *T* matrix, the wave-vector and mode resolved scattering rates can be computed according to Eq. 77.

1.2.3 Calculating thermal conductivity using Molecular Dynamics

In Sec. 1.2.2 we discussed how the DFT-BTE approach is able to provide accurate prediction of the thermal conductivities of various semiconductors, the only input information being the chemical composition of the system under study. This approach serves the important purposes of being parameter-free, fully predictive, and transferable to any material. Since it provides the most accurate values, it is often used to explore various experimental setups with much less associated costs. The translational symmetry of the systems under investigation allows the atomic vibrations to be described as collective modes or phonons facilitating the wave-vector and mode resolved computation of the thermal conductivities. However, for systems like amorphous materials that lack the transnational invariance, such a treatment is no longer feasible. Also for systems consisting of tens of thousands of atoms, the

DFT-BTE approach can not be used due to computational limitations. In such cases, one can profit from a more direct approach where the atomic trajectories can be computed in real space. To this end, molecular dynamics (MD) [122] can be used to calculate quantities like heat flux on the fly during the simulation as an ensemble average over atomic trajectories. MD presents an alternate means to calculate the thermal conductivity as opposed to the aforementioned DFT-BTE formalism. The commonly used MD methods for calculating thermal conductivity are the direct method [123–125], the equilibrium molecular dynamics (EMD) based on the Green-Kubo formula [126, 127], and the homogeneous non-equilibrium molecular dynamics (HNEMD) [128].

One of the most critical aspects in MD simulations is describing the atomic trajectories using a force field. Classical empirical potentials are the simplest way to describe the atomic interactions due to their low numerical complexity. However, they suffer from two major drawbacks, namely, accuracy and transferability, since they do not consider the electronic interactions in the system and they are usually parameterized for a particular set of physical properties, respectively. Hence, they are better suited to obtaining trends in thermal conductivity prediction rather than accurate numbers. More sophisticated quantum semi-empirical schemes are available which offer better accuracy than the empirical potentials but are also more expensive [129]. Finally, the most fundamental and superior, therefore most expensive methods are the fully-quantum *ab initio* techniques [130-132]. Studies on molecular dynamics in conjunction with BTE has also been carried out to calculate the phonon related properties and thermal conductivity using both the classical empirical potentials and first principles methods [133-136]. A comparison of different potentials and techniques in terms of their accuracy and computational costs for calculating the lattice thermal conductivity has attracted sustained scientific efforts [123, 135, 137-141]. In the present study, we have used the Stillinger-Weber (SW) potential [142] to calculate the thermal conductivity of bulk and defect-laden (vacancies) silicon using both GK and HNEMD methods. SW potential is known to accurately describe elastic properties, yield strengths, phonon dispersion curves, and thermal-expansion coefficients [123].

From a mathematical and physical point of view, the MD method can be described

as an initial value problem where the positions and momenta of a set of atoms are allowed to evolve from an initial configuration by numerically integrating Newton's equations of motion,

$$m_i \ddot{\mathbf{r}}_i = \mathbf{F}_i = -\nabla V(\mathbf{r}_i). \tag{99}$$

Central to the calculation of the thermal conductivity using MD is the computation of the heat current \mathbf{J} which is the rate of change of thermal energy transfer through a given surface. It characterizes the spatial average of the local energy transport property and is given as [123]:

$$\mathbf{J} = \frac{1}{\Omega} \frac{d}{dt} \sum_{i} \mathbf{r}_{i} \epsilon_{i}(t)$$
(100)

where Ω is the volume of the system and $\epsilon_i(t)$ the total energy of atom *i* which is the sum of kinetic and potential energies. A generic MD algorithm to calculate the heat current using classical empirical potentials is shown in Fig. 1.11. Within the *Born-Oppenheimer approximation* in MD simulations (called classical MD), the nuclear mass is approximated as a classical point mass wherein the quantum mechanical character of the nucleus is disregarded and the electrons are assumed to stay in the ground state when the atoms move. The simulation typically starts with setting the required parameters, which include, the initial positions of the atoms, the total length of time the simulation will run, the duration of time between successive simulation steps (Δt) , the potential describing the atomic interactions, etc.. Once the parameters are set, the system is allowed to thermalize and equilibrate at the desired temperature, in the NPT ensemble, which is accomplished by modifying the equations of motion using desired integrators. Next, the computation of relevant quantities like $\langle \mathbf{J} \rangle$, $\langle \mathbf{J} \cdot \mathbf{J} \rangle$ is carried carried out in the NVE ensemble or using desired integrators, which are also stored at regular time intervals.

In the following, we present the theory behind the GK and HNEMD methods used in the present thesis.

1.2.3.1 Equilibrium MD (GK method)

As the name suggests, the Green-Kubo method represents an EMD technique where the simulations are carried out in thermodynamic equilibrium and κ_{ℓ} is calculated



Figure 1.11: MD algorithm to calculate the ensemble average of the heat current and HCACF, which are used to calculate κ_{ℓ} , consisting of two parts: (a) Equilibration and thermalization at a desired temperature T for a certain time period. (b) Calculation of relevant quantities.

according to the Green-Kubo formula [126, 127]. It relates the fluctuations of the heat current vector, \mathbf{J} , to κ_{ℓ} via the fluctuation-dissipation theorem as:

$$\kappa_{\ell} = \frac{1}{3k_B V T^2} \int_0^\infty \langle \mathbf{J}(\mathbf{0}) \otimes \mathbf{J}(t) \rangle dt, \qquad (101)$$

where k_B is the Boltzmann constant, V the volume of the system, T the temperature and $\langle \mathbf{J}(\mathbf{0}) \otimes \mathbf{J}(t) \rangle$ the heat current auto-correlation function (HCACF) where $\langle \bullet \rangle$ represents the ensemble average. HCACF describes the correlation strength between values of the signals of the heat current separated by a time lag t. With the GK method the full second-order thermal conductivity tensor can be calculated, however, for a material with cubic symmetry Eq. 101 gives a scalar as an output. In practice, the simulation is performed on discrete MD steps of length Δt and the integral in Eq. 101 is replaced with a sum as [123]:

$$\kappa_{\ell}(\tau_M) = \frac{\Delta t}{k_B V T^2} \sum_{m=1}^{M} \sum_{n=1}^{N-m} \frac{J(n)J(m+n)}{(N-m)},$$
(102)

where τ_M is the maximum correlation time given by $M\Delta t$ until which summation is carried out, and J(m+n) is the value of the heat current at time step m+n. From Eq. 102 it is evident that the total number of simulation steps N should be larger than the number of summation steps M.

The Green-Kubo method is prone to two potential errors in calculating κ_{ℓ} as follows [143]:

1. Averaging error: Within MD, the ensemble average $C(t) = \langle \mathbf{J}(\mathbf{0}) \otimes \mathbf{J}(\mathbf{t}) \rangle$ in Eq. 101 is calculated as a time-average from the data of a single MD simulation using the ergodic hypothesis as:

$$C(t) = \lim_{\tau_N \to \infty} \frac{1}{\tau_N} \int_0^{\tau_N} J(n) J(m+n) dn = \lim_{\tau_N \to \infty} C_{\tau_N}(t), \qquad (103)$$

where, $C_{\tau_N}(t)$ is an estimate of the correlation function C(t) for a finite simulation time $\tau_N = N\Delta t$ and is given in Eq. 102 as:

$$C_{\tau_N}(m) = \sum_{n=1}^{N-m} \frac{J(n)J(m+n)}{(N-m)}.$$
(104)

N should ideally be infinite, however a simulation can only be carried out for a finite time duration, which gives rise to the *averaging error*. In order to minimize the averaging error, which is equivalent to increasing the value of N, we have averaged the C(t) also over several independent simulations with different initial conditions [123, 138, 144].

2. Truncation error: In Eq. 101 the integration of C(t) should be carried out ideally till infinity. But in practice, it is only carried out for a finite correlation time $\tau_M = M\Delta t$ which adds to the averaging error already present due to finiteness of τ_N [143]. This truncation of the correlation time is called as the *truncation error*. A judicious choice has to be made to select the correct value of τ_M , as too small τ_M would underestimate κ_ℓ and too big a value would lead to large statistical errors generated by the cross-correlation functions. This can be seen in Fig. 1.12 that as auto-correlation function (green) decays it crosses the cross-correlation functions or noise after the correlation time marked with a red line. Therefore, the summation to calculate κ_ℓ in Eq. 102 should only be carried out till τ_M reaches the red line. The noise can be calculated with the cross-correlation functions as [138]:

$$\zeta(t) = \sqrt{\frac{\langle J_x(0)J_y(t)\rangle^2 + \langle J_y(0)J_z(t)\rangle^2 + \langle J_z(0)J_x(t)\rangle^2}{3}}.$$
 (105)



Figure 1.12: Schematic illustration of κ_{ℓ} calculation with the GK method. It can be seen that with increasing τ_M the error bars in the value of κ_{ℓ} also get bigger. The red line indicates the correlation time after which the HCACF (blue line) is dominated by the noise (green line).

1.2.3.2 Homogeneous non-equilibrium molecular dynamics

The HNEMD method was originally proposed by Evans [128,145] and later extended to three-body potentials [139], multi-body potentials [146], and mixtures and alloys [147] by Mandadapu et al.. In this method the thermal transport process is considered as a mechanical problem where a fictitious time-independent external force field (\mathbf{F}_e) is used to mimic the effect of a thermal gradient. Such a force field is essentially used to as a perturbation to the Nosé-Hoover [145] thermostated equations of motion which are then used for the calculation of the transport coefficients. For a single element, N-body system, the underlying equations of motion are then given as [148]:

$$\dot{\mathbf{r}}_{i} = \frac{\mathbf{p}_{i}}{m_{i}} + \mathbf{C}_{i}\mathbf{F}_{e}$$

$$\dot{\mathbf{p}}_{i} = \mathbf{F}_{i} + \mathbf{C}_{i}\mathbf{F}_{e} + \zeta\mathbf{p}_{i}$$

$$\dot{\zeta} = \frac{1}{Q} \left(\sum_{i=1}^{N} \frac{\mathbf{p}_{i} \cdot \mathbf{p}_{i}}{m_{i}} - 3Nk_{B}T\right),$$
(106)

where \mathbf{p} is the atomic momentum, ζ is the thermodynamic fraction coefficient associated with the Nosé-Hoover thermostat and Q the external reservoir mass-like parameter (with units of energy-time²) which affects the period and amplitude of the thermal fluctuations [145]. \mathbf{C}_i and \mathbf{D}_i are the second-order tensor phase variables which describe the coupling of the system to the applied external field \mathbf{F}_e .

For the resulting non-equilibrium system, using ergodic hypothesis and linear response theory, the long-time ensemble average of the heat current vector $\mathbf{J}(t)$ can be shown to be proportional to small values of the external force field \mathbf{F}_{e} . For such a case, the constant of proportionality is the GK formula for the heat transport coefficient tensor [148]:

$$\frac{\langle \mathbf{J}(t) \rangle}{VT} = \left[\frac{1}{k_B V T^2} \int_0^\infty \langle \mathbf{J}(0) \otimes \mathbf{J}(t) \rangle dt \right] \mathbf{F}_e = \boldsymbol{\kappa}_\ell \mathbf{F}_e.$$
(107)

The HNEMD method circumvents the calculation and integration of the HCACF required in the GK method. In practice, \mathbf{F}_e is applied in one single direction (F_{ex}) for a particular set of calculations and therefore only a scalar value of κ_{ℓ} is obtained in Eq. 107.

Three different methods can be used to deduce the thermal conductivity from the estimates of $\langle J_x(t) \rangle$ corresponding to a range of force fields $F_{ex}^i, i = 1, \ldots, n$ as follows [139]:

- 1. Gradient: In this method, the $\frac{\langle J_x^i(t) \rangle}{VT}$ values are calculated and plotted versus respective F_{ex}^i , and a least-squares fit of the function $\kappa_\ell F_{ex}$ is obtained. The slope of this fit is identified as the thermal conductivity. It is assumed that the fit passes through origin such that $\lim_{F_{ex}\to 0} J_x = 0$.
- 2. Mean: Here, the thermal conductivity is taken to be the average over all the calculated values of $\kappa_{\ell}^{i} = \frac{\langle J_{x}^{i}(t) \rangle}{VTF_{ex}^{i}}$, i.e., $\kappa_{\ell} = n^{-1} \sum_{i=1}^{n} \kappa_{\ell}^{i}$.
- 3. Extrapolation: This approach is similar to the gradient one, except that here κ_{ℓ}^{i} is plotted versus F_{ex}^{i} and a least-squares fit of the function $\kappa_{\ell} + mF_{ex}$ is obtained between the two. The fit is extrapolated to $F_{ex} = 0$ and the intercept is identified as the true κ_{ℓ} .

It should be noted that, while calculating κ_{ℓ} using the above three methods, only those points that fall under the linear regime should be included in the fit or the average. The points that deviate strongly from the linear regimes in Fig. 1.13 have to be omitted. Thus, in the HNEMD method it is critical to find the linear regime to correctly predict the true thermal conductivity.



Figure 1.13: Schematic illustration of κ_{ℓ} calculation with the HNEMD method. (a) Gradient method. (b) Mean method. (c) Extrapolation method.

2 Summary of published journal articles and contributions

2.1 Extrinsic doping of half-Heusler compounds

Robin Stern, Bonny Dongre, and Georg KH Madsen; *Nanotechnology*, **2016**, 27(33), 334002.

Abstract:

Controlling the p- and n-type doping is a key tool to improve the power-factor of thermoelectric materials. In the present work we provide a detailed understanding of the defect thermochemistry in half-Heusler compounds. We calculate the formation energies of intrinsic and extrinsic defects in state of the art n-type TiNiSn and p-type TiCoSb thermoelectric materials. It is shown how the incorporation of online repositories can reduce the workload in these calculations. In TiNiSn we find that Ni- and Ti-interstitial defects play a crucial role in the carrier concentration of TiNiSn. Furthermore, we find that extrinsic doping with Sb can substantially enhance the carrier concentration, in agreement with experiment. In case of TiCoSb, we find Sc_{Ti}, Fe_{Co} and Sn_{Sb} being possible p-type dopants. While experimental work has mainly focussed on Sn-doping of the Sb site, the present result underlines the possibility to p-dope TiCoSb on all lattice sites.

Contribution:

Defect formation energy and carrier concentration calculations for the TiCoSb system, evaluation and interpretation of the data. Writing - review and editing the manuscript.

2.2 Exceptionally Strong Phonon Scattering by B Substitution in Cubic SiC

Ankita Katre, Jesús Carrete, Bonny Dongre, Georg KH Madsen, and Natalio Mingo; *Physical Review Letters*, **2017**, 119(7), 075902.

Abstract:

We use *ab initio* calculations to predict the thermal conductivity of cubic SiC with different types of defects. An excellent quantitative agreement with previous experimental measurements is found. The results unveil that B_C substitution has a much stronger effect than any of the other defect types in 3C-SiC, including vacancies. This finding contradicts the prediction of the classical mass-difference model of impurity scattering, according to which the effects of B_C and N_C would be similar and much smaller than that of the C vacancy. The strikingly different behavior of the B_C defect arises from a unique pattern of resonant phonon scattering caused by the broken structural symmetry around the B impurity.

Contribution:

Evaluating the Frobenius norm of the V_K matrices. Interpretation and visualization of the data. Writing - review and editing the manuscript.

2.3 Resonant phonon scattering in semiconductors

Bonny Dongre, Jesús Carrete, Ankita Katre, Natalio Mingo, and Georg KH Madsen; Journal of Materials Chemistry C, **2018**, 6(17), 4691-4697.

Abstract:

Boron impurities have recently been shown to induce resonant phonon scattering in 3C-SiC, dramatically lowering its thermal conductivity. The B-doped 3C-SiC is associated with an off-center relaxation of the B atom, inducing a local transition from T_d to C_{3v} symmetry. Similar relaxations in B and N-doped diamond, with a similarly large effect on the interatomic force constants (IFCs), fail to produce resonances. Here we develop an intuitive understanding of such dopant-induced resonant phonon scattering in semiconductors with the help of a 1D monoatomic chain model. We find that the phenomenon is connected to a slight asymmetry in the relaxed position of the defect, with its origin in two or more minima of the potential energy surface in close proximity. The large perturbation they introduce in the IFCs is the essential ingredient of a resonance.

Contribution:

Partial conception of the study, data curation, formal analysis, investigation, methodology, software, validation, visualization Writing - original draft, reviewing and editing the manuscript.

2.4 Ab initio lattice thermal conductivity of bulk and thin-film α -Al₂O₃

Bonny Dongre, Jesús Carrete, Natalio Mingo, and Georg KH Madsen; *MRS Communications*, **2018**, 8(3), 1119-1123.

Abstract:

The thermal conductivities (κ) of bulk and thin-film α -Al₂O₃ are calculated from first principles using both the local density approximation (LDA) and the generalized gradient approximation (GGA) to exchange and correlation. The room temperature single crystal LDA value ~39 W/m K agrees well with the experimental values ~35-39 W/m K, whereas the GGA values are much smaller ~26 W/m K. Throughout the temperature range, LDA is found to slightly overestimate κ , whereas GGA strongly underestimates it. We calculate the κ of crystalline α -Al₂O₃ thin films and observe a maximum of 79% reduction for 10 nm thickness.

Contribution:

Partial conception of the study, data curation, formal analysis, investigation, methodology, software, validation, visualization. Writing - original draft, reviewing and editing the manuscript.

2.5 Comparison of the Green–Kubo and homogeneous non-equilibrium molecular dynamics methods for calculating thermal conductivity

Bonny Dongre, Tao Wang, and Georg KH Madsen; *Modelling and Simulation in Materials Science and Engineering*, **2017**, 25(5), 054001.

Abstract:

Different molecular dynamics methods like the direct method, the Green-Kubo (GK) method and homogeneous non-equilibrium molecular dynamics (HNEMD) method have been widely used to calculate lattice thermal conductivity (κ_{ℓ}). While the first two methods have been used and compared quite extensively, there is a lack of comparison of these methods with the HNEMD method. Focusing on the underlying computational parameters, we present a detailed comparison of the GK and HNEMD methods for both bulk and vacancy Si using the Stillinger-Weber potential. For the bulk calculations, we find both methods to perform well and yield κ_{ℓ} within acceptable uncertainties. In case of the vacancy calculations, HNEMD method has a slight advantage over the GK method as it becomes computationally cheaper for lower κ_{ℓ} values. This study could promote the application of HNEMD method in κ_{ℓ} calculations involving other lattice defects like nanovoids, dislocations, interfaces.

Contribution:

Partial conception of the study, data curation, formal analysis, investigation, methodology, software, validation, visualization. Writing - original draft, reviewing and editing the manuscript.

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Extrinsic doping of the half-Heusler compounds

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Abstract

Controlling the p- and n-type doping is a key tool to improve the power-factor of thermoelectric materials. In the present work we provide a detailed understanding of the defect thermochemistry in half-Heusler compounds. We calculate the formation energies of intrinsic and extrinsic defects in state of the art n-type TiNiSn and p-type TiCoSb thermoelectric materials. It is shown how the incorporation of online repositories can reduce the workload in these calculations. In TiNiSn we find that Ni- and Ti-interstitial defects play a crucial role in the carrier concentration of TiNiSn. Furthermore, we find that extrinsic doping with Sb can substantially enhance the carrier concentration, in agreement with experiment. In case of TiCoSb, we find Sc_{Ti}, Fe_{Co} and Sn_{Sb} being possible p-type dopants. While experimental work has mainly focussed on Sn-doping of

the Sb site, the present result underlines the possibility to p-dope TiCoSb on all lattice sites.

Keywords: half-Heusler compounds, defect thermochemistry, DFT repository

(Some figures may appear in colour only in the online journal)

1. Introduction

Energy efficiency has become more and more important in recent years. For that purpose thermoelectric materials are of great interest, since they can convert a temperature gradient into an electric field thereby enabling the recovery of waste heat as electric energy. The performance of a thermoelectric material is measured by the dimensionless figure of merit $zT = \frac{S^2 \sigma T}{\kappa}$, with *S* the Seebeck coefficient, σ the electrical conductivity, *T* the temperature and κ the thermal conductivity.

Among the thermoelectric materials, half-Heusler compounds (HHCs) have received great interest [1]. Experiments have shown thermoelectric properties, such as zT > 1.2 for nanostructured n-type MNiSn_{1-x}Sb_x, M=Ti, Zr and Hf [2–4] and zT = 0.9 - 1.0 for p-type MCoSb_{1-x}Sn_x [5–7], which are comparable to other state of the art thermoelectric materials.

zT can be improved by isoelectronic alloying which introduces mass-disorder scattering of phonons thereby lowering the thermal conductivity. Interestingly, solubility limits can also be taken advantage of to introduce a 'natural' nanostructuring, which further lowers the thermal conductivity [4, 7]. Another possibility to improve the performance by chemical substitution is to optimize the power factor $S^2\sigma$ of the material. This can be achieved by doping the material with electron donating or accepting atoms to reach an optimal carrier concentration. In TE materials this typically means a carrier concentration around $10^{20}-10^{21}$ cm⁻³. Taking a state-of-the-art TE HHC like Ti_x(Zr_yHf_{1-y})_{1-x}NiSn_{1-x}Sb_x one would thus think of the isovalent alloying of Ti, Zr and Hf as a handle to lower the thermal conductivity. The doping of the Sn site by Sb, thereby introducing one extra valence electron per dopant, can be thought of as a handle to optimize the electronic power factor.

Dopants can be seen as point defects in the host structure. Point defects occur naturally in any kind of material even in the absence of extrinsic dopants. They can be seen as an exchange of atoms between a distant reservoir and the host structure. If the material is non-metallic, defects can also occur in charged states. This fact is taken advantage of in the fabrication of p-type and n-type semiconductors. The formation energy of the defects control the doping limits of the material, where the dopability increases with low defect formation energies.

The main experimental work has been on optimizing the carrier concentration by substituting the Sn site, either by an

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electron donating Sb substitution, Sb_{Sn} in TiNiSn or a hole donating Sn substitution, Sn_{Sb}, in TiCoSb [2, 8-12]. Some attempts have also been made to p-dope TiCoSb by Sc_{Ti} [13], Ta_{Ti} [14], Fe_{Co} [15] and Ge_{Sb} [16] but the most successful still seems to be Sn_{Sb} [6, 12]. A special interest of HHCs is their chemical versatility [17] and the possibilities to substitute each lattice site independently and it is very possible that extrinsic doping has not been explored fully. At the same time, intrinsic defects have been found to play an important role in producing carriers in HHC. If TiNiSn is grown under Ni-rich conditions interstitial Ni defects (Ni_{Int}) are formed at the full Heusler positions [18-21]. Furthermore, it has also been found that under Ti rich conditions, where the growth of the TiNiSn will be in equilibrium with the Ti rich phases Ti₂Ni₂Sn, Ti₂Sn and Ti₃Sn, also Ti form electron donation interstitials [21].

The carrier concentration in HHC is thus an intricate interplay between intrinsic and extrinsic dopants and growth conditions. In this study, we show how extrinsic doping of TiNiSn and TiCoSb can significantly increase the carrier concentration. We considered different experimental conditions by treating the chemical potentials of the constituents and the dopants as variables and explored under which conditions optimal results for the power factor are achieved. We discuss how the increasing availability of external databases of density functional theory (DFT) energies are very useful in this step.

2. Method

The most commonly used first principles method for the calculation of defect formation energies is DFT within the supercell approach, where the defect is located in a cell with a finite number of atoms [22-25]. This cell is supposed to be large enough to reach the dilute limit, which means that a periodic repetition of this cell does not lead to defect-defect interactions. Within this approach we define the defect formation energy as [26, 27]

$$E_{D^{(q)}}(\mu_e) = E_{f,D^{(q)}} - \sum_{\alpha} n_\alpha \Delta \mu_\alpha + q \mu_e.$$
(1)

The first term is the defect formation energy with respect to the reference states of the defect forming atoms and involves the calculations on (charged) supercell. n_{α} is the number of atoms, that are transferred to the crystal (n > 0) or to the reservoir (n < 0). The energy to exchange atoms with the reservoir is captured in the chemical potentials $\Delta \mu_{\alpha}$ of the defect forming atoms. If the defect carries the charge q, then the defect formation energy also depends on the electron chemical potential μ_{e} .

2.1. Supercell calculation of the defect formation energy

In the defect formation energy

$$E_{f,D^{(q)}} = E_{D^{(q)}} - E_{\text{bulk}} - \sum_{\alpha} n_{\alpha} E_{\alpha}$$
(2)

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 $E_{D^{(q)}}$ and E_{bulk} are the energies of the supercell with and without the defect, E_{α} are the reference energies of the defect forming atoms and n_{α} , as in equation (1), the transferred atoms.

Charged defect states were realized by changing the number of electrons in the supercell. Due to periodic boundary conditions, the resulting net charge of the cell has to be compensated by a jellium background charge, which is realized by setting the average electrostatic potential to zero. In this case, the Kohn–Sham eigenvalues are only defined up to a constant, which depends on the average crystal potential and the choice of pseudopotential. The total energies of the supercells containing charged defects and the pure bulk material are corrected by [24]

$$\Delta E_{\rm pa}(D^{(q)}) = q \left[V_{\rm R}(D^{(q)}) - V_{\rm R}^{\rm bulk} \right] + \Delta \varepsilon_{\rm VBM},\tag{3}$$

where $V_{\rm R}$ are the potential energies at given reference points, far from the defect and $\Delta \varepsilon_{\rm VBM}$ aligns the valence band maximum of the defected and non-defected cell. Furthermore, the electrostatic interaction of the charged defect with their periodic images can not simply be overcome by using larger cells, since the Coulomb interaction is rather long range. To correct this effect we used the method by Makov and Payne [28].

Thus, the energy of the defect containing supercell is given by

$$E_{D^{(q)}} = E_{D^{(q)}}^{0} + \Delta E_{\text{pa}}(D^{(q)}) + \Delta E_{\text{MP}}(q), \qquad (4)$$

where $E_f^0(D^{(q)})$ is the uncorrected energy of the defect containing supercell as in equation (1). $\Delta E_{\rm MP}$ accounts for the correction of the electrostatic interaction.

2.2. Chemical potential domain

The chemical potentials of the atoms forming a defect in the host material represent the energies of the reservoirs, with which they are exchanged and can change according to the experimental scenario. However, specific bounds are set by competing phases, that limit the allowed chemical potential domain of a stable host material. To map out the chemical potentials that represent a stable host material a number of conditions have to be fulfilled. First, the chemical potentials have to equal the potential energy of the material

$$\Delta \mu_{\rm Ni} + \Delta \mu_{\rm Ti} + \Delta \mu_{\rm Sn} = \Delta H \,({\rm TiNiSn}). \tag{5}$$

To make sure that the constituents do not precipitate in their reference state, they have to satisfy

$$\Delta \mu_{\rm Ni} \leqslant 0; \ \Delta \mu_{\rm Ti} \leqslant 0; \ \Delta \mu_{\rm Sn} \leqslant 0. \tag{6}$$

The chemical potential domain is further constrained by the formation energies of the competing phases. This leads to the general condition

$$k\Delta\mu_{\rm Ni} + l\Delta\mu_{\rm Ti} + m\Delta\mu_{\rm Sn} \leqslant \Delta H ({\rm Ni}_k {\rm Ti}_l {\rm Sn}_m).$$
(7)

For example, the chemical potentials of Ni and Sn have to fulfill the condition

$$\Delta \mu_{\rm Ni} + \Delta \mu_{\rm Sn} \leqslant \Delta H \,({\rm NiSn}) \tag{8}$$



Figure 1. Schematic illustration of the flow for the three parts of equation (1).

since NiSn is a stable structure that can precipitate under certain conditions. To get an accurate answer in which chemical potential domain the desired structure is stable, the list of conditions has to be complete. Similar conditions have to be considered, if impurities are added. Taking as an example Sb doping, one of the important competing phases is TiNiSb, which is one of the few stable HHC whose valence electron count does not fulfill the 18 electron rule. The presence of TiNiSb leads to the condition

$$\Delta \mu_{\rm Ni} + \Delta \mu_{\rm Ti} + \Delta \mu_{\rm Sb} \leqslant \Delta H \,(\rm NiTiSb). \tag{9}$$

The formation energies of the competing phases, equations (5)–(9), can be calculated using DFT or extracted from on-line repositories. Since both the chemical potentials and the defect formation energies are given with respect to the same reference states, the formation energies necessary for calculating the chemical potential limits can be extracted from on-line repositories. This is illustrated schematically in figure 1. Both the AFLOWlib and the Materials Project have APIs that adhere to the REST architectural constraints [29, 30]. Comparing the chemical potential ranges calculated here with those obtained from AFLOWlib and Materials Project, the main difference comes from the Ti₂Ni₂Sn phase not being present in the online data-bases, despite it being a known experimental phase in equilibrium with the HHC phase [21, 31].

2.3. Defect concentrations

In thermal equilibrium the concentration of a given defect, $c_{D^{(q)}}$, will be determined by a minimum in the Gibbs free energy landscape

$$\frac{\partial G}{\partial c_{D^{(q)}}} = 0. \tag{10}$$

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Approximating the free energy by the defect formation energy, means that the concentration is given by

$$c_{D^{(q)}}(\mu_e, T; \Delta\mu_\alpha) = \exp\left(-\frac{E_{D^{(q)}}(\Delta\mu_\alpha, \mu_e)}{k_BT}\right).$$
(11)

In general, each lattice site can only accept one defect and we do not consider such exclusion effects of defects that are located at the same lattice site. In the dilute limit this will not affect the concentration of the individual defects significantly. Charged defects are considered to donate electrons to the R Stern et al

conduction band or to accept electrons from the valence band. Charge neutrality of the crystal requires

$$n_h(\mu_e, T) - n_e(\mu_e, T) = -\sum_{D^{(q)}} q c_{D^{(q)}}(\mu_e, T; \Delta \mu_\alpha).$$
 (12)

In the dilute limit, the band structure is approximately the same as for the pure host material. The number of holes is given by

$$n_{h} = \int_{-\infty}^{\varepsilon_{\text{VBM}}} n(\varepsilon) (1 - f(\varepsilon, \mu_{e})) d\varepsilon$$
(13)

and the number of electrons

$$n_e = \int_{\varepsilon_{\rm VBM}}^{\infty} n(\varepsilon) f(\varepsilon, \, \mu_e) \mathrm{d}\varepsilon, \qquad (14)$$

where $n(\varepsilon)$ is the density of states. Since the defect energy equation (1) depends on the electron chemical potential, equation (12) has to be solved self-consistently, which can be done with standard root-finding algorithms.

2.4. Computational procedure

The primitive unitcell of the half-Heusler structure consists of three interpenetrating fcc lattices with positions (0, 0, 0), (1/4, 1/4, 1/4) and (3/4, 3/4, 3/4). We studied all intrinsic defects, such as vacancies, antisites and interstitial atoms on the full Heusler position (1/2, 1/2, 1/2). For the defect calculations, we used large supercells with 192 atoms per unitcell for TiNiSn and 96 atoms per unitcell in TiCoSb. We used $3\times3\times3$ and $5\times5\times5$ kpoints for TiNiSn and TiCoSb respectively and relaxed the positions of the atoms in the cell. We considered Cu, Sb and V as extrinsic defects in TiNiSn and Sc, Y, La, Fe, Ge and Sn in TiCoSb. Calculations were performed for all possible substitutional and interstitial sites. Calculations were performed with the VASP code [32]. As exchange correlation functional we used a generalized gradient approximation [33] and a plane wave cut-off of 350 eV in both cases.

3. Results and discussion

The relevant chemical potentials for doping TiNiSn are shown in figure 2(left). We have chosen four sets of chemical potentials representing Ti-poor and Ni-rich (point 1), Sn-rich (point 2), Ti-rich (point 3) and Ni-rich, Sn-poor (point 4) growth conditions. Figure 2(right) shows the $E_{D^{(q)}}$ as a function of μ_a for the intrinsic defects. Mainly the results confirm the experimental observations, namely that the most stable intrinsic defects are the Ni_{Int} and Ti_{Int} [21]. At this point it should be pointed out that, due to an incorrect alignment of the potentials equation (3), $E_{f,D^{(q)}}$ of the negatively charged interstitial defects were underestimated in our earlier work [21]. This however does not change the main conclusion, namely that the interstitial NiInt and TiInt are the most stable intrinsic defects in TiNiSn. At Sn-rich growth conditions (point 2), the formation of Ni and Ti interstitial defects is suppressed by the low chemical potential of Ni and Ti, figure 2.



Figure 2. (left) The allowed chemical potential domains (colored area) of TiNiSn. White regions correspond to growth conditions under which competing phases are formed. Competing phases in the quaternary Sb–Ti–Ni–Sn system are shown in color. All chemical potentials are shown in the $\Delta \mu_{\text{Ni}}$ and $\Delta \mu_{\text{Ti}}$ plane, thus $\Delta \mu_{\text{Sn}}$ is given implicitly. (right) Defect formation energies with respect to μ_e . According to the chosen sets of chemical potentials (p1–p4) the defect formation energies take different values. The positive slope results from a positively charged state of the defects and vice versa.



Figure 3. (left) The allowed chemical potential domains (colored area) of TiCoSb. White regions correspond to growth conditions under which competing phases are formed. Competing phases in the quaternary Fe/Sn–Ti–Co–Sb system are shown in color. The colored area in the stable domain shows the competing phases of Sn with the corresponding colorbar on the left. The inset in the top right shows the competing phases of Fe with the colorbar on the right. All chemical potentials are shown in the $\Delta\mu_{Co}$ and $\Delta\mu_{Ti}$ plane, thus $\Delta\mu_{Sb}$ is given implicitly. (right) Defect formation energies with respect to μ_e . According to the chosen sets of chemical potentials (p1–p4) the defect formation energies take different values. The positive slope results from a positively charged state of the defects and vice versa.

Figure 2(right) also illustrates that, independent of conditions Cu_{Ni} and V_{Ti} have a high formation energy, making V and Ti unfavorable for doping. In contrast to that the extrinsic Sb_{Sn}^{1} defect is the lowest energy positively charged defect. This is in good agreement with the available experimental information, where it is found that doping the Sn site with Sb is known to significantly increase the electrical conductivity and leads to an improved power factor of the material [8–11]. To a certain degree the low energy of the Ni_{Int} and Sb_{Sn} can be related to the known experimental full Heusler TiNi₂Sn and non 18 electron half Heusler TiNiSb phases. TiNiSb has a similar lattice constant of $a_{NiTiSb} = 5.872$ Å compared to $a_{TiNiSn} = 5.941$ Å.

Figure 3 illustrates the chemical potential ranges and defect formation energies for TiCoSb. Similar to the TiNiSn case, figure 2, we have chosen four sets of chemical potentials representing Ti-poor and Co-rich (point 1), Sb-rich (point 2), Ti-rich (point 3) and Co-rich, Sb-poor (point 4) growth conditions. Furthermore, we illustrate the defect formation

energies in figure 3(right). Comparing figure 2(right) and figure 3(right), the defect thermodynamics of the two compounds at first sight look very different. The differences are mainly due to two reasons, namely the larger band gap and stability region found in TiCoSb. Taking as an example Tipoor and Co/Ni rich point 1, it is clear that the Co¹_{Int}, respectively the Ni_{Int}, defect dominates at the VBM. As a result of the positive charge (and slope with μ_{e}) this defect does not make TiCoSb intrinsically n-doped, as opposed to TiNiSn which has a smaller band gap. As expected the Colnt and Ni_{Int} defects are destabilized at the Co/Ni poorest point (point 2) studied. This upward shift of Ni_{Int} is however only about 0.4 eV, whereas the Co_{Int} defect is shifted upwards by almost 1 eV at point 2 compared to point 1 due to the larger stability region of the TiCoSb. A further obvious difference is the formation of negatively charged defects in TiCoSb, such as Vac_{Ti} at p1, close to the CBM. These will make it difficult to n-dope TiCoSb, and their presence is clearly related to the larger band gap found in TiCoSb. The multivalent character of several of these defects, e.g. Sb_{Ti} is also clear from the



Figure 4. Carrier concentration due to charged defects in TiCoSb as a function of growth temperature. Full lines correspond to the chemical potential of p1, dotted lines to p2 and dashed lines to p4.

dome like shape of the lines, meaning that positive defects dominate close to the valence band whereas negative defects dominate close to the conduction band. A further result of the multivalent character is that both the Ti_{Sb} and Sb_{Ti} will be negatively charged close to the conduction band.

No negatively charged intrinsic defects are low in energy at the VBM, figure 3(right), and a low carrier concentration of undoped TiCoSb can be expected. However, it is also seen that positively charged defects are relatively high in energy at the VBM, figure 3(right), which makes it possible to extrinsically dope the system. The obvious choices are the substitutional defects with one lesser valence electron such as Sc_{Ti}, Y_{Ti}, La_{Ti}, Fe_{Ti}, Ge_{Sb} or Sn_{Sb}. We have tested all of these, but find that only the substitutions from the same period, i.e. Sc_{Ti}, Fe_{Ti} and Sn_{Sb}, have low formation energies. These are plotted in figure 3. It is clear that in the Sb-poorest point, the Sn_{Sb} defect is low in energy. However an interesting point is that especially the ScTi defect looks very favorable.

Scandium as a favorable dopant can be further underlined by calculating the charge carrier concentration due to the defects. The chemical potential dependence of the defect formation energies, equation (1), means that also the concentrations of the defects change with respect to the chosen set of chemical potentials. Furthermore, for charged defects, the formation energy depends on the electron chemical potential μ_{a} , which has to be determined self-consistently for each temperature to satisfy the charge neutrality condition equation (12). The resulting carrier concentration is shown in figure 4. It is seen that Sn doping in Sb-poor growth conditions would indeed lead to a significant increase in carriers in agreement with experiment [7]. However, it is also clear that in the Ti-poor and the Ni-poor limits, the Sc_{Ti} and Fe_{Ni} defects respectively are more efficient dopants. This is somewhat surprising considering that the bulk of experimental work is on Sn doping. It is however in reasonable agreement with the findings of Ouardi et al [13]. Here it was found that a strong doping of TiCoSb with Sc can lead to an R Stern et al

almost metallic state with a very low Seebeck coefficient [13]. While this sample was clearly not of TE interest, the present results could indicate that a systematic study of Sc or Fe doped TiCoSb, in combination with a carefully controlled nano-structure [5-7], could be worth further investigation. We also want to underline that even though they were found to be less favorable than Sc for doping TiCoSb, Y and La doping could be interesting for the phase-separated samples where also Zr and Hf rich phases are present.

4. Conclusion

In summary, we calculated the formation energies of intrinsic and extrinsic defects in TiNiSn and TiCoSb under various growth conditions.

We have shown that positively charged Ni and Ti interstitials dominate among the intrinsic defects in TiNiSn, especially under Ti- and Ni-rich conditions. Among the extrinsic defects only the experimentally known Sb_{Sn} defect has a sufficiently low formation energy suitable for n-doping TiNiSn.

In contrast to TiNiSn TiCoSb is not intrinsically n-dopable, due to the larger band gap and stability region in TiCoSb. This leads to high formation energies of the positively charged intrinsic defects in the band gap. As extrinsic dopants we found Sc_{Ti}, Fe_{Co} and Sn_{Sb} as possible p-type dopants, thus enabling to dope TiCoSb on all three lattice sites.

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Exceptionally Strong Phonon Scattering by B Substitution in Cubic SiC

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We use *ab initio* calculations to predict the thermal conductivity of cubic SiC with different types of defects. An excellent quantitative agreement with previous experimental measurements is found. The results unveil that B_C substitution has a much stronger effect than any of the other defect types in 3*C*-SiC, including vacancies. This finding contradicts the prediction of the classical mass-difference model of impurity scattering, according to which the effects of B_C and N_C would be similar and much smaller than that of the C vacancy. The strikingly different behavior of the B_C defect arises from a unique pattern of resonant phonon scattering caused by the broken structural symmetry around the B impurity.

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Silicon carbide (SiC) plays a fundamental role in many emerging technologies, ranging from biomedical sensors to optoelectronics, power electronics, and photovoltaics [1-9]. Most notably, this material has been termed the "linchpin to green energy" that may replace Si-based technology in power electronics [1], owing partly to its large lattice thermal conductivity κ . From the many stable polytypes of SiC [10], two of the hexagonal ones, 6H-SiC and 4H-SiC, have been extensively studied and widely used [10-12]. In contrast, the structurally less complex cubic polytype of SiC with the zinc-blende structure (3C-SiC) is much less well understood, despite presumably having the best electronic properties [13], and, as we will see, possibly a higher κ than the other polytypes. This is partly due to the difficulty in synthesizing high quality crystals, although recent improvements in 3C-SiC growth techniques have prompted a renewed interest in it [13].

Surprisingly, the reference measurements of κ on pure undoped 3C-SiC are over 20 years old and little detail is known about the quality of the samples [10,14]. The reference value of κ for the 3C phase is perplexingly lower than that for the structurally more complex 6H phase, raising doubts about whether this is truly an intrinsic property or just a consequence of the defective, polycrystalline quality of the 3C-SiC samples. A very recent study [15] has shown that structural complexity and thermal conductivity are inversely correlated in the series of hexagonal phases of SiC, contrary to historical measurements, which could be afflicted with similar problems [10,14]. It is then clear that to understand the conduction properties of 3C-SiC, and to harness its full potential, one must first comprehend the way defects affect it. As we show here, by comparing predictive ab initio calculations with experiments on defective samples, a richer physical picture emerges, unveiling striking differences in the way different dopants affect κ . It also indirectly suggests that the intrinsic κ of defect-free 3C-SiC should be much

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higher than previously reported and surpass that of the 6H phase.

In this Letter, we compare our theoretical results to the measured $\kappa(T)$ curves for doped samples of 3*C*-SiC [16]. We use an *ab initio* approach to quantify the phonon scattering rates of N_C substitutional defects. The predicted κ is in excellent agreement with the experimental results. This then allows us to explain the effect of codoping with N and B, and shows that B impurities scatter phonons 2 orders of magnitude more strongly overall than N or Al impurities, and as strongly as C vacancies. We identify resonant phonon scattering as the reason for this behavior, resulting from distortion and broken symmetry around the B atom. We then show this resonant scattering behavior to be a general phenomenon that can take place for strong enough perturbations.

 κ for cubic structures can be obtained from a complete phonon picture as explained in Refs. [17,18]. We use an iterative scheme to solve the full linearized Boltzmann transport equation (BTE) and calculate κ of 3*C*-SiC as implemented in the ALMABTE code [19]. Details about the calculations are presented in the Supplemental Material [20], which includes Refs. [17–19,21–30].

The calculated κ for defect-free single-crystal 3*C*-SiC is shown as the brown dashed line in Fig. 1 and is in good agreement with earlier calculations [31]. The value of κ at 300 K is 552 W/m K, which is about ~70% higher than the experimentally reported κ (320 W/m K) [14,32]. It also surpasses the experimental κ at 300 K for the 6*H*-SiC phase by ~10% [32]. Inclusion of Si and C isotope scattering slightly lowers the calculated κ (orange dashed line in Fig. 1), but the values remain much larger than the experimental ones.

The calculated κ for the defective structures of 3*C*-SiC are compared with experiments on polycrystalline samples from Ref. [16] in Fig. 1. The additional contribution of the grain boundaries to the scattering rate is included in the standard way as $\tau_{jq,grain}^{-1} = |v_{jq}|/L_{grain}$, where $|v_{jq}|$ is the norm of the



FIG. 1. Calculated κ of 3*C*-SiC including, progressively, anharmonic phonon scattering, isotope scattering, grain boundary scattering (— $L_{\rm grain} = 0.8 \ \mu$ m), and different concentrations of defects [— $2.2 \times 10^{20} \ {\rm cm^{-3}} \ {\rm N_C} (0.45\%)$, – – $8 \times 10^{20} \ {\rm cm^{-3}} \ {\rm N_C} (1.63\%)$, — $6.6 \times 10^{20} \ {\rm cm^{-3}} \ {\rm N_C} (1.3\%)$, $2.6 \times 10^{20} \ {\rm cm^{-3}} \ {\rm B_C} (0.5\%)$, and – – $1.32 \times 10^{21} \ {\rm cm^{-3}} \ {\rm N_C} (2.7\%)$, $1.23 \times 10^{21} \ {\rm cm^{-3}} \ {\rm B_C} (2.5\%)$]. The experiments are from Morelli *et al.* [14] and Ivanova *et al.* [16].

phonon group velocity vector for a phonon mode $j\mathbf{q}$ (*j* represents the phonon branch and \mathbf{q} the wave vector) and L_{grain} is the grain size. Employing $L_{\text{grain}} = 0.8 \ \mu\text{m}$ for all the samples yields good agreement with experiment.

The black filled triangles in Fig. 1 are the experimental measurements on the polycrystalline bulk sample without any dopant [16]. The other experimental results are for the N-doped, and N- and B-codoped *n*-type samples in Ref. [16]. The case of N-only doping demonstrates the predictive power of the *ab initio* approach. As N in SiC can be considered as a shallow donor [33–35] and each dopant contributes one electron per defect atom, the concentrations of N_C defects can be expected to be the same as the carrier concentration. Using the carrier concentrations for different N-doped 3*C*-SiC samples reported in Ref. [16] yields excellent agreement between the calculated and the experimental κ for the whole temperature range in Fig. 1 (blue lines and symbols). This confirms the reliability of the *ab initio* approach.

The case of B and N codoping is considered next. B substitutes for C in 3*C*-SiC when it is grown in Si-rich conditions [36–38]. The fact that the undoped samples in Ref. [16] are *n* type with a reasonably high carrier concentration ($\approx 10^{17}$ cm⁻³) would indicate the formation of vacancies at C sites and in turn Si-rich growth conditions [39]. Because of codoping, the carrier concentrations given in Ref. [16] correspond to the difference between the donor and acceptor concentrations, and thus they do not uniquely determine the defect densities. In this case, we determine the individual defect densities by keeping the difference in concentrations equal to the experimental carrier concentration. The calculation matches the whole

FIG. 2. 3*C*-SiC κ variation with defect concentration for Al_{Si}, N_C, Vac_C, and B_C defects. The low value of κ associated with the B_C defect is related to its anisotropic lattice relaxation seen in the inset (and in the Supplemental Material [20]). The changes in the nearest-neighbour interatomic distances are directly proportional to the bond-width variations shown in the inset.

temperature dependent experimental curve only if the individual concentrations are 1.3% and 0.5% for $N_{\rm C}$ and B_{C} , respectively (Fig. 1, upper green line and circles). The relative concentrations of the other codoped sample were similarly derived yielding 2.7% and 2.5% of N_{C} and B_{C} defects, respectively (lower green line and circle in Fig. 1). Our calculations capture the correct experimental trend of a big reduction in κ seen when B_C defects, even in smaller concentrations than N_C, are introduced in the samples (Fig. 1). This evidences the much stronger phonon scattering strength induced by B_C defects. Furthermore, Fig. 2 shows the dependence of κ on impurity concentration, and confirms the anomalously large scattering from B_C defects. This behavior of the B_C defects seems the only possible explanation of the very low κ (42 and 19 W/mK at 300 K) measured for the codoped samples. Otherwise, to achieve the same low thermal conductivities by N doping alone would require the $N_{\rm C}$ concentrations in excess of 20%, which are obviously unrealistic.

A look at the phonon scattering rates in Fig. 3(b) provides more clues about boron's atypical behavior. Scattering by substitutional impurities comes from two sources: the mass difference between the impurity atom and the one it replaces, and the local change in the interatomic force constants (IFCs) around the impurity in response to structural relaxation and a modified chemical environment. In cases like Ge impurities in Si, the mass term dominates because Si and Ge have similar chemical bonding properties but very different masses [40,41]. The other extreme is the case of vacancies, where the host atom is absent and the only contribution comes from IFC differences. The B-induced scattering rates in Fig. 3(b) are a striking 2 orders of magnitude larger than the N-induced ones, and they are comparable to those of the C vacancy. This is



FIG. 3. (a) Phonon DOS of SiC and (b) scattering rates of phonons by different defects (with a concentration of 10^{20} cm⁻³), isotopes, and phonon-phonon interactions at 300 K.

surprising because the absolute value of the mass difference between B and C is nearly the same as between N and C. A calculation including only mass differences, and neglecting IFC differences does indeed predict very similar scattering rates for B and N impurities (see Fig. S1 of the Supplemental Material [20]). Therefore, the large scattering rates for B must come from the different changes in IFCs. However, scattering by Al substitutionals is not nearly as large as that of B, despite both species belonging to the same column in the periodic table, which might lead one to expect similar chemical bonding properties.

Figure 4 shows the norm of the changes in the on-site IFC submatrices. Since translation symmetry imposes a set



FIG. 4. Frobenius norm of the changes in the on-site IFC submatrices of the atoms (*i*) around the defects with respect to the perfect 3C-SiC structure as a function of the distance of the atoms from the defect center (*d*).

of linear constraints on each row of the IFC matrix, the change in the on-site terms probes the overall change in the IFCs related to each atom. The results shown in the figure confirm that the largest changes happen in the case of the vacancy. On the other hand, the B_C defect shows a rather large asymmetry in the first-neighbor shell, which may explain the increased scattering. To be able to analyze the contribution to scattering from this asymmetry, we define a symmetric perturbation matrix V_{sym} containing only the part of the total perturbation matrix V (see details in the Supplemental Material [20]) calculated by averaging V over the four space-group operations that just permute the four nearest neighbors of the defect center. Hence, V can be split as a sum of this symmetric term plus an asymmetric term containing the remainder of the total perturbation: $\mathbf{V} = \mathbf{V}_{sym} + \mathbf{V}_{asym}$. Figures 2 and 3 show the variation of κ with defect concentration and the phonon-defect scattering rates induced by the artificial defect represented by V_{sym} . Likewise, the norm of the changes in the on-site IFC submatrices due to $\mathbf{V}_{\rm sym}$ is shown in Fig. 4. It can be seen that the symmetrization process does indeed bring the values more in line with those corresponding to the symmetric perturbations N_C and Al_{Si}. Accordingly, the symmetrized B_C perturbation yields thermal conductivities very similar to those from Alsi impurities, and much larger than those for the same concentration of true B_C impurities, as shown in Fig. 2.

The asymmetry in IFCs is caused by an asymmetry in the relaxed structure of the B_C defect. While both N and Al lead to relaxations around the impurity maintaining tetrahedral (T_d) symmetry, the relaxation around B breaks the symmetry and the impurity gets closer to three of its four nearest neighbors showing threefold (C_{3v}) symmetry [Fig. 2 (inset); see also Ref. [38]]. The asymmetrical relaxed structure of the B_C defect is a manifestation of the complex chemistry of boron [42]. Some insight into the different chemical behaviors of N and B with respect to Si can be gained from a look at their binary compounds. While the most stable silicon nitride is Si₃N₄, with a relatively simple structure, silicon borides have stoichiometries from SiB₃ to SiB₄₀ and very complex unit cells with hundreds of atoms [43,44]. The stoichiometry and the structure of silicon borides suggest an affinity of B for low coordination with Si. Thus, the relaxation of the B defect atom away from one of its four neighboring atoms in 3C-SiC can be interpreted as a movement towards lower coordination. This type of relaxation is however not uncommon for an extrinsic defect in tetrahedral semiconductors, and can arise in the context of DX centers

Although the above reasoning shows that symmetry breaking affects the perturbation for B_C impurities, this does not yet explain its exceptionally large effect on κ . To understand it, let us take another look at the scattering rates and the phonon density of states (DOS) of SiC in Fig. 3. The scattering rates for B_C display a prominent peak at

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about 33 rad/ps. A similarly large peak is observed for the vacancy at a slightly higher frequency. Such a peak is notably smaller or almost absent for the Al_{Si} and N_C defects. The rates for the symmetrized B_C impurity are also shown (B_C sym), displaying much smaller values and a much lower peak than the original B_C perturbation. This peak is the signature of resonant scattering. Resonances are quasibound states in the continuum of propagating states. They are infinitely extended, but have a large probability around the localized perturbation that causes them. They manifest themselves as peaks in the phonon scattering cross section σ of the scatterer near the frequency of the resonance. The Green's function approach that we use to compute defect scattering rates accounts for the full scattering to all orders. so it perfectly captures the effect of resonances, which would not appear in truncated perturbative approaches.

A direct way to identify resonant scattering is via the scattering T matrix (see the expression in the Supplemental Material [20]), which is fundamentally related to the cross section [24,45]. Prominent peaks in the imaginary part of the trace of the scattering T matrix, shown in Fig. 5(a), correspond to resonances. In Fig. 5(a), these resonances are much easier to identify than from the cloud of scattering rate points in Fig. 3. The figure clearly displays large resonances for B_C and C vacancies (Vac_C), but not for the symmetrized B_C, N_C and Al_{Si}.

According to scattering theory, as the intensity of the localized perturbation grows stronger, increasingly sharper resonances start to develop at the lower frequency spectrum [46]. In the present case, this would imply that resonances might show up for impurities other than B_C or C vacancies, if only their perturbations were stronger. To verify this, we have artificially multiplied the perturbation by a constant factor α , and have recalculated σ for a longitudinal-acoustic phonon of frequency 33 rad/ps (the resonant frequency for the B_C defect), as a function of α . The value $\alpha = 1$ corresponds to the true perturbation. Figure 5(b) confirms that for sufficiently large α , every impurity is able to develop resonant scattering. Figure 5(b) suggests the qualitative concept of an effective native "strength" of the defect: the B_C and C vacancy defects are associated with a larger strength, manifested as a larger cross section at small α and an earlier onset of the resonance with an increase in α . This strength is the result of a complex interplay involving the magnitude of the different changes in the IFCs and their symmetry. In the B_C case, the broken symmetry due to the T_d to C_{3v} transition leads to a visibly enhanced strength with respect to the symmetrized case, seen in Fig. 5(b), despite the overall change in the perturbation matrices in Fig. 4 not being drastic. Similar strong effects of the T_d to C_{3v} symmetry transition for extrinsic defects in tetrahedral semiconductors are also seen for charge carrier scattering [47,48].

These results have significant implications for the SiC industry. B-doped SiC has shown promising results in



FIG. 5. (a) Trace of the imaginary part of the scattering **T** matrix for different impurities, showing a resonance for B and a vacancy. (b) Scattering cross section σ for the longitudinal-acoustic mode at an angular frequency of 33 rad/ps, as a function of scattering strength for different impurities. Similar resonance peaks for the B_C defect are also seen for transverse-acoustic phonon modes at ~33 rad/ps (see Fig. S4 in the Supplemental Material [20]).

photovoltaics, power electronics, and many more applications [49–53]. However, the drastic thermal conductivity reduction associated with B doping can affect device efficiency and lifetime. Thus, balancing the improvement of electronic and luminescent properties with the detrimental effects on thermal conductivity is an important factor to consider when selecting the right dopants for these applications.

In conclusion, B_C substitutional impurities in cubic SiC scatter phonons much more strongly than N_C or Al_{Si} impurities, and comparably to C vacancies. For N impurities to reduce κ as much as B impurities do, the concentration of the former has to be roughly 30 times larger than that of the latter. This could not have been guessed from mass difference considerations. It emerges from *ab initio* calculations, which are clearly supported by previous experimental measurements. This striking behavior is caused by the symmetry transition from T_d

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to C_{3v} around the B impurity upon relaxation, which leads to strong resonant scattering of acoustic phonons in the angular frequency range between 33 and 50 rad/ps. If only the symmetric part of the perturbation is kept, the resonance disappears and the calculated effect becomes similar to that of Al substitutionals, thus showing a significant impact of defect-induced symmetry breaking on the thermal conductivity of SiC. However, symmetry breaking by itself is not a sufficient condition, as seen in the case of N defects in diamond [45], where lattice distortions do not lead to resonant scattering. Furthermore, the calculations presented suggest that single-crystalline, defect-free cubic SiC can achieve a thermal conductivity about 1.7 times higher than the largest reported measured value on this polytype, and above those of other polytypes.

The results shown here point to a general phenomenon, whereby lattice distortions induced by defects showing a T_d to C_{3v} transition in different tetrahedrally bonded semiconductors [47,54] may develop into a phonon resonance and lead to enhanced scattering. This should be relevant to many rapidly evolving technologies. In complex semiconductors there will usually be several possible doping scenarios for reaching a desired carrier concentration, and the sensitivity of the phonon scattering to the specific defect thus opens up an important new route in semiconductor design.

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Exceptionally strong phonon scattering by B substitution in cubic SiC: Supplementary Material

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I. COMPUTATIONAL DETAILS

A. Lattice thermal conductivity

The lattice thermal conductivity κ for isotropic compounds can be expressed as [1, 2]

$$\kappa = \frac{1}{3} \sum_{j} \int \frac{\mathrm{d}\mathbf{q}}{(2\pi)^3} C_{j\mathbf{q}} v_{j\mathbf{q}}^2 \tau_{j\mathbf{q}} \tag{1}$$

where $v_{j\mathbf{q}}$, $C_{j\mathbf{q}}$ and $\tau_{j\mathbf{q}}$ represent the group velocity, contribution to the specific heat, and relaxation time for phonons in mode $j\mathbf{q}$. Here, j stands for the phonon branch index and \mathbf{q} for the wave vector. The inverse of the phonon relaxation time, $\tau_{j\mathbf{q}}^{-1}$, is the phonon scattaring rate. This expression holds as long as none of the scattering mechanisms breaks the isotropy of the crystal. This can be true even for anisotropic defects, as long as their orientations are randomly and uniformly distributed.

B. Total scattering rate

For the system under study in this work, the total phonon scattering rate $\tau_{j\mathbf{q}}^{-1}$ can be written as the sum of four contributions from different scattering mechanisms:

$$\tau_{j\mathbf{q}}^{-1} = \tau_{j\mathbf{q},\text{anh}}^{-1} + \tau_{j\mathbf{q},\text{iso}}^{-1} + \tau_{j\mathbf{q},\text{def}}^{-1} + \tau_{j\mathbf{q},\text{grain}}^{-1}.$$
 (2)

where τ_{anh}^{-1} is due to the intrinsic anharmonicity of the crystal that enables three-phonon processes, τ_{iso}^{-1} to isotopic mass disorder, τ_{def}^{-1} to crystallographic defects and τ_{grain}^{-1} to the presence of grain boundaries. Anharmonic scattering is characterized using the method described in Refs. 1 and 2, based on *ab-initio* calculations of the third-order interatomic force constants (IFCs) of the perfect 3C-SiC crystal. τ_{iso}^{-1} is obtained using the scheme developed by Tamura *et al.* in Refs. 3 and 4, which only requires knowledge of the phonon spectrum and the natural isotopic abundances. The expression for τ_{grain}^{-1} is given in the main text. The next section is devoted to $\tau_{jq,def}^{-1}$.

C. Phonon scattering by defects

An expression for τ_{def}^{-1} can be obtained by adding up the scattering rates due to all possible elastic phonon scattering processes $|j\mathbf{q}\rangle \rightarrow |j'\mathbf{q}'\rangle$ as [5],

$$\tau_{j\mathbf{q},\mathrm{def}}^{-1} = \pi \chi_{\mathrm{def}} \frac{\Omega}{V_{\mathrm{def}}} \frac{1}{\omega_{j\mathbf{q}}} \sum_{j'\mathbf{q}'} \left| \langle j'\mathbf{q}' \, | \, \mathbf{T} \, | \, j\mathbf{q} \rangle \right|^2 \delta \left(\omega_{j'\mathbf{q}'}^2 - \omega_{j\mathbf{q}}^2 \right), \tag{3}$$

where χ_{def} is the number fraction of defects, V_{def} the volume of a defect, Ω the volume which is used to normalize $|j\mathbf{q}\rangle$, and ω the angular frequency of phonons. The **T** matrix is given as,

$$\mathbf{T} = \left(\mathbf{I} - \mathbf{V}\mathbf{g}^{+}\right)^{-1}\mathbf{V} \tag{4}$$

where \mathbf{g}^+ is the causal Green's function for the perfect structure, \mathbf{V} the perturbation matrix connecting the perfect and defective systems, and \mathbf{I} the identity matrix. However, it is more convenient to dispense with the sum over outgoing phonon modes by using the optical theorem [6]:

$$\tau_{j\mathbf{q},\mathrm{def}}^{-1} = -\chi_{\mathrm{def}} \frac{\Omega}{V_{\mathrm{def}}} \frac{1}{\omega_{j\mathbf{q}}} \Im\left\{ \langle j\mathbf{q} \, | \, \mathbf{T} \, | \, j\mathbf{q} \rangle \right\}.$$
(5)

 \mathbf{V} can be decomposed as a sum of contributions from the changes in mass (\mathbf{V}_M) and in force constants (\mathbf{V}_K) between the perfect and defective structures:

$$\mathbf{V} = \mathbf{V}_K + \mathbf{V}_M \tag{6}$$

 $\mathbf{2}$

More specifically, the mass term \mathbf{V}_M is diagonal and its only nonzero elements correspond to onsite terms for the defect. Their values are $-\frac{M'_i - M_i}{M_i} \omega^2$, where M' and M are the masses of the defect and of the original atom at the *i*-th site, respectively, and ω is the angular frequency of the incoming phonon. Hence, \mathbf{V}_M is independent of the structural distortions around the defect. Those effects are included in the \mathbf{V}_K matrix, which is computed from the differences between the IFCs for defective (\mathbf{K}') and perfect (\mathbf{K}) structures as $\mathbf{V}_{K,i\alpha,k\beta} = \frac{K'_{i\alpha,k\beta} - K_{i\alpha,k\beta}}{\sqrt{M_i M_k}}$. Here *i*, *k* are atom indices and α, β represent Cartesian axes.

Since the perturbations are represented in real space, the need arises to impose a cutoff radius $r_{\rm cut}$ for structural distortions. The changes in IFCs are taken into account up to second nearest-neighbours of all the atoms within this $r_{\rm cut}$. A large $r_{\rm cut} = 5.5$ Å (corresponding to the sixth neighbour shell in 3C-SiC) is chosen for all the defects. Changes beyond this cutoff are found to be very small. Nevertheless, it is necessary to apply a numerical correction to the "raw" \mathbf{V}_K to make this cutoff strict. In particular, this ensures that all sets of IFCs fulfil the so called "sum rules" expressing the conservation of momentum or, in other words, the homogeneity of space. In practice, this is achieved by restricting \mathbf{V}_K to a subspace of atomic displacements from which rigid translations have been removed. Let \mathbf{u}_{α} be the vector with component (i, β) equal to $\delta_{\beta\alpha}$, representing a rigid displacement of all atoms along Cartesian axis α . The restriction operator is defined as:

$$\mathbf{P} = \mathbf{I} - \sum_{\alpha} \mathbf{v}_{\alpha} \otimes \mathbf{v}_{\alpha},\tag{7}$$

where $\mathbf{v}_{\alpha} = \mathbf{u}_{\alpha}/|\mathbf{u}_{\alpha}|$. This operator is applied on $\tilde{\mathbf{V}}_{K} = \mathbf{K}' - \mathbf{K}$ simply as

$$\tilde{\mathbf{V}}_{K}^{\text{cut}} = \mathbf{P}\tilde{\mathbf{V}}_{K}\mathbf{P},\tag{8}$$

after which $\mathbf{V}_{K}^{\text{cut}}$ is trivially obtained from $\tilde{\mathbf{V}}_{K}^{\text{cut}}$. As a matter of fact, we use an iterative scheme, looping over Eq. 8 with $\tilde{\mathbf{V}}_{K} = \tilde{\mathbf{V}}_{K}^{\text{cut}}$, until the final $\mathbf{V}_{K}^{\text{cut}}$ components beyond the r_{cut} are negligible. This ensures that no corrections to the force constants for atoms beyond r_{cut} are made.

D. Parameters for *ab-initio* calculations

The harmonic and anharmonic IFCs for 3C-SiC are calculated with a finite displacement scheme for a $5 \times 5 \times 5$ supercell of the rhombohedral primitive cell (spacegroup F-43m). The supercell contains 250 atoms. As a check, the harmonic IFCs are also obtained for a $4 \times 4 \times 4$ supercell. The maximum difference in angular frequency ω at the Γ -point is a mere 0.3 rad/ps.

All *ab-initio* calculations, including both the structural relaxation and the force calculations needed for computing the IFCs, are carried out using the projector-augmented-wave method [7] as implemented in the density functional theory package VASP [8], with the local density approximation to exchange and correlation [9]. The equilibrium lattice parameter obtained for perfect 3C-SiC is a = 4.33 Å.

Force constants for the B_C , N_C and Al_{Si} substitutional defects are calculated using $5 \times 5 \times 5$ containing one defect atom. A $4 \times 4 \times 4$ supercell is used for the carbon vacancy.

The atomic coordinates of the defective supercell are relaxed keeping the cell volume fixed before calculating the IFCs. The relaxation is iterated to avoid any imaginary phonon frequencies at the Γ -point of the Brillouin zone for the supercell. A small displacement of the defect atom or its nearest-neighbors is introduced before the start of the relaxation so as to avoid the system getting trapped in a saddle point of the energy surface.

To extract the second- and third-order IFCs from the *ab-initio* calculated forces, we use the Phonopy [10] package and our own third-order.py code [1] respectively.

The Born effective charges and the dielectric tensor calculated with VASP are also included to account for the non-analytical correction to the dynamical matrix for a correct reproduction of LO-TO phonon splitting in 3C-SiC [11].

To compute the defect scattering, the Green's functions are calculated on a $18 \times 18 \times 18$ grid using the tetrahedron method to integrate over the Brillouin-zone [12]. All the scattering rates are calculated on a $24 \times 24 \times 24$ q-point mesh. The calculations of the Green's functions, the scattering rates τ_{anh}^{-1} , τ_{iso}^{-1} , τ_{def}^{-1} , τ_{grain}^{-1} and the final κ are performed using the almaBTE code, developed in house [13].

II. DEFECTS AS MASS PERTURBATIONS



FIG. 1: Phonon scattering rates from B_C , N_C , and Al_{Si} substitutional defects (in concentration of 10^{20} cm⁻³) with only mass perturbation contributions, from isotopes and from phonon-phonon interaction at 300 K.

Fig. 1 shows the defect scattering rates from B_C , N_C , and Al_{Si} taking into account only the contribution from V_M in Eq. (6). Slightly stronger scattering rates are obtained for the N_C defect than for B_C and Al_{Si} . However, it is clear that the contributions from all these defects are extremely weak when compared to mass-disorder and anharmonic scattering if the V_K term is neglected in Eq. (6).

III. ANHARMONIC SCATTERING OF ACOUSTIC PHONONS



FIG. 2: Anharmonic scattering rates of SiC at 300K for each acoustic branch (two transverse-acoustic: TA1 and TA2, and one longitudinal-acoustic: LA). To avoid the overlap in the plots, we have scaled TA1 and LA mode by 10^2 and 10^{-2} respectively.

The anharmonic scattering contribution from the transverse-acoustic and longitudinal-acoustic phonon modes of SiC as a function of phonon frequencies are shown in Fig. 2. It can be seen that all the acoustic phonon modes follow an ω^2 behaviour with a slight spread which is expected due to dependence of phonon scattering rates on wave-vector and polarization along with frequencies.



FIG. 3: Visual representation of the changes in the interatomic distances for defective supercells containing a single (a) Al_{Si} , (b) N_C , (c) Vac_C , or (d) B_C defect in 3C-SiC. The changes in the nearest-neighbour interatomic distances are directly proportional to the bond width variations seen in the figure. The colour gradient from red to blue is used to show the depth of the bond cage structure (front to back).

IV. STRUCTURAL DISTORTION WITH DEFECTS

Fig. 3 shows a 3D representation of the bond length variations in defective 3C-SiC supercells. The defect is located in the centre of the structure. The lines represent the bonds between the nearest neighbour atoms in 3C-SiC, and their thicknesses are directly proportional to the variations in the bond lengths. Thus, lines are thicker near the defect centre and become thinner with increasing distance from the defect centre, Fig. 3. The colour gradient (red to blue) provides depth perspective to help discriminate between the bonds at the front and back in this 3D structure.

The B_C defect, unlike the others, shows a surprising anisotropic behaviour of the bond length variation after the structural relaxation as seen in Fig. 3(d). Furthermore, the perturbations near the defect centre are larger than for the other two defects at C site, N_C and Vac_C , Fig. 3(b) and (c).

 $\mathbf{5}$

V. SCATTERING CROSS-SECTION FOR $B_{\rm C}$ DEFECT

 $\mathbf{6}$



FIG. 4: Scattering cross-section (σ) as a function of scattering strength factor (α) for B_C defect in 3C-SiC. The resonance is seen for both transverse-acoustic and longitudinal-acoustic modes.

Fig. 4 shows the scattering cross-section for B_C defect as a function of scattering strength factor (α). Similar to the LA mode seen in Fig.5(b) in the main text, TA modes at ~33 rad/ps also exhibits resonance peak at $\alpha = 1$.

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Check for updates Resonant phonon scattering in semiconductors Bonny Dongre, [®]^a Jesús Carrete, [®]^a Ankita Katre, [®]^b Natalio Mingo^b and

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Boron impurities have recently been shown to induce resonant phonon scattering in 3C-SiC, dramatically lowering its thermal conductivity. The B-doped 3C-SiC is associated with an off-center relaxation of the B atom, inducing a local transition from T_d to C_{3v} symmetry. Similar relaxations in B and N-doped diamond, with

Received 15th February 2018, Accepted 3rd April 2018 DOI: 10.1039/c8tc00820e lowering its thermal conductivity. The B-doped 3C-SiC is associated with an off-center relaxation of the B atom, inducing a local transition from T_d to C_{3v} symmetry. Similar relaxations in B and N-doped diamond, with a similarly large effect on the interatomic force constants (IFCs), fail to produce resonances. Here we develop an intuitive understanding of such dopant-induced resonant phonon scattering in semiconductors with the help of a 1D monoatomic chain model. We find that the phenomenon is connected to a slight asymmetry in the relaxed position of the defect, with its origin in two or more minima of the potential energy surface in close proximity. The large perturbation they introduce in the IFCs is the essential ingredient of a resonance.

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1 Introduction

Extrinsic doping of semiconductors dates back to the mid-twentieth century and has found uses in such important technologies as power electronics, optoelectronics, photovoltaics, thermoelectrics, and bio-sensors to cite a few.^{1,2} The need to identify the effect of a single dopant on the properties of a semiconductor has acquired a paramount importance today, to the extent of opening a new field, solotronics.3 The effect of defect induced lattice distortions on various physical properties like charge carrier scattering⁴ or thermal conductivity5,6 has been studied. In our previous work, we showed the presence of exceptionally strong phonon scattering in cubic SiC containing boron substitutions on carbon sites (B_C substitutions).⁶ The phonon scattering leads to a drastically reduced thermal conductivity, κ , for boron-doped 3C-SiC. This can have detrimental effects on device efficiency and lifetime, and have serious implications for the usage of particular dopants in semiconductor materials.

On a more fundamental level, the B_C results also point to a general phenomenon whereby lattice distortions induced by substitutions can cause resonant scattering of phonons in semiconductors. In ref. 6, we found that the unusually high scattering was related to a symmetry breakdown around the B atom. The atomic environment of the dopant B atom experiences a transition from T_d to C_{3v} symmetry after atomic relaxation. This transition is connected to a large change in interatomic force constants (IFCs). However, no detailed connection between the structural transition and the large IFC perturbation has been established. This is underlined by the fact that in an earlier study of nitrogen doping of diamond no resonant scattering was observed, despite the symmetry breaking transition of the dopant nitrogen being associated with a larger relaxation than that of boron in 3C-SiC.⁵ Therefore, understanding the detailed mechanism is essential to help identify other potential superscatterers and to guide the choice of dopants during device design.

In the present work we fill this gap by first exploring the influence of charge on the relaxation and phonon scattering of the $B_{\rm C}$ and $N_{\rm C}$ defects in 3C-SiC and diamond. We confirm the previous reports5,6 that a large asymmetric distortion around N⁽⁰⁾_C in diamond fails to show any resonant scattering whereas a small distortion around B_C⁽⁰⁾ does produce resonant scattering in 3C-SiC. A review of the studies of intrinsic and extrinsic point defects in 3C-SiC shows that even though there have been some experimental and computational works on doping 3C-SiC with boron⁷⁻⁹ and nitrogen,¹⁰⁻¹² stability of the charged states of these defects is not fully understood. Furthermore, nothing is known about the influence of the charged state of the defect on its phonon scattering properties. Therefore we calculate the defect formation energies (DFEs) of the charged defects in 3C-SiC and diamond, and find that the -1 and +1 charge states of the B_C and N_C defects respectively are stable in the band gap along with their neutral charge states. This suggests that all the respective defects are present in 3C-SiC and diamond according to the Boltzmann distribution.

The study of phonon scattering from an atomistic Green's function perspective revolves around the **T** matrix, which connects the Green's functions of the perturbed and unperturbed lattices. The **T** matrix combines the effect of the perturbation itself – caused by differences in mass and force constants – with the properties of the host lattice. We speak of resonant phonon scattering when significant peaks appear in **T** and in the scattering rates as functions of phonon frequency. Resonances can occur

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at any frequency, but they matter the most when they occur at relatively low frequencies in the dispersion relation, because the scattering of the low-frequency acoustic phonons is otherwise described by a Rayleigh like behavior. As the acoustic phonons typically carry most of the heat in semiconductors and insulators, the experimental signature of a resonance at low frequencies is a drastic reduction of lattice thermal conductivity even at moderate defect concentrations.

In order to develop an intuitive understanding of resonant phonon scattering, here we reproduce the effect in a simple 1D monoatomic chain, where the shape of the energy landscape can be easily controlled. By using a Tersoff-like potential on three contiguous atoms of the chain we obtain a double well potential energy landscape. Then, by progressively increasing bond-strength parameter of the potential, we systematically reduce the distance between the two minima thereby reducing the energy barrier between them. We find that in the case of the 1D chain a large IFC perturbation arises when the two minima in the potential energy landscape are so close to each other that their curvatures are modified. Resonant phonon scattering at low frequencies is clearly observed when the minima are very close. This phenomenon is characterized by a phonon reflectivity approaching unity and prominent peaks in the trace of the imaginary part of the T matrix, also at low frequencies.

Considering the original case of B_C and N_C in 3C-SiC and diamond in light of our analysis of the 1D model, we establish that a rather small lattice distortion associated with two or more close energy minima in the potential energy landscape is a necessary condition for having resonant phonon scattering. In addition, a low slope of the acoustic phonon bands, and consequently a large density of states, of the unperturbed host is identified as a necessary condition.

2 Methodology

2.1 Scattering rates

Within the atomistic Green's function formalism, the retarded phonon Green's function of the unperturbed host lattice (g^+) is used to calculate the T matrix given the perturbation matrix V as:¹³

$$\mathbf{T} = (\mathbf{I} - \mathbf{V}\mathbf{g}^{\dagger})^{-1}\mathbf{V},\tag{1}$$

where I is the identity matrix. Hence, once the Green's function of the unperturbed host lattice and the T matrix are known, the Green's functions of the perturbed lattice can be calculated according to the Dyson equation:

$$\mathbf{G}^{+} = \mathbf{g}^{+} (\mathbf{I} + \mathbf{T} \mathbf{g}^{+}). \tag{2}$$

The elastic scattering rate due to defect–phonon interactions, τ^{-1} , is frequency and wave-vector dependent. It can be calculated for a particular phonon branch index *i* and a given wave vector **q** by adding up the scattering rates due all possible elastic phonon scattering processes $|i\mathbf{q}\rangle \rightarrow |i'\mathbf{q}'\rangle$ as:¹⁴

$$\frac{1}{\tau_{i\mathbf{q}}} = \pi n_{def} V_{uc} \frac{1}{\omega_{i\mathbf{q}}} \sum_{i'\mathbf{q}'} |\langle i'\mathbf{q}'|\mathbf{T}|i\mathbf{q}\rangle|^2 \delta(\omega_{i'\mathbf{q}'}^2 - \omega_{i\mathbf{q}}^2), \qquad (3)$$

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where n_{def} is the volumetric concentration of the point defects, V_{uc} the volume of the unit cell, and ω the angular frequency of phonons. Eqn (3) is the rigorous equivalent of Fermi's golden rule in exact time-independent perturbation theory. It is obtained from the Lippmann–Schwinger equation, which uses the perturbation to establish a connection between the unperturbed and perturbed phonon wave functions. Eqn (3) can be reduced to a more convenient form using the optical theorem:¹³

$$\frac{1}{\tau_{i\mathbf{q}}} = -n_{\text{def}} V_{\text{uc}} \frac{1}{\omega_{i\mathbf{q}}} \Im\{\langle i\mathbf{q} | \mathbf{T} | i\mathbf{q} \rangle\}.$$
(4)

Eqn (4) removes the need to sum over outgoing phonon modes as well as the problem of satisfying the energy conservation, represented by the Dirac delta function in eqn (3), when sampling the phonon frequencies on a finite grid.

V is defined as:

$$= \mathbf{V}_{\mathbf{M}} + \mathbf{V}_{\mathbf{K}}.$$
 (5)

 $\mathbf{V}_{\mathbf{M}}$ and $\mathbf{V}_{\mathbf{K}}$ account for changes in mass and force constants between the perfect and defective structures, respectively. $\mathbf{V}_{\mathbf{M}} = -\frac{M_j' - M_j}{M_j} \omega^2$ is diagonal and is nonzero only for the onsite terms of the defect. M_j' and M_j are the masses of the defect and the original atom at the *j*-th site, respectively, and ω is the angular frequency of the incoming phonon. $\mathbf{V}_{K,j\alpha,k\beta} = \frac{K'_{j\alpha,k\beta} - K_{j\alpha,k\beta}}{\sqrt{M_j M_k}}$ where **K**' and **K** are the IFCs for defective

and perfect structures respectively. j, k are atom indices and α, β represent Cartesian axes.

2.2 Defect thermochemistry

The structures and potential energy surfaces of the defects depend on a range of factors like the number and charge states of the defects as well as the chemical potentials of the atoms exchanged with the reservoir and the electrons in the system. The presence of the defects in thermodynamic equilibrium will be determined by the DFE:

$$E_{\mathbf{D}^{(q)}}(\mu_{\rm e}) = E_{{\rm f}, \mathbf{D}^{(q)}} - \sum_{a} n_{\rm a} \Delta \mu_{\rm a} + q \mu_{\rm e}, \tag{6}$$

where $E_{\rm f,D^{(q)}}$ is the defect formation energy with respect to the reference states, given as:

$$E_{f,D^{(q)}} = E_D^{(q)} - E_{bulk} - \sum_a n_a E_a,$$
 (7)

 n_a is the number of atoms of kind *a* that are exchanged with the reservoirs at chemical potentials $\Delta \mu_a$. $E_{\rm I}^{(q)}$ are calculated using a supercell approach. The following section gives the computational details and ref. 15 the details of the applied corrections due to the compensating jellium background charge and the interactions between the periodic arrangement of charged defects.

In a binary system like SiC the formation energies are defined with respect to the chemical potentials corresponding to Si- and C-rich growth conditions. The allowed respective chemical potentials are calculated by carefully restricting the formation of different intrinsic competing phases like SiC₂,

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 SiC_3 in the system. Similar conditions have to be obeyed if impurities are added. In case of boron doping this includes restricting the formation of competing phases like BC, B₄C, SiB, SiB₃. In case of nitrogen doping the competing phases include binaries like CN, C₂N, Si₃N₄ and ternaries like SiCN, SiC₂N₄.

2.3 Computational details

The total energy as well as the force calculations are done using the projector-augmented-wave method¹⁶ as implemented in the VASP code,¹⁷ with the Perdew–Burke–Ernzerhof (PBE) exchange and correlation functional.¹⁸ The calculated equilibrium lattice parameter for perfect 3C-SiC is a = 4.37 Å and for diamond is a = 3.57 Å. We calculate the DFEs and IFCs using a 5 × 5 × 5 supercell, containing 250 atoms of the rhombohedral primitive cell (space group $F\bar{4}3m$) to avoid defect–defect interactions. For the DFEs a 4 × 4 × 4 *k*-point mesh and for the IFCs a single Γ -point are used.

Structural relaxations for the defective structures are carried out iteratively, allowing the atomic coordinates to relax and keeping the cell volume fixed such that there is no imaginary frequency at the Γ -point of the Brillouin zone of the supercell. To this end, the defect atom is given a small initial displacement before the start of the relaxation in order to avoid the system getting trapped in a saddle point of the potential energy land-scape. The harmonic IFCs for the bulk and defect-containing 3C-SiC and diamond are calculated with a finite displacement scheme. We use the Phonopy¹⁹ package to extract the second-order IFCs from the *ab initio* calculated forces.

To compute the defect scattering for 3C-SiC and diamond, the Green's functions are calculated on a 27 × 27 × 27 and 29 × 29 × 29 grid, respectively, using the linear tetrahedron method for integration over the Brillouin zone.²⁰ The scattering rates are then calculated on $24 \times 24 \times 24$ and $26 \times 26 \times 26$ **q**-point meshes for 3C-SiC and diamond, respectively. In the case of 3C-SiC a non-analytical correction is added to the dynamical matrix to correctly reproduce the LO–TO splitting.²¹ The non-analytical correction to the dynamical matrix is not required for the defect–laden systems, as we only need the perturbation matrix, eqn (5), for which no correction is required. All these calculations are performed using our in-house almaBTE code.²²

3 Results and discussion

The scattering rates for all the defects are shown in Fig. 1. For the two non-charged substitutional defects, $B_C^{(0)}$ and $N_C^{(0)}$, our results agree with the ones in ref. 6, which were obtained using the local density approximation, thereby validating the presence of a resonance in case of the $B_C^{(0)}$ defect in 3C-SiC. The resonant scattering is two to three orders of magnitude higher than the other defects. The increased scattering is key to explaining the very low thermal conductivity experimentally observed for boron-doped 3C-SiC. $B_C^{(-1)}$, does not exhibit resonant scattering, Fig. 1. One would typically think of the substitutional



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Fig. 1 Scattering rates for 3C-SiC (circles) and diamond (plus signs) for different dopants with their respective charge states at a concentration of 10^{21} defects per cm³.

boron on a carbon position as a hole-donating (negatively charged) defect. This apparent contradiction can be understood in terms of the defect formation energies shown in Fig. 2. It can be seen that both the neutral and respective charged states, -1 for the B_C defect and +1 for the N_C defect, are present in the band-gap. The $B_C^{(0)}$ and $N_C^{(+1)}$ defects are more stable near the valence band maximum whereas the $B_C^{(-1)}$ and $N_C^{(0)}$ defects are more stable near the conduction band minimum. In a p-doped sample, as the experimentally investigated boron-doped SiC,⁹ one would thus expect both $B_C^{(-1)}$ to be present according to a Boltzmann distribution.

Despite all the defects introducing a similar mass perturbation, there is a stark difference in phonon scattering caused by each defect. This underlines the fact that the underlying contribution to



Fig. 2 Defect formation energies vs. electronic chemical potential (μ_e) for 3C-SiC using the experimental bandgap.²³ $\mu_e = 0$ corresponds to the valence band maximum (VBM) and $\mu_e = 2.4$ is the conduction band minimum (CBM). (a and b) Correspond to Si and C rich growth conditions respectively.

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Fig. 3 The phonon band structure of 3C-SiC (blue) and diamond (red) along with the absolute values of the real (right) and imaginary (middle) parts of the Green's function.

phonon scattering from factors like Green's functions of the host, the lattice relaxation around the defect, and resultant force constant perturbation all play an important role. The effect of Green's functions on phonon scattering can be understood with the help of Fig. 1 and 3. Fig. 1 illustrates how the scattering rates of defects in diamond tend to be lower than those in 3C-SiC. This is in direct relation with Fig. 3 which shows the real and imaginary parts of the trace of the Green's functions for 3C-SiC and diamond with their respective phonon band structures. The negative trace of the imaginary part of the Green's function corresponds to the density of states (DOS) of the system. As would be expected from the high phonon velocities in diamond, it can be seen that the magnitude of the DOS for diamond is considerably smaller than that of 3C-SiC.

A large DOS in combination with a large force constant perturbation are required to have eigenvalues of the Vg^+ matrix approach unity resulting in a resonance, eqn (1). Intuitively, this implies that a low DOS in diamond, seen in Fig. 3, inhibits the phonon scattering as there are not enough phonon modes available for scattering, at small frequencies in particular.

In addition to a "large" Green's function, the Vg^+ matrix can approach unity due to a "large" perturbation matrix, V. Taking the Frobenius norm of the IFC perturbation matrices, Table 1, as a gauge for the magnitude of the IFC perturbation, we obtain the largest perturbations for $B_{C}^{(0)}$ and $N_{C}^{(0)}$ defects in diamond, and $B_{\rm C}^{(0)}$ in 3C-SiC. The resonance for the $B_{\rm C}^{(0)}$ and $N_{\rm C}^{(0)}$ defects in diamond are suppressed by the low DOS, Fig. 3. In agreement with the analysis in our earlier paper,⁶ the perturbations with a large $\|\mathbf{V}\|_{\mathrm{F}}$ are associated with a structural transition from T_{d} to C_{3v} symmetry around the defect. Interestingly, the magnitude of the perturbation caused by the B⁰_C defect in diamond, where the bond lengths differ by only 0.025 Å, is larger than that caused by the $N_{\rm C}^0$ defect in diamond, where the bond lengths differ by 0.509 Å, Table 1. Similarly, the B⁰_C in SiC, which causes the resonance, is associated with a small structural asymmetry of 0.047 Å. The distortions around these defects are illustrated

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Table 1 Frobenius norm of the IFC perturbation matrices **V**, $\|V\|_F = \sqrt{\sum V_i^2}$, for the eight charged and non-charged defects studied here. The nearest neighbor distances are also listed where d_1 is the shortest and d_2 the longest distance. For the three asymmetric cases, $B_c^{(0)}$ and $N_c^{(0)}$ in diamond and $B_c^{(0)}$ in SiC, where $d_1 \neq d_2$ there are three short distances, d_1 , and one long, d_2

| | SiC | | | Diamond | | |
|----------------|---|-----------|-----------|--|-----------|-----------|
| | $\left\ \mathbf{V} \right\ _{F} \left(e V \; \mathring{A}^{-2} \right)$ | d_1 (Å) | d_2 (Å) | $\left\ \mathbf{V} \right\ _{\mathrm{F}} \left(e V \; \mathring{A}^{-2} \right)$ | d_1 (Å) | d_2 (Å) |
| $B_{C}^{(0)}$ | 41.7 | 1.923 | 1.970 | 54.0 | 1.582 | 1.607 |
| $B_{C}^{(-1)}$ | 20.4 | 1.911 | 1.911 | 18.6 | 1.586 | 1.586 |
| $N_{C}^{(0)}$ | 35.8 | 1.923 | 1.923 | 48.6 | 1.484 | 1.993 |
| $N_{C}^{(+1)}$ | 28.8 | 1.918 | 1.918 | 37.6 | 1.563 | 1.563 |

in Fig. 4. The results would thus indicate that a symmetry breaking structural transition is necessary for a large IFC perturbation, but that the magnitude of the perturbation has an inverse relation with the magnitude of the asymmetry.

To understand this somewhat counter-intuitive relation, we introduce a simple infinite 1D monoatomic chain. The unperturbed chain has only one degree of freedom per atom. The atoms in the chain have mass m = 1 and are bonded by simple harmonic potentials with force constants k = 1 in an arbitrary system of units. Fig. 5(a) shows the characteristic phonon dispersion. The trace of the imaginary and real parts of the Green's function, calculated



Fig. 4 Displacement of atoms around defect in the asymmetrically relaxing defects. The length of the red arrows indicate the magnitude and direction of the displacement vectors. (a) The B atom in SiC moves away from one of the four Si neighbors towards the plane of the other three. (b) One of the four C atoms in diamond moves further away from the B atom as compared to the other three. (c) N moves away from one of the C atoms towards the plane of the other three causing the highest asymmetry.

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Fig. 5 Phonon dispersion curve, and trace of the imaginary and real part of the retarded Green's function, g², for the 1D chain as the black line. Also shown as colored lines are the trace of the real and imaginary parts of the perturbed Green's functions, G², pertaining to the three defect atoms. The color coding follows that of different potentials shown in Fig. 6. The negative trace of the imaginary part of Green's function corresponds to the DOS. While the DOS is usually calculated as a function of the frequency (ω), the Green's function is calculated as a function of frequency squared. However, since the phonon dispersion is plotted here as a function of frequency.

using a decimation technique,²⁴ are shown in Fig. 5(b and c), respectively.

To explore the effect of symmetry lowering relaxations on the IFCs and phonon scattering we then introduce a defect in the 1D-chain by replacing the k = 1 interactions between three contiguous atoms by a simple bond order potential. We label these three atoms L, D and R, Fig. 6 (top). The unperturbed symmetric situation can be thought of as corresponding to the minima of the overlap of the L–D and R–D interatomic potential curves. A small geometric distortion from the high symmetry (non-perturbed) structure results in two competing minima. In this situation the R–D interatomic potential will strongly perturb that of the L–D and *vice versa*. A large geometric distortion means that the potential energy surface around one minimum is only weakly perturbed.

Similar ideas have a long history in chemistry. The Bell-Evans-Polanyi principle (see discussion in ref. 25) for example, can be interpreted such that when the potential energy is described by two parabolas, the transition state is the intersection of both parabolas and it is lowered if the local minimum of the higher energy minimum parabola is lowered and *vice versa*. Similarly, the Lippincott-Schroeder potential explains the hydrogen bond in terms of overlapping Morse like potentials.²⁶ It gives a simple and intuitive explanation of the strong hydrogen bond²⁷ where the potential energy surface changes from a hydrogen localized at one oxygen atom, over a low barrier hydrogen bond, where localization can depend on whether the bond is hydrogenated or deuteronated,²⁸ to a centered situation, where the hydrogen is situated approximately midway between the two oxygen atoms.



Fig. 6 The potential energy curves of the defect-containing 1D chain as a function of the displacement of the central defect atom from the central position. Curves are shown for increasing *B* values of 0.26 (blue), 0.30 (orange), 0.34 (green) and 0.38 (red). The potential curves are labeled with the Frobenius norm of the **V** matrix in arbitrary units. The potential energy curves are obtained by relaxing the system and then calculating its energy when moving the defect atom D (central atom in the three Tersoff-bonded atoms) towards its right R and left L neighbors. *d* is the distance between the defect atom and the center of the two neighbor atoms.

To quantify this interpretation we make a model where the defect is introduced by modifying the interactions among three particular contiguous atoms of the chain. These three atoms behave according to a bond-order potential, V_{ij} , described by a modified Tersoff form²⁹ given as:

$$V_{ij} = f_{\rm C}(r_{ij})[f_{\rm R}(r_{ij}) + b_{ij}f_{\rm A}(r_{ij})], \qquad (8)$$

where $f_{\rm R}$ is the repulsive pair potential, $f_{\rm A}$ is the attractive pair potential associated with bonding, and $f_{\rm C}$ is a cutoff function chosen to include only the first nearest neighbors. r_{ij} is the distance between atoms *i* and *j*. The attractive and repulsive part of the potential are simple exponential functions:

$$f_{R}(r) = A \exp(-\lambda_{1}r),$$

$$f_{A}(r) = -B \exp(-\lambda_{2}r),$$
(9)

where *A*, *B*, λ_1 , and λ_2 are constants. We choose A = 1, $\lambda_1 = 1.0$ and $\lambda_2 = 0.2$. *B* is systematically varied to control the bond strength. b_{ij} in eqn (8) represents a measure of the bond order and is a function of the local environment. We use an expression like that of the Tersoff potential with $\beta = 40$, n = 23and $\lambda_3 = \lambda_2$. As the chain is always linear, the bond-order contribution is independent of the bond angle term that is present in the original Tersoff potential.²⁹ The IFCs required to

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calculate the ${\bf V}$ matrix for the 1D chain are obtained by relaxing the atomic positions and evaluating

 K_i

$$_{j} = \frac{1}{\sqrt{m_{i}m_{j}}} \frac{\partial^{2}U}{\partial u_{i}\partial u_{j}},$$
(10)

where m_i is the mass and u_i is the displacement of atom *i*, using automatic differentiation.

The Tersoff potential for the 1D chain is tweaked in such a fashion that it produces degenerate double well minima in the potential energy surface as shown in Fig. 6. This means that the central atom D prefers to sit more closer to either of the identical nearest neighbors, L and R, than in the central position. This behavior mimics the one observed with the T_d to C_{3v} symmetrybreaking relaxation around the $B_{C}^{(0)}$ defect in 3C-SiC, where the B atom relaxes slightly off center and closer to one of the Si atoms in the first nearest neighbor Si atom tetrahedron around it, see Fig. 4a. Keeping all other parameters fixed, we change the value of B to get different atomic relaxations as shown in Fig. 6. As can be seen in Fig. 6, successive increases in the value of bond-strength parameter, B, result in the two minima of the double well potential moving closer and the barrier decreasing, in agreement with the Bell-Evans-Polanyi principle. The perturbation matrix with the largest norm is found at B = 0.34 (green line) after which the potential energy landscape reduces to a single well minimum.

The lowering of the transition barriers in Fig. 6 with increasing *B* strongly modifies the curvature of the potential energy landscape. This corresponds to an increase in perturbation of the force constants as compared to the perfect system, shown as the Frobenius norm of the **V** matrix $(||\mathbf{V}||_F)$. $||\mathbf{V}||_F$ is maximum for the green curve, after which it falls down again as there is a single minima in the potential energy surface. This is reflected in the presence of resonant scattering in the 1D chain, Fig. 7a for the green line which represents the potential with an almost negligible transition barrier. Also shown in Fig. 7b is a distinct peak in the imaginary part of the trace of the T matrix at near zero frequency.

An alternative measure of phonon scattering in the 1D chain is the phonon reflectivity (R),³⁰ *i.e.*, the fraction of the energy carried by phonons that is reflected at a given frequency. For a system with only one phonon branch it is expressed as

$$R_q = \frac{\left|\left\langle \psi_q^* | \mathbf{T}_q | \psi_q \right\rangle \right|^2}{\left| 2\omega_q v_q \right|^2},\tag{11}$$

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where ψ_q and v_q are the wave function and group velocity for a particular wave vector q, respectively. Fig. 7c can be understood with the help of the perturbed Green's functions, calculated according to eqn (2), and shown in Fig. 5. Just like the imaginary part of the trace of the unperturbed Green's function, \mathbf{g}^+ , corresponds to the DOS of the unperturbed system, Fig. 5b, the imaginary part of the trace of the block of \mathbf{G}^+ pertaining to the defect atoms gives us the projected density of states (pDOS) of the perturbed system. As expected the peak in \mathbf{G}^+ aligns well with peak in the trace of the **T** matrix, Fig. 7b.

Availability of phonon modes around the defect atoms is a necessary but not sufficient condition for them to couple with the incoming phonons from the bulk. A low projected DOS around the defect atoms in the perturbed system will thus lead to a higher reflectivity of the incoming phonons. Fig. 5(b) shows how the peak of the projected DOS moves to lower frequencies as the perturbation increases in Fig. 6 and only phonon modes which are close to a rigid translation can pass through the defective segment. The same kind of correlation between pDOS and reflectivity can be observed in the non-resonant cases by comparing Fig. 5(b) with Fig. 7c: the increased density of states in the range $\omega \in [0.5, 0.7]$ leads to a steep fall in the reflectivity in that regime. In contrast, the exceptionally high reflectivity of the green curve in Fig. 7c at very low frequencies is caused by the corresponding peak in the T matrix and unavailability of phonon modes at higher frequencies, see Fig. 5(b) green line.

4 Conclusion

The phonon scattering due to the B_C^{-1} , $B_C^{(0)}$, $N_C^{(0)}$ and $N_C^{(+1)}$ point defects in tetrahedrally bonded diamond and 3C-SiC is calculated using a T-matrix formalism. With the help of a simple 1D monoatomic chain we show that a resonance occurs when the defect relaxes in a way that produces a very small lattice distortion. Such a small lattice distortion leads to a strong perturbation of the potential energy surface surrounding the defect. The consequent strong IFC perturbation results in resonant scattering. This behavior is observed for the $B_C^{(0)}$ defect in 3C-SiC which undergoes a small lattice distortion during the T_d to C_{3v} transition upon relaxation. A similar distortion by the $B_C^{(0)}$ defect in diamond fails to cause any resonance, due to low density of states in diamond.

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We conclude that in tetrahedrally bonded semiconductors, dopants which cause a rather small lattice distortion due the T_d to C_{3v} transition might result in significantly higher phonon scattering as compared to the ones that undergo large lattice distortions or relax symmetrically. The intuitive picture of IFC perturbations developed with the help of the 1D chain could help understand how the dopants effect the local bonding environment in other systems. The insight developed into the fundamentals of resonant phonon scattering by point defects with the help of the 1D-chain model can also help in identifying superscatterers so that their presence in the system could be controlled more effectively. More generally, this could enhance our understanding of the use of dopants to achieve desired properties in device design.

Conflicts of interest

There are no conflicts to declare.

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Communications

Research Letter

Ab initio lattice thermal conductivity of bulk and thin-film α-Al₂O₃

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Abstract

The thermal conductivities (κ) of bulk and thin-film α -Al₂O₃ are calculated from first principles using both the local density approximation (LDA) and the generalized gradient approximation (GGA) to exchange and correlation. The room temperature single-crystal LDA value ~39 W/m K agrees well with the experimental values ~35–39 W/m K, whereas the GGA values are much smaller ~26 W/m K. Throughout the temperature range, LDA is found to slightly overestimate κ , whereas GGA strongly underestimates it. We calculate the κ of crystalline α -Al₂O₃ thin films and observe a maximum of 79% reduction for 10 nm thickness.

Corundum (α -Al₂O₃) is a material of high technological importance due to its varied applications such as dielectric insulators in complementary metal-oxide semiconductor (CMOS) devices, substrate for growing silicon and gallium nitride, hightemperature structural ceramics, anti-corrosive coatings, and optical devices. This can be attributed to its excellent mechanical strength, high-temperature thermal stability, large band gap (8.8 eV), and high dielectric constant (9.0).^[1,2] In spite of its widespread usage, most research has focused on its electrical^[3,4] and chemical^[5,6] interface properties.

Thermal device design, on the other hand, is of utmost importance as the CMOS transistor gate lengths are scaled below 45 nm.^[7] InGaAs-based MOS stacks supported on Al₂O₃ have recently been shown to present better breakdown characteristics due to the high thermal conductivity of Al₂O₃.^[8] Nevertheless, the latest measurements on the thermal conductivity of single-crystal^[2] and amorphous thin films^[9,10] of Al₂O₃ are almost two decades old and are in contradiction with earlier results.^[11] Effect of grain size and impurity phonon scattering on κ in polycrystalline α -Al₂O₃ has also been studied.^[12] There are some recent studies on thermal transport in polycrystalline porous alumina layers, and membranes.^[13–15] However, there are no computational studies of the thermal conductivities of bulk and thin-film Al₂O₃, and in this study we fill this gap.

We report the calculated bulk, and the in-plane and crossplane thin-film lattice thermal conductivities (κ_1) of α -Al₂O₃ with varying cross-sections. κ_1 calculated using the full iterative solution to the Boltzmann transport equation (BTE) and the relaxation time approximation (RTA) agree well with each other. From now on κ_1 is simply referred as κ . For the bulk single crystals, we find a value of ~39 W/m K for LDA at 300 K, which is consistent with the experimental values of $\sim 35^{[2]}$ and ~ 39 W/m K,^[11] whereas the GGA value ~ 26 W/m K is considerably smaller. For the thin films, it is found that the reduction in κ already sets in around 40 µm and for a 10 nm film thickness $\sim 79\%$ reduction is observed.

The thermal conductivity tensor, $\kappa^{\alpha\beta}$, is calculated by carrying out the full BTE computations, i.e., solving the linearized BTE while accounting for all scattering terms as^[16]:

$$\kappa^{\alpha\beta} = \sum_{\lambda} C_{\lambda} v_{\lambda}^{\alpha} F_{\lambda}^{\beta}, \qquad (1)$$

where α and β are the Cartesian coordinates and λ comprises of both the phonon branch index *j* and wave vector **q**. C_{λ} is the mode λ contribution to the specific heat, *v* the group velocity and *F* is the solution of the linearized BTE written in the form:

$$\mathbf{F}_{\lambda} = \tau_{\lambda} (\mathbf{v}_{\lambda} + \mathbf{\Delta}_{\lambda}). \tag{2}$$

In Equation (2), τ_{λ} is the lifetime of mode λ . $\tau_{\lambda} \mathbf{v}_{\lambda}$ is the RTA phonon mean free path and Δ_{λ} accounts for the deviation of the population of a specific phonon mode from the RTA prediction. The detailed expression for Δ_{λ} and the full iterative solution to the BTE can be found in Ref. 17.

Considering the Taylor series of the potential energy up to the third-order term, the total scattering rate τ^{-1} is calculated as a sum of the contributions from inelastic three-phonon and elastic two-phonon scattering processes as:

$$\tau^{-1} = \tau_{3ph}^{-1} + \tau_{2ph}^{-1}.$$
 (3)

The expressions for the three-phonon scattering rates as well as the isotopic contribution to the two-phonon scattering can be

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found in Refs. 17 and 18, respectively. In the present work, only isotope scattering is considered, but in a more general scenario, other contributions to the two-phonon elastic scattering can come from, for example, point defects,^[19,20] nanoparticles,^[21] and dislocations.^[22]

The in-plane (\parallel) and cross-plane (\perp) effective thin-film RTA thermal conductivities are calculated according to the methodology developed in Ref. 16, as:

$$\kappa_{\rm eff}(I) = \sum_{\lambda} S_{\lambda}(I) C_{\lambda} |\mathbf{v}_{\lambda}| \Lambda_{\lambda} \cos^2 \Theta_{\lambda}.$$
(4)

Here *I* is the film thickness, $\Lambda(T) = |\mathbf{v}| \pi(T)$ the mean free path, and Θ is the angle between the group velocity and the transport axis. The suppression function, *S*, accounts for the additional phonon scattering induced by the film boundaries. We account for the crystal anisotropy by evaluating the wavevector-resolved *S* on a mode-by-mode basis, as discussed in Ref. 16. For the in-plane transport, the Cartesian vector \mathbf{n} , which denotes the film normal, is perpendicular to the vector \mathbf{u} along which the thermal transport is to be evaluated (see inset Fig. 4), whereas for the cross-plane transport, the two are parallel to each other.

For the in-plane transport, S is defined according to the Fuchs–Sondheimer formalism as^[16]:

$$S_{\parallel} = \frac{1 - p \exp(-1/K_{\parallel}) - (1 - p)K_{\parallel}[1 - \exp(-1/K_{\parallel})]}{1 - p \exp(-1/K_{\parallel})},$$
(5)

where $K_{\parallel} = \hat{\Lambda}_{\pm}/I$ is the effective Knudsen number and $0 \le p \le 1$ the specularity, meaning that for p = 0 the film boundaries act as perfectly absorbing black bodies, whereas p = 1 would denote perfectly reflective boundaries. The calculations are carried out in a transformed coordinate system as explained in Ref. 16 and the symbol ^ corresponds to quantities expressed in transformed coordinates. Similarly, for the cross-plane transport where the film boundaries are considered to act as perfectly absorbing black bodies, the suppression function takes the form:

$$S_{\perp} = \frac{1}{1 + 2K_{\perp}} \tag{6}$$

and the Knudsen number is simply evaluated without the need for coordinate transforms as, $K_{\perp} = \Lambda |\cos\Theta|/I$.

The total energy as well as the force calculations are done using the projector-augmented-wave method^[23] as implemented in the VASP code,^[24] with both the local density approximation (LDA)^[25] and the generalized gradient approximation (GGA) to exchange and correlation. For GGA the Perdew–Burke–Ernzerhof exchange and correlation functional^[26] is used. The experimental and calculated equilibrium lattice parameters for α -Al₂O₃ are shown in Table I.

The atomic positions and the volume of the unit cell for both LDA and GGA structures are relaxed until the energy and the forces are converged up to 10^{-8} eV and 10^{-7} eV/Å, respectively. The second- and third-order interatomic force constants (IFCs)

Table I. Lattice parameters for $\alpha\text{-}Al_2O_3.$ The LDA and GGA values are from this work.

| | <i>a</i> (Å) | α | Vol (Å ³) |
|---------------------|--------------|--------|-----------------------|
| Exp ^[27] | 5.13 | 55.28° | 84.89 |
| LDA | 5.10 | 55.36° | 83.50 |
| GGA | 5.18 | 55.31° | 87.52 |
| | | | |

are extracted using $4 \times 4 \times 4$ and $3 \times 3 \times 3$ supercells, containing 640 and 270 atoms, respectively, of the rhombohedral primitive cell, using just the Γ -point. For the second-order IFC calculations, we use the Phonopy^[28] software package, and for the third-order IFCs, we use our in-house code thirdorder.py.^[17] The bulk thermal conductivity is calculated using a $18 \times 18 \times 18$ *q*-point mesh for both LDA and GGA calculations using our in-house code ALMABTE.^[16] As α -Al₂O₃ is polar, a non-analytical correction is added to the dynamical matrix to correctly reproduce the LO–TO splitting (see Fig. 2).^[29]

 α -Al₂O₃ belongs to the trigonal crystal system and has space group R_3^2c [167]. In the conventional description, its crystal structure is composed of six molecular units (30 atoms) and can be described as a nearly close-packed ABAB stacking of oxygen ions. The aluminium ions occupy two-thirds of the octahedral interstitial sites along the *c*-axis (a_3^c) of the hexagonal coordinate system, i.e., the [0001] direction. The primitive unit cell is composed of two molecular units of Al₂O₃ (ten atoms). The relationship between the two lattices can be seen in Fig. 1. The lattices are oriented in such a fashion that the [0001] direction of the conventional lattice and the [111] direction of the primitive lattice are both parallel to the *z* direction in the Cartesian coordinate system.

The calculated LDA and GGA phonon band structures and the corresponding density of states of α -Al₂O₃ are shown in Fig. 2. We get an excellent agreement of the LDA dispersion with the inelastic neutron scattering dispersion, as also obtained earlier by Heid et al.^[30] The LDA frequencies are significantly higher than the GGA values at the Brillouin zone boundaries. This agrees with the fact that the LDA relaxed structure volume is ~5% smaller than GGA (Table I). It is also seen that the slope of the graphs along the Γ -*Z* and Γ -*X* directions which correspond to the group velocities along the a_3^c and the a_1^c axes, respectively, are only slightly different. This small difference in the group velocities is also reflected in a small anisotropy in the thermal conductivity values along the respective directions, as we will see later.

Figure 3 shows the calculated BTE and experimental thermal conductivities of α -Al₂O₃. Our values are in very good agreement with the single-crystal experimental values in the literature.^[2,11] The relatively more recent single-crystal values by Cahill et al.^[2] are found to be in better agreement to the LDA values than GGA. Whereas, for the earlier results compiled by Slack,^[11] a good agreement with LDA is found up till

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Figure 1. Crystal structure of a-Al₂O₃ in the conventional (black) and primitive (blue) lattices, with a_1^p , a_2^p , and a_3^p being the primitive lattice vectors and a_1^c , a_2^c , and a_3^c being the conventional lattice vectors.

room temperature. For higher temperatures, the Slack data fall off more rapidly than both the LDA and the more recent experimental results. This high-temperature deviation can be seen as a difference in the experimental techniques used for different temperature regimes in the results compiled by ${\rm Slack}.^{[11]}$ It should also be noted that some of these high-temperature values are even lower than the κ of 90% dense polycrystalline samples measured by Smith et al.,^[13] which is unrealistic. Williams et al.^[12] measured the κ for a sample of 99.3% dense polycrystalline α -Al₂O₃ with a grain size of 7.2 µm and obtained a value of 31.7 W/m K at 303 K, Fig. 3. However, with our LDA calculations, this reduction is only observed for a grain size of 0.5 µm. The agreement of the experimental thermal conductivity values with the LDA results is also in line with the excellent agreement of the LDA and experimental phonon dispersions (Fig. 2). Earlier calculations by some of us have also shown better agreement of LDA thermal conductivities with the experimental ones as compared with those obtained with GGA.^[32]

Throughout the temperature range, the experimental values lie between the LDA and GGA values. As can be seen in Table I, the LDA lattice volume is smaller than the experimental one which is again smaller than that obtained with GGA. This translates to LDA having stronger interatomic interactions and larger second- and third-order IFCs. The influence on κ will thus be a competition between the increased group velocities and third-order scattering rates. In the present case, we do indeed find a lower thermal conductivity with phonon softening (Fig. 2) whereas, in other cases, even a slight increase in κ has been found in connection with phonon softening.^[33]



Figure 2. LDA and GGA phonon bandstructure and density of states (DOS) of α -Al₂O₃. The black dots are the data from the inelastic neutron scattering experiments from Ref. 31.

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Figure 3. Effective thermal conductivity ($\kappa_{eff} = Tr(\kappa^{\alpha\beta})/3$) of α -Al₂O₃ compared with the experimental results. The black and the yellow dots are the single-crystal data from Cahill et al.^[2] and Slack.^[11] respectively. The red crosses are for the 99.3% dense polycrystalline samples from Williams et al.,^[12] whereas the gray crosses are for 90% dense polycrystalline samples from Smith et al.^[13]

The room temperature LDA in-plane and cross-plane thermal conductivities of α -Al₂O₃ for thicknesses varying from 10 nm to 100 µm are shown in Fig. 4. We find that for crossplane transport along the a_3^c axis (green curve with plus signs) reduction in κ starts already around 20–30 µm film thickness. A 50% reduction is observed at ~80 nm, where as ~80% is observed at 10 nm film thickness. It can be observed that the cross-plane reduction in κ is much higher than the in-plane reduction. This is a direct consequence of the fact that the suppression function (*S*), by its construction, contributes more to



Figure 4. Thermal conductivity of α -Al₂O₃ films calculated at p = 0.2. The green and purple curves correspond to the calculations with transport axis being parallel to, and perpendicular to the α -axis of the conventional cell in Fig. 1, respectively. The open circles correspond to the in-plane transport, whereas the plus signs denote the cross-plane transport as shown by the corresponding **u** vectors in the inset.

the scattering in the cross-plane direction than the in-plane direction.

The bulk values for transport along both the a_3^c axis and the basal plane are recovered for ~40 µm film thickness. We observe that the ratio of thermal conductivity along the a_3^c axis to the one in the basal $a_1^c - a_2^c$ plane is 1.1 which agrees well with the experimental value at 300 K.^[11] This slight anisotropy in the κ values is related to the aforementioned small difference in the group velocities along the a_1^c and a_3^c axes.

In conclusion, we have reported the first-principles calculations of the bulk, and in-plane and cross-plane lattice thermal conductivities of α -Al₂O₃ for varying film thicknesses. The LDA values are 1.5–1.8 times higher than GGA values throughout the temperature range. A very good agreement between the LDA values and the recent experimental values by Cahill et al.^[2] was found. We have calculated the thin-film thermal conductivities of crystalline α -Al₂O₃ for thicknesses varying from 100 µm to 10 nm. A maximum of ~79% reduction was observed in κ for 10 nm film thickness.

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Comparison of the Green–Kubo and homogeneous non-equilibrium molecular dynamics methods for calculating thermal conductivity

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Abstract

Different molecular dynamics methods like the direct method, the Green–Kubo (GK) method and homogeneous non-equilibrium molecular dynamics (HNEMD) method have been widely used to calculate lattice thermal conductivity (κ_{ℓ}). While the first two methods have been used and compared quite extensively, there is a lack of comparison of these methods with the HNEMD method. Focusing on the underlying computational parameters, we present a detailed comparison of the GK and HNEMD methods for both bulk and vacancy Si using the Stillinger–Weber potential. For the bulk calculations, we find both methods to perform well and yield κ_{ℓ} within acceptable uncertainties. In case of the vacancy calculations, HNEMD method has a slight advantage over the GK method as it becomes computationally cheaper for lower κ_{ℓ} values. This study could promote the application of HNEMD method in κ_{ℓ} calculations involving other lattice defects like nanovoids, dislocations, interfaces.

Keywords: Green-Kubo, HNEMD, Stillinger-Weber, thermal conductivity, vacancies

(Some figures may appear in colour only in the online journal)

1. Introduction

Due to miniaturization of devices, increasing thermal loads and higher efficiency demands there is an ever-growing demand for materials with tailored thermal conductivities (κ) [1]. On one hand, devices like high power semiconductor electronic devices and lasers require high κ

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for efficient heat removal which is critical to their performance. On the other hand, very low κ is required in thermoelectric devices whose performance is inversely proportional to κ .

In semiconductors and insulators κ is dominated by the lattice part κ_{ℓ} . Classical molecular dynamics (MDs) simulations are a powerful tool for calculating κ_{ℓ} due to their atomic resolution that helps to understand the underlying mechanisms leading to a specific κ_{ℓ} . The conceptually simplest MD method for calculating κ_{ℓ} is the direct method [2–6] where a temperature gradient is applied over a simulation box and the thermal conductivity is extracted from Fourier's law. However, the temperature gradients that must be applied are orders of magnitude larger than in experiments. Furthermore, the long mean free paths of the low frequency phonons make it difficult to converge the results [7].

An alternate MD method for calculating κ_{ℓ} is the Green–Kubo (GK) method [8]. The GK method applies linear response theory to the fluctuations of the heat current in a homogeneous equilibrium system. It requires integration of the auto-correlation function, which makes the method numerically challenging to apply. Another technique called homogeneous non-equilibrium molecular dynamics (HNEMD) circumvents the calculation of the auto-correlation function. The HNEMD method was initially proposed by Evans to calculate κ_{ℓ} [9], who applied it to systems with pairwise interactions. The technique was subsequently applied to study systems with higher-order interactions among the particles [10–12].

To design materials with desired thermal conductivities, understanding the effects of defects is of prime importance. Defects like vacancies, dislocations, interfaces etc are inevitably present in materials of technological interest. Such defects break the symmetry of the crystal structures and scatter the phonons thereby affecting the energy transported by phonons in solids. Vacancies in particular are very important because of their high concentrations at elevated temperatures. They act both as a large mass perturbation and perturb the bonding in the lattice and therefore strongly effect κ_{ℓ} [13–16].

There has not been a systematic comparison of HNEMD with other methods in literature. In this work we fill this gap by doing a systematic comparison of the GK and HNEMD methods in terms of their computational efficiencies and statistical errors when calculating κ_{ℓ} . We perform calculations on both bulk-Si and Si with varying concentrations of vacancies using the Stillinger–Weber (SW) potential [17].

2. Background

In order to calculate κ_{ℓ} with the GK and HNEMD methods, calculation of the heat current is essential. The heat current J is a vector quantity that characterizes the change with time of the spatial average of the local energy and is given as

$$\boldsymbol{J} = \frac{1}{\Omega} \frac{\mathrm{d}}{\mathrm{d}t} \sum_{i} \boldsymbol{r}_{i}(t) \epsilon_{i}(t), \tag{1}$$

where Ω is the volume of the system and ϵ_i and \mathbf{r}_i are the total energy [2] and coordinate vector of atom *i*.

2.1. The GK method

The GK method [18, 19] is an equilibrium MDs approach that relates J to κ_{ℓ} via the fluctuation-dissipation theorem,

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$$\kappa_{\ell} = \frac{1}{k_{\rm B} V T^2} \int \langle \boldsymbol{J}(0) \otimes \boldsymbol{J}(t) \rangle \mathrm{d}t, \qquad (2)$$

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where, $k_{\rm B}$ is the Boltzmann constant, V the volume of the system, T the temperature and $\langle J(0) \otimes J(t) \rangle$ the heat current auto-correlation function (HCACF). In general, κ_{ℓ} is a second-order tensor but in a material with cubic symmetry it reduces to a scalar. The discretized form of the HCACF, equation (2), is given as

$$\kappa_{\ell} = \frac{\Delta t}{k_{\rm B} V T^2} \sum_{m=1}^{M} \sum_{n=1}^{N-m} \frac{J(m+n)J(n)}{N-m},\tag{3}$$

where Δt is the length of a single MD timestep and *M* determines the length of the correlation time given by $M\Delta t$ over which the integration is done. J(m + n) is the heat current at MD timestep m + n. It should be noted that the number of integration steps *M* must be less than the total number of simulation steps *N*.

Two potential errors can arise while calculating κ_{ℓ} via equation (3). First of all, the correlation function $\langle J(0) \otimes J(t) \rangle$ is usually calculated as a time-average from the data of a single simulation and using a finite averaging time $\tau_N = N\Delta t$ in equation (3) which leads to an averaging error. Secondly, there is a truncation error related to *M*. Ideally *M* should be so that the HCACF has decayed to zero [2]. Too small *M* would underestimate κ_{ℓ} and a too large value would lead to large statistical errors as the heat current is dominated by noise after a certain correlation time [20].

2.2. Homogeneous non-equilibrium MDs

In HNEMD a fictitious force field is used to mimic the effect of a thermal gradient. It uses the linear response theory to calculate the transport coefficients in which the long-time ensemble average of the heat current vector, $\langle J(t) \rangle$, for the resulting non-equilibrium system can be shown to be proportional to the external force field, F_e , when the latter is sufficiently small [9, 21].

The detailed implementation of the HNEMD method for systems governed by three-body potentials can be found in [12]. The equation to consider is,

$$\frac{\langle \boldsymbol{J}(t)\rangle}{VT} = \left[\frac{1}{k_{\rm B}VT^2} \int_0^\infty \langle \boldsymbol{J}(0) \otimes \boldsymbol{J}(t)\rangle \mathrm{d}t\right] \boldsymbol{F}_{\rm e} = \kappa_\ell \boldsymbol{F}_{\rm e}.$$
(4)

It shows a linear relationship between the external perturbation field F_e and the induced heat current J(t). The constant of proportionality (κ_l) is the GK formula for the heat transport coefficient tensor, equation (2). In this way, the thermal conductivity can be obtained without explicitly calculating the auto-correlation functions. Hence, one can circumvent the problems related to the calculation and integration of autocorrelation functions associated with the GK method described above.

3. Results and discussion

We carried out all the simulations in silicon system on a $6 \times 6 \times 6$ supercell containing 1728 atoms and with a lattice parameter of 5.431 Å using the SW potential [17] and the LAMMPS package [22]. The choice of the parameters was based on previous finite size dependence studies done on silicon using MD techniques [2, 20, 23]. In each simulation, after the velocity initialization the system was equilibrated under zero pressure at 1000 K (NPT ensemble).



Figure 1. (a) Representative HCACF for Si (SW potential) as a function of $\tau_M = M\Delta t$, normalized to the value at t = 0 (Blue line). (b) Thermal conductivity of Si calculated by the direct integration of the HCACF, with the redline showing τ_c . The blue line depicts the averaged thermal conductivity over 5 independent simulations (green lines). Also shown in the inset is κ_ℓ calculated for the total correlation time of 300 ps and error bars can be seen growing rapidly after 65 ps (red line) because of the calculations being dominated by noise.

3.1. Bulk conductivity

From the GK method the thermal conductivity was obtained through equation (3). The HCACF was sampled at every timestep for better accuracy of the correlation integral. The simulations were then run in the NVE ensemble for the calculation and sampling of the HCACF. A time step of $\Delta t = 1.0$ fs was chosen to ensure long-time stability of the HCACF.

The averaging error can be minimized either by performing one simulation for a very large number of time steps or by carrying out multiple independent simulations for smaller time durations. We have applied the latter technique in which the simulations can be run in parallel and we collected a total of 60 ns of data comprising of 5 independent simulations of N = 12 ns (12×10^6 timesteps) each. These independent simulations vary only with respect to the random seed provided for generating the initial atomic velocities [2, 20]. The total correlation length for a single simulation was 300 ps (3×10^5 timesteps).

In order to minimize the truncation error, we employed the idea of a maximum significant correlation time (τ_c) [24] to determine an optimum *M*. Figure 1(a) shows the ensemble averaged HCACF together with the noise (green line) which is estimated as the root mean square of the heat current cross-correlation functions [20],

$$\zeta = \sqrt{\frac{\langle J_x(t)J_y(0) \rangle^2 + \langle J_y(t)J_z(0) \rangle^2 + \langle J_z(t)J_x(0) \rangle^2}{3}}.$$
(5)

 τ_c is the time after which the noise crosses and becomes larger than the HCACF and is shown as a red line in figure 1(a). The HCACF can be seen to decay and at $\tau_M \equiv \tau_c \simeq 65$ ps (red line) the noise overtakes the HCACF.

Next, κ_{ℓ} was calculated by direct integration of the HCACF. Figure 1(b) shows the value of κ_{ℓ} versus the correlation time. The integration till $\tau_c = 65 \text{ ps}$ gives a value of $49.6 \pm 1.5 \text{ W} (\text{m K})^{-1}$. This value is in good agreement to the other GK calculations $53.3 \pm 5.2 \text{ W} (\text{m K})^{-1}$ [4, 24], lower than but consistent with $66 \pm 16 \text{ W} (\text{m K})^{-1}$ [2]. It is also slightly lower than $53 \pm 3 \text{ W} (\text{m K})^{-1}$ reported by Howell *et al* [20] because they

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Figure 2. The running average of components of the heat current **J** in the x, y and z directions for Si with $F_{\rm e} = 8 \times 10^{-5} \text{ Å}^{-1}$ applied in the x direction.

calculated κ_{ℓ} by integrating till ∞ an exponential function fitted to the values of κ_{ℓ} averaged over five independent samples. They mentioned that the contribution to the total value of κ_{ℓ} by correlation times greater than τ_c is <5%. Recently, Jones *et al* [24] proved that the relative error in the estimate of κ_{ℓ} is bounded by the ratio of maximum significant correlation time (τ_c) and the total simulation time *K* as $2\sqrt{\tau_c/K}$, which in our case reduces to $\approx \sqrt{M/N}$. This limits the relative error to be less than 6.5%, which is consistent with our results.

From the HNEMD method the thermal conductivity was obtained through equation (4). A time-independent external perturbation field F_e was applied in the *x* direction. The calculations were carried out for a total of 22 F_e values ranging from 1×10^{-5} to 3×10^{-4} (Å⁻¹) at 1000 K for 5×10^6 time steps each of duration of 0.55 fs and running averages of the heat currents were collected for each simulation. Figure 2 shows the behavior of the running average of the heat current with the external perturbation field, $F_e = 8 \times 10^{-5}$ Å⁻¹. As can be seen in the figure, the initial fluctuations of heat current are very high and they stabilize at ≈ 2000 ps. Consequently, we choose to cut off sampling $\langle J \rangle$ at t = 2750 ps. This lead to a bulk thermal conductivity of 53.4 W (m K)⁻¹ at 1000 K, see figure 3(a). Cutting the sampling at t = 2400 ps lead to $\kappa_{\ell} = 52.6$ W (m K)⁻¹, underlining that the results are well converged.

We have considered two methods for calculating κ_{ℓ} from $\langle J(t) \rangle$. In the gradient method the slope of a least-squares fit of $\langle J_x(t) \rangle / VT$ versus F_e is identified as the thermal conductivity, equation (4). We assume that the intercept is zero. In the mean method κ_{ℓ} is calculated by averaging the κ_{ℓ} 's obtained from several individual runs with varying F_e . For bulk-Si, the values of thermal conductivity calculated by the gradient and mean methods are $\kappa_{\ell} = 53.4 \pm 1.9 \text{ W (m K)}^{-1}$ figure 3(a) and $53.2 \pm 6.7 \text{ W (m K)}^{-1}$ figure 3(b), respectively. The values are in good internal agreement the GK calculations as well as the earlier HNEMD calculations [12].

One observation is that the determination of the range where κ_{ℓ} depends linearly on F_e is important. For the bulk-Si runs, it can be seen in figure 3(a) that the values of κ_{ℓ} deviate strongly from a linear behavior for $F_e > 2 \times 10^{-5} \text{ Å}^{-1}$. The other possible shortcoming of the HNEMD method is that it is inefficient for very small values of F_e . At very small values of F_e all the three components of J are almost equal suggesting that the system is still in equilibrium. Due to this, the estimation of the ratio $\langle J(t) \rangle / TF_e$ becomes very difficult, as $\langle J_x(t) \rangle$ approaches zero for these values. Hence, it is crucial to determine a range of F_e that is large enough to obtain reasonable values of $\langle J_x(t) \rangle / TF_e$ and small enough for the system to be

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Figure 3. (a) Running average of heat current J as a function of F_e in bulk (red) and defected Si with five randomly distributed vacancies (green). The thermal conductivity is obtained via the gradient method. (b) κ_{ℓ} as a function of F_e used to obtain the thermal conductivity via the mean method for both bulk and vacancy Si.

in the linear non-equilibrium range [12]. A fine scan over different values of F_e is required to correctly estimate κ_{ℓ} .

3.2. Influence of vacancies on κ_{ℓ} of Si

In order to compare the performance of GK and HNEMD methods in defected structures, we carried out κ_{ℓ} calculations for 1 to 10 (0.06–0.57 atomic %) randomly distributed vacancies in the 6 × 6 × 6 Si supercell (1728 atoms in bulk) at 1000 K. To minimize the interaction of vacancies among themselves, the vacancies were distributed in such a manner that no two vacancies were within the second nearest neighbor distance of one another.

Although, both the methods agree well in terms of thermal conductivity predictions for defect structures, figure 4(a), we would like to point out that for the defected structures the calculation of κ_{ℓ} becomes easier with HNEMD method. This is illustrated as follows. In section 3.1 we saw that one of the shortcomings of the HNEMD method is the difficulty in determining the linear range of $\langle J_x(t) \rangle/VT$ versus F_e . However, in our calculations for defected Si, we observed that as the vacancy concentration increases $\langle J_x(t) \rangle/VT$ versus F_e remains linear for higher and higher values of F_e . This can be observed in figure 3(a) which shows a comparison of the linear regimes in bulk and defected Si. It can be clearly seen in figure 3(a) that one has to do a fine scan over F_e values in case of bulk to find out the exact linear range. The relation between $\langle J_x(t) \rangle/VT$ and F_e becomes nonlinear already around $F_e = 2 \times 10^{-5} \text{ Å}^{-1}$, whereas in case of defect structure the plot is still linear for values as high as $40 \times 10^{-5} \text{ Å}^{-1}$. This behavior is also illustrated in figure 3(b) where, for bulk the κ_{ℓ} values deviate for higher F_e whereas for the defected structure they are stable. Hence, in case of defected structures one can obtain the linear range and therefore κ_{ℓ} using fewer values of F_e thereby reducing the computational cost.

We found an inverse power-law like decay of κ_{ℓ} against the vacancy concentration, *c*, for both GK and HNEMD methods confirming a good agreement between the two methods, figure 4(a). Following the discussion above, we performed κ_{ℓ} calculations at 700 K using only HNEMD method. An inverse power-law decay for κ_{ℓ} versus *c* was also observed at 700 K, as shown in figure 4(b). We also tried to fit exponential functions to κ_{ℓ} 's but the standard deviation for the fit values was orders of magnitude higher than the power-law fit.



Figure 4. (a) Comparison of GK and HNEMD methods with regards to κ_{ℓ} versus vacancy concentration for Si at 1000 K. (b) κ_{ℓ} versus vacancy concentration for Si at 700 K.

Hence we can establish that the thermal conductivity falls according to inverse power-law with increasing vacancy concentration in crystalline Si. Our results agree well the literature [14, 16, 25].

4. Conclusions

We have done a detailed study of the GK and HNEMD methods for calculating κ_{ℓ} in bulk and defected Si and highlighted the advantages and disadvantages of each method. We have discussed the underlying parameters of the two methods and shown that by a judicious choice both the methods performed equally well for κ_{ℓ} calculations in bulk Si. The GK method in the above fashion produces very accurate values of thermal conductivity within statistical uncertainties. With the GK method the entire lattice thermal conductivity tensor can be calculated from one simulation, unlike the HNEMD method which necessitates several simulations in each direction to achieve the same. At the same time the GK method can suffer from averaging and truncation errors which makes it more cumbersome than the HNEMD method. Both the GK and the HNEMD method require several independent simulations to get a κ_{ℓ} with a low uncertainty. These simulations in the respective methods are not interdependent and can be run in parallel. The HNEMD method has an advantage over the GK method as it generates lesser statistical errors and reduces the necessary computation time by combining the elements of both equilibrium and non-equilibrium MD simulations. Specially in case of defect structures HNEMD can be advantageous.

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title Predictive calculation of point-defect phonon scattering in semiconductors

supervisors Uni. Prof. Georg K. H. Madsen and Univ. Prof. Dr. Ernst Kozeschnik description Calculation of the point defect scattering rates in semiconductor devices in a predictive manner using the inhouse almaBTE package. Ab initio interatomic forces are used to compute the force-constants of the perfect and defect-laden systems, which are then used as inputs to obtain the scattering rates in T-matrix atomistic

Master thesis

Green's functions approach.

thermal conductivity of bulk and vacancy silicon.

title The effect of a vacancy on the thermal conductivity of Stillinger-Weber silicon

supervisors Uni. Prof. Georg K. H. Madsen and Prof. Ralf Drautz description Comparison of Green-Kubo and HNEMD molecular dynamics methods for calculating

Publications

- o "Exceptionally Strong Phonon Scattering by B Substitution in Cubic SiC"; A Katre, J Carrete, B Dongre, GKH Madsen, and N Mingo; Physical Review Letters 119 (7), 075902 [2017]
- o "Resonant phonon scattering in semiconductors"; B Dongre, J Carrete, A Katre, N Mingo, and GKH Madsen; Journal of Materials Chemistry C 6 (17), 4691-4697 [2018]

- "Extrinsic doping of the half-Heusler compounds"; <u>R Stern</u>, **B Dongre**, GKH Madsen; *Nanotechnology* 27 (33), 334002 [2016]
- "Ab initio lattice thermal conductivity of bulk and thin-film α-Al₂O₃"; <u>B Dongre</u>, J Carrete, A Katre, N Mingo, and GKH Madsen; MRS Communications 8 (3), 1119-1123 [2018]
- "Comparison of the Green-Kubo and homogeneous non-equilibrium molecular dynamics methods for calculating thermal conductivity"; <u>B Dongre</u>, T Wang, <u>GKH Madsen</u>; *Modelling and Simulation in Materials Science and Engineering* 25 (5), 054001 [2017]

Selected Talks and Poster Presentations

- Talk: "Resonant phonon scattering in semiconductors"; B Dongre, J Carrete, A Katre, N Mingo, and GKH Madsen; Proceedings of MRS Spring Meeting; 02-06/04/2018; Phoenix, USA
- Talk: "Resonant phonon scattering in semiconductors"; B Dongre, J Carrete, <u>A Katre, N Mingo, and GKH Madsen</u>; 33. WORKSHOP Novel Materials and Superconductivity; 11-17/02/2018; Bundessport und Freizeitzentrum (BSFZ) Obertraun, Austria
- Talk: "Point defect phonon scattering and thermal conductivity in Silicon"; <u>B</u> <u>Dongre</u>, and GKH Madsen; *Proceedings of DPG Spring Meeting*; 19-24/03/2017; Dresden, Germany
- POSTER: "Predictive all-scale lattice thermal conductivity"; <u>B Dongre, T</u> Wang, and GKH Madsen; 612. WE-Heraeus-Seminar on Electrons and phonons:Interfaces and interactions; 03 - 06/04/2016; Physikzentrum Bad Honnef, Germany

Experience

Vocational

Executive Engineer, LTSSHF, Surat, Gujarat, India.

Academic

Research Assistant, ICAMS, Ruhr Universiät Bochum, Germany.

Skills

2011 2013

2015

2014

Codes almaBTE, VASP, WIEN2K, GPAW, ASE, AiiDA Languages Python, C++ $\,$

Languages

English Near native / fluent German Basic communication skills Hindi Native

Mother Tongue