

Proceedings of The Canadian Society for Mechanical Engineering International Congress 2018
CSME International Congress 2018
May 27-30, 2018, Toronto, On, Canada

Thermal conductivity of β -Arsenene under biaxial tensile strain: A first principle study

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Abstract— A first principle study is conducted to explore the phonon thermal transport in a buckled arsenene monolayer (β -As) subjected to tensile strain. The results showed that the thermal conductivity first decreases with strains from 0% to 1%, then it increases with strains from 1% to 5%, and finally it decreases with strains from 5% to 9%. The maximum thermal conductivity occurs at strain of 5%, which is 1.45 times higher than that of unstrained arsenene. Phonon properties are investigated to understand the causes of this thermal response to strain.

*First Principle; Arsenene; Strain; Thermal conductivity
Phonon Properties*

I. INTRODUCTION

Since the discovery of graphene, two-dimensional (2D) materials have attracted a great deal of attention. The appealing thermal [1] and electrical [2] properties of graphene have motivated the scientific community to explore for other 2D materials. This effort has resulted in many other nanomaterials added to the 2D family such as silicene, germanene, boron nitride (BN) and transition metal dichalcogenides (TMDCs) [3,4]. Very recently, group-VA monolayers such as phosphorene (P), arsenene (As), antimonene (Sb) and bismuthene (Bi) have attracted significant attention. As opposed to graphene that does not have a band gap, group-VA monolayers have band gaps in the range of 1-2.5eV [5,6,7], making them intriguing for electronic and optoelectronic applications. From a thermal point of view, materials of this family have a much lower thermal conductivity than graphene [8], making them more suitable for thermoelectric applications. There are two possible atomic structures for these materials: buckled (known as β) and puckered (known as α). The thermal conductivity of buckled structure is isotropic while the puckered structure has a highly anisotropic thermal conductivity in the zigzag and the armchair directions [8]. The focus of this paper is on buckled structures. Figure 1 shows a schematic of the group-VA buckled structure, in which atoms are arranged on a honeycomb lattice similar to graphene, with two atoms per unit cell. What makes these structures different from graphene is the non-zero buckling height d between two atomic planes

(Fig. 1). The minimum and maximum value of d are exhibited by β - phosphorene and β - bismuthene, respectively.

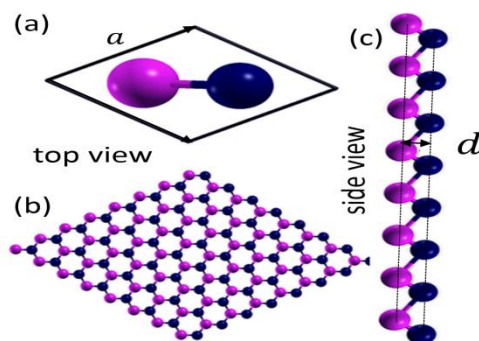


Figure 1. Lattice structure of group-VA monolayers: (a) unit cell (b) a 7×7 supercell (c) side view of the supercell. All atoms are the same kind, any of the group-VA elements (P, As, Sb or Bi). Different colors are used to show atoms in the upper and lower planes.

Apart from the value of accurately predicting the thermal conductivity of these novel materials, it is of paramount importance to understand how to tune the thermal conductivity. For that, it is necessary to investigate the thermal transport from a phonon transport perspective. 2D materials are commonly subjected to residual strains in real applications, and it is well known that strain has a considerable effect on the phonon properties and the thermal conductivity of 2D materials. Many studies have been conducted on the effects of strain on 2D materials such as graphene, stanene, germanene and silicene [1,9]. These studies revealed that tensile strain might increase or decrease the thermal conductivity. Also, tensile strain increases the dependency of the thermal conductivity to sample size. Zhang et al. [10] studied the effect of strain on phonon transport of β -Sb based on Boltzmann transport equation (BTE) under single relaxation time approximation (RTA) [11]. They considered strains ranging from -6% to 6%. Based on their results, the buckled structure of β -Sb is not stable for strains less than -1%. For strains from -1% to 6%, they found that the thermal conductivity increases by increasing strain. For instance, the thermal conductivity of β -Sb under tensile strain of 6% is about three times higher

than that of unstrained structure. However, there are still intriguing questions that need to be answered. For example, is the variation of the thermal conductivity with strain similar in other group-VA 2D materials? What will be the effect of higher tensile strain values on the phonon properties and thermal conductivity of other members of the group-VA family? In this work, we address these questions investigating the thermal properties of β -As, using a rigorous first-principle density functional theory (DFT) approach. We considered the effect of tensile strain (0-9%) on the thermal conductivity and phonon properties of β -As. The rest of this paper is organized as follows: Section II discusses the computational approach, Section III presents the harmonic and anharmonic phonon properties for different strain levels. Finally, Section IV summarizes the key findings.

II. COMPUTATIONAL APPROACH

The methodology here is based on a full solution of the BTE [11]. Having the harmonic and anharmonic interatomic force constants (IFCs), the BTE can be iteratively solved for the three-phonon scattering lifetime τ_λ of different phonons. Then, the thermal conductivity along the α direction, $\kappa_{\alpha\alpha}$, is

$$\kappa_{\alpha\alpha} = \frac{1}{Ah} \sum_{\lambda(\mathbf{k},p)} \hbar \omega_\lambda \frac{\partial n_\lambda^0}{\partial T} v_\lambda^\alpha v_\lambda^\alpha \tau_\lambda \quad (1)$$

where $\lambda(\mathbf{k}, p)$ shows a phonon mode with \mathbf{k} being the phonon wave vector and p the polarization branch, A is the unit cell area, h is the thickness of the material, ω is the phonon frequency, T is temperature, v_λ^α is the phonon group velocity in the direction α , and n_λ^0 is the phonon occupation number given by the equilibrium Bose-Einstein distribution.

The DFT calculations were conducted by the QUANTUM ESPRESSO (QE) package [12] with projected augmented wave (PAW) pseudopotential and generalized gradient approximation (GGA) exchange-correlation. First, the structure is fully optimized to obtain the relaxed lattice constant. We used an electronic wave-vector grid of $25 \times 25 \times 1$ for the Brillouin zone (BZ) integration, and the plane-wave cutoff was set to 70Ry. We also considered a vacuum of 20 Å between β -As monolayers to avoid interaction between adjacent layers. The relaxed lattice constant and buckling height of β -As is found to be $a_0=3.61\text{Å}$ and $d=1.40\text{Å}$, respectively (Fig 1). These values are in excellent agreement with previously reported values in [8,13]. Then, the percentage of applied strain is defined as

$$\epsilon = \frac{a - a_0}{a_0} \times 100 \quad (2)$$

where a is the lattice constant of the strained structure. Strains values studied here are 0%, 1%, 3%, 5%, 7% and 9%. For each value of strain, the phonon calculations are performed on a phonon wave-vector grid of $7 \times 7 \times 1$. The anharmonic IFCs

were calculated based on supercells, using a finite-difference method within the *thirdorder* package[11]. We used a $5 \times 5 \times 1$ supercell, and atomic interactions were considered up to the tenth nearest neighbor. Finally, the thermal conductivities are calculated using ShengBTE code [11] on an $80 \times 80 \times 1$ phonon wave-grid vector. Rigorous convergence tests with respect to all DFT settings implemented here showed that using the parameters described above led to fully converged phonon properties and thermal conductivities.

Based on Eq. (1), the thermal conductivity depends on the thickness h of the unit cell. However, the definition of h is controversial among 2D materials. Here, the value of h is considered the same as the length of the unit cell along the z direction, i.e., 20Å , the same strategy as previously used in [10].

III. RESULTS AND DISCUSSION

Figure 2 shows the variation of the lattice thermal conductivity of β -As with strain (0-9%) at 300K. The thermal conductivity first decreases with strains from 0% to 1%, and then it increases with strains from 1% to 5%. For 5% of strain, the thermal conductivity exhibited its maximum value, which was 1.45 times higher than that of strain 0%. This critical value of strain that resulted in a maximum conductivity, was also observed in silicene, germanene and stanene [9]. Thermal conductivity reduction occurs for strain values higher than 5%. In contrast to what was found in Ref. [10], an increase in the thermal conductivity of β -Sb from 0% to 1% of strain, we found here that the thermal conductivity of β -As slightly decreases from 0% to 1% of strain. Moreover, in Ref. [10], the authors did not consider strain percentages higher than 6%. Based on our results, we conclude that the thermal conductivity response of group-VA 2D materials to strain may differ although they are similar in structure. Also, considering a wider range of strain (in the elastic region) is necessary to obtain a comprehensive picture of the thermal response of 2D materials to strain. Figure 3 shows the variation of the thermal conductivity of β -As for temperatures in the range of 200 to 1000 K. The relative difference of the thermal conductivity between 0% and 5% of strain decreases from 49% at 200K to 43% at 1000K.

Now, we analyze the harmonic and anharmonic phonon properties to shed light into the mechanism responsible for the thermal conductivity variation of β -As with strain. Harmonic properties such as phonon dispersion and phonon group velocity govern the thermal transport in nanomaterials. As an example, the anisotropic thermal conductivity of puckered phosphorene and arsenene (α -P and α -As) is directly related to the anisotropic group velocities near the center of BZ [14, 15]. Fig. 4 illustrates the phonon dispersion curve along highly

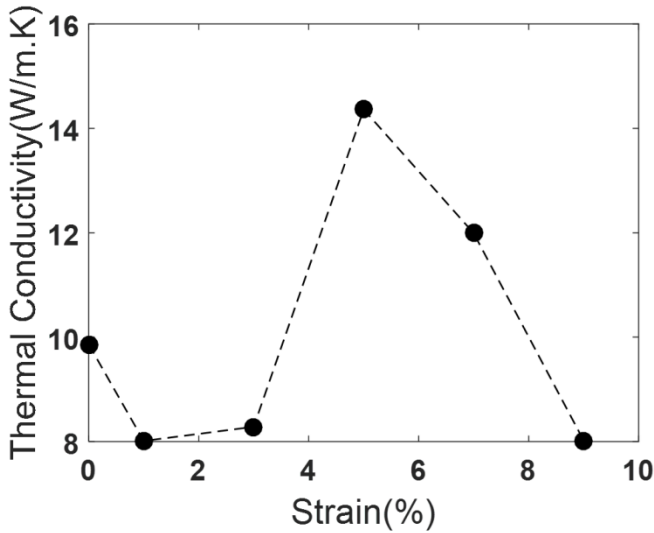


Figure 2. Strain variation of the thermal conductivity of β -As with strain at 300K.

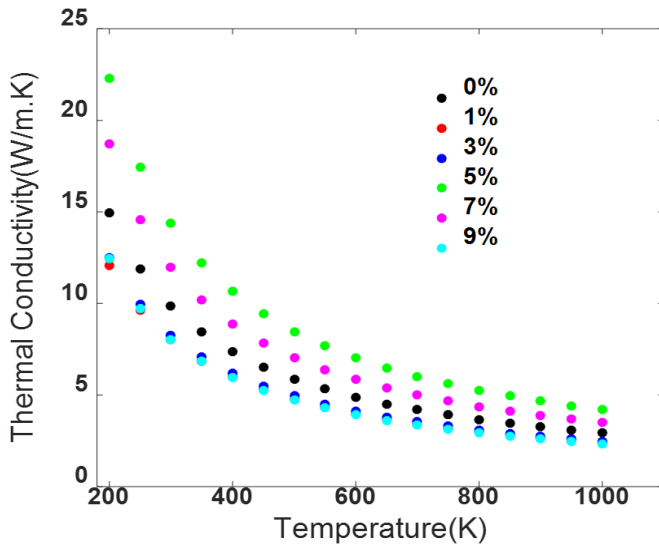


Figure 3. Variation of the thermal conductivity of β -As with temperature for different strain levels.

symmetric directions of the Brillouin zone for strains from 0% to 6%. There are two atoms in the unit cell β -As. Thus, there are six phonon branches: three acoustic modes called ZA, TA and LA; and three optical modes. Fig. 4 shows that increasing strain has not identical effects on different phonon modes. For example, as strain increases the ZA mode becomes more linear (higher phonon frequencies), and the LA mode exhibits a lower slope (lower phonon frequencies). The TA mode is less affected by strain compared to LA and ZA. Optical modes are also affected by strain. All optical modes become lower for higher strains. The same effect was also observed in graphene, silicene, stanene, germanene, and β -Sb [1,9,10].

The group velocity of a phonon mode is defined as the derivative of the phonon frequency with respect to the wave vector. Based on Eq. (1), the thermal conductivity has a strong dependence on the group velocity. We present the group velocity of all phonon modes for strain values of 0%, 3%, 5% and 7% in Fig. 5. In correlation with the responses of the phonon dispersion branches, the strain does not have the same impact on the group velocities of different phonon modes. Regarding the ZA mode, the group velocity near the center of the BZ increases with increasing strain. The group velocity of the ZA near the Γ -point is 0.36 km/s for strain 0% and increases to 1.30 km/s as strain increases to 7%. However, this is not the case for higher phonon frequencies of the ZA mode. As shown in Fig. 5, phonon group velocities of the ZA mode decreases as strain increases from 0% to 7%. Based on Eq. (1), this effect reduces the thermal conductivity. Considering the TA mode, the group velocity decreases near the Γ -point as strain increases. The group velocity is 3.07 km/s in unstrained β -As, and it is 2.68 km/s for strain of 7%. For other frequencies of the TA mode, considerable changes are not observed.

The reduction in group velocities as strain increases is also observed in the LA modes in Fig. 5. Unstrained β -As has the highest group velocities which decrease with increasing strain. In consequence, one could infer that the trend observed in group velocities of the acoustic modes leads to smaller thermal conductivities as strain increases. Group velocities of the three optical modes generally increases as strain increases, which is more obvious in the first two optical modes. However, since the group velocities of optical modes are smaller in magnitude than those of acoustic modes, it is predicted that the most important contribution in thermal conductivity of β -As comes from acoustic phonon modes. Therefore, regarding the group velocities, strain has a decreasing effect on thermal conductivity, as previously reported for β -Sb[10].

The other phonon property that has a crucial role in determining the thermal conductivity of a material is the phonon lifetime. Based on Eq. (1), higher phonon lifetimes result in higher thermal conductivities. The phonon lifetime of the acoustic and optical modes obtained from the iterative solution of BTE is plotted in Fig. 6. Since optical modes have smaller phonon lifetimes and group velocities than acoustic phonon modes, here we limit our discussion to the acoustic modes. Considering the ZA mode, the phonon lifetimes of the low-frequency phonons at 0% of strain are the highest. As shown in Fig. 6, the ZA mode of the unstrained structure has higher phonon lifetimes in the low-frequency region while the phonon lifetimes for 3%, 5% and 7% of strain in the same region are almost the same. However, the situation is different in the high-frequency region. As the strain increases from 3% to 5%, the phonon lifetimes of the ZA mode increases. To summarize, in the low-frequency region, the unstrained structure has the highest lifetimes among all strains considered. In the high-frequency region, 7% and 5% strains

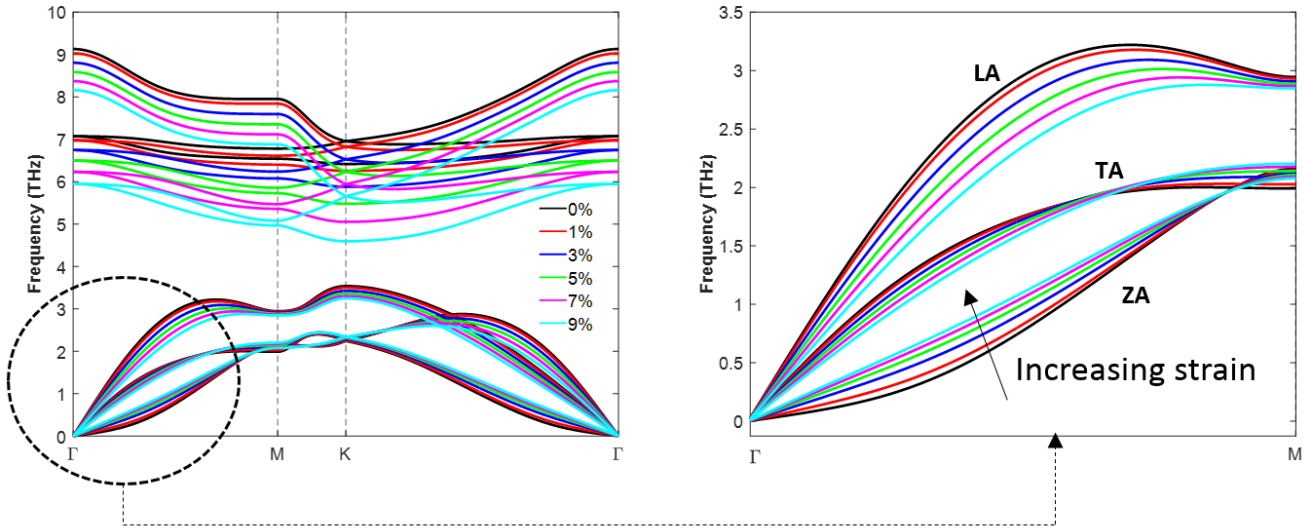


Figure 4. The phonon dispersion of buckled arsenene for different values of tensile strain.

result in higher phonon lifetimes than 1%, which in turn exhibits higher lifetimes than 3%. The situation is different in β -Sb [10], where the phonon lifetimes of the ZA mode were found to increase as strain increases from -1% to 6%, both in the low- and the high-frequency region. Regarding the TA and LA phonon modes, the phonon lifetimes increased as strain increased, except for the 0% and 3% strains, with 3% resulting in lower lifetimes than 1%. Overall, for all strain levels considered here, as strain increases, the phonon lifetimes of TA, LA and high-frequency ZA modes also increase. The only exception is for 3% strain, which resulted in lower lifetimes than those for 0% in all acoustic modes. Based on what has been discussed in this section, there is an interplay between group velocities and phonon lifetimes as strain increases. Group velocities are lower at higher strains, while phonon lifetime increases with increasing strain. This interplay is the main reason for the up and down variation of the thermal conductivity versus strain in buckled Arsenene.

IV. CONCLUSION

In this work, strain effects on the phonon properties and thermal conductivities of buckled arsenene have been investigated. Six different strains have been considered ranging from 0% to 9%. We found that thermal conductivity decreases as strain increases from 0% to 1%, then it increases for strains in the range of 1% to a critical value of 5%. Afterward, it decreases for strains between 5% and 9%. Harmonic and anharmonic phonon properties have been analyzed to understand the causes of this variation. We observed that the cause of this variation is the interplay between the responses of the group velocities and phonon lifetimes of the acoustic modes to strain. The variation of the thermal conductivity of buckled arsenene with strain is

different than that observed in other materials of the same family, such as buckled antimonene. This study revealed that tensile strain can have different effects on different 2D materials, even if they belong to the same family with similar structure.

ACKNOWLEDGMENT

This work was supported by the Natural Science and Engineering Research Council of Canada (NSERC), through the Discovery and the Collaboration Research and Development (CRD) grant program. Computations were performed on the GPC supercomputer at the SciNet HPC Consortium. SciNet is funded by the Canada Foundation for innovation under the auspices of Compute Canada; the Government of Ontario; Ontario Research fund- Research Excellence; and the University of Toronto.

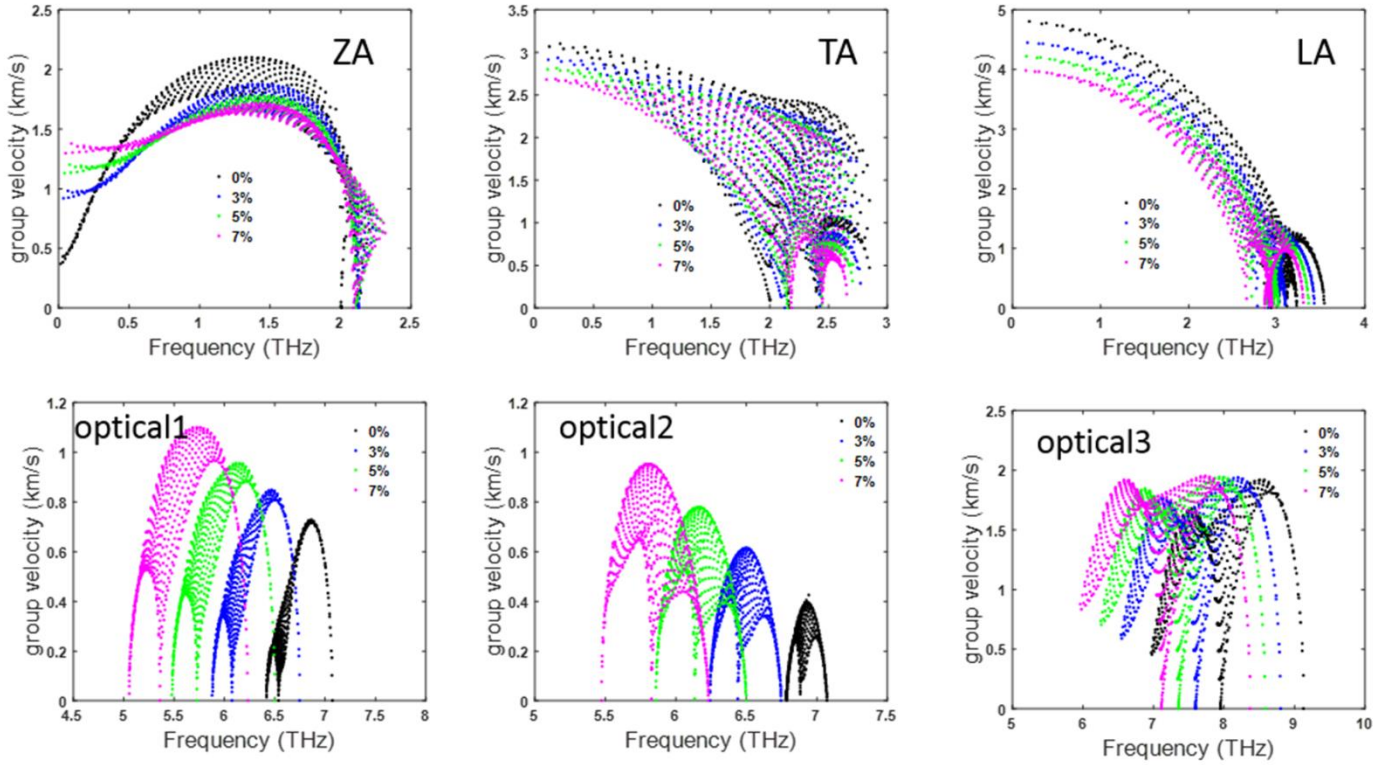


Figure 5. The phonon group velocity of acoustic and optical modes for strains of 0%, 3%, 5% and 7%.

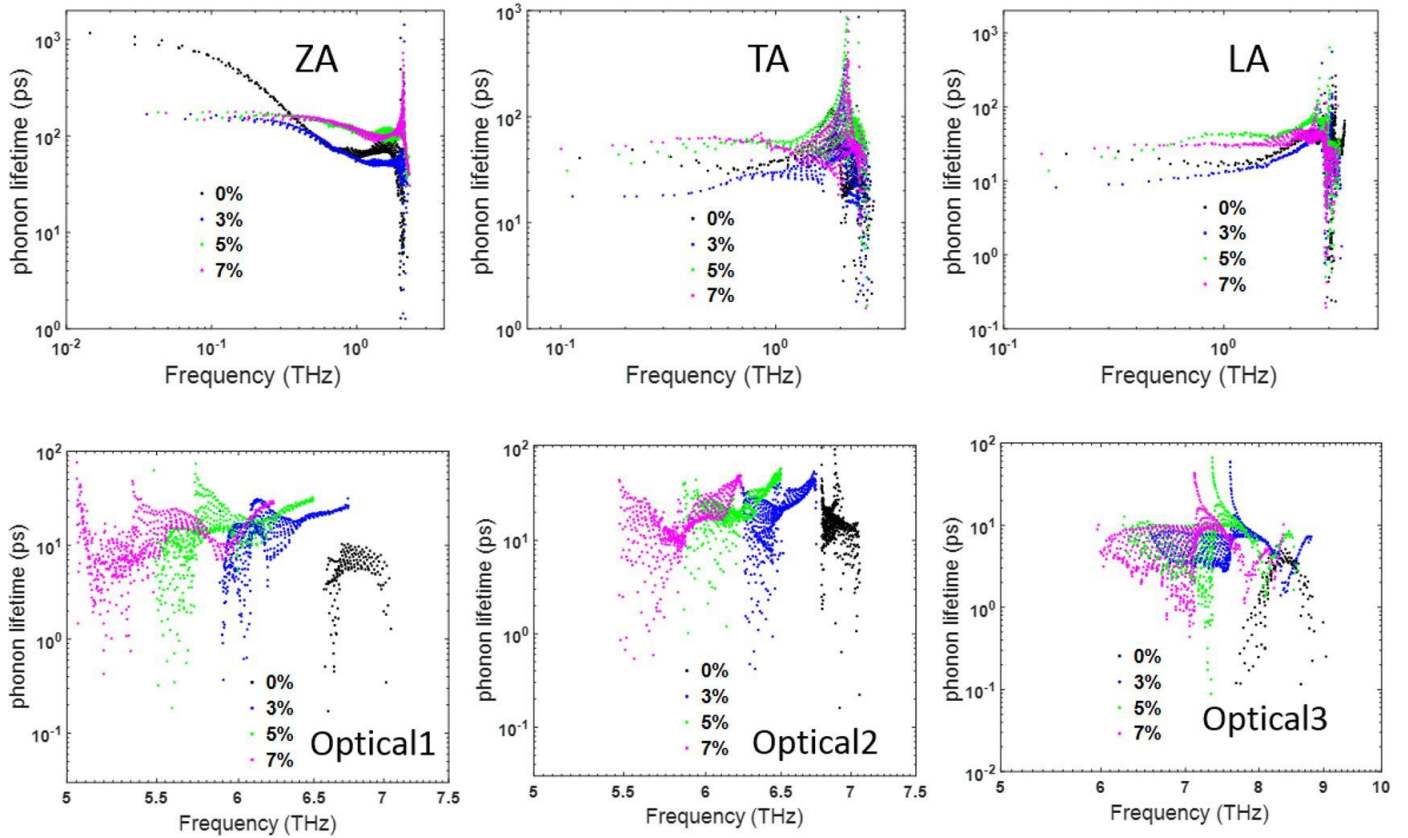


Figure 6. The phonon lifetime of acoustic and optical modes for strains of 0%, 3%, 5% and 7

REFERENCES

- [1] Y. Kuang, L. Lindsay, S. Shi, X. Wang, and B. Huang, "Thermal conductivity of graphene mediated by strain and size," *Int. J. Heat Mass Transf.*, vol. 101, pp. 772–778, 2016.
- [2] K. S. Novoselov, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, A. A. Firsov, and A. K. Geim, "Electric Field Effect in Atomically Thin Carbon Films," *Science (80-.)*, vol. 306, no. 5696, pp. 666–669, 2004.
- [3] C. Da Silva, F. Saiz, D. A. Romero, and C. H. Amon, "Coherent phonon transport in short-period two-dimensional superlattices of graphene and boron nitride," *Phys. Rev. B*, vol. 93, no. 12, pp. 1–10, 2016.
- [4] C. da Silva, J. Sborz, D. A. Romero, and C. H. Amon, "Thermal response of boron nitride and boron nitride-graphene nanosheets to uniaxial tensile strain," in *Proceedings of the Canadian Society for Mechanical Engineering International Conference (CSME)*, 2014, pp. 1–5.
- [5] S. Zhang, M. Xie, F. Li, Z. Yan, Y. Li, E. Kan, W. Liu, Z. Chen, and H. Zeng, "Semiconducting Group 15 Monolayers: A Broad Range of Band Gaps and High Carrier Mobilities," *Angew. Chemie - Int. Ed.*, vol. 55, no. 5, pp. 1666–1669, 2016.
- [6] C. Kamal and M. Ezawa, "Arsenene: Two-dimensional buckled and puckered honeycomb arsenic systems," *Phys. Rev. B - Condens. Matter Mater. Phys.*, vol. 91, no. 8, 2015.
- [7] H. Liu, A. T. Neal, Z. Zhu, Z. Luo, X. Xu, D. Tománek, and P. D. Ye, "Phosphorene: An unexplored 2D semiconductor with a high hole mobility," *ACS Nano*, vol. 8, no. 4, pp. 4033–4041, 2014.
- [8] G. Zheng, Y. Jia, S. Gao, and S. H. Ke, "Comparative study of thermal properties of group-VA monolayers with buckled and puckered honeycomb structures," *Phys. Rev. B*, vol. 94, no. 15, pp. 1–6, 2016.
- [9] Y. D. Kuang, L. Lindsay, S. Q. Shi, and G. P. Zheng, "Tensile strains give rise to strong size effects for thermal conductivities of silicene, germanene and stanene," *Nanoscale*, vol. 8, no. 6, pp. 3760–3767, 2016.
- [10] A.-X. Zhang, J.-T. Liu, and S.-D. Guo, "Strain effects on phonon transport in antimonene from a first-principles study," *Phys. Chem. Chem. Phys.*, vol. 19, pp. 14520–14526, 2017.
- [11] W. Li, J. Carrete, N. A. Katcho, and N. Mingo, "ShengBTE: A solver of the Boltzmann transport equation for phonons," *Comput. Phys. Commun.*, vol. 185, no. 6, pp. 1747–1758, 2014.
- [12] P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, A. Dal Corso, S. De Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos, . Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Sclauzero, A. P. Seitsonen, A. Smogunov, P. Umari, and R. M. Wentzcovitch, "QUANTUM ESPRESSO: A modular and open-source software project for quantum simulations of materials," *J. Phys. Condens. Matter*, vol. 21, no. 39, 2009.
- [13] B. Peng, D. Zhang, H. Zhang, H. Shao, G. Ni, Y. Zhu, and H. Zhu, "The conflicting role of buckled structure in phonon transport of 2D group-IV and group-V materials," *Nanoscale*, vol. 9, no. 22, pp. 7397–7407, 2017.
- [14] A. Jain and A. J. H. McGaughey, "Strongly anisotropic in-plane thermal transport in single-layer black phosphorene," *Sci. Rep.*, vol. 5, no. 1, p. 8501, 2015.
- [15] M. Zeraati, S. M. Vaez Allaei, I. Abdolhosseini Sarsari, M. Pourfath, and D. Donadio, "Highly anisotropic thermal conductivity of arsenene: An ab initio study," *Phys. Rev. B*, vol. 93, no. 8, pp. 1–5, 2016.