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Temperature-dependent phonon spectrum of transition metal dichalcogenides calculated from the spectral energy density: Lattice thermal conductivity as an application

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I. INTRODUCTION

A new era of nanodevice engineering has been started after fabricating an isolated single layer of graphite named graphene. Although this carbon allotrope has many extraordinary properties, its zero band gap, which imposes a challenge for possible band-gap engineering, is its main setback for device applications. Hexagonal boron nitride (h-BN) is another planar two-dimensional (2D) material, and contrary to the graphene, it has an intrinsic band gap; however, being an insulator restricts its applications, especially for electronics. Although this carbon allotrope has many extraordinary properties, its zero band gap, which imposes a challenge for possible band-gap engineering, is its main setback for device applications. Despite the outstanding properties make them ideal candidates, particularly for flexible electronic and optoelectronic devices [9–14] and thermoelectric applications [15–19].

Since thermal and mechanical properties of materials are crucial in any device applications, many experimental and theoretical investigations have been carried out in order to determine the temperature-dependent properties of single-layer TMDs [20]. First-principles calculations [21,22] estimated a positive thermal expansion coefficient at low temperature for most common TMDs, which are WS2, WSe2, MoS2, and MoSe2, while it was reported to be negative for graphene [23]. Besides, they have much smaller thermal conductivities compared to graphene and h-BN. For instance, the thermal conductivity of MoS2 is reported as 34.5 Wm−1 K−1 from the confocal micro-Raman method [24]. However, it is measured as 13.3 Wm−1 K−1 in vacuum conditions [25]. Similarly, there are experimental and theoretical studies reporting low cross-planar thermal conductivity in WSe2 [26–28]. On the other hand, the lattice thermal conductivity of single-layer WSe2 at room temperature is estimated to be as high as 53 Wm−1 K−1 based on first-principles calculations [29,30]. Clearly, more studies are necessary in order to resolve the diverse results about the thermal properties of TMDs.

All thermal properties are directly or indirectly related to the phonon spectrum which could be obtained from experimental and theoretical studies reporting low cross-planar thermal conductivity in WSe2 [26–28]. On the other hand, the lattice thermal conductivity of single-layer WSe2 at room temperature is estimated to be as high as 53 Wm−1 K−1 based on first-principles calculations [29,30]. Clearly, more studies are necessary in order to resolve the diverse results about the thermal properties of TMDs.

Predicting the mechanical and thermal properties of quasi-two-dimensional (2D) transition metal dichalcogenides (TMDs) is an essential task necessary for their implementation in device applications. Although rigorous density-functional-theory–based calculations are able to predict mechanical and electronic properties, mostly they are limited to zero temperature. Classical molecular dynamics facilitates the investigation of temperature-dependent properties, but its performance highly depends on the potential used for defining interactions between the atoms. In this study, we calculated temperature-dependent phonon properties of single-layer TMDs, namely, MoS2, MoSe2, WS2, and WSe2, by utilizing Stillinger-Weber–type potentials with optimized sets of parameters with respect to the first-principles results. The phonon lifetimes and contribution of each phonon mode in thermal conductivities in these monolayer crystals are systematically investigated by means of the spectral-energy-density method based on molecular dynamics simulations. The obtained results from this approach are in good agreement with previously available results from the Green-Kubo method. Moreover, detailed analysis of lattice thermal conductivity, including temperature-dependent mode decomposition through the entire Brillouin zone, shed more light on the thermal properties of these 2D crystals. The LA and TA acoustic branches contribute most to the lattice thermal conductivity, while ZA mode contribution is less because of the quadratic dispersion around the Brillouin zone center, particularly in MoSe2 due to the phonon anharmonicity, evident from the redshift, especially in optical modes, by increasing temperature. For all the considered 2D crystals, the phonon lifetime values are compelled by transition metal atoms, whereas the group velocity spectrum is dictated by chalcogen atoms. Overall, the lattice thermal conductivity is linearly proportional with inverse temperature.

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density-functional-theory (DFT)–based calculations at zero temperature. First-principles studies based on the Boltzmann transport equation (BTE) deal with a perfect crystal lattice, neglecting the rippling behavior in single-layer materials; moreover, they mostly consider three phonon processes. Raman methods are one of the most common approaches for experimental studies, and they are very sensitive to sample quality and size. Furthermore, mixed modes and Raman forbidden modes restrict the measurement of frequencies of all phonon modes, and the obtained lifetimes rely on laser absorption. Classical molecular dynamics (MD) simulation is a powerful alternative to overcome all of the aforementioned problems, but its performance depends on the accuracy of interatomic potential [31]. In previous works, we have developed parameters for Stillinger-Weber (SW)–type potential for TMDs [32,33], and it was shown that the obtained thermal properties are in good agreement with first-principles calculations. As it is quantitatively shown in Ref. [34], the exact prediction of MD thermal conductivity is given by the Green-Kubo method, where thermal transport properties are driven from the fluctuation-dissipation theorem [35,36]. However, one drawback of the Green-Kubo method is the lack of possibility of investigating the contribution of different phonon modes and evaluation of phonon lifetimes, which is very important in compiling the thermal conductivity. On the other hand, phonon lifetimes and mode contributions are accessible utilizing the spectral-energy-density (SED) method, which considers all anharmonic effects as well [37]. Although SED method is widely used in studying 2D materials and their heterostructures [38–42], the investigation of TMDs based on SED is limited [33,43]. Furthermore, most of the previous reports are restricted to optical modes at the Γ point or along the high-symmetry paths. In this work, we present a systematic study of phonon frequencies and lifetimes of TMDs in the full Brillouin zone using mode decomposition and the SED method. Contributions of different modes to thermal conductivity are obtained utilizing the Callaway model within the relaxation-time approximation (RTA) [44]. Then, in order to assess the accuracy and limitations of all the mentioned approaches, our results are compared with those from literature obtained from first-principles calculations and Green-Kubo methods, and they are in good agreement, especially at high temperatures.

II. METHOD

The SW potential [45] used in this study has the following form:

\[
E = \sum_i \sum_{j \neq i} \phi_2(r_{ij}) + \sum_i \sum_{j \neq i} \sum_{k \neq j} \phi_3(r_{ij}, r_{ik}, \theta_{ijk}),
\]

\[
\phi_2(r_{ij}) = A_{ij} \left( \frac{B_{ij}}{r_{ij}} - 1 \right) \exp \left( -\frac{\rho_{ij}}{r_{ij} - r_{ij}^{\text{max}}} \right),
\]

\[
\phi_3(r_{ij}, r_{ik}, \theta_{ijk}) = K_{ijk} \exp \left[ -\frac{\rho_{ij}}{r_{ij} - r_{ij}^{\text{max}}} + \frac{\rho_{ik}}{r_{ik} - r_{ik}^{\text{max}}} \right] \times (\cos \theta_{ijk} - \cos \theta_{0,ijk})^2,
\]

where the two- and three-body interactions are defined by \( \phi_2 \) and \( \phi_3 \), respectively. The summations in Eq. (1) run over neighbors of atom \( i \) within the radius \( r_{ij}^{\text{max}} \) and \( \theta_{ijk} \) is the angle between two bonds of atom \( i \). Sets of the optimized parameters and more details are presented in previous works [32,33]. There are two different approaches for obtaining phonon dispersion curves using MD. The first one is based on Green’s function [46,47] and the other method utilizes SED [37]. The first approach is known to be unstable near the Γ point [47,48]. SED is computationally more expensive but considers all anharmonic effects and generates stable results in the entire Brillouin zone, and it is widely used for investigating the phonon properties of 2D materials. It is shown that mode decomposition is not necessary, and it is possible to use any arbitrary orthogonal set instead of normal mode coordinates [49]. However, mode decomposition makes the study much easier, especially when the dispersion curves of different modes are close to each other. Within the framework of SED the function \( \psi(k, j|\tau) \) is defined as

\[
\psi(q, j|\tau) = \sum_{\alpha,\beta} \left[ \sum_n \nu_{\alpha}(n, \beta|\tau) \exp(-i\Omega_{\alpha}(q)) \right] e_\alpha^*(b|q, j),
\]

where \( q \) is the wave vector, \( \alpha \) shows each of the Cartesian components of velocity of the \( \alpha \)th basis of the \( n \)th lattice unit cell, and \( e_\alpha^*(b|q, j) \) is the \( j \)th normal mode of the perfect crystal lattice. It is shown that the frequency and lifetime of each phonon mode can be obtained by fitting a Lorentzian function,

\[
\frac{I}{1 + \left( \frac{\omega - \omega_0}{\chi} \right)^2},
\]

to the power spectrum of \( \psi(q, j|\tau) \). Here, \( \omega_0 \) is the phonon frequency, \( \chi \) gives the phonon lifetime, and \( I \) is the peak magnitude. Under the relaxation-time approximation, the contribution of each phonon branch to the lattice thermal conductivity in terms phonon lifetimes \( \tau \) and group velocities \( v_g = \frac{\partial \omega}{\partial q} \) is given by

\[
\kappa_j = \frac{1}{V} \sum_q c_{ph}[v_g(q) \cdot \mathbf{e}]^2 \tau(q),
\]

where \( \kappa_j \) denotes the lattice thermal conductivity along the direction \( j \), \( V \) is the volume of the system, and \( \mathbf{e} \) is the unit vector in the direction of the thermal conductivity. \( c_{ph} \) is the phonon specific heat and its usual classical form is simple in terms of Boltzmann constant \( (k_B) \). In order to consider the quantum correction at low temperatures, we adapted the quantum-mechanical form given below:

\[
c_{ph}(\omega) = \frac{(\hbar\omega)^2}{k_B T} \exp(h\omega/k_BT) [\exp(h\omega/k_BT) - 1]^2.
\]

All MD simulations in this study have been carried out using the open source program LAMMPS [50,51]. In all cases a 70x70 (14,700 atoms) triclinic computational cell is relaxed for 500 ps in an isothermal-isobaric (NPT) ensemble. Then the simulation cell constructed using lattice parameters obtained from NPT run and the velocities are recorded in a microcanonical (NVE) ensemble run, which lasted for \( 2^{20} \) with time step of 0.5 fs. Periodic boundary conditions are considered in all three dimensions. In order to obtain the averaged power spectrum, 16 different simulations are performed. The
TEMPERATURE-DEPENDENT PHONON SPECTRUM OF …

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Fig. 1. Phonon dispersion curves of 2D WS₂, WSe₂, MoS₂, and MoSe₂ structures calculated by SED approach at different temperatures.

Brillouin zone is sampled using a 35×35 mesh, which is dense enough for the convergence of the summation in Eq. (5).

III. RESULTS AND DISCUSSION

First we examined the temperature-dependent phonon frequencies through the entire Brillouin zone for all the considered materials, WS₂, WSe₂, MoS₂, and MoSe₂, by using phonon-mode decomposition. Previously, Feng et al. [49] studied the effect of temperature on phonon modes of PbTe and showed that at very high temperatures the harmonic phonon modes are not adequate for decomposing the power spectrum. Although the modes of a perfect lattice are used for decomposition in this study, within the considered temperature ranges, up to 500 K the eigenvectors of these modes are quite accurate to decompose the full power spectrum, as demonstrated in the example of performance of phonon-mode decomposition shown in Fig. S1 of the Supplemental Material [52].

The calculated phonon dispersion curves along the high-symmetry directions for five different temperatures (100–500 K) are shown in Fig. 1. The results, particularly for acoustic frequencies, are in very good agreement with those previously predicted by first-principles approaches. As clearly seen in the figure, the acoustic frequencies do not change notably with temperature compared to the optical frequencies. The most prominent temperature effect is observed on the optical modes of MoSe₂, which exhibits considerable redshift by increasing temperature. The evident difference indicates much stronger phonon anharmonicity in this material than the other considered TMDs.

Following the SED calculations, we determined the phonon-mode lifetimes τ along with the mode frequencies.

In Fig. 2 the calculated room temperature τ of acoustic modes and an optical mode which has the most contribution in thermal conductivity are presented within the entire first Brillouin zone. The same representations for the other considered temperature values are given in the Supplemental Material [52] as well. The calculated τ values corresponding to the acoustic branches are approximately an order of magnitude longer than the ones calculated for optical modes. For acoustic branches of all the considered materials, the calculated τ values at the phonon wave vectors q close to zone center are notably higher. The variation of τ from zone center to zone boundary is very broad and sharp for Mo-based systems, whereas this variation is very narrow for W-based systems. This characteristic is more evident for the ZA mode. Also, the τ values for W-based systems are clearly higher than those calculated for Mo-based systems. The unusual comparable κ values of heavier W- and lighter Mo-based layers, previously predicted and also obtained in this study, might be related with this notable difference. As anharmonicity is increased from WS₂, WSe₂, and MoS₂ to MoSe₂, depicted from the frequency shifts in phonon dispersion in Fig. 1, phonon lifetimes are decreased, consequently. The distribution of lifetimes at different q points varies with temperature, and the overall trend in lifetimes is only decreasing the mean value by increasing the temperature.

As depicted in Eq. (5), another important physical property which has significant contribution on lattice thermal properties is the phonon group velocity, vₔ. Here, the mode and wave vector decomposed vₔ of all the considered materials are calculated by a finite difference derivative of phonon frequencies obtained with the SED approach within the entire Brillouin zone. In Fig. 3, the magnitude of calculated group velocities at room temperature is displayed as a similar form with the lifetimes presented above, where vₔ data for various other temperatures are reported in the Supplemental Material [52] as well. While τ spectrum characteristics are dominated by the transition metal atoms, here the vₔ spectrum is dictated by the chalcogen atoms, S and Se. This can be explained...
by the fact that total ionic mass in the unit cell is one of the primary factors for the maximum frequency of acoustic modes, and hence the Debye temperatures. Among the acoustic modes, the ZA branch has quadratic dispersion, a feature of 2D systems, that can be observed from circularly symmetric increasing $v_g$ around the zone center, $\Gamma$ point.

By using Eq. (5) we have investigated lattice thermal conductivity of these materials from the accurately calculated phonon frequency, lifetime, and group velocity spectrums that are obtained by the SED method, achieving highly improved statistical convergence. This approach enables us mode decomposition at any general $q$ point, and therefore we can determine the contribution of each mode to the total lattice thermal conductivity, as opposed to other approaches such as Green-Kubo formula. In Fig. 4 the contribution of each mode in thermal conductivity at room temperature is presented.

As expected, most of the contribution is from the acoustical modes; however, there is a non-negligible contribution from optical modes in WS$_2$, WSe$_2$, and MoS$_2$. On the contrary, the contribution of optical modes of MoSe$_2$ is almost negligible, which is in contrast to the calculated finite $v_g$ values, similar both in WSe$_2$ and MoSe$_2$. This contrast can be explained by the highly anharmonic nature of MoSe$_2$ observed in both as highly suppressed optical phonon lifetimes, as seen in Fig. 2, and a shift in optical frequencies by temperature, as seen in Fig. 1. Not only optical modes but also the relatively low contribution of the ZA mode compared to the other acoustical modes and other materials might be another evidence for anharmonicity.

Despite the influence of lifetimes as discussed above, the similar thermal conductivity contributions calculated for acoustic modes of materials with the same chalcogen atom clearly represent the dominant effect of group velocities on final $\kappa$ values. Therefore, one can conclude that the lattice thermal conductivity scales with total ionic mass in the unit cell for these 2D materials due to the trivial relation between the $v_g$ and ionic mass in any system possessing the same crystal structure.

The contribution of acoustic modes to the lattice thermal conductivity as a function of temperature is shown in Fig. 5. Most of the contribution comes from the LA and TA branches, while the ZA mode contribution is less, especially in MoSe$_2$, due to the anharmonicity as discussed above. Overall, in all considered systems, $\kappa$ decreases with increasing temperature, approximately proportional with inverse temperature, similar to the other 2D systems [53].

Finally, we predicted the temperature-dependent total lattice thermal conductivity values from SED analysis based on MD simulations. The calculated room temperature values, 91.66, 89.43, 39.94, and 29.05 Wm$^{-1}$K$^{-1}$ for WS$_2$, MoS$_2$, WSe$_2$, and MoSe$_2$, respectively, clearly indicate again the dominant role of the chalcogen atom (total ionic mass of the cell) on the overall thermal conductivity. The variation of $\kappa$ as a function of temperature is depicted in Fig. 6, along
The systematic investigation conducted in this work shows that the SED approach used together with classical molecular dynamics calculations is very convenient to study the temperature-dependent phonon properties and lattice thermal conductivity. Utilizing multicomposition facilitates carrying out a detailed analysis based on mode-decomposed lifetimes, group velocities, and lattice thermal conductivity, which paves the way to tailor $\kappa$ of these materials. Thus, with this approach one can also fairly estimate the thermal effects of extended systems, such as the defects and heterostructure constituted in large supercell systems, which is not available with methods based on Green-Kubo and first-principles approaches. The most prominent temperature effect is observed on the optical modes of MoSe$_2$, which exhibits considerable redshift by increasing temperature. The evident difference indicates much stronger phonon anharmonicity in this material than the other considered TMDs. On these binary systems, transition metal atoms drive the phonon lifetime values, whereas chalcogen atoms dictates the group velocity spectrum. Most of the contribution to the $\kappa$ values arise from the LA and TA acoustic branches, while the ZA mode contribution is less, particularly in MoSe$_2$, due to the anharmonicity and quadratic dispersion around the Brillouin zone center. In conclusion, for all the considered 2D crystals, $\kappa$ is linearly proportional with inverse temperature.

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IV. CONCLUSIONS

with the values from the other available methods [29,54]. The total lattice thermal conductivity varies linearly with inverse temperature, as predicted previously for mode decomposed values. There is an overall agreement between the results of different methods, as clearly seen in the figure. The SED method adopted in this study, slightly underestimates, but within the error bars, the $\kappa$ values compared with the Green-Kubo results, which is probably due to the Callaway-approach-based equation used here [59]. It is possible to include a correction in terms of lifetimes of normal and umklapp processes which cannot be separated from SED analysis. Moreover, the $\kappa$ values obtained by both MD based approaches are systematically smaller than the first-principles solution of the phonon Boltzmann transport equation, PBTE. This is due to the well-known fact that the Maxwell-Boltzmann distributed phonon excitations in the classical molecular dynamics simulations enhance the anharmonic interactions, unlike the Fermi-Dirac distributed excitations of phonon modes in PBTE calculations.
