Effects of van der Waals interactions on the phonon transport properties of tetradymite compounds

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Abstract

Unlike tremendous works on the electronic structures of tetradymite compounds, studies of their thermal properties are relatively rare. Here, first-principles calculations and Boltzmann theory are combined to investigate the phonon transport of such kind of layered materials. Using four binary tetradymites as prototypical examples, it is interesting to find that the weak van der Waals (vdW) interactions play an important role in determining their lattice thermal conductivities, which are obviously higher than those without the consideration of vdW, especially for the out-of-plane direction. In principle, such enhanced phonon transport can be attributed to the decreased interlayer spacing caused by the presence of vdW, which effectively reduces the strong anharmonicity of the systems. Indeed, we observe relatively smaller Grüneisen parameter together with larger phonon group velocity and relaxation time. Our theoretical work demonstrates the vital importance of the seemingly weak vdW forces in predicting the phonon transport properties of various layered structures.

1. Introduction

During the past few decades, tetradymites have attracted much attention in the field of thermoelectric (TE) materials and topological insulators (TIs) due to the existence of heavy elements and small band gaps [1]. The well-known examples are the binary tetradymites Bi$_2$Te$_3$, Bi$_2$Se$_3$, Sb$_2$Te$_3$ and Sb$_2$Se$_3$, which are found to be well-established TE materials and their electronic and transport properties have been subject to numerous studies, both experimentally and theoretically [2–9]. Meanwhile, all these four compounds have been confirmed to be three-dimensional (3D) TIs with similar band inversion caused by the spin–orbit coupling, and feature inherent gapless surface states which behave as a single Dirac cone in the Brillouin zone [10–13].

Although extensive experimental and theoretical studies have been performed on the tetradymites, most of them are focused on the electronic and topological properties. The investigations of their phonon transports are less known. By performing classical molecular dynamics (CMD) simulations, Huang and Kaviany [14] firstly established a set of complicated interatomic potentials to calculate the lattice thermal conductivity of Bi$_2$Te$_3$. Using the same approach, Qiu and Ruan [15] developed a simpler two-body potentials for Bi$_2$Te$_3$ by fitting the results from density functional calculations. It should be mentioned that the precision of CMD strongly depends on appropriate selection of interatomic potentials [16], which may lead to certain discrepancy in the calculated lattice thermal conductivity compared with the experimentally measured value [17]. On the other hand, Sosso et al [18] theoretically predicted the Raman, infrared ray and phonon spectra of crystalline Sb$_2$Te$_3$. Although their results are overall consistent with the experimental
data, the lack of appropriate exchange and correlation functionals tends to underestimate the frequency of longitudinal acoustic phonons. In principle, due to the presence of van der Waals (vdW) interactions in the tetradymites with layered structure, one should include vdW functionals for high-level density functional theory (DFT) calculations. However, the effects of such weak interactions are generally assumed to be negligible, and standard DFT calculations without consideration of vdW functional can well reproduce/predict most physical results for many decades. Only in recent years, it was found that the seemingly weak vdW forces may have real effects on certain physical properties of some layered systems. For instance, using the GW method with optB86b-vdW functional, Cheng et al predicted a band gap of 157 meV for the Bi2Te3 that is much closer to the experimental value [19]. Surprisingly, the rhombohedral Sb2Se3 was proven to be also topologically non-trivial if the vdW interactions are explicitly taken into account [13, 20]. All these findings make it reasonable to expect that the intrinsic vdW may also play an important role in precisely determining other fundamental properties of tetradymites such as the phonon transport, which is so far less known to the best of our knowledge.

In this work, using four binary tetradymites (Bi2Te3, Bi2Se3, Sb2Te3 and Sb2Se3) as prototypical examples, we give a first-principles study on their phonon transport properties, and the results with and without consideration of the vdW forces are both discussed for comparison. It is surprising to find that the seemingly weak interlayer interactions actually play a very important role in predicting their lattice thermal conductivities, which are obviously higher than those obtained without vdW. The underlying physical mechanisms are explored in terms of the structural, harmonic and anharmonic properties of such layered systems.

2. Computational method

The optimized structures of the four binary tetradymites can be obtained by performing DFT calculations [21–23], where the projector-augmented wave [24, 25] method is adopted as implemented in the Vienna ab initio simulation package [26]. The exchange–correlation energy is in the form of Perdew–Burke–Ernzerhof (PBE) with the generalized gradient approximation [27]. The energy cutoff is set to 500 eV and the Brillouin zone is sampled with an 11×11×11 Monkhorst-Pack k mesh [28]. To include the effect of vdW, the so-called optB86b-vdW [13] is selected after carefully checking various functional forms.

For the phonon properties, we use the finite displacement method to derive the harmonic and anharmonic interatomic force constants (IFCs) by using 4×4×4 and 3×3×3 supercells, respectively. The codes are embedded in the so-called PHONOPY [29] package and the THIRDORDER.PY script. Besides, the fourth nearest neighbors are imposed to achieve converged third-order IFCs. The thermal transport properties can be computed by solving the phonon Boltzmann transport equation, which is implemented in the ShengBTE program [30]. A fine q-mesh of 25×25×25 is used to obtain converged lattice thermal conductivity.

3. Results and discussion

As shown in figure 1, the binary tetradymites Bi2Te3, Bi2Se3, Sb2Te3 and Sb2Se3 all have the same rhombohedral crystal structure with space group of R3m. The primitive cell consists of five atoms, and it is usually convenient to show the layered structure using the hexagonal unit cell with 15 atoms. The system can be viewed as five atomic layers arranged along the c direction in the sequence of Te(Se)1–Bi(Sb)–Te(Se)2–Bi(Sb)–Te(Se)1 held by covalent bonds, known as the quintuple layers (QLs). Unlike the strong coupling between two atomic layers inside one QL, the vdW interactions between adjacent QLs are much weaker. However, it should be noted that the vdW is a dominant factor in correctly determining the interlayer spacing (d_eqm), which was previously found to have pronounced effects on the electronic and topological properties of tetradymites [13, 18, 19]. As summarized in table 1, the lattice parameters (a) predicted by the standard DFT calculations with PBE functional tend to be overestimated compared with the experimental values [31–34]. Such a problem can be effectively addressed by considering the vdW functionals, where the form of optB86b-vdW was confirmed to be the best that can well reproduce the lattice parameters of some tetradymites [13]. It is thus reasonable to choose such a functional exclusively to predict the real crystal structures of all the four binary tetradymites. Indeed, we see from table 1 there is obvious reduction of the interlayer spacing when the vdW is considered, which also leads to slightly decreased volume of the primitive cell.

It is interesting to check if the weak vdW interactions could also affect the thermal properties of these tetradymites. Figure 2 shows the phonon dispersion relations of the Bi2Te3, Bi2Se3, Sb2Te3 and Sb2Se3. Since there are five atoms in the primitive cell of each system, we observe 15 phonon branches where three are the
Figure 1. The crystal structure of binary tetradymites. The primitive cell, QLs and interlayer spacing (d_{eqm}) are also marked.

Table 1. The lattice constant (a), layer spacing (d_{eqm}), and volume of the primitive cell (Ω) for the binary tetradymites Bi₂Te₃, Bi₂Se₃, Sb₂Te₃ and Sb₂Se₃ calculated with standard PBE and PBE + optB86b-vdW functionals. The available experimental results are also listed for comparison.

| Variable | Methods         | Bi₂Te₃ | Bi₂Se₃ | Sb₂Te₃ | Sb₂Se₃ |
|----------|-----------------|--------|--------|--------|--------|
| a (Å)    | Exp.            | 10.48  | 9.84   | 10.45  | 9.81   |
|          | Standard PBE    | 11.00  | 10.70  | 10.76  | 10.45  |
|          | PBE + optB86b   | 10.71  | 10.11  | 10.41  | 9.80   |
| d_{eqm} (Å) | Standard PBE | 3.15   | 3.40   | 3.08   | 3.29   |
|          | PBE + optB86b   | 2.87   | 2.79   | 2.71   | 2.62   |
| Ω (Å³)   | Standard PBE    | 182.98 | 158.31 | 170.72 | 146.09 |
|          | PBE + optB86b   | 178.78 | 149.67 | 163.01 | 135.62 |

There are no imaginary frequencies which suggest that all the four binary tetradymites are dynamically stable, no matter the vdW functional is included or not. Due to the larger mass of constituent atoms, the maximum phonon frequencies of those four compounds are all smaller than 210 cm⁻¹. Among them, the Bi₂Te₃ exhibits the lowest value (140 cm⁻¹) and the Sb₂Se₃ has the highest (205 cm⁻¹), which is negatively correlated with their atomic mass as generally assumed. However, we find that the Bi₂Se₃ has a relatively higher cutoff frequency (175 cm⁻¹) compared with the Sb₂Te₃ (165 cm⁻¹), despite the former possesses a larger total atomic mass. It is thus reasonable to expect that there exists stronger interatomic bonding of Bi–Se than that of Sb–Te [1, 35]. Furthermore, we find some hybridizations between acoustic and low-frequency optical branches of all the four compounds, which suggests that the inherent phonon–phonon scatterings are more likely to occur and the systems could have lower thermal conductivities [36]. On the other hand, we see that the dispersion relations with and without the consideration of vdW functional are almost the same for the optical branches. However, the presence of vdW tends to increase the phonon group velocity of the acoustic branches along the Γ–Z direction so that a larger lattice thermal conductivity can be expected. In another word, such effect should become more pronounced along the z direction, as discussed in the following.

Table 2 summarizes the calculated lattice thermal conductivities (κ_l) of the binary tetradymites Bi₂Te₃, Bi₂Se₃, Sb₂Te₃ and Sb₂Se₃. For comparison, the results without the vdW functional are also included. It should be mentioned that in the present work, we focus on the effects of the vdW interactions on the phonon transport and only consider the lattice thermal conductivity at 300 K (the effect of thermal expansion was previously investigated by Hellman et al using temperature-dependent IFCs [37]). We see that the in-plane thermal conductivities are obviously larger than those along the out-of-plane direction, which is generally found for layered structures [38–40]. It should be mentioned that, if the vdW is explicitly considered in the calculation, the κₗ of the Bi₂Te₃, Bi₂Se₃ and Sb₂Te₃ agree well with those found previously [1, 37, 41]. On the other hand, including the vdW leads to increased thermal conductivities for all the four
Figure 2. The phonon dispersion relations of the four binary tetradymites Bi$_2$Te$_3$, Bi$_2$Se$_3$, Sb$_2$Te$_3$ and Sb$_2$Se$_3$, where the red and black lines indicate the results calculated with and without vdW functionals, respectively.

Table 2. Lattice thermal conductivities (in-plane/out-of-plane) of the binary tetradymites Bi$_2$Te$_3$, Bi$_2$Se$_3$, Sb$_2$Te$_3$ and Sb$_2$Se$_3$ calculated with and without the consideration of vdW interactions. The change percentages are also listed. The unit of the thermal conductivity is W m$^{-1}$ K$^{-1}$.

| Compounds    | $\kappa_l$ (with vdW) | $\kappa_l$ (w/o vdW) | Change percentage |
|--------------|------------------------|----------------------|------------------|
| Bi$_2$Te$_3$ | 1.82/0.90              | 1.65/0.25            | 9%/72%           |
| Bi$_2$Se$_3$ | 2.60/0.43              | 2.49/0.36            | 4%/16%           |
| Sb$_2$Te$_3$ | 2.06/1.13              | 1.81/0.27            | 12%/76%          |
| Sb$_2$Se$_3$ | 2.64/1.22              | 1.60/0.20            | 39%/84%          |

investigated systems, especially for those along the out-of-plane direction, which is consistent with obviously enhanced phonon dispersion relations along the $\Gamma$–Z direction discussed above. For example, the thermal conductivities of Sb$_2$Se$_3$ increase respectively by 39% and 84% along the in-plane and out-of-plane directions when the vdW functional is explicitly included in the calculations. Such a surprising finding indicates that the generally assumed weak vdW forces are actually of vital importance in predicting the phonon transport properties of layered systems, and a deep understanding of the physical mechanisms involved is quite necessary.

We now focus on the Sb$_2$Se$_3$ where the effect of vdW is the strongest among the four investigated binary tetradymites. Table 3 summarizes the contributions of each phonon branch to the lattice thermal conductivity of the Sb$_2$Se$_3$ calculated with and without consideration of the vdW, where we see that the heat transport is mainly governed by the three acoustic branches, especially for the out-of-plane direction. Together with figure 2(d), such a finding can be used to qualitatively explain the obvious increase of the lattice thermal conductivity when the vdW is taken into considerations. To go into the details, we know that the lattice thermal conductivity can be expressed as $\kappa_l = \frac{1}{\Omega} \sum c_i v_i^2 \tau_i$, where $\Omega$, $c$, $v$ and $\tau$ are the volume of the primitive cell, the heat capacity, the group velocity, and the relaxation time, respectively. The summation is over all the phonon modes. As shown in figure 2(d), the phonon dispersion relations of three acoustic branches along the $\Gamma$–Z direction are obviously enhanced when the vdW functional is included, which means that they have a larger group velocity. Indeed, our calculated $v$ increases from 954 m s$^{-1}$ (747 m s$^{-1}$) to 2490 m s$^{-1}$ (1875 m s$^{-1}$) for the LA (TA) mode at the $\Gamma$ point. Table 4 summarizes the average values of the relaxation time ($\tau$) for the LA, TA, ZA and OP phonon modes. It is found that considering the vdW leads to a significantly larger $\tau$, especially for the LA and TA modes. Indeed, the overall average relaxation time is calculated to be 6.06 ps and 3.13 ps for the system with and without vdW.
Table 3. Contributions of each phonon branch to the lattice thermal conductivity of the Sb$_2$Se$_3$, calculated with and without the consideration of vdW interactions.

| vdW  | Direction | LA (%) | TA (%) | ZA (%) | OP (%) |
|------|-----------|--------|--------|--------|--------|
| With | In-plane  | 22.1   | 19.5   | 20.8   | 37.6   |
|      | Out-of-plane | 31.2   | 28.8   | 24.9   | 15.1   |
| W/o  | In-plane  | 25.3   | 20.2   | 25.1   | 29.4   |
|      | Out-of-plane | 48.6   | 45.6   | 2.5    | 3.3    |

Table 4. Average values of the phonon relaxation time ($\tau$, in unit of ps) and Grüneisen parameter ($\gamma$) for each phonon branch of the Sb$_2$Se$_3$, calculated with and without the consideration of vdW interactions.

| Variable | vdW | LA | TA | ZA | OP |
|----------|-----|----|----|----|----|
| $\tau$   | With | 8.43 | 8.21 | 5.50 | 2.11 |
|          | W/o  | 3.94 | 3.03 | 4.57 | 0.97 |
| $\gamma$ | With | 0.97 | 0.66 | 1.58 | 1.92 |
|          | W/o  | 4.77 | 2.49 | 2.67 | 2.10 |

Figure 3. The Grüneisen parameter and the energy change with respect to the relative lattice constant of the Sb$_2$Se$_3$, where the vdW interactions are considered in (a) and (c), and ignored in (b) and (d). The red and black lines in (c) and (d) are fitted by the three-order polynomial.

forces, respectively. All these observations suggest that the effect of vdW is to increase both the phonon group velocity and the relaxation time so that a larger lattice thermal conductivity of Sb$_2$Se$_3$ can be expected.

In principle, the phonon relaxation time of a given system is closely related to its anharmonicity, which can be characterized by the so-called Grüneisen parameter ($\gamma$). As known [42–44], a smaller $\gamma$ means a weaker phonon scattering strength and therefore a longer relaxation time which consequently leads to a higher lattice thermal conductivity. Indeed, we see from figures 3(a) and (b) that the Sb$_2$Se$_3$ with vdW considered exhibits obviously smaller $\gamma$, especially for the LA, TA, and ZA branches which are previously confirmed to be the dominant contribution to the lattice thermal conductivity. As can be also found from table 4, the average Grüneisen parameter ($\bar{\gamma}$) of these three acoustic branches shows a significant reduction when the vdW functional is explicitly included in the calculations. In particular, the calculated total $\gamma_{\text{tot}}$ is also decreased from 2.29 to 1.69, suggesting the reduced phonon anharmonicity and thus enhanced lattice thermal conductivity. As a further evidence, we plot in figures 3(c) and (d) the energy change ($\Delta E$) with
respect to the relative lattice constant \((a/\Delta a_0)\) of the Sb\(_2\)Se\(_3\). For comparison, the results with and without vdW are both shown. It is found that \(\Delta E\) can be well fitted by a cubic polynomial, where the coefficient of the third-order term is respectively 72 and 92 for the calculations with and without vdW. That is, the system with vdW explicitly included exhibits relatively smaller anharmonicity as discussed above. It is noted that similar results can be found in other binary tetradymites, which are summarized in supplementary table 1 and figure 1 (https://stacks.iop.org/NJP/23/083002/mmedia). It should be noted that the inclusion of the vdW functional also enhances the in-plane thermal conductivity, which is more pronounced for the Sb\(_2\)Se\(_3\). The reason is that the vdW force is not completely along the out-of-plane direction, and its in-plane component could also affect the corresponding phonon transport. To have a better understanding, we plot in supplementary figure 2 the atomic displacement parameters along the in-plane direction for the Se atom at the QL edge of Sb\(_2\)Se\(_3\) (i.e. the Se1 in figure 1). We see that the in-plane vibration of the Se atom is obviously smaller when the vdW force is included, which suggests a lower anharmonicity and thus a higher thermal conductivity. Of course, the major effect of the vdW force on the phonon transport is along the out-of-plane direction.

Before concluding our discussions, it should be mentioned that the effect of vdW on the lattice thermal conductivity can be also understood by a simple physical picture. For the layered structures such as the Sb\(_2\)Se\(_3\), the coexistence of strong covalent bonding inside the QL and much weaker vdW force between neighboring QLs leads to inherently strong phonon anharmonicity, which will be diminished at smaller interlayer distance when the seemingly weak vdW force is presented. As a consequence, lower lattice thermal conductivity can be expected.

### 4. Conclusion

In conclusion, we demonstrate by DFT calculations and Boltzmann transport theory that the weak vdW interactions actually have pronounced effects on the phonon transport properties of the layered tetradymites. The physical origin is that considering the vdW leads to obviously reduced interlayer distance, which can effectively weaken the strong phonon anharmonicity of the system, as confirmed by the decrease of the Grüneisen parameter, as well as the increase of the group velocity and relaxation time. As a consequence, all the four investigated tetradymites exhibit larger lattice thermal conductivities in the presence of vdW, especially for those along the out-of-plane direction. Our work emphasizes the very important role of the usually ignored vdW interactions in accurately predicting the lattice thermal conductivity of the tetradymite compounds, and should be also applied in other layered systems such as transition metal dichalcogenides and various heterostructures of two-dimensional materials.

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### Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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