First-principles study of lattice thermal conductivity of Td–WTe$_2$

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Keywords: WTe$_2$, lattice thermal conductivity, anisotropy

Abstract

The structural and thermal properties of bulk Td–WTe$_2$ have been studied by using first-principles calculations based on the simple Klemens model and an iterative self-consistent method. Both methods show that lattice thermal conductivity is anisotropic, with the highest value in the (001) plane, and lowest one along the c-axis at 300 K. The calculated average thermal conductivity of WTe$_2$ is in agreement with the experimental measurement. The size dependent thermal conductivity shows that nanostructuring of WTe$_2$ can possibly further decrease the lattice thermal conductivity, which can improve the thermoelectric efficiency. Such extremely low thermal conductivity, even much lower than WSe$_2$, makes WTe$_2$ having many potential applications in thermal insulation and thermoelectric materials.

Introduction

Tungsten telluride (WTe$_2$), as a typical transition-metal dichalcogenide (TMD), has attracted great attention recently owing to the interesting physical properties [1–12], such as non-saturating giant positive magnetoresistance [1, 3], superconductivity [8, 9] and high carrier mobilities [5]. Unfortunately, the extremely large positive magnetoresistance can only be observed at low temperature which limits the applications of WTe$_2$ magnetoresistance devices. The thermal transport properties are a key consideration to accelerate the application of WTe$_2$, which are likely to demonstrate thermally limited performance. In addition, thermal conductivity plays a crucial role to improve the thermoelectric efficiency, which has become an important subject to design the high-efficiency thermoelectric materials which can convert waste heat into usable electrical energy [13].

Recently, the thermal properties of TMD materials have attracted great interest due to their potential applications in ultralow thermal conductivity devices [14] and thermoelectric devices [15–19]. WTe$_2$ is a semimetal which is also a potential thermoelectric material [20], and we can further improve its thermoelectric performance by doping. The performance of thermoelectric materials depends on the figure of merit $ZT$ [21]. One effective way to increase $ZT$ is to reduce the thermal conductivity without affecting electronic conductivity [22]. Moreover, ultralow thermal conductivity is required to prevent the back-flow of heat from the hot end to the cool one. Therefore, it is crucial to search for ultralow thermal conductivity materials in thermoelectric applications. It was recently found that the cross-plane thermal conductivity ($\kappa_c$) of disordered WSe$_2$ thin films is as low as 0.05 W m$^{-1}$ K$^{-1}$ [14] which is the lowest $\kappa$ ever reported for a dense solid to this date. According to the classical theory [23, 24], WTe$_2$ should possess lower thermal conductivity than WSe$_2$ due to the heavier atom mass and lower Debye temperature in WTe$_2$. However, unlike the electronic properties of WTe$_2$, which have been intensively explored, the study on the thermal properties is still in its infancy [25–28]. The experiment measurement showed the thermal conductivity of polycrystalline WTe$_2$ is 0.8 W m$^{-1}$ K$^{-1}$ [28], which didn’t
exhibit the anisotropy of thermal transport. Besides, the polycrystalline samples have many boundary scattering which can not give the intrinsic thermal conductivity of WTe₂.

In this paper, we have calculated the isochoric specific heat, Debye temperature, and the intrinsic lattice thermal conductivity from the first principles calculations. We find that the thermal conductivity of WTe₂ is anisotropic, and much lower than that of WSe₂. The size-dependent thermal conductivity of WTe₂ is also discussed.

Computational details

The first-principles calculations are performed by using the density functional theory as implemented in the Vienna ab initio simulation package [29–31]. The Perdew–Burke–Ernzerhof of generalized gradient approximation (GGA) is chosen as the exchange-correlation functional [32]. The vdW-DF of correlation functional [33, 34] is used in our calculation in order to take into account van der Waals (vdW) forces, which are expected to play a crucial role in bulk WTe₂. The cutoff energy of planewaves is set as 600 eV, and a Monkhorst–Pack [35] k-mesh of 14 × 7 × 3 is used to sample the Brillouin zone in the structure optimization. The internal coordinates and lattice constants are optimized until the atomic forces became less than 10⁻³ eV Å⁻¹.

For Td–WTe₂, the intrinsic lattice thermal conductivity is dominated by phonons, and the interaction between phonons and electrons can be neglected safely as the electronic density of states (DOS) near the Fermi surface is quite small [8]. In this work, finite displacement method is used for harmonic phonon properties with Phonopy package [36]. Thermal conductivity is calculated with two methods for comparing. Firstly, we calculated thermal conductivity with Klemens model, in which the umklapp phonon–phonon scattering processes are calculated using the relaxation time approximation [37–39]. It only includes the contribution of acoustic phonons within a Debye approximation and the optic phonon branches are omitted, as thermal transport usually dominated by acoustic phonons. This method has been successfully applied to predict the thermal conductivity of many materials, such as graphene [37, 40], graphene nanoribbons [41], monolayer MoS₂ sheet [42], and Phosphorene [43]. Secondly, an iterative self-consistent method is used for solving the phonon Boltzmann transport equation (BTE) to calculate the lattice thermal conductivity with the ShengBTE code [44]. It is based on the second-order (harmonic) and third-order (anharmonic) interatomic force constants (IFCs) combined with an iterative self-consistent algorithm to solve the BTE, and has also successfully predicted the thermal conductivities of many materials [45–47]. We use a 3 × 2 × 1 supercell which contains 72 atoms for calculations of second-order IFCs, and a 2 × 2 × 1 supercell with a 7 × 4 × 3 k-mesh is used for the third-order IFCs. The third-order IFCs including fourth nearest-neighbor interactions are obtained by the thirdorder script in ShengBTE [44].
Results and discussion

The space group of bulk WTe$_2$ is Pnm$2_1$. The octahedron of Te is slightly distorted and the W atoms displace from their ideal octahedral sites, forming zigzag metal–metal chains along $a$-axis [48] as shown in figure 1. The crystal structure is fully optimized using the GGA and GGA+vdW methods. The calculated structural parameters are listed in table 1. Taking the experimental ambient volume [48] as a reference, we find the difference between calculated and experimental volumes of 15.82% in GGA method and 2.88% in GGA+vdW method. Obviously, the GGA+vdW scheme performs much better. From table 1, we can find that the inclusion of vdW interactions reduces all the lattice parameters ($a$, $b$, and $c$). But the largest difference between the two methods is found for the $c$ parameter, i.e., the direction perpendicular to the WTe$_2$ layers. The distance between two adjacent layers ($d$ in figure 1) is also better described by GGA+vdW. Therefore, we conclude that the vdW forces dominate the interlayer interaction and are essential in order to obtain the accurate lattice parameters in WTe$_2$. Therefore all of the following results are based on the GGA+vdW method.

The calculated phonon dispersion and DOS are shown in figure 2. The phonon frequencies are in the range of 0–232 cm$^{-1}$. It can be found that all of the phonon frequencies are positive in the Brillouin zone, which indicates that the structure of WTe$_2$ is dynamically stable. Since the primitive cell of WTe$_2$ contains twelve atoms, thirty-six independent vibration modes can be found, in which three are acoustic modes (two transverse and one longitudinal) and the remaining modes correspond to optical ones. The phonon dispersions are well consistent with previous reports [8].

According to the results of the phonon dispersion, the isochoric specific heat capacity $C_v$ of bulk WTe$_2$ is calculated. The temperature dependent heat capacity is presented in figure 3(a). It can be seen the isochoric specific heat capacity shows the expected $T^3$ law behavior in the low-temperature limit, and attains the saturation value (74.8 J mol$^{-1}$ K$^{-1}$), which is known as Dulong–Petit classical limit. Compared with the experimental constant-pressure specific heats $C_p$ [26] as shown in figure 3, it is found that the $C_p$ are systemically larger than the $C_v$ which is related to the thermal expansion caused by anharmonicity effects [49].

### Table 1. Calculated structural parameters of bulk WTe$_2$. Experimental ones are listed for comparison. $d$ is the nearest interlayer distance shown in figure 1.

| Lattice parameter (Å) | GGA | GGA+vdW | Expt.$^*$ |
|-----------------------|-----|---------|----------|
| $a$                   | 3.502 | 3.500   | 3.477    |
| $b$                   | 6.332 | 6.291   | 6.249    |
| $c$                   | 15.910 | 14.232  | 14.018   |
| $d$                   | 3.764 | 2.906   | 2.868    |
| $V$ ($\text{Å}^3$)    | 352.82 | 313.40  | 304.63   |

$^*$ Reference [48].
The Debye temperature $\theta_D$ is known as an important fundamental parameter closely related to many physical properties such as specific heat, elastic constant, and melting point [50]. We obtain the Debye temperature based on Debye model by fitting the calculated specific heat capacities. Debye temperature $\theta_D$ as a function of temperature is exhibited in figure 3(b). As the temperature varies from 0 to 500 K, $\theta_D$ increases quickly and then reaches a constant about 263 K. The zero temperature $\theta_D(T \rightarrow 0)$ is 137.0 K, which is in good agreement with the experimental one (133.8 K) [26].

The thermal conductivities of WTe$_2$ at 300 K calculated with two methods are listed in table 2. For both the Klemens model and iterative self-consistent method, the intrinsic thermal conductivity propagating on (001) plane is much higher than that along [001] direction, and the $\kappa$ of WTe$_2$ on (001) plane is slightly anisotropic. We can find the values that Klemens model gives are slightly smaller than iterative self-consistent method. Furthermore, the result of Klemens model indicates the max value of $\kappa$ is along $a$-axis while it is along $b$-axis in the result of ShengBTE, though the difference of $\kappa$ along the two directions is quite small with both methods. The thermal conductivity of WSe$_2$ is also calculated for comparing as we expect WTe$_2$ may possess lower thermal conductivity than WSe$_2$. For WSe$_2$, the calculated thermal conductivities by iterative self-consistent method are consistent with the ones in [19], but they are much larger than the values of Klemens model. The difference of the two methods is small for WTe$_2$, while is large for WSe$_2$. It may result from that there is an obvious frequency gap between acoustic and optic phonon branches [19] which can reduce its intrinsic thermal resistance [51] for WSe$_2$, while there is no gap for WTe$_2$. Nevertheless, both methods show that the thermal conductivities of WSe$_2$ are also anisotropic and they are higher than WTe$_2$ in all directions, which is expected due to the heavier atom mass of Te. Compared with the less-justified Klemens model, the iterative self-consistent method is more reliable, therefore, we will mainly discuss the lattice thermal conductivity based on the results using the iterative self-consistent method in the following.

Table 2. Comparison of the lattice thermal conductivities of WTe$_2$ and WSe$_2$ obtained from various studies at 300 K.

|        | WTe$_2$ (W m$^{-1}$ K$^{-1}$) | WSe$_2$ (W m$^{-1}$ K$^{-1}$) |
|--------|-------------------------------|-------------------------------|
|        | Calc$^a$ | Calc$^b$ | Expt$^c$ | Calca | Calcb | Calcd | Expte |
| [100]  | 9.84     | 9.03     | 69.58    | 15.00  | 50    | 9.7   |
| [010]  | 11.06    | 7.69     | 0.8      | 69.58  | 14.59 | 50    | 9.7   |
| [001]  | 1.04     | 0.45     | 7.02     | 0.90   | 6     | 2.09  |

$^a$ Calculated using iterative self-consistent method with ShengBTE code.
$^b$ Calculated with Klemens model.
$^c$ [28].
$^d$ [19].
$^e$ [52].
As we expected, the thermal conductivity of WTe$_2$ is lower than that of WSe$_2$. For instance, the lowest $\kappa$ of WTe$_2$ is 1.04 W m$^{-1}$ K$^{-1}$ along [001] direction, while the lowest value for WSe$_2$ is about six times higher at 7.02 W m$^{-1}$ K$^{-1}$ along the same direction. The thermal conductivity of WTe$_2$ is much lower than that of WSe$_2$ because of the heavier atom mass and lower Debye temperature in WTe$_2$. We estimate the averaged thermal conductivity is about 2.60 W m$^{-1}$ K$^{-1}$ using the Matheissen’s rule, while the average value of Klemens model is 1.22 W m$^{-1}$ K$^{-1}$. The smaller thermal conductivity measured in experiments (0.8 W m$^{-1}$ K$^{-1}$) compared to the theoretical values can be due to the defect and/or boundary scattering effects in polycrystalline samples.

In order to compare the temperature dependent $\kappa$ of WTe$_2$ and WSe$_2$, we present the calculated lattice thermal conductivities of WTe$_2$ and WSe$_2$ from 200 to 500 K based on the iterative self-consistent method with ShengBTE in figure 4. We can see that the thermal conductivity of WTe$_2$ is much lower than that of WSe$_2$ not only at the room temperature, but also in the whole calculated temperature range. It is also shown that both of their lattice thermal conductivities decrease with the rise of temperature following a $T^{-1}$ relationship due to the stronger phonon-phonon scattering at the higher temperature.

Besides, we find the obvious anisotropy of thermal conductivity in both materials. The thermal conductivities in [001] direction are much lower than those propagating on (001) plane. This kind of anisotropy of thermal conductivity between in-plane and cross-plane is due to their vdW bound layered structure which has
also been found in other layered materials [53]. The in-plane thermal conductivity in WTe$_2$ is a factor of $\sim$10 times larger than the $c$-axis thermal conductivity, which is almost the same of WSe$_2$. The in-plane thermal conductivities of WTe$_2$ are also a little anisotropic while WSe$_2$ shows isotropic which is ascribed to their different crystal symmetry. Figure 5 shows the in-plane thermal conductivity of WTe$_2$ at 300 K based on the iterative self-consistent method with ShengBTE to understand the anisotropy of in-plane thermal conductivity. It can be seen the in-plane thermal conductivity is 9.84–11.06 W m$^{-1}$ K$^{-1}$ at 300 K, and the maximum is along [010] direction while the minimum is along [100] direction.

To further understand the anisotropy of thermal conductivity, we have calculated the group velocities of phonons of WTe$_2$, which are closely relevant to the lattice thermal conductivity of a material. The group velocities along [100], [010] and [001] directions, as a function of frequency, are plotted in figure 6. It can be seen that the group velocities decrease with the increase of phonon frequency along each direction, which is because the optical modes are usually less dispersive than the acoustic ones. In addition, the phonon group velocities along [001] direction are significantly lower than the other two directions because of the weak inter-layer vdW interactions along the [001] direction. Therefore, the phonon velocity is anisotropic which has significantly effect on the lattice thermal conductivity [54]. The larger phonon velocities in the direction [100] and [010] result in a larger lattice thermal conductivity in these directions, and smaller ones in [001] are responsible for smaller thermal conductivity.

![Figure 6. Group velocities of phonons along [100], [010], and [001] directions in WTe$_2$, respectively.](image)

![Figure 7. Cumulative thermal conductivity $\kappa$ with respect to phonon MFP in WTe$_2$ along [100], [010] and [001] directions, respectively.](image)
An important question on the thermal conductivity of real materials is the size dependence. In order to understand the size effect on the thermal transport, it is instructive to calculate the cumulative thermal conductivity which associates with accumulated contributions up to a mean-free path (MFP) cutoff $L$ with the formulas in [35]. We calculate the cumulative thermal conductivities of WTe$_2$ along [100], [010] and [001] directions at 300 K using the iterative self-consistent method as shown in figure 7. The total accumulation for each direction firstly increases as $L$, then gradually approaches a plateau. It can be seen that the cumulative thermal conductivities in [010] and [001] directions decrease quickly when the $L$ is less than about 200 nm, while the critical point of such quick decrease is around 100 nm for [100] direction. Phonons with MFP below 200 nm contribute about 85% $\kappa$ for the [010] and [001] directions. While for $L < 100$ nm, phonons with MFP contribute about 95% $\kappa$ for the [100] direction. Therefore, the nanostructuring approach is a promising way to further reduce the lattice thermal conductivity. The material may have a high thermoelectric efficiency when it is in an appropriate size, while it can keep its electronic conductivity with doping.

**Conclusion**

We have investigated the structural properties and the intrinsic lattice thermal conductivity of bulk WTe$_2$ from first principles. It is found that vDW force plays an important role in the inter-layer interaction of WTe$_2$. Our calculations indicate that the thermal conductivity of WTe$_2$ is anisotropic, and the highest thermal conductivity (11.06 W m$^{-1}$ K$^{-1}$ at 300 K) is along $b$-axis, while the lowest one is along $c$-axis (1.04 W m$^{-1}$ K$^{-1}$ at 300 K). The averaged thermal conductivity is 2.60 W m$^{-1}$ K$^{-1}$. The anisotropic group velocities of phonon are responsible for the anisotropy of thermal conductivity. In addition, the WTe$_2$ has the ultralow low cross-plane thermal conductivity which is even lower than that of WSe$_2$. We also studied the size dependent thermal conductivity of WTe$_2$. Our results indicate that introducing nanostructure can possibly further decrease the lattice thermal conductivity in WTe$_2$. Our work shields more light on potential applications of WTe$_2$ in thermal insulation and thermoelectric materials.

**Acknowledgments**

This work was supported by the National Key Project for Basic Research of China (Grant no. 2015CB659400), NSFC (Grant nos. 11474150 and 11525417, 11374137, 11547030), China Postdoctoral Science Foundation (2014M551544), and the Opening Project of Shanghai Key Laboratory of High Temperature Superconductors (14DZZ2260700).

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