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A systematic investigation of thermal conductivities of transition metal dichalcogenides

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ABSTRACT

Although the thermal conductivities of MoS_2 and WS_2 have been reported by some experimental and theoretical studies, the results are inconsistent. Here, thermal transport properties of twelve types of single layer transition metal dichalcogenides (TMDs) MX_2 (M = Cr, Mo, W; X = O, S, Se, Te) are investigated systematically, by solving Boltzmann transport equation based on first-principle calculations. After accurate considering the size effect and boundary scattering, we find that our calculations can fit the experimental results very well. Moreover, diverse transport properties in TMDs are revealed, and an abnormal dependence of thermal conductivity on atomic mass is observed. In most MX_2 structures, the thermal conductivities decrease with the increase of mass of atom M or X. However, the thermal conductivities of sulfides MS_2 and selenides MSe_2 increase as the M changes from Cr to Mo to W, which is contradictory to our traditional understanding. A detailed calculation indicates that the abnormal trend is originated from the rapid increase of phonon relaxation time. Our studies provide important information for thermal transport abilities in TMDs.

1. Introduction

The zero band gap of graphene constricts its applications in some fields, such as electronics and optoelectronics, even if it possesses unique physical and chemical properties [1–4]. Therefore, finding semiconductors with suitable band gaps has become a focus in the field of two dimensional (2D) materials [5–9]. The single layer transition metal dichalcogenides (TMDs) are good candidates, which are generally in the form of honeycomb MX_2 (M is transition metal while X is chalcogen) [6,7,10]. They exhibit excellent electronic and optoelectronic properties. For example, the carrier mobility of a MoS_2 transistor can approach 200 cm^2/VS, and its on/off ratio approaches 10^8 at room temperature [10,11]; high-performance light-emitting transistors and field-effect transistors based on MoS_2 and WS_2 have also been synthesized [11–14]. Besides the transition metal sulfides, oxides, selenides and tellurides are also found to be semiconductors showing potential applications as electronic and optoelectronic devices [7,15]. Most of the TMDs have been synthesized successfully, which further stimulates extensive interests in the research community of these rich 2D materials [16,17].

Followed by the studies of electronic and optoelectronic properties of TMDs, the thermal transport properties have attracted attentions gradually [18–21], because of crucial roles in the practical applications, such as heat dissipation, phononics and thermoelectric devices. As a typical material of TMDs, the thermal conductivity of MoS_2 is numerously investigated by experiment and theory. Zhang et al. and Liu et al. reported that their measured thermal conductivities are approximate 85 W/m K, with the sample size $d \approx 5$ μm (width) and $L \approx 15$ μm (length) [18,22]. Sahoo et al. reported that the thermal conductivity of MoS_2 with size $d \approx 4$ μm and $L \approx 10$ μm is 52 W/m K [19]. While Yan et al. demonstrated that a smaller circle sample (≈1.2 μm) have a much smaller value 34.5 W/m K [23]. Therefore, the experimental values obtained are dependent on the samples. Theoretically calculated thermal conductivities based on various methods present different results, such as 103 W/m K from Boltzmann transport equation [24], 1.5 W/m K [25] and 6.0 W/m K [21] from molecular-dynamics simulations and 23.3 W/m K from the Green's function method [26]. These results not only are different from each other, but also have great disparities with the experimental values. Monolayer WS_2 is another typical TMD whose thermal conductivity has been studied [20,24]. A theoretic work revealed that WS_2 possesses high thermal conductivity 140 W/m K [24], however, a experimental work reported that the value is only 32 W/m K [20]. Obviously, a systematic study of thermal conductivities of

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TMDs is necessary, on one hand to clarify the disparities between experimental and theoretical results, on the other hand to obtain a united description of thermal transport properties of the 2D materials.

In this paper, we investigate systematically thermal conductivities of twelve honeycomb MX_2 (M = Cr, Mo, W; X = O, S, Se, Te) compounds. In the approaches of dealing with thermal transport, the Green's function method is constricted in the phonon ballistic transport region while molecular-dynamics simulation is strongly related to the classical empirical potentials. Therefore, in many cases, the calculated results based on the two methods deviate from the experimental data. Here, we use Boltzmann transport equation [27–29] combined with first-principle method [30,31] to calculate thermal conductivities of the TMDs. It is found that the thermal transport properties show significant size effect. By considering the boundary scattering and the effect of length, our calculated results agree with the experimental results well. The thermal conductivities of the twelve MX_2 compounds as a function of length are predicted. In addition, an abnormal dependence of thermal conductivity on the mass is found: as X = S and Se, the thermal conductivities of MX_2 increase with the mass of atom M rather than decrease, which is contradictory to normal understanding. Underlying transport mechanisms are analyzed by heat capacity, phonon group velocity, phonon relaxation time and phonon dispersion.

2. Computational method

The thermal conductivity κ of TMD is calculated by solving the Boltzmann transport equation (BTE), which is expressed as [27–29]:

$$\kappa = \sum C_v v_s(q)^2 \tau_s(q) = \frac{k_b}{4\pi h}\sum_s \int_{q_{\min}}^{q_{\max}} \frac{\exp[\hbar\omega_s(q)/k_bT]}{[\exp[\hbar\omega_s(q)/k_bT]-1]^2} q \times [\hbar\omega_s(q)/k_bT]^2 \times v_s(q)^2 \times \tau_s(q)dq, \quad (1)$$

where s and q are phonon branches and wave vectors, respectively; C_v, $v_s(q)$ and $\tau_s(q)$ are heat capacity, phonon group velocity and phonon relaxation time, $\omega_s(q)$ is phonon frequency k_b is Boltzmann parameters, h is the thickness of single layer MX_2 that chosen as layer distance in bulk structure, and T is the temperature. The $\omega_s(q)$ can be extracted from the phonon spectrum, and the $v_s(q)$ is calculated from $v_s(q) = d\omega_s(q)/dq$. The heat capacity C_v can also be expressed in the frequency presentation, by integrating over the partial phonon density of states ($PDOS(\omega)$) of different particle (N) [29,32]:

$$C_v = k_b \sum_N \int_0^\infty \left\{ [\hbar\omega/k_bT]^2 \times \frac{\exp[\hbar\omega/k_bT]}{[\exp[\hbar\omega/k_bT]-1]^2} PDOS(\omega) \right\} d\omega. \quad (2)$$

To determine the phonon relaxation time $\tau_s(q)$, two types of phonon scattering mechanisms are considered here, including intrinsic phonon-phonon scattering and phonon boundary scattering. The intrinsic phonon-phonon scattering process is studied by considering the three-phonon Umklapp scattering [27,33]:

$$\tau_s^U(q) = \frac{1}{\gamma_s(q)^2} \frac{M v_s(q)^2}{k_B T} \frac{\omega_{s,\max}}{\omega_s(q)^2}, \quad (3)$$

where $\omega_{s,\max}$ is the maximum frequency of branch s, m is the total mass of atoms in a unit cell, $\gamma_s(q)$ is Grüneisen parameters that can be obtained from the phonon spectrum by $\gamma_s(q) = -Vd\omega_s(q)/\omega_s(q)dV$ [26,34]. The phonon boundary scattering can be evaluated as [27,29]:

$$\tau_s^B(q) = \frac{d}{v_s(q)} \frac{1+p}{1-p}, \quad (4)$$

where d is the width of a sample, and p is the specularity parameter which characterizes the fraction of specularity of scattered phonons depending on the roughness of the edge, ranging from 0.0 for a completely rough edge to 1.0 for a perfectly smooth edge. Then, according to the Matthiessen's rule, $\tau_s(q)$ can be found by combine the phonon-phonon Umklapp scattering and phonon boundary scattering together [35]:

$$\frac{1}{\tau_s(q)} = \frac{1}{\tau_s^U(q)} + \frac{1}{\tau_s^B(s,q)}. \quad (5)$$

It is noted that the phonon mean free path (MFP) cannot exceed the physical length L of the sample, and thus the phonons should be excluded if they cannot satisfy the following formula [28], and meanwhile the low-bound cut-off frequencies for each branch are determined,

$$v_s(q)\tau_s^U(q) < L. \quad (6)$$

The first principle calculations for phonon spectra are accurately performed by the Vienna ab initio simulation package (*VASP*) based on density functional theory [30]. The generalized gradient approximation with Perdew-Burke-Ernzerhof exchange-correlation potential (GGA-PBE) is adopted, with plane wave cut-off energy 450 eV. The total energy convergence is chosen as 1.0×10^{-8} eV, and structure optimization is performed until the force acting on each atom is less than 1.0×10^{-7} eV. In addition, the calculations are performed on a $5 \times 5 \times 1$ supercell structure, which is large enough to obtain reliable harmonic and anharmonic phonon properties [24,36].

3. Results and discussion

In Fig. 1, the effects of width d and length L on the thermal conductivity κ of MoS_2 are shown. To describe the boundary scattering in detail, the effect of p is also considered. Three length values L = 4, 10 and 15 μm, corresponding to sample lengths in four experiments, are selected. If L is fixed, κ increases rapidly at small d followed by convergence at large d ($d \geqslant L$). The effect of p also becomes weak with the increase of d. This is reasonable because the influences of the boundary scattering are weakened in the sam-

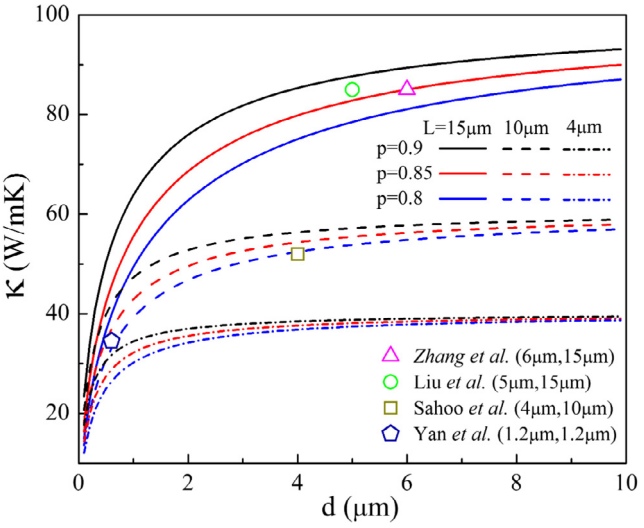

Fig. 1. Thermal conductivity κ of MoS_2 as a function of width d with different p and length L, respectively, at T = 300 K. The single symbols are experimental results from Zhang et al. in Ref. [18], Liu et al. in Ref. [22], Sahoo et al. in Ref. [19] and Yan et al. in Ref. [23] with different sample sizes (d, L).