Few-Layer PdSe₂ Sheets: Promising Thermoelectric Materials Driven by High Valley Convergence

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ABSTRACT: Herein, we report a comprehensive study on the structural and electronic properties of bulk, monolayer, and multilayer PdSe₂ sheets. First, we present a benchmark study on the structural properties of bulk PdSe₂ by using 13 commonly used density functional theory (DFT) functionals. Unexpectedly, the most commonly used van der Waals (vdW)-correction methods, including DFT-D2, optB88, and vDW-DF2, fail to provide accurate predictions of lattice parameters compared to experimental data (relative error > 15%). On the other hand, the PBE-TS series functionals provide significantly improved prediction with a relative error of <2%. Unlike hexagonal two-dimensional materials like graphene, transition metal dichalcogenides, and h-BN, the conduction band minimum of monolayer PdSe₂ is not located along the high symmetry lines in the first Brillouin zone; this highlights the importance of the structure–property relationship in the pentagonal lattice. Interestingly, high valley convergence is found in the conduction and valence bands in monolayer, bilayer, and trilayer PdSe₂ sheets, suggesting promising application in thermoelectric cooling.

INTRODUCTION

Two-dimensional (2D) materials, including graphene, transition metal dichalcogenides, and phosphorene, have attracted much attention in recent years due to their remarkable properties and great potential in nanoelectronic, catalytic, energy conversion and storage, spintronics, superconductor, and even biological applications.1−25 Recently, studies on a new 2D carbon allotrope, penta-graphene,26 have brought 2D materials with pentagonal structures under the spotlight. Unlike hexagonal graphene, pentagonal graphene is an indirect bandgap semiconductor with a sizable bandgap of ~1.30 eV. This makes 2D PdSe₂ promising for application in field effect transistors (FETs) with a high current on/off ratio and low power dissipation. It was reported that the FET constructed by the PdSe₂ bilayer exhibited an on/off ratio of up to 10⁶, together with a high electron mobility of ~158 cm² V⁻¹ s⁻¹.33 More importantly, PdSe₂ remains highly stable even after exposure to air for 60 days,33 demonstrating a potential for practical applications in many important fields.

In this paper, we report a systematic study of the lattice structure and electronic properties of bulk and few-layer (1−5 layers) PdSe₂. We conducted a benchmark study on the structural properties of bulk PdSe₂ by using 13 different density functional theory (DFT) functionals and found that the PBE-TS + SCS functional can reproduce the experimentally obtained lattice structure of bulk PdSe₂, because it provides
Figure 1. (a) Crystal structure of bulk PdSe2. The red and white spheres represent Pd and Se atoms, respectively. (b) The Brillouin zone path of bulk PdSe2 primitive cell. (c) The electronic band structure of bulk PdSe2, calculated by the PBE-TS + SCS method. The Fermi level has been set to zero and indicated by the dashed line.

Table 1. Lattice Parameters (in Å) a, b, and c, Calculated Using Different DFT Functionals, and the Relative Error (Δ) of Bulk PdSe2 with Respect to the Experimental Data

| Method          | a       | Δ (%)  | b       | Δ (%)  | c       | Δ (%)  |
|-----------------|---------|--------|---------|--------|---------|--------|
| expt (ref 47)   | 5.7457  |        | 5.8679  |        | 7.6976  |        |
| PBE             | 5.779   | 0.63   | 5.931   | 1.09   | 8.495   | 9.62   |
| PBE-D2          | 6.196   | 7.83   | 6.196   | 5.58   | 6.193   | −19.55 |
| PBE-D3 + ZP     | 6.198   | 7.87   | 6.178   | 5.62   | 6.192   | −19.55 |
| PBE-D3 + BJ     | 6.179   | 7.54   | 6.178   | 5.30   | 6.173   | −19.81 |
| PBE-dDsC        | 6.208   | 8.05   | 6.210   | 5.82   | 6.201   | −19.44 |
| optPBE          | 6.310   | 9.81   | 6.310   | 7.53   | 6.303   | −18.12 |
| optB86b         | 6.220   | 8.26   | 6.221   | 6.01   | 6.212   | −19.30 |
| optB88          | 6.268   | 9.09   | 6.269   | 6.83   | 6.258   | −18.70 |
| vdW-DF2         | 6.512   | 13.34  | 6.513   | 10.99  | 6.524   | −15.24 |
| PBE-TS          | 5.862   | 2.03   | 5.953   | 1.46   | 7.590   | −1.40  |
| PBE-TS + HI     | 5.859   | 1.98   | 5.955   | 1.48   | 7.591   | −1.38  |
| PBE-TS + SCS    | 5.851   | 1.83   | 5.947   | 1.34   | 7.694   | −0.05  |
| PBE-TS + MBD    | 5.838   | 1.61   | 5.945   | 1.32   | 7.496   | −2.62  |

an appropriate description of interlayer interaction. Multilayer PdSe2 sheets were all found to be indirect bandgap semiconductors. Interestingly, we identified convergence in energy of both the conduction and valence bands in monolayer, bilayer, and trilayer PdSe2, indicative of their excellent thermoelectric properties.

### RESULTS AND DISCUSSION

#### Structural and Electronic Properties of Bulk PdSe2

It is well known that van der Waals (vdW) interaction plays a dominant role in layered materials like graphite and hexagonal boron nitride. Thus, accurate theoretical description of the interlayer interaction is of great importance in the investigation of physical properties of layered materials. Herein, the structural properties of bulk PdSe2 are studied using 13 different DFT functionals, including PBE, PBE-D2, PBE-D3 with zero damping (PBE-D3 + ZP), PBE-D3 with Becke Johnson damping (PBE-D3 + BJ), PBE-dDsC, optPBE, optB86b, optB88, vdW-DF2, PBE-TS, PBE-TS + HI, PBE-TS + SCS, and PBE-TS + MBD functionals. Figure 1a shows the atomic structure of bulk PdSe2; it has an orthorhombic structure with a Pbca space group. The experimental lattice parameters of the crystal are \( a = 5.7457 \) Å, \( b = 5.8679 \) Å, and \( c = 7.6976 \) Å. Our computed lattice parameters of bulk PdSe2 are summarized in Table 1 and are compared with the available experimental data. Obviously, the PBE functional cannot describe the interlayer interaction in bulk PdSe2 because it cannot reproduce the \( c \) lattice constant accurately. Meanwhile, the PBE-D2, PBE-D3 + ZP, PBE-D3 + BJ, and PBE-dDsC functionals makeover binding results and underestimate the interlayer spacing in comparison with experimental data. These functionals predict the \( c \) lattice constants to be \( 6.173 - 6.201, \sim 1.5 \) Å smaller than the experimental value. They also predict larger \( a \) and \( b \) lattice constants compared with the experimental data. vdW-DF functional, including optPBE, optB86b, optB88, and vdW-DF2 series methods, also fail to predict the lattice structure of bulk PdSe2. The calculated values of the \( c \) lattice constants (6.303, 6.212, 6.258, and 6.524 Å, respectively) are significantly smaller than the experimental data. Interestingly, the PBE-TS series functionals result in a significantly better agreement with the experimental data than other methods. Specifically, for the computed values obtained by PBE-TS + SCS, the mean relative errors with respect to the experimental data are only 0.05% for the lattice constants \( a, b, \) and \( c \), respectively. In theory, PBE-D2 is based on an empirical correction to the total energy in the form of a pairwise interaction, whereas optB86b and vdW-DF2 are based solely on the global charge density. On the other hand, the TS approaches refine these basic corrections with an improved description of the nonlocal effect. On the basis of the above discussion, it is found that the PBE-TS + SCS functional leads to a reasonable and accurate prediction of the lattice parameters of bulk PdSe2.

Next, we focus on the electronic properties of bulk PdSe2. Its Brillouin zone and electronic band structure are shown in Figure 1b,c, respectively. Bulk PdSe2 is metallic in nature with many bands across the Fermi level (Figure 1c). We also calculated the band structure of bulk PdSe2 in the presence of
spin–orbit coupling (SOC) (Figure S1). Both combinations of methods predict that bulk PdSe₂ is metallic, being fully consistent with the recently reported experimental results.³³ Clearly, accurate prediction of the lattice structure is vital for the theoretical prediction of the electronic properties.

Lattice Structure and Electronic Properties of Monolayer PdSe₂. Next, we focus on monolayer PdSe₂. Figure 2a shows the optimized structure of the PdSe₂ monolayer: every primitive cell of monolayer PdSe₂ contains two Pd atoms and four Se atoms in a pentagonal arrangement. Unlike the isotropic penta-graphene,²⁶ PdSe₂ has an anisotropic structure. The optimized lattice constants are \( a = 5.71 \) Å and \( b = 5.90 \) Å, which are in good agreement with the previous results.³³,⁴⁹ In a primitive cell, each Pd atom forms four bonds with four Se atoms, while each Se atom forms two bonds with two Pd atoms and one bond with another Se atom. Because of its anisotropy, two types of Se are defined in a primitive cell, denoted as Se₁ and Se₂ (Figure 2a). The bond lengths of Pd–Se₁, Pd–Se₂, and Se₁–Se₂ are 2.45, 2.46, and 2.42 Å, respectively, while the bond angles of Se₁–Pd–Se₂, Se₁–Pd–Se₂, and Pd–Se₁–Pd are 93.6, 86.4, and 113.7°, respectively. The side view (Figure 2a) shows a large buckling height of 0.75 Å, much larger than that of penta-graphene (0.6 Å).²⁶

The band structure and density of states (DOSs) of monolayer PdSe₂ are calculated by the PBE-TS + SCS method. The Fermi level has been set to zero and indicated by the dashed line. (c) The Brillouin zone path of PdSe₂ primitive cell.

The bandstructure and density of states (DOSs) of monolayer PdSe₂ are shown in Figure 2b. It can be found that the PdSe₂ monolayer is an indirect bandgap semiconductor. Interestingly, the conduction band minimum (CBM) of PdSe₂ is not located along the high symmetry lines like other 2D semiconducting materials such as MoS₂,⁵⁰ and phosphorene.⁵¹ It is located at the \( \Lambda \) point, which is along the \( \Gamma \) and \( M \) (0.385, 0.5, 0) lines (Figure 2c). Meanwhile, the valence band maximum (VBM) is located at the \( \Gamma \)–X line, marked as \( \Sigma \). The bandgap calculated by PBE-TS + SCS is 1.381 eV, which is slightly larger than the value (1.3 eV) reported by Oyedele et al.³³ In general, this difference is due to the large uncertainty in the prediction of an unoccupied band by commonly used exchange–correlation functional.⁵² Since both Pd and Se are heavy elements, the band structure of the PdSe₂ monolayer was checked by considering SOC (Figure S2). The spin–orbit splitting of the conduction band around the \( S \) point is ~28 meV; however, no significant spin–orbit splitting appears at the CBM and VBM. The PBE-TS + SCS + SOC method yields a bandgap of 1.376 eV, similar to that predicted by the PBE-TS + SCS method. We also calculated the band structure of the PdSe₂ monolayer by HSE06 functional (Figure S2b).³³ The HSE06 gap (2.203 eV) is much larger than that obtained by the PBE-TS + SCS method. Moreover, the band structure predicted by the PBE-TS + SCS + HSE06 method has a profile similar to the PBE-TS + SCS result. Thus, the PBE-TS + SCS method is reliable for predicting the electronic properties of PdSe₂ layers.

Structural and Electronic Properties of Few-Layer PdSe₂ Stacks. Next, we investigated the structural and electronic properties of bilayer PdSe₂. Figure 3a shows that the first possible stacking pattern of bilayer PdSe₂ is named \( \alpha \)-PdSe₂ (AB stacking), which starts from the bulk stacking sequence, and the structure symmetry is \( C_{2v} \). Due to \( C_{2v} \) symmetry, one PdSe₂ layer can rotate 180° with respect to the adjacent layer, to yield the other possible stacking pattern, \( \beta \)-PdSe₂, which has a lower symmetry of \( C_{2v} \). The transverse displacement between the two adjacent layers is considered to search for the most stable stacking pattern. The translational degree of freedom was obtained by varying \( \Delta x, \Delta y \) in the range of \( [0, a] \) and \( [0, b] \), respectively, with a \( 20 \times 20 \) grid. At each grid point, all atoms were allowed to relax. The energetically favorable bilayer PdSe₂ stacking was assessed using the potential energy surface (PES) as a function of the relative position between the two sheets (Figure 3c,d). The minimum relative energy was obtained at a relative shift \( \Delta x = 0.00, \Delta y = 0.00 \) for \( \alpha \)-PdSe₂ and \( [0.00, 0.00, 0.05] \) for \( \beta \)-PdSe₂. The corresponding structures are shown in Figure 3e,f. \( \alpha \)-PdSe₂ has lower energy than \( \beta \)-PdSe₂. However, the energy difference is only 10.85 meV for the studied supercell, corresponding to 0.90 meV/atom. The resulting interlayer spacing is 3.95 and 4.07 Å, respectively, indicating the presence of vdW interaction between the adjacent PdSe₂ layers. Interestingly, after forming the bilayer structure, charge is redistributed in the region between the layers, thereby changing the covalent bonds within each layer. Consequently, the lattice parameters of bilayer PdSe₂ significantly increased: the lattice parameter \( a \) increased by 0.05 Å on moving from monolayer to bilayer, with the corresponding increase in the lattice parameter \( b \) being 0.02 Å.
Next, to evaluate the binding strength, we calculated the interlayer binding energy \( E_b \), defined as the atom-averaged energy difference between the separated layers and bound layers, and is given as the following equation

\[
E_b = \frac{2 \times E\text{monolayer} - E\text{bilayer}}{2 \times N\text{atom}}
\]

(1)

where \( E_b \) is the interlayer binding energy (meV/atom), \( E\text{monolayer} \) is the energy of a PdSe\(_2\) monolayer, \( E\text{bilayer} \) is the total energy of the bilayer, and \( N\text{atom} \) is the number of atoms per layer. According to this definition, a larger absolute value of \( E_b \) implies a more stable stacking phase. The \( E_b \) for \( \alpha\)-PdSe\(_2\) and \( \beta\)-PdSe\(_2\) are 62.04 and 61.14 meV/atom, respectively, corresponding to 0.3498 and 0.3447 J/m\(^2\). These values are even smaller than that in graphite (0.37 J/m\(^2\)). That is why PdSe\(_2\) can be easily exfoliated from its bulk crystals.

Here, the well-studied graphite is considered for comparison to estimate the natural abundance of different stacking patterns of PdSe\(_2\). There are two phases of graphite in nature: AB and ABC stacking, with the \( E_b \) of AB-graphite (55.15 meV/atom) being only 0.35 meV/atom larger than the ABC-graphite (54.80 meV/atom). As a matter of fact, the natural abundance of AB-graphite is \( \sim \)80%. Here, the \( E_b \) of \( \alpha\)-PdSe\(_2\) is higher than its \( \beta \) counterpart by up to 0.90 meV/atom, which is much higher than that in graphite, indicating that \( \alpha\)-PdSe\(_2\) plays a dominant role in bilayer PdSe\(_2\).

Figure 4 shows \( E_b \) as a function of interlayer distance. Only the results of \( \alpha\)-PdSe\(_2\) are shown because it is energetically most stable. The distance–energy points can be fitted to the empirical potentials within the Buckingham potential\(^{55,55}\) and the Lenard-Jones (LJ) potential\(^{59}\)

\[
E = Ae^{-\beta h} + C/h^6
\]

(2)

\[
E = 4\epsilon[(\sigma/h)^{12} - (\sigma/h)^6]
\]

(3)

In 2 and 3, \( A, B, C, \epsilon, \), and \( \sigma \) are the fitting parameters. A nonlinear fitting process yields \( A = -3.301 \text{ eV, } B = 0.479 \text{ Å}^{-1}, \) and \( C = 5.261 \times 10^6 \text{ meV Å}^6 \) for the Buckingham potential, and \( \epsilon = 0.4016 \text{ meV} \) and \( \sigma = 2.957 \text{ Å} \) for the LJ potential.

The band structures of the PdSe\(_2\) bilayer with \( \alpha \) and \( \beta \) phases (Figure 5) show that they are also indirect bandgap semiconductors like monolayer PdSe\(_2\). However, due to the quantization effect, the bandgap reduces to 0.832 and 0.847 eV for \( \alpha\)-PdSe\(_2\) and \( \beta\)-PdSe\(_2\), respectively.

Figure 5. Electronic band structures of bilayer PdSe\(_2\): (a) \( \alpha\)-PdSe\(_2\) and (b) \( \beta\)-PdSe\(_2\) calculated by the PBE-TS + SCS method. The Fermi level has been set to zero and indicated by the dashed line.

Convergence in Energy of Band Edge. On the basis of the band structure of multilayer PdSe\(_2\), we would like to emphasize its promise in thermoelectric applications. In thermoelectric effect, the efficiency of its thermal-to-electric energy conversion is usually evaluated in terms of a dimensionless figure of merit \( ZT \), given by the following equation

\[
ZT = S^2\sigma T/\kappa
\]

(4)

where \( S, \sigma, T, \) and \( \kappa \) are the Seebeck coefficient, electrical conductivity, operating temperature, and thermal conductivity, respectively. For a real material with multiple sub-bands, if each conduction valley can be treated as noninteracting, the entire transport coefficient in a band can be summed from those of the constituent conduction valleys by assuming a parallel conductor model

\[
S = \sum_{i=1}^{N} \frac{S_i}{\sigma_i}, \quad \sigma = \sum_{i=1}^{N} \sigma_i
\]

(5)

On the basis of this model, both the two valleys have contribution to the total electrical conductivity while the total Seebeck coefficient remains unchanged. Therefore, the power factor, \( P = S^2\sigma \), significantly increased. This concept of band convergence has been applied to control the valley degeneracy in PbTe\(_1-x\)Sn\(_x\) alloys\(^{60}\), Mg\(_2\)Si\(_{1-x}\)Sn\(_{x}\) solid solutions\(^{61}\).
MoS$_2$, and phosphorene, to improve their thermoelectric performance. For example, Hong et al. predicted that ZT of MoS$_2$ can be greatly enhanced by tuning the thickness because the valley degeneracy leads to a significant enhancement in electrical conductivity, while the Seebeck coefficient vanishes.

The PdSe$_2$ monolayer is a potential high-performance thermoelectric material because of its reported high Seebeck coefficients (>200 $\mu$V/K). Furthermore, convergence of electronic bands also occurs in monolayer and few-layer PdSe$_2$, as schematically shown in Figure 7. For the PdSe$_2$ monolayer, in addition to the CBM at the $\Lambda$ point, there is another valley in the conduction band (CBM + 1) at the $\Lambda + 1$ point along the $S$–$Y$ high symmetry line (Figures 2c and 7). The bottom of this valley is only 29 meV (PBE-TS + SCS calculation) higher in energy than that in the $\Lambda$ valley (Table 2), which is smaller than 52 meV (2 times the thermal energy at room temperature, denoted hereafter as $2k_B T_{300K}$). By employing PBE-TS + SCS + SOC calculation, the energy difference is decreased to 16 meV (Table 2). The SOC splitting of the conduction band at the $\Lambda + 1$ point is only 28 meV (Figure S2a); thus, also highly likely to make contribution to the electrical conductivity. Interestingly, in addition to the VBM at the $\sum$ point along the $\Gamma$–$X$ high symmetry line, there is another valley in the valence band (VBM − 1) at the $\sum − 1$ point along the $Y$–$\Gamma$ high symmetry line (Figures 2c and 7a). The energy difference between these two valleys is only 36 meV (Table 2), which is also smaller than $2k_B T_{300K}$. For the $\alpha$-PdSe$_2$ bilayer, the energy difference between CBM and CBM + 1 increases to 49 meV, which is smaller than $2k_B T_{300K}$ similar to the monolayer (Table 2). This indicates that the thermoelectric transport occurs through both CBM and CBM + 1 valleys. Furthermore, there is another valley in the valence band at the $\Gamma$ point (Figures 5a and 7b), the top of this valley is 23 meV lower in energy than that in the $\sum$ valley (Table 2). Therefore, both the $\sum$ and $\Gamma$ valleys contribute to the electrical conductivity. For the $\beta$-PdSe$_2$ bilayer, energy difference between the CBM and CBM + 1 is 35 meV, while the energy difference between the VBM and VBM − 1 is 21 meV (Table 2). Both these values are smaller than those in $\alpha$-PdSe$_2$. For the PdSe$_2$ trilayer, the energy difference between the CBM and CBM + 1 is 35 meV, while the energy difference between the VBM and VBM − 1 is 21 meV (Table 2).

**Table 2. Energy Difference $\Delta_{\text{CBM}}$ and $\Delta_{\text{VBM}}$ in Few-Layer PdSe$_2$ Sheets ($N = 1$–5)**

| $N$ | $\Delta_{\text{CBM}}$ (meV) | $\Delta_{\text{VBM}}$ (meV) |
|-----|-----------------|-----------------|
|     | PBE-TS + SCS    | PBE-TS + SCS + SOC |
| 1   | 29              | 16              |
| 2 ($\alpha$) | 49              | 49              |
| 2 ($\beta$) | 35              | 34              |
| 3   | 55              | 55              |
| 4   | 56              | 55              |
| 5   | 56              | 56              |

$62^{−64}$ and phosphorene,$^{65}$ to improve their thermoelectric performance. For example, Hong et al.,$^{62}$ predicted that ZT of MoS$_2$ can be greatly enhanced by tuning the thickness because the valley degeneracy leads to a significant enhancement in electrical conductivity, while the Seebeck coefficient vanishes. The PdSe$_2$ monolayer is a potential high-performance thermoelectric material because of its reported high Seebeck coefficients (>200 $\mu$V/K).$^{66}$ Furthermore, convergence of electronic bands also occurs in monolayer and few-layer PdSe$_2$, as schematically shown in Figure 7. For the PdSe$_2$ monolayer, in addition to the CBM at the $\Lambda$ point, there is another valley in the conduction band (CBM + 1) at the $\Lambda + 1$ point along the $S$–$Y$ high symmetry line (Figures 2c and 7). The bottom of this valley is only 29 meV (PBE-TS + SCS calculation) higher in energy than that in the $\Lambda$ valley (Table 2), which is smaller than 52 meV (2 times the thermal energy at room temperature, denoted hereafter as $2k_B T_{300K}$). By employing PBE-TS + SCS + SOC calculation, the energy difference is decreased to 16 meV (Table 2). The SOC splitting of the conduction band at the $\Lambda + 1$ point is only 28 meV (Figure S2a); thus, also highly likely to make contribution to the electrical conductivity. Interestingly, in addition to the VBM at the $\Sigma$ point along the $\Gamma$–$X$ high symmetry line, there is another valley in the valence band (VBM − 1) at the $\Sigma − 1$ point along the $Y$–$\Gamma$ high symmetry line (Figures 2c and 7a). The energy difference between these two valleys is only 36 meV (Table 2), which is also smaller than $2k_B T_{300K}$. For the $\alpha$-PdSe$_2$ bilayer, the energy difference between CBM and CBM + 1 increases to 49 meV, which is smaller than $2k_B T_{300K}$ similar to the monolayer (Table 2). This indicates that the thermoelectric transport occurs through both the CBM and CBM + 1 valleys. Furthermore, there is another valley in the valence band at the $\Gamma$ point (Figures 5a and 7b), the top of this valley is 23 meV lower in energy than that in the $\Sigma$ valley (Table 2). Therefore, both the $\Sigma$ and $\Gamma$ valleys contribute to the electrical conductivity. For the $\beta$-PdSe$_2$ bilayer, energy difference between the CBM and CBM + 1 is 35 meV, while the energy difference between the VBM and VBM − 1 is 21 meV (Table 2). Both these values are smaller than those in $\alpha$-PdSe$_2$. For the PdSe$_2$ trilayer, the energy difference between the CBM and CBM + 1 is 35 meV, while the energy difference between the VBM and VBM − 1 is 21 meV (Table 2).
VBM and VBM − 1 is only 8 meV (Table 2). However, the energy difference between the CBM and CBM + 1 is 55 meV (Table 2), which is larger than 2kBT_{300 K}, suggesting that thermoelectric transport occurs only through the Δ valley. Finally, for the PdSe₂ tetralayer and pentalayer, the energy differences between the CBM and CBM + 1 are always larger than 2kBT_{300 K}, while the VBM occurs at the Γ point and the valley degeneracy vanishes (Table 2).

To justify theoretical analysis, next, based on the band structure obtained from DFT, we further use the Boltzmann transport equation within constant relaxation time approximation to calculate different transport properties, i.e., Seebeck coefficient S, electrical conductivity σ, and power factor P, as follows: \[ σ = \frac{N^0}{eT} (\frac{N^0}{e})^{-1} \] \[ S = \frac{1}{eT} (\frac{N^0}{e})^{-1} \] \[ N^0 = \frac{e^2}{m^*} \sum_{E_k} \Delta E \left[ \frac{\beta \exp(\beta (E_k - \mu))}{(1 + \exp(\beta (E_k - \mu)))^2} \right] D(E_k) E_k \] \[ (E_k - \mu)^n \] Here, e is the charge of the carrier, T is the temperature, E_k is the electron energy, r is the relaxation time, m* is the effective mass of the charge carrier, μ is the electron chemical potential, and \( D(E_k) \) is the DOS. As acoustic phonon scattering is the dominant scattering mechanism for carrier relaxation time in the low energy region, Qin et al.\(^{49}\) calculated the electron/hole relaxation time of monolayer PdSe₂ by the deformation potential theory, which is 2.73 × 10⁻¹⁴ s for electron. Here, we adopted this value and used m* = 0.19m_e in our calculation.\(^{49}\) The carrier concentration \( n \) is defined as \[ n = \int D(E - \mu) \times f(E - \mu) \times dE \] Here, rigid-band approximation\(^{68}\) is used, which assumes that the shape of the band structure does not change under light doping, but only shifts the Fermi level up (down) for n-type (p-type) doping, respectively.

First, the transport properties of n-type monolayer PdSe₂ as a function of n are shown in Figure S5. It is clear that σ increases with the increase in n, whereas the Seebeck coefficient S decreases with the increase in the carrier concentration, which is in good agreement with the previous report.\(^{66}\) Therefore, there is an optimal carrier concentration \( n_{\text{Max}} \) (∼1.5 × 10¹² cm⁻²) yielding the maximum attainable value of power factor \( P_{\text{Max}} \). The dependence of transport properties on carrier concentration is similar to those observed in other nanoscale thermoelectric materials.\(^{59,70}\)

Next, using the n-type α-PdSe₂ bilayer as an example, we explore the importance of valley degeneracy on thermoelectric performance. The conduction band of the α-PdSe₂ bilayer is shown in Figure 8a, where the CBM and the CBM + 1 bands are highlighted in red and blue, respectively. The energy difference between the CBM and the CBM + 1 (ΔCBM) is 49 meV (Table 2). Then, we artificially changed the ΔCBM to 10, 30, 50, 70, and 90 meV and calculated the partial density of states (PDOSs), which are shown in Figure S6. Because there is no report about the electron relaxation time of bilayer PdSe₂, we focus on the related change of the maximum attainable P as a function of ΔCBM. The ratio R is defined as \( R = \frac{P(\Delta_{\text{CBM}})}{P(\Delta_{\text{CBM}} = 10 \text{ meV})} \), where \( P(\Delta_{\text{CBM}}) \) is the maximum attainable power factor of the considered case and \( P(\Delta = 10 \text{ meV}) \) is the maximum attainable power factor for the sample with Δ = 10 meV. It is clear that the ΔCBM significantly affects the P value of the α-PdSe₂ bilayer. As the ΔCBM increases, P gradually decreases, owing to the low valley degeneracy. The maximum attainable power factor for a system with ΔCBM = 90 meV is only 62% of that with ΔCBM = 10 meV, emphasizing the importance of valley degeneracy on thermoelectric performance.

**CONCLUSIONS**

In summary, we systematically investigated the structural and electronic properties of multilayer PdSe₂ using vdW-corrected DFT computations. We first employed 13 different vdW-correction methods to predict the accurate geometric and electronic structures of bulk PdSe₂. The overall accuracies for different correction methods are compared and the PBE-TS + SCS functional is found to exhibit the best performance. Accurate prediction of the lattice parameters is vital for theoretical prediction of the electronic properties of bulk PdSe₂. The metallic properties in bulk are in good agreement with the reported experimental data. On the other hand, monolayer PdSe₂ is an indirect bandgap semiconductor with a bandgap of 1.381 eV. For bilayer PdSe₂, we search possible stacking patterns using a systematic study of the potential energy surface. The minimum potential corresponds to the AB stacking pattern. The interlayer interaction between the two separate layers induced a significantly reduced bandgap of 0.832 eV, which can be further reduced to 0.308 eV by increasing the number of layers to five. Interestingly, valley convergence is found in the band structures of monolayer, bilayer, and trilayer PdSe₂, leading to a significant improvement in thermoelectric performance. Our results denote that few-layer PdSe₂ is a new category of promising material for future nanoelectronic and thermoelectric applications.

**COMPUTATIONAL METHODS**

The calculations were performed by using the projector-augmented plane-wave method within the DFT framework in the code of Vienna ab initio simulation package.\(^{72,73}\) Calculations were conducted with a Monkhorst-Pack k-point mesh of 10 × 10 × 1 and a cut-off energy of 350 eV, which provide good convergence. A vacuum region larger than 15 Å was used to eliminate the interaction between the adjacent periodic images in the study of few-layer PdSe₂. In geometry optimization, atomic coordinates were relaxed until the maximum atomic force became smaller than 0.01 eV/Å.
Electronic band structures of bulk, monolayer, α-PdSe2, bilayer, β-PdSe2, bilayer, trilayer, tetralayer, and penta-layer PdSe2 are calculated by the PBE-TS + SCS + SOC method; electronic band structures of monolayer PdSe2 are calculated by the PBE-TS + SCS + HSE06 method; electronic transport coefficients of monolayer PdSe2 at room temperature as a function of carrier concentration; band structures and PDOSs of the CBM and the CBM + 1 states of the α-PdSe2 bilayer with different energy difference between the CBM and the CBM + 1 (PDF)

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**Notes**

The authors declare no competing financial interest.

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