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Thermoelectric properties of 1 T monolayer pristine and Janus Pd dichalcogenides

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Abstract

In this paper, we investigate the stability and thermoelectric properties of 1 T PdSSe, PdSTe and PdSeTe Janus structures using density functional theory (DFT). All three systems are narrow gap semiconductors with indirect bandgaps of 0.94 eV, 0.33 eV and 0.34 eV respectively. Compared to transition metal dichalcogenide (TMD) monolayers, PdS₂ and PdSe₂ are semiconductors with wider indirect bandgaps of 1.29 eV and 0.69 eV respectively. Phonon dispersion calculations demonstrate that all pristine and Janus structures are mechanically stable despite the presence of negligible negative frequencies around the Γ point in PdSTe and PdSeTe. Inspection of the lattice thermal conductivity (κ_L) shows that these structures are slightly anisotropic in the x and y directions except for PdSe₂ which shows a higher degree of anisotropy. Influenced by the values of κ_L , the thermal electronic conductivity (κ_e), the electronic conductivity (σ) and the Seebeck effect (S), the figure of merit along the x (ZT^x) and y (ZT^y) directions register the largest values in the case of electron doping for the PdSe₂ and PdSeTe 2D crystals. Interestingly, the figures of merit of the Janus structures are larger than their corresponding pristine PdX₂ ($X = S, Se$) structures. Once synthesized, such information is crucial for the implementation of the PdXY ($Y = Se, Te$) structures in industrial applications.

Keywords: density functional theory, Janus structure, group velocity, specific heat capacity, lattice thermal conductivity, figure of merit (ZT)

(Some figures may appear in colour only in the online journal)

1. Introduction

Due to its outstanding properties [1–5], graphene, the two dimensional (2D) form of carbon, has marked the history of the 21st century condensed matter and nanoscale physics since it was first exfoliated mechanically from graphite in 2004 [6]. It is a null gap semiconductor, with linear and isotropic bands around the K point in the reciprocal hexagonal Brillouin zone and vanishing density of states at the Fermi level. These characteristics made the charge carriers in graphene behave as relativistic massless particles that are described by the Dirac equation [2, 3]. One consequence is a high electrical conductivity larger than that of aluminium [1, 7]. Moreover, graphene

has important mechanical properties such as fracture toughness, significant in the area of engineering [8] as well as a high modulus of elasticity (~ 1100 GPa) [9], making it almost 200 times stronger than steel.

Despite the above remarkable properties, graphene lacks two features, pivotal in the field of electronics and superconductivity: firstly it is not suitable for device electronics since it has a zero band gap. Applying an external electric field perpendicular to a bilayer graphene system [10] or p -doping using Al, B, NO₂ and NH₃ (alternatively n -doping using nitrogen and alkali metals) [11–14] opens a bandgap. Secondly, it is not a superconductor because of the low carrier density at the Fermi level. However recently, some researchers were able to enhance superconductivity in graphene by doping it with Ca [15] or by means of lithium deposition [16].

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Twisting a ‘sandwich’ of two graphene layers by a unique (magic) angle [17] also seems to be a promising technique to make graphene superconducting.

All of the tremendous properties of graphene as well as the ‘missing’ characteristics mentioned above paved the way for scientists to explore hundreds of possible stable 2D structures that might have a non zero band gap and/or possess some distinct physical and electronic properties necessary for the development of optoelectronic and energy devices. These structures, which were either predicted using DFT or synthesized experimentally, fall into different groups, the simplest of which are the 2D analogues of three dimensional systems such as silicene [18], germanene [19], stanene [20], antimonene [21], borophene [22, 23], phosphorene [24], arsenene [25] and very recently diamondene [26].

The second category of 2D structures, whose exploration has skyrocketed in the last few years, involve transition metal dichalcogenides (TMDs); they are represented by the chemical formula MX_2 , where M is a transition metal and X is usually S, Se or Te. One of the reasons why such systems gained so much fame is the indirect to direct band gap transition in both monolayer [27] and multilayered forms [28]: whilst bulk MoX_2 and WX_2 are indirect band gap semiconductors, their 2D analogues are direct band gap semiconductors of 1.88 eV and 2.03 eV respectively [29]. Thanks to the adjustability of their optical and electronic properties, they constitute an advantage over zero gap graphene and hexagonal boron nitride (BN) monolayers having a large bandgap of ~ 6 eV [30]. 2D TMD monolayers, in particular, have a wide range of applications such as transistors [31, 32], catalysts [33, 34], batteries [35, 36], etc. $\text{MoS}_2/\text{MoSe}_2$ monolayer nanoscale transistors have been already manufactured with high on/off ratios [37, 38]. The stability, as well as the electronic features of other TMD monolayers (M = Ti, Zr, Hf, V, Nb, Ta, Cr) [39–44] have also been extensively reported.

Very recently, researchers have shifted their attention to other exotic 2D materials, derived from the TMDs called Janus structures, hoping that these might have better properties than their pristine counterparts. Adopted from Roman mythology, the term ‘Janus’ widely used by the scientific community, refers to materials with different properties on two opposing sides or faces; starting from MX_2 , one of the ‘X’ elements can be substituted by another element ‘Y’ to form the Janus MXY structures. For example, replacing Sulfur in MS_2 by Selenium produces MSSe whilst substituting it by Tellurium gives MSTe .

Although such research is still at its infancy, some have made various achievements: MoSSe monolayers have been synthesized by different experimental strategies [45] including the sulfurization of a monolayer of MoSe_2 [46]. On a theoretical basis, most research focuses on the electronic structure and stability of Janus systems [47] while few papers discuss the phonon transport and their thermoelectric properties [48, 49]. More excitingly, experimental and theoretical discussions on graphene based 2D Janus materials [50] have lately emerged.

In this work, we focus on the electronic properties, stability and thermoelectric properties of the PdXY Janus TMDs derived from 1 T monolayers of PdX_2 (X = S, Se; Y = S, Se, Te). Throughout this manuscript, the word ‘pristine’ will refer to the PdX_2 structures. Generally the urge to acquire knowledge about the thermoelectric performance in any 2D structure is the belief that these have a higher thermoelectric efficiency than their 3D bulk analogues [51]; consequently they can be better candidates for the fabrication of thermoelectric generators, used for instance in research stations in the arctic and antarctic region [52], or in thermoelectric cooling devices and various temperature measurement applications [53].

As far as the PdX_2 structures in their various symmetrical forms are concerned, they have been previously considered by many authors: the electronic band structure as well as the stability of PdS_2 , through phonon dispersion calculations, are studied in [54], claiming that the most stable form is with planar tetra-coordinate Pd atoms and covalent S–S bonds. [55] proposes an ultrathin crystal device based on 1 T monolayers and bilayers of PdS_2 that present interesting features needed for the production of FETs in 2D electronic devices. The experimental growth of bulk PdSe_2 and the transition to a few layer structure show that the latter possesses intrinsic ambipolar characteristics, that seem promising for the fabrication of FET devices [56]. Strain applied on a PdSe_2 monolayer obtained by selenizing a Pd(111) surface is discussed in [57]. In addition, pentagonal 2D monolayer of PdSe_2 is shown to have a high thermoelectric performance through doping [58]. To the best of our knowledge, no one has previously investigated the thermoelectric features of 1 T monolayer pristine and Janus Pd structures.

The paper is organized as follows: in section 2, the thermoelectric theory will be discussed in details. The computational details of the electronic structure, phonon calculations as well as the thermoelectric properties will follow in section 3. The presentation and discussion of the obtained results are the main subject of section 4. Finally, section 5 contains a summary of the most important conclusions achieved in this work.

2. Thermoelectric theory

It is well known that the thermoelectric performance is measured through the so-called figure of merit (ZT) dimensionless parameter given by:

$$ZT = S^2 \sigma T / (\kappa_e + \kappa_L), \quad (1)$$

where S is the Seebeck coefficient, T is temperature (in K), σ is the electronic conductivity and κ_e and κ_L are the thermal electronic and thermal lattice conductivities respectively. A thermoelectric device is usually at its best if $ZT \geq 1$. From equation (1), increasing ZT means increasing $S^2 \sigma$ (called the power factor (PF)) and/or decreasing $(\kappa_e + \kappa_L)$. Within the Boltzmann transport theory [59, 60], the tensor components $\{\alpha, \beta \equiv x, y, z\}$ of the above physical quantities are defined by:

$$\begin{aligned}\kappa_e^{\alpha\beta}(E) &= \sum_{n,k} \tau_{n,k} v_g^\alpha(n,k) v_g^\beta(n,k) \delta(E - E_{n,k}) \\ \sigma^{\alpha\beta}(T, \mu) &= \frac{e^2}{NV} \int \sum_{n,k} \tau_{n,k} v_g^\alpha(n,k) v_g^\beta(n,k) \delta(E - E_{n,k}) \\ &\quad \times \left[-\frac{\partial f(T, E, \mu)}{\partial E} \right] dE \\ S^{\alpha\beta}(T, \mu) &= \frac{1}{eVT\sigma^{\alpha\beta}(T, \mu)} \int \kappa_e^{\alpha\beta}(E - \mu) \\ &\quad \times \left[-\frac{\partial f(T, E, \mu)}{\partial E} \right] dE,\end{aligned}$$

where e , N and V are the electron's charge, the number of $\mathbf{k}$ points sampled and the volume of the unit cell respectively. f is the Fermi–Dirac distribution function, μ the chemical potential, equivalent to the Fermi energy (E_F) at 0 K, and v_g^α is the α 's component of the group velocity of the carriers. $E_{n,k}$ and $\tau_{n,k}$ are the energy and the electronic relaxation time of the n th electronic band at the k th point.

Similarly the lattice thermal conductivity, also described by its tensor components $\{\alpha, \beta\}$, is evaluated by summing over the contributions of all phonon wave vectors ($\mathbf{q}$) and dispersion branches (s) such that:

$$\kappa_L^{\alpha\beta} = \frac{1}{NV} \sum_{\mathbf{q},s} c_v(\mathbf{q},s) v_g^\alpha(\mathbf{q},s) v_g^\beta(\mathbf{q},s) \tau(\mathbf{q},s),$$

$c_v(\mathbf{q},s)$ being the specific heat capacity and $\tau(\mathbf{q},s)$ the phonon lifetime for the ($\mathbf{q},s$) phonon mode.

3. Computational details

All electronic structure calculations were performed within DFT using the Quantum Espresso (QE) code [61]. We use the norm-conserving Troullier–Martins pseudopotential [62] to describe the interaction between the valence electrons and the ion cores and a scalar relativistic Perdew–Burke–Ernzerhof (PBE) parametrization [63] for the exchange correlation functional. Well converged results were produced using a $24 \times 24 \times 1$ $\mathbf{k}$ point grids in the reciprocal Brillouin zone and a plane wave energy cutoff of 75 Ry, needed for subsequent phonon spectrum calculations. A tight geometry relaxation was applied until the forces acting on each atom in the unit cell is 5×10^{-4} Ry au $^{-1}$ and the pressure is less than 0.16 kbar. The long range electron correlations are accounted for through the Van der Waals (VdW) corrections following Grimme's semi-empirical method [64, 65].

In order to model a 2D system within the QE code, the structures are taken to be periodic in the plane where the atoms belong, and separated by a vacuum distance of at least 15 Å along the perpendicular direction to restrain the interaction with their periodic images. The converged results from QE are then fed into the PHONOPY code [66], based on the frozen phonon (supercell) approach [67, 68], to obtain the phonon dispersion spectrum and deduce the group velocities (v_g) and specific heat capacities (c_v) at various temperatures.

The electronic properties, namely S , σ and κ_e were computed using the BoltzWann code [69] which is adapted to deal with 2D structures. This package is implemented in the QE code and makes use of Wannier functions [70]. Grids of $140 \times 140 \times 1$ were sufficient to converge calculations at temperatures equal to or higher than 300 K. The electronic relaxation time is calculated via the electron–phonon Wannier (EPW) package [71, 72] also implemented in the QE code, where $\mathbf{k}$ and $\mathbf{q}$ grids of $120 \times 120 \times 1$ each were used in the computation. EPW obtains the imaginary part of the electron self-energy $\text{Im}(\Sigma_{n,\mathbf{k}}^{\text{el-ph}})$ for each electronic state n making use of the ultra dense electron phonon matrices obtained in a previous step. This allows the determination of the electronic relaxation time for band n and point $\mathbf{k}$ as $\tau_{n,\mathbf{k}} = \hbar / (2 \text{Im}(\Sigma_{n,\mathbf{k}}^{\text{el-ph}}))$. Since the BoltzWann software requires a single constant value for the electronic relaxation time, separate averages of $\tau_{n,\mathbf{k}}$ over points belonging to the maximum valence and minimum conduction bands were only considered. These represent hole and electron relaxation times respectively, required for the examination of the effect of doping on the thermoelectric properties of the structures in question.

The phonon relaxation time (τ_{ph}), mainly due to the phonon–phonon scattering, as well as the lattice thermal conductivity (κ_L) are obtained via the PHONO3PY code [73] by solving the linearized phonon Boltzmann equation within the single mode relaxation time approximation (RTA). To guarantee convergence, second order interatomic force constants (IFC) were obtained using a $6 \times 6 \times 1$ supercell whilst third order ones were computed using a $3 \times 3 \times 1$ supercell and $100 \times 100 \times 1$ $\mathbf{q}$ -point meshes.

4. Results and discussions

4.1. Electronic bands and density of states

Figure 1 shows the top view of the 2D 1 T PdX₂ TMDs and PdXY Janus materials, {X, Y} being S, Se or Te. PdSSe and PdSTe are theoretically constructed from the 2D pristine PdS₂ by substituting the top (or bottom) layer of S by Se and Te respectively. In a similar manner, PdSeTe is formed by replacing the top (or bottom) Se layer of PdSe₂ by Te. Therefore all structures belong to the hexagonal geometry [74] and spacegroup P-3m1. The formation energies ϵ_f of the 1 T pristine and Janus structures will be calculated as:

$$\epsilon_f(\text{PdX}_2) = E_{\text{PdX}_2} - (E_{\text{Pd}}/n_{\text{Pd}} + 2E_X/n_X)$$

$$\begin{aligned}\epsilon_f(\text{PdXY}) &= E_{\text{PdXY}} - E_{\text{Pd}}/n_{\text{Pd}} \\ &\quad - E_X/n_X - E_Y/n_Y\end{aligned}$$

E_{PdX_2} and E_{PdXY} being the total energies of the structures, (E_{Pd} , E_X and E_Y) are the energies of the bulk Pd, X and Y crystals respectively and (n_{Pd} , n_X , n_Y) are the numbers of atoms in their unit cells. Columns 2–6 of table 1 give the equilibrium lattice parameters (a_{eq}), the optimized bond lengths and the formation energies for the six structures. The tabulated values show negative formation energies meaning that they are all energetically favorable.

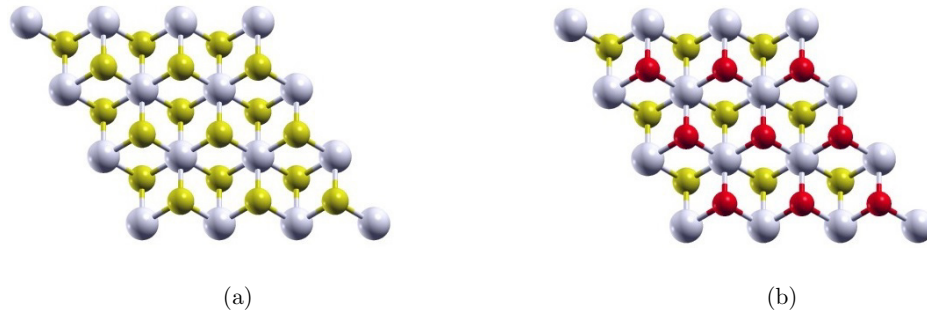


Figure 1. Top view of the unit cell of (a) the 1 T Pd dichalcogenides where the grey balls are Pd atoms and the yellow ones represent S, Se or Te. (b) The 1 T Janus structures; red and yellow colors refer to the X and Y elements.

Table 1. Values of the equilibrium lattice parameters, bond lengths, formation energies, in-plane stiffness constant (C) as well as band gap values of the 1 T PdX₂/PdXY structures. Corresponding references are indicated for comparison.

Structure	a_{eq} (Å)	Pd–S (Å)	Pd–Se (Å)	Pd–Te (Å)	ϵ_f (eV Å ⁻¹)	C (N m ⁻¹)	Band gap (eV)
PdS ₂	3.51, 3.55 ^a , 3.56 ^b	2.40	—	—	−1.78	74.45	1.29, 1.28 ^c , 1.24 ^b
PdSe ₂	3.67, 3.73 ^a , 3.74 ^d	—	2.53	—	−1.91	56.51	0.69, 0.67 ^e , 0.84 ^c , 1.10 ^d
PdSSe	3.59	2.43	2.50	—	−1.81	61.32	0.94
PdSTe	3.73	2.48	—	2.62	−1.58	40.96	0.33
PdSeTe	3.81	—	2.57	2.64	−1.78	39.41	0.34

^a Rasmussen and Thygesen [79].

^b Saraf *et al* [78].

^c Ahmad [77].

^d Liu *et al* [57].

^e Miró *et al* [80].

Young's modulus (Y) is one of the parameters that describe the elastic properties of a structure. However since our structures are 2D monolayers, the thickness (which is in the 3rd dimension) can be ill-defined. Therefore, we discuss instead the elasticity of the materials in terms of the in-plane stiffness constant C [75]. This is simply done by plotting the 'strain—no strain' energy difference $\Delta E = E(w) - E(w = 0)$ versus $w = (a - a_{eq})/a_{eq}$, a being the lattice parameter under strain. It was obtained by adding and subtracting incremental values of 0.2 Bohrs to a_{eq} to induce various pressures (strain) on the unit cell. The energies for each a (and therefore for each w) are then calculated. $E(w)$ and $E(w = 0)$ represent these energies at $a \neq a_{eq}$ and at equilibrium respectively. A polynomial function of the 4th order best fits the values obtained. Mathematically, $E(w) = b_1 + b_2w + b_3w^2 + b_4w^3 + b_5w^4$. C is defined as $C = (\partial^2 E(w)/\partial w^2)/A_0$, where A_0 is the area of the hexagonal unit cell at equilibrium given by $3\sqrt{3}a_{eq}^2/2$. Since $w = 0$ at equilibrium, C reduces to $2b_3/A_0$. The values of the stiffness constants for all pristine as well as the Janus structures can be found in the 7th column of table 1.

We notice that C decreases as we move from PdSSe to PdSeTe similar to what happens in PdX₂ dichalcogenides as X changes from S to Se. Pristine PdX₂ structures have values comparable to MS₂, MSe₂ and MTe₂ ($M = \text{Hf, Zr, Ti}$) [47] respectively, which are smaller than those obtained for the MoX₂ [76] and WS₂ [47] monolayers. The Janus PdXY structures have in plane stiffness constants also close to those belonging to $M = \text{Ti, Zr, Hf}$ and less than those corresponding to $M = \text{Mo, W}$ [47].

Figure 2 exhibits the electronic band structures and the respective DOS of the 1 T pristine and Janus structures. All systems show indirect band gaps which is similar to most Janus structures studied so far except for MoSeTe, WSSe and WSeTe which demonstrate direct band gaps [47]. The 8th column of table 1 includes the values of the bandgaps. Our calculations based on the PBE pseudopotential indicate that both PdS₂ and PdSe₂ (figures 2(a) and (b)) are semiconductors with respective bandgaps 1.29 and 0.69 eV. On the other hand, PdSSe (figure 2(c)) is a semiconductor with bandgap 0.94 eV, smaller than that of PdS₂. Likewise PdSTe and PdSeTe are narrow gap semiconductors with bandgaps 0.33 eV and 0.34 eV respectively as shown in figures (2)(d) and (e).

Our values of the bandgaps and lattice parameters were compared to others based on the ultrasoft Perdew–Zunger (PZ) pseudopotential [77] and on PBE-PAW [78] amongst others [79, 80]. While our PdS₂ bandgap shows excellent agreement with other calculations, that of PdSe₂ seems to be underestimated compared to the experimental value only reported for pentagonal PdSe₂ monolayer [57]. Despite this fact, it is important to note that other than being computationally demanding, the combination of ultrasoft or hybrid pseudopotentials [81] with the EPW package, needed to obtain the electron and hole relaxation times, might be problematic since not all types of pseudopotentials are implemented. On the other hand, our lattice parameters agree well with other values in the literature with a difference of just 2% for the case of PdSe₂. It is not possible to compare results corresponding to the Janus structures since they were not treated before.

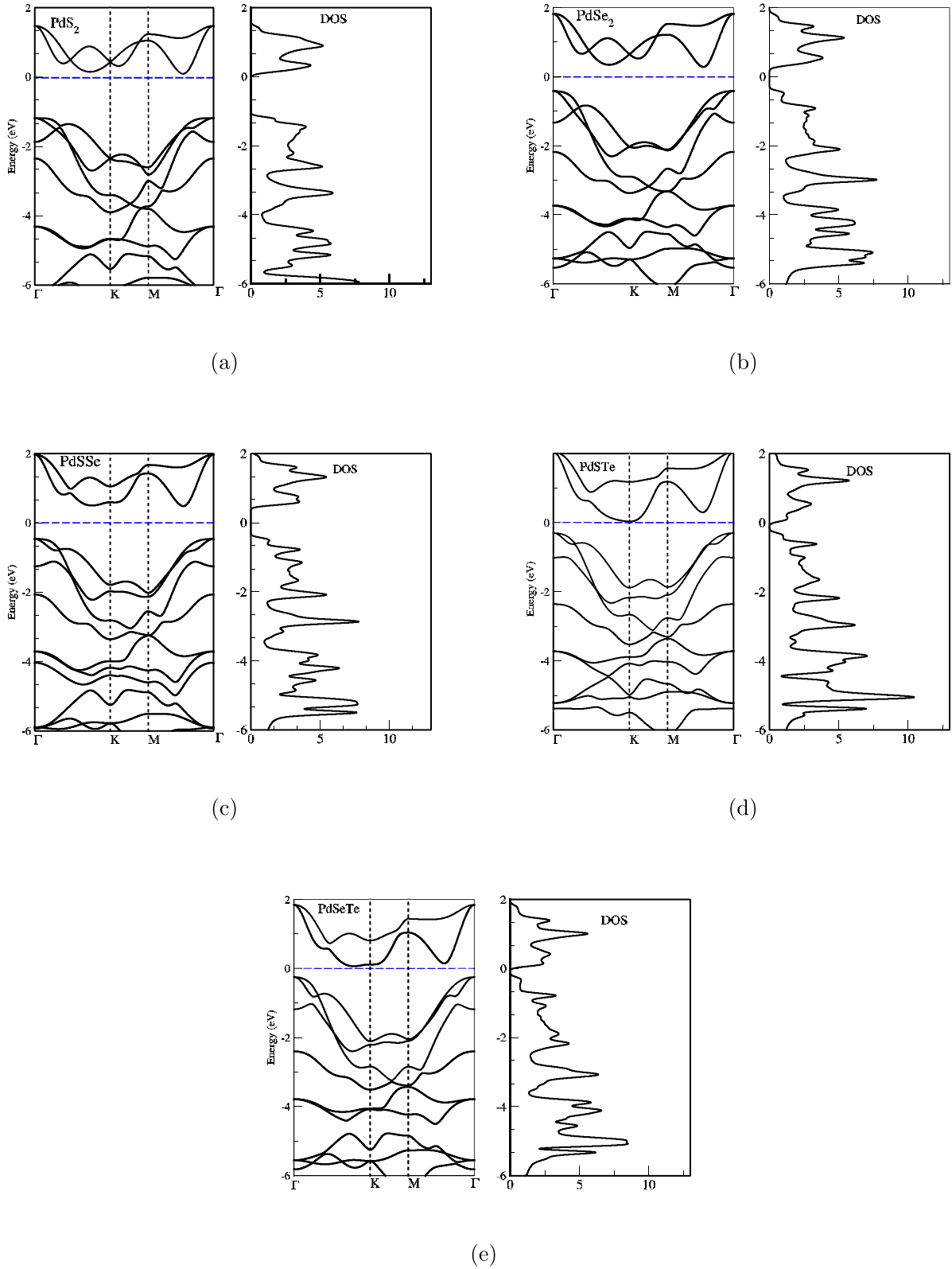


Figure 2. The electronic band structures and DOS of the PdX₂ systems and their respective PdXY Janus analogues along the Γ -K-M- Γ path in the Brillouin zone. The dashed horizontal blue lines represent the positions of the Fermi energy.

4.2. Phonon dispersion and stability

All Janus structures have three atoms per unit cell and therefore nine phonon dispersion branches are expected to be seen: the lowest three acoustic modes (A) and the upper six optical

modes (O). Both acoustic and optical modes can be either transverse (T), longitudinal (L) or flexural (Z). ZA and ZO modes are out-of-plane whereas LA, TA, LO, and TO are usually in plane modes of vibration. By analyzing the phonon branches of the Janus systems in figures 3(c)–(e), we notice

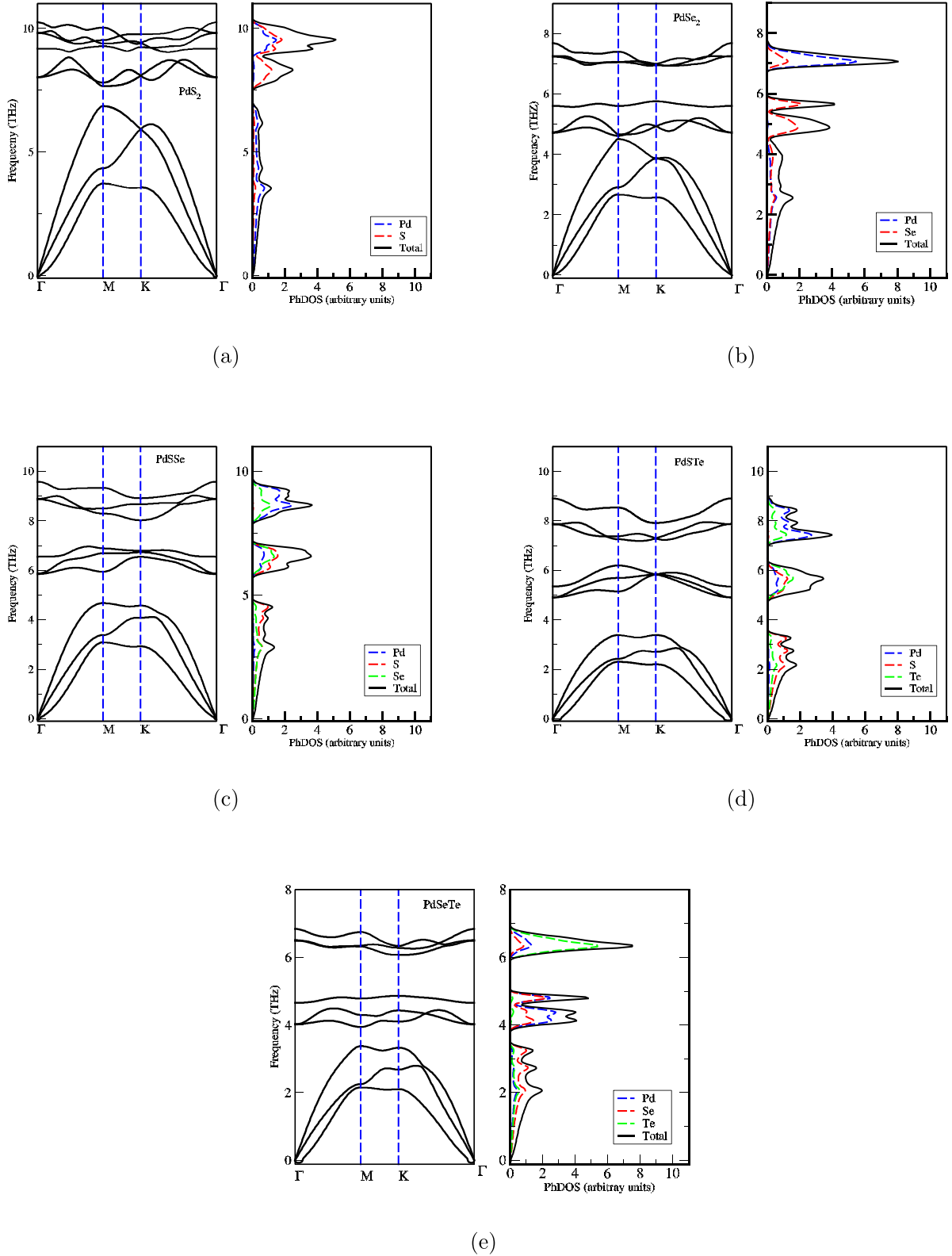


Figure 3. Phonon dispersion curves and PhDOS for the pristine and Janus Pd structures. All are stable showing acoustic-optical and optical-optical bandgaps which widen up as PdX_2 transits to PdXY .

that all frequencies are mostly positive, except for some very small negative frequencies (not exceeding -0.1 THz) appearing in the vicinity of the Γ point. It can therefore be asserted that all Janus structures are mechanically stable. It

can be also detected that, in the vicinity of the Γ point, the ZA mode has a parabolic behavior whereas it is linear for the LA and TA modes. This characteristic has been linked to low dimensional systems [82].

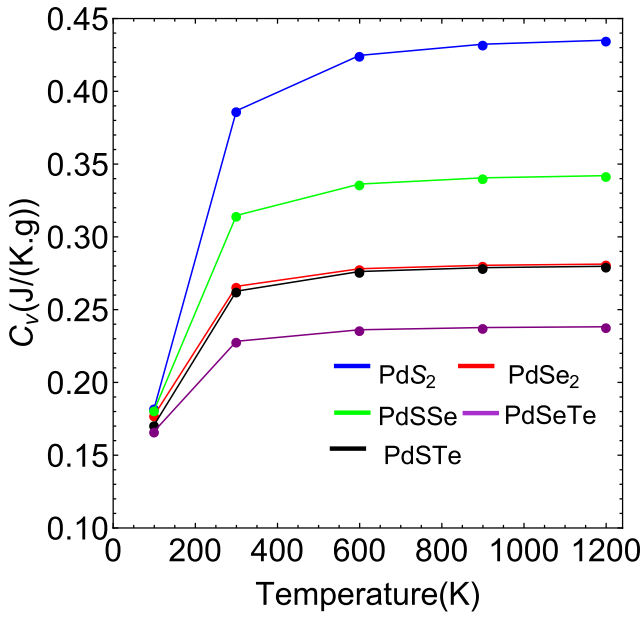


Figure 4. Specific heat capacity at constant volume c_v , as a function of temperature, for the PdX_2/PdXY materials, in units of $\text{J} (\text{K} \cdot \text{g})^{-1}$.

Moreover, we observe phonon bandgaps between acoustic and optical modes and between the optical modes themselves; the acoustic-optical bandgaps in PdSSe and PdSTe are larger than those in pristine PdS_2 . In a similar manner, PdSeTe has wider acoustic-optical bandgaps compared to pristine PdSe_2 . Usually large acoustic-optical phonon bandgaps signal vast phonon lifetimes which lead to inefficient scattering. Also widening of optical-optical bandgaps is perceived in the pristine PdX_2 as X changes from S to Se . We realize that in all structures, the LO-TO splitting at the Γ point is very small (between 0.003 and 0.021 THz) and can be safely neglected. Moreover, the LA and TA modes that were degenerate at the K point in PdS_2 split in the PdSSe and PdSTe structures; the same observation can be deduced for PdSeTe and PdSe_2 .

The phononic partial density of states (PhDOS) shows some interesting behavior. In PdS_2 , Pd has the highest contribution to the acoustic modes while S mainly contributes to the six optical modes. In PdSe_2 , Se is mainly responsible for the acoustic and the low lying optical modes while Pd mainly contributes to the highest three optical modes.

In PdSSe , the acoustic and the low lying optical modes are primarily composed of Se and S whereas the PhDOS for the three highest optical modes is mainly due to Pd. The situation is different for the PdSTe where S has the highest contribution to the acoustic modes while Pd and Te contribute the most within the three highest and three lowest optical mode regions respectively. Interestingly, the major contributions of Pd and Te get swapped in PdSeTe where Pd is chiefly responsible for the low lying optical modes and Te for the three highest optical modes. Both the large bandgaps observed in the dispersion curves and the proximity of the acoustic modes might

Table 2. Values of c_v ($\text{J} (\text{K} \cdot \text{g})^{-1}$) for the 1 T PdXY and PdX_2 structures at different temperatures.

Structure	100 K	300 K	600 K	900 K	1200 K
PdSSe	0.181	0.314	0.336	0.340	0.342
PdSTe	0.171	0.263	0.276	0.278	0.279
PdSeTe	0.166	0.228	0.236	0.237	0.238
PdS_2	0.182	0.386	0.425	0.432	0.435
PdSe_2	0.177	0.266	0.278	0.280	0.282

also play an important role in determining the values of the electron-phonon coupling in such materials; however, this will not be pursued further as it is out of the scope of the present work.

The dependence of the specific heat capacity (c_v) on temperature for the pristine and Janus structures is displayed in figure 4. Among the pristines, PdS_2 has the highest c_v at all temperatures. On the other hand, PdSSe has the highest value of c_v and PdSeTe has the lowest. All structures have their c_v very close to each other at low temperatures and reach saturation values at temperatures $T \geq 800$ K. It is also clear that c_v decreases as we go from PdS_2 to PdSSe and becomes even lower in PdSTe ; this is also seen by comparing PdSe_2 and PdSeTe . The detailed values of the specific heat capacities are reported in table 2.

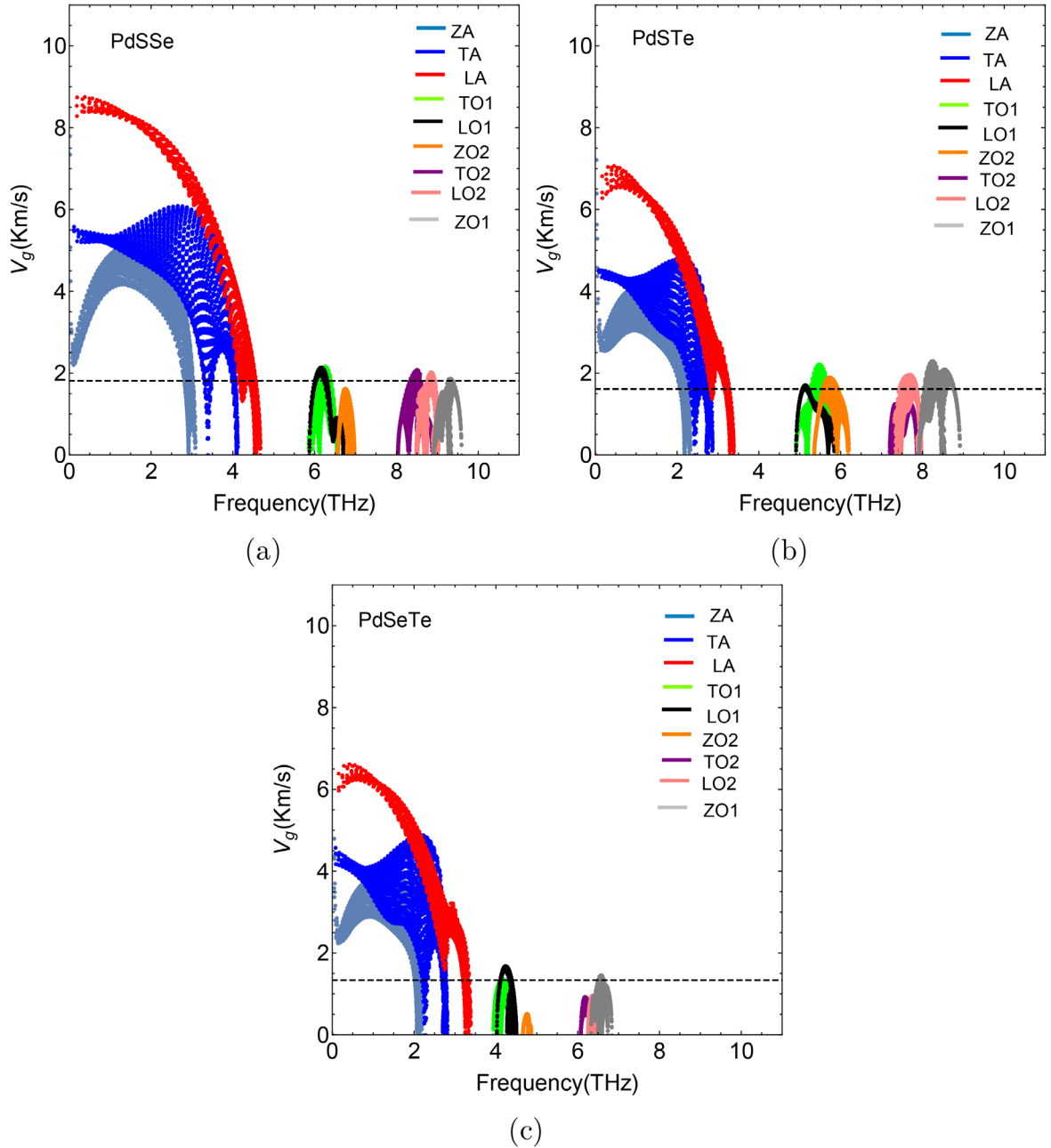
Figure 5 shows the contribution of each of the acoustic and optical modes (labeled as flexural, transverse or longitudinal) to the group velocities of the Janus structures. The average group velocity (v_g) has also been computed and represented by horizontal dashed lines. We realize that the average $v_g = 1.81 \text{ km s}^{-1}$, 1.61 km s^{-1} and 1.34 km s^{-1} for the PdSSe , PdSTe and PdSeTe respectively. These results can be understood by noticing that PdSSe has the highest contributions of both the acoustic modes with a maximum group velocity of $\sim 8.7 \text{ km s}^{-1}$. Acoustic modes are less involved in both PdSTe and PdSeTe where their maximum v_g only reaches $\sim 7 \text{ km s}^{-1}$. It is also obvious that the optical modes contribute less in PdSeTe than in the other Janus structures and extend over a smaller frequency range. Although not shown for the sake of simplicity, pristine 2D TMDs have average group velocities of 2.51 km s^{-1} and 1.70 km s^{-1} for PdS_2 and PdSe_2 respectively.

The contributions of the different modes to the phonon relaxation time τ_{ph} at $T = 300$ K are plotted in figures 6(a) and (b). By computing the average phonon relaxation time for all structures, we infer that PdS_2 (pristine) and PdSeTe (Janus) register the highest values (5.5 ps and 3.89 ps respectively) and thus have the lowest phonon scattering rates.

Figures 7(a) and (b) show the ratio of the thermal lattice conductivities along the x (κ_L^{xx}) and y (κ_L^{yy}) directions as well as the average value of κ_L (κ_L^{av}), given by $(\kappa_L^{xx} + \kappa_L^{yy})/2$. At $T = 300$ K, κ_L^{av} for the PdSSe Janus structure has a value of $2.85 \text{ W} (\text{m} \cdot \text{K})^{-1}$ whereas PdSeTe and PdSTe have κ_L^{av} of $1.21 \text{ W} (\text{m} \cdot \text{K})^{-1}$ and $1.09 \text{ W} (\text{m} \cdot \text{K})^{-1}$ respectively. Compared to PdS_2 , which has a κ_L^{av} of $7.10 \text{ W} (\text{m} \cdot \text{K})^{-1}$, both

Table 3. Maximum values of ZT^{xx} and ZT^{yy} , for the case of electron doping, for the PdX_2 and $PdXY$ structures at temperatures $T = 300, 600$ and 900 K.

Structure	ZT^{xx}_{max}			ZT^{yy}_{max}		
	300 K	600 K	900 K	300 K	600 K	900 K
PdS_2	0.09	0.28	0.41	0.08	0.29	0.42
$PdSe_2$	0.34	0.63	0.73	0.41	0.68	0.77
$PdSSe$	0.27	0.54	0.66	0.27	0.65	0.58
$PdSTe$	0.25	0.52	0.57	0.26	0.53	0.58
$PdSeTe$	0.40	0.64	0.65	0.42	0.65	0.65

**Figure 5.** Group velocities in km s^{-1} for the 2D $PdXY$ Janus structures. $PdSSe$ has the highest average value of v_g (represented by the dashed horizontal lines) whilst $PdSeTe$ has the smallest.

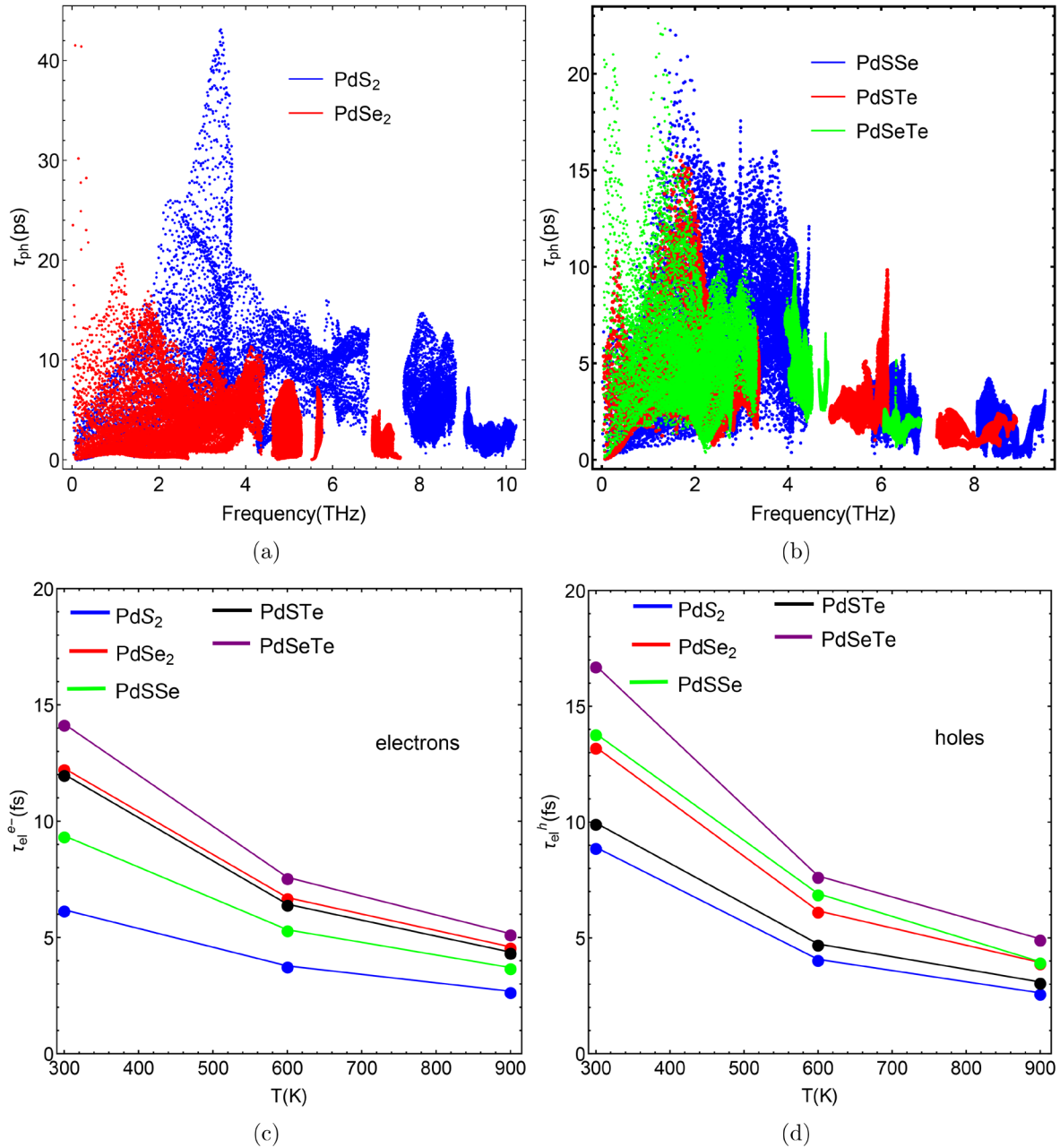


Figure 6. The phonon relaxation time τ_{ph} at different acoustic and optical frequencies for the (a) pristine and (b) Janus semiconductors. (c) Electronic relaxation times (τ_{el}^{e-}) and (d) hole relaxation times (τ_{el}^h) for Janus and pristine structures.

PdSSe and PdSTe have smaller lattice thermal conductivities. Analogously, PdSe₂ has a higher κ_L^{av} ($1.51 \text{ W (m} \cdot \text{K)}^{-1}$) than PdSeTe.

At room temperature, these values are small when compared to those of graphene ($\sim 1600 \text{ W (m} \cdot \text{K)}^{-1}$) [83], γ -graphyne ($76.40 \text{ W (m} \cdot \text{K)}^{-1}$) [84], blue phosphorene ($130 \text{ W (m} \cdot \text{K)}^{-1}$) [85] but higher than those belonging to other 1 T 2D TMD such as TaSe₂ ($0.39 \text{ W (m} \cdot \text{K)}^{-1}$) and NbSe₂ ($0.13 \text{ W (m} \cdot \text{K)}^{-1}$) [86].

κ_L^{av} can be always perfectly fitted to a function of the form $a_1 + a_2/T + a_3/T^2$. These are shown as dashed curves in figure 7 for the PdS₂ and PdSSe cases. All Janus structures are

slightly thermally anisotropic with $\kappa_L^{yy}/\kappa_L^{xx}$ ranging between 0.91 and 1.02. This is not the case for pristine PdSe₂ which is highly anisotropic ($\kappa_L^{yy}/\kappa_L^{xx} \sim 0.67$ at 300 K). For $T \geq 300 \text{ K}$, all structures maintain these ratios unaltered.

4.3. Thermoelectric properties

In this section, the variation of the Seebeck coefficient, electronic conductivity as well as the electronic thermal conductivities as a function of the chemical potential μ , will be discussed giving some insight on how thermal properties respond to electron/hole doping. The zero reference on the

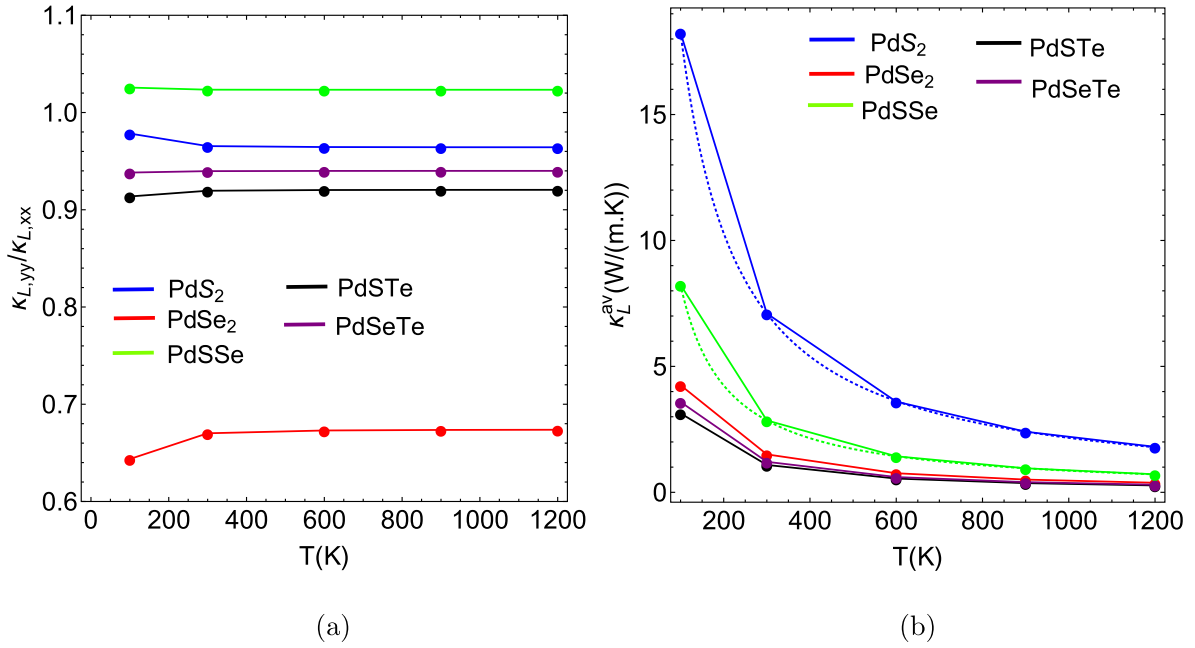


Figure 7. (a) All structures are slightly anisotropic except for PdSe₂ which shows a significant anisotropy. (b) κ_L^{av} decreases with increasing temperature. The dotted blue and green curves are fitting functions to PdS₂ and PdSSe systems respectively. The fitting parameters are $a_1 = -0.11 \text{ W (m} \cdot \text{K)}^{-1}$, $a_2 = 2322.77 \text{ W m}^{-1}$, $a_3 = 48\,605.60 \text{ W} \cdot \text{K m}^{-1}$ for PdS₂ and $a_1 = -0.01 \text{ W (m} \cdot \text{K)}^{-1}$, $a_2 = 877.97 \text{ W m}^{-1}$, $a_3 = 529.12 \text{ W} \cdot \text{K m}^{-1}$ for PdSSe. The other systems can be equally fitted.

x -axis will represent a chemical potential equal to E_F , that is the case of an undoped system. The rigid band approximation (RBA) [87] will be used to model n (electron) and p (hole)-doping without the addition of impurities by changing the value of the chemical potential. Shifting the Fermi energy towards the conduction band adds more electrons and leads to n -doped systems. Besides, shifting E_F towards the valence bands will produce p -doped systems. This allows the definition of both electron (τ_{el}^e) and hole (τ_{el}^h) relaxation times.

The variation of the electronic relaxation times with temperature are shown in figures 6(c) and (d). Only results corresponding to $T = 300, 600$ and 900 K will be illustrated as these are more relevant to practical applications. As temperature increases, both electronic relaxation times decrease. At $T = 300$ K, PdSSe has relaxation times (9.37 fs for electrons/13.81 fs for holes) compared to (12.01 fs for electrons/9.96 fs for holes) for PdSTe and (14.17 fs for electrons/16.75 fs for holes) for PdSeTe. This trend continues to be seen as the temperature rises. Among all structures, PdS₂ has the lowest electronic relaxation times (6.18 fs for electrons/8.91 fs for holes).

Figure 8 displays the average power factor ($PF_{av} \equiv S_{av}^2 \sigma_{av}$) at various temperatures T , where $S_{av} = (S^{xx} + S^{yy})/2$ and $\sigma_{av} = (\sigma^{xx} + \sigma^{yy})/2$. Continuous (solid) graphs represent electron doping as opposed to the dashed curves that depict hole doping regions. Since the RBA method assumes a fixed band structure that does not change with temperature and/or small doping and consequently is independent of μ , calculations will be strictly done for $-0.5 \text{ eV} \leq \mu - E_F \leq 0.5 \text{ eV}$. In principle $\tau_{n,k} = \tau_{el}^h$ is used for calculations within the range $\mu - E_F < 0$ while $\tau_{n,k}$ is substituted by τ_{el}^e for $\mu - E_F > 0$. At ambient temperature, a peak value of $4.28 \mu\text{W (m} \cdot \text{K}^2)^{-1}$

is obtained for PdSSe in the case of electron doping whilst the highest PF_{av} for the pristine structures is noted for PdSe₂ with a value of $4.51 \mu\text{W (m} \cdot \text{K}^2)^{-1}$.

Another important thermoelectric property is κ_e that measures how heat is carried by the free electrons in the material. The average electrical thermal conductivity ($\kappa_e^{av} = (\kappa_e^{xx} + \kappa_e^{yy})/2$) is plotted for the same range of $\mu - E_F$ with the same relaxation times used in the PF calculations. Figure 9 shows that at room temperature systems, PdSeTe has an optimal value of $12.10 \text{ W (m} \cdot \text{K)}^{-1}$ among the Janus structures whereas for the pristines, PdSe₂ registers a maximum value of $8.60 \text{ W (m} \cdot \text{K)}^{-1}$. Within the range considered, these values occur at $\mu - E_F \sim 0.5 \text{ eV}$.

The figures of merit of the pristine and Janus structures along the x direction (ZT^{xx}) are exhibited in figure 10. The thermoelectric performance along the y direction (ZT^{yy}) is not shown on the graphs because for the majority of the systems, no big deviations from the values of ZT^{xx} are detected except for PdSe₂ whose values are somehow disparate. Details of the peak values of ZT^{xx} and ZT^{yy} , at $T = 300, 600$ and 900 K, for both electron and hole doping can be found in tables 3 and 4. Larger figures of merit are seen to be due to electron doping. Among the Janus structures, PdSeTe has the highest figure of merit at all temperatures with $ZT^{xx} = 0.40, 0.64$ at 300 and 600 K occurring at $\mu - E_F \sim 0.06$ and 0.04 eV .

At a temperature of 300 K, the thermoelectric performance of PdSSe and PdSTe is 3 and 2.7 times larger than that of PdS₂. Figures 11(a) and (b) monitor the ratio $ZT_{max}^{xx}(\text{PdXY})/ZT_{max}^{xx}(\text{PdX}_2)$ where $X = \text{S, Se}$ and $Y = \text{Se, Te}$ for both electron and hole doping. The above ratio is always greater than 1 at all temperatures which gives the Janus structures an advantage over their pristine analogues. In both types of doping, this

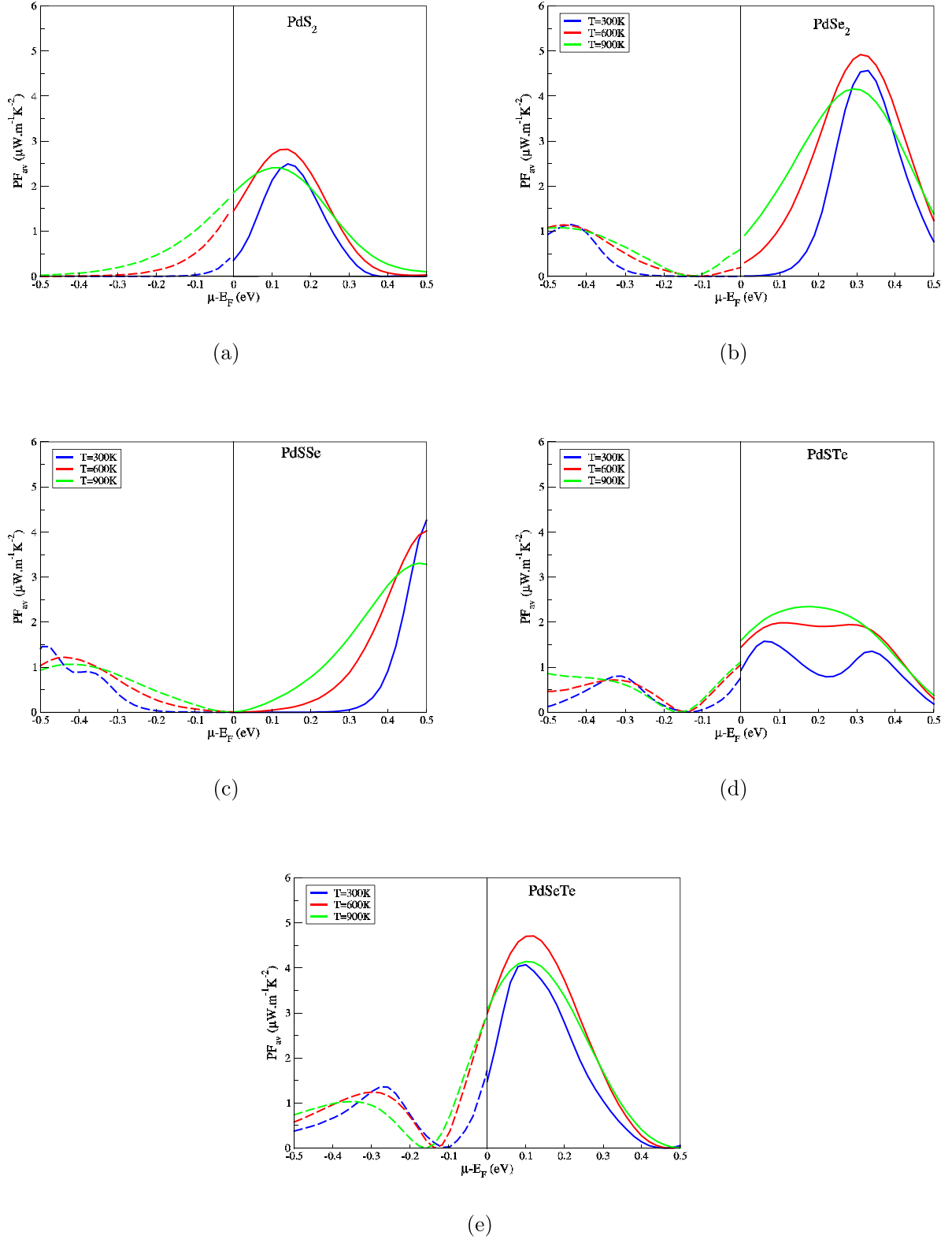


Figure 8. The average power factor (PF_{av}) for the pristine and Janus 1 T Pd structures showing regions of both electron (solid) and hole doping (dashed). At $T = 300$ K, $PdSe_2$ has its maximum PF around $\mu - E_F = 0.33$ eV. The Janus $PdSSe$ system has the optimal peak value at $\mu - E_F = 0.50$ eV. A vertical line at $\mu - E_F = 0$ separates hole and electron doping regimes.

ratio is largest at $T = 300$ K and decreases (remaining >1) as the temperature rises meaning that the Pd Janus structures are better thermoelectric devices than some of the pristines, especially at ambient temperatures. Experimentally, this implies that once $PdSSe$ and $PdSTe$ are synthesized from PdS_2 , they

will possess a bigger ZT_{max}^{xx} . Likewise, $PdSeTe$ synthesized from $PdSe_2$ has a larger optimal figure of merit.

Compared to other 2D dichalcogenides, the maximum ZT of 1 T $PdSe_2$ is observed to be higher than those of the 2D 2H MoS_2 [88] and 2H $MoSe_2$ [89] with values 0.11 and 0.1 at 500

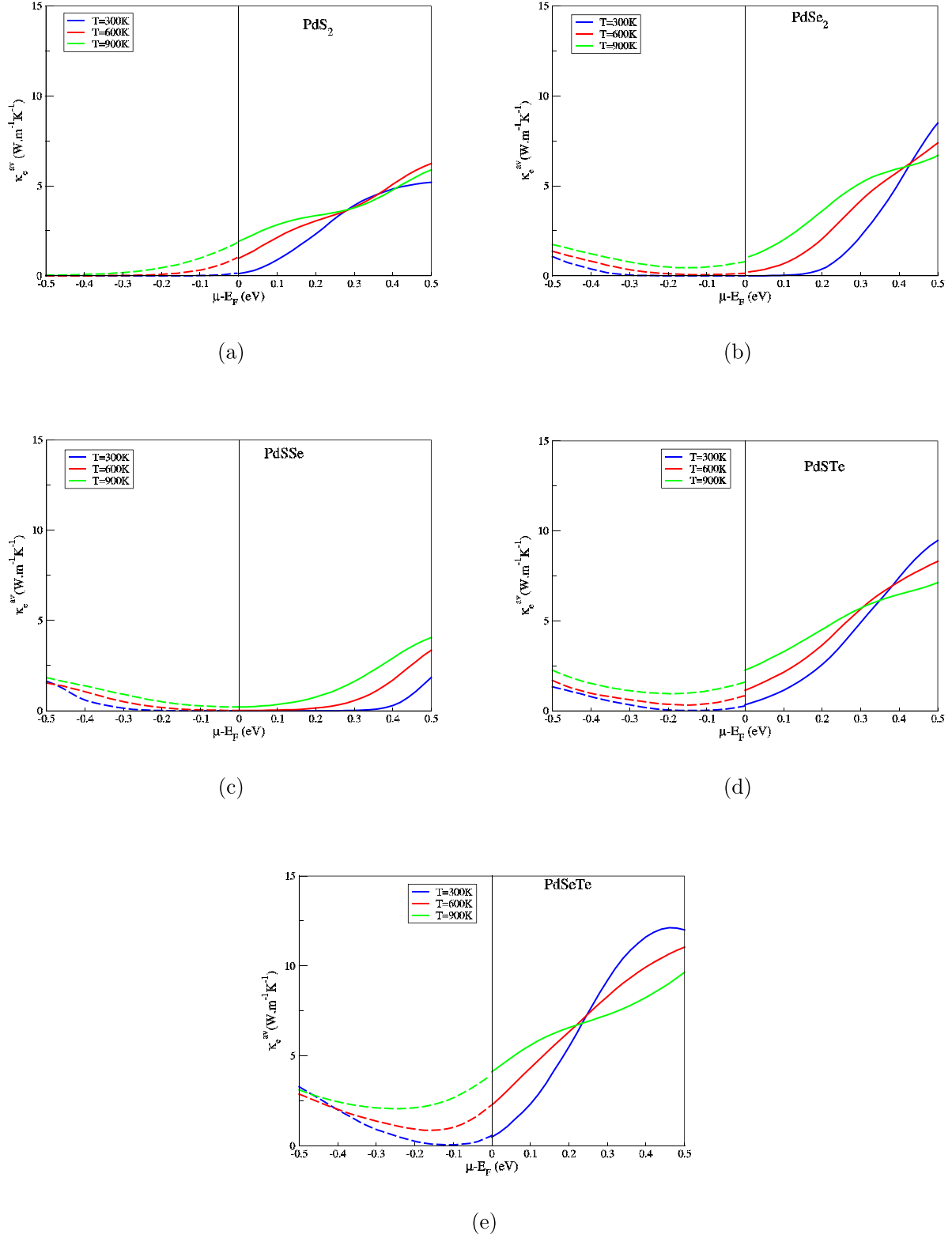


Figure 9. κ_e^{av} for the pristine and Janus 1 T Pd structures. At room temperature and within the range considered, PdSeTe has the highest value amongst all structures. Maxima occur for $\mu - E_F > 0$. Electron and hole doping regions are separated by a vertical line at $\mu = E_F$.

and 1200 K respectively. The pentagonal PdSe₂ monolayer of [58] shows that the structure has $ZT_{\max}^{xx} = 1.1$ at 300 K, almost 3.25 times larger than our 1 T system at the same temperature. Guo *et al* [49] discusses the 1 T ZrS₂ and Janus ZrSSe structures calculating just the electronic part of the figure of merit

(ZT_e) over a very small range of electron and hole concentrations. Although the values obtained reach almost 0.9 they are expected to be lower since κ_L was not taken into account.

By looking at figures 8–10, it is important to note that the thermoelectric properties discussed above show some

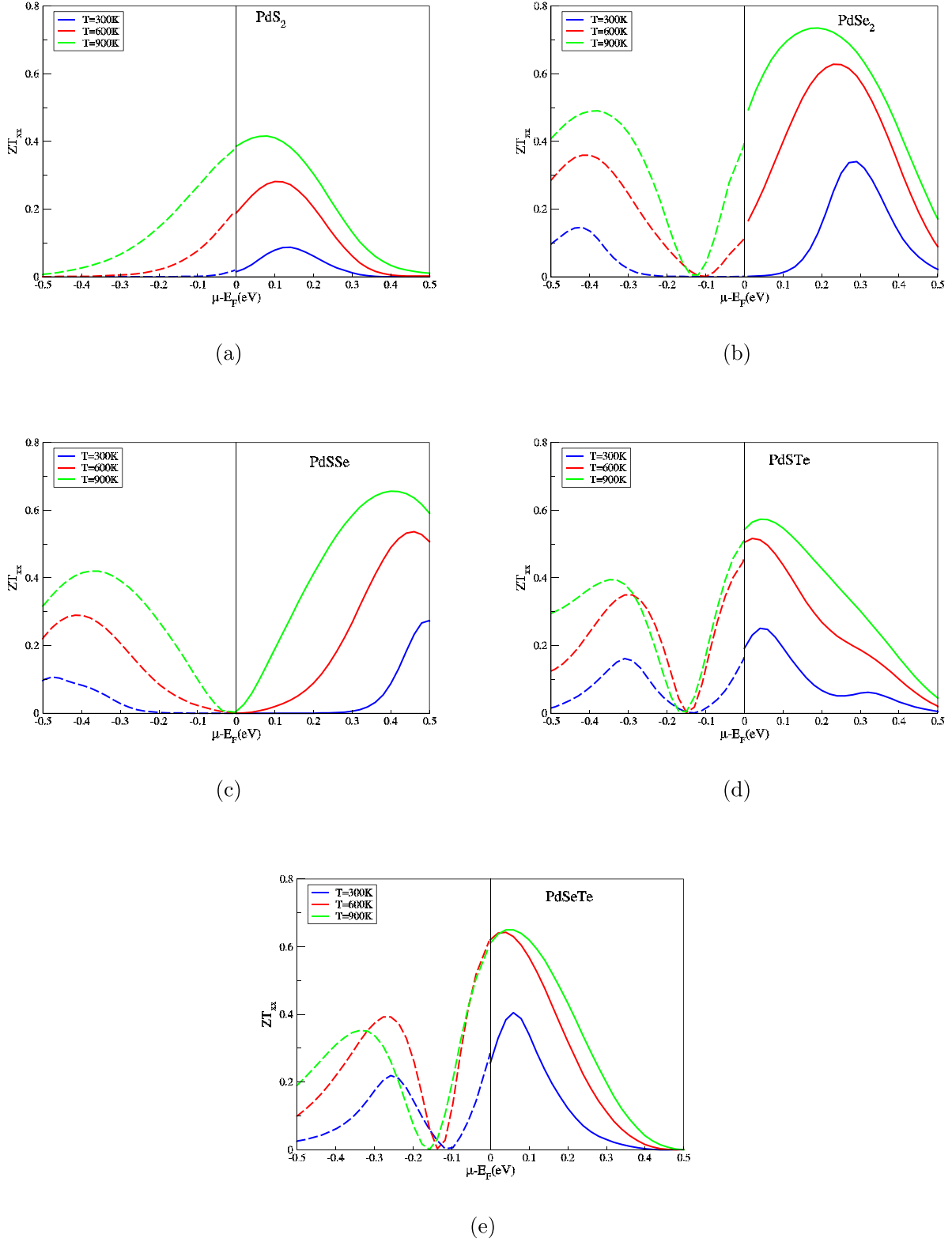


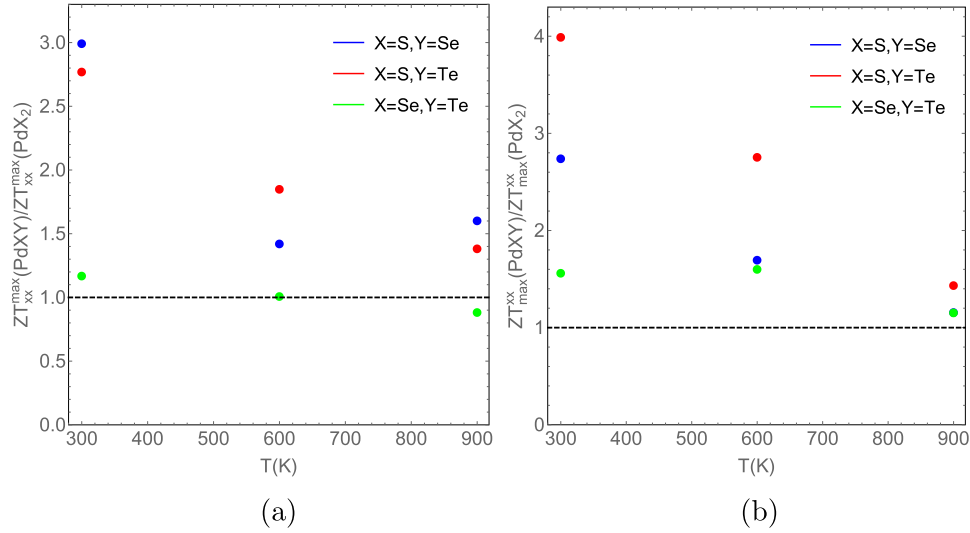
Figure 10. ZT^{xx} for the pristine and Janus 1 T Pd dichalcogenides in the case of electron (solid) and hole (dashed) doping for $\mu - E_F \in [-0.5 \text{ eV}, 0.5 \text{ eV}]$. Electron doping provides an optimal thermoelectric performance thus favoring n -doped semiconductors. At 900 K, ZT_{max}^{xx} reaches 0.65 for PdSeTe and 0.73 for PdSe₂.

‘discontinuity’ at values very close to E_F . This is mainly due to the usage of two different relaxation times for the electron and hole doping regimes and possibly due to numerical inaccuracies in the calculations since they are mostly noticeable

for the PdSe₂ and PdSTe cases. Nevertheless, these differences are rather small for ZT. As an example, at 600 K PdSe₂ has a ZT^{xx} equal to 0.115 and 0.125 at E_F using both relaxation times, giving rise to an error of 8%. At 900 K, these values

Table 4. Same as in table 3 for the case of hole doping. Optimal values are smaller than those obtained for the electron doping. Note that PdSe₂ shows some considerable anisotropy.

Structure	$ZT_{\max}^{xx}$			$ZT_{\max}^{yy}$		
	300 K	600 K	900 K	300 K	600 K	900 K
PdS ₂	0.04	0.17	0.36	0.04	0.17	0.37
PdSe ₂	0.14	0.36	0.49	0.19	0.43	0.55
PdSSe	0.11	0.29	0.42	0.09	0.28	0.42
PdSTe	0.16	0.47	0.52	0.17	0.46	0.51
PdSeTe	0.22	0.52	0.49	0.23	0.51	0.49

**Figure 11.** $ZT_{\max}^{xx}(\text{PdXY})/ZT_{\max}^{xx}(\text{PdX}_2)$ for both electron and hole doping. Janus structures have better thermoelectric performance than their related pristine structures at all temperatures (as explained in the text). (a) Electron doping. (b) Hole doping.

become 0.396 and 0.420 which is equivalent to an error of 6%. Similarly for PdSTe at 600 K, the values register 0.47 and 0.50 for hole and electron relaxation times respectively giving a difference of 6%. At 900 K, this difference is smaller (4%). This means that these values can still be used to describe the thermoelectric performance for the $\mu = E_F$ undoped case.

5. Conclusion

This paper focuses on the calculation of thermoelectric properties of 1 T 2D Pd pristine (PdX₂) and Janus (PdXY) structures with X = S, Se and Y is either S, Se or Te using a PBE Troullier–Martins pseudopotential, which is more viable to employ jointly with the packages used in the computation. All structures are semiconductors with variable indirect gaps. The Janus structures, which were not considered before, are mechanically stable showing positive frequencies on the phonon dispersion curves.

The thermoelectric properties show that the thermal lattice conductivities κ_L for both PdX₂ and PdXY systems are hardly anisotropic in both the x and y directions as the tensor components indicate, except for pristine PdSe₂ dichalcogenides whose $\kappa_L^{yy}/\kappa_L^{xx} \sim 0.67$. Figure of merit calculations for the Janus structures exhibit tiny differences in the maximum

values of ZT along the two directions in the structures' plane. Again an exception is pristine PdSe₂ manifesting an anisotropy with a ratio $ZT_{\max}^{yy}/ZT_{\max}^{xx} \sim 1.35, 1.19$ and 1.12 at $T = 300, 600$ and 900 K respectively for the case of hole doping. The Janus PdSeTe (PdSTe) has the highest (lowest) maximum values at almost all temperatures. Our results point to the fact that a maximum thermoelectric performance is achieved through electron doping, thus favoring n -doped semiconductors for the systems at hand.

Although there are almost no publications targeting the thermoelectric performance of 2D dichalcogenides (pristines and Janus), the figures of merit of the Janus Pd systems seem to be low compared to other types of 2D materials; however they are still higher than the corresponding pristines in both cases of electron and hole doping. Although Pd has become even rarer than gold and consequently should in principle be costly, PdXY thermoelectric devices can be an improvement over those using their pristine analogues: hypothetically, if devices made from PdSSe and PdSTe can at some point be manufactured, they will have a better performance over those fabricated using PdS₂. A similar argument is valid for PdSeTe and PdSe₂. Ways to further enhance the thermoelectric performance of the Janus structures could be to place a defect or to form a system of various layers, which will be the goal of a future work in progress.

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