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Single-Layer Janus Type Platinum Dichalcogenides and Their Heterostructures

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Abstract

Ultra-thin two-dimensional Janus type platinum dichalcogenide crystals formed by two different atoms at opposite surfaces are investigated by performing state-of-the-art density functional theory calculations. Firstly, it is shown that single-layer PtX_2 structures (where X=S, Se or Te) crystallize into the dynamically stable 1T phase and are indirect band gap semiconductors. It is also found that the substitutional chalcogen doping in all PtX_2 structures is favorable via replacement of surface atoms with smaller chalcogen atom and such process leads to the formation of Janus type platinum dichalcogenides (XPtY, where X and Y stand for S, Se or Te) which are novel single-layer crystals. While all Janus structures are indirect band gap semiconductors as their binary analogs, their Raman spectra show distinctive features that stem from broken out-of-plane symmetry. In addition, it is revealed that the construction of Janus crystals enhances the piezoelectric constants of PtX_2 crystals significantly both in the in-plane and in the out-of-plane directions. Moreover, it is shown that vertically stacked van der Waals heterostructures of binary and ternary (Janus) platinum dichalcogenides offer wide-range electronic features by forming bilayer heterojunctions of type-I, type-II and type-III. Our findings reveal that Janus type ultra-thin platinum dichalcogenide crystals are quite promising materials for optoelectronic device applications.

I. INTRODUCTION

Interest in the field of two dimensional (2D) single-layer materials triggered by the synthesis of graphene¹ has also led to emergence of novel ultra-thin materials exhibiting remarkable optical, electronic and mechanical properties.^{2–4} Apart from one-atom-thick graphene, single-layers of transition metal dichalcogenides (TMDs) such as MoS_2 , $MoSe_2$, WS_2 and WSe_2 have also been added to the library of 2D crystals.^{5–20}

Among TMDs, bulk platinum dichalcogenides (PtX₂, where X=S, Se, or Te) were quite demanded materials owing to their properties such as complete renewability,²¹ enhanced adhesion,²¹ semi-metallic electronic structure,^{22,23} high optoelectronic efficiency,²⁴ and enhanced photo- and electro-catalytic behavior.^{25,26} However, recently, 2D single-layer crystals of PtSe₂, with high structural stability in air and high photo-responsivity^{27–29}, has been successfully synthesized by direct selenization of the Pt(111) substrate.³⁰ In addition, theoretical studies revealed that single-layer PtS₂ (PtSe₂) is a semiconductor with a band gap of 1.6 eV³¹ (1.2 eV²⁸) having the potential for solar energy harvesting.

Recently, various techniques such as the construction of both vertical and lateral heterostructures have been applied to 2D materials in order to combine their different properties in a material.^{32,33} Although, such combination is experimentally feasible, the size and quality of the heterostructure are strongly influenced by the synthesis technique which may limit their applications. Moreover, recent studies have revealed that the synthesis of Janus type 2D materials can be an efficient way to enrich the functionality of a 2D crystal since different monolayers can be combined in a single-layer with strong chemical bondings.³⁴ The fact that the two surfaces of Janus materials have different properties inspired the development of nanodevices in the fields of chemistry, biology, and physics.^{35–40} Furthermore, recent theoretical studies have reported the energetic feasibility of Janus type single-layer crystals such as In_2SSe ,⁴¹ MoSe₂,⁴² MXY (M = Mo,W and X/Y = S, Se, Te).^{43,44} It was shown that intrinsic out-of-plane electric field induced in single-layer Janus crystal leads to significant Rashba spin splitting in electronic band dispersion of WSeTe.⁴³ In addition, syntheticallysynthesized Janus single-layer of TMDs have found to be displaying higher piezoelectric performance than commonly used materials.⁴⁴

In this study, motivated by the recent studies demonstrating the successful large-area chalcogen replacement in ultra-thin structures, we investigate the structural, vibrational,

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 and electronic properties of single-layers of Janus-type platinum chalcogenides and their vertical heterojunctions. The paper is organized as follows: Details of the computational methodology are given in Sec. III. The structural, phononic, electronic, and elastic properties of the single-layer PtX_2 are discussed in Sec. III A while those for their Janus crystals are presented in Sec. III B. Heterojunctions of Janus structures are discussed in Sec. III C. Finally, Sec. IV is devoted to the conclusion.

II. COMPUTATIONAL DETAILS

Density functional theory (DFT) calculations were performed using the Vienna *ab-initio* Simulation Package (VASP).^{45,46} The Perdew-Burke-Ernzerhof (PBE)⁴⁷ form of generalized gradient approximation (GGA) was adopted to describe electron exchange and correlation. The van der Waals (vdW) correction to the PBE functional was done using the density functional theory long-range dispersion correction (DFT-D2) method of Grimme.⁴⁸

The kinetic energy cutoff for a plane-wave basis was set to 400 eV. For the convergence criterion of self-consistent calculations in ionic relaxations, the total energy difference between the consecutive steps was taken to be 10^{-6} eV. The total force on the atoms in the primitive unitcell was reduced to a value of less than 10^{-5} eV/Å while the pressures on the lattice were decreased to values less than 1.0 kbar in all directions. To eliminate interaction between the adjacent layers, at least 18 Å of vacuum space was inserted. Analysis of the charge transfers in the structures was determined by using Bader technique.⁴⁹ For the band alignment calculations, the dipole corrections were taken into account in order to compensate the effect of induced out-of-plane dipole moment in Janus structures.

The cohesive energy per formula E_{Coh} was calculated by using the formula as $E_{Coh} = [n_1E_1 + n_2E_2 - E_{ML}]/n_{tot}$, where E_1 and E_2 represent the energies of single isolated two atoms, respectively. E_{ML} stands for the total energy of the 1T-PtX₂ structure, n_{tot} , n_1 and n_2 denote the total number of atoms, number of Pt and X atoms within the unitcell, respectively. The vibrational properties were calculated with PHONOPY code⁵⁰ that uses finite-displacement method. Phonon eigenfrequencies in whole Brillouin Zone (BZ) and phonon eigenvectors were calculated in a 75-atom supercell. In addition, the first-order off-resonant Raman spectra were obtained by calculating the derivative of polarizability in the crystal with respect to each vibrational phonon mode at the Γ point.

TABLE 1: The calculated parameters for single-layers of PtS₂, PtSe₂, and PtTe₂ are: the lattice constants, a=b; the atomic distance between Pt and X atoms (X=S, Se, Te), d; the thickness of single-layer, h; the cohesive energy per atom, E_{Coh} ; the charge donation from Pt to chalcogenide atom, $\Delta \rho$; work function, Φ ; total magnetic moment, μ ; frequencies of Raman-active phonon modes A_{1g} and E_g; intra-layer force constant per unit area between Pt and X atoms, out-of-plane (α_{Pt-X}^{\perp}) and in-plane $(\alpha_{Pt-X}^{\parallel})$ components; in-plane and out-of-plane macroscopic static dielectric constants, $\epsilon_{xx} = \epsilon_{yy}$ and ϵ_{zz} ; in-plane stiffness, C; and Poisson's ratio, ν .

| | a=b | d | h | E_{Coh} | $\Delta \rho$ | Φ | μ | A_{1g} | \mathbf{E}_{g} | α_{Pt-X}^{\perp} | $\alpha_{Pt-X}^{\parallel}$ | $\epsilon_{xx} = \epsilon_{yy}$ | ϵ_{zz} | С | ν |
|----------|----------------|------|------|-----------|---------------|--------|-----------|----------------------|----------------------|-------------------------|-----------------------------|---------------------------------|-----------------|-------|------|
| | (\AA) | (Å) | (Å) | (eV) | (e^{-}) | (eV) | (μ_B) | (cm^{-1}) | (cm^{-1}) | (N/m^3) | (N/m^3) | — | _ | (N/m) | _ |
| PtS_2 | 3.57 | 2.40 | 2.46 | 4.68 | 0.4 | 6.07 | 0 | 324.4 | 284.3 | $1.9{	imes}10^{21}$ | 1.4×10^{21} | 3.97 | 1.22 | 99 | 0.29 |
| $PtSe_2$ | 3.69 | 2.52 | 2.68 | 4.42 | 0.0 | 5.36 | 0 | 200.5 | 169.1 | $1.6{\times}10^{21}$ | 1.1×10^{21} | 7.52 | 1.50 | 88 | 0.31 |
| $PtTe_2$ | 3.92 | 2.69 | 2.90 | 4.28 | -0.3 | 4.30 | 0 | 153.1 | 124.8 | $1.3{	imes}10^{21}$ | $0.9{	imes}10^{21}$ | 10.64 | 1.61 | 73 | 0.31 |

III. RESULTS

A. Single-Layers of PtX_2

1. Structural Properties

The atomic structures of PtX₂ are shown in Figure 1(a). The single-layer PtX₂ crystal structures exhibits hexagonal symmetry and trigonal primitive unitcell in their 1T phase in which each Pt atom is surrounded by six X atoms forming a near-octahedral [PtX₆]⁴⁻ unit. For single-layer PtS₂, PtSe₂, and PtTe₂, the optimized lattice parameters (a=b) are calculated to be 3.57, 3.69 and 3.92 Å, respectively. As presented in Table 1, the length parameters in the structural properties such as bond distances and geometric thickness (which is defined to be the vertical distance between uppermost and lowermost chalcogenide atoms) enlarge with the increasing atomic radius. The cohesive energy per formula in the unitcell is calculated to be 4.68 eV for single-layer PtS₂, whereas those for PtSe₂ and PtTe₂ are found as 4.42 and 4.28 eV, respectively. As the atomic radius of the chalcogenide atom increases from S to Te, the bond length between Pt-X atoms increases which reveals the existence of relatively weaker bonds that means the required energy to remove the chalcogenide atom from the structure decreases. The cohesive energies are calculated by



Figure 1: (a) Top side of the geometric structures of PtS_2 , $PtSe_2$, and $PtTe_2$. Yellow, blue, green, and brown colors show S, Pt, Se, and Te atoms, respectively. (b) Phonon band diagrams of PtS_2 , $PtSe_2$, $PtTe_2$, respectively. (c) Normalized Raman activity plot of PtX_2 single-layers. All Raman activities are normalized to the volume of the primitive unitcell of each crystal structure. (d) Electronic band structures of PtS_2 , $PtSe_2$, $PtTe_2$.

using the formula given in Section 2 in which the energies of single isolated atoms are considered at 0 $^{\circ}$ K. In addition to cohesive energies, the heat of formation can be calculated by using the same formula. As reported in CMR data base⁵⁶, the heat of formations for

 PtS_2 , $PtSe_2$, and $PtTe_2$ are -0.385, -0.413, and -0.392 eV/atom. However, for the calculation of heat of formation the standart state of the constituent atoms (energy of an isolated atom is calculated at 300 °K at 1 atm pressure) are taken into account. Therefore, since the standart state of each individual atom depends on their standart compounds, similar trend on cohesive energies may not be expected.

According to Bader charge analyses, formation of single-layer PtS_2 can occur by donation of 0.4 e^- from each Pt atom to S atoms. In addition, while $PtTe_2$ single-layer is formed by 0.3 e^- transfer from each Te to Pt atom, in $PtSe_2$ crystal structure bonds are formed without any charge transfer between Pt and Se. Apparently, $PtSe_2$ single-layer has entirely covalent bonds while PtS_2 and $PtTe_2$ have partially ionic bonding character.

2. Raman Activity, Elastic Properties and Electronic Characteristics

The dynamical stability of the single-layer 1T-PtX_2 structures are verified by calculating their phonon band structures through the whole BZ. As shown in Figure 1(b), all singlelayers of PtX_2 s are free from imaginary frequencies in the whole BZ, indicating that they are dynamically stable. In the 3-atom primitive unitcell, each single-layer exhibits nine phonon branches three of which are acoustic and the remaining six have optical character.

While there is a large gap ($\sim 55 \text{ cm}^{-1}$) between acoustic and optical phonon branches of PtS₂, for PtSe₂ and PtTe₂ crystals mid-frequency optical modes overlap with acoustic modes at the M symmetry point. As a result of the planar symmetry in 1T phase, six optical modes in PtX₂ structures consist of two doubly degenerate in-plane and two non-degenerate out-of-plane phonon modes. For the single-layer PtS₂, the out-of-plane modes A_{2u} and A_{1g} occur at frequencies 317.3 cm⁻¹ and 324.4 cm⁻¹, respectively while two doubly degenerate in-plane modes: E_g and E_u have frequencies 284.3 cm⁻¹ and 305.2 cm⁻¹, respectively at the Γ point. In addition, single-layers of PtSe₂ and PtTe₂ have A_{2u} (223.0 and 177.0 cm⁻¹, respectively), A_{1g} (200.5 and 153.1 cm⁻¹, respectively) out-of-plane phonon modes, while they have two doubly degenerate E_g (169.1 and 124.8 cm⁻¹, respectively) and E_u (218.3 and 178.8 cm⁻¹, respectively) in-plane modes.

The group theory analysis reveal that 1T-PtX_2 which belongs to the D_{3d} point group possess three Raman active phonon modes. The optical phonon modes, E_g , are attributed to the in-plane vibration of chalcogenide atoms against each other while the non-degenerate

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 A_{1g} mode represents the out-of-plane vibration of chalcogenide atoms against each other (see the inset of Figure 1(c)). For the two optical phonon modes, A_{1g} and E_g , the force constant per unit area can be related to the phonon frequency by the equations;⁵³

$$\Omega_{A_{1g}} = \left(\frac{1}{2\pi c}\right) \sqrt{\frac{2\alpha_{Pt-X}^{\perp}}{\mu}},$$

$$\Omega_{E_g} = \left(\frac{1}{2\pi c}\right) \sqrt{\frac{2\alpha_{Pt-X}^{\parallel}}{\mu}},$$
(1)

where μ is the atomic mass per unit area and c is the speed of light. Due to the contribution of only chalcogenide atoms to the vibration, the total mass per unit area is equal to $2m_X$.

The calculated mass per unit area is 0.5×10^{-6} , 1.1×10^{-6} , and 1.6×10^{-6} (kg/m²) for PtS₂, PtSe₂, and PtTe₂, respectively. As seen from Table 1, when going from PtS₂ to PtTe₂, the heavier the chalcogen atom the smaller the force constants which is directly attributed to the weaker bonds formed by heavier chalcogenide atom. Therefore, soft crystals formed by heavier chalcogenide atoms display remarkable phonon softening in their spectrum as shown in Figure 1(b).

In all single-layers, the Raman activity of A_{1g} mode is smaller than that of E_g modes which occurs due to the relatively smaller contribution of ϵ_{zz} to the Raman tensors.⁵² In order to make a comparison between different single-layers, the Raman activities are normalized to the volume of each primitive unitcell. As seen in Figure 1(c), the Raman activity of each mode increases from PtS₂ to PtTe₂. Relatively larger atomic bond lengths result in larger dielectric constant which exhibits larger change of polarizability in the crystal when subjected to an incident light. Hence, increasing Raman activity of the phonon modes from PtS₂ to PtTe₂ can be attributed to the increase in macroscopic static dielectric constants (see Table 1).

The linear-elastic properties of 2D single-layer materials can be represented in terms of two independent constants; the in-plane stiffness, C, and the Poisson's ratio, ν . For determination of linear-elastic constants via energy-strain relation a 54-atom supercell is constructed for each crystal structures. Biaxial and uniaxial strains are applied for both tensile and compressive cases. The strain parameters ε_a and ε_b are varied between ± 0.015 with a step size of 0.005. Then, three different sets of data are calculated; (i) $\varepsilon_a=0$ and ε_b varying, (ii) $\varepsilon_b=0$ and ε_a varying and (iii) $\varepsilon_a=\varepsilon_b$ varying. At each configuration, the atomic positions are fully relaxed and the strain energy, E_S , is calculated by subtracting the total energy of the equilibrium state from the strained structure. Then, the calculated data is fitted to the equation; $E_S = c_1 \varepsilon_a^2 + c_2 \varepsilon_b^2 + c_3 \varepsilon_a \varepsilon_b$,⁵⁴ and the coefficients, c_i , are determined. Therefore, the in-plane stiffness, C, the measure of the rigidity of a material under applied external load, can be calculated by the formula; $C = (1/A_0)(2c - c_3^2/2c)^{55}$ where $c_1=c_2$ due to the in-plane isotropy and A_0 is the area of the unstrained supercell. As listed in Table 1, the C values are 99, 88, and 73 N/m from single-layer PtS₂ to PtTe₂. In agreement with the calculated in-plane component of intra-layer force constants ($\alpha_{Pt-X}^{\parallel}$); the larger the bond lengths, the smaller the in-plane stiffness. This decreasing trend demonstrates that as the in-plane stiffness decreases, the corresponding restoring forces in the structure become effective in a shorter range of applied strain, i.e. the harmonic strain region gets smaller for soft materials. A similar trend for in-plane stiffness values were reported in CMR data base (86, 71, and 65 N/m from single-layer PtS₂ to PtTe₂). Here slightly different values obtained by different theoretical methodologies can be better explained via experimental measurements.⁵⁶

In addition one can obtain the Poisson's ratio defined as the ratio of the transverse contraction strain to the longitudinal extension strain in the direction of the stretching force. Here the Poisson's ratio for *a*- and *b*-vectors are calculated in terms of the coefficients c_i as; $\nu_a = \nu_b = c_3/2c$. The Poisson's ratios display small changes from single-layer PtS₂ to PtTe₂ (0.29 for PtS₂, 0.31 for PtSe₂, and 0.31 PtTe₂). When compared with well-known TMDs, i.e. 0.25 for MoS₂,⁵⁷ 0.22 for WS₂,⁵⁷ and 0.23 for MoSe₂,⁵⁷ PtX₂ crystals exhibits larger responses to the applied load along the perpendicular direction. Such relatively large Poisson's ratios suggest more sensitive structural response to external loads which can be beneficial for nanoelastic applications.

The electronic band dispersions of the single-layers of 1T-PtX_2 through the whole BZ are shown in the Figure 1(d). It is found that all structures are indirect band gap semiconductors. The indirect band gaps of PtS₂, PtSe₂ and PtTe₂ are calculated to be 1.82, 1.34 and 0.34 eV, respectively. Therefore, the band gaps are inversely proportional to the atomic mass of their chalcogenide types. The VBM of single-layer PtS₂ resides between the *K* and Γ points while that of the other single-layers are located at the Γ point. It is seen from the Figure 1(d) that the VBM takes the shape of a sharper concave from PtS₂ to PtTe₂ with increasing effective mass. CBM shifts from within the Γ -M to within the Γ -*K*. The CBM of single-layer PtS₂ and PtSe₂ reside between the M- Γ points while the CBM of



Figure 2: The exchange energy formed by the transverse process between a host and a foreign chalcogenide atom in a large-scale platinum dichalcogenide single-layer.

single-layer $PtTe_2$ reside between the Γ and K points. As seen from the Figure 1(d) the CB edge in between the Γ and K points becomes energetically more favorable as the radius of the chalcogenide atom increases and it becomes CBM for single-layer $PtTe_2$. This behavior may be attributed to the increasing lattice parameters in the structure when compared to those of PtS_2 and $PtSe_2$.

3. Chalcogen Exchange in single-layers PtX_2

The exchange energies required to replace a single chalcogenide atom instead of the host chalcogenide atom are shown in Figure 2. The exchange energy is calculated by replacing a foreign chalcogenide atom to a host chalcogenide atom in a $3\times3\times1$ supercell by using the formula; $\Delta_{xc} = E_{tot}(Pt_9X_{18}) - E_{tot}(Pt_9X_{17}X'_1)$ where $E_{tot}(Pt_9X_{18})$ is the total energy of 3×3 supercell of the bare PtX_2 while $E_{tot}(Pt_9X_{17}X'_1)$ is that of the exchanged structure. Note that the chemical potential of the exchanged atom is set to be equal to its total energy in vacuum at 0 °K. By examining such exchange energy, it is possible to determine whether the replacement is obtained with or without external energy.

As seen in Figure 2, when one S atom is replaced by Se or Te in a single-layer PtS_2 , the exchange energies are found to be 0.33 and 1.11 eV, respectively. On the other hand, if S or Te exchanges with a Se atom in the $PtSe_2$, the required energies are calculated to be -0.32 and 0.20 eV, respectively. The minus sign indicates the process is exothermic, whereas the

positive sign means that an additional energy is required and the process is endothermic. In single-layer $PtTe_2$, the exchange of chalcogenide atoms, with S or Se atoms is found to require -0.13 and -1.03 eV, respectively. It is clearly seen that the exchanging a small chalcogenide atom instead of a larger chalcogenide atom is energetically favorable process. It is found that the replacing S atoms instead of Te atoms in single-layers of $PtTe_2$ is the energetically most favorable process.

B. Janus type Single-layers of XPtY

1. Structural Properties

Janus type ultra-thin platinum dichalcogenides are constituted completely two different chalcogenide surfaces. After a detailed analysis of single-layer 1T-PtX₂, we investigate the 1T phase of Janus, or in other words, ternary platinum dichalcogenide single-layer structures, 1T-XPtY. Figure 3(a) shows the crystal structure of the single-layer 1T-XPtY. In a Janus structure, platinum is sandwiched between upper chalcogenide (X) and bottom chalcogenide (Y) layers in 1T-phase.

As given in Table 2, the calculated lattice parameters (a=b) of ternary platinum dichalcogenides are 3.63, 3.75 and 3.81 Å for SePtS, TePtS and TePtSe, respectively. The atomic bond lengths between Pt atom and the upper (Se) and lower sides (S) are 2.50 and 2.43 Å in SePtS structure. On the other hand, for TePtS structure, the Pt-Te bond length is 2.62 Å while that of Pt-S is 2.57 Å. In single-layer TePtSe, the atomic bond lengths Pt-Te and Pt-Se are calculated as 2.64 and 2.57 Å, respectively. Moreover, the thicknesses are found to be 2.57, 2.70 and 2.80 Å for SePtS, TePtS, and TePtSe, respectively. In addition, the calculated cohesive energies are 4.53, 4.40 and 4.31 eV, for SePtS, TePtS and TePtSe, respectively. As we discussed in Section 3A, the same trend between cohesive energies and bond lengths in the structure are found for the Janus single-layers which is a result of the existing chalcogenide atoms in the Janus crystal. As mentioned for the bare PtX₂ crystals, cohesive energies simply display an increasing or decreasing trend depending on the atomic mass and radius of the chalcogenide atoms. For the thermodynamical stabilities of Janus crystals, the formation enthalpies at 0 °K are calculated by using the formula; $\Delta H=E_{tot}(PtXX')-0.5E_{tot}(PtX'_2)-0.5E_{tot}(PtX_2)^{55}$ where $E_{tot}(PtXX')$, $E_{tot}(PtX'_2)$, and



Figure 3: (a) Top and side views for the geometric structures of SePtS, TePtS, and TePtSe. Yellow, blue, green, and brown colors are for S, Pt, Se, and Te, respectively. (b) Phonon band diagrams A-like and E-like phonon branches are shown by \tilde{A} and \tilde{E} . (c) Normalized Raman activity plot of Janus single-layers. All Raman activities are normalized to the volume of the primitive unitcell of each crystal structure. (d) Electronic band structures of SePtS, TePtS, and TePtSe and the Fermi level is set to zero.

 $E_{tot}(PtX_2)$ denote the total energies of Janus and single-layers of PtX₂ and PtX'₂, respectively. The calculated formation enthalpies are 0.046, 0.075, and 0.243 eV/cell for SePtS, TePtSe, and TePtS, respectively. Our results reveal that when the mass difference between two chalcogenide atoms is smaller, the formation of their Janus crystal is more feasible.

It is seen that when a small atom is placed inside the structure instead of a large atom, lattice parameters, the bond lengths, the thickness, and the cohesive energies decrease accordingly. According to Bader charge analyses, in single-layer SePtS Pt donates $0.2 e^-$, S receives $0.2 e^-$, and Se has no charge transfer. Since charge transfers are obtained for TePtS and TePtSe, it is seen that Te donates $0.1 e^-$ to Pt and $0.3 e^-$ to S in TePtS, in TePtSe while Te donates $0.2 e^-$ to Pt and $0.1 e^-$ to Se.

2. Vibrational Properties and Raman Spectra

To verify dynamical stability of the Janus platinum dichalcogenide structures, the vibrational properties of the XPtY single-layers are investigated and the phonon band diagrams are shown in Figure 3(b). Similar to their binary analogs, Janus structures are also found free from the imaginary frequencies in the whole BZ indicating their dynamical stability. In addition, Janus single-layers exhibit three acoustical and six optical phonon branches.

As shown in Figure 3(b), the phonon band gaps are ~ 27 , 36 and 14 cm⁻¹ for single-layer SePtS, TePtS, and TePtSe, respectively. The phonon band gaps of XPtY structures become narrower and the phonon bands soften from SePtS to TePtS and TePtSe. This can also be attributed to different atomic masses, as the mass of chalcogenide atom increases the corresponding vibrational frequencies decrease.

Differing from the single-layers of PtX₂ crystals, single-layers of XPtY Janus structures exhibit additional Raman active phonon modes originating from the broken inversion symmetry. The single-layers of XPtY structures exhibit six Raman active phonon modes two of which are non-degenerate out-of-plane modes while the remaining four are doubly-degenerate having in-plane vibrational character. Since the two chalcogenide atoms are different, their vibrations with respect to the Pt layer are not symmetric. Thus, depending on the atomic mass, i.e. on the atomic bond lengths, the Raman activities differ from one structure to another. For instance, the phonon mode \widetilde{A}_{2u} has the smallest Raman activity when the total Pt-X bond length is the smallest, i.e. for single-layer SePtS structure. The activity

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of this mode gets larger for single-layer SPtTe and decreases for single-layer SePtTe. The reason for this behavior is the vibrational character of the atoms in the phonon mode. As seen on the right panel of Figure 3(c), one of the chalcogenide atoms is stationary and do not contribute to the vibration. In S-based XPtY structures, Raman activity increases from SePtS to TePtS because of the increasing mass of stationary chalcogenide atom. By the same analogy, the \widetilde{E}_u mode exhibits the same behavior since it represents the in-plane vibration of Pt and lighter chalcogenide atoms. For the \widetilde{A}_{1g} mode the same trend is found because in S-based XPtY structures the vibration of Se and Te atoms dominate that of S atom. When the second chalcogenide atom is changed from Se to Te, the dipole between Pt and Te atoms increases due to the larger atomic bond in Pt-Te. Therefore, the Raman activity of the A_{1g} increases from SePtS to TePtS. However, in single-layer TePtSe the vibration of Pt and Se atoms have almost the same strength while the vibration of Te dominates the motion. Finally, when we analyze the E_q mode, it is seen that the Raman activity increases from SePtS to TePtSe. In all single-layer XPtY structures, the Pt atom and the lighter chalcogenide atom vibrate along the same direction while the heavier chalcogenide atom vibrates in opposite direction. Therefore, the Raman activity increases when the bond length between Pt and the heavier chalcogenide atom increases.

TABLE 2: The calculated parameters for single-layers of SePtS, TePtS, and TePtSe are: the lattice constants, a=b, the atomic distance between Pt and X atoms (X=S, Se, Te), d; the thickness of single-layer, h; the cohesive energy per formula, E_{Coh} ; the charge donation from Pt to chalcogens, $\Delta \rho$; work function, Φ ; net magnetization in the primitive cell, μ ; in-plane and out-of-plane macroscopic static dielectric constants, $\epsilon_{xx} = \epsilon_{yy}$ and ϵ_{zz} ; in-plane stiffness, C; and Poisson's ratio, ν .

| | a = b | d_{Pt-Se} | \mathbf{d}_{Pt-S} | \mathbf{d}_{Pt-Te} | h | E_{Coh} | $\Delta \rho$ | Φ_{Pt-Se} | Φ_{Pt-S} | Φ_{Pt-Te} | μ | $\epsilon_{xx} = \epsilon_{yy}$ | ϵ_{zz} | \mathbf{C} | ν |
|--------|---------|----------------|---------------------|----------------------|----------------|-----------|---------------|----------------|---------------|----------------|-----------|---------------------------------|-----------------|--------------|------|
| _ | (Å) | (\AA) | (Å) | (Å) | (\AA) | (eV) | (e^{-}) | (eV) | (eV) | (eV) | (μ_B) | _ | — | (N/m) | |
| SePtS | 5 3.63 | 2.50 | 2.43 | - | 2.57 | 4.53 | 0.2 | 5.31 | 6.09 | - | 0 | 6.80 | 1.46 | 93 | 0.30 |
| TePtS | 5 3.75 | - | 2.57 | 2.62 | 2.70 | 4.40 | -0.1 | - | 5.95 | 4.48 | 0 | 8.59 | 1.51 | 78 | 0.29 |
| TePtSe | e 3.81 | 2.57 | - | 2.64 | 2.80 | 4.31 | -0.2 | 5.11 | - | 3.05 | 0 | 9.07 | 1.55 | 76 | 0.31 |

3. Elastic and Electronic Properties

Using the same methodology, the in-plane stiffness and Poisson's ratio are calculated for the Janus type single-layer structures. As listed in Table 2, the C values are 93, 78, and 76 N/m for SePtS, TePtS and TePtSe, respectively. Apparently, the larger the interatomic distance, the smaller the stiffness. The decreasing trend of the in-plane stiffness also matches well with the change in cohesive energy. When these values are analyzed in terms of the individual in-plane stiffness and Poisson's ratio, in all single-layers XPtY the in-plane stiffness is determined by heavier chalcogenide atom. It is seen that the Te-based single-layers of XPtY, TePtS and TePtSe, exhibit the same ν (0.31) values which are dominated by the Te atom while for the single-layer of SePtS the ν is found to be close to that of PtS₂.

The electronic band diagrams of single-layer XPtY are shown in Figure 3(d). It is seen that Janus structures of SePtS, TePtS and TePtSe are indirect band gap semiconductors with band gap of 1.56, 0.86 and 0.82 eV, respectively. In Janus structures replacement of small atoms by larger atoms simply leads to the narrowing of the band gap. While the band structure of SePtS is detemined by both and S and Se states, electronic bands of Te-including Janus single-layers mainly composed of Te states. Compared with their binary analogs, character of VBM and CBM in single-layer XPtY structures are significantly different. It is seen that VBM of Janus structures shifts to the Γ point and take the shape of a sharper concave from SePtS to TePtSe with increasing effective mass. However, differing from the binary analogs, CBM of Janus structures shifts from the Γ -M to the K symmetry point.

4. Piezoelectric Properties

Piezoelectricity or piezoelectric effect is known as the generating electric dipole moment as a response for the applied mechanical stress in a non-centrosymmetric material. Theoretical predictions and experimental observations have demonstrated the enhancement of piezoelectric constants in 2D limit.^{58–62}

In the case of 1T-phase TMDs, because of the centrosymmetry of the structure, the piezoelectric constants are expected to be very small as compared to 1H-phase TMDs. For the calculation of piezoelectric constants, one needs the elasticity tensor whose elements are then related to the piezoelectric coefficients, e_{ij} , and piezoelectric constants, d_{ij} , by the

TABLE 3: For the monolayers of PtX_2 and XPtY Janus crystals the relaxed-ion; Elastic constants, C_{ij} , piezoelectric coefficients, e_{ij} , and the corresponding piezoelectric strain constants, d_{ij} . Note that all the elastic and piezoelectric constants are renormalized by the *c* lattice parameter in 2D limit.

| | C_{11} | C_{12} | e_{11} | e_{31} | d_{11} | d_{31} |
|-------------------------|----------|----------|----------|----------|----------------------|----------------------|
| | (N/m) | (N/m) | (pC/m) | (pC/m) | $(\mathrm{pm/V})$ | (pm/V) |
| PtS_2 | 107.5 | 31.5 | 0.29 | 0.13 | 3.8×10^{-3} | 0.9×10^{-3} |
| PtSe_2 | 97.4 | 30.0 | 0.38 | 0.20 | 5.6×10^{-3} | $1.5{\times}10^{-3}$ |
| PtTe_2 | 80.5 | 24.7 | 1.00 | 0.11 | $1.8{	imes}10^{-2}$ | $1.3{	imes}10^{-3}$ |
| SePtS | 101.6 | 30.3 | 75.00 | 58.30 | 1.0 | 0.44 |
| TePtS | 84.8 | 25.1 | 235.50 | 321.40 | 4.0 | 2.9 |
| TePtSe | 83.9 | 25.8 | 152.00 | 262.30 | 2.6 | 2.4 |

equation;⁵⁹

$$d_{11} = \frac{e_{11}}{C_{11} - C_{12}},\tag{2}$$

$$d_{31} = \frac{e_{31}}{C_{11} + C_{12}},\tag{3}$$

where C_{ij} stands for the second-order elastic constants. The relaxed-ion elastic constant are listed in Table 3. Due to the D_{3d} symmetry of 1T-phase, $C_{11}=C_{22}$ while $C_{12}=C_{21}$ and such a symmetry exists also for piezoelectric coefficients and constants. As given by the in-plane stiffness values in Table 1 and 2, a similar trend is found for the elastic constants, C_{11} and C_{21} , which decrease as the atomic radius increases in 1T-PtX₂ crystals.

As listed in Table 3, the calculated piezoelectric coefficients, e_{ij} , are negligibly small as compared to 1H-TMDs monolayers. It was experimentally observed for 1H monolayer MoS₂ that the in-plane piezoelectric coefficient, e_{11} , is 294 pC/m⁶³ (308 pC/m in our case which reveals the reliability of the methodology). However, in the case of 1T-PtX₂ crystals, the e_{11} values are found to be 0.29, 0.38, and 1.00 pC/m for single-layer PtS₂, PtSe₂, and PtTe₂, respectively which are negligibly small as compared to monolayer MoS₂ (294 pC/m⁶³). A similar increasing trend from S to Te atom was reported for MX₂ (M=Mo or W, X=S, Se, or Te) structures⁶⁴. The corresponding piezoelectric constants, d₁₁, are listed in Table 3 which are also negligibly small as compared to 1H-TMDs. This is a result of the in-plane centrosymmetry in 1T-phase crystal structures. In addition, the out-of-plane piezoelectric coefficients and the corresponding piezoelectric constants, e_{31} and d_{31} , are also calculated and found to be comparable to those of e_{11} and d_{11} . The finite out-of-plane piezoelectric constant arises from the non-centrosymmetric crystal structure of the 1T-phase in the out-of-plane direction.

When the Janus structures of PtX_2 crystals are formed, due to the broken in-plane and out-of-plane symmetries, the piezoelectric constants are significantly enhanced. The inplane piezoelectric coefficients are found to be 75.00, 235.50, and 152.00 for SePtS, TePtS, and TePtSe, respectively and the corresponding piezoelectric constants are 1.0, 4.0, and 2.6 pm/V which are at the order of 10^{-3} for the PtX₂ structures. In addition to the broken in-plane symmetry in the Janus crystals, an additional out-of-plane degree of freedom allows one to have piezoelectric behavior in that direction. The calculated e_{31} and d_{31} values are listed in Table 3 which follow the similar trend to what was reported for XMoY and XWY Janus crystals⁴⁴. In the Janus crystal two chalcogenide atoms are different thus, when an external strain is applied different amounts of charges are accumulated on different sides of the crystal which results in a net electric dipole moment.

C. Vertical van der Waals heterostructures

Vertical vdW heterostructures of ultra-thin materials have been the focus of interest due to the idea of Lego type construction and combining properties of different single-layers in one structure.^{65,66} Since binary and ternary platinum dichalcogenides are ultra-thin semiconductor materials, their vdW heterostructures and band alignments present broad variety to achieve different electronic characters. In this section, we focus on possible vdW heterostructures and their electronic heterostructure types. Band alignments of binary and ternary (Janus type) platinum dichalcogenides are shown in Figure 4. Note that the dipole correction is considered in band alignment calculations to construct the exact type of alignment of the heterostructure. For this purpose, an external dipole moment in the out-of-plane direction is introduced to compensate the effect of induced dipole moment.

In type-I (straddling) heterojunctions, VBM and CBM are from the same individual layer. These type heterostructures are common in superlattices and desirable for light emitting applications. As seen in Figure 4(b), it is found that the type-I vdW heterostructures can



Figure 4: (a) The band alignments of binary and ternary platinum dichalcogenides. In XPtY, workfunction values are determined for X surface and vacuum level set to zero. (b) The table of all possible vdW heterostructures types. For Janus structures the bands are aligned according to the surface of X type atom. Yellow, blue and red boxes in the table indicate type-I, II and III heterostructures, respectively. Schematic representation of a heterostructure SPtSe/TePtSe are also shown in the table.

be formed by PtS₂/SPtSe, PtS₂/SPtTe, PtTe₂/SePtS, PtTe₂/TePtS, SePtS/SePtTe and SPtSe/SPtTe.

If both VBM and CBM of one structure are lower than the VBM and CBM of the other structure, electrons are confined in one structure, while holes are confined in the other structure. In this case, heterostructure type is called as type-II or staggered type heterojunction. Owing to separation of electrons and holes to different layers, the lifetime of radiative recombinations are increased; thus, these type heterostructures can be used for photocatalytic, photovoltaics and photodetection applications. PtS₂/PtSe₂, PtS₂/SePtS, PtS₂/SePtTe, PtS₂/TePtS, PtSe₂/SePtSe, PtSe₂/SePtTe, PtSe₂/SPtSe, PtSe₂/SPtTe, PtSe₂/TePtS, SePtS/TePtS, SePtTe/TePtS, SPtSe/SePtTe and SPtTe/SePtTe vdW heterostructures are found to form type-II heterojunctions.

In a type-III (broken) heterojunction, the CBM of one structure lies below the VBM of

the other one. Such heterojunctions not only allow semimetal-to-semiconductor transitions but also lead to formation of interface excitons and coexistence electron and holes. We found that PtS₂/PtTe₂, PtS₂/TePtSe, PtSe₂/PtTe₂, PtSe₂/TePtSe, PtTe₂/SePtTe, PtTe₂/SPtSe, PtTe₂/SPtTe, PtTe₂/TePtSe, SePtS/TePtSe, SPtSe/TePtS, SPtSe/SePtS, SPtSe/TePtSe, SPtTe/TePtS, SPtTe/TePtSe, TePtS/TePtSe and TePtSe/SePtTe are type-III heterojunctions.

IV. CONCLUSIONS

In the present work, the structural, electronic, and vibrational properties of the singlelayers of PtX₂ and Janus type XPtY (where X/Y=S, Se, Te) were investigated by performing *ab*-initio calculations. It was shown that single-layer PtX₂ structures are dynamically stable structures in 1T phase and display three characteristic Raman active phonon modes at the Γ point that can be observed by Raman measurements.

Furthermore, it was found that formation of Janus type platinum dichalcogenide crystals having two different atoms at opposite surfaces is possible via chalcogen exchange and all XPtY are dynamically stable. In addition, in their Raman spectrum, Janus XPtY structures exhibit additional three Raman-active modes stemming from broken out-of-plane symmetry. Electronically, similar to their binary analogs, all Janus type platinum chalcogenide structures were calculated to be indirect band gap semiconductor. Moreover, the construction of Janus crystals enhances the piezoelectric constants of PtX_2 crystals significantly and adds a new degree of freedom for piezoelectricity in out-of-plane direction. The vdW heterostructures of binary and ternary platinum dichalcogenides were also investigated. It was found that 36 possible vdW heterostructures create ultra-thin heterojunctions of type-I, II, and III. Our study reveal that Janus type platinum dichalcogenide crystals are novel stable materials having wide-range of electronic character.

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TOC Graphic

.

2

PtTe₂ SePtS

Monolayer PtX

PtSe₂

لفالى طفالي

Monolayer Janus XPtY

Chief Parts

800

PtS,

• e₁₁

• e_{31}^{+}

TePtS TePtSe

400

300

200

100

0

000

Piezoelectric Coefficients (pC/m)



- 59
- 60

