Two-Dimensional Disorder in Black Phosphorus and Monochalcogenide Monolayers

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Supporting Information

ABSTRACT: Ridged, orthorhombic two-dimensional atomic crystals with a bulk Pnma structure such as black phosphorus and monochalcogenide monolayers are an exciting and novel material platform for a host of applications. Key to their crystallinity, monolayers of these materials have a 4-fold degenerate structural ground state, and a single energy scale $E_C$ (representing the elastic energy required to switch the longer lattice vector along the x- or y-direction) determines how disordered these monolayers are at finite temperature. Disorder arises when nearest neighboring atoms become gently reassigned as the system is thermally excited beyond a critical temperature $T_c$ that is proportional to $E_C/k_B$. $E_C$ is tunable by chemical composition and it leads to a classification of these materials into two categories: (i) Those for which $E_C \geq k_B T_m$ and (ii) those having $k_B T_m > E_C \geq 0$, where $T_m$ is a given material’s melting temperature. Black phosphorus and SiS monolayers belong to category (i); these materials do not display an intermediate order−disorder transition and melt directly. All other monochalcogenide monolayers with $E_C > 0$ belonging to class (ii) will undergo a two-dimensional transition prior to melting. $E_C/k_B$ is slightly larger than room temperature for GeS and GeSe, and smaller than 300 K for SnS and SnSe monolayers, so that these materials transition near room temperature. The onset of this generic atomistic phenomena is captured by a planar Potts model up to the order−disorder transition. The order−disorder phase transition in two dimensions described here is at the origin of the Cmcm phase being discussed within the context of bulk layered SnSe.

KEYWORDS: 2D atomic materials, black phosphorus, layered monochalcogenides, phase transitions, structural degeneracies, molecular dynamics

Monolayers of layered orthorhombic materials1−18 can become disordered at room temperature.

Graphene19,20 and other 2D atomic materials such as hexagonal boron nitride and transition-metal dichalcogenide monolayers21,22 have a nondegenerate structural ground state that is key to their stability at room temperature. On the other hand, the ridged structure of black phosphorus monolayers and other materials with a similar atomic structure leads to their celebrated anisotropic electron and optical properties.2 At the same time, such unique atomic arrangement has striking consequences for crystalline order23−36 that remain unexplored up to date.

Indeed, the remarkable multifunctionality of ferroelectrics largely originates from the degeneracies of their structural ground state,37 and degeneracies of the structural ground state lead to well-known mechanical instabilities in two-dimensional critical lattices at finite temperature as well.38 If the structural ground state of black phosphorene (BP), black arsenene, and monochalcogenide monolayers (MMs) turned out to be degenerate, this family of two-dimensional materials must necessarily and inevitably display in-plane disorder at finite temperature. Structural degeneracies may even be key to explain the Pnma−Cmcm transition seen in bulk samples that has drawn considerable excitement in the thermoelectric community.10,39 Structural degeneracies of two-dimensional atomic materials may open the door for new physics and may also lead to new and completely unexplored material functionalities that could be controlled with temperature.

This study contains a discussion of degeneracies of the structural ground state of monolayers with a Pnma structure at zero temperature; the determination of an energy $E_C$ that depends on atomic number and sets the energy scale for elastic transitions among degenerate ground states; Car−Parrinello molecular dynamics (MD) calculations at finite temperature (carried out on a code that employs localized orbital basis sets) that permit relating the specific heat and an order parameter to
E_{\text{cr}}; and a coarse-grained in-plane (clock) Potts model with \( q = 4 \) that matches the MD data up to the order–disorder transition at a critical temperature proportional to \( E_{\text{cr}}/k_B \), where \( k_B \) is Boltzmann constant. The two-dimensional (2D) order–disorder transition discovered here must have profound consequences for all material properties, including degradation propensity, and it can be experimentally verified by scanning tunneling microscopy,\(^{10}\) temperature-dependent polarized Raman measurements, specific heat measurements, among other methods.

**Results and Discussion. Structural Degeneracies at Zero Temperature.** The degeneracy of the structural ground state at zero temperature is generic to all monolayers having a Pnma structure, and it is discussed within the context of a GeS monolayer (Figure 1) next.

The first source of degeneracy seen on the elastic energy landscape\(^{10}\) (Figure 1a) stems from the fact that the elastic energy—the total energy at zero temperature as a function of lattice parameters \( a_1 \) and \( a_2 \)—is degenerate upon exchange of lattice parameters \( E(a_1, a_2) = E(a_2, a_1) \). The degeneracy is highlighted with star-like patterns at ground states \( B \) and \( A \). The four degenerate ground states are named \( A_1, A_2, B_1, \) and \( B_2 \) and assigned in-plane arrows that label them uniquely.

The four degenerate structural ground states \( A_1, A_2, B_1, \) and \( B_2 \) on Figure 1b occur when specific triads of atoms \( 1 \rightarrow 0 \rightarrow 2, 3 \rightarrow 0 \rightarrow 4, 3 \rightarrow 0 \rightarrow 1, \) or \( 4 \rightarrow 0 \rightarrow 2 \) create nearest-neighbor bonds, and this in-plane bond structure can be identified with four in-plane arrows: \( \rightarrow, \leftarrow, \downarrow, \uparrow \).\(^{24}\) These atoms form an extra bond to the lower sublayer making the structure 3-fold coordinated, but that lower layer reassigns bonds in a similar manner making a discussion of its rearrangement unnecessary.

It is possible to reassign a nearest-neighbor bond at zero temperature (or to turn arrows by \( \pm \pi/2 \)) by means of the elastic distortion shown by the white dashed curve on Figure 1a that converts ground state \( A_1 (A_2) \) with bonding atoms \( 1 \rightarrow 0 \rightarrow 2 \) (3 → 0 → 4)—onto ground state \( B_1 (B_2) \), where atoms \( 1 \rightarrow 0 \rightarrow 3 \) (4 → 0 → 2) bond.

Indeed, the distortion highlighted by the dashed white curve on Figure 1a includes the saddle point \( C \) where all 4 atoms bond to atom 0, turning the original zigzag structure onto an unstable “checkerboard” structure with an energy cost \( E_C \). When the bond to the lower plane is included, this checkerboard structure is 5-fold coordinated. The structure must loose some bonds as the elastic deformation along the white dashed path continues from point \( C \) to point \( B \), being equally likely to turn into decorations \( B_1 \) or \( B_2 \), which are both 3-fold coordinated. This is how bonds are reassigned at zero temperature. When the lower sublayer (seen in white on Figure 1b) is considered, one sees that two chemical bonds per unit cell are reassigned when structure \( A_1 (A_2) \) turns onto structure \( B_1 (B_2) \).

Direct transitions from decoration \( A_1 (\rightarrow) \) to decoration \( A_2 (\leftarrow) \) (\( B_1 (1) \) onto \( B_2 (1) \)) are more costly as they require reassigning twice as many bonds: \( 1 \rightarrow 0 \rightarrow 2 \rightarrow 3 \rightarrow 0 \rightarrow 4 \) (or \( 3 \rightarrow 0 \rightarrow 1 \rightarrow 4 \rightarrow 0 \rightarrow 2 \)), or a \( \pi \)-arrow rotation on Figure 1b. These transitions can be achieved in two elastic cycles (for instance, from \( \rightarrow \) to \( \uparrow \), back to \( \rightarrow \)). The reassignment of nearest-neighbors is at the core of the 2D disorder to be discussed later on.

**Tuning the Elastic Energy Barrier \( E_C \) with Atomic Number \( Z \).** The average atomic number \( Z \) is defined as follows:

\[
Z = \frac{1}{4} \sum_{i=1}^{4} Z_i \tag{1}
\]

where the sum is over the four atomic elements on a unit cell, each having atomic number \( Z_i \). It will be shown that both \( a_1/a_2 \) and \( E_C \) evolve with \( Z \) now.

The magnitude of \( E_C \) was determined through stringent calculations with the VASP code\(^{41,42}\) whose details are provided as Supporting Information. As indicated previously, Car–Parrinello MD calculations will also be necessary to verify our main claim, and these calculations are prohibitively expensive on any computational code that employs plane-wave sets. For that reason \( E_C \) was also computed with the SIESTA code,\(^{43}\) as that code will permit carrying out MD calculations at the expense of making a choice for the localized basis set in which electronic wave functions are to be expanded. Our choice of basis set, described in the Methods section, is such that the magnitude of the lattice constant for BP agrees reasonably well among these two computational tools.

The values of \( a_1/a_2 \) and \( E_C \) averaged over their magnitude from three different calculations are displayed in Figure 2 and Table 1 (see Methods). Light compounds such as BP or SiS monolayers (\( Z = 15 \)) have the largest values of \( a_1/a_2 \) and \( E_C \). On the other hand, ultrathin Pb-based monochalcogenides (\( Z > 48 \)) have a rock-salt structure so that \( a_1/a_2 = 1 \) and \( E_C = 0 \). All remaining monochalcogenide monolayers (MMs) have values of \( a_1/a_2 \) and \( E_C \) lying somewhere in between, which implies a vast tunability of \( a_1/a_2 \) and \( E_C \) with atomic number.

Bond covalency is gradually sacrificed with increasing atomic number to favor a higher atomistic coordination and a weaker (i.e., metallic) bonding. In previous work, we showed that group-IV two-dimensional materials turn from a 3-fold to a 9-fold-coordinated phase with increasing atomic number.\(^{26}\) In the present case, a 3-fold-coordinated structure evolves toward a 5-fold-coordinated one with increasing \( Z \). Being more specific, \( a_1/a_2 \rightarrow 1 \) decays quite rapidly with \( Z \) and regardless of the numerical approach employed. We fit:
Switch in between Degenerate Ground States for BP and 12 parameters are given in the main text (see Methods). Temperature, and the Elastic Energy Barrier and constants decreases exponentially with the mean atomic number.

(a) The ratio \(a_1/a_2\) among orthogonal in-plane lattice constants decreases exponentially with the mean atomic number \(Z\), and \(a_1/a_2\) decays exponentially with \(Z\) as well. \(E_C/k_B < 300\) K (and \(a_1/a_2 \leq 1.1\)) for \(Z \geq 30\), prompting the question whether 3-fold coordinated GeSe, SnS, and SnSe monolayers are disordered near room temperature. Structures with \(a_1 \approx a_2\) display a 5-fold-coordinated and nondegenerate ground state with \(E_C \approx 0\). Solid lines are fits whose parameters are given in the main text (see Methods).

(b) The ratio \(E_C/k_B\) required to switch in between Degenerate Ground States for BP and 12 MMs with numerical parameters \(d = 37,650\) K and \(c_k = 1/6\) (this trendline is shown as a straight line in Figure 2b).

Experimental values for the melting temperature \(T_m\) of bulk compounds are reported in Table 1 as well. We make an additional point by assuming that the melting temperature of monolayers is relatively close to \(T_m\). Then, \(T_m\) permits a classification of these two-dimensional materials into two groups: (i) those having \(E_C \geq k_B T_m\) and (ii) those where \(k_B T_m > E_C \geq 0\). Black phosphorus and SiS monolayers belong to category (i). Given the error bars in \(E_C\), SiSe appears to be borderline between class (i) and (ii). All other MMs belong to class (ii).

The classification introduced in previous paragraph can be used to draw a direct connection to experiments on BP monolayers: Most theory developed for BP has been carried out under the implicit assumption that its atomistic structure does not drastically change in between 0 K and room temperature, and this is confirmed by experiments. Such agreement appears to counter the statement that materials with a \(Pnma\) structure undergo an order–disorder transition. But its rather large magnitude of \(E_C\)—higher than its melting temperature—prevents this material from thermally exploring its degenerate ground states up until it melts and thus solves the apparent contradiction.

The significance of Equation 3 can hardly be overstated, for it indicates that \(E_C\) is tunable by the choice of compound in Table 1, all the way from 0 K and up to temperatures above \(T_m\). In stark contrast to BP monolayers, some MMs will undergo a 2D order–disorder transition, so that the implicit assumption that structural symmetries obtained at zero temperature remain unchanged at finite temperature does not hold true for many MMs.

Two-Dimensional Disorder at Finite Temperature. So far, elastic transitions among \(q = 4\) degenerate ground states at zero temperature have been studied, and the energy \(E_C(Z)\) required to cycle among these four structures via elastic strain at zero temperature was established. It will now be proven that the generic existence of four ground states with a finite energy barrier \(E_C(Z)\) to switch among these structures leads to two-dimensional disorder on materials belonging to class (ii) by means of a realignment of nearest-neighbor bonds at finite temperature.

Previous assertion will be demonstrated with Car–Parrinello molecular dynamics (MD) calculations performed for 1000 fs at 30, 300, and 1000 K on periodic supercells containing 576 atoms with all unit cells initially set to the \(A_1\) decoration. These calculations permit establishing that materials with \(E_C > k_B T_m\) belonging to category (i) do not show bond reassignment at any of these temperatures, and that materials belonging to category (ii) having \(E_C/k_B < 300\) K do show disorder at room temperature.
Nelson makes a point that relevant thermodynamical phenomena can be described without recourse to full atomistic detail: coarse-grained descriptions with effective parameters extracted from atomistic data increase our intuition of the observed phenomena. Following this philosophy, an atomic bond was drawn if interatomic distances lie within 10% of their value on the structure at 0 K. The total energy equilibrates within 500 fs (Supporting Information), and Figure 3a shows a snapshot at the 1000 fs step for a BP monolayer ($Z = 15$ and $E_C = 5159 \pm 75$ K) on a periodic $12 \times 12$ supercell at 300 K. The vertical zigzag patterns shown by black bonds consistent with a $A_1$ decoration (Figure 1b) that are characteristic of materials with a $Pnma$ structure can clearly be resolved throughout the dynamical evolution. The zigzag pattern remains unchanged throughout the entire MD evolution, and Figure 3a, thus demonstrates that a BP monolayer retains its $Pnma$ structure up to room temperature as it was hypothesized in previous subsection.

To investigate the hypothesis of two-dimensional disorder created from reassignment of nearest-neighbor bonds on MMs qualitatively, we disclose whether the vertical zigzag patterns (characteristic of a material with all unit cells set to the $A_1$ decoration) become altered at finite temperature at two time steps, a task simplified by visualizing the upper sublayer only.

We show in Figure 3b the time evolution of the atomic positions for atoms belonging to the upper sublayer of SiSe at 300 K ($Z = 24$ and $E_C = 730 \pm 446$ K). As expected from its large value of $E_C$, the vertical zigzag pattern can be seen on the figure at all times (the pattern is shown at 500 fs in orange, and 950 fs in black solid lines). The lack of nearest neighbors being
Tables 2. Evolution of Average Lattice Parameters $\langle a_1 \rangle$, $\langle a_2 \rangle$, and Their Ratio versus Temperature ($T$) for $12 \times 12$ Supercells of BP and Eight MM

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$\langle a_1 \rangle$ (Å)</th>
<th>$\langle a_2 \rangle$ (Å)</th>
<th>$\langle a_1 \rangle/\langle a_2 \rangle$</th>
<th>$\langle a_1 \rangle$ (Å)</th>
<th>$\langle a_2 \rangle$ (Å)</th>
<th>$\langle a_1 \rangle/\langle a_2 \rangle$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>4.628 ± 0.000</td>
<td>3.364 ± 0.000</td>
<td>1.375 ± 0.000</td>
<td>5.039 ± 0.000</td>
<td>3.728 ± 0.000</td>
<td>1.352 ± 0.000</td>
</tr>
<tr>
<td>30</td>
<td>4.625 ± 0.050</td>
<td>3.364 ± 0.033</td>
<td>1.375 ± 0.028</td>
<td>5.029 ± 0.058</td>
<td>3.733 ± 0.077</td>
<td>1.347 ± 0.042</td>
</tr>
<tr>
<td>300</td>
<td>4.628 ± 0.181</td>
<td>3.368 ± 0.103</td>
<td>1.374 ± 0.096</td>
<td>5.054 ± 0.187</td>
<td>3.748 ± 0.272</td>
<td>1.348 ± 0.140</td>
</tr>
<tr>
<td>1000</td>
<td>4.632 ± 0.388</td>
<td>3.384 ± 0.207</td>
<td>1.369 ± 0.198</td>
<td>5.090 ± 1.298</td>
<td>3.861 ± 1.302</td>
<td>1.318 ± 0.780</td>
</tr>
</tbody>
</table>

Although illustrative of the atomistic phenomena at play, it is possible to go beyond the visual evidence provided in Figures 3 and 4 in arguing for the two-dimensional transition, and in Table 2 we infer whether the two-dimensional order–disorder transition has occurred from the ratio of the average lattice constants $\langle a_1 \rangle/\langle a_2 \rangle$ on $12 \times 12$ supercells at finite temperature (see Methods).

As shown in Figure 3c, the onset of the transition is dictated by reassignment of nearest neighbors. Reassignment occurs as the atomic structure explores the four degenerate ground states displayed in Figure 1b once temperature reaches a magnitude similar to $E_C/k_B$. Reassignment leads to the macroscopic increase (decrease) of the average local lattice parameter along the vertical (horizontal) direction (see Figure 1b) as local strain is released, and hence onto a macroscopic structure in which $\langle a_1 \rangle \approx \langle a_2 \rangle$.

BP and SiSe do preserve the magnitude of the ratio $\langle a_1 \rangle/\langle a_2 \rangle$ to a large extent, which is consistent with their values of $E_C$ equal to 5519 ± 75 K and 730 ± 221 K, respectively (Table 1). As seen qualitatively on Figures 3a and b, these compounds do preserve their original two-dimensional $Pnma$ structure until they melt. On the other side of the energy scale set by $E_C$, PbS has $\langle a_1 \rangle/\langle a_2 \rangle = 1$, which is consistent with its magnitude of $E_C$ = 0 K. All other materials listed in Table 2 are predicted to undergo a 2D order–disorder transition before melting.

Indeed, GeS displays a drastic decrease of $\langle a_1 \rangle/\langle a_2 \rangle$ in between 300 and 1000 K (its magnitude drops from 1.156 ± 0.106 down to 1.048 ± 0.541). This significant drop in between these two temperatures is consistent with a transition temperature of the order of $E_C = 653 ± 221$ K displayed in Table 1. Analogously, GeSe has a sharp decrease on $\langle a_1 \rangle/\langle a_2 \rangle$, going from 1.084 ± 0.116 at 300 K, down to 1.016 ± 0.541 at 1000 K. This also means that a two-dimensional order–
disorder transition is occurring roughly after 300 K. Table 1 predicts a transition temperature close to 300 K (E_C = 220 ± 76 K). We will be able to determine the exact transition temperature for GeS and GeSe later on.

Additionally, SnS has E_C = 63 ± 0 K for SnS, which implies that a significant drop on \( \langle a_1 \rangle/\langle a_2 \rangle \) must occur in between 30 and 300 K. Accordingly, Table 2 points to a decrease from 1.041 ± 0.021 down to 1.003 ± 0.096 in between those temperatures.

According to Table 1, GeTe and SnSe should transition at temperatures in between 30 and 300 K. Both compounds do show a decrease of \( \langle a_1 \rangle/\langle a_2 \rangle \) in between 30 and 300 K on the second significant digit, but that decrease is not as drastic as the one registered on the other compounds. Each calculation leading to a data point in Table 2 consumed about one month of uninterrupted computing, and it appears as if these two compounds may still require additional MD steps to reach a smaller ratio. As far as we know, the MD tool we employ does not offer a numerically sound way to restart a MD calculation. Nevertheless, degeneracies of the ground state lead to mechanical instability at finite temperature,38 and we cannot think of a physical mechanism that will alter the assumption that GeTe and SnSe will continue to reduce their ratio \( \langle a_1 \rangle/\langle a_2 \rangle \) on MD runs performed over longer periods of time. The Potts model, to be introduced later on, will also help us in bringing all numerical results onto a coarse model that describes all the phenomena observed in our MD calculations.

SnTe presents a different kind of numerical challenges. This material has a ratio of \( \langle a_1 \rangle/\langle a_2 \rangle = 1.02 \) at 0 K and a barrier E_C roughly larger than 1 meV. E_C is (roughly) the energy difference per unit cell among the ordered and the disordered phases one is attempting to resolve. This numerical consideration makes it increasingly challenging to do better on this material: its magnitude of E_C is minuscule in comparison with the other materials listed in Table 1.

A final physical consideration must be added to the discussion of SnS, SnSe, SnTe, and PbS on Table 2: lattice constants lose their meaning on a molten (i.e., noncrystalline) phase, so the increase on \( \langle a_1 \rangle/\langle a_2 \rangle \) at 1000 K with respect to their magnitude reported at 300 K on these compounds should not be given a heavy weight.

Table 2 continues to build the evidence toward a generic 2D order−disorder transition, and we next report the transition temperature \( T_c \) for GeS and GeSe through a study of the evolution of energetics and order parameters with an increased temperature resolution.
Energetics and Order Parameter as a Function of Temperature. In Figure 5a and b we address the thermal evolution of the energy and the order parameter for GeS and GeSe with increased resolution. To proceed with celerity, these MD calculations were performed on periodic 8 × 8 supercells. The total energy, averaged from 500 to 1000 fs at a given temperature is labeled $\langle E(T) \rangle$, and it has kinetic and configurational (i.e., potential) energy contributions. According to the equipartition theorem, the kinetic energy is proportional to temperature, with $c$ the proportionality constant. This way, the configurational energy $\langle U(T) \rangle$ displayed for GeS and GeSe in Figure 5a and b is $\langle U(T) \rangle = (E(T)) - cT$. The similar trends on $\langle U(T) \rangle$ and its thermal derivative obtained for two different MMs provides yet additional proof of the generality of the two-dimensional order-disorder transition. In a manner consistent with Figure 3, atomistic trajectories from MD calculations are given in Figure 5d for GeS and GeSe at increasing temperatures. Incipient reassignments of nearest neighbors at the onset of the order-disorder transition are shown as well.

Phase transitions lead to drastic changes in the specific heat $C_p \equiv d(E(T))/dT = d(U(T))/dT + c$ at zero pressure. $\langle U(T) \rangle$ is a monotonically increasing function of temperature, and it has two marked changes of slope that lead to two peaks on the finite-difference temperature derivative $\Delta U(T)/\Delta T$ in Figure 5a and b. These two peaks correspond to phase transitions from a crystalline onto a disordered two-dimensional phase, and from the disordered two-dimensional phase onto a molten phase, respectively. The focus of this manuscript is on the 2D order-disorder transition. According to Figure 5a and b, the transition temperature $T_c$ is 510 K for GeS (Z = 24), and at 382 K for GeSe (Z = 33). There is a proportionality among $T_c$ obtained from MD calculations (red vertical lines in Figure 5) and $E_c/K_b$ from Table 1 (shown in a green vertical lines in Figure 5a and b), so that Car-Parrinello MD results do validate the basic intuition drawn from Figures 1 and 2.

The order parameter $\langle a_i \rangle/\langle a_j \rangle$ for GeS and GeSe transitions onto a value close to unity at $T_c$, a fact that can be better appreciated in the numerical derivative plots $\Delta \langle \langle a_i \rangle/\langle a_j \rangle \rangle/\Delta T$ shown as the lowermost subplots in Figure 5a and b. Figure 5 reproduces the magnitudes of this ratio reported in Table 2 at 0, 30, 300 and 1000 K on larger supercells. Figure 5a and b continue to provide further numerical validation to the hypotheses set forth in discussing Figures 1 and 2 and continue to provide further numerical validation to the hypotheses set forth in discussing Figures 1 and 2 and demonstrate in an even more convincingly manner the unavoidable disordered nature of MMs at finite temperature.

The two-dimensional order-disorder transition is quite relevant for practical room-temperature applications based on MMs, and a model that describes it is provided next.

2D Order–Disorder Transition and Potts Model. Starting with a crystalline structure in which all unit cells have an $A_1$ (↔) decoration, a local energy penalty equal to $J = E_{C_1}$ is given to a neighboring unit cell that reassigns two bonds in acquiring the $B_1$ (↑) or the $B_2$ (↓) decoration. A direct transition from a $A_1$ (↔) to a $A_3$ (↔) decoration requires reassigning four bonds and is thus given an energy penalty equal to 2J. This prescription leads to a 2D (clock) Potts model with $q = 4$ states whose dynamical behavior is characterized by an in-plane spin Hamiltonian on a square lattice with the following nearest-neighbor coupling:

$$\hat{H} = -J \sum_{\langle ij \rangle} \cos(\theta_i - \theta_j)$$

In previous equation, $\theta_i$ and $\theta_j$ can take any of the four ($q = 4$) values 0 (↔), $\pi/2$ (↑), $\pi$ (↓), or $3\pi/2$ (↓). At low temperatures, the transition with energy penalty $J$ becomes dominant, and the system behaves as if there was just a single coupling. Figure 5c displays the predictions from the model, which reproduces the temperature dependence of the configurational energy $\langle U \rangle$ and $\langle a_i \rangle/\langle a_j \rangle$ from Car-Parrinello MD, a remarkable agreement in light of the simplicity of the model and the complexity of the ab initio calculations: Potts model provides an appealingly simple physical picture for the 2D order–disorder transition.

It is impossible to sample larger cells with the ab initio method, so Potts model was employed to increase sampling statistics which leads to domain sizes shown in Figure 6 on supercells containing 60 × 60 unit cells, corresponding to an area of 30 × 30 nm². At $T = 1.3J/k_B$, it is highly unlikely to see domains with arrows pointing in opposite direction along the same direction due to the higher energy cost required to create such configuration, and intriguing "vortex" configurations can be observed as well.

Structural disorder implies the existence of electronic disorder. Indeed, the electronic wave functions below and above the Fermi energy seen in Figure 7 for disordered 2D SnSe exhibit drastic changes at room temperature when contrasted with their appearance on a crystalline structure at 0 K.

Valleytronics, piezoelectricity, and shift photovoltaics applications have been predicted for fully crystalline phases; the results provided here thus constrain the choice of materials for these applications near room temperature. At a fundamental level, it will be interesting to explore how these predictions become altered in the presence of 2D disorder, something that is the subject of forthcoming work.

Conclusion. In summary, the ridged structure of black phosphorus and of layered monochalcogenides leads to 2D disorder as in-plane nearest-neighbors become reassigned at finite temperature. A second transition from this disordered 2D lattice onto a gas phase occurs at a larger temperature, with the remarkable exception of a BP monolayer which has no visible

Figure 6. Potts model is employed to ascertain domain sizes at experimentally relevant scales. A vortex structure seen on the disordered state has been highlighted as a zoom-in, and unrelaxed atomistic models are attached to highlight the inherent atomic disorder.
temperature and zero pressure were carried out with the VASP41,42 (PBE, Method 1) and SIESTA 43 codes (PBE, bound solids. constants and bulk moduli of layered materials and tightly ref 51, the BH pseudopotential produces accurate lattice of the chemical elements employed in this work.52 According to deployment of pseudopotentials for the SIESTA code for most Method 2; and BH, Method 3). This required a dedicated Berland-Per Hyldgaard (BH) 51 exchange-correlation func-
tionals were carried out on unit cells containing four atoms through the 2D order parameter. This model describes the full-scale energetics already presents here call to investigate the properties recently predicted on crystalline samples (valleytronics, shift-current photovoltaics, and piezoelectronics)15–18 as 2D disorder sets in. Having $T_c = 510$ K, GeS monolayers appear as the proper crystalline material platform—already available in the bulk form—for the pursuit of MM-based applications that require crystallinity of the 2D lattice at room temperature. These results apply to freestanding monolayers, and it may be possible to raise the magnitude of the transition temperature $T_c$, through thermal coupling to a substrate or in the bulk.

The predictions contained here illustrate classic results from the theory of phase transitions and disorder in two-dimensions at work in this novel family of 2D atomic materials. **Methods.** Density-functional theory calculations with the Perdew–Burke–Ernzerhof (PBE)30 and the van der Waals Berland-Per Hyldgaard (BH)51 exchange-correlation functionals were carried out on unit cells containing four atoms to determine the elastic energy barrier $E_C$ in Table 1, with the VASP$^{31,42}$ (PBE, Method 1) and SIESTA$^{43}$ codes (PBE, Method 2; and BH, Method 3). This required a dedicated deployment of pseudopotentials for the SIESTA code for most of the chemical elements employed in this work.32 According to ref 51, the BH pseudopotential produces accurate lattice constants and bulk moduli of layered materials and tightly bound solids.

All calculations on single unit cells leading to $E_C$ on Table 1 were performed with a $18 \times 18 \times 1$ k-point sampling. SIESTA calculations had a large mesh cutoff (used for computing the potential energy on a real-space grid) of 300 Ry. In addition, the electronic density was converged down to $5 \times 10^{-6}$.

Car–Parrinello MD calculations with Method 3 at constant temperature and zero pressure were carried out with the SIESTA code at temperatures of 30, 300, and 1000 K for 1000 steps (with a 1 fs time step) on periodic supercells containing 576 atoms. These calculations employed a single k-point, a reduced mesh cutoff of 200 Ry, and a reduced tolerance on the electronic cycle of $10^{-4}$, and require about a full month to end for a given temperature, running on 128 processors.

A more detailed analysis of the total energy as a function of temperature for GeS and GeSe monolayers was performed on smaller periodic $8 \times 8$ supercells containing 256 atoms, still employing a single k-point, a reduced mesh cutoff of 200 Ry, and a reduced tolerance on the electronic cycle of $10^{-4}$. Calculation of an individual data point on Figures $5(a-b)$ accrues 2 weeks running on 128 processors.

The average lattice constants $\langle a_1 \rangle$ and $\langle a_2 \rangle$ were obtained for nine compounds from the distances among each of the four atoms on a given unit cell with respect to the position of said basis atoms in neighboring unit cells once thermal equilibrium was reached, leading to an average over $12 \times 12 \times 500$ individual values from SIESTA calculations with BH pseudopotentials that is reported up to three significant digits in Table 2. By definition $\langle a_1 \rangle = a_1$ and $\langle a_2 \rangle = a_2$ on the crystalline structures at 0 K, whose values were then obtained from single unit cell calculations. Values of $a_1$ and $a_2$ at 0 K are consistent with these shown in Table 1, which were in turn obtained as averages at zero temperature over the three different computational methods. $\langle a_1 \rangle$ and $\langle a_2 \rangle$ are also indicators of the numerical precision being achieved in our MD calculations.

All SIESTA calculations reported on this paper were performed using standard basis sets with an energy shift of 0.01 eV; this choice was made because that the lattice constants for BP agree among SIESTA and VASP reasonably well: (4.635, 3.302), (4.625, 3.345), and (4.627, 3.365) Å from VASP with PBE pseudopotentials, SIESTA with PBE pseudopotentials, and SIESTA with Berland–Per Hyldgaard pseudopotentials, respectively.

Monte Carlo calculations of the configurational energy and the order parameter as predicted from the Potts model were carried on supercells of increasing size with an in-house algorithm.

Figure 7. Structural disorder creates electronic disorder: The states (a) above and (b) above the Fermi level for SnSe at 0 K. State (c) below and (d) above the Fermi level for SnSe corresponding to the snapshot at 300 K shown in subplot (e).
MD movies for GeS at 30, 300, and 1000 K (ZIP)
Details of the calculation of $E_C$ for BP and a demonstration of thermal equilibration achieved after 500 fs (PDF)

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**Notes**
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