

Framework for identifying non-van der Waals two-dimensional materials

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Two-dimensional (2D) materials are categorized into van der Waals (vdW) and non-vdW types. However, no relevant descriptors have been proposed for identifying non-vdW 2D materials. Here, we identify the non-vdW 2D materials by calculating the thickness dependence of total energy of thin films truncated from surfaces. The non-vdW 2D materials exhibit a deviation from the law of finite-thickness excess energy (FTEE) inverse to the number of layers in the monolayer limit. This framework is applied to single-component systems, which successfully identifies non-vdW 2D materials including silicene and goldene that are overlooked in the dimensional analysis of the parent crystals. The anomalies of FTEE at specific thickness are found in Pb and Ga thin films, supporting the creation of plumbene and gallene. The framework is also applied to multicomponent systems with cubic and hexagonal symmetry (zincblende- and fluorite-types and tungsten carbide- and PtSbBa-types, respectively). Among them, several non-vdW 2D materials are identified to be dynamically stable. Structural transformation from hexagonal to almost tetragonal symmetry is observed in metallic TiS and ZrTe thin films. Our framework is useful for identifying non-vdW 2D materials.

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I. INTRODUCTION

Since the successful exfoliation of graphene from graphite [1], other two-dimensional (2D) materials that exhibit interesting properties have been explored. Several geometric approaches have been used to identify a few thousands of layered materials among several material databases. As the pioneering work, Lebegue *et al.* identified about 100 van der Waals (vdW) materials that have a large interlayer distance along the *c* axis [2]. Ashton *et al.* developed a topology-scaling algorithm determining the dimensionality of the parent materials and identified 800 candidate materials in the Materials Project (MP) database [3]. Mounet *et al.* also identified about 1000 vdW materials using the Inorganic Crystal Structure Database (ICSD) and the Crystallographic Open Database (COD) [4]. Given the 2D structure prototypes, the element substitutions are employed to expand the family of 2D materials systematically, which led to the development of the Computational 2D materials Database (C2DB) [5]. A combinatorial creation of candidate monolayers with a symmetry-based approach predicted 6500 compounds [6]. More recently, synthetic 2D structures (e.g., MoSi₂N₄ [7]) having no 3D counterparts have been extensively investigated. Machine learning algorithms have been used to generate 2D structures that are different from the known prototypes [8].

Although their parent materials are classified into non-vdW (nonlayered) materials, several 2D materials have been synthesized experimentally, such as Xenes [9,10] including

silicene [11], plumbene [12], and goldene [13], and binary and ternary 2D compounds [14–16]. This means that more than tens of thousands of non-vdW 2D candidate materials have been overlooked in constructing 2D materials database. Predicting 2D materials consists of energy evaluation, phonon calculations, and finite-temperature molecular dynamics (MD) simulation [17]. Non-vdW 2D materials have been explored by truncating a monolayer from a specific surface of the 3D counterparts, and then their exfoliation, cohesive, and formation energies and dynamical stabilities at zero and finite temperatures have been investigated [18–25]. Experimentally synthesized 2D materials should satisfy the stability criteria. However, it is still under debate whether *any* 2D materials satisfying the criteria can be synthesized experimentally because many predicted 2D materials have not been synthesized yet. It will be interesting to explore a different approach to predict 2D materials specific to non-vdW systems. In this paper, we provide an approach for identifying non-vdW 2D materials based on the energy variation of thin films in the monolayer limit.

So far, first-principles high-throughput calculations, as well as data mining, have provided many vdW 2D materials having interesting properties such as magnetism [26], superconductivity [27], and heavy-fermion state [28]. The 2D semiconductors have also been explored for next-generation electronics and optoelectronics [29,30]. The present work provides how to search non-vdW 2D candidate materials, which will provide a platform to pave the way for the physics and their interesting applications.

II. METHODS

A. Basic idea

Let us consider the carbon, silicon, and germanium crystals in the diamond structure and truncate thin films from the

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(111) surface. If the film thickness is decreased, the electronic character in the occupied states changes from sp^3 to sp^2 and the thin films are transformed into multilayered graphene, silicene, and germanene at a specific thickness. This is a hypothetical creation of 2D materials from non-vdW materials. Therefore, it is important to study the energy variation of thin films for exploring non-vdW 2D materials, which may reflect such a 3D-2D transformation.

For a quantitative discussion, we define the finite-thickness excess energy (FTEE) as $\Delta E_\alpha(N) = E_\alpha(N)/N - E_{\text{bulk}}$, where $E_\alpha(N)$ and E_{bulk} are the total energy per unit cell of N -layer thin film and bulk, respectively. The subscript α is the index specifying the surface cut, e.g., Si(111). The FTEE includes the excess energy due to the surface and finite-size effects, which becomes negligible in the bulk limit.

Theorem. $\Delta E_\alpha \propto N^{-1}$ for large N .

Proof. We assume that the surface relaxation occurs only at the top and bottom layers. The N layer thin film consists of $(N - 2)$ bulk layers and two surface layers, where the chemical bonds on the surface are different from those in the bulk. If N is large enough to ignore the interaction between the upper and bottom surfaces, we can express the total energy of this system as $E_\alpha(N) \simeq (N - 2)E_{\text{bulk}} + 2E_{\text{surf}}^\alpha$, where E_{surf}^α is the energy of the α surface layer for large N . Thus, one obtains $\Delta E_\alpha(N) = E_0/N$, where the factor $E_0 = 2(E_{\text{surf}}^\alpha - E_{\text{bulk}})$ is independent of N .

On the contrary, $\Delta E_\alpha(N = 1) = E_{\text{mono}}^\alpha - E_{\text{bulk}}$ with E_{mono}^α being the total energy of a monolayer having the α surface. If E_{mono}^α is equal to $-E_{\text{bulk}} + 2E_{\text{surf}}^\alpha$, the N^{-1} law exactly holds. If a parent non-vdW material can take the 2D form as a metastable structure, E_{mono}^α is significantly lowered. In this case, one will observe a breakdown of the N^{-1} law. In this paper, we propose that “a downward deviation from the N^{-1} scaling of ΔE_α at $N = 1$ ” is a good indicator to identify non-vdW 2D materials.

When the N^{-1} law holds, one obtains $\ln \Delta E_\alpha(N) = -\ln N + C$ with a constant C . To identify the deviation from the N^{-1} law, we calculate the following quantity:

$$p_\alpha(N) = \frac{d \ln \Delta E_\alpha}{d \ln N} \simeq \frac{\ln \Delta E_\alpha(N + 1) - \ln \Delta E_\alpha(N)}{\ln(N + 1) - \ln N}. \quad (1)$$

If $p_\alpha(N) = -1$, the N -layer thin film exactly follows the N^{-1} law. The inequality of $p_\alpha(1) > -1$ indicates a downward deviation from the N^{-1} law.

B. Computational details

We used Quantum Espresso (QE) [31] to perform density-functional theory (DFT) calculations and used the Perdew-Burke-Ernzerhof (PBE) functional [32] in the pslibrary1.0.0 [33]. The $4f$ states of lanthanides were treated as the core states. As we study thin films with a few layers, we included the vdW correction within Grimme’s DFT-D3 level [34]. In each compound, the energy cutoff for wavefunction E_{cut} was set to be the highest E_j plus 10 Ry, where E_j is the suggested value for atom j , and the energy cutoff for charge density was set to be $10E_{\text{cut}}$. The k -point distance of $\Delta k \leq 0.15 \text{ \AA}^{-1}$ was assumed along the in-plane axes, and the vacuum layer was set to be $20 \text{ \AA}$ to avoid the spurious interactions between periodic images. The smearing parameter of 0.015 Ry

was used [35]. The total energy in the self-consistent field (scf) calculations was converged within 10^{-6} Ry , and the total energy and forces in the geometry relaxation were converged within 10^{-4} Ry and 10^{-3} a.u. , respectively. Spin-polarized calculations were performed and ferromagnetic states were assumed in the initial condition except for bcc Cr. Spin-orbit coupling (SOC) was included for Po. In the electron density-of-states (DOS) calculations for Ga, TiS, and ZrTe, we assumed $\Delta k \leq 0.075 \text{ \AA}^{-1}$ in the non-scf calculations and treated the delta function as a Gaussian function with a broadening of 0.1 eV .

We performed phonon calculations within density-functional perturbation theory (DFPT) [36] implemented in QE [31]. Before calculating phonon dispersions, we reoptimized the crystal structures with high accuracy: the total energy in the scf calculations was converged within 10^{-12} Ry , and the total energy and forces in the geometry relaxation were converged within 10^{-5} Ry and 10^{-4} a.u. , respectively. As the DFPT calculations with DFT-D3 are not implemented in QE, the vdW correction within DFT-D2 [37] was assumed. The convergence parameter (tr2_ph) in the force constant calculations was set to be 10^{-14} a.u. The q grids used were $3 \times 3 \times 1$ for TiS and WC, $4 \times 4 \times 1$ for ZrTe and NbN, and $6 \times 6 \times 1$ q for YHSe and HoHSe thin films. The acoustic sum rule was imposed by considering the Born-Huang invariance and the Huang conditions in the lattice potential [38]. In addition, first-principles MD simulations, switched back to DFT-D3, were performed by using QE [31]. The supercell sizes used were $6 \times 6 \times 1$ for SrCl_2 , CdF_2 , YHSe, and HoHSe (108 atoms) and $5 \times 5 \times 1$ for TiS and ZrTe thin films (100 atoms). The volume of the unit cell was fixed, the ionic temperature was kept at 300 K by adapting the velocity scaling, and the Newton’s equation was integrated by using the Verlet algorithm with a time step of 1 fs .

C. Models of thin films

Throughout the work, we visualized crystal structures by using VESTA [39], constructed models of thin films by using the surface module implemented in atomic simulation environment (ASE) [40], and searched the primitive cell for each model by using spglib [41].

1. Single-component systems

For single-component systems, we study metallic elements from Li to Po and nonmetallic elements including C, Si, Ge, and As. We used ASE [40] to obtain the experimental lattice constants and crystal structure type for each element. Most of the metallic elements have either face-centered cubic (fcc), body-centered cubic (bcc), or hexagonal close-packed (hcp) structures except for Ga (orthorhombic), In (body-centered tetragonal, bct), α -Sn (diamond), Sb (rhombohedral), Bi (rhombohedral), and Po (simple cubic). In the present work, Mn (cubic), Pm, Sm (rhombohedral), and Hg (rhombohedral) are not studied because of their complex or unknown geometry. C, Si, and Ge have diamond structure and As has rhombohedral structure. We considered thin films up to $N = 8$.

To construct N -layer thin films, we need to determine the surface index α for each element. Since 3D metals have

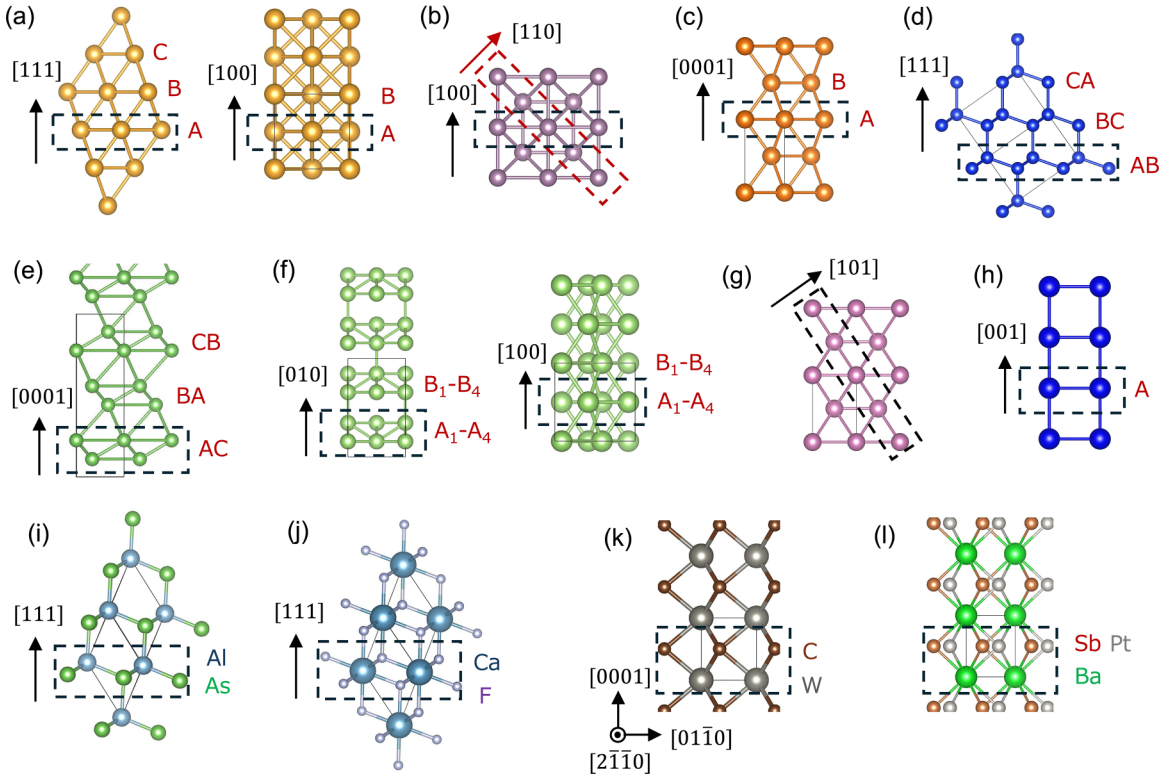


FIG. 1. Crystal structure of non-vdW 3D compounds. (a) fcc, (b) bcc, (c) hcp, (d) diamond, (e) As (hexagonal), (f) Ga (orthorhombic), (g), In (bct), (h) Po (simple cubic), (i) AlAs (zincblende), (j) CaF_2 , (k) WC, and (l) PtSbBa-type structures. The dashed line indicates $N = 1$ thin film that corresponds to (a) hexagonal and square, (b) square and monoclinic, (c) hexagonal, (d) buckled honeycomb, (e) buckled honeycomb, (f) rectangular, (g) monoclinic, (h) square, (i) buckled honeycomb, (j) 1T, (k) buckled honeycomb, and (l) 1T Janus structures (assuming that Sb atoms move along the $[0001]$ direction). See Table I for details.

close-packed structure, we truncate thin films from nearly close packed surfaces of fcc, bcc, and hcp metals, i.e., the (111) and (100) surfaces for fcc metals, the (110) and (100) surfaces for bcc metals, and the (0001) surface for hcp metals. The N layer thin films derived from fcc (111) and hcp (0001) , fcc (100) and bcc (100) , and bcc (110) surfaces have hexagonal, tetragonal, and monoclinic (or centered rectangular) symmetry, respectively, and include N atoms in the unit cell. Each layer has one atom and is alternately stacked along the surface-normal direction. See Figs. 1(a)–1(c) for the crystal structures and Table I for the stacking pattern.

It is known that Si, Ge, Sn, As, Sb, and Bi have buckled honeycomb structure in the monolayer limit. To obtain such structures, we truncate thin films from the (111) surface of Si, Ge, and Sn in the diamond structure and the (0001) surface of As, Sb, and Bi in the hexagonal structure [Figs. 1(d) and 1(e)]. By using ASE [40] and spglib [41], we obtain N -layer thin films including $2N$ atoms per cell, where each buckled honeycomb layer has two atoms. The stacking sequence is different between diamond and rhombohedral (hexagonal) systems, as listed in Table I.

Ga has the orthorhombic cell including eight atoms in the cell. Following the work by Kochat *et al.* [42], we truncate thin films from the (010) and (100) surfaces, as shown in Fig. 1(f). The N -layer thin films have $4N$ atoms in the cell (see Table I for details). We next consider thin films of bct In. Bauernfeind *et al.* reported the formation of In monolayer in the hexagonal structure [43]. We thus truncate N -layer thin

films from the (101) surface having $2N$ atoms per cell [see Fig. 1(g) and Table I for details]. The ratio of lattice constants is $a/b \simeq 1.82$, which is nearly equal to $\sqrt{3} \simeq 1.73$ for the hexagonal structure. Finally, we consider thin films derived from Po (001) , as shown in Fig. 1(h). The square lattice is stacked in N -layer thin films including N atoms in the cell.

2. Multicomponent systems

Mounet *et al.* predicted that no vdW 2D materials are present in the cubic crystal system based on high-throughput DFT calculations [4]. To investigate what cubic crystals become non-vdW 2D materials, we apply our approach to zinc-blende-type (AB) and fluorite-type (AB_2 or A_2B) systems. This is because many of these have been predicted to serve as non-vdW 2D materials based on formation energy and phonon calculations [19,24].

For the zincblende-type structure, we considered III-V materials AB ($A = \text{Al, Ga, and In}$; $B = \text{P, As, and Sb}$), i.e., nine systems in total. These have the diamond structure, while the nearest-neighbor atoms are different species. The AB thin films have the same stacking sequence as the diamond Si (111) listed in Table I, e.g., $N = 1$ thin film corresponds to the buckled honeycomb structure and A and B atoms are located at A and B sites, respectively [see Fig. 1(i)].

We considered AB_2 and A_2B fluorite-type semiconductors (A indicates metallic elements and B indicates chalcogen and halogen atoms) [24]. We studied 21 systems including

TABLE I. 2D Bravais lattices, stacking sequences, and crystal coordinates of layers in thin films derived from various surfaces of representative elements. Each layer is separated by “|” in the stacking sequence. Each layer is projected onto $z = 0$ plane, so that the z -coordinate is omitted. The exceptions are the thin films truncated from DIA(111) and HEX(0001). These are regarded as ABC-stacked buckled honeycomb layers, and each layer consists of two hexagonal planes with different orders ($AB \rightarrow BC \rightarrow CA$ or $AC \rightarrow BA \rightarrow CB$). The sum of two pairs among z_A , z_B , and z_C is subject to zero in our notation (e.g., $z_A = -z_B$ and the thickness of $2|z_A|$ for AB layer). The thin films derived from Ga(010) and Ga(100) have $a/b = 1.03$ and $a/b = 1.67$, respectively, and each layer consists of four atoms. For Ga(010), $\delta = 0.0846$ and each layer is puckered. For Ga(100), $\delta_x = 0.1557$ and $\delta_y = 0.0846$. $\theta(x)$ is the Heaviside step function having unity for $x \geq 0$ and zero for $x < 0$. The monoclinic lattice derived from BCC(110) and BCT(101) has $\gamma \simeq 54.7^\circ$ and 61.2° , respectively, with keeping $a = b$. FCC, face-centered cubic; BCC, body-centered cubic; HCP, hexagonal close-packed; DIA, diamond; HEX, hexagonal; ORC, orthorhombic; BCT, body-centered tetragonal; CUB, cubic; SQ, square; MCL, monoclinic; REC, rectangular.

Element	Plane	2D lattice	Stacking	Crystal coordinates
Cu	FCC(111)	HEX	A B C	A(0, 0), B(1/3, 2/3), C(2/3, 1/3)
Cu	FCC(100)	SQ	A B	A(0, 0), B(1/2, 1/2)
W	BCC(100)	SQ	A B	A(0, 0), B(1/2, 1/2)
W	BCC(110)	MCL	A B	A(0, 0), B(1/2, 1/2)
Mg	HCP(0001)	HEX	A B	A(0, 0), B(1/3, 2/3)
Si	DIA(111)	HEX	AB BC CA	A(0, 0, z_A), B(1/3, 2/3, z_B), C(2/3, 1/3, z_C)
As	HEX(0001)	HEX	AC BA CB	A(0, 0, z_A), B(1/3, 2/3, z_B), C(2/3, 1/3, z_C)
Ga	ORC(010)	REC	A ₁ -A ₄ B ₁ -B ₄	A ₁ (1/2 + δ , 1/2, - z), A ₂ (1 - δ , 0, - z), A ₃ (δ , 1/2, z), A ₄ (1/2 - δ , 0, z) B _i ($x(A_i)$, $y(A_i) + 1/2 - \theta(y(A_i) + 1/2 - 1)$, $z(A_i)$) A ₁ (1/2 - δ_x , 1/2 - δ_y), A ₂ (δ_x , 1 - δ_y), A ₃ (1/2 + δ_x , 1/2 + δ_y), A ₄ (1 - δ_x , δ_y) B _i ($x(A_i) + 1/2 - \theta(x(A_i) + 1/2 - 1)$, $y(A_i)$)
Ga	ORC(100)	REC	A ₁ -A ₄ B ₁ -B ₄	
In	BCT(101)	MCL	A B	A(0, 0), B(1/2, 1/2)
Po	CUB(001)	SQ	A	A(0, 0)

five fluorides (AF_2 with $A = \text{Ca, Sr, Ba, Cd, and Pb}$), two chlorides (ACl_2 with $A = \text{Sr and Ba}$), and 14 chalcogenides (A_2B with $A = \text{Li, Na, K, and Rb}$; $B = \text{O, S, Se, and Te}$) except for K_2O and Rb_2O . A atoms form the fcc structure and B atoms occupy the tetrahedral sites for AB_2 , and vice versa for A_2B . The thin films derived from the (111) surface consist of the ABC stacking of hexagonal $A(B)$ monolayers sandwiched by $B(A)$ atoms. The thin films at $N = 1$ correspond to the 1T structure [see Fig. 1(j)].

In the present work, we calculated the total energy of these films derived from their (111) surfaces up to $N = 8$, where $2N$ and $3N$ atoms are included in the unit cell for zincblende-type and fluorite-type systems, respectively. The crystal structures of the bulk were extracted from the MP database [44] by using pymatgen [45].

It should be noted that PbF_2 monolayer derived from the (110) surface is more stable than that from the (111) surface, and exhibits negative Poisson's ratio, where the thickness increases when laterally stretched [24]. We also investigated PbF_2 thin films derived from the (110) surface up to $N = 5$ with $6N$ atoms in the unit cell.

Many vdW 2D materials belonging to the hexagonal crystal system have been studied for twenty years. To explore non-vdW 2D materials with the hexagonal symmetry, we investigated the materials with the space group of $P\bar{6}m2$ and extracted binary and ternary systems with ICSD numbers from the MP database (on March 26th, 2025) [44] by using pymatgen [45]. The crystals containing noble gas and actinide atoms are excluded, the energy above the hull is assumed to be less than 0.01 eV/atom, and the number of sites is set to be two or three. We then obtained 28 materials including 9 tungsten carbide-type (WC, B_h) and 19 PtSbBa-type structures

[46]. The WC-type structure consists of the hexagonal W and C layers that are stacked alternately along the [0001] direction [see Fig. 1(k)]. The stacking sequence is the same as that of the hcp structure. The PtSbBa-type structure consists of the hexagonal Ba and PtSb layers, where PtSb forms the BN-type structure [see Fig. 1(l)]. Note that only LiAsBa (mp-10616), HoHSe (mp-24012), and YHSe (mp-28797) have finite band gap [44]. We calculated the total energy of thin films up to $N = 8$, where $2N$ and $3N$ atoms are included in WC-type and PtSbBa-type structures, respectively.

III. RESULTS AND DISCUSSION

In the following, we focus only on the energetically favorable structures. From total energy calculations for fcc and bcc metals, we have confirmed that thin films derived from the fcc(111) and bcc(110) surfaces are more stable than those derived from the (100) surfaces. We have also confirmed that thin films derived from Ga(010) surfaces are more stable than those from Ga(100). Thus, the surface orientation of thin films is determined for all systems. For brevity, the surface index α is omitted in $\Delta E_\alpha(N)$ and $p_\alpha(N)$ below.

We considered thin films of elements up to $N = 8$ except for Ga (up to $N = 5$). However, it was difficult to obtain the scf convergence for Sc (8), Ti (8), V (6,7,8), Cr (6,7,8), Fe (5,6,7,8), Co (7,8), Ni (8), Nb (6,8), In (8), Ba (5,6,7,8), Eu (7,8), Yb (5,6,7,8), Lu (8), and W (8), where integers in parenthesis indicate N . We also obtained no convergence in some of multicomponent systems with hexagonal systems for large N . Assuming different atomic positions and/or spin configurations in the initial model may be necessary to improve the scf convergence and geometry optimization. Still, the N^{-1}

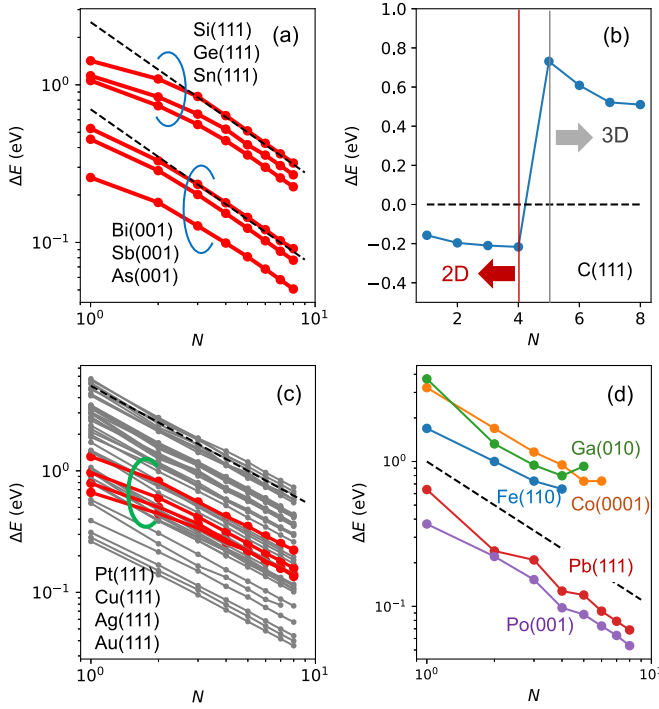


FIG. 2. ΔE vs N for the single-component systems. (a) Si, Ge, Sn, As, Sb, and Bi, (b) C, (c) fcc, bcc, and hcp metals, and (d) Ga, Fe, Co, Pb, and Po. The dashed line in log-log plots (a), (c), and (d) indicates $\Delta E \propto N^{-1}$. The curves with $p(1) > -0.7$ are colored in red. (b) The carbon diamond exhibits $\Delta E < 0$ for $N \leq 4$, indicating a 3D-2D (diamond-graphene) transition at $N = 4$. (d) A minimal value or dip structure is found for Ga ($N = 4$), Co ($N = 5$), Pb ($N = 2$ and 4), and Po ($N = 4$) thin films.

law is satisfied for lesser N . The thin films showing a strong deviation from N^{-1} law will be treated in Fig. 2(d).

A. Single-component system

Figure 2(a) shows ΔE of N -layer thin films for Si, Ge, Sn, As, Sb, and Bi. ΔE is inversely proportional to N for large N , suggesting that our theorem is valid for $N \geq 3$. The curves deviate from the N^{-1} law at $N = 1$ and 2 and $p(1)$ is larger than -0.7 . This indicates that the thin films in the monolayer limit are no longer bulk and tend to change into 2D materials.

Carbon should be studied separately because the diamond structure is metastable. As N is decreased, ΔE becomes suddenly negative at $N = 4$ [see Fig. 2(b)]. This indicates a 3D-2D transition. The thin films with $N \geq 5$ still form the diamond structure with the sp^3 bonds, while those with $N \leq 4$ are regarded as N -layered graphene with the sp^2 bonds.

For metallic elements from Li to Po, we plotted ΔE as a function of N in Fig. 2(c), if the curve satisfies $-1.3 \leq p(N \geq 2) \leq 0.7$ (i.e., the curve almost follows the N^{-1} law). When we move on to $N = 1$, we can identify goldene [$p(1) = -0.58$] having hexagonal lattice [see Fig. 3(a)]. This finding is consistent with the experimental synthesis [13]. We also identify silverene (-0.65), copperene (-0.69), and platinumene (-0.68), whose $p(1)$ is close to that of Bi (-0.68). Our calculation predicts $p(1) = -1.11$ for In, suggesting that

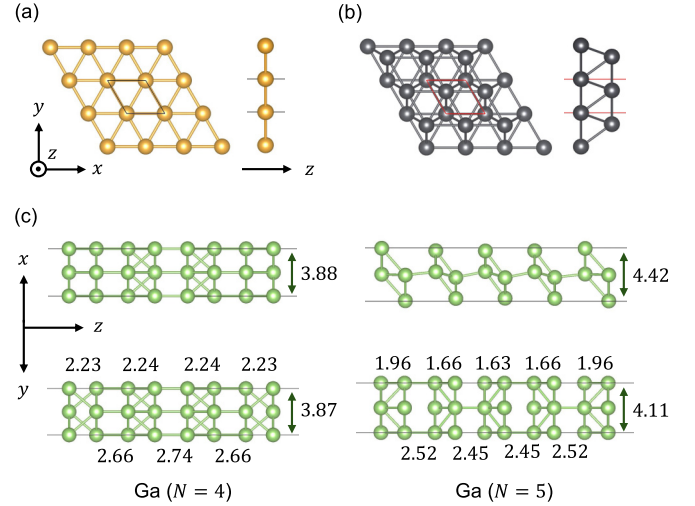


FIG. 3. Crystal structure of N -layer thin films for elemental metals. (a) Hexagonal Au ($N = 1$), (b) buckled honeycomb Pb ($N = 2$), and (c) Ga ($N = 4$ and 5). The thickness of each layer and the inter-layer distance (Å) are indicated for Ga thin films, where these values are compared with the bulk values of 1.43 and 2.37 Å, respectively. The lattice constants, a and b , are also indicated.

the free-standing In monolayer does not exist, whereas the In monolayer may be supported by SiC(0001) substrate [43].

If the N dependence of ΔE does not satisfy $-1.3 \leq p(N \geq 2) \leq 0.7$, the curves are plotted in Fig. 2(d). For Pb thin films, ΔE is significantly small at $N = 2$ and 4, resulting in $p(2) = -0.35$ and $p(4) = -0.28$. Such thin films relaxed to mono- and bilayers in the buckled honeycomb structure [see Fig. 3(b)]. The 2D Pb in the honeycomb structure is known as plumbene, which has been synthesized on a $\text{Pd}_{1-x}\text{Pb}_x(111)$ alloy surface [12]. The thin films in our calculations relaxed to high-buckled phase, i.e., for $N = 2$ thin film the lattice constant and thickness are 3.46 and 2.70 Å, respectively. The high-buckled phase is metallic, while the low-buckled phase with lattice constant of 4.934 Å becomes a topological insulator [47].

For Ga(010) thin films, ΔE takes a minimal value at $N = 4$ and increases with decreasing N . To understand this anomaly at $N = 4$, we investigated the difference of crystal structures between $N = 4$ and 5 thin films. We found that (i) δ , the atomic displacement parameter along the x direction introduced in Table I, is exactly zero at $N = 4$, while δ keeps finite value at $N = 5$; (ii) the thickness d of each layer is large at $N = 4$ ($d \simeq 2.24$ Å), compared to that at $N = 5$ ($d = 1.63 \sim 1.96$ Å) and the bulk value of 1.43 Å, as shown in Fig. 3(c); and (iii) the lattice constants at $N = 4$ (3.88 Å) are smaller than those at $N = 5$ ($a = 4.42$, $b = 4.11$ Å) and the bulk value ($a = 4.49$ Å, $b = 4.52$ Å). We also found that (iv) the electron DOS at $N = 4$ is nearly flat around the Fermi energy and the contributions from 4s and 3p states are almost equal, while the DOS for $N = 5$ thin films and bulk is large around ± 1 eV because of the large contribution from 3p and 4s states below and above the Fermi energy, respectively (see Fig. 4). These results imply that $N = 5$ is a lower bound for stabilizing 3D Ga, and below $N = 4$, 2D Ga is formed. This is similar to carbon, where 3D-2D transition occurs at $N = 4$. It

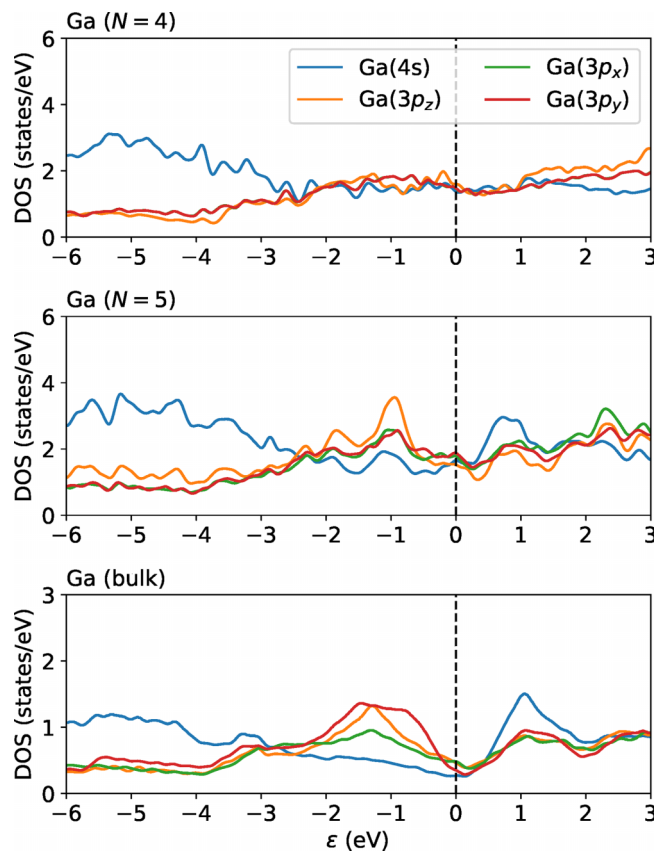


FIG. 4. Projected DOS per cell for Ga(010) thin films with $N = 4$ and 5 and Ga bulk. The overall feature of $N = 5$ thin film is similar to that of 3D bulk. The energy is measured from the Fermi level.

Po is known to crystallize into the simple cubic structure in bulk. The poloniumene in the square lattice structure (2D Po) truncated from the (001) surface has been predicted to be dynamically stable [48]. The present calculation predicts $p(1) = -0.74$. It is interesting that a dip ΔE is found at $N = 4$ [$p(4) = -0.48$]. We observed that the in-plane lattice constant a_{in} at $N = 3$ (3.390 Å) and $N = 4$ (3.372 Å) is similar to the lattice constant of bulk ($a_{\text{bulk}} = 3.374$ Å).

Above $N = 5$ (3.358 Å), a_{in} increases monotonically and approaches a_{bulk} with N .

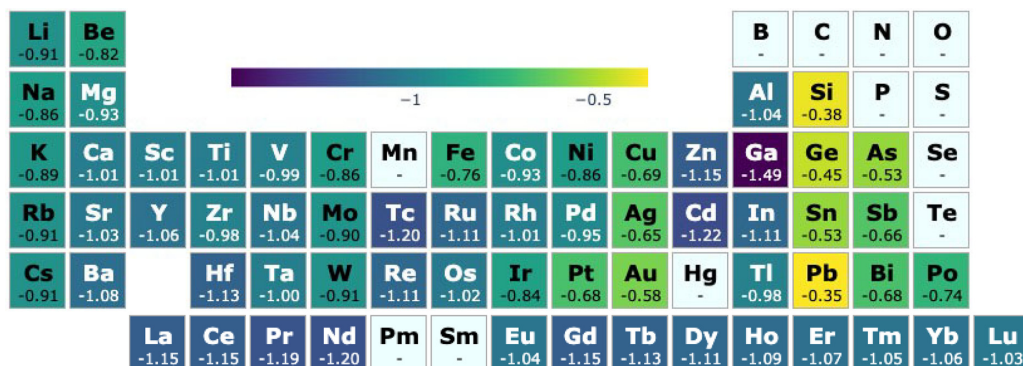
A deviation from the N^{-1} law is also found in Fe(110) and Co(0001) thin films: For Fe, the decrease in ΔE is slow as N is increased, and for Co, $\Delta E(N=5)$ is almost equal to $\Delta E(N=6)$. In these systems, we could not find structural anomalies across the N . It is desirable to study whether a magic N exists in Fe and Co thin films, but this is left for future work.

In this way, the energy variation calculations of thin films enable us to identify the single-component non-vdW 2D materials that have been synthesized through experiments, validating our approach. The results are summarized in Fig. 5. We apply our method to more complex systems below.

B. Cubic crystal system

Figures 6(a) and 6(b) show ΔE as a function of N for thin films of III-V materials and fluorite-type materials, respectively. The III-V materials exhibit the N^{-1} law for $N \geq 5$, while the deviation from the N^{-1} law is large for some systems, e.g., $p(5) = -1.27$ for AlP and $p(6) = -0.77$ for AlSb. All curves show a strong curvature around $N = 2-3$ and $p(1) > -0.5$. AlP shows $p(2) \simeq 0$ because for the $N = 2$ thin film, P atoms move from the inner to the outer region of thin films, terminating the upper and bottom surfaces. The crystal structure at $N = 2$ is different from the double-layer honeycomb structure reported in Ref. [19]. Atomic displacements within a layer need to be assumed in the initial geometry to reproduce the latter. Still, the present calculations suggest that III-V materials adopt non-vdW 2D structures.

The fluorite-type materials also follow the N^{-1} law, as shown in Fig. 6(b). A deviation from the N^{-1} law is observed in SrCl_2 (-0.51) and CdF_2 (-0.67) at $N = 1$. The previous study has reported that these 1T structures are dynamically stable [24]. Note also that PbF_2 thin films derived from the (110) surface have $p(1) = -0.77$, which is more negative than the Bi monolayer (-0.68). These monolayers are dynamically stable because they show no imaginary frequencies in phonon calculations (PBE) [24]. We have confirmed their dynamical stabilities through first-principles MD simulations at 300 K, as shown in Fig. 7 for SrCl_2 and CdF_2 and Fig. 2(c) in Ref. [24] for PbF_2 . It is noteworthy that



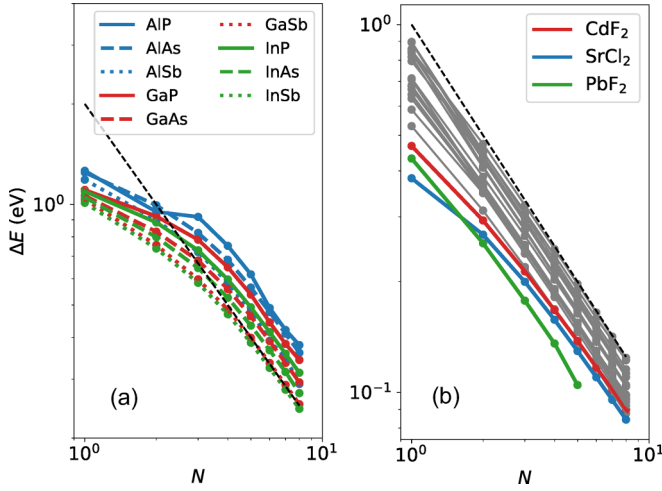


FIG. 6. The N dependence of ΔE of thin films with the (111) surface for (a) III-V materials and (b) the fluorite-type materials. The dashed line indicates $\Delta E \propto N^{-1}$. All III-V materials exhibit $p(1) > -0.5$ and AlP has $p(2) \simeq 0$. In (b), the ΔE - N curve is colored if $p(1) > -0.7$. The curve of $\text{PbF}_2(110)$ thin films, which are more stable than $\text{PbF}_2(111)$ thin films, is also colored.

SrCl_2 and CdF_2 monolayers have a band gap of 5.76 eV and 3.85 eV (PBE) and serve as wide-gap semiconductors [24], and PbF_2 monolayer exhibits negative Poisson's ratio and serves as a 2D auxetic material [24].

C. Hexagonal crystal system

Figure 8(a) shows ΔE versus N for hexagonal systems. It is anomalous that TiS, ZrTe, WC, and NbN thin films show a minimal ΔE at $N = 2$. As shown in Fig. 8(b), the optimized geometry has the rectangular (almost tetragonal) cell consisting of two buckled rectangular lattices stacked along the z axis. Metallic ($M = \text{Ti, Zr, W, and Nb}$) and semiconducting ($X = \text{S, Te, C, and N}$) atoms in the upper layer are located above X and M atoms in the bottom layer, respectively. For the TiS film, the lattice constant is $a = 3.286 \text{ \AA}$ and $b = 3.299 \text{ \AA}$ ($b/a \simeq 1.004$), and the M - X bonds and the z axis form an angle of $\theta = 2.7^\circ$ because Ti and S atoms

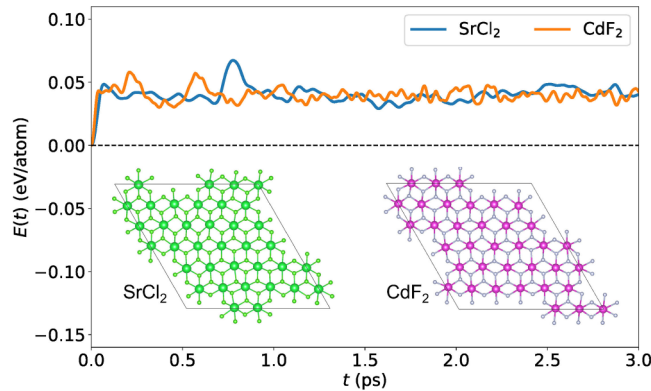


FIG. 7. First-principles MD runs at 300 K for 1T SrCl_2 and CdF_2 monolayers. A $6 \times 6 \times 1$ supercell is assumed (108 atoms). (Inset) Top view of atomic distribution at 3 ps.

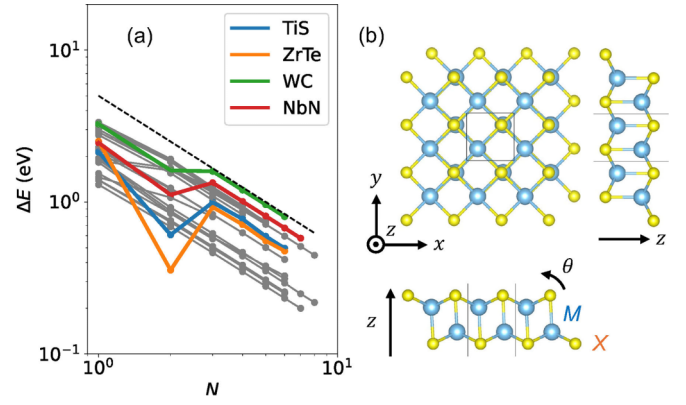


FIG. 8. (a) ΔE as a function of N for hexagonal systems with $P\bar{6}m2$. MX systems including TiS, ZrTe, WC, and NbN take a minimal ΔE at $N = 2$. (b) Crystal structure of the $N = 2$ MX thin films with the rectangular cell.

in each layer shift along the x axis differently (space group $P\bar{1}$). For the other films, b/a is less than 1.001 and $\theta \simeq 0^\circ$ (space group $Pmmn$). TiS and ZrTe thin films are dynamically stable, which is confirmed by phonon dispersion calculations (see Fig. 9) and first-principles MD simulations at 300 K [see Figs. 10(a)–10(c)]. However, WC and NbN thin films are unstable: Imaginary frequencies are observed around X point for WC and along ΓX line for NbN (see Fig. 9). We have confirmed that the eigenvectors of unstable mode have large values along the out-of-plane direction.

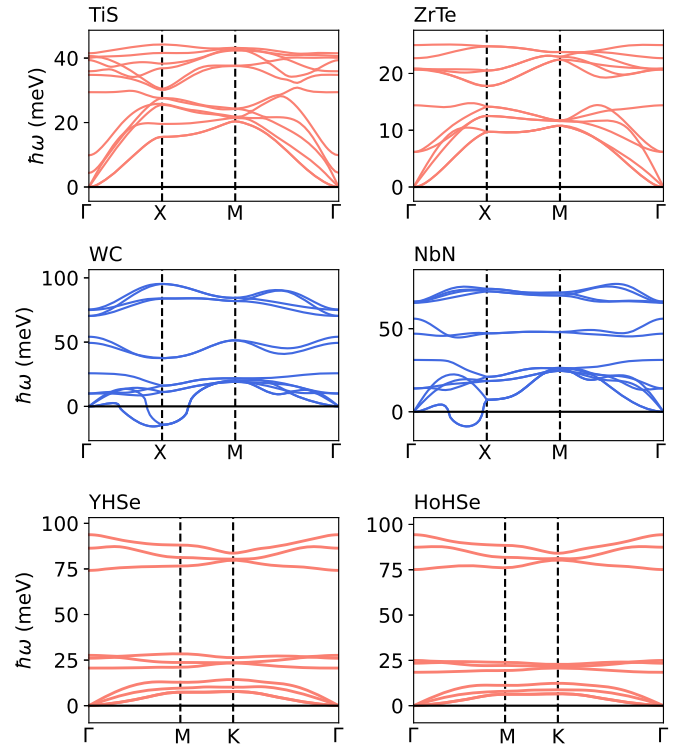


FIG. 9. Phonon dispersions of TiS, ZrTe, WC, and NbN thin films at $N = 2$ and YHSe and HoHSe thin films at $N = 1$ (within DFT-D2). Negative energy indicates the imaginary phonon energy of the unstable mode.

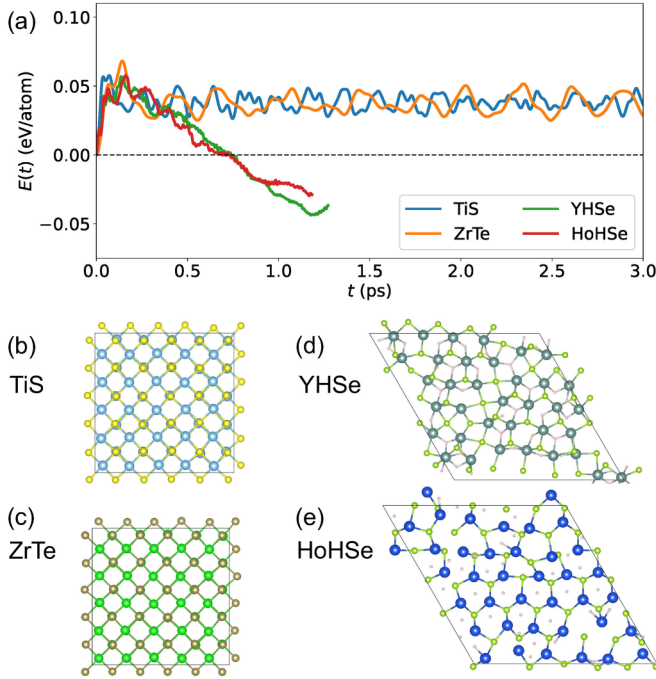


FIG. 10. (a) First-principles MD runs at 300 K. A $5 \times 5 \times 1$ supercell (100 atoms) is assumed for TiS and ZrTe thin films at $N = 2$, and a $6 \times 6 \times 1$ supercell (108 atoms) is assumed for YHSe and HoHSe thin films at $N = 1$. (b)–(e) Top view of atomic distribution at 3 ps. TiS and ZrTe are stable, whereas YHSe and HoHSe thin films are disordered.

Note that in the initial optimization only TiS was transformed into a rectangular cell at $N = 1$ and 2. With distortion, we reoptimized ZrTe, WC, NbN, and MoP thin films at $N = 1$ and 2 and obtained tetragonal cells. Only MoP keeps the hexagonal symmetry in the optimization calculations. Note also that the distorted TiS film with $\theta = 2.7^\circ$ [see Fig. 8(b)] was obtained by sequentially displacing Ti and S atoms to remove imaginary phonon frequencies at Γ point. It is worth noting that in our previous calculations for 2D Xenos [20], Ti and Zr layers prefer the buckled square structure to the buckled honeycomb structure, whereas Mo and W layers have the buckled honeycomb structure and Nb layer has the square structure with $N = 3$.

Figure 11 shows the electronic structure of $N = 2$ TiS and ZrTe thin films. Several bands cross the Fermi level on the ΓX and ΓM lines, showing metallic behavior. The projected DOS shows that the electron states around the Fermi energy are dominated by the d_{zx} and d_{zy} characters of metallic atoms, and a peak around $\varepsilon = -1.5$ eV originates from the d_{zx} , d_{zy} , and $d_{x^2-y^2}$ states, whereas the chalcogen p states appear around -4 eV.

We have also identified that RHSe ($R = Y$ and Ho) show a deviation from the N^{-1} law at $N = 1$. In the parent crystal, 2H-type RSe₂ layers are stacked along the c axis but Se layers are shared with adjacent RSe₂ layers, and H atoms form the triangular lattice in the same plane of R [see Fig. 1(l)]. In the monolayer, we observe that H atoms move to the upper side of the R layer, and obtain Janus 1T-type monolayers, where the triangular lattice of R is sandwiched by H and

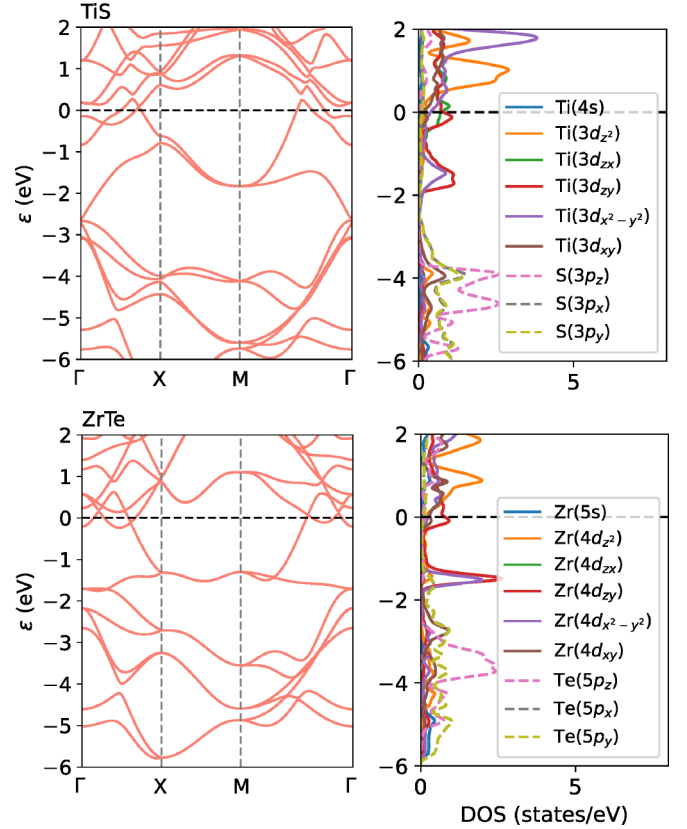


FIG. 11. Electronic band structure and projected DOS of TiS and ZrTe thin films with $N = 2$. The energy is measured from the Fermi level. The curves between the d_{zx} and d_{zy} components of Ti and Zr atoms, as well as those between p_x and p_y components of S and Te atoms, almost overlap.

Se layers. This is stark contrast with the existing Janus monolayers that are artificially created from transition metal dichalcogenides [49]. No imaginary frequencies were observed in their phonon calculations, showing that they are dynamically stable (see Fig. 9). However, by running finite-temperature MD simulations, they were disordered because of movement of hydrogen atoms [see Figs. 10(a), 10(d), and 10(e)] and therefore highly buckled. To stabilize these systems, thicker films and/or different terminations may be needed.

D. Discussion

Before closing, we discuss a possible reason why goldene [13] is so unique and serves as a non-vdW 2D material. For single-component semiconductors classified as covalent crystals, the interatomic bonds can be changed into in-plane bonds, which are preferable for the formation of 2D materials. Therefore, it is not trivial how to stabilize goldene with metallic bonds. The goldene has a hexagon-shaped Fermi surface [see Fig. 12(a)]. The electron states on each edge exhibit mainly in-plane bond character (17% 6s, 27% 6p_x + 6p_y, and 56% 5d_{xy} + 5d_{x²-y²}), and the 6p_x + 6p_y components are enhanced to 65% on each vertex by reducing the 5d character. A similar trend has been observed in the previous calculations within PBE [50]. The in-plane character allows the goldene to be robust against perturbations. On the other hand, aluminene

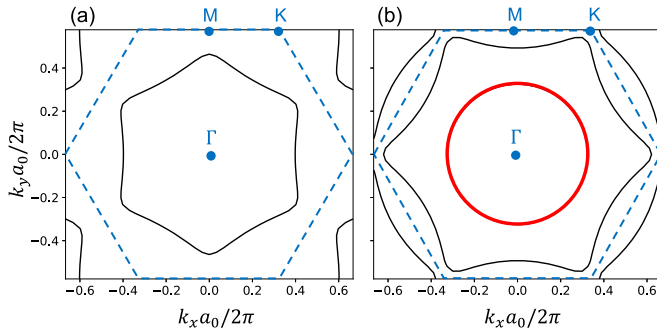


FIG. 12. The Fermi surface of (a) Au and (b) Al monolayers in the hexagonal structure. Dashed line indicates the boundary of the first Brillouin zone. The circular (red) and deformed hexagonal Fermi surfaces in Al monolayer exhibit out-of-plane and in-plane bond characters, respectively (see main text).

(2D Al) has a circular Fermi surface with p_z character and a deformed hexagon-shaped Fermi surface with s , p_x , and p_y characters [see Fig. 12(b)]. The coexistence of p_x , p_y , and p_z states on the Fermi surface is not preferable for stabilizing a 2D flat sheet, giving rise to buckling [20] or 3D crystallization when subjected to perturbations.

In the construction of a 2D materials database [2–6,8], identifying vdW 2D materials starts from exploring layered materials among 3D crystals, followed by estimating the exfoliation energy, calculating phonon dispersions, and performing first-principles MD simulations. On the other hand, for identifying non-vdW 2D materials, the first two procedures (i.e., exploration of layered systems and exfoliation energy calculations) are replaced with truncating thin films from a specific surface, calculating $\Delta E(N)$, and analyzing the N dependence.

The exfoliation energy divided by the surface area A [51] has often been used for predicting several vdW 2D materials. However, the magnitude of FTEE per area is not important for predicting non-vdW 2D materials. For example, $\Delta E(1)/A$ of silicene and goldene was estimated to be 110 and 90 meV/Å², respectively, which are larger than that of graphene (21 meV/Å² [51]). On the other hand, $\Delta E(1)/A$ of Rb(110) monolayer was estimated to be 12 meV/Å², which is smaller than that of silicene, goldene, and graphene. However, $p(1) = -0.91$ for Rb monolayer and such a monolayer has not been synthesized yet. In this way, we have not focused on the magnitude of FTEE and therefore ignored the constant factor from surface area.

It should be emphasized that a magic N (different from unity) exists to stabilize thin films. In the present work, we have identified $N = 2$ and 4 Pb (i.e., mono- and bilayer plumbene [12]), $N = 4$ Ga (i.e., gallene [42]), $N = 5$ Co, $N = 4$ Po, $N = 2$ AlP, and $N = 2$ TiS and ZrTe thin films. Exploring magic N would also be essential to identify non-vdW 2D materials. The surface relaxation and structural transformation will play an important role in understanding their stability. A slight distortion of the initial geometry may help the thin films to relax into more stable structures by breaking the initial symmetry. Investigation of the details is left for future work.

IV. CONCLUSIONS

In conclusion, we proposed that a downward deviation from the N^{-1} law of FTEE is an indicator for identifying non-vdW 2D materials. Several 2D materials that are absent from the existing databases have been revisited. Among single-component systems, silicene [$p(1) = -0.38$] and goldene [$p(1) = -0.58$] exhibit a strong deviation from the N^{-1} law at $N = 1$, which are representative semiconducting and metallic monolayers, respectively. Pb and Ga thin films have magic $N (\geq 2)$, where the FTEE becomes small, which corresponds to plumbene and gallene, respectively. For multicomponent cubic systems, nine III-V semiconductors and three fluorite-type materials (SrCl₂, CdF₂, and PbF₂) exhibit a deviation from the N^{-1} law at $N = 1$. Metallic TiS and ZrTe thin films show a structural transformation from hexagonal to rectangular (almost tetragonal) lattice at $N = 2$.

This work can be extended by considering different parent crystal structures, surface cuts, spin distribution, and initial geometry, and using more advanced exchange-correlation functionals, in combination with high-throughput calculations. Predicting physical properties will further stimulate experimental syntheses of non-vdW 2D materials.

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DATA AVAILABILITY

The data that support the findings of this article are openly available [52].

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