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Pentagon-based 2D materials: Classification, properties and applications

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ABSTRACT

Since penta-graphene (PG), a two-dimensional (2D) carbon allotrope exclusively composed of five-membered rings, was proposed in 2015, a great deal of effort has been devoted to the rational design and synthesis of pentagon-based 2D materials with novel properties and promising applications. As a result, over one hundred new pentagonal 2D materials have been theoretically predicated, and some of them have been experimentally synthesized. Due to the unique geometries of these materials, they exhibit many interesting properties, including negative Poisson's ratio, intrinsic piezoelectricity, giant out-of-plane second harmonic generation susceptibility, ferromagnetism with high Curie temperature and topological quantum state, and have broad applications. In this paper, we review the recent progress made in this emerging field, and classify all the pentagonbased 2D structures reported so far based on their geometric characteristics and space groups. Especially, we highlight the major breakthroughs that have occurred over the past several years, discuss the unexpected physical properties that have enabled these materials to bridge many disciplines in science and technology, and analyze the potential applications in metal-ion batteries, thermoelectricity, photocatalysis, electrocatalysis, and heterojunction. The challenges and opportunities in this field are also discussed for future study.

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1. Introduction

1.1. Mathematical models

Pentagon is well known to mathematicians for its golden ratio (0.618) and as the building block of the fifth Platonic solid, a dodecahedron composed of 12 pentagonal faces. In chemical science, many pentagonal molecules, such as cyclopentane, furan, pyrrole, thiofene, terthienyl, tetrathiafulvalene, five-membered sulfur-pnictogen ring SN_2P_2 [1], aromatic pentagonal anion $P_2N_3^-$ [2], and fullerene C_{20} [3] have been discovered. However, in physics, because there is no five-fold rotational symmetry in crystals, different from regular triangles, squares and hexagons, *regular* pentagons cannot tile the Euclidean plane, namely, it is impossible to achieve perfect mosaic in 2D space with *regular* pentagons. This led to the introduction of a well-known mathematical proposition proposed by Karl Rheinhardt in 1918: How to cover the Euclidean plane using only identical copies of the same shape pentagons leaving no gaps and with no overlaps. During the past 100 plus years, mathematicians have found 15 types of irregular pentagons that can tile the Euclidean plane, as shown in Fig. 1. The 15th one was found in 2015, and was reported in *Science News*.

1.2. From models to materials

Going beyond pentagonal molecules and clusters, Balaban mathematically surveyed some hypothetical forms of carbon, including two planar pentagonal configurations [6]. We proposed a 2D carbon allotrope composed entirely of pentagons, penta-graphene (PG) [7], based on extensive theoretical simulations, which resembles the mathematical pattern of type-4 pentagonal tiling in Fig. 1 It can be chemically exfoliated from T12-carbon [8]. According to *ab initio* molecular dynamics simulations [7], when H₂ molecules are introduced to a 4-layer (001) thin film of T12-carbon, they tend to break the C–C bonds, leading to the exfoliation of a partially hydrogenated PG sheet from T12-carbon. Then, the PG sheet can be obtained *via* dehydrogenation process.

Because of its unique atomic configuration and exceptional properties, PG has not only received considerable attention, but has also become a new structural model for other 2D pentagon-based structures, leading to the emergence of many new 2D materials, from the unitary pentagon-based sheets (penta-silicene [9,10], penta-germanene [11] and penta-tellurene [12]) to binary pentagon-based sheets (penta-CN₂ [13], penta-B₂C [14], penta-BN₂ [15], penta-PdSe₂ [16] *etc.*), ternary systems (penta-BCN [17], penta-CNP [18], penta-PdSSe [19], penta-Zn₂C₂P₂ [20], *etc.*), and their hydrogenated/fluorinated derivatives [21–24]. So far, 126 pentagon-based binary and ternary 2D structures have been proposed. Among them, many structures are obtained from the atomic configuration of PG by replacing or partially replacing the carbon with other atoms. Some of them have been synthesized, including penta-PdSe₂ [16,25], penta-PdS₂ [26,27], penta-NiN₂ [28], and pentagonal silicene nanoribbons [29]. These pentagon-based 2D materials exhibit interesting physical and chemical properties, such as negative Poisson's ratio [7,15,18,30–36], spontaneous polarization and intrinsic piezoelectricity [17,18,37], second harmonic generation [38], ferroelectricity [10], and ferromagnetism [39–49]. More details about the geometries and properties can be found in our database of pentagon-based 2D structures [50].



Fig. 1. 15 types of irregular pentagons that can tile the Euclidean plane with no overlaps and no gaps. *Source:* Adapted from Ref. [4], licensed under the Creative Commons Attribution-Share Alike 4.0 International license [5]. We added the recognized numbering for each tiling.

The studies on pentagon-based 2D materials have revealed a wealth of information on the structure–property relationships of materials, provided new insights into problems of technological interest, and laid the foundations for their applications in various fields, including metal-ion batteries [51–58], spintronics [45,59–63], thermoelectricity [64–67], water splitting [32,34–36,42,58,68–74], gas sensors [15,75–77], and heterojunctions [78–81].

1.3. Synthesis of pentagon-based 2D structures

In addition to the extensive efforts made in predicting new pentagon-based 2D structures and discovering their intriguing properties, a number of pentagon-based sheets have been successfully synthesized, which has significantly promoted this research field. Here we summarize the major breakthroughs in the synthesis of pentagon-based materials.

Pentagonal silicene nanoribbon is the first synthesized pentagon-based material, where Cerdá et al. [29] used a clean Ag(110) surface as the substrate, which was obtained by repeatedly sputtering of Ar^+ ions and subsequently annealing at 750 K, and then deposited silicon atoms on the surface at the evaporation rate of 0.03 mL min⁻¹ in an ultrahigh vacuum system (base pressure $< 9 \times 10^{-11}$ Torr). The geometry of the silicene nanoribbons can be controlled by the temperature of the Ag substrate, where an isolated single-strand nanoribbon was obtained when the substrate was kept at room temperature, and an ordered double-strand nanoribbon was obtained when the substrate was heated at 443 K. Espeter et al. [82] and Sheng et al. [83] used similar procedure to prepare pentagonal silicene nanoribbons. Instead of the evaporation rate, the key parameters to control the growth of the pentagonal nanoribbons were given by the growth rate of 0.01 Å min⁻¹ and temperature (1300 K) of the heated silicon source, respectively. In addition, they both found that when the substrate was heated to ~500 K, the product would be the double-strand nanoribbons. As shown in Fig. 2(a-b), clear pentagonal units were observed in the noncontact atomic force microscopy (nc-AFM) images of the single- and double-strand nanoribbons [83]. These synthesis procedures are highly dependent on the lattice match between the substrate and the nanoribbon in the atomic level.

Going beyond penta-nanoribbons of silicon, penta-PdSe₂ was the first synthesized pentagon-based 2D sheet. It was initially prepared by exfoliating its bulk counterpart in a top-down approach, but now was commonly synthesized from its corresponding atomic sources using bottom-up approaches. In a typical top-down synthesis procedure, Oyedele et al. [16] synthesized the bulk PdSe₂ in the pyrite phase by melting stoichiometric amounts of elementary substance Pd and Se in a sealed evacuated quartz ampule under a vacuum condition. The ampule was placed in a single-zone thermal furnace, slowly heated up to 850 °C for 50 h, and then slowly cooled down, the graphite-like layered geometry of bulk PdSe₂ was obtained, based on which the monolayer and few-layered penta-PdSe₂ sheets were prepared by the micromechanical exfoliation of the bulk PdSe₂. Das et al. [86] reported that the exfoliation could also be performed using the "Scotch tape" method. Such top-down method is only suitable for the bulk materials with layered pentagon-based structures.

While, due to the energy low-lying feature of penta-PdSe₂ [87], bottom-up approaches have been developed for its mass production. In a typical chemical vapor deposition (CVD) approach reported by Gu et al. [88], Pd and Se powders were used as the precursors. Pd powder was placed in the central zone and heated to 800 °C, and Se powder was placed in the upstream zone and heated to 350 °C. The evaporated Se was carried by inert carrier gas (Ar, flow rate 50~150 sccm)



Fig. 2. Experimental nc-AFM images of (a) single- and (b) double-strand pentagonal silicene nanoribbons. (c) Experimental transmission electron microscopy of penta-PdSe₂ synthesized by CVD. (d) Experimental scanning tunneling microscopy image of penta-PdSe₂ synthesized by MBE. *Source*: (a-b) Adapted with permission from Ref. [83]; (c) and (d) adapted with permission from Ref. [84], and [85], respectively.

and reacted with the heated Pd source. The penta-PdSe₂ product was deposited on SiO₂/Si substrate in the downstream. A similar CVD process was used to prepare few-layered penta-PdS₂, as reported by Zhang et al. [27], where evaporated elemental S reacted with Pd. It was also found by Wei et al. [89] that PdCl₂ powder can be used as Pd source, which reduced the heating temperature from 800 °C to 500 °C. In addition, Hoffman et al. [90] etched the few-layered penta-PdSe₂ sheets prepared by the CVD *via* exposing them to mild O₂+Ar plasma at 20 °C and 15 mTorr for 15 s with a gas flow rate of 40 standard cubic centimeter per minute (sccm), and found that thinner penta-PdSe₂ sheets can be obtained at higher O₂ concentrations. Das et al. [86] reported a similar etching process using mild SF₆ plasma carried by N₂ at room temperature and the pressure of 20 mTorr with a lower flow rate (2 and 6 sccm), where the thickness of resulting few-layered penta-PdSe₂ sheet reduced linearly with the exposure time to the plasma.

In addition to the CVD method, molecular beam epitaxy (MBE) synthesis of penta-PdSe₂ was also [85] conducted in an ultrahigh vacuum (base pressure 2.0×10^{-10} mBar) scanning tunneling microscopy (STM) system, where a nitrogendoped 6H-SiC(0001) wafer (terminated by high-quality graphene and heated to 500 K) was used as the substrate. Pd and Se sources were simultaneously evaporated from an electron-beam evaporator and a standard Knudsen diffusion cell with a flux ratio of 1:10, and were deposited on the substrate, thus forming few-layered penta-PdSe₂. The high-resolution images of penta-PdSe₂ from both the CVD and MBE approaches are presented in Fig. 2(c-d), showing that the lattice parameters are consistent with those of theoretical predictions.

Different from using the bottom-up CVD and MBE approaches at ambient/low pressure, penta-NiN₂ was synthesized with Ni and N₂ in a diamond anvil cell at high pressure [28]. In the procedure of the synthesis, N₂ was used as both reagent and pressure-transmitting medium. By exerting a high pressure of $3.1 \sim 4.0$ GPa together with laser-heating, few-layer penta-NiN₂ was synthesized, demonstrating that the high-pressure approach is promising for the synthesis of pentagon-based sheets.

It is worth mentioning that the concept of exfoliation can be extended beyond the splitting of layered bulk materials. For example, Puthirath et al. [91] reported the liquid exfoliation of iron pyrite, and found the clue that the antiferromagnetic penta-FeS₂ may exist in the mixed product. By performing an ultrasonic treatment on iron pyrite powder dispersed by N, N-dimethylformamide for 25 h, the chemical bonds between Fe and S atoms in the iron pyrite can be broken, indicating that these stimulations are sufficient enough to overcome the energy between a 2D sheet and its bulk counterpart. Thus, exfoliation methods can be used in the preparation of pentagon-based sheet as long as its corresponding pentagon-based layered bulk counterpart has comparable energy with the pentagon-based sheet.

From the above discussion on the synthesis of pentagon-based materials, it can be concluded that the energy profile of a structure can partly determine the feasible choices of synthesis procedures. Thus, the formation energy E_{form} of some pentagon-based sheets, defined as the energy change in synthesizing a 2D sheet from its corresponding elemental substances are summarized in Table 1. For example, the formation energy for a binary material with the chemical formula $M_x X_y$ can be defined as $E_{\text{form}} = [E(M_x X_y) - x E(M) - y E(X)]/(x + y)$, here $E(M_x X_y)$, E(M), and E(X) are the total energy of the material on a per chemical formula basis, the energy of one M and X atom in their bulk phases, respectively. The positive/negative value of E_{form} implies that the reaction consumes/releases energy, respectively. One can expect that penta-CNP [18], CoBiS [92] and the penta-NbX (X = S, Se, Te) family [93], etc. with negative formation energy could be synthesized from elemental substances using bottom up approaches. In addition, the energy or exfoliation energy in these reports, namely, $E_{\text{form}} = E(\text{sheet}) - E(\text{bulk})$, here E(sheet) and E(bulk) are the energies of the 2D sheet and its bulk counterpart on per atom basis, respectively. This exfoliation-related formation energies of penta-FeAsS, PtPN, penta-NiP₂, and penta-PtP₂ are comparable with that in penta-FeS₂ [91], indicating that the exfoliation of their bulk counterparts could be also possible.

Motivated by the rapid advances in theoretical design and experimental synthesis of pentagon-based materials, we timely review the current progress made in this field. Especially, for the first time, we systematically classify all the reported structures into different phases based on their lattice symmetries and structural features. We also elucidate the relationship between the geometric configurations and their properties.

heoretical formation energy	Eform	(in	eV/atom)	of	pentagon-based	2D	sheets.
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Structure	Phase	Eform	Ref.
penta-B ₂ C	α	0.610	[58]
penta-CN ₂	α	0.61	[13]
penta-C ₂ Al ₄	α	0.595	[58]
penta-P ₂ C	α	0.174	[58]
penta-C ₂ Ga ₄	α	0.797	[58]
penta-As ₂ C	α	0.522	[58]
penta-NC ₂	α	1.485	[58]
penta-AlN ₂	α	0.11	[39]
penta-SiC ₂	α	0.605	[58]
penta-SiN ₂	α	-0.14	[13]
penta-PC ₂	α	0.672	[58]
p-GeC ₂	α	0.915	[58]
penta-SiC ₅	α	0.988	[58]
penta-C ₅ P	α	0.925	[58]
penta-C5As	α	1.339	[58]
penta-CNP	α'	-0.29	[18]
penta-FeAsS	α'	0.348 ^a	[43]
H-Pt ₂ N ₄	β	-1.67	[24]
CoBiS	eta'	-0.133	[92]
PtPN	$\beta^{\prime\prime}$	0.174 ^a	[94]
pp-Fe ₄ N ₂	γ	-0.238	[95]
penta-FeS ₂	γ	0.48 ^a	[91]
penta-NiP ₂	γ	0.543 ^a	[96]
penta-PtN ₂	γ	-0.93	[24]
penta-PtP ₂	γ	0.410 ^a	[61]
penta-NbS	γ'	-0.600	[93]
penta-NbSe	γ'	-0.503	[93]
penta-NbTe	γ'	-0.215	[93]

Note:

^aEnergy difference between the sheet and its bulk counterpart.

2. Classification of pentagon-based 2D structures

Despite the fruitful research on mathematically tiling 2D plane with identical irregular pentagons, it is challenging to design pentagon-based 2D structures because the atoms and chemical bonds in real materials are completely different from the mathematical nodes and line segments in the known tiling patterns shown in Fig. 1. In materials, the coordination numbers of the atoms and the bond angles are highly restricted by the shape of hybridized atomic orbitals. In addition, pentagon fusion induces large strain energy, as described by the "isolated-pentagon rule" for fullerenes [97]. As a result, the shared nodes/segments in the tiling patterns, together with the symmetry constraints, limit the choice of elements to form stable pentagon-based 2D materials.

Inspired by the prediction of PG [7], more than one hundred pentagon-based 2D structures have been proposed, as listed in our database [50], and it has been found that type-2 and type-4 pentagonal tilings can be used for the design of pentagon-based 2D structures. As shown in Fig. 3(a), the original type-2 pentagonal tiling requires $\angle A + \angle C = 180^{\circ}$ and |AE| = |BC| = x. By further setting |AB| = |CD|, i.e., y = z, one can see that the two obtuse angles ($\angle A$) and two acute angles ($\angle C$) from four different pentagonal units share one vertex and form two sets of vertical angles in the tiling pattern. For the simplest case, where each node in this tiling pattern is replaced by one atom alone, nodes A and C correspond to the four-fold coordinated atom M, and nodes B, D and E correspond to the three-fold coordinated atom X in the atomic configuration of a real pentagon-based sheet, leading to a binary chemical formula, MX₂. Similarly, in the type-4 pentagonal tiling, nodes A and C, and the remaining nodes correspond to the four-fold coordinated atom X respectively. This results in the chemical formula, MNX₄, where each node is occupied by one atom alone. For the Cairo pentagonal tiling, a special case of the type-4 pentagonal tiling, where x = y, atoms M and N are the same element, and the chemical formula is simplified to MX₂. While in the case that N and X are the same element, the formula becomes MX₅. It is worth mentioning that the three-fold coordinated X atoms in all the above cases are in the form of X₂ dimer, which could be the origin of a number of intriguing properties of such materials [98].

In this review, we focus on the stable pentagon-based binary and ternary 2D structures reported so far with their stabilities confirmed by using *ab initio* molecular dynamics simulations and phonon spectra. Among these structures, we classify the pentagon-based sheets with one atom on one node into the different categories based on their space group symmetries and structural characteristics, including α -, β -, and γ -phases. We further categorize the pentagonal sheets obtained by replacing the three- and four-fold coordinated atoms in the γ -phase sheets by two same atoms on the top and bottom sides of the sheets occupying one node from their top views, respectively, as the derivatives of the γ -phase based on their space group symmetries, namely, γ '- and γ "-phases. We further classify the other pentagonal sheets that



Fig. 3. (a) Schematics of the type-2 and type-4 pentagonal tiling patterns. Insets are the corresponding pentagonal units. (b) Classification of pentagon-based sheets in different phases.

tile the Euclidean plane by using non-identical pentagonal units. They are considered as the derivatives of the α - and β -phases based on their space group symmetries and structural characteristics, labeled α '-, α ''-, β '-, and β ''-phases. The top and side views of a representative structure for each category together with the number of the structures in each phase are given in Fig. 3(b). While the compositions, main properties and potential applications of all the pentagon-based structures with the chemical formula MX₂ are summarized in Table 2. This table shows that these materials possess various properties: They can have negative Poisson's ratio, may be semiconducting or metallic, ferromagnetic or antiferromagnetic, topological insulating or semi-metallic. For instance, the experimentally synthesized penta-PdSe₂ is semiconducting, possesses negative Poisson's ratio, and can be used as a catalytic and thermoelectric material. The details of the geometries, properties and applications of all the pentagon-based 2D materials reported so far will be discussed in Sections 2, 3–5, and Section 6, respectively. For clarity, in this review, we add the prefix "penta-" to the names of pentagon-based 2D structures that satisfy the definition of the pentagonal tiling.

2.1. α -Phase: Type-4 tiling with buckling

Among all the reported pentagon-based 2D materials, there are 36 binary compounds that have the chemical formula MX_2 with the tetragonal space group symmetry of $P-42_1m$ (no. 113), and feature the Cairo pentagonal tiling, i.e., the type-4 pentagonal tiling geometric structure. These penta-MX₂ sheets have the same space group symmetry with PG, and can be obtained by replacing the four- and three-fold coordinated carbon atoms in the geometry of PG with M and X atoms, respectively. We classify them as α -phase pentagonal 2D structures. The tetragonal symmetry of these penta-MX₂ sheets confines their lattice parameters by a = b and $\gamma = 90^{\circ}$. The two M atoms and four X atoms in their unit cells occupy the Wyckoff positions 2b (0, 0, 0.5) and 4e (x, x + 0.5, z), respectively. In these structures, the dimers formed by the three-fold coordinated X atoms are parallel to the crystal plane defined by the four-fold coordinated M atoms, while the M atoms are sandwiched between the two layers of X₂ dimers on the top and bottom sides. This leads to the quasi-2D sheets with buckling and the breakage of centrosymmetry in their geometries. Thus, among them, the 2D semiconductors would exhibit piezoelectricity and nonlinear optical properties because of the non-centrosymmetry. The M atom is selected from the group IIA, IB, IIB, IIIA, IVA or VA elements in the periodic table, as shown in Table 2. The X atom is from non-metallic elements of the group IVA, VA, and VIA, and forms X₂ dimers containing either $\sigma(sp^2 - sp^2)$ bonds with π bonds or $\sigma(sp^3 - sp^3)$ bonds with lone-pair electrons. Some of these structures have been proven to be the ground state atomic configurations of their chemical formula, MX₂, such as T-GeP₂ [99] and penta-ZnS₂ [38]. This indicates the possibility of synthesizing these pentagon-based structures.

Nine other pentagon-based structures with the chemical formula, $MNX_4(MX_5)$ patterned in the type-4 pentagonal tiling with a finite thickness of buckling have also been proposed. They are also classified as the α -phase pentagonal structures. They possess the tetragonal space group of *P*-4 (no. 81), and can be considered as the four-coordinated sites in the α -phase penta-MX₂ alternately occupied by M and N(X) atoms. The choice of elements in penta-MNX₄(MX₅) has not been systematically explored yet. The reported cases are penta-MP₅ (M = B, Al, Ga, In) [100,101] and the systems obtained by isoelectronic atomic substitutions of PG, namely, penta-SiC₅ [102], *p*¹-Ge_{0.5}Sn_{0.5}C₂ and *p*¹-Si_{0.5}Ge_{0.5}C₂ [103].

Site M Site X	Group IIA	Group IIIB-VIIB	Group VIII	Group IB	Group IIB	Group IIIA	Group IVA	Group VA	
Group IIIA			NFe ₂				$\begin{array}{c} CB_2 \bullet CAl_2 \\ CGa_2 \end{array}$	PB ₂ 8	
Group IVA		MnC ₂				BC₂ ●	$\begin{array}{c c} \operatorname{SiC}_2 & & \operatorname{GeC}_2 \bullet \\ \operatorname{SnC}_2 & & \\ \end{array}$	$\begin{array}{c} NC_2 \bullet \\ PC_2 \bullet \end{array}$	
Group VA	BeP₂ ●	MnN ₂ 8	$\begin{array}{c c} NiN_2 \bullet NiP_2 \bullet \\ NiAs_2 & NiSb_2 \bullet \\ RhN_2 \bullet PdN_2 \bullet \\ PdP_2 \bullet PdAs_2 & \\ PtN_2 \bullet PtP_2 \bullet \\ PtAs_2 & \\ \end{array}$			$ BN_2 \\ BP_2 \\ AlN_2 \\ GaN_2 \\ S $	$\begin{array}{c} CN_2 \bullet CP_2 \bullet \\ CAs_2 \bullet CSb_2 \bullet \\ SiN_2 \bullet SiP_2 \bullet \\ SiAs_2 \bullet SiSb2 \bullet \\ GeP_2 \bullet GeBi_2 \bullet \end{array}$		
Group VIA	BeS₂ ●	MnS ₂ MoS ₂ WSe ₂	FeS2 CoS2 NiS2 NiS2 NiSe2 NiTe2 PdS2 PdS2 PdSe2 PdTe2 PtS2 PtSe2 PdTe2 P	$CuS_2 \bullet$ $AgS_2 \bullet$ $AgS_2 \bullet$	$\begin{array}{c c} ZnO_2 \\ ZnS_2 \\ ZnS_2 \\ CnSe_2 \\ CdS_2 \\ CdS_2 \\ CdSe_2 \\ \end{array}$		$\begin{array}{c} CS_2 & CSe_2 \\ CTe_2 & SiS_2 \\ SiSe_2 & SiTe_2 \\ GeS_2 & GeSe_2 \\ GeTe_2 & SnS_2 \\ SnSe_2 & SnSe_2 \\ SnSe_2 & SnTe_2 \\ SnTe_2 & PbS_2 \\ PbSe_2 & PbTe_2 \\ \end{array}$		
MA ₂ : α-ph	MA ₂ : α -phase • Negative Poisson's ratio			Ferromagnetic Thermoelectric					
MA ₂ : β-phase MA ₂ : γ-phase		Semico Metallio	SemiconductingMetallic		erromagne ogical	tic \bigcirc S	Second harmonic generation Catalytic		

Compositions, and theoretically identified properties and potential applications of some penta-MX₂ sheets in α -, β -, and γ -phases

2.2. β -Phase: Type-2 tiling with buckling

The pentagon-based PdSe₂ monolayer represents another category of the 15 pentagon-based 2D structures with the monoclinic space group symmetry of $P2_1/c$ (no. 14) and puckered morphology reported so far. It was first proposed by Wang et al. in 2015 [87], and was found that the pentagon-based configuration of PdSe₂ is lower in energy than 1T-MoS₂-like configuration [87]. Penta-PdSe₂ monolayer was synthesized *via* exfoliating its pyrite-phase bulk counterpart in 2017 by Oyedele et al. [16] and Chow et al. [25], respectively. Later on, the bottom-up approaches like molecular beam epitaxy [85] and chemical vapor deposition [84,88,90,104] have also been applied to mass-produce few-layered penta-PdSe₂ sheets for the properties studies in optical and electronic devices, which partially evidences the energy-low-lying nature of the penta-PdSe₂ configuration. Similarly, few-layered penta-PdS₂ sheets have been prepared *via* spin coating [26] and chemical vapor deposition [27].

The geometric configuration of penta-PdSe₂ is hereby classified as β -phase, which is also known as the pyrite-type structure [72]. The tiling pattern of penta-PdSe₂ and its analogues were initially considered as the type-4 Cairo pentagonal tiling [16,96]. Subsequent studies pointed out that it is actually in the type-2 pentagonal tiling [41,105]. Unlike the geometries of the α -phase penta-MX₂ sheets, the M atoms in the β -phase sheets are in the planar four-fold coordinated dsp^2 -like hybridization, leading to the centrosymmetry in these structures, while the X₂ dimers are tilted against the crystal plane defined by the M atoms. The M and X atoms occupy the Wyckoff positions 2b (0, 0, 0.5) and 4e (*x*, *y*, *z*), respectively. The monoclinic symmetry of the β -phase MX₂ sheets guarantees the lattice angle $\gamma = 90^{\circ}$, and the lattice parameters *a* and *b* are no longer identical due to the deviations in M–X bond lengths. For instance, the two different Pd–Se bond lengths in penta-PdSe₂ are 2.45 and 2.48 Å, respectively, corresponding to $x \neq y$ in the top panel of Fig. 3(a). Different from the main-group M atoms in the α -phase MX₂ sheets, the M atoms in β -phase MX₂ prefer the group VIII transition metal (TM) atoms. This is because they require the planar dsp^2 -like hybridization rather than the tetrahedral sp^3 -like hybridization (Table 2). The X atoms in β -phase sheets are restricted to chalcogens and their isoelectronic species, such as hydrogenated P and N atoms [23,24], where the terminal hydrogen atoms are not included in the pentagonal transition metal (Table P and N atoms [23,24], where the terminal hydrogen atoms are not included in the pentagonal framework.

2.3. γ -Phase: Type-4 tiling without buckling

In addition to the α - and β -phase sheets with finite thickness of buckling, there are 31 other pentagon-based planar sheets patterned in the type-4 pentagonal tiling with the tetrahedral space group symmetry *P*4/*mbm* (no. 127). In these structures, the M atoms are in the planar four-fold coordination, while the three-fold coordinated X atoms are in sp^2 -like

hybridization, forming X_2 dimers on the lattice plane defined by the M atoms. The tetrahedral space group symmetry confines their lattice parameters by a = b and $\gamma = 90^{\circ}$, and the M and X atoms in their unit cells occupy the Wyckoff positions 2b (0, 0, 0.5) and 4 h (x, x + 0.5, 0.5), respectively. We classify the 29 pentagon-based planar sheets as γ -phase structures, as shown in Fig. 3(b). These structures are initially found in some stretched α -phase MX₂ sheets like penta-B₂C [14], penta-AlN_{2.39}, and penta-SiN₂ [106], while α -SnX₂ (X = S, Se, Te) [59] sheets are the first reported intrinsically planar structures. They are further extended to the family of pentagonal group-IVA dichalcogenides (p-MX₂, M = C, Si, Ge, Sn, Pb; X = S, Se, Te) [62]. Here, all the M atoms in the γ -phase structures are from the p-block elements in the periodic table. The planar four-fold coordination of these atoms can be explained with the mechanism of the stabilized planar four-fold coordinated C atoms proposed by Hoffmann et al. [107]. Such coordination has been found to mostly exist in metal complexes and fenestranes, as it is stabilized by the delocalization of the electrons in p_{τ} orbital of the planar four-fold coordinated *p*-block atoms *via* back donating and π bonding [108]. Meanwhile, the follow-up work on the design of the γ -phase MX₂ structures focuses on TM atoms like Mn, Mo, Ni, Pd and Pt, as shown in Table 2. This is because they prefer the planar four-fold coordinated dsp^2 hybridization to the tetrahedral sp^3 hybridization [109–111]. Recently, a new γ -phase structure with p-block element N on the M site and transition-metal atom Fe on the X site was proposed [95], where the chemical bonds between the adjacent Fe are partially contributed by the $d_{x^2-y^2}$ orbitals. Some of the γ -phase structures have also been found to be the ground state structures, including pp-Fe₄N₂ [95], penta-PdN₂ [112], and penta-PtN₂ [112]. All of them are promising to be synthesized experimentally as suggested by the recent synthesis of their isoelectronic system, penta-NiN₂, under high pressure [28].

2.4. Other pentagonal tilings

In addition to the conventional pentagon-based sheets discussed above, there are some other pentagon-based 2D structures, where certain nodes are occupied by one atom on each side of the sheets. Based on the Cairo pentagonal tiling pattern, Pan's group proposed a new structure, in which the top and bottom sites of M nodes are occupied by the four-fold coordinated *p*-block atoms (B, C, P, and the chalcogen atoms S, Se, Te) on both sides of the lattice plane defined by the five-fold coordinated TM X atoms [Fig. 3(b)]. Examples include penta-CrS [42], penta-TaB [40], penta-ZrC [40], penta-NbSe [93], *etc.* Eventually, they have found 17 such pentagon-based structures with the chemical formula, MX. All these structures possess the tetrahedral space group symmetry of P4/mbm (no. 127), which is the same as that of the γ -phase MX₂ sheets. Therefore, we term them as the γ '-phase pentagonal structures. Yuan et al. [60] took another approach by doubling the X₂ dimers on both sides of the lattice plane defined by the consequently eight-coordinated M atoms, leading to the configuration of penta-RuS₄ [see Fig. 3(b)]. It also possesses the tetrahedral space group symmetry P4/mbm (no. 127), and thus is classified as the γ ''-phase structure.

In recent years, pentagon-based sheets composed of several non-identical pentagonal units have also been proposed. They are different from any of the conventional pentagonal tiling patterns shown in Fig. 1, where the Euclidean plane is tiled by using only identical copies of the same shape pentagons. Such unconventional pentagon-based sheets are classified as variants of the α - and β -phase MX₂ sheets based on their similarities in geometries and the choice of elements. For example, we proposed some ternary pentagon-based sheets, including penta-BCN [17] and penta-CNP [18] with the monoclinic space group symmetry of $P2_1$ (no.4). They can be obtained by replacing the X_2 dimers in the α phase sheets, namely, PG and penta-CN₂, with the polarized radicals BN and NP, respectively. Thus, they are classified as α '-phase. Similarly, two different configurations of β -phase-based ternary structures have been identified. One of them, represented by pentagonal PdSSe and PdSeTe [19] and classified as β '-phase, also features the P2₁ (no.4) symmetry, but is different from the α '-phase sheets in that the polarized SSe and SeTe radicals cross the lattice plane defined by the Pd atoms. While the other pentagonal PdSSe structure in the Pc (no.7) space group symmetry [68] that differs from β '-phase PdSSe [19] in the direction of spontaneous polarization is classified as β "-phase. In the β '-phase PdSSe, the polarization cancels each other out in the out-of-plane direction, while in the β "-phase PdSSe, that of the SSe radicals adds up to a dipole moment in the out-of-plane direction due to their ordered alignment in that direction. The difference between α' and β' - phases of the ternary pentagon-based structures is not well defined for the structures without α - and β -phase analogues; that is, penta-FeAsS proposed by Liu et al. [43], which is classified as the α '-phase in this review since the AsS radicals do not cross the lattice plane defined by the Fe atoms. Another kind of ternary pentagon-based structures, for instance, the one proposed by Kilic et al. [36], can be obtained by changing the element of an M atom and its neighbors along the lattice vector **b** in a $\sqrt{2} \times \sqrt{2}$ supercell of an α -phase penta-MX₂ unit cell. This results in the chemical formula, MNX₄, and is thus classified as α "-phase. The unit cell of such structure contains two M, two N and eight X atoms, and possesses the orthorhombic space group symmetry of Pma2 (no.28). A fourth approach is to change the element of every other X_2 dimer in a penta-MX₂ sheet, i.e., penta-Zn₂C₂P₂ proposed by Liu et al. [20] Also, a total of 23 plausible approaches to ternary pentagon-based 2D structures beyond the pentagonal tiling patterns have been proposed by Bravo et al. [19] based on symmetry analysis. They include the α' -, β' -, and β'' -phases discussed above, but lack the pentagon-based 2D configurations containing more than six atoms in the unit cells, like the α "-phase structures. Moreover, the geometry of the first pentagon-based sheet beyond the pentagonal tiling, i.e., penta-BN [15,113], was obtained by replacing every other N_2 dimer with polarized radical BN in penta-BN₂ [15]. This could lead to the pentagon-based sheets with up to quaternary chemical formulas if the radical would not contain B and N atoms. The geometries of α' -, α'' -, β' -, and β'' phase sheets together with other special cases are also plotted in Fig. 3(b), showing there is a lot of room for the design of pentagon-based sheets beyond the pentagonal tiling patterns.

There are also a number of 2D structures that can be viewed as the assembly of a series of pentagon-based sublattices, which are not summarized in this review article. For instance, PdPX (X = S, Se), proposed by Jing et al. [114], can be viewed as the two β "-phase PdPX sheets bonded in the out-of-plane direction *via* P–P bonds, and PP-VTe₂, proposed by Li et al. [115], can be viewed as two distorted β -phase VTe₂ sheets bonded in the out-of-plane direction *via* V–Te bonds. Very recently, a few-layer PdPX sheets have both been synthesized [116–118].

3. Mechanical properties

The mechanical properties of the pentagon-based sheets reported so far have been thoroughly studied with the main focus on their mechanical stability, Young's modulus and Poisson's ratio. The mechanical stability of a material is described by Born–Huang criteria [119] based on the elastic tensor components C_{ij} with *i* and *j* ranging from 1 to 6 under Voigt notation [120]. It is used to denote the types (tensile and shear) and directions of the stress and strain, respectively. For a 2D system, all the tensor components in the out-of-plane direction are zero, and only C_{11} , C_{12} , C_{22} and C_{66} are nonzero. As a result, the criteria are reduced to $C_{11} > 0$, $C_{22} > 0$, $C_{66} > 0$, and $C_{11} > C_{22} > C_{12}^2$ for 2D systems with orthorhombic symmetry, and can be further reduced to $C_{11} > 0$, $C_{66} > 0$, and $C_{11} > C_{12}$ for tetragonal 2D systems. Note that the C_{ij} of 2D materials is usually reported in the unit of GPa nm (equivalent to N/m) rather than GPa. This is because the side area of a 2D sheet is ill-defined due to the arbitrary vacuum space, and the arbitrariness can be canceled out by multiplying the C_{ij} with its lattice parameter *c*. Thus, the units of the related quantities like Young's modulus and piezoelectric strain tensor all change accordingly.

3.1. Young's modulus

All linear mechanical properties can be evaluated from the elastic tensor components C_{ij} . The Young's modulus Y for the orthorhombic and tetragonal pentagon-based sheets as a function of the direction of tensile strain can be deduced from C_{ii} using the equation below,

$$Y(\theta) = \frac{C_{11}C_{22} - C_{12}^2}{C_{11}\sin^4\theta + C_{22}\cos^4\theta + \left(\frac{C_{11}C_{22} - C_{12}^2}{C_{66}} - 2C_{12}\right)\sin^2\theta\cos^2\theta},\tag{1}$$

where θ is the angle between the *x* axis and the direction of in-plane tensile strain. For reference, in the α -, β - and γ -phase pentagon-based sheets and their derivatives, the lattice vectors **a** and **b** correspond to the positive directions of the *x* and *y* axes, i.e., $\theta = 0^{\circ}$ and 90°, respectively. The results, calculated from the reported raw C_{ij} data, are summarized in Table 3, which shows the stiffness of the 2D structures under external stress.

It has been found that the structures constructed by lighter elements have larger Young's moduli. For instance, for the isoelectronic penta-MX₂ sheets, the Young's moduli of α -phase penta-CN₂ and penta-X₂C (X = P, As, Sb) are 315, 60.33, 37.32, and 8.65 GPa nm [13,34], and those of β -phase penta-PdX₂ (X = S, Se, Te) along the x/y directions are 56.5/78.3, 37.7/61.5, and 23.2/51.0 GPa nm, respectively [35]. They decrease as the atomic mass of the X atoms increases. It is also the case for the M atoms; for example, the Young's moduli of penta-SiN₂ [13] and p-GeC₂ [36] are lower than those of penta-CN₂ [13] and PG [7], respectively. The main reason for this trend is that light elements usually have smaller atomic size, leading to stronger binding, thus larger force constants, which add up to the high Young's moduli. In the contrast, heavy X atoms, like As and Se on the three-fold coordinated sites, cannot effectively form π bonds in between due to the large bond length of the X-X bond, and heavy transition metal M atoms like Pd and Pt on the four-fold coordinated sites can lead to back-donating, where their d electrons fill in the antibonding orbitals of the X_2 dimers. Thus, the light-element pentagon-based structures tend to have larger Young's moduli. For the ternary derivatives of the α - and β -phase sheets, for instance, penta-CNP as the derivative of penta-CN₂ and penta-P₂C, and β '- and β ''-phase PdSSe as the derivatives of β -phase penta-PdS₂ and penta-PdSe₂, the Young's moduli of these derived structures all fall in between those of their binary counterparts. For the β -phase MX₂ sheets, except for the hydrogenated ones (PtP₂H₂ and H-Pt₂N₄), their Young's moduli along the y axis are larger than those along the x axis by up to 100%. For instance, the Young's moduli of β -phase penta-PdSe₂ along the lattice vectors \boldsymbol{a} and \boldsymbol{b} are 37.7 and 61.5 GPa nm [35], respectively, showing significant anisotropy in stiffness. Meanwhile, for the α - and β -phase MX₂ sheets with the same chemical formula (MS₂, M = Ni, Zn, Ag, and Cd) [72], the Young's moduli of the α -phase structures, except for the α -phase penta-NiS₂ sheet, are larger than those of the β -phase structures in both axial directions. This suggests a trend: the α -phase sheets are stiffer than the β -phase sheets, as evidenced by penta-ZnS₂ with the Young's moduli of 34.5 and 8.18 (x)/21.21 (y) GPa nm for its α - and β -phase structure, respectively. This can be understood from the difference in their bond lengths of these structures. For the α and β -phase sheets with the same chemical formula MX₂, the M–X bonds in the former are shorter than those in the latter, as the sp^3 -like orbitals in the α -phase sheets are more localized around the M atom than the dsp^2 -like orbitals in the β -phase sheets. The shorter bond length leads to a stronger chemical bond, and thus, the α -phase sheets with stronger M-X bonds possess larger Young's moduli.

Calculated results for the lattice parameters a and b (in Å), axial Young's modulus Y (in GPa nm), axial Poisson's ratio v, and electronic band gap E_g (in eV) of PG and pentagon-based 2D compounds (\uparrow for spin-up, \downarrow for spin-down, and M for metallic) at the HSE06 level without SOC unless otherwise noted.

Structure	Phase	Lattice parameters	Ŷ	ν	Eg	Ref.
PC.	a	3.64	263.8	-0.068	3 25	[7]
nonta PoD	u	5.04	205.0	0.000	0.80	[121]
penta-ber ₂	α	5.24	-	-	0.80	[121]
penta-BeS ₂	α	4.65	28.50	0.13	2.56	[122]
penta-BC ₂	α	4.017	-	-	M ^b	[123]
penta-BN ₂	α	3.63	224	-0.03	М	[15]
nenta-PaB	a	4 50	_	_	Mb	[124]
ponta P C	a	2 0 2 4	16 627	0.006	2.45	[[2]]
penta-b ₂ C	ά	3.934	10.037	0.900	2.43	[30]
penta-CN ₂	α	3.31	315	0.07	6.53	[13]
penta-C ₂ Al ₄	α	5.110	-	-	-	[58]
penta-P ₂ C	α	4.09	60.33	0.53	2.64	[34]
penta-C ₂ Ga ₄	α	5.010	_	_	1.37	[58]
nenta-As ₂ C	a	4 36	37 32	0.64	2.09	[34]
penta_Sh_C	a	179	8 65	0.89	1 35	[3/]
penta-502e	u	2,417	8.65	0.05	1.55	[122]
penta-INC ₂	α	3.417	-	-	IVI ^S	[123]
penta-AIN ₂	α	-	-	-	3.0 (↑), 0.9 (↓) ⁹	[39]
		4.44	-	-	-	[44]
penta-SiC ₂	α	4.409	140.857	0.033	2.41	[58]
penta-SiN ₂	α	4.04	152	-	5.19	[13]
nenta_P_Si	~	4 88	_	_	2.69	[125]
penta 1251	u	-1.00 F 02	52.0	0.410	2.05	[71]
penta-SIAS ₂	ά	5.05	33.9	0.418	2.53	[/1]
penta-SD ₂ SI	α	5.53	-	-	1.53	[126]
penta-B ₂ P	α	4.53	-	-	M (↑), ~1.0 (↓) ^p	[124]
penta-PC ₂	α	4.141	175.22	-0.083	M	[58]
penta-MnC ₂	α	4.630	_	_	$\sim 0.2 (\uparrow), \sim 2.4 (\downarrow)^{b}$	[123]
α -MnS ₂	a	5.67	59.93	0.11	3 32	[72]
a NiS	a	5 79	84.05	0.16	2.54	[72]
u-10152	u	5.28	54.95	0.10	2.34	[72]
α -cus ₂	α	5.50	54.00	0.27	IVI	[72]
penta-ZnO ₂	α	4.49	43.88	-0.14	4.53	[31]
penta-ZnS ₂	α	5.07	34.5	0.03	3.34	[38]
penta-ZnSe ₂	α	5.24	26.3	0.13 ^c	2.53	[70]
penta-N ₂ Ga	α	4.52	-	-	$\sim 0.9 (1)^{b}$	[124]
n-GeCa	α	4 602	12165	0.069	2.23	[<u>36</u>]
nenta_CeP	~	5.02	45 53	0.20	2 72	[99]
CoDi	u	5.02	45.55	0.20	2.72	[10]
Gebl ₂	α	5.831	-	=	$\sim 1.2^{\circ}$	[19]
penta- γ PdS ₂	α	5.65	-	-	1.30	[127]
α -AgS ₂	α	6.00	34.26	0.33	M	[72]
α -CdS ₂	α	5.46	20.38	0.09	3.35	[72]
penta-CdSe ₂	α	5.54	16.8	0.23 ^c	2.41	[70]
p-SnC ₂	α	5.045	81.23	0.175	1.36	[36]
β -SnS ₂	α	6 6 3 6	_	_	M ^b	[59]
B SpSo	~	6 608			0.1460	[50]
ρ-5115C2	u	0.058	-	-	0.140	[55]
β -Sn1e ₂	α	7.325	-	-	0.160	[59]
penta-BP5	α	4.544	-	-	2.68	[100]
penta-AlP ₅	α	4.89	-	-	2.73	[101]
penta-SiC ₅	α	4.022	171.182	0.052	2.69	[58]
n^1 -Sio - Geo - Co	α	4 506	131.33	0.050	2.28	1361
penta_C-P	~	3 801	206 865	0.018	M	[58]
penta-C ₅ 1	u	102	200.005	0.018	2.75	[101]
penna-GdP5	α	4.92	-	-	2./3	
p^{1} -Ge _{0.5} Sn _{0.5} C ₂	α	4.825	95.49	95.49	1.78	[36]
penta-C₅As	α	4.024	-	-	-	[58]
penta-InP ₅	α	5.06	-	-	2.78	[101]
penta-BCN	α'	3.67(a), 3.63(b)	223.45 (x), 189.03 (v)	0.022(x), 0.026(y)	2.81	[17]
H-BCN	α'	358(a) 354(b)	$178.8(x)$ 170.3 $(y)^{c}$	$0.14(x) 0.13(y)^{c}$	5.63	1371
nonta CNP	a'	3.30(a), 3.51(b)	222 (y) 180 (y)	$0.025 (y) 0.026 (y)^{\circ}$	2.65	[10]
penta-CNP	α,	5.72(u), 5.09(b)	223(x), 189(y)	0.023(x), 0.020(y)	2.02	[10]
penta-FeAsS	α	5.81(a), 5.78(b)	-	-	0.52	[43]
p^2 -Si _{0.5} Ge _{0.5} C ₂	α''	6.376 (a), 6.366 (b)	136.83 (x), 137.32 (y)	0.008(x), 0.008(y)	2.14	[36]
p^2 -Si _{0.5} Sn _{0.5} C ₂	α''	6.709 (a), 6.627 (b)	116.60 (x), 112.13 (v)	0.039(x), 0.041(y)	1.35	[36]
p^2 -Ge _{0.5} Sn _{0.5} C ₂	α''	6.831(a), 6.798(b)	109.06(x), 105.54(v)	0.038(x), 0.039(v)	1.54	36
$nenta-CoS_{2}$	ß	5337(a) 5432(b)		_	2.24	[41]
penta_NiS	P B	5,35,(a),5,352(b) 5,215(a),5,226(b)	580(y) 025 (y)	0.062(x) 0.008(x)	2.2.1	[25]
penna-mis2	Р	$J_{21} = (u), J_{22} = (D)$	$30.3(x), 32.3(y)^{-1}$	$0.002 (x), 0.098 (y)^{-1}$	2.40	[33]
	0	5.21(a), 5.32(b)	58.83 (X), 94.11 (Y)	-0.01(x), -0.02(y)	2.45	[/2]
penta-NiSe ₂	β	5.512 (a), 5.702 (b)	$37.4(x), 72.8(y)^{c}$	-0.018 (x), -0.036 (y)	2.27	[35]
penta-NiTe ₂	β	5.955 (a), 6.261 (b)	22.6 (x), 60.6 $(y)^{c}$	-0.037 (x), -0.100 (y)	1.89	[35]
β -ZnS ₂	β	5.83 (a), 5.48 (b)	8.18 (x), 21.21 (y)	0.16(x), 0.41(y)	2.47	[72]
penta-PdS ₂	β	5.472 (a), 5.571 (b)	56.5 (x), 78.3 (v) ^c	$0.038(x), 0.053(v)^{c}$	2.14	35
penta-PdSe ₂	ß	5.744(a), 5.919(b)	$37.7 (x), 61.5 (y)^{\circ}$	$0.025(x), 0.040(y)^{\circ}$	2.16	[35]
1	r [.]	5.75(a) 5.92(b)	_	$0.027 (x) -0.022 (y)^{c}$		[33]
		J. J		$(n_{j}, 0.022 (y)$		[~]

(continued on next page)

Table 3 (continued).

Structure ^a	Phase	Lattice parameters	Y	ν	E_{g}	Ref.
nenta_PdTe-	ß	6.146(a) $6.439(b)$	$232(y) 510(y)^{c}$	-0.001(x) -0.002(y)	1 90	[35]
penta-rure ₂	ρ	0.140(u), 0.433(b)	23.2(x), 51.0(y)	-0.001(x), -0.002(y)	1.50	[33]
p-AgS ₂	β	5.95(a), 6.06(b)	20.34 (x), 25.06 (y)	0.28(x), 0.35(y)	IVI	[72]
β -CdS ₂	β	6.01 (a), 5.96 (b)	8.57(x), 18.19(y)	0.02(x), 0.03(y)	2.53	[72]
H-Pt ₂ N ₄	β	4.81	221	0.18	2.70	[24]
PtP ₂ H ₂	β	5.861 (a), 5.810 (b)	$105.0 (x), 82.5 (y)^{c}$	$0.14(x), 0.11(y)^{c}$	3.34	[23]
penta-PtS ₂	В	5.46(a), 5.56(b)	-	_	1.98 ^b	[128]
nenta_PtSe_	R	5.75(a) 5.91(b)	_	_	1.65 ^b	[128]
penta-ribe2	ρ	5.75(u), 5.51(b)	-	-	1.05	[120]
penta-PtTe ₂	β	6.11(a), 6.42(b)	-	-	1.45	[128]
CoBiS	β'	5.987 (a), 5.867 (b)	69.88(x), 47.25(y)	$0.35(x), 0.25(y)^{c}$	0.5	[92]
PdSSe	β'	5.619 (a), 5.754 (b)	-	-	$\sim 2.3^{d}$	[19]
		_	45.86(x), 69.15(y)	0.064(x), 0.096(y)	2.10	[73]
DdSoTo	R'	5939(a) $6168(b)$	_	_	$\sim 2.0^{d}$	[10]
C-A-C	ρ ο"	5.555(u), 0.108(b)	-			[13]
COASS	P	5.75 (<i>a</i>), 5.69 (<i>b</i>)	$74.70(x), 51.03(y)^{2}$	$0.12(x), 0.08(y)^{2}$	0.34 (↑), 0.64 (↓)	[129]
penta-PdSSe	$\beta^{\prime\prime}$	5.54 (a), 5.70 (b)	-	-	2.34	[68]
		-	45.79 (x), 69.18 (y)	0.064 (x), 0.097 (y)	2.06	[73]
penta-PdSTe	β''	6.00(a), 5.81(b)	61.98 (x), 35.43 $(y)^{c}$	0.075(x), 0.043(y)	2.14	[74]
nenta-PdSeTe	' β″	617(a)593(b)	$56.21(x).29.66(y)^{\circ}$	0.061(x) = 0.032(y)	2.06	74
DrDN	ρ β"	5.30(a), 5.33(b)		-	1.60	
- CC	ρ	5.50 (u), 5.25 (b)	-	-	1.00	
$p-CS_2$	γ	5.44	-	-	IVI	[62]
p-CSe ₂	γ	5.99	-	-	M	[62]
p-CTe ₂	γ	6.45	-	-	M	[62]
pp-Fe ₄ N ₂	ν	5.15	-	_	M (↑), 0.74 (↓)	95
n_SiS_	7	6.18	_	_	M	[62]
p-5152	Y	0.10	-	-		[02]
p-515e ₂	γ	6.55	-	-	IVI	[62]
p-SiTe ₂	γ	7.16	-	-	M	[62]
penta-MnN ₂	γ	4.80	112.25	0.18 ^c	M (↑), 1.12 (↓) ^b	[46]
β -FeS ₂	ν	5.604	108.5°	0.12 ^c	0.31	[47]
penta_NiN_	24	153	168.8	0 130	1 10	[130]
penta-Ming	Y	4.55	117.42	0.150	0.010	
penta-NIP ₂	γ	5.552	117.42	0.229	0.818	[96]
penta-NiAs ₂	γ	5.89	97.22	0.25	0.55	[131]
penta-NiSb ₂	γ	6.464	-	-	M ^b	[132]
n-GeS2	ν	6.42	-	_	М	[62]
n-CeSe	24	677	_	_	0.065	[62]
p GCSC2	Y	7.20			0.005	[02]
p-Gere ₂	γ	7.30	-	-	0.044	[02]
sp-MoS ₂	γ	6.04	-	-	M (↑), ~0.25 (↓) ⁵	[45]
penta-RhN ₂	γ	4.810	-	-	M	[133]
penta-PdN ₂	γ	4.87	128.4	0.118	0.92	[130]
penta-PdP ₂	v	5 86	105.88	0.30	0.74	1311
penta_PdAs_	7	6 19	84 20	0.34	0.80	[131]
n CnC	Y	0.15	04.25	0.54	0.00	[[]]]
p-31132	γ	0.01	-	-	0.193	[02]
p-SnSe ₂	γ	7.15	-	-	0.345	[62]
p-SnTe ₂	γ	7.74	-	-	0.317	[62]
WSe ₂	γ	6.439	_	-	M (↑), ~0.09 (↓) ^b	[134]
nenta-PtN ₂	, 1/	481	222.5	0 167	1 11	1301
penta PtP.	7	5.83	136.77	0.29	0.54	[131]
penta DtAs	Y	5.05 C 1C	106.72	0.23	0.19	[101]
penita-PtAS ₂	γ	0.10	100.72	0.52	0.10	
$p-PbS_2$	γ	6.99	-	-	0.222	[62]
p-PbSe ₂	γ	7.33	-	-	0.617	[62]
p-PbTe ₂	γ	7.91	-	-	0.715	[62]
nenta-BN	_	3 7 5	133.4 ^c	0.04	$\sim 1^{b}$	1151
ponta TiP	24	5 901	54.20	0.01	М	[125]
penta-m	Y,	1.05	17.00	0.478	ivi a sh	
penta-VS	γ΄.	4.95	17.0	0.68	MB	[48]
penta-CrS	γ'	4.92	127.3 ^c	0.19 ^e	2.378	[42]
penta-CrSe	γ'	5.03	109.8 ^c	0.28 ^c	2.522	[42]
penta-CrTe	ν'	5.25	77.0 ^c	0.31 ^c	1.298	421
nenta-MrS	24	471	36.0	0.48°	Mb	[48]
pointa Millo	r	472	20.0	0.10	n a b	
penta-res	γ'	4./3	30.0	0.48	IVI-	[48]
penta-ZrC	γ'	5.92	-	-	M ^D	[40]
penta-ZrP	ν'	6.379	64.10	0.452	M ^b	[135]
nenta-NbS	V	5 4 3 9	105 ^c	0.40 ^c	М	[03]
ponta NhCo	r d	5 5 2 9	85 0 ^C	0.42	M	[02]
penna-muse	Υ,	5.520	0.0	0.44	111	[32]
penta-NbTe	γ'	5.666	64.7°	0.44	0.027	[93]
penta-HfC	γ'	5.85	-	-	M ^D	[40]
penta-HfP	γ'	6.302	54.37	0.538	М	[135]
nenta-TaR	V	5 69	_	_	M ^b	[40]
Penna nub	1	0.00			•••	[10]

(continued on next page)

Table 3 (continued).

Structure ^a	Phase	Lattice parameters	Y	ν	E_{g}	Ref.
penta-TaC	γ'	5.58	-	-	M ^b	[40]
penta-WB	γ'	5.46	-	_	M ^b	[40]
penta-RuS ₄	γ''	5.318	-	_	0.070 ^e	[60]
penta-Zn ₂ C ₂ P ₂	-	5.205 (<i>a</i>), 98.96° (γ)	35.5 (<i>x</i>), 61.1 (<i>y</i>)	0.12 (x), ~0.2 (y)	1.16	[20]

Note:

^aOnly the first reported complete data sets are included, unless data from follow-up reports are complementary or qualitatively inconsistent. ^bCalculated at the PBE level.

^cCalculated from raw data in corresponding reference.

^dCalculated at the HSE06 level with SOC.

^eCalculated at the PBE level with SOC.

3.2. Poisson's ratio

The Poisson's ratio v, defined as the negative ratio of the transverse strain to the corresponding axial strain, can be calculated by using the following equation:

$$\upsilon(\theta) = \frac{C_{12} \left(\sin^4 \theta + \cos^4 \theta\right) - \left(C_{11} + C_{22} - \frac{C_{11}C_{22} - C_{12}}{C_{66}}\right) \sin^2 \theta \cos^2 \theta}{C_{11} \sin^4 \theta + C_{22} \cos^4 \theta + \left(\frac{C_{11}C_{22} - C_{12}^2}{C_{66}} - 2C_{12}\right) \sin^2 \theta \cos^2 \theta},\tag{2}$$

where C_{ij} is the elastic tensor components and θ is the angle between the *x* axis and the direction of in-plane tensile strain. Normally, this ratio is positive as most materials expand in the lateral directions of the strain when subjected to a compression. It is closely related to the internal strain at the interfaces of the materials. The calculated results of Poisson's ratios for PG and other pentagon-based 2D structures are summarized in Table 3. One can see that some penta-sheets in α - and β -phase possess negative Poisson's ratio (NPR) due to their special geometries.

Actually, materials with NPR are rarely seen in nature. For pentagon-based 2D materials, PG was the first one to be found to possess NPR. The origin of such auxetic behavior was schematically illustrated by analyzing the response of sp^2 hybridized C atoms in PG unit cell when the lattice is uniaxially stretched [7]. For the α -phase sheets, NPR has also been found in some isoelectronic and electron-rich systems of PG, including penta-ZnO₂ [31], penta-X₂C (X = P, As, Sb) [34], penta-BN₂ [15,30], penta-PC₂ [58], penta-CNP [18], and penta-CN₂ [136]. Among them, the NPR feature of penta-ZnO₂ and penta-BN₂ is restricted to the directions close to the lattice vectors \boldsymbol{a} and \boldsymbol{b} , as shown in Table 3, while that of the penta-X₂C family, penta-CN₂, and penta-CNP is only found near their diagonal directions. For penta-BN₂, NPR exists in all directions. For the β -phase sheets, NPR has been found in penta-PdSe₂ [32,33] and some of its isoelectronic species, such as penta-NiSe₂, penta-NiTe₂, and penta-PdTe₂ [35]. They all show robust NPR features regardless of the direction of the external stress. This property labels these pentagon-based 2D materials as auxetic materials or metamaterials, which could have applications in nano-mechanical devices. Since the γ -phase materials do not show NPR, it is intuitive to speculate that the NPR in these α - and β -phase sheets could be attributed to their buckled geometries. The thickness of the α - and β -phase sheets tends to decrease when stretched along an in-plane direction, while the atoms in the sheets would be pushed out along the transverse direction with almost unchanged bond length due to the strong inter-atomic forces [34]. Thus, the elongation in the transverse direction results in the NPR when it overwhelms the compression in that direction. In addition, Winszewski et al. [137] proposed a model to explain the NPR in PG, where all the chemical bonds are described as springs with one single harmonic force constant k_s regardless of the chemical difference and the connection between the changes in the bond angles and the strain energy is described by another harmonic force constant $k_{\rm a}$. They demonstrated that NPR can exist in the materials with the geometry of PG when the chemical bonds are strong and bond angles are flexible, indicating that the geometry of the α -phase pentagon-based sheets indeed represents a new auxetic configuration.

Being the opposite of negative Poisson's ratio, ultra-high Poisson's ratio has also been found in some pentagon-based sheets. Typically, the Poisson's ratio of penta-B₂C and penta-Sb₂C reaches 0.906 [58] and 0.89 [34], which are both close to the upper limit of $\nu = 1$ constrained by the Born–Huang criteria for the α - and γ -phase systems with tetragonal symmetry. This indicates that the area covered by penta-B₂C/penta-Sb₂C sheet almost remains constant under the axial tensile strain.

3.3. Ideal strength

In addition to the linear mechanical properties that describe the scenarios near the equilibrium state of materials, the intrinsic mechanical properties beyond the domain of Hooke's law, like the ideal strength and the ultimate tensile strain, determine the behavior of material under extreme stress and strain. The ideal strength is the upper limit to the mechanical strength of a defect-free crystal, determining how much strain the material can withstand before failing. Usually, it can be obtained from the peak value of stress on the stress-strain curve. By applying small uniaxial/biaxial

Structure	Phase	Ultimate t	ensile strain	Ideal strer	ıgth	Ref.
		Biaxial	Uniaxial	Biaxial	Uniaxial	
PG	α	17.1% ^a	17%	-	_	[7,36]
penta-BN ₂	α	12%	-	~ 10.4	-	[15]
penta-P ₂ C	α	18%	24%	19.44	14.92	[34]
penta-As ₂ C	α	18%	27%	14.33	11.79	[34]
penta-Sb ₂ C	α	18%	30%	10.41	9.39	[34]
penta-SiC ₂	α	16%	21%	-	-	[36]
$p-GeC_2$	α	12%	16%	-	-	[36]
p-SnC ₂	α	7%	16%	-	-	[36]
penta-BP5	α	20%	18%	4.1	2.93	[100]
p ¹ -Si _{0.5} Ge _{0.5} C ₂	α	14%	18%	-	-	[36]
p^1 -Ge _{0.5} Sn _{0.5} C ₂	α	10%	12%	-	-	[36]
p^2 -Si _{0.5} Ge _{0.5} C ₂	$\alpha^{\prime\prime}$	13%	15% (x), 21% (y)	-	-	[36]
p^2 -Si _{0.5} Sn _{0.5} C ₂	α''	10%	15% (x), 19% (y)	-	-	[36]
p^2 -Ge _{0.5} Sn _{0.5} C ₂	$\alpha^{\prime\prime}$	9%	10% (x), 14% (y)	-	-	[36]
penta-BN	-	12%	-	${\sim}7.0$	-	[15]
penta-NiN ₂	γ	-	\sim 12%	-	8.9	[133]
penta-RhN ₂	γ	-	\sim 11.6%	-	9.7	[133]
penta-PdN ₂	γ	-	\sim 8%	-	5.0	[133]
penta-PtN ₂	γ	-	$\sim 11.2\%$	-	11.9	[133]

Calculated	ultimate	tensile	strain	and	ideal	strength	(in	GPa	nm)	for	PG	and	some	pentagon	-based	2D	compounds

^aDetermined by phonon instability.

tensile strain increments to simulate the effect of external tensile stress, the value of external tensile stress is represented by the negative value of the internal stress in the strained lattice, and the tensile strain corresponding to the ideal strength is termed ultimate tensile strain. The calculated ideal strength and ultimate tensile strain for PG and some other pentagon-based 2D sheets are summarized in Table 4.

A high ultimate tensile strain and a high ideal strength are desired for functional 2D materials, and the penta- X_2C family (X = P, As and Sb) performs well in these aspects [34]. Especially, under biaxial tensile strain, the largest known values of both ultimate tensile strain (18%) and ideal strength (19.44 GPa nm) were both found in penta- P_2C . While, under uniaxial tensile strain, the records for the known ultimate tensile strain (30%) and ideal strength (14.92 GPa nm) were held by penta- Sb_2C and penta- P_2C , respectively.

It is also worth mentioning that the theoretical phonon instability of the stretched sheets can happen before the ultimate tensile strain [138]. Thus, the ultimate tensile strain and the ideal strength obtained from the stress–strain curve might be slightly overestimated. For example, imaginary phonon modes arose in PG under a biaxial tensile strain of 17.2% [7], indicating that the ultimate tensile strain of PG under biaxial tensile strain should be 17.1% as determined by its phonon instability, which outperforms that of graphene (\sim 15%) [138]. This also indicates that the ultimate tensile strain and ideal strength taken from the stress–strain curve should be carefully reexamined from the perspective of phonon instability.

4. Electronic properties

The analysis of the electronic structures of pentagon-based 2D structures is crucial for revealing their electronic transport properties near the equilibrium states, and for investing their potential applications in electronic devices like transistors. In this section, based on the space group symmetry of these structures, we provide insight into the band degeneracy in their electronic band structures, and discuss the carrier mobility in these structures based on the deformation potential theory and the electron–phonon coupling. We also cover the analysis on the topological edge states in these structures.

4.1. α -Phase materials

Due to their tetragonal symmetry, the first Brillouin zone of the α -phase penta-MX₂ sheets can be represented by the high symmetry path Γ (0.0, 0.0, 0.0) \rightarrow X (0.5, 0.0, 0.0) \rightarrow M (0.5, 0.5, 0.0) \rightarrow Γ . The high symmetry point M is also denoted as S in some reports. Brave et al. [123] studied the symmetry of these structures and reported that when magnetism and spin-orbit coupling (SOC) are not included, the system keeps the two-fold degenerated spin-up and spin-down energy states due to the time-reversal symmetry, and a further two-fold band degeneracy along the high symmetry path X \rightarrow M is protected by the screw axis symmetry $\{2_{001} | \frac{1}{2}, \frac{1}{2}, 0\}$. This is because the irreducible representations are conjugated with each other, as shown in Table 5 and Fig. 4(a–e). Such degeneracy together with the energy band gap E_g between the energy bands leads to the indirect semiconducting feature of not only the isoelectronic species of PG like penta-SiC₂ [139], penta-CdS₂ [140], penta-ZnS₂ [38], but also the systems that lose or gain *four* valence electrons per unit cell, like penta-B₂C [14], and penta-CN₂ [13] [Fig. 4(a) and (e)]. In addition, the Fermi levels in the isoelectronic species of

Table 5 Character table of the α -phase penta-sheets with space group P-42₁m at

k-point (u , 0.5, 0) on the high	n-symmetry path $X \rightarrow$	M (path Y).
Symmetry operation	Ι	$\left\{2_{001} \left \frac{1}{2}, \frac{1}{2}, 0 \right. \right\}$
Y ₁	1	$\omega = e^{i\pi u}$
Y ₂	1	$-\omega$

PG precisely separate the occupied valence bands with bonding features and the unoccupied conduction bands with antibonding features. The gained/lost electrons in the other α -phase MX₂ structures lead to antibonding features in the valence band maximum (VBM)/bonding features in the conduction band minimum (CBM), respectively [13,14,99]. The electronic band gaps of each family of semiconducting isoelectronic α -phase sheets follow the trend that the structures with heavier atoms possess lower band gaps. For example, the band gaps of penta-CN₂ and the penta-X₂C (X = P, As, Sb) family decrease monotonously from 6.53 to 1.35 eV with the increasing atomic number [13,34]. The similar trend has also been found in bulk covalent semiconductors as described by the following empirical equation [141,142],

$$E_{\rm g} = p \frac{1}{\rho^{\alpha} \sum_{i} w_{i} f_{i} \left(r_{\rm c}/r_{\rm a} \right)^{\beta}} \sqrt{\frac{H \left(\chi_{\rm a} \right) H \left(\chi_{\rm c} \right)}{H \left(n_{\rm a} \right) H \left(n_{\rm c} \right)}} + q,\tag{3}$$

where subscript a/c denotes the anions/cations, ρ is the bond electron density, *i* stands for nonequivalent chemical bonds, w_i is the proportion of bond *i* in the structure, $f_i = 1 - (\chi_a - \chi_c)/(\chi_a + \chi_c)$ is the covalence of bond *i*, *r* is the radius of atoms and r_c/r_a represents the polarization of the bond, χ is the Pauling electronegativity, *n* is the principal quantum number of valence electrons, $H(x_n)$ is the weighted harmonic mean of the data set x_n , and p, q, α , and β are system-dependent constants. This formula shows the relationship between the energy band gap E_g and the characteristic parameters of the composing atoms. Heavier atoms from the same group in the periodic table possess lower electronegativity χ , and the larger principal quantum number *n*, leading to lower band gaps when used to construct pentagon-based sheets. From the perspective of chemical bonds, molecular orbitals, and linear combination of atomic orbitals, the transition from the VBM to the CBM should overcome the binding energy of the covalent bonds, which is lower for chemical bonds containing heavy atoms, and is represented by electronegativity and principal quantum number in the above equation. More interestingly, for the systems that gain or lose *two* valence electrons per unit cell, metallicity arises in most cases due to the two-fold degeneracy in energy bands, i.e., penta-BN₂ [15,30], penta-NC₂ [123], penta-PC₂ [123], penta-PB₂ [124], penta-BP₂ [124], α -CuS₂ [72], and α -AgS₂ [72], as is the case with the systems shown in Fig. 4(b) and (d). While, an uncommon *p*-orbital ferromagnetism that arises in penta-AlN₂ [39] will be discussed in the following Section 5.1.

The first Brillouin zone of the α -phase penta-MNX₄(MX₅) sheets is also represented with the high symmetry path $\Gamma \rightarrow X \rightarrow M \rightarrow \Gamma$. However, no band degeneracy is found along the $X \rightarrow M$ path, since the $\left\{2_{001} \mid \frac{1}{2}, \frac{1}{2}, 0\right\}$ symmetry is broken due to the different M and N atoms. In spite of the difference in band degeneracy, the energy band structure of penta-MNX₄(MX₅) is similar to that of its isoelectronic α -phase penta-MX₂ counterparts in both band dispersions and semiconducting nature. For instance, penta-BP₅ [100] [Fig. 4(f)] together with the penta-MP₅ (M = Al, Ga, In) family [101], and penta-CN₂ [13] [Fig. 4(e)] are all semiconducting with wide indirect band gaps.

4.2. β -Phase materials

The first Brillouin zone of the β -phase MX₂ sheets can be represented by the high symmetry path $\Gamma \rightarrow X \rightarrow M \rightarrow Y$ (0.0, 0.5, 0.0) $\rightarrow \Gamma$ when the lattice vector **c** is perpendicular to the 2D crystal plane. The band degeneracy features of the β phase sheets are shown in Fig. 4(g-i). When magnetism and SOC are not considered, the two-fold band degeneracy other than the spin degeneracy is found along the $X \rightarrow M$ and $M \rightarrow Y$ paths, which is protected by the symmetry operations $\{m_{100} | \frac{1}{2}, \frac{1}{2}, 0\}$ and $\{2_{100} | \frac{1}{2}, \frac{1}{2}, 0\}$, respectively, as shown in Table 6. And such two-fold degeneracy is still preserved when SOC is considered, as indicated by the irreducible representations of the double space group of the β -phase sheets [144], while the spin degeneracy is broken. In addition to the band degeneracy features in the β -phase MA₂ structures, the band dispersions of these structures are also similar to each other. This is due to the similar evolution of the energy levels of the atomic orbitals in the corresponding M/A elements due to the same crystalline field, which is determined by the coordination and hybridization of atoms. Take β -phase penta-PdSe₂ as an example, where the Pd²⁺ has the electronic configuration of [Kr]4 d^8 , and its empty 5s, 5 p_x , 5 p_y , and $4d_{x^2-y^2}$ orbitals are hybridized, forming dsp^2 -like orbitals. They are saturated by the four neighboring Se atoms in sp^3 -like hybridization, thus, making all the 4d orbitals of Pd fully occupied. For nonmagnetic β -phase structures with more valence electrons than that of penta-PdSe₂, the band dispersion is almost unchanged only with an up-shift of the Fermi level. All of the β -phase systems are semiconducting with indirect band gaps, except β -AgS₂ [72], which is intrinsically metallic due to its two extra valence electrons per unit cell with respect to that of penta-PdSe₂ and the two-fold degeneracy in its nonmagnetic energy band, similar to the case of α -AgS₂ [72]. The band gaps of the β -phase structures generally follow the trend that the structures with heavier atoms possess lower band gaps, while there are some exceptions, i.e. the band gap of penta-PdSe₂ (2.16 eV) is larger than that of penta-PdS₂ (2.14 eV), and the band gap of penta-PdTe₂ (1.90 eV) is larger than that of penta-NiTe₂ (1.89 eV) [35]. This



Fig. 4. Theoretical electronic band structure of (a) penta-B₂C, (b) penta-BC₂, (c) penta-SiC₂, (d) penta-BN₂, (e) penta-CN₂, (f) penta-BP₅, (g) penta-PdSe₂, (h) β -AgS₂, (i) β -ZnS₂, (j) γ -phase SnSe₂, (k) penta-NiP₂, (l) penta-NbTe, (m) penta-CrTe, (n) penta-BCN, (p) β '-phase PdSeTe, (q) p^2 -Si_{0.5}Ge_{0.5}C₂.

Source: (a-g) Adapted with permission from Ref. [13–15,100,123,143], and [65]; (h-i) adapted with permission from Ref. [72]; (j-q) adapted with permission from Ref. [17,19,42,60,62,93,96], and [36], respectively.

Г - э	h	10	c
١d	D	Ie	o

Character table for the β -phase penta-sheets with space group P2₁/b11 at *k*-points (0.5, ν , 0) and (u, 0.5, 0) on the high-symmetry path X \rightarrow M (path G) and M \rightarrow Y (path V), respectively.

Symmetry operation	Ι	$\left\{m_{100} \left \frac{1}{2}, \frac{1}{2}, 0 \right. \right\}$
<i>G</i> ₁	1	$-\omega_1$
G ₂	1	$\omega_1 = e^{i\pi v}$
Symmetry operation	Ι	$\left\{2_{100} \left \frac{1}{2}, \frac{1}{2}, 0\right.\right\}$
<i>V</i> ₁	1	$\omega_2 = e^{i\pi u}$
<i>V</i> ₂	1	$-\omega_2$

can be attributed to the bond electron density term ρ , the covalence term f_i and the polarization term r_c/r_a in the Eq. 3, where heavy cations lead to weak covalence, large anions lead to a low r_c/r_a value, and heavy atoms generally lead to large lattice parameters and low bond charge density, resulting in an increased band gap if they overcome the decrease caused by the average electronegativity and principal quantum number.

4.3. γ -Phase materials

The first Brillouin zone of the γ -phase MX₂ sheets can be described with the high symmetry path $\Gamma \rightarrow X \rightarrow M \rightarrow \Gamma$, same as that of the α -phase sheets. The two-fold degeneracy along the X \rightarrow M path is symmetry-protected whether SOC is considered or not. This is due to the fact that the irreducible representations in both space group and double space group are either second-order or conjugated with one another [144], as shown in Fig. 4(j-k), and Table 7 for the symmetry operations $\{2_{001} | \frac{1}{2}, \frac{1}{2}, 0\}$, $\{m_{001} | 0, 0, 0\}$ and $\{m_{010} | \frac{1}{2}, \frac{1}{2}, 0\}$. Most of the known γ -phase MX₂ sheets containing TM atoms are isoelectronic species of penta-NiN₂, which are two valence electrons short per unit cell with respect to β -phase penta-PdSe₂. Taking penta-NiN₂ as an example, the Ni atom in +2 valence possesses fully occupied 3*d* orbitals after being saturated by the four neighboring N atoms. While, the N atom is in sp^2 -like hybridization as indicated by its planar three-fold coordination, because N atom is one valence electron less than Se, leading to a higher bond order in N₂ dimers for satisfying the octet rule. Therefore, we conclude that the difference between the planar configurations of these γ -phase sheets and the buckled ones of the β -phase sheets is due to the different number of valence electrons of the X atoms in these two systems. This is further confirmed by the change in the pentagonal framework of PtN₂ and

Character table of the γ -phase penta-sheets with space group P4/mbm at *k*-point (*u*, 0.5, 0) on the high-symmetry path X \rightarrow M (path Y).

Symmetry operation	Ι	$\left\{2_{001} \left \frac{1}{2}, \frac{1}{2}, 0\right. \right\}$	$\{m_{001} 0,0,0\}$	$\left\{m_{010} \left \frac{1}{2}, \frac{1}{2}, 0 \right. \right\}$
Y ₁	1	$\omega = e^{i\pi u}$	1	ω
Y ₂	1	ω	-1	$-\omega$
Y ₃	1	$-\omega$	-1	ω
Y ₄	1	$-\omega$	1	$-\omega$

PtP₂ before and after hydrogenation [23,24]. The PtN₂ and PtP₂ sheets in γ -phase planar configuration are transformed into β -phase buckled configuration after hydrogenation, because the N–H and P–H radicals can be viewed as isoelectronic species of S atoms, and thus, hydrogenated PtN₂ and PtP₂ are isoelectronic species of β -phase penta-PdSe₂ rather than the penta-NiN₂. Among the semiconducting γ -phase MX₂ structures, a general correlation between the heavy atoms in the sheets and the lower band gaps was also found with some exceptions (like the case of penta-PdP₂ and penta-PdAs₂ [131]) to be attributed to the bond electron density, the covalence, and the polarization terms in the *Eq.* 3, as explained in the above section. While, all the γ -phase IVA–VIA compounds, except *p*-PbS₂ and *p*-PbSe₂, are metals/semimetals at the HSE06 level when SOC is not considered. Some of them, for instance, the γ -phase PbSe₂ sheet exhibits a type-I nodal-line band structure around the high symmetry point Γ [Fig. 4(j)]. While penta-NiP₂ and most of its isoelectronic species tend to possess direct band gaps at the high symmetry point M, as shown in Fig. 4(k). Penta-NiSb₂ [132], also an isoelectronic species of penta-NiP₂, possesses an intrinsic type-III Dirac cone at the Fermi level, which is constructed by a flat band and an ordinary tilted band. It can be tuned into type-I/II Dirac cones *via* biaxial tensile/compressive strain. All of these electronic structures differ from the typical indirect semiconducting nature of the α - and β -phase sheets.

4.4. Other pentagon-based materials

The first Brillouin zone of the γ '-phase penta-MX structures [Fig. 4(1-m)] and γ "-phase penta-RuS₄ [Fig. 4(n)], together with their band degeneracy are similar to those of the γ -phase MX₂ structures. This is because they possess the same space group symmetry. Thus, we skip the detailed discussions on those materials, and move to the electronic structures of the ternary pentagon-based structures. For the α '-, β '- and β "-phase 2D structures with the orthorhombic symmetries like P2₁, the first Brillouin zone of these ternary pentagon-based sheets can be represented with the high symmetry path $\Gamma \rightarrow X \rightarrow M \rightarrow Y \rightarrow \Gamma$, like that of the β -phase sheets. The two-fold band degeneracy along the M \rightarrow Y (or M \rightarrow X, depending on the selection of lattice vectors **a** and **b**) path is found due to the screw axis symmetry {2₀₁₀ | 0, $\frac{1}{2}$, 0} in these structures, as shown in Fig. 4(o-p). Meanwhile, for the α "-phase 2D structures with the orthorhombic Pma2 symmetry, the first Brillouin zone is also represented with the high symmetry path $\Gamma \rightarrow X \rightarrow M \rightarrow Y \rightarrow \Gamma$, and the two-fold band degeneracy is found along the M \rightarrow Y path, as illustrated in Fig. 4(q).

4.5. Carrier mobility

2D materials with high carrier mobility [150,151] can have applications in high-performance field-effect transistors. The pentagon-based sheets in all phases are no exception. The carrier mobility μ of 2D materials is usually expressed by the Bardeen–Shockley formula, as given in *Eq.* (4) within the deformation potential (DP) theory, which is used for the α - and γ -phase sheets where the *x* and *y* directions are equivalent.

$$\mu_{x} = \mu_{y} = \frac{2e\hbar^{3}C_{2D,x}}{3k_{B}T\left(m_{x}^{*}\right)^{2}E_{1,x}^{2}},$$
(4)

where m_x^* , $C_{2D,x}$, and $E_{1,x}$ are the effective mass, the in-plane elastic modulus, and the deformation potential along the *x* axis, respectively. While, for the materials in other phases like in the β -phase with anisotropic effective mass, the carrier mobility can be expressed by *Eq.* (5),

$$\mu_{x} = \frac{e\hbar^{3}C_{2D,x}}{k_{B}T(m_{x}^{*})^{\frac{3}{2}}(m_{y}^{*})^{\frac{1}{2}}E_{1,x}^{2}}}$$

$$\mu_{y} = \frac{e\hbar^{3}C_{2D,y}}{k_{B}T(m_{x}^{*})^{\frac{1}{2}}(m_{y}^{*})^{\frac{3}{2}}E_{1,y}^{2}},$$
(5)

where m_y^* , $C_{2D,y}$, and $E_{1,y}$ are the effective mass, the in-plane elastic modulus, and the deformation potential along the y axis, respectively. The carrier mobilities of the pentagon-based structures based on the DP theory are summarized in Table 8. However, it should be mentioned that the Bardeen–Shockley formula was proposed for isotropic systems, while Eq. (5) is a simple expansion of Eq. (4). For example, when studying the carrier mobility along the x axis, it completely ignores the scattering processes introduced by the phonons propagating along the y axis because the formula only includes the deformation potential and elastic modulus along the x axis. A properly generalized form of this formula is deduced

Structure	Phase	μ_e	μ_h	Ref.
PG	α	2.274	0.127	[145]
penta-P ₂ C	α	$0.912 \sim 0.954^{a}$	$0.031 \sim 0.145^{a}$	[34]
penta-As ₂ C	α	0.147	$0.105 \sim 15.2^{a}$	[34]
penta-Sb ₂ C	α	$0.194 \sim 0.195^{a}$	$0.363 \sim 0.752^{a}$	[34]
penta-SiC ₂	α	0.25	1.9, 0.13 ^b	[69]
		0.0274	0.2588	[143]
penta-SiAs ₂	α	2.085	8.422	[71]
T-GeP ₂	α	2.63 ^c	0.249 ^c	[99]
penta- γ PdS ₂	α	0.00252	_	[127]
penta-PdS ₂	β	0.003940(x), 0.013749(y)	0.164415(x), 0.063194(y)	[65]
1 2	,	0.004097(x), 0.016911(y)	0.033925(x), 0.009173(y)	[87]
		0.00156(x), 0.00856(y)	_	[127]
penta-PdSe ₂	β	0.017713(x), 0.063021(y)	0.148592(x), 0.399768(y)	[65]
1 2	,	0.015992(x), 0.021159(y)	0.192899(x), 0.149803(y)	[64]
		0.002910(x), 0.022901(y)	0.053455(x), 0.018459(y)	[32]
penta-PdTe ₂	в	0.026855(x), 0.054575(y)	0.292489(x), 0.745475(y)	[65]
PtP ₂ H ₂	β	0.116(x), 0.161(y)	0.097(x), 0.177(y)	[23]
22	r	$0.174(x), 0.238(y)^{c}$	$0.106 (x), 0.226 (y)^{c}$	[23]
PdSSe	β'	0.002073(x), 0.005431(y)	0.083173(x), 0.065302(y)	[73]
PdSSe	β"	0.000585(x), 0.001325(y)	0.252044(x), 0.092850(y)	[73]
penta-NiP ₂	v	1.7	2.6	[146]
F 2	1	0.0786074	0.8544841	[96]
		0.0067695°	0.0006541 ^c	[96]
		$0.54 \sim 0.71^{a}$	$4.45 \sim 6.35^{a}$	[131]
penta-NiAs ₂	ν	2.2	2.9	[146]
F	1	$4.97 \sim 5.50^{a}$	$3.11 \sim 4.95^{a}$	[131]
		1 47	193	[67]
penta-PdP ₂	ν	1.23	13.77	[147]
penta i ai 2	T	1.3	1.3	[146]
		$2.71 \sim 3.96^{a}$	$60.84 \sim 84.25^{\circ}$	[131]
		4 312	14.60	[148]
penta-PdAs ₂	ν	1.81	51.56	[147]
penta i anoz	T	19	51.4	[146]
		$4.18 \sim 5.64^{a}$	$31.74 \sim 89.64^{a}$	[131]
		2 99	54 11	[148]
		1 27	34 27	[67]
nenta-PtN ₂	1/	11.27	9 36	[149]
penta 1 tiv2	Y	21.9	13.2	[143]
nenta-PtP ₂	1/	14.4	3.8	[146]
penta i ti 2	r	$11.79 \sim 15.36^{a}$	5.0° 5 38~ 5 57 ^a	[131]
penta-PtAs _a	1/	25.6	72	[146]
penta 10.62	r	$836 \sim 1309^{3}$	$427 \sim 621^{a}$	[120]
		17.07	4.80	[67]
nenta-NhTe	×′	2 <i>A</i> 2	2.60	[03]
$penta-7p_{-}C_{-}P_{-}$	Y	2.72 6 2211 (v) 0 0145 (v)	0.0075(x) 0.8680(y)	[30]
Penna-Zingegrig	-	0.2211(x), 0.0143(y)	0.0373 (x), 3.0003 (y)	[20]

Note:

^aThe mobilities along the equivalent x and y directions in a tetragonal lattice were found to be different.

^bValues of each degenerate band.

^cEvaluated at the HSE06 level, others at the PBE level.

by Lang et al. [152] as follows, which has been proved to be reliable for anisotropic systems like layered transition metal dichalcogenides [153].

$$\begin{cases} \mu_{x} = \frac{e\hbar^{3} \left(\frac{5C_{11}+3C_{22}}{8}\right)}{k_{B}T(m_{x}^{*})^{\frac{3}{2}}(m_{y}^{*})^{\frac{1}{2}} \left(\frac{9E_{1,x}^{2}+7E_{1,x}E_{1,y}+4E_{1,y}^{2}}{20}\right)}{e\hbar^{3} \left(\frac{3C_{11}+5C_{22}}{8}\right)} \\ \mu_{y} = \frac{e\hbar^{3} \left(\frac{3C_{11}+5C_{22}}{8}\right)}{k_{B}T(m_{x}^{*})^{\frac{1}{2}}(m_{y}^{*})^{\frac{3}{2}} \left(\frac{4E_{1,x}^{2}+7E_{1,x}E_{1,y}+9E_{1,y}^{2}}{20}\right)}{20} \end{cases}$$
(6)

Although the carrier mobility of the same structure from different reports is not always the same quantitatively, many of the reported carrier mobilities are above 10^3 cm² V⁻¹ s⁻¹. The most significant one among them is the hole mobility μ_h of penta-PdAs₂, which is as high as $\sim 5 \times 10^5$ cm² V⁻¹ s⁻¹, as reported by several groups [67,131,146–148]. While the lowest one is the electron mobility μ_e of β "-phase PdSSe along the *x* axis, i.e. 5.85 cm² V⁻¹ s⁻¹. For the β -phase sheets and

their derivatives, it has been found that the carrier mobilities along different axial directions are significantly different. It is well-known that different functionals treat the exchange correlation interactions of electrons in different ways, thus, resulting in different values of the carrier mobility. For example, as compared with the commonly used PBE functional, the HSE06 functional provides more accurate electronic band gap with a steeper band dispersion and a smaller effective mass, thus, leading to a larger carrier mobility, as is the case with PtP₂H₂, where the carrier mobility at the HSE06 level is about 1.5 times larger than that at the PBE level [23].

Besides, it is also worth mentioning that the carrier mobility of 2D systems calculated based on the DP theory could be overestimated in orders of magnitude with respect to experimental results, as found in black phosphorus [151,154]. For instance, the values of μ_e and μ_h for penta-PdSe₂ monolayer were calculated to be in the range of 29~630 and 184~3998 cm² V⁻¹ s⁻¹, respectively, based on the DP approach [32,64,65], and the value of μ_h is an order of magnitude larger than that of μ_e . While, by using the self-energy relaxation time approximation [155] in the electronphonon coupling scheme, a more accurate method, the corresponding values of penta-PdSe₂ monolayer were found to be 2.5~13.2 and 7.1~9.7 cm² V⁻¹ s⁻¹ [156], respectively, depending on the crystalline orientation. The values of μ_e and μ_h for 4-layered penta-PdSe₂ were calculated to be 121.9~167.8 and 13.1~20.1 cm² V⁻¹ s⁻¹ [156], respectively. These values are comparable to experimental results in both the absolute value and the relative magnitude of μ_e and μ_h [16,25,84,86,88,157,158], where the optimized field-effect mobility of electrons and holes were found to be in the range of 88~294 and 10~57 cm² V⁻¹ s⁻¹, respectively for multilayered penta-PdSe₂ sheets. In addition, both theoretical and experimental results show thickness-dependent electronic transport properties in penta-PdSe₂. This highlights the importance of carefully studying the carrier mobility for both monolayer and multilayer systems, although it is difficult to measure the carrier mobility in penta-PdSe₂ monolayer.

4.6. Topological quantum states

It has been demonstrated that many bulk and 2D crystalline materials are topologically nontrivial [159–161], which is also the case with some pentagon-based 2D materials. For example, a number of semiconducting α - and γ -phase MX₂ sheets have been found to be topological insulators with quantum spin Hall effect, including α -phase SnX₂ (X = Se, Te) [59], γ -phase SnX₂ (X = S, Se, Te) [59], γ -phase *p*-PbX₂ (X = S, Se, Te) [62], and penta-RuS₄ [60]. They exhibit conductive edge states, as shown in Fig. 5(a–e), and their topological features were confirmed by the calculated topological invariant $Z_2 = 1$ [162]. The topological states in these pentagon-based sheets originate from the band inversion between the in-plane p_x , p_y orbitals and the out-of-plane p_z orbitals of both M and X atoms due to the crystal field effect and spin–orbit coupling, as shown in the bottom panels in Fig. 5(a–c).

Li et al. [45] reported another intriguing pentagon-based topological material, *sp*-MoS₂, which is a γ -phase pentagonal structure. It exhibits quantum anomalous spin Hall effect as confirmed by the first Chern number, C = -2. Its topological chiral edge states along the high-symmetry path Γ -M [Fig. 5(e)] are contributed from the d_{xz} and d_{yz} orbitals of the Mo atoms, leading to a quantum anomalous Hall conductivity of 370 Ω^{-1} cm⁻¹ ($\sim 2 e^2/h$). Detailed discussions on the ferromagnetism in *sp*-MoS₂ can be found in Section 5.1. This study was followed up by the research on WSe₂ [134], an isoelectronic species of MoS₂, whose edge state is shown in Fig. 5(f). The Chern number *C* and the quantized Hall conductivity of WSe₂ were found to be -1 and $-470 \ \Omega^{-1} \ cm^{-1}$, respectively. It is also worth noting that the electronic structure of penta-MnN₂ [46] is analogous to that of *sp*-MoS₂ [45] and WSe₂ [134]. This implies that the topological behaviors of some pentagon-based materials might have been overlooked.

5. Other physical properties

Besides the previously discussed unique properties such as negative Poisson's ratio, ultrahigh ideal strength and intriguing electronic properties, other physical properties of pentagon-based 2D materials have also been attracted extensive attention with intensive explorations. In this section, we review some typical physical properties of these pentagonbased materials, including magnetism, lattice thermal conductivity, piezoelectricity, second harmonic generation, and ferroelasticity.

5.1. Magnetism

Magnetism is one of the important physical properties of materials, which usually arises in crystalline structures containing TM atoms with partially occupied *d* or *f* orbitals, where the unpaired electrons are coupled *via* exchange interactions to form long-ranged ferromagnetic (FM), antiferromagnetic (AFM), or ferrimagnetic (FiM) coupling configurations, exhibiting intrinsic magnetism. Since the discovery of the giant magnetoresistance effect, finding new magnetic materials for spintronic devices has been hotly pursued. Considerable research has also been performed on the magnetic behavior of pentagon-based 2D materials in recent years. It has been found that many β - and γ -phase structures containing TM as the M atoms are magnetic, including the FM *sp*-MoS₂ [45], penta-WSe₂ [134], penta-MnN₂ [112], penta-CoAsS [129] and penta-AlN₂ [39], and the AFM penta-CoS₂ [41], FeS₂ [47], penta-FeASS [43], and penta-CoBiS [92]. In the following, we discuss magnetism in pentagonal 2D materials by focusing on penta-metal-chalcogenide and penta-metal-nitride sheets.



Fig. 5. Theoretical conductive edge states and schematic of the band inversion in (a) α -phase SnTe₂, (b) γ -phase SnTe₂, (c) penta-RuS₄. Theoretical conductive edge states in (d) *p*-PbS₂, (e) *sp*-MoS₂, (f) WSe₂. (a-b) Adapted with permission from Ref. [59]; (c-f) adapted with permission from Ref. [45,60,62], and [134], respectively.

We begin with the discussion of magnetism in pentagonal metal-chalcogenide sheets. It is well-known that molybdenum disulfide (MoS₂) sheets are nonmagnetic either in their conventional 1H- or 2T-phase [163,164]. However, it was found when MoS₂ sheet is in pentagonal configuration, named sp-MoS₂ [45], becomes an intrinsic ferromagnet with a magnetic moment of 2 $\mu_{\rm B}$ on the Mo site and a high Curie temperature of 200 K, as shown in Fig. 6(a). It behaves as a half semimetal, and possesses spin-polarized Dirac fermions around the Fermi level, where the linear dispersion of spin-up sub-band is dominated by the Mo d_{xz} and d_{yz} orbitals, intrinsically different from the p_z orbital of group-IVA elemental monolayers such as graphene or silicene. Moreover, when spin-orbit couplings are included, the magnetic Dirac band is gapped, hosting quantized conductance channels. This work shows that a nonmagnetic 2D material can become magnetic in some cases when its geometric structure is changed to a pentagonal configuration due to the crystal-field effect. For instance, in penta-MoS₂, according to the crystal-field theory, the energies of d orbitals of the planar four-fold coordinated Mo atom are in decreasing order of $d_{x^2-y^2}$ (for dsp^2 hybridization), d_{xy} , d_{z^2} , and degenerated d_{xz} and d_{yz} , and the energy of the p_z orbital of Mo is higher than all of these d orbitals. However, the d_{z^2} and the p_z orbitals of Mo atom can be stabilized in the γ -phase pentagon-based sheets as they are included in the lattice-wide conjugated π bond. And, specifically, such inversion between d_{z^2}/p_z and d_{xz}/d_{yz} orbitals in energy level, together with the electronic structure of the sp^2 hybridized S atoms in the dimer, results in the partially occupied d_{xz} and d_{vz} orbitals in the sp-MoS₂, leading to the ferromagnetic coupling.

In the geometric structure of *sp*-MoS₂ sheet [45], when the Mo atom is replaced with Co, penta-CoS₂ [41] can be obtained. Based on DFT+U method, it was found that the penta-CoS₂ sheet is an AFM semiconductor with an indirect band gap of 2.24 eV, and magnetocrystalline anisotropy energy (MAE) shows that the easy axis of the AFM ordering is along the *b* axis with a sizable MAE of 153 μ eV per Co ion. By calculating the magnon frequencies at different spin-spiral vectors, the Néel temperature was found to be 20.4 and 13.3 K in the mean field and random phase approximations, respectively. Although the energy difference between the FM and AFM configurations strongly depends on biaxial strain, the ground state remains the AFM ordering in the strain range of $-4\% \sim +4\%$, as shown in Fig. 6(b).



Fig. 6. Change of the calculated magnetic moment with temperature in (a) *sp*-MoS₂, (c) CoAsS, and (d) penta-MnN₂. (b) Calculated energy difference between the AFM and FM states in penta-CoS₂. (a–d) Adapted with permission from Ref. [41,45,129], and [46], respectively.

The AFM coupling ordering in penta-CoS₂ sheet follows the Goodenough–Kanamori rules [165,166], which state that the type of magnetic ordering depends on the metal–nonmetal–metal bond angle for the superexchange interactions between two metal ions linked by a nonmetal ion. If their angle is close to 90°, the resulting magnetic ordering is FM; if it is greater than 90°, the corresponding ordering is AFM. The calculated Co–S–Co angle is 118.5°, therefore, the AFM ordering is preferable over the FM due to the superexchange interactions, as predicted by the theoretical work on penta-CoS₂ sheet [41]. The magnetic coupling between the two Co ions is mediated by the bridging non-metallic S ions. This can be understood by that one electron in the *d* orbitals (e.g., in spin-up d_{z^2}) of a Co ion overlaps with one of the p_z orbitals overlaps with the spin-down p_z) of the bridging S ion to form a π bond, while a remaining spin-up electron in the p_z orbital overlaps with the spin-down d_{z^2} orbital in another Co ion. The net effect of such superexchange interactions leads to the AFM ordering. In the ground state, each Co ion carries a magnetic moment of 1.19 μ_B . Similarly, replacing Co with Fe, penta-FeS₂ sheet can be obtained, where the magnetic coupling between the Fe ions is also AFM [47], as is the case with penta-CoS₂ sheet.

The magnetic properties of penta-CoS₂ sheet can be further turned by replacing one S in the S₂ dimer with As atom, leading to pentagonal CoAsS sheet [129]. It was found that the replacement induces the magnetic transition from the AFM to FM due to the higher electronegativity of As atom, resulting in a weakened bridging role on the superexchange interactions between the Co ions. The Currie temperature of the penta-CoAsS sheet was found to be 95 K based on Monte Carlo simulation, as shown in Fig. 6(c). In addition, the magnetocrystalline anisotropy energy was found to be significantly enhanced to 460 μ eV/Co ion, much higher than that of 153 μ eV/Co ion of the penta-CoS₂ sheet because of the heavier mass of As ions associated with stronger SOC as compared with S ions. In the ground state, each Co ion carries a magnetic moment of 2 μ_B , larger than the value of 1.19 μ_B in penta-CoS₂ sheet.

As discussed above, the magnetic properties of penta- CoS_2 sheet can be effectively modulated by replacing one S with As atom, due to the change of the SOC associated with their mass difference. It would be very interesting to know if the As atom in penta-CoAsS is further replaced by an even heavier one like Bi, how the magnetic properties change? Recently, it was found [92] that the penta-CoBiS sheet is indeed mechanically, dynamically and thermally stable, and the magnetic coupling between the Co ions switches to AFM with the FM state higher in energy by 53.46 meV. The local magnetic moment on Co site was found to be 1.82 μ_B . More interestingly, this penta-CoBiS sheet has an in-plane easy axis and possesses large intrinsic Dzyaloshinskii–Moriya interaction [167] because of the broken inversion symmetry and a strong SOC originated from heavy Bi atom. The Néel temperature was predicted to be 206.59 K, much higher than the value of 20.4 K of penta-CoS₂ sheet.

In addition, it was found that the AFM ground states exist in penta-CrX (X=S, Se, Te) monolayers [42], and each Cr ion carries a magnetic moment of 2.91, 2.92, and 3.02 μ_{B} , for X=S, Se, Te, respectively, due to the superexchange interactions

between the Cr ions mediated by X ion. These three pentagonal sheets are semiconductors with band gap of 2.38, 2.52, and 1.30 eV, decreasing from S to Se and Te.

Besides penta-metal-chalcogenide sheets, the magnetic properties of pentagonal metal-nitride sheets are also interesting. The main reasons are: (1) the atomic radius of N is smaller than that of S atom, which can shorten the distance between the metal ions in pentagonal metal-nitride sheets and enhance the magnetic coupling; (2) Compared with S, N atom is more effective in mediating the magnetic couplings. For example, Mn₂ is an AFM dimer, it becomes FM when N is introduced [168]. While for Mn atom, because of its special electronic configuration of $3d^54s^2$, it has been widely used for the design of various magnetic materials, especially for 2D FM monolayers. For instance, a graphene-like hexagonal MnN monolayer, named Hex–MnN, is FM with Tc above room temperature (368 K) [169]. While, interestingly, Zhao et al. found [46] when the structural unit is changed to pentagon, the resulting penta-MnN₂ sheet not only has a FM ground state, but also exhibits a high Currie temperature $T_{\rm C}$ of 913 K, and can be further improved to 956 K when the biaxial tensile strain of 3% is applied. The AFM and NM states are higher than the FM one in energy by +0.42 eV and +3.12 eV per cell, respectively, as shown in Fig. 6(d). The local magnetic moment on each Mn and N is 3.6 $\mu_{\rm B}$ and $-0.3 \mu_{\rm B}$, respectively, leading to a net magnetic moment of 6.0 $\mu_{\rm B}$ per unit cell containing two Mn and four N atoms. The penta-MnN₂ sheet is half-metallic, the spin-up channel shows metallic characteristics whereas the spin-down channel is semiconducting with a band-gap of 1.12 eV. Compared to the hexagonal MnN monolayer [169], the exchange interaction between the Mn atoms is significantly enhanced in penta-MnN₂ due to its unique geometric configuration with pentagonal structural units containing N₂ dimers. In addition, it was found [49] that the penta-MnN₂ sheet displays a large perpendicular magnetic anisotropic energy of 0.207 meV/Mn, which is one or two orders of magnitude larger than those of bulk Co (65 μ eV/atom), Fe (1.4 μ eV/atom) and Ni (2.7 μ eV/atom) [170]. As to the magnetic order of pp-Fe₄N₂ with a unique Fe–Fe bond [95], a similar trend was found. Despite the antiferromagnetic nature of Fe_2 dimers [171], pp- Fe_4N_2 is ferromagnetic with a magnetic moment of 3.5 $\mu_{\rm B}$ on each Fe atom. The pp-Fe₄N₂ sheet is also half-metallic with a semi-metallic spin-up channel and a semiconducting spin-down channel, and a high Curie temperature of 428 K.

It is also interesting that the graphene-like AlN sheet [172,173] is nonmagnetic, however, the penta-AlN₂ sheet is a FM semiconductor with a band gap of 0.3 eV and a Curie temperature of 22 K [44]. The magnetic moment comes from the unpaired electron on the $\pi_{2p_z}^*$ orbital.

In the last part of this section, we discuss the Ising model for the magnetism of penta-sheets with the Cairo pentagonal lattice [174] to explore the general features.

The Hamiltonian of the Cairo pentagonal Ising model can be expressed as

$$H = -J_1 \sum_{\langle i,j \rangle} s_i s_j - J \sum_{\langle k,l \rangle} s_k \tau_l, \tag{7}$$

where *s* is for the spin of three-fold coordinated atom, and τ is for the spin of the four-fold coordinated atom, and $s_i = \pm 1$ and $\tau_l = \pm 1$. J_1 corresponds to the interaction between s_i and s_j , *J* is for the exchange interaction between spin s_k and spin τ_l , as shown in Fig. 7(a). Although the theoretical model only considered the nearest-neighbor magnetic coupling, the magnetic moments on the four-fold coordinated atoms couple *indirectly* with each other through the three-fold coordinated atoms. While it is necessary to include the next nearest-neighbor coupling for a better description of the magnetic behaviors of the penta-sheets with the magnetic atom on the four-fold coordinated sites. The magnetic phase diagram, total magnetization and specific heat [174] can be further derived, as shown in Fig. 7(b-d). One can see that the magnetic properties depend on the exchange interaction parameters *J* and *J*₁, which can be modulated by placing different atoms on the 3- and 4-coordinated sites and by changing the symmetry of the lattice, thus, resulting in rich magnetic behaviors like FM, FiM, and frustrated states (FRU), as observed in above discussed β - and γ -phase penta-sheets. The results predicted with the Ising model are qualitatively consistent with the DFT ones for the magnetism of penta-sheets.

5.2. Lattice thermal conductivity

Thermal conductivity is of great importance for technological applications in thermoelectric conversion and in thermal management where materials with high or low thermal conductivity are both required in different scenarios. The lattice thermal conductivity κ_L , which overwhelms the electronic thermal conductivity in semiconductors, is usually calculated by solving the Boltzmann transport equation based on the scattering processes of phonons,

$$\frac{\mathrm{d}f_{\lambda}}{\mathrm{d}t} = \left.\frac{\partial f_{\lambda}}{\partial t}\right|_{\mathrm{diffusion}} + \left.\frac{\partial f_{\lambda}}{\partial t}\right|_{\mathrm{scattering}} = -\nabla T \cdot \boldsymbol{v}_{\lambda} \frac{\partial f_{\lambda}}{\partial T} + \left.\frac{\partial f_{\lambda}}{\partial t}\right|_{\mathrm{scattering}} = 0,\tag{8}$$

where f_{λ} and \mathbf{v}_{λ} are the phonon distribution function and group velocity of the phonon mode λ , respectively. Lattice thermal conductivity can be calculated from the following equation,

$$\kappa_{L}^{\alpha\beta} = \frac{1}{k_{\rm B}T^{2}\Omega N} \sum_{\lambda} f_{0} \left(f_{0} + 1\right) \left(\hbar\omega_{\lambda}\right)^{2} v_{\lambda}^{\alpha} F_{\lambda}^{\beta},\tag{9}$$

where α and β denote the projections along axial directions *x*, *y* and *z*, Ω is the volume of the cell, f_0 is the Bose–Einstein distribution, and F_{λ} corresponds to the expansion of f_{λ} against the temperature gradient ∇T . In the scattering



Fig. 7. (a) Theoretical configuration with spin and exchange interaction, (b) magnetic phase diagram, (c) temperature dependence of the total magnetization, and (d) specific heat as function of temperature. *Source:* (a–d) Adapted with permission from Ref. [174].

processes of phonons, the energy and crystal momentum of the absorbed and emitted phonon modes are conserved, namely, $\Sigma \omega_{\lambda,absorb} = \Sigma \omega_{\lambda,emit}$ and $\Sigma q_{\lambda,absorb} = \Sigma q_{\lambda,emit} + G$, where G is a linear combination of the reciprocal lattice vectors and the nonzero G leads to Umklapp scattering.

By considering the three-phonon scattering processes, the lattice thermal conductivities κ_L of some α -, α' -, β -, and γ -phase sheets were calculated. These include PG [106,175,176], penta-silicene [11], penta-germanene [11], pentagonal tellurene [12], penta-CN₂ [176,177], penta-SiC₂ [106], penta-SiN₂ [106], penta-X₂C (X=P, As, Sb) [178], penta-PdX₂ (X = S, Se Te) family [65], penta-PtX₂ (X = S, Se Te) family [66], penta-MN₂ (M =Ni, Pd, Pt) family [133], and penta-MAs₂ (M =Ni, Pd, Pt) family [67], as listed in Table 9. The κ_L of isoelectronic species of the α -phase MX₂ structures decreases significantly with the increase of atomic mass. For instance, κ_L of the penta-X₂C family drops by three orders of magnitude from 1027 W m⁻¹ K⁻¹ in penta-CN₂ [177] to 0.72 W m⁻¹ K⁻¹ in penta-Sb₂C [178], and κ_L of PG and penta-CN₂ is also reduced to 101 [106] and 185 W m⁻¹ K⁻¹ [106] when the four-fold coordinated C atom is replaced by Si. In the β -phase sheets, it was found that the κ_L of penta-PdX₂ and penta-PtX₂ families falls in the range of 10⁰ ~10¹ W m⁻¹ K⁻¹ [65,66], and the value of κ_L along the stiff y direction is larger than that along the soft x direction. A decrease in κ_L with the increase of the atomic mass of X atoms was found in these β -phase sheets, though no such relation was found for the M atoms, indicating that the p-block X atoms in β -phase sheets play a more important row in κ_L than the TM atoms. Similarly, the κ_L of the γ -phase penta-MN₂ family and penta-MAs₂ family falls in the range of 10² [133] and 10⁰ W m⁻¹ K⁻¹ [67], respectively, and no general relationship was found between the κ_L and the atomic mass of M atoms. Interestingly, the κ_L values of the penta-PdAs₂ (2.9 W m⁻¹ K⁻¹) [67] and penta-PtAs₂ (3.6 W m⁻¹ K⁻¹) [67] are numerically close to those of β -phase penta-PdSe₂ (2.91 W m⁻¹ K⁻¹) [65] and penta-PtAs₂ (3.12 W m⁻¹ K⁻¹) [66] along their x direction, respectively

Hu and co-workers studied the effect of stain on the lattice thermal conductivity κ_L of some α -phase MX₂ sheets, including penta-SiC₂ and penta-SiN₂. They found that the former exhibits an unusual nonmonotonic up-and-down κ_L -strain relationship, while the latter has 1 order of magnitude enhancement due to the strain induced phase transformation from the buckled α -phase to the planar γ -phase [106], as shown in Fig. 8(a). They further studied the effect of lone-pair electrons on the thermal conductivity of penta-CN₂, and made the conclusion that lone-pair electrons in 2D penta-based materials do not necessarily lower down the κ_L [176]. The mechanism of the enhanced lattice thermal conductivity



Fig. 8. (a) Calculated lattice thermal conductivity of PG, penta-SiC₂, and penta-SiN₂ (from top to bottom) as a function of external strain. (b) Schematic diagram for the mechanism of the enhanced theoretical lattice thermal conductivity by lone-pair electrons in penta-CN₂. *Source:* (a-b) Adapted with permission from Ref. [106,176], respectively.

by lone-pair electrons is schematically illustrated in Fig. 8(b). Very recently, Zhang et al. [156] studied the change of lattice thermal conductivity of penta-PdSe₂ with its thickness, and found an intriguing trend that the lattice thermal conductivity of odd-layered penta-PdSe₂ sheets is ~50% lower than that of the even-layered sheets, which is different from the weak dependence of lattice thermal conductivity on the stacking thickness of PG [179]. The calculated lattice thermal conductivities of these few-layered penta-PdSe₂ at 300 K are in the range of 10~30 W m⁻¹ K⁻¹, which agree well with the values measured by using micro-Raman thermometry (10.95 and 15.58 W m⁻¹ K⁻¹ along the *x* and *y* directions, respectively [180]).

5.3. Piezoelectricity

Piezoelectric materials can be electrically polarized under an externally applied strain, namely, can generate internal electrical charge under applied mechanical stress, or *vice versa*. Intrinsic piezoelectric response can only occur in the materials that have semiconducting electronic feature and any noncentrosymmetric crystallographic point groups except D_4 (432), because in materials with such crystal point group symmetry, any changes in local electronic dipoles under external stress are always canceled out by their symmetric equivalents. It is known that the spontaneous electronic dipoles can lead to enhanced piezoelectric response. In recent years, 2D piezoelectric materials have attracted increased attention because the surface effect and surface modification of 2D materials can lead to altered piezoelectric properties, as is the case with graphene [183–185]. Thus, significant progress is also made in pentagon-based 2D piezoelectric materials. In principle, semiconducting α -, α '-, β '- and β "-phase pentagon-based sheets possess piezoelectricity because they all lack centrosymmetry.

The piezoelectric response of a material is usually described by the piezoelectric stress tensor $e_{ijk} = \partial P_i / \partial \varepsilon_{jk}$ and the piezoelectric strain tensor $d_{ijk} = \partial P_i / \partial \sigma_{jk}$, which are correlated by the equation

$$e_{ijk} = \sum_{j'k'} d_{ij'k'} C_{j'k'jk},$$
(10)

where P_i is the polarization, ε_{jk} and σ_{jk} are the in-plane strain and the corresponding stress, respectively, and $C_{j'k'jk}$ is the elastic modulus. The subscripts *ijk* and *j'k'jk* can also be reduced using the Voigt notation [120]. After removing the terms related to the nonexistent out-of-plane strain/stress in 2D materials, the above formula is simplified as follows:

$$\begin{pmatrix} e_{11} & e_{12} & e_{16} \\ e_{21} & e_{22} & e_{26} \\ e_{31} & e_{32} & e_{36} \end{pmatrix} = \begin{pmatrix} d_{11} & d_{12} & d_{16} \\ d_{21} & d_{22} & d_{26} \\ d_{31} & d_{32} & d_{36} \end{pmatrix} \begin{pmatrix} C_{11} & C_{12} & C_{16} \\ C_{21} & C_{22} & C_{26} \\ C_{61} & C_{62} & C_{66} \end{pmatrix}.$$

Structure	Phase	κ _L	Ref.
PG	α	167 ^a	[181]
		645	[175]
		197.85	[106]
		252.95	[176]
penta-silicene	α'	1.66 (x), 1.29 (y)	[11]
penta-germanene	α'	0.38 (x), 0.30 (y)	[11]
pentagonal tellurene	-	0.28	[12]
penta-CN ₂	α	660.71	[176]
		1027	[177]
penta-P ₂ C	α	75.27	[178]
penta-As ₂ C	α	19.11	[178]
penta-Sb ₂ C	α	0.72	[178]
penta-SiC ₂	α	101	[106]
penta-SiN ₂	α	185	[106]
penta-BCN	α'	98 ^b	[182]
penta-PdS ₂	β	4.34 (x), 12.48 (y)	[65]
penta-PdSe ₂	β	2.91 (x), 6.62 (y)	[65]
penta-PdTe ₂	β	1.42 (x), 5.90 (y)	[65]
penta-PtS ₂	β	4.27 (x), 8.86 (y)	[66]
penta-PtSe ₂	β	3.12 (x), 7.05 (y)	[66]
penta-PtTe ₂	β	1.77 (x), 5.17 (y)	[66]
penta-NiN ₂	γ	610	[133]
penta-PdN ₂	γ	350	[133]
penta-PtN ₂	γ	120	[133]
penta-NiAs ₂	γ	5.9	[67]
penta-PdAs ₂	γ	2.9	[67]
penta-PtAs ₂	V	3.6	[67]

Calculated lattice thermal conductivity κ_L (in W m⁻¹ K⁻¹) of some pentagon-based structures at room temperature.

Note:

^aCalculated using classical equilibrium molecular dynamics simulations. ^bCalculated using semi-empirical methods.

Table	10

Nonzero piezoelectric strain and stress tensor components d_{ij} and e_{ij} with Voigt notation in the different phases of pentagon-based sheets.

Phase	Nonzero d_{ij}	Nonzero e _{ij}
α	$d_{31} (= -d_{32}), d_{36}$	e_{31} (= $-e_{32}$), e_{36}
$\alpha' \& \beta'$	$d_{16}, d_{21}, d_{22}, d_{36}$	<i>e</i> ₁₆ , <i>e</i> ₂₁ , <i>e</i> ₂₂ , <i>e</i> ₃₆
α''	d ₃₁ , d ₃₂	e ₃₁ , e ₃₂
β''	d_{11}, d_{12}, d_{26}	<i>e</i> ₁₁ , <i>e</i> ₁₂ , <i>e</i> ₂₆

For the pentagon-based sheets in the different phases, the nonzero components of piezoelectric tensors are further reduced due to their symmetry constraints. The resulting nonzero piezoelectric strain tensor components d_{ij} and nonzero piezoelectric stress tensor components e_{ij} are listed in Table 10. According to their geometric characteristics, all semiconducting α -phase MX₂ and MX₅ sheets should possess pure out-of-plane piezoelectric response, while the α '- and β '-phase sheets should have both in-plane and out-of-plane piezoelectric responses, because they lack both the mirror symmetry along the *x*-y plane and the two-fold rotational symmetry along the *x* and *z* axes.

The piezoelectric properties of some ternary pentagon-based sheets have been recently studied. For instance, Zhao et al. studied the piezoelectric properties of penta-BCN [17]. They found that penta-BCN exhibits significant piezoelectric responses in its in-plane direction with the major nonzero piezoelectric strain tensor d_{16} of 1.72 pm/V and high spontaneous polarization of 3.17×10^{-10} C/m due to its unique atomic configuration with noncentrosymmetric and semiconducting features, and particularly due to the existence of the orderly arranged B–N polar bonds. Later on, Sun et al. [18] found that the piezoelectric properties of penta-CNP are more outstanding compared with penta-BCN because the N–P polar bond is stronger than the B–N polar bond in penta-BCN, leading to a larger spontaneous polarization of 4.33×10^{-10} C/m. A significant intrinsic piezoelectric response with d_{16} of 1.80 pm/V was found. For clarity, the results are summarized in Table 11. Note that the spontaneous polarization in both of the two structures is larger than that of *h*-BN (2.71 × 10⁻¹⁰ C/m) [186]. The absolute value of the out-of-plane piezoelectric response d_{36} is 0.076 and 0.1 pm/V for penta-BCN [17] and penta-CNP [18], respectively, which is larger than that of PG (0.065 pm/V) [187], but much smaller than that of the out-of-plane piezoelectric response in the Janus half-hydrogenated half-fluorinated PG sheet [0.69 pm/V (d_{31})] [188], since the α - and α '-phase sheets do not possess out-of-plane spontaneous polarization, whereas the Janus sheet can exhibit such polarization. A follow-up study showed that hydrogenated PG [187,188]. This may imply

Theoretical piezoelectric stress tensor e (in 10^{-10} C/m) and piezoelectric strain tensor d (in pm/V) of the ternary pentagon-based sheets. For comparison, the corresponding theoretical results for the hydrogenated penta-BCN (H-BCN) are also listed in this table.

Structure	e ₂₁	e ₂₂	e ₁₆	e ₃₆	<i>d</i> ₂₁	<i>d</i> ₂₂	<i>d</i> ₁₆	d ₃₆	Ref.
penta-BCN	1.93	-1.24	1.80	-0.08	0.878	-0.678	1.72	-0.076	[17]
penta-CNP	2.37	-1.21	1.78	-0.11	1.39	-0.69	1.80	-0.1	[18]
H-BCN	0.89	0.48	1.15	0.01	0.462	0.213	1.03	0.009	[37]
Structure	<i>e</i> ₁₁	e ₁₂	e ₂₆		<i>d</i> ₁₁	<i>d</i> ₁₂	d ₂₆		Ref.
CoAsS	-2.47	1.38	1.09		-3.52	3.10	2.02		[129]

Table 12

Nonzero SHG susceptibility tensor components χ_{ij} under the Voigt notation in different phases of pentagon-based sheets.

Phase	Nonzero χ_{ij}
$ \begin{array}{c} \alpha \\ \alpha' \& \beta' \\ \alpha'' \\ \beta'' \end{array} $	$\begin{array}{l} \chi_{14} \ (= \ \chi_{25}), \ \chi_{15} \ (= - \ \chi_{24}), \ \chi_{31} \ (= - \ \chi_{32}), \ \chi_{36} \\ \chi_{14}, \ \chi_{16}, \ \chi_{21}, \ \chi_{22}, \ \chi_{23}, \ \chi_{25}, \ \chi_{34}, \ \chi_{36} \\ \chi_{15}, \ \chi_{24}, \ \chi_{31}, \ \chi_{32}, \ \chi_{33} \\ \chi_{11}, \ \chi_{12}, \ \chi_{13}, \ \chi_{15}, \ \chi_{24}, \ \chi_{26}, \ \chi_{31}, \ \chi_{32}, \ \chi_{33}, \ \chi_{35} \end{array}$

that such reduction of the in-plane piezoelectric responses could be general for hydrogenated pentagon-bases sheets as hydrogenation would weaken the polarity of the polar bonds.

Apart from the piezoelectricity in the α '-phase sheets, Liu et al. [129] reported strong in-plane piezoelectric responses in β "-phase CoAsS, as shown in Table 11. While its piezoelectric stress tensor components e_{ij} are comparable with those of penta-CNP, its piezoelectric strain tensor components d_{ij} are larger by up to 5 times in magnitude, because the elastic constants of CoAsS (e.g., $C_{11} = 75.44$ N/m) are smaller than those of penta-CNP (e.g., $C_{11} = 173.32$ N/m), as summarized in Table 3.

It is worth to mention that the piezoelectric stress tensor components e_{ij} in monolayer β -phase pentagonal sheets would vanish due to the centrosymmetry in these systems. Whereas, the reported nonzero results [189], within $10^{-13} \sim 10^{-15}$ C/m order of magnitude, might be from numerical errors.

5.4. Second harmonic generation

The second harmonic generation (SHG) of light is a nonlinear optical effect where photons with the angular frequency ω are "combined" into new photons with the doubled angular frequency 2ω . This phenomenon has been observed in many systems like metal surfaces [190], plasmonic nanostructures [191], and centrosymmetric systems containing electric quadrupoles [192], while the most extensively studied systems so far are the crystals lacking centrosymmetry [193–196], where the electric dipoles under electric field of the light play an important role. The prominent features in the SHG susceptibility are generally caused by either single-photon resonance at angular frequency 2ω or two-photon resonance at angular frequency ω .

The SHG of 2D layered materials has attracted increasing interest motivated by the flexibility of photon generation, manipulation, transmission, detection, and imaging for the applications of modern on-chip nanophotonic devices [197]. In general, all the piezoelectric materials can be used for SHG due to the absence of centrosymmetry in these systems. Therefore, the α -, α '-, α ''-, β '- and β "-phase pentagon-based sheets can exhibit the essential features of SHG.

The intensity of SHG responses can be represented by the SHG susceptibility tensor components χ_{ijk} , as defined by the equation

$$\Delta P_i = \varepsilon_0 \sum_{jk} \chi_{ijk} E_j E_k, \tag{11}$$

where E_j/E_k is the electric field of light, and ΔP_i is the nonlinear polarization. Similar to the dielectric function, the value of SHG susceptibility is described by a complex number, where the real and imaginary parts correspond to the intensity of polarization and the hysteresis of the SHG response, respectively. Unlike the non-existence of out-of-plane strain and stress in 2D materials, the out-of-plane incident electric field and the resulting dipole remain universal, so that all nonzero SHG susceptibility tensor components allowed by symmetry can exist in these pentagon-based sheets. A summary of the non-zero tensor components for these piezoelectric materials (with the subscript *jk* simplified by the Voigt notation [120]), is given in Table 12. Unlike a majority of previously reported 2D materials whose SHG responses are restricted to the inplane directions due to the existence of the in-plane mirror symmetry [196,198,199], the pentagon-based sheets possess not only in-plane but also out-of-plane SHG responses. This is because the excited electron dipoles in both directions are allowed due to the lack of centrosymmetry and in-plane mirror symmetry in these structures.

Shen et al. studied the out-of-plane SHG response in penta- ZnS_2 monolayer [38]. They found that the imaginary part of the out-of-plane susceptibility is up to -8 pm/V for the incident photons with the energy of 3.19 eV [38]. This peak in



Fig. 9. (a) Calculated imaginary part of nonzero SHG susceptibility of penta- ZnS_2 . (b) Electron transitions contributed to the peak in the SHG response in penta- ZnS_2 , and (c) corresponding electronic states. Dependence of experimental SHG intensity in PdSe₂ on the layer number (d), and the anisotropy of experimental integrated SHG intensities (e) for 4L PdSe₂. The purple dots in (e) indicate the polar plot of experimental integrated SHG intensities excited by the 880 nm laser, and the corresponding fitting result is denoted by the solid red curve. *Source:* (a-c) Adapted with permission from Ref. [38]; (d-e) adapted with permission from Ref. [200].

the SHG response of penta-ZnS₂ was found to coincide with the imaginary part of its dielectric function at the doubled photon energy of 6.38 eV. This connection was explained by the following recursion formula of the *n*th-order perturbation to the density matrix $\rho^{(n)}$ with respect to the incident electric field *E*,

$$\frac{\partial \rho^{(n)}}{\partial t} = \frac{1}{i\hbar} \left\{ \left[H_0, \rho^{(n)} \right] + \left[-e\mathbf{r} \cdot \mathbf{E}, \rho^{(n-1)} \right] \right\},\tag{12}$$

where the 2nd-order perturbation to density matrix $\rho^{(2)}$, which corresponds to the SHG responses, can be obtained from the Hamiltonian of the system and the 1st-order perturbation term $\rho^{(1)}$, which represents the electronic structure and dielectric responses of penta-ZnS₂. The contribution of the dielectric response is further distributed to direct transitions in the reciprocal space, and to specific electronic states concerning the polarized Zn–S bonds in penta-ZnS₂, as illustrated in Fig. 9 (a–c).

Besides penta-ZnS₂ monolayer, the SHG of penta-PdSe₂ multilayers was also studied [88,200,201]. Although penta-PdSe₂ monolayer has centrosymmetry due to the C_{2h} (2/m) point group and $P2_1/c$ (No. 14) space group, even-numbered β -phase penta-PdSe₂ layers have been found to possess a C_{2v} (mm2) point group and $Pca2_1$ (No. 29) space group with a broken inversion symmetry [16,88,200,201]. For bilayer (BL) and four-layer (FL) PdX₂ (X=S, Se), the SHG susceptibility tensor has five independent nonzero elements, i.e., $\chi_{xxy}^{(2)}$, $\chi_{yyx}^{(2)}$, $\chi_{yyy}^{(2)}$, $\chi_{yzz}^{(2)}$ and $\chi_{zyz}^{(2)}$ [201]. Among the nonzero SHG susceptibility elements, $\chi_{yxx}^{(2)}$ and $\chi_{yyx}^{(2)}$ spectra show a pronounced peak with almost the same maximum value of ~1.2 × 10³ pm/V at slightly different photon energies of 3.1 and 3.3 eV, respectively. The $\chi_{yyy}^{(2)}$ spectrum of BL PdS₂ exhibits the second maximum of 0.9 × 10³ pm/V at 1.6 eV, while for BL PdSe₂, the $\chi_{yyy}^{(2)}$ spectrum of BL PdSe₂ has a broad twin peak of magnitude of 1.1 × 10³ pm/V centered at ~1.9 eV. For FL PdSe₂, $\chi_{yyy}^{(2)}$ and $\chi_{yxx}^{(2)}$ spectra peak at 1.2 and 1.7 eV with the large maximum values of 0.94 × 10³ and 1.2 × 10³ pm/V. All the values of $\chi^{(2)}$ spectra for the FL PdS₂ structures are generally smaller than the corresponding spectra of the BL PdS₂ structures, and the maximum magnitude of $\chi^{(2)}$ can reach 1.4 × 10³ pm/V for bilayer PdSe₂ at 1.9 eV and 1.2 × 10³ pm V⁻¹at 3.1 eV for bilayer PdS₂.

Recently, the SHG properties of few-layer PdSe₂ nanoflakes were measured at the excitation wavelengths of 800 and 880 nm [88,200]. For the monolayer region, the detected SHG signal was negligible. When the laser spot was switched to the bilayer area, strong signals can be observed at 400 nm [200]. In order to further demonstrate the dependence of the SHG signal on the number of PdSe₂ layers, the spatial mapping was implemented. Fig. 8(d) shows the SHG signal excited at the fixed wavelength of 880 nm in 1–8 L PdSe₂. The integrated intensity of SHG varied with the layer numbers, represented by the blue dots. One can see that the SHG signals from even-numbered layers of PdSe₂ are much stronger as compared with those from odd-numbered layers and the bulk PdSe₂, which are almost negligible. Among the even-layered penta-PdSe₂ sheets, the highest SHG signal was found in the four-layered system at the wavelength of 440 nm, corresponding to the photonic excitation at 880 nm and the photon energy of 1.41 eV [200]. The SHG susceptibility of the 4L system was measured to be 51.7 pm/V, which is comparable with that of multilayered graphene [202]. The experimental results for the 4L PdSe₂ sample are not in agreement with the theoretical ones [201], one of the possible reasons is that the flakes was used in measurement while an ideal 2D sheet was used in calculation. In addition, as shown in Fig. 8(e), the SHG response of multi-layered penta-PdSe₂ is highly anisotropic, depending on the direction of electric field of light, especially the SHG intensity along 90 degrees is much stronger than that of zero direction.

5.5. Ferroelasticity

Parallel to ferroelectricity and ferromagnetism, the strain-induced ferroelasticity in 2D materials has also received increasing attention in recent years. Ferroelastic materials can be characterized by a phase transformation under applied strain, and the new phase usually has a different crystal structure or different crystal orientation. These processes help minimize the internal strain and the total energy. Ferroelastic materials have great potential for applications in devices like switches, force sensors, and nonvolatile memory devices under ambient conditions [203].

Zhang et al. [127] studied the ferroelastic responses in penta-PdS₂ with four phases: the penta- α , penta- β , penta- γ , and $\delta \text{ PdS}_2$ phase. Penta- α , penta- β , and penta- $\gamma \text{ PdS}_2$ are purely composed of pentagonal structural units with similar lattice constants, while δ PdS₂ possesses a highly anisotropic structure that is the same as blue phosphorus [204]. They all are semiconducting with direct band gaps of 1.98, 0.96, 1.30 and 1.81 eV, respectively. Among the four allotropes, penta- α PdS_2 was successfully synthesized [26,27]. There are six types of ferroelastic transitions, namely, the lattice rotation in penta- α PdS₂, the transformation between penta- α PdS₂ and penta- β PdS₂, the transformation between penta- α PdS₂ and penta- γ PdS₂, the transformation between penta- β PdS₂ and penta- γ PdS₂, the transformation between penta- α PdS₂ and δ PdS₂, and the lattice rotation in δ PdS₂. Specifically, the ferroelasticity in penta- α PdS₂ can lead to the lattice rotation under uniaxial tension with an energy barrier of 0.13 eV/atom, and the phase transformation to δ PdS₂ under shear strain with an energy barrier of 0.24 eV/atom, as shown in Fig. 10(a), where the uniaxial tension and compression induced energy curves intersect at the lattice length of 5.54 Å due to the structural anisotropy of penta- α PdS₂. When the lattice **a** is larger than 5.54 Å, the penta- α PdS₂ phase becomes energetically unstable, leading to lattice rotation along with energy release. The ferroelastic transition from the penta- α phase to penta- β phase has an energy barrier of 0.10 eV/atom. The penta- α phase transforms into the penta- γ phase requires an energy barrier of 0.12 eV/atom, while the ferroelastic switching between the penta- β phase and penta- γ phase needs a rather small energy barrier of 0.02 eV per atom. It is worthy to note that these ferroelastic transformations are different from the mechanism in PdS₂ pyrite-phase counterpart, where the lattice rotation *via* switching between van der Waals and covalent interactions plays the role [205–207].

Based on an analysis of the order-parameters and free-energy expansion defined by the Landau theory of continuous phase transitions, pure ferroelastic transitions with no spontaneous polarization can widely exist in the 21 out of 32 crystal point groups [208], while the corresponding space groups include those of the α -phase (*P*-42₁m), β -phase (*P*2₁/*c*) and γ -phase (*P*4/*mbm*) pentagon-based sheets. Thus, the ferroelasticity of pentagon-based PdS₂ and the corresponding pathways could also be observed in other pentagon-based 2D materials with similar geometric structures. One can expect that all β -phase MX₂ sheets can display ferroelasticity when the lattice vectors **a** and **b** are switched and X₂ dimers are rotated, like the case in Fig. 10(b). While, in principle, all pentagon-based sheets with stable α - and β -phase configurations in the same chemical formula MX₂, i.e., NiS₂ [35,72], ZnS₂ [38,72], CdS₂ [72], and SnX₂ (X = S, Se, Te) [59], could also show ferroelasticity *via* phase transformation, like the case in Fig. 10(c). Meanwhile, the two different configurations of penta-MnN₂ [46,49] with different magnetic moment and a 3% difference in their lattice parameters, as discussed in Section 5.1, could also be viewed as a ferroelastic response under biaxial tensile/compressive strain, leading to a family of pentagon-based 2D multiferroic materials [209]. And the other pentagon-based sheets, like the γ -, γ' -, and γ'' -phase, might also possess ferroelastic transitions according to the symmetry analysis, although the exact reaction pathways in these structures remain unrecovered.

5.6. Linear optics

Linear optical properties of 2D materials have attracted great attention, since materials with proper optical properties can be used in opto-electronic applications like photodetectors, solar cells, *etc.* Shortly after its synthesis, it was found that penta-PdSe₂ is promising for self-powered photodetector, showing the necessity of studying the linear optical properties of other pentagon-based materials to find more candidates for these opto-electronic applications. Theoretically, all linear



Fig. 10. (a) Schematic diagram of the crystal orientation rotation of penta- α PdS₂ under tensile strain and the phase transformation between penta- α PdS₂ and δ PdS₂ under shear strain. Theoretical energy barriers and reaction pathways of the ferroelastic processes for the transition (b) between penta- α PdS₂ and its rotated forms, and (c) between penta- α PdS₂ and penta- γ PdS₂. *Source:* (a-c) Adapted with permission from Ref. [127].

optical properties, including the absorption coefficient $I(\omega)$, the refraction index $n(\omega)$, the energy loss spectra $L(\omega)$, and the reflectivity $R(\omega)$ can be obtained from the complex dielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) + i \cdot \varepsilon_2(\omega)$ as follows,

$$I(\omega) = \sqrt{2}\omega \left[\sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)} - \varepsilon_1(\omega) \right]^{1/2}$$
(13)

$$n(\omega) = \frac{\sqrt{2}}{2} \left[\sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)} + \varepsilon_1(\omega) \right]^{1/2}$$
(14)

$$L(\omega) = \frac{\varepsilon_2(\omega)}{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)}$$
(15)

$$R(\omega) = \left| \frac{[\varepsilon(\omega)]^{1/2} - 1}{[\varepsilon(\omega)]^{1/2} + 1} \right|^2$$
(16)

Since the electronic band gap of the semiconducting pentagon-based sheets spans in a wide range from the low value of 0.1 eV [62,93] to the high value of 6.53 eV for penta-CN₂ [13], and the onsets and peaks of their linear optical responses also spreads in a wide range in the spectrum. For example, the narrow-band-gap semiconductors like penta-MP₂ and penta-MAs₂ (M = Ni, Pd, Pt) show considerable linear optical absorption in the infrared, visible and ultraviolet region [131,146], while the semiconductors with their band gaps in the range of 1.6 \sim 3.1 eV, like the penta-X₂C (X = P, As, Sb) [34], penta-NiX₂ and penta-PdX₂ (X = S, Se, Te) [35] families, show good absorption in the visible and ultraviolet spectrum, but the wide-band-gap semiconductors, like penta-ZnO₂, only absorb light in the ultraviolet region [31]. These pentagon-based sheets with different band gaps and absorption profiles could be used in tandem solar cells for achieving high power conversion efficiency. In addition to the most extensively studied linear optical absorption properties, a low reflectivity (< 0.005) in the infrared and visible spectrum was predicted in penta-ZnO₂, high reflectivity up to 0.35 was found in

Calculated specific capacity (in mA h g^{-1}), diffusion barrier (in eV), and average open-circuit voltage (in V) of some pentagon-based sheets for Liand Na-ion battery anodes.

Materials	Phase	Adsorbed ion	Specific capacity	Diffusion barrier	OCV	Ref.
penta-BN ₂	α	Li	2071	0.05	0.18	[51]
penta-SiC ₂	α	Li	1028.7	0.052	-	[52]
penta-PC ₂	α	Na	975	0.055	-	[58]
penta-B ₂ C	α	Li	1594	0.094	-	[53]
		Na	2391	0.042	-	[53]
penta-C₅P	α	Na	1767	0.034	-	[58]
penta-BCN	α'	Li	2183.12	0.14	-	[55]
		Na	1455.41	0.16	-	[55]
penta-CoS ₂	β	Li	653.31	0.21	-	[56]
		Na	326.77	0.15	-	[56]
penta-PtN ₂	γ	Li	480.53	0.25	0.44	[54]
		Na	480.53	0.14	0.41	[54]
PG/penta-BN ₂	-	Li	1054.35	0.02	0.93	[57]
		Na	1054.35	0.20	0.74	[57]

penta-BeP₂ [121] and penta-As₂C [210], and moderate refraction index up to 2.1 in the visible spectrum was reported in H-Pt₂N₄ [24].

However, the linear optical properties calculated based on the PBE and HSE06 functionals might be inaccurate because the effect of excitons is not included, which is robust in 2D systems [211,212]. A more accurate evaluation of these properties would require the *GW* calculations [213–215], which treat an electron and the cloud of positive charges induced by its negative charge as one quasiparticle. Efforts have been made to acquire the quasiparticle band structure of PG [216] and penta-PdSe₂ [217]. However, the excitonic binding energy and the linear optical properties at *GW* level have not been reported yet.

6. Potential applications

The unique properties of pentagon-based materials provide the basis for their vast potential applications. In the following, we particularly discuss the applications in metal-ion batteries, thermoelectricity, photocatalysis, electrocatalysis, and heterojunction.

6.1. Anode materials of metal-ion batteries

Due to the large specific surface area, 2D materials as anode for Li/Na/K-ion batteries have been extensively studied [218–220]. The specific capacity, open-circuit voltage (OCV) and diffusion barriers are evaluated for some pentagonbased sheets, as summarized in Table 13 and Fig. 11. Among the existing studies, the α - and α '-phase sheets constructed by light elements, such as penta-BN₂ [51], penta-SiC₂ [52], penta-PC₂ [58], penta-B₂C [53], penta-C₅P [58], penta-BCN [55], and the PG/penta-BN₂ heterostructure [57], they all possess significant theoretical capacities for Li-/Na-ion battery anodes in the magnitude of 10³ mA h g⁻¹. The maximum specific capacity for Li- and Na-ion battery anodes was found in penta-BCN (2183.12 mA h g⁻¹) [55] and penta-B₂C (2391 mA h g⁻¹) [53], respectively, which are much higher than those of graphite (372 mA h g⁻¹ for Li-ion battery and ~100 mA h g⁻¹ [221] for Na-ion battery), and are higher than those of hexagon-based 2D graphene analogues like B₂S (1498 mA h g⁻¹) [223] due to the multi-layered adsorption configuration. The diffusion barriers for Li/Na ions along the most preferred diffusion pathways on penta-BN₂, penta-SC₂, and penta-B₂C are all below 0.1 eV. While the corresponding values on other pentagon-based sheets all below 0.25 eV, indicating the easy migration of Li/Na ions on these pentagon-based materials. For the 2D pentagonal systems like penta-CoS₂ and penta-PtN₂ containing heavy atoms, the specific capacity can respectively reach up to 653.31/326.77 [56] and 480.53/480.53 [54] mA h g⁻¹ for Li/Na-ion batteries [54,56], which are higher than those of the hexagon-based 2D materials are potential candidates for Li-/Na-ion batteries). These studies suggest that pentagon-based 2D materials are potential candidates for Li-/Na-ion battery anodes.

6.2. Thermoelectricity

The performance of thermoelectric materials can be evaluated by the dimensionless figure of merit *ZT* value, $ZT = S^2 \sigma T/(\kappa_e + \kappa_L)$, where *S* is the Seebeck coefficient, σ is the electrical conductivity, $\kappa_e = L\sigma T$ is the electrical thermal conductivity (*L* is the empirical Lorenz number), and κ_L is the lattice thermal conductivity. Semiconductors with low lattice thermal conductivity and high electrical conductivity usually exhibit good thermoelectric performances. The thermoelectric properties of monolayer penta-PdSe₂ were first theoretically studied by Singh's group in 2015 [224]. They found high Seebeck coefficients (> 200 μ V/K) for both *p*- and *n*-type up to high doping level (~2 × 10¹³ cm⁻²). Later on,



Fig. 11. Optimized adsorption configuration and theoretical voltage profile for (a) penta-BN₂, (b) penta-BCN and (c) PG/penta-BN₂ heterostructure as Li-ion battery anode, (d) penta-PC₂, (e) penta-C₅P, (f) penta-B₂C, and (g) penta-PtN₂ as Na-ion battery anode. *Source:* (a-c) Adapted with permission from Ref. [51,55], and [57], respectively; (d-e) adapted with permission from Ref. [58]; (f-g) adapted with permission from Ref. [53,54], respectively.

Oin et al. [64] further calculated the lattice thermal conductivity and the ZT value of monolayer penta-PdSe₂, and indicated that monolayer penta-PdSe₂ is a promising thermoelectric material with the ZT value of 1.1 along the x direction for p-type doping at room temperature. Lan et al. [65] expanded this study to penta-PdX₂ (X = S, Se, Te) family. They found that the ZT value of this family member increases with the decrease of the lattice thermal conductivity. The thermoelectric performance of the *p*-type sheets prevails over that of the *n*-type sheets. The optimized ZT values for *p*-type penta-PdS₂, penta-PdSe₂, and penta-PdTe₂ at 300 K are 0.85, 1.18, and 2.42, respectively, which are larger than those of the commercial thermoelectric material Bi₂Te₃ (about 0.8), as shown in Fig. 12(a), demonstrating that penta-PdX₂ monolayers are potential anisotropic thermoelectric materials. Similarly, the thermoelectric properties of the penta-PtX₂ (X = S, Se, Te) [66] and penta-MAs₂ (M = Ni, Pd, Pt) [67] families were studied. The optimized ZT values in the penta-PtX₂ family are 0.58, 1.75, and 2.60 at 300 K for penta-PtS₂, penta-PtSe₂, and penta-PtTe₂, respectively, which are also found in their p-type sheets, as shown in Fig. 12(b). The increase in optimized ZT values with the decrease of the lattice thermal conductivity was also found in this system. While, in the penta-MAs₂ family, different from the preference of p-type doping for better thermoelectric performance, the optimized ZT value for penta-PdAs₂ is found in its n-type sheet, respectively, as shown in Fig. 12(e). The temperature dependence of ZT in the pentagon-based structures were also studied, where the increase of ZT value with the increasing temperature was found in most systems [Fig. 12(c-e)], whereas the optimized ZT value for penta-PtAs₂ is inert to temperature beyond 500 K [Fig. 12(f)]. In addition to these promising theoretical predictions, it is encouraging that the thermoelectric devices based on few-layer penta-PdSe₂ nanoflakes have been prepared [158].

6.3. Photocatalysis

The intrinsic high specific surface area of 2D materials provides the advantage for adsorption and catalysis. In the family of pentagon-based 2D structures, the capability of gas adsorption on such sheets has been widely reported. For instance, O_2 adsorption on penta-BN₂ [15], N_2 adsorption on penta-TiP, penta-ZrP and penta-HfP [135], O_2 and CO adsorption on penta-SiC₂ [75], N_2 , O_2 , CO_2 and H_2O adsorption on penta-PdS₂ [76], and H_2 and CO_2 adsorption on penta-C₂N [77]. These show that pentagon-based sheets can serve as 2D catalysts. Among the semiconducting pentagon-based sheets, those satisfying certain band-alignment criteria, namely, the VBM/CBM (versus the vacuum level) slightly below/above the oxidation/reduction potential of certain half-reactions, can have potential applications in photocatalysis, where the photon excited carriers stimulate the adsorbed reactants crossing the energy barrier to form new species.

Taking the widely studied water splitting reaction as an example, the redox potential φ of O_2/H_2O and H^+/H_2 as a function of pH can be expressed by $\varphi(O_2/H_2O) = (-5.67 + 0.0591 \times \text{pH}) \text{ V}$ and $\varphi(H^+/H_2) = (-4.44 + 0.0591 \times \text{pH})$ V, respectively. As summarized in Table 14, a number of pentagon-based sheets in α -, α "-, β -, and β '-phases satisfy the criteria in both acidic (pH = 0) and neutral (pH = 7) environments. While, penta-As₂C [34], α -NiS₂ [72], β -ZnS₂ [72], and penta-PdS₂ [35] show a preference for either acidic or neutral environment, providing the capability to tune on/off the water splitting reaction. It is also worth noting that the capability of pentagon-based sheets as photocatalysts for water splitting can be further tuned by external strain, as reported in penta-Zn₂C₂P₂ [20], since the VBM and CBM are both functions of external strain. The CO₂ splitting reaction, which is another photocatalytic process of great significance, has been studied for penta-GeP₂ [99], which can convert CO₂ into CO. The redox potentials of CO₂/CO and O₂/H₂O in half-reactions can be expressed as $\varphi(CO_2/CO) = (-4.32 + 0.0591 \times \text{pH}) \text{ V}$ and $\varphi(O_2/H_2O) = (-5.67 + 0.0591 \times \text{pH}) \text{ V}$,



Fig. 12. Theoretical *ZT* value of (a) *p*-type penta-PdX₂ (X = S, Se, Te) and (b) *p*-type penta-PtX₂ (X = S, Se, Te) as a function of hole concentration. (c) Theoretical *ZT* value of *p*-type penta-PtX₂ as a function of temperature. Theoretical *ZT* value of (d) penta-NiAs₂, (e) penta-PdAs₂, and (f) penta-PtAs₂ as a function of temperature and chemical potential. *Source:* (a) Adapted with permission from Ref. [65]; (b–c) adapted with permission from Ref. [66]; (d–f) adapted with permission from Ref. [67].

respectively. It was found that penta-GeP₂ can be used as photocatalysts for CO₂ splitting. Since both the water and CO₂ splitting reactions include the O_2/H_2O half-reaction, and the redox potentials of CO₂/CO and H⁺/H₂ reactions are close to each other in value, therefore, most candidates as photocatalysts for water splitting could also service as photocatalysts for CO₂ splitting.

6.4. Electrocatalysis

In contrast to the photocatalytic properties of some semiconducting pentagon-based sheets, the metallic pentagonbased sheets are more suitable for applications in electrocatalysis. The free energy change ΔG of each step in the reaction pathway is adopted to describe the activity instead of an overall redox potential. It is expressed by the formula $\Delta G = \Delta E + \Delta E_{\text{ZPE}} + T \Delta S$, where ΔE , ΔE_{ZPE} , and ΔS are the difference in adsorption energy, zero-point vibrational energy, and entropy between the reactants and the products, respectively. The metallic structures are superior to the semiconductors in which ΔG of the pathways with charged reactants can be easily tuned by applying external electric potentials.

Taking the most studied hydrogen evolution reaction (HER) as an example, it involves the adsorption of hydrogen atoms (H*) on the catalyst in the first step and the formation of H₂ in the second (final) step. The HER activity is determined by the ΔG_{H*} of the adsorption step according to the volcano curve [225], and low $|\Delta G_{H*}|$ is preferred. It was found that the adsorption of H* on the penta-MA configuration is on the bridge site between adjacent TM atoms, and the ΔG_{H*} at an optimized hydrogen coverage, as shown in Table 14, can reach a nearly ideal value of -0.03 eV. For reference, Pt is the well-commercialized electrocatalyst for HER with ΔG_{H*} of -0.09 eV [225]. As for penta-PdSe₂, its pristine 2D sheet is not suitable for catalyzing HER due to the high ΔG_{H*} over 1 eV [32], while high HER activity has been confirmed *via* electrochemical experiments [226], which is attributed to both Pd and Se atoms at the edge of the finite 2D sheet. The activity of other reactions like oxygen evolution reaction (OER) and N₂ reduction on the pentagon-based sheets are also studied. For example, penta-SiAs₂ can be used for overall water splitting (both HER and OER on a single catalyst) under an external voltage of 1.47 V [71], and penta-TiP can reduce N₂ to NH₃ at the external voltage of 0.72 V [135], showing great potential for water splitting nitrogen fixation.

6.5. Heterostructures

Distinct electronic transport properties have been found in heterostructure devices formed by two juxtaposed materials instead of the pristine crystals of their parent constituents. These properties lead to potential applications of

Calculated capability of the pentagon-based sheets as photocatalysts for water splitting in different environments, and the adsorption free energy of $H^* \Delta G_{H*}$ (in eV) for the pentagon-based sheets as electrocatalysts for HER.

Structure	Water splitti	ng	Ref.	Structure	$\Delta G_{\mathrm{H}*}$	Ref.
	pH = 0	pH = 7				
penta-B ₂ C	×	√	[58]	penta-SiAs ₂	0.72	[71]
penta-P ₂ C	\checkmark	\checkmark	[34,58]	penta-PdSe ₂	1.175	[32]
penta-As ₂ C	×	\checkmark	[34,58]	β' -phase PdSSe	1.64	[73]
penta-SiC ₂	\checkmark	\checkmark	[36,58,69]	β'' -phase PdSSe	1.55	[73]
penta-SiAs ₂	\checkmark	\checkmark	[71,72]	penta-VS	-0.03	[48]
α -MnS ₂	\checkmark	\checkmark	[72]	penta-FeS	-0.03	[48]
α -NiS ₂	×	\checkmark	[72]	penta-ZrC	-0.13	[40]
penta-ZnS ₂	\checkmark	\checkmark	[72]	penta-NbS	0.117	[93]
penta-ZnSe ₂	\checkmark	-	[70]	penta-NbSe	-0.156	[93]
p-GeC ₂	×	\checkmark	[36,58]	penta-NbTe	-0.193	[93]
α -CdS ₂	\checkmark	\checkmark	[72]	penta-HfC	0.20	[40]
penta-CdSe ₂	\checkmark	-	[70]	penta-TaB	-0.15	[40]
p^1 -Si _{0.5} Ge _{0.5} C ₂	\checkmark	\checkmark	[36]	penta-TaC	0.28	[40]
p^2 -Si _{0.5} Ge _{0.5} C ₂	\checkmark	\checkmark	[36]	penta-WB	-0.03	[40]
penta-NiS ₂	×	\checkmark	[72]			
	\checkmark	\checkmark	[35]			
penta-NiSe ₂	\checkmark	\checkmark	[35]			
penta-NiTe ₂	\checkmark	\checkmark	[35]			
β -ZnS ₂	×	\checkmark	[72]			
penta-PdS ₂	\checkmark	×	[35]			
penta-PdSe ₂	\checkmark	\checkmark	[32]			
penta-PdTe ₂	\checkmark	\checkmark	[35]			
β' penta-PdSSe	\checkmark	\checkmark	[68]			
	\checkmark	Х	[73]			
β'' penta-PdSSe	\checkmark	×	[73]			
	-	\checkmark	[74]			
β'' penta-PdSTe	-	\checkmark	[74]			
eta'' penta-PdSeTe	-	\checkmark	[74]			
penta-CrS	\checkmark	-	[42]			
penta-CrSe	\checkmark	-	[42]			

heterostructures in optoelectronic devices [227] and transistors [228]. Usually, electric current crossing the heterojunction is hindered by the Schottky barrier. For van der Waals (vdW) metal–semiconductor junctions [229], where no chemical bonds are formed between their interfaces, and the chemical disorders and Fermi-level pinning found in conventional heterojunctions can be avoided. In such cases, the Schottky barrier can be described by the Schottky-Mott rule, where the intrinsic Schottky barriers in field-effect transistors are determined by $\Phi_n = \Phi_m - \chi$ and $\Phi_p = I - \Phi_m$, where Φ_m is the Fermi level of metallic source/drain, χ is the electronic affinity and I is the ionization energy of semiconducting channel, the *n* is for electron and *p* is for hole. An ohmic contact is formed when Schottky barrier is tuned to zero, and thus heterostructures with low Schottky barriers are desired for electronic devices with low power dissipation.

For the semiconducting and metallic pentagon-based sheets with comparable lattice parameters, for example, penta-BN₂ and PG, a vertical heterostructure [230] between them can be formed with high thermal stability [79], which could be used in micro-nano electronic devices like field-effect transistors. The electronic band structure of the penta-BN₂/PG heterostructure, as shown in Fig. 13(a), possesses features of the two individual 2D structures, though their two-fold band degeneracies along the high-symmetry path X–M are not preserved due to the breakage of $\{2_{001} | \frac{1}{2}, \frac{1}{2}, 0\}$ symmetry. This indicates a vdW contact between the two sheets. The band alignment of the penta-BN₂/PG heterostructure and PG, as demonstrated in Fig. 13(c), leads to an *n*-type Schottky contact with the Schottky barriers of ~1 eV for both electrons and holes, and the Schottky barrier height can be further tuned by applying tensile and compressive strain.

In addition, the contacts between β -phase penta-PdSe₂ and metal surfaces/graphene have also been studied by our group [80]. The strong interactions are found in all the vertical contacts between the β -phase penta-PdSe₂ and the metal surfaces, as summarized in Table 15. While, a vdW contact is found in the penta-PdSe₂/graphene heterojunction, which is also an *n*-type Schottky contact with a low Schottky barrier of 0.22 eV for electrons, as shown in Fig. 13(d). Similarly, the contact between penta-PdSe₂ and another theoretically proposed 2D Dirac material termed ZT–MoSe₂ was reported by Jakhar et al. [81] They predicted a *p*-type Schottky contact with a low Schottky barrier of 0.06 eV, as shown in Fig. 13(e), and they found that the Schottky barrier can be tuned with external pressure and electric field to achieve ohmic contact. Note that the Schottky barriers in heterostructures could be inaccurate because the band alignment is usually evaluated at the PBE level for practical reasons, resulting in an underestimated electronic band gap and inaccurate band edges.

Meanwhile, a number of heterostructures between penta-PdSe₂ and other 2D [231,232]/3D [233,234] materials have been prepared in experiments, and some of their properties match the theoretical predictions. For example, the *n*-type nature of the penta-PdSe₂/graphene contact [80] is confirmed in the synthesized heterojunction between few-layer PdSe₂



Fig. 13. Calculated electronic band structure of (a) PG/penta-BN₂ and (b) penta-PdSe₂/ZT-MoSe₂ heterostructure. Theoretical band alignment of (c) PG/penta-BN₂ heterostructure and free-standing PG, (d) penta-PdSe₂/graphene heterostructure and free standing penta-PdSe₂, and (e) penta-PdSe₂ /ZT-MoSe₂ heterostructure and free standing penta-PdSe₂.

Source: (a, c) Adapted with permission from Ref. [79]; (b, e) adapted with permission from Ref. [81]; (d) adapted with permission from Ref. [80].

Table 15											
Calculated	Schottky	barrier Φ	p_n and q	b_p (in	eV) of	the he	terojunctions	containing	pentagon-based	2D materials.	

Metallic constituent	Semiconducting constituent	Φ_n	$arPsi_p$	Note	Ref.
graphene	PG	0.42	1.69	vdW contact, <i>n</i> -type	[78]
penta-BN ₂	PG	1.06	1.16	vdW contact, <i>n</i> -type	[79]
Ag (111)	penta-PdSe ₂	0.87	0.56	<i>p</i> -type	[80]
Au (111)	penta-PdSe ₂	0.62	0.81	<i>n</i> -type	[80]
Cu (111)	penta-PdSe ₂	0.79	0.64	<i>p</i> -type	[80]
Ti (0001)	penta-PdSe ₂	0.58	0.85	n-type	[80]
Pb (111)	penta-PdSe ₂	0.76	0.67	<i>p</i> -type	[80]
graphene	penta-PdSe ₂	0.22	-	vdW contact, <i>n</i> -type	[80]
ZT-MoSe ₂	penta-PdSe ₂	1.09	0.06	vdW contact, <i>p</i> -type	[81]

and graphene [235]. These heterostructures were designed as self-powered infrared photodetectors for image sensing applications [233,234,236–244].

7. Conclusions and outlook

Mathematical pattern provides the playground for new materials design, as shown in C_{20} and C_{60} . The former corresponds to a dodecahedron and the latter to a truncated icosahedron in mathematics. In this review, we began with the introduction of the 15 types of pentagonal tiling that tile the Euclidean plane leaving no gaps and with no overlaps found by mathematicians during the past 100 plus years. These mathematical models are very different from the geometric configurations of the widely studied graphene, MXene, black phosphorus, dichalcogenides, and trichalcogenides, providing novel structural skeletons for the design and synthesis of new 2D materials. Penta-graphene and the more than 100 pentagon-based materials can be considered as the material realization of these mathematical models. These pentagon-based 2D materials exhibit rich physical and chemical properties, which can change from semiconducting to metallic and topological quantum state, and from nonmagnetic to antiferromagnetic, ferrimagnetic and ferromagnetic, showing unprecedented potentials for applications. We conclude that pentagon is another important structural unit that can lead to a paradigm shift in new materials design and synthesis.

The pentagon-based 2D structures reported so far can be mainly classified into three major phases (α , β , and γ) and their derivatives (α' , α'' , β'' , β'' , γ' , and γ'') according to their symmetries and structural characteristics. They exhibit different properties for the materials in different phases. We discuss their novel properties and potential applications in the fields like mechanics, electronics, spintronics, energy, and catalysis, *etc.*, as shown in Fig. 14. We also probe the underlying structure–property relationship.



Fig. 14. Theoretically proposed distinct physical properties and potential applications of pentagon-based sheets. *Source:* Illustrations for these properties and applications (from piezoelectricity to ferroelasticity, clockwise) are adapted with permission from Ref. [17,36,38,45,46,80,135,245,245], and [127], respectively.

The α -phase MX₂ and α -MNX₄(MX₅) sheets, which can be considered as the rationally atomic substitutions of PG, feature the type-4 pentagonal tiling with buckled geometries. The existence of noncentrosymmetry in these structures leads to universal piezoelectricity and second harmonic generation responses in these materials. These properties can be further enhanced by the breakage of the four-fold rotational symmetry in the derived α '-phase structures.

The β -phase MX₂ sheets, represented by the synthesized penta-PdSe₂ and penta-PdS₂, are an alternative phase of the transition-metal dichalcogenides in the type-2 pentagonal tiling with a finite thickness of buckling. For the materials in this phase, piezoelectric responses and second harmonic generation are forbidden due to the existence of centrosymmetry. While intrinsic ferroelasticity arises due to the difference of the geometries between their *x* and *y* directions. These features together with their anisotropies can further lead to the tunable lattice thermal conductivity and carrier mobility in these materials.

The γ -phase MX₂ sheets, represented by the synthesized penta-NiN₂, also feature the type-4 pentagonal tiling but have planar configurations, where piezoelectric responses and second harmonic generation are also forbidden because of the existence of centrosymmetry in these planar geometries. While the conjugated π orbitals throughout the lattice plane can lead to topological quantum states in a number of such structures, displaying topological quantum behaviors.

The current challenges and future directions in this field are as follows:

(1) Developing new synthesizing strategies to fabricate the predicted pentagon-based 2D materials. Since the discovery of annulation reactions in organic chemistry, it has been of great interest to design and synthesize molecules and crystalline structures composed purely of pentagonal units, as shown in Fig. 15. Currently, only a few of pentagon-based 2D materials, such as pentagonal Si nanoribbon [29], penta-PdSe₂ [16,25,85], and penta-NiN₂ sheet [28] have been synthesized by surface growth on substrate surface [29,85], exfoliation [16,25], and high-pressure method [28]. More effective preparing technologies are highly desirable for controllable synthesis and mass-production.

(2) Maturing penta-sheet-based devices. 2D materials provide the playground for ultrathin devices. For instance, graphene has been used for straight waveguides [246], channel switching [247], and electro-refractive modulation [248]. MXene has been used for wearable strain sensors [249], pressure sensors [250], and gas sensors [251], but less attention has been paid to penta-sheet-based devices.

(3) Expanding atom-based to cluster-based pentagonal 2D materials. Currently, the reported pentagon-based 2D materials employ atoms as their basic units, while cluster-based materials can exhibit novel properties commonly absent



Fig. 15. Roadmap from pentagon to fused pentagon, penta-cage, penta-ribbon and 2D materials. *Source:* Illustrations for penta-Si nanoribbon, penta-PdSe₂ and penta-NiN₂ are adapted with permission from Ref. [16,29], and [28], respectively.

in conventional materials consisting of individual atoms [252]. For instance, the band structures of cluster-based materials are from the overlap of cluster orbitals, while those of conventional crystals come from the overlap of atomic orbitals. Such extension would significantly expand the family of pentagon-based 2D materials with many unpredictable properties.

(4) Applying new theoretical methods for a better understanding of the intrinsic properties of pentagon-based 2D materials. For instance, lattice thermal conductivity by considering the four-phonon scattering effect in calculation [253–256], the effect of electron–phonon coupling on carrier mobility and electronic thermal conductivity [257–261], and phonon spectra at finite temperature based on the self-consistent phonon theory [262,263]. Such theoretical studies would greatly deepen our understanding of structure–property relationship of pentagon-based 2D materials.

In short, synergetic study between theory and experiment is highly desired so that more pentagon-based 2D materials with Earth-abundant elements and novel properties can be synthesized and replace some rare or expensive ones for energy storage and conversion as well as for nano devices, thus expanding the family of 2D materials with diversities and new functionalities.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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