Negative Poisson’s ratio of sulfides dominated by strong intralayer electron repulsion†

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Geometrical variations in a particular structure or other mechanical factors are often cited as the cause of a negative Poisson’s ratio (NPR). These factors are independent of the electronic properties of the materials. This work investigates a class of two-dimensional (2D) sulfides with the chemical formula MX₂ (M = Ti, Cr, Mn, Fe, Co, X = S) using first-principles calculations. Among them, monolayered TiS₂, CrS₂, and MnS₂ were found to exhibit a structure-independent NPR. The strong strain response of intra-layer interactions is responsible for this unique phenomenon. This can be traced to the lone pair of electrons of the S atoms and the weak electronegativity of the central atoms in multi-orbital hybridization. Our study provides valuable insights and useful guidelines for designing innovative NPR materials.

1 Introduction

Poisson’s ratio (PR) is a significant parameter describing the fundamental mechanical properties of materials. PR is defined as the ratio of the transverse elastic strain to the longitudinal elastic strain of a material.1–3 In principle, when stretching (pressing) stresses are applied in one direction, the material tends to shrink (expand) in the transverse direction. Most materials show a positive Poisson’s ratio (PPR) following this convention. In rare cases, however, the material will expand laterally when subjected to a single uniaxial tensile stress, resulting in a NPR.4–10 These materials, also referred to as auxetic materials, could possess interesting mechanical properties11–17 like high strength, light weight, high designability, and good performance in impact resistance and energy absorption.18 NPR materials have been used in biomedicine,19 aerospace,20 armor,2 intelligent manufacturing,22 and other fields.23 Conventionally, auxetic materials are realized by internal macroscopic structure design to ensure lateral expansion when the object is stretched.

In recent years, researchers have discovered NPR effects in materials with specific molecular structures. For example, some two-dimensional (2D) crystals were found to display a NPR, which has attracted a great deal of attention. NPR has been reported in a variety of existing and predicted 2D materials.24–30 The impressive properties of 2D materials have increased their prominence in scientific exploration, uncovering new avenues for research into auxetic phenomena. Prominent illustrations of such materials include graphene,31–33 transition metal dichalcogenides (TMDs),34 and transition metal halides.35 The low-dimensional effects of 2D materials cause quantum confinement, making them more prone to exhibiting new physical properties. Novel NPR phenomena are anticipated in 2D materials due to this confinement. Currently, 2D NPR materials are uncommon, and the ones that have been found are α-phosphorene,36 δ-phosphorene,37 black phosphorus (BP),38 TiN,39 Ag₂S,40 Zn₂C,41 Cd₂C,42 SnSe,43 Be₅C₂,44 WN₄,45 and SiSe.46 The emergence of 2D NPR materials has revealed that the intrinsic NPR is closely linked to their distinctive geometrical structures. Consequently, further exploration of an intrinsic NPR in 2D materials, such as wrinkled and square materials with specific lattice structures,47–49 is being pursued to uncover new NPR materials. However, it is important to note that intrinsic NPRs are typically attributed to unique geometries, such as the re-entrant mechanism, rather than their electronic properties. For example, the NPR of materials with wrinkles, such as black phosphene,50 arises from the geometrical variations. More recently, Yu et al.51 discovered that the NPR behavior in the 1T-TMD material is governed by electronic effects through the filled electronic orbitals. The inherent NPR behavior is not solely influenced by its exceptional geometry, but also by its electronic attributes. Thus, other distinct NPR mechanisms exist besides the geometry effect-dominated configuration.
This work reports on new 2D sulfides whose intrinsic NPR behavior was determined using a first-principles approach. These sulfides are unique in terms of their geometrical structure and, more significantly, the micro-origin of their NPR. All single-layer sulfides belong to the MX$_2$ type (X = Ti, Cr, Mn, Fe, Co, X = S). Most notably, the monolayer MX$_2$ exhibits a geometric structure-independent NPR. Unlike the previously reported NPR, which was dominated by the re-entry mechanism, this behavior cannot be explained by the geometrical structure alone, since the same MX$_2$ configuration exhibits very different Poisson ratios. The appearance of this NPR in an MX$_2$ monolayer can be explained by its unique response to intra-layer interactions. Moreover, it has been demonstrated that MX$_2$ monolayers exhibit kinetic, thermal, and mechanical stability. The combination of these properties with the NPR makes MX$_2$ a promising contender for nanoelectronics and micromechanics applications.

2 Computational details

The CASTEP module of Materials Studio software was utilized for theoretical calculations.\textsuperscript{54,52} Self-consistent periodic density-functional theory (DFT)\textsuperscript{53,54} was employed with the Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional\textsuperscript{55} via the generalized gradient approximation (GGA). The energy cutoff was set at 450 eV. The self-consistent field (SCF) tolerance was set at 5.0 $\times$ 10$^{-7}$ eV per atom. The convergence criteria for maximum stress, maximum displacement, maximum force, and energy were confined to be less than 0.02 GPa, 5.0 $\times$ 10$^{-4}$ Å, 0.01 eV Å$^{-1}$, and 5.0 $\times$ 10$^{-6}$ eV atom$^{-1}$, respectively.\textsuperscript{56} The k-point grid was set to be 9 $\times$ 9 $\times$ 5. Our previous calculations verified these parameter settings.\textsuperscript{57} To ensure the consistency and reliability of the currently chosen DFT method, we selected chalcopyrite-structured sulfide-type LiMS$_2$ (M = Sc, Ti, V, Cr, Mn, Fe, Co, and Ni) materials with the same space group for comparison with available data in the literature. (See Table S1, and Fig. S1, ESI).\textsuperscript{58} As shown in Table S1 [ESI], the LiMS$_2$ (M = Sc, Ti, V, Cr, Mn, Fe, Co, and Ni) crystallographic parameters optimized using our DFT method are in good agreement with those of LiMS$_2$ in the literature, which ensures the consistency and reliability of the currently selected DFT method.

The elastic constants represent the amount of elasticity of a material, which is a very important physical quantity for the mechanical properties of materials. According to Voigt notation, elastic constants are always expressed as a 6 $\times$ 6 matrix [C$_{ij}$], and C$_{ij}$ represents the elastic constants with indices i and j labeled as xx = 1, yy = 2, zz = 3, yz = 4, zx = 5, and xy = 6. For 2D materials, only in-plane strain and stresses are allowed, whereas the z direction is strain and stress-free (i.e., C$_{ij}$ = 0 for i = 3 or j = 3).\textsuperscript{59} Hence, the linear elastic constitutive relationship of a 2D material can be expressed as\textsuperscript{60}

\[
\begin{bmatrix}
\sigma_{11} \\
\sigma_{22} \\
\sigma_{12}
\end{bmatrix} = \begin{bmatrix}
C_{11} & C_{12} & C_{16} \\
C_{21} & C_{22} & C_{26} \\
C_{16} & C_{26} & C_{66}
\end{bmatrix} \begin{bmatrix}
\varepsilon_{11} \\
\varepsilon_{22} \\
2\varepsilon_{12}
\end{bmatrix}
\]

where $\sigma_{ij}$ is the stress tensor and $\varepsilon_{ij}$ is the strain tensor. The relaxed- and clamped-ion elastic constants C$_{ij}$ were calculated using the finite difference (i.e., strain–stress) method in the CASTEP module of Material Studio software, i.e., the stresses generated by small applied strains were calculated using a strain range $-3\% < \varepsilon < 3\%$, using the same first-principles parameters as in this paper. The in-plane Young’s modulus (YM) $Y(\theta)$ and PR $\nu(\theta)$ of a material are closely related to its anisotropy. They are functions of the direction angles $\theta$, which can be expressed as follows:\textsuperscript{64}

\[
Y(\theta) = \frac{C_{11}C_{22} - C_{12}^2}{C_{11}\sin^4 \theta + A\sin^2 \theta \cos^2 \theta + C_{22}\cos^2 \theta},
\]

\[
\nu(\theta) = \frac{C_{12}\sin^2 \theta - B\sin^2 \theta \cos^2 \theta + C_{12}\cos^2 \theta}{C_{11}\sin^2 \theta + A\sin^2 \theta \cos^2 \theta + C_{22}\cos^2 \theta},
\]

where C$_{ij}$ are the elastic constants, $A = (C_{11}C_{22} - C_{12}^2)/C_{66} - 2C_{12}$ and $B = C_{11} + C_{22} - (C_{11}C_{22} - C_{12}^2)/C_{66}$.

The phonon calculations utilized the infinite displacement method within a 4 $\times$ 4 $\times$ 1 supercell. During the calculations, the Device Studio program offers functions for visualizing, modeling, and simulating. We performed calculations of electron localization functions (ELFs) and charge densities using the DS-PAW\textsuperscript{62} software integrated in the Device Studio program,\textsuperscript{63} based on DFT. Molecular dynamics (MD)\textsuperscript{64} simulations were conducted in the NVT ensemble using a 4 $\times$ 4 $\times$ 1 supercell at 300 K for 10 ps. Periodic boundary conditions have been used throughout the entire simulation. To ensure precise simulation results, we added a vacuum layer of 15 Å to all models. This eliminates periodic interactions. During the calculations, M$_2$S$_5$’s bottom layer remains fixed. The universal force field (UFF) was utilized as the force field for MD simulations, as well as for optimizing the model and assigning charges for accurate calculations. The quasi-Newton method was used for geometry optimization calculations. A quasi-Newton method was used to minimize the initial model until the gradient was less than 0.1 kcal mol$^{-1}$.

The ground state structures of 2D sulfides were investigated using the unbiased crystal structure AnaLYsis by Particle Swarm Optimization (CALYPSO)\textsuperscript{65–70} structure search method. A set of chemical formulas was mainly considered, and the initial structure was randomly constructed via plane-group symmetry operations followed by relaxation. The structure search simulation was stopped after 20 generations. To avoid interactions between neighboring layers due to periodicity, all monolayer structures were separated by a vacuum space of at least 15 Å in the Z-direction.

3 Results and discussion

Initially, we identified over 700 materials from the Materials Project database using the unbiased CALYPSO method and the first-principles calculations. We then mined the data to identify 2D compounds with compliant specific lattice and flexural geometries. The results indicate that we have successfully identified five stable compounds with MX$_2$ (M: Ti, Cr, Mn, Fe, Co; X: S) stoichiometry as the most promising candidates, see Fig. 1. The series of 2D chemical compounds has a flexural
structure where transition metal M atoms are sandwiched between two layers of S atoms. The M atom each forms a quasi-tetrahedron with its neighboring S atom. Furthermore, this group of sulfide compounds differs significantly from the previously reported 1-H and 1-T TMDs, featuring a completely new structure. The unique geometry of this new material may result in the manifestation of intriguing properties.

3.1 Structural properties

The atomic structures of the monolayer transition metal sulfides MS₂ (M = Ti, Cr, Mn, Fe, and Co) are shown in Fig. 2a. All the materials are rectangular cells with space group I4̅2d, with the protocell having eight S atoms along with four M atoms, which is a different geometrical configuration from that of the 1T-TMDs. It presents a pronounced folded structure, where the zigzag-shaped structure is connected by M-S bonds. M²⁺ is bonded to four equivalent S²⁻ atoms to form corner-sharing MS₄ tetrahedra. Interestingly, monolayer MS₂ shares similar nonmetallic encapsulation properties to TMDs, i.e., the metallic M-layer is sandwiched by the nonmetallic S-layer, forming a nonmetallic cage structure. Furthermore, the central M-atoms form a four-coordination bond with the S-atoms, while the two outer layer S-atoms have an equivalent three-coordination configuration. Table 1 shows that the symbols a, b, and θ represent the lattice constants along the X- and Y-directions and their characteristic angles, correspondingly. Fig. 2b presents a diagram demonstrating the participation of locally symmetric atoms in the NPR evolution process.

3.2 Stability verification

To evaluate the stability of the MS₂ monolayer, we initially computed its cohesive energy to inspect its interatomic binding and structural stability. The cohesive energy is calculated as $E_{coh} = (xE_M + yE_S - E_{M_S})$, where $E_M$, $E_S$, and $E_{M_S}$ are the energy values for the individual M, S atoms, the MS₂ monolayer in the cell, and the x and y values denote the number of atoms of the corresponding element in sulfides, respectively. Table 1 demonstrates that the cohesion energy follows the trend of TiS₂ (5.17 eV atom⁻¹) > CrS₂ (4.79 eV atom⁻¹) > MoS₂ (4.70 eV atom⁻¹) > FeS₂ (4.64 eV atom⁻¹) > CoS₂ (4.29 eV atom⁻¹), which suggests that the 2D MS₂ is strongly bonded and exhibits high stability. Since the cohesion energy of MoS₂ observed experimentally is 5.02 eV per atom,⁷¹ we expect TiS₂ to be more stable based on the calculated cohesive energy. In addition, the formation energies ($E_f$) of the MS₂ compounds have been calculated as $E_f = (E_{M_S} - xE_M - yE_S)/(x + y)$, where $E_{M_S}^{bulk}$ and $E_M^{bulk}$ denote the energies of the M and S atoms, respectively, in their respective bulk phases. Table 1 shows that negative formation energies suggest favorable energetics of the 2D structures. Lower formation energies drive the structures towards lower energy states, resulting in more stable configurations. These findings indicate that these structures have the potential to be synthesized experimentally. Then, a comparison of the experimentally known MS₂ 2D material with the crystal structure we used reveals that the geometry of the former is dominated by the $P6_3/mmc$ space group, i.e., phase 1T with octahedral coordination and phase 2H with trigonal prismatic coordination,⁷² ⁷³ whereas the structure under discussion is that of an M⁺ bonded to four equivalent S⁻ atoms bonded to form the angle-sharing MS₄ tetrahedron, which crystallizes in the tetragonal I4̅2d space group with different spatial symmetries. Moreover, it has a more complex arrangement, the protocells are larger than the 1T and 2H phases, and the atoms are more tightly connected. There are few reports on this novel structure. The different phases have different structures, stability, and properties, as well as different application scenarios. Therefore
exploring new material structures with their unique properties will greatly broaden the future application areas and solve related problems.

To assess the dynamic and thermal stability of the monolayer MS$_2$, we conducted phonon calculations and MD simulations. The results demonstrate that the monolayer MS$_2$ exhibits robust dynamic and thermal stability, which is discussed in greater detail in Note 1 and Fig. S2 (ESI†). To ensure mechanical stability, the Born–Huang criterion$^7$ must be satisfied, which requires $C_{11}$, $C_{12}$, and $C_{66}$ > 0 and $C_{11} + C_{22} > 2C_{12}$, where $C_{ij}$ represents the elastic constants. Table 2 shows the values of $C_{11}$, $C_{22}$, $C_{12}$, and $C_{66}$ for the MS$_2$ monolayer, all of which meet the mechanical stability requirements. These results provide strong evidence of the stability of the monolayer MS$_2$.

### 3.3 Mechanical properties

YM is a physical measure that characterizes the ability of a material to withstand elastic deformation, and flexible materials have a low YM.$^{78}$ As depicted in Fig. S3 (ESI†), Fig. 2c and d, all compounds, except CrS$_2$, MnS$_2$, and CoS$_2$, exhibit varying degrees of anisotropy in their YM and PR. This indicates dissimilar mechanical responses to the identical amount of strain along diverse orientations. As demonstrated in Table 2, the YM of MS$_2$ falls within the range of 13–27 N m$^{-1}$. Additionally, the smaller Y(θ) value compared to graphene and BN suggests improved flexibility. These results align with prior studies on 2D materials.

### Table 1

<table>
<thead>
<tr>
<th>Compound</th>
<th>$a$ (Å)</th>
<th>$b$ (Å)</th>
<th>$\theta$ (°)</th>
<th>Cohesive energy (eV per atom)</th>
<th>Formation energy (eV per atom)</th>
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<td>TiS$_2$</td>
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<td>5.83</td>
<td>107.74</td>
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<td>−1.38</td>
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<td>CrS$_2$</td>
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<td>5.42</td>
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<tr>
<td>MnS$_2$</td>
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<td>5.44</td>
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<td>4.70</td>
<td>−0.58</td>
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<tr>
<td>FeS$_2$</td>
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<td>5.27</td>
<td>109.14</td>
<td>4.64</td>
<td>−0.49</td>
</tr>
<tr>
<td>CoS$_2$</td>
<td>5.09</td>
<td>5.09</td>
<td>109.94</td>
<td>4.29</td>
<td>−0.14</td>
</tr>
</tbody>
</table>

Fig. 2 (a) The views of the geometry structures of MS$_2$ (M = Ti, Cr, Mn, Fe, and Co). The coordination environments of the M atoms are presented in rectangular shapes with dashed lines. (b) Localized lattice morphology and atoms of MS$_2$. (c) NPR versus orientation for monolayer MS$_2$. (d) PPR versus orientation for monolayer MS$_2$. 

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ensuring the reliability of the methodology used. For instance, we obtained a $Y(\theta)$ value of 333 N m$^{-1}$ for graphene, which is consistent with the predicted values in ref. 76 (334 N m$^{-1}$) and ref. 77 (332 N m$^{-1}$), as well as the measurements in ref. 79 (340 N m$^{-1}$). These low values are indicative of the excellent flexibility possessed by MS$_2$ and can be attributed to its flexural properties. Fig. S4 (ESI†) displays the results of PR calculations for strain. TiS$_2$ has the most extensive range of PR, ranging from 0.2 to 0.2, compared to other binary compounds of MS$_2$, see Fig. S4 (ESI†) and Fig. 2. It is worth noting that even though the MS$_2$ compounds share a structural resemblance, NPRs have been detected in TiS$_2$, CrS$_2$, and MnS$_2$. TiS$_2$, CrS$_2$, and MnS$_2$ achieved significantly higher NPR values of 0.17, 0.37, and 0.51, respectively, which are distinctly higher than those of borophene ($\nu = 0.053$), PN ($\nu = 0.078$), penta-graphene ($\nu = 0.068$), and W$_2$C ($\nu = 0.43$). The in-plane PR of this structure is unique compared to other configurations. This emerging NPR cannot be attributed to conventional geometrical mechanisms, as no NPR behavior has been observed in other MS$_2$ monolayers. This phenomenon is believed to be linked to robust coupling between particular orbitals, which cannot be explained solely based on geometry. A comparable occurrence has been noted in 1T-TMDs. The distinction lies in the fact that MS$_2$ compounds undergo comparable orbital hybridization among themselves, but not all of them manifest NPR behavior. As such, the emergence of a NPR in MS$_2$ presents new and valuable leads in comprehending the regulation of NPR behavior by electronic effects.

### 3.4 The mechanism underlying the NPR

To investigate the origin of the NPR, we provide a mechanistic explanation by analyzing the development of a tetrahedron composed of S$_1$, S$_2$, S$_3$, and S$_4$, and transition metal M atoms as displayed in Fig. 2b and 3a, b. Uniaxial strain causes neighboring S atoms to move apart as depicted in Fig. 3a. When a force is applied in the X-direction, S$_4$ atoms move further away, increasing the angle $\theta$ and leading to NPR. Similarly, in Fig. 3b, a strain in the Y-direction causes S$_3$ atoms to move downwards, moving M atoms towards the X-axis, ultimately leading to a NPR. The NPR originated from the tetrahedral flattening caused by uniaxial strains. However, it should be noted that the mechanisms underlying the geometries are insufficient to explain the newly discovered NPR. Specifically, only TiS$_2$, CrS$_2$, and MnS$_2$ exhibit a NPR, while the remaining MS$_2$ compounds do not. To further elucidate this newly discovered NPR, we will examine the geometric and electronic responses of all monolayers of MS$_2$ when subjected to strain in the X-axis direction. The geometrical response along the X-axis is expressed in the distance $d$ between the atoms of MS$_2$, which in turn depends on the geometrical variation of the lattice atoms on the tetrahedron. The key parameters,

<table>
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<tr>
<th></th>
<th>$C_{11}$</th>
<th>$C_{12}$</th>
<th>$C_{22}$</th>
<th>$C_{66}$</th>
<th>$E_x$</th>
<th>$E_y$</th>
<th>$v_x$</th>
<th>$v_y$</th>
<th>$v^*$</th>
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<tr>
<td>TiS$_2$</td>
<td>17.65</td>
<td>-3.04</td>
<td>17.65</td>
<td>5.39</td>
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<td>17.13</td>
<td>-0.17</td>
<td>-0.17</td>
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<tr>
<td>CrS$_2$</td>
<td>14.95</td>
<td>-5.53</td>
<td>14.95</td>
<td>14.70</td>
<td>12.90</td>
<td>12.90</td>
<td>-0.37</td>
<td>-0.37</td>
<td>-0.51</td>
</tr>
<tr>
<td>MnS$_2$</td>
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<td>-7.81</td>
<td>19.24</td>
<td>16.33</td>
<td>16.06</td>
<td>16.06</td>
<td>-0.41</td>
<td>-0.41</td>
<td>-0.48</td>
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<tr>
<td>FeS$_2$</td>
<td>23.47</td>
<td>5.13</td>
<td>23.47</td>
<td>13.98</td>
<td>22.35</td>
<td>22.35</td>
<td>0.22</td>
<td>0.22</td>
<td>0.22</td>
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<tr>
<td>CoS$_2$</td>
<td>30.89</td>
<td>11.12</td>
<td>30.89</td>
<td>9.95</td>
<td>26.89</td>
<td>26.89</td>
<td>0.36</td>
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<tr>
<td>BN (this work)</td>
<td>288.4</td>
<td>63.12</td>
<td>288.4</td>
<td>113.2</td>
<td>274.5</td>
<td>274.5</td>
<td>0.22</td>
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<tr>
<td>BN (ref. 76)</td>
<td>290</td>
<td>64</td>
<td>290</td>
<td>112</td>
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<td>Graphene (this work)</td>
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<td>Graphene (ref. 77)</td>
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<td>72</td>
<td>349</td>
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<td>334</td>
<td>0.206</td>
<td>0.206</td>
<td>0.20</td>
</tr>
</tbody>
</table>

Ref. 76, 77, 79

![Fig. 3](image-url) The localized atomic displacements corresponding to the NPR along the (a) X and (b) Y directions, respectively. The blue and orange indicate forced and responsive strain-driven atomic displacements, respectively.
Fig. 4  Geometric evolution under strain. (a) Local lattice morphology and atoms with symmetrical motion in MS₂, and (b) the MS₂ geometric evolution of the tetrahedron under two different modal strains (NPR and PPR). (c) Relationship between MS₂ characteristic angle and electronegativity. (d) Comparison of ICOHP between MS₂ compounds with different compositions. (e) and (f) The ELF of TiS₂ at 0% and 4% strain, respectively. (g) and (h) The ELF of CoS₂ at 0% and 4% strain, respectively.
i.e., distance $d_{S_2-S_4}$ and characteristic angle $\theta$ ($\angle S_2 MS_1$), are thus obtained, see Fig. 3a and b.

Moving on, we will demonstrate additional pathways for NPR production by describing the microscopic deformation mechanism of $MS_2$, as shown in Fig. 4a and b. When subjected to a tensile strain, two opposite geometrical modes take place, as depicted in Fig. 4b. Firstly, on applying tension along the $X$-axis direction, the $M$ atoms shift downward due to their attractive interactions with $S_3$ and $S_4$ atoms, resulting from the robust bonding interactions between the $M$ atoms and their four adjacent atoms. If the interaction between $S$ atoms cannot be discounted, then the attractive force from the $M$ atoms and the $S$ atoms’ lateral repulsive force will affect the $S_1$ and $S_2$ atoms. The resulting forces cause the $S_2$ atoms to rotate and move away from the $M$ atoms, resulting in the NPR. On the other hand, if the $S-S$ interaction is negligible, the $M$ atoms’ attraction towards the $S_1$ and $S_2$ atoms becomes dominant. The structure experiences transverse contraction (PPR) when subjected to tensile strain in the $X$-direction. The two modes, with opposite and competing contributions, have varying effects on the geometrical evolution of the structure. However, we also note that the geometrical variation is insufficient to account for the emerging NPR since both NPR and PPR effects are present in this group of compounds. Therefore, it is anticipated that the electronic structure of the material, including the electronic status of the atoms, has a crucial role in the interactions between the sulfur atoms, thereby exerting a significant impact on the material’s PR.

Fig. 5 Charge densities of (a) TiS$_2$, (b) CrS$_2$, (c) MnS$_2$, (d) FeS$_2$ and (e) CoS$_2$. 
3.5 Basic understanding of the NPR from orbital evolution

To demonstrate this emerging NPR, we provide an example of the geometrical variations and electronic response of a single-layer MS$_2$ when strain is imposed in the $X$-direction. When tensile strain is applied, the geometrical responses of the three MS$_2$ (TiS$_2$, CrS$_2$, and MnS$_2$) with NPR behavior demonstrate consistent behavior, namely, an increase in the eigenangle $\theta$. In contrast, the other two MS$_2$ (FeS$_2$ and CoS$_2$), which do not exhibit the NPR behavior, exhibit a decrease in eigenangle $\theta$, as shown in Fig. S5 (ESI†). The results indicate that the emergence of the NPR in geometrical evolution is associated with an increase in the characteristic angle $\gamma$, as illustrated in Fig. 4a and b. An increase in the characteristic angle $\theta$ indicates that the intra-layer interactions are stronger and that the S atoms have the opportunity to move away from the M atoms in the center, due to the combined forces. This allows the sulfide to overcome the PPR mode and produce NPR. Based on the above analysis, we compared the relationship between the characteristic angle and the electronegativity of monolayer MS$_2$, as shown in Fig. 4c. Monolayers of TiS$_2$, CrS$_2$, and MnS$_2$ exhibit stronger strain responses for intralayer interactions than monolayers of FeS$_2$ and CoS$_2$ due to their smaller characteristic angle $\theta$, see Fig. 4c. The strength of intra-layer interatomic reactions is more likely to increase as the eigenangle decreases. The strong intra-layer interaction response is shown in Fig. 4e–h and stems from the overlap of the intra-layer wave functions. This overlap can be visualized in the ELF. When stretching strain is imposed, the superposition of the electron cloud between sulfur atoms in the TiS$_2$ monolayer becomes deeper (refer to Fig. 4e and f). In contrast, the superposition in CoS$_2$ is comparatively weak (see Fig. 4g and h), resulting in a weaker intralayer repulsion. To measure the strength of the intra-layer interaction response, we extracted the integrated crystal orbital Hamiltonian population (ICOHP) between S$_1$ and S$_2$ atoms, see Fig. 4d. Increasing the strain by 4% results in a more than 30% increase in the interlayer ICOHP of monolayer TiS$_2$, significantly faster than the increase observed in monolayer CoS$_2$ (which increases by no more than 5%). The growth rate of monolayer MS$_2$ follows the order TiS$_2$ > CrS$_2$ > MnS$_2$ > FeS$_2$ > CoS$_2$ in terms of ICOHP. The ICOHP’s rapid growth indicates a stronger response to intra-layer interactions, allowing the material to transition gradually from the emergence of a NPR to a PPR as the response weakens.

![Fig. 6 The PDOS of (a) TiS$_2$, (b) CrS$_2$, (c) MnS$_2$, (d) FeS$_2$ and (e) CoS$_2$.](image-url)
A strong intra-layer response causes the characteristic angle $\theta$ of monolayer MS$_2$ to increase, ultimately resulting in geometric structure-independent NPR behavior. For further comparison, we have also included in Fig. 5 and Fig. S6 (ESI†) the charge density calculations and the full ELF for the MS$_2$ compounds, which allow a clear comparison of the interactions of the S atoms around them and the degree of intralayer response.

To improve our understanding of the emerging NPR in this new sulfide monolayer, we calculated the projected density of states (PDOS) and the electron density difference map (Fig. S7, ESI†) of the MS$_2$ monolayer. According to the electron density difference map, the charges of the transition metal M and S atoms are redistributed during the chemical bonding process, with the M atoms presenting a state in which they lose electrons, while the S atoms gain electrons, thus allowing the observation of electronic interactions, i.e., the transfer of electrons from the M atoms to the S atoms. Fig. 6 displays the PDOS of the MS$_2$ monolayer, where the S-p and M-d orbitals contribute significantly more than the other orbitals in the bonded state. In conjunction with Fig. 6, it can be observed that electrons in the d orbitals of transition metal M atoms enter the metal–sulfur bond. Additionally, we observed that the energy of the s-electrons in the S-atoms is considerably lower than that of the bonded electrons in the M-atoms, forming lone pairs of electrons. During the evolution of S atoms in NPR materials, complex orbital hybridizations such as sp$^3$d are formed, resulting in smaller bond angles than those of sp$^3$ or sp$^2$ hybridization. The bonding pairs are compressed and the bond angles are smaller due to the large repulsive force exerted by the lone pair of electrons on the sulfur atom. The PDOS diagram shows that the number of s-electrons is decreased compared to those in the previous compounds. This implies that the effect of lone pair electrons on bond angles is diminishing. The charge density in Fig. 5 also supports this observation, indicating a gradual weakening of interactions between the S atoms due to variations in the electronic structure. In addition, the electronegativities of Ti, Cr, and Mn are 1.54, 1.66, and 1.55, respectively. The electronegativities of Fe and Co (1.83 and 1.88) are larger, as shown in Fig. 4c. Due to the small electronegativity of the central atom, the bonding electron pairs move away from it, resulting in a smaller bond angle and reduced repulsive forces between the bonding pairs. Therefore, the repulsive force between the two M-S bonds decreases, bringing them closer and resulting in smaller bond angles. In summary, these electronic factors cause a change in the characteristic angle of MS$_2$, resulting in stronger intralayer interactions when subjected to tensile strain due to a smaller characteristic angle. This leads to NPR modes, as shown in Fig. 4b, ultimately resulting in the unique NPR behavior of MS$_2$.

4 Conclusions

In conclusion, we proposed novel 2D sulfides with a NPR and comprehensively investigated the Poisson’s ratio behavior of these MX$_2$-type (M = Ti, Cr, Mn, Fe, Co, X = S) sulfide monolayers. The monolayers TiS$_2$, CrS$_2$, and MnS$_2$ show inherent NPR behavior when strain is applied. Unlike the previously reported NPR dominated by the re-entry mechanism, this phenomenon can be ascribed to the strong strain response of the intra-layer interactions powered by electronic effects. By tracking the key parameter (eigenangle $\theta$) during the geometric evolution, it is possible to gain a deeper understanding of the origin of NPR: the NPR mode (strong interactions between S atoms) and the PPR mode (effects between S atoms). All MS$_2$ monolayers exhibit the same evolutionary path, but TiS$_2$, CrS$_2$, and MnS$_2$ show stronger responses because of the smaller angle $\theta$. The response of TiS$_2$, CrS$_2$, and MnS$_2$ is also stronger. The strong interaction within the layer is due to the lateral repulsion caused by the accumulated charges within the layer. This interaction is quantified by ELF and ICOHP. The phenomenon is caused not only by the geometrical structure but also by the interaction between the lone pairs of electrons of the S atoms in the coordination environment of MS$_2$, along with the varying strengths and weaknesses of the electronegativity of the central atoms in multiorbital hybridization. Studying the distinctive NPR mechanism can provide precious ideas and directions for screening and designing novel NPR materials.

Data availability

The data supporting this article have been included as part of the ESI†.

Conflicts of interest

There are no conflicts to declare.

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