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Carrier Doping Modulate Magnetoelectronic, and Magnetic Anisotropic Properties of Two-Dimensional MSi_2N_4 (M = Cr, Mn, Fe, and Co) Monolayers

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ABSTRACT

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Through extensive density functional theory (DFT) calculations, our investigation delves into the stability, electrical characteristics, and magnetic behavior of monolayers (MLs) of MSi₂N₄. Computational analyses indicate intrinsic antiferromagnetic (AFM) orders within the MSi₂N₄ MLs, as a result of direct exchange interactions among transition metal (M) atoms. We further find that $CrSi_2N_4$ and $CoSi_2N_4$ MLs with primitive cell (pcell) exhibit half-metallic properties, with respective spin- β electrons' gaps of 3.661 and 2.021 eV. In contrast, MnSi₂N₄ and FeSi₂N₄ MLs with pcell act as semiconductors, having energy gaps of 0.427 and 0.282 eV, respectively. When SOC is considered, the $CrSi_2N_4$, $MnSi_2N_4$ and $FeSi_2N_4$ MLs are metals, while the $CoSi_2N_4$ ML is semiconductor. Our findings underscore the dynamic and thermodynamic stability of MSi₂N₄ MLs. We have also explored the influence of carrier doping on the electromagnetic attributes of MSi₂N₄ MLs. Interestingly, charge doping could transform $CrSi_2N_4$, $MnSi_2N_4$, and $CoSi_2N_4$ MLs from their original AFM state to a ferromagnetic (FM) order. Moreover, carrier doping transformed CrSi₂N₄ and CoSi₂N₄ MLs from spin-polarized metal to halfmetal (HM). It is of particular note that doping of $CrSi_2N_4$ MLs with +0.9 e/pcell or more holes caused a switch in the easy axis (EA) to the [001] axis. The demonstrated intrinsic AFM order, excellent thermodynamic and kinetic stability, adjustable magnetism, and half-metallicity within the

 MSi_2N_4 family suggest promising potential for applications in the real m of spintronics.

1. INTRODUCTION

Since the discovery of graphene,¹ the first two-dimensional (2D) material, through mechanical exfoliation, there has been a great interest in 2D materials owing to their exemplary electrical,² thermal,² mechanical,^{3,4} and chemical catalytic⁵ properties. The potential for such materials is incredibly vast.⁶⁻⁸ Nonetheless, the existence of long-range magnetic order at finite temperatures in these materials was considered unfeasible due to thermal fluctuations as per the Mermin-Wagner theorem.⁹ Initially, 2D FM materials had not yet been synthesized. The lack of 2D FM materials limits 2D materials' application in the spintronics and electronics. However, the synthesis of the layered 2D FM CrI₃ has sparked new excitement in this field.¹⁰ Following the discovery of CrI₃, the successful synthesis and characterization of other layered 2D FM materials¹¹⁻¹³ such as Fe₃GeTe₂,¹⁴ Cr₂Ge₂Te₆,^{15, 16} and 2H-VSe₂¹⁷ have occurred, these materials are anticipated to invigorate spintronics, data storage, magnetic electronic devices and magnetostrictive material development.¹⁸⁻²⁰ Hence, the research and enhancement of 2D FM materials possess profound significance due to their promising potential applications.^{21, 22}

The layered MoSi₂N₄²³ MLs have interesting properties.²⁴⁻²⁹ This material's paramagnetic properties,³⁰ however, limit its application in

spintronics.^{31, 32} Encouragingly, there exist several common methods to manage the magnetic ground state of 2D materials, including charge doping,³³ defect engineering,³⁴ stress engineering,³⁵ magnetic field manipulation,³⁶ intercalation,^{37, 38} and optical control.³⁹ Among these, charge doping is a practical and effective method⁴⁰ to modulate the electromagnetic properties of 2D materials,⁴¹ and the utilization of computational techniques may help alleviate the high experimental costs.

This paper studies MSi_2N_4 MLs due to their exceptional performance. Employing first-principles calculations based on DFT, we execute systematic research on MSi_2N_4 . We investigate the geometry, electronic structure, stability, and magnetism of MSi_2N_4 MLs, and uncover the origin of the AFM ground state. Besides, $CrSi_2N_4$ and $CoSi_2N_4$ MLs with FM orders are half-metallic. Charge doping enables the transition of magnetic order in $CrSi_2N_4$ and $MnSi_2N_4$. Additionally, charge doping prompts a switch in the EA of $CrSi_2N_4$ from [100] to [001] directions. Overall, this study propels the research trajectory of 2D magnetic materials, fostering their broad applications in the domain of spintronics.

2. COMPUTATIONAL DETAILS

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The geometries of MSi_2N_4 are searched by adopting the particle-swarm optimization (PSO) method with the CALPSO code and ASAP.⁴² The plane-wave basis Vienna ab initio simulation package (VASP) code⁴³ is used to calculate MSi_2N_4 MLs. Perdew–Burke–Ernzerhof (PBE)⁴⁴ is

adopted to deal with valence electrons. The range-separated hybrid Heyd-Scuseria-Ernzerhof (HSE06)45,46 functional and GGA+U method47 is applied to deal with the strong-correlated correction to the valence electrons, respectively. The effective onsite Coulomb interaction parameters (U) are set to be 4.6 eV ($CrSi_2N_4$ and $MnSi_2N_4$), 6.0 eV (FeSi₂N₄), 7.6 eV (CoSi₂N₄). The exchange interaction parameters (J_0) are set to be 0.6 eV ($CrSi_2N_4$, $MnSi_2N_4$ and $CoSi_2N_4$), 0.5 eV ($FeSi_2N_4$), respectively. Therefore, the effective U_{eff} ($U_{eff} = U - J_0$) are set as 4.0 eV $(CrSi_2N_4 \text{ and } MnSi_2N_4)$, 5.5 eV (FeSi_2N_4), 7.0 eV (CoSi_2N_4), and the corresponding references supporting these settings are shown in the Supporting Information. These U_{eff} are used in the calculation of the magnetic anisotropy energy (MAE), phonon spectra, and ab initio molecular dynamics (AIMD) simulation. Lattice constant c along zdirection is set as 23 Å. The distance between adjacent interlayer atoms is 17 Å. The kinetic energy cutoff is set as 520 eV for all MSi₂N₄ MLs. The criteria of energy and force are 10⁻⁶ eV and 10 meVÅ⁻¹, respectively. The geometry optimization and energy computation are adopted $3 \times 3 \times 1$ and $9 \times 9 \times 1$ Monkhorst–Pack k-grids, respectively. The SOC is considered in calculation. After self-consistent calculation, total energies are evaluated by the noncollinear nonself-consistent calculations. The MAE is calculated with an energy cutoff of 600 eV, and the corresponding energy criterion is 1×10^{-8} eV. The corresponding k-grid is adopted $20 \times 20 \times 1$ with no

symmetry constriction. Based on the finite displacement method, the

phonon spectra and the phonon density of the states (PHDOS) are calculated in Phonopy package.⁴⁸ To calculate phonon spectra and the PHDOS, a $4\times4\times1$ cell is adopted. The corresponding criteria of energy is set as 10^{-8} eV and the Hellmann–Feynman force is 1 meVÅ⁻¹, respectively. 6000 uniform k-points along high-symmetry lines are adopted to get phonon spectra. AIMD simulation is also used to prove geometry stability. The constant moles–volume–temperature ensemble with a Nosé–Hoover thermostat⁴⁹ is used at 300 K. The time step is 1 fs and the total time is 10 ps. To eliminate the effect of periodic boundary condition in smaller system size, a 2×2×1 cell (supercell) is adopted in AIMD simulation.

3. RESULTS AND DISCUSSION

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3.1. Geometries of MSi₂N₄ MLs. The ML geometries of MSi₂N₄ have been computed and verified through the application of PSO⁴² and ASAP methodologies, founded on crystallographic structural analysis. Fig S1 displays the optimal pcell configuration for the MSi₂N₄ MLs, whilst Fig 1a-c exhibits the optimal geometries for the respective supercells. As indicated in Table 1, the determined lattice constants for MSi₂N₄ MLs are as followed: 2.909 Å for CrSi₂N₄, 2.920 Å for both MnSi₂N₄ and FeSi₂N₄, and 2.875 Å for CoSi₂N₄. Conversely, the MoSi₂N₄ ML exhibits a lattice constant of 2.910 Å. Atomic radii values of M and Mo are 118 pm (Cr), 117 pm (Mn), 117 pm (Fe), 116 pm (Co), and 130 pm (Mo), respectively.



Fig 1. Optimized geometries with (a) top and (b, c) side views of MSi₂N₄ MLs. The left, medium, and right balls at the bottom of Fig 1c represent M, Si, and N atoms, respectively.

This leads to comparable lattice parameters across the different MSi_2N_4 configurations. The interatomic distances between element M and nitrogen atoms have been calculated to be 2.049, 2.052, 2.052, and 2.048 Å, respectively.⁵⁰ These distances exhibit minor variation due to the atomic radii similarities between the M elements. Further details pertaining to the MSi_2N_4 can be referenced from Table 1. The optimized geometries for the MSi_2N_4 MLs have been represented visually in Fig 1a-c. The values for d_1 , d_2 , d_3 , and d_{M-N} outlined in Table 1, have been annotated in Fig 1c. For example, the d_1 presents the distance from the top N atom to the bottom N atom.

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System	$a_0(\text{\AA})$	$d_1(\text{\AA})$	$d_2(\text{\AA})$	d_3 (Å)	$d_{\text{M-N}}(\text{\AA})$
CrSi ₂ N ₄	2.909	6.879	1,174	1.750	2.049
$MnSi_2N_4$	2.920	6.858	1.170	1.745	2.052
FeSi ₂ N ₄	2.920	6.858	1.170	1.745	2.052
CoSi ₂ N ₄	2.875	6.989	1.199	1.762	2.048

Table 1. Calculated Lattice Constants a_0 , Total Energies E_t , and Several^{/D3CP05032G}

3.2. Electronic and Magnetic Properties of MSi_2N_4 . Initially, our investigation is focused on the electromagnetic characteristics of a pcell. Each MSi_2N_4 pcell is composed of one M atom, two Si atoms, and four N atoms, each demonstrating spin charge densities as delineated in Fig S2a-d. The magnetic moments (MMs) attributed to each M atom equate to 2.56 (M = Cr), 3.31 (Mn), 3.84 (Fe), and 2.51 (Co) μ_B , in contrast with the MMs of silicon and nitrogen atoms, which approach 0 μ_B . An assessment of the band structure and partial density of state (PDOS) for MSi_2N_4 has been computed and presented in Fig S3a-d, indicating that $CrSi_2N_4$ and $CoSi_2N_4$ MLs operating with the pcell are HMs, while $MnSi_2N_4$ and $FeSi_2N_4$ MLs function as semiconductors. Besides, the band structures with SOC with magnetic axis along [001] are also calculated, considering the existence of M in the MSi_2N_4 and $FeSi_2N_4$ MLs, the bands cross the Fermi-level, For $CrSi_2N_4$, $MnSi_2N_4$ and $FeSi_2N_4$ MLs, the bands cross the Fermi-level,

thus, they are metals. More specifically, $MnSi_2N_4$ ML is a metal based on the SOC calculation results, while it is a semiconductor based on the band structures without SOC. So, it is different between the band structures without SOC and these with SOC. For CoSi₂N₄ ML, the VBM of it is located at the Γ point, while the CBM is located at the F point, shown in Fig 2d. Therefore, the $CoSi_2N_4$ ML is semiconductor with an indirect band of 0.370 eV. Comprehensive data regarding the electromagnetic properties of MSi₂N₄ MLs can be found in the Supporting Information.



Fig 2. Band structures of (a) $CrSi_2N_4$, (b) $MnSi_2N_4$, (c) $FeSi_2N_4$ and (d) $CoSi_2N_4$ MLs. The dots colored by red present the electrons' channel.

Subsequently, supercells of MSi₂N₄ MLs were studied to authenticate the ground state of the MSi₂N₄ compound. Analysis of the magnetic

properties of M atoms was conducted to discern the magnetic order, as displayed in Fig 3a-c. Each M atom contributes 2.51 (Cr), 3.31 (Mn), 3.72 (Fe), and 2.55 (Co) $\mu_{\rm B}$ MM, with four M atoms present in a supercell. The FM order in the supercell yields 8.00 ($CrSi_2N_4$), 12.00 ($MnSi_2N_4$), 16.00 (FeSi₂N₄), and 11.35 (CoSi₂N₄) μ_B MM, suggesting that the MM of MSi₂N₄ is principally contributed by M atoms, as demonstrated in Table 2. In addition to the FM order, the AFM configuration was also examined. For the AFM orders of the MSi₂N₄ MLs, two M atoms contribute positive MMs of 2.173, 3.194, 3.640, and 2.536 $\mu_{\rm B}$, while the other two M atoms contribute an equal and opposite MM, leading to a total MM of 0.0 $\mu_{\rm B}$ for all considered MSi₂N₄ MLs. Fig 3a-c showcases the spin charge density of MSi_2N_4 for both FM and AFM orders. We define ΔE_{FM-AFM} as followed: $\Delta E_{\rm FM-AFM} = E_{\rm FM} - E_{\rm AFM}$, which presents the energy differences between FM and AFM orders of MSi₂N₄ MLs. The energies of AFM orders of MSi₂N₄ MLs E_{AFM} are set as 0 eV. The result shows that the energies of the FM orders $E_{\rm FM}$ are the highest among all calculated magnetic orders of the MSi₂N₄ MLs. The $\Delta E_{\text{FM-AFM}}$ is shown in Table 2.

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To comprehend why MSi_2N_4 MLs exhibit an AFM orientation, we delved into the underlying mechanism. Each M atom within the MSi_2N_4 MLs is surrounded by six N ligands. The N-Cr-N bond angles are precisely 69.898°, 90.440°, and 131.615°, while the N-Mn-N bond angles measure

Table 2. MM (μ_B) and the Energy Differences ΔE_{FM-AFM} (meV) of MSt₂N₄^{9/D3CP05032G} MLs between FM and AFM Orders. The MM/M Appeared in the Table Represents the Moment Contributed by M Atoms.

System	$\Delta E_{\mathrm{FM-AFM}}$	М	М	MM/M		
		FM	AFM	FM	AFM	
CrSi ₂ N ₄	438	8.00	0	2.51	± 2.17	
$MnSi_2N_4$	1235	12.00	0	3.31	± 3.19	
FeSi ₂ N ₄	547	16.00	0	3.72	± 3.64	
$CoSi_2N_4$	138	11.35	0	2.55	± 2.54	

69.539°, 90.703°, and 131.498°. In the case of FeSi₂N₄ ML, the N-Fe-N bond angles are 69.539°, 90.702°, and 131.498°. For Co, the N-Co-N bond angles are 70.113°, 90.294°, and 131.679, respectively. Analysis of the Integrated Density of States (IDOS) of d-electrons suggested that M atoms contained between 4 to 7 electrons within d-orbitals. The presence of these electrons led to a direct exchange interaction that resulted in an AFM coupling. Concurrently, the FM coupling was seen to arise from superexchange interaction, in line with the Goodenough-Kanamori-Anderson rule⁵¹⁻⁵³ as controlled by the superexchange theorem. These two distinct exchange interactions were observed, with the direct exchange interaction between the M atoms playing a decisive role in defining the ground state, as depicted in Fig S9a. This implies that the direct exchange



Fig 3. Spin charge densities of (a) AFM and (b) FM orders of $CoSi_2N_4$. The isovalue is 0.05 $e/Å^3$ in (a), and 0.04 $e/Å^3$ in (b), respectively. The red and blue colors represent spin- α and spin- β electrons, respectively. The spin-polarized band structure and PDOS of (c) $CrSi_2N_4$, (d) $MnSi_2N_4$, (e) FeSi₂N₄, and (f) $CoSi_2N_4$ MLs, respectively. The solid and dashed lines represent spin- α and spin- β electrons, respectively.

interaction among the M atoms proved stronger than the superexchange interaction, as illustrated in Fig S9a, b. Consequent to this analysis, MSi₂N₄ demonstrates an AFM ground state, contrasting to that of MoSi₂N₄. The MSi₂N₄ MLs with AFM orders were identified as either spin-unpolarized

metals ($CrSi_2N_4$ and $CoSi_2N_4$) or semiconductors ($MnSi_2N_4$ and $FeSi_2N_4^{039/D3CP05032G}$), with respective energy gaps of 1.539 and 0.234 eV, as illustrated in Fig 3dg. Additional data on the magnetic and electronic properties of the MSi_2N_4 MLs are provided in Fig S10 in the Supporting Information.

3.3. Electronic and Magnetic Properties of Carriers-Doped MSi₂N₄. Carriers-doped 2D materials have been realized by several methods,⁵⁴⁻⁵⁷ such as self-doping caused by intrinsic defects,⁵⁸ bulk doping induced by the substrate,⁵⁹ spontaneous polarization associated with the substrate,⁶⁰ and so on.⁶¹ The doping value is up to $10^{14} \sim 10^{15} \text{ e/cm}^2$ in some experimental studies⁵⁴⁻⁵⁶ or theoretical research,⁶²⁻⁶⁵ so the chosen doping values in this work are reasonable. Additionally, carrier doping methodologies^{40, 66} have been frequently employed to modulate the performance characteristics of 2D materials. Hence, further investigations are warranted to scrutinize the effects of carrier doping on the magnetic and electronic properties of MSi₂N₄ MLs.

Our calculated findings indicate that charge doping exerts an influence on the properties of these MLs. Notably, carrier doping within MSi_2N_4 MLs can instigate a magnetic phase transition due to alterations in the number and structure of MSi_2N_4 valence electrons. These modifications have implications for the energy of each magnetic configuration, in compliance with the Goodenough-Kanamori-Anderson rules. Furthermore, carrier doping can initiate an electronic phase transition, effectively

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converting MSi_2N_4 MLs from semiconductor to HM. Recognizing the potential for magnetic configuration regulation of MSi₂N₄ is vital, given the promising future of 2D FM materials in various applications such as integrated chips, spintronic devices, magnetic storage, and quantum information technology.⁶⁷ The charge doping could cause magnetic phase transformation from AFM to FM orders in MSi₂N₄. The energy differences between AFM and FM orders (ΔE) are defined as $\Delta E = E_{AFM} - E_{FM}$, where E_{AFM} means the energy of MSi₂N₄ with AFM order, while E_{FM} means energy with FM order. The relation between ΔE and doped charges is shown in Fig 4a-d. When -0.3 e/pcell (-0.0409 $e/Å^2$) charges are injected in the pcell of the CrSi₂N₄ ML, the ΔE is -0.816 eV. As more negative charges are introduced, the ΔE is decreased to -0.982 eV (-0.6 e/pcell) and -1.110 eV (-0.9 *e*/pcell), respectively. When the holes (positive charges) are doped, the ΔE is further increased to -0.442 eV (+0.1 e/pcell), 0.194 $(+0.3 \ e/pcell)$, 1.078 $(+0.6 \ e/pcell)$, and 1.646 eV $(+0.9 \ e/pcell)$, respectively. The magnetic phase transition is observed in the CrSi₂N₄ ML when +0.25 e/pcell holes are doped, as shown in Fig 4a. ΔE increases as more positive charges or fewer negative charges are doped. It means that the superexchange interaction is strengthened and the direct exchange interaction is weakened. Following the investigation of CrSi₂N₄ MLs, the magnetic properties of doped MnSi₂N₄ MLs are explored. The total energy difference (ΔE) of MnSi₂N₄ initially diminishes and subsequently escalates,

as demonstrated in Fig 4b. The nadir of ΔE is observed when $MnSi_2N_4^{polstormatchilder}$ MLs are in their undoped state, with a minimum value of -1.235 eV. Notably, a magnetic phase transition is evident in MnSi₂N₄ MLs upon the



Fig 4. Electron and hole dope the MSi₂N₄ MLs. ΔE of (a) CrSi₂N₄, (b) $MnSi_2N_4$, (c) $FeSi_2N_4$, (d) $CoSi_2N_4$ change with doped charges. The q in this figure presents the number of doped charges.

introduction of +0.54 e/pcell (+0.0731 e/Å²) holes, as illustrated in Fig 4b. The ΔE plots for both FeSi₂N₄ and MnSi₂N₄ MLs exhibit a V-shaped pattern, as evidenced in Fig 4b, c. A persistent AFM order characterizes $FeSi_2N_4$, whereas $CoSi_2N_4$, upon carrier doping, predominantly exhibits an FM order, as shown in Fig 4d.

The foregoing discussion reveals that carrier doping can influence the magnetic characteristics of MSi_2N_4 MLs. Additionally, it appears that

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View Article Online carrier doping also mediates changes in electronic properties. As illustrated in Fig 5, $CrSi_2N_4$ in its undoped state behaves as a metal, whereas undoped MnSi₂N₄ exhibits semiconductor characteristics. The metallic nature of $CrSi_2N_4$ persists with the introduction of -0.8 or -0.3 *e*/pcell electrons. However, with the addition of +0.2 e/pcell holes, the CrSi₂N₄ MLs transitions into HM, as delineated in Fig 5c. This shift is noteworthy as it occurs upon the introduction of $+0.2 \ e/pcell$ holes, suggesting a lower threshold for the modulation of electronic properties compared to magnetic transitions. As Fig 5c-e indicate, the states proximate to the Fermi level in HM are primarily attributed to spin- α electrons. The transition of CrSi₂N₄ from semiconductor to HM is attributable to the repositioning of some electrons initially residing at the Fermi level, which are "pumped" out of the valence band maximum (VBM) of CrSi₂N₄ when positive charges are incorporated. This carrier doping modifies the Fermi surface, thereby triggering the transition. With regard to $MnSi_2N_4$, doping with -0.6 or -0.3 e/pcell charges imparts metallic characteristics, whereas in its undoped state, $MnSi_2N_4$ behaves as a semiconductor. The introduction of +0.6 or +0.9 e/pcell electrons induces a shift to HM, as presented in Fig 5f, g. Here, as in $CrSi_2N_4$, the states at the MnSi₂N₄ ML's Fermi level in HM phase are predominantly due to spin- α electrons. Moreover, HM phase persists when charges are introduced in the CoSi₂N₄ ML, with additional details provided in the Supporting Information (Fig S11).



Fig 5. Band structures of the electrons or holes doped $CrSi_2N_4$ and MnSi₂N₄ MLs, calculated with HSE06 functional. The band structures of $CrSi_2N_4$ are doped with (a) -0.8 (b) -0.3, (c) 0.2, (d) 0.5, (e) +0.8 *e*/pcell. $MnSi_2N_4$ are doped with (f) -0.6, (g) -0.3, (h) 0, (i) 0.6, (j) 0.9 e, respectively. The red and blue lines represent spin- α and spin- β electrons, respectively.

3.4. Magnetocrystalline Anisotropy. The MAE is normally defined as the difference in total energy for moment alignment along an EA and a hard axis.^{35, 68} The elevation of the magnetic axis is defined as θ and the azimuth of the magnetic axis is defined as ϕ . The relation between the energies of the systems with high symmetry and (θ, ϕ) is as followed:⁶⁹

$$\Delta E_0 = K_1 \cos^2 \theta + K_2 \cos^4 \theta + K_3 \cos 3\phi = E - E_{[001]}$$
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In the above equation, E is the energy in a certain elevation and azimuth (θ, ϕ) . $E_{[001]}$ represents the energy with EA along [001] direction. Similarly, $E_{[100]}$ and $E_{[010]}$ could be defined. K_1 and K_2 are the quadratic and quadratic coefficients in the equation 1, respectively. The relation between ΔE_0 and (θ, ϕ) is shown in Fig 6a. Previous literature⁷⁰ indicates that ΔE_0 and ϕ are independent. Besides, the conclusion could be drawn from the symmetry of the MSi_2N_4 MLs that each of MSi_2N_4 MLs has a D_{3h} point group.⁵⁸ As a result, K_3 is equal to 0. Therefore, the equation 1 is corrected into the following equation:

$$\Delta E_0 = K_1 \cos^2 \theta + K_2 \cos^4 \theta \tag{2}$$

For MnSi₂N₄ ML, when $E = E_{001}$ and $\theta = \pi/2$, ΔE_0 reaches the maximum value (0 meV, taken as the reference energy). However, it reaches the minimum value when $\theta = 0$. The EA tends to be IMA (inplane magnetic anisotropy, along [100] direction). The relation between ΔE_0 and θ is revealed in Fig 7a. In calculation, U_{eff} is set as 4.6 eV. The relations of ΔE_0 (unit: meV) of different charges doped MnSi₂N₄ ML with θ are as followed: $\Delta E_0 = -0.209 \cos^2 \theta \ (+0.6 \ e), \ \Delta E_0 = -0.168 \cos^2 \theta \ (+0.7 \ e),$ $\Delta E_0 = -0.144 \cos^2 \theta \ (+0.8 \ e), \text{ and } \Delta E_0 = -0.120 \cos^2 \theta \ (+0.9 \ e). E_{[100]} \text{ and } E_{[001]}$ are used to present energy of the system whose θ of the magnetic axis is 0 and 90 degrees, respectively. Then MAE could be presented as the following equation:

When MAE is negative, the direction of the EA tends to be in the plane, and it is called as IMA. By the way, when the EA prefers to be perpendicular to the plane, it is called perpendicular magnetic anisotropy (PMA). MnSi₂N₄ is a 2D material, and it is expected that MnSi₂N₄ ML has



Fig 6. Information about MAE of $CrSi_2N_4$. (a) Relationship between ΔE_0 and (θ, ϕ) is shown in a stereogram. (b) ΔE_0 of CrSi₂N₄ with different doped charges varies as elevation changes. The black, red, yellow, green, cyan, blue and purple dotted lines represent ΔE_0 of CrSi₂N₄ with doped charges of +0.3, +0.4, +0.5, +0.6, +0.7, +0.8, and +0.9 *e*/pcell holes, respectively. (c) Red arrows represent the direction of EA of $MnSi_2N_4$. (d) Relation between ΔE_0 of CrSi₂N₄ and azimuthal. The black, red, yellow,

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green, cyan, blue and purple dotted lines represent ΔE_0 of $\text{CrSi}_2 \mathbb{N}_4^{\text{Dim}} \mathbb{N$

a considerable MAE compared with three-dimensional material. The calculation results reveal that the MAE of MnSi₂N₄ ML is -0.209 (+0.6 e/pcell), -0.168 (+0.7 e/pcell), -0.144 (+0.8 e/pcell), and -0.120 meV (+0.9 e/pcell), respectively. Negative MAE indicates that MnSi₂N₄ prefers IMA, as shown in Fig 6c. The MAE of MnSi₂N₄ decreases with the increase of doped charges, as shown in Fig 7a, b. CrSi₂N₄ is similar to that of MnSi₂N₄ ML. The U_{eff} is also set as 4.0 eV for MnSi₂N₄ ML. The relations between ΔE_0 (unit: μ eV) and θ are revealed in Fig 6b. Besides, the relations between ΔE_0 of CrSi₂N₄ ML with different carrier doping and θ are as followed:

$$\Delta E_0 = -7.45 \cos^2 \theta + 4.52 \cos^4 \theta \ (+0.3 \ e) \tag{4}$$

$$\Delta E_0 = -2.61 \cos^2 \theta \ -0.95 \cos^4 \theta \ (+0.4 \ e)$$
 (5)

$$\Delta E_0 = -31.77 \cos^2\theta \ (+0.5 \ e) \tag{6}$$

$$\Delta E_0 = -38.76 \cos^2 \theta \ (+0.6 \ e) \tag{7}$$

$$\Delta E_0 = -9.59 \cos^2 \theta \ (+0.7 \ e) \tag{8}$$

$$\Delta E_0 = -3.93 \cos^2 \theta \ (+0.8 \ e) \tag{9}$$

$$\Delta E_0 = 3.77 \cos^2 \theta \ (+0.9 \ e) \tag{10}$$

The MAE of $CrSi_2N_4$ ML is -2.93 (+0.3 *e*/pcell), -3.56 (+0.4 *e*/pcell), -

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31.78 (+0.5 *e*/pcell), -38.77 (+0.6 *e*/pcell), -9.59 (+0.7 *e*/pcell), -3.93 ($\pm 0.8^{/D3CP05032G}$ *e*/pcell), and 3.76 (+0.9 *e*/pcell) µeV, respectively, shown in Fig 6d. MAEs of CrSi₂N₄ decrease first and then increase. Interestingly, when +0.9 *e*/pcell electrons are introduced, the negative MAE value substituted for positive one, which means EA of CrSi₂N₄ ML has changed from [100] to [001] directions. Accordingly, there is a switch for CrSi₂N₄ from IMA to PMA.

In order to clarify the switch of EA, it is necessary to determine the contribution of each atomic orbital to the MAE of $CrSi_2N_4$ and $MnSi_2N_4$. Besides, explaining the relation between MAEs (MAE of $CrSi_2N_4$ and $MnSi_2N_4$) and doped charges is urgent. To accomplish the above objectives, tight binding and second-order perturbation theory are used to calculate the MAE.⁵⁹ According to the canonical formula,⁷¹ each atom's contribution to MAE can be calculated by using the following formula:

$$MAE_{i} = \left[\int E_{f}(E - E_{F})[n_{i}^{[100]}(E) - n_{i}^{[001]}(E)]\right]$$
(11)

where the MAE_i present the MAE contributed by atom i, the $n_i^{[100]}$ and $n_i^{[001]}$ mean the density of state in [100] and [001] directions, respectively. Given the symmetry of MSi₂N₄ MLs (D_{3h} group), $E_{[010]}$ is equal to $E_{[100]}$.³³ The following formula is used to calculate total MAE:

$$MAE_{tot} = \sum_{i} MAE_{i}$$
(12)

where the MAE_{tot} is the sum of MAE_i . Given the second-order perturbation theory,⁷² MAE can be calculated by the following equation:





Fig 7. (a) ΔE_0 of doped MnSi₂N₄ ML varies as elevation changes. The black, red, green and blue dotted lines represent ΔE_0 of MnSi₂N₄ with +0.6, +0.7, +0.8, and +0.9 *e*/pcell doped charges vary as elevation changes. (b) ΔE_0 of MnSi₂N₄ with different doped charges vary as azimuthal changes. The black, red, green and blue dotted lines represent ΔE_0 of

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MnSi₂N₄ with +0.6, +0.7, +0.8, and +0.9 *e*/pcell doped charges varies as $^{\text{DO}+10.1039/\text{D3}CP05032G}$ azimuthal changes. Orbital-resolved MAE of MnSi₂N₄ ML with doped charges of (c, f, i) +0.6, (d, g, j) +0.8, and (e, h, k) +1.0 *e*/pcell, respectively. The orbital-resolved MAEs contributed by (c, d, e) Mn, (f, g, h) Si, and (i, j, k) N atoms are shown in Fig 7, respectively.

where + and – mean spin- α and spin- β states, ξ , L_x and L_z represent the SOC constant, angular momentum operators in [100] and [001] directions, respectively. и and o represent unoccupied and occupied states, respectively. $E_{\rm u}$, $E_{\rm o}$ present energies of occupied and unoccupied states, respectively. MAE is primarily composed of spin orbit matrix element and energy difference. According to equation 4, MAE is related to density of the Fermi-level. The matrix element differences states near $|\langle o^{-} | L_{z} | u^{-} |^{2} - |\langle o^{-} | L_{x} | u^{-} \rangle|^{2}$ and $|\langle o^{+} | L_{z} | u^{-} |^{2} - |\langle o^{+} | L_{x} | u^{-} \rangle|^{2}$ of p and dorbitals are calculated, which are shown in Table 3 and Table 4.

To explain the change of MAE with doped charges, atomic orbital resolved MAE is researched, and the corresponding results are shown in Fig 7c-k and Fig 8a-i, respectively. The MAE of $CrSi_2N_4$ is relatively low. Each atom's contribution to the MAE is shown in Table S1. The hybridization between Cr's *d* orbitals is also investigated. It could be concluded that the hybridization between Cr atoms' d_{z^2} and d_{yz} contributes positively to MAE (corresponds to the matrix differences 3 for

Table 3. Matrix Differences of <i>d</i> Orbitals along [001] and [100] Directions in	050320
equations 6 and 7	

			o^+					0 ⁻		
u ⁻	\mathbf{d}_{xy}	d_{yz}	d_{z^2}	d _{xz}	$\mathbf{d}_{x^2-y^2}$	d_{xy}	d_{yz}	d_{z^2}	d _{xz}	$\mathbf{d}_{x^2 - y^2}$
d_{xy}	0	0	0	1	-4	0	0	0	-1	4
d_{yz}	0	0	3	-1	1	0	0	-3	1	-1
d_{z^2}	0	3	0	0	0	0	-3	0	0	0
d_{xz}	1	-1	0	0	0	-1	1	0	0	0
$d_{x^2-y^2}$	-4	1	0	0	0	4	-1	0	0	0

the d-orbitals) from 0.040 (+0.6 *e*/pcell) to 0.051 (+0.9 *e*/pcell) meV. The hybridization between Cr atoms' d_{x^2,y^2} and d_{xy} make negative contribution to MAE (corresponds to the matrix differences -4 for the Cr atom's d-orbitals) from -0.060 (+0.6 *e*/pcell) to -0.033 (+0.9 *e*/pcell) meV. More information about the hybridization between Cr's *d* orbitals could be found in Fig 8a-i. According to the above result, we can conclude that the negative contribution (to MAE) of the hybridization between Cr atoms' d_{x^2,y^2} and d_{xy} decreases with the doped charges. Besides, the positive contribution (to MAE) of the hybridization between Cr atoms' d_{y^2} and

Table 4. Matrix Differences of *p* Orbitals along [001] and [100] Directions

		<i>0</i> ⁺			0 ⁻	
u^-	$p_{\rm y}$	p_{z}	$p_{\rm x}$	p_{y}	$p_{\rm z}$	$p_{\rm x}$
p_{y}	0	1	-1	0	-1	1
<i>p</i> _z	1	0	0	-1	0	0
p _x	-1	0	0	1	0	0

in equations 6 and 7

increases with the doped charges. These could explain that the MAE's $d_{\rm vz}$ sign reverses. The MAE's sign reverses, which means the transformation of EA.



Fig 8. Orbital-resolved MAE of $CrSi_2N_4$ ML with doped charges of (a, d, g) +0.6, (b, e, h) +0.7, and (c, f, i) +0.9 e/pcell, respectively. The orbitalresolved MAEs contributed by (a, b, c) Cr, (d, e, f) Si, and (g, h, i) N atoms are shown in this figure, respectively.

3.5. Dynamical and Thermal Stability. The phonon dispersion curve and the PHDOS are calculated, as shown in Fig 9a-d. The results show there is no imaginary phonon mode, thus the dynamic stability of MSi_2N_4 is predicted. The highest vibration frequency contributed by M is 11.97 (Cr), 6.53 (Mn), 5.28 (Fe) and 5.23 (Co) THz, respectively, which decreases with atomic number increasing. In addition, the PHDOS is mainly contributed by M atom for the low frequency ($0 < \varepsilon < 10$ THz), while it is mainly contributed by N and Si atoms for the high frequency $(\varepsilon > 10 \text{ THz})$. This difference is due to the different atomic weight between Si, N and M atoms. Specifically, the M atoms (atomic weight: 52.00, 54.94, 55.85, and 58.93) are heavier than Si (atomic weight: 28.09) and N atoms (atomic weight: 14.01). Thus, the high frequency phonons are mainly contributed by the silicon and nitrogen atoms, while the low frequency phonons are mainly contributed by the M atoms, as shown in Fig 9a-d. M atoms contribute thermal conductivity majorly at low temperatures by the low-frequency phonons. However, thermal conductivity is majorly contributed by silicon and nitrogen atoms at high

temperatures with the high-frequency phonons. Since the MSi_2N_4 MLs are $^{\text{View Article Online}}_{\text{MLS}}$ composed of the same non-metallic atoms, and these non-metallic atoms are lighter than the M and Mo atoms, the maximum vibration frequency of MSi₂N₄ is close to that of MoSi₂N₄.⁷³



Fig 9. (a–d) Phonon spectrum and PHDOS of (a) $CrSi_2N_4$, (b) $MnSi_2N_4$, (c) $FeSi_2N_4$, and (d) $CoSi_2N_4$ MLs. The green, blue, pink, wine red, orange, cyan lines represent Si, N, Cr, Mn, Fe, and Co atoms' projected phonon

DOS, respectively. (e–h) AIMD of evaluation of energies at the $PBE^{1}U^{0}U^{0}D3CP05032G}$ level for 10 ps at 300 K. The total energies of (e) $CrSi_2N_4$, (f) $MnSi_2N_4$, (g) $FeSi_2N_4$, and (h) $CoSi_2N_4$ are shown in Fig 9e-h, respectively.

To predict the thermal stability of MSi_2N_4 family, the widely used AIMD simulation, which is applied in studying the stability of materials, is performed at 300K. The result shows that the total energies of MSi_2N_4 fluctuated around -219.65 (Cr), -216.77 (Mn), -207.41 (Fe), and -198.58 eV (Co) at 300 K, as shown in Fig 9e-h. The total energies of MSi_2N_4 increase with the atomic number. The phase transition occurs in $CoSi_2N_4$ ML, and the energy of $CoSi_2N_4$ ML decreases during this phase transition. More information about the dynamical and thermal stability of the MSi_2N_4 is shown in Fig S12 in the Supporting Information.

4. CONCLUSIONS

In summary, we employed DFT calculations to investigate the structural, electronic, and magnetic properties of ML MSi_2N_4 . We discovered that intrinsic MSi_2N_4 MLs exhibit either metallic or semiconducting behavior, coupled with AFM orders. We further investigated the impact of carrier doping on these systems. Our results indicate that upon doping with +0.25 e/pcell ($CrSi_2N_4$)/ +0.54 e/pcell ($MnSi_2N_4$) or more positive carriers, the magnetic orders of both $CrSi_2N_4$ and $MnSi_2N_4$ MLs transition to FM states. Moreover, charge doping appears to be a viable strategy to modulate the

electronic properties of these MLs. Indeed, CrSi₂N₄ and MnSi₂N₄^{E 1010339/D3CP05032G} transition from their initial states as metals or semiconductors into HM upon the introduction of +0.5 e/pcell / +0.6 e/pcell charges, respectively.Further injection of positive charges results in an initial increase followed by a decrease in the MAE of $CrSi_2N_4$ beyond +0.6 *e*/pcell charge doping. Interestingly, carrier doping of $+0.9 \ e$ /pcell causes a switch in the EA direction from [100] to [001] in the $CrSi_2N_4$ ML. This phenomenon is attributable to the reduced negative hybridization contribution between Cr atoms' $d_{x^2-y^2}$ and d_{xy} orbitals and the increased positive hybridization contribution between Cr atoms' d_{z^2} and d_{yz} orbitals, resulting from the introducing additional positive charges. On the other hand, the MAE of MnSi₂N₄ diminishes with charge doping, which can be ascribed to the decreasing negative hybridization contribution between Mn atoms' $d_{\rm xy}$ and $d_{x^2-y^2}$ and the increasing positive hybridization contribution between d_{z^2} and d_{yz} , d_{xy} and d_{xz} . Our findings highlight the Mn atoms' excellent tunable electromagnetic properties of MSi₂N₄ MLs. We are hopeful that this study will serve as a springboard for further theoretical and experimental investigations in the burgeoning field of 2D magnetic materials.

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