

Stacking-engineered tunability of electronic and magnetic states in Nb₃I₈ nanofilmsPanpan Wang¹, Xiaolei Li¹, Jinhua Gu¹, Weiguang Chen², Chunyao Niu¹, and Zhili Zhu^{1,3,*}¹*School of Physics and Laboratory of Zhongyuan Light, Zhengzhou University, Zhengzhou 450001, China*²*College of Physics and Electronic Engineering, Zhengzhou Normal University, Zhengzhou, Henan 450044, China*³*Institute of Quantum Materials and Physics, Henan Academy of Science, Henan 450046, China*

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Both monolayer and bilayer Nb₃I₈ were theoretically predicted to be magnetic, whereas bulk Nb₃I₈ was experimentally observed to exhibit a nonmagnetic (NM) ground state. In this work, we pursue the origin of bulk NM behavior and the evolution of magnetism in Nb₃I₈ nanofilms using first-principles calculations. We identified three distinct stacking types in bilayer Nb₃I₈, further categorized into nine specific configurations. Strikingly, the HH-AA stacking configuration adopts an NM ground state, while the other eight configurations stabilize as antiferromagnetic (AFM) states. The magnetization loss in HH-AA stacking originates from charge transfer from interfacial I atoms to Nb atoms, driving the Nb₃ trimer's transition from [Nb₃]⁸⁺ ($S = 1/2$) to [Nb₃]⁷⁺ ($S = 0$). Furthermore, multilayer Nb₃I₈ films with bulk stacking exhibit layer-dependent oscillations between ferromagnetic (FM) and NM states, alternating with odd and even layer counts. The NM ground state of bulk Nb₃I₈, which consists of alternating HH-AA and TT-AC stacking sequences, results from the moment quenching in HH-AA stacking over the AFM coupling in TT-AC stacking. Our findings establish Nb₃I₈ as a promising platform for stacking-engineered functionalities. Its stacking diversity not only broadens the functional landscape of two-dimensional materials but also reveals hidden correlations between structural degrees of freedom and electronic/magnetic responses.

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I. INTRODUCTION

Over the past two decades, two-dimensional (2D) materials have attracted tremendous research interest due to their fascinating emergent properties, which enable diverse device applications [1–7]. Following the discovery of intrinsic ferromagnetism in CrI₃ monolayers (MLs) [8,9], the field of 2D magnetism has rapidly expanded, exploring diverse material families such as the hexagonal Cr₂Ge₂Te₆ [10], transition metal trihalides like MX₃ ($M = \text{Pt}$ and Pd , $X = \text{Br}$ and I) [11], and other relevant materials like MnBi₂Te₄, TcSiTe₃, etc. [10,12–20]. Recently, Nb₃X₈ ($X = \text{Cl}$, Br , or I) [21–27] MLs have emerged as a class of intrinsic magnetic 2D materials. Notably, Nb₃I₈ ML was predicted to exhibit room-temperature ferromagnetism ($T_C \sim 307$ K), while bilayer and trilayer structures show antiferromagnetic (AFM) ordering, demonstrating layer-dependent magnetic behavior [22,23]. However, experimental measurements have observed a nonmagnetic (NM) ground state in bulk Nb₃I₈ [28]. To date, the origin of bulk NM behavior and the evolution of magnetism in Nb₃I₈ nanofilms remain unclear.

The bulk Nb₃I₈ crystal was first synthesized in 1993 [29], which demonstrates a layered van der Waals (vdW) structure, characterized by six layers per unit cell (space group $D_{3d}^5-R\bar{3}m$, No. 166) [23]. Given the six-layered unit cell of bulk Nb₃I₈, its bilayer is expected to possess multiple possible stacking configurations. It is known that weak interlayer vdW interactions enable the manipulation of both rotational and translational degrees of freedom between layers, facilitating the development of materials with unique stacking symmetries and functionalities [30–36]. A pivotal direction in this field is the stacking-tunable magnetism in vdW-layered materials. This phenomenon has been most extensively studied in CrI₃ multilayers, where the interlayer magnetic coupling can be reversibly switched between AFM and ferromagnetic (FM) states through external stimuli such as electrostatic gating, pressure, or twisting the stacking angle [11,35,37–39]. This principle may hold the key to resolving the Nb₃I₈ puzzle. So, there may exist special correlations between the interlayer stacking orders and electronic/magnetic responses in Nb₃I₈ nanofilms.

In this work, we investigate the interlayer stacking of Nb₃I₈ nanofilms and its influence on electronic and magnetic properties using first-principles calculations. We identify three distinct stacking orders in bilayer Nb₃I₈, further classified into nine specific configurations, namely, HH-AA, HH-AB, HH-AC, TT-AA, TT-AB, TT-AC, HT-AA, HT-AB, and HT-AC. This stacking diversity arises from the noncentrosymmetric I-Nb-I sandwich structure of Nb₃I₈ ML. Intriguingly, the HH-AA stacking exhibits a complete moment quenching, in which the local magnetic moments of Nb atoms present in

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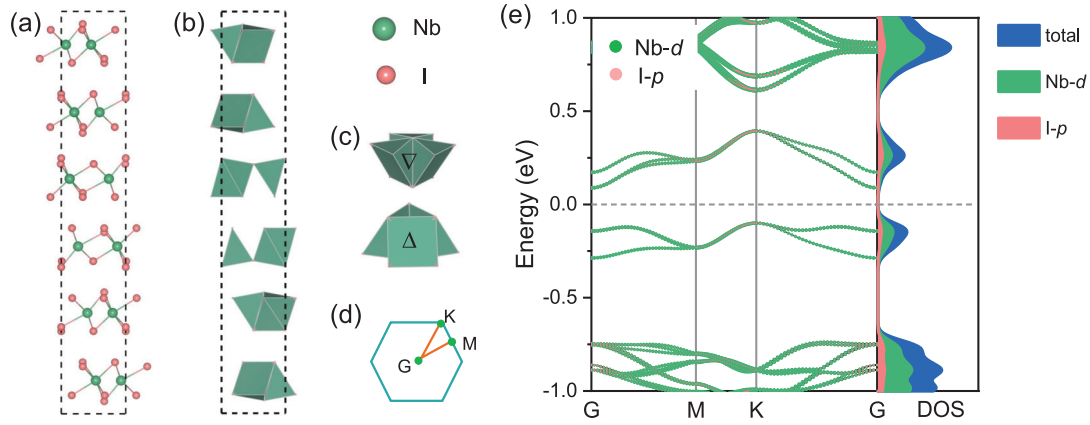


FIG. 1. (a) Ball-and-stick model and (b) polyhedral representation of the bulk Nb₃I₈ structures. (c) Two Nb₃I₁₀ cluster units in HH orientation. (d) Projected Brillouin zone for the (001) surface. (e) Band structure and density of states of the bulk Nb₃I₈.

isolated MLs are fully suppressed, resulting in an NM ground state. This effect results from charge transfer from interfacial I atoms to Nb atoms, driving the Nb₃ trimer's transition from [Nb₃]⁸⁺ ($S = 1/2$) to [Nb₃]⁷⁺ ($S = 0$). In contrast, the remaining eight configurations stabilize in AFM ground states. These results demonstrate stacking-dependent magnetism in Nb₃I₈ bilayers, suggesting potential AFM-to-NM transitions via stacking control. Furthermore, multilayer Nb₃I₈ films with bulk stacking sequence exhibit layer-dependent oscillations between FM and NM states, alternating with odd and even layer counts. The NM ground state of bulk Nb₃I₈, which consists of alternating HH-AA and TT-AC stacking sequences, results from the dominant moment quenching in HH-AA stacking over the AFM coupling in TT-AC stacking. Our findings establish Nb₃I₈ as a promising stacking-tunable magnetic material. The diversity of stacking configurations not only broadens the functional scope of 2D materials but also provides a platform for exploring hidden correlations between structural degrees of freedom and electronic/magnetic responses.

The paper is organized as follows. In Sec. II, we briefly describe the method and details of the density functional theory (DFT) calculations. In Sec. III, we illustrate the diversity of stacking configurations in bilayer Nb₃I₈. The layer and stacking-dependent electronic and magnetic properties of Nb₃I₈ nanosheets are discussed in detail. In Sec. IV, we conclude this work with a brief summary.

II. COMPUTATIONAL METHODS

Our density functional theory calculations were performed using the generalized gradient approximation and the projector augmented wave method [40,41] as implemented in the VIENNA *AB INITIO* SIMULATION PACKAGE [42,43]. Dispersion correction with the optB86b functional [44] was adopted for structure-related calculations, which was proved to be accurate in describing the structural properties of layered materials. A uniform Monkhorst-Pack k -mesh of $9 \times 9 \times 1$ was adopted for integration over the Brillouin zone [45]. A plane-wave cutoff energy of 400 eV was used during the structural relaxations. A sufficiently large distance of $c > 15$ Å along the out-of-plane direction was adopted to elimi-

nate interaction between each layer. The convergence of the calculations was verified using a higher plane-wave cutoff energy of 500 eV and a denser k -mesh of $11 \times 11 \times 1$, with no significant changes observed in the total energy and key properties. All structures were fully relaxed until the total energies converged up to 10^{-4} eV and the Hellmann-Feynman forces were less than 0.01 eV/Å. The band gaps were verified using the nonlocal Heyd-Scuseria-Ernzerhof (HSE06) hybrid functional calculation [46,47] with a Hartree-Fock mixing parameter of 0.25. A plane-wave cutoff energy of 400 eV and a $7 \times 7 \times 1$ k -point grid were adopted, ensuring convergence for the electronic and magnetic properties. The phonon calculations employed a supercell approach, as implemented in the Phonopy code [48].

III. RESULTS AND DISCUSSION

As shown in Fig. 1(a), bulk Nb₃I₈ exhibits a layered vdW crystal structure consisting of six layers per unit cell. Each layer contains eight iodine (I) atoms and three niobium (Nb) atoms, with Nb atoms sandwiched between two atomic sheets of I. Notably, the Nb atoms form a distorted kagome lattice characterized by triangular Nb₃ trimers, where the intratrimer Nb-Nb distance differs from the intertrimer distance. Furthermore, the two sheets of I atoms are not equivalent, leading to the formation of an essentially flat I sheet and a corrugated I sheet. Therefore, each Nb₃I₈ layer is composed of distorted octahedra formed by I and Nb atoms, thus breaking inversion symmetry.

The optimized lattice constants are $a = b = 7.62$ Å and $c = 41.68$ Å, consistent with experimental results [29]. To examine the electronic structures of bulk Nb₃I₈, we performed spin-polarized and non-spin-polarized calculations within the generalized gradient approximation (GGA) method. Notably, both calculations yield NM ground states, aligning with experimental observations of NM behavior in bulk Nb₃I₈ [28]. Given the partially filled 4d subshells of Nb, we tested the effect of Hubbard U corrections in bulk Nb₃I₈. Strikingly, the ground state exhibits strong U dependence (Table S1 and Fig. S1 of the Supplemental Material [48]). Specifically, an AFM ground state emerges for $U > 1.5$ eV. Since this non-robust behavior under U correction, we did not include the

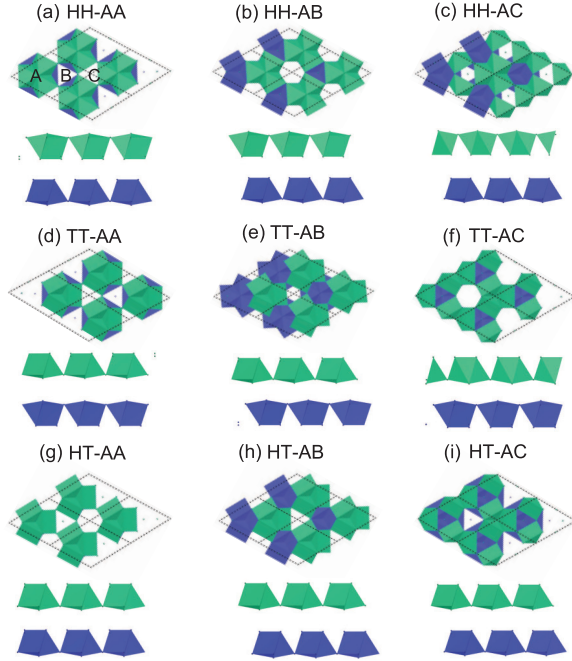


FIG. 2. Top and side views of (a) HH-AA, (b) HH-AB, (c) HH-AC, (d) TT-AA, (e) TT-AB, (f) TT-AC, (g) HT-AA, (h) HT-AB, and (i) HT-AC stacking configurations of bilayer Nb_3I_8 . The first and second layers are colored in green and blue, respectively.

Hubbard U correction in subsequent calculations to ensure methodological consistency. The calculated Perdew-Burke-Ernzerhof (PBE) band structure and density of states (DOS) for bulk Nb_3I_8 are shown in Fig. 1(e). The results confirm its semiconducting character with an indirect band gap of $E_g = 0.19$ eV. The DOS near the Fermi level are dominated by Nb atoms, with a slight contribution from I atoms. Additionally, the band structures of bulk Nb_3I_8 were computed using both the PBE + U ($U = 1.0$ eV) and HSE06 functionals. As shown in Fig. S3 of the Supplemental Material [48], the negligible difference between the PBE and PBE + U results suggests that the electronic structure is insensitive to local Hubbard U corrections for $U \leq 1.0$ eV [49]. The HSE06 functional yields a larger band gap ($E_g = 0.28$ eV) while maintaining the overall band dispersion, thereby validating the electronic structure picture obtained from PBE calculations. The measured band gap of bulk Nb_3I_8 in experiments is 0.52 eV [50]. It should be noted that gravitational-wave (GW) calculations, while potentially more accurate, are prohibitively expensive for the large Nb_3I_8 unit cell. Additionally, the underestimation of the band gap may be partly attributed to excitonic effects not captured in standard DFT. We note that while the absolute energy scales are sensitive to the exchange-correlation treatment, the relative trends and physical mechanisms governing the stacking-tunable magnetism in Nb_3I_8 remain robust.

Following our initial characterization of bulk Nb_3I_8 , we now focus on the interlayer stacking of its bilayer. Intriguingly, as shown in Fig. 2, we identify three distinct stacking orders in bilayer Nb_3I_8 . Based on the relative orientation of Nb_3I_{10} cluster units between layers [see Fig. 1(c)], these distinct orders are designated as head-to-head (HH), tail-to-

TABLE I. Relative stability of different magnetic states for each stacking configuration. For each system, the total energy of the ground state is set to zero. ΔE_{NM} , ΔE_{FM} , and ΔE_{AFM} denote the energy differences of the NM, FM, and AFM states relative to the ground state, respectively. E_b represents the binding energy of bilayer Nb_3I_8 for each stacking configuration.

Structure	ΔE_{NM} (meV)	ΔE_{FM} (meV)	ΔE_{AFM} (meV)	E_b (eV/ML)
HH-AA	0	—	—	−0.56
HH-AB	64.90	10.60	0	−0.46
HH-AC	72.58	5.39	0	−0.33
TT-AA	90.01	3.93	0	−0.25
TT-AB	86.46	3.81	0	−0.47
TT-AC	72.19	13.93	0	−0.53
HT-AA	45.97	26.73	0	−0.46
HT-AB	70.95	7.68	0	−0.38
HT-AC	60.93	12.99	0	−0.43

tail (TT), and head-to-tail (HT) stacking. Each order can be further classified into AA, AB, and AC stacking according to the relative lateral shift between layers, where A, B, and C denote specific stacking sites illustrated in Fig. 2(a). Strikingly, unlike conventional 2D systems typically limited to a few stacking orders, we demonstrate that bilayer Nb_3I_8 exhibits significant stacking diversity, encompassing nine distinct configurations. To verify the structural stability of bilayer Nb_3I_8 across different stacking configurations, we carried out phonon dispersion calculations. As shown in Fig. S2 of the Supplemental Material [48], the resulting spectra exhibit no imaginary frequencies, which confirms their dynamical stability. This diversity originates directly from the unique inversion-symmetry-breaking I-Nb-I sandwich structure of the ML, as previously discussed.

It is well established that ML Nb_3I_8 exhibits an FM ground state, whereas the bulk phase is NM. To systematically investigate the ground-state properties of the bilayer Nb_3I_8 , we performed NM, FM, and AFM calculations for each stacking configuration to evaluate their relative stability. Given that ML Nb_3I_8 has been predicted to exhibit in-plane FM ordering [21–23], the AFM configurations in our calculations correspond to opposite interlayer spin alignments while maintaining the same intralayer spin orientation. The relative stability of different magnetic states for each configuration is presented in Table I. Intriguingly, the HH-AA stacking configuration exhibits an NM ground state, while the remaining eight configurations stabilize as AFM states. We also performed calculations with spin-orbit coupling (SOC) included to evaluate the SOC effect on the magnetism of the bilayer Nb_3I_8 . The results demonstrate that SOC does not significantly alter the magnetic ground states. Specifically, the HH-AA stacking configuration adopts an NM ground state, while the other eight configurations stabilize in an AFM state. These findings are consistent with the results obtained without SOC. To assess the interlayer interactions, we calculated the binding energy, defined as $E_b = (E_{\text{tot}} - 2E_{\text{ML}})/2$, where E_{tot} is the total energy of the bilayer ground state and E_{ML} is the total energy of an isolated ML. The results reveal strong interlayer coupling, with the HH-AA stacking being the most stable ($E_b = -0.56$ eV/ML), followed by the TT-AC

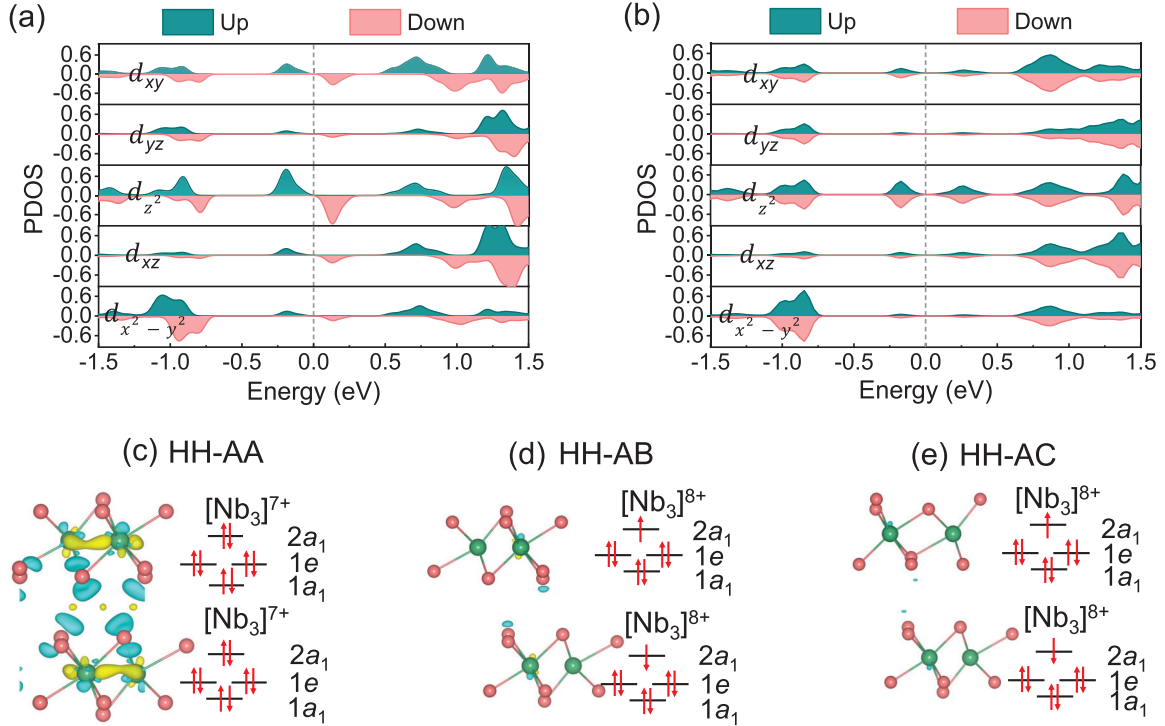


FIG. 3. PDOS for (a) ML Nb_3I_8 and (b) HH-AA stacked bilayer. Charge density difference plots (left) and corresponding Nb_3 trimer molecular orbital schematics (right) for (c) HH-AA, (d) HH-AB, and (e) HH-AC stacking configurations. Yellow and cyan indicate charge accumulation and depletion, respectively. The isosurface value is $0.002 \text{ e}/\text{\AA}^3$.

stacking ($E_b = -0.53 \text{ eV/ML}$). This energetic preference for HH-AA and TT-AC stacking provides a natural explanation for the bulk structure of Nb_3I_8 , which consists of alternating HH-AA and TT-AC stacking sequences [see Fig. 1(b)]. To quantitatively characterize the magnetic interactions in the bilayer Nb_3I_8 with different stacking configurations, we extracted the exchange parameters by evaluating the total energy differences between various spin configurations. A simplified model was used to describe the magnetism in the bilayer Nb_3I_8 , which includes only the nearest-neighbor intralayer and interlayer exchange interactions [28]. Our results show that the intralayer exchange is strongly FM with coupling constants about $2 \text{ meV}/\mu_B^2$, while the interlayer exchange is AFM and stacking dependent, with coupling constants ranging from 0.04 to $0.51 \text{ meV}/\mu_B^2$ (see Table S2 of the Supplemental Material [48]).

Nevertheless, the electronic and magnetic properties of Nb_3I_8 bilayers concerned with stacking orders remain to be fully elucidated. It is known that ML Nb_3I_8 exhibits an FM ground state [21–23], where each Nb_3 trimer shares seven electrons, resulting in a local magnetic moment of $1.0 \mu_B$. However, the bilayer Nb_3I_8 displays stacking-dependent ground states, including NM and AFM ground states. Most strikingly, the HH-AA stacking manifests moment quenching, in which the local magnetic moments of Nb atoms present in isolated MLs are entirely quenched. This dramatic suppression of magnetism underscores the critical role of interlayer stacking in governing the electronic and magnetic behavior of the bilayer Nb_3I_8 .

To pursue the origin of magnetization loss in the HH-AA stacked bilayer Nb_3I_8 , we first explore the interlayer

coupling strengths across all nine stacking configurations. Notably, the HH-AA stacking exhibits the strongest coupling strength of approximately $-22.76 \text{ meV}/\text{\AA}^2$. We then conducted a detailed analysis of the electronic structure of the HH-AA bilayer. For comparison, the projected density of states (PDOS) on the atomic orbitals of ML Nb_3I_8 was calculated and presented in Fig. 3(a). The results illustrate that ML Nb_3I_8 is a spinpolarized semiconductor, and the DOS near the Fermi level are dominated by the d_{z^2} , d_{xy} , and d_{xz} orbitals of Nb atoms. Strikingly, the HH-AA stacked bilayer shows markedly different electronic properties compared to the ML, as evidenced by the complete suppression of spin polarization [Fig. 3(b)]. This dramatic transformation directly results from the strong interlayer coupling in the HH-AA configuration.

To further elucidate the moment quenching, the differential charge densities for HH-stacked configurations were calculated and plotted in Figs. 3(c)–3(e). As shown in Fig. 3(c), the results demonstrate significant charge redistribution in the HH-AA bilayer, with pronounced charge accumulation around Nb atoms in both layers and depletion around interfacial I atoms. In contrast, HH-AB and HH-AC bilayers show negligible charge transfer [Figs. 3(d) and 3(e)]. To quantify interfacial charge transfer in the HH-AA stacked bilayer Nb_3I_8 , we computed the planar-averaged charge density difference (see Fig. S4 of the Supplemental Material [48]). Numerical integration reveals a net transfer of 0.99 electrons from the interfacial region to Nb_3 trimer, with each Nb atom gaining approximately 0.33 electrons. This substantial charge redistribution, primarily from interfacial I atoms to Nb sites, serves as the fundamental mechanism for the observed moment quenching.

This mechanism can be further clarified by analyzing the molecular orbitals of Nb_3 trimers, whose splitting behavior is strongly tied to crystal symmetry. The bulk Nb_3I_8 has a space group of $R\bar{3}m$, whereas the 2D form of ML Nb_3I_8 belongs to $P\bar{3}m1$. Under C_{3v} symmetry, the $5d$ orbitals of Nb first split into t_{2g} and e_g . The strong covalent bonding within each Nb_3 trimer further splits these orbitals into distinct energy levels. As shown in Fig. S5 of the Supplemental Material [48], the t_{2g} orbitals of the Nb atoms give rise to the energy levels $1e$, $1a_1$, $2e$, $2a_1$, $3e$, and $1a_2$, which correspond to the irreducible representations under C_{3v} symmetry. Here, e is the basis function of $(d_{x^2-y^2}, d_{xy})(d_{xz}, d_{yz})$, while a_1 corresponds to d_{z^2} . Each Nb_3 trimer shares seven d electrons, yielding a valence state of $[\text{Nb}_3]^{8+}$. Thus, the $[\text{Nb}_3]^{8+}$ trimer carries an unpaired electron ($S = 1/2$), yielding a local magnetic moment of $1.0 \mu_B$, reflecting the underlying mechanism as in the FM monolayer and AFM bilayer Nb_3I_8 . As shown in Fig. 3(a), a group of molecular orbitals within $[-0.5, 0.5]$ eV, mainly composed of Nb d_{xy} and d_{z^2} orbitals, are partially occupied. Population analysis indicates that each Nb atom hosts about 0.3 unpaired electrons at these energies, collectively contributing to the total local magnetic moment of $\sim 1.0 \mu_B$. Crucially, in the HH-AA bilayer, the interfacial charge transfer of ~ 1.0 electron to the three Nb atoms induces a valence state transition from $[\text{Nb}_3]^{8+}$ to $[\text{Nb}_3]^{7+}$. As evidenced in Fig. 3(c), the unpaired spin present in the isolated ML becomes fully saturated in the HH-AA bilayer, resulting in a net spin $S = 0$ and complete quenching of the magnetic moment. In stark contrast, the Nb_3 trimers preserve their $[\text{Nb}_3]^{8+}$ valence configuration in both HH-AB and HH-AC bilayers, as evidenced by the negligible charge density variation around Nb sites. Consequently, these stacking configurations retain spin polarization and stabilize in AFM ground states [Figs. 3(d) and 3(e)]. For TT and HT stacking orders, our calculations reveal significant interfacial charge redistribution in TT-AB, TT-AC, and HT-AA bilayers. Notably, this charge reorganization occurs primarily at the interface without substantially altering the electronic density around Nb atoms in either layer (see Fig. S6 of the Supplemental Material [48]). Therefore, the Nb_3 trimer in TT and HT stacking orders will approximately preserve the $[\text{Nb}_3]^{8+}$ valence state, explaining their AFM ground states across all six configurations.

We now examine the electronic properties of the bilayer Nb_3I_8 across different stacking configurations. As shown in Fig. 4, the HH-AA bilayer exhibits an NM semiconductor with an indirect band gap of $E_g = 0.15$ eV, while the remaining eight configurations display AFM semiconducting behavior with stacking-dependent band gaps ranging from 0.08 to 0.16 eV. Notably, for both HH and TT stacking configurations, the spin-polarized band structures are degenerate due to the inversion symmetry linking the top and the bottom layer. In contrast, for HT stacking, the lack of inversion symmetry results in a k -point-dependent spin splitting, yielding the gap difference between spin-up and spin-down channels. For example, the HT-AB bilayer has the band gaps of $E_{g,\uparrow} = 0.09$ eV and $E_{g,\downarrow} = 0.16$ eV, respectively. The semilocal PBE scheme may underestimate the band gap. In order to remedy such a potential inaccuracy in the PBE, we perform hybrid DFT calculations with the HSE06 functional. The corrected band gap of HH-AA bilayer is $E_g = 0.25$ eV, which is about

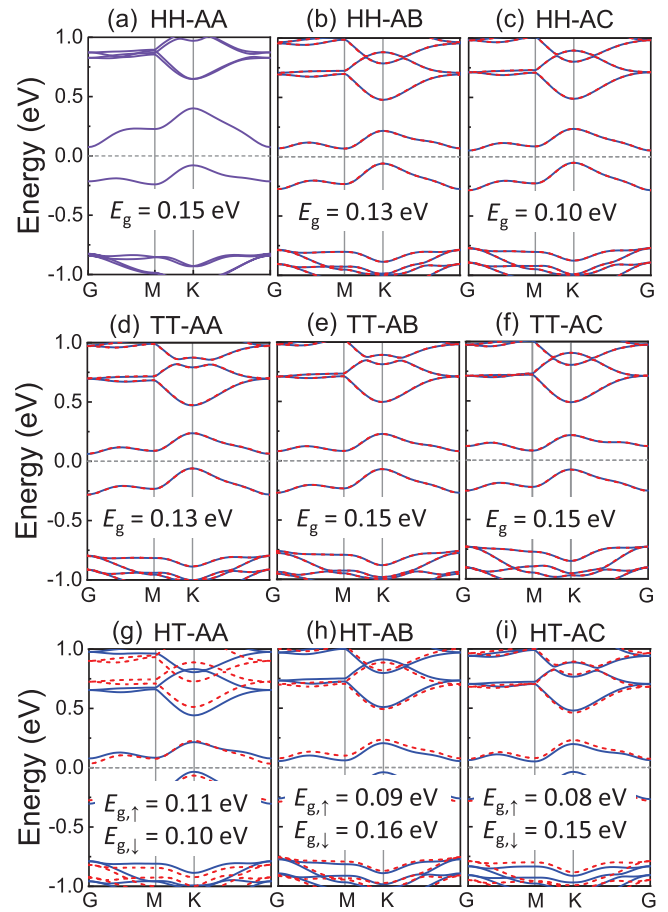


FIG. 4. Band structures for (a) HH-AA in the NM ground state, spin-polarized band structures for (b) HH-AB, (c) HH-AC, (d) TT-AA, (e) TT-AB, (f) TT-AC, (g) HT-AA, (h) HT-AB, and (i) HT-AC stacking configurations in AFM ground states. The Fermi level is set to zero. Blue (red) bands represent the spin-up (spin-down) channel.

0.1 eV larger than that of the PBE result (see Fig. S7 of the Supplemental Material [48]). These results demonstrate that while bilayer Nb_3I_8 is a narrow-gap semiconductor, its electronic structure can be effectively tuned through interlayer stacking engineering.

To give a further insight into the interlayer coupling in HH-AA stacking, we conducted a detailed study on the influence of interlayer spacing on its magnetic properties. Figure 5 shows the evolution of both magnetic moment and coupling strength as a function of interlayer distance in the HH-AA bilayer. Our results reveal that the moment quenching is strongly correlated with interlayer coupling strength. Notably, the demagnetization effect disappears when the interlayer spacing exceeds $4.42 \text{ \AA}$. Meanwhile, the Nb atoms in each layer regain local magnetic moments, indicating a phase transition from an NM to an AFM ground state. The local magnetic moment of each Nb_3 trimer in the phase transition region is $\pm 0.3 \mu_B$. As the interlayer spacing further increases, the local magnetic moment almost increases to $\pm 1.0 \mu_B$ at $4.82 \text{ \AA}$, near to the values observed in the other eight stacking configurations.

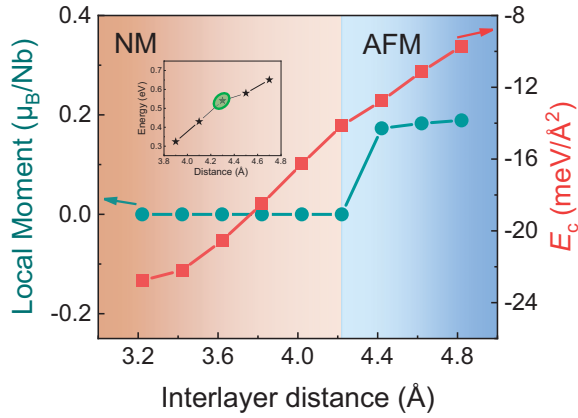


FIG. 5. Local magnetic moment of Nb atom as well as coupling strength as a function of the interlayer distance in HH-AA bilayer. The inset shows the variation of total energy with interlayer distance, where the green circle indicates the magnetic transition point.

Finally, we explored the electronic and magnetic properties of multilayer Nb_3I_8 films with bulk stacking sequences. As depicted by the schematic lines in Fig. 6, a simplified interlayer-coupling model shows that the multilayer Nb_3I_8 films comprise alternating HH-AA and TT-AB stacking sequences. Importantly, the moment quenching behavior of HH-AA stacking remains robust in these multilayer structures. Since the HH-AA stacking has a stronger coupling strength than that of TT-AC stacking, the moment quenching of HH-AA stacking dominates over the AFM coupling of TT-AC stacking in multilayer Nb_3I_8 sheets. Therefore, the even-layered films ($n = 2, 4$, and 6) adopt NM states through paired HH-AA stacking. In contrast, odd-layered films ($n = 3$ and 5) exhibit FM states due to the unpaired layer lacking HH-AA stacking. The oscillatory NM-FM behavior captured by this model stems from the competition between the dominant moment quenching of HH-AA stacking and the weaker AFM coupling (J_{inter}) of TT-AC stacking. The FM state in odd-numbered layers specifically arises from an unpaired ML,

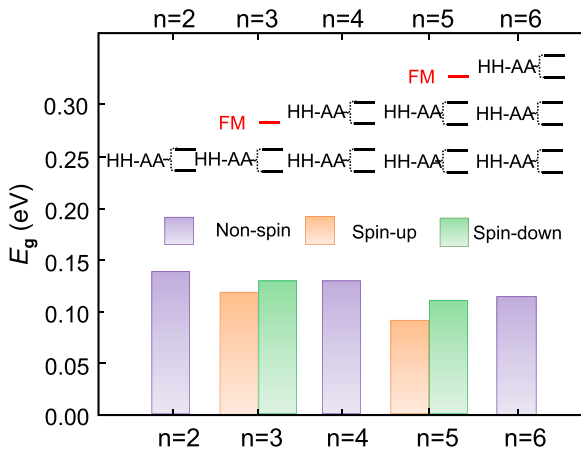


FIG. 6. Band gaps of multilayer Nb_3I_8 as a function of layer counts. Each line denotes a single-layer stacking into a multilayer Nb_3I_8 with a bulk stacking sequence. Black (red) lines denote paired (unpaired) layers with (without) HH-AA stacking.

whose robust ferromagnetism is inherited from the strong intralayer FM coupling (J_{intra}) of an isolated Nb_3I_8 sheet. This mechanism not only explains the layer-dependent magnetic behavior in few-layer systems but also accounts for the NM ground state observed in bulk Nb_3I_8 . The band structures of multilayer Nb_3I_8 sheets were calculated and presented in Fig. S8 of the Supplemental Material [48]. It was found that the band gap decreases with the increased layer number. The even-layered sheets ($n = 2, 4$, and 6) are NM semiconductors with the band gaps of $0.15, 0.14$, and 0.13 eV, respectively. On the other hand, the odd-layered sheets ($n = 3$ and 5) exhibit AFM semiconducting characters, which have spin-up band gaps of $E_g = 0.14$ and 0.12 eV, and spin-down band gaps of $E_g = 0.13$ and 0.10 eV, respectively. Given that odd-layered films reflect the FM properties of Nb_3I_8 ML, which has a Curie temperature (T_C) of ~ 307 K, the predicted oscillation in multilayer films is expected to persist at room temperature.

IV. CONCLUSIONS

In summary, we systematically investigated the interlayer stacking of Nb_3I_8 nanofilms based on the first-principles calculations. We identified three distinct stacking orders in bilayer Nb_3I_8 , further categorized into nine specific configurations, which offers an unprecedented degree of flexibility for materials engineering. This stacking diversity arises from the noncentrosymmetric I-Nb-I sandwich structure of ML Nb_3I_8 . The electronic and magnetic characteristics of the bilayer Nb_3I_8 exhibit remarkable sensitivity to interlayer stacking. Notably, the HH-AA configuration displays moment quenching (NM ground state) through interfacial charge redistribution, while the other eight configurations stabilize in AFM states. Furthermore, multilayer Nb_3I_8 sheets demonstrate layer-parity-dependent oscillations between NM and FM states, alternating with odd- and even-layer counts. The NM ground state of bulk Nb_3I_8 results from the dominant moment quenching in HH-AA stacking over the AFM coupling in TT-AC stacking. The predicted stacking orders in the bilayer Nb_3I_8 may be realized via advanced nanofabrication techniques like strain engineering or scanning probe manipulation. Furthermore, their stacking-dependent magnetic properties could be verified using techniques such as magnetic force microscopy and polarized Raman spectroscopy. These findings open avenues for designing Nb_3I_8 -based multifunctional materials where stacking configurations are spatially patterned to create atomic-scale quantum devices.

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DATA AVAILABILITY

The data that support the findings of this article are openly available [51].

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