Strain-tunable electronic and magnetic properties of Nb$_3$I$_8$ multilayer

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The study of novel 2D platforms implementing magnetism in tunable van der Waals (vdW) homo- and hetero-structures paves the way to innovative spintronics and magnetic devices. In this study, we unravel the intriguing properties of few-layer Nb$_3$I$_8$ vdW systems from first principles, showing that specific magnetic orderings can be tuned using several degrees of freedom, such as film thickness, stacking geometry, and strain or even a combination of them. All these aspects are explored here, giving a comprehensive view of this novel and promising magnetic material.

Keywords: van der Waals materials, layer-dependent magnetism, spintronics, straintronics.

I. INTRODUCTION

In the last years, two-dimensional (2D) materials have been attracting tremendous research interest. Their interesting properties, induced by the combination of surface effects and quantum confinement, can be exploited to realize 2D platforms-based electronic devices for a wide range of technological applications [1–3]. The out-of-plane van der Waals (vdW) interactions allow the integration of highly different 2D materials, that can thus be viewed as building blocks of new materials showing novel properties and exotic phenomena unavailable in the single-layer constituents. An unprecedented number of degrees of freedom, such as order and number of layers [4–6], the twist angle among them [7–10], and the distance between two consecutive single layers (interlayer distance) [11, 12] can be tuned to achieve this goal.

Among these degrees of freedom, strain engineering deserves a special mention, since it offers a viable approach to control electronic, magnetic, and optical properties, often referred to as “straintronics”. Indeed, it has been extensively demonstrated that many properties might show a strong dependence on the lattice structures [13–16]. The higher flexibility and elasticity than most three-dimensional (3D) crystals [17, 18] and the reduced atomic coordination have allowed straintronics in 2D systems to expand rapidly and provide remarkable results for different classes of 2D materials.

Since the recent discovery of intrinsic magnetism in monolayers of CrI$_3$ [19], the exploration of 2D intrinsic magnetic materials has been exponentially increasing [20]. In particular, 2D platforms combining ferromagnetism with room Curie temperature $T_C$ and conventional semiconductors open a new pathway to realize spintronic applications based on the use of both charge and spin degrees of freedom in electronic devices, such as next-generation quantum logic chips and nonvolatile magnetic memories with increased densities [21, 22]. Some examples are the first observed CrI$_3$ and Cr$_2$Ge$_2$Te$_6$ [23], or those exhibiting high $T_C$, such as V$_3$I$_8$ [24], MnS$_2$ [25], VSe$_2$ [26], and Nb$_3$I$_8$ [27], all inheriting the magnetic ordering from the transition metal d-orbitals.

Nb$_3$I$_8$ is a recently synthesized 2D material [28] with a predicted ferromagnetism at the room temperature ($T_C \sim$ 307 K) and a layer-dependent magnetism, being ferromagnetic (FM) in monolayer form and anti-FM (AFM) in bilayer and trilayer forms [27]. Also, Nb$_3$I$_8$ monolayer actually is a “ferrovalley” material, because it exhibits an intrinsic spontaneous valley polarization of 107 meV and, thus, the anomalous valley Hall (AVH) effect without external tunings [29]. All these observations make Nb$_3$I$_8$ an ideal candidate for spintronics and valleytronics applications.

So far, several routes have been experimentally applied and theoretically predicted to control the magnetic states in the most recently discovered 2D materials. Electrostatic doping applied to bilayer CrI$_3$ significantly affects the interlayer exchange coupling, providing a phase transition from the layered AFM state of two FM layers with opposite spin directions to an FM state [30, 31]. An out-of-plane pressure of 2.70 GPa on bilayer CrI$_3$ destroys the AFM state to favor an FM ordering [32, 33], whereas an out-of-plane pressure of 2.45 GPa on trilayer CrI$_3$ can create coexisting domains of three phases, one ferromagnetic and two antiferromagnetic, or can induce an FM ordering [33]. Strain engineering was shown to affect the magnetic properties of several 2D magnets, such as FM-AFM phase transition of monolayer CrI$_3$ [34] and transition metal trichalcogenides [35], valley polarization and metal-semiconductor and/or magnetic phase transitions of CoSe$_2$ structures [36], the superexchange interactions and the Curie temperature of Cr$_2$Ge$_2$Te$_6$ [37].

All these experimental evidences and theoretical predictions clearly bring out that strain engineering reveals as one of the most promising “control knobs” to engineer the electronic and, to an even larger extent, magnetic properties of 2D magnetic materials. With this motivation, the present work is focused on a detailed analysis...
of the intriguing electronic and magnetic properties of the less explored Nb$_3$I$_8$, to unravel its potentialities for spintronic and valleytronic applications. State-of-the-art first-principles calculations in the framework of density functional theory (DFT) are carried out to bring out the effects of the (in-plane) biaxial strain on the electronic and magnetic properties of Nb$_3$I$_8$ in monolayer, bilayer, and trilayer forms. All these systems are investigated in two different stacking geometries, to establish a possible interplay between thickness, stacking, strain, and magnetism. We accurately describe the competition between different magnetic phases and the strain-induced band gap engineering, showing intriguing properties, such as possible transitions between magnetic states. As it will be better detailed in the next, due to the peculiar nature of Nb$_3$I$_8$, accurate first-principles calculations should definitely take into account two fundamental interactions, that is, vdW interlayer interaction (by an appropriate choice of the exchange-correlation functional) and on-site Coulomb repulsion for Nb 4d-electrons (for example, using a DFT+$U$ scheme). All these are carefully included in our analysis, accompanied by a systematic study of the convergence of the presented results with respect to all parameters involved in the calculations.

The paper is organised as follows. In Sec. II we present the computational methods and technical details of our calculations. In Sec. III we show and discuss the electronic and magnetic properties of Nb$_3$I$_8$ films, with special focus on their dependence on the thickness, strain and stacking geometry. Finally, in Sec. IV, we summarize our results and draw some conclusions.

II. METHODS

All calculations are performed using DFT as implemented in the Quantum-ESPRESSO package (version 6.6) [38–40], based on plane waves and pseudopotentials. The generalized gradient approximation (GGA) is used with projector-augmented wave (PAW) pseudopotentials [41] based on the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional [42] to represent the atomic cores [43]. The plane wave basis set is truncated using a cutoff energy of 60 Ry for the plane waves and 480 Ry to represent the charge density in all calculations. An adequate vacuum space of $\approx 20$ Å was set between periodic replicas along the direction orthogonal to the planes (assumed to be the $z$ direction), in order to avoid spurious interactions induced by the periodic boundary conditions. The Brillouin zone (BZ) of the $1\times1\times1$ unit cell was sampled using an $8\times8\times1$ Monkhorst-Pack $k$-point grid [44], grids for $n\times n \times 1$ supercells were scaled accordingly. These $k$-point grids have been used for both structural relaxation and total energy calculations.

The vdW interaction has been self-consistently accounted for using the rev-vdW-DF2 [45] exchange-correlation functional, that has been proven to be successful in the description of 2D vdW heterostructures with an hexagonal lattice [10] and, in particular, provides a good agreement with the available experimental data on Nb$_3$I$_8$ [27]. Based on previous reports, the on-site Coulomb repulsion of Nb 4d electrons is taken into account by means of the DFT+$U$ method [46–48] with $U = 2$ eV. For all the considered systems, the lattice parameters have been optimized using spin-polarized calculations. The atomic positions have been fully optimized by means of the Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm [49–52], with a convergence criterion such that the total energy difference between consecutive structural optimization steps is less than $10^{-5}$ Ry and that all components of all the forces acting on the atoms are less than $10^{-4}$ Ry/Bohr.

In-plane, biaxial strain $\varepsilon = (a - a_0)/a_0$, where $a_0$ is the unstrained lattice parameter and $a$ is the strained lattice parameter, has been applied to the considered structures, ranging from $-7.5\%$ to $7.5\%$ in steps of $2.5\%$. Thickness effects have been studied by considering monolayer, bilayer, and trilayer forms, which will be referred to as Nb$_3$I$_8$-nL ($n = 1, 2, 3$), respectively. Moreover, the effect of the stacking geometry has been introduced by comparing the bulk stacking, that is the natural order of the layers as they would be arranged in the bulk form, and the $A^n$ stacking, that is constructed by piling $n$ layers with the same planar coordinates.

The ground state analysis is performed on the nonmagnetic (NM) and several magnetic states for each system. In particular, since it turns out that Nb$_3$I$_8$-1L has a magnetic ground state with an FM ordering of the spins, magnetic ordering in thin films with 2 or 3 layers has been carefully investigated. Indeed, while preserving the in-plane FM ordering, inter-layer interaction might induce a FM or AFM out-of-plane ordering of the spins, thus giving rise to spin “stacking sequences”, such as $\uparrow\uparrow\ldots$ or $\uparrow\downarrow\uparrow\ldots$.

To conclude this section, it should be pointed out that, mostly as far as the magnetic properties are concerned, accurate convergence tests with respect to the calculation parameters (BZ sampling, plane wave and charge density cut-offs, and so on) are needed. In this respect, we refer to the appendix of Ref. [27], where a detailed discussion of the convergence of the magnetic stability, band structure, Curie temperature may be found.

III. RESULTS AND DISCUSSION

A. Unstrained systems

Nb$_3$I$_8$ is a layered transition metal halide belonging to the family of Nb$_3$X$_8$ (X = Cl, Br, I) crystals, having six layers per unit cell (u.c.) in its bulk structure (space group $D_{3d}^5 - R\bar{3}m$, No. 166) [53]. Each single layer shows an I-Nb-I sandwich structure, where the Nb atoms form triangular Nb$_3$ clusters with $d_1 \approx 2.96$ Å-length sides of an irregular Kagome lattice, due to the $d_2 \approx 4.65$ Å distance separating neighbor Nb$_3$ clusters (see Fig. 1(a)).
FIG. 1. Top (a) and side (b) view of a Nb$_3$I$_8$-1L $3 \times 3$ supercell. Green and purple spheres represent Nb and I atoms, respectively. The irregular Kagomé lattice for Nb atoms can be recognized in the panel (a), with the first-neighbor $d_1 \simeq 2.95$ Å and second-neighbor $d_2 \simeq 4.65$ Å Nb-Nb distances evidenced by red arrows.

Each Nb atom is covalently bonded to a distorted octahedral environment of I atoms, as shown in Fig. 1. Furthermore, the hexagonal u.c. contains three Nb atoms and eight I atoms, and the two sheets of I atoms are not equivalent. Starting from Nb$_3$I$_8$-1L, the bulk stacking is obtained by performing particular transformations of the latter. For instance, the second layer results from the inversion operation of the first one with respect to a triangular Nb cluster center (inversion center), whereas the third layer is shifted with respect to the first one of a certain quantity.

Nb$_3$I$_8$-1L is an intrinsic 2D cluster magnet [27, 29], since the magnetic moments of $1 \mu_B$ are delocalized on the Nb$_3$ clusters and result from the seven electrons shared by the Nb atoms (as it will be clearly shown by the spin density isosurfaces shown in the following). The ground state is FM ad is separated from the NM state by an excitation energy of $\sim 174$ meV, that protects the magnetic ground state from the thermal fluctuations even at high temperatures. Indeed, as calculated in Ref. [27], such a system exhibits a Curie temperature $T_C \sim 307$ K. The calculated lattice parameter is 7.621 Å and the corresponding band structure is shown in Fig. 2, describing a semiconducting system with a spin-up channel band gap $E_{g,\uparrow}$ of 0.552 eV and a spin-down channel band gap $E_{g,\downarrow}$ of 1.273 eV (highlighted by the shaded orange regions in the figure). It should be pointed out that other magnetic states, arising in larger (e.g., $2 \times 2$) supercells, can be devised, at an energy of one or few tens of meV higher than the FM ground state [27]. This is an interesting point because, despite the FM state is definitely stable over a wide range of temperatures, phase transitions between different magnetic states could easily occur under suitable conditions (e.g., applied magnetic fields).

By assuming the (most stable) FM spin ordering within a single layer, the question arises on whether, after stacking two or more layers on top of each other with a given stacking geometry, consecutive layers preferentially carry out the same spin or opposite spins (thus giving rise to a “mixed” spin configuration, with all triangular Nb clusters in the same plane exhibiting parallel spins, but with a spin flip when moving form one layer to a nearby one). This is a key concept because the possibility of obtaining a “layered” and eventually tunable (by means of electrostatic doping or out-of-plane pressure) magnetism paves the way to a wide range of applications, as already inferred for CrI$_3$ [30, 31].

Let us start our analysis from Nb$_3$I$_8$-2L, for which both bulk and $A^2$ stackings have been explored (optimized lattice parameters are 7.620 Å and 7.624 Å, respectively). Among the possible spin orderings, we have considered: FM (all Nb clusters in both planes carry the same spin, with a resulting non-zero magnetization); AFM$_x$ (all Nb clusters in the same plane carry the same spin, but the two different planes carry opposite spins and the resulting
FIG. 3. AFM spin patterns in Nb$_{3}$I$_{8}$-2L: (a) “stripy-2L”, (b) “Néel-2L”, and (c) “reverted-Néel-2L” states. Top views are shown for (a) and (b) because top and bottom planes show the same magnetic ordering. In (c), both the top (left) and side (right) views are shown. In all cases, Nb atoms in the same triangular cluster carry out the same spin. Yellow (blue) isosurfaces correspond to positive (negative) spin density. We can easily distinguish: (a) alternating rows with opposite spins in the stripy-2L state; (b) alternating clusters with opposite spins along both a$_{1}$ and a$_{2}$ crystallographic directions in the Néel-2L state; (c) same pattern as in the Néel-2L state for the reverted-Néel-2L state, but spins are reverted in the bottom plane.

magnetization is zero); AFM$_{xy}$ requiring a $2 \times 2$ supercell (two out of the four Nb clusters in each plane carry a spin up, the other two a spin down, with the resulting magnetization being zero for each plane). The latter configuration is compatible with different spin patterns, that will be referred to as “stripy-2L”, “Néel-2L”, and “reverted-Néel-2L” states, which are shown in Fig. 3 through their spin densities, each one obtained as difference between spin-up and spin down electron charge density. The stripy-2L state shows the spin distributed, in each plane, according to alternating rows, and the same pattern is identically repeated on the two layers. In the Néel-2L state the in-plane pattern is such that each pair of Nb clusters along a supercell diagonal carry the same spin, and the same pattern is identically repeated on the two layers. Finally, the reverted-Néel-2L state is obtained by reverting the spins of the Néel-2L state in the second layer, such that to a spin-up cluster on the top layer corresponds a spin-down cluster in the bottom layer and similarly for spin down. FM and AFM$_{xy}$ will also be referred to in the following as $\uparrow \uparrow$ and $\uparrow \downarrow$, respectively, to better highlight the relative spin orientation between the two layers.

It turns out that, regardless of the stacking geometry, the lowest-energy spin pattern is always that of the AFM$_{z}$ state (exactly as for CrI$_{3}$). The relative energy with respect to the latter of the other patterns as described above are reported in Tab. I for both $A^{2}$ and bulk stacking. The energies are reported per Nb$_{3}$I$_{8}$ formula unit (f.u.), so as to allow a straightforward comparison between $1 \times 1$ and $2 \times 2$ supercells. The FM state energy is $\sim 77$ meV/f.u. and $\sim 6$ meV/f.u. higher than the ground AFM$_{z}$ state in the bulk and the $A^{2}$ stacking, respectively. The same calculated energies of the NM state (spin polarization turned off in the calculations) are much larger, $\sim 103$ and $\sim 292$ meV/f.u., respectively.

As far as FM and AFM$_{xy}$ states are concerned, for $A^{2}$ stacking the former is separated from the AFM$_{z}$ state by few meVs, whereas the latter by 10-20 meV. On the other hand, for bulk stacking, they all lay at quite high energies (comparable with that of the NM state), but AFM$_{xy}$-reverted-Néel-2L is situated about 10 meV above the AFM$_{z}$ state. All these results reveal a fundamental role played by the deposition steps in the experimental fabrication of real samples, since the $A^{2}$ stacking tends to stabilize magnetism versus nonmagnetic solutions compared to the bulk stacking and the opposite concerns the stability of AFM$_{z}$ versus other magnetic patterns. As such, the magnetic phase diagram and its dependence on the temperature can be modified by effect of the stacking geometry.

The effect of the stacking geometry also emerges from the analysis of the spin-polarized band structure. In Fig. 4, the band structure for both $A^{2}$ and bulk stacking is shown for the lowest-energy AFM$_{z}$ state. It can be clearly inferred that for bulk stacking spin-up and spin-down channels provide almost identical band structures (see Fig. 4(b)), with a very tiny difference between the corresponding gaps, $E_{g,\uparrow}$ = 0.544 eV and $E_{g,\downarrow}$ = 0.537 eV. This can be ascribed to the inversion symmetry operation of the bulk stacking. On the other hand, for $A^{2}$ stacking, although the overall band structures look similar, the breaking of the inversion symmetry results in a k-point dependent spin splitting, yielding the band gaps $E_{g,\uparrow}$ = 0.481 eV and $E_{g,\downarrow}$ = 0.562 eV (see Fig. 4(a)).

At this stage, one might wonder about what would happen if thicker films with an odd number of layers would be considered. Since the AFM$_{z}$ magnetic order-

| Magnetic state | $\Delta E$ (meV/f.u.) |
|---------------|---------------------|
| NM            | 292.1               |
| FM            | 5.6                 |
| AFM$_{xy}$-Néel-2L | 21.2            |
| AFM$_{xy}$-reverted-Néel-2L | 15.6          |
| AFM$_{xy}$-stripy-2L | 21.2          |

TABLE I. Relative stability for different magnetic states of Nb$_{3}$I$_{8}$-2L for both bulk and $A^{2}$ stacking. $\Delta E$ is the energy difference per formula unit with respect to the lowest-energy state, that in both cases corresponds to the AFM$_{z}$ state, i.e., the in-plane FM magnetic ordering with AFM ordering between the top and bottom planes. NM stands for nonmagnetic state, FM for ferromagnetic state (both planes carry the same spin), whereas Néel-2L, reverted-Néel-2L, and stripy-2L states are as described in the text. The energies are calculated per Nb$_{3}$I$_{8}$ formula unit.
ing was proven to be the most stable for Nb$_3$I$_8$-2L, we analyzed similar patterns for Nb$_3$I$_8$-3L. In other words, given an in-plane FM ordering of the spins, different out-of-plane spin-stacking sequences were considered: ↑↑↑ (FM), analogous of the FM state of Nb$_3$I$_8$-2L; ↑↓↑, where neighbor layers carry opposite spin and obtained from FM by flipping the central layer spin; ↑↑↑, obtained from FM by flipping the spin of one of the outermost layers.

The optimized lattice parameters are 7.627 Å for the bulk stacking and 7.622 for the $A^3$ stacking. The AFM interlayer spin ordering (that is, ↑↑↑) has proven to be the most stable configuration, in agreement with what already reported for trilayer CrI$_3$ [33]. In Tab. II, we report the energies of all the other considered states with respect to the ↑↓↑ ordering, referred to one Nb$_3$I$_8$ f.u., for both bulk and $A^3$ stacking. Again, the stacking geometry reveals its central role, in that for bulk stacking several tens of meV separate ↑↑↑ and ↑↓↑ from the ground state. On the other hand, they lay only ∼12 and ∼6 meV from the ground state.

As far as the ground-state spin-polarized band structure is concerned, we do not expect any degeneracy for both stacking geometries, since no inversion symmetry operation can be identified. Indeed, the bulk stacking shows a semiconducting band structure for both spin channels with $E_{g,↑} = 0.547$ eV and $E_{g,↓} = 0.559$ eV (see Fig. 5(a)), whereas the $A^3$ stacking provides $E_{g,↑} = 0.436$ eV and $E_{g,↓} = 0.498$ eV (see Fig. 5(b)).

B. Strained systems

Strain engineering directly impacts on the electronic properties because it affects the interactions between the atoms composing the lattice. In particular, since the magnetism arises from the exchange interactions between the magnetic atoms belonging to the lattice, strain can be devised as an effective degree of freedom for tuning the magnetic couplings and, as a consequence, move the system state within the magnetic phase diagram in an absolutely unpredictable way. Here, we analyze in-plane compressive or tensile strain ranging from −7.5% to 7.5% in terms of lattice constant variations and discuss to what extent it can induce magnetic phase transitions.

Let us start our analysis from Nb$_3$I$_8$-IL. NM, FM, AFM$_{xy}$-stripy-1L and AFM$_{xy}$-Néel-1L magnetic orderings are considered (the last two patterns are the same as shown in Fig. 3, by keeping in mind that the figure has been conceived for bilayers whereas here we are dealing with monolayer systems).

While the FM magnetic ordering turns out to be always the lowest-energy state as for the unstrained monolayer for all the considered values of tensile and compressive strain, larger compressive strain makes the different magnetic states closer in energy. This can be easily evinced from Fig. 6, where the difference between the total energy of the NM or AFM magnetic configurations and the lowest-energy FM state is reported as a function of the applied strain. It is possible to distinguish a com-

| Magnetic state | $\Delta E$ (meV/f.u.) |
|---------------|-----------------------|
| NM            | 422.7                 |
| ↑↑↑           | 11.9                  |
| ↑↑↓           | 5.9                   |

TABLE II. Relative stability for different magnetic states of Nb$_3$I$_8$-3L for both bulk and $A^3$ stacking. $\Delta E$ is the energy difference per formula unit with respect to the lowest-energy state, that in both cases corresponds to the ↑↑↑ (AFM) state, i.e., the FM magnetic ordering with AFM ordering between the top, middle and bottom plane. ↑↑↑ stands for the (ferromagnetic) ordering where all planes carry out the same spin, opposite to that of the third plane.

FIG. 4. Spin-up (left panels) and spin-down (right panels) band structure along the $\Gamma - K - M - \Gamma$ path in the first BZ of Nb$_4$I$_8$-2L (in the lowest-energy magnetic configuration) for (a) $A^3$ and (b) bulk stacking. Zero energy corresponds to the top valence band. The band structure shows a semiconducting behavior, with the energy gap highlighted, for each spin channel, by a shaded orange region.
FIG. 5. Spin-up (left panels) and spin-down (right panels) band structure along the Γ − K − M − Γ path in the first BZ of Nb₃I₈-3L (in the lowest-energy magnetic configuration) for (a) A³ and (b) bulk stacking. Zero energy corresponds to the top valence band. The band structure shows a semiconducting behavior, with the energy gap highlighted, for each spin channel, by a shaded orange region.

FIG. 6. Relative stability of different magnetic orderings in Nb₃I₈-1L. ∆E = E − E_FM is the energy difference between the energy of a given configuration and that of the lowest energy, FM state: “Néel-1L” and “stripy-1L” configurations are considered.

The projected density of states (PDOS) onto atomic orbitals, shown in Fig. 8, reveals that, almost independently of the strain, the top valence bands are mostly dominated by hybridized Nb(d) and I(p) orbitals, with

common behavior to each magnetic state: energy differences increase (decrease) with an increasing tensile (compressive) strain. This is a striking result because it demonstrates the possibility of using strain as a control knob to stabilize the magnetic phase during the deposition steps, since a sufficiently high tensile (compressive) strain enhances (reduces) the energy difference between NM and FM states. From the analysis of the spin densities, it is clear that the FM state is characterized by the magnetization of the Nb₃ triangular clusters, each carrying a 1 µ_B magnetic moment, that is, a 1/2 spin. By identifying each cluster with its total 1/2 spin, such systems appears as a triangular lattice of 1/2 spins, whose stability can be tuned with strain. In particular, tensile strain enhances the stability of this phase against the others (since cluster-cluster couplings that might induce other magnetic orderings are weakened because of the increased intercluster distance).

If we now move to the electronic properties, the effect of strain is clearly visible also in the band structure. This can be evinced from Fig. 7, where the band structures of Nb₃I₈-1L in the presence of a ±7.5\% strain are reported. In general, in the strong tensile strain regime, the electronic bands exhibit a flattening deriving from the increasing of the in-plane interatomic distances, as expected. An unexpected effect of the strain on the band structure concerns the band gap variation: by tuning the strain from compressive to tensile, a decrease (increase) of the spin-up (spin-down) channel band gap is observed, as shown in Fig. S1 of the Supplemental Material (SM). Such an opposite behavior for spin-up and spin-down channel may be ascribed to the number and nature of electronic bands in proximity of the energy gap region. As it will be further clarified in a while from the projection of the energy bands onto atomic orbitals, the relative weight of I and Nb orbitals to those bands is differently influenced by the strain for the two spins, with a direct effect onto the energy gaps. We could expect that this intriguing peculiarity might be unveiled from absorption experiments, as an example.

An in-depth analysis also shows that upon increasing strain a decreasing of the monolayer thickness is observed, ranging from ~ 4.57 Å for a ~7.5 \% strain to ~ 3.67 Å for a 7.5 \% strain, to be compared with 4.08 Å of the unstrained bilayer (that is indeed intermediate between the other two). In other words, tensile (compressive) strain tends to weaken (enhance) the interatomic interaction along the z direction.

The projected density of states (PDOS) onto atomic orbitals, shown in Fig. 8, reveals that, almost independently of the strain, the top valence bands are mostly dominated by hybridized Nb(d) and I(p) orbitals, with
FIG. 7. Spin-up (left panels) and spin-down (right panels) band structure along the $\Gamma - K - M - \Gamma$ path in the first BZ of $\text{Nb}_3\text{I}_8$-1L (in the lowest-energy magnetic configuration) under a (a) $-7.5\%$ and (b) $7.5\%$ strain. Zero energy corresponds to the top valence band. The band structure shows a semiconducting behavior, with the energy gap highlighted, for each spin channel, by a shaded orange region.

FIG. 8. PDOS of $\text{Nb}_3\text{I}_8$-1L in the lowest-energy FM configuration onto I($p$), Nb($d$) and Nb($p$) orbitals. The largest considered compressive ($-7.5\%$) and tensile ($7.5\%$) strains, together with the unstrained system are considered. Zero energy corresponds, for each system, to the top valence band. Positive (negative) values of the PDOS correspond to spin-up (spin-down) bands.

The larger contribution coming from the former. However, by looking at an energy window $\sim 0.4$ eV below the top valence band, the integrated PDOS shows that, on going from the largest compressive strain to the unstrained system to the largest tensile strain the I($p$) contribution to the total PDOS changes from $45\%$ to $32\%$ to $30\%$, respectively. We can infer that the compressive strain can significantly enhance the hybridization between I and Nb orbitals, whereas the opposite effect is observed in the case of tensile strain.

Moving to the layered systems, it turns out that the strain does not alter the ground-state magnetic ordering, with exception of $\text{Nb}_3\text{I}_8$-2L at large compressive strain, as detailed below. In other words, adjacent layers always carry opposite spin in the lowest-energy state ($\uparrow \downarrow$ for $\text{Nb}_3\text{I}_8$-2L and $\uparrow \downarrow \uparrow$ for $\text{Nb}_3\text{I}_8$-3L).

In Figs. 9 and 10, the energy differences of different magnetic orderings relative to the lowest-energy state are reported, as a function of the applied strain and for both bulk and $A^2$ stackings. A particularly important effect is observed for $\text{Nb}_3\text{I}_8$-2L in the bulk stacking: at $-7.5\%$ strain and below, a phase transition to a NM state occurs, since Nb magnetic moments monotonically vanish, as illustrated in Fig. 11. This does not hold for the $A^2$ stacking, providing further proof of the deposition steps importance for the expected magnetic state of the system.

Finally, as shown in Figs. S2 and S3 of the SM for $\text{Nb}_3\text{I}_8$-2L and -3L, respectively, strain can significantly affect the band structures, giving rise to non-
IV. CONCLUSIONS

This work explores the novel and intriguing magnetic and electronic properties of few-layer Nb$_3$I$_8$ vdW nanofilms, showing how and to what extent the magnetism and magnetic ordering can be considered as tunable properties as a function of the film thickness, applied strain, stacking geometry and the combined effect of these three parameter. By considering one-, two-, and three-layer systems, we have shown different magnetic patterns that might be energetically favored among the many possible. Spin densities are mostly localised on Nb atoms. In particular, we argued that within each plane, a FM ordering is energetically favored, with parallel spins on all Nb atomic sites. However, as one or more layer are added, the lowest-energy configuration is that corresponding to an in-plane FM ordering and an out-of-plane AFM ordering of the spins (that is, two consecutive layers carry opposite magnetizations). On the other hand, other magnetic patterns have been shown possible, with energy 10-20 meV above the lowest-energy state, where spin triangles, driven by Nb$_3$ cluster natively present in the lattice, show up.

We explored both $A^n$ and bulk stacking, showing that the stacking geometry might significantly affect the electronic and magnetic properties. Similarly, strain effects have been observed, from band flattening taking place for tensile stress, to more dispersed bands with increasing contribution from I orbitals for large modulus compressive stress.

Interestingly, a transition to a NM state shows up when bulk-stacked two-layer systems under $-7.5\%$ strain are considered. Moreover, the strain is also capable of enhance or weaken (according to its sign) the energy differences between different possible magnetic orderings, paving the way to a strain-tunable magnetic response.

All these results shed light on new and intriguing properties of this novel material, bringing it among the possible candidates to implement more complex magnetic responses, in user-designed homo- and hetero-structures.

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FIG. S1. Spin-up \((E_{g,\uparrow})\) and spin-down \((E_{g,\downarrow})\) energy gap of Nb$_3$I$_8$-1L (in the lowest-energy FM configuration) as a function of the strain. We can notice the decreasing (increasing) behavior of \(E_{g,\uparrow}\) \((E_{g,\downarrow})\) when tuning the strain from compressive to tensile.
FIG. S2. Spin-up (left panels) and spin-down (right panels) band structure of Nb$_3$I$_8$-2L (in the lowest-energy magnetic configuration) along the $\Gamma - K - M - \Gamma$ path in the first Brillouin zone for (a) $A^2$ stacking, $-7.5\%$ strain, (b) $A^2$ stacking, $7.5\%$ strain, (c) bulk stacking, $-7.5\%$ strain, and (d) bulk stacking, $7.5\%$ strain. Zero energy corresponds to the top valence band. The band structure shows a semiconducting behavior, with the energy gap highlighted, for each spin channel, by the (orange) shaded region.
FIG. S3. Spin-up (left panels) and spin-down (right panels) band structure of Nb$_3$I$_8$-3L (in the lowest-energy magnetic configuration) along the $\Gamma - K - M - \Gamma$ path in the first Brillouin zone for (a) $A^3$ stacking, $-7.5\%$ strain, (b) $A^4$ stacking, $7.5\%$ strain, (c) bulk stacking, $-7.5\%$ strain, and (d) bulk stacking, $7.5\%$ strain. Zero energy corresponds to the top valence band. The band structure shows a semiconducting behavior, with the energy gap highlighted, for each spin channel, by the (orange) shaded region.