Tunable electronic and magnetic properties of thin Nb$_3$I$_8$ nanofilms: interplay between strain and thickness

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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 nanofilms from first principles, showing how and to what extent 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 charming 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 [1–9]. The out-of-plane van der Waals (vdW) interactions allow the integration of deeply different 2D materials, that can thus be viewed as elementary building blocks of new heterostructures 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 [10], 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 deserves a special mention, since it offers a viable approach to engineer the electronic, magnetic, and optical properties [13–16] of 2D nanostructures. The reduced atomic coordination and the enhanced flexibility and elasticity that 2D materials often exhibit when compared with most three-dimensional (3D) crystals [17–18] have boosted the development of this new field, referred to as “straintronics”.

As far as ground-state magnetism is concerned, several avenues have been devised so far to gain a precise and predictable control over the magnetic states in a number of recently discovered 2D materials. For example, it has been argued that charge doping and/or external strain can significantly affect and modify magnetic phase transitions and exchange interaction [19], and are being explored as feasible routes to tune the magnetic ordering in both monolayer ad multilayers systems [20–27].

Since the recent discovery of intrinsic magnetism in monolayers of CrI$_3$ [28], the exploration of 2D intrinsic magnetic materials has been exponentially increasing [29]. Among the many, we can mention CrI$_3$ and Cr$_2$Ge$_2$Te$_6$ [30], or those exhibiting high Curie temperature $T_C$, such as V$_3$I$_8$ [31], MnS$_2$ [32], VSe$_2$ [33], and Nb$_3$I$_8$ [34], all inheriting the magnetic ordering arising from the transition metal $d$-orbitals. In particular, 2D platforms combining ferromagnetism with room $T_C$ and conventional semiconductors open new avenues to implement spintronic applications based on the use of both the charge and the spin degrees of freedom, for example, in next-generation quantum logic chips and nonvolatile magnetic memories with increased densities [35–36].

Nb$_3$I$_8$ is a recently synthesized 2D material [37] 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 antiferromagnetic (AFM) in bilayer and trilayer forms [34]. 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 effect without external tunings [35]. All these observations make Nb$_3$I$_8$ an ideal candidate for spintronics and valleytronics applications, as even revealed by recent experimental and theoretical studies [39]. Nevertheless, a comprehensive explanation of the intriguing electronic and magnetic properties of few-layer Nb$_3$I$_8$ is still missing, so the present work aims to unveil its potentialities for spintronics applications contributing to the search of novel materials with improved or new functionalities. 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. In particular, we will assess and describe the competition and relative stability between different magnetic phases and the band-gap dependence.
on the applied strain.

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). Both 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. This will be better detailed in the next section.

The paper is organized 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) [11,43]. The generalized gradient approximation (GGA) is used with projector-augmented wave (PAW) pseudopotentials [44] based on the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional [45] to represent the atomic cores [46]. 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 $\sim 20$ Å is 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 $1 \times 1 \times 1$ unit cell was sampled using an $8\times8\times1$ Monkhorst-Pack $k$-point grid [47], grids for $n \times n \times 1$ supercells were scaled accordingly to guarantee the same accuracy with respect to the $k$-point grid of all calculations. 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 [18] 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$_8$ [31]. The supplemental material (SM), in Sec. I, reports typical intralayer binding curves calculated within this approach, characterized by binding energies that are typical of vdW systems.

Based on previous reports [49], the on-site Coulomb repulsion of Nb 4d electrons, responsible, as we shall see, of the magnetic behavior of the material, is taken into account by means of the DFT + $U$ method [50,53] with $U = 2$ eV. The SM, in Sec. III, contains a number of tests showing that, upon changing $U$ within a reasonable range, the reported properties do not exhibit significant variations. In particular, we have verified the stability of the ground-state magnetic ordering, that will be discussed in Sec. III] against $U$. Occupied Kohn-Sham levels do show changes within 0.1-0.2 eV, whereas unoccupied levels shift by much larger energies. This allows to conclude that the main conclusions of the present paper should not be affected by the chosen value of $U$.

The in-plane lattice parameter of all the considered systems has been optimized using spin-polarized calculations. The atomic positions have been fully optimized using spin-polarized calculations. These converge in steps of 2.5%. Thickness effects have been studied by considering monolayer, bilayer, and trilayer nanofoils, which will be referred to as Nb$_3$I$_8$-nL with $n = 1, 2, 3$, respectively.

The effect of the stacking geometry has been assessed for Nb$_3$I$_8$-2L and Nb$_3$I$_8$-3L, by comparing the bulk stacking, that is the natural order of the layers as they would be arranged in the bulk form, and the AA stacking, constructed by piling different layers with the same planar coordinates.

The ground-state analysis is performed on the non magnetic (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 in-plane FM ordering of the spins, the inter-layer magnetic ordering in thin nanofoils with two or three layers has to be carefully investigated. Indeed, while preserving the in-plane FM ordering, the inter-layer interaction might induce either FM or AFM out-of-plane ordering of the spins, thus giving rise to different spin “stacking sequences”, such as $↑↑\ldots$ or $↑↓↑\ldots$. This will be better detailed in the next.

Spin-orbit coupling (SOC) has not been included in the calculations, because it does not appear to significantly affect the main conclusions of the paper. An example is shown in Sec. II of the SM, that allows to conclude that the calculated band structures with the inclusion of the SOC do not differ from those calculated in the absence of it.

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. [34], where a detailed discussion of the convergence of the magnetic stability, band structure, Curie temperature may be found.
FIG. 1. Top (a) and side (b) view of a Nb\textsubscript{3}I\textsubscript{8}-1L \(3 \times 3\) supercell. Green and pink spheres represent Nb and I atoms, respectively. The irregular Kagomé lattice formed by Nb atoms can be recognized in the top view, together with the first-neighbor \(d_1 \approx 2.95\) Å and second-neighbor \(d_2 \approx 4.65\) Å Nb-Nb distances evidenced by red and green bonds respectively. This gives rise to alternating, inequivalent triangles \[39, 40\]. The ground-state spin polarization distribution \(\rho_\uparrow - \rho_\downarrow\) is shown in (c) with the yellow isosurfaces, corresponding 25\% of the maximum value.

FIG. 2. Spin-up (left) and spin-down (right) band structure along the \(\Gamma - K - M - \Gamma\) path in the first BZ of Nb\textsubscript{3}I\textsubscript{8}-1L. Zero energy corresponds to the top valence band. The band structure shows a semiconducting behavior, with the spin-up and spin-down energy gaps highlighted by a shaded orange region and occupied (unoccupied) bands depicted in black (red).

III. RESULTS AND DISCUSSION

A. Unstrained nanofilms

1. Bulk Nb\textsubscript{3}I\textsubscript{8}

Nb\textsubscript{3}I\textsubscript{8} is a layered transition metal halide belonging to the family of Nb\textsubscript{3}X\textsubscript{8} (X = Cl, Br, I) crystals, having six layers per unit cell (u.c.) in its bulk structure (space group \(D_{5d}^2 - R\overline{3}m\), No. 166) \[58\]. Each single layer shows an I-Nb-I sandwich structure, where the Nb atoms are arranged into a two-dimensional planar lattice of triangular Nb\textsubscript{3} clusters with side \(d_1 \approx 2.96\) Å, separated by a \(d_2 \approx 4.65\) Å distance, as sketched in Fig. 1(a). As evidenced in Fig. 1(b), each Nb atom is covalently bonded to a distorted octahedral environment of I atoms, that in turn form a top and a bottom layer that are not equivalent.

2. Nb\textsubscript{3}I\textsubscript{8}-1L

Nb\textsubscript{3}I\textsubscript{8}-1L is an intrinsic 2D cluster magnet \[34, 38\], since the magnetic moment per unit cell of 1 \(\mu_B\) is distributed over the Nb\textsubscript{3} clusters and results from the seven electrons shared by the Nb atoms. This is depicted in Fig. 1(c), showing the spin polarization isosurfaces in the FM
ground state. The NM solution is separated by an energy of \( \sim 174 \text{ meV} \) from the ground state, that protects the magnetic ground state from the thermal fluctuations even at high temperatures. Such a circumstance is supported by the calculations reported in Ref. [31], where it is shown that such system exhibits a Curie temperature \( T_C \sim 307 \text{ K} \). The calculated lattice parameter is \( 7.62 \text{ Å} \) and the corresponding band structure is shown in Fig. 2, describing a semiconducting system with a spin-up channel band gap \( E_{g,↑} = 0.552 \text{ eV} \) and a spin-down channel band gap \( E_{g,↑} = 1.273 \text{ eV} \) (highlighted by the shaded orange regions in the figure). It should be pointed out that other and more complex magnetic states, arising in larger (e.g. \( 2 \times 2 \)) supercells, can be devised, at an energy from one to few tens of meV higher than the FM ground state [34]. 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).

The dynamical stability of \( \text{Nb}_3\text{Is}-1\text{L} \) has been demonstrated both experimentally (isolated monolayers have been successfully obtained onto suitable substrate [59]) and theoretically (from the calculated phonon spectrum, as obtained within the same theoretical framework as that of the present work [19]). It should be pointed out that, as far as the multilayer and the strained nanofilms considered in the next are concerned, the assessment of the dynamical stability has not be carried out, being computationally quite demanding and out of the scope of the present work. Here, we are going to conceptually support, with the presented results, how the interplay between magnetism, stacking and strain makes \( \text{Nb}_3\text{Is} \) an ideal candidate for novel magnetic devices and functionalities, that certainly demand for further work and investigation.

To conclude the discussion on \( \text{Nb}_3\text{Is}-1\text{L} \), the in-plane magnetic coupling, leading to the discussed FM magnetic ordering, can be estimated by building a \( 2 \times 2 \) supercell, as difference between the FM ground state energy and the energy obtained after flipping just one of the spins, out of the four available. The magnetic coupling so obtained is about 23 meV. Such result seems independent on the size of the supercell, since the same value is obtained for a \( 3 \times 3 \) supercell.

### 3. Stacking

Starting from \( \text{Nb}_3\text{Is}-1\text{L} \), the next layer with bulk stacking is obtained by applying to the former suitable in-plane coordinate transformations. For instance, the second layer results from applying a spatial inversion operation with respect to the center of an \( \text{Nb}_3 \) cluster (inversion center), whereas the third layer results from the first one after applying a suitable fractional translation. On the other hand, multilayer nanofilms with AA stacking can be easily obtained by just replicating the first layer at suitable distances, at fixed in-plane coordinates.

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 \( \text{Nb}_3 \) 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 [20 21].

#### 4. \( \text{Nb}_3\text{Is}-2\text{L} \)

For \( \text{Nb}_3\text{Is}-2\text{L} \) we explored both bulk and AA stackings, that reveal an in-plane optimized lattice parameter quite similar to that of \( \text{Nb}_3\text{Is}-1\text{L} \) (\( \sim 7.62 \text{ Å} \)).

As far as the magnetic ordering is concerned, the most straightforward configuration to be conceived is that of stacking the two layers (with either bulk or AA stacking) with in-plane FM ordering, same as that of \( \text{Nb}_3\text{Is}-1\text{L} \) (see Fig. 1(c)). In this respect, each layer becomes an “elementary” building block of the multilayer film, carrying a \( \pm 1 \mu_B \) magnetic moment per unit cell (all \( \text{Nb}_3 \) clusters belonging to the same plane carry the same spin). The remaining degree of freedom is that of the relative sign of such moment between the two layers. Therefore, we can conceive two different out-of-plane orderings, that will be referred to as FM or \( ↑↑ \) (where both layers have a \( +1 \mu_B \) magnetic moment and the total magnetization is non-zero as well) and AFM\(_z\) or \( ↑↓ \) (where the two layers carry opposite spins, each layer as a non-zero magnetization whereas the total magnetization is zero).

However, aimed at giving a more comprehensive picture of the possible magnetic patterns and their relative stability, \( 2 \times 2 \) supercells were also employed, to explore configurations where each single layer carries a zero total magnetization (two out of the four \( \text{Nb}_3 \) clusters in each plane carry a spin up, the other two a spin down, each plane has a zero magnetization and the total magnetization is zero as well). These configurations will be referred to as AFM\(_{xy}\) and are compatibles with different spin patterns, named “stripy-2L”, “Néel-2L”, and “reverted-Néel-2L” states. These patterns, together with FM and AFM\(_z\), are sketched in Fig. 3. In the stripy-2L ordering, spin up and spin down in each plane are distributed according to alternating rows, and the same pattern is identically repeated in the two layers. In the Néel-2L ordering spin up and spin down in each plane are distributed according to the supercell diagonal (that is, \( \text{Nb}_3 \) clusters belonging to the same 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 flipping the spins of the Néel-2L state in the second layer, such that to a spin-up in the top layer cor-
FIG. 3. $2 \times 2$ supercell and spin patterns investigated for Nb$_3$I$_8$-2L. The naming follows the same convention as in the text. Nb$_3$ clusters are highlighted with triangles. Red (blue) triangle background refers to spin-up (spin-down), also depicted with up (down) green arrows. It is evident that FM and AFM$_z$ are characterized by a non-zero magnetization of each Nb$_3$I$_8$ single layer whereas the total magnetization is not zero only for FM.

responds a spin-down in the bottom layer and the other way around for spin-down. The spins densities associated with the AFM$_{xy}$ orderings are reported in Sec. I of the SM for the sake of completeness.

In the following we report the analysis of the different FM, AFM$_z$ and AFM$_{xy}$ magnetic orderings. The relative energy of each magnetic pattern with respect to the lowest-energy AFM$_z$ ordering is reported in Tab. I for both AA and bulk stacking. The energies are reported per $1 \times 1$ unit cell (u.c.), so as to allow a straightforward comparison between $1 \times 1$ and $2 \times 2$ supercells. It turns out that, regardless of the stacking geometry, the magnetic ground state definitely turns out to be much more stable than the NM solution and that AFM$_z$, among the considered ones, is always the lowest-energy spin pattern. Such circumstance at least partly distinguishes Nb$_3$I$_8$ from CrI$_3$. Indeed, as far as the latter is concerned, while a similar interlayer AFM$_z$ ordering has been argued for the bilayer, a stacking-dependent magnetism shows up [60–62], that seems to lack in Nb$_3$I$_8$. However, in the case of Nb$_3$I$_8$ the stacking geometry plays a role in the relative stability of different magnetic states. Indeed, AFM$_{xy}$ orderings, as depicted in Fig. 3, depending on the stacking, show higher energies, ranging from about 10-20 meV to about 100 meV. On the other hand, the FM state energy is $\sim 77$ meV/u.c. and $\sim 6$ meV/u.c. higher than AFM$_z$ in the bulk and the AA stacking, respectively. These results reveal that an important role might be played by the deposition steps in the fabrication of real samples, in that the stability of the AFM$_z$ ordering against other magnetic orderings gets much more pronounced for bulk stacking. 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 AA 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 linking the top and the bottom layer in the bulk stacking. On the other hand, for AA 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)). The presence or lack of inversion symmetry for the two stackings can also be easily identified.
in the charge transfer plots, reported in Sec. I of the SM and showing the ground-state electronic charge difference between Nb$_3$I$_8$-2L and the isolated top and bottom layer.

5. Nb$_3$I$_8$-3L

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 ordering, corresponding to AFM coupling between two consecutive layers, was proven to be the most stable for Nb$_3$I$_8$-2L, we analyzed similar patterns for Nb$_3$I$_8$-3L. Given the in-plane FM ordering in each layer, different out-of-plane spin-stacking sequences were considered: ↑↑↑, analogous of the FM state of Nb$_3$I$_8$-2L; ↑↑↓, where neighbor layers carry opposite spin and obtained from the first by flipping the central layer spin; ↑↑↓, obtained from the first by flipping the spin of one of the outermost layers. The optimized lattice parameters are 7.63 Å and 7.62 Å for the bulk and the AA stacking, respectively. The ↑↑↑ ordering, corresponding to AFM coupling between each pair of consecutive layers, has been proven to be the most stable configuration, in agreement with what already reported for trilayer CrI$_3$ [22]. In Tab. II we report the relative energies per u.c. of all the considered magnetic states with respect to the lowest-energy ↑↑↑ ordering, for both bulk and AA 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 lie only ≃12 and ≃6 meV from the ground state in the AA stacking.

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 AA stacking provides $E_{g,↑} = 0.436$ eV and $E_{g,↓} = 0.498$ eV (see Fig. 5(b)).

As a final remark, we should point out that the out-of-plane AFM magnetic coupling can be estimated, from our results, to be of the order of 6 meV for AA stacking and 80 meV in bulk stacking. Such a coupling is calculated as the energy needed to flip the spin of a whole layer starting from an otherwise AFM$_z$ magnetic configuration and can inferred from both the results for Nb$_3$I$_8$-2L (as $E_{↑↓} - E_{↑↑}$ in Table I) and those for Nb$_3$I$_8$-3L (as $E_{↑↑↓} - E_{↑↑↑}$ in Table II). As such, we can conclude that, while the stacking seems not to be able to modify the lowest-energy magnetic configuration, bulk stacking can definitely make it more stable than it is in the AA stacking.

B. Strained nanofilms

Applied strain can directly impact 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 across the magnetic phase diagram in an absolutely unpredictable way. Here, we analyze in-plane compressive or tensile biaxial 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.

1. Nb$_3$I$_8$-1L

Let us start our analysis from Nb$_3$I$_8$-1L. Here, two main questions arise: the first is about whether the strain might stabilize other magnetic phases against the stable FM phase found for the unstrained monolayer. Second, whether and to what extent the electronic properties of a given magnetic phase may change as an effect of the strain.

Aimed at giving an answer to the first question, besides the NM and FM orderings previously discussed for Nb$_3$I$_8$-1L, here we consider also, for the sake of complete-

| Magnetic state       | ΔE (meV/u.c.) | AA stacking | bulk stacking |
|----------------------|--------------|-------------|---------------|
| NM                   | 292.1        | 103.0       |               |
| FM (↑↑)              | 5.6          | 76.7        |               |
| AFM$_{xy}$-Néel-2L  | 21.2         | 96.2        |               |
| AFM$_{xy}$-reverted-Néel-2L | 15.6 | 13.7 |               |
| AFM$_{xy}$-stripy-2L | 21.2         | 96.2        |               |

TABLE I. Relative stability for different magnetic states of Nb$_3$I$_8$-2L for both bulk and AA stacking. ΔE is the energy difference between the considered state and the lowest-energy one, that for both stackings corresponds to the AFM$_z$ (↑↓). NM stands for nonmagnetic state, FM for ferromagnetic state (both layers 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 1 × 1 unit cell (u.c.).

| Magnetic state       | ΔE (meV/u.c.) | AA stacking | bulk stacking |
|----------------------|--------------|-------------|---------------|
| NM                   | 422.7        | 276.7       |               |
| ↑↑↑                  | 11.9         | 79.5        |               |
| ↑↑↓                  | 5.9          | 78.0        |               |

TABLE II. Relative stability for different magnetic states of Nb$_3$I$_8$-3L for both bulk and AA stacking. ΔE 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 the same spin and ↑↑↓ for the ordering where two consecutive planes carry 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 Γ−K−M−Γ path in the first BZ of Nb$_3$I$_8$-2L (in the lowest-energy magnetic configuration, AFM$_z$) for (a) AA 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 Nb$_3$I$_8$-3L (in the lowest-energy magnetic configuration, ↑↓↑) for (a) AA 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.

ness, two other configurations, that is, AFM$_{xy}$-stripy-1L and AFM$_{xy}$-Néel-1L (with definitions similar to those of Fig. 3, by keeping in mind that the figure has been conceived for bilayers whereas here we are dealing with a monolayer).

The FM magnetic ordering turns out to be stable against strain effects for all the considered values of tensile and compressive strain. However, larger compressive strain makes the different magnetic states closer in energy to be contrasted with tensile strain that instead further stabilizes the FM state. This can be be easily inferred from Fig. 6 where the relative energy of different magnetic configurations is reported versus the applied 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 and between different magnetic states. The explanation of such behavior requires to remind that, as previously stated, the origin of magnetism in Nb$_3$I$_8$ stands in the irregular Kagomé lattice, where each Nb$_3$ triangular cluster carries a 1/2 spin. The magnetic interactions between those clusters are modified by strain, in particular because an enhanced or reduced inter-cluster distance.

Now we turn to the second question, that was about strain-induced effects on the electronic properties. To this aim, in Fig. 7 the spin-up and spin-down band structures of Nb$_3$I$_8$-1L in the presence of a ±7.5% strain are reported. As a general remark, in the strong tensile strain regime, the electronic bands exhibit a flattening deriving from the increased in-plane interatomic distances. A more intriguing 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 we show in Fig. 7(c). 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 contribution 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.

As a final remark, we would like to point out that strain-induced effect on the electronic structure can also be related to the change in the orbital hybridization following structural modification. As an example, we report in Fig. 8 the projected density of states (PDOS) onto atomic orbitals. Almost independently of the strain, the top valence bands are mostly dominated by hybridized Nb(d) and I(p) orbitals, with the larger contribution coming from the former. However, by looking at an energy window ∼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.

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 parameters. 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 shown to be mostly localized on the Nb$_3$ triangular clusters natively present into the irregular Kagomé lattice. In particular, we argued that within each plane a FM ordering is energetically favored, with parallel spins on all Nb atomic sites. In this respect, a single Nb$_3$I$_8$ layer behaves as a “macroscopic” spin carrying a 1 $\mu_B$ magnetic moment per unit cell. However, as one or more layer are stacked on the first, the inter-layer magnetic interaction drives the system to an out-of-plane AFM ordering of the spins, such that two consecutive layers carry opposite magnetizations. On the other hand, other, both in-plane and out-of-plane magnetic patterns have been shown to be feasible, with energies depending on the stacking geometry and the nanofilm thickness. In particular, the out-of-plane AFM magnetic coupling results more (less) stable in the presence of bulk (AA) stacking, demonstrating how stacking might play a fundamental role for designing
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 Nb$_3$I$_8$-1L (in the lowest-energy magnetic configuration, FM) under (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. (c) 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.

new magnetic materials and devices with given functionalities.

Similarly, strain effects have been evidenced, from band flattening taking place for sufficiently large tensile stress, to more dispersed bands with increasing contribution from I orbitals for large modulus compressive stress.

Interestingly, the strain is also capable of enhancing or weakening (according to its sign) the energy differences between different possible magnetic orderings, paving the way to a strain-tunable magnetic response.

The magnetic coupling, responsible for the in-plane FM and the out-of-plane AFM orderings has been estimated from total energy differences. It turns out that it is required an energy of about 23 meV to flip a single spin within a single FM layer. On the other hand, about 6 meV for AA stacking and 80 meV for bulk stacking per unit cell are required to flip the spin of a whole layer starting from two antiferromagnetically coupled layers.

All these results, also combined with recent experimental and theoretical outcomes on the bulk counterpart [39], 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. Our outcomes represent a step forward in the search of thickness-dependent and strain-tunable magnetism in 2D van der Waals materials, which is currently object of intense and ongoing research [63].

Future work could involve the study of defected Nb$_3$I$_8$ vdW nanofilms, with the aim of bringing out, depending on the defect nature and concentration, the two-fold role that might be played, especially in a magnetic system, by the impurities: on one hand, unwanted defects might at least partially destroy the desired (e.g., magnetic) properties. On the other hand, intentionally induced impurities might represent a novel degree of freedom to enhance those properties [64–66]. Moreover, a thorough study of valley polarization and its interplay with strain would be desirable, as being investigated in other classes of two-dimensional materials [67–69].
FIG. 8. PDOS of Nb$_3$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.

FIG. 9. Relative stability of the ↑↑ magnetic ordering in Nb$_3$I$_8$-2L for both AA and bulk stacking as a function of the strain, referred to that of the lowest-energy ↑↓ state ($\Delta E = E_{↑↑} - E_{↑↓}$).

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FIG. 10. Relative stability of different magnetic orderings in Nb$_3$I$_8$-3L for both AA and bulk stacking as a function of the strain. $\Delta E = E - E_{↑↓↑}$ is the energy difference between the energy of a given configuration and that of the lowest-energy, ↑↓↑ state.

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