1. Introduction

Bulk transition metal dichalcogenides (TMDs) of the form TCh2, where T is a transition metal and Ch is a chalcogen (S, Se, Te), are very versatile systems as their electronic and structural properties can be tuned not only by varying their chemical composition but also by synthesizing different polytypes having the same chemical formula. The variation of the local coordination of the transition metal ion in different polytypes of a given TMD leads to completely different physical properties [1]. For example, 1T-TaS2 with Ta in octahedral coordination, is a correlated system which ground state is still very debated (Mott insulator or correlated metal) [2–5] while 2H-TaS2, with Ta in trigonal prismatic coordination, is a metal (the 1T and 1H polytypes are reported in figure 1). However, this tunability cannot be completely exploited as not all bulk TMDs can be synthesized in 1T and 2H polytypes either because the appropriate chemical and thermodynamical preparation conditions are unknown or because the energetic is unfavorable. This is the case of bulk 1T-TiSe2 that has never been synthesized in the 2H polytype or, vice versa, of bulk 2H-NbSe2 and 2H-NbS2 that crystallize in the 2H polytype and not in the 1T one, although it has been reported [6] that 1T-NbS2 bulk can be synthesized under very special conditions.

Since different TCh2 planes are bounded together by the weak van der Waals interaction, it makes possible to isolate single layers of a large class of transition metal dichalcogenides [7, 8] (a single layer here refers to a trilayer TCh2 unit). The exfoliation of bulk TMDs into bi-dimensional crystals, beside being interesting in itself as it allows to investigate a variety of phenomena in low dimension, paves the way to different synthesis techniques, unfitted for bulk systems but feasible in few layers flakes. An example is the phase transition between the hexagonal and monoclinic phases of monolayer MoTe2 achieved by electrostatic doping [9] or the transition between the 2H and 1T′ phases obtained by liquid exfoliation [8, 10].

More recently it has been shown that the 1T-NbSe2 polytype can be stabilized either as a sin-
Single layer on top of bilayer graphene kept at 500 °C–590 °C during epitaxy [11] or by applying a pulsed local field through the STM tip at the surface of bulk 2H-NbSe2 [12].

The physical properties of single layer 1T-NbSe2 turned out to be completely different from that of single layer 1H-NbSe2 as the former is a spin 1/2 Mott-Jahn Teller insulator undergoing a $\sqrt{3} \times \sqrt{3}$ charge density wave [11, 13] (CDW), while the latter is a metal undergoing a $3 \times 3$ CDW [14–16]. Most important, it has been recently shown [13] that density functional theory (DFT) calculations with local LDA/GGA kernels do not explain the stabilization of the 1T-NbSe2 single layer phase with respect to the 1H one, as this transition occurs via a correlated mechanism involving vibrations and the stabilization of a magnetic state that can be addressed within the DFT + U approximation. Thus, given the broad perspectives offered by these new synthesis techniques, theoretical calculations can be used to spot new TMD phases that can be experimentally accessed and to describe their structural and electronic properties, since the accuracy of DFT in these systems has been thoroughly verified [17, 18].

Bulk 2H-NbS2 is isoelectronic and isostructural to 2H-NbSe2, however it stands somewhat at odd with respect to other transition metal dichalcogenides as it displays no CDW at low temperature [19]. On the contrary, when NbS2 single-layer is grown on Nitrogen-doped 6H-SiC(0001) terminated with single or bilayer graphene, it adopts the 1H-NbS2 polytype and STM images show a $3 \times 3$ reconstruction [20], but if 1H-NbS2 is grown epitaxially on Au(111) no CDW is detected [21]. Given the different properties of NbS2 in the bi-dimensional limit, it is natural to investigate the possible stability of other polytypes and the formation of magnetic and CDW phases.

In this work, by using density functional theory calculations, we investigate the possible synthesis of single layer 1T-NbS2 together with its structural, vibrational and electronic properties. We study the stability with respect to the single layer phase and we calculate magnetic couplings.

2. Computational details

Density functional theory calculations are performed using the QUANTUM ESPRESSO code [22, 23]. For Nb (Ta)
we use ultra-soft pseudopotentials from Vanderbilt distributions [24] including semicore states and two projectors for s and p channels and valence configuration 4s², 4p⁶, 4d⁴, 5s², 6s², 5p⁶, 5d³. For S (Se) we use norm-conserving pseudopotentials with empty d-states in valence and the following valence configuration 3s², 3p⁴, 3d⁶ (4s², 4p³, 4d²).

We use an energy cutoff up to 45 Ry (540 Ry for the charge density) for all the calculations. For the exchange correlation energy we take the generalized gradient approximation (GGA) and the GGA + U one.

The charge density integration over the Brillouin Zone (BZ) is performed using an uniform \(20 \times 20 \times 1\) Monkhorst and Pack grid [25] for the 1T and 2H-polytypes (\(6 \times 6 \times 1\) and \(5 \times 5 \times 1\) for the \(\sqrt{13} \times \sqrt{13}\) and \(4 \times 4\) CDW phases respectively) and a 0.01 Ry gaussian smearing. For the total energy comparison among magnetic solutions of the \(\sqrt{13} \times \sqrt{13}\) reconstruction we reduce the smearing to 0.0001 Ry increasing the BZ grid to \(12 \times 12 \times 1\). For the evaluation of exchange constants we use super-cells: we scale the BZ sampling grid to assure the same density used in the other calculations. The surface is simulated by considering a supercell with about 10 Å of vacuum along the c-axis between the periodic images. We use the theoretical in-plane lattice parameters and perform full structural optimization of the internal degrees of freedom. Phonon modes in the undistorted 1T-phase are calculated in linear response theory [22, 23] over 19 phonon wave-vector mesh in the irreducible BZ using an uniform \(20 \times 20 \times 1\) reciprocal space mesh for sampling the electronic states.

### 3. Results and discussion

#### 3.1. High-symmetry 1T-NbS₂ structure.

We start by performing geometrical optimization of the undistorted 1T-NbS₂ structure (3 atoms/cell). For completeness and to achieve a better understanding of the transition metal/chalcogen hybridization, we also calculate the theoretical GGA structural parameters and electronic structures of 1T-NbSe₂, 1T-TaS₂ and

![Figure 2. Band structures for TCh₂ compounds (T = Nb, Ta; Ch = S, Se) in the 1T-polytype. The size of the circles is proportional to the Nb²⁺ character of the eigenvalues, the percentage of the largest Nb²⁺ component at \(\Gamma\) for each system is as follows: (a) 1T-NbS₂ \{Nb²⁺(\(\Gamma\)) = 47\%\}. (b) 1T-NbSe₂ \{Nb²⁺(\(\Gamma\)) = 54\%\}. (c) 1T-TaS₂ \{Nb²⁺(\(\Gamma\)) = 46\%\}. (d) 1T-TaSe₂ \{Nb²⁺(\(\Gamma\)) = 54\%\}.](image)

Table 2. Calculated energy difference among different polytypes and CDW phases. The energy differences are in mRy/Nb. In the last two columns the theoretical equilibrium lattice constants with and without \(U\) (\(a\) and \(a_U\) respectively) are reported in Å, \(U = 2.87\) eV for all the calculations. The experimental in-plane lattice parameter for bulk 2H-NbS₂ is 3.31 Å [31]. The (*) means we have two different CDWs with the same periodicity, practically degenerate in energy. The (FM) acronym indicates the ferrimagnetic solution.

| System | \(\Delta E\) | \(\Delta E_U\) | \(a\) | \(a_U\) |
|--------|-------------|-------------|-----|-------|
| 1H     | 0.0         | 0.0         | 3.346| 3.326 |
| 1T     | +7.2        | +4.2        | 3.360| 3.357 |
| 4×4    | +5.8*       | +1.9        | 13.485| 13.428 |
| \(\sqrt{13} \times \sqrt{13}\) | +4.3        | +1.2        | 12.200| 12.123 |
| \(\sqrt{13} \times \sqrt{13}\) (FM) | +4.4        | +0.5        | 12.198| 12.126 |

Monkhorst and Pack grid [25] for the 1T and 2H-polytypes (\(6 \times 6 \times 1\) and \(5 \times 5 \times 1\) for the \(\sqrt{13} \times \sqrt{13}\) and \(4 \times 4\) CDW phases respectively) and a 0.01 Ry gaussian smearing. For the total energy comparison among magnetic solutions of the \(\sqrt{13} \times \sqrt{13}\) reconstruction we reduce the smearing to 0.0001 Ry increasing the BZ grid to \(12 \times 12 \times 1\). For the evaluation of exchange constants we use super-cells: we scale the BZ sampling grid to assure the same density used in the other calculations. The surface is simulated by considering a supercell with about 10 Å of vacuum along the c-axis between the periodic images. We use the theoretical in-plane lattice parameters and perform full structural optimization of the internal degrees of freedom. Phonon modes in the undistorted 1T-phase are calculated in linear response theory [22, 23] over 19 phonon wave-vector mesh in the irreducible BZ using an uniform \(20 \times 20 \times 1\) reciprocal space mesh for sampling the electronic states.
1T-TaSe$_2$ high symmetry phases. We obtain the lattice parameter and internal coordinates reported in table 1. As it can be seen the sulfur dichalcogenides are somewhat compressed in the basal plane with respect to Se dichalcogenides. The smaller in-plane parameter is accompanied by a smaller chalcogen height ($h_{Ch}$) and a smaller tetragonal distortion of the octahedral crystal symmetry around the transition metal ion. This is relevant as the electronic structures of all these highly symmetric polytypes are similar but with important differences that can be in part attributed to the amount of Jahn–Teller trigonal distortion of the octahedral crystal field around the transition metal and in part to the alignment of the chalcogen and transition metal levels [26, 27].

In more details, the octahedral crystal field splitting leads to triply degenerate $t_{2g}$ orbitals ($d_{x^2-y^2}$, $d_{z^2}$, $d_{xy}$) and doubly degenerate $e_g$ orbitals ($d_{3z^2-r^2}$, $d_{yz}$) at higher energy (we adopt here the same convention of [27] for the crystal axes). The trigonal distortion of the octahedron is identified by the bond angles centered at the transition metal ion and having bonds to the nearest chalcogens (see picture in table 1). In an undistorted octahedron $\alpha = \beta = 90^\circ$, while in the present cases there is a substantial deviation from the ideal values.

The crystal field for a trigonal distorted octahedron splits the $t_{2g}$ orbitals in a twofold degenerate state ($d_{x^2-y^2}$, $d_{xy}$) and a single degenerate $d_{z^2-r^2}$ state. We label this energy separation at zone center ‘apparent Jahn–Teller splitting’. In the case of 1T-NbS$_2$ and 1T-TaS$_2$, the apparent trigonal Jahn–Teller splitting at the $\Gamma$ point is positive (namely the band originating from the $d_{z^2-r^2}$ state is higher in energy with respect to the twofold degenerate one arising from the $d_{x^2-y^2}$ and $d_{xy}$ atomic orbitals) and very similar in magnitude for both systems, as it can be seen in figure 2. Surprisingly, in selenides, despite a larger distortion, the apparent Jahn–Teller splitting is almost zero or negative. This apparent contradiction can be solved by considering the hybridization between the transition metal $t_{2g}$ bands and the other occupied chalcogen bands at zone center (labeled ‘h’ in figure 2). In sulfides, this separation is larger than in NbS$_2$, mainly due to the larger energy misalignment between the sulfur 3$p$ and the Nb 4$d$ or Ta 5$d$ states. The situation is very different in selenides, where the hybridization between the Se $p$ states and the Ta or Nb $d$ states is strong (stronger in Nb than in Ta) and leads to completely counterintuitive results with respect to crystal field theory. For example, the larger octahedral distortion occurs in NbSe$_2$, but here we find an apparent negative Jahn–Teller splitting. Finally, in TaSe$_2$, the apparent Jahn–Teller splitting is almost zero as the crystal field and the hybridization
perfectly cancels out and the $t_{2g}$ bands become almost threefold degenerate at zone center. Furthermore the top of what were the chalcogen $p$-bands in sulfides becomes mixed with $d$-states in selenides (particularly evident in NbSe$_2$).

The different magnitude of the hybridization explains why in sulfides one expect $t_{2g}$ manifolds separated by the chalcogen states while in selenides the character is more entangled [13].

Finally, it is worth mentioning that as the 1T-polytype breaks the inversion symmetry, we investigate the magnitude of relativistic effects in 1T-NbS$_2$ finding them negligible, as expected given the relatively light atoms involved.

Having understood the electronic structure of the highly symmetric phase in comparison with other 1T compounds, we compare the energy of single layer 1T-NbS$_2$ with the 1H-NbS$_2$ polytype. We find that 1H is more stable by approximately 7.2 mRy/Nb (see also table 2), similarly to what happens for the NbSe$_2$ case[28–30]. This large energy difference prevents an highly symmetric 1T phase to form in experiments.

In order to inspect for possible CDW instabilities, we then calculate the phonon dispersion of single layer 1T-NbS$_2$. As shown in figure 3 we found strongly unstable phonon modes. To better identify the wavevector of the most unstable phonon frequencies in the BZ, we also perform a bi-dimensional plot of the instability.
in figure 3. At the harmonic level we find that the two most likely instabilities have wavevector compatible with a $\sqrt{3} \times \sqrt{3}$ [32] and a $4 \times 4$ CDWs.

### 3.2. Charge density wave phases

We perform geometrical optimization within the GGA approximation in $4 \times 4$ and $\sqrt{3} \times \sqrt{3}$ supercells starting from initial configurations obtained by displacing the atomic coordinates following the patterns of the most unstable phonon modes. In both cases, we find structures that are substantially more stable than the highly symmetric ones. In the case of a $4 \times 4$ supercell, we find two different reconstructions that are practically degenerate in energy (see figure 4). Both $4 \times 4$ CDW, however, seems to try to form some kind of star-of-David reconstruction, but the non-ideal periodicity hinders the complete formation. This is confirmed by the fact that $\sqrt{3} \times \sqrt{3}$ is the most stable reconstruction, with an energy gain of $\approx 2.9$ mRy/Nb with respect to the highly symmetric $1T$-$Nb_S_2$ phase, however still with an energy loss of $\approx 4.3$ mRy/Nb with respect to the highly symmetric $1H$-$Nb_S_2$ phase.

The optimized $\sqrt{3} \times \sqrt{3}$ structure is shown in figure 4 (we also report the Wyckoff positions in appendix A), and it is dynamically stable (see appendix B). The relative energy differences among the different phases considered are reported in table 2.

The non-magnetic electronic structure in the $\sqrt{3} \times \sqrt{3}$ phase is shown in figure 5 (top). It is characterized by the presence of an extremely flat band at the Fermi level having a non-negligible $d_{z^2-\sigma}$ character related to the central Nb atom in the star. The flat band is isolated from the others and is located in the middle of the gap, this is in analogy with what happens in $1T$-$TaS_2$ [4, 32–35] and in contrast with the $1T$-$NbSe_2$ case [13, 29, 30] where the flat band is entangled with chalcogen states.

In order to disentangle the effects of chemistry and distortion in determining the energy position of the flat band with respect to the chalcogen states, we calculate the non-magnetic electronic dispersions of (i) $NbS_2$ CDW structure in which we substitute the $S$ atoms with $Se$ keeping, however, the structure unchanged (labeled ‘$1T$-$NbS_2$ str.; $Se$ PP’ in figure 5), (ii) $NbS_2$ using the crystal structure of $1T$-$NbSe_2$ in the CDW phase (labeled ‘$1T$-$NbSe_2$ str.; $S$ PP’ in figure 5). These calculations should be directly compared with the case of $NbSe_2$ reported in figure 3 of [13] (left panel) where, at the GGA level, the flat band lies in the middle of Se states and is not isolated from the others. This comes mostly from a $0.25$ eV upshift of the lower occupied states at zone center.

Calculation (i) allows us to determine the effect of alignment between $Se/S$ states with $Nb$ ones. As it can be seen the effect of replacing the $S$ with a $Se$ pseudo-potential is an up-shift of the chalcogen states at zone center, in agreement with what happens in the ideal high-symmetry undistorted $1T$-$NbS_2$/$1T$-$NbSe_2$ phases (see figure 2). However this up-shift is still not large enough to mix the flat band with the other occupied bands, as it happens in the $\sqrt{3} \times \sqrt{3}$ phase of $1T$-$NbSe_2$ [13]. If, on the contrary, we use the $NbSe_2$ $\sqrt{3} \times \sqrt{3}$ structure with the $S$ pseudopotential, as in calculation (ii), we see that the results is to up-shift mostly the chalcogen states very close to the flat band. However, this is not what happens in the $\sqrt{3} \times \sqrt{3}$ phase of $1T$-$NbSe_2$ as in this system, at the GGA level, the top of the $Se$ states at $\Gamma$ are empty and are at higher energies then the flat band. It follows that the effect is not properly chemical neither structural, but it is a cooperative effect of the two. This aspect is a general feature strictly related to the chalcogen atom involved in the compound. In fact the same behavior is observable also in $TaS_2$ and $TaSe_2$ (see [4, 13, 33]).

As shown in figure 5 (top), the $Nb_{d_{z^2-\sigma}}$ band is extremely flat, with a dispersion of $\sim 0.016$ eV. This implies a small Fermi velocity, a low kinetic energy and an high peak in the density of the states at the Fermi level. It is then natural to expect electronic instabilities to occur. We then perform spin-polarized calculations stabilizing an insulating ferrimagnetic solution with

![Figure 6. Spin resolved electronic band structures for the $\sqrt{3} \times \sqrt{3}$ phase obtained in GGA (left panel) and in GGA + U approximation (right panel); solid (dashed) lines are related to majority (minority) spin states. The size of the circles is proportional to the central Nb $d_{z^2-\sigma}$ character of the eigenvalues. The percentage of the central Nb $d_{z^2-\sigma}$ component for the flat bands at $\Gamma$ are 9.5% for the majority (12% for the minority) component in the GGA approximation and 6.2% for the majority (16% for the minority) component in the GGA + U one.](image-url)
an energy loss of about 0.1 mRy/Nb with respect to the metallic non-magnetic $\sqrt{13} \times \sqrt{13}$ reconstruction (see table 2). Thus, even in the absence of an Hubbard term, GGA stabilizes a magnetic state.

The magnetic bands are reported in figure 6 (left), as we can see, in the ferrimagnetic configuration, the system results to be semiconductor with a gap of about 0.15 eV. The flat band is split in two, one is fully occupied and the second one is empty, so that the total magnetic moment is $1 \mu_B$. By referring to the left panel in figure 4, the magnetic moments are 0.21 $\mu_B$ on the red sites, 0.04 $\mu_B$ on the blue ones and negligible contributions on the others. It is worth to underline that the magnetic structure is still unstable (4.4 mRy/Nb) with respect to the 1H one.

The insurgence of magnetism induces a weak hardening of some $A_{2g}$ modes, in principle detectable as a Raman shift (see appendix B). However, given the correlated nature of the problem and the key role of the DFT + U approximation in determining total energies, as shown in 1T-NbSe$_2$ [13], we perform DFT + U calculations using the method in [36]. The $U$ parameter is computed self-consistently from first principles [36], we obtain $U = 2.87$ eV. This value is similar to those found for 1T-TaS$_2$ [4] and 1T-NbSe$_2$ [13] compounds.

We first perform structural optimization of the high-symmetry 1T-NbS$_2$ and 1H-NbS$_2$ single-layer structure within DFT + U. For the 1H-polypype, we find that the in-plane lattice parameter in DFT + U is in slightly better agreement with the one measured in the bulk than in the GGA case (see table 2), suggesting that DFT + U gives a slightly better energetic then GGA, as it happens in NbSe$_2$ [13]. As it can be seen, the energy difference between the 1H and 1T undistorted polytypes is now reduced.

We then optimize the geometry in the CDW phase with DFT + U obtaining a small contraction of the in-plane lattice constants (see table 2, the Wyckoff positions are reported in appendix A). Also the magnetic structure is slightly different from the GGA result: a stronger ferrimagnetic solution with magnetic moments of 0.41 $\mu_B$ on the red sites, 0.03 $\mu_B$ on the blue ones and negligible antiferromagnetic contributions from the other sites is stabilized (we refer to the left panel in figure 4 for color labeling). The total magnetic moment per unit cell is of $1 \mu_B$. The magnetic moment on the central atom is thus almost the double of the one found in spin-polarized GGA (while the total spin is of course still 1/2). Moreover, as shown in table 2, the CDW magnetic solution has an important energy gain with respect to the 1T-polypype and it is almost degenerate with the 1H one (0.5 mRy of energy difference).

This energy difference is slightly smaller than the one found between 1H-NbSe$_2$ highly symmetric polytype and the 1T-NbSe$_2$ charge density wave phase. This suggest that 1T-NbS$_2$ can be synthesized with a similar experimental procedure to the one used for NbSe$_2$ [11, 12].

In figure 6 we report the band structure for the magnetic solution obtained in DFT + U compared with the ones obtained in GGA. The band-gap between the flat band is now more than twice that in spin-polarized GGA ($\sim 0.41$ eV) and is not the fundamental gap as the minority spin flat bands is pushed inside the empty $d$-conduction bands. The fundamental gap is $\sim 0.35$ eV and involves transitions between $d$-orbitals of different Nb atoms.

It is important to underline that we are considering the contribution of static correlations, in this way dynamical effects can, in principle, stabilize a paramagnetic insulating state. Nevertheless, it is remarkable that even in the regime of weak correlations (GGA) we stabilize a magnetic solution. This seems to suggest that magnetism is robust in this system. However, in the case of a such flat band, the electron-electron interaction is always in the non-perturbative regime. This paves the way to possible correlated states such as spin liquids [37] or superconductivity [38].

Finally we evaluate the nearest-neighbor ($J_1$) and next-nearest-neighbor ($J_2$) exchange constants between different star of David clusters in a ferromagnetic Hubbard model described by the following Hamiltonian:

$$\hat{H} = -J_1 \sum_{\langle i,j \rangle} \hat{S}_i^z \cdot \hat{S}_j^z - J_2 \sum_{\langle\langle i,j \rangle\rangle} \hat{S}_i^z \cdot \hat{S}_j^z.$$

We adopted a super-cell approach and considered a ($2\sqrt{13} \times 3\sqrt{13}$) cell with different collinear magnetic configurations. It is important to note that we obtain similar total energies for all the spin configurations taken into account.

The calculated ferromagnetic exchange couplings are $J_1 = 9.5$ K and $J_2 = 0.4$ K, in line with the parameters describing the similar NbSe$_2$ compound [30]. From that the system results to have a ferromagnetic ground state between different stars.

4. Conclusions

In this work we investigated by first principles the possible formation of single-layer 1T-NbS$_2$ as well as its structural, electronic and dynamical properties in the high symmetry phase and in the CDW one with different degrees of correlation and allowing for magnetic solutions.

We demonstrate that the 1T undistorted ($1 \times 1$) polytype is highly unstable towards a $\sqrt{13} \times \sqrt{13}$ reconstruction. Within the GGA + U approximation, the $\sqrt{13} \times \sqrt{13}$ structural distortion and the formation of a ferrimagnetic state cooperate in stabilizing the 1T-NbS$_2$ phase in single layer form that becomes comparable in energy with that of the 1H polytype. Thus, we predict that this system can be synthesized with similar techniques to those used for single layer 1T-NbSe$_2$ [6, 11, 12].
Finally, it is interesting to underline that in this system, magnetism occurs in an ultraflat band, isolated from all the others and having a marked $d_{z^2} - r^2$ character on the central Nb atom in the star. Spin polarized calculations without any Hubbard mean field term, recover the insulating state by stabilizing magnetism (although with a fairly small gap). In this respect, sulfides are odd with 1T-NbSe$_2$ where the flat band is strongly hybridized with Se states and the Hubbard interaction is needed to disentangle it from the other bands. 1T-NbS$_2$ in the $\sqrt{13} \times \sqrt{13}$ is then a prototype system where the presence of an ultraflat band produces magnetism even at very moderate values of $U/t$.

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### Appendix A

We report the relaxed Wyckoff positions for the low temperature $\sqrt{13} \times \sqrt{13}$ CDW (non-magnetic) phase in the non magnetic solution (NM: black curves) and in the ferrimagnetic one (FM: red curves).

### Table A1.

| $C = (0, 0, 0)$ | Multiplicity | Wyckoff label | $x$ | $y$ | $z$ |
|----------------|--------------|----------------|-----|-----|-----|
| Nb             | 1            | a              | 0.00000 | 0.00000 | 0.00000 |
| Nb             | 6            | g              | 0.28854 | 0.07046 | 0.00044 |
| Nb             | 6            | g              | 0.63662 | 0.15249 | $-0.00124$ |
| S              | 6            | g              | 0.05083 | 0.17491 | 0.13591 |
| S              | 6            | g              | 0.35363 | 0.25132 | 0.15360 |
| S              | 6            | g              | 0.48561 | 0.19908 | 0.87839 |
| S              | 2            | d              | 0.33333 | 0.66667 | 0.88017 |
| S              | 6            | g              | $-0.02692$ | 0.40822 | 0.11972 |

### Table A2.

| $C = (0, 0, 0)$ | Multiplicity | Wyckoff label | $x$ | $y$ | $z$ |
|----------------|--------------|----------------|-----|-----|-----|
| Nb             | 1            | a              | 0.00000 | 0.00000 | 0.00000 |
| Nb             | 6            | g              | 0.28891 | 0.07059 | 0.00036 |
| Nb             | 6            | g              | 0.63634 | 0.15237 | $-0.00097$ |
| S              | 6            | g              | 0.05072 | 0.17451 | 0.13662 |
| S              | 6            | g              | 0.35369 | 0.25129 | 0.13419 |
| S              | 6            | g              | 0.48561 | 0.19901 | 0.87358 |
| S              | 2            | d              | 0.33333 | 0.66667 | 0.87248 |
| S              | 6            | g              | $-0.02695$ | 0.40829 | 0.12062 |

Figure B1. Phonon dispersion for the $\sqrt{13} \times \sqrt{13}$ CDW phase in the non magnetic solution (NM: black curves) and in the ferrimagnetic one (FM: red curves).
Table B1. Raman active frequencies for the $\sqrt{3}\times\sqrt{3}$ CDW phase obtained in non magnetic (NM) and Ferrimagnetic (FM) phases (in GGA approximation).

| Point group | $\omega_{NM}$ (cm$^{-1}$) | $\omega_{FM}$ (cm$^{-1}$) |
|-------------|--------------------------|--------------------------|
| $E_2$       | 63.9                     | 61.6                     |
| $A_2$       | 64.6                     | 64.6                     |
| $A_g$       | 82.1                     | 83.2                     |
| $E_2$       | 84.4                     | 88.6                     |
| $E_g$       | 93.3                     | 91.5                     |
| $A_g$       | 94.2                     | 97.9                     |
| $E_2$       | 106.0                    | 105.4                    |
| $A_g$       | 119.5                    | 120.2                    |
| $A_g$       | 121.2                    | 121.7                    |
| $A_g$       | 142.9                    | 146.3                    |
| $A_g$       | 164.0                    | 166.7                    |
| $E_2$       | 179.7                    | 180.4                    |
| $E_g$       | 211.1                    | 211.1                    |
| $E_g$       | 218.8                    | 218.8                    |
| $A_g$       | 221.3                    | 221.6                    |
| $E_2$       | 226.9                    | 227.1                    |
| $E_2$       | 236.2                    | 236.3                    |
| $A_g$       | 242.2                    | 242.4                    |
| $E_2$       | 243.7                    | 243.6                    |
| $E_2$       | 257.7                    | 258.6                    |
| $E_2$       | 261.6                    | 261.7                    |
| $A_g$       | 262.3                    | 262.7                    |
| $A_g$       | 266.8                    | 266.7                    |
| $E_2$       | 268.1                    | 268.4                    |
| $E_2$       | 276.7                    | 276.9                    |
| $E_2$       | 283.9                    | 283.6                    |
| $A_g$       | 286.0                    | 285.5                    |
| $A_g$       | 298.7                    | 298.7                    |
| $E_2$       | 303.4                    | 303.2                    |
| $E_2$       | 307.5                    | 306.9                    |
| $A_g$       | 346.5                    | 346.5                    |
| $E_2$       | 349.9                    | 351.7                    |
| $E_2$       | 357.5                    | 357.9                    |
| $A_g$       | 358.9                    | 359.1                    |
| $A_g$       | 366.7                    | 371.0                    |
| $E_2$       | 378.4                    | 379.0                    |
| $A_g$       | 392.8                    | 394.1                    |
| $E_2$       | 393.0                    | 395.1                    |

is dynamically stable. The Raman active modes are reported in table B1. The insurgence of magnetism causes a weak hardening of $A_2g$ frequencies at around 90 and 366 cm$^{-1}$ (we register shift of around 4 ÷ 5 cm$^{-1}$, see table B1).

References

[1] Wilson J A, Di Salvo F J and Mahajan S 1975 Adv. Phys. 24 117
[2] Fazekas P and Tosatti E 1980 Physica B + C 99 183–7
[3] Fazekas P and Tosatti E 1979 Phil. Mag. B 39 229
[4] Darancet P, Mills A J and Marianetti C A 2014 Phys. Rev. B 90 045134
[5] Ngankeu A S et al 2017 Phys. Rev. B 96 195147
[6] Carmalt C J, Manning T D, Parkein I P, Peters E S and Hector A L 2004 J. Mater. Chem. 14 290–1
[7] Novoselov K S, Jiang D, Schedin F, Booth T, Khotkevich V V, Morozov S and Geim A K 2005 Proc. Natl Acad. Sci. 102 10451
[8] Coleman J N et al 2011 Science 331 568
[9] Wang Y et al 2017 Nature 550 487
[10] Eda G, Yamaguchi H, Voiry D, Fujita T, Chen M and Chhowalla M 2011 Nano Lett. 11 5111
[11] Nakata Y, Sugawara K, Shimizu R, Okada Y, Han P, Hitosugi T, Ueno K, Sato T and Takahashi T 2016 NPG Asia Mater. 8 e321
[12] Bischoff J, Auwärter W, Barth J V, Schifferin A, Fuhrer M and Weber B 2017 Chem. Mater. 29 9907–14
[13] Calandra M 2018 Phys. Rev. Lett. 121 026401
[14] Xi X, Zhao L, Wang Z, Berger H, Forró L, Shan J and Mak K F 2015 Nat. Nanotechnol. 10 765
[15] Ugeda M et al 2016 Nat. Phys. 12 92
[16] Calandra M, Mazin I and Mauri F 2009 Phys. Rev. B 80 241108
[17] Zhuang H L and Hennig R G 2013 J. Phys. Chem. C 117 20440–5
[18] Rasmussen F A and Thygesen K S 2015 J. Phys. Chem. C 119 13169–83
[19] Leroux M, Tacon M L, Calandra M, Cario L, Mészáros M, Diener P, Borriksen E, Bosak A and Rodière P 2012 Phys. Rev. B 86 155125
[20] Lin H, Huang W, Zhao K, Lian C, Duan W, Chen X and Ji S H 2018 Nano Res. 11 4722
[21] Stan R M, Mahatha S K, Bianchi M, Sanders C E, Caciol D, Hofmann P and Jill A M 2019 Phys. Rev. Mater. 3 044003
[22] Giannozzi P et al 2009 J. Phys.: Condens. Matter 21 395502
[23] Giannozzi P et al 2017 J. Phys.: Condens. Matter 29 465901
[24] Vanderbilt D 1990 Phys. Rev. B 41 7892–5
[25] Monkhorst H and Pack J D 1976 Phys. Rev. B 13 5188–92
[26] Whangbo M and Canadell E 1992 J. Am. Chem. Soc. 114 9587
[27] Mattheiss L F 1973 Phys. Rev. B 8 3719
[28] Calandra M and Mauri F 2005 Phys. Rev. Lett. 95 237200
[29] Kaniil E, Berges J, Schnuff G, Rinner M, Scher M, Sangiovanni G and Wehling T O 2018 J. Phys.: Condens. Matter 30 325601
[30] Pasquier D and Yazeyev O V 2018 Phys. Rev. B 98 045114
[31] Jellinek F, Brauer G and Müller H 1960 Nature 185 376
[32] Ge Y and Liu A Y 2010 Phys. Rev. B 82 155133
[33] Miller D C, Mahanat S D and Duxbury P M 2018 Phys. Rev. B 97 045133
[34] Albertini O R, Zhao R, McCann R L, Feng S, Terrones M, Freericks J K, Robinson J A and Liu A Y 2016 Phys. Rev. B 93 214109
[35] Liu A Y 2009 Phys. Rev. B 79 220515
[36] Cococcioni M and de Gironcoli S 2005 Phys. Rev. B 71 035105
[37] Law K T and Lee P A 2017 Proc. Natl Acad. Sci. 114 6966–7000
[38] Cao Y, Fatemi V, Fang S, Watanabe K, Taniguchi T, Kasirae E and Jarillo-Herrero P 2018 Nature 556 43–50

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Appendix B

We compute the phonon dispersion for the $\sqrt{3}\times\sqrt{3}$ CDW phase in GGA approximation for the non magnetic and the ferrimagnetic solutions. We calculate the dynamical matrix at zone center and then Fourier interpolate the dynamical matrices on the full Brillouin zone. Results are reported in figure B1. All frequencies are positive revealing the CDW phase of both structures obtained in GGA and GGA + U belongs to the P3 space group (group number 147), and the Wyckoff positions are reported in tables A1 and A2 respectively.