# Strong spin-orbit splitting and magnetism of point defect states in monolayer WS<sub>2</sub>

Wun-Fan Li,\* Changming Fang, and Marijn A. van Huis
 Soft Condensed Matter, Debye Institute for Nanomaterials Science,
 Utrecht University, Princetonplein 5, 3584CC Utrecht, The Netherlands
 (Received 9 June 2016; revised manuscript received 29 August 2016; published 16 November 2016)

The spin-orbit coupling (SOC) effect has been known to be profound in monolayer pristine transition metal dichalcogenides (TMDs). Here we show that point defects, which are omnipresent in the TMD membranes, exhibit even stronger SOC effects and change the physics of the host materials drastically. In this article we chose the representative monolayer WS<sub>2</sub> slabs from the TMD family together with seven typical types of point defects including monovacancies, interstitials, and antisites. We calculated the formation energies of these defects, and studied the effect of spin-orbit coupling (SOC) on the corresponding defect states. We found that the S monovacancy (V<sub>S</sub>) and S interstitial (adatom) have the lowest formation energies. In the case of V<sub>S</sub> and both of the W<sub>S</sub> and W<sub>S2</sub> antisites, the defect states exhibit strong splitting up to 296 meV when SOC is considered. Depending on the relative position of the defect state with respect to the conduction band minimum (CBM), the hybrid functional HSE will either increase the splitting by up to 60 meV (far from CBM), or decrease the splitting by up to 57 meV (close to CBM). Furthermore, we found that both the W<sub>S</sub> and W<sub>S2</sub> antisites possess a magnetic moment of 2  $\mu_B$  localized at the antisite W atom and the neighboring W atoms. The dependence of SOC on the orientation of the magnetic moment for the W<sub>S</sub> and W<sub>S2</sub> antisites is discussed. All these findings provide insights in the defect behavior under SOC and point to possibilities for spintronics applications for TMDs.

DOI: 10.1103/PhysRevB.94.195425

# I. INTRODUCTION

The transition metal dichalcogenides (TMDs) are a member of the layered two-dimensional (2D) van der Waals (vdW) materials, in which the atoms are bound by intralayer chemical bonding and interlayer vdW bonding. Among many other TMDs, the molybdenum dichalcogenides and tungsten dichalcogenides (MX<sub>2</sub>, M = Mo or W, and X = S, Se, or Te) are the group 6 branch of the whole TMD family and have attracted much scientific attention. Theoretically, the most stable structure of MX<sub>2</sub> consists of one layer of transition metal atoms sandwiched by two layers of chalcogen atoms with a prismatic coordination, forming the so-called 1H form [1]. Due to the weak interlayer vdW interaction, TMDs can be exfoliated from bulk into the few-layer or monolayer (ML) forms. When reducing the number of lavers from bulk to ML, the band gap of TMDs evolves from an indirect band gap to a direct band gap with an increased gap size due to quantum confinement [2,3]. The layer-dependent tunability of the electronic structure together with other distinct physical properties of ML TMDs make them promising candidates of applications in fields like electronics, optoelectronics, spintronics and valleytronics, sensing, and catalysis [4–7].

There are two effects governing the band structure (BS) of  $MX_2$ , namely crystal field (CF) splitting and spin-orbit (SO) splitting ( $\Delta_{SO}$ ). These two effects strongly affect the electronic properties of  $MX_2$  and influence in particular the *d* bands of the transition metal.

According to crystal field theory, the five formerly degenerate d bands of the transition metal will split in energy if the transition metal is bonded to other ligands (the chalcogen atoms in our case), and the pattern of the energy splitting is dependent on the metal-ligand coordination geometries. For

The spin-orbit coupling (SOC) effect has been discovered for bulk  $MX_2$  materials in the last few decades [11,12], and for ML MX<sub>2</sub> in recent years [13-16]. In bulk MX<sub>2</sub>, the system possesses both the space inversion symmetry  $[E_{\downarrow}(\vec{k}) =$  $E_{\downarrow}(-\vec{k})$ ] and time inversion symmetry  $[E_{\downarrow}(\vec{k}) = E_{\uparrow}(-\vec{k})]$ . The net result is spin degeneracy in reciprocal space when no external magnetic field is present:  $E_{\perp}(\vec{k}) = E_{\uparrow}(\vec{k})$ . However, in the case of ML MX<sub>2</sub>, because of the lack of space inversion symmetry, the spin states are expected to split under SOC. Especially, the band splitting can be as large as 463 meV for the valence band maximum (VBM) of ML WSe<sub>2</sub> at the Kpoint in the first Brillouin zone [16]. For pristine ML  $WS_2$ , the band splitting is also large at 433 meV [16]. Based on symmetry arguments [13,16], for ML MX<sub>2</sub> only the orbitals with magnetic quantum number  $m_l \neq 0$  will participate SO splitting. Furthermore, because the X atoms are rather light, their p orbitals are not affected by the SOC effect. Lastly, as indicated in the BSs of ML WS2 in the SM [10] (Fig. S4), the VBM and conduction band minimum (CBM) are dominated by the  $d_{z^2}$  ( $m_l = 0$ ),  $d_{xy}$  ( $m_l = -2$ ), and  $d_{x^2-y^2}$  ( $m_l = 2$ ) orbitals. As a result, only the  $d_{xy}$  and  $d_{x^2-y^2}$  orbitals will have the SO splitting.

ML MX<sub>2</sub> in the 1H phase, the transition metal is surrounded by six chalcogen atoms in a trigonal prismatic coordination (Fig. 1). Consequently, the *d* bands split according to their orientations—the more they are along the direction of the M-X bond, the higher in energy they will be due to the electron-electron repulsion with the X orbitals. As shown in Fig. 1, the  $d_{z^2}$  orbital is the lowest in energy, and the  $d_{x^2-y^2}$ and  $d_{xy}$  orbitals are higher in energy. The  $d_{xz}$  and  $d_{yz}$  orbitals are the highest in energy [8,9]. The Supplemental Material (SM) [10] shows the decomposed band structures of both bulk and ML WS<sub>2</sub> which illustrate the CF splitting of the *d* bands (Figs. S3 and S4). The order of increasing energy is  $d_{z^2} < d_{x^2-y^2} = d_{xy} < d_{xz} = d_{yz}$  for both bulk and ML WS<sub>2</sub>, as expected.

<sup>\*</sup>Corresponding author: w.f.li@uu.nl



FIG. 1. Schematic of the energy splitting of the transition metal d bands under the crystal field. The coordination is trigonal prismatic.

Besides the novel physical properties of pristine TMDs, atomic point defects are omnipresent in the materials. Furthermore, adatom adsorption and doping on ML MX<sub>2</sub> is especially achievable by virtue of their 2D surface nature. Both the naturally occurring and chemically or physically introduced point defects in MX<sub>2</sub> will extensively modulate the physical properties such as charge transport, magnetism, optical absorption, and absorbability [17–33], thus control the applicability of the material. The crucial role of point defects has triggered many studies to investigate their behavior in ML MX<sub>2</sub>. Liu et al. identified the atomic defects and visualized their migrations on ML MoS<sub>2</sub> [34]. Komsa et al. found that electron beam irradiation generates sulfur monovacancies  $(V_S)$ and also cause these defects to migrate and aggregate [35,36]. Zhou et al. carried out a joint experiment and theory study and investigated several types of defects and their influence on the electronic structure of ML MoS<sub>2</sub> synthesized by chemical vapor deposition (CVD) [37]. Among the single vacancy, vacancy complexes, and antisite complexes, they found that the  $V_S$  is the predominant point defect. First-principles calculations confirmed that V<sub>S</sub> has the lowest formation energy among all the defect kinds. Hong et al. did a systematic study which shows the route dependence of predominant point defect types [38]. In ML MoS<sub>2</sub>, synthesized by CVD and mechanical exfoliation (ME), V<sub>S</sub> is the only dominating point defect, whereas in ML MoS<sub>2</sub> fabricated by physical vapor deposition (PVD), the antisites Mo<sub>S2</sub> and Mo<sub>S</sub> are the dominant point defects. They also found that the Mos antisite possesses a local magnetic moment around the Mo defect site. From the theoretical perspective, several exhaustive works have been done to study the point defects systematically by virtue of density functional theory (DFT) [39–41]. Their results predict that in ML MX<sub>2</sub>, the  $V_S$  and sulfur interstitial  $S_i$  have the lowest formation energy.

Despite the significance of SOC and point defects for ML MX<sub>2</sub> systems, to the best of our knowledge thus far no study has been conducted on the SOC effect on the electronic structure of defective ML MX<sub>2</sub>. Therefore, here we investigate how the SOC effect will change the band structure (BS) of ML MX<sub>2</sub> when different types of point defects are present. We chose systematically three categories of point defects: monovacancies ( $V_S$  and  $V_W$ ), interstitials ( $S_i$  and  $W_i$ ), and antisites (S<sub>W</sub>, W<sub>S</sub>, and W<sub>S2</sub>). For conciseness, the ML WS<sub>2</sub> slabs containing these defects are abbreviated as  $V_{S}$ -WS<sub>2</sub>,  $V_{W}$ -WS<sub>2</sub>,  $S_{i}$ -WS<sub>2</sub>,  $W_{i}$ -WS<sub>2</sub>,  $S_{W}$ -WS<sub>2</sub>,  $W_{S}$ -WS<sub>2</sub>, and  $W_{S2}$ -WS<sub>2</sub>, respectively. The relaxed structure of each point defect is shown in Fig. 2. We chose  $WS_2$  as a representative of the MX<sub>2</sub> family as the physical and chemical properties of all the MX<sub>2</sub> members are very similar, and thus the results of  $WS_2$  are expected to be applicable to other  $MX_2$  systems.

Defect-induced magnetic moments on 2D materials are important for spintronics applications as exemplified by graphene [42,43], phosphorene [44], and ML germanane [45]. The orientation of the magnetic moments can be tuned as a degree of freedom by gating, doping, or functionalization, making the host 2D materials candidates for high-Curietemperature materials with diluted magnetism strongly desired for high magnetic information storage density [43]. As such, we were motivated to also study the magnetic moments found in  $W_S$ - $WS_2$  and  $W_{S2}$ - $WS_2$  in the context of spintronics applications of dilute magnetic moments.

After describing the computational settings, we will first discuss the formation energies of the selected defect species. We then chose  $V_S$ ,  $S_i$ ,  $W_S$ , and  $W_{S2}$  for further investigation of the SO defect state splitting. We found that SOC causes strong defect state splitting in the cases of  $V_S$  and  $W_{S2}$ , with the magnitude of the band splitting up to 194 meV for  $V_S$  and 167 meV for  $W_{S2}$ , respectively. In addition, we also found that both  $W_S$  and  $W_{S2}$  antisites possess a magnetic moment around the antisite W atom, which is contrary to the previous study of  $MoS_2$  [38]. The findings in this work provide a deeper insight in the point defect physics of  $MX_2$  and will help developing potential applications of  $MX_2$  in electronics and spintronics.



FIG. 2. The relaxed structures of all the defective ML WS<sub>2</sub> supercells. The vacancies are denoted by light blue circles. The defect sulfur atoms are marked in red, and defect tungsten atoms in blue. The arrows indicate the directions and magnitudes of the relaxations.

## **II. COMPUTATIONAL DETAILS**

All calculations were performed using the DFT code VASP [46–48] within the projector-augmented wave (PAW) framework [49]. The exchange and correlation energies were described using the generalized gradient approximation (GGA) formulated by Perdew, Burke, and Ernzerhof (PBE) [50,51]. We mention here that studying magnetism and spin splitting in combination with SOC should ideally be treated on the basis of current density functional theory (CDFT) [52,53], where appropriate functionals are presently being developed [54,55]. The VASP code that was used in the present work treats the problem an approximate way, by incorporating relativistic effects by a scalar relativistic Hamiltonian with SOC in a perturbation treatment [56,57]. The GGA-PBE functional has been widely used for spin-splitting calculations, and it was shown that the magnitude of spin splitting in bulk WS<sub>2</sub> predicted by using the GGA-PBE functional matched perfectly with the result from experiment [58]. In addition, concerning the calculation of magnetic anisotropy energy (MAE), the results from GGA-PBE agreed well with the values calculated using the local density approximation (LDA) and with experimental values [57].

The cut-off energy of the wave functions and the augmentation functions were 400 and 550 eV, respectively. The van der Waals correction with the optB88-vdW density functional [59] was used as at the beginning of this study the bulk  $WS_2$  was also included [60]. The supercell size of the ML  $WS_2$  was  $6 \times 6$  in the x-y plane, and the vacuum along the z direction was larger than 16 Å. These dimensions of the supercell were sufficiently large to avoid the artificial defectdefect interaction. A  $\Gamma$ -centered 2  $\times$  2  $\times$  1 k mesh was used. The thresholds of energy convergence and force convergence were  $10^{-4}$  eV and  $10^{-2}$  eV/Å, respectively. We examined the SOC effect and found that it does not affect the structure but only influences the electronic properties of WS<sub>2</sub>, therefore we only included SOC after geometry relaxation to obtain the band structure (BS) and DOS for the systems. We first performed the geometry relaxation and total energy calculation with only vdW correction included (without SOC). Then we turn on SOC, and exclude vdW correction for calculating the electronic properties (BS and DOS) of the relaxed geometry. Spin-polarized (SP) calculations were performed for every point defect species, and only the W<sub>S</sub> and W<sub>S2</sub> antisites were found to be magnetic due to their unpaired electrons. The magnetism of W<sub>S</sub>-WS<sub>2</sub> and W<sub>S2</sub>-WS<sub>2</sub> was further investigated by noncollinear calculations.

The initial geometry of each point defect configuration was chosen based on previous theoretical studies [40,41]. The stringent setting described above guarantees a good convergence of defect formation energy within 0.01 eV.

In addition to standard DFT calculations, we also performed the more advanced hybrid functional (HSE06) [61] calculations for the defective ML WS<sub>2</sub> which shows defect state splitting under SOC (the V<sub>S</sub>-WS<sub>2</sub>, W<sub>S</sub>-WS<sub>2</sub>, and W<sub>S2</sub>-WS<sub>2</sub>). The goal of these HSE+SOC calculations is to investigate how HSE will affect the defect state splitting. The HSE calculations were performed on the DFT-relaxed geometries and we found that HSE relaxation gave almost identical geometries compared to traditional DFT. We set the fraction of Hartree-Fock exchange functional to 0.168 by fitting the calculated band gap of ML WS<sub>2</sub> to the experimental value. This fraction gives us a band gap of 2.04 eV, which is very close to the experimental value of 2.05 eV [62]. In the HSE+SOC calculations only the  $\Gamma$  point was included as we did a test for V<sub>S</sub>-WS<sub>2</sub> and W<sub>S</sub>-WS<sub>2</sub> and found that a 2 × 2 × 2 *k* mesh only improves the band gap for 7 meV for V<sub>S</sub>-WS<sub>2</sub>, and for 13 meV for W<sub>S</sub>-WS<sub>2</sub>. Therefore, we believe that  $\Gamma$  is sufficient in our case. Our SO splitting of the top valence bands of perfect ML WS<sub>2</sub> calculated by DFT is 430 meV, which is perfectly matching the previous DFT-PBE result of 433 meV [16]. The HSE increases this splitting considerably to 517 meV.

# **III. RESULTS AND DISCUSSION**

#### A. Defect formation energy

The formation energy  $E_f$  of a neutral defect is defined as [63]

$$E_f = E_{\text{defect}} - E_{\text{perfect}} + \sum_i n_i \mu_i.$$
(1)

In Eq. (1),  $E_{defect}$  is the total energy of the defective system,  $E_{perfect}$  is the total energy of the perfect system,  $n_i$  is the number of atoms being added (plus) or removed (minus) from the perfect system, and  $\mu_i$  is the chemical potential of the added or removed atom. The added/removed atom is imagined to be taken from/put to an atomic reservoir, and the chemical potentials  $\mu_i$  are needed to reflect the chemical environment surrounding the system.  $\mu_i$ 's are not fixed, but they are variables with the following boundaries [39–41,64]:

$$E_{\rm WS_2} - 2E_{\rm S} \leqslant \mu_{\rm W} \leqslant E_{\rm W},\tag{2a}$$

$$\frac{1}{2}(E_{\rm WS_2} - E_{\rm W}) \leqslant \mu_{\rm S} \leqslant E_{\rm S}.$$
(2b)

The calculated defect formation energies are listed in Table I dependent on W-rich or S-rich chemical potentials.

The next step is to choose relevant defect types for further study of the effect of SOC on electronic properties of the defective ML WS<sub>2</sub> slabs. Table I provides a simple criterion in terms of defect formation energy:  $V_S$  and  $S_i$  possess the lowest formation energies in both the W-rich and S-rich conditions, thus it is sensible to select them for more detailed study. Although the W<sub>S</sub> and W<sub>S2</sub> antisites have a higher formation energy, it has been reported that the Mo<sub>S</sub> and Mo<sub>S2</sub> antisites are the predominant point defects in MoS<sub>2</sub> synthesized by

TABLE I. Formation energies (in eV) of the defects selected in this study

	W-rich	S-rich
$\overline{V_s}$	1.689	2.897
V <sub>w</sub>	6.345	3.928
Si	2.419	1.211
Wi	5.317	7.733
Sw	8.219	4.594
Ws	5.380	9.005
W <sub>S2</sub>	6.838	11.671



FIG. 3. The band structures calculated with or without SOC for the selected  $WS_2$  slabs. NSP stands for non-spin-polarized non-SOC calculations, and spin-up and spin-down stand for the spin-polarized calculations, respectively. Here the Fermi level is marked in red. The defect state splitting can be clearly seen in the case of  $V_S$  and  $WS_2$ . However, the splitting is suppressed for  $S_i$ .

physical vapor deposition (PVD). Therefore, the  $W_S$  and  $W_{S2}$  antisites are also included in the present study [38].

### B. Defect state splitings under SOC

As seen in Ref. [65] and Fig. S4 in the SM [10], the valence bands of MX<sub>2</sub> are composed of the  $p_x$  and  $p_y$  orbitals of the X atoms (here S atoms), and the  $d_{xy}$ ,  $d_{x^2-y^2}$ , and  $d_{z^2}$  orbitals of the M atoms (here W atoms). The  $d_{xz}$ ,  $d_{yz}$  orbitals are far from the band gap region. Furthermore, Fig. 4 indicates that the top valence bands and the bottom conduction bands consist mainly of the *d* orbitals of W atoms. The only *p* orbital present is the  $p_z$  orbital from the S atoms, and it does not split under SOC.

The calculated BSs with and without SOC are shown in Fig. 3. We can see from Figs. 3 and 4 that irrespective of the type of point defects, the VBM of  $WS_2$  always splits into two bands under SOC.

# i. Vs

As discussed in the Introduction, only the W  $d_{xy}$  and  $d_{x^2-y^2}$  orbitals will undergo SO splitting. This is the case for V<sub>S</sub>. The defect states are composed of the the linear combinations of W  $d_{xy}$  and  $d_{x^2-y^2}$  orbitals, which formerly degenerate are now

split into two bands. The magnitude of the SO splitting for  $V_S$  is 194 meV. The HSE+SOC calculation gave a SO splitting of 252 meV, which is 58 meV larger than the DFT+SOC value. This substantial energy difference shows the necessity of hybrid functionals in calculating the SO splitting of the defect states.

ii. S<sub>i</sub>

In the case of  $S_i$ , the only defect state is composed of the  $p_x$  and  $p_y$  orbitals of the interstitial S atom, which do not split under SOC. This defect state is hidden in the top valence bands.

#### iii. W<sub>S</sub>

For W<sub>S</sub>, the defect states are also composed of W  $d_{xy}$  and  $d_{x^2-y^2}$ , but they do not split when SOC is included in the calculations. Further eigenstate analysis shows that the reason for the defect states to be kept degenerate is that the spin projections of these states in the SOC BS are all on the  $m_x$ - $m_y$  plane ( $m_x, m_y$ , and  $m_z$  are the magnetization axes), in contrast to the defect states of the other three defect kinds where the spin projections are either mostly on or along the  $m_z$  axis (in the case of W<sub>S2</sub>,  $+m_z$  for spin-up and  $-m_z$  for spin-down). As a result, the spin states are not split even when SOC



(d)  $W_S$ 

(e)  $W_{S2}$ 



FIG. 4. The energy level diagram of the WS<sub>2</sub> systems at the  $\Gamma$  point. The valence bands are colored in red, defect states in green, and conduction bands in blue. The Fermi level  $E_F$  is marked in cyan. The electrons which contribute to magnetism for W<sub>S</sub> and W<sub>S2</sub> antisites are labeled in light green. The major orbital components of each band are indicated, where the orbitals in bold are the most predominant ones. The dotted lines show the SO splittings of the energy bands. The magnitude of the SO splitting ( $\Delta$ ) is also shown in magenta, the values for  $\Delta$  in parentheses were calculated by HSE+SOC.

is present. We performed a second calculation in which the magnetization was constrained along the  $m_z$  axis and thus the defect states indeed split. This allows us to examine the effect of the orientation of magnetization on the defect state splitting. We also found that the  $m_z$ -constrained magnetic configuration is 38.9 meV higher in energy (for HSE, the value is 58.4 meV) than the  $m_x$ - $m_y$ -relaxed magnetic ground state. This finding suggests that the W<sub>S</sub>-WS<sub>2</sub> is a magnetically anisotropic material and that the easy axis lies on the  $m_x$ - $m_y$  plane.

In Figs. 3 and 4 we show the BS and the band energies at  $\Gamma$  of the  $m_z$ -constrained W<sub>S</sub>-WS<sub>2</sub>. There are six defect states for  $W_S$ - $WS_2$  as shown in Fig. 4(d). Three of these states are spin-up, and the other three are spin-down. For each spin species, the two degenerate states with a lower energy are composed of  $d_{xy}$  and  $d_{x^2-y^2}$  of the antisite W atom, and the state higher in energy originates from the  $d_{z^2}$  orbital. It is worth mentioning that the spin-up  $d_{xy}$  and  $d_{x^2-y^2}$  orbitals are occupied by two unpaired electrons which are the source of the magnetic moment of W<sub>S</sub>-WS<sub>2</sub> as will be discussed in the next section. Under SOC, the  $d_{xy}$  and  $d_{x^2-y^2}$  orbitals split into two bands and each of these bands is a linear combination of  $d_{xy}$ and  $d_{x^-y^2}$ . For spin-up, this splitting is 296 meV, which is the highest  $\Delta_{SO}$  among all the WS<sub>2</sub> defects studied in this paper. For spin-down, the splitting is 87 meV. The smaller  $\Delta_{SO}$  for spin-down may be related to the fact that the spin-down defect states are much higher in energy than the spin-up states, thus they are closer to the CBM which are the  $d_{7^2}$  orbitals that do not exhibit SO splitting. The consequence is that the spin-down defect states are hybridized with the  $d_{z^2}$  conduction bands and thus their  $\Delta_{SO}$  is reduced. This argument is supported by the wave function analysis, which shows that both the  $d_{xy}$  and  $d_{x^2-y^2}$  orbitals approximately have a  $\frac{1}{3} d_{z^2}$  character.

The  $\Delta_{SO}$  from HSE+SOC are 356 and 62 meV for spin-up and spin-down, respectively. With HSE, the SO splitting of the spin-up defect states increases significantly (60 meV) similar to the case of V<sub>S</sub>-WS<sub>2</sub>. However, for the spin-down defect states, with HSE the SO splitting decreases by 25 meV. The reason for the decreased  $\Delta_{SO}$  for spin-down defect states is that HSE pushes these states further into the conduction band region, thereby enhancing the mixing with the  $d_{z^2}$  orbitals.

# iv. $W_{S2}$

W<sub>S2</sub> is the most complicated case among the chosen defects. It involves ten defect states—five are spin-up and five are spin-down. As indicated in Fig. 4(e), without SOC, the five defect states for each spin type can be categorized into three groups: two groups of doubly degenerate states which are lower in energy, and a single  $d_{z^2}$  orbital higher in energy. The mixing of the conduction  $d_{z^2}$  band with the spin-down  $d_{xy}$  and  $d_{x^2-y^2}$  defect bands is even stronger in the case of W<sub>S2</sub>-WS<sub>2</sub> as the spin-down defect  $d_{z^2}$  state is already in the conduction band region. The two sets of doubly degenerate states are composed of the linear combinations of the  $d_{xy}$  and  $d_{x^2-y^2}$  orbitals of the antisite W atom, and will split into four states if SOC is present. Thus, for W<sub>S2</sub>-WS<sub>2</sub>, there are four sets of SO splittings. The  $\Delta_{SO}$  of each split set is 121, 105, 167, and 138 meV, respectively, with ascending energy.

In contrast to DFT, HSE calculation for  $W_{S2}$ -WS<sub>2</sub> relaxed the magnetization onto the  $m_x$ - $m_y$  plane. Therefore, we again constrained the magnetization along the  $m_z$  axis. The constrained configuration is less stable than the relaxed one by 23.5 meV. For the magnetically constrained W<sub>S2</sub>-WS<sub>2</sub>, HSE again enhances the splittings which are not close to CBM [the first three splittings in Fig. 4(e)]. The increments are 46, 38, and 33 meV, respectively. In contrast, for the fourth splitting HSE decreases  $\Delta_{SO}$  by 57 meV. One noteworthy feature is that the spin-up splittings are always larger than the spin-down splittings.

### C. Magnetic moments of the W<sub>S</sub> and W<sub>S2</sub> antisites

We found that both W<sub>S</sub> and W<sub>S2</sub> defects possess a magnetic moment of 2  $\mu_B$ . This is different from the result of Ref. [38], which indicated that for MoS<sub>2</sub>, only Mo<sub>S</sub>-MoS<sub>2</sub> has a magnetic moment but not Mos2-MoS2. These magnetic moments are generated by the unpaired spin-up electrons residing on the  $d_{xy}$ and  $d_{x^2-y^2}$  defect states, as indicated by Figs. 4(d) and 4(e). These states split under SOC. We defined the spin density as the difference between the spin-up charge density and the spin-down charge density  $\rho = \rho_{\uparrow} - \rho_{\downarrow}$  to visualize the magnetic moment distribution around the defect site. The resulting spin density plots are presented for both antisite defects in Fig. 5. At first glance, the magnetic moment seems to be fully localized on the antisite W atom, however for both  $W_S$  and  $W_{S2}$ , the *d* orbitals of the neighboring W atoms contribute to the magnetic moment as well, and to a lesser extent also the next-nearest-neighboring (NNN) W atoms are involved. For W<sub>S2</sub>, the magnetic moment spreads to both the nearest-neighboring (NN) and NNN W atoms.

We compared the ratio between the magnetic moment at the defect W atom and the total magnetic moment ( $\mu_r = \frac{\mu(W_{def})}{\mu(all)}$ ) to give a semiquantitative description of the distribution of the magnetic moment. We used the VASP default atomic radii for W (1.455 Å) and S (1.164 Å) to perform the spherical integration of the spin density. We calculated  $\mu_r$  using DFT (spin polarized), DFT+SOC, and HSE+SOC methods. For W<sub>S</sub>,  $\mu_r$ (DFT) = 88.4%,  $\mu_r$ (DFT+SOC) = 88.0%, and  $\mu_r$ (HSE+SOC) = 98%, respectively. For W<sub>S2</sub>, the corresponding values were lower at 53.1%, 53.5%, and 66.6%, respectively. In addition, we also found that the magnetic moment distribution shown in Fig. 5 has a triangular shape with a side length of around 6.4 Å in both cases. Therefore, these two antisite defects could also be named magnetic "superatoms" [38].



FIG. 5. Spin density plots of (a)  $W_S$  and (b)  $W_{S2}$  antisites calculated by DFT. The spin-up charge density is marked in red and the spin-down density in green. The isosurface level is 0.002 *e*/Å<sub>3</sub>.



FIG. 6. TDOS plots for both the non-spin-polarized (NSP) and spin-polarized (SP)  $W_S$  and  $W_{S2}$  antisites. The vertical blue solid lines indicate the Fermi level. The colored dotted lines map the NSP  $\rightarrow$  SP splitting of the defect bands.

Therefore, one can conclude that, first, for W<sub>S</sub> the magnetic moment is almost solely localized on the defect W atom, yet for W<sub>S2</sub> the magnetic moment is centered at the defect W atom, but half of it spreads to the NN and NNN W atoms. Second, with the HSE hybrid functional, the magnetic moment is more localized on the defect atom, yielding a higher  $\mu_r$ .

In order to trace back the origin of these magnetic moments, we compared the total energy and the density of states (DOS) of both the non-spin-polarized (NSP) and spin-polarized (SP) solutions of W<sub>S</sub>-WS<sub>2</sub> and W<sub>S2</sub>-WS<sub>2</sub>. It was found that the NSP solutions are significantly higher in energy than the SP counterparts. The energy difference E(SP) - E(NSP) is 402 meV for  $W_S$ -WS<sub>2</sub> and 151 meV for  $W_{S2}$ -WS<sub>2</sub>. Therefore, both antisite configurations are indeed spin polarized and are magnetic. The DOS plots of both the NSP and SP solutions for  $W_{S}$ - $WS_{2}$  and  $W_{S2}$ - $WS_{2}$  in Fig. 6 show clearly the magnetism. By combining Fig. 6, Fig. 4, and the projected DOSs (PDOSs) (Fig. S2 in the SM [10]), we performed a thorough eigencharacter analysis of the defect states, revealing that these states are composed of the d orbitals of the antisite W atom which are numbered for each antisite in Fig. 6. For  $W_{S}$ -WS<sub>2</sub>, group 1 is composed of the  $d_{xy}$  and  $d_{x^2-y^2}$  orbitals and group 2 is characterized by the  $d_{z^2}$  orbital. For  $W_{S2}$ -WS<sub>2</sub> there are three groups of defect states. Groups 1 and 2 are both composed of the  $d_{xy}$  and  $d_{x^2-y^2}$  orbitals. However, they are now mixed with the  $d_{7^2}$  orbital to different extents. Group 2 is more heavily mixed with the  $d_{r^2}$  orbital than group 1. Group 3 is simply the  $d_{z^2}$  orbital. Furthermore, for both antisite defects, only the spin-up part of peak 1 is under the Fermi level and is occupied by two electrons from the  $d_{xy}$  and  $d_{x^-y^2}$  orbitals of the antisite W atom. Therefore the magnetism and its origin are confirmed.

## **IV. CONCLUSION**

In this study we calculated the formation energies of seven different configurations of point defects including monovacancies, interstitials, and antisites. We found that among the point defects, V<sub>S</sub> and S<sub>i</sub> possess the lowest formation energies;  $E_f(V_S) = 1.689$  eV in a W-rich chemical environment, and  $E_f(S_i) = 1.211$  eV under a S-rich chemical environment. We selected the V<sub>S</sub>, S<sub>i</sub>, W<sub>S</sub>, and W<sub>S2</sub> defects to investigate the SOC band splitting of the defect states. We have shown that the SO splitting depends on both the orbital constitution and the orientation of magnetization of the defect states. The states having the  $d_{xy}$  and  $d_{x^2-y^2}$  character will undergo significant SO splitting when the magnetization is oriented along the  $m_z$  magnetization axis. The as-generated SO splittings are 194 meV for V<sub>S</sub>, 296 and 87 meV for W<sub>S</sub>, and 121, 105, 171, and 138 meV for W<sub>S2</sub>. The hybrid functional HSE enhances the SO splitting up to 60 meV if the defect state is not close to CBM. However, it decreases the SO splitting up to 57 meV if the defect state is close to CBM. For S<sub>i</sub> no SO splitting was found as the defect state is composed solely by the  $d_{z^2}$  and  $p_z$  orbitals. We also found that not only W<sub>S</sub>, but also the W<sub>S2</sub> defect possesses a local magnetic moment of 2  $\mu_B$  around the antisite W atom due to the two unpaired spin-up electrons occupying the  $d_{xy}$  and  $d_{x^2+y^2}$  defect states. The antisite W atom together with its NN and NNN W atoms thus form the so-called magnetic superatom.

#### V. OUTLOOK

The results presented in this article provide insights into the SOC behavior of the ML WS<sub>2</sub> containing the most common point defects. These results are expected to be extendable to other ML MX<sub>2</sub> systems. In particular, the controllability of these SO split states are worth further investigation as they are highly promising in spintronics applications. It would be interesting to examine whether the spins can flip when an electric field is applied. Also, considering the frequent occurrence of the M<sub>X2</sub> antisites generated during the PVD synthesis of the ML MX<sub>2</sub> membranes [38], it will be interesting to increase the concentration of M<sub>X2</sub> antisite defects and examine the interaction of the magnetic moments and their arrangement over space. Further development of this topic is beyond the scope of the present paper and will be addressed in future works.

## ACKNOWLEDGMENTS

This project is financially supported by the Dutch science foundation NWO via a VIDI grant (Grant No. 723.012.006). W.F.L. acknowledges Torbjörn Björkman and Hugo Aramberri for their discussion on the SOC calculations, and Jyh-Pin Chou for his practical instruction on VASP settings and insight of interpreting the SOC band structures.

- C. Ataca, H. Şahin, and S. Ciraci, J. Phys. Chem. C 116, 8983 (2012).
- [2] K. F. Mak, C. Lee, J. Hone, J. Shan, and T. F. Heinz, Phys. Rev. Lett. 105, 136805 (2010).
- [3] A. Kuc, N. Zibouche, and T. Heine, Phys. Rev. B 83, 245213 (2011).
- [4] Q. H. Wang, K. Kalantar-Zadeh, A. Kis, J. N. Coleman, and M. S. Strano, Nat. Nanotechnol. 7, 699 (2012).

- [5] R. Roldán, J. A. Silva-Guillén, P. López-Sancho, F. Guinea, E. Cappelluti, and P. Ordejón, Ann. Phys. (Berlin) 526, 347 (2014).
- [6] T. Heine, Acc. Chem. Res. 48, 65 (2015).
- [7] R. Ganatra and Q. Zhang, ACS NANO 8, 4074 (2014).
- [8] M. Chhowalla, H. S. Shin, G. Eda, L.-J. Li, K. P. Loh, and H. Zhang, Nat. Chem. 5, 263 (2013).
- [9] H. Schmidt, F. Giustiniano, and G. Eda, Chem. Soc. Rev. 44, 7715 (2015).
- [10] See Supplemental Material at http://link.aps.org/supplemental/ 10.1103/PhysRevB.94.195425 for discussion on the limitations of vdW and SOC in the VASP code, derivation of the boundaries of the chemical potentials for the W and S atoms, density of states plots for all the ML WS<sub>2</sub> slabs, orbital decomposed charge densities of the band structures of perfect bulk and ML WS2 unitcells, and orbital decomposed band structures of perfect and defective ML WS<sub>2</sub> supercells.
- [11] T. J. Wieting and M. Schlüter, eds., *Electrons and Phonons in Layered Crystal Structures* (Springer, Netherlands, 1979).
- [12] R. Coehoorn, C. Haas, and R. A. de Groot, Phys. Rev. B 35, 6203 (1987).
- [13] Z. Y. Zhu, Y. C. Cheng, and U. Schwingenschlögl, Phys. Rev. B 84, 153402 (2011).
- [14] D. Xiao, G.-B. Liu, W. Feng, X. Xu, and W. Yao, Phys. Rev. Lett. 108, 196802 (2012).
- [15] W. Feng, Y. Yao, W. Zhu, J. Zhou, W. Yao, and D. Xiao, Phys. Rev. B 86, 165108 (2012).
- [16] K. Kośmider, J. W. González, and J. Fernández-Rossier, Phys. Rev. B 88, 245436 (2013).
- [17] C. Ataca, H. Şahin, E. Aktürk, and S. Ciraci, J. Phys. Chem. C 115, 3934 (2011).
- [18] Y. Ma, Y. Dai, M. Guo, C. Niu, J. Lu, and B. Huang, Phys. Chem. Chem. Phys. 13, 15546 (2011).
- [19] C. Ataca and S. Ciraci, J. Phys. Chem. C 115, 13303 (2011).
- [20] E. W. K. Koh, C. H. Chiu, Y. K. Lim, Y-W. Zhang, and H. Pan, Int. J. Hydrogen Energy 37, 14323 (2012).
- [21] J.-W. Wei, Z.-W. Ma, H. Zeng, Z.-Y. Wang, Q. Wei, and P. Peng, AIP Adv. 2, 042141 (2012).
- [22] H. Qiu, T. Xu, Z. Wang, W. Ren, H. Nan, Z. Ni, Q. Chen, S. Yuan, F. Miao, F. Song, G. Long, Y. Shi, L. Sun, J. Wang, and X. Wang, Nat. Commun. 4, 2642 (2013).
- [23] D. Liu, Y. Guo, L. Fang, and J. Robertson, Appl. Phys. Lett. 103, 183113 (2013).
- [24] A. Carvalho and A. H. Castro Neto, Phys. Rev. B 89, 081406(R) (2014).
- [25] J. Chang, S. Larentis, L. F. R. Emanuel Tutuc, and S. K. Banerjee, Appl. Phys. Lett. **104**, 141603 (2014).
- [26] S. Yuan, R. Roldán, M. I. Katsnelson, and F. Guinea, Phys. Rev. B 90, 041402(R) (2014).
- [27] P. Rastogi, S. Kuma, S. Bhowmick, A. Agarwal, and Y. S. Chauhan, J. Phys. Chem. C 118, 30309 (2014).
- [28] S.-C. Lu and J.-P. Leburton, Nanoscale Res. Lett. 9, 676 (2014).
- [29] P. K. Chow, R. B. Jacobs-Gedrim, J. Gao, T.-M. Lu, B. Yu, H. Terrones, and N. Koratkar, ACS Nano 9, 1520 (2015).
- [30] H. Liu, N. Han, and J. Zhao, RSC Adv. 5, 17572 (2015).
- [31] A.-M. Hu, L. ling Wang, W.-Z. Xiao, G. Xiao, and Q.-Y. Rong, Comp. Mater. Sci. 107, 72 (2015).
- [32] W. Zhao, Z. Ghorannevis, L. Chu, M. Toh, C. Kloc, P.-H. Tan, and G. Eda, ACS Nano 7, 791 (2012).
- [33] H. Li, S. Liu, S. Huang, D. Yin, C. Li, and Z. Wang, Ceram. Int. 42, 2364 (2015).

- [34] Z. Liu, K. Suenaga, Z. Wang, Z. Shi, E. Okunishi, and S. Iijima, Nat. Commun. 2, 213 (2011).
- [35] H.-P. Komsa, J. Kotakoski, S. Kurasch, O. Lehtinen, U. Kaiser, and A. V. Krasheninnikov, Phys. Rev. Lett. 109, 035503 (2012).
- [36] H.-P. Komsa, S. Kurasch, O. Lehtinen, U. Kaiser, and A. V. Krasheninnikov, Phys. Rev. B 88, 035301 (2013).
- [37] W. Zhou, X. Zou, S. Najmaei, Z. Liu, Y. Shi, J. Kong, J. Lou, P. M. Ajayan, B. I. Yakobson, and J.-C. Idrobo, Nano Lett. 13, 2615 (2013).
- [38] J. Hong, Z. Hu, M. Probert, K. Li, D. Lv, X. Yang, L. Gu, N. Mao, Q. Feng, L. Xie, J. Zhang, D. Wu, Z. Zhang, C. Jin, W. Ji, X. Zhang, J. Yuan, and Z. Zhang, Nat. Commun. 6, 6293 (2015).
- [39] J.-Y. Noh, H. Kim, and Y.-S. Kim, Phys. Rev. B **89**, 205417 (2014).
- [40] H.-P. Komsa and A. V. Krasheninnikov, Phys. Rev. B 91, 125304 (2015).
- [41] S. Haldar, H. Vovusha, M. K. Yadav, O. Eriksson, and B. Sanyal, Phys. Rev. B 92, 235408 (2015).
- [42] R. R. Nair, I.-L. Tsai, M. Sepioni, O. Lehtinen, J. Keinonen, A. V. Krasheninnikov, A. H. C. Neto, M. I. Katsnelson, A. K. Geim, and I. V. Grigorieva, Nat. Commun. 4, 2010 (2013).
- [43] W. Han, R. K. Kawakami, M. Gmitra, and J. Fabian, Nat. Nanotechnol. 9, 794 (2014).
- [44] A. Hashmi and J. Hong, J. Phys. Chem. C 119, 9198 (2015).
- [45] M. Sun, Q. Ren, Y. Zhao, S. Wang, J. Yu, and W. Tang, J. Appl. Phys. 119, 143904 (2016).
- [46] G. Kresse and J. Hafner, Phys. Rev. B 49, 14251 (1994).
- [47] G. Kresse and J. Furthmüller, Comput. Mat. Sci. 6, 15 (1996).
- [48] G. Kresse and J. Furthmüller, Phys. Rev. B 54, 11169 (1996).
- [49] P. E. Blöchl, Phys. Rev. B 50, 17953 (1994).
- [50] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
- [51] J. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 78, 1396 (1997).
- [52] G. Vignale and M. Rasolt, Phys. Rev. Lett. 59, 2360 (1987).
- [53] G. Vignale and M. Rasolt, Phys. Rev. B **37**, 10685 (1988).
- [54] S. Rohra and A. Görling, Phys. Rev. Lett. 97, 013005 (2006).
- [55] J. W. Furness, J. Verbeke, E. I. Tellgren, S. Stopkowicz, U. Ekström, T. Helgaker, and A. M. Teale, J. Chem. Theory Comput. 11, 4169 (2015).
- [56] D. Hobbs, G. Kresse, and J. Hafner, Phys. Rev. B 62, 11556 (2000).
- [57] S. Steiner, S. Khmelevskyi, M. Marsmann, and G. Kresse, Phys. Rev. B 93, 224425 (2016).
- [58] D. W. Latzke, W. Zhang, A. Suslu, T.-R. Chang, H. Lin, H.-T. Jeng, S. Tongay, J. Wu, A. Bansil, and A. Lanzara, Phys. Rev. B 91, 235202 (2015).
- [59] J. Klimeš, D. R. Bowler, and A. Michaelides, J. Phys.: Condens. Matter 22, 022201 (2010).
- [60] Please refer to the SM for more details [10].
- [61] A. V. Krukau, O. A. Vydrov, A. F. Izmaylov, and G. E. Scuseria, J. Chem. Phys. **125**, 224106 (2006).
- [62] G. L. Frey, R. Tenne, M. J. Matthews, M. S. Dresselhaus, and G. Dresselhaus, J. Mater. Res. 13, 2412 (1998).
- [63] C. G. V. de Walle and J. Neugebauer, J. Appl. Phys. 95, 3851 (2004).
- [64] Please refer to Sec. II in the SM for the derivation [10].
- [65] J. E. Padilha, H. Peelaers, A. Janotti, and C. G. Van de Walle, Phys. Rev. B 90, 205420 (2014).