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# Interface depended electronic and magnetic properties of vertical CrI<sub>3</sub>/WSe<sub>2</sub> heterostructures

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Owing to the great potential applications in information processing and storage, two-dimensional (2D) magnetic materials have recently attracted significant attention. Here, using first-principles calculations, we investigate the electronic and magnetic properties of the van der Waals CrI<sub>3</sub>/WSe<sub>2</sub> heterostructures. We find that after forming heterostructures, monolayer CrI<sub>3</sub> undergoes a direct to indirect band gap transition and its gap size is greatly reduced. In particular, the out-plane spin quantization axis of monolayer CrI<sub>3</sub> is tuned into in-plane for most stacking configurations of CrI<sub>3</sub>/WSe<sub>2</sub>. We further reveal that the transition of the easy magnetization direction is mainly originated from the hybridization between Cr-d and Se-p orbitals. These theoretical results provide a useful picture for the electronic structure and magnetic anisotropy behaviors in vertical CrI<sub>3</sub>/WSe<sub>2</sub> heterostructures.

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## Introduction

As triggered by graphene,<sup>1,2</sup> two-dimensional (2D) materials such as hexagonal BN<sup>3</sup> and transition metal dichalcogenides (TMDs),<sup>4,5</sup> have become the focus of intensive studies during the past decade because of their unique properties and the great promise for novel applications. Among them, materials with long-range ferromagnetic order are most desirable for applications in spintronics devices.<sup>6</sup> However, most 2D materials in their pristine forms are intrinsically nonmagnetic, and the magnetic moments introduced by dopants, defects, edges, or coupling to ferromagnetic substrates<sup>7</sup> are mostly very local. Therefore, the recently fabricated 2D intrinsic ferromagnetic materials, such as chromium germanium telluride (Cr<sub>2</sub>Ge<sub>2</sub>Te<sub>6</sub>, (ref. 8)), CrI<sub>3</sub> (ref. 9) and VSe<sub>2</sub>,<sup>10</sup> have attracted much attention for the promised applications as high-density magnetic memories and spintronic applications at the nanoscale.

CrI<sub>3</sub> is layered van der Waals material with order ferromagnetically, the Curie temperature ( $T_c$ ) is 61 K for bulk<sup>11–14</sup> and 45 K for monolayer.<sup>9</sup> Monolayer CrI<sub>3</sub> is a semiconductor<sup>9,15</sup> with the band gap of 1.2 eV.<sup>16–18</sup> By including spin–orbit coupling (SOC), the band gap will decrease to 0.9 eV.<sup>16,18</sup> The magnetism arises from the partially filled d orbitals of the Cr<sup>3+</sup> ion, and the magnetocrystalline anisotropy favours an out-plane spin

orientation.<sup>12</sup> It has been demonstrated that the magnetic properties of CrI<sub>3</sub> can be controlled by strain,<sup>19–23</sup> electric fields<sup>24–28</sup> and magnetic fields.<sup>21,29</sup>

To combine the advantages of two different 2D materials, stacking them into a heterostructure has been proven to be an effective way.<sup>30,31</sup> Until now, many kinds of 2D heterostructures have been fabricated successfully in experiments,<sup>32–34</sup> and their physical properties have been predicated theoretically.<sup>35–39</sup> For magnetic materials, it is known that they can be integrated with many other materials, including conductors<sup>40</sup> and semiconductors.<sup>41</sup> Recently, increasing attention has been paid to the 2D ferromagnetic heterostructures. For example, by the electrostatic doping in CrI<sub>3</sub>/graphene heterostructures, Jiang *et al.* found that the saturation magnetization can be tuned up to 40% experimentally.<sup>25</sup> A theoretical study<sup>16</sup> on CrI<sub>3</sub>/graphene heterostructure indicated that a Chern insulating state can be achieved. Moreover, it is possible to control the spin and valley pseudospin properties of WSe<sub>2</sub> by constructing CrI<sub>3</sub>/WSe<sub>2</sub> ferromagnetic heterostructure.<sup>42,43</sup> However, some questions still need to be answered. For example, what are the interfacial (stacking type) effects on the electronic and magnetic properties of this kinds of heterostructures? Is it possible to tune the magnetic anisotropy energy (MAE) in CrI<sub>3</sub>/WSe<sub>2</sub> heterostructures?

In this paper, by using first principle calculations, we report the interface effects on the electronic structure and magnetic properties in 2D ferromagnetic CrI<sub>3</sub>/WSe<sub>2</sub> heterostructures. We consider three different stacking types for both bilayer and triple layer vertical heterostructures. The tuneable band gap and magnetic properties can be found and understood with the help of orbital hybridization and SOC effects.

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## Computational methods

The structural and electronic properties of monolayer CrI<sub>3</sub>, bilayer and triple layer CrI<sub>3</sub>/WSe<sub>2</sub> heterostructures were computed using the DFT and projector-augmented wave method (PAW)<sup>44</sup> implemented in the VASP code.<sup>45</sup> The Perdew–Burke–Ernzerhof (PBE) functional<sup>46</sup> was used to describe the exchange–correlation interaction. The plane wave basis was expanded up to a cutoff energy 550 eV. Grimme's semiempirical DFT-D3 scheme for dispersion correction<sup>47</sup> was employed to describe the van der Waals (vdW) interactions between the CrI<sub>3</sub> and the WSe<sub>2</sub> layers. In the direction perpendicular to the sheet, 5 nm thickness was selected to avoid any spurious interaction with the image sheets. For each configuration, the atomic coordinates and in-plane supercell parameters were fully relaxed, until the Hellmann–Feynman force on each atom became smaller than 0.01 eV Å<sup>-1</sup> and the total energy was converged to be within 10<sup>-6</sup> eV. The 2D Brillouin zones were sampled by an 14 × 14 × 1 *k*-point grid mesh.<sup>48</sup> Spin polarization was taken into the account, and the effect of SOC was also introduced for the calculations of the electric properties. In addition, to include the interactions between 3d orbits of Cr atoms, the DFT+U methods described by Dudarev<sup>49</sup> were used. Here, in the electronic calculations, the on-site Coulomb parameter (*U*) and the exchange parameter (*J*) were selected as *U* = 2.7 eV and *J* = 0.7 eV,<sup>17,48</sup> respectively.

## Results and discussion

As shown in Fig. 1a, monolayer CrI<sub>3</sub> is a I–Cr–I sandwich structure where each Cr is surrounded by six first neighboring I atoms. In the Cr atomic layer, the Cr atoms form a honeycomb lattice. Owing to the octahedral symmetry, the five d-orbitals (*d*<sub>xy</sub>, *d*<sub>xz</sub>, *d*<sub>yz</sub>, *d*<sub>x<sup>2</sup>-y<sup>2</sup></sub>, *d*<sub>z<sup>2</sup></sub>) of Cr are split into three half-filled *t*<sub>2g</sub> orbitals and two empty *e*<sub>g</sub> orbitals.<sup>17</sup> The magnetization comes directly from the honeycomb Cr lattice. The orbital configuration of the I<sup>-</sup> ion (5s<sup>2</sup>5p<sup>6</sup>) has a very strong SOC, which results in antisymmetric exchange effects and anisotropic symmetric

exchange effects.<sup>17</sup> In Fig. 2, we show the band structures of monolayer CrI<sub>3</sub> without and with SOC, where the direct band gaps are 1.05 eV and 0.72 eV, respectively. These results are consistent with previous DFT calculations.<sup>16–18</sup>

We discuss here the bilayer CrI<sub>3</sub>/WSe<sub>2</sub> and trilayer WSe<sub>2</sub>/CrI<sub>3</sub>/WSe<sub>2</sub> heterostructures. For monolayer CrI<sub>3</sub> and WSe<sub>2</sub>, the optimized lattice parameter is 7.002 Å and 3.321 Å, respectively. In bilayer CrI<sub>3</sub>/WSe<sub>2</sub> heterostructure, monolayer CrI<sub>3</sub> (1 × 1) stacked on monolayer WSe<sub>2</sub> (2 × 2) vertically. The trilayer WSe<sub>2</sub>/CrI<sub>3</sub>/WSe<sub>2</sub> heterostructure has a sandwich structure, in which the monolayer CrI<sub>3</sub> (1 × 1) is surrounded by two layers of WSe<sub>2</sub> (2 × 2). Therefore, the lattice mismatch between CrI<sub>3</sub> (1 × 1) and WSe<sub>2</sub> (2 × 2) is about 5.42%. In both bilayer and triple layer heterostructures, the lattice parameter of adopted that of CrI<sub>3</sub> lattice (7.002 Å), and the WSe<sub>2</sub> layer has been enlarged uniformly. As shown in Fig. 1b–d, three kinds of vertical stacking types have been considered in the present calculation, bi-Se, bi-T and bi-W for bilayer heterostructures. For bi-Se CrI<sub>3</sub>/WSe<sub>2</sub> heterostructure, as shown in Fig. 1b, only one Cr atom is located on the top of a W atom in a unit cell. Similarly, for the bi-W configuration, one Cr atom is located on the top of a I<sub>2</sub> pair in a unit cell (see Fig. 1d). For the bi-T configuration as shown in Fig. 1c, one Cr atom is located on the top of W atom, and the other Cr atom located on the top of I<sub>2</sub> atom. In the trilayer WSe<sub>2</sub>/CrI<sub>3</sub>/WSe<sub>2</sub> heterostructures, the CrI<sub>3</sub>/WSe<sub>2</sub> stacking in tri-Se, tri-T and tri-W configurations are similar to those in bi-Se, bi-T and bi-W configurations, and the two WSe<sub>2</sub> layers are stacked by the AA type.

As can be seen from the data in Table 1, the bi-Se (tri-Se) stacking type is the most favourite configuration in the bilayer (trilayer) heterostructures, which is 6.33 (23.19) and 85.40 (18.76) meV per cell more stable than bi-T (tri-T) and bi-W (tri-W). Meanwhile, the -Se configuration also has the shortest interlayer distance (0.6654 nm for bi-Se, 0.6667 nm for tri-Se), compared with those of -T (0.6674 nm for bi-T and 0.6668 nm for tri-T) and -W (0.6685 nm for bi-W and 0.6842 for tri-W) configurations. Even so, it is noted that the energy differences between different stacking configurations are relatively small and their interlayer distances are comparable, suggesting the superlubricity in the vertical CrI<sub>3</sub>/WSe<sub>2</sub> heterostructures, which has been found in bilayer graphene.<sup>50</sup> Moreover, the Bader charge analysis<sup>51</sup> suggests that, the -Se configurations have less

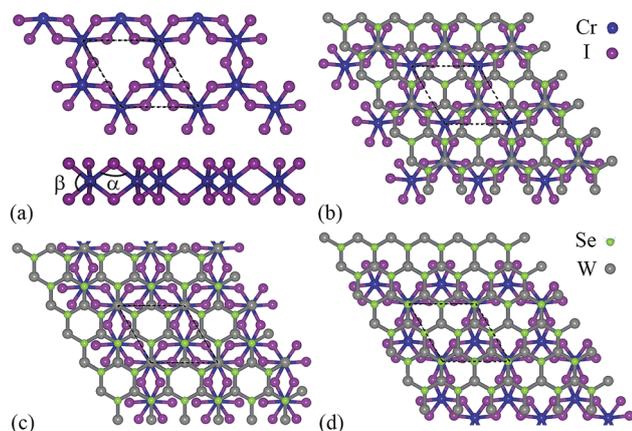


Fig. 1 The structure model for (a) monolayer CrI<sub>3</sub> (upper: top view, lower: side view), and (b–d) CrI<sub>3</sub>/WSe<sub>2</sub> heterostructures with different stacking way ((b) Se-site, (c) top-site and (d) W-site).

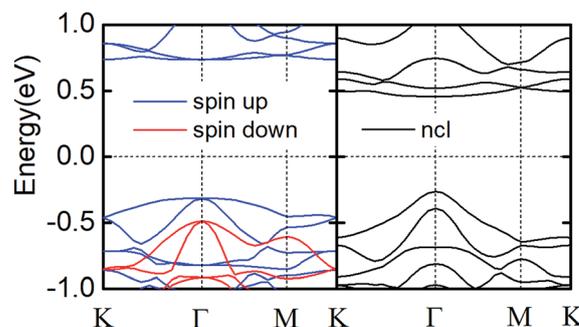


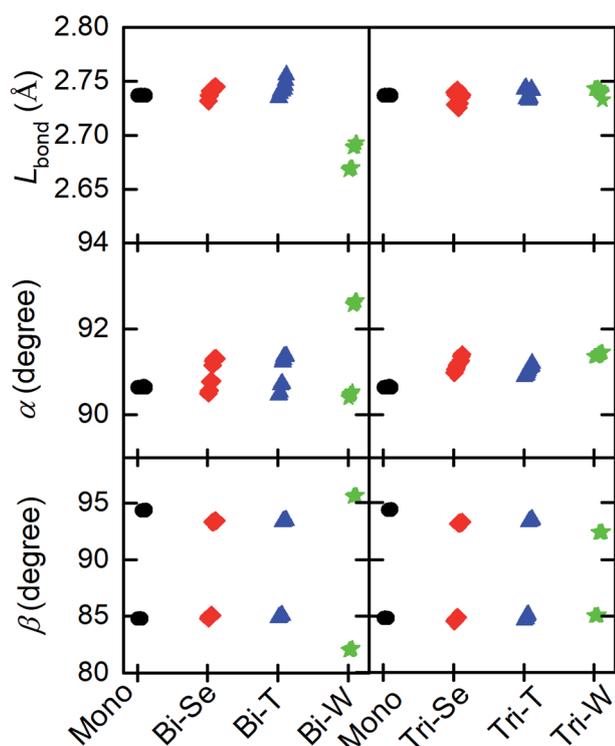
Fig. 2 Band structure of monolayer CrI<sub>3</sub> without (left panel) and with (right panel) SOC.



**Table 1** The calculated relative energy ( $E_r$ , meV per cell), inter-layer distance ( $d$ , nm) and the inter-layer charge transfer ( $Q$ , electrons per cell) for bi-layer and tri-layer  $\text{CrI}_3/\text{WSe}_2$  heterostructures. SOC has been included in all calculations

	$E_r$	$d$	$Q$
Bi-Se	0	0.6654	0.009
Bi-T	6.33	0.6674	0.012
Bi-W	85.40	0.6685	0.014
Tri-Se	0	0.6667	0.007
Tri-T	23.19	0.6668	0.015
Tri-W	18.76	0.6842	0.023

inter-layer charge transfer (0.009 electrons per cell for bi-Se, and 0.007 electrons per cell for tri-Se) than -T and -W configurations. The electronic properties and magnetic properties of  $\text{CrI}_3$  are known to rely on its structural properties. Fig. 3 shows that, the distribution of the bond length (Cr-I,  $L_{\text{bond}}$ ) and bond angles ( $\alpha$ :  $\angle \text{I-Cr-I}$ ,  $\beta$ :  $\angle \text{Cr-I-Cr}$  as labelled in Fig. 1a) of  $\text{CrI}_3$  in monolayer (black dots), bilayer (left panel) and trilayer (right panel) heterostructures. For the case of monolayer  $\text{CrI}_3$ , according to our calculation, the lattice constant,  $L_{\text{bond}}$ ,  $\alpha$  and  $\beta$  are 7.002 Å, 2.737 Å, 90.6° and 94.5° (84.8°), respectively. These results are consistent with previous theoretical results.<sup>12,13,19,24</sup> When forming  $\text{CrI}_3/\text{WSe}_2$  heterostructures, the inter-layer van de Waals interaction makes both the bond length and the bond angles of  $\text{CrI}_3$  slightly changed. As shown in Fig. 3, the bond information of  $\text{CrI}_3$  in bi-Se and tri-Se are closer with the monolayer case, which are responsible for the lower formation



**Fig. 3** Bond length ( $L_{\text{bond}}$ ) and bond angle ( $\alpha$  and  $\beta$ ) for bilayer and trilayer  $\text{CrI}_3/\text{WSe}_2$  heterostructures with three different stacking models.

energy indicated in Table 1. Nevertheless, both the bond angle and bond length have been interrupted by the  $\text{WSe}_2$  layer in bilayer and triple layer  $\text{CrI}_3/\text{WSe}_2$  heterostructures. The bond angle of  $\alpha$  and  $\beta$  accounts the ferromagnetic superexchange symmetry.<sup>24</sup> Therefore, the electronic properties and magnetic properties of  $\text{CrI}_3$  in heterostructure are supposed to be different from those of monolayer  $\text{CrI}_3$ .

We then next discuss the electronic and magnetic properties of the  $\text{CrI}_3/\text{WSe}_2$  heterostructures. When stacked into heterostructure, as shown in Fig. 4 for bilayer and Fig. 5 for triple layer  $\text{CrI}_3/\text{WSe}_2$  heterostructures, the band structure of  $\text{CrI}_3$  depends on the interlayer interactions. Firstly, we can also see from the band structures is that, the band alignment in both bilayer and triple layer  $\text{CrI}_3/\text{WSe}_2$  heterostructures can be categorized into staggered type (type-II). Secondly, compared with the band gap of monolayer  $\text{CrI}_3$  (see Fig. 2), *i.e.*, 1.05 eV (without SOC) and 0.72 eV (with SOC), band gap of  $\text{CrI}_3$  in heterostructures is larger. Without (with) SOC, band gap of  $\text{CrI}_3$  in bilayer heterostructures is 1.13 (1.12), 1.13 (1.07) and 1.19 (0.90) eV for bi-Se, bi-T and bi-W, respectively. For trilayer  $\text{CrI}_3/\text{WSe}_2$  heterostructures, the band gaps without (with) SOC are 1.07 (1.07) eV for tri-Se, 1.07 (1.04) eV for tri-T and 0.96 (1.01) eV for tri-W, respectively (see Fig. 5). Thirdly, the direct-to-indirect band gap transition can be found from monolayer  $\text{CrI}_3$  to  $\text{CrI}_3/\text{WSe}_2$  heterostructures. For monolayer  $\text{CrI}_3$ , either with or without SOC (see Fig. 2), the band gap is direct. However, for both bilayer and triple layer  $\text{CrI}_3/\text{WSe}_2$  heterostructures, the inter-layer interaction tuned the band gap to indirect (without considering SOC). When considering the SOC, tri-Se still have indirect band gap, in which the valence band maximum (VBM) is located at  $\Gamma$  point, but the conduction band minimum (CBM) is located at K point (see Fig. 5). As shown in Fig. 4 and 5, less than 0.1 eV energy difference at different K points in the flat conductance bands. Then, it is easier to switch between the direct band gap and indirect one by using different interlayer interactions. It is found that the CBM is contributed by Cr, I and W atoms, then the SOC effect mainly resulting from  $\Gamma^-$  atoms is one reason for the direct to indirect change.

Magnetic anisotropy originating mainly from SOC effects,<sup>17,30</sup> is an important parameter when it comes to 2D magnets as it is qualitatively related to their magnetic stability. MAE is defined as the difference between energies corresponding to the magnetization in the in-plane and out-plane directions ( $\text{MAE} = E_{\text{m//a}} - E_{\text{m//c}}$ ), in which  $E_{\text{m//a}}$  is the energy for the in-plane magnetization, and  $E_{\text{m//c}}$  is the energy for the out-plane magnetization. A positive (negative) value of MAE indicated the out-plane (in-plane) easy axis. Taking SOC effects into account, the total energies  $E_{\text{m//a}}$  and  $E_{\text{m//c}}$  can be achieved through noncollinear calculations, and then the MAE can be evaluated. Consistent with the previous calculations<sup>12,18,19,21</sup> and experimental results,<sup>13,17</sup> because of the strong SOC in the heavier iodine ions,<sup>17</sup> the easy axis for monolayer  $\text{CrI}_3$  is out-plane with MAE 0.73 meV per Cr atom.

One most interesting finding is that, as shown in Table 2, the out-plane easy axis in monolayer  $\text{CrI}_3$  changed into in-plane in  $\text{CrI}_3/\text{WSe}_2$  heterostructures with almost all kinds of stacking types. The only exception is tri-T, which is still out-plane easy



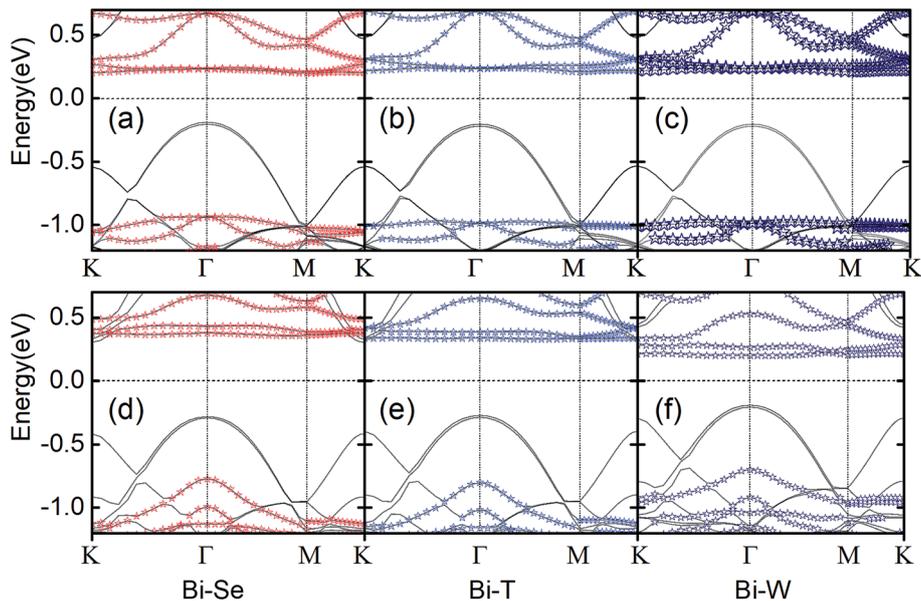


Fig. 4 Band structure of bilayer  $\text{CrI}_3/\text{WSe}_2$  heterostructures without (a–c) and with (d–f) SOC for bi-Se (a and d), bi-T (b and e) and bi-W (c and f) stackings. The grey lines are band of the heterostructure, and stars are band mainly contributed from  $\text{CrI}_3$  layer. The bandgap is indirect without SOC, but tuned direct for bi-T and bi-W stackings after the SOC have been considered.

axis with MAE 0.03 meV per Cr. Remarkable large MAE can be found for the most stable stacking configurations in both bilayer and triple layer  $\text{CrI}_3/\text{WSe}_2$  heterostructures, *i.e.*, 0.17 meV per Cr and 0.23 meV per Cr for bi-Se and tri-Se, respectively.

Noteworthy, the charge transfer in bilayer heterostructures (see Table 1) can result in a net dipole moment. With the dipole correction, our calculation indicated that the MAE and magnetic moment can be changed about 0.001 meV per Cr and

0.001  $\mu_B$  per Cr, respectively. In Fig. 6a, take bi-Se  $\text{CrI}_3/\text{WSe}_2$  heterostructures as an example, we compared the wave function characteristics at the G point Cr d and Se  $p_z$  orbitals between out-plane and in-plane easy axis. It can be seen clearly that, the hybridizations take place between  $\text{Cr}_{d_{xz,yz}}$ ,  $\text{Cr}_{d_z^2}$  and  $\text{Se}_{p_z}$  orbitals, as the results of the interlayer interaction between  $\text{CrI}_3$  layer and  $\text{WSe}_2$  layer. This should be responsible for the easy axis transition in  $\text{CrI}_3/\text{WSe}_2$  heterostructures as suggested in Fe/MgO interfaces.<sup>52</sup> The only exception is the tri-T  $\text{CrI}_3/\text{WSe}_2$

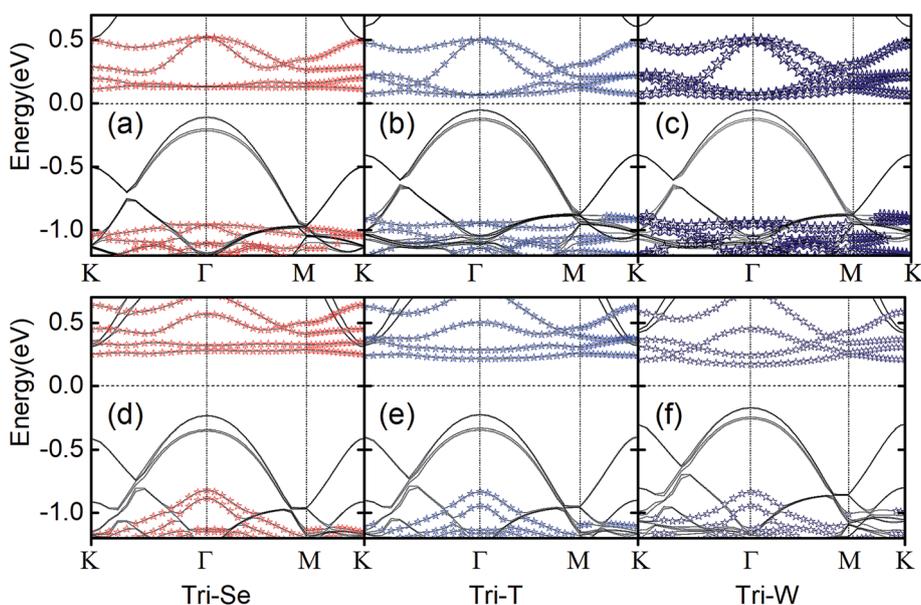


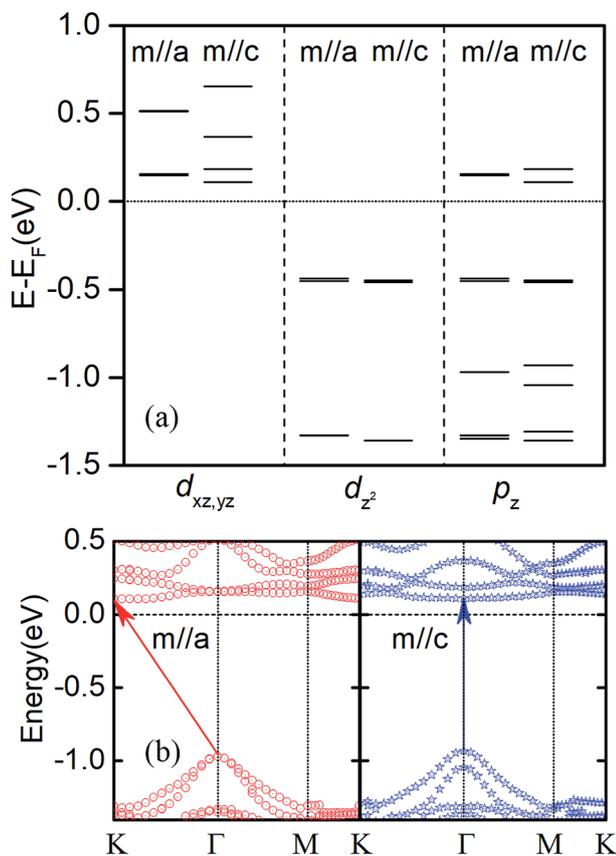
Fig. 5 Band structure of triple layer  $\text{CrI}_3/\text{WSe}_2$  heterostructures without (a–c) and with (d–f) SOC for tri-Se (a and d), tri-T (b and e) and tri-W (c and f) stackings. The grey lines are band of the heterostructure, and stars are band mainly contributed from  $\text{CrI}_3$  layer.



**Table 2** The magnetization directions for bi-layer and tri-layer CrI<sub>3</sub>/WSe<sub>2</sub> heterostructures. The MAE (in units of meV per Cr) is also listed in the bracket, a positive (negative) value indicated the out-plane (in-plane) easy axis

	-Se	-T	-W
Monolayer	Out-plane (0.73)		
Bi	In-plane (-0.17)	In-plane (-0.03)	In-plane (-0.02)
Tri	In-plane (-0.23)	Out-plane (0.03)	In-plane (-0.04)

heterostructure, in which the out-plane easy axis is maintained. Therefore, except for applying the in-plane external magnetic field,<sup>18</sup> we demonstrated here that the spin direction can be shifted from out-plane to in-plane by stacking with the WSe<sub>2</sub> layer. The easy axis direction should be another reason for the direct-to-indirect band gap transition. We calculated the band structures for bi-Se CrI<sub>3</sub>/WSe<sub>2</sub> heterostructure with two different magnetic moment orientations (m//a and m//c) as shown in Fig. 6b. For m//a, the CBM located at K point, but the VBM is located at  $\Gamma$  point, which makes the band gap indirect. For m//c, however, both the CBM and VBM located at  $\Gamma$  point, then the band gap is direct. Moreover, it can be also found in Fig. 6b and 4a, both the CBM and VBM are degenerated at  $\Gamma$  point for m//



**Fig. 6** (a) Effects of spin axis on the wave function characteristics at  $\Gamma$  points for Cr d and Se p<sub>z</sub> orbitals for bi-Se CrI<sub>3</sub>/WSe<sub>2</sub> heterostructures. (b) Band structure of bi-Se CrI<sub>3</sub>/WSe<sub>2</sub> heterostructures for the magnetic moment along the in-plane a axis (left panel) out-of-plane c axis (right panel). The arrows show that the bandgap is indirect with m//a and direct with m//c.

a and without SOC. It is known that, the CBM at  $\Gamma$  point is mainly results from p<sub>x</sub> and p<sub>y</sub> orbitals of I atom.<sup>18</sup> When the SOC is included and with the out-plane easy axis, the energy split for VBM and CBM at  $\Gamma$  point. Therefore, the transition of easy axis from out-plane to in-plane is one reason for the direct-to-indirect band gap switch.

## Conclusions

To summarize, our first-principles calculations unveil the effect of interfaces on the electronic and magnetic properties of vertical CrI<sub>3</sub>/WSe<sub>2</sub> heterostructures. We find that the -Se stacking is the most stable configuration in either bilayer or triple layer CrI<sub>3</sub>/WSe<sub>2</sub> heterostructures. The switch between direct and indirect band gap can be found mainly because of the SOC effects of the p orbitals of I atoms. Most importantly, originated from hybridizations between d orbitals of Cr atoms and p orbital of Se atoms, the easy axis transition from the out-plane of monolayer CrI<sub>3</sub> to in-plane for almost all stacking type of both bilayer and triple layer CrI<sub>3</sub>/WSe<sub>2</sub> heterostructures is found. All these theoretical results constitute a useful picture of vertical CrI<sub>3</sub>/WSe<sub>2</sub> heterostructures for the interface effect on the electronic and magnetic behaviors and provide vital guidance in designing novel spintronic 2D devices.

## Conflicts of interest

There are no conflicts to declare.

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