

Large spin-orbit splitting in the conduction band of halogen (F, Cl, Br, and I) doped monolayer WS₂ with spin-orbit coupling

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Spin-orbit (SO) splitting in the conduction-band minimum (CBM) of monolayer WS₂ plays a pivotal role in spintronics for spin-valley coupled electron. Using first-principles calculation, a large SO splitting at the *K* point in the CBM is achieved in halogen doped monolayer WS₂ (83.55 meV for F doped $4 \times 4 \times 1$ supercell) because of the strong spin-orbit coupling induced by the asymmetric electric field. We further clarify that the asymmetric electric field originates from the stronger trigonal prismatic ligand field and asymmetric surface charge distribution incurred by halogen doping. More importantly, halogen doping could be used to lift the degeneracy of *K* and *K'* valleys in the CBM of monolayer WS₂ by breaking the time-reversal symmetry. This research proposes a feasible method to enlarge the SO splitting in the CBM of transition-metal dichalcogenides, advancing their application in valley spintronic devices.

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I. INTRODUCTION

Spin-orbit coupling (SOC) leads to coupled spin and valley physics in monolayer transition-metal dichalcogenides (TMDs), making possible controls of spin polarization [1], spin Hall effect [2], and valley Hall effect [3] in these two-dimensional materials [4]. Enhancing the SOC in monolayer TMDs is a key concern in the application of future electronic, optical, and valleytronic devices [5–8]. As a fundamental interaction in TMDs, SOC originates from the movement of electrons in a crystal's intrinsic electric field [9], and spin-orbit (SO) splitting is derived from asymmetric potential gradient (electric field) in the vicinity of the nuclei. Two alternative mechanisms exist for this SO splitting in monolayer TMDs, related to different sources of the electric-field asymmetry: the special trigonal prismatic ligand field (Dresselhaus effect) [10] and the surface charge distribution (Rashba effect) [2]. Both cases propose the possibility of designing and fabricating spintronic devices based on TMDs. However, application is hampered by the limited spin-orbit interaction of the currently available TMDs, and thus inevitably needs low operation temperatures, long channel lengths, and ultrahigh purity materials to avoid spin-flip scattering [11]. In this respect, it is highly desirable to achieve a relatively large SO splitting in both valence-band maximum (VBM) and conduction-band minimum (CBM) [12].

Recently, the SO splitting bands and spin valley for monolayer TMDs near the main energy gaps were calculated by tight-binding models [13–15], and have been experimentally confirmed [16–18]. Using density functional theory (DFT) calculation, the SO splittings at the *K* points in the VBM of monolayer MoS₂, MoSe₂, WS₂, and WSe₂ were 148, 183, 426, and 456 meV, respectively [11]. This SO splitting in the VBM can be strongly affected by multiple external stimuli, such as in-plane tensile strain and electric/magnetic fields

perpendicular to the basal planes in monolayer TMDs [19–23]. However, SO splittings in the CBM were only between 3 and 30 meV [24,25]. It should be noted that the SO splitting in the CBM plays a significant role in the spintronic properties such as spin-conserving scattering [6,26–28]. But up to now, little attention was paid to modulating SO splitting in the CBM of TMDs. Absor *et al.* have recently reported the modification of the SO splitting at the *Q* point closing to the *K* point in the CBM by applying strain [28], neglecting the *K* point which manifests great importance. Searching for a suitable adjustment method to achieve a large valley-dependent SO splitting at the *K* point in the CBM is a great challenge.

In this work, due to large carrier mobility of monolayer WS₂ and higher stability of mixed TMDs compounds by halogen modification [6,29], we employ halogen doping in monolayer WS₂ to improve SO splitting at the *K* point in the CBM through DFT+SOC calculations and crystal-field theory analysis. The halogen doping causes an asymmetric electric field and enhances the SOC interaction, which evidently gives rise to a large SO splitting (e.g. 83.55 meV with F doping) as well as a huge orbit moment at the *K* point in the CBM. Interestingly, the conduction-band splitting decreases with the impurity radius increasing. Meanwhile, large valley polarization at the *K* and *K'* points in the CBM of monolayer WS₂ could be reached by breaking the time-reversal symmetry by means of halogen doping. This attractive property can contribute to better improvement of optoelectronic and valley spintronic devices.

II. COMPUTATIONAL METHODS

To get insight into the electronic properties of a monolayer WS₂ doped with halogen impurities, the spin-polarized DFT calculations are performed using the Vienna *Ab-initio* Simulation Package (VASP) with the projector augmented wave (PAW) potentials [30–32]. DFT calculation was performed at a single point at the generalized gradient approximation (GGA)

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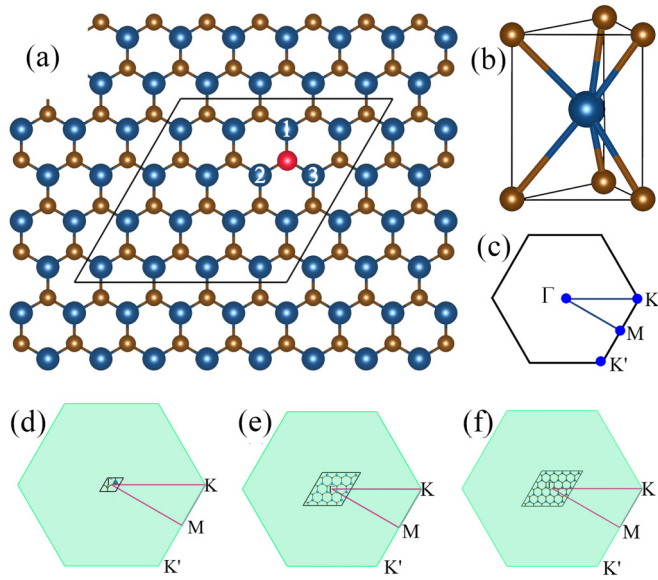


FIG. 1. (a) The relaxed structure for possible substitutional dopants in the $4 \times 4 \times 1$ monolayer WS_2 supercell. The brown, blue, and red balls represent S, W, and dopant (F, Cl, Br, and I) atoms, respectively. (b) The structure for trigonal prisms monolayer WS_2 . (c) The first Brillouin zone of the monolayer WS_2 . (d)–(f) The detailed first Brillouin zones of undoped monolayer WS_2 for the unit cell, $4 \times 4 \times 1$ supercell and $5 \times 5 \times 1$ supercell, respectively.

lattice geometry. First, the GGA scheme was employed for the fully relaxed structure optimization using conjugate gradient. The structure relaxations were carried out with a 450-eV plane-wave cutoff. The self-consistent total-energy difference and the convergence criterion for forces on atoms were set to 10^{-4} eV and 0.01 eV/Å, respectively. A minimum of 15 Å of vacuum perpendicular to the monolayer WS_2 was added to avoid spurious interaction between the periodic images of the sheets. Then, the static state of $4 \times 4 \times 1$ supercells and $9 \times 9 \times 1$ k -point mesh was calculated using Perdew-Burke-Ernzerhof (PBE) [33] and Heyd, Scuseria and Ernzerhof (HSE) methods [34] for the treatment of exchange-correlation energy, respectively. $4 \times 4 \times 1$ supercells consist of 48 atoms with an S atom substituted by a F, Cl, Br, or I atom [Fig. 1(a)]. In addition, we simulated the dopant in $5 \times 5 \times 1$ supercells and $3 \times 3 \times 1$ k -point mesh using the PBE functional. $5 \times 5 \times 1$ supercells consist of 75 atoms with an S atom substituted by a F, Cl, Br, or I atom. To take into consideration the band-folding effect of undoped supercells, the unit cell of monolayer WS_2 was also calculated to make a comparison.

Based on the static states mentioned above, we calculated the corresponding band structures. Note that SOC and un-SOC are considered in our work to calculate the band structure and charge density. From now on, the calculated methods are referred to PBE, PBE + SOC, HSE, and HSE + SOC, respectively.

III. RESULTS AND DISCUSSION

The crystal structure of monolayer WS_2 is characterized by the symmetry of hexagonal space group $P\bar{6}m2$ (D_{3h}^1) (no. 187). In the prismatic unit cell, the W atom sits in the

TABLE I. The physical parameters of $4 \times 4 \times 1$ monolayer WS_2 supercell. d (Å) is the bond lengths between the three nearest tungsten and sulfur (or halogen) atoms in pure (or halogen doped) supercell. E_f (eV) is the formation energies of halogen substitutional dopants in WS_2 under W-rich and S-rich conditions.

Model		Bond length	E_f (W rich)	E_f (S rich)
Pure	$d_{\text{S-W1}}$	2.4141		
	$d_{\text{S-W2}}$	2.4141		
	$d_{\text{S-W3}}$	2.4141		
F doped	$d_{\text{F-W1}}$	2.3208	−2.5207	0.5293
	$d_{\text{F-W2}}$	2.3169		
	$d_{\text{F-W3}}$	2.3173		
Cl doped	$d_{\text{Cl-W1}}$	2.5383	−1.3199	1.7301
	$d_{\text{Cl-W2}}$	2.5385		
	$d_{\text{Cl-W3}}$	2.5384		
Br doped	$d_{\text{Br-W1}}$	2.6884	−0.9170	2.1330
	$d_{\text{Br-W2}}$	2.6871		
	$d_{\text{Br-W3}}$	2.6870		
I doped	$d_{\text{I-W1}}$	2.8722	−0.3968	2.6532
	$d_{\text{I-W2}}$	2.8716		
	$d_{\text{I-W3}}$	2.8713		

center of a trigonal prismatic coordination, being bound to six S atoms by strong covalent bonds as shown in Fig. 1(b). The monolayer WS_2 is direct gap semiconductor with the VBM and CBM at the K (K') point of the hexagonal Brillouin zone as displayed in Fig. 1(c). Both the unit cell and the $n \times n$ supercell WS_2 share the same Brillouin zone, where n is a positive integer greater than 1. The detailed first Brillouin zones of the unit cell, $4 \times 4 \times 1$ supercell, and $5 \times 5 \times 1$ supercell are shown in Figs. 1(d)–1(f), respectively [35]. The absence of inversion symmetry leads to strong modifications of the electronic and optical properties compared with the bulk counterpart. By examining the optimized lattice of pure and halogen doped $4 \times 4 \times 1$ supercells, the calculated bond lengths $d_{\text{S-W}}$ and $d_{\text{halogen-W}}$ are given in Table I. It is noticeable that the monolayer WS_2 has an equal value of $d_{\text{S-W}} = 2.4141$ Å between the three nearest S-W atoms [Fig. 1(a)]. In halogen doped monolayer WS_2 , the bond lengths of the three $d_{\text{halogen-W}}$ are unequal. Besides, the bond lengths of $d_{\text{F-W}}$ for F doping are slightly shorter than that in a pure supercell ($d_{\text{S-W}} = 2.4141$ Å), while the $d_{\text{halogen-W}}$ are longer in the case of Cl, Br, and I doping. It clearly indicates that the doping systems still maintain the trigonal prismatic coordination, but their symmetry reduces to $P3m1$ (C_{3v}^1) (no. 156).

To analyze the influence of halogen doping on the stability of monolayer WS_2 , impurity formation energy (E_f) of a particular substitutional dopant is given by Eq. (1) as

$$E_f = E_{\text{WS}_2:X} - E_{\text{WS}_2} - u_X + u_S, \quad (1)$$

where X represents the chemical elements of halogen. $E_{\text{WS}_2:X}$ and E_{WS_2} are the total energies of halogen doped WS_2 monolayer and pristine $4 \times 4 \times 1$ supercells, respectively. The chemical potentials u_X and u_S are the substitutional halogen atom and the S atom, respectively. u_X is obtained from the free

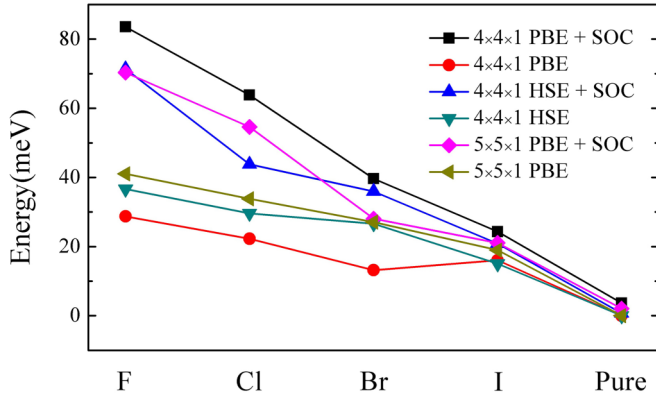


FIG. 2. The splitting at the K point in CBM of pure and halogen doped monolayer WS_2 under different calculated models and methods. Here, black and red lines indicate $4 \times 4 \times 1$ supercells calculated with PBE + SOC ($\Delta_{\text{SOC}}^{\text{CBM}}$) and PBE (Δ^{CBM}), respectively. Blue and dark cyan lines indicate $4 \times 4 \times 1$ supercells calculated with HSE + SOC ($\Delta_{\text{SOC}}^{\text{CBM}}$) and HSE (Δ^{CBM}), respectively. Magenta and dark yellow lines indicate $5 \times 5 \times 1$ supercells calculated with PBE + SOC ($\Delta_{\text{SOC}}^{\text{CBM}}$) and PBE (Δ^{CBM}), respectively.

molecule X_2 (F_2 , Cl_2 , Br_2 , and I_2). The growth of engineered WS_2X should not be an equilibrium process but a kinetic process, which depends on the experimental growth conditions of W-rich, S-rich, or anything in between. Under the S-rich condition, u_S is calculated from the ground-state energy of the S_2 molecule. Under the W-rich condition, the W is assumed to be in thermodynamic equilibrium with the bulk solid phase, and thus, their chemical potentials are fixed at the value u_W . Then u_S is obtained by the growth condition

$$2u_S + u_W = u_{\text{WS}_2}. \quad (2)$$

The calculated results are summarized in Table I. The formation energies E_f (eV) of the halogen atom doped WS_2 monolayer under W-rich are much less than those under the S-rich growth condition, indicating that halogen doping in the WS_2 monolayer are easier to implement under the W-rich growth condition. The formation energy of the doped compounds is negative in the W-rich condition, indicating that the doped compounds are easy to form and more stable than the pure one. The trend of stability of such compounds under the W-rich growth condition is consistent with that obtained from calculating the cohesive energies [29]. From Table I, we can also conclude that F doping is energetically more favorable than other halogen elements.

To understand details of the SO splitting at the K point in the CBM of pure and halogen doped monolayer WS_2 under different calculated models and exchange-correlation potential functionals, we calculated the band structures of the unit cell using PBE + SOC, $4 \times 4 \times 1$ supercells using PBE + SOC, PBE, HSE + SOC, and HSE, and the $5 \times 5 \times 1$ supercell using PBE + SOC and PBE. The quantitative values of the SO splitting at the K point in the CBM are summarized in Fig. 2. It is noticeable that the SO splitting is strongly affected by the exchange-correlation functional [23]. This is likely because PBE is the local electron exchange functional, whereas HSE addresses the influence of the nonlocal part of the exchange correlation [25]. The SO splitting in the $4 \times 4 \times 1$ supercell

using the PBE + SOC method with same dopant system is the largest. The band gap of pure monolayer WS_2 calculated by using the HSE hybrid functional is 2.45 eV, which is much larger than the 1.97 eV in experiment [36]. However, the band gap 1.95 eV using the PBE method is in good agreement with experiment [36]. This is likely because of an error cancellation: due to quenched Coulomb screening that has been explored in detail for graphene [37], large exciton binding energies of TMD materials roughly compensate for the band-gap underestimation at the PBE functional [23]. Therefore, PBE is the most ideal functional for calculating monolayer WS_2 . We will mainly treat $4 \times 4 \times 1$ supercells using the PBE functional to study the SO splitting in the following.

In our PBE + SOC calculation, the absence of inversion symmetry in monolayer WS_2 , different from the bulk one [12], leads to valley-dependent optical selection rules for interband transitions at K (K') points [38]. Nevertheless, the conduction-band splitting at the K valley in pure WS_2 is negligible due to its relatively small structure asymmetry [Fig. 3(a)]. Thus a significant change of the band splitting is expected by halogen doping, which can strongly modify the structure symmetry and the electronic properties of monolayer WS_2 . Figures 3(a)–3(e) reveal the band structures of pure and halogen doped $4 \times 4 \times 1$ monolayer WS_2 supercell with PBE + SOC. The zero energy point was set to the Fermi level of the VBM in pure monolayer WS_2 , and the doped systems were corrected by aligning the vacuum potentials of these systems [39]. Similar band structures of halogen doped WS_2 are obtained, and a SO splitting ($\Delta_{\text{SOC}}^{\text{CBM}}$) at the CBM is clearly observed as labeled with $c1$ and $c2$ at the K valley in Figs. 3(f)–3(j), which are the enlarged images of the red frame in Figs. 3(a)–3(e), respectively. We take the 83.55-meV SO splitting in the F doped one as an example, which plays a pivotal role in the spintronic phenomena for spin-conserving scattering [28]. To quantitatively show the effect of different halogen elements on the SO splitting, the values of SO splitting for F, Cl, Br, and I doped WS_2 were summarized in Fig. 2 (black line). Interestingly, the SO splitting decreases with the increase of radius of the dopant atom. The similar trend is observed in the systems of $4 \times 4 \times 1$ supercells with HSE + SOC and $5 \times 5 \times 1$ supercells with PBE + SOC (Fig. 2, blue and magenta lines). The black and magenta lines in Fig. 2 also indicate that the SO splitting values of the CBM decrease with reducing impurity concentration using PBE + SOC.

In order to better understand the physical origin of the observed spin splitting, we have calculated the partial charge density of bands $c1$ and $c2$ at the K point, and charge density difference for halogen-doped $4 \times 4 \times 1$ monolayer WS_2 supercells, as shown in Figs. 4(a)–4(c). In halogen doped monolayer WS_2 , the bands $c1$ and $c2$ mainly originate from tungsten d antibonding states, with a feeble contribution from the p orbital of the sulfur or halogen atoms, as indicated in Figs. 4(a) and 4(b). After introducing halogen into WS_2 , the charges of W and S atoms redistribute, where electrons flow into the neighbored halogen atoms [Fig. 4(c)] and decrease the positive polarity of the W atoms as well as the Coulomb attraction between tungsten atoms and the sulfur (or halogen atoms). To better evaluate the quantity of charges transferred from the tungsten atom to the halogen atom, total orbital charges of atoms around the dopants are summarized in Table II. We noticed that the

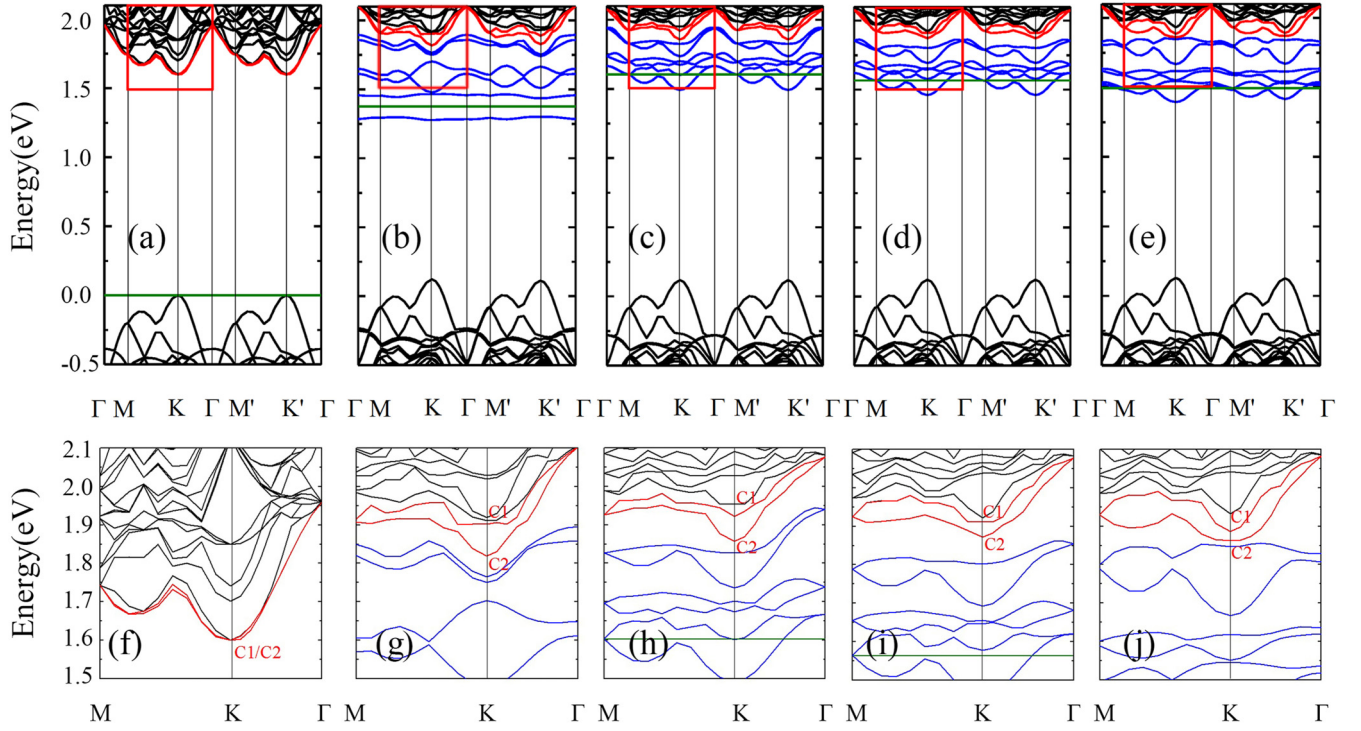


FIG. 3. (a)–(e) Band structures of $4 \times 4 \times 1$ supercells for pure and halogen (F, Cl, Br, and I) doped monolayer WS_2 calculated with PBE + SOC. (f)–(j) Enlarged images of the red frame in (a)–(e), respectively. Here, the black, red, blue curve and light green straight line indicate the conduction bands, the lowest split conduction bands ($c1$ and $c2$), impurity levels, and Fermi-level energy, respectively.

charge transfer would decrease in more diluted doped $5 \times 5 \times 1$ supercells [Fig. 4(d) and Table II]. The asymmetric electric field caused by halogen doping breaks inversion symmetry,

resulting in strong SOC and the subsequent large SO splitting [40]. This will make it possible to control spin and valley in doped monolayer TMD materials.

We now attempt to make a deep insight into the origin of the asymmetric electric field based on trigonal prismatic ligand field (Dresselhaus effect) and surface electric field (Rashba

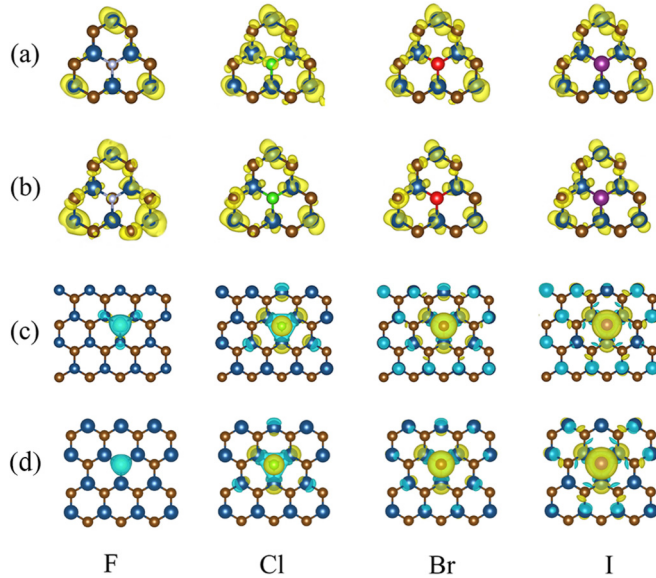


FIG. 4. The partial charge density of $c1$ (a) and $c2$ (b) at the K point, and the charge density difference of F, Cl, Br, and I doped monolayer WS_2 for $4 \times 4 \times 1$ supercells (c) and $5 \times 5 \times 1$ supercells (d) with PBE + SOC. In (a) and (b), the isosurface level is $0.004 \text{ eV}/\text{bohr}^3$. In (c) and (d), the yellow (light blue) region indicates the charge accumulation (depletion), the isosurface level is $0.01 \text{ electron}/\text{bohr}^3$.

TABLE II. Orbital charge population for atoms around dopant (F, Cl, Br, and I) in $4 \times 4 \times 1$ and $5 \times 5 \times 1$ monolayer WS_2 calculated with PBE + SOC. $\Delta(e)$ is the difference value of the total orbital charge for S and W atoms after halogen doping.

		$4 \times 4 \times 1$ supercell		$5 \times 5 \times 1$ supercell	
	Atoms	Total charge	$\Delta(e)$	Total charge	$\Delta(e)$
Pure	S	3.721		3.721	
	W	10.143		10.143	
F doped	S	3.726	0.005	3.727	0.006
	F	6.05		6.046	
	W	10.084	−0.059	10.092	−0.051
Cl doped	S	3.724	0.003	3.724	0.003
	Cl	5.087		5.083	
	W	10.111	−0.032	10.113	−0.030
Br doped	S	3.725	0.004	3.722	0.001
	Br	4.862		4.857	
	W	10.113	−0.030	10.116	−0.027
I doped	S	3.726	0.005	3.722	0.001
	I	4.295		4.292	
	W	10.117	−0.026	10.119	−0.024

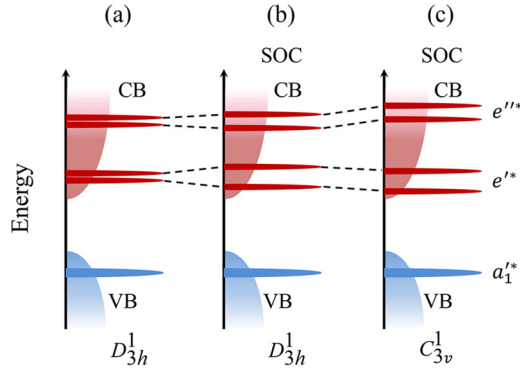


FIG. 5. Ligand-field level diagram of W d orbitals in trigonal prismatic ligand field for monolayer WS_2 (a) without doping, SOC not included, (b) without doping, SOC included, and (c) with F doping, SOC included.

effect), and try to clarify how they cause the strong SOC in halogen doped WS_2 . In the trigonal prismatic ligand field of monolayer WS_2 , heavy metal W d orbitals have a crystal-field splitting. The splitting pattern arises in a six-coordinated transition-metal complex of D_{3h}^1 or C_{3v}^1 symmetry of crystal structure space group [23], and the energies split into two doubly degenerate $m = \pm 2$ levels e'^* ($d_{x^2-y^2}$ and d_{xy}) and $m = \pm 1$ levels e''^* (d_{xz} and d_{yz}), and the single $m = 0$ level $a_1'^*$ ($d_{3z^2-r^2}$), as shown in Fig. 5. The d orbit electron wave functions have been calculated by Huisman *et al.* [41] using a series of spherical harmonics, where the single $m = 0$ level $a_1'^*$ has the lowest energy.

In addition, the pure monolayer WS_2 has the symmetry of hexagonal space group $P\bar{6}m2$ (D_{3h}^1). It is clear that in the case of the trigonal prismatic coordinated W atom, the adjacent S atom hardly affects the ligand field while the W atom has a high spin state according to the Hund principle. In its high spin state, the majority spin electrons will half fill up the lowest $a_1'^*$ orbit, the spin channel e'^* and e''^* orbitals, which are crucial for producing a large SO splitting in the CBM as will be discussed below. At the W ground state, both the spin e'^* doublet and the e''^* doublet are partially filled. In this situation, the levels of double degenerate e'^* may be lower than the e''^* , as the interorbital Coulomb interaction of e'^* is remarkable due to their common in-plane characters [Fig. 5(a)]. The majority spin d_{xy} orbital electrons could promote the higher lying e''^* doublet to a higher state and reduce the interorbital Coulomb repulsion. This may compensate for the energy cost associated with the strong SOC interaction and the trigonal prismatic ligand field excitation [42]. Note that the CBM lies just below the e'^* orbitals, due to the occupation of electrons in the broad conduction band in n -type WS_2 [43]. Thus the CBM splitting is mainly determined by d orbital splitting and spin-orbit moment, both derived from separation of lower energy e'^* and higher energy e''^* orbitals. Taking account of the SOC interaction, the degeneration of e'^* and e''^* orbitals are removed. The partially-filled e''^* doublet will yield the occupied orbit in the up-spin channel shifting to higher energy, while the e'^* doublet will make the occupied orbit shift to lower energy, thus giving an orbital moment. Figure 5(b) depicts the splitting of d levels for the W atom under the SOC interaction.

The trigonal prismatic field (Dresselhaus effect) causes the conduction-band splitting with the absence of degeneration of e'^* and e''^* orbitals.

We now turn towards the splitting in d orbitals of the halogen doped monolayer WS_2 . The D_{3h}^1 group for pure monolayer combines the C_s^1 and C_{3v}^1 symmetry groups. Because C_s^1 is broken with the entry of halogen atoms, the doped systems preserve the hexagonal space group $P3m1$ (C_{3v}^1). In particular, we select F doped WS_2 as a representative system to discuss in detail, since the other halogens present similar electronic structures. When doped with an F atom, one additional p orbit electron becomes spatially extended, and the interorbital Coulomb interaction between the W cation and ligand anion increases. Due to the enhanced p - d covalence, the ligand field effect gets stronger. As a result, the e'^* is pushed to a high ligand field level, while the e''^* is pushed to a low ligand field level. Meanwhile, a more asymmetric electric field is obtained in a doped system compared with the pure one, thus generating a larger spin-orbital moment and d -orbital splitting in energy, as shown in Fig. 5(c).

Besides increasing trigonal prismatic ligand field, halogen doping also causes the change of the surface electric field. The halogens are expected to act as a source of n -type doping for monolayer WS_2 , since they have one additional p orbital electron [44]. The band structure in Fig. 3(b) shows that the F-doped $4 \times 4 \times 1$ monolayer WS_2 supercell has a magnetic ground state, and extra electrons are added to the occupied impurity level at about 55 meV below the CBM. Notably, a magnetic moment of approximately $1\mu_B$ ($0.97\mu_B$) from the p - d exchange between F $2p$ and W $5d$ orbitals has been formed, which indicates a potential diluted ferromagnetism property [45]. This reveals that the fluorine atoms are not fully ionized, which could be attributed to the strong spontaneous spin polarization in doping systems. Due to the excess electron from fluorine injecting, an asymmetric electric field is produced by charge redistribution near the fluorine anion, which results in a spin-polarized orbit moment at the K point. To sum up, halogen doping brings a larger spin-orbital moment as well as a magnetic moment of the W atom, and thus breaks the electric-field symmetry, causing a strong SOC effect. As a result, F doping gives rise to a remarkable SO splitting (83.55 meV) at the K point in the CBM of monolayer WS_2 , promising a way to form materials with diluted ferromagnetism property.

We have also researched the Cl, Br, and I doped $4 \times 4 \times 1$ monolayer WS_2 supercells (isoelectronic to F) by PBE + SOC and PBE, in analogy to that of F substitution. We find that in our PBE+SOC calculation, the SO splittings at the K point in the CBM are 63.84, 39.61, and 24.30 meV for Cl, Br, and I, respectively (see black line in Fig. 2). Here halogen doping leads to band splittings of 22.26, 13.17, and 16.04 meV in the case of no-considering SOC, respectively (see red line in Fig. 2). Interestingly, the SO splitting decreases with the increase of radius of dopant atom, as depicted in Fig. 2. In order to clarify this phenomenon, the partial charge distribution of halogen in bands $c1$ and $c2$ should be concerned [Figs. 4(a) and 4(b)]. We can clearly see that the contribution of the doping atoms in bands $c1$ and $c2$ weakens with the increase of the radius for different halogen atoms. In addition, the difference of partial charge distribution in bands $c1$ and $c2$ decreases

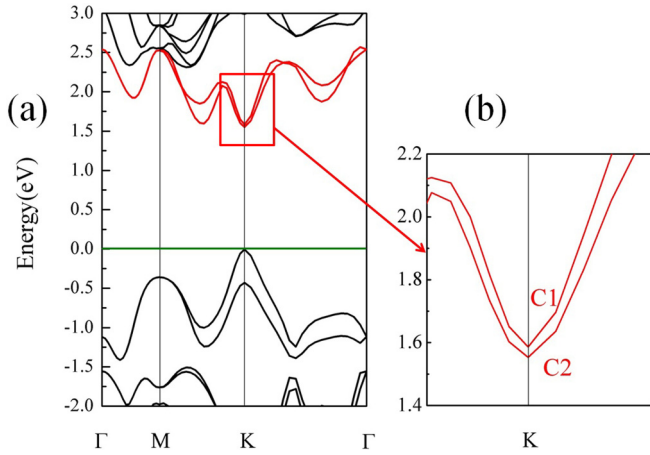


FIG. 6. (a) Band structure of unit cell for pure monolayer WS_2 calculated with PBE + SOC. (b) Enlarged image of the red frame in (a).

gradually. The F atom contributes to the $c2$ band instead of the $c1$ band, while the Cl atom contributes to $c1$ band, regardless of the $c2$ band. The Br atom has less contribution to the $c1$ band than the Cl and F atoms. And the iodine atom almost has no contribution to bands $c1$ and $c2$ because the additional electron remains unpaired and is localized around the impurity [46].

From the other aspect, the charges of W and S atoms transfer when doped with halogen, that the vicinity charges for halogen atom accumulate more with the increase of the atom radius, considering the same total number (385 for $4 \times 4 \times 1$ supercell) of valence charge in our system [Fig. 4(c)]. Consequently, both cases including the disaffinity of partial charge density of bands and charge transfer between W atom and S (or halogen) atoms lead to an asymmetric surface charge distribution and a huge orbit moment. This asymmetry evidently gives rise to a relatively larger Rashba spin splitting of surface states. We could know that from crystal-field theory, the ligands are ordered by the size of the induced splitting in trigonal prismatic ligand field (Dresselhaus effect): $\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$. As a combination of Rashba effect and Dresselhaus effect, a large SO splitting of 83.55 meV is achieved in the CBM at the K point with F doping.

In order to consider the band-folding effect of the undoped monolayer WS_2 supercell, we have further calculated band structures of the unit cell using PBE + SOC methods (Fig. 6). The SO splitting at the K point in the CBM of the unit cell is 26 meV, which is in good agreement with the result reported [25]. However, the SO splitting of $4 \times 4 \times 1$ supercells is 3.66 meV [Fig. 3(f)]. Note that the SO splitting decreases with increasing the size of the simulation model. This is likely because of the reduction of wave vector k near the zone center as a result of the band folding. The large SO splittings in doped supercells using PBE + SOC (83.55 meV for F doped $4 \times 4 \times 1$ supercell) indicate that the increase of SO splitting mainly originates from the halogen doping. The n -type doped WS_2 with strong SOC interaction exhibits a high on/off current ratio at room temperature, along with high charge carrier density and mobility at low temperatures (reported by Ovchinnikov *et al.* [6]). These unique electronic properties of WS_2 accompanying larger SO splitting indicate great potential applications in electronic, optical, spintronic, and valleytronic devices [5–8].

More importantly, a large valley polarization in conduction bands (lifting of the degeneracy of spin and valleys at the K and K' points) is caused by halogen doping. We also take the F doping $4 \times 4 \times 1$ monolayer WS_2 supercell using PBE + SOC as an example. Band structures of pure and halogen doped monolayer WS_2 with the SOC are shown in Figs. 3(a)–3(e). As expected, spin degeneracy and degenerate valleys at the K and K' points are obtained for the pure system [Fig. 3(a)], whereas the band structure of F doped monolayer WS_2 [Fig. 3(b)] reveals large valley polarization in conduction bands, because the F $2p$ orbitals have the additional electron as compared to the S $3p$ orbitals, and the excess electron breaks the time-reversal symmetry [8]. The energy difference between the CBM at the K and K' points amounts to 13.83 meV. In addition, similar valley polarizations occur in Cl, Br, and I doped systems, but the values are smaller than that of the F doped one [see Figs. 3(c)–3(e)]. It is exciting to achieve a monolayer TMD material with valley polarization in the conduction bands via nonmagnetic dopants. Based on our calculated results regarding a large SO splitting and valley polarization in halogen doped monolayer WS_2 , we predict that the halogen-nitrogen family codoping would increase SO splitting and valley polarization in the CBM in monolayer TMDs. On the premise of ensuring the compensation of charges, a p - n junction-like monolayer TMD with large SOC could be realized, owing to the larger asymmetric electric field by codoping, which originates from getting both strong ligand field and asymmetric surface charges.

IV. SUMMARY

The SO splitting in the CBM gets significantly enhanced by doping halogen atoms (F, Cl, Br, and I) in monolayer WS_2 , using the first-principles calculation. We find that halogen doping leads to an asymmetric electric field in monolayer WS_2 . This results in a sizable orbital moment as well as a large SO splitting (83.55 meV for F doped $4 \times 4 \times 1$ supercell using PBE + SOC) at the K point of CBM considering the strong SOC interaction from the enhanced trigonal prismatic ligand field and increased asymmetric surface charge. And halogen doping also breaks the time-reversal symmetry, leading to the large valley polarization in the conduction band. As can be identified, band structures of $4 \times 4 \times 1$ supercells using PBE + SOC and HSE + SOC, and $5 \times 5 \times 1$ supercells using PBE + SOC follow a similar trend: the SO splitting decreases with the increase of the radius of a dopant atom. The SO splitting values decrease with diluting the dopant concentration. Due to large SO splitting in the conduction band, these two-dimensional materials manifest great potential applications in optoelectronic, spin electronic, and valley spintronic devices.

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