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Article

Hidden spin polarization in the 1*T*-phase layered transition-metal dichalcogenides MX_2 (M = Zr, Hf; X = S, Se, Te)

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ABSTRACT

The recent discovery of hidden spin polarization emerging in layered materials of specific nonmagnetic crystal is a fascinating phenomenon, though hardly explored yet. Here, we have studied hidden spin textures in layered nonmagnetic 1*T*-phase transition-metal dichalcogenides MX_2 (M = Zr, Hf; X = S, Se, Te) by using first-principles calculations. Spin-layer locking effect, namely, energy-degenerate opposite spins spatially separated in the top and bottom layer respectively, has been identified. In particular, the hidden spin polarization of β-band can be easily probed, which is strongly affected by the strength of spin–orbit coupling. The hidden spin polarization of ξ-band locating at high symmetry M point (conduction band minimum) has a strong anisotropy. In the bilayer, the hidden spin polarization is preserved at the upmost Se layer, while being suppressed if the $ZrSe_2$ layer is taken as the symmetry partner. Our results on hidden spin polarization in 1*T*-phase dichalcogenides, verifiable by spin-resolved and angle-resolved photoemission spectroscopy (ARPES), enrich our understanding of spin physics and provide important clues to search for specific spin polarization in two dimensional materials for spintronic and quantum information applications.

1. Introduction

Layered transition-metal dichalcogenides (TMD) in the form of MX_2 (M = Metal, X = S, Se, Te) have attracted intensive attentions thanks to the fact that they serve as a playground for diverse fundamental phenomena and potential applications [1–11]. Depending on how the chalcogenide atoms are sitting on each side of the metal layer, there are two polymorphs for monolayer TMDs: 1*T*-phase with D_{3d} point group and 2*H*-phase with D_{3h} point group. The physical properties of molybdenum disulfide (MoS_2) with the 2*H* structure, as a representative two-dimensional (2D) TMDs, have been widely studied. It exhibits a series of intriguing attributes that are different from its bulk form, including switchable thickness-dependent band gap [12], strong photoluminescence [13], special magnetic structure by transition metal doping [14–16], and nonlinear Rashba spin splitting under external electric field [17]. Compared with 2*H* TMDs, 1*T*-phase TMDs receive relatively less attention, but might also possess outstanding properties. For example, 1*T*-phase zirconium and hafnium dichalcogenides are considered for photovoltaic applications due to their suitable band gap for visible light absorption [18,19]. Moreover, the monolayer TMDs with CdI_2 type structure are expected to realize low lattice thermal conductivity and enhanced figure of merit (Z_T) due to the strong hybridization of low-lying optical modes with acoustic modes [20–22].

Spin-orbit coupling (SOC) can induce spin polarization in nonmagnetic three-dimensional (3D) crystals when the inversion symmetry is broken, as manifested by the bulk Rashba-type (referred to as R-1) and Dresselhaus-type (referred to as D-1) effects [23,24]. Recently, a new insight indicates that fundamental spin polarization effects can originate from the local asymmetry (atomic site group) rather than the global asymmetry (bulk space group) [25]. Consequently, the doubly degenerate bands due to inversion symmetry and time reversal symmetry in nonmagnetic centrosymmetric materials could have opposite polarization, each spatially localized on one of the two separate sectors forming the inversion partners. In other words, spin-layer locking effect, where spin polarization spatially separated in two real space sectors forming the inversion partners, can be invoked, which introduces type-2 Rashba (R-2) and Dresselhaus (D-2) effects. Compared with the R-1 effect under a large internal electric field, the R-2 effect may have advantages for electrically tunable spintronics devices due to the easy manipulation of spins via the application of an external electric field [26–28].

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In experiment, hidden spin-polarized bulk bands in an inversion-symmetric bulk TMDs (for example, bulk WSe_2 [29] and bulk MoS_2 [30]) have been observed. A lot of theoretical works have been reported on hidden spin polarization in centrosymmetric materials [31,32]. Moreover, Bruyer et al. [33] proposed the possibility of combining ferroelectricity and Rashba-like spin splitting in monolayer 1*T*-phase transition-metal dichalcogenides MX_2 (M = Mo, W; X = S, Se, Te). Recently, helical spin texture with spin-layer locking in monolayer $PtSe_2$ has been revealed by combining spin- and angle-resolved photoemission spectroscopic (spin-ARPES) measurements [34]. Such spin physics including a local Rashba effect possesses a great potential for building electric-field-tunable spintronic devices. The investigation of hidden spin polarization in two-dimensional materials with local centrosymmetry opens a new era. Therefore, prediction and realization of hidden spin polarization in layered materials becomes an important research frontier for materials science and quantum physics.

In this work, we present a systematic study on the hidden spin polarization in 1*T*-phase layered TMDs MX_2 (M = Zr, Hf; X = S, Se, Te) based on accurate first-principles calculations. Our results show that spin-layer locking exists in 1*T*-phase monolayer and bilayer MX_2. In particular, the spin-layer locking is most significant for the β-band in valence, which is strongly affected by the strength of spin-orbit coupling and can be easily explored in experiment. The conduction band minimum of ξ-band, located at the high symmetry M point, has a strong anisotropy in helical hidden spin texture. The helical hidden spin texture of bilayer $ZrSe_2$ is preserved if the upmost Se layer is considered as the inversion symmetry partner, while being suppressed with the upper $ZrSe_2$ layer as a whole considered as the inversion symmetry partner. The hidden spin polarization in 1*T*-phase TMDs can be verified by spin-resolved angle-resolved photoemission spectroscopy. This work sheds new light on hidden spin structures to enrich our understanding of spin polarization physics and provides important clues for designing new materials with specific spin texture and spintronic applications.

2. Methods

The optimized geometry and electronic structure of 1*T*-phase MX_2 materials are obtained from first-principles plane wave calculations within density functional theory (DFT) as implemented in the Vienna *ab initio* simulation package (VASP) [35–37]. The projector augmented-wave (PAW) method [38] and Perdew-Burke-Ernzerhof (PEB) exchange-correction functional [39] are used. A cutoff energy of 500 eV for the plane-wave basis set and a Monkhorst-Pack mesh [40] of $12 \times 12 \times 1$ for the Brillouin zone integration are employed for relaxation and $21 \times 21 \times 1$ for self-consistent calculations. Spin-orbit coupling is taken into account to obtain the spin texture. Spin-orbit coupling is calculated by a perturbation $\sum_{i,l,m} V_l^{SO} \vec{L} \cdot \vec{S} |l,m,i\rangle\langle l,m,i|$ to the pseudopotential, where $|l,m,i>$ is the angular momentum eigenstate of the *i*th atomic site [41]. The spin polarization is evaluated by projecting the calculated wavefunction $|\phi\rangle$ on the spin and orbital basis of each atomic site $C_{i,l,m,\eta}\langle\phi|(s_\eta \otimes |l,m\rangle_{ii}\langle l,m|)|\phi\rangle$ and then summing $C_{i,l,m,\eta}$ for a given spin direction and sector that contains a number of atomic sites in the unit cell. In order to eliminate the spurious interaction between two adjacent monolayers, a vacuum layer larger than 17 Å is adopted in the calculations. All the structures are fully relaxed by using the conjugate gradient method until the maximum Hellmann-Feynman forces acting on each atom is less than 0.01 eV/Å. The phonon dispersion is calculated using density functional perturbation theory [42] as implemented in phonopy code [43].

3. Results and discussion

3.1. Atomic structure of 1*T*-phase MX_2

Bulk MX_2 (M = Zr, Hf; X = S, Se, Te) has a stable 1*T*-phase layered structure with weak interlayer interactions, corresponding to the CdI_2-type trigonal structure with $P\bar{3}m1$ space group (No. 164, D_{3d}). In each layer, the transition metal M atoms are sandwiched by the top and bottom chalcogen X layers with inversion symmetry, where the M atoms are octahedrally coordinated by the X atoms. The atomic structure of MX_2 is shown in Fig. 1. In monolayer MX_2, the top layer chalcogens X (red dotted rectangle online) and bottom layer chalcogens X (blue dotted rectangle online) are the inversion symmetry partners, which can be distinguished as the upper-sector and down-sector (labeled up- and down-component, respectively). Meanwhile, in the bilayer $ZrSe_2$, either we choose the upmost Se (Se1) and the bottom Se (Se4) layer as inversion symmetry partners, or the upper and bottom $ZrSe_2$ layer to form the complete symmetry partners for the bilayer $ZrSe_2$ (see Fig. 1).

Note that the possible polymorphs in monolayer MX_2 can only be of trigonal (*T*) or hexagonal (*H*) symmetry [44]. The lattice constants of 1*T*-phase monolayer Zr-compounds (ZrS_2, $ZrSe_2$, $ZrTe_2$) are calculated to be 3.68, 3.80 and 3.95 Å, respectively. For comparison, the lattice constants of 1*T*-phase monolayer Hf-compounds (HfS_2, $HfSe_2$, $HfTe_2$) are calculated to be 3.64, 3.76 and 3.97 Å, respectively. All these values are obtained on the level of DFT with PBE functional, and are well consistent with previous results [20–22]. The 2*H*-phase of monolayer Zr- and Hf-compounds is dynamically unstable judged from the phonon dispersion relation (see Fig. S1a and b online for monolayer $ZrSe_2$ as an example) and the fact that the energy of 2*H*-phase is several hundred meV higher than that of the corresponding 1*T*-phase (Table S1 online). Therefore, we focus on the dynamically stable, 1*T*-phase of monolayer TMDs as shown in Fig. 1a.

3.2. Electronic structure and spin textures of monolayer $ZrSe_2$

We first investigate the electronic structure of monolayer $ZrSe_2$ as an example. The band structure of monolayer $ZrSe_2$ is shown in Fig. 2a, where the conduction bands (CB) and valence bands (VB) are shown in the upper and lower panel, respectively. It is consistent with experimental band structure measured by ARPES [45]. Note that all the energy bands are doubly degenerate because of the inversion symmetry and time reversal symmetry.

Fig. 2b shows the orbital-projected electronic band structure. The bottom three conduction bands (labeled as **θ**, **η** and **ξ** in Fig. 2a, respectively) is mainly composed of the 4*d* orbitals of Zr atoms. The conduction band minimum (CBM) is located at the high symmetry M point, which is mainly composed of d_{xz}, d_{z^2} orbitals of Zr atoms and a part of out-plane p_z orbital of Se atoms. Moreover,

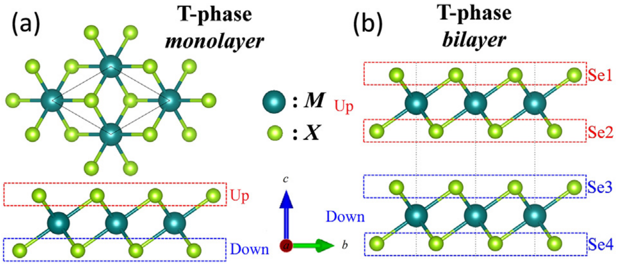

Fig. 1. (Color online) Atomic structure for the 1*T*-phase of layered MX_2 materials. (a) The top and side view of 1*T*-phase MX_2 monolayer. The thin black line denotes the unit cell. (b) Side view of 1*T*-phase (AA-stacking) bilayer MX_2.

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