Manipulation of valley splitting for the WSe$_2$/NiCl$_2$ heterostructure by adjusting the interlayer spacing and constructing a NiCl$_2$/WSe$_2$/NiCl$_2$ heterojunction

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Abstract

The electronic band structure and valley splitting of the WSe$_2$/NiCl$_2$ heterostructure have been investigated by density functional theory and Berry curvature calculations. We demonstrate that the valley polarization of monolayer WSe$_2$ is induced due to the magnetic proximity effect caused by the single layer of ferromagnetic NiCl$_2$. The magnitude of valley splitting depends on the stacking configurations of WSe$_2$/NiCl$_2$, and the maximum value of valley splitting reaches $-11.87$ meV. Large valley splitting can be achieved by adjusting the layer spacing and constructing a NiCl$_2$/WSe$_2$/NiCl$_2$ heterojunction with Ni spins arranged in parallel between two NiCl$_2$ sheets. The valley-contrasting Berry curvature between the K and K' valleys suggests that the WSe$_2$/NiCl$_2$-based heterostructure could potentially be used as a valleytronic device to realize the valley-polarized anomalous Hall effect as both spin and valley filter.

1. Introduction

The success of research in graphene [1] has developed interest in the study of other single-layer 2D materials, such as silicene [2], black phosphorus [3], and transition metal dichalcogenides (TMDCs) [4–6]. TMDCs, such as MX$_2$ (M = Mo, W and X = S, Se), are semiconducting graphite analogues composed of a layer of atoms covalently bonded; the stacks of these layers are held together by van der Waals interactions [7, 8]. Recently, the atomically thin 2D layered TMDCs have been extensively investigated due to their unique electronic properties and coupled spin-valley degrees of freedom [8, 9]. The monolayer of TMDCs possesses a pair of inequivalent valleys in the vicinities of the vertices of hexagonal Brillouin zone (BZ) [10]. TMDCs are considered good candidates for the valley and the Berry phase-related physics, also called valleytronics, due to the strong spin–orbit coupling, valley-contrasting Berry curvature, and broken intrinsic inversion symmetry [11–13].

In valleytronics applications of monolayer TMDCs, the valley polarization between K and K' should be introduced to exploit the valley degrees of freedom. The broken inversion symmetry of monolayer TMDCs could separate the paired valleys K and K' in the momentum space; however, the energy degeneracy still remained because it is protected by the time-reversal symmetry [13]. A key factor to achieve valley polarization is to lift the valley degeneracy by breaking the time-reversal symmetry. Previous studies have shown many ways of lifting the K–K' valley degeneracy. The optical pumping with circularly polarized light is one way to achieve valley polarization; however, optical pumping is difficult to robustly manipulate and inapplicable for practical valleytronic applications [14–16]. Other studies have shown that the magnetic field can be applied to lift the valley degeneracy. However, a large intensity of magnetic field is needed. For instance, the small valley splitting values in monolayer WSe$_2$ and MoSe$_2$ were approximately $0.2$ meV T$^{-1}$ [17, 18] and $0.12$ meV T$^{-1}$ [19], respectively. Recent studies have shown that the proximity-induced...
Zeeman effect is an effective strategy to achieve considerable valley splitting with a large effective Zeeman field (EZF). A giant valley splitting has been theoretically predicted in MoTe2/EuO (440 T EZF) [20], MoS2/EuS (20 T EZF) [21], and MoS2/CoO (152 T EZF) [22]. The enhanced valley splitting in monolayer WSe2 by exploiting the magnetic proximity effect from the EuS substrate was experimentally reported; the substrate provides the EZF of 12 T [23, 24]. Xu et al also reported the valley splitting and polarization in the WSe2/CrI3 heterostructure and detected a large EZF of approximately 13 T [25].

Monolayer NiCl2, which can be successfully fabricated from its layered bulk crystals, is a promising 2D intrinsic ferromagnetic (FM) semiconductor with an energy band gap of 2.4–2.8 eV [26, 27], and the FM Curie temperature is 120 K [28]. A recent study found that the cleavage energy of NiCl2 is 0.223 J m−2, which is smaller than that of graphite, thereby implying that it can be easily exfoliated down to the monolayer [28]. In this work, we theoretically study the electronic and valleytronic properties of the WSe2/NiCl2 heterostructure by first principle calculation. The results show that the K–K′ valley degeneracy is lifted with a large valley splitting (−11.87 meV). The K–K′ valley splitting depends on the stacking types that possess varying interlayer spacing. A large valley splitting can be achieved by building a NiCl2/WSe2/NiCl2 heterojunction. The result of the calculated Berry curvature indicates that the valley Hall effects could occur in this WSe2/NiCl2 heterostructure.

2. Computational details

Our calculations, including geometric relaxation and electronic structure calculation, were performed by using density functional theory (DFT) on the basis of projector augmented wave implemented in the VASP package [29, 30]. The exchange correlation potential was described with Perdew–Burke–Ernzerhof of the generalized gradient approximation; the van der Waals interaction was considered using the DFT-D2 method [31]. In structural optimization, consideration of spin–orbit coupling (SOC) has nearly no effect on the structural properties such as the bond length and bond angle by our test calculations. Therefore, in order to save computing resources and speed up the calculation, we did not consider SOC in structural optimization, but in the calculation of electronic structure. An energy cutoff of 450 eV was employed for the plane-wave basis set. A 15 × 15 × 1 k-sampling generated by the Monkhorst-Pack scheme for the BZ was adopted. During the structural relaxation, the energy convergent criterion was 10−5 eV per unit cell. The force convergent criterion on all relaxed atoms was less than 0.02 eV Å−1. We conducted test calculations for U values ranging from 3 eV to 6.5 eV with J = 0 eV to include the strong on-site Coulomb interaction in NiCl2 [32]. The result indicated that the magnetic moment and lattice constant showed a weak dependence on the U value, while the band gap was sensitive to it. The values of 4.0 and 0 eV for U and J, respectively, were suitable for the further calculations of the electronic structure because the calculated band gap of 2.59 eV is in agreement with the experimental value of 2.4–2.8 eV of the parameters. The in-plane lattice constants of the optimized free-standing monolayer WSe2 and NiCl2 were 3.40 and 3.49 Å, respectively. These values are in good agreement with the previous theoretical study, thereby resulting in a 2% lattice mismatch of the WSe2/NiCl2 heterostructure. In the Berry curvature calculation of the WSe2/NiCl2 heterostructure, we used the maximally localized Wannier function method, as implemented in the WANNIER90 package, to construct real-space maximally localized Wannier functions (MLWFs) after obtaining the self-consistent ground state of the system under study [33].

3. Results and discussion

3.1. Geometric structure of the WSe2/NiCl2 heterostructure

We considered six possible stacking configurations (T1–T6) in the WSe2/NiCl2 heterostructure (figures 1(a)–(f)): (a) Se right above the midpoint of the Ni–Clup bond; (b) Se over Ni and W over Cldn; (c) Se over Clup and W over Ni; (d) Se over Clup and W over Cldn; (e) Se over Clup and W over Ni; (f) Se over Ni and W over Clup. Meanwhile, we defined d as the distance between the lower layer Se atoms and the Clup atoms (figure 1(a)). The top and side views of NiCl2 and WSe2 are shown in figures 1(b) and (g), respectively. The BZ with the high symmetry points and the k-path used for presenting the band structures are shown in figure 1(i). After fully relaxing the structures, we calculated the binding energies of the six configurations by using the following formula [34]:

\[ E_b = (E_h - E_w - E_n) / N, \]  

where \( E_h \) and \( E_w \) and \( E_n \) are the total energies of the WSe2/NiCl2 heterostructure and isolated monolayers WSe2 and NiCl2, respectively; and \( N(N = 6) \) is the total number of atoms in the heterostructure. The calculated interlayer spacing, binding energies, and valley splitting are shown in table 1. The results of the
Figure 1. Top and side views of (a)–(f) the T1–T6 structural models for WSe2/NiCl2, (g) monolayer WSe2, and (h) monolayer NiCl2. (i) Hexagonal BZ and k-path used for presenting the band structures. The grey, yellow, brown, and green spheres represent W, Se, Ni, and Cl atoms, respectively.

Table 1. Calculated equilibrium interlayer spacing $d$ between WSe2 and NiCl2, interlayer binding energy $E_b$ per atom of the six stacking configurations (T1–T6), and valence splitting $\Delta VB$, conduction splitting $\Delta CB$, and total valley splitting $\Delta KK'$ of the four stable configurations (T1, T2, T5, and T6) for the WSe2/NiCl2 heterostructure.

| Stacking | $d$ (Å) | $E_b$ (meV) | $\Delta VB$ (meV) | $\Delta CB$ (meV) | $\Delta KK'$ (meV) |
|----------|---------|-------------|------------------|------------------|------------------|
| T1       | 3.137   | −1.3041     | 2.34             | 3.52             | 1.18             |
| T2       | 3.192   | −1.2997     | −5.64            | 3.49             | 9.13             |
| T3       | 3.719   | −1.2591     | −            | −            | −            |
| T4       | 3.712   | −1.2597     | −            | −            | −            |
| T5       | 3.215   | −1.3        | 8.6             | −3.27            | −11.87           |
| T6       | 3.171   | −1.3036     | 7.36             | −3.65            | −11.01           |

binding energies show that all the six stacking configurations can stably exist due to their negative values with only a little energy difference [34]. The binding energies and interlayer spacing of T1, T2, T5, and T6 are significantly smaller than those of T3 and T4, thereby indicating that the T1, T2, T5, and T6 configurations are more stable and have a stronger interfacial interaction than the T3 and T4 configurations. Further, the phonon spectra were calculated for six possible stacking configurations (T1–T6) as shown in figure S1 (https://stacks.iop.org/NJP/22/103061/mmedia). It is clear that the phonon dispersion of T1, T2, T5 and T6 has no imaginary frequencies, which indicates that T1, T2, T5 and T6 are dynamically stable. Therefore, in the following discussion we only consider the four configurations, T1, T2, T5, and T6.

3.2. $K$–$K'$ valley splitting in WSe2/NiCl2

In this part, we study the valley splitting of the WSe2/NiCl2 heterojunction. The $K$ and $K'$ valleys for pristine single layer WSe2 energetically degenerate (figure 2(a)). When WSe2 is placed on a magnetic substrate, the $K$–$K'$ valley degeneracy is lifted due to the exerted exchange field (figure 2(b)). The electrons in the two valleys can be selectively excited by the $\sigma^+$ and $\sigma^-$ photons because of the conservation of the angular momentum required by optical transition selection rules and the opposite valley angular
momentum in the $K$ and $K'$ valleys [11]. Accordingly, the $K$–$K'$ valley splitting can be characterized by the optical transition energy difference between the $E(\sigma^+)$ and $E(\sigma^-)$ [i.e., $\Delta KK' = E(\sigma^+) - E(\sigma^-)$] [35]. The valley spin subbands in the spin-up state are labeled as $VB_1'$, $CB_1'$, $VB_2$, and $CB_2$, and they are labeled as $VB_2'$, $CB_2'$, $VB_1$, and $CB_1$ in the spin-down state (figure 2(b)). These subbands are involved in the optical excitation and valley polarization of WSe$_2$. The $K$–$K'$ valley splitting can be also expressed as $\Delta KK' = \Delta CB - \Delta VB$, where $\Delta VB = E_{VB1}' - E_{VB1}$ and $\Delta CB(\Delta CB = E_{CB1}' - E_{CB1})$ stand for the valley splitting of valance band (VB) and conduction band (CB), respectively. We calculated the band structures of $T_1$, $T_2$, $T_3$ and $T_6$ stacking configurations (figure S2), which show that the band dispersion are similar with only a little detailed difference. Figures 3(a) and (b) show the band structure of $T_5$, with NiCl$_2$, respectively. The charge density difference of $T_5$ is shown in figure 3(c), where the yellow (blue) regions represent the net charge gain (loss). The charges at the interfaces are redistributed. The Se atoms close to the interface lose charges, while a significant charge accumulation occurred in the interfacial Cl atoms. Based on the Bader charge analysis, we find that the amount of 0.05e has been transferred from the WSe$_2$ to NiCl$_2$, showing slightly a covalent bonding character. The DOS show that the CB minimum is dominated by the states of Ni and Cl atoms, while the states of W and Se atoms mainly contribute to the VB maximum, exhibiting a quasi-II-type band alignment because the NiCl$_2$ DOS within 0.05–0.5 eV are involved in the band gap (figure 3(a)).

The valley splitting value of $T_3$ stack is the largest among the four stacking configurations. Hence, we calculated the charge density difference and density of states (DOS) for $T_3$, and the results are shown in figures 3(a) and (c), respectively. The charge density difference $\Delta \rho$ is defined as follows:

$$\Delta \rho = \rho - \rho(WSe_2) - \rho(NiCl_2), \quad (2)$$

where $\rho$, $\rho(WSe_2)$ and $\rho(NiCl_2)$ represent the charge densities of the heterostructure, monolayer WSe$_2$, and NiCl$_2$, respectively. The side view of charge density difference of $T_3$ is shown in figure 3(c), where the yellow (blue) regions represent the net charge gain (loss). The charges at the interfaces are redistributed. The Se atoms close to the interface lose charges, while a significant charge accumulation occurred in the interfacial Cl atoms. Based on the Bader charge analysis, we find that the amount of 0.05e has been transferred from the WSe$_2$ to NiCl$_2$, showing slightly a covalent bonding character. The DOS show that the CB minimum is dominated by the states of Ni and Cl atoms, while the states of W and Se atoms mainly contribute to the VB maximum, exhibiting a quasi-II-type band alignment because the NiCl$_2$ DOS within 0.05–0.5 eV are involved in the band gap (figure 3(a)).

We further adjusted the interlayer spacing ($d$) and calculated the corresponding valley splitting for $T_3$ to examine the effect of interfacial distance on the valley splitting (figure 3(d)). In the structural models, $d$ takes nine values, namely, 2.9, 3.0, 3.1, 3.3, 3.5, 3.7, 3.9, 4.1 and 4.3 Å, around the most stable value.

**Figure 2.** (a) Illustration of $K$–$K'$ valley degeneracy, $E(\sigma^+)$ and $E(\sigma^-)$ represent the interband optical transition energies of the right-hand ($\sigma^+$) and left-hand ($\sigma^-$) circularly polarized photons, respectively. (b) Illustration of lifting of $K$–$K'$ valley degeneracy. $\Delta VB$ and $\Delta CB$ stand for the valley splitting of VB and CB, respectively.
Figure 3. Calculated band structure and DOS of T5 with (a) NiCl₂ magnetized upward, and with (b) NiCl₂ magnetized downward. The insets show the magnified band region near the $K$ and $K'$ valleys. (c) Side views of the charge density differences for the T5 model of the WSe₂/NiCl₂ heterostructure. The yellow (blue) regions represent the net charge gain (loss). (d) Relationship between interlayer spacing $d$ and valley splitting changes. The dashed line represents the most stable distance. $\Delta V_B$ and $\Delta C_B$ represent the valence and conduction valley splitting, respectively. $\Delta K K'$ represents the valley splitting.

(3.215 Å) of interlayer spacing. After structural optimization, the results show that the minimum value of $d$ is 3.015 Å. The valley splitting expands with the decrease in the interlayer spacing. However, the interfacial interaction is weakened, and $\Delta C_B$, $\Delta V_B$ and $\Delta K K'$ are reduced when $d$ is increased. The optimized $d$ value of 3.015 Å corresponds to the valley splitting of $-19.4$ meV. And when the value of $d$ is 4.32 Å, the splitting valley basically disappears. This finding indicates that the valley splitting can be effectively adjusted by changing interlayer spacing $d$.

3.3. Valleytronic properties of the WSe₂/NiCl₂ heterostructure

We address the character of the Berry phase of the WSe₂/NiCl₂ heterostructure. This study takes T₅ as an example. Berry curvature $\Omega(k)$ is an odd function of $k$ in the presence of time reversal symmetry and an even function in the presence of spatial inversion symmetry [36]. In WSe₂/NiCl₂, the time inversion symmetry is broken, thereby allowing nonzero values for $\Omega(k)$ and the valley contrasting properties. The nonzero Berry curvature can change the motion of carriers and make the system exhibit certain special transport properties, such as the valley Hall effect [37]. These effects enable valley polarization through electric or magnetic fields to be generated and detected, and the free storage and processing of information in the valley can be utilized [19, 38]. According to the Kudo equation, the Berry curvature can be expressed as the summation of all occupied contributions [39, 40]:

$$\Omega(k) = -\sum_{n} \sum_{n' \neq n} f_n \frac{2 \text{Im} \langle \psi_{nk} | v_x | \psi_{n'k} \rangle \langle \psi_{n'k} | v_y | \psi_{nk} \rangle}{(E_n - E_{n'})^2}$$

where $f_n$ is the Fermi–Dirac distribution function, $v_{x(y)}$ is the velocity operator, and $|\psi_{nk}\rangle$ is the Bloch wave function with eigenvalue $E_n$. To ensure the calculation accuracy of the Wannier base functions, we first plotted the tight binding band structure using MLWFs shown in figure 4(a). We found that the band dispersion coincided well with the DFT result (figure 3(a)), indicating that the produced Wannier base functions were sufficiently localized and the accuracy of the calculation was ensured. Figures 4(b) and (c) demonstrate that the calculated Berry curvature at the $K$ and $K'$ valleys of WSe₂/NiCl₂ are nonzero and
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opposite, similar to monolayer WSe$_2$. This finding suggests that the magnetic proximity effect induced by NiCl$_2$ maintains the valley-contrastive characteristic of monolayer WSe$_2$. Under an in-plane longitudinal electric field, the Berry curvature will give rise to an anomalous transverse velocity $v_\perp$ for Bloch carriers (electrons or holes), $v_\perp \sim E \times \Omega(k)$ [41], and the carriers at the $K$ and $K'$ valleys will achieve opposite transverse velocity owing to the opposite signs of their Berry curvature. An illustration of the carrier movement is shown in the insets of figure 4(c), where the plane corresponds to the $xy$ plane of the WSe$_2$/NiCl$_2$ heterostructure. Compared with the band structure shown in figure 3(a), it is found that the spin-up holes at the $K'$ valley will move toward the upside in the presence of an in-plane external electric field due to their negative Berry curvatures. If the magnetic ordering of NiCl$_2$ is reversed from up to down (figure 3(b)), the spin-down holes at the $K$ valley will act as free carriers and move toward the downside since they have positive Berry curvatures. The hole carriers with $K$ or $K'$ nature will accumulate at one transverse edge, and then a sizable voltage can be measured owing to the anomalous Hall effect. Thus, the 2D WSe$_2$/NiCl$_2$-based heterostructure could potentially be used as a valleytronic device to realize the valley-polarized anomalous Hall effect and filter carriers with certain spin and valley indexes.

3.4. $K$--$K'$ valley splitting in NiCl$_2$/WSe$_2$/NiCl$_2$

We have increased the heterostructure from two to three layers to achieve a huge valley splitting. A layer of WSe$_2$ exists between the two layers of NiCl$_2$. According to our above calculated results, we found that $T_1$ is the most stable configuration and the valley splitting value of $T_5$ is the largest among the four stable configurations $T_1$, $T_2$, $T_3$, and $T_5$. So, four structures ($A_1$, $A_2$, $A_3$, and $A_4$) are constructed on the basis of the above-mentioned $T_1$ and $T_5$ ($A_1$ and $A_2$ correspond to $T_1$; $A_3$ and $A_4$ correspond to $T_5$) (figure 5(a)). Two types of spin alignments of the NiCl$_2$ layers are considered to study the valley splitting properties. In the first case, the Ni spins are aligned in parallel between the two NiCl$_2$ sheets, denoted as $\uparrow\uparrow$. The first and second arrows represent the identical Ni spins in the two NiCl$_2$ sheets. In the second case, Ni spins at the top and bottom NiCl$_2$ sheets are in an antiparallel alignment. We label this case as $\uparrow\downarrow$. The calculated band structures of stacking configurations $A_1$, $A_2$, $A_3$, and $A_4$ are shown in figure S3. The interlayer spacing and valley splitting of the four stacking configurations are illustrated in table 2. The valley splitting of $\uparrow\downarrow$ is notably weaker than that of $\uparrow\uparrow$. $A_4(\uparrow\uparrow)$ possesses the largest value ($-19.94$ meV) of $\Delta K\Delta K$ among the four configurations, and its band structure is shown in figure 5(b). In the parallel alignment $\uparrow\uparrow$, the valley splitting for $A_1$, $A_2$, $A_3$, and $A_4$ is distinctly larger than the corresponding double-layer heterostructure WSe$_2$/NiCl$_2$. This finding indicates that the magnetic effect of the two NiCl$_2$ sheets is more greatly enhanced than that of the single NiCl$_2$ sheet in WSe$_2$/NiCl$_2$. In the antiparallel alignment $\uparrow\downarrow$, the valley splitting for $A_2$, $A_3$, and $A_4$ is notably smaller than corresponding double-layer heterostructure WSe$_2$/NiCl$_2$. This finding indicates that the magnetic effect of the two NiCl$_2$ sheets is greatly weakened. However, the magnetic field effect from the two NiCl$_2$ sheets does not completely disappear due to the unequal interlayer spacing between $d_1$ and $d_2$ (table 2); thus, the valley splitting still exist. In the $A_1$ stacking, the valley splitting of $\uparrow\downarrow$ has increased compared with $T_1$ of WSe$_2$/NiCl$_2$. These results further verify the critical role of the stacking configurations in the valley splitting in WSe$_2$/NiCl$_2$. One may pretreat a trilayer NiCl$_2$/WSe$_2$/NiCl$_2$ sample in a magnetic field to ensure a parallel alignment of the Ni spins in the two NiCl$_2$ sheets to achieve an enhanced valley splitting. This prediction needs further experimental verification. In any case, the heterojunction of the sandwich structure can also be used to adjust the valley splitting.

Figure 4. (a) Band structure calculated by MLWFs. (b) Contour map of the Berry curvature in the 2D BZ. (c) Berry curvature along the high-symmetry lines of the WSe$_2$/NiCl$_2$ heterostructure for the Fermi level located inside the band gap. The insets illustrate the carriers moment for the $K$ and $K'$ valleys.
4. Conclusions

In summary, we have calculated the structural properties, electronic properties, and Berry curvature of the WSe$_2$/NiCl$_2$ and NiCl$_2$/WSe$_2$/NiCl$_2$ heterostructures by first principle calculations in combination with MLWFs. The results demonstrate that valley splitting exists in T$_1$, T$_2$, T$_5$ and T$_6$ stacking configurations for the heterostructure. This result shows that valley splitting is sensitive to the arrangement of atoms between the two layers of the heterostructure. The valley splitting of the T$_5$ configuration can be changed by adjusting the layer spacing. The valley splitting can also be adjusted by aligning the Ni spins of the two NiCl$_2$ sheets and constructing a heterostructure of a sandwich structure NiCl$_2$/WSe$_2$/NiCl$_2$. The Berry curvature and spin splitting are opposite at the K and K$'$ valleys of the WSe$_2$/NiCl$_2$ heterostructure, thereby enabling simultaneous polarization and locking of the valley and spin quantum degrees of freedom. The results demonstrate that the WSe$_2$/NiCl$_2$-based heterostructure can be widely used in next generation multifunctional valleytronic devices for the anomalous Hall effect as both spin and valley filter.

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