Magnetic properties of bilayer VI₃: Role of trigonal crystal field and electric-field tuning

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The magnetic properties of two-dimensional VI₃ bilayer are the focus of our first-principles analysis, highlighting the role of trigonal crystal-field effects and carried out in comparison with the CrI₃ prototypical case, where the effects are absent. In VI₃ bilayers, the empty a₁₆ state - consistent with the observed trigonal distortion - is found to play a crucial role in both stabilizing the insulating state and in determining the inter-layer magnetic interaction. Indeed, an analysis based on maximally-localized Wannier functions allows to evaluate the interlayer exchange interactions in two different VI₃ stackings (labelled AB and AB’), to interpret the results in terms of virtual-hopping mechanism, and to highlight the strongest hopping channels underlying the magnetic interlayer coupling. Upon application of electric fields perpendicular to the slab, we find that the magnetic ground-state in the AB’ stacking can be switched from antiferromagnetic to ferromagnetic, suggesting VI₃ bilayer as an appealing candidate for electric-field-driven miniaturized spintronic devices.

I. INTRODUCTION

Boosted by the experimental discovery of intrinsic magnetism in atomically thin layers of CrI₃, Cr₂Ge₂Te₆ and Fe₃GeTe₂, two-dimensional (2D) van der Waals (vdW) magnets have recently received an increasing attention. Interestingly, the control of 2D magnetism in few atomic layers is enabled by external electric field or by electron-hole doping making them particularly appealing for potential spintronic applications.

Among those materials, VI₃, belonging to the family of transition-metal (M) trihalides MX₃ (X = Cl, B, and I) with honeycomb arrangement of the metal cations (similar to the most studied CrI₃), has recently emerged as a potential 2D ferromagnet. It is known since more than 30 years ago that, in the bulk form, VI₃ becomes ferromagnetic below a Curie temperature of T_c ≃ 55 K, similar to CrI₃ (with T_c ≃ 68 K). Conversely, the structural properties are still under debate. Experimental characterizations of the crystal structure have in fact reported that VI₃ undergoes a structural phase transition around 79 K, changing its symmetry across still unclear phases: the high-temperature (HT) crystal structure was proposed to be either trigonal P3₁[1] or rhombohedral R̅3̅m[2] or monoclinic C2/m structure[3]. The low-temperature (LT) crystal structure was proposed to be either C2[4] or R3m[5]. Optical and electrical transport measurements have clearly showed bulk VI₃ to be a semiconductor with an optical band gap of ∼ 0.67 eV[6]. However, from the theoretical point of view, the understanding and modeling of the electronic properties are the focus of present debate. Some studies have in fact reported that bulk VI₃ is a Mott-insulator with a bandgap of about 1 eV[7], whereas others have claimed a half-metallic character[8].

In a thin-film limit, to the best of our knowledge, no experimental studies have been reported for atomic layers of VI₃. On the theoretical side, current studies are controversial with respect to the electronic properties, in analogy to the situation for the corresponding bulk phase. In particular, by analysing electronic properties in the VI₃ monolayer, in Ref[9] a Mott-insulator ground state is proposed, reported to be lower in energy than the half-metallic state (by ∼0.3 eV/f.u). Other attempts to explain the Mott-insulator ground state have also been reported: the authors in Ref[10] have proposed orbital-ordered phases accompanying the lattice distortion, while the authors of Ref[11] ascribed the gap opening to combined effects of spin-orbit coupling (SOC) and Hubbard U correlations. On the other hand, a consensus is reached with respect to the magnetic properties of a VI₃ single layer: current theoretical characterizations report a ferromagnetic (FM) exchange coupling between first V-site neighbors, i.e. FM intra-layer coupling. The inter-layer magnetic stability has also been investigated for bilayer VI₃. In particular in Ref[12] it is reported that the inter-layer magnetic stability is sensitive to the layer stacking, in line with previous works on bilayer CrI₃[13]. For the sake of completeness, we mention that in Ref[14] it is claimed bilayer VI₃ to show a stacking-independent ferromagnetic ground state, but considering the half-metallic state rather than the Mott-insulating one.

A deep understanding of the VI₃ electronic structure is needed to interpret the related magnetic properties, both in the monolayer and in the bilayer case. In this study, we therefore focus on the crucial role of trigonal crystal field effects in determining the VI₃ insulating behaviour and the related magnetic properties. As a counterexample, we consider the prototypical 2D magnet, i.e. CrI₃ (where trigonal crystal field effects are absent), and...
we carry out a one-to-one comparison between VI$_3$ and CrI$_3$. In particular, we first focus on the monolayer and discuss crystal field effects (Section III A) and density of states (Section III B). Then we move to the the magnetic properties of bilayer halides, by considering two different stacking arrangements. We concentrate on the interlayer exchange coupling, interpreting it in terms of virtual hopping mechanisms, highlighting the most efficient hopping paths (Section IV A) and addressing the effects of an external electric field in tuning the magnetic stability (Section IV B). Finally, we draw our conclusions in Section V.

II. COMPUTATIONAL METHOD

Density-functional theory (DFT) calculations were performed using the VASP code$^{23}$ within the generalized gradient approximation (GGA$^{24}$). The van der Waals (vdW) interactions were included for bilayer structure calculations. The rotationally invariant GGA + $U$ method was employed to account for correlation effects$^{25}$.

On-site Coulomb interaction for transition-metal 3$d$ orbitals was considered with an effective $U$ of 2.0 eV$^{24,26}$. Semiconducting and metallic states are initialized via the density matrix within the GGA+$U$ scheme$^{27}$. Brillouin zone integrations were performed using a $k$-point grid of $6 \times 6 \times 1$ for the structure optimization. Band structures and density of states (also including electric fields) were calculated by using $12 \times 12 \times 1$ $k$-points mesh. Electric fields are applied perpendicularly to the surface by saw-tooth-like potential with dipole correction$^{27}$. The maximally-localized Wannier functions (MLWFs) were calculated by using WANNIER90 tool$^{28}$ interfaced with the VASP code.

III. RESULTS FOR MONOLAYER VI$_3$

A. Crystal-field effects

First we focus on the difference between VI$_3$ and CrI$_3$ monolayers, as far as crystal field effects are concerned. In particular, both VI$_3$ and CrI$_3$ show the magnetic atom coordinated to six I atoms, forming edge-sharing octahedra and resulting in octahedral crystalline electric field (CEF) splitting of the $d$ orbitals into the two-fold $e_g$ and three-fold $t_{2g}$ states. The $t_{2g}$ state can be further split into a doublet $e'_g$ and a singlet $a_{1g}$ state to reduce the band energy, i.e. a Jahn-Teller (JT) effect in trigonal symmetry$^{29,30}$. This effect leads to the trigonal lattice distortion, but such JT-distortion is not remarkable in this system. The I-Cr-I bond angle in CrI$_3$ is almost 90° (i.e. a cubic octahedron), while the I-V-I angle in VI$_3$ approaches 89.9°. As such, it exhibits a trigonal distortion - elongation along the $z$ axis - still preserving spatial inversion symmetry [see Fig. 1(a) and (b)]. Fig. 1(c) and (d) show the difference in CEF splitting for VI$_3$ and CrI$_3$ respectively: as schematically represented, the JT-induced splitting allows for the band gap opening in VI$_3$ by half-filling the majority $e'_g$ channel and leaving the $a_{1g}$ empty in the case of V $d^2$. On the other hand, CrI$_3$ is unaffected both because of the Cr $d^3$ valence and the almost cubic CEF.

Within the global Cartesian $\{xyz\}$ coordinate system, the $a_{1g}$ and $e'_g$ states are written in the form$^{29}$:

$$|a_{1g}\rangle = 3z^2 - r^2$$
$$|e'_g\rangle = \frac{1}{\sqrt{2}} \left( \sqrt{2} (x^2 - y^2) - zx \right)$$
$$|e'_{g1}\rangle = \frac{1}{\sqrt{3}} \left( \sqrt{2} xy + yz \right)$$

(1)

where the $z$ axis is parallel to the out-of-layer direction (i.e. perpendicular to the slab). According to the different local crystal field effects, we projected the Bloch functions onto the local MI$_6$ octahedral coordinate system $\{x'y'z'\}$ for CrI$_3$ (with basis axes directed along the Cr-I bonds), and onto the Cartesian $\{xyz\}$ system for VI$_3$ [see Fig. 1(e) and (f)]

![Figure 1. Distortion of the crystal structure in (a) VI$_3$ and (b) CrI$_3$. The distortion does not change the bond length but alters the bond angle, leading to a trigonal elongation along the $z$-direction. (c) and (d) show the crystal field splitting of $d$ levels in V $3d^2$ and Cr $3d^3$, respectively. Five 3$d$ Wannier functions reflect the trigonal CEF states in monolayer VI$_3$ (e) and cubic CEF states in monolayer CrI$_3$ (f). The isosurface levels of the Wannier functions were set at 1.5 $a_0^{-3/2}$ (yellow) and $-1.5 a_0^{-3/2}$ (blue), where $a_0$ is the Bohr radius.](image)
After the projection and maximally localization process, the Wannier functions converged into localized orbitals, as shown in Fig. 1(e) and (f): orbitals shapes are in agreement with the \( e_g (a_{1g}, e'_g) \) states splitting induced by the trigonal CEF in VI\(_3\), and the \( e_g - t_{2g} \) states induced by the cubic CEF in CrI\(_3\). In particular, for the latter, it is possible to recognize the \( |3z^2 - r^2 \rangle \) orbital shape for the \( a_{1g} \) state (occupying the empty space at the center of the \( I_3 \) triangle and pointing along the \( z \)-direction) and mixed shapes from the \((|x^2 - y^2 \rangle, |zx \rangle)\) and \((|xy \rangle, |yz \rangle)\) orbitals for the \( e'_g1 \) and \( e'_g2 \) states respectively, according to Eq. (1).

B. Density of states

In line with previous works, our DFT calculations on monolayer VI\(_3\) converged to two different electronic states, corresponding to half-metallic[17] and Mott-insulator states[18,19]: the two \( V \ d^2 \) electrons occupy \( t_{2g} \) states as \( a_{1g} e'_g \) and \( e'_g a_{1g} \), respectively. We found that the insulating state (with a direct band gap of \( \sim 0.39 \) eV at the \( \Gamma \) point for \( U = 2.0 \) eV) is lower in energy than the half-metallic state by \( 1.8 \) eV/f.u. Therefore, we will focus hereafter on the Mott insulator state as the ground state. Although Yang et al. proposed that the insulating ground state of monolayer VI\(_3\) is stabilized by spin-orbit coupling (SOC) splitting rather than by CEF splitting, here we remark that the crystal field splitting is energetically dominant over the SOC effect, as usually seen in 3d transition-metal compounds[18,19]. In fact, when including SOC in our band structure calculations, we observed that it affects the width and energy bands related to the I-\( p \) states, but it does not significantly change the \( V \ 3d \) band structure. Moreover, as we focus here on the \( e'_g a_{1g} \) state, eventual SOC induced splitting would not affect the mechanisms and conclusions presented in this study.

The partial density of states (DOS) for monolayer CrI\(_3\) and VI\(_3\) are shown in Fig. 2. DOS are resolved for each MLWF state, clearly showing the trigonal CEF states. In particular, Cr-\( d \) states are split into \( e_g \), \( a_{1g} \), \( e'_g \) trigonal CEF states. In particular, \( e'_g \) is the lowest energy state with a broad distribution due to the \( pd \) hybridization below the Fermi level, similar to CrI\(_3\). On the other hand, the CEF splitting shows a different behaviour of the empty \( d \) states: the \( a_{1g} \) state becomes the lowest energy state, while the \( e'_g \) state still lies in the same energy region as the minority Cr-\( t_{2g} \) state. This is related to the fact that the \( e'_g \) state has more bonding character with surrounding I-\( p \) state than the \( a_{1g} \) state (compare the orbital shapes in Fig. 1(e)); therefore, the \( pd \) hybridization shifts unoccupied \( e'_g \) level up and occupied I-\( p \) level down.

IV. RESULTS FOR BILAYER VI\(_3\)

A. Electronic properties and inter-layer magnetic stability

Let us now consider the case of bilayer VI\(_3\), showing a similar atomic structure to its bulk counterpart. In particular, we studied two structures corresponding to \( R3 \) and \( C2/c \) phases in bulk VI\(_3\)[20]. The difference between
First, we remark that the robustness of the intra-layer FM spin ordering is demonstrated by calculating the energy difference between FM and Néel type antiferromagnetic AFM spin configurations in VI₃ monolayer, i.e. \( \Delta E = E_{\text{AFM}} - E_{\text{FM}} = 12.8 \text{ meV/f.u.} \). The V magnetic moment was calculated as 2.16 \( \mu_B \). We then address the magnetic properties of bilayers, by calculating the total energy between inter-layer FM and AFM orders for the two stackings in bilayer VI₃ and compared the results with those obtained in CrI₃. In bilayer VI₃, the interlayer FM and AFM spin configurations are very close in energy; nevertheless, the FM order is favored in the AB-stacking, while the AFM order is favored in AB’ stacking, as reported in Table 1. Differently, in bilayer CrI₃, the FM order is favored in both AB and AB’ stacking pattern. Noteworthy, the inter-layer FM order in AB’ stacking is only slightly more stable than the AFM order, the energy differences being rather sensitive to used on-site Coulomb \( U \) values, therefore not allowing a direct comparison with previous works on bilayer CrI₃. In any case, according to the energy differences reported in Table 1 the magnetic stability in bilayers VI₃ and in CrI₃ AB-stackings results to be weak. As such, it may lead to an easy control of the magnetism by either external electric fields or electrostatic doping.

To understand the magnetic stability, we evaluated the magnetic exchange interactions between V atoms by fitting total energies calculated in AB and AB’ stacking to the Heisenberg Hamiltonian. Here we assume the Heisenberg Hamiltonian,

\[
H = \sum_{\langle i,j \rangle} J_{ij} s_i \cdot s_j,
\]

where \( J_{ij} \) are the isotropic Heisenberg coupling constant between spin sites \( i \) and \( j \) and \( s_i \) is the unit vector pointing to the direction of the spin at site \( i \). A parallel spin (FM) configuration is favored when \( J < 0 \) and an anti-parallel (AFM) spin configuration is favored when \( J > 0 \).

In addition to the intra-layer (in-plane) first nearest-neighbor coupling (\( J_\parallel \)), we thus considered inter-layer couplings (\( J_1 \) and \( J_2 \) in AB stacking; \( J_1' \), \( J_2' \), \( J_3' \) and \( J_4' \) in AB’ stacking) as schematically illustrated in Fig. 3. The associated atomic pairs distances are reported in Table 1. In particular, we performed calculations to estimate \( J_2' \) and \( J_4' \) in a \( 2 \times 1 \times 1 \) supercell via the four-state energy mapping method. This method allows to consider one specific pair of spins and remove the background interactions, therefore allowing the calculation of the inter-layer magnetic exchange coupling constants of interest.

In Table 1 we report the estimated exchange coupling constants for bilayer VI₃ and CrI₃.

For VI₃, the intra-layer exchange coupling favors parallel spin state, while the inter-layer coupling eventually favors parallel spin state in AB-stacking and anti-parallel spin states in AB’-stacking, (cfr Table 1). In closer detail, in AB stacking, \( J_1 \) favours anti-parallel coupling (0.81 meV), while \( J_2 \) favours parallel coupling (−0.24 meV).

![FIG. 3. (a, b) Top views and (c, d) side views of atomic structure in bilayer VI₃ in AB and AB’ stacking. The red and orange hexagons represents honeycomb structure of V atoms in top and bottom layers, and gray balls represent I atoms. The black arrow indicates the vector which connects equivalent atoms located in two layers and shows how the top layer is sliding with respect to the bottom layer. Inter-layer exchange coupling \( J_{ij} \) in bilayer VI₃ for (e) AB and (f) AB’ stacking.](image-url)
Since there is one $J_1$ bond and nine $J_2$ bonds per unit cell, overall the ferromagnetic configuration is more stable. In AB’ stacking, both $J_1'$ and $J_2'$ favour anti-parallel coupling (0.1 meV and 0.21 meV), thus dominantly contributing to the inter-layer AFM coupling stability. For CrI₃, the intra-layer and inter-layer exchange coupling basically favor parallel spin states in both AB stacking and AB’ stacking.

In order to shed light on the microscopic mechanism behind the stacking-dependent magnetic couplings, we recall the “virtual hopping” idea based on the Hubbard model. In particular, we discuss the results in terms of the virtual inter-layer hopping of $e_g$-$t_{2g}$ states supported by the inter-layer M-I-I-M super-exchange effect. In the weak hopping limit, the inter-site hopping can be treated as a perturbation to the ground state in which magnetic ordering does not affect the energy. When the hopping process is allowed between occupied and unoccupied states, it in turn contributes to the ground state energy through the second-order contribution as the effective exchange energy $J_{\text{eff}} = 2t^2/U$ with hopping integral $t$ and Coulomb repulsion $U$, the process being called “virtual hopping”. If we consider the direct hopping between occupied and unoccupied 3d states at the transition metal sites, the parallel-spin configuration is favored if the hopping is strong between majority- and majority-spin states; on the other hand, the anti-parallel spin configuration is favored if the hopping between majority- and minority-spin states is strong. In order to discuss the virtual hopping process, we extracted the hopping parameters by using a MLWF basis set, as illustrated in Fig. [4](e) and (f). Note that the Wannier functions are centered at V and Cr sites and spreading the tail to I sites, so that our virtual hopping process implicitly includes the pd hybridization process. The same concept can be found in Anderson’s original work on super-exchange interaction.

Figure [4] shows the inter-layer hopping paths with the corresponding MLWFs which are responsible for the exchange energy in bilayer VI₃ and CrI₃. Here we select three types of inter-layer exchange couplings: first neighbor and second neighbor ($J_1$ and $J_2$) interactions in AB stacking; first neighbor ($J_1'$) interaction in AB’ stacking. The calculated hopping integrals corresponding to these exchange couplings are shown in Table. [III]

In AB-stacking bilayer VI₃, the trinodal CEF levels and the two-electron occupation make $J_1$ positive (anti-parallel-spin-favored). The hopping between $e_{g2}^\uparrow$ and $a_{1g}^\downarrow$ states are calculated to be negligible ($t \sim 0.0$ meV), thus not contributing to the magnetic interaction. On the other hand, the hopping between $e_{g2}^\downarrow$ and $e_{g1}^\uparrow$ states is sizable ($t = 1.0$ meV), which may be responsible for the anti-parallel-spin-favored exchange interaction. In AB-stacking bilayer CrI₃, in contrast, the negative (parallel-spin-favored) $J_1$ can be explained by a sizeable hopping between occupied $d_{x^2-y^2}$ state and unoccupied $d_{x^2-y^2}$ state ($t = 0.6$ meV). This is consistent with previous works, claiming that the $e_{g2}$-t₂g hopping leads to the FM coupling. As shown in Fig. [4](d), the diagonally elongated lobes of $d_{x^2}$ and $d_{x^2-y^2}$ orbitals show a path through Cr-I-I-Cr sites with $d_{x^2}$ and $d_{x^2-y^2}$ hybridization, where the first pd hybridization shows π-like and the second shows σ-like bonding. The second neighbor.

| Table II. Number of equivalent bonds per unit cell $N$, bond distance between transition-metal sites $d$, and calculated exchange coupling constants $J_{ij}$ in AB and AB’ stacking for bilayer VI₃ and CrI₃. |
|---|---|---|---|---|---|---|---|---|---|---|
| | AB stacking | | AB’ stacking | |
| | $J_{ij}$ | $J_1$ | $J_2$ | $J_{ij}$ | $J_1'$ | $J_2'$ | $J_1$ | $J_2$ |
| VI₃ | $N$ | 6 | 1 | 9 | 6 | 1 | 9 |
| | $d$ (Å) | 3.95 | 6.66 | 7.74 | 3.95 | 7.04 | 7.05 | 8.07 | 8.95 |
| | $J_{ij}$ (meV) | -3.20 | 0.81 | -0.24 | -4.46 | 0.10 | 0.21 | 0.04 | -0.04 |
| CrI₃ | $N$ | 6 | 1 | 9 | 6 | 2 | 2 |
| | $d$ (Å) | 3.95 | 6.57 | 7.68 | 3.95 | 7.00 | 7.02 | 8.03 | 8.92 |
| | $J_{ij}$ (meV) | -7.03 | -0.82 | -0.69 | -8.11 | -0.18 | -0.23 | -0.29 | 0.25 |
The microscopic mechanism of the tunable magnetic stability can be explained by invoking again the virtual hopping idea. The DOS projected onto V-$d$ orbital state of top and bottom layers in AB’ stacked bilayer VI$_3$ is shown in Fig. 5(c) and (d). Without electric field, the DOS relative to the top and bottom layer lie in the same energy range. As discussed above, there is a competition between parallel-spin hopping and anti-parallel-spin hopping in determining the first-neighbor exchange coupling $J'_1$. Since the energy difference between $e_{g}^{↑}$ and $a_{1g}^{↑}$ state ($\Delta \varepsilon_{g}^{↑} = 2.9$ eV) is much larger than the energy difference between $e_{g}^{↑}$ and $a_{1g}^{↑}$ state ($\Delta \varepsilon_{p}^{↑}=1.4$ eV), one may think that a parallel-spin configuration is favored. However, $J'_1$ is found to be slightly AFM-favored. This is because the anti-parallel spin hopping ($t_{p} = -3.1$ meV) is stronger than the parallel-spin hopping ($t_{g} = -1.1$ meV), resulting in a stronger AFM effective exchange coupling $J_{eff} \propto t_{p}^{2}/\Delta \varepsilon$. Upon electric fields, the $a_{1g}$ orbital state of the top layer is shifted up, while it is shifted down in the bottom layer (cfr Fig. 5). The band gap becomes narrower due to the shift of DOS and in turn decreases the difference of orbital energy levels, while the hopping integral is not significantly affected. Overall, this increases the tendency toward FM stability, eventually switching the favored magnetic configuration from AFM to FM.

### V. CONCLUSIONS

By means of first-principles calculations, we investigated the magnetic stability in bilayer VI$_3$ and compared our results with the corresponding well-studied case of CrI$_3$. In particular, the magnetic exchange interactions have been analyzed by evaluating the hopping integrals between MLWFs projected onto 3$d$ orbital states at V and Cr sites. We found out that the trigonal crystal field...
TABLE III. Hopping integrals calculated by MLWF basis set between occupied and unoccupied d orbital states in parallel- ($t_{gg}$) or anti-parallel ( $t_{e}$) spin configurations. Three types of hopping integrals, $t_1$, $t_2$, and $t'$, corresponding with inter-layer exchange couplings $J_1$, $J_2$, and $J_1''$ are listed. $\Delta \epsilon$ labels the difference between two eigenenergy for the MLWFs relevant to the hopping process, corresponding to $\Delta \epsilon_{1\uparrow\uparrow}$ and $\Delta \epsilon_{1\downarrow\downarrow}$ in the main text. The dominant hopping values relevant to the exchange couplings and those illustrated in Fig. are highlighted in bold.

|     | Hopping $t_{\uparrow\uparrow}$ | Hopping $t_{\downarrow\downarrow}$ | Hopping $t_{\downarrow\downarrow}'$ |
|-----|-------------------------------|----------------------------------|----------------------------------|
| VI$_3$ | $\alpha_1 g_{\uparrow\uparrow}$ | $\alpha_1 g_{\downarrow\downarrow}$ | $\alpha_1 g_{\downarrow\downarrow}'$ |
|      | $\epsilon_0 - \epsilon_0$ | $\epsilon_0 - \epsilon_0$ | $\epsilon_0 - \epsilon_0$ |
|      | $\epsilon_0 - \epsilon_0$ | $\epsilon_0 - \epsilon_0$ | $\epsilon_0 - \epsilon_0$ |
|      | $\epsilon_0 - \epsilon_0$ | $\epsilon_0 - \epsilon_0$ | $\epsilon_0 - \epsilon_0$ |
|      | $\Delta \epsilon$ (eV) | 0 | 1.4 |
| $t_1$ (meV) | -3.6 | 2.1 | 0.0 |
| $t_2$ (meV) | -0.7 | 1.1 | -1.6 |
| $t'$ (meV) | 3.6 | 1.0 | -1.1 |
| CrI$_3$ | $\epsilon_g - \epsilon_g$ | $\epsilon_g - \epsilon_g$ | $\epsilon_g - \epsilon_g'$ |
|      | $\epsilon_g - \epsilon_g$ | $\epsilon_g - \epsilon_g$ | $\epsilon_g - \epsilon_g$ |
|      | $\epsilon_g - \epsilon_g$ | $\epsilon_g - \epsilon_g$ | $\epsilon_g - \epsilon_g$ |
|      | $\Delta \epsilon$ (eV) | 0 | 1.5 |
| $t_1$ (meV) | 0.9 | 0.6 | 0.7 |
| $t_2$ (meV) | 0.6 | 1.5 | 0.8 |
| $t'$ (meV) | 2.1 | 1.3 | 1.4 |

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REFERENCES

1. B. Huang, G. Clark, E. Navarro-Moratalla, D. R. Klein, R. Cheng, K. L. Seyler, D. Zhong, E. Schmidgall, M. A. McGuire, D. H. Cobden, W. Yao, D. Xiao, P. Jarillo-Herrero, and X. Xu, Nature 546, 270 (2017).
2. C. Gong, L. Li, Z. Li, H. Ji, A. Stern, Y. Xia, T. Cao, W. Bao, C. Wang, Y. Wang, Z. Q. Qiu, R. J. Cava, S. G. Louie, J. Xia, and X. Zhang, Nature 546, 265 (2017).
3. Y. Deng, Y. Yu, Y. Song, J. Zhang, N. Z. Wang, Z. Sun, Y. Yi, Y. Z. Wu, S. Wu, J. Zhu, J. Wang, X. H. Chen, and Y. Zhang, Nature 563, 94 (2018).
4. B. Huang, G. Clark, D. R. Klein, D. MacNeill, E. Navarro-Moratalla, K. L. Seyler, N. Wilson, M. A. McGuire, D. H. Cobden, D. Xiao, W. Yao, P. Jarillo-Herrero, and X. Xu, Nature Nanotechnology 13, 544 (2018).
5. S. Jiang, J. Shan, and K. F. Mak, Nature Materials 17, 406 (2018).
6. E. S. Morell, A. León, R. H. Miwa, and P. Vargas, 2D Materials 6, 025020 (2019).
7. S. Jiang, L. Li, Z. Wang, K. F. Mak, and J. Shan, Nature Nanotechnology 13, 549 (2018).
8. M. A. McGuire, H. Dixit, V. R. Cooper, and B. C. Sales, Chemistry of Materials, Chemistry of Materials 27, 612 (2015).
9. N. Sivadas, S. Okamoto, X. Xu, C. J. Fennie, and D. Xiao, Nano Letters, Nano Letters 18, 7658 (2018).
10. D. Soriano, C. Cardoso, and J. Fernández-Rossier, Solid State Communications 299, 113662 (2019).
11. P. Jiang, C. Wang, D. Chen, Z. Zhong, Z. Yuan, Z.-Y. Lu, and W. Ji, Phys. Rev. B 99, 144401 (2019).
12. J. Kim, K.-W. Kim, B. Kim, C.-J. Kang, D. Shin, S.-H. Lee, B.-C. Min, and N. Park, Nano Letters, Nano Letters.
