Ferroelectricity and ferromagnetism in a VOI$_2$ monolayer: Role of the Dzyaloshinskii-Moriya interaction

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Multiferroics with intrinsic ferromagnetism and ferroelectricity are highly desired but rather rare, while most ferroelectric magnets are antiferromagnetic. A recent theoretical work [Tan et al., Phys. Rev. B 99, 195434 (2019)] predicted that oxyhalides VOX$_2$ (X: halogen) monolayers are two-dimensional multiferroics by violating the empirical $d^0$ rule. Most interestingly, the member VOI$_2$ are predicted to exhibit spontaneous ferromagnetism and ferroelectricity. In this work, we extend the previous study on the structure and magnetism of VOI$_2$ monolayer by using density-functional theory and Monte Carlo simulation. The presence of the heavy element iodine with a strong spin-orbit coupling gives rise to an effective Dzyaloshinskii-Moriya interaction in the polar structure, which favors a short-period spiral magnetic structure.. Another interesting result is that the on-site Coulomb interaction can strongly suppress the polar distortion thus leading to a ferromagnetic metallic state. Therefore, the VOI$_2$ monolayer is either a ferroelectric insulator with spiral magnetism or a ferromagnetic metal, instead of a ferromagnetic ferroelectric system. Our study highlights the key physical role of the Dzyaloshinskii-Moriya interaction.

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I. INTRODUCTION

Since the discovery of CrI$_3$ monolayer [1] and Cr$_2$Ge$_2$Te$_6$ few layers [2] in 2017, two-dimensional (2D) crystals with intrinsic ferromagnetism have attracted a great deal of attention boosting both experimental and theoretical research. New 2D ferromagnets have been experimentally confirmed, including VSe$_2$ monolayer [3] and Fe$_3$GeTe$_2$ monolayer [4], and even more have been predicted [5–11]. At the same time, 2D ferroelectric materials have also become booming since the discovery of SnTe monolayer [12] and CuInP$_2$S$_6$ few layer [13] in 2016.

An interesting topic is the crossover of 2D magnetic materials and polar materials, i.e., 2D multiferroics, which represents a newborn field of research. In the past decades, the multiferroics in three-dimensional crystals have been extensively studied, but has not widely extended to the 2D families [14–18]. Only until very recently, some 2D materials have been predicted to be multiferroic [19–25]. Not only the type-I multiferroics but also the type-II multiferroics have been designed such as Hf$_2$VC$_2$F$_2$ monolayer with Y-type noncollinear spin texture [19]. Very recently, Tan et al. predicted that oxyhalides VOX$_2$ (X: halogen) monolayers are two-dimensional multiferroics by violating the empirical “$d^0$ rule,” which is a main driving force for proper ferroelectricity as in BaTiO$_3$ [26]. The most interesting member is VOI$_2$, which is predicted to have ferromagnetic (FM) and ferroelectric (FE) orders [21], a very rare but highly desired property.

In the present work, we extend the previous study about VOI$_2$ monolayer [21] by considering both the spin-orbit coupling (SOC) and Hubbard-U correction, which were not taken into account in Ref. [21]. In this system, due to the presence of heavy element I, the SOC effect should influence the structural and magnetic properties. For 3$d$ orbitals of V, the Hubbard correlation should also be considered. Although in the spin-polarized density-functional theory (DFT) calculation, the role of Hund coupling has been partially considered, in practice an additional $U$ is needed in many cases. Indeed, our calculations find that the combined effect of both SOC and Hubbard-U correction is crucial for discussing the ferromagnetism and ferroelectricity in VOI$_2$ monolayer.

II. COMPUTATIONAL METHODS

Our first-principles calculations were performed on the basis of spin-polarized DFT implemented in the Vienna Ab initio Simulation Package (VASP) code [27,28]. For the exchange-correlation functional, the PBE parametrization of the generalized gradient approximation (GGA) was used [29] and the Hubbard $U$ was applied using the Dudarev parametrization [30]. In addition, the Heyd-Scuseria-Ernzerhof (HSE06) functional [31] is also adopted to compare with the GGA+$U$ result. The SOC was considered in all calculations, including the structural relaxation. The energy cutoff is fixed at 600 eV, and the V’s 2$p$ and $d$ electrons were treated as valence states. The $k$-point grid of $11 \times 11 \times 1$ is employed to sample the Brillouin zone for the minimal unit cell and accordingly

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TABLE I. The DFT-calculated magnetic coefficients (meV) for the spin model. The spin is normalized to unit one. Spin-polarized GGA with SOC is adopted. For the Dzyaloshinskii-Moriya vectors, those components below 0.01 meV are considered as zero.

<table>
<thead>
<tr>
<th>$K_b$</th>
<th>$K_c$</th>
<th>$J_a$</th>
<th>$J_b$</th>
<th>$J_{ab}$</th>
<th>$D_a$</th>
<th>$D_b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.11</td>
<td>0.54</td>
<td>−2.15</td>
<td>−0.69</td>
<td>−0.72</td>
<td>(0, 0, 0)</td>
<td>(0, 0, 0.89)</td>
</tr>
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FIG. 2. (a) The four collinear magnetic orders, which are calculated to extract the values of $J_a, J_b$, and $J_{ab}$. (b), (c) The two 120° noncollinear magnetic orders, which are calculated to extract the Dzyaloshinskii-Moriya interactions along $a$-/b direction, respectively.

By mapping the DFT energy to aforementioned Hamiltonian, these Dzyaloshinskii-Moriya interactions can be calculated based on $3 \times 1 \times 1$ and $1 \times 3 \times 1$ supercells with two spiral-spin configurations with opposite chirality. The noncollinear spin angles between two neighboring V$_4^+$ sites were set as 120°, as shown in Figs. 2(b) and 2(c), which own different energy contribution from Dzyaloshinskii-Moriya interaction but identical energy contribution from others. The calculated values are summarized in Table I. It is clear that only the $c$ component of $D_b$ is nonzero, while the $a$ component of $D_a$ is too small ($<0.01$ meV). We also checked the source of such $D_b$ by simply replacing I with Cl in this polar structure; then the magnitude of $D_b$ becomes (0, 0, 0.008) meV. Therefore here the heavy element iodine indeed contributes mainly to the SOC-induced Dzyaloshinskii-Moriya interaction.

Then, a classical spin model Hamiltonian can be constructed as

\[ H = J_a \sum_{\langle i,j \rangle} S_i \cdot S_j + J_b \sum_{\langle m,n \rangle} S_m \cdot S_n + J_{ab} \sum_{\langle k,l \rangle} S_k \cdot S_l + D_a \cdot \sum_{\langle i,j \rangle} S_i \times S_j + D_b \cdot \sum_{\langle m,n \rangle} S_m \times S_n + \sum_i \left[ K_c (S_i^z)^2 + K_b (S_i^y)^2 \right], \]  

(1)

where $S_i$ is the normalized spin ($|S| = 1$) at site; $\langle a/b \rangle$ denotes to the NN along the $a/b$ axis; $\langle \rangle$ represents the NNN along the diagonal direction; $K_{b/c}$ stands for the single-ion anisotropy coefficient.

Based on the above DFT coefficients and Hamiltonian [Eq. (1)], a Monte Carlo simulation was used to simulate the magnetic ordering of VOI$_2$ monolayer. According to the heat capacity [Fig. 3(a)], there is a peak at $T_C \sim 21$ K indicating a magnetic phase transition. The MC snapshot below $T_C$ confirms a spiral order, as shown in Fig. 3(b). The spins rotate in the $ab$ plane and the propagation vector of spiral is along the $b$ axis. The period or magnetic spiral is $\sim 15$ unit cells (about 6 nm) according to the MC simulation [see Fig. 3(b)].

Above results based on pure spin-polarized GGA+SOC have confirmed the ferroelectricity but ruled out the ferromagnetism. Then it is necessary to double check the Hubbard-$U$ correction, which may affect the electron structures seriously especially for partially occupied 3$d$ orbitals. In the following, the spin-polarized GGA+$U$+SOC calculations were performed for the structural relaxation, as shown in Fig. 4(a). With increasing $U_{ef}$ ($= U - J$ as defined in the Dudarev approach [29]), the lattice shrinks in the $a$ axis but elongates...
FIG. 4. Structure and polarization as a function of $U_{\text{eff}}$, calculated with SOC and without SOC. (a) Lattice constants $a$ and $b$. (b) The O–V–I bond angle $\Phi$. Inset: the top view of a unit cell. (c) Ferroelectric polarization.

in the $b$ axis. Such tendency suppresses the polar distortion, as evidenced in the V–O–I bond angle $\Phi$ [see Fig. 4(b)]. When $U_{\text{eff}} > 0.4$ eV, the polar distortion completely disappears ($\Phi = 90^{\circ}$) and the space group becomes $Pmmm$ (i.e., the paraelectric state). The spin-polarized GGA+$U$ calculations without SOC show similar tendency but the critical $U_{\text{eff}}$ are larger, as compared in Fig. 4.

The electronic structure is also sensitive to $U_{\text{eff}}$. The density of states (DOS) of VOI$_2$ monolayer calculated by GGA+SOC and GGA+$U$/SOC ($U_{\text{eff}} = 1$ eV) are shown in Fig. 5(a) for comparison. Surprisingly, the VOI$_2$ monolayer turns to be metallic when $U_{\text{eff}} = 1$ eV, while originally it is a semiconductor. The spin-polarized GGA+$U$ calculations without SOC show similar tendency but the critical $U_{\text{eff}}$ are larger, as compared in Fig. 4.

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the itinerant of electrons, which will strengthen the long-range exchange $J_{ab}$. While for the Dzyaloshinskii-Moriya interaction, as shown in Fig. 6(b), it changes following the behavior of polar distortion [Fig. 4(b)] since it is directly determined by the symmetry. In particular, for the nonpolar structure, $D_b$ becomes zero. With the increasing exchange interactions and decreasing Dzyaloshinskii-Moriya interaction, the spin-spiral period of VOI$_2$ monolayer will become longer and longer, and finally the system becomes a ferromagnetic metal.

Finally, the HSE06+SOC approach has been used to verify above GGA+$U$+SOC calculation. The HSE06+SOC optimization leads to even stronger polar distortion (e.g., $\Phi = 83.54^\circ$) than the GGA+SOC result ($\Phi = 85.03^\circ$). Correspondingly, the polarization obtained in the HSE06+SOC calculation is 258 pC/m, which is larger than that of GGA+SOC (225 pC/m). Then the stronger Dzyaloshinskii-Moriya interaction and spiral spin texture is expectable.

IV. CONCLUSION

The structural, electronic properties, electric polarization, as well as magnetic property of VOI$_2$ monolayer have been studied systematically via spin-polarized GGA+SOC and GGA+$U$+SOC methods. Our results have confirmed but, at the same time, go beyond the previous work [21]. In particular, our work revealed the key role of antisymmetric Dzyaloshinskii-Moriya interactions which is significant in VOI$_2$ monolayer. Our conclusion is that VOI$_2$ monolayer is either a ferroelectric magnet with spiral-spin configuration (in the low-$U$ limit or using the HSE method), or a ferromagnetic metal without ferroelectricity (in the large-$U$ side), instead of the expected ferroelectric ferromagnet. Our work will stimulate future experimental verifications and predictions of for new 2D multiferroic materials.

Note added. Recently, we became aware of a recent theoretical work on VOI$_2$ monolayer [36], which reported a similar noncollinear spin order as ground state.

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