Interplay of spin magnetism, orbital magnetism, and atomic structure in layered van der Waals ferromagnet VI$_3$

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Recently discovered ferromagnetism of the layered van der Waals material VI$_3$ attracts much research attention. Despite substantial progress, in the following important aspects no consensus has been reached: (i) a possible deviation of the easy axis from the normal to the VI$_3$ layers, (ii) a possible inequivalence of the V atoms, (iii) the value of the V magnetic moments. The theoretical works differ in the conclusions on the conduction nature of the system, the value and the role of the V orbital moments. To the best of our knowledge there is no theoretical works addressing issues (i) and (ii) and only one work dealing with the reduced value of the V moment. By combining the symmetry arguments with density functional theory (DFT) and DFT+$U$ calculations we have shown that the antidimerization distortion of the crystal structure reported by Son et al.

Phys. Rev. B 99, 041402(R) (2019) must lead to the deviation of the easy axis from the normal to the VI$_3$ layers in close correlation with the experimental results. The antidimerization accompanied by the breaking the inversion symmetry leads to the inequivalence of the V atoms. Our DFT+$U$ calculations result in large value $\sim 0.8 \mu_B$ of the V orbital moments of the V atoms leading to reduced total V moment in agreement with a number of experimental results and with the physical picture suggested by Yang et al.

Phys. Rev. B 101, 100402(R) (2020)]. We obtained large intraatomic noncollinearity of the V spin and orbital moments revealing strong competition between effects coursed by the on-site electron correlation, spin-orbit coupling, and interatomic hybridization since pure intraatomic effects lead to collinear spin and orbital moments. Our calculations confirm the experimental results of strong magnetoelastic coupling revealing itself in the strong dependence of the magnetic properties on the distortion of the atomic structure.

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I. INTRODUCTION

The search for new magnetic 2D materials for spintronic applications is one of the hot topics of the present-day solid state physics (see, e.g., Ref. 1 for a review). In recent few years, much research attention has been attracted to the layered van der Waals (vdW) trihalide VI$_3$.$^{3,6–15}$ The conclusions of different studies of VI$_3$ appeared to contain both important agreements and important differences. Thus the experimental works agree on the insulating nature of the system, and ferromagnetic type of the magnetic structure.$^{3,6–11,14}$ In most studies the $z$ axis, orthogonal to the VI$_3$ layers, is treated as the easy axis, and all V atoms are considered to be equivalent. On the other hand, there are experimental reports pointing to significant deviation of the easy axis from the $z$ axis (Ref. 8, supplementary material to Ref. 3) and the inequivalence of the V atoms.$^9$ Remarkably, there is no consensus also on the value of the V magnetic moments: the reported experimental estimations differ strongly. Taking as an example the moments obtained in the measurements in magnetic field parallel to the $z$ axis we find the following values (all in $\mu_B$): 2.47 (Ref. 8), 2.0 (Ref. 3), 1.3 (Ref. 3), 1.2 (Ref. 6), 0.95 (Ref. 14).

On the theoretical side, all publications consider the ferromagnetic state with the easy $z$ axis and equivalent V atoms.$^{2,5,10,11}$ All studies find the V spin moment close to $2.0 \mu_B$. Some works$^{2,5,10,11}$ compare this value with experimental magnetic moment claiming good agreement. The orbital moment (OM) is usually not reported. An important exception is a recent work by Yang et al.$^{11}$ arguing that in the ground state the V atoms have a large OM of about $1 \mu_B$. This magnetic state was obtained in the DFT+$U$ calculation taking into account the correlation of the V 3d electrons. The large OM opposite to the spin moment leads to the reduced value of the total atomic moment.

Another important difference in the conclusions of the theoretical studies concerns the conduction nature of the system. Several works (Refs. 2,10) report the half-metallic electronic structure and find Dirac or Weyl states close to the Fermi energy in the conducting spin-up subsystem. Other works obtain Mott insulator state in agreement with experiment.$^{5,11,13}$ In Ref. 11 the authors discuss the possibility of the convergence of the DFT+$U$ calculations to different states that can explain difference of the results obtained within apparently similar theoretical approaches.

The goal of the present paper is to contribute to the understanding of VI$_3$ in the following aspects. First, we address the findings of the experimental works that, despite their importance, have not yet been treated theoretically. As mentioned above, these findings are the deviation of the easy axis from the normal to the VI$_3$ layers and the inequivalence of the V atoms. Another characteristic feature of our work is a systematic attention paid to the properties of the atomic OMs. In general, the OMs play important role in the magnetism of various types of systems. They provide insight into the physical consequences of spin-orbit coupling (SOC). In particular, the properties of the OMs are known to be closely related.
with the properties of the magnetic anisotropy (see, e.g., Refs. [18–21]). In the case of $V_3$ the attention to the OMs is additionally stimulated by the experimental reports of reduced values of the atomic moments and by the physical picture suggested in Ref. [11] whose crucial feature is a large OM of the V atoms. We also contribute to the discussion of the multiple convergence of the calculations taking into account electron correlations within the framework of the DFT+U approach.

Our theoretical methodology consists in the combination of the symmetry-based analysis of magnetic states with the DFT and DFT+U calculations. The strong feature of the symmetry treatment is a wide independence of the drawn conclusions from the details of the approach used in the calculation of the electronic properties. On the other hand, the symmetry analysis does not provide quantitative estimates of the physical quantities. Therefore, we perform the DFT based calculations to evaluate the magnitudes of the symmetry-predicted effects.

The paper is organized as follows. In Sec. II we describe the method of calculations. Section III presents the atomic structure and discusses the symmetry aspects of the study. Section IV contains the results of the calculations and their discussion. Section V is devoted to the conclusions.

II. METHOD OF CALCULATIONS

The calculations are performed with the augmented spherical waves (ASW) method22,23, generalized to deal with noncollinear magnetism and spin-orbit coupling24. The generalized gradient approximation (GGA) to the energy functional25 is employed in the calculations. The DFT+U method in the form suggested by Dudarev et al.26 was applied to examine the influence of the on-site correlation of the 3d electrons on the magnetic moments and energies of magnetic configurations. We used the $U_{eff}$ parameter equal to 0.2 Ry (∼2.72 eV) what is a reasonable value for this material27,28. The most of calculations were performed with $k$-mesh $12\times12\times12$.

An important quantity of the DFT+U approach is the orbital density matrix $n$ of the correlated atomic states. It enters the method with the prefactor $U$ leading to the orbital dependence of the electron potential29:

$$V_{m,m'} = -U(n_{m,m'} - \frac{1}{2}\delta_{m,m'}).$$

In the paper we work in the basis of complex spherical harmonics $Y_{lm}$. We consider the correlation of the V 3d electrons. Therefore the orbital quantum number $l$ is equal to 2 and the orbital dependence of the potential is given by the dependence on the magnetic quantum number $m$. All other indices characterizing orbitals are omitted. The diagonal elements $n_{m,m}$ of the orbital density matrix give the occupations of the corresponding $m$ orbitals. Examples of the implementation of the $n$ matrix calculation within the DFT methods can be found in Refs. 27,28.

The operator of the spin-orbit coupling is taken in the form:

$$H_{so} = \frac{1}{(2\pi)^2} \int \frac{dV^+}{r} \left[ \begin{array}{c} \frac{1}{M^2} \frac{dV^+}{dr} \\ 0 \\ \frac{1}{M^2} \frac{dV^-}{dr} \end{array} \right] \sigma_z \hat{l}_z + \frac{1}{M^2} \frac{dV^+}{dr} \sigma_y \hat{l}_y$$

where $V^+$ and $V^-$ are spin-up and spin-down electron potentials,

$$V^{av} = \frac{1}{2}(V^+ + V^-)$$

and

$$M_n = \frac{1}{2}(1 - \frac{1}{c^2} V^{\alpha}) \quad \alpha = av, +, -.\quad (4)$$

$\sigma_x, \sigma_y, \sigma_z$ are the Pauli matrices and $\hat{l}_x, \hat{l}_y, \hat{l}_z$ are the operators of the components of the orbital momentum, $r$ is the distance from the center of atomic surface, $c$ is the light velocity. The SOC is taken into account for both V and I atoms.

We calculate the vectors of spin $m^s_\nu$ and orbital $m^o_\nu$ moments of the $\nu$th atom as:

$$m^s_\nu = \sum_{kn} \int_{\Omega_n} \psi^\dagger_{kn} \sigma \psi_{kn} d\mathbf{r} \quad (5)$$

$$m^o_\nu = \sum_{kn} \int_{\Omega_n} \psi^\dagger_{kn} \hat{l} \psi_{kn} d\mathbf{r} \quad (6)$$

where $\sigma = (\sigma_x, \sigma_y, \sigma_z)$ and $\hat{l} = (\hat{l}_x, \hat{l}_y, \hat{l}_z)$, $\psi_{kn}$ is the wave function of the Kohn-Sham state corresponding to wave vector $\mathbf{k}$ and band index $n$. The sum is taken over occupied states. The integrals are carried out over $\nu$th atomic sphere.

Due to the orbital-dependent potential term (Eq. 1) the occupied orbitals tend to lower their energies whereas empty orbitals tend to increase their energies. This feature makes the DFT+U approach an adequate tool for the study of the enhancement of the orbital magnetic moment. It is well known that standard DFT calculations underestimate the value of the OM. There is a similarity in the physical mechanisms of the OM enhancement within the DFT+U method24 and the method of the orbital polarization correction by Eriksson et al.29,30. The latter approach is based on the simulation of the intraatomic second Hund’s rule in the DFT calculations. There is, however, an important difference in the scale of the terms responsible for the orbital polarization enhancement. In the DFT+U scheme the scale is governed by the Hubbard parameter $U_{eff}$ whereas in the second Hund’s rule this is a usually smaller parameter often referred to as $B$. 

The hybridization of the correlated states with the states of ligands produces physical mechanism counteracting the energy shifts of the correlated states. This results in a complex interplay of intraatomic and interatomic interactions that is taken into account in the DFT+$U$ calculations.

III. CRYSTAL LATTICE AND SYMMETRY ASPECTS

A. Undistorted $R3\bar{3}$ atomic structure

The system experiences structural phase transition at $\sim$80 K that is above the temperature of the magnetic phase transition. One VI$_3$ layer consists of the honeycomb V lattice and two I layers lying above and below the V layer (Fig. 1b). The neighboring VI$_3$ layers are weakly bounded through the vdW interaction. The stacking of the layers we consider is ABC. The structural phase transition leads to the distortion of the honeycomb lattice. Son et al. describe this distortion in terms of antidimerization (AD) of the V atoms. We performed calculations for both $R3\bar{3}$ and distorted (Fig. 1b) atomic lattices. In this section we discuss the symmetries of the lattices and their physical consequences.

We begin with the symmetry properties of VI$_3$ in the $R3\bar{3}$ crystal lattice. The $R3\bar{3}$ crystal structure has 6 symmetry operations. The two generators of the symmetry group are 120°-rotation about the z axis, $C_{3z}$, and space inversion.

The unit cell contains two formula units of VI$_3$. The equivalence of the atoms belonging to one unit cell does not follow from the translational invariance of the lattice and, if present, must be the consequence of the point symmetry operations. The $C_{3z}$ axes go through the positions of the V atoms leaving them invariant under $C_{3z}$ rotation. On the other hand, the inversion transposes the two V atoms in the unit cell revealing their equivalence. For the I atoms, the $C_{3z}$ operation permutes cyclically 1-3 and 4-6 atoms whereas the inversion transposes pairs of atoms: 1 ↔ 4, 2 ↔ 6, 3 ↔ 5. As a result, all I atoms are equivalent. In general, the magnetic structure can reduce the symmetry of the system below the symmetry of the atomic lattice. In VI$_3$, the ferromagnetic structure with moments parallel to the z axis preserves the symmetry operations of the lattice.

The symmetry analysis performed above can be used to address the following important question: Can the $z$ axis be the easy axis of the ferromagnetic VI$_3$ with $R3\bar{3}$ structure? This question is equivalent to the question whether the ferromagnetic structure with the moments parallel to the $z$ axis is distinguished by symmetry with respect to the magnetic structures obtained by the infinitesimal deviations of the atomic moments from the...
z direction. Indeed, if the z axis is not distinguished by symmetry it is just one of the continuum of axes that, before the concrete numerical study is carried out, appear as equally possible realizations of the easy axis. The probability that one axis selected by us from the continuum of formally equivalent axes corresponds to the desired property is negligible. In this case, the calculation started with the atomic moments oriented parallel to the z axis is predicted to result in the deviation of the moments from this axis. In the iterative process, the moments tend to assume self-consistent directions. These directions are accidental in the sense that they are not characterized by an additional symmetry and cannot be determined without direct calculations.

On the other hand, if a selected axis is distinguished by symmetry with respect to the axes obtained by infinitesimal deviations, we deal with the symmetry constraint on the magnetic structure (or, equivalently, symmetry protection of the magnetic structure). The calculations started with symmetry protected directions of the atomic moments preserve these directions during iterations. The symmetry protected directions of the magnetic moments are natural candidates for the magnetic easy axis.

Applying these general principles to VI$_3$ in $R \bar{3}$ we notice that the $C_{3z}$ symmetry operation is disturbed by any deviation of the V moments from the z axis. This makes the z direction of the V moments to be symmetry protected and reveals the z axis as a symmetry supported option for the easy axis. Both spin and OMs of the V atoms must be collinear to the z axis to satisfy the symmetry constraint. Therefore, they must be collinear also to each other. However, for the moments induced on the I atoms the situation is different. The symmetry operations transform I atoms into each other and, therefore, impose constraints not on the directions of the moments of individual atoms but on the relative directions of the moments of different atoms: If a symmetry operation $\alpha$ transforms the position of atom $i$ in the position of atom $j$, it also transforms the moment of atom $i$ in the moment of atom $j$. Since there is no symmetry operation ‘responsible’ for preserving the collinearity of the I moments to the z axis, the symmetry analysis predicts the deviation of the I moments from the z axis. As there is no symmetry requirement of equal deviations of the spin and orbital moments, the spin and orbital moments of the I atoms are expected to deviate by different angles and to become noncollinear to each other. As a general rule, always when the atomic moments assume accidental directions, the spin and orbital moments of the same atom are noncollinear. The calculations fully confirmed the predictions following from the symmetry analysis.

IV. RESULTS OF CALCULATIONS

A. DFT calculations

In the calculations for the $R \bar{3}$ lattice we used experimental lattice parameters $a=6.835 \text{ Å}$, $c=19.696 \text{ Å}$. In Fig. 3a, we show the density of states (DOS) calculated without account for the SOC and electron correlations. The characteristic feature of the electronic structure is its half-metallic nature: the spin-up subsystem is metallic and spin-down subsystem is insulating. The spin moment is exactly 2 $\mu_B$ per formula unit (FU). The value of the V spin moment is 2.124 $\mu_B$. The OM is quenched.

There is a group of the spin-up V 3d states around the Fermi level that plays important role in the discussion of the results of the DFT+$U$ calculations presented below. This group of states is associated with $t_{2g}$ orbitals originating in the crystal-field splitting of the V 3d states in the octahedral environment of the I ligands. To recall, the splitting of the 3d states to $t_{2g}$ and $e_g$ subshells appears in the standard consideration of the influence of the octahedral ligand environment on a 3d atom. In the case of VI$_3$ crystal the octahedron axes are different from the z axis and are not symmetry axes of the crystal. Although the models based on the treatment of the crystal-field splitting of the V 3d states in the octahedral environment are useful for qualitative considerations they are a substantial simplification of the real physical situation. The DFT-based calculations reflect more closely the actual complexity of the system. The results of these
FIG. 3: Densities of states. Above the abscissa axis are the spin-up DOSs, below the abscissa axis are the spin-down DOSs. Black lines present total DOSs in numbers of states per 1 eV and formula unit, blue and red lines present partial V 3d and I DOSs per one atom. The energy origin is at the Fermi level in the cases of metallic state [panels (a) and (b)] and at the bottom of the valence band in the insulating states [panels (c) and (d)]. (a) Calculation without SOC and $U=0$. (b) Calculation with SOC and $U=0$. (c) Calculation without SOC and $U=2.72$ eV. (d) Calculation with SOC and $U=2.72$ eV.

Calculations will be the basis of our considerations. Keeping this comment in mind, we for brevity will refer to the spin-up DOS peak around the Fermi energy as $t_{2g}$-peak.

The account for the SOC does not change the general structure of the DOS (Fig. 3b) leading, however, to important differences in the details. Strictly speaking, the DOS is not now half-metallic since the SOC mixes spin-up and spin-down states and, therefore, there is no 100% spin-polarization of the electronic states at the Fermi level. On the other hand, the contribution of the spin-down states at the Fermi level is small and hardly noticeable in Fig. 3b. The spin moment of V is $2.145 \mu_B$. The V OM is unquenched and assumes the value of $-0.075 \mu_B$ where negative sign means the direction opposite to the direction of the spin moment. The spin and orbital moments of the V atoms are collinear to the $z$ axis.

To illustrate the origin of the nonzero V OM we show in Fig. 4 the $m$-resolved V 3d DOSs. The partial DOS corresponding to a given $m$ is obtained by projecting of the electron states to complex spherical harmonic $Y_{2m}$. The sum of the $m$-resolved DOSs gives the total V 3d DOS. The complex spherical harmonics are defined with respect to the $z$ axis. The nonzero atomic OM is the result of different occupation of the $m$ and $-m$ states [see also Eq. (8)]. Without SOC (Figs. 3a-c), DOS$_m$=DOS$_{-m}$ and the $z$ projection of the OM is zero. With SOC taken into account (Figs. 3d-f), DOS$_m$$\neq$DOS$_{-m}$ and the $z$ projection of the OM is unquenched.

In Sec. IV B we will discuss the results of the DFT+U calculations where the orbital density matrix $n$ enters the secular matrix of the method and influences directly the formation of the electronic structure. Since the symmetry determined properties of the occupation matrix are identical in both DFT and DFT+U calculations it is useful to consider these properties already here. The calculations give the following form of the $n$ matrix

$$
\begin{pmatrix}
\ast & 0 & 0 & \ast & 0 \\
0 & \ast & 0 & \ast & 0 \\
0 & \ast & 0 & 0 & \ast \\
\ast & 0 & \ast & 0 & 0 \\
0 & \ast & 0 & \ast & \ast
\end{pmatrix}
$$

Equation (7) shows a spin-diagonal block of matrix $n$. The rows and columns of the matrix are numbered with the magnetic quantum number $m = 2, 1, 0, -1, -2$. The asterisks, $\ast$, present nonzero elements of the matrix: the
The nonzero off-diagonal elements of $n$ reveal that the symmetry supports the hybridization of the pairs of the atomic orbitals: orbital $m=2$ with orbital $m=-2$ and orbital $m=1$ with orbital $m=-1$. The origin of this hybridization can be explained as follows. The symmetry operations of the rotation about the $z$ axis by angles $0^\circ$, $120^\circ$ and $240^\circ$ form an abelian group with three one-dimensional irreducible representations: $\Gamma_1(1,1,1)$, $\Gamma_2(1,\epsilon^2,-\epsilon)$, $\Gamma_3(1,\epsilon,-\epsilon^2)$ where $\epsilon=\exp(i2\pi/3)$ and the numbers in the parentheses correspond to the three symmetry operations. The $m=0$ spherical harmonic transforms according to $\Gamma_1$, $m=2$ and $m=-1$ harmonics transform according to $\Gamma_2$ and $m=1$ and $m=-2$ harmonics transform according to $\Gamma_3$. The non-zero off-diagonal elements of $n$ reflect the hybridization between orbitals belonging to the same irreducible representation.

The elements of the $n$ matrix determine the value of the OM. The $z$ component of the OM, $m_{oz}$, is determined by the diagonal elements

$$m_{oz} = \sum_m n_{m,m},$$

whereas the $x$ and $y$ components, $m_{ox}$ and $m_{oy}$, depend on the values of the off-diagonal elements

$$m_{ox} \pm im_{oy} = \sum_m (2 \mp m)[3 \pm (m-1)]^{1/2} n_{m,m \mp 1}. \tag{9}$$

In general, nonzero off-diagonal elements can lead to nonzero $x$ and $y$ components of the OM. However, this needs nonzero elements $n_{m,m'}$ with $|m-m'|=1$. In our case, these matrix elements are zero that leads to vanishing $x$ and $y$ components of the OM. Therefore, the form of the calculated $n$ matrix is consistent with the conclusion about the collinearity of the V OM to the $z$ axis made above.

For the magnetic moments of the I atoms the calculations with account for SOC gave the following results. The spin moments have the value of 0.023 $\mu_B$ and deviate from the negative direction of the $z$ axis by $0.5^\circ$. The OM have the value of 0.022 $\mu_B$ and deviate from the negative direction of the $z$ axis by $7.3^\circ$. The in-plane projections of the I moments compensate each other. The directions of both spin and OM are close to the negative direction of the $z$ axis. This feature corresponds to the expectation based of the third Hund’s rule: for an isolated I atom the spin and OM are parallel to each other. On the other hand, the sizable deviations of the moments from the $z$ axis manifest the influence of the lattice. The fact that the induced I spin moments deviate much weaker from the $z$ axis than the induced I OM reflects a stronger influence of the atomic lattice on the orbital degrees of freedom.

**B. DFT+U calculations**

Although our DFT calculations discussed in Sec. IV A provide some insight into the formation of the properties of the system, they result in the metallic state contradicting the experiments revealing the formation of an insulating state. As most of the previous theoretical studies, to deal with the Mott insulating state of VI$_3$ we made use of the DFT+U method.

Indeed, the calculations result in the splitting of the $t_{2g}$ DOS peak and the formation of the insulating gap between occupied and empty states. A remarkable result of our DFT+U calculations is the possibility to obtain self-consistent insulating states of VI$_3$ with strongly different character of the splitting of the $t_{2g}$ peak. This possibility of different self-consistent results of the DFT+U calculations is in correlation with the conclusions of Wang et al.\cite{13}. We, however, emphasize that our calculations did not give a metallic state of VI$_3$ as reported in Ref.\cite{13}. Importantly, the different insulating states obtained in our calculations are connected with the formation of different OM. In this respect our results agree with the physical picture suggested by Yang et al.\cite{12}. It is also worth noting that in Ref.\cite{13} the possibility of two different orbital ordered states is discussed where both insulating states have zero OM.

In Fig. 3, we show the DOS obtained with $U=2.72$ eV with and without SOC being neglected. At the beginning of the iterations the $n$ matrix was set to zero. In the absence of the SOC the OM remained quenched in the iterations that is reflected in the property that the partial DOS corresponding to magnetic quantum number $m$ is identical to the partial DOS corresponding to $-m$ (Fig. 3b). This degeneracy combined with the interorbital hybridization, $m=-2$ with $m=1$ and $m=2$ with
$m=-1$ (see Sec. IIIA), leads to the joint shift to lower energies of the occupied parts of the corresponding four partial DOS. These states are separated by a gap from the empty peak of predominantly $m=0$ states (Fig. 3).

On the other hand, if we include the SOC already the first iteration results in the different occupation of the $m$ and $-m$ orbitals unquenching the OM. This orbital polarization is strongly enhanced in the course of the DFT+U iterations leading to the splitting of the occupied and empty states (Figs. 3c-5f) and large orbital moment of $-0.782\, \mu_B$. The occupied partial DOSs correspond now mainly to the hybridized $m=-2$ and $m=1$ orbitals and to the $m=0$ orbital (Fig. 5f).

We obtained also the self-consistent state with distinctly smaller V OM of $0.111\, \mu_B$. This calculation was performed as follows. First the SOC was switched on only on the V atoms. We obtained the V OM of $0.093\, \mu_B$. Then the SOC was switched on also on the I atoms. In this case, the structure of the $m$-DOSs and, therefore, the nature of the splitting of $t_{2g}$ peak (Fig. 5c-i) is rather close to the case with quenched OM (Fig. 5d-f). The energy of the state with small OM is $\sim 34$ meV/FU higher than the energy of the state with large OM.

The possibility to obtain insulating states with different OM can be interpreted as follows. There are two different aspects to mention. On one hand, the hybridization with the environment of various $m$-orbitals of the electron states belonging to the $t_{2g}$ DOS peak is not strong enough to counteract efficiently the splitting tendencies initiated by the on-site correlation governed by the $U$ parameter. Therefore the insulating gap can appear between states with different types of atomic orbitals. The types of the states that become stronger occupied and, therefore, lower their energy leading to the insulating gap determine the value of the OM formed by the occupied states. On the other hand, the interatomic hybridization is also an important factor that cannot be neglected. This, in particular, is reflected in the closely correlated behavior of the pairs of the partial $m$-DOSs: $m=-2,1$ and $m=2,-1$. In an isolated atom, the states corresponding to different values of $m$ do not hybridize.

Although the account for on-site correlations changes the values of the atomic moments, the symmetry properties remain intact. As the result, the V spin and orbital moments are collinear to the $z$ axis. Since, however, the V spin moments changes only weakly while the orbital moment increases by more than 10 times, the total V moment decreases strongly to the value of $1.362\, \mu_B$. The large value of the V OM is in agreement with the physical picture suggested in Ref. 11 and with the reduced magnetization values reported in a number of experimental works.

Examining the calculated I moments, we find that the I spin moments deviate from the negative direction of the $z$ axis by $4.3^\circ$ whereas the deviation of the orbital moments reaches $27.5^\circ$. We conclude that the correlation of the V $3d$ electrons is transferred by means of interatomic hybridization to the I states leading to strong enhancement of the deviation of the I moments from the $z$ axis and, as a result, to strong enhancement of the intraatomic noncollinearity of the spin and orbital moments.

C. Distorted atomic structure

1. AD-Distortion with preserved inversion symmetry

As discussed in Sec. IIIA, the AD-distortion reduces the lattice symmetry. Since the $z$ axis is not a symmetry axis of the system it cannot be the easy axis and the V moments are predicted to deviate from the $z$ axis. On the other hand, the inversion symmetry remains intact that preserves the equivalence of the V atoms and the collinearity of the moments of the V atoms. The direction of the moments is ‘accidental’ in the sense that it cannot be predicted on the symmetry basis. Therefore, although the V spin moments are parallel to each other and the V orbital moments are parallel to each other, the spin moments are noncollinear to the orbital moments. Also the consequences of the AD-distortion for the symmetry properties of the I atoms are discussed in Sec. IIIA.

The calculations for the AD-distorted structure confirm the predictions of the symmetry analysis. If we start with the V moments parallel to the $z$ axis, after the first iteration the moments deviate from the $z$ direction reflecting the breaking of the symmetry protection of the collinearity to the $z$ axis. The magnetic moments of different V atoms remain parallel to each other. However, the spin and orbital moments of the same atom become noncollinear. As expected, the form of the $n$ matrix changes compared with Eq. 7; the off-diagonal matrix elements responsible for the $x$ and $y$ components of the OM are now nonzero.

To determine the easy axis direction we performed the following set of calculations. We constrained several directions of the V spin moments in the $xy$ plane. For each of these directions specified, by angle $\theta_s$, other quantities were allowed to relax towards self-consistency. The total energy of the system as the function of $\theta_s$ is presented in Fig. 6. We see that at $\theta_s=0$ the slope of the curve is nonzero and, therefore, this state does not correspond to an extremum of energy. This feature confirms the results of the symmetry analysis. With increasing $\theta_s$, the energy first decreases. Then it becomes rather flat reaching a flat minimum at $\sim 35^\circ$. For $\theta_s$ above $\sim 60^\circ$ the energy quickly increases revealing the presence of strong magnetic anisotropy in the system.

At each iteration the calculated direction of the V spin moment given by angle $\theta'_s$ is not equal to the initial direction given by $\theta_s$. Due to constraint, this difference is neglected and the initial value $\theta_s$ is preserved in the iterations. In Fig. 6, we plot the difference $\theta'_s - \theta_s$ as a function of $\theta_s$. This difference becomes zero at $\sim 35^\circ$ showing that the position of the energy minimum corresponds to the unconstrained self-consistent state.

Another point of interest is the properties of the orbital
moment. As stated above on the basis of the symmetry arguments, the spin and orbital moments of the V atoms in the distorted lattice become noncollinear. We denote as $\theta_a$ the angle of the deviation of the calculated orbital moment from the negative direction of the $z$ axis. In Fig. 6a, we present $\theta_o$ and $\theta_s$, $\theta_o$, as functions of $\theta_s$. We obtain remarkably strong noncollinearity of the two V moments. The angle between the moments is $23^\circ$ for $\theta_s=0^\circ$. It decreases almost linearly with the increase of $\theta_s$. At $\theta_s \sim 35^\circ$ two moments become collinear. With further increase of $\theta_s$, the noncollinearity increases again. At $\theta_s=90^\circ$ the angle between spin and orbital moments reaches $35^\circ$.

A number of important conclusions can be derived from these graphs. First, the interval of the variation of the orbital moment direction is distinctly smaller than the interval of the variation of $\theta_s$. This reveals a limited influence of the spin moment direction on the direction of the orbital moment. The competing stronger influence is exerted by the lattice. Second, in the self-consisted state at $\theta_s \sim 35^\circ$ the two atomic moments are almost collinear. The angle of $\sim 35^\circ$ specifying the direction of the easy axis is in very good correlation with the experimental measurement.

It is also interesting to inspect the magnitudes of the spin and orbital atomic moments as the functions of $\theta_s$. The corresponding data are plotted in Figs. 6b-e. The variation range of the spin moment value of the is distinctly smaller than the variation range of the orbital moment. A flat maximum of the spin moment is reached at $\sim 35^\circ$, that is very close to the direction of the easy axis. In the same region the magnitude of the orbital moment assumes its minimum (Fig. 6b). The minimum of $m_s$ close to the the easy axis direction appears surprising taking into account that the widely accepted analysis of Bruno predicts the maximal value of the OM for the easy axis direction. However, if we take into account that the direction of the OM deviates from the direction specified by $\theta_s$ and consider the value of the projection of vector $\mathbf{m}_o$ on the constrained direction of the spin moment we obtain the curve characterized by a flat maximum at $\sim 35^\circ$ (Fig. 6e). The behavior of the projection of the OM on the constrained direction of the spin moment correlates with the Bruno’s conclusion. Nevertheless, it is worth emphasizing that the Bruno’s treatment deals with elemental 3d ferromagnets in a highly symmetric atomic lattice whereas we investigate a compound with low symmetry lattice and strong SOC on ligands. Therefore, more complex relationships between physical quantities should be expected.

For completeness we include some information on the properties of the I moments. First, we will take the case of $\theta_s=0^\circ$. As predicted by the symmetry analysis, the I atoms become inequivalent. The I spin moments of atoms 1-3 have the values 0.040, 0.013, 0.014 $\mu_B$ and deviate from the $z$ axis by 1°, 12° and 9°, respectively. The OMs have the values 0.022, 0.034 and 0.033 $\mu_B$ deviating by 18°, 34° and 34° from the $z$ axis. As a result we have a complex magnetic configuration with strong intraatomic noncollinearity of the spin and orbital moments and strong noncollinearity of the inducing and induced moments. For the self-consistent state corresponding to $\theta_s=35^\circ$ we obtained the values of the I orbital moments 0.024, 0.036, and 0.035 $\mu_B$ that are very close to the values for $\theta_s=0^\circ$. The noncollinearity with respect to the V moments is given by 2°, 10°, and 10° that is now distinctly smaller than in the case of $\theta_s = 0^\circ$.

2. AD-Distortion combined with broken inversion symmetry

As discussed in Sec. IV C 1, the preserved inversion symmetry of the AD-distorted atomic structure is responsible for the equivalence of the V atoms and collinearity of their magnetic moments. Consequently, the breaking of the inversion symmetry must lead to the inequivalence of the V atoms and noncollinearity of their V moments. In this work we will consider the distortion of the I environment of the V atoms simulated by the shift of all V atoms along the $y$ axis keeping the positions of the I unchanged. This shift leads to the breaking
of the inversion symmetry. These calculations have a model character and are not based on the experimental information on this type of the atomic lattice distortion.

We considered three values of the shift $\delta_1=0.034$ Å, $\delta_2=2\delta_1$, $\delta_3=4\delta_1$. For all three cases we performed calculations with the directions of the V spin moments constrained parallel to the $z$ axis. As expected, the V atoms in this type of lattice are inequivalent. For the smallest shift $\delta_1$ we obtained very small difference in the value of the spin moments of the V atoms: $m_s$(V1)=2.092, $m_s$(V2)=2.086 $\mu_B$. However, for the orbital moments the difference is considerable: the values of the moments are 0.735 and 0.608 $\mu_B$, the deviations from the $z$ axis are 20$^\circ$ and 28$^\circ$. For shift $\delta_2$ we obtained large difference between the values of the spin moments $m_s$(V1)=2.020 $m_s$(V2)=1.355 $\mu_B$. For the orbital moments we get the values 0.667, 0.688 $\mu_B$ and the deviation angles 13$^\circ$ and 24$^\circ$. For the largest shift $\delta_3$, the spin moments are 2.064 and 0.035 $\mu_B$. The values and deviations of the orbital moments are 0.628 and 0.015 $\mu_B$ and 26$^\circ$ and 141$^\circ$.

Analysis of these data shows that distortion of the I environment of the V atoms has strong influence on the magnetic moments of the V atoms. This influence is complex and nonlinear with respect to the value of the distortion. For the smallest distortion $\delta_1$ the spin moments of the two V atoms remain almost equal whereas the values and directions of the orbital moments differ considerably. Doubling the shift we obtain strong drop of $m_s$(V2) which looses a half of its value. Surprisingly, here the values of the orbital moments are rather close to each other. For the largest shift $\delta_3$ we obtain dramatic change of the magnetism of the V2 which is now nearly nonmagnetic.

The model calculations discussed in this section show (i) the distortion of the I environment of the V atoms has a strong effect on the magnetic characteristics of the V atoms. (ii) As predicted the inversion symmetry breaking leads to the inequivalence of the V atoms. This feature correlates with the experimental results of Gati et al. (iii) The character of the changes is strongly non-linear with respect to the strength of the distortion. This means that quantitative conclusions about the properties of the system need precise information on the character of the lattice distortions.

V. CONCLUSIONS

Recently discovered ferromagnetism of the layered vdW material VI$_3$ attracts much research attention, both theoretical and experimental. Despite substantial progress, in some important aspects no consensus has been reached. Among the experimental questions where no consensus is achieved are (i) the deviation of the easy axis from the normal to the VI$_3$ layers, (ii) a possible inequivalence of the V atoms, (iii) the value of the V magnetic moments. The theoretical works differ in the conclusions on the conduction nature of the system, the value and the role of the V orbital moments. To the best of our knowledge there is no theoretical works addressing issues (i) and (ii) and only one work dealing with the reduced value of the V moment and explaining it by the formation of a large orbital moment.

By combining the symmetry arguments with DFT and DFT+U calculations we have shown that the distortion of the crystal structure suggested by Son et al. must lead to the deviation of the easy axis from the normal to the VI$_3$ layers in close correlations with the experimental results reported in Ref. 38. The AD accompanied by the distortion of the I environment of the V atoms leads to the breaking of the inversion symmetry and inequivalence of the V atoms.

In agreement with earlier works our calculation show that the DFT+U method provides a proper account for the interplay between interatomic hybridization and on-site electron correlations leading to the formation of the Mott insulating state. The standard DFT calculations give a metallic state of VI$_3$ contradicting the experimental results.

Our DFT+U calculations result in large values of the OMs of the V atoms leading to reduced total V moment, in agreement with a number of experimental results and with the physical picture suggested by Yang et al. We obtained large intraatomic noncollinearity of the V spin and orbital moments revealing strong competition of the effects caused by the on-site electron correlation, SOC, interatomic hybridization.

Our calculations confirm the experimental result of strong magneto-elastic interaction revealing itself in the strong dependence of the magnetic properties on the distortion of the atomic structure. This makes the account for the lattice distortion crucial for the understanding of the magnetic properties of VI$_3$.

Our study agrees with previous reports about possibility of the multiple convergence of the DFT+U method. However, in contrast to Ref. 15 in our calculations all converged states are Mott insulators. The different states are characterized by different values of the OM with the state with the large OM being the lowest in energy.

We hope that our study contributes importantly to the understanding of the magnetic properties of VI$_3$ and will stimulate further experimental and theoretical investigations of VI$_3$ and other vdW and 2D magnets.

VI. ACKNOWLEDGMENTS

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The comparison of the energies of the ferromagnetic states of the $R^3$ atomic structure and the structure with the AD distortion gives for the distorted structure the energy gain of about 0.2 eV per formula unit.