Orbital and magnetic ordering in single-layer FePS$_3$: A DFT+$U$ study

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I. INTRODUCTION

The study of two-dimensional (2D) magnetic ground states has gained special interest after the discovery of stable long-range ferromagnetic (FM) and antiferromagnetic (AFM) order in monolayer CrI$_3$ and FePS$_3$, respectively [1,2]. The ideal candidates for 2D magnets are layered van der Waals materials such as the transition-metal dichalcogenides [3], chromium trihalides [1] and transition-metal phosphorous trichalcogenides [4]. These materials hold significant promise for technological applications, especially in the field of spintronics and nanomagnetism [5]. Therefore, a deep understanding of the magnetic exchange mechanisms in 2D system is essential. In this way, it is possible to find out which exchange coupling controls the magnetic properties of the ground state and how the system selects a special order when decreasing the temperature. Here, we investigate the magnetic ordering in FePS$_3$, a 2D Ising antiferromagnet with a Néel temperature of 116–120 K in bulk [6,7]. In advantage over other 2D materials, Ramos et al. [8] claimed the optical response of FePS$_3$ over a broad range of the electromagnetic spectrum, from infrared to ultraviolet. Its band gap of about 1 eV [8–11] makes FePS$_3$ suitable for infrared detection while applications in ultraviolet photodetectors [12] and in nonlinear optics [13] have been reported as well. In addition, pure bulk FePS$_3$ displays antiferromagnetic ordering below 120 K [6,14] while its magnetic and structural properties can be tuned easily [15] by chemical modification. That is why this material, similar to the low-temperature 2D magnet CrI$_3$, is a suitable candidate for the next step in spintronics towards AFM 2D spintronic devices [5] operating at low temperatures.

From the structural point of view, bulk FePS$_3$ is a 2D layered material. Figure 1 shows the unit cell of one monolayer. To visualize the crystal structure, it is better to write Fe$_2$P$_2$S$_6$, which means that in each layer, every Fe ion is surrounded by bipyramidal (P$_2$S$_6$)$^{4-}$ anions. In this way, each Fe is octahedrally bonded to six S atoms while each P is bonded to three S atoms and one P atom.

The Fe$^{2+}$ ions in FePS$_3$ have the maximum magnetic moment compatible with their charge state, i.e., their spin is $S = 2$. Leaving away all the other ions for clarity, the positions of the Fe$^{2+}$ ions, and thus of their spins, can be described by a distorted honeycomb lattice. Two opposite sides of each hexagon are slightly (between 0.017 and 0.19 Å according to different experimental sources [14,17]) longer than the other four sides, see Fig. 2. This difference has a crucial effect on the type of magnetic exchange interaction between Fe atoms. Another important feature of the magnetism in FePS$_3$ is its strong out-of-plane easy axis, which renders stable magnetic order even in the monolayer limit. According to the Hohenberg-Mermin-Wagner theorem [18,19] in a system with isotropic interactions, thermal fluctuations in 2D would prevent the spontaneous symmetry breaking required to form a low-temperature ordered state. Therefore, some anisotropic interaction, e.g., magnetic single-ion anisotropy, is required in 2D systems to get a ground state with long-range magnetic order [1]. However, despite many experimental and theoretical investigations [14,20–26], the magnetic unit cell of the ground state of FePS$_3$ is still under debate. Leaving aside possible complications in the three-dimensional material related to stacking order, several authors [14,22] assumed an identity of the structural and the magnetic unit cell, containing two Fe$^{2+}$ ions each. Consequently, all Fe-Fe bonds along a ferromagnetically aligned chain would be identical in length. In contrast, LeFlem et al. [23] proposed a unit cell with four Fe$^{2+}$ ions...
FIG. 1. (Top row) Octahedral and tetrahedral environment of Fe and P ions in FePS$_3$, respectively. The primitive cell of the FePS$_3$ monolayer (Middle) in side view and (Bottom) in top view. The brown, grey, and yellow spheres denote the Fe, P and S atoms, respectively. Each Fe atom is surrounded by six S ions. The P dimer, oriented perpendicular to the plane of view, sits in the center of the Fe honeycomb. Magnetic exchange interactions between Fe ions are governed by the S ions as the mediating links between them. Data in this figure, as well as in Figs. 3, 4, and 7, were drawn using the VESTA software [16].

in which the ferromagnetically aligned Fe chains run along an alternating sequence of short and long Fe-Fe bonds. This proposal was taken up later by other researchers [27–29], e.g., to explain the observation of Brillouin-zone folding effects in measured Raman spectra [7]. Note that the FM chains in both models are rotated by 60° in the plane, see Fig. 3.

The so far unresolved issue of the relation between lattice distortion and magnetic ground state motivated us to carry out a comprehensive computational study of the magnetic properties employing the DFT+$U$ approach (density functional theory plus on-site electron-electron repulsion). In

the literature, spin model Hamiltonians had considered exchange interactions only up to the third-nearest neighbors of the Fe atoms [20,21], and the difference between short and long Fe-Fe bonds had been ignored in the Hamiltonian parametrization. Moreover, higher-order (in the spin variable) couplings, such as the Dzyaloshinskii-Moriya interaction and biquadratic couplings, had been neglected so far. We find that $U = 2.22$ eV can produce the experimental band gap of 1.23 eV. Interestingly, we find that the magnetic exchange interaction is ferromagnetic and antiferromagnetic along the long bonds and short bonds, respectively. This assignment turns out to be robust with respect to changes in the $U$ parameter. We conclude that the magnetic ground state consists of ferromagnetic spin chains running along the long bonds that couple antiferromagnetically among each other. In addition, we propose a model spin Hamiltonian that includes anisotropic spin interactions that are of crucial importance for 2D magnets, as well as an interaction up to forth neighbors, such that the fall-off of magnetic interactions with distance, as it is expected for a magnetic insulator, can be seen.

The paper is structured as follows. In Sec. II the details of the DFT and Monte Carlo calculations are presented. Section III is devoted to electronic properties as well as the derivation of the spin Hamiltonian and the different aspects of exchange interactions in the determination of the magnetic ground state of the FePS$_3$ monolayer. Finally, in Sec. IV a summary is given.

II. COMPUTATIONAL DETAILS

As a single crystal, iron phosphorous trichalcogenide crystallizes in the monoclinic structure with space group C2/m. The Fe atoms occupy the $4g(0,y,0)$ sites, P atoms occupy the $4i(x,0,z)$ and S atoms occupy $4i(x,0,z)$ and $8j(x,y,z)$ sites, respectively. Structural parameters can be found in Ref. [14].
We used the so-defined lattice parameters and atomic positions as starting point for our calculations of a FePS$_3$ monolayer. To generate an isolated layer, the lattice parameter perpendicular to the layers (c axis) of the bulk structure was increased to 20 Å.

We employ two different computational approaches for our first-principles calculations: For calculating the single-site magnetic anisotropy and anisotropic interactions between spins that rely on a relativistic description of electrons as well as for the biquadratic interaction which needs a noncollinear scheme, we use an all-electron full-potential linearized augmented plane-wave (FPLAW) method. For large systems consisting of many atoms with collinear spins, computationally more efficient calculations were carried out with the Quantum-Espresso (QE) [32] code in the framework of the spin-polarized DFT. We approximate the exchange-correlation energy using the generalized gradient approximation (GGA) in the Perdew-Burke-Ernzerhof parametrization [33].

For a better description of the low-temperature ground state of FePS$_3$, we used GGA+$U$ approach to correct on-site electron-electron interaction ($U$) for the 3$d$ orbitals of the Fe atoms, following Dudarev’s approach which includes a spherically symmetric effective on-site Coulomb repulsion $U_{\text{eff}}$. Since QE is a plane-wave code, GBRV ultrasoft pseudopotentials [34] for the elements Fe, P, and S are employed to describe the interaction of the valence electrons with the ionic core. The optimized cut-off energies of 50 and 480 Ry have been used for expanding the wave functions and charge density, respectively, in plane waves.

Some magnetic modeling parameters, such as the single-ion anisotropy (SIA) and the Dzyaloshinskii-Moriya (DMI), require the inclusion of spin-orbit interaction, and therefore a relativistic treatment of the electrons. For an accurate treatment of these aspects, we employ the FPLAW method, as implemented in the FLEUR code [35]. The cut-off energy of the plane-wave expansion in the interstitial region is set to $k_{\text{max}} = 3.8$ a.u.$^{-1}$. The muffin-tin radii of Fe, P, and S atoms are set to 2.8, 1.49 and 1.90 a.u., respectively. Although the FLEUR code allows for a more general treatment of the on-site electron-electron interaction, we chose to set the on-site Hund exchange to zero to stay compatible with the QE calculations.

In order to determine the type of magnetic order of the ground state, we define a model spin Hamiltonian:

$$H_{\text{spin}} = H_{\text{Heis}} + \frac{1}{2} B \sum_{n,n} (\vec{S}_i \cdot \vec{S}_j)^2 + \frac{1}{2} D \sum_{n,n} \vec{D}_{ij} \cdot (\vec{S}_i \times \vec{S}_j) + \Delta \sum_i (\vec{S}_i \cdot \vec{d}_i)^2,$$

where $\vec{S}_i$ represents direction of magnetic spins, $H_{\text{Heis}}$ is the usual Heisenberg Hamiltonian (for details see below), $B$, $D$, and $\Delta$ are the strengths of biquadratic, DMI and SIA, respectively. Moreover, unit vectors $\vec{D}_{ij}$ and $\vec{d}_i$ show the direction of the DMI and the easy axis of magnetization at each site $i$, respectively. It should be noted that the direction of DMI is determined by Moriya rules [36]. Due to the centrosymmetric 2/m point group symmetry, the FePS$_3$ monolayer has a mirror plane perpendicular to the $b$ axis. According to the Moriya rules, when a mirror plane includes two ions, the $D$ vector should be perpendicular to the mirror plane.

For the determination of $B$, $D$ and $\Delta$ with FLEUR, we consider the primitive cell (2 Fe atoms, 10 atoms in total) and a $10 \times 10 \times 1$ Monkhorst-Pack $k$-point mesh. The biquadratic interaction originates from electron hopping, and in terms of a tight-binding description it can be obtained in fourth order from a perturbation theory [37,38]. For extracting the $B$ term from DFT calculations, we rotate the spins of the two Fe atoms pointing in opposite direction around the $c$ axis in such a way that the sum of them remains zero, $S_x + S_z = 0$. In this way, the energy due to the Heisenberg term is degenerate and the total energy differences are attributed to $B$ only. It should be noted that in the calculation of $B$ spin-orbit coupling (SOC) has not been considered, and the anisotropic terms are quenched. For the anisotropic exchange interactions, we need to consider the effect of SOC (GGA+$U$+SOC). Care must be taken in the selection of appropriate spin configurations that allow us to extract the values of $D$ and $\Delta$ from total energy differences. Therefore, pairs of configurations are constructed in such a way that their energies, as given by the
Heisenberg term, are degenerate before turning on SOC. For SIA, we consider a pair of magnetic configurations in which all spins are oriented along the c axis or along the b axis, respectively. For these configurations, the DMI term vanishes in GGA+U+SOC calculations. For obtaining the strength of $D$, we need to consider two different magnetic configurations in which two spins are oriented on the a axis and the negative b axis for the first, and the a axis and the positive b axis for the second one. In this way, the $\Delta$ term vanishes in GGA+U+SOC calculations. From energy difference of each pair of configurations, the $\Delta$ and $D$ can be extracted.

With the aim to characterize the low-temperature magnetic ground state of FePS$_3$, Monte Carlo simulations of classical spins on a lattice have been performed using the replica-exchange method [39]. We use two-dimensional lattices consisting of $N \times L^2$ spins, where $L = 10$ is the linear size of the simulation cell and $N$ is the number of spins ($N = 2$ for the primitive cell). For checking phase transition at low temperature, different sizes of the simulation cell from $L = 8$ to $L = 14$ are considered. For the thermal equilibrium and data collection, we consider $3 \times 10^8$ Monte Carlo steps (MCs) per spin at each temperature.

### III. RESULTS AND DISCUSSION

#### A. Geometric and electronic structure

It is well known from previous studies that in FePS$_3$ the Fe$^{2+}$ ions are in the high-spin state of Fe. Consequently at one Fe atom five electrons are pointing spin-up while one electron is spin-down and occupies a single 3$d$ orbital. Of course, at Fe atoms with opposite magnetic moment the role of spin-up and spin-down electrons is interchanged. Due to the rather large distance between the Fe$^{2+}$ ions, the interaction between the 3$d$ orbitals of different Fe ions is weak, yet decisive for the magnetic ground state. Since the energies of the orbitals on the 3$d$ shell are split up by the crystal field of the surrounding sulfur anions, unequal occupation of the 3$d$ orbitals, and hence orbital ordering, are to be expected. Thus, the DFT + $U$ method is mandatory for a correct description of electronic structure. Several approaches are possible to determine a suitable value for $U$: We found that we are able to reproduce the experimental band gap by choosing $U = 2.22$ eV. For this purpose, we rely on the most recent experimental value of 1.23 eV [8], discarding an older optical absorption measurement that had estimated a band gap of $\sim$1.6 eV [10] as outdated. This value of $U$ is of the same order as the value $U = 2$ eV used in Ref. [20]. Alternatively, we estimated $U$ using density functional perturbation theory (DFPT) [40] which is implemented in the QE code. This calculation has been done by considering the primitive cell of FePS$_3$ (containing 10 atoms), and a value of $U = 4.89$ eV is obtained. Since the DFT + $U$ calculations have been done using two codes, we compared the obtained gap to make sure that different implementations of DFT+$U$ have no effect on the results. The gaps obtained from the QE and theFLEUR code are in good agreement for each $U$ parameter.

We started by performing a number of explorative calculations to investigate the interplay between structure and magnetic order at low temperature. For this purpose we used a $(1 \times 2)$ cell which includes four Fe ions and allows us to build ferromagnetic zigzag chains of spins, either running along the long or the short Fe-Fe separations, as illustrated in Fig. 3. We started from the experimental geometry [14] and optimized the geometry using self-consistent forces obtained with the GGA+U method. In particular, we optimized both the lattice vectors and the positions of the atoms in the cell for both spin configurations shown in Fig. 3. In both cases, it is found that the Fe-Fe distances are unequal; two

![Image of different collinear magnetic configurations](image-url)

**FIG. 4.** Different collinear magnetic configurations that we use for obtaining $J$ parameters. The yellow, grey, and brown spheres are S, P, and Fe ions, respectively. The red arrow shows the direction of the magnetic moment on each Fe ion. Note that some Fe-Fe distances (the vertical ones in the plots) are about 4% larger than the others, and hence all six configurations shown are nonequivalent. Top row shows (from left to right), Néel, long-bond zigzag, and short-bond zigzag configurations. Our DFT + $U$ calculations show that the long-bond zigzag is the global minimum ground state. Bottom row shows additional collinear configurations considered.
The energies plotted in the graph are for numbered spin configurations correspond to those shown in Fig. 4. The energies plotted in the graph are for U_{eff} = 2.22 eV. The standard fitting error for each U_{eff} is ~2%.

opposing edges of the Fe hexagons are longer than the others by 0.14 Å and 0.13 Å for long-bond and short-bond spin configurations, respectively. The lattice constants determined for the two spin structures differ by less than 0.4%. Having spins ferromagnetically aligned in the zigzag chain passing through the long Fe-Fe bonds is found to be always energetically more favorable than the alignment along the short bonds, or any other spin structure in this cell. Moreover, we find this trend to be independent on the value of U. To construct the spin Hamiltonian, it is therefore justified to work with the optimized lattice constants and atomic positions of the ground-state spin configuration, the long-bond zigzag chain, and to use this fixed geometries for all additional geometries shown in Fig. 4 whose energies are reported in Fig. 5. The optimized distances between the Fe atoms which are used to derive J parameters are summarized in Table I. Using U = 2.22 eV, the two different nearest-neighbor distances are determined as d_{ia} = 3.44 Å and d_{ib} = 3.58 Å, see Fig. 2. Thus, the obtained results show that the distance between the nearest Fe neighbors differs by d_{ib} - d_{ia} = 0.14 Å; this agrees well with the structure determination by neutron scattering at low temperature by Lançon et al. [14] who obtained 0.19 Å while earlier experiments [17] using x-ray diffraction at room temperature in magnetically disordered samples had found a smaller value of 0.017 Å. We will later argue that this distortion has a crucial effect on exchange interaction and magnetic properties of the ground state. The obtained lattice parameters for the primitive unit cell (a = 6.017 Å and b = 6.052 Å and \gamma = 119.86°) are in good agreement with experimental values [14] of bulk samples (a = 5.940 Å and \gamma = 121.29°).

Calculations of the electronic band structure and the orbital-projected density of states of the magnetic ground state for both values of U are shown in Fig. 6. While the band structure obtained with U = 2.22 eV reproduces the experimental gap of 1.23 eV, the calculation with U = 4.89 eV gives a much wider band gap. The projected density of states show that for U = 2.22 eV this gap is opened up by the intra-atomic Coulomb repulsion between the occupied 3d_{x^2-y^2} orbitals and the remaining unoccupied 3d orbitals. For the larger U_{eff} value, the occupied 3d state of Fe is pushed down even further in energy and energetically overlaps with the valence bands, hence the larger band gap encountered in this case. A Löwdin analysis indicates that all 3d states for spin majority are fully occupied while for spin minority the Löwdin charges in the individual orbitals for U_{eff} = 4.89 eV are 0.03, 0.35, 0.18, 0.60, 0.15 for d_{x^2}, d_{y^2}, d_{xy}, d_{x^2-y^2} and d_{3y^2-r^2}, respectively. By decreasing the U_{eff} parameter, the hybridization between the 3d orbitals of Fe and the p orbitals of P and S gets slightly weaker, so that for U_{eff} = 2.22 eV the d_{x^2-y^2} orbital has less mixing with other orbitals, and the respective Löwdin charges are 0.02, 0.31, 0.13, 0.61, and 0.15. We conclude that U_{eff} = 2.22 eV is a suitable choice to concurrently reproduce both the crystal structure and the electronic structure of the AFM FePS_3 monolayer.

As indicated by the Löwdin charges in the U_{eff} = 2.22 eV case, only a single orbital of the 3d shell, the in-plane d_{x^2-y^2} orbital, is occupied. Thus, the electronic ground state of FePS_3 shows orbital ordering. To illustrate its role, a partial charge density plot of the highest occupied band at the \Gamma point is displayed in Fig. 7. It show that the spatial orientation of the in-plane Fe 3d orbital with respect to the crystal axes changes between the two Fe atoms in the structural unit cell. In addition, sulfur p orbitals oriented within the plane are involved in forming this electronic band. The alternating rotation of the Fe 3d orbital allows for a bonding overlap (same sign of the orbital lobes) between the S atom and both Fe atoms for the long Fe-Fe distance in the distorted hexagon. This finding explains why the long-bond zigzag chain is energetically preferred. Another aspect of orbital ordering is the unusually large orbital moment of Fe in this system. Using the Berry curvature approach [41], we find the orbital moment of each Fe to equal 0.77 and 0.8 \mu_B for U_{eff} = 2.22 eV and 4.89 eV, respectively. We believe that the reason for such a large orbital moment can be understood in analogy to the orbital moment of a free Fe atom which is determined by Hund’s rule. In this system, Fe^{2+} is in a 3d^6 state. We thus expect 4 \mu_B as spin moment, and DFT yields 3.46 \mu_B for U_{eff} = 2.22 eV. The difference is related to induced magnetic moments at the S and P ions. Moreover, for 3d^6 the quantum numbers m_L do not add up to zero, which means the orbital moment is not quenched and points in the direction perpendicular to the plane. As a

![Graph](image-url)
FIG. 6. (Top row) Band structure and (Bottom row) projected density of states (PDOS) of the AFM long-bond zigzag structure for $U_{\text{eff}} = 4.89$ and 2.22 eV, respectively. For band structures, the green and blue colors denote spin up and spin down, respectively. Due to the absolute spin being zero for AFM long-bond zigzag, the two spin channels collapse to each other. When $U_{\text{eff}}$ is decreased, the contribution of the $d_{x^2-y^2}$ orbital to the highest occupied bands increases. This is the reason why in the band structure with $U_{\text{eff}} = 2.22$ eV the two topmost valence bands are split off. These calculations were done in the $(2 \times 2)$ cell also used for the calculations of the $J$ parameters.

consequence, the effect of SOC and its related exchange interactions cannot be neglected, and there is a strong tendency for the spin to align with the orbital moment perpendicular to the plane.

Because of the sensitivity to orbital ordering, we found out that great care must be taken when converging the electronic self-consistency cycle in the DFT + $U$ calculation. In particular, the choice of the starting point for the density matrix used to represent the electronic state of the single spin-down electron in the DFT + $U$ scheme has an influence on the converged result and must be checked carefully.

B. Magnetic exchange interactions

Next we map the information obtained from our DFT+$U$ calculations onto a Heisenberg Hamiltonian

$$H_{\text{Heis}} = -\frac{1}{2} \sum_{i \neq j} J_{ij} (\vec{S}_i \cdot \vec{S}_j).$$

Motivated by the orbital ordering leading to long and short distances between Fe neighbors, we allow for a differentiation of the first-neighbor $J$ parameters into $J_{1a}$ (= short) and $J_{1b}$ (= long) interactions. Since previous calculations had indicated a rather long range of the exchange interactions, despite the semiconducting character of FePS$_3$, we decided to include interactions up to the fourth-nearest neighbors. Therefore, collinear magnetic configurations were calculated in a quite large $(2 \times 2)$ supercell using the QE code. The total energies for all possible 15 collinear structures were calculated to find the global minimum. The six configurations lowest in energy shown in Fig. 4 were used to determine five exchange parameters. Concerning the quality of the fit, consult Fig. 5. Note that, unlike in previous work [20,21] the so-called stripy magnetic pattern was not included in the fit because our calculations indicate that its energy is much higher than those of the other configurations.
TABLE II. Calculated Heisenberg couplings \( J_i \) (meV) up to the fourth neighbors, biquadratic exchange interaction \( B \) (meV), Dzyaloshinskii-Moriya exchange interaction \( D \) (meV) and single ion anisotropy \( \Delta \) (meV) for different \( U_{\text{eff}} \) (eV) parameters. Negative and positive values denote antiferromagnetic and ferromagnetic exchange interaction, respectively. Note that \( |S| = 1 \) has been used in the definition of the spin Hamiltonian. Using the obtained couplings, we perform MC simulations to find the Curie-Weiss \( (\theta_{\text{CW}}) \) and Néel \( (T_N) \) temperatures (K). We compare to experimental data from Refs. \([6,7,42,43]\).

| \( U_{\text{eff}} \) | \( J_{1a} \) | \( J_{1b} \) | \( J_2 \) | \( J_3 \) | \( J_4 \) | \( \Delta \) | \( D \) | \( B \) | \( T_N \) | \( \theta_{\text{CW}} \) |
|---|---|---|---|---|---|---|---|---|---|---|
| 4.89 | −3.48 | 3.63 | −0.67 | −3.62 | 0.29 | 0.71 | −0.57 | −1.00 | 48.88 | −67.25 |
| 3.89 | −3.87 | 3.98 | −1.14 | −4.01 | 0.20 | 0.73 | −0.39 | −1.37 | 51.42 | −73.12 |
| 2.89 | −3.80 | 4.13 | −1.30 | −5.11 | 0.66 | 0.80 | −0.36 | −1.80 | 63.80 | −85.01 |
| 2.22 | −3.26 | 4.01 | −1.24 | −5.71 | 1.50 | 0.89 | −0.34 | −2.10 | 70.00 | −101.57 |
| exp. | | | | | | | | | 104 – 120 | −112 |

C. Spin Hamiltonian and Monte Carlo simulation

Now we proceed to discuss the features of the effective spin Hamiltonian, to find the ground state in a large simulation cell, and to calculate the finite-temperature properties of FePS\(_3\) monolayer. To avoid any ambiguity due to the debatable value of the \( U \) parameter, we investigate the dependence of the properties on this parameter systematically, varying it between the value determined from the band gap, \( U = 2.22 \) eV, and the value from DFPT, \( U = 4.89 \) eV. Table II summarizes calculated \( H \) terms for the different \( U_{\text{eff}} \) parameters, as well as \( T_N \) and Curie-Weiss temperature \( (\theta_{\text{CW}}) \), which has been obtained by means of MC simulations using the Hamiltonian of Eq. (1).

For all \( U_{\text{eff}} \) parameters, exchange interaction for \( J_{1a} \) and \( J_{1b} \) is AFM and FM, respectively. This means that FM chains run along the long Fe-Fe bond and couple to each other antiferromagnetically along the short bond. This is in agreement with the long-bond zigzag ground state [23]. Interestingly, some interactions are antiferromagnetic \( (J_{1a} \) and \( J_3 \), negative sign), while others are ferromagnetic \( (J_{1b} \) and \( J_6 \), positive sign). The value of \( J_1 \) is the smallest, thus ensuring that the magnetic exchange interaction falls off with distance, as one would expect in an insulating material. In absolute terms, \( J_1 \) has the largest value, larger than \( J_{1a} \). The dominance of \( J_{1a} \), which is responsible for the preferred antiparallel spin alignment between neighboring chains is getting even more prominent when a small value of \( U \) (as dictated by the experimentally known electronic band gap) is employed. Remarkably, the small difference between \( d_{1a} \) and \( d_{1b} \) goes along with a different sign of the interactions \( J_{1a} \) and \( J_{1b} \), the latter being ferromagnetic. While this may seem surprising at first, we note that also in other 2D magnetic systems, such as Cr-trihalides, it has been reported that the exchange parameter may change its sign if the bond distances and bond angle change even by small amounts [44]. In a wider context, this can be seen as a consequence of the Kanamori-Anderson-Goodenough rules [45–47] that emphasize the role of the bond angle at the anion connecting two cations. The governing principle is the dependence of the exchange interaction on the orientation of the anion \( p \) orbital relative to the bond axis between the magnetic cations. For more long-ranged interactions, the connectivity of the lattice sites (mediated via the \( 3p \) orbitals of P and S ions) governs the super-exchange mechanism. According to the strong-coupling perturbation theory, adding an extra intermediate ion (site-connection) increases the order of the perturbative expansion. Therefore, the super-exchange interaction does not reach zero with increasing distances as quickly as in other materials, e.g., in oxides.

As can be seen from Table II, the strengths of \( \Delta \) and \( D \) increase with decreasing \( U_{\text{eff}} \) which satisfies Anderson’s rule [46]. Previous reports [14,20,25] did not mention the effect of DMI in this system. They considered only the effect of the out-of-plane SIA which is responsible for the symmetry breaking required to have an ordered ground state in a 2D system. Here, our calculations show that the direction of the \( D \) vector is along the \( c \) axis due to the lack of inversion symmetry and helps SIA to break rotational symmetry. Our MC simulations show that without considering the effect of \( \Delta \) and \( D \), at finite temperature not all spins are oriented perpendicular to the plane. Besides increasing \( T_N \), the effect of \( \Delta \) and \( D \) is to create perfect Ising-AFM order with spins pointing along the \( c \) axis. The negative value of \( B \) favors the collinear coupling of spins. This feature also helps the system to settle in the Ising-AFM state. The presence of a biquadratic interaction in FePS\(_3\) has been suggested by Wildes et al. [27] when analyzing the experimental neutron scattering pattern and magnetoelastic effect.

As a major result of the Monte Carlo simulations, we present the temperature dependence of the specific heat in Fig. 8 for \( U_{\text{eff}} = 2.22 \) eV. The value of \( T_N \) is estimated from

![FIG. 8. Plot of the specific heat versus temperature obtained from Monte Carlo simulations of the spin Hamiltonian for lattices with the linear sizes \( L = 8 \) to \( L = 14 \) for \( U_{\text{eff}} = 2.22 \) eV. The divergence, seen as a peak of specific heat in the simulations, is used to read off the Néel temperature. The observation that the peak height increases with increasing \( L \) is indicative of a phase transition.](image-url)
the location of the peak. We observe that this peak becomes higher by increasing the simulation lattice size which is a confirmation of a phase transition taking place. We obtain the Curie-Weiss temperatures (θ_{CW}) by a linear fitting of the inverse susceptibility in the temperature range between 150 and 300 K. The negative values of θ_{CW} indicate that the ground state has AFM order. In addition, θ_{CW} increases monotonically with decreasing U_{eff} which can be related to the enhancement of exchange interactions, in good agreement with Anderson’s theory of super-exchange [46]. According to the definition [48] of the frustration index f = |θ_{eff} - θ_{CW}|, it is between 1 to 10 for all U_{eff}, indicating that this is a lightly frustrated system.

While the obtained θ_{CW} is close to the experimental value, the obtained T_N for U_{eff} = 2.22 eV still falls short of the experimentally measured value. We note that other reports of first-principles based MC simulations for this material have also not been fully successful to obtain the exact Néel temperature [20]. A possible reason could be the neglect of spin-phonon coupling [49–51] in our simulation. If FePS₃ undergoes a spin-Peierls transition, a gap in the magnetic excitation spectrum would result that is indeed observed in inelastic neutron scattering experiments [14]. Taking the gapped excitation spectrum into account, we expect a higher Néel Hamiltonian for a single layer of FePS₃ with Heisenberg exchange interactions [52].

The cell with (at least) four Fe atoms and consists of chains of biquadratic interactions and single-ion anisotropy. The three latter terms jointly result in the preferred alignment of Fe magnetic moments perpendicular to the crystallographic plane which has led to the characterization of FePS₃ as an Ising antiferromagnet. A series of calculations with different values U_{eff} of the on-site Coulomb interactions in the Fe 3d shell has been carried out to ensure the robustness of the results. All calculations show that due to orbital ordering the honeycomb lattice formed by the Fe atoms is not ideal; two opposite sides of the Fe hexagons are longer than the others. We observe that calculated magnetic exchange couplings along the long bonds and short bonds are FM and AFM, respectively. As a consequence, the magnetic ground state must be described by a unit cell with (at least) four Fe atoms and consists of chains of parallel magnetic moments running across the long bonds. In an attempt to reproduce both the electronic band gap and the Néel temperature, we conclude that a value of U_{eff} = 2.22 eV is a reasonable choice, but there is room for improvement by including more subtle effects such as spin-lattice coupling.

IV. CONCLUSION

In summary, using DFT calculations we determined a spin Hamiltonian for a single layer of FePS₃ with Heisenberg exchange up to the forth neighbor, the nearest-neighbor DM and biquadratic interactions and magnetic excitations are beyond the scope of our current work.

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