Unusual Spin Exchanges Mediated by the Molecular Anion \( \text{P}_2\text{S}_6^{4-} \): Theoretical Analyses of the Magnetic Ground States, Magnetic Anisotropy and Spin Exchanges of MPS\(_3\) (\(M = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}\))

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Abstract: We examined the magnetic ground states, the preferred spin orientations and the spin exchanges of four layered phases MPS\(_3\) (\(M = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}\)) by first principles density functional theory plus onsite repulsion (DFT + U) calculations. The magnetic ground states predicted for MPS\(_3\) by DFT + U calculations using their optimized crystal structures are in agreement with experiment for \(M = \text{Mn}, \text{Co} \) and \(\text{Ni}\), but not for \(\text{FePS}_3\). DFT + U calculations including spin-orbit coupling correctly predict the observed spin orientations for \(\text{FePS}_3\), \(\text{CoPS}_3\) and \(\text{NiPS}_3\), but not for \(\text{MnPS}_3\). Further analyses suggest that the \(1/2 \) spin direction observed for the \(\text{Mn}^{2+}\) ions of \(\text{MnPS}_3\) is caused by the magnetic dipole–dipole interaction in its magnetic ground state. Noting that the spin exchanges are determined by the ligand p-orbital tails of magnetic orbitals, we formulated qualitative rules governing spin exchanges as the guidelines for discussing and estimating the spin exchanges of magnetic solids. Use of these rules allowed us to recognize several unusual exchanges of MPS\(_3\), which are mediated by the symmetry-adapted group orbitals of \(\text{P}_2\text{S}_6^{4-}\) and exhibit unusual features unknown from other types of spin exchanges.

Keywords: magnetic ground state; spin exchange; magnetic anisotropy; molecular anion; MPS\(_3\); magnetic orbitals; qualitative rules

1. Introduction

In an extended solid, transition-metal magnetic cations \(M\) are surrounded by main-group ligands \(L\) to form \(\text{ML}_n\) (typically, \(n = 3–6\)) polyhedra, and the unpaired spins of \(M\) are accommodated in the singly occupied d-states (i.e., the magnetic orbitals) of \(\text{ML}_n\). Each d-state has the metal d-orbital combined out-of-phase with the p-orbitals of the surrounding ligands \(L\). The tendency for two adjacent magnetic ions to have a ferromagnetic (FM) or an antiferromagnetic (AFM) spin alignment is determined by the spin exchange between them, which takes place through the M-L-M or M-L . . . L-M exchange path [1–4]. Whereas the characteristics (e.g., the angular and distance dependence) of the M-L-M exchanges is conceptually well understood [5–8], the properties of the M-L . . . L-M exchanges involving several main-group ligands have only come into focus in the last two decades [1–4]. Furthermore, the character of a M-L . . . L-M exchange can be modified if the L . . . L contact is bridged by a d\(^0\) metal cation \(A\) to form a L . . . A . . . L bridge [1–4]. What has not been well understood so far is the M-L . . . L-M exchange in which the L . . . L contact is an integral part of the covalent framework of a molecular anion made up of main group elements (e.g., the \(\text{P}_2\text{S}_6^{4-}\) anion in MPS\(_3\), where \(M = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}\)), which might be termed the M-(L-L)-M exchange to emphasize its difference from the M-L-M, M-L . . . L-M and M-L . . . A . . . L-M exchanges.
In the present work we examine the M-(L-L)-M spin exchanges in the layered phases MPS$_3$ (M = Mn [9–11], Fe [9–11], Co [10,11], Ni [10,11]), which crystallize with a monoclinic structure (space group C2/m, no. 12). Each layer of MPS$_3$ is made up of the molecular anions P$_2$S$_6^{4-}$ possessing the structure of staggered ethane (i.e., a trigonal antiprism structure) (Figure 1a,b). The molecular anions P$_2$S$_6^{4-}$ form a trigonal layer (Figure 1c) with the P-P bonds perpendicular to the layer, and a high-spin M$^{2+}$ cation occupies every S$_6$ octahedral site (deviations from a trigonal symmetry caused by the monoclinic distortions are less than 1°). Thus, each MPS$_3$ layer consists of a honeycomb arrangement of M$^{2+}$ cations. With the c*-direction of the MPS$_3$ taken as the z-direction, the P-P bond of each P$_2$S$_6^{4-}$ is parallel to the z-direction (||z), and each MS$_6$ octahedron is arranged with one of its three-fold rotational axes along the ||z|-direction.

To a first approximation, it may be assumed that each MPS$_3$ layer has a trigonal symmetry (see below for further discussion), so there are three types of spin exchanges to consider, i.e., the first nearest-neighbor (NN) spin exchange J$_{12}$, the second NN spin exchange J$_{13}$, and the third NN exchange J$_{14}$ (Figure 1d). J$_{12}$ is a spin exchange of the M-L-M type, in which the two metal ions share a common ligand, while J$_{13}$ and J$_{14}$ are nominally spin exchanges of the M-L…L-M type, in which the two metal ions do not share a common ligand. In describing the magnetic properties of MPS$_3$ in terms of the spin exchanges J$_{12}$, J$_{13}$ and J$_{14}$, an interesting conceptual problem arises. Each P$_2$S$_6^{4-}$ anion is coordinated to the six surrounding M$^{2+}$ cations simultaneously (Figure 1c,d), so one P$_2$S$_6^{4-}$ anion participates in all three different types of spin exchanges simultaneously with the surrounding six M$^{2+}$ ions. Furthermore, the lone-pair orbitals of the S atoms of P$_2$S$_6^{4-}$, responsible for the coordination with M$^{2+}$ ions, form symmetry-adapted group orbitals, in which all six S atoms participate (for example, see Figure 1e). Consequently, there is no qualitative argument with which to even guess the possible differences in J$_{12}$, J$_{13}$, and J$_{14}$. Over the past two decades, it became almost routine to quantitatively determine any spin exchanges of a magnetic solid by performing an energy-mapping analysis based on first principles DFT calculations. From a conceptual point of view, it would be very useful to have qualitative rules with which to judge whether the spin exchange paths involving complex intermediates are usual or unusual.

A number of experimental studies examined the magnetic properties of MPS$_3$ (M = Mn [9,11–14], Fe [9,11,15–18], Co [11,19], Ni [11,20]). The magnetic properties of MPS$_3$ (M = Mn, Fe, Co, Ni) monolayers were examined by DFT calculations to find their potential use as single-layer materials.
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A number of experimental studies examined the magnetic properties of MPS3 (M = Mn, Fe, Co, Ni) by electronic structure calculations and analyze the spin exchanges of their spin lattices.

Other quantities of importance for the magnetic ions M of an extended solid are the preferred orientations of their magnetic moments with respect to the local coordinates of the MLn polyhedra. These quantities, i.e., the magnetic anisotropy energies, are also readily determined by DFT calculations including spin orbit coupling (SOC). For the purpose of interpreting the results of these calculations, the selection rules for the preferred spin orientation of MLn were formulated [2,3,22–24] based on the SOC-induced interactions between the highest-occupied molecular orbital (HOMO) and lowest-unoccupied molecular orbital (LUMO) of MLn. With the local z-axis of MLn taken along its n-fold rotational axis (n = 3, 4), the quantity needed for the selection rules is the minimum difference, |ΔLz|, in the magnetic quantum numbers Lz of the d-states describing the angular behaviors of the HOMO and LUMO. It is of interest to analyze the preferred spin orientations of the M2+ ions in MPS3 (M = Mn, Fe, Co, Ni) from the viewpoint of the selection rules.

Our work is organized as follows: Section 2 describes simple qualitative rules governing spin exchanges. The details of our DFT calculations are presented in Section 3.1. The magnetic ground states of MPS3 (M = Mn, Fe, Co, Ni) are discussed in Section 3.2, the preferred spin orientations of M2+ ions of MPS3 in Section 3.3, and the quantitative values of the spin exchanges determined for MPS3 in Section 3.4. We analyze the unusual features of the calculated spin exchanges via the P2S64− anion in Section 3.5, and investigate in Section 3.6 the consequences of the simplifying assumption that the honeycomb spin lattice has a trigonal symmetry rather than a slight monoclinic distortion found experimentally. Our concluding remarks are summarized in Section 4.

2. Qualitative Rules Governing Spin Exchanges

2.1. Spin Exchange between Magnetic Orbitals

For clarity, we use the notation (ϕi, ϕj) to represent the spin exchange arising from the magnetic orbitals ϕi at the magnetic ion sites A and B, respectively. It is well known that (ϕi, ϕj) consists of two competing terms [1–4,25]

\( (\psi_i, \psi_j) = J_F + J_{AF} \) (1)
The FM component $J_F (> 0)$ is proportional to the exchange repulsion,

$$J_F \propto K_{ij}$$  \hspace{1cm} (2)

which increases with increasing the overlap electron density $\rho_{ij} = \varphi_i \varphi_j$. In case when the magnetic orbitals $\varphi_i$ and $\varphi_j$ are degenerate (e.g., between the $t_{2g}$ states or between $e_g$ states of the magnetic ions at octahedral sites), the AFM component $J_{AF} (< 0)$ is proportional to the square of the energy split $\Delta e_{ij}$ between $\varphi_i$ and $\varphi_j$ induced by the interaction between them,

$$J_{AF} \propto - (\Delta e_{ij})^2 \propto -(S_{ij})^2$$  \hspace{1cm} (3)

The energy split $\Delta e_{ij}$ is proportional to the overlap integral $S_{ij} = \langle \varphi_i | \varphi_j \rangle$, so that the magnitude of the AFM component $J_{AF}$ increases with increasing that of $(S_{ij})^2$. If $\varphi_i$ and $\varphi_j$ are not degenerate (e.g., between the $t_{2g}$ and $e_g$ states of the magnetic ions), the magnitude of $J_{AF}$ is approximately proportional to $-(S_{ij})^2$.

2.2. $p$-Orbital Tails of Magnetic Orbitals

The spin exchanges between adjacent transition-metal cations $M$ are determined by the interactions between their magnetic orbitals, which in turn are governed largely by the overlap and the overlap electron density that are generated by the $p$-orbitals of the ligands present in the magnetic orbitals (the $p$-orbital tails, for short) [1–4]. Suppose that the metal ions $M$ are surrounded by main-group ligands $L$ to form $ML_6$ octahedra. In the $t_{2g}$ and $e_g$ states of an $ML_6$ octahedron (Figure 3a,b), the $d$-orbitals of $M$ make antibonding combinations with the $p$-orbitals of the ligands $L$. Thus, the $p$-orbital tails of the $t_{2g}$ and $e_g$ states are represented as in Figure 4a,b, respectively, so that each $M$-$L$ bond has the $p_{\sigma}$ and $p_{\pi}$ tails in the $t_{2g}$ and $e_g$ states, respectively, as depicted in Figure 4c. The triple-degeneracy of the $t_{2g}$ and the double-degeneracy of the $e_g$ states are lifted in a $ML_6$ square pyramid and a $ML_4$ square plane, both of which have a four-fold rotational symmetry; the $t_{2g}$ states ($xz$, $yz$, $xy$) are split into ($xz$, $yz$) and $xy$, and the $e_g$ states ($3z^2 - r^2$, $x^2 - y^2$) into $3z^2 - r^2$ and $x^2 - y^2$. Nevertheless, the description of the ligand $p$-orbital tails of the $d$-states depicted in Figure 4c remains valid.

![Figure 3](image1.png)

**Figure 3.** (a) The $t_{2g}$ states and (b) the $e_g$ states of a $ML_6$ octahedron.

![Figure 4](image2.png)

**Figure 4.** The $p$-orbital tails of (a) the $t_{2g}$ and (b) the $e_g$ states of a $ML_6$ octahedron. (c) The $p_{\sigma}$ and $p_{\pi}$ orbitals of the ligand $p$-orbital tails.
2.3. Spin Exchanges in Terms of the p-Orbital Tails

In this section, we generalize the qualitative rules of spin exchanges formulated for the magnetic solids of Cu$^{2+}$ ions [4]. Each Cu$^{2+}$ ion has only one magnetic orbital, i.e., the $x^2-y^2$ state in which each Cu-L bond has a p$_{\sigma}$ tail. The d-electron configuration of the magnetic ion is $(t_{2g})^3(e_{g}^\uparrow)^2(t_{2g}^\downarrow)\ell^0(e_{g}^\downarrow)\ell^0$ in Mn$_2$S$_3$, $(t_{2g})^3(e_{g}^\uparrow)^2(t_{2g}^\downarrow)\ell^2$ in Fe$_2$S$_3$, $(t_{2g})^3(e_{g}^\uparrow)^2(t_{2g}^\downarrow)^2(e_{g}^\downarrow)\ell^0$ in Co$_2$S$_3$, and $(t_{2g})^3(e_{g}^\uparrow)^2(t_{2g}^\downarrow)^3(e_{g}^\downarrow)\ell^0$ in Ni$_2$S$_3$. Thus, the Mn$^{2+}$, Fe$^{2+}$, Co$^{2+}$, and Ni$^{2+}$ ions possess 5, 4, 3, and 2 magnetic orbitals, respectively. For magnetic ions with several magnetic orbitals, the spin exchange $J_{AB}$ between two such ions located at sites A and B is given by the sum of all possible individual exchanges $(\psi_i, \psi_j)$,

$$J_{AB} = \frac{2}{n_An_B} \sum_{i \in \Lambda} \sum_{j \in B} (\psi_i, \psi_j) \propto \sum_{i \in \Lambda} \sum_{j \in B} (\psi_i, \psi_j)$$

(4)

where $n_A$ and $n_B$ are the number of magnetic orbitals at the sites A and B, respectively. Each individual exchange $(\psi_i, \psi_j)$ can be FM or AFM depending on which term, $J_F$ or $J_{AF}$, dominates. Whether $J_{AB}$ is FM or AFM depends on the sum of all individual $(\psi_i, \psi_j)$ contributions.

2.3.1. M-L-M Exchange

As shown in Figure 5, there occur three types of M-L-M exchanges between the magnetic orbitals of $t_{2g}$ and $e_g$ states.

![Figure 5. Three-types of M-L-M spin exchanges between t$_{2g}$ and e$_g$ magnetic orbitals.](image)

If the M-L-M bond angle $\theta$ is 90$^\circ$ for the $(e_g, e_g)$ and $(t_{2g}, t_{2g})$ exchanges, and also when $\theta$ is 180$^\circ$ for the $(e_g, t_{2g})$ exchange, the two p-orbital tails have an orthogonal arrangement so that $(\psi_i, \psi_j) = 0$ (i.e., $J_{AF} = 0$). However, the overlap electron density $\rho_{ij}$ is nonzero (i.e., $J_F \neq 0$), hence predicting these spin exchanges to be FM. When the $\theta$ angles of the $(e_g, e_g)$ and $(t_{2g}, t_{2g})$ exchanges increase from 90$^\circ$ toward 180$^\circ$, and also when the angle $\theta$ of the $(e_g, t_{2g})$ exchange decreases from 180$^\circ$ toward 90$^\circ$, both $J_{AF}$ and $J_F$ are nonzero so that the balance between the two determines if the overall exchange $(\psi_i, \psi_j)$ becomes FM or AFM. These trends are what the Goodenough–Kanamori rules [5–8] predict.

2.3.2. M-L . . . L-M Exchange

There are two extreme cases of M-L . . . L-M exchange. When the p$_{\sigma}$-orbital tails are pointing toward each other (Figure 6a), the overlap integral, $(\psi_i | \psi_j)$, can be substantial if the contact distance L . . . L lies in the vicinity of the van der Waals distance. However, the overlap electron density $\rho_{ij} = \psi_i \psi_j$ is practically zero because $\psi_i$ and $\psi_j$ do not have an overlapping region. Consequently, the in-phase and out-of-phase states $\Psi_+$ and $\Psi_-$ are split in energy with a large separation $\Delta\Psi$. Thus, it is predicted that the M-L . . . L-M type exchange can only be AFM [1–4]. When the L . . . L linkage is bridged by a d$^0$ cation such as V$^{5+}$ or W$^{6+}$, for example, only the out-of-phase state $\Psi_-$ is lowered in energy by the d$_{\pi}$ orbital of the cation A, reducing the $\Delta\Psi$ so that the M-L . . . A . . . M exchange becomes weak (Figure 6b). Conversely, when the p-orbital tails of the M-L . . . L-M exchange path have an orthogonal arrangement (Figure 7a), the overlap integral, $(\psi_i | \psi_j)$, is zero, making the M-L . . . L-M exchange weak. If the L . . . L linkage of such an exchange path is bridged
by a $d^0$ cation, the out-of-phase state $\Psi$. level is lowered in energy enlarging $\Delta e_{ij}$ so that the M-L...A...L-M becomes strongly AFM (Figure 7b) [2–4].

![Figure 6](image)

**Figure 6.** Interactions between the magnetic orbitals in the M-L...L-M exchange where their p$_\sigma$ tails are pointing to each other. The large energy split $\Delta e_{ij}$ of the M-L...L-M exchange in (a) is reduced by the $d_\pi$ orbital of the $d^0$ cation A in the M-L...A...L-M exchange in (b).

![Figure 7](image)

**Figure 7.** Interactions between the magnetic orbitals in the M-L...L-M exchange where their p$_\sigma$ tails have an orthogonal arrangement. The small energy split $\Delta e_{ij}$ of the M-L...L-M exchange in (a) is enlarged by the $d_\pi$ orbital of the $d^0$ cation A in the M-L...A...L-M exchange in (b).

In the M-L...A...L-M exchange of Figure 7, the vanishingly small $\Delta e_{ij}$ of the M-L...L-M exchange results because the two p$_\sigma$ tails have an orthogonal arrangement. A very small $\Delta e_{ij}$ for the M-L...L-M exchange occurs even if the two M-L bonds are pointing to each other as in Figure 6 when one M-L bond has a p$_\sigma$ tail and the other has a p$_\pi$ tail, and also when both M-L bonds have p$_\pi$ tails. Such M-L...L-M spin exchanges become strong in the corresponding M-L...A...L-M exchanges.

### 2.3.3. Qualitative Rules Governing Spin Exchanges

The above discussions are based on the observation that the nature of a spin exchange, be it the M-L-M, M-L...L-M or M-L...A...L-M type, is governed by the ligand p-orbital tails present in the magnetic orbitals of the spin exchange path. The essential points of our discussions can be summarized as follows:

a. For an individual $(\phi_i, \phi_j)$ exchange of a M-L-M type, the $(t_{2g'}, t_{2g})$ and $(e_g, e_g)$ exchanges are FM if the bond angle $\theta$ is $90^\circ$, and so is the $(t_{2g}, e_g)$ exchange if the bond angle $\theta$ is $180^\circ$. These exchanges become AFM when the bond angles $\theta$ deviate considerably from these values.

b. An individual $(\phi_i, \phi_j)$ exchange of a M-L...L-M or M-L...A...L-M type can only be AFM if not weak.

c. A strong individual $(\phi_i, \phi_j)$ exchange of a M-L...L-M is weakened by the $d^0$ metal cation A in the M-L...A...L-M exchange, but a weak individual $(\phi_i, \phi_j)$ exchange...
of a M-L . . . L-M is strengthened by the presence of a d\(^0\) metal cation A in the M-L . . . A . . . L-M exchange.

d. When a magnetic ion has several unpaired spins, the spin exchange between two magnetic ions is given by the sum of all possible individual \((\phi_i, \phi_j)\) exchanges.

These qualitative rules governing spin exchanges can serve as guidelines for exploring how the calculated spin exchanges are related to the structures of the exchange paths and also for ensuring that important exchange paths are included in the set of spin exchanges to evaluate by the energy-mapping analysis.

3. Results and Discussion

3.1. Details of Calculations

We performed spin-polarized DFT calculations using the Vienna ab initio Simulation Package (VASP) [26,27], the projector augmented wave (PAW) method, and the PBE exchange-correlation functionals [28]. The electron correlation associated with the 3d states of M (M = Mn, Fe, Co, Ni) was taken into consideration by performing the DFT+U calculations [29] with the effective on-site repulsion \(U_{\text{eff}} = U - J = 4\) eV on the magnetic ions. Our DFT + U calculations carried out for numerous magnetic solids of transition-metal ions showed that use of the \(U_{\text{eff}}\) values in the range of 3 – 5 eV correctly reproduce their magnetic properties (see the original papers cited in the review articles [1–3,22,24]).

The primary purpose of using DFT + U calculations is to produce magnetic insulating states for magnetic solids. Use of \(U_{\text{eff}} = 3 – 5\) eV in DFT + U calculations leads to magnetic insulating states for magnetic solids of Mn\(^{2+}\), Fe\(^{2+}\), Co\(^{2+}\), and Ni\(^{2+}\) ions. The present work employed the representative \(U_{\text{eff}}\) value of 4 eV. We carried out DFT + U calculations (with \(U_{\text{eff}} = 4\) eV) to optimize the structures of MPS\(_3\) (M = Mn, Fe, Co, Ni) in their FM states by relaxing only the ion positions while keeping the cell parameters fixed and using a set of \((4 \times 2 \times 6)\) k-points and the criterion of \(5 \times 10^{-3}\) eV/Å for the ionic relaxation. All our DFT + U calculations for extracting the spin-exchange parameters employed a \((2a, 2b, c)\) supercell, the plane wave cutoff energy of 450 eV, the threshold of \(10^{-6}\) eV for self-consistent-field energy convergence, and a set of \((4 \times 2 \times 6)\) k-points. The preferred spin direction of the cation M\(^{2+}\) (M = Mn, Fe, Co, Ni) cation was determined by DFT + U + SOC calculations [30], employing a set of \((4 \times 2 \times 6)\) k-points and the threshold of \(10^{-6}\) eV for self-consistent-field energy convergence.

3.2. Magnetic Ground States of MPS\(_3\)

We probed the magnetic ground states of the MPS\(_3\) phases by evaluating the relative energies, on the basis of DFT + U calculations, of the AF1, AF2 and AF3 spin configurations shown in Figure 2 as well as the FM, AF4, AF5, and AF6 states depicted in Supplementary Materials, Figure S1. As summarized in Table 1, our calculations using the experimental structures of MPS\(_3\) show that the magnetic ground states of MnPS\(_3\) and NiPS\(_3\) adopt the honeycomb state AF1 and the ||\(a\)-chain state AF2, respectively, in agreement with experiment. In disagreement with experiment, however, the magnetic ground state is predicted to be the ||\((a + b)\)-chain state AF3 for FePS\(_3\), and the honeycomb state AF1 for CoPS\(_3\). Since the energy differences between different spin ordered states are small, it is reasonable to speculate if they may be affected by small structural (monoclinic) distortion. Thus, we optimize the crystal structures of MPS\(_3\) (M = Mn, Fe, Co, Ni) by performing DFT + U calculations to obtain the structures presented in the supporting material. Then, we re-determined the relative stabilities of the FM and AF1–AF6 states using these optimized structures. Results of these calculations are also summarized in Table 1. The optimized structures predict that the magnetic ground states of MnPS\(_3\), CoPS\(_3\) and NiPS\(_3\) are the same as those observed experimentally, but that of FePS\(_3\) is still the ||\((a + b)\)-chain state AF3 rather than the ||\(a\)-chain state AF2 reported experimentally. This result is not a consequence of using the specific value of \(U_{\text{eff}} = 4\) eV, because our DFT + U calculations for FePS\(_3\) with \(U_{\text{eff}} = 3.5\) and 4.5 eV lead to the same conclusion.
Table 1. Relative energies (in meV/formula unit) obtained for the seven ordered spin states of MPS$_3$ (M = Mn, Fe, Co, Ni) from DFT + U calculations with $U_{\text{eff}} = 4$ eV. The numbers without parentheses are obtained by using the experimental structures, and those in parentheses by using the structures optimized by DFT + U calculations.

|     | Mn     | Fe       | Co       | Ni       |
|-----|--------|----------|----------|----------|
| FM  | 33.77  | 31.25    | 71.46    | 45.00    |
|     | (33.36)| (25.10)  | (55.00)  | (42.04)  |
| AF1 | 0 (0)  | 12.24    | 0 (5.70) | 6.50     |
|     |        | (5.16)   |          | (7.11)   |
| AF2 | 15.54  | 12.92    | 45.05    | 0 (0)    |
|     | (15.50)| (7.93)   |          |          |
| AF3 | 14.25  | 0 (0)    | 34.02    | 0.35     |
|     | (14.21)|          | (24.99)  | (0.34)   |
| AF4 | 14.72  | 20.85    | 22.16    | 52.40    |
|     | (14.45)| (18.57)  | (26.00)  | (49.53)  |
| AF5 | 12.77  | 15.79    | 157.25   | 33.62    |
|     | (12.58)| (12.95)  | (158.33) | (31.98)  |
| AF6 | 17.24  | 10.57    | 140.58   | 16.43    |
|     | (17.07)| (6.33)   | (143.05) | (15.21)  |

To resolve the discrepancy between theory and experiment on the magnetic ground state of FePS$_3$, we note that the magnetic peak positions in the neutron diffraction profiles are determined by the repeat distances of the rectangular magnetic structures, namely, $a$ and $b$ for the AF2 state (Figure 2b), and $a'$ and $b'$ for the AF3 state (Figure 2c). In both the experimental and the optimized structures of FePS$_3$, it was found that $a = a' = 5.947$ Å and $b = b' = 10.300$ Å. Thus, for the neutron diffraction refinement of the magnetic structure for FePS$_3$, the AF2 and AF3 states provide an equally good model. In view of our computational results, we conclude that the AF3 state is the correct magnetic ground state for FePS$_3$.

The experimental and optimized structures of MPS$_3$ (M = Mn, Fe, Co, Ni) are very similar, as expected. The important differences between them affecting the magnetic ground state would be the M-S distances of the MS$_6$ octahedra, because the d-state splitting of the MS$_6$ octahedra is sensitively affected by them. The M-S distances of the MS$_6$ octahedra taken from the experimental and optimized crystal structures of MPS$_3$ are summarized in Table 2, and their arrangements in the honeycomb layer are schematically presented in Figure 8. All Mn-S bonds of MnS$_6$ in MnPS$_3$ are nearly equal in length, as expected for a high-spin d$^5$ ion (Mn$^{2+}$) environment. The Fe-S bonds of FeS$_6$ in the optimized structure of FePS$_3$ are grouped into two short and four long Fe-S bonds. This distinction is less clear in the experimental structure. The Co-S bonds of CoS$_6$ in the experimental and optimized structures of CoPS$_3$ are grouped into two short, two medium and two long Co-S bonds. However, the sequence of the medium and long Co-S bonds is switched between the two structures. In the experimental and optimized structures of NiPS$_3$, the Ni-S bonds of NiS$_6$ are grouped into two short, two medium and two long Ni-S bonds. This distinction is less clear in the experimental structure. Thus, between the experimental and optimized structures of MPS$_3$, the sequence of the two short, two medium and two long M-S bonds do not switch for M = Fe and Ni whereas it does for M = Co. The latter might be the cause for why the relative stabilities of the AF1 and AF2 states in CoPS$_3$ switches between the experimental and optimized structures.
Table 2. The M-S bond distances (in Å) of the MS$_6$ octahedra in MPS$_3$ (M = Mn, Fe, Co, Ni) obtained from the experimental and the optimized crystal structures, which are shown without and with parentheses, respectively.

|        | Mn       | Fe      | Co      | Ni      |
|--------|----------|---------|---------|---------|
|        | 2.627 (2.632) | 2.546 (2.525) | 2.485 (2.492) | 2.457 (2.453) |
|        | 2.627 (2.632) | 2.546 (2.526) | 2.485 (2.492) | 2.457 (2.453) |
|        | 2.625 (2.635) | 2.547 (2.571) | 2.504 (2.525) | 2.462 (2.457) |
|        | 2.625 (2.635) | 2.547 (2.572) | 2.504 (2.525) | 2.462 (2.457) |
|        | 2.634 (2.639) | 2.549 (2.572) | 2.491 (2.537) | 2.465 (2.461) |
|        | 2.634 (2.639) | 2.549 (2.573) | 2.491 (2.537) | 2.465 (2.461) |

Figure 8. The arrangements of the M-S bond lengths of the MS$_6$ octahedra in MPS$_3$. The short M-S bonds are represented by blue lines, the medium M-S bonds by red lines, and the long M-S bonds by black lines.

3.3. Preferred Spin Orientation of MPS$_3$

3.3.1. Quantitative Evaluation

We determine the preferred spin orientations of the M$^{2+}$ ions in MPS$_3$ (M = Mn, Fe, Co, Ni) phases by performing DFT + U + SOC calculations using their FM states with the \( ||z \) and \( \perp z \) spin orientations. For the \( \perp z \) direction we selected the \( ||a\) direction. As summarized in Table 3, these calculations predict the preferred spin orientation to be the \( ||z \) direction for FePS$_3$, and the \( ||x \) direction for MnPS$_3$, CoPS$_3$ and NiPS$_3$. These predictions are in agreement with experiment for FePS$_3$ [9,18], CoPS$_3$ [19], and NiPS$_3$ [20], while this is not the case for MnPS$_3$ [9,12,14,31]. Our DFT + U + SOC calculations for the AF1 state of MnPS$_3$ show that the \( ||x \) spin orientation is still favored over the \( ||z \) orientation just as found from the calculations using the FM state of MnPS$_3$. The Mn$^{2+}$ spins of MnPS$_3$ were reported to have the \( ||z \) orientation in the early studies [9,12], but were found to be slightly tilted away from the z-axis (by 8°) [14,31]. In our further discussion (see below), this small deviation is neglected.

Table 3. Relative energies (in K per formula unit) of the \( ||z \) and \( \perp z \) spin orientations of the M$^{2+}$ ions in the FM states of MPS$_3$ (M = Mn, Fe, Co, Ni) obtained by DFT + U + SOC calculations. The results calculated by using the optimized (experimental) structures are presented without (with) the parentheses.

|        | MnPS$_3$ $^a$ | FePS$_3$ $^b$ | CoPS$_3$ | NiPS$_3$ |
|--------|--------------|--------------|-----------|-----------|
| \( \perp z \) | 0 (0) | 20.0 (21.8) | 0 (0) | 0 (0) |
| \( ||z \) | 0.3 (0.3) | 0 (0) | 3.8 (5.2) | 0.8 (0.7) |

$^a$ The same result is obtained by using the AF1 state, which is the magnetic ground state of MnPS$_3$. $^b$ The same results are obtained from our DFT+U calculations with \( U_{eff} = 3.5 \) and 4.5 eV.
3.3.2. Qualitative Picture
Selection Rules of Spin Orientation and Implications

With the local z-axis of a ML₆ octahedron along its three-fold rotational axis (Figure 1a), the t₂g set is described by {1a, 1e'}, and the e₉ set by {2e'}[22–24], where

\[
1a = 3z^2 - r^2
\]

\[
\{1e'\} = \left\{ \sqrt{\frac{1}{3}}xy - \sqrt{\frac{1}{3}}xz, \sqrt{\frac{1}{3}}(x^2 - y^2) - \sqrt{\frac{1}{3}}yz \right\}
\]

\[
\{2e'\} = \left\{ \sqrt{\frac{1}{3}}xy + \sqrt{\frac{1}{3}}xz, \sqrt{\frac{1}{3}}(x^2 - y^2) + \sqrt{\frac{1}{3}}yz \right\}
\]

Using these d-states, the electron configurations expected for the M²⁺ ions of MPS₃ (M = Mn, Fe, Co, Ni) are presented in Figure 9. In the spin polarized description of a magnetic ion, the up-spin d-states lie lower in energy than the down-spin states so that the HOMO and LUMO occur in the down-spin d-states for the M²⁺ ions with more than the d⁵ electron count, so only the down-spin d-states are shown for FePS₃, CoPS₃, and NiPS₃ in Figure 9a–c. For MnPS₃ with d⁵ Mn²⁺ ion, the HOMO is represented by the up-spin 1e', and the LUMO by the down-spin 1a and 2e' (Figure 9d).

![Figure 9](image-url)

**Figure 9.** Electron configurations of the M²⁺ (M = Mn, Fe, Co, Ni) ions of (a) FePS₃, (b) CoPS₃, (c) NiPS₃, and (d) MnPS₃ in the spin polarized description. In (a–e), the up-spin d-states lying below the down-spin t₂g states are not shown for clarity.

In terms of the d-orbital angular states |L, Lz⟩ (L = 2, Lz = −2, −1, 0, 1, 2), the 1e' state consists of the |2, ±2⟩ and |2, ±1⟩ sets in the weight ratio of 2:1, and the 2e' state in the weight ratio of 1:2 ratio. Consequently, the major component of the 1e' set is the |2, ±2⟩ set, while that of the 2e' set is the |2, ±1⟩ set.

The selection rules of the spin orientation are based on the |ΔLz| value between the HOMO and LUMO of ML₆. If the HOMO and LUMO both occur in the up-spin state or in down-spin states (Figure 9a–c), the ||z spin orientation is predicted if |ΔLz| = 0, and the ⊥z spin orientation if |ΔLz| = 1. When |ΔLz| > 1, the HOMO and LUMO do not interact under SOC and hence do not affect the spin orientation. Between the 1a, 1e' and 2e' states, we note the following cases of values:

\[
|\Delta L_z| = 0 \left\{ \begin{array}{l}
\text{between the major components of the 1e' set} \\
\text{between the major components of the 2e' set}
\end{array} \right.
\]

\[
|\Delta L_z| = 1 \left\{ \begin{array}{l}
\text{between 1a and the minor component of 1e'} \\
\text{between 1a and the major component of 2e'} \\
\text{between the major components of 1e' and 2e'}
\end{array} \right.
\]
We now examine the preferred spin orientations of MPS$_3$ from the viewpoint of the selection rules and their electron configurations (Figure 9). The d-electron configuration of FePS$_3$ can be either (d↑)$^5$(1e')$_1$ or (d↑)$^5$(1a) $_1$ (Figure 9a), where the notation (d↑)$^5$ indicates that all up-spin d-states are occupied. The (d↑)$^5$(1e')$_1$ configuration, for which $\Delta L_z = 0$, predicts the $\|z$ spin orientation, while the (d↑)$^5$(1a)$_1$ configuration, for which $\Delta L_z = 1$, predicts the $\perp z$ spin orientation. Thus, the (d↑)$^5$(1a)$_1$ configuration is correct for the Fe$^{2+}$ ion of FePS$_3$. Since this configuration has the degenerate level 1e' unevenly occupied, it should possess uniaxial magnetism [2,3,22–24] and hence a large magnetic anisotropy energy. This is in support of the experimental finding of the Ising character of the spin lattice of FePS$_3$ [16] or the single-ion anisotropic character of the Fe$^{2+}$ ion [17,18]. The d-electron configuration of CoPS$_3$ can be either (d↑)$^5$(1e')$_2$ or (d↑)$^5$(1a)$_1$(1e')$_1$ (Figure 9b). The (d↑)$^5$(1e')$_2$ configuration, for which $\Delta L_z = 1$, predicts the $\perp z$ spin orientation, while the (d↑)$^5$(1a)$_1$(1e')$_1$ configuration, for which $\Delta L_z = 0$, predicts the $\| z$ spin orientation. Thus, the (d↑)$^5$(1e')$_2$ configuration is correct for the Co$^{2+}$ ion of CoPS$_3$. Since this configuration has the degenerate level 1e' evenly occupied, it does not possess uniaxial magnetism [2,3,22–24] and hence a small magnetic anisotropy energy. The d-electron configuration of NiPS$_3$ is given by (d↑)$^5$(1a)$_1$(1e')$_2$ (Figure 9c), for which $\Delta L_z = 1$, so the $\perp z$ spin orientation is predicted in agreement with experiment.

Let us now consider the spin orientation of the Mn$^{2+}$ ion of MnPS$_3$. First, it should be noted that, if the HOMO and LUMO occur in different spin states as in MnPS$_3$ (Figure 9d), the selection rules predict the opposite to those found for the case when the HOMO and LUMO occur all in up-spin states or all in down-spin states [2,3,22–24]. Namely, the preferred spin orientation is the $\| z$ spin orientation if $\Delta L_z = 1$, but the $\perp z$ spin orientation if $\Delta L_z = 0$ [2,3,22–24]. According to Equation (7), $\Delta L_z = 1$ for the Mn$^{2+}$ ion of MnPS$_3$, which predicts the $\perp z$ orientation as the preferred spin direction in agreement with the quantitative estimate of the magnetic anisotropy energy obtained from the DFT + U + SOC calculations, although this is in disagreement with experiment [5,8–10]. It has been suggested that the $\| z$ spin orientation is caused by the magnetic dipole–dipole (MDD) interactions [13]. This subject will be probed in the following.

### Magnetic Dipole–Dipole Interactions

Being of the order of 0.01 meV for two spin-1/2 ions separated by 2 Å, the MDD interaction is generally weak. For two spins located at sites i and j with the distance $r_{ij}$ and the unit vector $\vec{e}_i$ along the distance, the MDD interaction is defined as [32]

$$
\left( \frac{g^2 \mu_B^2}{a_0^3} \right) \left( \frac{a_0}{r_{ij}} \right)^3 \left[ -3(\vec{S}_i \cdot \vec{e}_{ij}) (\vec{S}_j \cdot \vec{e}_{ij}) + (\vec{S}_i \cdot \vec{S}_j) \right]
$$

(8)

where $a_0$ is the Bohr radius (0.529177 Å), and $(g\mu_B)^2/(a_0)^3 = 0.725$ meV. The MDD effect on the preferred spin orientation of a given magnetic solid can be examined by comparing the MDD interaction energies calculated for a number of ordered spin arrangements. In summing the MDD interactions between various pairs of spin sites, it is necessary to employ the Ewald summation method [33–35]. Table 4 summarizes the MDD interaction energies calculated, by using the optimized structures of MPS$_3$ (M = Mn, Fe, Co, Ni), for the $\| z$ and $\| x$ spin directions in the AF1, AF2 and AF3 states. The corresponding results obtained by using the experimental structures of MPS$_3$ are summarized in Table S1.

...
Table 4. Relative energies (in K per formula unit) of the $\|x$ and $\|z$ spin orientations calculated by MDD calculations for the M$^{2+}$ ions of MPS$_3$ (M = Mn, Fe, Co, Ni) in the AF1, AF2 and AF3 states using the optimized crystal structures.

|                | MnPS$_3$ | FePS$_3$ | CoPS$_3$ | NiPS$_3$ |
|----------------|----------|----------|----------|----------|
|                | $\|x$    | $\|z$    | $\|x$    | $\|z$    |
| AF1            | 0.48     | 0.17     | 0.36     | 0.12     |
| AF2            | 0.00     | 0.35     | 0.00     | 0.26     |
| AF3            | 0.55     | 0.38     | 0.38     | 0.27     |

These results can be summarized as follows: for the $\|z$ spin orientation, the AF1 state is more stable than the AF2 and AF3 states. For the $\|x$ spin orientation, the AF2 state is more stable than the AF1 and AF3 states. The $\|x$ spin direction of the AF2 state is more stable than the $\|z$ spin direction of the AF1 state. However, none of these results can reverse the relative stabilities of the $\|z$ and $\|x$ spin directions determined for FePS$_3$, CoPS$_3$, and NiPS$_3$ from the DFT + U + SOC calculations (Table 3). The situation is slightly different for MnPS$_3$, which adopts the AF1 state as the magnetic ground state. For MnPS$_3$ in this state, the MDD calculations predict that the $\|z$ spin orientation is more stable than the $\|x$ spin orientation by 0.3 K per formula unit (Table 4). Note that this prediction is in agreement with the experimental observation. Consequently, for MnPS$_3$ the MDD interaction dominates over the SOC effect which is plausible because of the half-filled shell electronic configuration. This is because the AF1 magnetic structure is forced on MnPS$_3$; in terms of purely MDD interactions alone, the $\|z$ spin orientation in the AF2 state is most stable.

3.4. Quantitative Evaluations of Spin Exchanges

Due to the monoclinic crystal structure that MPS$_3$ adopts, each of the exchanges $J_{12}, J_{13}$ and $J_{14}$ (Figure 10a) are expected to split into two slightly different spin exchanges (Figure 10b) so that there are six spin exchanges $J_1$–$J_6$ to consider. To extract the values of the six spin exchanges $J_1$–$J_6$ (Figure 3), we employ the spin Hamiltonian expressed as:

$$H_{\text{spin}} = - \sum_{i>j} J_{ij} \hat{S}_i \cdot \hat{S}_j \quad (9)$$

![Figure 10](image-url)

Figure 10. (a) Three kinds of spin exchange paths in each honeycomb layer of MPS$_3$. (b) Two kinds of the spin exchanges resulting from $J_{12}, J_{13}$ and $J_{14}$ due to the loss of the trigonal symmetry in the MPS$_3$ honeycomb layers. In (b), the numbers 1–6 refer to $J_1$–$J_6$, respectively.
Then, the energies of the FM and AF1–AF6 states of MPS$_3$ (M = Mn, Fe, Co, Ni) per 2 $\times$ 2 $\times$ 1 supercell are written as:

$$E_{FM} = (-16J_1 - 8J_2 - 16J_3 - 32J_4 - 16J_5 - 8J_6)S^2$$
$$E_{AF1} = (+16J_1 + 8J_2 - 16J_3 - 32J_4 + 16J_5 + 8J_6)S^2$$
$$E_{AF2} = (-16J_1 + 8J_2 - 16J_3 + 32J_4 + 16J_5 + 8J_6)S^2$$
$$E_{AF3} = (-8J_2 + 16J_3 + 16J_5 + 8J_6)S^2$$
$$E_{AF4} = (+16J_1 - 8J_2 - 16J_3 + 32J_4 - 16J_5 - 8J_6)S^2$$
$$E_{AF5} = (+8J_2 + 16J_3 - 16J_5 + 8J_6)S^2$$
$$E_{AF6} = (-8J_2 + 16J_3 + 16J_5 - 8J_6)S^2$$

where $S$ is the spin on each M$^{2+}$ ion (i.e., $S = 5/2, 2, 3/2$ and $1$ for M = Mn, Fe, Co, and Ni, respectively). By mapping the relative energies of the FM and AF1–AF6 states determined in terms of the spin exchange $J_{ij}$ onto the corresponding relative energies obtained from the DFT + U calculations (Table 1), we find the values of $J_{ij}$ listed in Table 5. (The spin exchanges of MPS$_3$ determined by using their experimental crystal structures are summarized in Table S2.)

**Table 5.** Spin exchanges $J_{ij}$ obtained (for the optimized structures of MPS$_3$ (M = Mn, Fe, Co, Ni) from DFT + U calculations with $U_{eff} = 4$ eV) by simulating the relative energies of the FM and AF1–AF6 states with the six spin exchanges.

|       | Mn   | Fe   | Co   | Ni   |
|-------|------|------|------|------|
| $J_1$ | 1.00 | 0.37 | 0.05 | −0.25|
| $J_2$ | 0.87 | −0.32| −0.91| −0.14|
| $J_3$ | 0.06 | 0.36 | −0.55| 0.04 |
| $J_4$ | 0.05 | 0.07 | 0.04 | −0.01|
| $J_5$ | 0.34 | 0.86 | 0.11 | 0.99 |
| $J_6$ | 0.33 | 1.00 | 1.00 | 1.00 |

With the sign convention adopted in Eq. 1, AFM exchanges are represented by $J_{ij} < 0$, and FM exchanges by $J_{ij} > 0$. From Table 5, the following can be observed:

a. In all MPS$_3$ (M = Mn, Fe, Co, Ni), $J_1 \neq J_2$, $J_3 \neq J_4$, and $J_5 \neq J_6$, reflecting that the exchange paths are different between $J_1$ and $J_2$, between $J_3$ and $J_4$, and between $J_5$ and $J_6$ (Figure 10).

b. $J_1 \approx J_2 < 0$, $J_3 \approx J_4 \approx 0$, and $J_5 \approx J_6 < 0$ for MnPS$_3$, while $J_1 \approx J_2 > 0$, $J_3 \approx J_4 \approx 0$, and $J_5 \approx J_6 < 0$ NiPS$_3$. To a first approximation, the electron configurations of MnPS$_3$ and NiPS$_3$ can be described by $(t_{2g})^6(e_g)^2$ and $(t_{2g})^6(e_g)^2$, respectively. That is, they do not possess an unevenly occupied degenerate state $t_{2g}$.

c. In FePS$_3$ and CoPS$_3$, $J_1$ and $J_2$ are quite different, and so are $J_3$ and $J_4$. While $J_3$ and $J_6$ are comparable in FePS$_3$, they are quite different in CoPS$_3$. The electron configurations of FePS$_3$ and NiPS$_3$ can be approximated by $(t_{2g})^6(e_g)^2$ and $(t_{2g})^6(e_g)^2$, respectively. Namely, they possess an unevenly occupied degenerate state $t_{2g}$.

d. The strongest exchange is $J_1$ in MnPS$_3$, but $J_6$ in other MPS$_3$ (M = Fe, Co, Ni).

e. The second NN exchange $J_3$ is strongly FM in CoPS$_3$, while the third NN exchange $J_6$ is very strongly AFM in CoPS$_3$ and NiPS$_3$.

From the viewpoints of the expected trends in spin exchanges, the observation (e) is quite unusual. This will be discussed in the next section.
3.5. Unusual Features of the M-L…L-M Spin Exchanges

3.5.1. Second Nearest-Neighbor Exchange

As pointed out in the previous section, the second NN exchange $J_3$ of CoPS$_3$ is strongly FM despite that it is a M-L…L-M exchange to a first approximation. This implies that the $J_3$ component in some $(\varphi_i, \varphi_j)$ exchanges is nonzero, namely, the overlap electron density associated with those exchanges is nonzero. This implies that the p-orbital tails of the two magnetic orbitals are hybridized with the group orbitals of the $P_2S_6^{4-}$ anion, i.e., they become delocalized into the whole $P_2S_6^{4-}$ anion. Each MS$_6$ octahedron has three mutually orthogonal “MS$_6$ square planes” containing the $yz$, $xz$ and $xy$ states (Figure 11a). At the four corners of these three square planes, the p-orbital tails of the d-states are present (Figure 3a).

Figure 11. (a) Three MS$_4$ square planes of a MS$_6$ octahedron, containing the $xy$, $xz$ and $yz$ states of an MS$_6$ octahedron. (b–d) Three cases of the CoS$_4$ square planes containing the $t_{2g}$ magnetic orbitals in the $J_3$ exchange path of CoPS$_3$.

The lone-pair orbitals of the S atoms are important for the formation of each MS$_6$ octahedron. Due to the bonding requirement of the $P_2S_6^{4-}$ anion, such lone pair orbitals become symmetry-adapted. An example in which the p-orbitals of all the S atoms are present is shown in Figure 1e.

With the $(t_{2g})^5(e_g)^2$ configuration, the Co$^{2+}$ ion of CoPS$_3$ has five electrons in the $t_{2g}$ level, namely, it has only one $t_{2g}$ magnetic orbital. This magnetic orbital is contained in one of the three CoS$_4$ square planes presented in Figure 11b–d. When the S p-orbital at one corner of the $P_2S_6^{4-}$ anion interacts with a d-orbital of M, the S p-orbitals at the remaining corners are also mixed in. Thus, when $P_2S_6^{4-}$ anion shares corners with both MS$_4$ square planes of the $J_3$ exchange path, a nonzero overlap electron density is generated, thereby making the spin exchange FM. For convenience, we assume that the magnetic $t_{2g}$ orbital of the Co$^{2+}$ ion is the $xy$ state. Then, there will be not only the $(xy, xy)$ exchange, but also the $(xy, x^2−y^2)$ and $(x^2−y^2, xy)$ exchanges between the two Co$^{2+}$ ions of the $J_3$ path. All these individual exchanges lead to nonzero overlap electron densities by the delocalization of the p-orbital tails with the group orbitals of the molecular anion $P_2S_6^{4-}$. In other words, the spin exchange $J_3$ in CoPS$_3$ is nominally a M-L…L-M, which is expected to be AFM by the qualitative rule, but it is strongly FM. It is clear that, if the L…L linkage is a part of the covalent framework of a molecular anion such as $P_2S_6^{4-}$, a nominal M-L…L-M exchange can become FM for a certain combination of the d-electron count of the metal M and the geometries of the exchange path.

3.5.2. Third Nearest-Neighbor Exchange

Unlike in MnPS$_3$ and FePS$_3$, the M-S…S-M exchange $J_6$ is unusually strong in CoPS$_3$ and NiPS$_3$ (Section 3.3). This is so despite that the S…S contact distances are longer in CoPS$_3$ and NiPS$_3$ than in MnPS$_3$ and FePS$_3$ (i.e., the S…S contact distance of the $J_6$ path in MPS$_3$ is 3.409, 3.416, 3.421 and 3.450 Å for M = Mn, Fe, Co and Ni, respectively). We note that a strong M-L…L-M exchange (i.e., a spin exchange leading to a large energy split $\Delta \psi$) becomes weak, when the L…L contact is bridged by a d$^0$ cation like, e.g., $V^{5+}$ and $W^{6+}$ to form the M-L…A…L-M exchange path (Figure 6b), because the out-of-phase combination $\psi_-$ is lowered in energy by interacting with the unoccupied d$_{xy}$ orbital of the cation A. Conversely, then, one may ask if the
strength of a M-L . . . L-M spin exchange can be enhanced by raising the $\psi_-$ level. The latter can be achieved if the L . . . L path provides an occupied level of $\pi$-symmetry that can interact with $\psi_-$. As depicted in Figure 12a, the $J_6$ path has the two MS₄ square planes containing the $x^2-y^2$ magnetic orbitals (Figure 12b). The lone-pair group orbital of the S₆ rectangular plane (Figure 12c) of the P₂S₆⁴⁻ anion has the correct symmetry to interact with $\psi_-$, so that the $\psi_-$ level is raised in energy thereby enlarging the energy split between $\psi_+$ and $\psi_-$ and strengthening the $J_6$ exchange (Figure 12d). Although this reasoning applies equally to MnPS₃ and FePS₃, the latter do not have a strong $J_6$ exchange. This can be understood by considering Equation (1), which shows that a magnetic ion with several magnetic orbitals leads to several individual spin exchanges that can lead to FM contributions.

![Figure 12](image_url)

**Figure 12.** (a) The $J_6$ spin exchange path of MPS₃ (M = Co, Ni) viewed in terms of the MS₄ and P₂S₄ square planes. (b) The $x^2-y^2$ magnetic orbital of the MS₆ octahedron. (c) The S p-orbitals present at the corners of the P₂S₄ square plane. (d) How the M-S . . . S-M spin exchange is enhanced by the through-bond effect of the intervening P₂S₆ octahedron.

In view of the above discussion, which highlights the unusual nature of the second and third NN spin exchanges mediated by a molecular anion such as P₂S₆⁴⁻, we propose to use the notation M-(L-L)-M to distinguish it from M-L-M. M-L . . . L-M and M-L . . . A . . . L-M type exchanges. The notation (L-L) indicates two different ligand sites of a multidentate molecular anion, each with lone pairs for the coordination with a cation M. Such M-(L-L)-M exchanges can be strongly FM or strongly AFM, as discussed above. Currently, there are no qualitative rules with which to predict whether they will be FM or AFM. A similar situation was found, for example, for the mineral Azurite Cu₅(CO₃)₂(OH)₂, in which every molecular anion CO₃²⁻ participates in three different Cu-(O-O)-Cu exchanges. DFT + U calculations show that one of these three is substantially AFM, but the remaining two are negligible. So far, this observation has not been understood in terms of qualitative reasoning.

### 3.6. Description Using Three Exchanges

Experimentally, the magnetic properties of MPS₃ have been interpreted in terms of three exchange parameters, namely, by assuming that $J_1 = J_2 (= J_{12})$, $J_3 = J_4 (= J_{13})$, and $J_5 = J_6 (= J_{14})$. To investigate whether this simplified description is justified, we simulate the relative energies of the seven ordered spin states of MPS₃ by using the three exchanges $J_{12}$, $J_{13}$ and $J_{14}$ as parameters in terms of the least-square fitting analysis. Our results, summarized in Table 6, show that the standard deviations of $J_{12}$, $J_{13}$ and $J_{14}$ are small for MnPS₃ and NiPS₃, moderate in FePS₃, but extremely large in CoPS₃ (for details, see Figures S2-S5). The exchanges experimentally deduced for FePS₃ are $J_{12} = -17$ K, $J_{13} = -0.5$ K, and $J_{14} = 7$ K from neutron inelastic scattering measurements [17], $-17$ K $\leq J_{12} \leq -5.6$ K, $-7.2$ K $\leq J_{13} \leq 2.8$ K, and $0 \leq J_{14} \leq 10$ K from powder susceptibility measurements [9], and $J_{12} = -19.6$ K, $J_{13} = 10.3$ K, and $J_{14} = -2.2$ K from high field measurements [17]. These experimental estimates are dominated by $J_{12}$, but the theoretical
estimates of Table 6 by $J_{14}$. One might note from Table 6 that the magnetic properties of MnPS$_3$, FePS$_3$ and NiPS$_3$ can be reasonably well approximated by two exchanges, that is, by $J_{12}$ and $J_{14}$ for MnPS$_3$, by $J_{14}$ and $J_{12}$ for NiPS$_3$, and by $J_{14}$ and $J_{13}$ for FePS$_3$. However, this three-parameter description leads to erroneous predictions for the magnetic ground states of MPS$_3$; it predicts the AF1 state to be the ground state for both MnPS$_3$ and CoPS$_3$. This prediction is correct for MnPS$_3$, but incorrect for CoPS$_3$. In addition, it predicts that the AF2 and AF3 states possess the same stability for all MPS$_3$ (M = Mn, Fe, Co, Ni), and are the ground states for FePS$_3$ and NiPS$_3$. These two predictions are both incorrect.

| M  | Mn          | Fe          | Co          | Ni          |
|----|-------------|-------------|-------------|-------------|
| $J_{12}$ | $-15.5 \pm 0.4$ | $2.0 \pm 7.7$ | $-61.4 \pm 119.0$ | $36.3 \pm 4.3$ |
| $J_{13}$ | $-0.9 \pm 0.2$ | $-7.7 \pm 3.9$ | $60.7 \pm 55.3$ | $0.0 \pm 2.0$ |
| $J_{14}$ | $-5.3 \pm 0.3$ | $-20.9 \pm 4.5$ | $-59.1 \pm 95.6$ | $-186.0 \pm 3.4$ |

4. Concluding Remarks

Our DFT + U calculations for the optimized structures of MPS$_3$ (M = Mn, Fe, Co, Ni) reveal that, in agreement with experiment, the magnetic ground state of MnPS$_3$ is the AF1 state while those of CoPS$_3$ and NiPS$_3$ are the AF2 state. In disagreement with experiment, however, our calculations predict the AF2 state to be the magnetic ground state for FePS$_3$. Our DFT + U + SOC calculations show that, in agreement with experiment, the preferred spin orientation of FePS$_3$ is the $\parallel z$ direction while those of CoPS$_3$ and NiPS$_3$ are the $\perp z$ direction, and the Fe$^{2+}$ ion of FePS$_3$ exhibits uniaxial anisotropy. In disagreement with experiment, these calculations predict the preferred spin orientation for MnPS$_3$ to be the $\perp z$ direction. Our analyses suggest that the $\parallel z$ spin direction experimentally observed for the Mn$^{2+}$ ions arises from the magnetic dipole–dipole interactions in the AF1 magnetic state. We presented simple qualitative rules governing spin exchanges to be used as guidelines for gauging the nature of various spin exchanges. These rules allowed us to recognize several unusual exchanges of MPS$_3$; the second NN exchange $J_3$ of CoPS$_3$ is strongly FM while the third NN exchanges $J_6$ of CoPS$_3$ and NiPS$_3$ are very strongly AFM. These observations reflect the fact that the lone-pair orbitals of the $P_2S_6^{4-}$ ion, mediating the spin exchanges in MPS$_3$ are symmetry-adapted group orbitals, so the effect of coordinating one S atom to one $M^{2+}$ ion is felt by all the remaining five S atoms of $P_2S_6^{4-}$. The spin exchanges mediated by molecular anions, termed the M-(L-L)-M type exchanges, differ in nature from the M-L-M, M-L . . . L-M and M-L . . . A . . . L-M type exchanges. To find qualitative trends in the M-(L-L)-M type exchanges, it is necessary to further study the spin exchanges involving various other molecular anions.

Supplementary Materials: The following are available online. Figure S1: Ordered spin states, FM, AF4, AF5 and AF6 employed together with the states AF1, AF2 and AF3 (see the text) to determine the magnetic ground states as well as the spin exchanges $J_1$-$J_6$ of MPS$_3$ (M = Mn, Fe, Co, Ni). Figure S2–S5. Results of the least-square fitting the relative energies of the seven ordered spin states (FM, AF1-AF6) of MnPS$_3$, CoPS$_3$ and FePS$_3$, and NiPS$_3$. Table S1: Relative energies (in K per formula unit) of the $\parallel x$ and $\parallel z$ spin orientations obtained by MDD calculations for the $M^{2+}$ ions of MPS$_3$ (M = Mn, Fe, Co, Ni) in the AFM1, AF2 and AFM3 states using the experimental crystal structures. Table S2: Spin exchanges (in K) obtained for the experimental structures of MPS$_3$ (M = Mn, Fe, Co, Ni) from DFT + U calculations with $U_{\text{eff}} = 4$ eV.

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