Understanding neutron scattering data in YMn_2O_5 : An effective spin Hamiltonian

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We construct an effective spin Hamiltonian for YMn_2O_5 through analysis of first-principles density-functional theory results. Using our first-principles-derived spin Hamiltonian we calculate the magnon dispersion of this compound and compare with the experimentally measured spectra probed using inelastic neutron scattering. Our first-principles-derived set of magnetic interaction parameters show the importance of the Mn1-Mn2 interaction along the b axis, which was ignored in the literature. We provide justification in favor of our first-principles-derived parameters.

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I. INTRODUCTION

Materials like RMn_2O_5 ($R = \text{Y, Tb, Ho}, \dots$) have come to the limelight in recent years due to the coexistence of magnetic as well as ferroelectric order in them, a phenomenon often denoted as multiferroicity.² These materials are of further interest since in these materials magnetization, which acts as primary order parameter, drives the polarization, which acts as secondary order parameter, thereby ensuring the coupling between the two order parameters through the magnetoelectric effect. We focus on a specific member of this family, namely YMn_2O_5 . The magnetic behavior of YMn_2O_5 , similar to another compound of this series, TbMn_2O_5 , involves a series of transitions. Upon decreasing temperature, Mn spins order in an incommensurately modulated phase [$\mathbf{k} = (q_x, 0, q_z)$] at about 44 K, which turns out to be paraelectric. Lowering the temperature further, a commensurate antiferromagnetic phase with wave vector $\mathbf{k} = (\frac{1}{2}, 0, \frac{1}{4})$ appears, with finite ferroelectric polarization.³ Further lowering of temperature to 19 K, results into incommensurate magnetic structure with $\mathbf{k}_{ic} = (0.48, 0.0, 0.29)$, characterized with much smaller polarization values.⁴ This series of magnetic transitions is believed to be caused by the frustration in the Mn spin lattice. Since magnetism is the key player driving the various phenomena observed in these materials, understanding the various magnetic interactions in Mn spin lattice form a crucial part of the study of these materials. Estimates of magnetic exchanges have been obtained from *ab initio* total energy calculations of different magnetic configurations⁵ in TbMn_2O_5 as well as by fitting the experimental inelastic neutron scattering data for the low-temperature incommensurate phase⁶ in YMn_2O_5 . Both approaches mentioned above are based on a certain fitting procedure, either fitting to energies of some chosen spin configurations or fitting to scattering intensity scanned along specific directions. This may lead to nonuniqueness in the choice of parameters, as is inherent in any fitting procedure. In our study, we have calculated the magnetic exchanges for YMn_2O_5 from the effective Mn-Mn hopping interactions and energy level separations obtained in a first-principles-derived Wannier function basis, employing the

extended Kugel-Khomskii model.⁷ We have also calculated the exchange interactions through fitting of total energies of different arrangements of Mn spins. Our study shows that the results obtained through fitting of total energies depend strongly on the choice of spin configurations. While a subset of all possible spin configurations reproduces the trend observed in previous obtained interactions reported in Ref. 5 for TbMn_2O_5 , the other subset gives rise to a result that is similar to the trend obtained from hopping integrals and energy-level separations through the extended Kugel-Khomskii model. From the chemical point of view, as justified through exchange paths defined by overlap of effective Wannier functions, the results obtained from first-principles-derived hopping integrals and energy-level separations seem to be the more plausible estimates. We further validate our results in terms of calculation of magnon spectra of the constructed spin model and by comparing with the measured spin-wave spectra for the commensurate phase along the directions [100] and [010]. The measured spin wave was reported in Ref. 6, however that was for the low temperature incommensurate phase and reported for scans along [100] and [001] directions.

The rest of the paper is organized in the following manner. In Sec. II, we discuss the details of the theoretical and experimental techniques. The crystal structure of YMn_2O_5 compound is discussed in Sec. III. Results and discussions are presented in Sec. IV, which consists of several subsections. The basic electronic structure calculated for different magnetic configurations is presented in Sec. IV A. First-principles-based N th order muffin-tin orbital (NMT-O)-downfolding calculations to compute effective hopping interactions and energy-level separations and a construction of an effective spin Hamiltonian is described in Sec. IV B. This section also includes rigorous study of calculations of magnetic exchange interactions using total energy calculations of various spin configurations. In Sec. IV C, we present the justification of our derived spin Hamiltonian. It has been done by calculating the magnon spectra and by comparing with experimental measurements, as presented in Sec. IV C1 and the argument provided from a chemical point of view as presented in Sec. IV C2.

II. METHODS

A. Theoretical techniques

Electronic structure calculations have been carried out within density-functional theory (DFT) with a choice of generalized-gradient approximation (GGA)⁸ for the exchange-correlation functional. Calculations have been carried out in muffin-tin orbital based linear muffin-tin orbital (LMTO)⁹ and NMTO¹⁰ basis. The NMTO calculations for the construction of Wannier functions corresponding to effective Mn orbitals and the tight-binding Hamiltonian have been carried out with the self-consistent potentials borrowed from LMTO calculations. The total energy calculations for different spin configurations have been carried with a plane-wave basis and projector-augmented-wave (PAW) pseudopotentials as implemented in Vienna *ab initio* simulations package (VASP).¹¹ The consistency between the electronic structures computed within muffin-tin-orbital basis and plane-wave basis has been cross checked. For the calculations in plane-wave basis, the choice of plane-wave cutoff of 480 eV was found to provide a good convergence of the total energies. For self-consistent field calculation $4 \times 4 \times 6$ Monkhorst-Pack k -point mesh was used to have a good convergence. To accommodate the commensurate magnetic structure, a large supercell should be taken, which is computationally heavy. We, therefore, considered a $2 \times 1 \times 1$ supercell that is equivalent to considering the propagation vector $\mathbf{k} = (1/2, 0, 0)$ instead of experimentally observed propagation vector of $\mathbf{k} = (1/2, 0, 1/4)$. For the supercell calculations, we used $2 \times 4 \times 4$ Monkhorst-Pack k -points mesh.

B. Experimental technique

Large single crystals of YMn_2O_5 were grown by the flux method using $\text{B}_2\text{O}_3/\text{PbO}/\text{PbF}_2$ flux in a Pt crucible. Inelastic-neutron-scattering experiments were done on a single crystal of size of about $6 \times 5 \times 4 \text{ mm}^3$ on the cold triple-axis spectrometer TASP of SINQ at the Paul-Scherrer Institute. The spectrometer configuration was guide-vertically curved PG(002) monochromator-open-sample-open-horizontally curved PG(002) analyzer-open-

detector. The YMn_2O_5 crystal was placed inside a standard He cryostat with its [010] crystallographic axis vertical so that that the scattering plane of the spectrometer was ($h0l$). The sample was cooled down to $T = 25 \text{ K}$ and this temperature was maintained all throughout the experiment. The magnetic phase of YMn_2O_5 at this temperature was the magnetic phase with the propagation vector $\mathbf{k} = (\frac{1}{2}, 0, \frac{1}{4})$. The spin-wave dispersions along [100] and [001] were measured by doing constant- Q energy scans at $Q = (3/2 \pm q_h, 0, 1/4)$ and at $Q = (3/2, 0, 1/4 \pm q_l)$, respectively for different values of q_h and q_l ranging from the magnetic zone center to the zone boundary. In a second experiment, on the same spectrometer we measured the spin-wave dispersion from YMn_2O_5 at $T = 25 \text{ K}$ along [010] by reorienting the crystal vertical axis such that the scattering plane was ($2h, k, h$). The spin-wave dispersion along [010] was determined by doing constant- Q energy scans at $Q = (1/2, 1 \pm q_k, 1/4)$ for different values of q_k ranging from the magnetic zone center to the zone boundary. In the following, we have calculated and discussed the spin-wave dispersion of YMn_2O_5 only along [100] and [010] directions.

III. CRYSTAL STRUCTURE

YMn_2O_5 crystallizes in the orthorhombic space group ($Pbam$)¹³ with lattice parameters $a = 7.325 \text{ \AA}$, $b = 8.517 \text{ \AA}$, and $c = 5.675 \text{ \AA}$. The unit cell contains four formula units, built out of four distorted Mn1O_6 octahedra and four distorted Mn2O_5 square pyramids, with two inequivalent Mn sites, Mn1 and Mn2. The distorted Mn1O_6 octahedral and Mn2O_5 square pyramidal units are shown in Fig. 1(a). The plane containing Mn1 and Mn2 ions is buckled. All Mn2 sites are located in the same plane (the ab plane). The pyramids centered at two neighboring Mn2 sites in the ab plane are edge shared. The Mn1 atoms lie either below or above the Mn2 layer. The connection of Mn1-Mn2-Mn1-Mn2-Mn2 gives rise to pentagon geometry, as shown in Fig. 1(b), projected on to ab plane. Within the unit cell, there are two such pentagons that share their edges formed by Mn2-Mn2 bond, as shown in Fig. 1(c). In the c or out-of-plane direction, the Mn1O_6 octahedra share their edges to form chain-like structure, as

FIG. 1. (Color online) Crystal structure of YMn_2O_5 . (a) Basic structural units of distorted Mn1O_6 octahedra and Mn2O_5 square pyramid. (b) Mn1-Mn2 connection projected onto ab plane. The rectangular box represents the unit cell. (c) Blown-up view of the unit cell projected onto ab plane. (d) Mn1-Mn2 connection projected onto ac plane. Oxygen atoms have been represented with small balls, while the Mn atoms have been represented with large balls. Y atoms have been omitted for simplicity. In panel (a), different inequivalent oxygens are colored differently, while in the rest of the panels, to avoid complexity, they have been colored uniformly. Two inequivalent Mn atoms have been colored as magenta (dark grey) for Mn1 and golden (light grey) for Mn2. The dominant magnetic exchanges have been also marked.

shown in Fig. 1(d). The Y ions (not shown in the figure) are positioned in the layer separating two Mn1/Mn2 layers.

Since the $Pb2_1m$ structure has inversion symmetry, this cannot develop electric polarization. For YMn_2O_5 , it has, therefore, been suggested⁵ that the actual symmetry group is $Pb2_1m$, which allows polarization along the b axis. In a related compound, $TbMn_2O_5$, the ground-state structure was indeed found to be in the lower $Pb2_1m$ symmetry.¹⁴

IV. RESULTS AND DISCUSSION

A. Basic electronic structure

The electronic structure of YMn_2O_5 was calculated using LMTO as well as VASP. The top panel of Fig. 2 shows the non-spin-polarized density of states (DOS) computed in the plane-wave basis. The DOS are projected onto Mn1- d , Mn2- d , and O- p characters. The Mn- d and O- p hybridized electronic structure extend from an energy range of about -7.5 eV below the Fermi energy (E_F) to about 3.5 eV above E_F . The non-spin-polarized calculation gave rise to a metallic solution with states of dominant Mn- d character crossing E_F . The crystal-field split Mn1- e_g states, as well as Mn2- d_{xz} states

remain separated from the rest of the other Mn- d dominated states, by an energy gap of about 0.5 – 0.6 eV. Introduction of the spin-splitting through spin-polarized calculation, as shown in the middle panel of Fig. 2, results into an insulating solution with a tiny energy gap. The insulating gap occurs between the occupied Mn1- t_{2g} and Mn2- $d_{yz}, d_{x^2-y^2}, d_{3z^2-r^2}, d_{xy}$ (marked as Mn2- $d_{1,2,3,4}$ in the figure) states and the unoccupied Mn1- e_g and Mn2- d_{xz} (marked as Mn2- d_5) states. The orbital characters are obtained with a choice of a local coordinate system with the z axis pointing along Mn1-O4 (Mn2-O3) and the y axis pointing along approximate Mn1-O3 (Mn2-O4) bond directions for Mn1 (Mn2) within a right-handed coordinate system.

The magnetic moments at Mn1 and Mn2 sites turned out to be $2.81 \mu_B$ and $3.45 \mu_B$, respectively, indicating a charge disproportionate situation with a nominal valence of Mn^{4+} ($3d^3$) at Mn1 site and Mn^{3+} ($3d^4$) at Mn2 site. The calculation considering the antiferromagnetic (AF) structure consisting of zigzag AF chains running along the a direction,¹⁵ as described in Ref. 12, further increased the band gap to about 0.7 eV, as shown in the bottom panel of Fig. 2.

B. Magnetic model: NMTO-downfolding and total energy calculations

In order to calculate the magnetic exchange interactions connecting different magnetic sites, we adopted the following procedure. First, we used the LMTO method to compute the non-spin-polarized electronic structure. Starting from such an all-electron, self-consistent calculation, we defined the low-energy, few-band Hamiltonian involving only Mn- d degrees of freedom employing NMTO-downfolding technique. The NMTO-downfolding technique is engineered to produce a few-band Hamiltonian starting from a full DFT calculation by means of an energy-selective procedure of integrating out (downfolding) the degrees of freedom that are not of interest. For the present study, we kept active only the Mn- d and downfolded all other degrees of freedom. The NMTOs, constructed in the above-mentioned way, span only the Mn- d dominated states of an all-band calculation and nothing else, and therefore serve the purpose of effective Wannier functions corresponding to Mn- d -only Hamiltonian. The tight-binding Hamiltonian, defined in the basis of downfolded, Mn- d Wannier functions provide the effective Mn-Mn hopping integrals and the on-site energies. Since the downfolded Mn- d Wannier function is renormalized, in the sense that it contains the integrated out O- p character in its tail, the effective Mn- d -Mn- d hopping integrals contain the chemical information of the hopping path involving oxygen sites. The effective on-site energies and the dominant hopping integrals are listed in Table I. The dominant hopping integrals turned out to be those connecting Mn1 and Mn2 sites within a given pentagon. These interactions are marked in Fig. 1. The interactions, denoted as “3” (t_3 for the hopping interaction and J_3 for the corresponding magnetic interaction) and “4” (t_4 for the hopping interaction and J_4 for the corresponding magnetic interaction) involve a pair of Mn1 and Mn2 atoms, and the interaction, denoted as “5” (t_5 for the hopping interaction and J_5 for the corresponding magnetic interaction) involve a pair of two Mn2 sites. We note that the Mn1-Mn2 interaction proceeds

FIG. 2. Density of states of YMn_2O_5 computed in plane-wave basis. (a) Non-spin-polarized DOS projected onto Mn1- d (marked with dashed line), Mn2- d (marked with solid line), and O- p (marked as shaded area) characters. (b) Spin-polarized DOS computed with ferromagnetic alignment of Mn spins. (c) Spin-polarized DOS computed with antiferromagnetic alignment of Mn spins. Energy is plotted with respect to E_F (marked in the plots as a vertical dashed line).

TABLE I. On-site matrix elements and effective hopping integrals in electron volt calculated in the basis of downfolding Mn Wannier functions. The on-site energies have been measured with respect to E_F . The directions are given in units of lattice constant. The first block corresponds to on-site matrix elements at Mn1 site while the second block corresponds to on-site matrix elements at Mn2 site. The rest of the blocks correspond to hopping integrals, corresponding to t_3 , t_4 , and t_5 .

Direction	O_{Mn1}	Mn1/Mn1	e_{g1}	t_{2g1}	t_{2g2}	e_{g2}	t_{2g3}
[0.00 0.00 0.00]		e_{g1}	2.438	0.000	0.000	0.000	0.000
		t_{2g1}	0.000	-0.107	0.000	0.000	0.000
		t_{2g2}	0.000	0.000	-0.085	0.000	0.000
		e_{g2}	0.000	0.000	0.000	2.534	0.000
		t_{2g3}	0.000	0.000	0.000	0.000	-0.068
Direction	O_{Mn2}	Mn2/Mn2	d_{xy}	d_{yz}	d_{3z^2-1}	d_{xz}	$d_{x^2-y^2}$
[0.00 0.00 0.00]		d_{xy}	0.574	0.000	0.000	0.000	0.000
		d_{yz}	0.000	-0.193	0.000	0.000	0.000
		d_{3z^2-1}	0.000	0.000	0.016	0.000	0.000
		d_{xz}	0.000	0.000	0.000	2.352	0.000
		$d_{x^2-y^2}$	0.000	0.000	0.000	0.000	-0.098
Direction	t_3	Mn2/Mn1	d_{xy}	d_{yz}	d_{3z^2-1}	d_{xz}	$d_{x^2-y^2}$
[-0.08 0.35 0.16]		e_{g1}	0.279	-0.060	0.036	-0.023	-0.029
		t_{2g1}	-0.135	-0.120	0.129	-0.012	0.022
		t_{2g2}	-0.170	0.001	-0.021	-0.038	-0.055
		e_{g2}	0.249	-0.057	0.069	0.002	0.159
		t_{2g3}	0.069	0.116	-0.123	0.005	0.240
Direction	t_4	Mn1/Mn2	e_{g1}	t_{2g1}	t_{2g2}	e_{g2}	t_{2g3}
[-0.35 -0.15 0.16]		d_{xy}	-0.063	-0.074	-0.132	-0.131	0.008
		d_{yz}	0.034	0.019	0.202	-0.080	-0.001
		d_{3z^2-1}	0.099	0.202	0.128	-0.043	0.013
		d_{xz}	0.150	0.128	0.245	0.220	-0.015
		$d_{x^2-y^2}$	0.054	0.149	-0.049	0.015	-0.004
Direction	t_5	Mn2/Mn2	d_{xy}	d_{yz}	d_{3z^2-1}	d_{xz}	$d_{x^2-y^2}$
[0.15 -0.29 0.00]		d_{xy}	-0.066	0.011	-0.112	0.000	0.000
		d_{yz}	0.011	-0.098	-0.047	0.000	0.000
		d_{3z^2-1}	-0.112	-0.047	-0.037	0.000	0.000
		d_{xz}	0.000	0.000	0.000	0.060	0.039
		$d_{x^2-y^2}$	0.000	0.000	0.000	0.039	0.144

through corner sharing of Mn1O_6 octahedra and Mn2O_5 square pyramid via a single oxygen atom, while Mn2-Mn2 interaction proceeds through edge sharing of two Mn2O_5 square pyramids via two oxygen atoms. The out-of-plane interactions connecting two edge-sharing Mn1O_6 octahedra, denoted as t_1 or J_1 and t_2 or J_2 , are found to be negligible, but smaller compared to dominant in-plane interactions. For the sake of comparison with previous calculations, we will restrict ourselves only to in-plane interactions. As is seen from Table I, considering the on-site energy blocks, the distortion in Mn1O_6 octahedra and Mn2O_5 square pyramid makes all the five d states nondegenerate. However, the states at Mn1 site are grouped together into t_{2g} 's and e_g 's with t_{2g} and e_g states split by small energy differences of ≈ 0.02 – 0.1 eV within themselves. Similarly, the states at Mn2 site can be listed as d_{yz} , $d_{x^2-y^2}$, $d_{3z^2-r^2}$, d_{xy} , and d_{xz} in order of increasing energy, with small energy differences between d_{yz} , $d_{x^2-y^2}$, and $d_{3z^2-r^2}$. The exchange processes connecting Mn1 and Mn2, and that connecting two Mn2 sites, considering their level splitting and the nominal occupations can be depicted, as shown in Fig. 3. The energy cost corresponding to the ferromagnetic and antiferromagnetic spin arrangements,

calculated within the extended Kugel-Khomskii-like model is given by

$$\begin{aligned}
 \Delta E_{\text{Ferro}}^{\text{Mn1-Mn2}} &= - \sum_{l=1}^3 \frac{2t_{l,d_{xz}}^2}{U - J_H + \Delta_{l,d_{xz}}} \\
 &\quad - \sum_{r=1}^4 \sum_{eg} \frac{2t_{r,e_g}^2}{U - J_H + \Delta_{r,e_g}}, \\
 \Delta E_{\text{Antiferro}}^{\text{Mn1-Mn2}} &= - \sum_{l=1}^3 \sum_{p=1}^5 \frac{2t_{l,p}^2}{U + \Delta_{l,p}} \\
 &\quad - \sum_{r=1}^4 \sum_{eg} \frac{2t_{r,e_g}^2}{U + \Delta_{r,e_g}}, \\
 \Delta E_{\text{Ferro}}^{\text{Mn2-Mn2}} &= - \sum_{l=1}^4 \frac{2t_{l,d_{xz}}^2}{U - J_H + \Delta_{l,d_{xz}}}, \\
 \Delta E_{\text{Antiferro}}^{\text{Mn2-Mn2}} &= - \sum_{l=1}^4 \sum_{r=1}^5 \frac{2t_{l,r}^2}{U + \Delta_{l,r}},
 \end{aligned}$$

FIG. 3. (Color online) Superexchange processes connecting Mn1 and Mn2 [panel (a) and panel (b)] and that connecting two Mn2 atoms [panel (c) and panel (d)]. The exchanges denoted as J_3 and J_4 are of the first kind and the exchange denoted as J_5 is of the second kind.

where the summation over l , r , and e_g in the first expression runs over three t_{2g} states at Mn1 site, d_{yz} , $d_{x^2-y^2}$, $d_{3z^2-r^2}$, and d_{xy} states at Mn2 site, and two e_g states at Mn1 site, respectively. Similarly, the summation over l , p , r , and e_g in the first expression runs over three t_{2g} states at Mn1 site, five d states at Mn2 site, d_{yz} , $d_{x^2-y^2}$, $d_{3z^2-r^2}$, and d_{xy} states at Mn2 site, and two e_g states at Mn1 site, respectively. The summations over l and r in the last two expressions run over occupied four d levels and all five d levels at the Mn2 site, respectively.

The magnetic exchanges, can be computed from the difference between the energy cost corresponding to the ferromagnetic and antiferromagnetic spin arrangements. The magnetic exchanges, therefore, can be calculated from the knowledge of on-site energies and hopping integrals listed in Table I. Such an approach has been previously successfully used in the context of calculation of magnetic interactions in $\text{La}_2\text{NiMnO}_6$.¹⁶ Adopting such an approach requires a choice of Hubbard on-site correlation U and the Hund's exchange J_H . The magnetic exchange interactions calculated by using the NMTO-downfolding-derived on-site energies and hopping integrals in the energy expression given by Fig. 3 and assuming typical values of U and J_H of 5 and 1 eV are listed in Table II. All the in-plane, magnetic interactions turned out to be of antiferromagnetic nature. For comparison, the values quoted from the calculation of Wang *et al.*⁵ computed for the related material TbMn_2O_5 are also listed. For YMn_2O_5 and TbMn_2O_5 , being closely related in terms of similar phase transitions, crystal structure, and bond lengths, one may expect this comparison to be reasonable. Comparing the two parameter sets, we find that both methods find J_4 to be the strongest interaction, with comparable J_4 and J_5 values between two parameter sets. The J_3 value, however, is remarkably different between

the two parameter sets, with $J_3/J_4 = 0.90$ obtained from NMTO-downfolding-calculations and $J_3/J_4 = 0.09$ as given in Wang *et al.*⁵ We note that both the above-discussed parameter sets provide a rather different estimate of J_5 , compared to the estimate obtained by fitting the experimental inelastic-neutron-scattering data for the low-temperature incommensurate phase of YMn_2O_5 by Kim *et al.*,⁶ with $J_5/J_4 = 0.35$ (0.38) for NMTO (Wang *et al.*⁵) and $J_5/J_4 = 1.37$ in Kim *et al.* estimate.¹⁷

In order to probe this aspect in detail, we have explored energetics of the spin configurations in much more detail. While Wang *et al.*⁵ has considered only eight spin configurations, we have considered all the 2^{16} configurations possible, considering the $2 \times 1 \times 1$ supercell containing 16 Mn atoms, out of which only 166 are found to be nondegenerate. We found the magnetic moments at Mn1 ions in various assumed spin arrangements to range from 2.6–2.8 μ_B in conformity with the nominal Mn^{4+} configuration, while that at Mn2 ions in various assumed spin arrangements to range from 3.4–3.5 μ_B in conformity with the nominal Mn^{3+} configuration, indicating stabilization of same spin state of Mn atoms between different

TABLE II. Magnetic exchange interactions (in millielectron volt), J_3 , J_4 , and J_5 computed using the extended Kugel-Khomskii model and NMTO-downfolding-derived on-site energies and hopping matrix elements, as compared to that computed by Wang *et al.*⁵ for TbMn_2O_5 .

	J_3	J_4	J_5
NMTO-downfolding	−4.15	−4.61	−1.63
Wang <i>et al.</i> (Ref. 5)	−0.45	−4.92	−1.85

TABLE III. Magnetic configurations of the Mn ions for different states used to determine the magnetic interactions. The numbering of the Mn ions are as shown in Fig. 4. The last column gives the relative energies in meV. The obtained magnetic exchange integrals corresponding to each set (one FM and three AFM configurations) are also listed.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	ΔE
FM	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	0
AFM1	-	-	-	-	+	+	+	+	+	+	+	+	+	+	+	+	281
AFM2	+	+	+	-	-	-	-	+	+	+	+	-	-	-	-	+	-4
AFM3	-	+	+	+	+	-	-	-	-	+	+	+	-	-	-	-	62
Set I: Exchange integral (meV) $J_3 = -0.17$								$J_4 = -3.19$				$J_5 = -1.16$					
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	ΔE
FM	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	0
AFM1	-	-	-	-	+	+	+	+	+	+	+	+	+	+	+	+	281
AFM2	+	+	+	-	-	-	-	-	-	+	+	+	+	+	+	-	-151
AFM3	-	-	+	-	+	-	+	+	-	+	-	+	-	+	+	-	12
Set II: Exchange integral (meV) $J_3 = -0.50$								$J_4 = -3.40$				$J_5 = -1.01$					
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	ΔE
FM	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	0
AFM1	-	-	-	-	+	+	+	+	+	+	+	+	+	+	+	+	281
AFM2	+	+	+	-	-	-	+	+	+	-	-	-	+	+	+	-	270
AFM3	+	-	-	-	-	+	+	+	-	-	-	-	+	+	+	-	187
Set III: Exchange integral (meV) $J_3 = -3.92$								$J_4 = -4.33$				$J_5 = -1.31$					
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	ΔE
FM	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	0
AFM1	-	-	-	-	+	+	+	+	+	+	+	+	+	+	+	+	281
AFM2	-	-	-	-	+	+	+	+	+	+	-	-	-	-	-	-	24
AFM3	-	+	-	+	+	-	+	-	+	-	+	-	+	-	+	+	23
Set IV: Exchange integral (meV) $J_3 = -3.73$								$J_4 = -4.19$				$J_5 = -1.44$					

spin arrangements. We further find that all the assumed spin arrangements gave rise to same or similar orbital occupancies discarding different orbital ordering.

A few representative results are presented in Table III. Analyzing the results, we find an interesting situation; a certain restricted subset of all the possible configurations (e.g., listed as set I and set II in Table III) yields $J_3 \ll J_4$ similar to that obtained by Wang *et al.*,⁵ while there exists a variety of other configurations that yield substantially larger values of J_3 (e.g., listed as set III and set IV in Table III) similar to that predicted by NMTO-downfolding calculations. This points to rather nonuniqueness of the parameter sets obtained from fitting of total energies. There are 166 nondegenerate spin arrangements, therefore, 166 different values of total energies, which may be fitted to obtain three unknown quantities J_3 , J_4 , and J_5 . This is an overdetermined situation and would therefore depend on the subsets of energy values chosen to fit.

In order to establish the goodness of one parameter set over other, in the following section, we provide the analysis of the magnon spectra and the feasibility arguments on the basis of hopping paths.

C. Goodness of the calculated magnetic exchanges

1. Magnon dispersion: comparison with experiment

In order to check the goodness of the parameter sets, we calculated the magnon spectra of the spin model using

the standard many-body techniques. We used the Holstein-Primakoff transformation¹⁸ to convert from spins to a boson representation. Thereupon we diagonalized the matrix using the numerical implementation of Bogolubov transformation.¹⁹ We obtained the dispersions along the [100] and [010] directions. We considered the magnetic exchanges, restricted within the cell shown in Fig. 5. This involves, in addition to J_3 , J_4 , and J_5 , J_1 that connect Mn1 sites, one located below the Mn2 layer and another located above the Mn2 layer. In Wang *et al.*'s total energy calculations,⁵ the fitting procedure did not involve J_1 . In order to establish the ground-state commensurate spin structure as predicted in Ref. 12, we need to involve J_1 ,

FIG. 4. (Color online) The magnetic unit cell considered for total energy calculations of different magnetic configurations. Different Mn atoms have been numbered.

FIG. 5. (Color online) The cell used to carry out the magnon calculation. The atoms marked from 1–8 belong to the unit cell labeled as $\{i, j\}$. The magnetic exchanges with neighbors of Mn atoms belonging to neighboring unit cells (labeled as $\{i \pm 1, j\}$ or $\{i, j \pm 1\}$) are included in the Hamiltonian. The ground-state spin structure, considering the NMTO-derived magnetic exchanges are also shown with arrows.

which according to NMTO-downfolding calculations turned out to be of ferromagnetic nature, having a magnitude of $\approx 0.5 J_4$ (2.2 meV). Using NMTO-derived parameter sets, we obtained the magnetic ground state corresponding to an antiferromagnet with the ordering vector $(1/2, 0, 0)$. Since we neglected the out-of-plane interactions beyond J_1 , the ordering was obtained as $(1/2, 0, 0)$ instead of $(1/2, 0, 1/4)$, observed experimentally.

The corresponding Hamiltonian is thus given by $H = H_{\text{intra}} + H_{\text{inter}}$, where

$$H_{\text{intra}} = \sum_{ij} J_5(S_{3,i,j}S_{4,i,j} + S_{1,i,j}S_{6,i,j}) \\ + J_3(S_{2,i,j}S_{3,i,j} + S_{1,i,j}S_{5,i,j}) \\ + J_4(S_{4,i,j}S_{5,i,j} + S_{1,i,j}S_{2,i,j}) \\ + J_1(S_{2,i,j}S_{7,i,j} + S_{5,i,j}S_{8,i,j}) \\ + (J_4S_{1,i,j}S_{7,i,j} + J_3S_{3,i,j}S_{7,i,j}) \\ + (J_3S_{1,i,j}S_{8,i,j} + J_4S_{4,i,j}S_{8,i,j}),$$

while

$$H_{\text{inter}} = \sum_{ij} J_3(S_{4,i,j}S_{2,i,j+1} + S_{5,i,j}S_{6,i,j+1}) \\ + J_4(S_{5,i,j}S_{3,i+1,j} + S_{6,i,j}S_{2,i+1,j}) \\ + J_3(S_{6,i,j}S_{5,i,j-1} + S_{2,i,j}S_{4,i,j-1}) \\ + J_4(S_{2,i,j}S_{6,i-1,j} + S_{3,i,j}S_{5,i-1,j}) \\ + (J_4S_{3,i,j}S_{8,i-1,j} + J_3S_{4,i,j}S_{7,i,j+1}) \\ + (J_3S_{6,i,j}S_{8,i,j-1} + J_4S_{6,i,j}S_{7,i+1,j}) \\ + (J_4S_{7,i,j}S_{6,i-1,j} + J_3S_{7,i,j}S_{4,i,j-1}) \\ + (J_3S_{8,i,j}S_{6,i,j+1} + J_4S_{8,i,j}S_{3,i+1,j}).$$

$S_{n,i,j}$ is the spin at n -th Mn site within the cell $\{i, j\}$ (see Fig. 5 for notation). H_{intra} corresponds to interactions restricted to the central cell $\{i, j\}$, while H_{inter} corresponds to interactions connecting sites within $\{i, j\}$ cell to neighboring cells.

We computed the magnon dispersions considering different parameter sets that were obtained through NMTO-downfolding calculations and that obtained in Wang *et al.*,⁵

FIG. 6. (Color online) Calculated low-lying branches of magnon dispersion plotted along $[100]$ (left panels) and $[010]$ (right panels) directions compared to experimentally measured data considering different sets of magnetic interactions. Top-most panels: Magnon spectra calculated using parameter sets given by NMTO-downfolding calculations. Second panels from top: Magnon spectra calculated using parameter sets given by the calculation of Wang *et al.*⁵ Third panels from top: Magnon spectra calculated using parameter sets given by the study of Kim *et al.*⁶ Bottom panels: Experimentally measured data.

and compared those with experimental magnon spectra probed through inelastic neutron scattering. We also performed the calculation considering the parameter set provided in the recent study of Kim *et al.*⁶ The comparisons are shown in Fig. 6. The left-hand panels correspond to dispersions probed along $[100]$ direction while the right-hand panels correspond to dispersions probed along $[010]$ direction. The top-most panels correspond to calculations using NMTO-derived parameter sets, the second and third panels from the top correspond to calculations using parameter sets obtained in Wang *et al.*'s total energy calculations⁵ and that using parameter sets obtained in the recent study of Kim *et al.*,⁶ respectively. The bottom-most panels show the experimentally measured dispersions. Our calculated magnon dispersion has eight branches, due to the multiatom basis in the unit cell.²⁰ The experimental spectra captures only the lowest two branches, the higher ones are not captured within the instrumental limitations of the cold triple-axis spectrometer TASP. For comparison with the experimental spectra, we show only the lowest branches of the theoretical

FIG. 7. (Color online) Overlaps of the downfolded Mn-*d* NMTOs at two Mn1 and Mn2 sites. Plotted are the orbital shapes (constant-amplitude surfaces) with the lobes of opposite signs labeled by black (magenta) and yellow (cyan) at site Mn2(Mn1). (a) Corner-sharing Mn1-Mn2 overlap corresponding to interaction “3”. (b) Corner-sharing Mn1-Mn2 overlap corresponding to interaction “4.”

results that lie within the energy scale of the experimental data.

Considering Fig. 6, we notice that while the theoretically calculated dispersions along [100] differ from experiment for all chosen parameter sets, the theoretical results obtained using NMTO-derived parameter sets, along [010] are in much better agreement with the experiment, compared to other parameter sets. The parameter set of Wang *et al.*,⁵ shows no dispersion at all along the [010] direction, in sharp contrast with the experimentally measured data. We note, that the vector connecting Mn1 and Mn2 sites, corresponding to J_3 interaction is primarily directed along the *b* direction, while the vector connecting Mn1 and Mn2 sites, corresponding to J_4 interaction is primarily directed along the *a* direction (cf. Table I). The lack of dispersion of the magnon modes along the [010] direction considering the parameter sets given by Wang *et al.*’s total energy calculations⁵ is therefore expected as the value of the parameter J_3 was rather small in Wang *et al.*’s parameter set.⁵ The value of the parameter J_3 was also small in the parameter set of Kim *et al.*,⁶ producing also dispersionless magnon spectra along [010] direction. We note that the measured magnon spectra of YMn_2O_5 in the low-temperature incommensurate state at higher energies (10–20 meV), to which the fit was carried out by Kim *et al.*⁶ did not involve the dispersions along [010] direction. The improvement of the description of dispersion along [010] direction using NMTO-derived parameters, therefore, shows a clear evidence of the superiority of the NMTO-derived parameter sets over the existing parameter sets with small values of J_3 .^{5,6} Finally, though the NMTO-downfolding-derived parameter sets capture the behavior of the experimental spectra along [010] direction satisfactorily, the description along [100] direction is still not satisfactory. This may be due to the neglect of magnon-phonon interactions, which are shown to be important in these systems²¹ as well as neglect of single-ion anisotropy in the model, responsible for the helicoidal modulation in experimentally observed spin structure. Inclusion of magnon-phonon interaction through phonon calculations for different magnetic configurations is prohibitively difficult and will be taken up at a later date. At the end, it is interesting to note that in spite of the simplistic nature of our spin model, it

brings out nicely the importance of the magnetic exchange interaction, J_3 .

2. Superexchange paths: overlap of Wannier functions

Having established the goodness of the NMTO-derived parameter set with substantially large value of magnetic exchange interaction J_3 in terms of the calculated magnon spectra and its comparison with inelastic-neutron-scattering data, we provide further arguments based on the involved superexchange paths. As found by the NMTO study, the magnitude of J_3 is comparable to that of the largest interaction, J_4 , while the previous studies^{5,6} report substantially smaller value of J_3 compared to J_4 . We argue in the following that from a chemical point of view, it is logical to have J_3 comparable to J_4 . It might be noted that both J_3 and J_4 interactions connect a pair of Mn1 and Mn2 sites through corner-shared oxygens, with a very similar Mn-O-Mn bond angle (123° for J_3 and 132° for J_4 interaction). One would, therefore, expect the involved superexchange paths to be similar in two cases, giving rise to a similar nature of magnetic exchanges.

This expectation turned out to be true as shown in Fig. 7, where the overlap of two representative Mn-*d* Wannier functions placed at Mn1 and Mn2 sites have been plotted, corresponding to interactions “3” (left panel) and “4” (right panel) respectively. It shows in both cases that the overlap of the Wannier functions centered at Mn1 and Mn2 sites gives rise to equally strong superexchange paths formed by the overlap of weights situated at the connecting oxygen site.

V. CONCLUSION

In conclusion, we have calculated the magnetic exchange interaction for an effective magnetic model corresponding to the multiferroic compound YMn_2O_5 . Our calculated magnetic interactions differ from those reported earlier⁵ in connection with the related compound TbMn_2O_5 obtained from total energy calculations and those obtained by fitting the inelastic-neutron-scattering data for the low-temperature incommensurate phase of YMn_2O_5 ,⁶ in terms of substantially large value of Mn1-Mn2 interaction along the *b*-axis (J_3). Our first-principles-derived parameters seem to provide improved

agreement with the measured neutron-scattering data along [010] direction, probed using inelastic neutron scattering for the commensurate phase, justifying the importance of J_3 . The description of magnon dispersion along [100] direction is still not satisfactory with the dispersion width being narrower compared to experimentally measured data. This may be improved by going beyond spin-only models in terms of inclusion of magnon-phonon coupling and also going beyond the assumption of collinearity of ground state

to include the helicoidal modulation detected experimentally. Calculations to include these effects are currently underway.

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