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# Density Functional Analysis of the Spin Exchange Interactions and Charge Order Patterns in the Layered Magnetic Oxides $YBaM_2O_5$ (M = Mn, Fe, Co)

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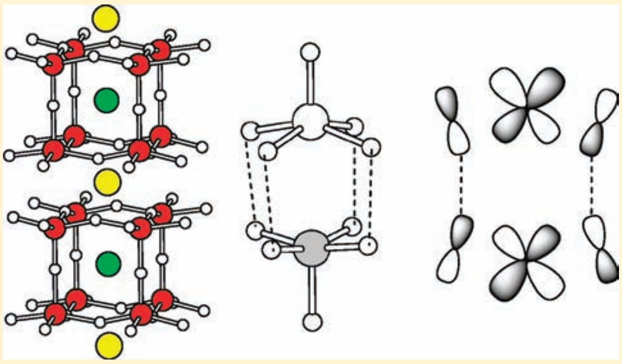
S Supporting Information

**ABSTRACT:** The spin and charge order phenomena of the layered magnetic oxides $YBaM_2O_5$ (M = Mn, Fe, Co) were analyzed on the basis of density functional calculations. We evaluated the spin exchange interactions of $YBaM_2O_5$ by performing energy-mapping analysis based on density functional calculations to find why they undergo a three-dimensional magnetic ordering at high temperature. We estimated the relative stabilities of the checkerboard and stripe charge order patterns of $YBaM_2O_5$ (M = Mn, Fe, Co) by optimizing their structures with density functional calculations to probe if the nature of the charge order pattern depends on whether their transition-metal ions are Jahn−Teller active.



## 1. INTRODUCTION

Transition-metal oxides based on perovskite-type structures exhibit rich physical properties associated with the charge, spin, and/or orbital order of their transition-metal cations. The layered magnetic oxides $YBaM_2O_5$ (M = Mn, Fe, Co) are quite special because they exhibit all three types of ordering phenomena. In the $M_2O_5$ slabs of $YBaM_2O_5$, the $MO_5$ square pyramids form the $M_2O_9$ dumbbell units by sharing their apical O atoms ($O_{ap}$), and these dumbbell units share their basal O atoms ($O_{bs}$) to form the $M_2O_5$ slabs parallel to the *ab*-plane. These slabs, containing a $Ba^{2+}$ ion in every $M_4$ cube, alternate with layers of $Y^{3+}$ ions along the *c*-direction (Figure 1). The transition-metal ions exist as $M^{2.5+}$ cations when their sites are equivalent in structure. This monovalence state of $YBaM_2O_5$ is stable at high temperatures, but lowering the temperature induces a charge order (i.e., charge disproportionation), $2\ M^{2.5+} \rightarrow M^{2+} + M^{3+}$, leading to a mixed-valence state. Two different types of charge order occur in the $M_2O_5$ slabs of $YBaM_2O_5$; $YBaMn_2O_5$ exhibits a checkerboard charge order (CCO) of the $M^{2+}$ and $M^{3+}$ ions (Figure 2a),[1−3] whereas both $YBaFe_2O_5$[4] and $YBaCo_2O_5$[5] show a stripe charge order (SCO) of the $M^{2+}$ and $M^{3+}$ ions with the stripes running along the *b*-direction (Figure 2b). $YBaMn_2O_5$ is similar to $YBaM_2O_5$ (M = Fe, Co) in spin order in that their magnetic ground states adopt a G-type antiferromagnetic (AFM) coupling between nearest-neighbor spins along the *a*-, *b*-, and *c*-directions.[2−5] Nevertheless, the SCO plus the G-type AFM spin order leads to zero overall moment (i.e., AFM state) for $YBaM_2O_5$ (M = Fe, Co), but the CCO plus the G-type AFM spin order to a nonzero overall moment (i.e., ferrimagnetic state) for $YBaMn_2O_5$.[1,3] Furthermore, $YBaMn_2O_5$ is different from $YBaM_2O_5$ (M = Fe, Co) in that the spin orientation is along the *c*-axis in $YBaMn_2O_5$,[2,3] but perpendicular to the *c*-axis in $YBaM_2O_5$ (M = Fe, Co).[4,5]

Because of their interesting physical properties, the layered oxides $YBaM_2O_5$ (M = Mn, Fe, Co) have been examined in a number of theoretical studies based on density functional theory (DFT) calculations.[6−13] Vidya et al.[8] found the ferrimagnetic state to be the ground state for $YBaMn_2O_5$, and showed the occurrence of the orbital order associated with the CCO in terms of charge-density plots. Xiang et al.[10] showed that the nature of the magnetic ground state of $YBaMn_2O_5$ depends on the ∠Mn−O−Mn angle of the Mn−O−Mn bridges in the *ab* plane. Hap et al.[11] examined $YBaFe_2O_5$ to show that the orbital order corresponds to the local distortions of the $FeO_5$ square pyramids. Vidya et al.[12] confirmed the ferrimagnetic ground state for $YBaMn_2O_5$ and the G-type AFM ground states for $YBaFe_2O_5$ and $YBaCo_2O_5$, and analyzed the Born effective charges to assess the charge orders of $YBaM_2O_5$ (M = Mn, Fe, Co). Using a model Hamiltonian and the assumption of the crystal field split pattern, $(xz, yz) < xy < z^2 < x^2{-}y^2$, for a $MO_5$ square pyramid with $C_{4v}$ symmetry, Wang et al.[14] investigated the relative stabilities of the CCO and SCO in $YBaMn_2O_5$ and $YBaCo_2O_5$ to suggest that the CCO is favored when there is no Jahn−Teller (JT) active ion, but the SCO is favored if there exist JT-active ions.

There are two aspects of $YBaM_2O_5$ (M = Mn, Fe, Co) that remain puzzling. One is that their three-dimensional (3D) magnetic ordering temperatures are high; the 3D AFM ordering

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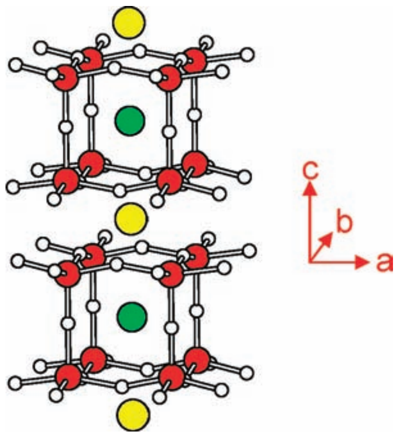

**Figure 1.** Perspective view of the crystal structure of $YBaM_2O_5$ (M = Mn, Fe, Co), where the red, white, green, and yellow circles represent the M, O, Ba, and Y atoms, respectively.

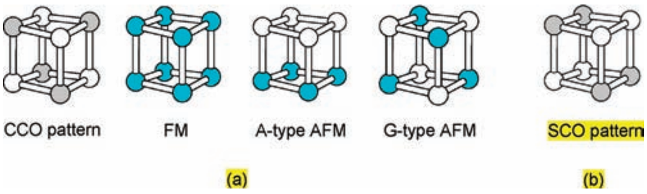

**Figure 2.** (a) Three ordered spin arrangements (namely, the FM, A-type AFM, and G-type AFM arrangements) of $YBaMn_2O_5$ with the CCO pattern employed to determine the U value appropriate for the DFT+U calculations. The $Mn^{3+}$ and $Mn^{2+}$ sites are identified by the gray and white circles, respectively, in the first diagram. The up-spin and down-spin Mn sites are indicated by cyan and white circles, respectively. The G-type AFM arrangement leads to the ferrimagnetic state. (b) The SCO pattern of $YBaM_2O_5$ (M = Fe, Co). The $M^{3+}$ and $M^{2+}$ sites are identified by the gray and white circles, respectively.

of $YBaFe_2O_5$ and $YBaCo_2O_5$ occurs at high temperatures (at $T_N$ = 430 K[4] and 330 K,[5] respectively), and so is the ferromagnetic ordering of $YBaMn_2O_5$ (167 K).[2] This implies that the M−O···O−M (M = Mn, Fe, Co) spin exchange interactions between adjacent $M_2O_5$ slabs along the *c*-axis is substantially strong. So far, there has been no systematic study on the spin exchange interactions of all three oxides $YBaM_2O_5$ (M = Mn, Fe, Co). In the neutron scattering study of $YBaFe_2O_5$ by Chang et al.,[15] the strength of the interslab Fe−O···O−Fe spin exchange was estimated to be only 1% of the Fe−O−Fe spin exchange within each $Fe_2O_9$ dumbbell.[15] Spiel et al.[13] extracted a few spin exchange parameters of $YBaFe_2O_5$ from their DFT calculations to compare with the experimental values of Chang et al.,[15] and reported only the average of the Fe−O···O−Fe and the Fe−O−Fe spin exchanges along the *c*-direction. Thus, it is timely and important to provide a comprehensive study of the spin exchange interactions for all $YBaM_2O_5$ (M = Mn, Fe, Co) on the basis of DFT calculations. The other puzzling aspect is if the nature of the charge order pattern of $YBaM_2O_5$ is determined by whether their $M^{2+}$ and/or $M^{3+}$ ions are JT-active or not. The crystal field split pattern, $(xz, yz) < xy < z^2 < x^2-y^2$, employed by Wang et al.[14] for a $MO_5$ square pyramid with $C_{4v}$ symmetry is appropriate only if the $\angle O_{ap}-M-O_{bs}$ angles of the $MO_5$ square pyramids are close to 90°.[16] In $YBaM_2O_5$ (M = Mn, Fe, Co) these angles are substantially greater than 90°,[17] which lowers the *xy* level below the (*xz*, *yz*) level, leading to the split pattern $xy < (xz, yz) < z^2 < x^2-y^2$.[16] As a consequence, the high-spin $Mn^{2+}$ and $Mn^{3+}$ ions of $YBaMn_2O_5$ are not JT-active, nor are the high-spin $Fe^{2+}$ and $Fe^{3+}$ ions of $YBaFe_2O_5$. Nevertheless, the CCO is found in $YBaMn_2O_5$, but the SCO in $YBaFe_2O_5$. Thus, it is questionable if the model Hamiltonian study of Wang et al.[14] is valid. It is important to quantitatively estimate the relative stabilities of the CCO and SCO in each of $YBaM_2O_5$ (M = Mn, Fe, Co) on the basis of DFT calculations.

**Table 1. Relative Energies[a] of the FM, A-type AFM, and G-type AFM Spin Arrangements[b] of $YBaMn_2O_5$[c]**

| *U* | FM | A-type AFM | G-type AFM |
|---|---|---|---|
| 0 eV | 0 | −323 | −412 |
| 1 eV | 0 | −267 | −295 |
| 2 eV | 0 | −213 | −199 |

[a] In meV per FU. [b] Defined in Figure 3. [c] Determined from the DFT+U calculations with *U* = 0, 1, and 2 eV.

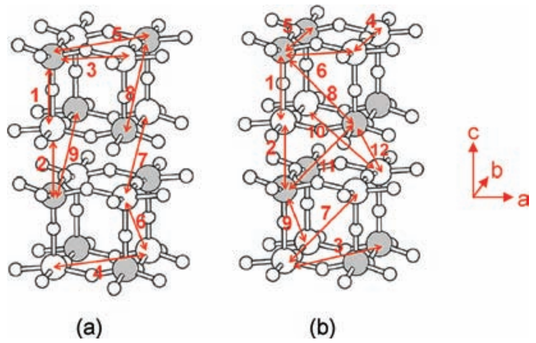

**Figure 3.** Spin exchange paths of $YBaM_2O_5$: (a) M = Mn and (b) M = Fe, Co. The $M^{3+}$ and $M^{2+}$ ions are represented by large gray and large white circles, respectively. The numbers 1, 2, 3, etc. represent the spin exchanges $J_1$, $J_2$, $J_3$, etc., respectively.

In the present work the aforementioned two questions are investigated. We evaluate the spin exchange interactions of all three oxides $YBaM_2O_5$ (M = Mn, Fe, Co) by performing energy-mapping analysis based on DFT calculations.[18] Then we estimate the relative stabilities of the CCO and SCO in $YBaM_2O_5$ (M = Mn, Fe, Co) by optimizing their structures in their magnetic ground state on the basis of DFT calculations.

## 2. DETAILS OF CALCULATIONS

Our spin-polarized density functional calculations employed the projector augmented wave method[19,20] encoded in the Vienna ab initio simulation package,[21] the generalized gradient approximation for the exchange and correlation corrections,[22] and the plane wave cutoff energy of 400 eV. The electron correlation associated with the M 3d states was taken care of by performing DFT plus on-site repulsion (DFT+U) calculations.[23] The DFT+U method is empirical in nature because one needs to determine the *U* value appropriate for a given magnetic system by performing a series of DFT+U calculations with several different *U* values.[24−26] For the $YBaM_2O_5$ (M = Mn, Fe, Co) system, the most important magnetic property to reproduce by DFT+U calculations is that they all adopt the G-type AFM spin arrangement as the magnetic ground state. The U value typically used for the transition-metal elements Mn, Fe, Co, and Cu is in the vicinity of 4 eV. For $YBaFe_2O_5$ and $YBaCo_2O_5$, the G-type AFM state is found to be the magnetic

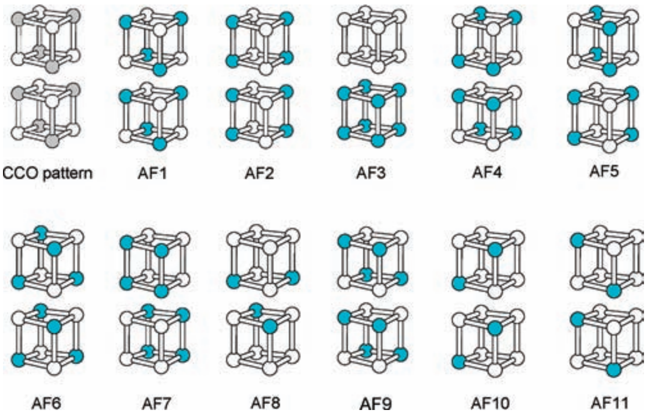

**Figure 4.** Ordered spin arrangements of $YBaMn_2O_5$ employed for the extraction of the nine spin exchange parameters $J_1$−$J_9$. The up-spin and down-spin Mn sites are indicated by cyan and white circles, respectively. The $Mn^{3+}$ and $Mn^{2+}$ sites are identified by the gray and white circles, respectively, in the first diagram.

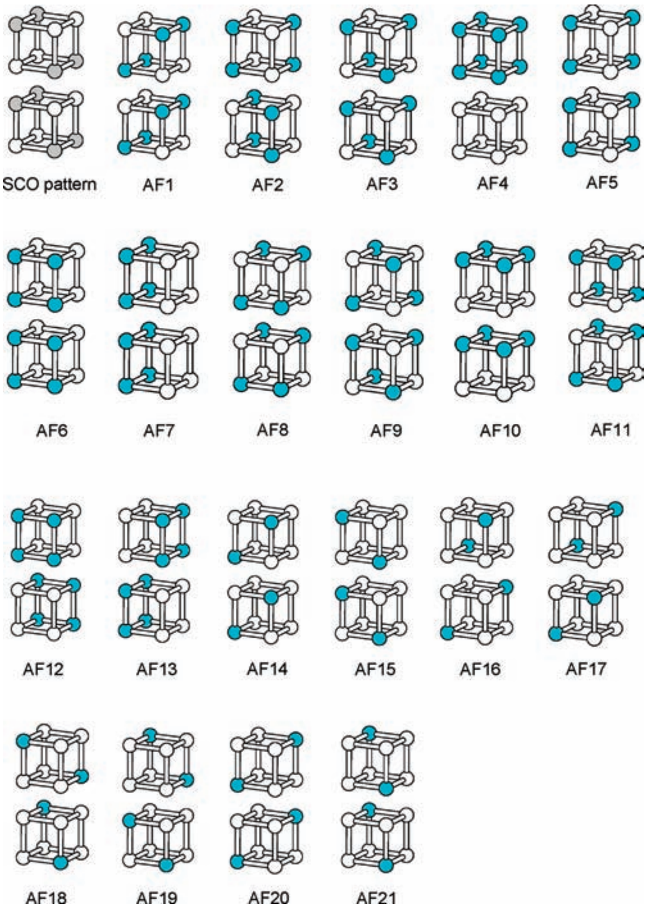

**Figure 5.** Ordered spin arrangements of $YBaM_2O_5$ (M = Fe, Co) employed for the extraction of the nine spin exchange parameters $J_1$−$J_{12}$. The up-spin and down-spin M sites are indicated by cyan and white circles, respectively. The $M^{3+}$ and $M^{2+}$ sites are identified by the gray and white circles, respectively, in the first diagram.

**Table 2. Relative Energies[a] of Various Ordered Spin States of $YBaM_2O_5$ (M = Mn, Fe, Co)[b]**

| M | AF1 | AF2 | AF3 | AF4 | AF5 | AF6 | AF7 |
|---|---|---|---|---|---|---|---|
| Mn | 0 | 192.7 | 137.4 | 238.4 | 95.5 | 110.0 | 70.1 |
| Fe | 131.9 | 212.6 | 0 | 325.8 | 183.7 | | 315.8 |
| Co | 128.6 | 245.9 | 0 | | | 241.7 | 119.5 |
| **M** | **AF8** | **AF9** | **AF10** | **AF11** | **AF12** | **AF13** | **AF14** |
| Mn | 138.8 | 147.1 | 9.4 | 137.1 | 139.1 | | |
| Fe | 69.7 | 18.3 | 235.9 | 90.9 | 142.0 | | 247.0 |
| Co | 123.7 | 240.9 | | 108.3 | 204.1 | 225.6 | 245.9 |
| **M** | **AF15** | **AF16** | **AF17** | **AF18** | **AF19** | **AF20** | **AF21** |
| Fe | 184.8 | 249.2 | 249.1 | 225.0 | 214.2 | 257.0 | 164.4 |
| Co | 125.3 | 241.7 | - | 119.5 | 123.7 | 240.9 | 121.5 |

[a] In meV per FU. [b] Determined from the DFT+U calculations.

ground state by using $U$ = 4 eV. For $YBaMn_2O_5$, however, the ferrimagnetic state resulting from the G-type AFM spin coupling is not the magnetic ground state if the $U$ value is greater than ∼1 eV (see Figure 2 and Table 1). A similar situation was found for the magnetic oxide $Ca_3CoMnO_6$,[26] which consists of trigonal arrangement of the $CoMnO_6$ chains made up of face-sharing $CoO_6$ trigonal prisms and $MnO_6$ octahedra; the magnetic ground state that has the ↑↑↓↓ spin arrangement of the $Co^{2+}$ and $Mn^{4+}$ ions is not reproduced by DFT+U calculations if the $U$ value for Mn is greater than 1 eV. Thus, in the present DFT+U calculations, we employed $U$ = 1 eV for $YBaMn_2O_5$ and $U$ = 4 eV for $YBaFe_2O_5$ and $YBaCo_2O_5$.

## 3. EVALUATION OF SPIN EXCHANGE INTERACTIONS

To examine why $YBaM_2O_5$ (M = Mn, Fe, Co) adopts the G-type AFM spin coupling, we evaluate the spin exchange parameters $J_1$−$J_9$ for $YBaMn_2O_5$ defined in Figure 3a, and $J_1$−$J_{12}$ for $YBaFe_2O_5$ and $YBaCo_2O_5$ defined in Figure 3b, by performing energy-mapping analysis based on DFT+U calculations. For this purpose, we first determine the relative energies of $YBaMn_2O_5$ for the ordered spin states listed in Figure 4, and those of $YBaM_2O_5$ (M = Fe, Co) for the ordered spin states listed in Figure 5. The relative energies of these states obtained from the DFT+U calculations are summarized in Table 2.

In extracting $N$ spin exchange parameters, the minimum number of ordered spin states needed in the mapping analysis is $N + 1$, which leads one-to-one mapping between the relative energy differences and the spin exchange parameters. For cases dealing with magnetic systems containing mixed-valence magnetic ions, there can be several different sets of $N + 1$ ordered spin states leading to slightly different values for the spin exchange parameters. In such cases, it is more reasonable to employ more ordered spin states than required for one-to-one mapping and carry out mapping analysis on the basis of least-squares fitting.[27]

The total spin exchange energies of the ordered spin states can be written in terms of the spin Hamiltonian,

$$\hat{H} = -\sum_{i<j} J_{ij}\hat{S}_i \cdot \hat{S}_j \qquad (1)$$

in which $J_{ij}$ (= $J_1$−$J_9$ for $YBaMn_2O_5$ and $J_1$−$J_{12}$ for $YBaFe_2O_5$ and $YBaCo_2O_5$) is the spin exchange parameter for the interaction between the spin sites $i$ and $j$ in $YBaM_2O_5$. In writing the expression for the total spin exchange energy of an ordered spin state, we employ the energy expressions for the ferromagnetic (FM) and AFM arrangements of a general spin dimer whose spin sites $i$ and $j$ possess $N_i$ and $N_j$ unpaired spins (hence, spins

**Table 3. Values of the Spin Exchange Parameters $J_i$ [a] of $YBaM_2O_5$ (M = Mn, Fe, Co)[b]**

| M | $J_1$ | $J_2$ | $J_3$ | $J_4$ | $J_5$ | $J_6$ | $J_7$ | $J_8$ | $J_9$ | $J_{10}$ | $J_{11}$ | $J_{12}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Mn | −12.9 | −8.6 | −2.7 | −0.2 | −1.6 | −0.5 | −0.9 | −0.1 | +0.7 | | | |
| Fe | −12.1 | −7.4 | −1.3 | −8.8 | −8.7 | −4.2 | +1.9 | +0.4 | +1.3 | −1.2 | −2.4 | −2.5 |
| Co | −17.3 | −2.8 | −0.7 | −3.2 | −16.9 | −10.0 | −0.5 | −0.4 | +0.1 | −0.5 | 0.0 | −0.5 |

[a] In meV. [b] Determined by mapping analysis based on DFT+U calculations.

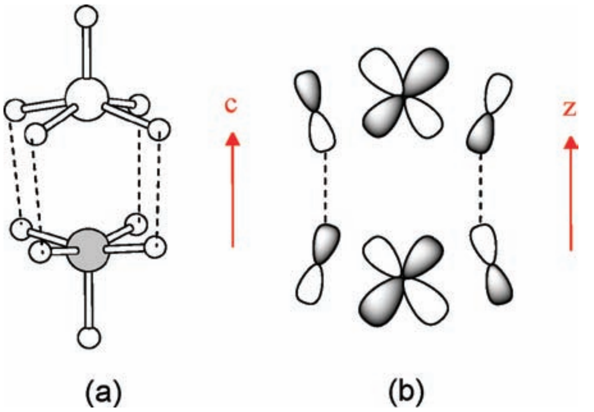

**Figure 6.** (a) Two $MO_5$ square pyramids associated with the M−O···O−M spin exchange $J_2$ of $YBaM_2O_5$ (M = Mn, Fe, Co), where the $M^{3+}$ and $M^{2+}$ sites are identified by the gray and white circles, respectively. (b) Magnetic orbitals (*xz* and/or *yz*) of the two $MO_5$ square pyramids enhancing the strength of the AFM spin exchange $J_2$.

$S_i = N_i/2$ and $S_j = N_j/2$), respectively.[28,29] Given $J_{ij}$ as the spin exchange parameter for this spin dimer, the energies of the FM and AFM arrangements of this spin dimer ($E_{FM}$ and $E_{AFM}$, respectively) are expressed as

$$E_{FM} = +N_iN_jJ_{ij}/4 = S_iS_jJ_{ij}$$

$$E_{AFM} = +N_iN_jJ_{ij}/4 = S_iS_jJ_{ij} \qquad (2)$$

(Note that $S = 5/2$ and 2 for the high-spin $Mn^{2+}$ and $Mn^{3+}$ ions, respectively, $S = 2$ and 5/2 for the high-spin $Fe^{2+}$ and $Fe^{3+}$ ions, respectively, and $S = 3/2$ and 2 for the high-spin $Co^{2+}$ and $Co^{3+}$ ions, respectively, in $YBaM_2O_5$.) The total spin exchange energy $E_{spin}$ per formula unit (FU) of an ordered spin arrangement, obtained by summing up all pairwise interactions, can be expressed as

$$E_{spin} = \sum_i C_iJ_i = C_1J_1 + C_2J_2 + C_3J_3 + \ldots \qquad (3)$$

where $C_i$ is the coefficient for the spin exchange parameter $J_i$. The $C_i$ values for the various ordered spin states for $YBaMn_2O_5$ are summarized in Supporting Information, Table S1, those for $YBaFe_2O_5$ in Supporting Information, Table S2, and those for $YBaCo_2O_5$ in Supporting Information, Table S3. In mapping the relative energies of the ordered spin states determined from the DFT+U calculations onto the corresponding energies expected from the total spin exchange energies, we carry out least-squares fitting analyses. The resulting spin exchange parameters of $YBaM_2O_5$ (M = Mn, Fe, Co) are summarized in Table 3.

For $YBaMn_2O_5$ the three strongest spin exchanges $J_1$, $J_2$, and $J_3$ are AFM and lead to the ferrimagnetic spin arrangement, as found experimentally.[3] For $YBaM_2O_5$ (M = Fe, Co), the five strongest spin exchanges $J_1$, $J_2$, $J_4$, $J_5$, and $J_6$ are AFM and lead to the G-type AFM spin arrangement, in agreement with experiment.[4,5] We note that $J_1$ and $J_3$ of $YBaMn_2O_5$ as well as $J_1$, $J_4$, $J_5$, and $J_6$ of $YBaM_2O_5$ (M = Fe, Co) are M−O−M superexchanges with large ∠M−O−M angles. Thus, they are predicted to be strongly AFM,[30] as confirmed from the present calculations.

A few exchange parameters of $YBaFe_2O_5$ were deduced in the neutron scattering study of Chang et al.[15] (The notations of their spin exchange parameters correspond to ours as follows: $J_1 = J_{23}^{c}$, $J_2 = J_{direct}$, $J_4 = J_{22}^{b}$, $J_5 = J_{33}^{b}$, and $J_6 = J_{23}^{a}$.) By using perturbation theory, Chang et al. estimated the $J_2/J_1$ ratio to be approximately 0.01, so they neglected $J_2$ in their analysis of the spin wave dispersion relations. However, our DFT+U calculations show that the $J_2$ exchanges of $YBaM_2O_5$ are quite strong, that is, $J_2/J_1$ = 0.67, 0.61, and 0.16 for M = Mn, Fe, and Co, respectively. As found in numerous magnetic oxides,[18,24,31] these M−O···O−M exchanges between the dumbbells along the c-direction (Figure 6a) are strongly AFM because their O···O contact distances are short [2.800 (×4) Å for $YBaMn_2O_5$, 2.753 (×2) and 2.838 (×2) Å for $YBaFe_2O_5$, and 2.796 (×2) and 2.829 (×2) Å $YBaCo_2O_5$]. Because of the short O···O contacts and the fact the $\angle O_{ap}-M-O_{bs}$ angles of the $MO_5$ square pyramids are greater than 90°,[17] the magnetic orbitals (e.g., *xz* and/or *yz*) of the $MO_5$ square pyramids associated with $J_2$ overlap substantially through their O 2p orbitals (Figure 6b) thereby making $J_2$ strongly AFM. Consequently, the 3D AFM ordering temperatures of $YBaFe_2O_5$ and $YBaCo_2O_5$ are high (i.e., $T_N$ = 430 K[4] and 330 K,[5] respectively), and the ferrimagnetic ordering temperature of $YBaMn_2O_5$ is substantially high as well (i.e., 167 K).[2] Thus, neglecting $J_2$ is not a good approximation.

By introducing another approximation, $J_{23} = (2J_{23}^{a} + J_{23}^{c})/3$, Chang et al.[15] obtained $J_{23}^{b} \approx -5.9$ meV, $J_{22}^{b} \approx -3.4$ meV, and $J_{23} \approx -6.0$ meV for $YBaFe_2O_5$. These estimates are comparable to the corresponding numbers of our calculations (i.e., −8.7, −8.8, and −6.8 meV, respectively). In their DFT study of $YBaFe_2O_5$,[13] Spiel et al. reported that $J_{23}^{b} = -10.0$ meV, $J_{22}^{b} = -4.3$ meV, $J_{23}^{a} = -4.2$ meV, and $\langle J_{23}^{c}\rangle \equiv (J_{23}^{c} + J_{direct})/2 = -5.6$ meV. The corresponding $J_{23}^{a}$ and $\langle J_{23}^{c}\rangle$ values of our calculations are −4.2 and −9.8 meV, respectively. Thus, the spin exchange parameters of Spiel et al. are comparable to ours.

## 4. PREFERRED CHARGE ORDER PATTERN

We now examine the energetic difference in the charge order patterns of $YBaM_2O_5$ (M = Mn, Fe, Co) in their magnetic ground states by performing DFT+U calculations. For this purpose, it is necessary to determine the relative energies of the CCO and SCO patterns of each $YBaM_2O_5$ (M = Mn, Fe, Co). For $YBaMn_2O_5$, we optimized the experimentally observed CCO structure. To obtain its hypothetical SCO structure, we started our optimization using the geometry of the experimentally observed SCO structure of $YBaFe_2O_5$. Our calculations show that the CCO structure is lower in energy than the SCO structure by 144 meV per FU for $YBaMn_2O_5$. For $YBaFe_2O_5$ and $YBaCo_2O_5$, we optimized their experimentally observed SCO structures. To find their hypothetical CCO structures, we began our optimization using the CCO structure of $YBaMn_2O_5$. The SCO structure is calculated to be more stable than the CCO structure by 133 meV per FU for $YBaFe_2O_5$, and by 50 meV per FU for $YBaCo_2O_5$. All these results are consistent with the experimental observations. The preference for the SCO over the CCO is considerably stronger for $YBaFe_2O_5$ than for $YBaCo_2O_5$ (133 vs 50 meV per FU), although JT-active ions are absent in $YBaFe_2O_5$ but present in $YBaCo_2O_5$. Therefore, the charge order patterns of $YBaM_2O_5$ (M = Mn, Fe, Co) are not determined by whether their transition-metal ions are JT-active or not.

## 5. CONCLUDING REMARKS

In $YBaM_2O_5$ (M = Mn, Fe, Co) the interslab M−O···O−M spin exchanges along the *c*-axis are strongly AFM. This together with the strong AFM intraslab spin exchanges explains why the 3D AFM ordering in $YBaM_2O_5$ (M = Fe, Co) takes place at temperatures well above the room temperature (i.e., $T_N$ = 430 K[4] and 330 K,[5] respectively) and why the ferrimagnetic ordering temperature of $YBaMn_2O_5$ is high (i.e., 167 K).[2] Our calculations show that the observed charge order patterns of $YBaM_2O_5$ (M = Mn, Fe, Co) are not determined by whether or not their transition-metal ions are JT-active.

## ASSOCIATED CONTENT

**Supporting Information.** Further details are given in Tables S1−S3. This material is available free of charge via the Internet at http://pubs.acs.org.

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