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Electronic and magnetic properties of double perovskite $\text{Dy}_2\text{MnCoO}_6$ by first-principles calculation

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Using first-principles calculation, we investigate electronic and magnetic properties of $\text{Dy}_2\text{MnCoO}_6$. A detailed structural optimization has been done and found that the orthorhombic structure with Mn (Co) ions aligning along the longest axis type is the most stable structure. Within the generalized gradient approximation, the spin polarized calculations predict $\text{Dy}_2\text{MnCoO}_6$ to be a half-metallic with ferromagnetic interaction between Mn and Co ions and antiferromagnetic interaction between Dy and Mn/Co ions. We also investigate the effect of Hubbard parameter (U) on the ground state magnetic structure. For all values of Hubbard U parameter the Co ions have nonzero magnetic moment; they do not lie in low-spin state, as in DyCoO_3 . © 2014 AIP Publishing LLC.

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I. INTRODUCTION

In the past several years, there has been considerable interest in developing multifunctional materials in which two or three of the properties, namely, ferromagnetism, ferroelectricity, and ferroelasticity, occur in single phase. The double perovskite with the formula $\text{A}_2\text{BB}'\text{O}_6$ (A is an alkaline rare earth or rare earth element and B and B' are transition metals) have been widely studied due to the diversity in their crystal structure and its potential applications—magneto-resistance,^{1,2} magnetocaloric effect,³ and magnetoelectric effect.⁴⁻⁶

The parent compound of $\text{Dy}_2\text{MnCoO}_6$ (DyMnO_3 and DyCoO_3) were found to be formed in orthorhombic structure ($Pbnm$).⁷ In DyCoO_3 , the Co^{3+} ions are diamagnetic (low spin $t_{2g}^6 e_g^0$, $S=0$) due to the high crystal field and the magnetic ordering temperature of Dy^{3+} is around 3.6 K. The metamagnetism was also observed in DyCoO_3 . In DyMnO_3 , an incommensurate antiferromagnetic ordering of Mn^{3+} ions sets around 39 K, and a second antiferromagnetic ordering of Dy^{3+} occurs at 5 K.⁸ The spontaneous polarization emerges due to spiral (cyclodial) magnetic ordering of Mn^{3+} moments at 18 K.⁹

$\text{DyMn}_{0.5}\text{Co}_{0.5}\text{O}_3$ crystallizes in orthorhombic structure with space group $Pnma$. It shows a spontaneous magnetic ordering around 85 K and also shows a metamagnetic behaviour results from the competition between magnetic anisotropy and exchange interaction under applied magnetic field. The magnetic properties of $\text{DyMn}_{0.5}\text{Co}_{0.5}\text{O}_3$ arise due to the superexchange interaction of $\text{Mn}^{4+}\text{-O-Co}^{2+}$. Around 5 K, the Dy and Mn-Co sublattices are aligned antiferromagnetically.^{10,11} However, no theoretical study has been carried out in order to understand the electronic and magnetic properties of $\text{DyMn}_{0.5}\text{Co}_{0.5}\text{O}_3$. The traditional idea was that the ferromagnetic ground state of the doped compounds, $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$,^{12,13} could be ascribed to $\text{Mn}^{3+}\text{-Mn}^{3+}$ interaction driven by structure transition; Co^{3+} ion has been considered to stay in low spin state ($3d^6$, $S=0$), like LaCoO_3

and DyCoO_3 . With this background, in this report, we try to study the electronic and magnetic properties of the double perovskite $\text{Dy}_2\text{MnCoO}_6$ using first-principles calculation. The calculated structural parameters and magnetic moments are compared with those of experimental results.

II. COMPUTATIONAL DETAILS

The calculations were performed using Cambridge Serial Total Energy Package (CASTEP).¹⁴ In this calculation, the Kohn-Sham wavefunctions of valence electrons are expanded to the basis set of plane waves within cutoff energy 500 eV. The interactions of electrons with ion cores were described by Vanderbilt-type nonlocal ultrasoft pseudopotentials.¹⁵ The exchange-correlation interactions were treated using generalized gradient approximation (GGA) within the scheme due to PBE (Perdew-Burke-Ernzerhof)¹⁶ and also GGA + U method. In the GGA + U method, the effective parameter $U_{\text{eff}} = U - J$ is adopted as an only input parameter, where U and J are Coulomb and exchange parameters, respectively. A Monkhorst-Pack mesh ($4 \times 3 \times 4$) of special points were chosen for sampling over Brillouin zone. Based on the convergence simulation, we chose the maximum convergent tolerant values of 10^{-5} eV, 0.03 eV/Å, and 0.001 Å for the maximum energy, -force, and -displacement, respectively.

III. RESULTS AND DISCUSSION

Structural optimizations and subsequent energy calculations were performed within GGA with ferromagnetic ordering of Mn and Co (with high spin) and possible positional ordering. Three different positional ordering for orthorhombic structure have been calculated:¹⁷ the layer by layer (2Co and 2Mn on the ac plane) (010), the Mn (or Co) aligning on the longest axis (101), and the interlacing in which each Mn (Co) atom surrounded by six nearest Co (Mn) neighbours (111), as shown in Figure 1. While doing geometry optimization by keeping lattice constants as experimental values, it is found that (101) positional ordering structure has lowest total

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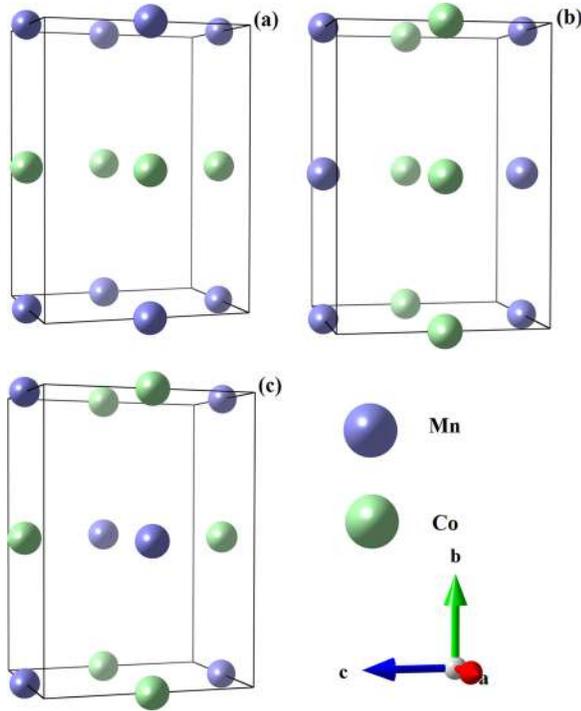


FIG. 1. (a) (010), (b) (101), and (c) (111) oriented Mn and Co layers of $\text{Dy}_2\text{MnCoO}_6$. These orientation is meant for cubic from which orthorhombic can be derived using $a^+b^-a^+$ (Glazer's notation).

energy than that of (010) and (111) by 31.78 meV and 44.42 meV. The optimized structure values for (101) positional ordering is given in Table I. A good agreement between experimental and theoretical values are observed. The ground-state structure possesses the monoclinic symmetry and the space group is $P2_1/m$ with an additional symmetry lowering due to different B cations (Mn and Co).

We calculated the density of states (DOS) with (101) positional ordering (Figure 2(a)) by the GGA method and found that the system possess half-metallic nature, in contrast to the experimentally observed insulating behaviour.¹¹ The failure of the GGA in describing the electronic structure of transition metal oxides is known to be associated with an inadequate description of the strong-correlation effects. The minority up-spin bands (Figure 2(a)) cross the Fermi level while majority down-spin bands exhibits a band gap of ~ 0.656 eV.¹⁷ In the approximate octahedral crystal field, the Mn and Co 3d states are split into upper e_g and lower t_{2g} states. In Figure 2(b), the Mn t_{2g} states (the arrow represents the spin direction) center at ~ -2.17 eV and e_g states at ~ -0.385 eV and also spread through Fermi level, while Co

TABLE I. Calculated positions of atoms in the unit cell and comparison with the experimental data (given in parentheses). The co-ordinates (Wyckoff positions) presented for comparison between calculated and real structures are in the $Pnma$ space group.

	x	y	z	Occupancy
Dy	0.0674 (0.0703)	0.25 (0.25)	0.9865 (0.9852)	1
Mn/Co	0(0)	0(0)	0.4998 (0.5)	0.5/0.5
O ₁	0.4694 (0.4662)	0.2499(0.25)	0.1014 (0.1006)	1
O ₂	0.3014 (0.2982)	0.0492 (0.0529)	0.6930 (0.6917)	1

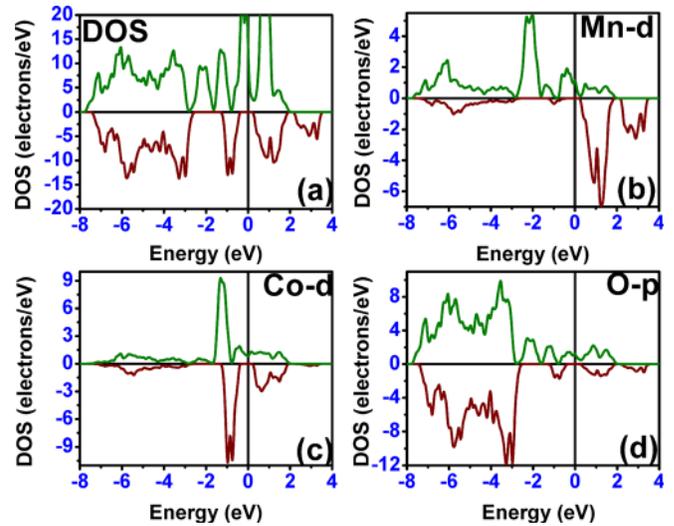


FIG. 2. Calculated (a) total DOS, Partial DOS of (b) Mn d, (c) Co d and (d) O p orbitals (minority spin states are shown as positive) using GGA method.

t_{2g} states center at ~ -1.26 eV and e_g states at ~ -0.4603 eV and also spread through Fermi level, as shown in Figure 2(c). The more dispersion of the e_g states of Mn and Co is due to larger overlap between e_g and O 2p states in comparison with that between t_{2g} and O 2p states (Figures 2(b)–2(d)). In $\text{Dy}_2\text{MnCoO}_6$, Mn e_g states partly overlap with empty Co e_g (Figures 2(b) and 2(c)), which induces the occupied Mn e_g to fill the empty Co e_g . This charge compensation mechanism brings the non Jahn-Teller active Mn^{4+} and Co^{2+} ions. A similar kind of mixed and variable valences has been experimentally found in $\text{La}_2\text{MnCoO}_6$.¹⁸

However, to the best of our knowledge, no detailed X-ray photoelectron spectroscopic (XPS) studies has been reported on $\text{Dy}_2\text{MnCoO}_6$ to identify the spin state of Mn and Co ions. One need to do XPS studies to understand the spin states of Mn and Co ions.

The magnetic moment of Mn, Co, and Dy ions are $\sim -3.66 \mu_B$, $\sim -0.54 \mu_B$, and $\sim 5.15 \mu_B$, respectively. Here, Co^{3+} do not lie in the low spin state ($t_{2g}^6 e_g^0$, $S = 0$),¹² they do have small magnetic moments much lesser than Mn ions, due to overlap of Co 3d and O 2p states (Figures 2(c) and 2(d)). The magnetic moment of O ion is $\sim \pm 0.02 \mu_B$, arises due to strong hybridization of Mn (Co) 3d-O 2p states and Dy 4f-O 2p states. From the values of the magnetic moments of Dy, Mn, and Co, one can conclude that Mn and Co ions are coupled ferromagnetically whereas the Dy ions interacts antiferromagnetically with Mn/Co sublattices and it is also experimentally observed.¹¹ A similar kind of behaviour has been experimentally observed in $\text{TbMn}_{0.5}\text{Co}_{0.5}\text{O}_{3.06}$ ¹⁹ and $\text{HoMn}_{0.5}\text{Co}_{0.5}\text{O}_3$.²⁰

The spin density of $\text{Dy}_2\text{MnCoO}_6$ is shown in Figure 3(a). The spin density illustrates graphically the difference between the up and down spin density. The spin density of Dy ions is antiparallel to that of Mn/Co ions, as shown in Figure 3(a). The antiferromagnetic interaction between Dy and Mn/Co sublattice can be ascribed to the exchange interaction between Dy 4f and Mn/Co 3d electrons, which are mediated by O 2p states. Figure 3(b) shows the spin density of Mn have quite spherical spin magnetic density due to its half filled e_g states ($t_{2g}^3 e_g^1$). The Co ions has star shaped spin magnetic density

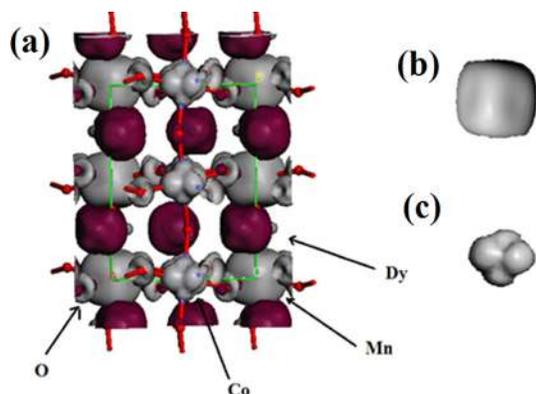


FIG. 3. Isosurfaces of the spin density of (a) $\text{Dy}_2\text{MnCoO}_6$ (isovalues ± 0.02 have been used); different colours correspond to the positive (violet) and negative (gray) values of the spin density, (b) isosurface of the spin density of Mn ions, and (c) isosurface of the spin density of Co ions.

owing to completely occupied t_{2g} states and spin polarized two e_g states, as shown in Figure 3(c).²¹ The O ions have both positive and negative isosurfaces of spin density, as shown in Figure 3(a), due to hybridization of O 2p states with 3d states of Mn/Co ions and 4f states of Dy.

In order to ensure the half-metallic nature and effect of the U_{eff} , we also perform the calculations by GGA + U method with $U_{\text{eff}} = U - J = 5$ eV for 4f states of Dy and 1 eV and 2 eV for 3d states of Mn and Co ions. Figures 4(a) and 4(b) show the DOS of $\text{Dy}_2\text{MnCoO}_6$ for $U = 1$ eV and 2 eV. Both figures confirm the half-metallic nature of $\text{Dy}_2\text{MnCoO}_6$. From Figures 4(a) and 4(b), it is seen that the orbital separation due to crystal field splitting of Mn/Co increases with increasing U_{eff} . When the value U_{eff} reaches 2 eV for Mn/Co ions and 5 eV for Dy ions, the magnetic moment of Mn and Co ions is $\sim -3.88 \mu_B$ and $\sim -0.40 \mu_B$ due to the suppressive effect of the U_{eff} on the presence of $\text{Mn}^{4+}\text{-Co}^{2+}$ ions and the band gap of the spin down states increases to 1.503 eV.

In real system, owing to random distribution of B-site cations (Mn and Co), one may expect a reduction of down-spin band gap with the assemblage of the same type

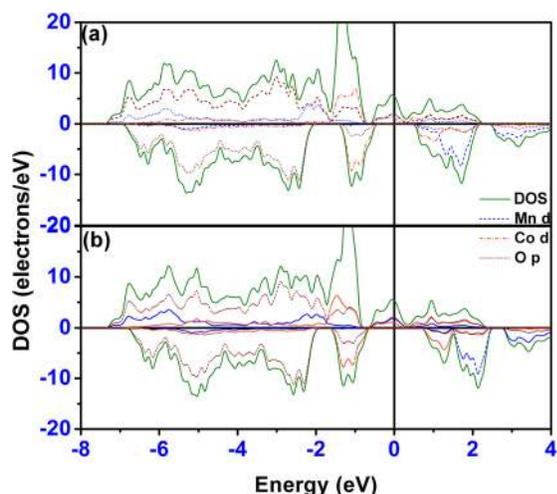


FIG. 4. Calculated total DOS and partial DOS of Mn, Co d, and O p orbitals (minority spin states are shown as positive) for $U_{\text{eff}} = 5$ eV for Dy, (a) $U_{\text{eff}} = 1$ eV for Mn/Co and (b) $U_{\text{eff}} = 2$ eV for Mn/Co.

transition metal or even destroy the band gap with an introduction of critical level of disorder. It should be mentioned that these calculations are indeed ordered calculations using the translational symmetry of the unit cell, but it is not in the case of a real disordered material. Since the unit cell contains 20 atoms, it is a small number for studying disorder materials and our probe is limited. Moreover, if a system experimentally approaches a chemically phase-separated scenario with a region having only Mn ions spatially separated from the region with only Co ions, such situations cannot be described within the present calculations. We have probed the limit where the disorder is still microscopic and does not lead to a larger length-scale phase separation.

IV. CONCLUSIONS

We have investigated electronic and magnetic properties of double perovskite $\text{Dy}_2\text{MnCoO}_6$ using first-principles calculation. The structural optimization has been done, and it is found that among three doping types for the orthorhombic structure, with the Mn (Co) ions aligning along the longest axis type is the most stable structure. Our results show that the ground state is half-metallic with Mn and Co ions interact ferromagnetically whereas Dy and Mn/Co ions interact antiferromagnetically. The band structure could be adjusted by introducing U_{eff} without altering electronic and magnetic characters. The Co ions of $\text{Dy}_2\text{MnCoO}_6$ are found to have magnetic moment in our calculations.

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