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Abstract. Magnetic property transition is essential for α-MnO₂, since ferromagnets have potential applications compared to antiferromagnets. Herein, the role of various substituents in the anion site (F, N) and cation site (Fe, Cr) on α-MnO₂·0.25H₂O is studied using first principle density functional theory calculations. From our calculations, we have shown that cation (Fe and Cr) substitutions are capable of tuning the antiferromagnetic ground state into ferromagnetic state than anion (F and N) substitutions. These results provide key ideas which are an indispensable need for multifunctional usage of this material.

INTRODUCTION

Among various polymorphs of manganese dioxide, α-MnO₂ is an interesting material since it possess tunnel cavity, which provides way to tune the physical and chemical properties by means of altering the concentration of chemical species present inside the cavity. The intrinsic magnetic ground state of α-MnO₂ is antiferromagnetic (AFM) - C2 type¹. It is reported that the magnetic property of this material is altered from AFM to a spin glass state by varying the concentration of K⁺ ions in the tunnel². The Mn vacancies known as Ruetschi defects³ and oxygen vacancies are the dominant point defects in this system. These defects are difficult to control during synthesize and it has a strong impact over its magnetic property. This study deals about the magnetic state transition upon the substitution of elements such as F, N, Fe and Cr on α-MnO₂.

COMPUTATIONAL DETAILS

We have studied α-MnO₂·0.25H₂O to understand its structural, electronic and magnetic properties using first principles density functional theory calculations as implemented in VASP⁴. In our calculations, projector augmented wave (PAW) pseudopotentials were used to represent the electron-ion interaction⁷ and Coulomb correlation corrected generalized gradient approximations (GGA+U) was employed to account the exchange-correlation energy⁶. The exchange energy (J) and on site cumbic interaction (U) terms used were 4.5 eV and 0.75 eV, respectively⁷. The ions relaxation was carried out using conjugate gradient algorithm for force minimization until the force on each ion reaches value lesser than 0.01eV/Å and the convergence criteria of 10⁻⁵ eV was set for electronic minimization. The spin polarized calculations were performed with FM (ferromagnetic) and AFM-C2 ordering. Brillouin zone (BZ) was sampled by 4 × 4 × 12 Monkhorst-Pack k-points along with the Gaussian smearing of 0.1 eV.
RESULTS AND DISCUSSION

\(\alpha\)-MnO\(_2\) has tetragonal crystal structure and belongs to space group 14/m, no.87, with lattice parameters of \(a = b = 9.77\ \text{Å}\) and \(c = 2.84\ \text{Å}\). It has eight formula units of MnO\(_2\) in the unit cell as shown in Fig. 1(a). In the structural framework, edge shared MnO\(_6\) octahedra lead to double chain along \(ab\) plane, and they share their corners to form tunnel structure along \(c\)-axis, with an area of 4.9x2.9 \(\text{Å}^2\), that facilitates the occupation of water molecules in the tunnel. The MnO\(_6\) octahedra are slightly distorted and the Mn-O bond distances differ in the range of 1.88 – 1.92 \(\text{Å}\) and along double chain, the Mn-Mn bond distance is shorter \((= 2.89\ \text{Å})\), while in corner shared octahedra region it is of longer distance with the value of 3.41 \(\text{Å}\). Moreover, there are two ways in which the Mn-O-Mn atoms are arranged, one is with the angle of 97° at the site in which Mn-Mn distance is short (2.88 \(\text{Å}\)) and the other is at long Mn-Mn (3.43 \(\text{Å}\)) distance where it is of 131°. Further, this system can be magnetically frustrated owing to their triangular lattice formation along \(c\)-axis by Mn atoms as shown in Fig.1(b). From our previous study\(^8\) we predicted that \(\alpha\)-MnO\(_2\).0.25 H\(_2\)O is an energetically feasible stoichiometry, as compared to others (\(\alpha\)-MnO\(_2\).\(x\) H\(_2\)O, \(x = 0, 0.125, 0.375\)). Our calculated lattice parameters match the experimental values\(^6\) within the error limit of 1%. The magnetic ground state of \(\alpha\)-MnO\(_2\) is found out to be AFM-C2 type\(^6\) and it is in agreement with the experiments as well as other theoretical results\(^1,10\). The energy difference between AFM-C2 and FM state is proportional to the exchange coupling constant which reveals the ground state magnetic ordering in the material. Those values are used to compare the strength of the creation of FM ordering in \(\alpha\)-MnO\(_2\).0.25H\(_2\)O when substituted with the elements such as Cr, Fe, N, and F with composition of 6.25% and is shown in Fig.2.

![Figure 1](https://example.com/figure1.png)

**FIGURE 1.** (a) Ball and stick models of \(\alpha\)-Mn2O\(_5\) in AFM-C2 type magnetic alignment, (b) triangular lattice arrangement of Mn atoms along \(c\)-axis. The blue, pink, white coloured pipes/balls represent Mn, O and H atoms, respectively. The red up and green down arrows represent the up and down spins, respectively.

To understand the role of anion on inducing FM in this material, anion such as F or N are substituted instead of O either at corner or edge site. The F substitution at corner sharing site (AFM-C2) is energetically more favourable than edge sharing substitution by75 meV/cell. The F substituted at the corner sharing site was found to be in the oxidation state of -1 and it is confirmed by the increase in the magnetic moment of nearby Mnto \(-3.7\) (Mn\(^{3+}\)) from \(-2.8\ \mu\text{B}\) (Mn\(^{4+}\)). The bond distances of F atom from Mn are 1.99 (Mn(1)-F) and 1.94 (Mn(2)-F) \(\text{Å}\). The shortest Mn-Mn (hereafter denoted as \(S_{M-M}\)) distance becomes 2.84 from 2.88 \(\text{Å}\), and the longest Mn-Mn (hereafter denoted as \(L_{M-M}\)) distance becomes 3.71 from 3.43 \(\text{Å}\) upon fluorine substitution at the corner sharing site. It resulted in the compression of \(S_{M-M}\) distance by 1.12%, but the \(L_{M-M}\) distance is elongated by about 8.40%. Except the substituted site, other \(L_{M-M}\) distance is 3.4 \(\text{Å}\). These bond length values confirm that there is a short range FM effect near substituted site due to strain effect but as an aggregate, it results in weak AFM compared to the pure material as shown in Fig. 2.

The N substitution at edge sharing site (AFM-C2) is more energetically favorable than corner sharing site by22.14 eV/cell. The substitution of nitrogen atom at edge sharing site for oxygen results N\(^3\) ions and is predicted by the change in the magnetic moment of nearby Mnto 2.1 (Mn\(^{3+}\)) from 2.8 \(\mu\text{B}\) (Mn\(^{4+}\)). In this case, not only the moment of Mn closer to N, but also other Mn moments are decreased to 2.4 (average) from 2.8 (average) \(\mu\text{B}\) indicating that these Mn atoms are well hybridized with oxygen atoms than pure and F substitution case. The calculated equilibrium bond distances for Mn(2)-N and Mn(3)-N are 1.87 and 1.85 \(\text{Å}\) respectively. Due to N substitution at O site, the Mn–Mn distance at edge sharing site becomes 2.87 from 2.88 \(\text{Å}\) and the Mn-Mn distance at corner sharing octahedra is 3.40 from 3.43 \(\text{Å}\). Thus there is a compression of \(S_{M-M}\) distance by 0.35% and \(L_{M-M}\) distance by 0.87% due to N substitution. Even though there is no significant strain effect, the major contribution to strong AFM ordering is originating from the
strong hybridization between Mn and O atoms. Thus the anion site substitutions in α-MnO$_2$·0.25H$_2$O do not favour FM ordering effectively.

To identify the role of cation substitution on inducing FM in this material, we substituted cations such as Cr or Fe instead of Mn in the structure. The magnetic moments at the Cr and Fe sites after substituted to the Mn site in α-MnO$_2$·0.25H$_2$O are 2.11 and 1.92 μ$_B$ respectively, which indicates that both Fe and Cr are in low spin configuration with +4 oxidation state after the substitution. The substitution results in the increase of shortest Mn-metal (Mn-Cr) distance to 2.90 Å and decrease of shortest Mn-metal distance (Mn-Fe) distance to 2.86 Å respectively, and are increases by 0.29% and decreases by 0.87% than un-substituted compound respectively. The calculated total DOS in Fig3(a) shows the semiconducting nature of Fe substituted α-MnO$_2$·0.25H$_2$O in FM configuration and the Fe-3d impurity states are raised near the Fermi level (E$_F$) indicating that more electrons are introduced into the material and is hybridized with O-2p states. The electron mediated semi-covalent exchange from d$^6$(Fe$^{4+}$) to d$^3$(Mn$^{4+}$) is the possible local superexchange mechanism between those atoms.

![FIGURE 2.](image)

To identify the role of cation substitution on inducing FM in this material, we substituted cations such as Cr or Fe instead of Mn in the structure. The magnetic moments at the Cr and Fe sites after substituted to the Mn site in α-MnO$_2$·0.25H$_2$O are 2.11 and 1.92 μ$_B$ respectively, which indicates that both Fe and Cr are in low spin configuration with +4 oxidation state after the substitution. The substitution results in the increase of shortest Mn-metal (Mn-Cr) distance to 2.90 Å and decrease of shortest Mn-metal distance (Mn-Fe) distance to 2.86 Å respectively, and are increases by 0.29% and decreases by 0.87% than un-substituted compound respectively. The calculated total DOS in Fig3(a) shows the semiconducting nature of Fe substituted α-MnO$_2$·0.25H$_2$O in FM configuration and the Fe-3d impurity states are raised near the Fermi level (E$_F$) indicating that more electrons are introduced into the material and is hybridized with O-2p states. The electron mediated semi-covalent exchange from d$^6$(Fe$^{4+}$) to d$^3$(Mn$^{4+}$) is the possible local superexchange mechanism between those atoms.

![FIGURE 3.](image)

Figure 3(b) shows the electronic structure of Cr substituted α-MnO$_2$·0.25H$_2$O in FM configuration which depicts the metallic nature of the compound due to the splitting of O-2p states at the Fermi level. The electronic states of transition metals are positioned deeper from E$_F$ compared to above case, implies that the Cr substitution introduces hole to the material. The possible superexchange mechanism in this case may be the hole mediated semicovalent exchange which leads to the delocalization of extra electron from d$^3$(Mn$^{4+}$) to d$^2$(Cr$^{4+}$). The above results clearly indicate that the cation substitutions lead the material to attain prominent FM nature more effectively than anion substitutions.
CONCLUSIONS

The effect of elemental substitution on the magnetic property of hydrated $\alpha$-MnO$_2$ is systematically studied by using the first principles density functional calculations. From our calculations, it is found that Fe, Cr substitutions on $\alpha$-MnO$_2$0.25H$_2$O results in weak FM ordering. But F substitution does not significantly alter the AFM property indicating that the effect of thus formed mixed charge state and strain in the lattice nearby the substitution site is feeble to influence the magnetic property. Furthermore N substitution instead of O in the lattice makes the compound more AFM and is due to increase in hybridization strength between Mn and O atoms. Therefore it is concluded that the cation site substitutions make the material to be ordered ferromagnetically when compared to the anion site substitutions and is due to the localization of electrons via semicovalent exchange interaction between the metal atoms.

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