Electronic Structure of LiMnO$_2$: A Comparative Study of the LSDA and LSDA+U methods

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Abstract

A first-principles electronic structure study of orthorhombic, monoclinic and rhombohedral LiMnO$_2$ has been carried out using the full-potential linearized augmented plane-wave method. The exchange and correlations have been treated within the local spin-density approximation (LSDA) and the LSDA+U methods. In the LSDA, the stable ground state is antiferromagnetic insulator for the orthorhombic and monoclinic structures but is ferromagnetic metal for the rhombohedral structure. The LSDA+U, on the other hand, predicts the ground state to be an antiferromagnetic insulator for all structures. We find that strong correlations change the density of states dramatically around the Fermi level. The LSDA+U predicts the nature of band gap to be a mixture of charge transfer and Mn $d \leftrightarrow d$ like excitations for orthorhombic and monoclinic LiMnO$_2$ and Mott-insulator for rhombohedral LiMnO$_2$ in agreement with the available experimental results. The inclusion of U increases the magnetic moment on Mn and gives a value in better agreement with experiment. However, Mn valency is not affected by the inclusion of U. We have also calculated X-ray emission photoelectron spectra for the orthorhombic and monoclinic LiMnO$_2$ by the LSDA and the LSDA+U methods. We find that LSDA+U gives better agreement with the available experimental results.

Key words: A. Layered transition metal oxides; D. Electronic structure; D. Magnetic structure

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1 Introduction

Transition metal oxides are interesting systems which exhibit phenomena such as metal-insulator transition, magnetic phase transition and charge-ordering etc [1,2,3]. The electronic structure description of transition metal oxides (TMO), which are strongly correlated systems, is very important and has been a subject of many ab-initio calculations on TMO [4,5,6]. These studies are mostly based on the local spin density approximation (LSDA) [7,8] and generalized gradient approximation (GGA) [9]. However, the LSDA and GGA fail in predicting many aspects of the electronic structure since the strong correlations between d electrons play an important role. Thus inclusion of strong correlations in the electronic structure calculations of TMO has been a challenging problem.

TMO are not only interesting from the basic physics point of view but have a great potential for technological applications. In particular, the layered LiMnO$_2$ has attracted a lot of attention during the last decade because of its potential use in rechargeable batteries [10,11,12]. LiMnO$_2$ in layered monoclinic structure was first synthesized by Armstrong et al. [11], which triggered a lot of experimental and theoretical activities on this system. Detailed study on the structural stability of LiMnO$_2$ was carried out by Mishra and Ceder [13]. They studied the effect of spin-polarization and magnetic ordering on the relative stability of various structures using the density functional theory (DFT) in the LSDA [7,8] and GGA [9]. The LSDA calculation gives metallic ferromagnetic (FM) ground state for the rhombohedral LiMnO$_2$ but the GGA calculation predicts antiferromagnetic (AFM) ground state. Terakura et al. [4] showed that the LSDA predicts metallic ground state for many transition metal oxides whereas experimentally these oxides are found to be insulators. They also showed that when AFM ordering is included in the LSDA calculations, the band gap can open up although it turns out to be smaller than the experimental gap [5]. However, the LSDA calculation performed by Galakhov et al. [14] on orthorhombic LiMnO$_2$ shows metallic AFM ground state. Also the magnetic moment on Mn was found to be smaller than the experimental work [15].

LiMnO$_2$ can exist in various phases such as orthorhombic, monoclinic, spinel etc., the ground state structure being orthorhombic (Pmmn) [16,15]. The favourable structure for rechargeable batteries is the layered rhombohedral (R3m). But Mn$^{3+}$ is a Jahn-Teller active ion in a rhombohedral environment and gives rise to a cooperative monoclinic distortion and as a result the rhombohedral phase is not stable. Doping of some elements such as Co can stabilize the rhombohedral structure which has been studied by Prasad et al. [17,18] using the GGA. But they found the stability of structure at about 32% [19] doping of Co which is very high as compared to the experimental value of
10% [20]. This can be attributed partially to the approximate treatment of correlation effects in the GGA.

As discussed above, several studies [13,14,17,18,19] indicate that neither the LSDA nor the GGA describes the electronic structure of LiMnO$_2$ satisfactorily. Thus for a better description of the electronic structure of this material the electron correlations between d-electrons must be included. The LSDA+U method [21,22] provides a simple way of incorporating correlations beyond the LSDA and GGA by introducing orbital dependent potential. The advantage of the LSDA+U method is the ability to treat simultaneously delocalized conduction band electrons and localized ‘d’ or ‘f’ electrons within the same computational scheme. The LSDA+U improves the electron-energy-loss spectra and parameters characterizing the structural stability of NiO [23,21] compared to the LSDA. Recent studies by the LSDA+U on some other oxides show the improvement over the LSDA results [6,24,25,26].

The aim of this paper is to study the effect of electron correlations on the ground state electronic structure properties and magnetic properties of LiMnO$_2$ using the LSDA+U method [21,22]. We hope that this calculation will be able to give correct ground state structure for various phases of LiMnO$_2$ and will provide starting point for future calculation with dopants. The electronic structure calculations have been done using the full-potential linearized augmented plane-wave (FLAPW) method [27]. We consider only orthorhombic, monoclinic and rhombohedral LiMnO$_2$. Since the value of U is not known for LiMnO$_2$ and there is no unique way of finding the value of U, we adopt the following procedure. We start our calculation for the orthorhombic structure with the value of U for MnO as given in the literature [28]. We then repeat the calculations using different values of U for orthorhombic, monoclinic, rhombohedral structures. The trends are similar with different values of U for orthorhombic, monoclinic and rhombohedral structures. Our LSDA+U results show that the ground state of rhombohedral LiMnO$_2$ is an AFM insulator although the LSDA shows it to be a FM metal. The band gap and magnetic moment of Mn increase in the LSDA+U as compared to the LSDA. The calculation of band structure and density of states (DOS) shows that the strongly correlated effects dominate over the crystal field effects. We have also calculated X-ray emission spectra (XES) [29,30] using the LSDA as well as the LSDA+U for the orthorhombic and monoclinic structures. The LSDA+U results at U=8.0 eV are closer to the experimental results.

The organization of paper is as follows. In Sec. II we provide computational details of the present work. In Sec. III we present our results and discuss them. Finally, we give our conclusions in Sec. IV.
2 Computational details

2.1 Method

The LSDA and LSDA+U methods have been discussed in great details in Ref. [7,8,21,22] and will not be discussed again. Here we give only the relevant computational details. We have used the full-potential linearized augmented plane-wave (FLAPW) method [27] in a scalar relativistic version without the spin-orbit coupling. The exchange and correlation potential has been included within the LSDA of the density functional theory [7,8]. To treat strong correlations, the localization of the \(d\)-states has been corrected by means of the LSDA+U method [21,22] which is the LSDA with an on-site Coulomb potential for the \(d\)-states. The double-counting term, which is already included in the LSDA, has been subtracted as given in Eq. (4) of Ref.[22]. For the LSDA+U calculations as described in Ref. [21,22], we need to know the Hubbard parameter \(U\) and the screened exchange energy \(J\) which is almost a constant about 1 eV [31]. We started our calculations for all \(\text{LiMnO}_2\) structures with the value of \(U=6.9\) eV and \(J=0.82\) eV for MnO as given in literature [28] and then repeated the calculations at different values of \(U\) without changing \(J\). The XES spectra were calculated using the formalism of Neckel et al. [29,30]. According to this method, K- and L-spectrum intensities of an atom \(A\) have the following proportionality

\[
I_K(E) \propto \frac{1}{3} E^3 M_A^2(p, 1s, \epsilon) \rho_p^A(\epsilon)
\]

\[
I_L(E) \propto E^3 (M_A^2(s, 2p, \epsilon) \rho_p^A(\epsilon) + \frac{2}{3} M_A^2(d, 2p, \epsilon) \rho_d^A(\epsilon))
\]

where \(E = \epsilon - \epsilon_{\text{core}}\) is the energy of the emitted x-ray with \(\epsilon\) and \(\epsilon_{\text{core}}\) being the energies for valence and core electrons respectively. \(\rho_l^A(\epsilon)\) is the \(l\)-component of the local (inside the atomic sphere \(A\)) DOS and \(M_A^2\) is the radial transition probability. The calculated spectra include broadening for the spectrometer and lifetime broadening for core and valence states. For Mn spectrum, we have used 0.9 eV and 0.75 eV broadening for core and valence lifetime and 0.5 eV for spectrometer while these parameter for O spectrum are 0.4 eV, 0.65 eV and 0.2 eV. The integration over the Brillouin zone in the self-consistency cycle is performed using 64, 100, and 113 k-points in irreducible Brillouin zone for the orthorhombic, rhombohedral and monoclinic \(\text{LiMnO}_2\) structures respectively. An improved tetrahedron method has been used for the Brillouin-zone integration [32]. The maximum \(l\) value in the radial sphere expansion is \(l_{\text{max}} = 10\), and the largest \(l\) value for the non-spherical part of the Hamiltonian matrix is \(l_{\text{max, ns}} = 4\). The cutoff parameters are \(R_{\text{mt}} K_{\text{max}} = 7\) for the plane wave and \(R_{\text{mt}} G_{\text{max}} = 14\) for the charge density. The number of plane waves
ranges from 11510 to 20853, depending on the structure of LiMnO₂.

2.2 Structure

The calculations are performed for orthorhombic, monoclinic and rhombohedral structures with space group Pnmm, C2/m and R3m respectively. The experimental lattice parameters are available for orthorhombic and monoclinic structures. Therefore, we have used experimental lattice constants for the orthorhombic [16] and monoclinic [11] structures. The rhombohedral structure is not a stable structure and its experimental lattice constants are not available. Therefore, the optimized lattice constants are used for the rhombohedral structure as given by Mishra and Ceder [13]. For the AFM and FM calculations, we construct a supercell of 16 atoms for the orthorhombic LiMnO₂. The AFM ordering is given in Fig. 1 for the orthorhombic structure. To get the supercell, we double the unit-cell of 8 atoms in the x-direction and arrange Mn atoms in AFM ordering along the x-direction and in FM ordering along the y-direction in both planes (z=0.4 and z=0.6). We have also checked our calculation using a bigger supercell of 32 atoms but the band gap and magnetic moments do not change significantly. On the other hand, the computational time increases drastically with increasing number of atoms in supercell. Thus we have chosen a supercell of 16 atoms for our calculations while 8 atoms cell have been used in Ref.[14]. For the monoclinic and rhombohedral structures the AF3 ordering has been used for the AFM case as suggested by Singh [33]. We have followed the construction of AFM structures as given by Prasad et al. [18] for the monoclinic and rhombohedral structures.

3 Results and Discussion

We have calculated the total energy for spin-polarized and non-spin-polarized configurations of the orthorhombic, monoclinic and rhombohedral LiMnO₂ structures using the LSDA and LSDA+U methods. In all cases we find that the non-spin-polarized configuration has higher energy than the spin-polarized configurations. Therefore, in the following, we shall discuss our results for only spin-polarized configurations for various structures. We will discuss the effect of different U values on electronic structure, magnetic moments and band gaps of these structures.
3.1 Electronic Structure

3.1.1 Orthorhombic LiMnO$_2$

The calculations have been done using the FM and AFM ordering of Mn in the orthorhombic structure. The AFM configuration has lower energy in both the LSDA and the LSDA+U calculations. As the value of $U$ is not known, we begin with $U=6.9$ eV, which is the value for MnO as given in the literature [28] and then repeat the calculations for different values of $U$.

Fig. 2 shows the calculated total and partial DOS for Mn and oxygen in the AFM configuration by the LSDA and the LSDA+U methods (for $U=8.0$ eV). The O-2p DOS is shown for the oxygen at two different planes of 2b site (O1 at $z=0.13$ and O2 at $z=0.60$). We shall first discuss the LSDA DOS which is shown in the panel (a). We see that the total DOS (top curve in left) in the occupied region near $E_F$ (0.0 to -3.0 eV) has a large contribution from Mn-d states as is evident from the partial DOS of Mn-d and O-2p states. The O-2p DOS mainly contributes in energy range -7.0 eV to -3.0 eV. The partial DOS of O-2p states at two different sites shows slight difference because the Mn-O bond lengths are different for these sites. We note that the crystal field splits Mn d-t$_{2g}$ and d-$e_g$ DOS giving rise to a band gap of 0.30 eV. This is in contrast to the result obtained by Galakhov etal. [14] using LMTO-ASA method [34] which shows the ground state to be a metallic AFM. This difference can be attributed to the difference in magnetic ordering, lattice parameter and atomic positions as well as the FLAPW method which treats potentials more accurately than the ASA. We have taken the AFM ordering along $\mathbf{a}$ direction while it is along $\mathbf{b}$ direction in Ref. [14]. The magnetic ordering also affects the magnetic moment of Mn [33] which is higher in the work of Galakhov etal. (3.45 $\mu_B$) [14] as compared to our results (3.29 $\mu_B$).

In the AFM ordering, the magnetic moment on Mn is 3.29 $\mu_B$ and each O sphere also gets polarized with a moment 0.05 $\mu_B$, while in FM ordering, the Mn has moment 3.43 $\mu_B$. The magnetic moment of Mn in the AFM state is smaller than the experimental value [15] of 3.69 $\mu_B$.

Now we discuss the LSDA+U results which are shown in panel (b) of Fig. 2. We see that the DOS in the occupied region from -3.0 eV to 0.0 eV has a large contribution from O-2p states and a small contribution from Mn-d states which is in sharp contrast to the LSDA result. This is due to the added electron-electron repulsion $U$, which pushes the minority bands up in energy by roughly $U/2$, and pushes the majority Mn-d bands down by roughly $U/2$. Thus the peaks in Mn d-t$_{2g}$ and d-$e_g$ DOS (majority bands) are shifted below $E_F$ by $\sim$4.0 eV. Because of these shifts the O-2p DOS increases near $E_F$ as shown in the lower panels of Fig.2 (b) and is comparable to Mn d-$e_g$ DOS (second panel of Fig. 2(b)) near $E_F$. Thus the band gap is created between O-
2p band and upper Mn-d band as well as between Mn d-d bands. The opening of the gap between O-2p and Mn-d bands is a signature of a charge-transfer insulator [2]. The shift in occupied majority spin Mn-d bands changes the band gap from Mn-d band splitting (crystal field effect) to a charge-transfer type O-2p and Mn-d gap with some contribution of Mn d-d like excitations. Thus the LSDA+U predicts it to be a mixture of charge-transfer and Mn d→d excitations like insulator in contrast to the LSDA, which predicts it to be a band insulator. Thus the inclusion of U qualitatively changes the electronic spectrum. The LSDA+U prediction is in agreement with experimental result [14] which shows the top of valence band in LiMnO₂ to be dominated by O-2p states. We also note that the band gap (1.95 eV) in the LSDA+U calculation is much larger than that in the LSDA calculation (0.30 eV). Thus we find that the strong correlation effects dominate over the crystal field effects.

The magnetic moments of Mn for AFM case is given in Table I. The U=0.0 eV value corresponds to the LSDA results. It is clear from Table I that Mn magnetic moment increases with increasing value of U and the experimental moment of Mn in AFM configuration is obtained at U=8.0 eV which is 3.69 \( \mu_B \) compared to 3.29 \( \mu_B \) without U. This shows that inclusion of U is important in these systems. Mn magnetic moment also increases in FM configuration from the LSDA value of 3.43 \( \mu_B \) to a value 3.71 \( \mu_B \) at U=8.0 eV. This is because in the LSDA+U, the electron occupation decreases in minority Mn-d states and increases in majority Mn-d states (see Table II).

We have also calculated the difference in total energy per unit cell between the AFM and FM ordering as a function of U. The difference between the energies of FM and AFM ordering decreases as we increase the value of U. We find that the magnetic ground state is not affected by the choice of U value and remains antiferromagnetic for all values of U (see Table III). At U=8.0 eV, the AFM configuration has an energy 0.05 eV per formula unit-cell below the FM configuration while this energy difference is 0.30 eV in the LSDA (U=0.0 eV). We have also calculated the band gap as a function of U and found that it too increases with increasing value of U.

### 3.1.2 Monoclinic LiMnO₂

Next we discuss the results for the monoclinic structure in FM and AF3 configurations. We have carried out calculations at different values of U similar to the orthorhombic case. The LSDA as well as LSDA+U, predict insulating state for both the magnetic orderings in monoclinic structure. The AF3 configuration has lower energy compared to the FM configuration in both the LSDA and the LSDA+U calculations. In Fig. 3, we show the calculated DOS for the AF3 ordering. Panel (a) shows the LSDA total DOS and the partial DOS for Mn d-\( t_{2g} \), d-\( e_g \) and O-2p states. As in the orthorhombic case (and
also rhombohedral case) Mn-d band splits in d-t_{2g} and d-e_g bands but there is further splitting of t_{2g} and e_g bands due to the cooperative Jahn-Teller distortion. The band gap arises due to this band splitting which is 0.61 eV. Note that without the Jahn-Teller splitting the system would be a metal as in the rhombohedral case (see next section). Mn-d bands contribute to the top of valence band (in energy range 0.0 eV to -3.0 eV) with a small contribution from O-2p bands, similar to the LSDA results of the orthorhombic case. The magnetic moment (see Table I) on Mn sphere is 3.29 \( \mu_B \) in the AF3 configuration and each O also get polarized with a moment 0.05 \( \mu_B \). In the FM ordering, the band gap is 0.17 eV and the magnetic moment on Mn and O are 3.42 \( \mu_B \) and 0.13 \( \mu_B \) respectively. We find good agreement between our LSDA results and the results reported by Singh [33].

We show the LSDA+U DOS (for U=8.0 eV) in panel (b) of Fig. 3. The occupied Mn-d bands are shifted towards lower energy (-4.0 eV to -7.0 eV) while the unoccupied Mn-d bands are shifted up in energy because of added electron-electron repulsion U. This increases the band gap by 1.19 eV. We see that the O-2p DOS increases around \( E_F \) in energy range 0.0 eV to -3.0 eV. Hence, the top of O-2p bands and the Mn-d bands merge, and so there is no high intensity peak structure in the total DOS in energy range 0.0 eV to -3.0 eV as seen in the LSDA. We note that the Mn d-t_{2g} and O-2p DOS have sharp peaks close to \( E_F \) and hence Mn-d states and O-2p states contribute significantly to the top of the valence band. Thus similar to the orthorhombic case, monoclinic LiMnO\(_2\) is also a mixture of charge-transfer type and Mn d\( \leftrightarrow \)d excitations like insulator. The band gap changes to 1.80 eV in presence of U while it is 0.61 eV in the LSDA. Thus we find that the electron-correlation effects tend to wash out distinct crystal field effects similar to the orthorhombic case.

Table I shows the magnetic moments and band gaps for different values of U for AF3 ordering. Mn magnetic moment increases to 3.79 \( \mu_B \) at U=8.0 eV. Mn magnetic moment increases with U in the case of FM ordering also which is 3.67 \( \mu_B \) at U=8.0 eV. This increase in Mn magnetic moment is similar to orthorhombic case. The AF3 configuration has lower energy by an amount 0.61 eV per formula unit compared to the FM configuration in LSDA and 0.17 eV per formula unit in LSDA+U (see Table III).

3.1.3 Rhombohedral LiMnO\(_2\)

In this section, we present results for the rhombohedral case in FM and AF3 configurations. Although this structure is unstable, it can be stabilized by doping with Co, Mg etc. [17,18]. Thus it would be interesting to see the effect of strong correlations on the electronic structure of rhombohedral LiMnO\(_2\) and compare with the earlier work [13]. Similar to the orthorhombic case, we have
used different values of \( U \) and fixed value of \( J \) for the LSDA+U calculations. The magnetic moment of Mn and band gap increase with increasing value of \( U \) for AF3 ordering. The LSDA predicts FM configuration as a lower energy state while LSDA+U gives AF3 insulator as the lower energy state. Fig. 4 shows the calculated total DOS for AF3 and FM configurations by the LSDA (panel (a)) and LSDA+U (for \( U=8.0 \) eV) (panel(b)). The LSDA predicts AF3 configuration to be a metal and FM configuration to be a half metal. This can be seen from Fig. 4 which shows finite DOS at \( E_F \) for AF3 as well as FM configurations (for minority spin) while the majority spin DOS shows gap at \( E_F \).

In the LSDA+U calculation, the band gap opens up with a value 0.85 eV and 3.18 eV at \( U=8.0 \) eV in AF3 and FM configurations respectively. The inclusion of \( U \) shifts the bands and opens up a gap at \( E_F \). In the AF3 configuration, the top of valance band has major contribution from Mn-d states in energy range -1.0 eV to 0.0 eV while O-2p contribution is in energy range -8.0 eV to -2.0 eV. The AF3 LSDA+U DOS are similar to monoclinic and orthorhombic LSDA DOS as it has strong Mn-d contribution at top of valence band. As the band gap is between Mn d-d bands, the insulating phase is a Mott-insulator. The nature of band gap is different between rhombohedral and monoclinic, orthorhombic structures because of their geometry differences. The Jahn-Teller distortion is responsible for the band gap in LSDA calculations of monoclinic and orthorhombic case while the inclusion of \( U \) has shifted the bands and created band gap in rhombohedral case.

In the LSDA, magnetic moment of Mn is 2.29 \( \mu_B \) and 1.82 \( \mu_B \) in AF3 and FM configuration respectively. Also there is a small magnetic moment on oxygen. The magnetic moments and band gap are given in Table I for AF3 configuration. Our LSDA results are in good agreement with earlier calculation [13]. Magnetic moment of Mn has a large change compared to the monoclinic structure in AF3 ordering (see Table I) because the LSDA gives an insulating AF3 ground state in monoclinic structure but it gives metallic FM ground state in rhombohedral structure.

The AF3 configuration has an energy 0.581 eV per formula unit below that of FM configuration in the LSDA+U and the FM configuration has an energy 0.52 eV per formula unit below that of AF3 configuration in the LSDA (see Table III). The energy difference in the LSDA+U is higher in this case as compared to the monoclinic and orthorhombic. This can be attributed to the difference in ground states by the LSDA in these structures.

Rather than presenting the full band structure we present a simple energy-level diagram which will help to understand our DOS results. Fig.5(a) schematically shows the energy-levels for Mn surrounded by O in an octahedral environment when U is assumed to be zero. Mn-d levels, in the crystal field shown in
the left hand side (in Fig. 5(a)), form bonding and antibonding levels after hybridization to O levels, as shown in the right hand side. The $dp\sigma$ levels arise from $\sigma$-bonding between Mn $t_{2g}$ and O-2p orbitals while the $dp\pi$ levels arise from $\pi$-bonding between Mn $t_{2g}$ and O-2p orbitals. The $\sigma$-bonding is usually much stronger than the $\pi$-bonding [35]. Thus the $dp\pi$ level has smaller O-2p contribution. Hence, the Mn d-d gap ($\Delta_{d-d}$) is smaller than O-2p Mn-d gap ($\Delta_{p-d}$) as shown in Fig. 5(a). This picture changes after the inclusion of U as shown in Fig. 5(b). Both $dp\pi$ and $dp\sigma$ levels shift downwards but the shift in $dp\pi$ level is larger compared to $dp\sigma$ level because of the smaller O-2p contribution in $dp\pi$ level. As a result, the $dp\pi$ and $dp\sigma$ levels lie roughly at the same energy. Thus the Mn d-d gap ($\Delta_{d-d}$) and O-2p Mn-d gap ($\Delta_{p-d}$) are of the same order (Fig. 5(b)). Let us now see how this energy level diagram helps us to understand our DOS results shown in Figs. 2-3. We first consider LSDA monoclinic case shown in Fig. 3a. We see that Mn d-$t_{2g}$ states mainly contribute around $E_F$ while O-2p states contribute well below $E_F$. This picture is similar to our energy level diagram shown in Fig. 5(a). When U is taken into account, we see from Fig. 3b that the $t_{2g}$ levels have been pushed down and O-2p contribution increases near $E_F$. Thus the picture is similar to Fig. 5(b). Fig. 2 can be understood in the similar fashion.

3.2 X-ray Emission Spectra

3.2.1 Orthorhombic LiMnO$_2$

To compare our work with the experimental data, we have calculated Mn L$\alpha$ and O K$\alpha$ X-ray emission spectra (XES) for the antiferromagnetic orthorhombic structure using the LSDA and LSDA+U at U=8.0 eV which is shown in Fig. 6. We have rescaled the intensity of calculated XES for better comparison with experimental result. In Mn L$\alpha$ XES, we see that the LSDA+U gives better agreement with experiment compared to the LSDA. In particular the region around peak 'B' of Mn spectrum produced by the LSDA+U shows much better agreement with the experimental results [14]. These differences in the LSDA and LSDA+U spectra can be understood in terms of DOS shown in Fig. 2, as the XES spectra have been calculated from Eqs. (1) and (2). In the LSDA spectrum, the feature 'A' corresponds to $t_{2g}$ DOS in energy range -7.0 eV to -3.0 eV and feature 'B' corresponds to $e_g$ DOS in energy range -2.5 eV to -1.0 eV. In the LSDA+U spectrum, the features 'A' and 'B' correspond to $t_{2g}$ DOS in energy range -7.0 to -3.0 eV and $e_g$ DOS in energy range -6.5 to -1.0 eV respectively. The peak 'B' is at -3.22 eV in the LSDA+U and at -2.56 eV in the LSDA while the experimental peak is seen at 3.3 eV. In the LSDA spectrum of O K$\alpha$, features 'D' and 'E' show the contribution of O(1)-2p and O(2)-2p states in energy ranges -7.0 to -3.0 eV and feature 'F' shows the contribution of O(2)-2p states in energy range -3.0 to 0.0 eV. However,
in the LSDA+U, only features 'D' and 'E' are present. The feature 'D' arises due to the contributions from O(1) and O(2) 2p-states in energy range -7.0 to -5.0 eV. The feature 'E' arises due to contributions from O(1) 2p-states in energy range -5.0 to -1.5 eV and O(2) 2p-states in energy range -5.0 eV to 0.0 eV. The O(2)-2p DOS does not have sharp peaks in energy range -3.0 eV to 0.0 eV and hence feature 'F' is absent in this case which is in agreement with experimental work [14]. The O Kα XES peak has maximum intensity at -4.2 eV in experimental work [14], which is seen in the LSDA calculation as well as in the LSDA+U calculation at -4.3 eV and at -4.1 eV respectively.

3.2.2 Monoclinic LiMnO₂

We have also calculated the Mn Lα and O Kα X-ray emission spectra for the AF3 monoclinic configuration by the LSDA and LSDA+U which is shown in Fig. 7. We see that inclusion of U drastically changes the spectrum. This is due to the change in the DOS caused by the inclusion of U. In Mn Lα spectrum, the peak 'B' and feature 'C' have large intensity in the LSDA calculation as compared to the LSDA+U while the feature 'A' has lower intensity. This change in intensity shifts the highest peak structure from -1.6 eV ('B' peak in the LSDA) to -5.2 eV ('A' feature in the LSDA+U). In the LSDA spectrum, the feature 'A' corresponds to \( t_{2g} \) as well as \( e_g \) DOS in energy range -7.0 to -3.0 eV and feature 'C' corresponds to \( t_{2g} \) DOS in energy range -1.0 eV to 0.0 eV. The peak 'B' corresponds to \( e_g \) DOS in energy range -2.5 eV to -1.5 eV. In the LSDA+U spectrum, feature 'A' corresponds to \( t_{2g} \) and \( e_g \) DOS in energy range -6.5 eV to -5.0 eV and feature 'C' has mainly contribution of \( e_g \) DOS around \( E_F \). The flat part of the spectrum between features 'A' and 'C' has contribution of \( t_{2g} \) and \( e_g \) DOS in energy range -5.0 eV to -1.0 eV. In the O Kα spectrum the peaks have lower intensity in the LSDA calculation compared to the LSDA+U calculation. The highest intensity is at -3.5 eV (feature 'D') in the LSDA calculation while it is at -1.7 eV in the LSDA+U. We note that the peaks 'E' and 'F' have been shifted to higher intensity in the LSDA+U calculation while feature 'D' remains absent due to change in DOS in energy range -7.0 eV to -5.0 eV as compared to the LSDA. The peaks 'E' and 'F' correspond to O-2p DOS in energy range -2.0 eV to -1.0 eV and -1.0 eV to 0.0 eV respectively in the LSDA calculations. In the LSDA+U spectrum, the peaks 'E' and 'F' have contribution of O-2p DOS in energy range -5.0 eV to -1.0 eV and -1.0 eV to 0.0 eV respectively. The inclusion of U changes the peak intensity for both Mn spectrum as well as oxygen spectrum. This effect of U in peak intensity is similar to the orthorhombic case but the change in peak intensity and the shift in highest intensity peak is larger in this case. This difference arises because of the difference in the DOS of both structures. In orthorhombic case, the \( e_g \) and \( t_{2g} \) DOS are mainly distributed in energy range -5.0 to -1.5 eV and -6.5 to -3.5 eV respectively. The \( t_{2g} \) DOS contributes to the peak at \( \approx -5.0 \) eV in XES spectrum and \( e_g \) DOS contributes to the peak
at -3.2 eV. In case of monoclinic, the $e_g$ and $t_{2g}$ DOS are distributed in energy range -6.5 to -1.0 eV and a sharp peak near $E_F$. The peak at -5.2 eV has contribution of $t_{2g}$ and $e_g$ DOS in energy range -6.5 eV to -5.0 eV and the flat part of spectrum between energy range -5.0 to -1.0 V has contribution of both $t_{2g}$ and $e_g$ DOS. The peak near 0.0 eV is mainly contributed by $e_g$ DOS. For monoclinic structure no X-ray emission experiment has been reported till now and it would be interesting to do such an experiment to verify our predictions.

3.3 Effect of U on Mn Valency

To see the effect of U on valency of Mn, we have examined the partial charges of Mn electrons in the LSDA and LSDA+U. Table II shows the partial charges of Mn in the AFM orthorhombic structure for the LSDA and LSDA+U. It is clear from Table II that the Mn 4s-states are fully ionized in the LSDA as well as in the LSDA+U. The partial charges of majority and minority $p$-states are not affected by inclusion of U while the partial charges in the majority Mn $d$-states have shifted from the minority Mn $d$-states. Hence the total number of Mn-d electrons do not change much which shows that the inclusion of U does not affect Mn valency in this case. We have noticed the similar effect of inclusion of U on Mn valency in the monoclinic and rhombohedral structure. The shift in charges occurs between the majority and the minority Mn-d electrons after inclusion of U. Thus we do not expect the change in Mn valency due to the inclusion of U.

4 Conclusions

Our study using the LSDA+U method shows that the electronic structures of orthorhombic, monoclinic and rhombohedral LiMnO$_2$ are significantly modified by inclusion of strong correlations. We have shown that the LiMnO$_2$ is an antiferromagnetic insulator by the LSDA+U for all structures while the LSDA predicts antiferromagnetic insulator for orthorhombic and monoclinic structures and FM metal for rhombohedral structure. The DOS calculations show a mixture of charge transfer and Mn d$\leftrightarrow$d excitation like insulator by the LSDA+U for monoclinic and orthorhombic LiMnO$_2$ in contrast to the LSDA result which shows a band insulator. On the other hand, the LSDA+U calculation for the rhombohedral LiMnO$_2$ shows it to be a Mott-insulator while the LSDA shows it to be a metal. We also note a large enhancement of the O-2p states at the top of valence band in the DOS of monoclinic and orthorhombic system by the LSDA+U. The calculated X-ray emission photoelectron spectra for orthorhombic and monoclinic structures show a decrease in peak intensity for Mn spectra and increase in peak intensity of oxygen spectra by
the LSDA+U as compared to the LSDA results. We find good agreement between the LSDA+U and experimental results at $U=8.0$ eV with respect to Mn magnetic moment, nature of band gap and X-ray emission photoelectron spectra for orthorhombic LiMnO$_2$. The DOS calculations show that the strong correlations change the DOS features dramatically around the Fermi level for all structures. We find that while the inclusion of $U$ increases Mn magnetic moments but it does not affect Mn valency.

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TABLE I. Band gap and magnetic moment ($m$) of Mn in the AFM orthorhombic LiMnO$_2$ and AF3 monoclinic and rhombohedral LiMnO$_2$ structure by the LSDA and LSDA+U at different U values (in eV).

| Structure  | $m$ ($\mu_B$) | LSDA | LDA+U |
|------------|---------------|------|-------|
|            |               | U=5.5 eV | U=6.9 eV | U=8.0 eV |
| Orthorhombic | 3.29          | 3.57 | 3.65 | 3.69 |
| Band Gap (eV) | 0.30          | 1.50 | 1.78 | 1.95 |
| Monoclinic  | 3.29          | 3.67 | 3.74 | 3.79 |
| Band Gap (eV) | 0.61          | 1.49 | 1.60 | 1.80 |
| Rhombohedral | 2.29          | 3.59 | 3.65 | 3.70 |
| Band Gap (eV) | 0.00          | 0.30 | 0.65 | 0.85 |

TABLE II. Partial charges of Mn in the AFM orthorhombic LiMnO$_2$ by the LSDA and LSDA+U at different U values (in eV).

| Charge Type | LSDA | LDA+U |
|------------|------|-------|
|            | U=5.5 eV | U=6.9 eV | U=8.0 eV |
| Majority   |       |       |       |
| $s$        | 0.09  | 0.09  | 0.09  | 0.09  |
| $p$        | 3.07  | 3.08  | 3.08  | 3.08  |
| $d$        | 3.90  | 4.01  | 4.04  | 4.05  |
| Total      | 7.06  | 7.18  | 7.21  | 7.22  |
| Minority   |       |       |       |
| $s$        | 0.07  | 0.08  | 0.08  | 0.08  |
| $p$        | 3.06  | 3.06  | 3.06  | 3.06  |
| $d$        | 0.64  | 0.47  | 0.42  | 0.39  |
| Total      | 3.77  | 3.61  | 3.56  | 3.53  |
TABLE III. Total energies (with respect to rhombohedral LiMnO$_2$ in FM configuration) of the orthorhombic, monoclinic and rhombohedral structures in ferromagnetic and antiferromagnetic configuration by the LSDA and LSDA+U at different U values (in eV).

|                  | LSDA | LDA+U                     |
|------------------|------|---------------------------|
|                  |      | U=5.5 eV  | U=6.9 eV  | U=8.0 eV  |
| Orthorhombic     |      |             |             |             |
| AF (eV)          | 0.276| -1.007      | -0.958     | -1.299     |
| FM (eV)          | 0.577| -0.916      | -0.886     | -1.249     |
| Monoclinic       |      |             |             |             |
| AF (eV)          | 0.285| -0.696      | -0.631     | -0.812     |
| FM (eV)          | 0.891| -0.496      | -0.451     | -0.640     |
| Rhombohedral     |      |             |             |             |
| AF (eV)          | 0.521| -0.592      | -0.588     | -0.581     |
| FM (eV)          | 0.00 | 0.00        | 0.00       | 0.00       |
FIGURE CAPTIONS

Fig. 1. Antiferromagnetic ordering for orthorhombic LiMnO$_2$ in two planes $z=0.4$ and $z=0.6$. Only Mn atoms are shown.

Fig. 2. Total DOS and the partial DOS of majority spin and minority spin Mn d-$t_{2g}$ bands and Mn d-$e_g$ bands for AFM orthorhombic LiMnO$_2$ (a) for the LSDA and (b) for the LSDA+U. The LSDA+U DOS corresponds to $U=8.0$ eV. The bottom two panels show the partial DOS of majority spin O-2p bands at two different planes. O1 and O2 correspond to 2b site at $z=0.13$ and $z=0.60$ respectively in $Pmmn$ space group. The dashed vertical line denotes the Fermi level $E_F$. The DOS for the majority spin is shown on the upside and DOS for the minority spin, on the downside.

Fig. 3. Total DOS and the partial DOS of majority spin and minority spin Mn d-$t_{2g}$ bands and Mn d-$e_g$ bands for AF3 monoclinic LiMnO$_2$ (a) for the LSDA and (b) for the LSDA+U ($U=8.0$ eV). The bottom panel shows the partial DOS of majority spin O-2p bands. The dashed vertical line denotes the Fermi level $E_F$. The DOS for the majority spin is shown on the upside and DOS for the minority spin, on the downside.

Fig. 4. Total DOS for AF3 and FM rhombohedral LiMnO$_2$ (a) for the LSDA and (b) for the LSDA+U ($U=8.0$ eV).

Fig. 5. Schematic energy level diagram of molecular orbitals for MnO$_6$ octahedron in LiMnO$_2$. (a) and (b) show the rough estimate for the LSDA and LSDA+U respectively.

Fig. 6. X-ray emission photoelectron spectra of Mn L$_\alpha$ and O K$_\alpha$ using the LSDA and LSDA+U and experimental result (Ref. 12) for orthorhombic case. The solid and dashed curves show the LSDA and LSDA+U ($U=8.0$ eV) results respectively and the dots, experimental result.

Fig. 7. X-ray emission photoelectron spectra of Mn L$_\alpha$ and O K$_\alpha$ using the LSDA and LSDA+U for monoclinic case. The solid line and dash line curves are showing the LSDA and LSDA+U ($U=8.0$ eV) results respectively. Upper panel shows Mn L$_\alpha$ spectrum and lower panel shows O K$_\alpha$ spectrum.
(a) LSDA

(b) LSDA+U

DOS (States/eV)

Energy (eV)

Mn 3d (e\textsubscript{g})

Mn 3d (t\textsubscript{2g})

O(1) 2p

O(2) 2p
(a) LSDA

(b) LSDA+U

DOS (States/eV)

Energy (eV)

Mn d(e_g)

Mn d(t_2g)

O 2p

Up

Dn

DOS  (States/eV)

Energy (eV)
(a) LSDA

(b) LSDA+U

Energy (eV)

DOS (States/eV)

AF3

FM

total

Up

Dn
Orthorhombic LiMnO$_2$

Mn L$\alpha$ XES

O K$\alpha$ XES

Energy (eV)

Intensity (arb. units)
Monoclinic LiMnO$_2$

Mn L$_\alpha$ XES

O K$_\alpha$ XES

Intensity (arb. units)

Energy (eV)