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Observation of self-regulating response in $\text{Li}_x\text{M}_y\text{Mn}_{2-y}\text{O}_4$ ($\text{M} = \text{Mn}, \text{Ni}$): A study using density functional theory

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ABSTRACT

Density functional theory is used to understand the response of the transition metal–oxygen octahedra in $\text{Li}_x\text{Mn}_2\text{O}_4$ and $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ to lithium intercalation and de-intercalation. Electronic structure computations on these compounds for $x = 0, 0.5$ and 1 indicate that the 3d DOS of Mn is almost unaffected to variations in x . On the other hand, the oxygen 2p-DOS and to a lesser extent Ni 3d DOS are found to be sensitive to perturbation. The observations are explained on the grounds of self-regulating response, characteristic of systems having localized d states that communicate with a covalent manifold.

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1. Introduction

Battery Materials such as $\text{Li}_x\text{Mn}_2\text{O}_4$, Li_xCoO_2 , etc. have recently started to attract the attention of Physicists because of their application in fundamental physics [1–5] besides their industrial importance as a green cathode material in solid state batteries. Charge state and lattice parameter are the foremost attributes dictating the physics and electrochemistry of materials. Charging or discharging (varying the state of charge of the battery) a lithium battery, employing cathode materials such as $\text{Li}_x\text{Mn}_2\text{O}_4$, causes a variation in the lithium stoichiometry (x). This x variation creates a variety of phase transitions, both structural and electronic. In our earlier work, we have studied using equations of classical physics, the variation in the Madelung energy [6] and lattice parameter [7] of $\text{Li}_x\text{Mn}_2\text{O}_4$ as a function of x and predicted an order–disorder type of transition in the material. In the present work, we study the angular momentum resolved DOS of $\text{Li}_x\text{Mn}_2\text{O}_4$ and $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ at different values of x .

Anderson and Haldane [8] had investigated the charge states of transition metal (TM) impurities in semiconductors using the Anderson Hamiltonian and reported that hybridization maintains

the charge around the TM atom almost a constant, irrespective of whether electrons are accepted by or donated to the d states. Following Anderson's work, researchers have studied layered oxides such as Li_xCoO_2 [9,10] and $\text{Na}_x\text{CoO}_2 \cdot n\text{H}_2\text{O}$ [11], respectively, using density functional theory (DFT) and a Hubbard Hamiltonian approach and observe that variation in x did not affect the charge around the TM. These authors [9,10] coin the term 'self-regulating response' to denote re-hybridization that stabilizes the d states towards a perturbation. In the present work, we observe and report a similar phenomenon in the case of spinel type $\text{Li}_x\text{Mn}_2\text{O}_4$ and $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$.

Before we go to the details of our work, it is pertinent to mention here that Harris et al. [12] have studied the interaction of hydrogen with metals like Al, Cu, Ag and Au and report that there is a Pauli repulsion between the filled σ molecular orbital of H_2 and the sp electrons in the metal. By contrast, in TMs having unfilled d-electron states of about the same energy, a re-hybridization can take place in which part of the sp electrons can escape into the d-orbitals minimizing the Pauli repulsion.

2. Computational details

Ab initio electronic structure calculations were performed for $\text{Li}_x\text{Mn}_2\text{O}_4$ ($x = 0, 0.5$ and 1) within the framework of DFT

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combined with the generalized gradient approximation (GGA), which is known to work well for manganese oxides. All the computations were performed on a primitive unit cell of $\text{Li}_x\text{Mn}_2\text{O}_4$ with two formula units on a personal computer (2.80 GHz Pentium-IV processor) using CASTEP [13]. P1 symmetry was adopted to study the Ni-substituted compound. Also, P1 symmetry was used to study $\text{Li}_x\text{Mn}_2\text{O}_4$ at $x = 0.5$.

3. Results and discussion

A comparison between the local electronic structures of Mn and O in $\text{Li}_x\text{Mn}_2\text{O}_4$ shows that while the triplet structure of Mn-3d DOS (Fig. 1) below the Fermi level shows least variations to x , the oxygen 2p-DOS (Fig. 2) shows a strong x -dependent triplet structure below the Fermi level. It is important to note here that at $x = 0.5$ the electronic structure of the eight oxygen atoms in the primitive unit cell of $\text{Li}_x\text{Mn}_2\text{O}_4$ are not identical. They segregate into two types each with a different DOS shape (spectral weight) and different charge states (Fig. 2).

We computed the angular momentum resolved charge state of an atom by integrating the area under the DOS below the Fermi level. To better characterize the response of the TM–oxygen octahedra to a perturbation, we find the difference in the charge (angular momentum resolved) enclosed around the site of an atom for different values of x (Table 1). We observe that the charge enclosed around the manganese site is a constant for all values of x , while that around the oxygen site shows significant changes with Li insertion/de-insertion. In other words, we can say that it is the oxygen backbone in $\text{Li}_x\text{Mn}_2\text{O}_4$ that responds to the charge/discharge of a lithium battery. The observation that it is the oxygen backbone that responds to Li insertion/de-insertion has already been noticed by Ceder et al. [14], for the case of Li_xCoO_2 . It is interesting to see that similar conditions prevail in the case of $\text{Li}_x\text{Mn}_2\text{O}_4$ also.

We extend similar computations on the nickel-substituted compound $\text{Li}_x\text{Ni}_y\text{Mn}_{2-y}\text{O}_4$. We find that the behavior of the electronic structure of this compound to perturbations (change in x) is very close to what has been noticed in $\text{Li}_x\text{Mn}_2\text{O}_4$. The interesting difference between $\text{Li}_x\text{Mn}_2\text{O}_4$ and $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ is that while the x variation maintains the charge around the Ni atom a constant,

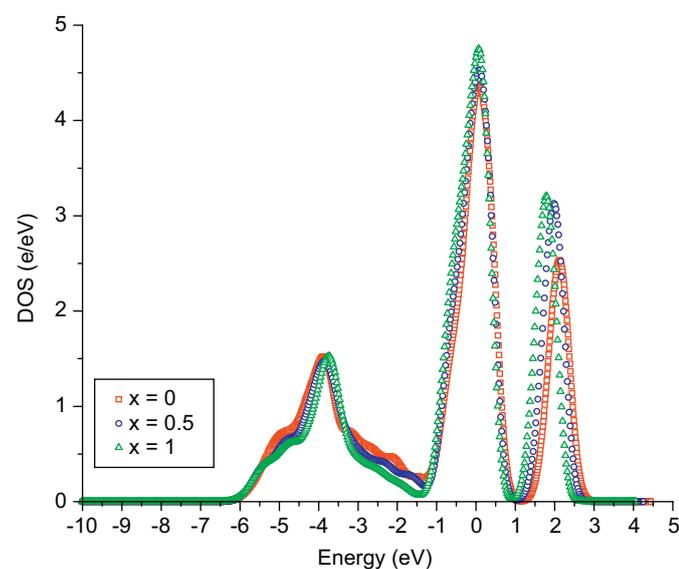


Fig. 1. GGA-projected densities of states for the Mn-3d states of $\text{Li}_x\text{Mn}_2\text{O}_4$ at $x = 0$ (red), $x = 0.5$ (blue) and $x = 1$ (green). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

there is a change in the spectral weight of the Ni-3d DOS (Fig. 4) in the close vicinity of the Fermi level. This behavior is not observed in the Mn-3d DOS of both $\text{Li}_x\text{Mn}_2\text{O}_4$ (Fig. 1) and $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (Fig. 3). The exact physical basis behind the observed change in the spectral weight is not immediately obvious. It is pertinent to mention here that a change in the hybridization is reported [15] to be the cause for a spectral weight transfer in the temperature-dependent UV-PES of a perovskite manganate.

Table 2 presents the bond population overlap studies providing information on the Mn-3d–O2p and Ni-3d–O2p hybridization. The Table demonstrates that as Li is inserted/de-inserted, the TM–oxygen hybridization changes and that this change is more significant in the Mn–O octahedra compared to the Ni–O octahedra. In summary, we find that x variation in $\text{Li}_x\text{Mn}_2\text{O}_4$ does not affect the charge on the Mn site though the formal oxidation state on the Mn atom decreases from 4 to 3.5, as per the charge conservation law, when x varies from 0 to 1. The charge on the Ni site in $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ also does not change with x variation, however, unlike the Mn-3d density of states, a slight change in the spectral weight of the Ni-3d density of states is noticed at the vicinity of the Fermi level. We also notice that there is a change in the Mn–O and Ni–O hybridization, when x varies from 0 to 1 and that the change in the Mn–O hybridization is more than that in the case of Ni–O hybridization.

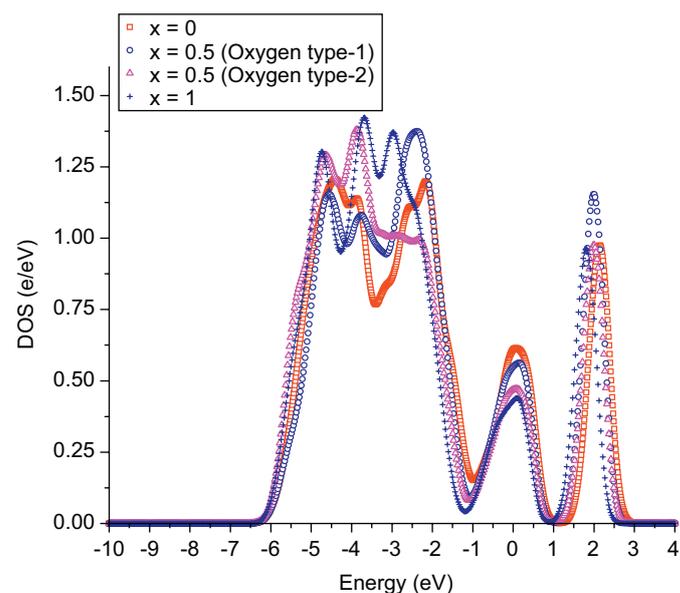


Fig. 2. GGA-projected densities of states for the O-2p states of $\text{Li}_x\text{Mn}_2\text{O}_4$ at $x = 0$ (Red), $x = 0.5$ and type I oxygen (blue), $x = 0.5$ and type II oxygen (rose) and $x = 1$ (navy blue). At $x = 0.5$, it can be seen that the electronic structure of the eight oxygen atoms are not identical. Four belong to one type (oxygen type-1) and the other four belong to another type (oxygen type-2). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1

Response of the Mn-3d, Ni-3d and O-2p orbitals in $\text{Li}_x\text{M}_y\text{Mn}_{2-y}\text{O}_4$ to a perturbation (O–I and O–II refer to the electronically different oxygen atoms at the intermediate value of x).

Atomic Orbital	$x = 0$ to $x = 0.5$	$x = 0.5$ to $x = 1$
O–I 2p-orbital	4.50–4.50 = 0	4.50–4.64 = –0.14
O–II 2p-orbital	4.50–4.65 = –0.15	4.65–4.64 = 0.01
Mn-3d-orbital	5.54–5.54 = 0	5.54–5.54 = 0
Ni-3d-orbital	8.31–8.30 = 0.01	8.30–8.34 = –0.04

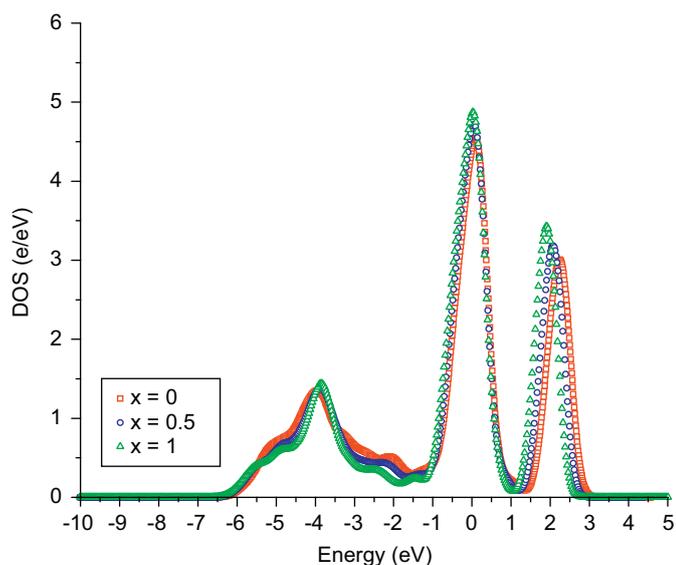


Fig. 3. GGA-projected densities of states for the Mn-3d states of $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ at $x = 0$ (red), $x = 0.5$ (blue) and $x = 1$ (green). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

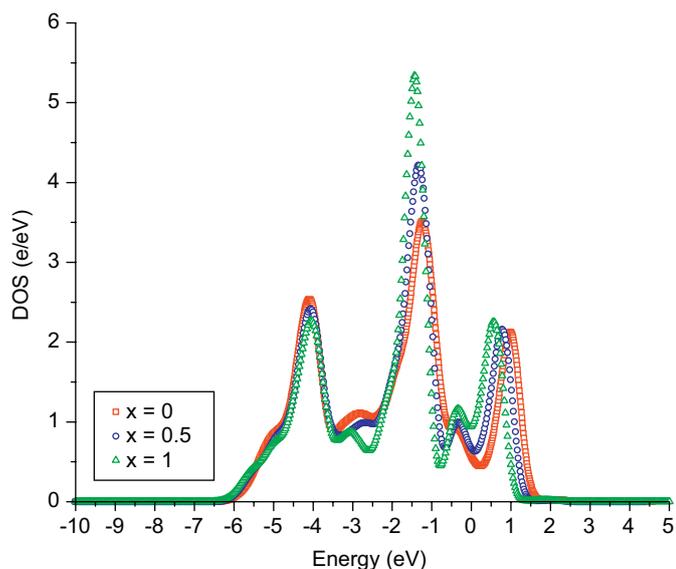


Fig. 4. GGA-projected densities of states for the Ni-3d states of $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ at $x = 0$ (red), $x = 0.5$ (blue) and $x = 1$ (green). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 2
Results of the bond population analysis for Mn–O in $\text{Li}_x\text{Mn}_2\text{O}_4$ and Mn–O, Ni–O in $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ at $x = 0, 0.5$ and 1.

x	LiMn_2O_4	$\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$	
	Mn–O	Mn–O	Ni–O
1	0.33	0.34	0.29
0.5	0.30, 0.34	0.35, 0.33	0.28, 0.30
0	0.30	0.31	0.28

4. Conclusion

Studies on the electronic structure of $\text{Li}_x\text{Mn}_{0.5}\text{Mn}_{1.5}\text{O}_4$, as a function of the lithium stoichiometry reveal the operation of the self-regulating response in this compound. The Mn-3d levels remain unaltered with variations in the x , though the formal oxidation state changes. The behavior of the Ni-3d levels is similar to that of the Mn-3d states as far as the charge state is concerned. However, the change in the Mn-3d O-2p hybridization with x variation is more, compared to that in the case of Ni-3d O-2p. We believe that this difference in the level of hybridization manifests as a change in the spectral weight of the Ni-3d DOS to variations in x , while no such change is noticed for the Mn-3d DOS. We further believe that this observation could guide us in the general understanding on the experimental observations reported by one of us [16] that the complex plane impedance spectra of nickel-doped lithium manganate showed a remarkable sensitivity towards UV perturbation compared to lithium manganate.

The phenomenon of preserving the d states from a perturbation at the cost of a re-hybridization between the metal d orbital and the ligand p orbital has been coined by earlier workers as ‘self-regulating response’ [9,10]. These researchers also question the necessity of the concept of formal oxidation states and literal charge transfer to understand the various signatures in the photo electron spectroscopy of TM oxides and point out that the re-hybridization associated with multiple oxidation states in such compounds is often falsely attributed to ‘charge ordering’ [17].

Observation of self-regulating response in lithium manganate thus demands further work to correctly understand electronic crystallization in this material, which is considered to be a prototype in the study of charge ordering, frustrated magnetism and thermodynamics of phase transition occurring in the earth’s mantle.

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