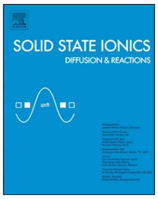
Solid State Ionics 321 (2018) 23–28

Contents lists available at ScienceDirect

Solid State Ionics

journal homepage: www.elsevier.com/locate/ssi



Electronic structure and magnetism of Li_x(Ni-Co-Mn)O_2 in view of KKR-CPA calculations

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ARTICLE INFO

Keywords:
Electronic structure
KKR-CPA
Li-ion battery
Density of states
Magnetic properties

MSC:
00-01
99-00

ABSTRACT

The Korringa-Kohn-Rostoker method with the coherent potential approximation (KKR-CPA) has been applied to study the electronic structure of Li_x(Co-Ni-Mn)O_2 cathode material. The influence of chemical disorder, such as vacancy defects on Li and O as well as Co/Ni/Mn alloying, on electronic density of states has been analyzed focusing on the magnetic properties onset in the aforementioned materials. It is found that local magnetic moments on transition metal atoms appear in Li_x(Co-Ni-Mn)O_2 when decreasing Li content. The largest moment was calculated on Mn atom ($\sim 1.5\mu_B$), while smaller magnetic moment was found on Co atoms ($\sim 0.2\mu_B$). On the whole, the KKR-CPA density of states of Li_x(Co-Ni-Mn)O_2 recall either strongly doped semiconducting-like behaviour or half-metallic character in non-magnetic and magnetic states, respectively, with the band gap markedly reduced when accounting for O vacancy defects in calculations.

1. Introduction

Lithium-ion battery materials are still considered to be the most promising energy converter/charger due to their excellent electrochemical parameters, and their industrial applications especially for power electronic devices are extremely important [1,2,3,4,5]. Moreover, outstanding commercial success of Li-ion cathode materials based on lithium cobaltate ($LiCoO_2$) caused that they became materials for personal use, which in turn demands more efficient functional parameters such as high energy density, long life-cycle, light-weight and safety.

In recent years, in order to have a deeper insight into electrochemical properties of Li-ion battery cathode materials, theoretical investigations based on DFT electronic band structure calculations have been undertaken in systematic way [6,7,8,9,10,11]. For instance, the impact of electronic structure features on the discharge curve in the series of compounds as A_xMO_2 (A = Li, Na; M = Mn, Co, Ni, Fe) and their solid solutions, have been recently notified based on detailed experimental and theoretical investigations [11,13,14]. Also, the step-like vs. continuous-like character of the discharge curve have been interpreted in terms of correlations between electronic structure and electrochemical properties in selected Li- and Na-ion cathode materials, respectively. Quite recently, it was found that substitution of Ni by lower cost and more accessible elements such as Co and Mn in $LiNi_{1-y-z}Co_yMn_zO_2$ cathode material, improved its electrochemical properties, namely crystal stability, initial capacity and life cycle [15,16,17,18]. The fact that experimentally investigated Li-ion battery materials commonly contain 3*d* transition metal elements (M = Mn, Fe, Co, Ni) directs attention to their possible magnetic properties. More precisely one can ask about local magnetic moments appearance in such materials and how magnetism can be affected when Li concentration changes.

The aim of this work is to show the evolution of total-, site-decomposed and l-decomposed density of states (DOS) in the whole range of Li concentration, starting our analysis from the reference Li_xCoO_2, next considering electronic and magnetic properties of 3*d* dopants (Mn and Ni) and then ending with highly disordered Li_x(Co-Ni-Mn)$O_{2-\delta}$ cathode material. We show that electronic structure features and resulting magnetic properties strongly depend on the chemical composition of the considered system. The enlightening of spin-polarised electronic structure behaviours, especially in the vicinity of the Fermi level, seems to be important to better understand the mechanisms responsible for electrochemical properties, if these systems exhibit magnetic order near battery operating temperature.

2. Computational details

The layered $LiMO_2$ with M = Co and Ni were reported to crystallize in the rhombohedral unit cell (α-$NaFeO_2$-type, space group $R\bar{3}m$) [19], whereas the crystal structure of $LiMnO_2$ was found to belong to

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https://doi.org/10.1016/j.ssi.2018.03.030
Received 30 October 2017; Received in revised form 27 March 2018; Accepted 29 March 2018

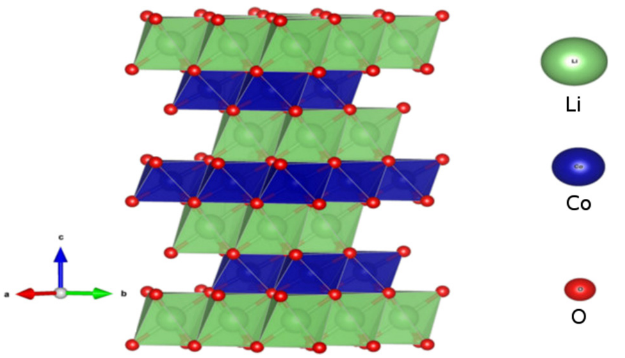

Fig. 1. KKR-CPA total and site-decomposed density of states in $LiCoO_2$ (image rendered with VESTA [31]).

orthorhombic (space group *Pnma*). In this work, we restrict our discussion to the rhombohedral structure only, and experimental lattice constants as well as atomic positions have been used to calculate electronic structure of ordered LiMO$_2$ compounds. In the case of disordered Li_x(Co-Ni-Mn)O_2 alloys, recently refined crystal data in two compositions $Li_xNi_{0.65}Co_{0.25}Mn_{0.1}O_2$ and $Li_xNi_{0.55}Co_{0.35}Mn_{0.1}O_2$ were employed [11] in KKR-CPA computations.

The crystal structure of $LiCoO_2$ is presented in Fig. 1. We can notice that the Li and Co atoms occupy the centers of two different edge-sharing [CoO_6]-octahedra, which results in formation of separate Li and Co layers. Hence, the layered structure of LiMO$_2$ is able to intercalate lithium into transition metals compounds.

Because of high degree of chemical disorder occurring in the considered materials (Li or O vacancy defects and Co/Ni/Mn alloying), the electronic structure calculations of such precise oxygen non-stoichiometry measurement solid solutions become much more complicated than the corresponding computations of ordered LiMO$_2$ compounds. The fully spin- and charge-self-consistent Green function Korringa-Kohn-Rostoker method (KKR) combined with the coherent potential approximation (CPA) was employed [21,22] to treat chemical disorder as random. It is worth noting that such approach allows to perform electronic structure calculations in the whole range of composition without changing the symmetry of the unit cell, which makes an important difference comparing with other computational methods based on supercell models of disordered systems. In the KKR-CPA computations, the crystal potential of the muffin-tin form was constructed within the local density approximation (LDA), applying the Perdew-Wang formula [23]. The Fermi energy (E_F) was determined accurately using the generalized Lloyd formula [24] and employing an elliptic contour in the complex energy plane. Total, site- decomposed and l-decomposed DOS were computed employing k-space integration technique over a dense mesh of small tetrahedrons in the irreducible part of the Brillouin zone. Because of the presence of transition metals, which commonly exhibit an intense d-like DOS peaks in the vicinity of E_F, the KKR-CPA calculations were carried out considering both non-spin-polarised and spin-polarised cases, expecting the onset of magnetic moments on these atoms.

3. Results and discussion

3.1. Mn and Ni impurities in $LiCoO_2$

Total electronic density of states of $LiCoO_2$ (Fig. 2) indicates semiconducting properties of this compound, since the Fermi level falls into the energy gap. Such electronic structure features arise from strong hybridisation of p − O states and d − Co states (with small admixture of s − Li states) leading to the separation between valence and conduction bands. It is worth noting that the states lying near top of valence states as well as near bottom of conduction states are dominated by d − Co states.

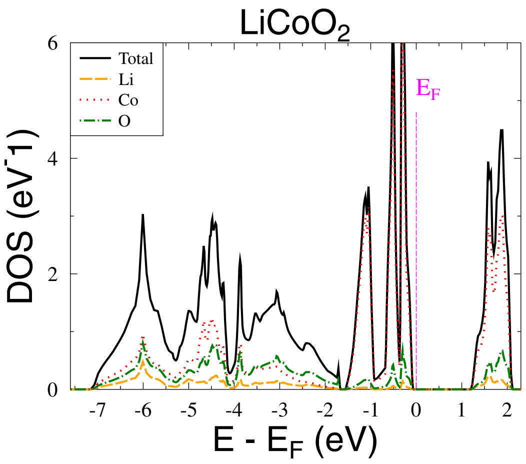

Fig. 2. KKR-CPA total and site-decomposed density of states in $LiCoO_2$.

It appears that the calculated energy gap may vary from 0.9 eV to 1.3 eV, depending on crystal data, and as already shown in Ref. [12], being very sensitive to the variation of z parameter of the O sites. It is worth noting that experimental energy gap reported in $LiCoO_2$ from optical measurements are rather scattered (1.7 eV [25], 2.1 eV [26], 2.5 eV [27] or 2.7 eV [28] from recent photoemission measurements). Our KKR value of E_g reflects the well-established LDA tendency to underestimate the band gap in semiconductors, which can be improved when employing e.g. GGA + U approach (E_g = 2.74 eV if using U = 4.91 eV for d − Co states [29]). Bearing in mind the LDA limits, we intend to demonstrate theoretically that the effect of chemical disorder is also important to better understand for example marked deviation between band gap of $LiCoO_2$ derived from optical and resistivity measurements (see e.g. 0.3 eV [14]).

The KKR calculations performed for other LiMO$_2$ compounds assuming the same unit cell symmetry as in $LiCoO_2$ resulted in the half-metallic character of DOS and integer value of a total magnetisation, i.e. 1 μ_B in $LiNiO_2$ and 2 μ_B in $LiMnO_2$, due to an appearance of local moments on Ni and Mn, respectively. This result can be understood in terms of the Stoner mechanism leading to energetically favourable DOS splitting for spin-up and spin-down electrons, when DOS value near E_F is sufficiently large. From Fig. 2, one can notice that it happens if the Fermi level is shifted into high DOS peak either above or below the energy gap. It prompted us to perform the spin-polarised KKR-CPA calculations of Ni and Mn impurities diluted in the semiconducting $LiCoO_2$ host to verify whether magnetic moments also appear at very low impurity concentration.

Actually, the role of the two elements substituted on Co-site is apparently different, since Mn is expected to shift E_F into valence band edge, while Ni acts in opposite way, moving the Fermi level into the conduction band edge. Since the d-like DOS peak near top of valence states are more enhanced than the corresponding ones near the bottom of conduction states, it is not surprising that the magnetic moment on Mn impurity in $LiCoO_2$ is only constituted (Fig. 3 a), unlike Ni one (Fig. 3 b). Interestingly, in the case of Mn the electronic DOS recalls the half-metallic behaviour due to finite viz. vanishing DOS for spin-up and spin-down electrons, respectively. The calculated magnetic moment on Mn impurity in $LiCoO_2$ is near 1.5 μ_B. Such value of μ_{Mn} is expected to be maintained when substituting Co (also Mn-Ni) with Mn in $LiCo_{1-x}Mn_xO_2$, since the computed Mn moment in the hypothetical $R\bar{3}m$-$LiMnO_2$ is also close to 1.5 μ_B.

3.2. Electronic structure of Li_x(Ni-Co-Mn)O_2

In order to study relative crystal stability of the Li_x(Ni-Co-Mn)O_2 solid solutions, the total energy KKR-CPA calculations were performed.