Effect of Co on the magnetism and phase stability of lithiated manganese oxides

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Abstract. We present first-principles calculations of the relative energies of various phases of lithiated manganese oxides with and without Co. We use the ultrasoft pseudopotential method as implemented in the Vienna *ab initio* simulation package (VASP). The calculations employ the local spin density approximation (LSDA) as well as the generalized gradient approximation (GGA). We consider monoclinic and rhombohedral structures in paramagnetic, ferromagnetic and antiferromagnetic (AF3) spin configurations. Spin-polarization significantly lowers the total energy in all cases. The effect of Co on the stability of these phases is discussed.

Keywords. Lithiated manganese oxides; first-principles calculations; VASP; phase stability; Co alloying.

1. Introduction

Mn oxides would be preferable to the Co oxides currently employed as cathode materials in commercially manufactured Li-batteries (Tarascon and Armand 2001), from the standpoint of cost and toxicity. The structural phase-transitions suffered by lithiated Mn oxides during oxidation-reduction between Mn oxidation states 3+ and 4+, however, degrade their performance in battery applications (Thackeray 1999). These structural phase transitions are thought to be driven by the Jahn–Teller effect for Mn-ions in an octahedral oxygen-neighbour environment (Marianetti *et al* 2001).

Alloying on the Mn sublattice may counteract the cooperative Jahn–Teller effect, which is instigated by the trivalent Mn ions, and thereby improve the performance of Mn-oxides in battery applications. Alloying the dioxide, $LiMnO_2$, by 10% Co (Armstrong *et al* 1998), for example, was found to suppress the monoclinic distortion (Armstrong and Bruce 1996; Capitaine *et al* 1996; Tabuchi *et al* 1998) that occurs in the unalloyed layered system. The alloying transforms the monoclinic system to the layered rhombohedral α-NaFeO$_2$ structure that is found for several lithiated transition metals dioxides (Aydinol *et al* 1997). Pure lithiated Mn dioxide is metastable with respect to the orthorhombic structure (Dittrich and Hoppe *et al* 1969). Transition to spinel occurs upon delithiation (Reed *et al* 2001).

The purpose of the present work is to explore theoretically the suppression of the Jahn–Teller distortion in layered $LiMnO_2$ by Co alloying. We present first-principles calculations within the local-spin-density-approximation (LSDA) framework, supplemented by the generalized gradient approximation (GGA) (Perdew and Wang 1992). Numerical calculations are performed with the VASP code (Kresse and Furthmüller 1996a, b), in which the ultrasoft-pseudopotential representation is implemented. A similar approach was previously employed by Mishra and Ceder (1999) to treat a series of lithiated Mn oxides, with several different crystal structures and stoichiometries. Their results for the relative stabilities were consistent with experiment, and provide evidence for the suitability of the LSDA–GGA framework for the treatment of structural properties. It should be borne in mind, however, that the insulating behaviour of many transition metal oxides is not accurately modeled within this framework. Higher-level treatments of electron correlation are still in a state of development, and are numerically intensive.

2. Calculational details

Calculations were performed for $LiMn_{1-x}Co_xO_2$ in the layered monoclinic (Armstrong and Bruce 1996; Capitaine *et al* 1996) and rhombohedral (Armstrong *et al* 1998) structures. To keep the unit-cell sizes relatively small, a concentration, $x = 0.25$, was employed in the alloyed systems. The corresponding cell contains 4 formula units, or 16 atoms. Calculations were also performed for the unalloyed systems, with $x = 0$.

Diffraction measurements on (other than layered) systems with composition Li_xMnO_2 show a commensurate antiferromagnetic structure in the orthorhombic phase (Greedan *et al* 1997) of $LiMnO_2$, but frustrated incommensurate magnetic structures in the spinel phase (Greedan *et al* 1998; Rodriguez-Carvajal *et al* 1998;

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Wills *et al* 1999a, b). Susceptibility measurements on monoclinic $LiMnO_2$ (Tabuchi *et al* 1998) and $LiAl_{0.05}Mn_{0.95}O_2$ (Jang *et al* 1999) suggest possible spin-glass behaviour. In the absence of a simple magnetic model for the layered monoclinic and layered rhombohedral crystal structures under consideration, we restrict our calculations to idealized spin configurations that are intended to reveal the basic behaviours. Calculations are performed for a ferromagnetic, a simple antiferromagnetic, and a nonmagnetic structure. For the monoclinic structure, we employ the commensurate antiferromagnetic structure proposed by Singh (1997), designated AF3, which has atoms with alternating spin directions along the *b* axis (see below). A similar antiferromagnetic structure is employed for the rhombohedral crystal.

In the real Co-alloyed materials, the arrangement of substitutional Co on the Mn sublattice is presumably disordered. The calculations described in this article, however, invoke periodic boundary conditions, and the Co-atom arrangement is therefore ordered. The neglect of disorder in the present treatment must therefore be kept in mind when comparing the theory with experiment.

The calculations presented here were performed using the first principles plane-wave ultrasoft pseudopotential framework, within the LSDA–GGA approximation (Kresse and Furthmüller 1996a, b). In previous work (Prasad *et al* 1999) on the materials under investigation, LSDA calculations were done with the full-potential linear muffin tin orbital method (Wills). Owing to the large numerical effort for this highly precise code (Wills), however, a full relaxation of the atomic coordinates and the cell parameters was not completed. With the VASP code, cell parameter and internal coordinate relaxations were performed for all of the systems studied.

Although the materials under consideration are insulating, the LSDA predicts metallic behaviour. To obtain an insulating energy gap in these materials, a treatment of electron correlation beyond the level of the LSDA–GGA is required. Correction of the LSDA for correlation by the $LDA + U$ (Bengone *et al* 2000) or by the GW approximation (Massidda *et al* 1997) would be desirable, although numerically intensive, for the large unit cells being considered.

2.1 *Monoclinic cell*

The unit cell of monoclinic $LiMnO_2$ ($NaMnO_2$ structure) contains two formula units. The observed lattice constants (Armstrong *et al* 1998) are $a = 5.44$ Å, $b = 2.81$ Å, $c = 5.39$ Å, and the monoclinic angle, $\boldsymbol{b} = 116°$. It is convenient to consider a cell in which $\mathbf{a}' = \mathbf{a} + \mathbf{b}$, $\mathbf{b}' = \mathbf{b} - \mathbf{a}$, and $\mathbf{c}' = \mathbf{c}$. In the AF3 structure, the spins along the *b c* axis are ordered ferromagnetically, and those along the *a'* axis, antiferromagnetically. This cell contains 4 formula units, and each layer of Li, M (Mn or Co), or O contains

4. With transition-metal (M) layer atoms at $(0, 0, 0)$, $(\frac{1}{2}, 0, 0)$, $(0, \frac{1}{2}, 0)$, and $(\frac{1}{2}, \frac{1}{2}, 0)$, the adjacent Li layer sites are obtained by a displacement of $(\frac{1}{4}, \frac{1}{4}, \frac{1}{2})$. The oxygen layers consist of $4i$ sites, and have two internal degrees of freedom, *x* and *z*. If one of the sites has coordinates $\mathbf{r}(1) = (x, 0, z)$, then the remaining seven sites in the primed coordinate system can be expressed in the form

$$\mathbf{r}(j) = \text{sgn}(j)\mathbf{r}(1) + n_1(j)(\tfrac{1}{2}, 0, 0) + n_2(j)(0, \tfrac{1}{2}, 0), \qquad (1)$$

where $\text{sgn}(j)$ is positive or negative when *j* is odd or even, and $n_1(j)$ and $n_2(j)$ are either 0 or 1. The crystallographic refinement by Armstrong *et al* (1998) yielded $x = 0.2723$, and $z = 0.7706$. The M layers contain either 4 Mn atoms $(x = 0)$, or 3 Mn and 1 Co atoms $(x = 0.25)$. A supercell could also be constructed by doubling the cell along the *c* axis. Since the magnetic coupling (either directly or via superexchange) is assumed to be primarily between Mn atoms within a given layer, a doubled cell within the layer was given primary attention. It appears, however, that doubling the cell along the *c*-axis gives similar results.

2.2 *Rhombohedral cell*

The layered rhombohedral ($NaFeO_2$) structure can be generated by cell unit vectors

$$\mathbf{A}_1 = a\hat{\mathbf{i}}, \ \mathbf{A}_2 = -\frac{1}{2}a\hat{\mathbf{i}} + \frac{\sqrt{3}}{2}a\hat{\mathbf{j}}, \ \mathbf{A}_3 = \frac{1}{2}a\hat{\mathbf{i}} + \frac{1}{3}\frac{\sqrt{3}}{2}a\hat{\mathbf{j}} + \frac{1}{3}c\hat{\mathbf{k}},$$

$$(2)$$

where *a* and *c* are the lattice constants, and $\hat{\mathbf{i}}, \hat{\mathbf{j}},$ and $\hat{\mathbf{k}}$ are cartesian unit vectors. The primitive unit cell that corresponds to cell vectors $\mathbf{A}_1$, $\mathbf{A}_2$, and $\mathbf{A}_3$ contains a single formula unit. The unit-cell dimension normal to the layers is *c*/3, one third the size of the conventional unit cell (see figure 2 in Aydinol *et al* 1997). To obtain a 4 formula unit cell, the first two cell vectors are doubled: $A'_1 = 2A_1$, $A'_2 = 2A_2$. For an atomic coordinate $\mathbf{r}(j) = x(j)\hat{\mathbf{i}} + y(j)\hat{\mathbf{j}} + z(j)\hat{\mathbf{k}}$, where *x* and *y* are in units of *a*, and *z* is in units of *c*/3, the corresponding cell vectors in the *A* system is

$$\mathbf{r}(j) = (x(j) + \frac{1}{\sqrt{3}}y(j) - \frac{2}{3}z(j), \frac{2}{\sqrt{3}}y(j) - \frac{1}{3}z(j), z(j)). \ (3)$$

To express $\mathbf{r}(j)$ in the A'_j-system, the coefficients of A'_1 and A'_2 in (3) are multiplied by 0.5.

The layer *z*-coordinates are $z(\text{Mn}) = 0$, $z(\text{Li}) = 0.5$, $z(O_1) = 1 - 3z_0$, $z(O_2) = 3z_0$, in units of *c*/3. Note that the unit cell contains two oxygen layers, labeled O_1, and O_2. The internal coordinate, z_0, is typically about 0.25 (Aydinol *et al* 1997).

The transition-metal-layer atomic coordinates (in the primed system) are $(0, 0, 0)$, $(\frac{1}{2}, 0, 0)$, $(0, \frac{1}{2}, 0)$, and $(\frac{1}{2}, \frac{1}{2}, 0)$, where the c-axis coordinate has been set to zero, as in the case of the monoclinic structure. The layers follow the ABC stacking sequence characteristic of fcc metals. The positions of the O_1 layer (a B-type layer, relative to the transition-metal layer, designated an A-type layer) are shifted by $(\frac{1}{2}, \frac{1}{2\sqrt{3}}, 1-3z)$ in (reduced) cartesian units. Using (3), and renormalizing the in-layer coordinates by a factor of 1/2, we obtain a shift, $\Delta r(O_1) = (z, \frac{1}{2}z, 1-3z)$ in primed-cell coordinates. Thus, the O_1 coordinates are obtained by shifting transition-metal layer coordinates by $\Delta r(O_1)$. In a similar way, we find $\Delta r(Li) = (0, \frac{1}{4}, \frac{1}{2})$, and $\Delta r(O_2) = (-z, -\frac{1}{2}z, 3z)$.

3. Results

The systems treated are specified by the alloy concentration, $z = 0.0$ or 0.25, the magnetic structure (either ferromagnetic (F) or antiferromagnetic (AF)), and the crystal structures (either monoclinic (m) or rhombohedral (r)). Considering the two different values of each of these three variables, eight systems were treated, altogether. The calculations were performed using a set of 36 special k-points generated with Monkhorst–Pack indices (4, 4, 4). Equal indices are appropriate, since the three unit cell axes for both the monoclinic and rhombohedral structures described above are comparable in length. For each system, the atomic coordinates and cell coordinates were relaxed to equilibrium. In the alloyed systems, symmetry is broken and the atomic coordinates do not correspond precisely to (1) and (3). Some rumpling of the layers is introduced, for example.

Most of the results quoted correspond to the GGA, although LSDA calculations were also performed. The GGA yielded more realistic structural predictions than LSDA in previous work by Mishra and Ceder (1999) on lithiated Mn oxides.

3.1 *Pristine system*

Before addressing the effect of alloying, we consider the results for the pristine system. We first note that the inclusion of spin polarization lowers the total energy by 2 to 4 eV per formula unit. This is not surprising, considering the large magnetic moment of Mn ($\sim 3\,\mu_B$) in these systems.

As was done by Mishra and Ceder, we compare the energies of different configurations with that for the rhombohedral cell with ferromagnetic ordering. The most stable unalloyed system treated in this work is the monoclinic cell with the AF3 antiferromagnetic structure. (The orthorhombic structure, which is not calculated here, is the most stable structure for the composition, $LiMnO_2$.) The energy difference

$$\Delta E(m, AF, 0) = E(m, AF, 0) -$$
$$E(r, F, 0) = -359(-375) \text{ meV/fu}, \quad (4)$$

where the third argument of E is the alloy concentration, z. The number in parentheses is that given by Mishra and Ceder, and values are normalized per formula unit (fu). The other two energy differences for the pristine system are

$$\Delta E(r, AF, 0) = -178(-36) \text{ meV/fu}, \quad (5)$$

and

$$\Delta E(m, F, 0) = -234(-248) \text{ meV/fu}. \quad (6)$$

The agreement between the present results and those of Mishra and Ceder for $\Delta E(m, F, 0)$ and $\Delta E(m, AF, 0)$ appears satisfactory, in view of the different cell sizes, k-point sampling, and perhaps other minor differences. The reason for the discrepancy in $\Delta E(r, AF, 0)$ is not clear. We obtained substantially different converged cell parameters, particularly c, from Mishra and Ceder for this case: $a = 2.95(2.90)$, and $c = 14.36(13.63)$.

3.2 *Alloy system*

As was the case for pristine system, we find that the inclusion of spin-polarization lowers the total energy of the alloyed system significantly. In the case of the alloyed system (0.25), as in the pure case, the most stable configuration, is found to be the monoclinic structure with AF3 magnetic order. The energy relative to the reference,

$$\Delta E(m, AF, 0.25) = -111 \text{ meV/fu}, \quad (7)$$

however, is much smaller. The monoclinic structure with ferromagnetic order is the next most stable system, with

$$\Delta E(m, F, 0.25) = 50 \text{ meV/fu}. \quad (8)$$

The results indicate that the monoclinic structure, with either type of magnetic order, is destabilized by alloying, when compared with the reference (rhombohedral ferromagnetic). A simple linear extrapolation of the results for the alloyed and pure systems would predict that the rhombohedral ferromagnetic system becomes stable only when the x exceeds about 0.32. Experiment, on the other hand, indicates that the rhombohedral structure is already stabilized at a concentration, $x = 0.1$. The LSDA–GGA calculations, therefore, overestimate the concentration at which the rhombohedral phase is stabilized by Co alloying. We note, however, that the experiments were conducted at room temperature and the calculations correspond to 0 K.

4. Discussion

Spin polarization plays an important role in determining the total energy and phase stability of the Mn-oxide systems under consideration. An accurate treatment of spin polarization is, therefore, essential for the simulation of their structural properties. The present work focuses on the effect of Co-alloying on the structural stability of $LiMnO_2$, which influences its performance as a Li-battery cathode (Armstrong *et al* 1998).

Employing the VASP code, we fully relax the atomic and cell coordinates within the framework of the LSDA–GGA, for both alloyed and unalloyed systems. We find that the predicted destabilizing effect of Co alloying on the monoclinic (in favour of the rhombohedral) structure is underestimated, relative to experiment. It is reasonable to attribute at least part of this discrepancy to shortcomings of the LSDA–GGA approximation. We note, however, two other factors that may contribute, viz. temperature and the disorder of the substitutionally-alloyed Co on the Mn-sublattice. Our calculations do not consider the effect of temperature on the magnetic structure (Tabuchi *et al* 1998; Jang *et al* 1999). At room temperature, $LiMnO_2$ appears to be a disordered local moment system, which makes the Jahn–Teller distortion in the monoclinic structure less robust than at lower temperatures. Furthermore, the disorder of the substitutional Co atoms, not included in the present calculations, is also expected to contribute to the destabilization of the monoclinic structure. This effect could, in principle, be investigated by the use of larger supercells.

Since the LSDA–GGA does not account for the insulating character of the present systems, other treatments of the electron–electron interaction would be of interest. For example, if Co occurs in the 2+ state (Park *et al* 1997), with the corresponding oxidation of Mn to 4+, this charge disproportionation would perhaps be washed out by screening in the LSDA–GGA. Among higher-level treatments of electron correlation, the GW (Massida *et al* 1997) and LDA + U (Bengone *et al* 2000) methods would be desirable, but computationally intensive for the large supercells treated in this work. A Hartree–Fock treatment (Mackrodt and Williamson 1998) might be worthwhile, although the spin-splitting is typically overestimated in that formulation.

Acknowledgements

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