First-principles calculations on \( \text{Li}_x\text{NiO}_2 \): phase stability and monoclinic distortion

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Abstract

The phase diagram of \( \text{Li}_x\text{NiO}_2 \) (0 < \( x < 1 \)) and the evolution of the monoclinic distortion as a function of the lithium content are calculated using a combination of first-principles energy methods and statistical–mechanics techniques. As a function of the temperature different ordered \( \text{Li}_x\text{NiO}_2 \) structures appear in the phase diagram at \( x = 0.25 \), 0.33, 0.4, 0.5 and 0.75. Noteworthy, a new and unsuspected phase, \( \text{Li}_0.4\text{NiO}_2 \), dominates the low-lithium region of the phase diagram. In agreement with experimental results, maxima in monoclinicity (\( a_m/b_m \)) are predicted to occur near \( \text{Li}_{0.75}\text{NiO}_2 \) and \( \text{Li}_{0.4}\text{NiO}_2 \). The coupling between the Li-vacancy ordering and the Jahn–Teller activity of \( \text{Ni}^{3+} \) ions plays a crucial role in the stability of ordered \( \text{Li}_x\text{NiO}_2 \) structures and is at the origin of the monoclinic distortion. As a result, the different electrochemical behavior of \( \text{Li}_x\text{NiO}_2 \) versus \( \text{Li}_x\text{CoO}_2 \) lies in the electronic nature of the involved transition metal cation.

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1. Introduction

\( \text{LiNiO}_2 \) has been the focus of significant attention due to its potential application as electrode in lithium batteries [1]. Its structure (see Fig. 1) can be viewed as an “ordered rock salt” in which alternate layers of \( \text{Li}^+ \) and \( \text{Ni}^{3+} \) ions occur in octahedral sites within the ccp oxygen array, making up a rhombohedral structure [2]. \( \text{LiNiO}_2 \) is isosstructural with \( \text{LiCoO}_2 \), the compound mostly used as positive electrode in rechargeable lithium batteries, though they behave fundamentally different. The \( \text{LiCoO}_2 \) system is well characterized [1], whereas in \( \text{Li}_x\text{NiO}_2 \) the sequence of phase transitions and ordered \( \text{Li}_x\text{NiO}_2 \) structures that occurs during the lithium intercalation/deintercalation is still unclear [1,3–7]. It is assumed that in the range 0.75 < \( x < 1 \) the rhombohedral symmetry of the starting compound is maintained. Between \( \text{Li}_{0.3}\text{NiO}_2 \) and \( \text{Li}_{0.75}\text{NiO}_2 \) a monoclinic region has been claimed to occur, and for compositions below \( \text{Li}_{0.3}\text{NiO}_2 \) a monoclinic symmetry is stable. Ordered structures have been proposed at \( \text{Li}_{0.25}\text{NiO}_2 \) [1,5], \( \text{Li}_{0.33}\text{NiO}_2 \) [1], \( \text{Li}_{0.6}\text{NiO}_2 \) [1,5,8,9], \( \text{Li}_{0.63}\text{NiO}_2 \) [1,9] and \( \text{Li}_{0.75}\text{NiO}_2 \) [1,5,9], though experimental evidence has been reported only at \( x = 0.25 \), 0.33 and \( \text{Li}_{0.63}\text{NiO}_2 \) [1,9].

Despite the potential Jahn–Teller (J–T) activity of \( \text{Ni}^{3+} \) cations, \( \text{LiNiO}_2 \) adopts rhombohedral symmetry in the R-3m space group at any temperature [10]. Removal of lithium from \( \text{LiNiO}_2 \) leads to monoclinic phase \( \text{Li}_x\text{NiO}_2 \) with 0.4 < \( x < 0.75 \) [1,3,4,9]. The origin of this large monoclinic region is controversial. One possible and obvious driving force is a cooperative distortion of \( \text{NiO}_2 \) octahedra [3,5,11] due to the Jahn–Teller effect of trivalent nickel ions. However, as has been claimed by some authors [1,9], this cause of the monoclinicity is somewhat unlikely: since a cooperative J–T distortion is not present in \( \text{LiNiO}_2 \), it is unlikely that a material with a lower concentration of J–T distorted \( \text{Ni}^{3+} \) octahedra could have a collective J–T distortion. Since lithium removal also creates vacancies, Li-vacancy ordering can take place. Hence, it has been speculated that such Li ordering may be the cause of the monoclinic distortion in partially delithiated \( \text{Li}_x\text{NiO}_2 \) [1,9].

As a first-principles calculation gives detailed information on the local structure as function of composition, it may be useful to further clarify the phase diagram of \( \text{Li}_x\text{NiO}_2 \) as well as the origin of the monoclinic distortion. First-principles refers to the use of quantum mechanics to determine the structure or properties of materials at 0 K. A combination of first-principles total energy calculations and statistical–mechanics allows to obtain finite-temperature thermodynamic properties. Here we report on the phase stability of \( \text{Li}_x\text{NiO}_2 \) as a function of concentration and temperature, and
examine the evolution of the monoclinic distortion with the lithium content at room temperature. We will show that the particular behavior found in Li\textsubscript{16}NiO\textsubscript{2} is related to the Jahn–Teller activity of Ni\textsuperscript{3+} ions coupled to the Li-vacancy ordering.

2. Method

The theoretical background to obtain a phase diagram from first-principles calculations can be found in some of our previous work [12–14]. The methodology followed in the Li\textsubscript{x}NiO\textsubscript{2} system for the phase diagram and monoclinicity is detailed in [14–16].

3. Results

3.1. Phase diagram

During the cycling of a lithium cell the lithium ions are reversibly removed from and reinserted into Li\textsubscript{x}NiO\textsubscript{2} creating or annihilating vacancies within the triangular lithium planes. Li-vacancy ordered structures can appear at several characteristic Li compositions depending on the relative magnitude of the first, second and further neighbor’s interactions [13,17]. In a first-principles study of the Li\textsubscript{16}CoO\textsubscript{2} system [12], we found the interactions between Li ions to be mainly repulsive and decaying with distance, as they are likely determinate by screened electrostatics and some oxygen displacement. In layered LiMO\textsubscript{2} different lithium planes are relatively far apart (\sim 5 Å) and are separated by the transition-metal layer, so in principle no important interlayer Li–Li interactions are expected, as was found in Li\textsubscript{16}CoO\textsubscript{2} [12,13]. Contrary to this, in Li\textsubscript{x}NiO\textsubscript{2} non-negligible attractive interactions exist between Li ions in different planes [14,16]. In particular we found that the interaction between Li ions that are on the extensions of linear O–Ni–O bonds is crucial for stabilizing some of the ordered ground states in the phase diagram [14]. In a comparative study [16], we found that all Li\textsubscript{x}NiO\textsubscript{2} structures with such 180° Li\textsubscript{A}–O–Ni\textsuperscript{3+}O–Li\textsubscript{B} configurations have lower energy than structures without these configurations but with the same in-plane lithium ordering.

Fig. 2 shows the calculated equilibrium phase diagram for Li\textsubscript{x}NiO\textsubscript{2}. Ordered structures of lithium ions and vacancies appear at Li\textsubscript{x}NiO\textsubscript{2} with \( x = 0.25, 0.33, 0.4, 0.5 \text{ and } 0.75 \) (gray regions in Fig. 1). These ordered regions are separated by domains of two-phase coexistence. At room temperature all phase transitions detected in this system are first order. Fig. 3 shows the predicted most stable Li-vacancy distribution at several ordered compositions. The most stable Li-vacancy arrangements for Li\textsubscript{0.25}NiO\textsubscript{2} and Li\textsubscript{0.33}NiO\textsubscript{2} in

Fig. 1. Schematic representation of the LiNiO\textsubscript{2} structure. Lithium ions in planes A and B are denoted with solid gray circles and diamonds. The diamonds are those Li ions that are at the extension of the Ni–O bond forming 180° Li\textsubscript{A}–O–Ni\textsuperscript{3+}O–Li\textsubscript{B} complexes. The cell with rhombohedral symmetry in the hexagonal setting is indicated by dashed lines. An hypothetical distortion of the Ni–O octahedra due to J–T effect is indicated by a dotted line, with the basic monoclinic cell indicated by bold lines.

Fig. 2. Calculated phase diagram of Li\textsubscript{x}NiO\textsubscript{2}. The gray areas represent ordered Li\textsubscript{x}NiO\textsubscript{2} regions. The insets show the Li-vacancy distribution in the ordered structures stable at room temperature. Li ions are denoted by circles and vacancies by squares.

Fig. 3. Lowest energy Li-vacancy arrangements in Li\textsubscript{16}NiO\textsubscript{2} at \( x \) values of 0.25, 0.33, 0.4 and 0.75. The big black circles denote the in-plane lithium orderings and the small black circles designate the positions of the Li ions in the adjacent plane. Dashed line indicates the 180 Li–O–Ni\textsuperscript{3+}O–Li configurations (see Fig. 1). Ni\textsuperscript{3+} ions are indicated by dark gray circles and Ni\textsuperscript{4+} ions by light gray circles.
the calculations agree with the experimental models from selected area electron diffraction data (SAED) [1]. We furthermore predicted particular ordered configurations at compositions \( \text{Li}_{0.75}\text{NiO}_2 \) and \( \text{Li}_{0.5}\text{NiO}_2 \), where a different ordering has been postulated [1,8,9] but no experimental characterization has been performed. In the region \( 0.5 < x < 0.75 \) first-principles calculations do not agree with the model proposed by Peres et al. to explain the ordered structure found by SAED in a sample of nominal composition \( \text{Li}_{0.63}\text{Ni}_{1.01}\text{O}_2 \) [9]. At \( \text{Li}_{0.4}\text{NiO}_2 \) we predict a stable phase with rows of nearest neighbors dumbbells. While this phase dominates the phase diagram at low-lithium concentration, it has not been considered in any previous work. Notice that at each composition the lowest energy structures gives a relation between ordering in successive planes so that \( \text{Li}-\text{Li} \) or vacancy–vacancy pairs exist along the O–Ni\(^{3+}\)O extensions, but never a Li–vacancy pair. These \( \text{Li}_x\text{O}–\text{Ni}^{3+}–\text{O}–\text{Li}_y \) complexes are shown by the dotted lines in Fig. 3.

The calculated phase diagram corresponds to stoichiometric \( \text{LiNiO}_2 \). However, in \( \text{LiNiO}_2 \) some departure from stoichiometry is unavoidable, and a compound \( \text{Li}_{1-x}\text{Ni}_{1+x}\text{O}_2 \) is obtained [1]. The introduction of some disorder in \( \text{LiNiO}_2 \) will decrease the temperature of the order–disorder transition. The disorder introduced by the Ni excess can also affect the character of the phase transformations.

### 3.2. Monoclinic distortion in \( \text{Li}_x\text{NiO}_2 \)

In a monoclinic cell a measure of the departure from the rhombohedral symmetry is given by the ratio between the \( a \) and \( b \) monoclinic lattice parameters, \( a_m/b_m \) (see Fig. 1). In an undistorted rhombohedral structure, this value would be \( \sqrt{3} \). Following the methodology detailed in [15] we have calculated the evolution of the monoclinicity \( a_m/b_m \) with the composition at room temperature. This result is shown in Fig. 4. Experimental data taken from Li et al. [4] are also plotted for comparison. In the region where experimentally monoclinicity is observed (\( 0.4 < x < 0.75 \)) the monoclinicity varies considerably as the stable Li-vacancy ordering varies with composition. The calculated \( a_m/b_m \) value decreases slightly in the range \( 1 < x < 0.8 \). Then around \( \text{Li}_{0.75}\text{NiO}_2 \) there is a maximum, followed by a drop in the monoclinicity. A second maximum appears near \( \text{Li}_{0.4}\text{NiO}_2 \). The calculated data in Fig. 4 are in qualitative agreement with the experimental data. However, some quantitative discrepancies in composition and magnitude between the experimental and calculated monoclinicity maxima seems to be present. This is likely due to the fact that experiments are always performed on non-stoichiometric \( \text{Li}_{1-x}\text{Ni}_{1+x}\text{O}_2 \) [1].

We have previously reported that in \( \text{Li}_x\text{NiO}_2 \) lithium ordering couples to orbital and Jahn–Teller ordering so as to produce long-range attractive interaction between Li ions in different planes [16]. In the previous section, we have shown that this \( 180^\circ \) \( \text{Li}_x\text{O}–\text{Ni}^{3+}–\text{O}–\text{Li}_y \) complexes are present in all the most stable \( \text{Li}_x\text{NiO}_2 \) structures. We review how the monoclinic distortion arises because of this unusual synergetic effect between the Li-vacancy ordering and the Jahn–Teller activity of \( \text{Ni}^{3+} \).

In an octahedral environment, the five \( d \) orbitals of a transition metal atom split in two groups; the \( t_2g \) group (\( d_{xy}, d_{xz}, d_{yz} \)) pointing away from oxygen atoms, and the \( e_g \) group (\( d_{x^2−y^2}, d_{z^2} \)). The latter overlap directly with the \( p_x, p_y \) and \( p_z \) oxygen orbitals forming bonding \( e_g \) bands and antibonding \( e_g^* \) bands. The antibonding \( e_g^* \) bands are predominantly \( d \) in character, and lie above the \( t_2g \) bands. Each oxygen at the vertex of \( \text{M} \) octahedral is also connected through the \( 2p_x, 2p_y, \) and \( 2p_z \) orbitals to the 2s orbital of a lithium ion, so that one of these lithium ions is “sharing” an \( O \) 2p orbital with \( \text{M} \) (see Fig. 8 in [16]). These Li 2s orbitals, oxygen 2p and metal \( e_g^* \) orbitals have the proper symmetry to hybridize. When the transition metal has empty \( e_g^* \) orbitals, as is the case in \( \text{LiCoO}_2 \), the hybridization of the \( e_g^* \) orbitals with Li 2s orbitals will not affect the energy. However, in \( \text{Li}_x\text{NiO}_2 \) the presence of Li ions at the extension of a Ni–O bond lowers the energy of that filled Ni \( e_g^* \) orbital. Since the energy of Jahn–Teller distortion is largest when charge is localized in completely filled spin orbitals, Li ions will preferentially hybridize with the same \( e_g^* \) orbital. This leads to attractive inter-planar Li interactions whenever those Li ions hybridize with the same \( e_g^* \) orbital, i.e. whenever they form a \( 180^\circ \) \( \text{Li}_x\text{O}–\text{M}–\text{O}–\text{Li}_y \) configuration. As we showed in the previous section, these interactions are crucial in the stability of ordered \( \text{Li}_x\text{NiO}_2 \) structures. Furthermore, the lining up of Li along one or two octahedral axis around \( \text{Ni}^{3+} \), with vacancies along the other one, produces a remarkably stable Jahn–Teller distorted configuration. In this way, at \( x = 0.4 \) and 0.75 the stable Li orderings are particularly conducive to Jahn–Teller distortion, thereby creating two maxima in the monoclinicity. In \( \text{Li}_x\text{NiO}_2 \) all Li sites are filled and the Jahn–Teller distortion is not assisted by the Li-vacancy ordering. Therefore, the distortion is expected to be somewhat smaller in magnitude, giving only a weak (in calculations) or non-existent (in experiments) Jahn–Teller distortion.

![Fig. 4. Calculated variation of \( a_m/b_m \) vs. \( x \) in \( \text{Li}_x\text{NiO}_2 \) at room temperature. Experimental data taken from [4] are also plotted for comparison.](image_url)
4. Summary

We have performed a first-principles investigation of phase stability in stoichiometric Li$_x$NiO$_2$ for $0 < x < 1$, and analyzed the evolution of the monoclinic distortion as a function of the lithium content. The calculated results are in good agreement with experiments. We explain the stability of ordered Li$_x$NiO$_2$ structures and the monoclinic distortion by long-range attractive inter-plane Li–Li interactions related to the charge distribution and electronic structure of the Ni$^{3+}$ ions. Therefore, the different electrochemical behavior found in isostructural Li$_x$NiO$_2$ and Li$_x$CoO$_2$ is due to the electronic nature of the involved M cations.

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