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First-principles theory of doping in layered oxide electrode materials

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Doping lithium-ion battery electrode materials LiMO_2 ($M = \text{Co}, \text{Ni}, \text{Mn}$) with impurities has been shown to be an effective way to optimize their electrochemical properties. Here, we report a detailed first-principles study of layered oxides LiCoO_2 , LiNiO_2 , and LiMnO_2 lightly doped with transition-metal (Fe, Co, Ni, Mn) and non-transition-metal (Mg, Al) impurities using hybrid-density-functional defect calculations. We find that the lattice site preference is dependent on both the dopant's charge and spin states, which are coupled strongly to the local lattice environment and can be affected by the presence of co-dopant(s), and the relative abundance of the host compound's constituting elements in the synthesis environment. On the basis of the structure and energetics of the impurities and their complexes with intrinsic point defects, we determine all possible low-energy impurity-related defect complexes, thus providing defect models for further analyses of the materials. From a materials modeling perspective, these lightly doped compounds also serve as model systems for understanding the more complex, mixed-metal, LiMO_2 -based battery cathode materials.

I. INTRODUCTION

Layered transition-metal oxides LiMO_2 ($M = \text{Co}, \text{Ni}, \text{Mn}$) and, especially, their derivatives such as $\text{Li}(\text{Ni}, \text{Co}, \text{Mn})\text{O}_2$ [NCM, also known as NMC] and $\text{Li}(\text{Ni}, \text{Co}, \text{Al})\text{O}_2$ [NCA] have been widely used as cathode materials in lithium-ion batteries.^{1,2} These materials are known to exhibit rich defect physics resulted from the ability of the transition-metal ions to exist in different charge and spin states and the strong coupling between charge, spin, and local atomic structures.³⁻⁵ Doping LiMO_2 with transition-metal and non-transition-metal impurities has been shown to be an effective way to optimize the electrochemical performance.⁶⁻¹⁹ Here, the impurities (i.e., dopants) can be incorporated into LiMO_2 at the transition-metal (M) and/or Li sites and the lattice site preference of some of the dopants may be dependent on the experimental conditions during synthesis. Understanding the effects of doping requires a detailed understanding of the interaction between the dopant and the host, including intrinsic point defects that may present in the host compound, under the synthesis conditions.

Computationally, there have been a number of first-principles studies of doping in LiMO_2 using density-functional theory (DFT) within the standard local-density approximation or generalized-gradient approximation or the DFT+ U extension (where U is the on-site Hubbard correction).²⁰⁻²⁷ These studies have provided useful information on several aspects of the doped materials, including their atomic and electronic structure and the solubility of the dopants. However, the methods used in these previous studies are known to have limited predictive power in complex transition-metal oxides. Even within the DFT+ U extension, Santana et al.,²¹ for example, showed that the results are strongly dependent on the choice of the U value for the $3d$ orbitals of the transition metal of the host. The problem becomes more challenging when the dopant itself is another transition metal. A more rigorous approach is thus needed to de-

scribe the physics of the doped LiMO_2 systems, including the ability to properly address the coupling between charge, spin, and local atomic structures.

In this work, we carry out a detailed and systematic study of doping in LiMO_2 using first-principles defect calculations based on a hybrid DFT/Hartree-Fock approach and our accumulated knowledge^{3,4} of the bulk properties and intrinsic point defects in the layered oxides. Specific impurities considered include Mg and Al, which have been reported to have beneficial effects on the performance of LiMO_2 , and transition metals Mn, Co, and Ni, often employed in ion substitution. From a materials modeling perspective, LiMO_2 doped with a low concentration of impurities can be considered as model systems for understanding the more complex, mixed-metal oxides such as NCM and NCA. For example, as a first approximation, Ni-rich materials $\text{LiNi}_{1-x-y}\text{Co}_x\text{Mn}_y\text{O}_2$ and $\text{LiNi}_{1-x-y}\text{Co}_x\text{Al}_y\text{O}_2$,²⁸ can be regarded as LiNiO_2 doped with (Co,Mn) and (Co,Al), respectively. Highly doped LiMO_2 materials such as $\text{NCM}_{1/3}$ and $\text{NCA}_{1/3}$ (i.e., $x = y = 1/3$) have been previously investigated.⁵ The focus of the current work is on the lattice site preference of the dopants, charge and spin states of the dopants and the transition-metal ions in the host, and effects of co-doping. This study will provide physical insights into the dopant-host interaction and possible effects on the electrochemical performance of LiMO_2 -based materials.

II. METHODOLOGY

The total-energy calculations are based on DFT with the Heyd-Scuseria-Ernzerhof (HSE06) screened hybrid functional,³⁰ as implemented in the Vienna *Ab Initio* Simulation Package (VASP).³¹ The Hartree-Fock mixing parameter (α) and the screening length are set to the standard values of 0.25 and 10 Å, respectively. The metal impurities in LiMO_2 , in the dilute doping limit, are modeled using 108-atom hexagonal supercells^{3,4} and a plane-

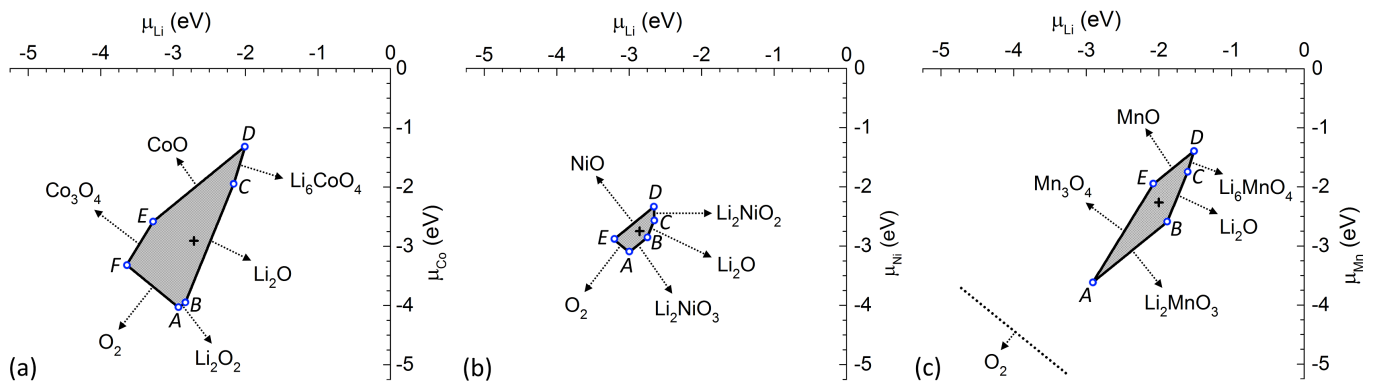


FIG. 1. Chemical-potential diagrams for LiMO_2 : (a) $M = \text{Co}$, (b) $M = \text{Ni}$, and (c) $M = \text{Mn}$, produced using data from Refs. 3 and 4. Only Li–M–O phases that define the stability region of LiMO_2 , shown as a shaded polygon, are included; in (c), O_2 is also included for reference. Point X inside the stability region [not to be confused with defect X in Eq. (1)] is marked by a cross. Explicit values of the atomic chemical potentials at representative points in the stability region are reported in Ref. 29.

wave basis-set cutoff of 500 eV; integrations over the supercell Brillouin zone are carried out using the Γ point. In these calculations, the lattice parameters are fixed to the calculated bulk values of LiMO_2 but all the internal coordinates are fully relaxed; the ferromagnetic spin configuration for the transition metal array in the lattice is used and spin polarization is included. Convergence with respect to self-consistent iterations is assumed when the total-energy difference between cycles is less than 10^{-4} eV and the residual forces are less than 0.01 eV/Å. We thus use the same calculation set-ups as in our previous work on bulk properties and intrinsic point defects in LiMO_2 ^{3,4} to ensure the transferability of the results.

The likelihood of an intrinsic defect, impurity or dopant (extrinsic defect), or defect complex X, hereafter often referred commonly to as “defect”, in charge state q being incorporated into a crystal is characterized by its formation energy, defined as

$$E^f(X^q) = E_{\text{tot}}(X^q) - E_{\text{tot}}(\text{bulk}) - \sum_i n_i \mu_i + q(E_v + \mu_e) + \Delta^q, \quad (1)$$

where $E_{\text{tot}}(X^q)$ and $E_{\text{tot}}(\text{bulk})$ are, respectively, the total energy of a supercell containing the defect X and that of a supercell of the perfect material. μ_i is the atomic chemical potential of species i (and is referenced to bulk metals or O_2 molecules at 0 K). n_i is the number of atoms of species i that have been added ($n_i > 0$) or removed ($n_i < 0$) to form the defect. μ_e is the electronic chemical potential, i.e., the Fermi level, that is, as a convention, referenced to the valence-band maximum (VBM) in the perfect bulk (E_v); the actual position of the Fermi level is determined by the charge neutrality condition that involves all defects and any other charge carriers that may be present in the material.^{3,4} Δ^q is the correction term to align the electrostatic potentials of the bulk and defect supercells and to account for finite-size effects on the total energies of charged defects, estimated following the procedure of Freysoldt et al.³² The total static dielectric con-

stants used in the calculation of Δ^q are 13.02, 15.45, and 32.52 for LiCoO_2 , LiNiO_2 , and LiMnO_2 , respectively.^{3,4}

The atomic chemical potentials of Li, M, and O in LiMO_2 are subject to thermodynamic constraints and can be used to represent the experimental situations, e.g., during materials preparation. These constraints are to ensure that the host compound LiMO_2 is thermodynamically stable.^{3,4} Figure 1 shows the chemical-potential diagrams for LiMO_2 in which the stability region is determined by considering equilibria with other Li–M–O phases. The results have been reported in Refs. 3 and 4 but are also produced here as we will frequently refer to these diagrams when discussing the results for the impurities. For the impurities in LiMO_2 , the lower limit of their chemical potentials is minus infinity and the upper limit is zero, with respect to the total energy per atom of the bulk metals. Stronger bounds on the impurity chemical potentials can be estimated based on other solubility-limiting phases formed between the impurities and the host constituents.³³ In the following, the chemical potentials of Mg, Al, Mn, Fe, Co, and Ni impurities are set as $\mu_{\text{Mg}} = -6.00$ eV, $\mu_{\text{Al}} = -9.00$ eV, $\mu_{\text{Mn}} = -6.00$ eV, $\mu_{\text{Fe}} = -5.00$ eV, $\mu_{\text{Co}} = -4.00$ eV, and $\mu_{\text{Ni}} = -4.00$ eV. These choices are somewhat arbitrary; however, they in no way affect the physics of what we are presenting as we are interested only in the relative formation energies of the impurities associated with different set of the atomic chemical potentials of the host constituents which correspond to different points in the chemical-potential diagram presented in Fig. 1. Formation energies for other values of the chemical potentials of the impurities, if desirable, can be easily obtained from the data we report.

We also investigate selected heavily doped LiMO_2 systems, using smaller, 24-atom hexagonal supercells. In these calculations, one (or two, in the case of co-doping) atom of the host is substituted by the impurity atom(s), and the cell volume and shape and internal coordinates are all relaxed. Integrations over the Brillouin zone are carried out using a Γ -centered $11 \times 6 \times 2$ k -point mesh to

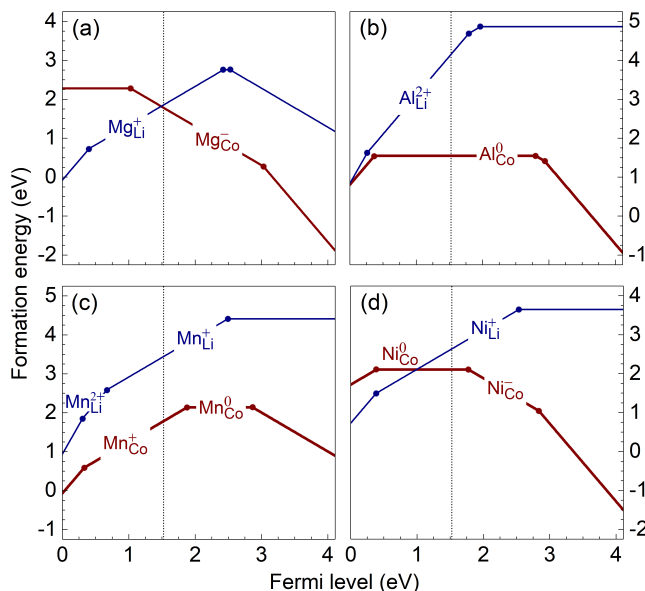


FIG. 2. Formation energies of substitutional impurities at the Li and Co lattice sites in LiCoO_2 obtained at point X [marked by a cross in the chemical-potential diagram in Fig. 1(a)], plotted as a function of Fermi level from the VBM to the conduction-band minimum (CBM) of the undoped compound: (a) Mg, (b) Al, (c) Mn, and (d) Ni. The slope in the energy plots indicates the charge state (q). For each defect, only the true charge states are indicated. The vertical dotted line marks the Fermi level of undoped LiCoO_2 , μ_e^{int} , determined by the intrinsic point defects as reported in Ref. 3

obtain high-quality electronic densities of states.

Finally, we note that smaller values of the mixing parameter α have also been employed in studies of the layered oxides using the HSE06 functional.³⁴ For reasonable choices of α values, however, the main difference is only in the calculated band-gap values; see Fig. 1 of Ref. 29. As discussed in Ref. 3 and references therein, the defect formation energy at the Fermi level determined by the charge neutrality condition is usually not sensitive to the calculated band gap, provided that the calculations can capture the essential physics near the band edges.

III. RESULTS AND DISCUSSION

A. LiCoO_2

Figure 2 shows the formation energies of substitutional Mg, Al, Mn, Fe, and Ni impurities at the Co and Li sites in LiCoO_2 , obtained under the conditions at point X in the chemical-potential diagram [Fig. 1(a)]. We find that each impurity has only one or two true charge states (hereafter also called elementary defects) among possible values of q ; the other charge states correspond to complexes consisting of the elementary defects and hole (η^+) or electron (η^-) polaron(s). Note that, in LiCoO_2 ,

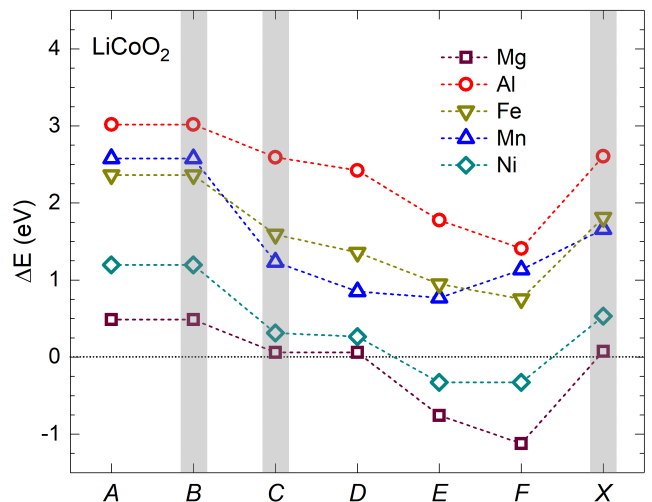


FIG. 3. Difference between the formation energies at the Co and Li sites, obtained under the conditions at points A–F and X in Fig. 1(a). $\Delta E > 0$ means the impurity is energetically more favorable at the Co site. Points B, C, and X can be regarded as representing more realistic synthesis conditions.

Co is stable as low-spin Co^{3+} ; η^+ (η^-) is the localized hole (electron) and local lattice distortion associated with the low-spin Co^{4+} (high-spin Co^{2+}) ion at the Co lattice site.³ Taken the Mn impurity as an example, Mn_{Co}^0 (i.e., high-spin Mn^{3+} at the Co site) and Mn_{Co}^+ (i.e., Mn^{4+} at the Co site) are elementary defects, as indicated in Fig. 2(c), whereas Mn_{Co}^- is a complex of Mn_{Co}^0 and η^- and Mn_{Co}^+ is a complex of Mn_{Co}^+ and η^+ . In this case, $q = 0$ and $+$ are true charge states; $q = -$ and $2+$ are regarded only as nominal charge states. Similarly, on the Li sublattice, Mn_{Li}^+ (i.e., high-spin Mn^{2+} at the Li site) and $\text{Mn}_{\text{Li}}^{2+}$ (i.e., high-spin Mn^{3+} at the Li site) are elementary defects; Mn_{Li}^0 is a complex of Mn_{Li}^+ and η^- .

In the following, we focus on the structure and energetics of the most stable defect configurations at the Fermi-level position of undoped LiCoO_2 , specifically at μ_e^{int} that is determined by the intrinsic point defects in the undoped compound for a given set of the atomic chemical potentials,³ e.g., as indicated by the vertical dotted line in Fig. 2. Under the conditions at point X in Fig. 1(a), chosen as representative conditions for the presentation purpose, Mg is most stable as Mg_{Co}^- (Mg_{Li}^+) on the Co (Li) sublattice, whereas Al is most stable as Al_{Co}^0 ($\text{Al}_{\text{Li}}^{2+}$), Mn as Mn_{Co}^+ (Mn_{Li}^+), and Ni as Ni_{Co}^0 (Ni_{Li}^+) on the Co (Li) sublattice; see Fig. 2. Fe (not included in the figure) is most stable as Fe_{Co}^0 (Fe_{Li}^+) on the Co (Li) sublattice. It is noted that, since the intrinsic-defect landscape (and hence the Fermi level μ_e^{int}) varies as a function of the atomic chemical potentials,³ the lattice site and charge (and spin) state preference of the impurities may also be different for different points in the chemical-potential diagram in Fig. 1(a), as discussed in more detail below.

To quantify the lattice site preference of the impuri-

TABLE I. Defect models for the impurities (dopants) in LiMO₂ (M = Co, Ni, Mn) under the conditions at different points in the chemical-potential diagrams (Fig. 1). Only the most stable configurations are included; other configurations that are close in energy are listed in the footnotes.

	Dopant	<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>	<i>E</i>	<i>F</i>	<i>X</i>
LiCoO ₂	Mg	Mg _{Co} ⁻ - η ⁺	Mg _{Co} ⁻ - η ⁺	Mg _{Co} ⁻ - η ⁺ ^a	Mg _{Co} ⁻ - Co _{Li} ⁺ ^b	Mg _{Li} ⁺ - V _{Li} ⁻	Mg _{Li} ⁺ - V _{Li} ⁻	Mg _{Co} ⁻ - η ⁺ ^c
	Al	Al _{Co} ⁰	Al _{Co} ⁰	Al _{Co} ⁰	Al _{Co} ⁰	Al _{Co} ⁰	Al _{Co} ⁰	Al _{Co} ⁰
	Fe	Fe _{Co} ⁰	Fe _{Co} ⁰	Fe _{Co} ⁰	Fe _{Co} ⁰	Fe _{Co} ⁰	Fe _{Co} ⁰	Fe _{Co} ⁰
	Mn	Mn _{Co} ⁺ - Li _{Co} ²⁻ - η ⁺	Mn _{Co} ⁺ - Li _{Co} ²⁻ - η ⁺	Mn _{Co} ⁰	Mn _{Co} ⁰	Mn _{Co} ⁺ - V _{Li} ^{-d}	Mn _{Co} ⁺ - V _{Li} ⁻	Mn _{Co} ⁰
	Ni	Ni _{Co} ⁰	Ni _{Co} ⁰	Ni _{Co} ⁰	Ni _{Co} ⁰	Ni _{Li} ⁺ - V _{Li} ⁻	Ni _{Li} ⁺ - V _{Li} ⁻	Ni _{Co} ⁰
LiNiO ₂	Mg	Mg _{Ni} ⁻ - η ⁺	Mg _{Ni} ⁻ - η ⁺	Mg _{Ni} ⁻ - η ⁺ ^e	Mg _{Li} ⁺ - η ^{-f}	Mg _{Li} ⁺ - η ^{-f}		Mg _{Ni} ⁻ - η ⁺ ^g
	Al	Al _{Ni} ⁰	Al _{Ni} ⁰	Al _{Ni} ⁰	Al _{Ni} ⁰	Al _{Ni} ⁰		Al _{Ni} ⁰
	Fe	Fe _{Ni} ⁰	Fe _{Ni} ⁰	Fe _{Ni} ⁰	Fe _{Ni} ⁰	Fe _{Ni} ⁰		Fe _{Ni} ⁰
	Mn	Mn _{Ni} ⁺ - η ^{-h}	Mn _{Ni} ⁺ - η ^{-h}	Mn _{Ni} ⁺ - η ⁻	Mn _{Ni} ⁺ - η ⁻	Mn _{Ni} ⁺ - η ⁻		Mn _{Ni} ⁺ - η ⁻
	Co	Co _{Ni} ⁰	Co _{Ni} ⁰	Co _{Ni} ⁰	Co _{Ni} ⁰	Co _{Ni} ⁰		Co _{Ni} ⁰
LiMnO ₂	Mg	Mg _{Li} ⁺ - V _{Li} ⁻ⁱ	Mg _{Mn} ⁻ - η ^{+j}	Mg _{Mn} ⁻ - Mn _{Li} ⁺	Mg _{Mn} ⁻ - Mn _{Li} ⁺	Mg _{Mn} ⁻ - Mn _{Li} ⁺		Mg _{Mn} ⁻ - Mn _{Li} ⁺ ^k
	Al	Al _{Mn} ⁰	Al _{Mn} ⁰	Al _{Mn} ⁰	Al _{Mn} ⁰	Al _{Mn} ⁰		Al _{Mn} ⁰
	Fe	Fe _{Mn} ⁰	Fe _{Mn} ⁰	Fe _{Mn} ⁰	Fe _{Mn} ⁰	Fe _{Mn} ⁰		Fe _{Mn} ⁰
	Co	Co _{Mn} ^l	Co _{Mn} ⁰	Co _{Mn} ⁰ - Mn _{Li} ⁺ ^m	Co _{Mn} ⁰ - Mn _{Li} ⁺	Co _{Mn} ⁰ - Mn _{Li} ⁺		Co _{Mn} ⁰ - Mn _{Li} ⁺ ⁿ
	Ni	Ni _{Mn} ⁻ - η ^{+o}	Ni _{Mn} ⁻ - η ^{+p}	Ni _{Mn} ⁻ - Mn _{Li} ⁺ ^q	Ni _{Mn} ⁻ - Mn _{Li} ⁺	Ni _{Mn} ⁻ - Mn _{Li} ⁺		Ni _{Mn} ⁻ - Mn _{Li} ⁺ ^r

^aMg_{Co}⁻ - Co_{Li}⁺ (+0.01 eV) and Mg_{Li}⁺ - η⁻ (+0.05 eV). ^bMg_{Li}⁺ - η⁻ (+0.05 eV). ^cMg_{Li}⁺ - V_{Li}⁻ (+0.21 eV). ^dMn_{Co}⁰ (+0.19 eV). ^eMg_{Li}⁺ - η⁻ (+0.15 eV). ^fMg_{Ni}⁻ - η⁺ (+0.08 eV) and Mg_{Ni}⁻ - Ni_{Li}⁺ (+0.20 eV). ^gMg_{Li}⁺ - η⁻ (+0.14 eV). ^hMn_{Ni}⁺ - Li_{Ni}²⁻ - η⁺ (+0.23 eV). ⁱMg_{Mn}⁻ - η⁺ (+0.12 eV). ^jMg_{Li}⁺ - Li_{Mn}²⁻ - η⁺ (+0.14 eV) and Mg_{Mn}⁻ - Mn_{Li}⁺ (+0.23 eV). ^kMg_{Mn}⁻ - η⁺ (+0.21 eV). ^lCo_{Li}⁺ - V_{Li}⁻ (+0.21 eV). ^mCo_{Mn}⁰ (+0.15 eV) and Co_{Mn}⁰ - Li_i⁺ (+0.21 eV). ⁿCo_{Mn}⁰ (+0.04 eV). ^oNi_{Li}⁺ - V_{Li}⁻ (+0.10 eV) and Ni_{Mn}⁻ - Mn_{Li}⁺ (+0.21 eV). ^pNi_{Mn}⁻ - Li_i⁺ (+0.15 eV) and Ni_{Mn}⁻ - Mn_{Li}⁺ (+0.21 eV). ^qNi_{Mn}⁻ - Li_i⁺ (+0.22 eV). ^rNi_{Mn}⁻ - η⁺ (+0.24 eV).

ties over the substitutional sites in LiMO₂, we define the energy difference

$$\Delta E = E^f(X_{Li}^{q1}) - E^f(X_M^{q2}), \quad (2)$$

where $E^f(X_{Li}^{q1})$ and $E^f(X_M^{q2})$ are the formation energies (at μ_e^{int}) of the lowest-energy defect configurations at the Li and M sites, respectively. Here, $\Delta E > 0$ means the impurity X is energetically more favorable as X_M^{q2} (i.e., at the M site) than as X_{Li}^{q1} (the Li site), whereas $\Delta E \sim 0$ indicates that the impurity can be incorporated both on the M and Li sites with almost equal concentrations.

Figure 3 shows the formation-energy difference between the Co and Li sites under the conditions at different points in the chemical-potential diagram [Fig. 1(a)]. We find that the impurities prefer the Co site over the Li site ($\Delta E > 0$), except Mg and Ni which can be energetically more favorable at the Co or Li site depending on the synthesis conditions. More specifically, when considered as isolated defects, Al is most stable as Al_{Co}⁰ (i.e., Al³⁺ at the Co site), Fe as Fe_{Co}⁰ (i.e., high-spin Fe³⁺ at the Co site), and Mn as Mn_{Co}⁺, independent of the atomic chemical potentials. Mg is most stable as Mg_{Co}⁻ (i.e., Mg²⁺ at the Co site) under the conditions at points *A* – *D* and *X* or Mg_{Li}⁺ (i.e., Mg²⁺ at the Li site) at points *E* and *F*. Finally, Ni is most stable as Ni_{Co}⁰ (i.e., low-spin Ni³⁺ at the Co site) under the conditions at points *A* – *C* and *X*, Ni_{Co}⁻ (i.e., high-spin Ni²⁺ at the Co site) at point *D*, or Ni_{Li}⁺ (i.e., Ni²⁺ at the Li site) at points *E* and *F*.

Overall, the lattice site preference of the impurities in LiCoO₂ does not have a simple dependence on the ionic-radius difference between the dopant and the substituted host ion, but is determined by both the dopant's charge and spin states and the relative abundance of the host's constituting elements in the synthesis environment. We note that the charge and spin states are coupled strongly to the local lattice environment and thus also determine the dopant's ionic radius. The relative abundance of the host constituents is represented by the atomic chemical potentials in our computational approach (see Sec. II).

We also consider a neutral (Ni,Mn) pair in LiCoO₂ with both dopants on the Co sublattice and find that it is most stable as (Ni²⁺, Mn⁴⁺), i.e., a complex of Ni_{Co}⁻ and Mn_{Co}⁺, which indicates charge transfer between the two impurities. The lowest-energy configuration of the pair corresponds to the shortest distance (2.82 Å) between oppositely charged defects Mn_{Co}⁺ and Ni_{Co}⁻, as expected due to the Coulomb interaction. In this configuration, the binding energy (E_b) of the complex is 0.67 eV with respect to isolated Ni_{Co}⁻ and Mn_{Co}⁺. It is noted that, as an isolated defect, Ni can be stable as Ni²⁺ or Ni³⁺ on the the Co sublattice, as presented earlier. Yet in the (Ni,Mn) pair the Ni²⁺ is always more stable. The results thus indicate that the dopant's charge and spin states can be affected by the presence of a co-dopant. It is also this impurity-impurity interaction between the transition-metal ions on the Co sublattice that causes the charge ordering observed in NCM_{1/3}.⁵ For comparison,

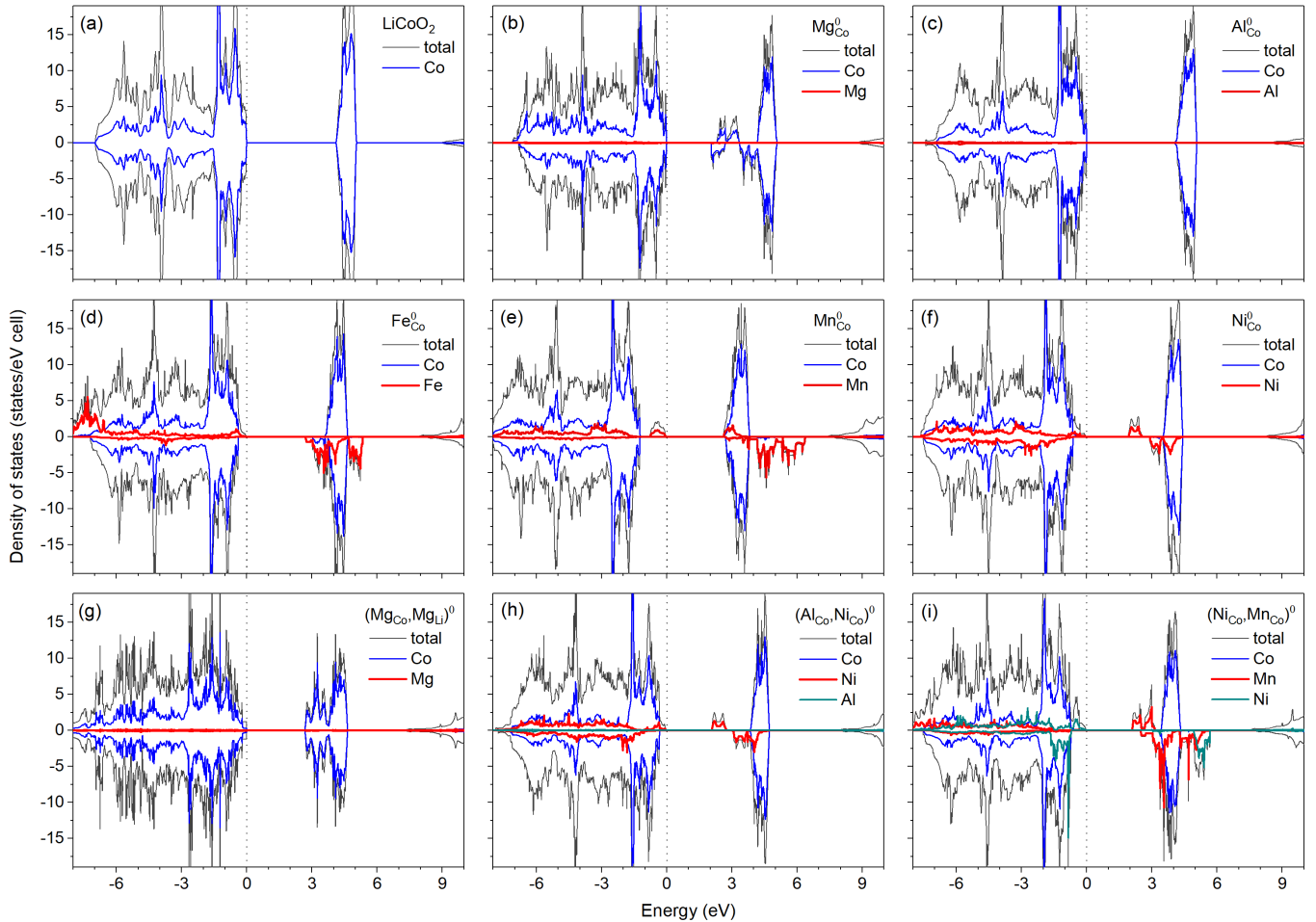


FIG. 4. Total and atomic-projected electronic densities of states of (a) undoped LiCoO_2 and heavily doped LiCoO_2 systems containing (b) Mg_{Co}^0 , (c) Al_{Co}^0 , (d) Fe_{Co}^0 , (e) Mn_{Co}^0 , (f) Ni_{Co}^0 , (g) $(\text{Mg}_{\text{Co}}, \text{Mg}_{\text{Li}})^0$, (h) $(\text{Al}_{\text{Co}}, \text{Ni}_{\text{Co}})^0$, and (i) $(\text{Ni}_{\text{Co}}, \text{Mn}_{\text{Co}})^0$. The zero of energy is set to the highest occupied state.

we find that a neutral (Ni, Al) pair in LiCoO_2 is stable as $(\text{Ni}^{3+}, \text{Al}^{3+})$, i.e., Ni_{Co}^0 and Al_{Co}^0 , and its total energy is almost independent of the pair distance ($E_b = 0$).

The impurities may occur in the material not as isolated defects but complexes with the intrinsic defects. On the basis of our results above regarding the most stable configurations of the impurities as well as those for the intrinsic defects under different sets of the atomic chemical potentials reported in Ref. 3, we carry out calculations for all possible low-energy impurity-related neutral complexes and identify the energetically most stable configurations. Table I summarizes the lowest-energy impurity-related defect complexes in LiCoO_2 under various preparation conditions. Since LiCoO_2 is often prepared under Li-rich conditions,^{3,35} the typical experimental conditions can be identified with approximately the region enclosing points *B*, *C*, and *X* in Fig. 1(a). Under these conditions, Mg can be present in LiCoO_2 in the form of the neutral complex $\text{Mg}_{\text{Co}}^- - \eta^+$; i.e., the incorporation of the Mg impurity at the Co site is charge-compensated by the creation of η^+ (i.e., Co^{4+}) in the host. The complex

has a binding energy $E_b = 0.65$ eV with respect to its isolated constituents. Al, Fe, and Ni are, on the other hand, most stable as Al_{Co}^0 , Fe_{Co}^0 , and Ni_{Co}^0 , respectively. Finally, Mn can be present in the form of the neutral complex $\text{Mn}_{\text{Co}}^+ - \text{Li}_{\text{Co}}^{2-} - \eta^+$ (at point *B*; $E_b = 2.19$ eV) or Mn_{Co}^0 (points *C* and *X*). Other defect complexes listed in Table I include $\text{Mg}_{\text{Co}}^- - \text{Co}_{\text{Li}}^+$ ($E_b = 0.49$ eV), $\text{Mg}_{\text{Li}}^- - \eta^-$ ($E_b = 0.50$ eV), $\text{Mg}_{\text{Li}}^+ - V_{\text{Li}}^-$ ($E_b = 0.51$ eV), $\text{Mn}_{\text{Co}}^+ - V_{\text{Li}}^-$ ($E_b = 0.42$ eV), and $\text{Ni}_{\text{Li}}^+ - V_{\text{Li}}^-$ ($E_b = 0.48$ eV).

In the case where the formation-energy difference ΔE is small, one should expect that the dopant is incorporated at both the Co and Li sites. For example, Mg-doped LiCoO_2 prepared under the conditions at point *C* in Fig. 1(a) has two defect complexes with almost equal formation energies: $\text{Mg}_{\text{Co}}^- - \eta^+$ and $\text{Mg}_{\text{Li}}^+ - \eta^-$, see Table I. These two complexes can combine to form $\text{Mg}_{\text{Co}}^- - \text{Mg}_{\text{Li}}^+$ which has Mg over both the Co and Li sites. Besides, it is expected that both isolated impurities and impurity-related defect complexes are present in real samples of the doped LiCoO_2 materials. The relative concentra-

tion of the complexes versus their isolated constituents is likely to be dependent on the total concentration of the dopants (and co-dopants, if present) and/or intrinsic point defects and their distribution in the materials.

Figure 4 shows the electronic densities of states (DOS) of selected heavily doped LiCoO₂ systems, obtained in calculations using the 24-atom supercells (see Sec. II). The defect models chosen for these calculations are those with the lowest energies under the conditions at points *C* and *X* reported in Table I; i.e., Mg_{Co}⁰ (i.e., Mg_{Co}⁻η⁺), Al_{Co}⁰, Fe_{Co}⁰, Mn_{Co}⁰, and Ni_{Co}⁰. The DOS of LiCoO₂ containing (Mg_{Co},Mg_{Li})⁰ (i.e., Mg_{Co}⁻ and Mg_{Li}⁺), (Al_{Co},Ni_{Co})⁰ (i.e., Al_{Co}⁰ and Ni_{Co}⁰), or (Ni_{Co},Mn_{Co})⁰ (i.e., Ni_{Co}⁻ and Mn_{Co}⁺) is also included. We find that the material stays non-metallic upon doping, which is consistent with our analysis of defect physics in LiCoO₂ reported previously according to which (charged) impurities are charge-compensated by intrinsic point defects and the Fermi level of the system cannot be shifted to the VBM or CBM.³ Focusing on the electronic structure near the band edges as it is relevant to the electrochemical properties,⁴ we find that, compared to the perfect bulk [Fig. 4(a)], the Mg doping strongly disturbs the conduction-band bottom with additional electronic states at ~2.0–4.0 eV coming from the Co⁴⁺ ion (i.e., η⁺), see Fig. 4(b). The doping of LiCoO₂ with Al has almost no change in the electronic structure near the band edges, see Fig. 4(c), whereas the Fe doping disturbs the band edges of the host compound, see Fig. 4(d). The Mn doping introduces electronic states associated with Mn³⁺ at ~-1.0–0.0 eV, see Fig. 4(e), whereas the Ni doping introduces electronic states associated with Ni³⁺ at ~2.0–3.5 eV, see Fig. 4(f). The electronic structure of the (Al,Ni)-doped system reflects that of the Al- and Ni-doped systems, see Fig. 4(h). The electronic structure of the (Ni,Mn)-doped system is characterized by the electronic states associated with Ni²⁺ at the valence-band top and those of Mn⁴⁺ at the conduction-band bottom, see Fig. 4(i). The calculated electronic structure is thus consistent with the details of the defect models.

Experimentally, it has been widely reported that Mg doping in LiCoO₂ enhances the electronic conductivity.^{6–10} Levasseur et al.,⁸ for example, found that the activation energy for electronic conduction decreases as increasing the Mg concentration. This observation can be understood in terms of the results presented above in which the incorporation of Mg into the material at the Co site results in the formation of the Mg_{Co}⁻ defect and the hole polaron η⁺. Equivalently, the incorporation of Mg into the Co sublattice can be regarded as acceptor-like doping:³⁶ Once the concentration of Mg_{Co}⁻ is higher than that of the lowest-energy negatively charged intrinsic defect, this acceptor-like defect will shift the Fermi level of the system from the position μ_e^{int} of undoped LiCoO₂ slightly toward to the VBM, thus lowering the formation energy and hence increasing the concentration of η⁺ (and other positively charged defects). The polarons remain in the samples

after preparation and act as athermal, preexisting current-carrying defects during subsequent electrical conductivity measurements or facilitate lithium extraction at the beginning of the delithiation process.^{3,37} Regarding the lattice site preference of Mg, Shim et al.³⁸ observed that the ratio between the Mg levels at the Co and Li sites is dependent on the thermal treatment temperature, which is consistent with our analysis regarding the dependence on the chemical potentials.

Regarding the other dopants, Al, Fe, and Mn were reported to be incorporated into LiCoO₂ at the Co site,^{17,39,40} in agreement with our results. Luo et al.¹⁷ was able to stabilize Mn⁴⁺ in the material. The defect model in this case could be one of those Mn_{Co}⁺-containing complexes listed in Table I. As for Ni, Liang et al.¹⁴ found that the amount of Ni that goes into the Li sublattice can be controlled through tuning the Li content, which is equivalent to tuning the atomic chemical potentials as discussed in the current work. Finally, Stoyanova et al.¹⁶ reported that in LiCo_{1-2x}Ni_xMn_xO₂ with *x* < 0.05, which can be regarded as (Ni,Mn)-doped LiCoO₂, the dopants are stable as Ni³⁺ and Mn⁴⁺, whereas in highly doped samples, *x* = 0.10, they are stable as Ni²⁺ and Mn⁴⁺. This can be understood as the following: At low dopant concentration, the probability of Ni and Mn being in the proximity of each other is low; as a result, the dopants are predominantly isolated defects, i.e., stable as Ni_{Co}⁰ (i.e., Ni³⁺) and Mn_{Co}⁺ (i.e., Mn⁴⁺) as discussed earlier. At higher concentrations, the observation can be understood in terms of our results for the (Ni,Mn) pair in which the dopants are stable as Ni²⁺ and Mn⁴⁺.

B. LiNiO₂

Figure 5 shows the formation energies of substitutional Mg, Al, Mn, Fe, and Co impurities in LiNiO₂, obtained under conditions at point *X* in Fig. 1(b). We find that each impurity has only one true charge state, as indicated in the figure, except Co_{Li} which can be stable as Co_{Li}⁺ (i.e., Co²⁺ at the Li site) or Co_{Li}²⁺ (i.e., Co³⁺ at the Li site) though the 2+ charge state is only stable in the range of the Fermi-level values far away from μ_e^{int}, the Fermi level of undoped LiNiO₂,³ and thus not really relevant. Other (nominal) charge states are defect complexes consisting of the elementary defects and hole (η⁺) or electron (η⁻) polarons. Note that, in LiNiO₂, Ni is stable as low-spin Ni³⁺ and the polaron η⁺ (η⁻) corresponds to low-spin Ni⁴⁺ (Ni²⁺) at the Ni site.³ Mn_{Ni}⁺ (i.e., Mn⁴⁺ at the Ni site), for example, is an elementary defect, whereas Mn_{Ni}⁰ is a complex of Mn_{Ni}⁺ and η⁻; Co_{Ni}⁰ (i.e., low-spin Co³⁺ at the Ni site) is an elementary defect, Co_{Ni}⁺ (Co_{Ni}⁻) is a complex of Co_{Ni}⁰ and η⁺ (η⁻).

Figure 6 shows the formation-energy difference at the Fermi level μ_e^{int} of undoped LiNiO₂ between the Ni and Li sites. The results indicate that all the impurities, except Mg, is energetically more favorable at the Ni site. Specifically, as isolated defects, Al is most stable as Al_{Ni}⁰

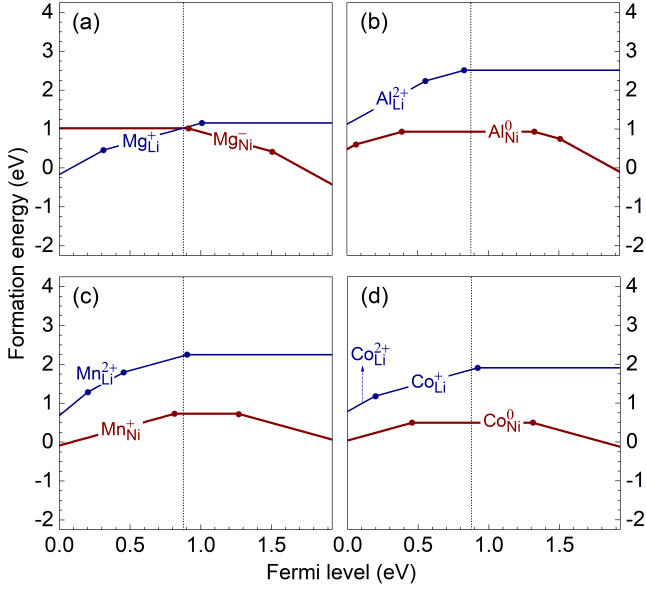


FIG. 5. Formation energies of substitutional impurities at the Li and Ni lattice sites in LiNiO₂ obtained at point X [marked by a cross in the chemical-potential diagram in Fig. 1(b)], plotted as a function of Fermi level from the VBM to the CBM of the undoped compound: (a) Mg, (b) Al, (c) Mn, and (d) Co. The slope in the energy plots indicates the charge state (q). For each defect, only the true charge states are indicated. The vertical dotted line marks the Fermi level of undoped LiNiO₂, μ_e^{int} , determined by the intrinsic point defects.³

(i.e., Al³⁺ at the Ni site), Fe as Fe_{Ni}⁰ (i.e., high-spin Fe³⁺ at the Ni site), Mn as Mn_{Ni}⁺, and Co as Co_{Ni}⁰, all independent of the atomic chemical potentials. Mg is most stable as Mg_{Ni}⁻ (i.e., Mg²⁺ at the Ni site) at points A and B, Mg_{Li}⁺ (i.e., Mg²⁺ at the Li site) at points D and E, and on both the Ni and Li sites with almost equal concentrations at C and X, see Fig. 6. Interestingly, we find that the ΔE curves for the impurities follow the same trend and are different from one another by only a constant. This is due to the fact that (i) μ_e^{int} of undoped LiNiO₂ is always determined by η^+ and η^- whose formation energies are independent of the atomic chemical potentials, i.e., μ_e^{int} is a constant,³ and (ii) the charge-state difference between the most stable configuration at the Ni site and that at the Li site is also a constant. As a result, ΔE for the impurities in LiNiO₂ depends on the atomic chemical potentials only through the term $\mu_{\text{Li}} - \mu_{\text{Ni}}$ which varies with different points in the chemical-potential diagram in Fig. 1(b) but is independent of the dopants' identity.

Explicit calculations of a neutral (Co,Mn) pair show that the impurities are stable as (Co³⁺,Mn⁴⁺) in LiNiO₂. Besides, they turn one Ni³⁺ of the host compound into Ni²⁺; i.e., there is charge transfer between Mn and one of the Ni host atoms. The whole (Co_{Ni},Mn_{Ni})⁰ complex can be regarded as consisting of Co_{Ni}⁰, Mn_{Ni}⁺, and η^- . This is consistent with the result discussed above that, as isolated defects, Co and Mn are most stable as Co_{Ni}⁰ and

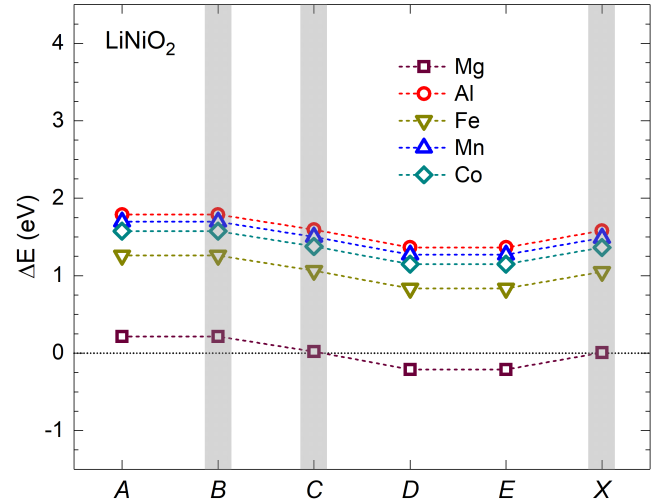


FIG. 6. Difference between the formation energies at the Ni and Li sites, obtained under the conditions at points A–E and X in Fig. 1(b). $\Delta E > 0$ means the impurity is energetically more favorable at the Ni site. The results under more realistic synthesis conditions (points B, C, and X) are highlighted.

Mn_{Ni}⁺, respectively, and the fact that η^- is easy to form in LiNiO₂.³ The lowest-energy configuration of the complex corresponds to the closest distance (2.89 Å) between the oppositely charged Mn_{Ni}⁺ and η^- . In this configuration, the complex has a binding energy of 0.70 eV with respect to its isolated constituents. For comparison, a neutral (Co,Al) pair is found to be stable as (Co³⁺,Al³⁺), i.e., Co_{Ni}⁰ and Al_{Ni}⁰ defects. The total energy of the pair is almost independent of the pair distance ($E_b \sim 0$ eV).

Like in the case of LiCoO₂, the impurities in LiNiO₂ may occur as complexes with the intrinsic point defects. Explicit calculations for all possible low-energy neutral complexes between the impurity and relevant intrinsic defects are carried out for LiNiO₂ and the results are summarized in Table I. We find that under more realistic synthesis conditions, such as in the region enclosing approximately points B, C, and X in Fig. 1(b), Mg can be present in the material in the form of the neutral complex Mg_{Ni}⁻- η^+ ($E_b = 0.54$ eV) and Mn in the form of Mn_{Ni}⁺- η^- ($E_b = 0.57$ eV). These two impurities are thus incorporated as negatively (positively) charged defects that are charge-compensated by hole (electron) polarons. The presence of the polarons as accompanying intrinsic defects of the impurities under all synthesis conditions is consistent with our previous study showing that η^+ and η^- are the lowest-energy intrinsic defects in LiNiO₂, a property that originates from the ability of low-spin Ni³⁺ in the layered oxide to undergo charge disproportionation: $2\text{Ni}^{3+} \rightarrow \text{Ni}^{4+} + \text{Ni}^{2+}$.³ The other impurities can be present as Al_{Ni}⁰, Fe_{Ni}⁰, and Co_{Ni}⁰, respectively; i.e., they are trivalent impurities; see Table I. Other defect complexes listed in Table I include Mg_{Li}⁺- η^- ($E_b = 0.38$ eV), Mg_{Ni}⁻-Ni_{Li}⁺ ($E_b = 0.44$ eV), and Mn_{Ni}⁺-Li_{Ni}²⁻- η^+ ($E_b = 1.62$ eV). The electronic structure of selected heav-

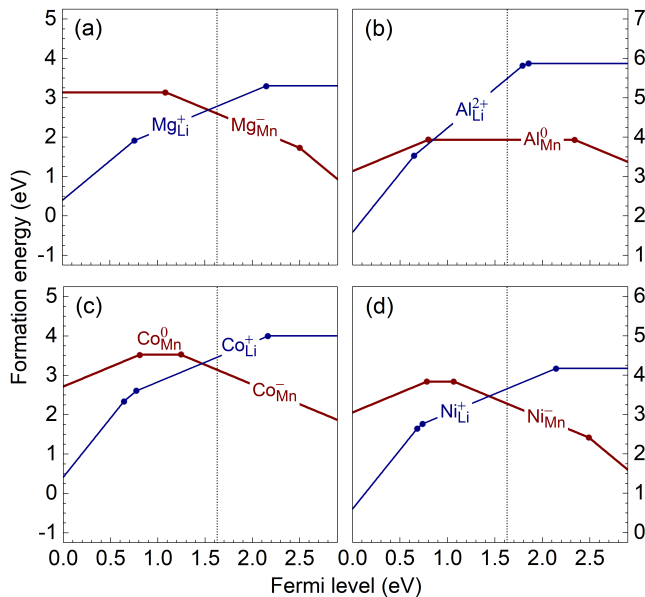


FIG. 7. Formation energies of substitutional impurities at the Li and Mn sites in LiMnO₂ obtained at point X [marked by a cross in the chemical-potential diagram in Fig. 1(c)], plotted as a function of Fermi level from the VBM to the CBM of the undoped compound: (a) Mg, (b) Al, (c) Co, and (d) Ni. The slope in the energy plots indicates the charge state (q). For each defect, only the stable charge states are indicated. The vertical dotted line marks the Fermi level of undoped LiMnO₂, μ_e^{int} , determined by the intrinsic point defects.⁴

ily doped LiNiO₂ systems is reported in Ref. 29.

Experimentally, Pouillier et al.¹⁹ reported that in Mg-doped LiNiO₂ samples, LiNi_{1-y}Mg_yO₂, a certain amount of Mg goes into the Li site, especially at $y \geq 0.10$. This is consistent with our results showing that Mg can be at the Ni and/or Li sites, see Fig. 6 and Table I. Other impurities were found to be incorporated at the Ni site,^{15,41} again, consistent with the computational results.

C. LiMnO₂

Figure 7 shows the formation energies of substitutional Mg, Al, Fe, Co, and Ni impurities at the Mn and Li sites in LiMnO₂, obtained under the conditions at point X in Fig. 1(c); defect configurations with true charge states, i.e., the elementary defects, are indicated. Other charge states are complexes of the elementary defects and hole (η^+) or electron (η^-) polarons. Note that, Mn is stable as high-spin Mn³⁺ in LiMnO₂ and the polaron η^+ (η^-) corresponds to Mn⁴⁺ (high-spin Mn²⁺) at the Mn site.⁴

Figure 8 shows the formation-energy difference at the Fermi level μ_e^{int} of undoped LiMnO₂ between the Mn and Li sites. The impurities are found to be more favorable at the Mn site, except under the conditions at point A where Mg at the Li site is slightly more favorable and Co and Ni can be on both the lattice sites. Specifically,

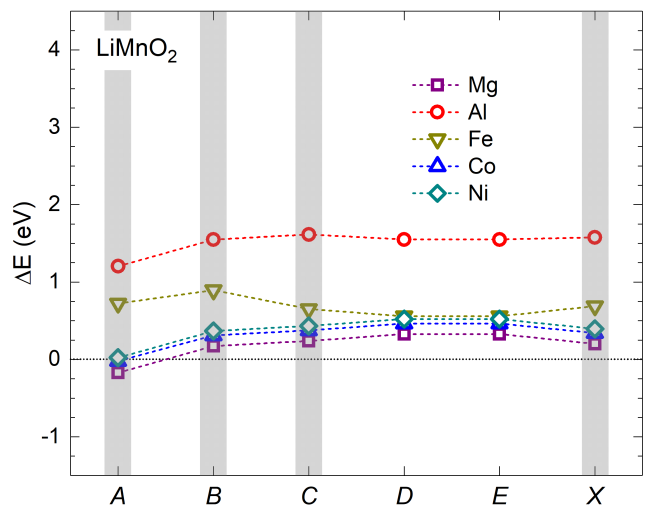


FIG. 8. Difference between the formation energies at the Mn and Li sites, obtained under the conditions at points A–E and X in Fig. 1(c). $\Delta E > 0$ means the impurity is energetically more favorable at the Mn site. The results obtained under more realistic synthesis conditions are highlighted.

as isolated defects, Al is stable as Al_{Mn}⁰ (i.e., Al³⁺ at the Mn site), Fe as Fe_{Mn}⁰ (i.e., high-spin Fe³⁺ at the Mn site), and Ni as Ni_{Mn}⁻ (i.e., high-spin Ni²⁺ at the Mn site). Mg is found to be most stable as Mg_{Mn}⁻ (i.e., Mg²⁺ at the Mn site) at points B–E and X or Mg_{Li}⁺ (i.e., Mg²⁺ at the Li site) at points A. Finally, Co is most stable as Co_{Mn}⁻ (i.e., high-spin Co²⁺ at the Mn site) at points B–E and X or Co_{Li}⁺ (i.e., high-spin Co²⁺ at the Li site) at point A. Ni and Co are thus stable as Ni²⁺ and Co²⁺, respectively, independent of the atomic chemical potentials.

For comparison, Prasad et al.,²⁵ based on an analysis of the metal-oxygen bond lengths, also found that Ni and Co are stable as Ni²⁺ and Co²⁺ in layered LiMnO₂. Regarding the lattice site preference, Kong et al.²⁷ showed that Ni and Co are energetically more favorable at the Mn site, which is in general consistent with our results (except those obtained under the conditions at point A). They, however, also indicated that Ni has a slightly larger tendency to occupy the Li site compared to Co, which appears to contradict our results reported in Fig. 8 where ΔE associated with Ni is slightly higher than that with Co. The discrepancy is likely due to the different computational approaches adopted in the two studies.

Explicit calculations of a neutral (Ni,Co) pair on the Mn sublattice shows that the impurities are stable as Ni²⁺ and Co³⁺ and one of the Mn³⁺ ions in the host compound is turned into Mn⁴⁺. There is thus charge transfer from Ni to one of the Mn host atoms. The whole pair is, in fact, a complex of Ni_{Mn}⁻, Co_{Mn}⁰, and η^+ . Though Co is most stable as Co²⁺ as an isolated defect as discussed above, here it is energetically more favorable as Co³⁺ due to the presence of Ni²⁺ and the formation of η^+ (i.e., Mn⁴⁺). The most stable configuration of the defect complex corresponds to the shortest distance (2.81

Å) between the oppositely charged defects Ni_{Mn}^- and η^+ . In this configuration, the complex has a binding energy of 0.37 eV with respect to its isolated constituents.

We also carry out calculations for all possible low-energy neutral complexes between the impurity and relevant intrinsic defects in LiMnO_2 . Table I summarizes the lowest-energy defect models for the doped materials. Under more realistic conditions, such as in the region enclosing approximately points *A*, *B*, *C*, and *X* in Fig. 1(c), Mg can be present in the material in the form of the neutral complex $\text{Mg}_{\text{Mn}}^- - \eta^+$ ($E_b = 0.35$ eV), $\text{Mg}_{\text{Li}}^+ - \text{V}_{\text{Li}}^-$ ($E_b = 0.29$ eV), or $\text{Mg}_{\text{Mn}}^- - \text{Mn}_{\text{Li}}^+$ ($E_b = 0.30$ eV), depending on the specific conditions. Al is most stable as Al_{Mn}^0 , Fe as Fe_{Mn}^0 , and Co as Co_{Mn}^0 or $\text{Co}_{\text{Mn}}^- - \text{Mn}_{\text{Li}}^+$ ($E_b = 0.28$ eV). Finally, Ni can be present in the material as $\text{Ni}_{\text{Mn}}^- - \eta^+$ ($E_b = 0.33$ eV) or $\text{Ni}_{\text{Mn}}^- - \text{Mn}_{\text{Li}}^+$ ($E_b = 0.31$ eV). It should be noted that, in addition to these lowest-energy defect models, those that have slightly higher energies are also reported in the footnotes of Table I. The other defect complexes associated with LiMnO_2 listed in Table I include $\text{Mg}_{\text{Li}}^+ - \text{Li}_{\text{Mn}}^{2-} - \eta^+$ ($E_b = 1.06$ eV), $\text{Co}_{\text{Li}}^+ - \text{V}_{\text{Li}}^-$ ($E_b = 0.26$ eV), $\text{Co}_{\text{Mn}}^- - \text{Li}_i^+$ ($E_b = 0.31$ eV), $\text{Ni}_{\text{Li}}^+ - \text{V}_{\text{Li}}^-$ ($E_b = 0.24$ eV), and $\text{Ni}_{\text{Mn}}^- - \text{Li}_i^+$ ($E_b = 0.32$ eV). All these complexes, except $\text{Mg}_{\text{Li}}^+ - \text{Li}_{\text{Mn}}^{2-} - \eta^+$, have rather small binding energies; as a result, they may dissociate into their isolated constituents, especially under thermal equilibrium at high temperatures.³³ The electronic structure of selected heavily doped LiMnO_2 systems is also calculated and reported in Ref. 29.

IV. CONCLUSIONS

We have carried out a detailed study of doping in layered oxides LiMO_2 , mainly in the dilute doping limit, using first-principles defect calculations based on a hybrid

DFT/Hartree-Fock approach. We find that Al, Fe, and Mn impurities are more favorable on the Co sublattice in LiCoO_2 , whereas Mg and Ni can be on the Co and/or Li sublattices depending on the synthesis conditions. In LiNiO_2 , Al, Fe, Mn, and Co are more favorable on the Ni sublattice; Mg can be incorporated on the Ni and/or Li sublattices. Finally, Mg, Al, Fe, Co, and Ni are energetically more favorable on the Mn sublattice in LiMnO_2 , except under the synthesis conditions where the system is close to an equilibrium with Li_2MnO_3 and Mn_3O_4 where Mg, Co, and Ni can be on the Mn and/or Li sublattices.

More importantly, we find that the lattice site preference is dependent not only on the ionic-radius difference between the doping element and the substituted host ion, which is related to the charge and spin states of the dopant at the substituted lattice site, but also on the relative abundance of the host compound's constituting elements in the synthesis environment. On the basis of the structure and energetics of the impurities and their complexes with intrinsic point defects, we have determined all possible low-energy impurity-related defect complexes in the doped materials. These defect models are useful for further analyses of the doped materials and in interpreting the experimental observations. Finally, the lightly doped LiMO_2 materials considered here can be regarded as model systems for understanding the more complex, mixed-metal, LiMO_2 -based battery electrode materials.

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