I. INTRODUCTION

Li$_x$CoO$_2$ is currently considered to be among the best cathode materials for rechargeable lithium batteries. Traditionally, this material is synthesized with a layered crystal structure having rhombohedral symmetry in which the Li and Co ions reside in alternating layers between close-packed planes of oxygen ions. In many ways, this layered structure is ideal for a cathode material: the Li ions can diffuse freely on a two-dimensional triangular grid within the Li layers and the voltage profile changes smoothly as the Li concentration is varied. The properties of this material have been investigated extensively both experimentally$^{1-3}$ and theoretically.$^{4-8}$

Within the last decade, synthesis routes proceeding at low temperature have produced a form of Li$_x$CoO$_2$ exhibiting cubic symmetry.$^{9-14}$ While there is still some controversy about the exact nature of its crystal structure, much evidence exists suggesting that the low-temperature (LT) form of Li$_x$CoO$_2$ has a modified spinel structure.$^{9,10}$ Although the actual material is likely to contain defects, the ideal crystal structure belongs to the F$d3m$ space group and has an fcc oxygen sublattice with the Co ions residing in the 16$d$ octahedral sites. The Li ions in this structure can occupy both the 8$a$ tetrahedral and 16$c$ octahedral sites. These sites form a connecting network of tunnels through which the Li ions can diffuse rapidly. Although presently the electrochemical cycling properties of LT Li$_x$CoO$_2$ do not compare well with those of the layered form, this phase is of importance because it is predicted by first-principles calculations to be thermodynamically more stable than the layered form at intermediate Li concentration.$^{15,16}$ This means that the layered form can potentially transform to spinel in a battery every time the material is delithiated. In fact, a recent TEM investigation$^{17}$ has shown that new diffraction spots consistent with those of spinel appear after repeated cycling of layered Li$_x$CoO$_2$.

In order to shed light on the properties of the spinel form of Li$_x$CoO$_2$, we have performed a first-principles investigation of the finite-temperature thermodynamic properties of this phase. The availability of two crystallographically distinct sites that the Li ions can occupy results in electrochemical properties that are distinct from those of layered Li$_x$CoO$_2$. We have used a lattice model derived from first principles to study the thermodynamic properties resulting from the configurational degrees of freedom of distributing Li ions and vacancies over the possible tetrahedral and octahedral sites within the CoO$_2$ spinel host. This technique has previously been applied to study layered Li$_x$CoO$_2$ (Refs. 6 and 7) as well as several other oxides.$^{5,18,19}$ By applying Monte Carlo simulations to this lattice model, we have calculated (i) the voltage intercalation curve, (ii) the Li distribution among tetrahedral and octahedral sites as a function of Li concentration, and (iii) the equilibrium phase diagram for spinel Li$_x$CoO$_2$. This information will help in further characterizing the LT form of Li$_x$CoO$_2$ and will be useful in detecting a potential transformation from layered Li$_x$CoO$_2$ to spinel after repeated cycling in a battery. Furthermore, since several other lithium transition-metal oxides such as Li$_x$MnO$_2$ assume the spinel crystal structure, the results obtained in this study will also contribute to the understanding of their electrochemical properties.

In the remainder of the text, we will refer to Li$_{1/2}$CoO$_2$ in which the Li ions occupy all the tetrahedral 8$a$ sites as ordered spinel (this structure is isomorphic with spinel MgAl$_2$O$_4$). We will refer to LiCoO$_2$ in which the Li ions occupy all the 16$c$ octahedral sites as modified spinel and we will call Li$_x$CoO$_2$ in which Li occupies either or both the octahedral and tetrahedral sites as simply spinel lithium cobalt dioxide.
II. METHODOLOGY

The thermodynamic properties of a material at finite temperature can be derived from its free energy. The free energy is determined both by the energetic interactions between the components of the material and by entropic effects associated with thermal excitations at finite temperature. In a system such as Li$_x$CoO$_2$, configurational excitations involving different arrangements of Li ions and vacancies within the metal oxide host constitute the most important contribution to the free energy. The effect of other excitations on phase stability, such as vibrational and electronic excitations, is for most purposes negligible.

The free energy of a system with configurational degrees of freedom can be calculated with standard statistical mechanics methods such as Monte Carlo simulations. All that is required is a model that accurately describes the energetics of different Li-vacancy arrangements within the CoO$_2$ host structure. This is done with a generalized lattice model based on the cluster expansion formalism. Within this formalism, occupation variables $\sigma_i$ are assigned to each Li site $i$ within the host. $\sigma_i$ is +1 if a Li ion resides at site $i$ and −1 if that site is empty. It can be shown that the configurational energy can be exactly expanded in terms of polynomials $\phi_\alpha$ of these occupation variables:

$$E = V_o + \sum_\alpha V_\alpha \phi_\alpha,$$

where

$$\phi_\alpha = \prod_{i \in \alpha} \sigma_i,$$

which corresponds to a product of occupation variables associated with Li sites belonging to the cluster $\alpha$. The clusters $\alpha$ are, for example, a nearest-neighbor pair cluster, a next-nearest-neighbor pair cluster, clusters containing three Li sites (i.e., a triplet cluster), etc. The coefficients $V_o$ and $V_\alpha$ are constant expansion coefficients and are called effective cluster interactions (ECI). The sum in Eq. (1) extends over all possible clusters of Li sites $\alpha$ within the host; however, in practice, Eq. (1) can be truncated such that terms corresponding to a limited set of small clusters remain in the expansion equation (1).

Numerical values for the ECI are to be determined with accurate first-principles total energy calculations. This can be done by calculating, from first principles, the energy of a set of structures with different Li-vacancy arrangements and then fitting a truncated form of Eq. (1) to the energy values of 17 different Li-vacancy arrangements in the cubic host. We used an inversion method based on linear programming techniques. The energies of the 17 different Li-vacancy configurations were calculated with the pseudopotential method in the local-density approximation (LDA) (nonspin polarized) as implemented in the Vienna ab initio simulation package. Ultrasoft pseudopotentials were used. For each structure, the cell parameters and the ionic positions were fully relaxed. The exchange and correlation potential used was that of Ceperley and Alder as parametrized by Perdew and Zunger. An energy cutoff of 600 eV was used for the plane-wave expansion. Convergence tests indicated that the calculated energies are converged to within 5 meV per Li$_x$CoO$_2$ formula unit with respect to the $k$-point meshes used.

Figure 1 shows the formation energies of 14 of the 17 structures used in the fit (three of the structures have a concentration greater than 1). The formation energies are defined as

$$\Delta_f E = E - xE_{LiCoO_2} - (1-x)E_{CoO_2},$$

where $E$ is the total energy per Li$_x$CoO$_2$ formula unit of a structure with a given Li-vacancy arrangement at a concentration $x$, $E_{CoO_2}$ is the energy of CoO$_2$ in the spinel phase and $E_{LiCoO_2}$ is the energy of LiCoO$_2$ in the spinel phase where all
the Li ions occupy the 16c octahedral sites (i.e., modified spinel). Among the 14 structures of Fig. 1 are configurations in which Li ions occupy only octahedral sites (crosses), tetrahedral sites (diamonds), and configurations in which both tetrahedral and octahedral sites are occupied simultaneously by Li ions (squares). We have also drawn the convex hull connecting the structures with the lowest formation energies to indicate the most stable structures among those considered with the pseudopotential method.

The cluster expansion determined by fitting to these energies contains ten terms (Table I). This includes ECI corresponding to the empty cluster \( V_o \), two point clusters (tetrahedral and octahedral sites), four pair clusters, and three multibody clusters. One type of pair cluster is between nearest-neighbor tetrahedral and tetrahedral sites. The other pair clusters correspond to the nearest- and second-nearest-neighbor pairs on the sublattice formed by the tetrahedral 8a sites and the nearest-neighbor pair on the sublattice formed by the octahedral 16c sites. The root-mean-square difference between the cluster expansion energy values and the pseudopotential energy values for the 14 structures of Fig. 1 is less than 5 meV per Li\(_x\)CoO\(_2\) formula unit.

To obtain thermodynamic properties for spinel Li\(_x\)CoO\(_2\), canonical and grand canonical Monte Carlo simulations were applied to the cluster expansion of Table I. Monte Carlo cells containing 3072 and 10368 Li sites (octahedral and tetrahedral) were used. 6000–8000 Monte Carlo passes per lattice site were performed at each temperature and chemical potential of which the last 4000 were used for averaging. Free energies were calculated by integrating the chemical potential from \( x = 0 \) and \( x = 1 \) (where the free energy equals the ground-state energy) to the desired concentration \( x \).

### IV. RESULTS

#### A. Voltage curve

An important property for lithium transition-metal oxides is the evolution of the voltage intercalation curve as a function of Li concentration. The voltage curve is related to the chemical potential of Li within the cathode host according to

\[
V(x) = -\frac{(\mu_{Li}^{\text{cathode}} - \mu_{Li}^{\text{anode}})}{zF},
\]

where \( z \) is the charge (in electrons) transported by Li in the electrolyte (i.e., \( z = 1 \) for Li), \( F \) is Faraday’s constant, \( \mu_{Li}^{\text{cathode}} \) is the chemical potential of Li in the cathode host, and \( \mu_{Li}^{\text{anode}} \) is the chemical potential of Li in the anode. We assume that the anode is metallic lithium and therefore \( \mu_{Li}^{\text{anode}} \) is constant at fixed temperature and equal to the free energy of pure metallic lithium. We have approximated \( \mu_{Li}^{\text{anode}} \) by the energy of pure lithium in the bcc phase. \( \mu_{Li}^{\text{cathode}}(x) \) is a direct output of the grand canonical Monte Carlo simulations.

Figure 2 illustrates the calculated voltage curve of Li\(_x\)CoO\(_2\) in the spinel phase at 300 K [Fig. 2(a)] and 600 K [Fig. 2(b)]. The voltage profile at 300 K clearly exhibits the abrupt jump in voltage at \( x = 0.5 \) characteristic of spinel Li\(_x\)MnO\(_2\) (Ref. 28) and Li\(_x\)TiO\(_2\). The plateau between \( x = 0.5 \) and \( x = 0.95 \) signifies a two-phase region.

<table>
<thead>
<tr>
<th>Cluster</th>
<th>ECI (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Empty cluster ( V_o )</td>
<td>166.9</td>
</tr>
<tr>
<td>2. Tetrahedral point cluster</td>
<td>168.6</td>
</tr>
<tr>
<td>3. Octahedral point cluster</td>
<td>174.1</td>
</tr>
<tr>
<td>4. Nearest-neighbor tetrahedral-tetrahedral pair</td>
<td>6.3</td>
</tr>
<tr>
<td>5. Second-nearest-neighbor tetrahedral-tetrahedral pair</td>
<td>0.3</td>
</tr>
<tr>
<td>6. Nearest-neighbor Octahedral-octahedral pair</td>
<td>29.1</td>
</tr>
<tr>
<td>7. Nearest-neighbor tetrahedral-octahedral pair</td>
<td>86.5</td>
</tr>
<tr>
<td>8. Octahedral triplet</td>
<td>8.8</td>
</tr>
<tr>
<td>9. Octahedral-tetrahedral-octahedral triplet</td>
<td>17.3</td>
</tr>
<tr>
<td>10. Quadruplet connecting 1 tetrahedral site with 3 octahedral sites</td>
<td>9.4</td>
</tr>
</tbody>
</table>
The increase in the occupation of the octahedral sites becomes significant at low Li concentrations. In fact, it is representative of a typical voltage curve for a layered phase in which no metal-insulator transition takes place. As Li is removed further, the tetrahedral sites are predominantly occupied and the concentration of the octahedral sites is lower than that of the tetrahedral position. Another quantity of interest is the energy increase associated with the simultaneous occupation of adjacent tetrahedral and octahedral sites. The energy of the crystal is predicted to increase by 250 meV if a Li ion is moved from an isolated tetrahedral site to one adjacent to an occupied octahedral site (in an otherwise empty CoO$_2$ host). This shows that the simultaneous occupation of adjacent tetrahedral and octahedral sites is energetically very unfavorable (this is also manifested by the large size of the ECI corresponding to the nearest-neighbor pair connecting adjacent tetrahedral and octahedral sites). Adjacent octahedra and tetrahedra share faces, which results in a strong electrostatic repulsion when these sites are occupied at the same time. The above simple results indicate that the Li ions will strive to reside in as many tetrahedral sites as possible, while at the same time, try to avoid as many nearest-neighbor tetrahedral-octahedral bonds as possible.

C. Site occupation

Figure 4 illustrates the concentrations in the tetrahedral and octahedral sites as a function of $x$ in Li$_x$CoO$_2$ as calculated in the Monte Carlo simulations. Figure 4(a) shows that only the octahedral sites are occupied at $x=1$ when the temperature is 300 K. As the Li concentration is reduced slightly, however, some tetrahedral sites start to be occupied. Nevertheless, the Monte Carlo simulations indicate that the probability that nearest-neighbor tetrahedral and octahedral sites are simultaneously occupied is very close to zero at all Li concentrations. In fact, this probability was found to be less than would be expected if the simultaneous occupation of adjacent tetrahedral and octahedral sites were uncorrelated. This implies that at these concentrations only tetrahedral sites in the vicinity of vacant octahedral sites are occupied by Li. At $x=0.95$, a two-phase region commences in which a lithiated spinel phase at $x=0.95$ where Li occupies mostly octahedral sites coexists with an ordered spinel phase at $x=0.5$ in which Li resides only in tetrahedral sites. At $x=0.5$, the Li ions occupy all the $8a$ tetrahedral sites while the octahedral sites are all empty. As Li is removed further, the tetrahedral sites are predominantly occupied and the concentration in the octahedral sites is low. Between $x=0$ and $x=0.5$, the spinel phase at 300 K forms a solid solution.

Figure 4(b) illustrates the octahedral and tetrahedral site occupancy at 600 K. At this temperature, the two-phase region above $x=0.5$ is absent, and a solid solution exists above this concentration. Figure 4(b) shows that as the overall Li concentration is reduced from $x=1$ to $x=0.5$, there is a gradual increase in the concentration of the tetrahedral sites with a simultaneous decrease in the concentration of the octahedral sites. Below $x=0.5$, the tetrahedral sites are predominantly occupied, though a non-negligible amount of Li ions also occupy the octahedral sites.

The increase in the occupation of the octahedral sites below $x=1/2$ with temperature is a result of the increased importance of entropy at higher temperature. Figure 4(c), which illustrates the site occupancy as a function of temperature at $x=1/2$, shows that the concentration of the octahedral sites increases gradually as the temperature is raised. Note that

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**B. Site energetics**

Many of the properties of spinel Li$_x$CoO$_2$ are determined by the availability to the intercalating Li ions of the two crystallographically distinct $8a$ and $16c$ sites. There are twice as many $16c$ sites as $8a$ sites and the energetics of the crystal are very different depending on which of these sites Li occupies. Figure 1, for example, shows that below $x=1/2$, the structures in which the Li ions occupy only the tetrahedral $8a$ sites are energetically more stable than the structures in which Li ions occupy octahedral $16c$ sites. Using the cluster expansion of Table I, we can investigate the relative stability of the two sites in more detail. The cluster expansion predicts that a single Li ion in an otherwise completely delithiated spinel CoO$_2$ host is more stable by 130 meV in a tetrahedral site than in an octahedral site. This indicates that the intrinsic site energy of the tetrahedral position is lower than that of the octahedral position. Another quantity of interest is the energy increase associated with bringing two isolated Li ions to adjacent tetrahedral and octahedral sites. The energy of the crystal is predicted to increase by 250 meV if a Li ion is moved from an isolated tetrahedral site to one adjacent to an occupied octahedral site (in an otherwise empty CoO$_2$ host). This shows that the simultaneous occupation of adjacent tetrahedral and octahedral sites is energetically very unfavorable (this is also manifested by the large size of the ECI corresponding to the nearest-neighbor pair connecting adjacent tetrahedral and octahedral sites). Adjacent octahedra and tetrahedra share faces, which results in a strong electrostatic repulsion when these sites are occupied at the same time. The above simple results indicate that the Li ions will strive to reside in as many tetrahedral sites as possible, while at the same time, try to avoid as many nearest-neighbor tetrahedral-octahedral bonds as possible.

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**FIG. 3.** Comparison of calculated voltage intercalation curves for spinel Li$_x$CoO$_2$ (dashed line) and layered Li$_x$CoO$_2$ (full line) at 300 K.
there is clearly no abrupt change in the octahedral and tetrahedral site occupancies by Li ions.

D. Phase diagram

Monte Carlo simulations give both information about the chemical potential as a function of Li concentration and temperature and about the equilibrium Li ordering within the host. Based on this information, it is possible to construct a phase diagram for spinel Li$_x$CoO$_2$ (Fig. 5). The calculated spinel Li$_x$CoO$_2$ phase diagram consists of a large miscibility gap between the outer limits of $x=0.5$ and $x=1.0$. The miscibility gap disappears above 420 K and a solid solution exists in which Li ions occupy both octahedral and tetrahedral sites. Below $x=0.5$, the Li ions predominantly occupy the tetrahedral sites and form a solid solution. Only below $T=150$ K do the Li ions order at $x=0.25$ (see Fig. 5) according to a second-order phase transformation. In this ordered phase, the Li ions occupy every other tetrahedral site. The formation energies as calculated with the pseudopotential method (Fig. 1) indicate that there should also be ordering at $x=0.125$ and $x=0.375$ (this is because these energy values lie on the convex hull in Fig. 1). Nevertheless, these ordered phases did not appear in the Monte Carlo simulations. We expect, therefore, that they have very low order-disorder transition temperatures.

We emphasize that the calculated phase diagram of Fig. 5 should only be viewed as a qualitative representation of the actual spinel Li$_x$CoO$_2$ phase diagram. In constructing the cluster expansion for this system, we have used the first-principles energy values of only 17 different Li-vacancy arrangements within the spinel CoO$_2$ host (since the unit cell of the spinel host is very large, it is currently computationally too expensive to calculate the energies of more Li-vacancy arrangements within this host). A cluster expansion derived from 17 energy values is usually sufficient to correctly predict the topology of a phase diagram; however, it is generally not enough to make accurate quantitative predictions about order-disorder transition temperatures. For this purpose, it would be necessary to construct the cluster expansion with the energies of 30–50 different Li-vacancy arrangements and to include the effects of lattice vibrations and electronic excitations.

V. DISCUSSION

One of the defining characteristics of the spinel phase is the large voltage step at $x=1/2$ in Li$_x$MO$_2$ where $M$ is a transition metal. It is observed experimentally in spinel Li$_x$MnO$_2$ and Li$_x$TiO$_2$ and predicted from first principles in this work for spinel Li$_x$CoO$_2$ [Fig. 2(a)]. For Li$_x$MnO$_2$, it is sometimes argued that the jump in voltage at $x=1/2$ is caused by a Jahn-Teller distortion of the MnO$_2$ host that is believed to start above a Li concentration of $x=0.5$. As shown in this work, the voltage step at $x=1/2$ is present even in the absence of a Jahn-Teller distortion. The sudden change in voltage is actually a result of the stability of ordered spinel at $x=1/2$. This can be seen from the calculated free-energy
The sharpness of the free energy around \( \text{LiMO}_2 \) as this would tend to flatten the free energy.

The discontinuity makes practical implementation of these materials in a battery difficult. To this end, it is necessary to diminish the stability of perfectly ordered spinel at \( x = 1/2 \) (with all the Li ions in the tetrahedral sites) as is evident in Fig. 6. It means the curvature at \( x = 1/2 \) is very sharp and hence the slope changes rapidly as a function of Li concentration at \( x = 1/2 \). The slope change is most pronounced slightly above \( x = 1/2 \). This is because the tetrahedral sites are saturated at \( x = 1/2 \) and further Li addition to the host must be accommodated by the energetically less favorable octahedral sites causing the free energy to rise sharply above \( x = 1/2 \).

The voltage profile of spinel Li\(_{2/3}CoO_2\) is likely to be representative of the phase diagrams for other lithium transition-metal oxides with the spinel structure. One important feature of Fig. 5 is the large miscibility gap between the bounds of \( x = 0.5 \) and \( x = 1 \). This miscibility gap results from a competition between filling tetrahedral sites while at the same time minimizing the number of occupied nearest-neighbor tetrahedral-octahedral pairs. This is most effectively done as a two-phase mixture of ordered \( \text{Li}_{1/2} \text{CoO}_2 \) where all the Li ions occupy tetrahedral sites and a lithiated spinel at high Li concentration where most Li ions occupy octahedral sites.

The voltage step starts to disappear at 600 K as a result of the reduction of the Li concentration in the tetrahedral sites and cause them to start occupying octahedral sites. This is clearly evident in Fig. 2(b) where the voltage step starts to disappear at 600 K as a result of the reduction of the Li concentration in the tetrahedral sites [Figs. 4(b) and 4(c)] of the spinel host. Lithium disorder smears out the free-energy curve around \( x = 1/2 \). In terms of doping with other metal ions, preference should be given to ions that stabilize the \( \text{LiMO}_2 \) structure and/or destabilize ordered spinel at \( \text{Li}_{1/2} \text{MO}_2 \).

The large qualitative difference between the voltage curves of the spinel and layered crystal structures (Fig. 3) can be attributed to the fact that spinels have two crystallographically distinct sites for Li while the layered phase has only one. In the layered phase, Li ions only occupy octahedral sites since the tetrahedral sites in the Li planes share faces with the oxygen octahedra surrounding the Co ions. The electrostatic repulsion between Co and Li in these sites is large making them energetically unfavorable. Removal of Li from the octahedral sites of the layered phase causes a gradual increase in the voltage curve. Only at particular concentrations in which Li ions order are there small plateaus and minor increases in the voltage curve. In the spinel phase, the particular arrangement of Co ions within the close-packed oxygen skeletal structure produces a set of tetrahedral sites (i.e., the \( \text{8a} \) sites within the \( \text{Fd}3 \text{m} \) space group) that do not share faces with the oxygen octahedra around the Co ions. Although the Li ions prefer the tetrahedral sites, the number of these sites is limited and Li must occupy octahedral sites above \( x = 0.5 \). In fact as \( x \) increases above 0.5, Li ions are displaced from the tetrahedral sites to the octahedral sites [see Figs. 4(a) and 4(b)] to avoid the simultaneous occupation of adjacent octahedral-tetrahedral sites.

The spinel structure is a common phase for the transition-metal oxides used in batteries. For example, it is readily stabilized in \( \text{Li}_2 \text{MnO}_3 \) and \( \text{Li}_2 \text{TiO}_3 \). Many of the qualitative features of the spinel phase diagram of Fig. 5 are determined by the symmetry of the spinel host structure and should therefore be independent of the type of transition metal. Hence, the phase diagram calculated for spinel Li\(_{2/3}CoO_2\) is likely to be representative of the phase diagrams for other lithium transition-metal oxides with the spinel structure. One important feature of Fig. 5 is the large miscibility gap between the bounds of \( x = 0.5 \) and \( x = 1 \). This miscibility gap results from a competition between filling tetrahedral sites while at the same time minimizing the number of occupied nearest-neighbor tetrahedral-octahedral pairs. This is most effectively done as a two-phase mixture of ordered \( \text{Li}_{1/2} \text{CoO}_2 \) where all the Li ions occupy tetrahedral sites and a lithiated spinel at high Li concentration where most Li ions occupy octahedral sites.

Similar though not as pronounced as at \( x = 1/2 \), the ordering at \( x = 1/4 \) below 150 K also creates a step in the voltage curve. This is illustrated in Fig. 7 in which the voltage curve between \( x = 0 \) and \( x = 0.5 \) at 100 K is plotted. Although this curve is calculated for a much lower temperature, it is similar to that observed for \( \text{Li}_2 \text{MnO}_3 \) at room temperature. The similarity in the two curves indicates that the observed step in voltage at \( x = 1/4 \) in \( \text{Li}_2 \text{MnO}_3 \) is consistent with Li ordering as is often claimed.28,32

One aspect of the phase diagram in Fig. 5 that is surprising is that the perfectly ordered spinel phase at \( x = 1/2 \) in which the Li ions occupy only the tetrahedral sites, does not have an order-disorder phase transition. Instead, as can be seen from Fig. 4(c), the Li ions are gradually excited into the octahedral sites over a large temperature interval. The average energy as calculated with the Monte Carlo simulations does not exhibit a discontinuity characteristic of a first-order phase transition, nor does it the heat capacity exhibit a divergence at any temperature. The absence of a unique order-disorder transition temperature is consistent with the fact that the high-temperature phase, in which the Li ions are distributed over both tetrahedral and octahedral sites exhibits the same symmetry as the perfectly ordered spinel phase \( \text{Li}_{1/2} \text{CoO}_2 \) in which the Li ions occupy exclusively the tetrahedral sites (i.e., the low- and high-temperature phases have
Co ions are excited out of the $16d$ sites as the Co ions remain in the $16d$ reduced. Note that the prediction that no phase transition at the same unit cell and belong to the same space group. Generally, phase transitions upon cooling occur from a phase with high symmetry to a new phase in which the symmetry is different symmetry than ordered spinel, and a phase transition upon heating can then be expected experimentally.

VI. CONCLUSION

We have investigated the thermodynamic properties of the spinel form of Li$_{1/2}$CoO$_2$ from first principles. Many of the electrochemical features characteristic of this phase are a result of the availability of two crystallographically distinct sites that the Li ions can occupy. By having implemented a first-principles generalized lattice model based on the cluster expansion formalism in Monte Carlo simulations, we have calculated (i) the intercalation voltage curve, (ii) the tetrahedral and octahedral site concentrations, and (iii) the equilibrium phase diagram. At room temperature, the voltage curve exhibits a step at $x=1/2$ having a height of more than 1 V. This voltage step is a result of the sharp curvature in the free energy that is caused by the strong stability of ordered spinel Li$_{1/2}$CoO$_2$ in which the Li ions occupy only the tetrahedral sites. As the temperature is raised, the step gradually smears out as a result of the increased occupation of the energetically less favorable octahedral sites due to thermal excitations. Below 420 K, a miscibility gap exists between $x=0.5$ and 1.0. The Li ions are predicted to order at $x=1/4$.

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31 This can be illustrated by the difference in two first-principles studies on layered Li$_x$CoO$_2$, one with 16 input structures (Ref. 8) and one with 36 input structures (Ref. 7).