Cation and vacancy ordering in Li_xCoO_2

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Using a combination of first-principles total energies, a cluster expansion technique, and Monte Carlo simulations, we have studied the Li/Co ordering in $LiCoO_2$ and Li-vacancy/Co ordering in the $\square CoO_2$. We find: ~i! A ground-state search of the space of substitutional cation configurations yields the CuPt structure as the lowest-energy state in the octahedral system $LiCoO_2$ ~and $\square CoO_2$), in agreement with the experimentally observed phase. ~ii! Finite-temperature calculations predict that the solid-state order-disorder transitions for $LiCoO_2$ and $\square CoO_2$ occur at temperatures (; 5100 K and ; 4400 K, respectively! much higher than melting, thus making these transitions experimentally inaccessible. ~iii! The energy of the reaction $E_{tot}(s, LiCoO_2)$ 2 $E_{tot}(s, \square CoO_2)$ 2 E_{tot}(Li, bcc) gives the average battery voltage $\overline{V}$ of a Li_xCoO_2/Li cell for the cathode in the structure s. Searching the space of configurations s for large average voltages, we find that s 5 CuPt @a monolayer ^111& superlattice# has a high voltage ($\overline{V}$ 5 3.78 V), but that this could be increased by cation randomization ($\overline{V}$ 5 3.99 V), by partial disordering ($\overline{V}$ 5 3.86 V), or by forming a two-layer $Li_2Co_2O_4$ superlattice along ^111& ($\overline{V}$ 5 4.90 V). @S0163-1829~98!00904-7#

I. INTRODUCTION

Much like the ABC_2 semiconductors (A,B 5 Al, Ga, or In and C 5 N, P, As, or Sb!, which exhibit cation ordering in a tetrahedrally coordinated network,[1] the Li$M$$O_2$ oxides[2,3] (M 5 3d transition metal! form a similar series of structures based on the octahedrally coordinated network with anions ~O! on one fcc sublattice and cations ~Li and M) on the other ~Fig. 1!. Cation arrangements in isovalent ~III-III-V! or heterovalent ~I-III-VI! semiconductor alloys have been observed[1] in the disordered, CuAu-type ~CA!, CuPt-type ~CP!, and chalcopyrite ~CH! structures ~bottom row of Fig. 1!, while cation arrangements in the oxides have been observed[2,3] in the disordered, CP, CH, $D4$, and $Y2$ structures ~top row of Fig. 1!. *Ab initio* total-energy calculations[1] have shown that in the tetrahedrally coordinated III-V semiconductor alloys, the CuPt structure is the least stable @due to the fact that it represents a stacking along the elastically hard ~111! direction#, while the chalcopyrite structure is most stable ~it possesses both the lowest electrostatic and strain energies!. Similar studies have been performed for the octahedrally coordinated networks of the spin alloy $Mn^{\uparrow}$S-$Mn^{\downarrow}$S and the lead chalcogenides.[4] In this paper, we examine the energetics and thermodynamics of cation ordering tendencies in the octahedral $LiCoO_2$ oxide, and compare to the tetrahedral semiconductor case, which is well studied. The $LiCoO_2$ compound is used as a cathode material in rechargeable Li batteries.[5–14] When Li is deintercalated from the compound, it creates a vacancy ~denoted $\square$) that can be positioned in different lattice locations. Hence, we will examine not only ~a! the Li/Co cation ordering ~different sites for Li and Co! properties of $LiCoO_2$ (x_{Li} 5 1), but also ~b! the vacancy/Co ordering ~different sites for $\square$ and Co! in $\square CoO_2$ (x_{Li} 5 0). A third type of ordering in these materials, vacancy/Li ordering in $Li_x\square_{1\,2\,x}CoO_2$ $(0 < x_{Li} < 1)$, is not treated here.

Our calculation proceeds in three steps: ~1! *Total-energy calculations:* We calculate the T 5 0 total energy of a set of ~not necessarily stable! ordered structures via the full potential, all-electron linearized augmented plane-wave method ~LAPW! ~Refs. 15 and 16! with all atomic positions fully relaxed via quantum mechanical forces. We then map those energies onto a ~2! *cluster expansion* ~CE!.[17–22] This expansion is a generalized Ising-like expression for the energy of an *arbitrary* substitutional cation arrangement. Once the coefficients of the expansion are known, the Ising-like expression may be easily evaluated for any cation configuration. Thus, one can calculate ~via first principles! the total energy of *a few* cation arrangements, but then effectively search the space of 2^N configurations ~where N is typically &10^4

are &1000 K.[1] The addition of Li vacancies lowers this transition to ;4400 K; however, this transition temperature is still too high to be observed. Thus, the finite-temperature calculations demonstrate that the observed disordered ~rock-salt! phase of $LiCoO_2$ is not thermodynamically stable, but is only stabilized kinetically.

~c! The intercalation reaction energy $E_{tot}(s, LiCoO_2)$ 2 $E_{tot}(s, \square CoO_2)$ 2 $E_{tot}(Li, bcc)$ gives the average battery voltage V

structure has one extra structural degree of freedom ~namely a c/a ratio! that the $D4$ structure does not have.[27]

We use N_s 5 8 configurations in the fitting procedure. These are shown in Fig. 1. The choice of end-point configurations requires some discussion. The nominal end-point configurations, LiO and CoO in the NaCl structure, do not obey the octet rule, as LiO has seven valence electrons/formula unit, while CoO has ~in addition to its filled t_{2g} shell! nine valence electrons/formula. As a result, these nominal structures have a very high energy. In the 1:1 structures $(LiO)_n(CoO)_n$, an electron will move from each CoO unit to fill the hole in the LiO unit, thus creating normal octet bonds. These ''charge-compensated'' end-point compounds $(LiO)^*$ and $(CoO)^*$ will have a lower energy than the nominal LiO and CoO. Our calculations thus consider only charge-compensated structures. Using the procedure of Wei, Ferreira, and Zunger[24] in treating heterovalent alloys, the conventional, high-energy ''end-point'' compounds LiO 1 CoO are not included in the CE because they are not charge compensated. Our CE could be used to *predict* the energies of $(LiO)^*$ 1 $(CoO)^*$, and we will see that this energy is indeed lower than that of nominal LiO 1 CoO. We and has access to a large database of structural energies, we

TABLE II. FLAPW calculated formation energies ~eV/formula unit! of various cation arrangements in $LiCoO_2$ and $□CoO_2$ 1 Li(bcc):$DH_f(s, LiCoO_2)$, $DH_f(s, □CoO_2)$ ~formation energies of s), and $DH_{react}(s)$ ~average intercalation voltage of $LiCoO_2$ relative to Li! are defined in Eqs. ~2!–~4!. V_{eq} is the equilibrium volume ~Å^3/formula unit! of $LiCoO_2$, and dV is the change in volume upon Li extraction @i.e., V_{eq}

vorable. This gives ~i! the T 5 0 K ground-state structures ~from a simulation of a finite-size cell initially at high temperature, and subsequently slowly cooled to a low temperature where all configurational changes proved to be energetically unfavorable!, ~ii! the pair-correlation functions or atomic short-range order present in the disordered alloy, and ~iii! the order-disorder transition temperature T_c.

III. T 5 0 FORMATION ENERGIES

A. Energetics of Li/Co ordering in $LiCoO_2$

The formation energies @Eq. ~2!# of $LiCoO_2$ in various cation arrangements are given in Table II and calculated structural properties are shown in Table III. We note that the $D4$ structure is only slightly higher in energy than the CuPt structure. This competition is interesting because $LiCoO_2$ has been synthesized in the $D4$ structure by solution growth at low temperature.[3,7–10,33–35] ~Although there was initially some discussion in the literature about this low-temperature synthesized phase being CuPt with imperfect long-range order,[7] it is now established that this phase is $D4$ ~or ''$D4$-like''!.[3,33,9,10,34] The near degeneracy of the calculated energies of the CuPt and $D4$ structures is simply a consequence of their identical pair and three-body correlations $\overline{\Pi}_f(s)$ noted above. We will see that the four-body interaction J_4 that distinguishes these structures is quite small, consistent with the small energy difference between CuPt and $D4$.

B. Energetics of □/Co ordering in $□CoO_2$

The formation energies @Eq. ~3!# of $□CoO_2$ in various □/Co arrangements are also given in Table II. These configurations correspond to various arrangements of Co and □. We note the following:

~1! The relative order of energetics is similar in $□CoO_2$ to that in $LiCoO_2$. There is only one qualitative difference: CH drops in energy significantly upon extraction of Li, and is lower in energy than the $Y2$ structure, whereas the reverse is true for $LiCoO_2$.

~2! The separation in energy between CuPt and $D4$ increases in $□CoO_2$ compared to $LiCoO_2$, due to the symmetry of the phases: Upon extraction of Li in the rhombohedral CuPt structure, the c/a ratio decreases significantly, providing a significant source of energy lowering for $□CoO_2$-CuPt. $D4$, on the other hand, is not a layered superlattice in any direction and has cubic symmetry. Hence, the cell parameters of $□CoO_2(D4)$ cannot distort in any preferred direction, and consequently, $□CoO_2(D4)$ does not relax as much as CuPt.

~3! The CuPt structure of $□CoO_2$ ~isostructural with $CdCl_2$) has an $ABC\ldots$ stacking of the cation planes. However, recent electrochemical measurements of Amatucci, Tarascon, and Klein[11] have succeeded in completely deintercalating Li from $LiCoO_2$, forming a $□CoO_2$ structure that is isostructural with CdI_2, with the stacking of planes in an $AAA\ldots$ arrangement ~see Fig. 3 and Table III! which we call ''CuPt (AAA).'' These two structure are not related to one another by substitutional degrees of freedom, and thus are not describable by a single cluster expansion. To examine these nonsubstitutional degrees of freedom, we have performed total-energy calculations of $□CoO_2$ in both the CuPt and CuPt (AAA) structures (CdI_2). Consistent with the observations of Amatucci, Tarascon, and Klein,[11] we find that the $□CoO_2$ in the AAA stacking is lower in energy than the CuPt structure by ; 0.05 eV/formula unit.

~4! We find that $LiCoO_2$ in the CuPt (AAA) structure ~Fig. 3! is higher in energy than the CuPt structure ~with ABC stacking! by ; 0.15 eV/formula unit, in agreement with the fact that the observed CuPt ground state in $LiCoO_2$ has ABC stacking.

C. Effect of cation arrangement on average voltages

Table II gives the calculated reaction energies given in Eq. ~4! for each of the cation arrangements s studied here.

The average voltages for all cation arrangements considered are in the ; 4 V range. In particular, the average voltage for $LiCoO_2$

input only charge-compensated compounds, and therefore can be used to predict the energies of charge-compensated (LiO)* 1 (CoO)*. We find from our CE of $LiCoO_2$ that (LiO)* 1 (CoO)* is 0.79 eV/formula unit lower in energy than the nominal, non-charge-compensated LiO 1 CoO. Similarly, the CE of $\square CoO_2$ predicts that ($\square$O)* 1 (CoO)* is 0.84 eV below the noncompensated compounds.

A. Ground states

The simulated annealing algorithm finds the CuPt structure as the low-temperature state. In Table II, we simply note that this structure was the lowest in energy of the eight structures calculated by LAPW. But, the simulated annealing prediction of the ground state demonstrates that CuPt is also the lowest-energy configuration out of an astronomical number of possible configurations ~without symmetry, there are ; 2^N possible configurations that the algorithm could explore, where N 5 4096). For our cluster expansion of $\square CoO_2$, the simulated annealing algorithm also finds CuPt as the lowest-energy substitutional configuration. As we have already shown above, nonsubstitutional configurations are even lower in energy for the $\square CoO_2$ system ~e.g., the CdI_2 structure!.

By combining the simulated annealing algorithm with the cluster expansion of average voltage, one can search for the cation configuration with *maximum* voltage. This search yields a phase separated ~LiO 1

CuPt phase should form with a long-range order ~LRO! parameter of nearly unity. Thus, antisite defects Li_{Co} or Co_{Li} are probably not formed under conditions of thermodynamic equilibrium. Also, since CuPt is completely ordered by 2000 K, even the *D*4 structure is not stabilized by thermodynamic factors ~i.e., thermal fluctuations in energy are smaller than the CuPt-*D*4 energy difference for temperatures of interest!. However, the *D*4 structure has been observed in low-temperature solution grown and laser ablation-grown samples, which are probably not equilibrium phases.

C. Properties of disordered and partially ordered cation arrangements

Using the CE, we can compute the energetics of *any* cation arrangement such as random alloys or any disordered ~short-range or long-range ordered! phases. These are examples of phases that are not directly accessible to first-principles calculations, but may be accessed via the cluster expansion. We show the cluster expansion energetics of several such phases in Table II.

Random alloy. The perfectly random alloy is a phase in which Li and Co atoms ~or □ and Co for $\square CoO_2$) are dis-

SRO parameters, $\overline{\mathrm{P}}_{0,n}$ measure the extent to which spatial *correlations* exist in disordered alloys. The SRO parameters used to compute the energetics of the first ten neighbor shells were obtained from a Monte Carlo simulation of the $LiCoO_2$ disordered alloy just above the order-disorder transition ~in parentheses are the values for fully ordered CuPt or *D*4): 2 0.06(0.0), 2 0.27(2 1.0), 1 0.03(0.0), 1 0.12(1 1.0), 1 0.02(0.0), 2 0.07(2 1.0), 2 0.02(0.0), 1 0.10(1.0), 2 0.01(0.0), and 2 0.01(0.0). Note that the energetic effect of SRO is to significantly lower the energy of the random phase in both $LiCoO_2$ and $\square CoO_2$ by 0.27 and 0.40 eV/formula unit, respectively.

Partial long-range order. There have also been reports of long-range ordered $LiCoO_2$ ~either CuPt or *D*4) with small quantities of Li on the Co sites, or vice versa. This amounts to a CuPt or *D*4 phase with partial LRO. If the LRO parameter *h* 5 1, then all Li and Co atoms reside completely on their own sublattice and LRO is perfect. However, for states of partial LRO, *h* , 1, and there is an amount (1 2 *h*/2) of intermixing between sublattices. For simplicity, we assume that there are no short-range correlations between the intermixed atoms. In Table II, we show the energetics of CuPt and *D*4 structures with LRO parameter *h* 5 0.88, corresponding to 6% of Li on the Co sites, and vice versa. The $LiCoO_2$ energies of CuPt and *D*4 are both raised by 0.16 eV/formula unit relative to the *h* 5 1 fully ordered phases, while the corresponding increases for $\square CoO_2$ is 0.20 and 0.17 eV/formula unit.

The cluster expansion of voltage can also be used to predict the average voltages of configurations not directly accessible to first-principles calculations ~Table II!. In particular, we see that the random alloy ~3.99 V! is predicted to have a higher average voltage than the ordered CuPt phase ~3.78 V!. Since this phase has been produced by laser ablation,[34] it would be interesting to measure its electrochemical properties, in order to compare with our predictions. The increase only energetic effects due to strain, one obtains the correct order of these three structures for both octahedral and tetrahedral systems as compared with LAPW.[37–39] One should note, however, that in the LiMO$_2$ series, there are systems other than M 5 Co that possess ground states other than CuPt, e.g., the CH and Y2 structures. Thus, clearly, strain-only arguments do not explain the totality of ordering tendencies in these compounds, as other effects must dominate in some systems.

Another distinction between the ordering tendencies of the octahedral LiCoO$_2$ system with those of the tetrahedral systems is in the energy scale. In Fig. 2, the energy scale of the tetrahedral systems is multiplied by a factor of 5, and is still smaller than the octahedral energy scale. The difference between the energy of the highest and lowest ordered compounds in the isovalent tetrahedral III-III-V$_2$ systems is dE(CuPt-CH) ; 0.1 eV/formula unit, in the heterovalent tetrahedral CuInSe$_2$ system it is dE(V2-CH) ; 0.7 eV/formula unit, whereas this difference in the octahedral systems is dE(V2-CuPt) ; 1.4 eV/formula unit in the LiCoO$_2$ system and dE(V2-CuPt) ; 2.4 eV/formula unit in □CoO$_2$. Thus the energetic effect of cation ordering is much more dramatic in the octahedrally coordinated networks.

VI. SUMMARY

Using a combination of first-principles total-energy calculations, a cluster expansion approach, and Monte Carlo simulated annealing, we have studied the cation ordering in LiCoO

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[27] For CuPt in the ideal geometry ~with all atoms in ideal rocksalt positions!, c/a 5 2A6 5 4.899, whereas the observed ~4.98! ~Ref. 13! and calculated values ~4.84! differ from this ratio ~Table III!.

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