

Phase separation in Li_xFePO_4 induced by correlation effects

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We report on a significant failure of the local density approximation (LDA) and the generalized gradient approximation (GGA) to reproduce the phase stability and thermodynamics of mixed-valence Li_xFePO_4 compounds. Experimentally, Li_xFePO_4 compositions ($0 \leq x \leq 1$) are known to be unstable and phase separate into LiFePO_4 and FePO_4 . However, first-principles calculations with LDA/GGA yield energetically favorable intermediate compounds and hence no phase separation. This qualitative failure of LDA/GGA seems to have its origin in the LDA/GGA self-interaction which delocalizes charge over the mixed-valence Fe ions, and is corrected by explicitly considering correlation effects in this material. This is demonstrated with LDA+U calculations which correctly predict phase separation in Li_xFePO_4 for $U-J \geq 3.5$ eV. The origin of the destabilization of intermediate compounds is identified as electron localization and charge ordering at different iron sites. Introduction of correlation also yields more accurate electrochemical reaction energies between $\text{FePO}_4/\text{Li}_x\text{FePO}_4$ and Li/Li^+ electrodes.

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First-principles calculations employing density functional theory have proven to be a powerful method in understanding the thermodynamic, structural and electronic properties of a large class of materials. The density functional is not known exactly, and is usually modeled within the local density approximation (LDA) or generalized gradient approximation (GGA). For many systems LDA or GGA gives remarkably good agreement with experiments, which has made these techniques valuable tools to predict the behavior of materials.¹ However, the self-interaction in LDA/GGA tends to delocalize electrons too much, and as such these methods are unable to capture precisely the Coulomb correlation effects in correlated electron systems like transition metal oxides. The resulting failure to predict many transition metal oxides as insulators has been well documented.² In this paper we show by means of olivine-type Li_xFePO_4 that the tendency for LDA/GGA to delocalize the d electrons in mixed-valence transition metal oxides also leads to a qualitative failure in predicting miscibility and phase stability by a surprisingly large magnitude. The role Coulombic correlations play in phase stability will be qualitatively probed.

LiFePO_4 , a naturally occurring mineral, has attracted much attention recently, as its superb thermal safety, non-toxicity and low cost make it the most likely candidate for rechargeable Li-batteries electrodes in large applications such as electric and hybrid vehicles.³⁻⁸ In a battery, lithium is electrochemically and reversibly cycled in and out of the LiFePO_4 material. As a result, the pseudo-binary FePO_4 - LiFePO_4 phase diagram, critical for the material's behavior as an electrode, has been well characterized experimentally.

Olivine-type LiFePO_4 and the de-lithiated structure FePO_4 have an orthorhombic unit cell with four formula units (FU) and space group $Pnma$ (see Fig. 1). The olivine-type structure contains a distorted hexagonal close-packing of oxygen anions, with three types of cations occupying the interstitial sites: (1) corner-sharing FeO_6 octahedra which are

nearly coplanar to form a distorted two-dimensional square lattice perpendicular to the a axis, (2) edge-sharing LiO_6 octahedra aligned in parallel chains along the b axis, and (3) tetrahedral PO_4 groups connecting neighboring planes or arrays. Electrochemical experiments and x-ray diffraction measurements have confirmed that no intermediate compound Li_xFePO_4 exists between FePO_4 and LiFePO_4 ,^{3,4} so that its phase diagram consists of a wide two-phase region with limited solubility on both the FePO_4 and LiFePO_4 sides. The magnetic structure of LiFePO_4 and FePO_4 was determined from neutron diffraction data.^{9,10} Below the Néel temperature $T_N = 50$ K⁹ and 125 K,¹⁰ respectively, the iron spins align in an antiferromagnetic (AFM) array, induced by Fe-O-Fe superexchange interactions between neighboring iron atoms.

The objective of this paper is to investigate the stability of compounds between the composition FePO_4 and LiFePO_4 and demonstrate that Coulomb correlations are essential in reproducing the absence of intermediate compounds. Different Li arrangements with 4 formula units are considered in the primitive cell. All possible symmetry-distinct decorations of the four Li sites give seven structures, including two end members ($x=0,1$), one structure at each of $x=0.25$ and 0.75 , and three at $x=0.5$, here named 0.5a,

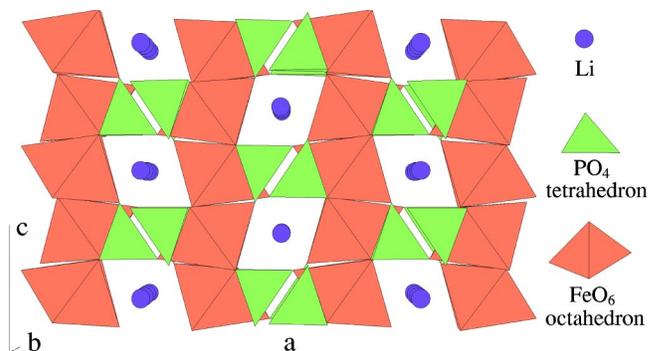
FIG. 1. Structure of LiFePO_4 with cation polyhedra.

TABLE I. Fractional positions of the four Li and four Fe atoms within the unit cell.

	Li 1	Li 2	Li 3	Li 4	Fe 1	Fe 2	Fe 3	Fe 4
x	0	0.5	0.5	0	0.28	0.22	0.78	0.72
y	0	0	0.5	0.5	0.25	0.75	0.25	0.75
z	0	0.5	0.5	0	0.98	0.48	0.52	0.02

0.5b and 0.5c. The structures 0.5a, 0.5b, and 0.5c have Li remaining at sites 1 and 2, 1 and 3, and 1 and 4, respectively (see Table I). All five intermediate structures have lower symmetry than the end members, and are monoclinic or triclinic.

Total energy calculations were performed for the seven structures in GGA (or LDA where explicitly stated) with the projector-augmented-wave method^{11,12} as implemented in the Vienna Ab-initio Simulation Package.¹³ An energy cutoff of 500 eV and appropriate k -point mesh were chosen so that the total ground state energy is converged within 3 meV per FU. All the atoms and cell parameters are fully relaxed at each structure. For $x=0.25$ and 0.75 the remaining S_2 point group symmetry has to be removed by imposing different initial magnetization on the irons to get the electronic ground state (see the following). The results in this paper represent the ferromagnetic (FM) spin-polarized configurations unless stated explicitly. Although the magnetic ground state of LiFePO_4 and FePO_4 is AFM,^{9,10} the difference in FM and AFM formation energies (defined in the following) is a few meV/FU in most cases, not exceeding 12 meV, and does not affect the qualitative analysis, which is clearer in the FM configuration. Iron is found to be always in the high-spin state, with the five majority spin $3d$ -orbitals occupied.

Here we define $\Delta E(x)$, the formation energy per FU of Li_xFePO_4 as

$$\Delta E(x) = E(x) - (xE(x=1) + (1-x)E(x=0)), \quad (1)$$

where $E(x)$ is the ground state total energy per FU for the structure with lithium concentration x . A negative formation energy means compound formation is energetically favorable. In order for phase separation to occur at room temperature, all intermediate structures should have positive formation energy, large enough to overcome the potential entropy gain in mixing. LDA results of $\Delta E(x)$ for all five structures are negative. Although GGA slightly increases the formation energy, the prediction remains qualitatively in disagreement with experiment (Table II).

Given that the true formation energies should all be positive, these errors are large and somewhat surprising, since formation energies are properly weighted energy differences

TABLE II. LDA and GGA formation energy (meV/FU) at different Li concentrations.

x	0.25	0.5a	0.5b	0.5c	0.75
LDA	-155	-255	-247	-136	-168
GGA	-135	-209	-197	-129	-138

between similar structures, and as such usually benefit from significant error cancellations. For example, in many binary alloys formation energies are only 100–200 meV/atom in magnitude, and hence large errors such as those found here would make them completely unreliable, which, based on the good agreement of many LDA/GGA studies with experiment, is not the case.¹⁴

To investigate whether Coulombic on-site effects could be related to this substantial failure of LDA/GGA we carried out rotationally invariant LDA+ U (GGA+ U , more accurately)¹⁵ calculations. The essence of the method can be summarized by the expression for the total energy

$$\begin{aligned} E_{\text{LDA}+U}[\rho, \hat{n}] &= E_{\text{LDA}}[\rho] + E_{\text{Hub}}[\hat{n}] - E_{\text{dc}}[\hat{n}] \\ &\equiv E_{\text{LDA}}[\rho] + E_U[\hat{n}], \end{aligned} \quad (2)$$

where ρ denotes the charge density and \hat{n} is the iron on-site $3d$ occupation matrix. The Hatree–Fock like interaction E_{Hub} from the Hubbard model replaces the double counting (dc) term E_{dc} representing the LDA on-site interaction. The U correction term $E_U \equiv E_{\text{Hub}} - E_{\text{dc}}$ is defined by Eq. (2). However E_{dc} is not uniquely defined, and here we consider three common approaches.¹⁶ The “around mean field” dc functional¹⁷ (dc1) yields low-spin iron, in disagreement with experiment.¹⁰ This is not surprising since dc1 usually works poorly in strongly correlated systems. We then compared formation energies with the dc functional defined in Ref. 15 (dc2) and with its spherically averaged version¹⁸ (dc3). The latter reads

$$E_{\text{dc}}(\hat{n}) = \frac{U-J}{2} \text{Tr} \hat{n} (\text{Tr} \hat{n} - 1) = \frac{U'}{2} \text{Tr} \hat{n} (\text{Tr} \hat{n} - 1), \quad (3)$$

$$E_U(\hat{n}) = \frac{U-J}{2} \text{Tr}(\hat{n}(1-\hat{n})) = \frac{U'}{2} \text{Tr}(\hat{n}(1-\hat{n})), \quad (4)$$

where we have defined $U' = U - J$. The formation energy with dc2 is very insensitive to a large range of J (0–2 eV) when U' is fixed, and agrees with dc3 results within 10 meV for $U' \geq 2$ eV. Therefore, we will use dc3, in which there is only one effective parameter, U' . We evaluate all results as function of U' , spanning the range from 0 to 5.5 eV. When calculating formation energies for a given U' , we assume U' to be the same for all structures. The choice of U' is a source of uncertainty in LDA+ U calculations. However, we present the results as a function of U' and will argue that the correct physics is obtained within a reasonable range of U' .

In Fig. 2 formation energies at different U' are shown as a function of Li concentration x . At each concentration ΔE increases with U' and becomes positive at intermediate U' (≈ 2.5 – 3.5 eV). The formation energies saturate to a nearly constant value around $U' \approx 3.5$ – 4.5 eV. The effect of the E_U term is to drive the Fe- $3d$ orbital occupation numbers to integer (0 or 1) values. As a result, the Fe ions tend to have integral occupancy even in the partially lithiated structures, and charge ordering occurs: we see distinct Fe^{3+} and Fe^{2+} in DFT+ U instead of the uniform $\text{Fe}^{(3-x)+}$ seen in LDA/GGA. For low U' values ($U' \lesssim 1$ eV) the four Fe ions

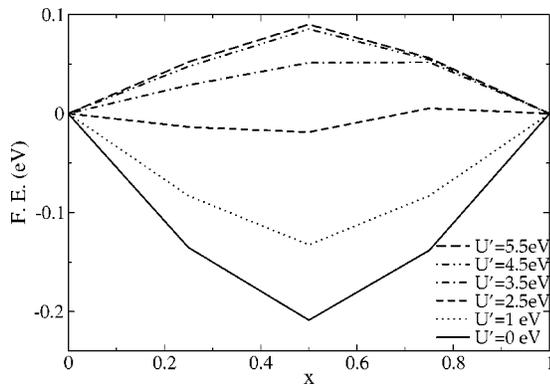


FIG. 2. Formation energy of Li_xFePO_4 at different x and U' values. Points at $x=0.5$ correspond to structure 0.5a.

in the unit cell have similar $3d$ electron occupancy and Fe-O bond lengths for all the intermediate structures. Therefore, little charge ordering occurs in this limit, even though the Fe ions occupy symmetrically distinct positions. We will call these Fe cations $(3-x)^+$ like. They are stable with respect to small perturbations in initial charge distribution. In the high limit of U' (≥ 3.5 or 4.5 eV) there are two types of Fe ions, one very similar to those in FePO_4 (which we call Fe^{3+} like) and the other similar to those in LiFePO_4 (called Fe^{2+} like). The designation $3(2)^+$ is only meaningful in that the Fe ions are similar to those in $\text{FePO}_4(\text{LiFePO}_4)$. The Fe-O hybridization gives them less than nominal charge. For $x=0.25(0.75)$ calculations imposing the symmetry of the structure on the charge density leads to two $3(2)^+$ like and two 2.5^+ like Fe ions. Only when symmetry is broken does a lower energy state with three $3(2)^+$ like and one $2(3)^+$ like ions form. In these structures the charge density has lower symmetry than what would be expected from the ionic positions and, hence, charge ordering occurs. As the analysis for all five structures is similar we choose $x=0.5a$ as a typical intermediate structure for further discussion.

In Fig. 3 $\Delta E(x=0.5a)$ is shown as a function of U' . We investigated AFM spin configurations in $x=0, 0.5a$ and 1 and found them to give only slightly lower total energies. The AFM ΔE (dotted line) is almost equivalent to the FM one with charge ordering (solid line). We also studied a “restricted” FM system at $x=0.5a$ where all four Fe ions have

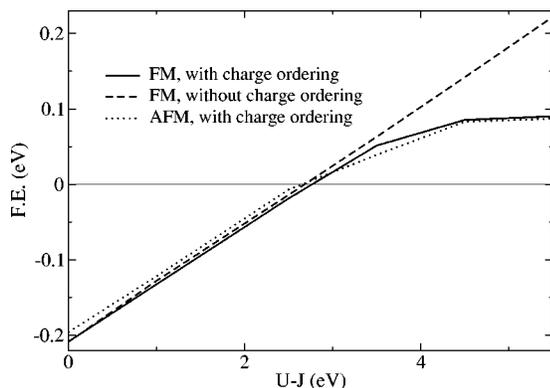


FIG. 3. Formation energy of structure 0.5a vs U' .

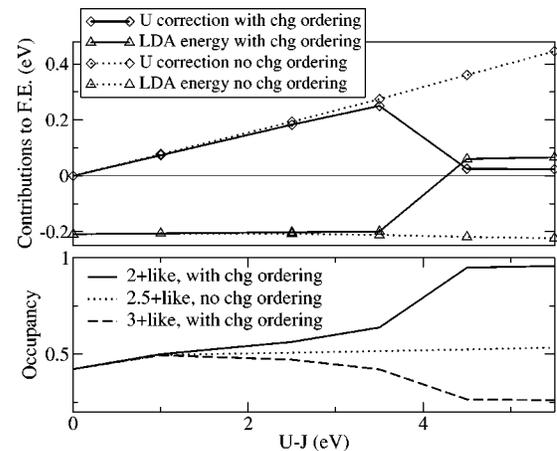


FIG. 4. Upper part: LDA (triangle) and U correction term (diamond) contributions to $\Delta E(x=0.5a)$ vs U' . Solid/dotted lines indicate presence/absence of charge ordering. Lower part: occupancy of the most occupied minority-spin orbital vs U' , for Fe 2^+ (solid line) and 3^+ (dashed line) in the charge-ordered state and for 2.5^+ (dotted line) in the state without charge ordering.

the same initial magnetization, ending up 2.5^+ like. Charge ordering is absent in this metastable state, which has higher total energy than the charge-ordered ground state. From Fig. 3 we can compare ΔE with and without charge ordering. Note that the curve with charge ordering levels off for $U \geq 4.5$ eV, which is explained in the following.

To study quantitatively the change in formation energies and electron distribution as U' is increased, the contributions to ΔE are separated into the LDA energy, ΔE_{LDA} , and the correction term, ΔE_U , with definitions analogous to ΔE in Eq. (1). The occupancy of the most occupied of the five minority-spin $3d$ -orbitals of iron is displayed in the lower part of Fig. 4. This orbital is most relevant because its occupation makes the difference between Fe^{3+} and Fe^{2+} . When charge ordering is absent, the occupation number does not change much with U' and stays near 0.5, as expected of a 2.5^+ like Fe cation. In contrast, the curves in the charge-ordered state separate beyond $U' \approx 1$ eV, with half of the ions becoming 2^+ like and the other half 3^+ like. These occupancies can help to explain ΔE in the upper part of the diagram. When charge ordering is absent (dotted lines) the four Fe cations in the $x=0.5a$ structure are equally affected by U' in terms of $3d$ occupation, as they are in $x=0$ and 1, and the changes in $\text{Tr}(\hat{n}(1-\hat{n}))$ in $\text{Li}_{0.5a}\text{FePO}_4$ are canceled by the weighted average of those in $x=0$ and 1 structures. As a result, the correction term ΔE_U is almost proportional to U' , explaining its linear behavior in Fig. 4. When the symmetry is sufficiently broken, ΔE_U will make Fe- $3d$ charge density order so as to create, as much as possible, orbitals with integer occupation. This comes at a cost to ΔE_{LDA} , which changes from large negative values at $U'=0$ to positive values. We see two possible reasons why ΔE_{LDA} increases when charge ordering occurs. Localization of the minority spin electrons into half of the Fe sites as Fe^{2+} obviously leads to an increase in kinetic energy. Additionally, since Fe^{2+} and Fe^{3+} have different Fe-O bond lengths, their

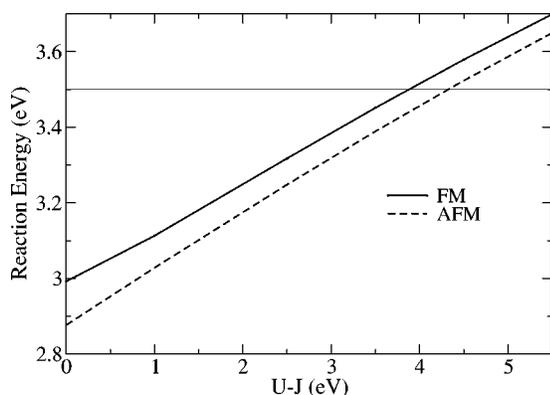


FIG. 5. Reaction energy in Eq. (5) per FU vs U' with FM and AFM configurations, respectively.

coexistence in one structure comes with a penalty in elastic energy. As the increase, relative to the LDA values, in ΔE_U is much smaller than in ΔE_{LDA} , the latter can be identified as the cause of phase separation.

The ground state electronic structure is also affected. The $x=0.5a$ compound is insulating when charge ordering occurs in LDA+ U , while it is metallic in LDA or LDA+ U without charge ordering. The end members are insulating in both LDA and LDA+ U .

A weakness of the LDA+ U method is that U is an external parameter, and some justification for the choice of it is required. Considering a realistic $J=1$ eV¹⁶ we find phase separation in the Li_xFePO_4 system for $U \geq 3.5$ eV + $J = 4.5$ eV. Above this cutoff the formation energies and orbital occupancies become less sensitive to U . The value of U for these systems is likely to be even higher than this cutoff. A recent *ab initio* computation of $U-J$ in the related Fe_2SiO_4 fayalite system suggests a value of 4.5 eV for iron.¹⁹

Another way to determine a physical value of U is to compare the calculated and experimental reaction energy of FePO_4 and Li to form LiFePO_4 .

$$\Delta E_{\text{reaction}} = (E_{\text{Li}} + E_{\text{FePO}_4} - E_{\text{LiFePO}_4}). \quad (5)$$

In this reaction Li^+ is inserted into the FePO_4 host and an electron is added to the d states, reducing Fe^{3+} to Fe^{2+} . Since the electron addition energy for Fe^{3+} is a significant component of this reaction energy, the result will depend on the value of U . Experimentally, this energy can be measured very accurately, as it is the equilibrium electrical potential between Li_xFePO_4 and Li-metal electrodes in a Li-electrolyte. In Fig. 5 the calculated potential is plotted as a function of U with FM and AFM spin configurations, respectively. The experimental voltage of 3.5 V⁴ is reached at $U - J \approx 4.2$ eV.

We have further confirmed that the positive formation energies obtained in Fig. 3 are not an artifact of using a single unit cell by calculating the energy of four other structures ($x=0.25$ or 0.75) with a doubled unit cell. We found all these formation energies to be within ± 10 meV of the results shown in Fig. 3. Positive formation energies in GGA was recently confirmed in Ref. 20.

In summary, we find that both LDA and GGA qualitatively fail to reproduce the experimentally observed phase stability and mixing energetics in the Li_xFePO_4 system. For $U - J > 3.5$ eV, LDA+ U calculations give positive ΔE , in agreement with experiments. Hence, we speculate that the experimentally observed phase separation is due to the cost in kinetic and elastic energies when Fe^{2+} and Fe^{3+} coexist in Li_xFePO_4 structures. This physics is not well captured by LDA/GGA, as the self-interaction causes a delocalization of the d electrons, resulting in electronically identical Fe ions. As a result, there is no phase separation in LDA/GGA, in clear disagreement with experiment.

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