

Lithium Battery Materials LiMPO_4 ($M = \text{Mn, Fe, Co, and Ni}$): Insights into Defect Association, Transport Mechanisms, and Doping Behavior

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The defect chemistry, doping behavior, and ion migration in olivine-type materials LiMPO_4 ($M = \text{Mn, Fe, Co, and Ni}$) are investigated by atomistic simulation techniques. The most favorable intrinsic defect type is found to be the cation antisite defect, in which Li and M ions exchange positions. Li migration is found to occur preferentially down [010] channels, following a curved trajectory. Defect association or binding energies for pair clusters composed of combinations of lithium vacancies, antisite cations, and small polaron species are investigated. Migration energies for divalent antisite cations on Li sites suggest that such defects would impede Li diffusion in LiMPO_4 to varying degrees. Calculation of dopant substitution energies for cations with charges +1 to +5 indicate that supervalent doping (e.g., Ga^{3+} , Ti^{4+} , Nb^{5+}) on either Li or M sites is energetically unfavorable and does not result in a large increase in electronic (small polaron) species.

1. Introduction

There is intensive research activity into alternative electrode materials for the next generation of rechargeable lithium-ion batteries, particularly for use in hybrid electric vehicles.^{1,2} Olivine-structured orthophosphates LiMPO_4 ($M = \text{Mn, Fe, Co, and Ni}$) have been proposed as viable alternatives to the conventional cathode material, LiCoO_2 .^{1–3} These olivine phosphates have good thermal stability, with high voltages versus the Li^+/Li couple.⁴ Moreover, the Fe and Mn members are environmentally benign and of low cost.

To date, most interest has focused on the LiFePO_4 phase,^{1–3} which is already in commercial use. Attention continues to be paid to the other transition metal systems,^{4–8} because any one of these would provide higher cell voltages than LiFePO_4 . Unfortunately these materials all suffer from a number of drawbacks that must be overcome before they can compete with LiFePO_4 . For example, LiMnPO_4 has poorer Li-ion conductivity than LiFePO_4 ,⁵ while the high upper charge voltages of LiCoPO_4 and LiNiPO_4 mean that

significant advances in electrolyte chemistry must be made before they can be put to use.^{6,7} LiNiPO_4 also exhibits extremely poor electronic conductivity and extremely low charge/discharge capacity.⁶

Low intrinsic electronic conductivity is one of the main difficulties of using all the LiMPO_4 ($M = \text{Mn, Fe, Co, and Ni}$) materials. Typically this is overcome through a combination of synthesis methods, such as preparing the material in nanoparticulate form with a coating of an electronically conductive phase such as carbon.^{2,9,10} In the case of LiFePO_4 , initial reports of supervalent cation doping¹¹ promised marked improvements in electronic conductivity of 8 orders of magnitude. However, subsequent studies suggest that this is not a true lattice doping effect but a result of carbon contamination from organic precursors and/or metallic-type conductive (secondary) phases being formed on particle surfaces under the highly reducing conditions used.^{12–14} Similar conclusions have been reached for LiCoPO_4 ,^{14,15} LiMnPO_4 ,¹⁴ and LiNiPO_4 .^{13,14}

Many researchers have also examined the electrochemical behavior of solid solutions of these systems, particularly $\text{LiM}_x\text{Fe}_{1-x}\text{PO}_4$.^{16–19} Given their similar ionic radii,²⁰ it

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might be expected that these four transition metals are mutually soluble within each system. In the case of $\text{LiCo}_x\text{Fe}_{1-x}\text{PO}_4$, neutron diffraction revealed that the Co^{2+} ions are distributed randomly over Fe^{2+} sites.²¹ Similarly, in our previous paper, we presented support for the solubility of Mn^{2+} , Co^{2+} , and Ni^{2+} on the Fe site in the LiFePO_4 system based on lattice energetics of dopant incorporation.²²

To understand the processes and structural features influencing the electrochemical behavior of these olivine phosphates, it is clear that fundamental knowledge of the underlying defect and transport properties is needed on the atomic scale. For instance, there has been recent speculation about the possibility of antisite defects and/or defect association (trapping) in LiFePO_4 affecting the diffusion behavior.^{23,24} Although such atomic level analysis is difficult to perform experimentally, atomistic simulation techniques provide a powerful means of investigating these key solid-state issues.

The present work extends our previous simulation studies of LiFePO_4 , where we examined the bulk defect chemistry and lithium transport²² and, more recently, surface structures and crystal morphology.²⁵ Here we present a systematic comparison of the energetics of intrinsic disorder, defect association, dopant incorporation, Li migration, and antisite cation migration in the four olivine-type materials LiMPO_4 ($M = \text{Mn, Fe, Co, and Ni}$).

2. Simulation Methods

This investigation uses well-established simulation techniques based on the Born model of solids. As these techniques are described in detail elsewhere,²⁶ only a general outline will be given here. All systems were treated as crystalline solids, with interactions between ions consisting of a long-range Coulombic component and a short-range component representing electron–electron repulsion and van der Waals interactions. The short-range interactions were modeled by use of the Buckingham potential:

$$\Phi_{ij}(r_{ij}) = A_{ij} \exp(-r_{ij}/\rho_{ij}) - C_{ij}/r_{ij}^6 \quad (1)$$

where r is the interatomic separation and A , ρ , and C are ion–ion potential parameters. An additional three-body term was used for the PO_4 units to take into account the angle-dependent nature and rigidity of O–P–O bonds, as used previously for LiFePO_4 ^{22,25} and other phosphates.²⁷ The three-body term took the form of a harmonic angle-bending potential about the P ion:

$$\Phi_{ijk} = \frac{1}{2} K_{ijk} (\theta - \theta_0)^2 \quad (2)$$

where K is the force constant and the angle θ_0 is the equilibrium bond angle for a PO_4 tetrahedron.

To provide a simple means of including effects of electronic polarization, we employed the shell model²⁵ for M^{2+} and O^{2-} ions. This method allows the polarization effects of charged defects to be taken into account and has proven effective in simulating dielectric properties of a wide range of ceramic oxides. As argued previously,²⁶ employing a formal charge model does not necessarily mean that the electron distribution corresponds to a fully ionic system, as the validity of the potential model is assessed primarily by its ability to reproduce observed crystal properties. In practice it is found that such models work well, even for compounds where there is undoubtedly a degree of covalency, such as aluminophosphates²⁷ and olivine silicates.²⁸ A key benefit of the formal charge model is that there are no ambiguities about the charge state when isovalent and aliovalent dopant substitution are considered.

The lattice relaxation about point defects, defect clusters, or migrating ions was calculated by an implementation of the Mott–Littleton scheme incorporated in the GULP code.²⁹ This method partitions a crystal lattice into two regions, with ions within the inner spherical region (on the order of >700 ions) immediately surrounding the defect relaxed explicitly. Relaxation of such a large number of ions is important for charge defects that introduce long-range electrostatic perturbations and is not easily treated by electronic structure methods. The outer region extends to infinity, with the outer lattice relaxation treated by quasi-continuum methods, since the defect forces here are relatively weak.

These techniques have been used successfully on a wide range of inorganic solids, including recent work on the fuel cell material LaBaGaO_4 ,³⁰ as well as spinel-type lithium battery materials LiMn_2O_4 and Fe_3O_4 .³¹

3. Results and Discussion

3.1. Structural Modeling. The starting point of the study was to reproduce the experimentally observed crystal structures.^{32–34} The olivine structure exhibited by LiMPO_4 materials is orthorhombic (space group $Pnma$), and consists of PO_4 tetrahedra with M^{2+} ions on corner-sharing octahedral positions ($4c$ sites in Wyckoff notation) and Li^+ ions on edge-sharing octahedral positions ($4a$ sites), the latter running parallel to the b axis. Most of the interatomic potentials were taken from our previous work on LiFePO_4 , while those for

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Table 1. Short-Range Potential Parameters

(a) Two-Body					
interaction	A (eV)	ρ (Å)	C (eV·Å ⁶)	Y (e) ^a	k (eV·Å ⁻²) ^b
Li ⁺ –O ²⁻	632.1018	0.2906	0.0	1.0	9999.0
Mn ²⁺ –O ²⁻	2601.394	0.278	0.0	3.42	95.0
Fe ²⁺ –O ²⁻	1105.2409	0.3106	0.0	2.997	19.26
Co ²⁺ –O ²⁻	1670.2416	0.2859	0.0	3.503	110.5
Ni ²⁺ –O ²⁻	1760.0	0.28	0.0	2.0	93.7
P ⁵⁺ –O ²⁻	897.2648	0.358 98	0.0	5.0	9999.0
O ²⁻ –O ²⁻	22 764.3	0.149	44.53	-2.96	65.0

(b) Three-Body		
bond type	K (eV·rad ⁻²)	θ_0 (deg)
O ²⁻ –P ⁵⁺ –O ²⁻	1.322 626	109.47

^a Shell charge. ^b Core–shell spring constant.

Table 2. Calculated and Experimental Structural Parameters of LiMPO₄ (M = Mn, Fe, Co, and Ni)

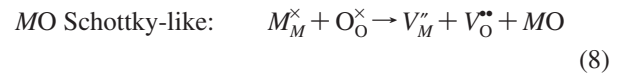
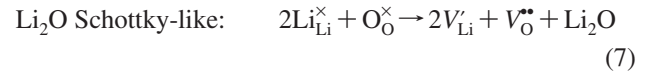
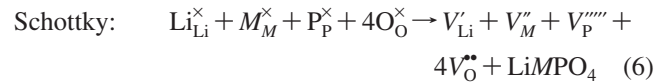
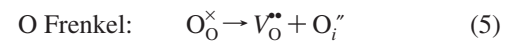
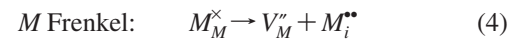
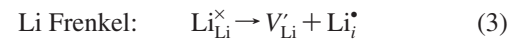
	a (Å)	b (Å)	c (Å)
LiMnPO ₄			
calc	10.5401	6.0874	4.6878
expt ^a	10.4310	6.0947	4.7366
Δ	0.1109	-0.0073	-0.0488
LiFePO ₄			
calc	10.3713	6.0216	4.6695
expt ^b	10.3377	6.0112	4.6950
Δ	0.0336	-0.0104	-0.0255
LiCoPO ₄			
calc	10.2428	5.9093	4.6418
expt ^c	10.2001	5.9199	4.6900
Δ	0.0428	-0.0106	-0.0482
LiNiPO ₄			
calc	10.1353	5.8432	4.6257
expt ^a	10.0275	5.8537	4.6763
Δ	0.1078	-0.0105	0.0506

^a Reference 32. ^b Reference 33. ^c Reference 34.

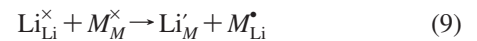
Mn²⁺–O²⁻, Co²⁺–O²⁻, and Ni²⁺–O²⁻ interactions were obtained by refining parameters from previous studies of their corresponding binary oxides. The potential parameters resulting from these refinements are listed in Table 1, with comparisons between the calculated unit cell parameters and those of the experimental crystal structures given in Table 2.

The calculated unit cell parameters deviate from experiment by at most 0.11 Å (in the case of LiMnPO₄) and in most cases much less; the same is found for the Li–O, M–O, and P–O bond lengths (see Supporting Information). As is observed experimentally, the simulated lattice parameters and unit cell volumes decrease across the series Mn, Fe, Co, Ni in accordance with Vegard’s law. This, combined with the excellent reproduction of the relatively complex olivine crystal structure, gives us confidence that the interatomic potential model can be used reliably in subsequent defect, dopant, and migration calculations.

3.2. Intrinsic Atomic Defects. A series of isolated point defect (vacancy and interstitial) energies were calculated for both systems. By combining these energies, the relative energies of formation of Frenkel and Schottky-type defects were determined. These take the following general forms (using Kröger–Vink notation), where $M = \text{Mn}^{2+}$, Fe^{2+} , Co^{2+} , or Ni^{2+} :

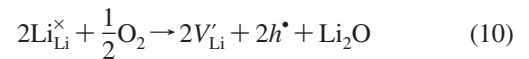


We also examined the Li/M “antisite” pair defect, which involves the exchange of an Li⁺ ion (radius 0.74 Å) with an M²⁺ ion (Mn²⁺ radius 0.83 Å, Fe²⁺ radius 0.78 Å, Co²⁺ radius 0.75 Å, and Ni radius 0.69 Å), according to



This type of defect is worth investigating since antisite or cation-exchange effects have been observed in the isostructural olivine silicates.³⁵

Off-stoichiometry defects (lithium deficiency or transition metal excess) were also considered according to



Our approach to electronic defects follows that used for other oxides (e.g., LiMn₂O₄ spinel³¹) in which we model the localized hole (h^{\bullet}) species (small polaron) on the transition metal ion as M^{3+} (see Supporting Information for details). Combining the calculated energies of isolated point defects and lattice energies, we can derive the energies for these intrinsic defect processes (eqs 3–11).

Examination of the results in Table 3 reveals three main points. First, the magnitude of the calculated energies suggests formation of M Frenkel, O Frenkel and Schottky defects is unfavorable. In particular, oxygen vacancies, oxygen interstitials, M²⁺ vacancies, and M²⁺ interstitials are highly unfavorable and thus unlikely to occur in any significant concentration.

Second, the most favorable intrinsic defect for all LiMPO₄ materials is the Li/M antisite pair (energy <1.50 eV), as predicted in our earlier study of LiFePO₄.²² This suggests that even at low temperatures there will be a small percentage of Li ions on M sites and M ions on Li sites; the concentration would be temperature-dependent and hence sensitive to experimental synthesis conditions. Structural analysis of hydrothermally synthesized LiFePO₄ suggests 3 mol % Fe on the lithium sites,²⁴ while a recently reported scanning transmission electron microscopy (STEM) study³⁶ confirms

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Table 3. Energies of Intrinsic Atomic Defects in LiMPO₄ (M = Mn, Fe, Co, and Ni)

disorder type	eq	energy (eV)			
		Mn	Fe	Co	Ni
Li Frenkel	3	1.97	2.15	2.32	2.38
M Frenkel	4	6.80	5.58	6.29	6.35
O Frenkel	5	7.32	5.46	6.71	8.65
full Schottky	6	33.58	25.30	29.96	33.20
Li ₂ O Schottky-like	7	7.36	6.33	6.97	6.95
MO Schottky-like	8	7.15	5.58	6.21	6.77
Li/M antisite	9	1.48	1.13	1.18	1.17
Li ⁺ deficiency	10	8.97	4.41	5.27	7.58
M ²⁺ excess	11	3.14	3.13	3.38	3.55

our earlier prediction of antisite defects in LiFePO₄, quoting a concentration of around 1%. Our present results demonstrate that such defects are general to the olivine-type phosphates LiMPO₄.

Such cation exchange is well-known in olivine silicates such as MgFeSiO₄³⁵ and can be rationalized in terms of the similar volumes and coordination environments of the two cation sites. In the LiMPO₄ materials, however, one consequence of this exchange is that an M ion on an Li site could block the lithium diffusion pathway, a point we return to in section 3.5.

Interestingly, in the Na analogue of the iron-containing system, NaFePO₄, the positions of the Na⁺ and Fe²⁺ ions are completely reversed (i.e., all Fe²⁺ are on 4a sites with the larger Na⁺ ion on 4c sites).³⁷ Consequently NaFePO₄ has very poor ionic conductivity, as the 4c sites on which the Na⁺ ions reside do not form a continuous network, unlike the 4a sites aligned along the [010] direction. This is also consistent with the low energies calculated for Na⁺ substitution in LiMPO₄ materials (see section 3.6).

Finally, the second lowest energies for all LiMPO₄ systems are found for the Li Frenkel defect (Table 3). This suggests that a minor population of such defects could be present at high temperatures. We note that intrinsic redox processes such as oxidation, reduction, and disproportionation were also considered. In general, the energies (all greater than 3.2 eV) suggest that oxidation (with V_{Li}[•] and M³⁺ formation) and reduction (with V_O[•] and M⁺ formation) of the olivine phosphate materials is difficult. This is consistent with the observation that these materials exhibit low intrinsic electronic conduction and that they do not show the oxygen nonstoichiometry found in other oxide cathode materials such as Li₂MnO_{3-δ}.³⁸

3.3. Defect Association. It is well established that the electrostatic and elastic interactions between point defects can lead to clustering or association. In the field of oxide-ion conductors in particular, it is known that defect clustering can add a binding (association) energy term to the conduction activation energy. For example, experimental and calculated binding energies for defect pair clusters in lanthanide-doped CeO₂ for use in solid oxide fuel cells fall in the range -0.1 to -0.6 eV.³⁹

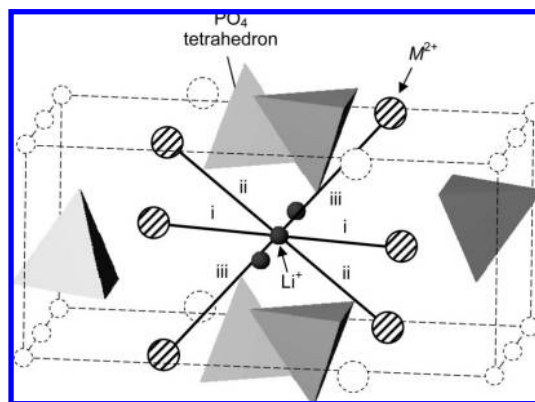


Figure 1. Cation neighbors relative to an Li site, showing three pairs of nonequivalent Li-M distances (Roman numerals indicate increasing interatomic distance), and surrounded by PO₄ tetrahedra. The other cations and unit cell are shown with dashed lines for clarity.

As there are a number of possible defects in the olivine orthophosphate systems, depending on temperature, initial stoichiometries, and lithium activity, several pair configurations of oppositely charged defects were considered. Indeed, the defect chemistry and possible association (trapping) in LiFePO₄ have been discussed recently by Maier and Amin,²³ where they note that detailed atomistic modeling is required to quantify the energies involved.

As demonstrated by previous studies on complex oxides,^{26,40} our simulation methods can model accurately the electrostatic, polarization, and elastic strain energies, which are the predominant terms in any local association process. The clusters considered comprised combinations of antisite defects, lithium vacancies, and hole species in the LiMPO₄ (M = Mn, Fe, Co, and Ni) systems.

The cluster binding energies (E_{bind}) were calculated from the general relationship

$$E_{\text{bind}} = E_{\text{cluster}} - \sum_{\text{component}} E_{\text{isolated}} \quad (12)$$

where a negative value indicates that the cluster is stable with respect to the isolated component defects. Energies of pairs of the most energetically favorable defects on neighboring cation sites were calculated relative to the same number of isolated defects. The defect pair clusters considered were (a) Li/M antisite defects, [Li_M[•]-M_{Li}[•]], (b) M ion on an Li site and a lithium vacancy, [M_{Li}[•]-V_{Li}[•]], (c) M³⁺ hole center (small polaron) and a lithium vacancy, [M_M[•]-V_{Li}[•]].

There are three nonequivalent Li-M interatomic distances to consider for configurations a and b (Figure 1). The lowest energies for each cluster type, listed in Table 4, were found for the shortest separation between defects.

Three key points can be identified from the results. First, all antisite clusters had negative binding energies, indicating that they are more stable than the isolated defects. This suggests that antisite defects will aggregate in the material, acting as precursors to larger clusters, as has recently been

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Table 4. Binding Energies of Defect Pair Clusters on Neighboring Cation Sites in LiMPO₄ (*M* = Mn, Fe, Co, and Ni)

defect cluster	binding energy (eV)			
	Mn	Fe	Co	Ni
[Li _{<i>M</i>} '-M _{<i>M</i>} Li]	-0.57	-0.44	-0.52	-0.54
[M _{<i>M</i>} Li'-V _{<i>M</i>} Li]	-0.65	-0.48	-0.57	-0.59
[M _{<i>M</i>} '-V _{<i>M</i>} Li]	-0.50	-0.39	-0.45	-0.64

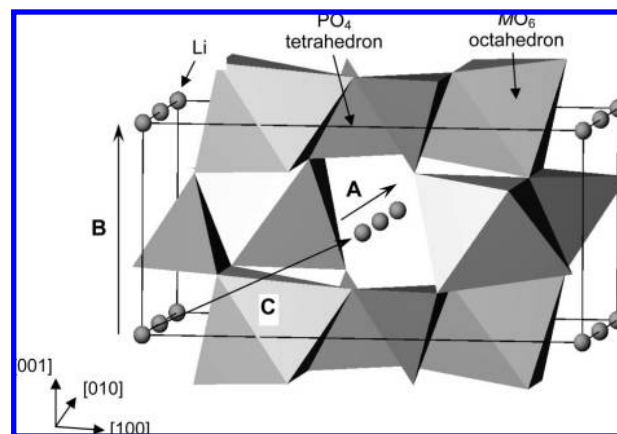
observed in LiFePO₄.³⁶ Although the binding energies are very similar for all four transition metals, the [Li_{Fe}'-Fe_{Li}}'] pair in LiFePO₄ and the [Li_{Mn}'-Mn_{Li}}'] pair in LiMnPO₄ were the most weakly and strongly bound, respectively.}}

Second, similar trends are found for clusters involving lithium vacancies and *M*²⁺ cations on lithium sites. The results reveal significant [M_{Li}'-V_{Li}}'] binding, which could lead to trapping of the migrating Li⁺ vacancies; as noted, such ions on the lithium site (M_{Li}'') could also hinder lithium diffusion along the *b*-axis channel.^{22,24} Because "trapping" introduces a further energy term to the lithium migration energy, this has implications for the lithium conductivity of these materials. The smallest binding energies are again found for the Fe system, which may favor higher lithium conduction rates compared to the others. The greatest trapping is predicted to occur in the LiMnPO₄ system. Although it is difficult to draw clear conclusions on the factors that lead to the small differences in binding energies for the four systems, as already mentioned, some of the key factors for defect association are electrostatic, polarization, and elastic strain (ion size) effects.}}

Finally, we find significant binding energies between the small polaron species (e.g., Fe³⁺ or Mn³⁺) and lithium vacancies, which are of relevance to the observed electronic conductivity; these results suggest the coupling or trapping of these charge carriers in Li_{1-x}MPO₄, as Mössbauer experiments have indicated that electron transport in Li_xFePO₄ occurs by small polaron hopping.⁴¹ Our results are compatible with GGA+U-type calculations that find a hole-vacancy binding energy in Li_{1-x}FePO₄ of greater than 500 meV.⁴²

3.4. Li Ion Migration. By use of atomistic simulation techniques, it is possible to examine various possible diffusion paths responsible for lithium conduction in these materials. Relaxation of the surrounding lattice (>700 ions) as an ion migrates through the structure is treated explicitly by these defect modeling methods.

Three possible migration paths were examined; these are labeled A–C in Figure 2 in order of shortest to longest jump distance. Path A involves migration between adjacent Li sites in the [010] direction, parallel to the *b* axis, with a jump distance of 2.9~3.0 Å. Path B involves migration in the [001] direction, parallel to the *c* axis, with a jump distance of 4.6~4.7 Å, while path C involves migration between the lithium channels in the [101] direction with the longest jump distance of 5.6~5.8 Å. Energy profiles for these mechanisms can be derived by calculating the energy of the migrating ion along the diffusion path, after relaxation of the surround-

**Figure 2.** Paths considered for lithium ion migration in olivine-structured phosphates LiMPO₄ (*M* = Mn, Fe, Co, and Ni).**Table 5. Mechanisms and Energies of Li Migration in LiMPO₄ (*M* = Mn, Fe, Co, and Ni)**

path ^a	migration energy, <i>E</i> _{mig} (eV)			
	Mn	Fe	Co	Ni
A [010]	0.62	0.55	0.49	0.44
B [001]	2.83	2.89	3.28	3.49
C [101]	2.26	3.36	3.41	3.99

^a Illustrated in Figure 2.

ing ions. The position of highest potential energy along the migration path corresponds to the activation energy of migration, *E*_{mig}. The migration energies for all compositions are listed in Table 5.

The results reveal that the lowest energy path for Li ion migration for all four materials is down the [010] channel, path A. High barriers of >2.2 eV are calculated for the other pathways (B and C), indicating that lithium ions cannot readily jump from one channel to another. By way of comparison, similar differences in activation energies are found between oxide ion migration (~0.9 eV) and cation migration (~2.3 eV) in the fast oxide ion conductor 8 mol % yttria-stabilized zirconia (YSZ),⁴³ in which cation migration is known to be orders of magnitude slower than oxide ion migration. This illustrates the strongly anisotropic nature of Li ion migration in the olivine phosphates. Our results are also consistent with electronic structure (density functional theory-type) calculations,⁴⁴ although in that study lower energy barriers of 0.1~0.3 eV were reported. Our calculated energies for LiFePO₄ and LiMnPO₄ are in accord with experimental activation energies of 0.63 eV for both LiFePO₄ and LiFe_{0.45}Mn_{0.55}PO₄.¹⁶

In the context of nanoparticle behavior, our recent LiFePO₄ surface simulations²⁵ showed that the (010) surface is prominent in the crystal morphology, in good agreement with experiment.⁴⁵ The exposure of this surface is significant since it is normal to the favored [010] conduction pathway.

Detailed structural analysis of the migrating ion shows that a curved migration path is taken between the adjacent lithium

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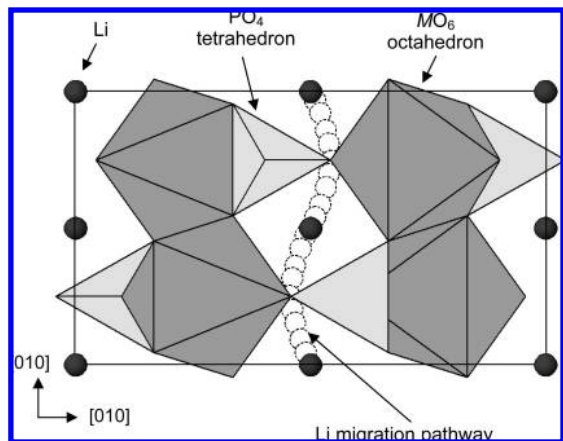


Figure 3. Schematic of curved migration pathway calculated for lithium ion migration in olivine-structured phosphates LiMPO_4 ($M = \text{Mn, Fe, Co, and Ni}$).

sites²² and not a direct linear path, as might be assumed. In each case, the migrating ion deviates from a linear path by around 0.5 \AA at its midpoint (Figure 3), while there is also a certain amount of lattice distortion around the diffusing lithium ion as it passes between the PO_4 and MO_6 polyhedra. More recently, neutron diffraction measurements of LiFePO_4 by Yamada et al.⁴⁶ confirm one-dimensional Li^+ diffusion, with a curved migration pathway between adjacent lithium sites, in excellent agreement with the present simulation results, as well as our earlier prediction.²² Similarly, magnetic susceptibility and X-ray absorption spectroscopy measurements reveal that the magnetic properties and electronic structure of single-crystal LiFePO_4 are different in the three axial directions.⁴⁷

These results contrast with a recent report that lithium ion diffusion in single crystals of LiFePO_4 was two-dimensional rather than one-dimensional.⁴⁸ However, two-dimensional transport with similar activation energies in the b and c directions is difficult to reconcile with the distinctly anisotropic nature of the orthorhombic olivine structure; for example, the corresponding Li–Li jump distances are highly disparate at $2.9\sim 3.0$ and $4.6\sim 4.7 \text{ \AA}$, respectively. Furthermore, tracer diffusion studies of another olivine-structured material, Fe_2SiO_4 , found Fe diffusion to be different along the three principal axes.⁴⁹

3.5. Antisite Cation Migration. Our defect calculations suggest that Li/M antisite defects are intrinsic to LiMPO_4 , and there is experimental evidence of a low concentration ($<3\%$) of Fe on Li sites in LiFePO_4 .²⁴ It may therefore be difficult to avoid M cations on Li sites blocking the diffusion pathways down $[010]$ channels, unless the antisite defect itself is mobile. Either scenario would likely reduce the electrochemical capacity.

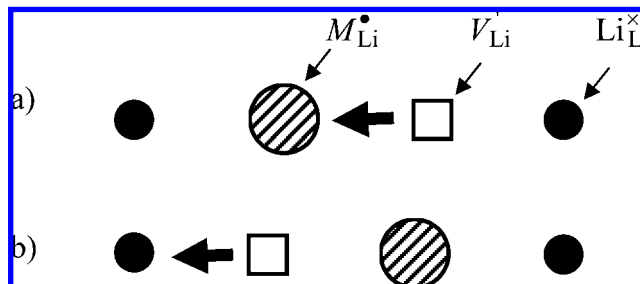


Figure 4. Schematic of two stages in migration of an Li vacancy (V_{Li}) down a $[010]$ channel of LiMPO_4 ($M = \text{Mn, Fe, Co, and Ni}$) near an antisite M cation (M_{Li}). (a) Exchange of V_{Li} and M_{Li} ; (b) exchange of V_{Li} and a lithium ion ($\text{Li}_{\text{Li}}^{\times}$).

Table 6. Energies of Antisite Cation (M_{Li}) Migration along $[010]$ in LiMPO_4 ($M = \text{Mn, Fe, Co, and Ni}$)

mechanism	E_{mig} (eV)
$\text{Mn}_{\text{Li}}^{\times} \rightarrow V_{\text{Li}}$	0.92
$\text{Fe}_{\text{Li}}^{\times} \rightarrow V_{\text{Li}}$	0.70
$\text{Co}_{\text{Li}}^{\times} \rightarrow V_{\text{Li}}$	0.81
$\text{Ni}_{\text{Li}}^{\times} \rightarrow V_{\text{Li}}$	1.33

In order to examine whether antisite defects affect long-range Li diffusion, the energy of migration of the divalent cation between lithium sites was calculated. This process can be viewed as an exchange of an antisite cation (M_{Li}^{\times}) with a lithium vacancy (as illustrated in Figure 4); the lithium vacancy would then continue to migrate in the opposite direction down the $[010]$ channel. A similar simulation procedure to that for Li migration was used, which allowed the lowest energy migration path to be determined. As for Li^+ migration, this was found to be a curved path between $4a$ sites (Figure 3).

All the calculated migration energies in Table 6 are $0.15\sim 0.7 \text{ eV}$ greater than the corresponding Li migration values, indicating lower antisite cation mobility compared to pure lithium diffusion. This suggests that antisite defects (M_{Li}^{\times}) would impede Li diffusion to varying degrees down $[010]$ channels. However, the most favorable migration energy (relatively low at 0.7 eV) is for LiFePO_4 , suggesting that a population of antisite defects in this system would have the least effect on lithium diffusion kinetics.

At this point it is interesting to examine overall trends in the energies of ion migration and defect association for LiMPO_4 systems. The magnitudes of the energies listed in Tables 4–6 reveal that the Fe system has a low lithium vacancy migration energy, the weakest $[M_{\text{Li}}^{\times}-V_{\text{Li}}]$ binding energy, and the lowest barrier to antisite cation migration. Combined, these results suggest higher lithium conduction rates in LiFePO_4 than in the other three systems.

3.6. Dopant Substitution. Reports that low-level ($<3\%$) doping of LiFePO_4 with cations (such as Al^{3+} , Zr^{4+} , and Nb^{5+}) produces orders-of-magnitude improvements in electronic conductivity¹¹ have stimulated considerable debate about the precise substitution mechanisms, nature of the conductive species, and, crucially, whether the dopant goes into the crystal lattice or if the enhanced conductivity is due to secondary effects such as carbon contamination and/or phosphide formation.^{12–14,16}

Our simulation methods can probe these issues by generating quantitative estimates of the relative energies of different

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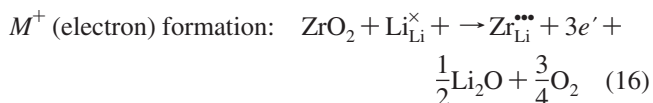
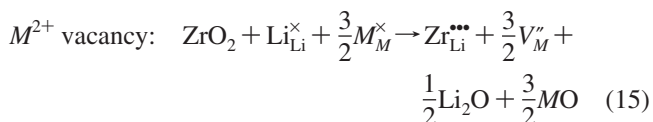
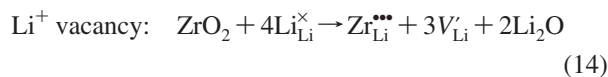
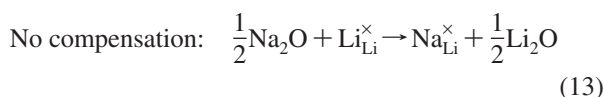
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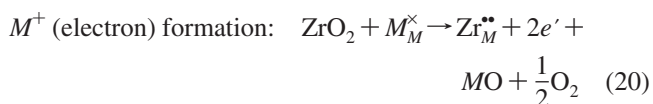
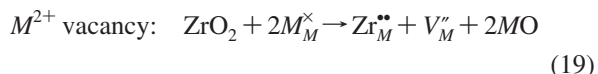
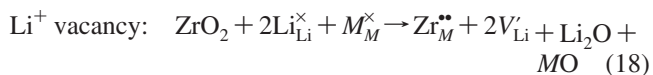
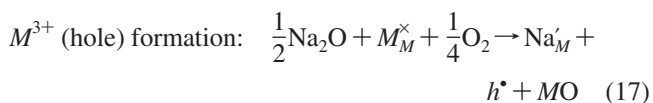
modes of dopant substitution. This can provide a useful systematic guide to the site selectivity for different dopant species and to trends in dopant solubility. In this study we have examined a range of dopants, from monovalent to pentavalent, in LiMPO₄, constituting a wider survey than current experimental reports.

For isovalent dopants (such as Na⁺ on Li⁺ or Mg²⁺ on M²⁺), no charge-compensating defect is required. However, for aliovalent dopants (whether donor ions such as Mg²⁺ on Li⁺ or Al³⁺ on M²⁺, or acceptor ions such as Na⁺ on M²⁺), the type of charge-compensating mechanism has not been clearly established from experiment and could consist of either Li vacancies, M vacancies, O vacancies, or electronic species (e.g., Fe⁺, Fe³⁺). We therefore calculated the overall substitution energy for a variety of different compensation mechanisms. With Na⁺ and Zr⁴⁺ as example dopant species on both Li and M sites (where M = Mn²⁺, Fe²⁺, Co²⁺, or Ni²⁺), incorporation mechanisms of the following types (normalized to a single dopant ion) were considered:

Li site



M site



The energies of these dopant substitution or solution reactions were calculated by combining the appropriate defect and lattice energy terms for each equation. Interatomic potentials used to model the corresponding binary oxides of the dopant cations were used in each case (given as Supporting Information). This systematic approach has been applied successfully to other oxide and silicate systems.^{40,50}

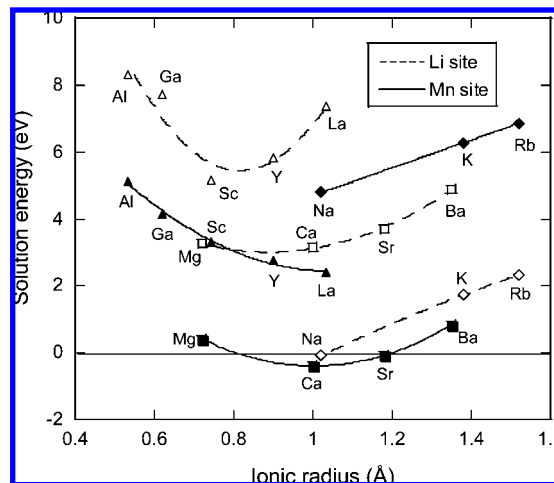


Figure 5. Solution energies versus dopant ionic radius for LiMnPO₄. Lines are a guide for the eye only.

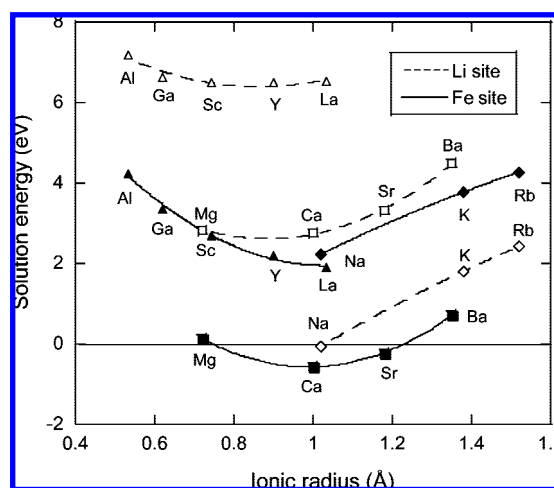


Figure 6. Solution energies versus dopant ionic radius for LiFePO₄. Lines are a guide for the eye only.

The dopant calculations were also carried out at the dilute limit, as is appropriate for examining low dopant concentrations.

Dopant incorporation, or solution, energies for a range of A⁺, A²⁺, and A³⁺ cation dopants with the most favorable charge compensation mechanisms are plotted as a function of ionic radius in Figures 5–8; because the solution energies for A⁴⁺ and A⁵⁺ dopants were much higher, these are listed separately in Table 7. Indeed, Nb⁵⁺ dopants on M²⁺ sites in LiMnPO₄ and LiNiPO₄ were found to be completely unstable.

These results indicate two main features. First, in all four LiMPO₄ materials the lowest energies are found for isovalent substitution; in particular, only Na doping for Li⁺ and divalent doping for M²⁺ were found to be favorable. This is consistent with the observed mutual solubility of Mg²⁺, Mn²⁺, Fe²⁺, Co²⁺, and Ni²⁺ in the various LiMPO₄ systems.^{6,15–19,21,24,51} However, these do not require any charge compensation and hence would not increase the number of charge carriers.

For example, Roberts et al.⁵² recently showed that Mg²⁺ is fully soluble on Fe sites in LiFePO₄ but does not go onto

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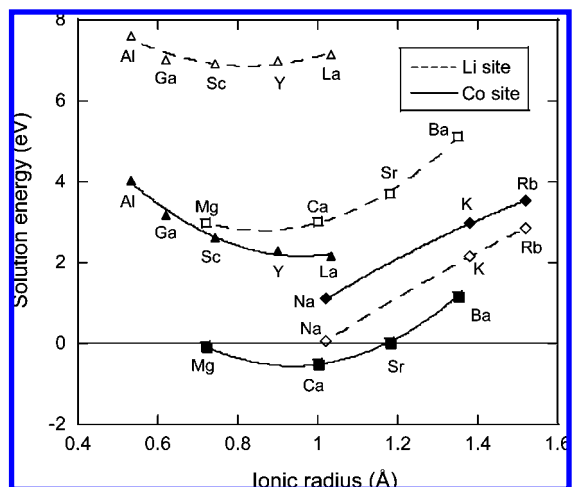


Figure 7. Solution energies versus dopant ionic radius for LiCoPO₄. Lines are a guide for the eye only.

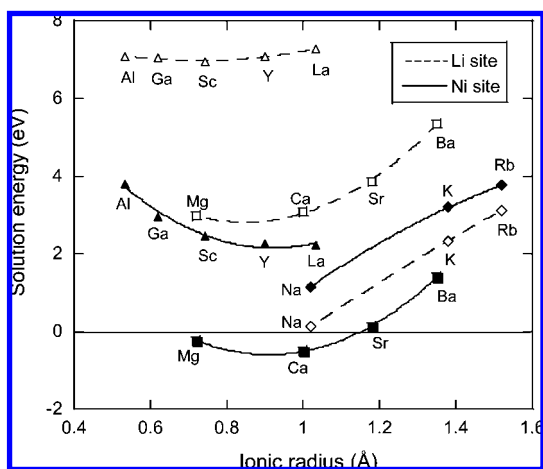


Figure 8. Solution energies versus dopant ionic radius for LiNiPO₄. Lines are a guide for the eye only.

Table 7. Solution Energies for Tetra- and Pentavalent Dopants in LiMPO₄ (*M* = Mn, Fe, Co, and Ni)

site	solution energy (eV/dopant)		
	Ti ⁴⁺	Zr ⁴⁺	Nb ⁵⁺
	LiMnPO ₄		
Li	11.0	12.5	17.9
Mn	7.6	6.8	NC ^a
	LiFePO ₄		
Li	10.7	10.6	13.5
Fe	6.0	5.7	7.7
	LiCoPO ₄		
Li	11.6	11.5	14.8
Co	6.3	7.3	12.5
	LiNiPO ₄		
Li	11.8	11.7	15.1
Ni	6.2	5.8	NC ^a

^a NC = nonconvergence of calculation.

the Li site. The LiFe_{0.9}Mg_{0.1}PO₄ system is reported to be more stable to capacity fade than undoped LiFePO₄,²⁴ although the incorporation of redox-inactive Mg²⁺ would reduce the effective electrochemical capacity. Interestingly, our results suggest that the most favorable dopant for M²⁺ is calcium, which to our knowledge has not been widely examined.

Second, a key result is that supervalent doping (especially of A⁴⁺ and A⁵⁺ ions) is energetically unfavorable in all LiMPO₄ systems. This strongly suggests that these ions are unstable within the crystal lattice and unlikely to be incorporated beyond low concentrations (<3%), in accord with our earlier study on LiFePO₄.²² For each system, the overall trends reveal that the greater the difference between the charges of the dopant and host ion, the higher the dopant incorporation energy (e.g., for the Li site, solution energies increase as Mg²⁺ < Ga³⁺ < Ti⁴⁺ < Nb⁵⁺). This indicates that electrostatic interactions dominate the energetics of dopant incorporation in these olivine-structured LiMPO₄ materials.

For both Li and *M* sites, the least favorable donor dopants were Ti⁴⁺ and Nb⁵⁺. The compensation mechanism for such supervalent dopants was found to be formation of M²⁺ vacancies, whereas compensation by a change in charge state of the transition metal (i.e., to give an M⁺ small polaron species) was much higher in energy. It is therefore unclear as to how supervalent doping could lead to a dramatic improvement in electronic conductivity.

Maier and Amin²³ also note that even if a small amount of supervalent (donor) dopant could enter the lattice to alter the transition metal's valence state, the number of native electronic carriers (holes) would decrease, effectively lowering the overall electronic conductivity, not increasing it. Furthermore, with suitable processing both LiFePO₄ and LiCoPO₄ can be made to exhibit conductivities as high as 10⁻⁴~10⁻² S cm⁻¹ in the absence of any dopants, demonstrating that doping need not be a major contributor to any improvements in conductivity.^{12,14,16}

Our simulation results also bear out other experimental reports. Butt et al.⁵³ obtained Raman data showing that Ti⁴⁺ is insoluble in LiNiPO₄, consistent with our results for this dopant. Wolfenstine¹⁵ also demonstrated that the electronic conductivity of LiCoPO₄ is not improved by doping, finding that the observed increase is due to the conductive Co₂P layer formed by carbothermal reduction. Delacourt et al.¹² attempted to dope LiFePO₄ with Nb⁵⁺ but were unsuccessful, while Ellis et al.¹⁴ showed that aliovalent dopants Al, Y, Cr, and Zr do not contribute to the high conductivity observed in LiMPO₄ treated at high temperatures under carbothermal or reducing conditions.

4. Conclusions

This systematic survey of the cathode materials LiMPO₄ (*M* = Mn, Fe, Co, and Ni) used atomistic simulation techniques to provide detailed insights into defect, dopant, and ion migration properties relevant to their electrochemical behavior. The main results can be summarized as follows:

(1) The observed crystal structures of all four phases were successfully reproduced by our potential models. The most favorable intrinsic defect in LiMPO₄ systems is the antisite defect, for which a small population (<2%) of Li⁺ and M²⁺

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(53) Butt, G.; Sammes, N.; Tompsett, G.; Smirnova, A.; Yamamoto, O. *J. Power Sources* **2004**, *134*, 72.

ions is expected to exchange sites; this would be temperature-dependent and hence sensitive to experimental synthesis conditions.

(2) Lithium ion diffusion follows a nonlinear, curved trajectory down the [010] channel, with relatively low migration energies (ca. 0.4~0.6 eV). High barriers of >2.2 eV for other pathways indicate that lithium ions cannot readily span the large jump (>4.5 Å) between channels. This one-dimensional transport mechanism is consistent with the strongly anisotropic nature of the orthorhombic olivine structure.

(3) Defect association effects could have a strong effect on the transport properties of LiMPO_4 . Association or binding energies of ca. -0.5 eV are found for $[\overset{\bullet}{M}_{\text{Li}}-\overset{\bullet}{V}_{\text{Li}}]$ pair clusters, which has implications for lithium conductivity as M^{2+} cations on Li sites could lead to trapping of the migrating Li^+ vacancies. Significant binding energies (ca. -0.4 to -0.6 eV) were also found between small polaron species and lithium vacancies, $[\overset{\bullet}{M}_{\text{M}}-\overset{\bullet}{V}_{\text{Li}}]$, which suggests the trapping or coupling of these charge carriers in $\text{Li}_{1-x}\text{MPO}_4$.

(4) The calculated migration energies (0.7~1.3 eV) for divalent antisite cations ($\overset{\bullet}{M}_{\text{Li}}$) jumping between two lithium sites down [010] channels suggests that such antisite defects would impede Li diffusion to varying degrees. However, the lowest antisite migration energy (0.7 eV) is for LiFePO_4 , suggesting that any antisite defects in this system would have the least effect on lithium diffusion kinetics.

(5) Of the four systems, the weakest binding energies for all defect pair clusters were found for LiFePO_4 . The overall

trends in the energies of ion migration and defect association suggest higher lithium insertion/extraction rates, and thus better electrochemical performance, in LiFePO_4 compared with the other three systems.

(6) A variety of dopants with charges of +1 to +5 were examined for both Li^+ and M^{2+} substitution. Low favorable energies were found only for Na^+ substitution on the Li^+ site and isovalent dopants (e.g., Mg^{2+}) on the M^{2+} site. In contrast, supervalent doping (especially Ti^{4+} and Nb^{5+}) appears unfavorable on both Li^+ and M^{2+} sites in all four phases; the charge-compensation mechanism found for such doping in LiMPO_4 does not alter the M^{2+} valence state and hence is unlikely to contribute to high electronic conductivity. These results are in accord with recent experimental reports of unsuccessful incorporation of significant levels (>3%) of aliovalent dopants to enhance electronic conductivity.

Acknowledgment. We thank the EPSRC for funding as part of the Supergen Energy Storage Consortium (Grant EP/D031672/1). We are also grateful to J. Maier, C. Masquelier, and L. F. Nazar for useful discussions.

Supporting Information Available: List of potential parameters for hole species and dopant cations and comparison of calculated and experimental bond lengths for the four olivine phosphates LiMPO_4 ($M = \text{Mn, Fe, Co, and Ni}$). This information is available free of charge via the Internet at <http://pubs.acs.org>.

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