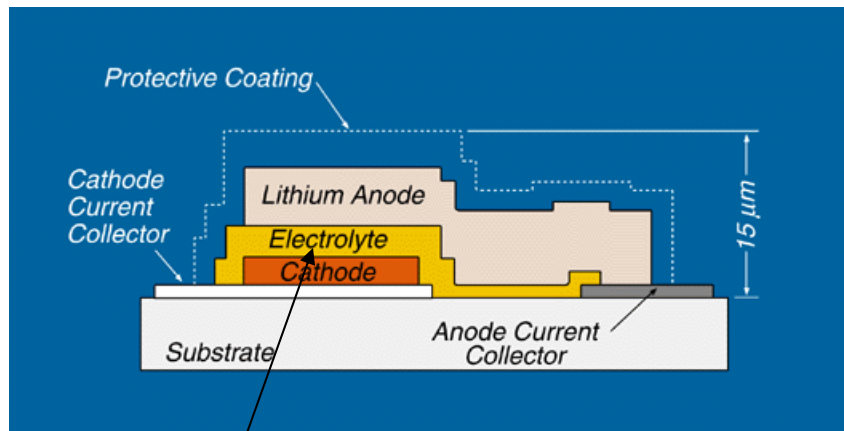


Li ion diffusion mechanism in the crystalline electrolyte $\gamma\text{-Li}_3\text{PO}_4$

Yaojun Du and N. A. W. Holzwarth

The structure of thin film battery³



Solid state electrolyte could be made very thin to overcome to the low ion-conductivity. Such as LiPON (Li_3PO_4)

LiPON electrolyte based on Li_3PO_4 , that is chemically and physically stable. is developed by ORNL¹.

Conductivities of various Li_3PO_4 -based materials are measured²

$$\sigma(T) = \frac{K}{T} e^{-E_A/kT}$$

material	E_A (eV)	σ (S cm ⁻¹) ^a
$\gamma\text{-Li}_3\text{PO}_4$	1.24	$4.2 \cdot 10^{-18}$
$\text{Li}_{2.88}\text{PO}_{3.73}\text{N}_{0.14}$	0.97	$1.4 \cdot 10^{-13}$
$\text{Li}_{2.7}\text{PO}_{3.9}$	0.68	$6.6 \cdot 10^{-8}$
$\text{Li}_{3.3}\text{PO}_{3.9}\text{N}$	0.56	$2.4 \cdot 10^{-6}$

a. Measured at 25 °C

1. B. Wang et al., J. of Solid State Chemistry **115**, 313 (1995).
2. J. B. Bates et al., Solid State Ionics **53-56**, 647 (1992).
3. <http://www.ms.ornl.gov/researchgroups/Functional/BatteryWeb/CrossSection.html>

Goal and Outline

For single crystal. Intrinsic carriers are created as Li vacancy-interstitial pair (Frenkel pair), which yields¹

$$\sigma \cdot T \sim ne^{-E_m/kT} = e^{-(E_m+E_f/2)/kT}$$

For doped crystal. extrinsic carriers are created as doped, which yields

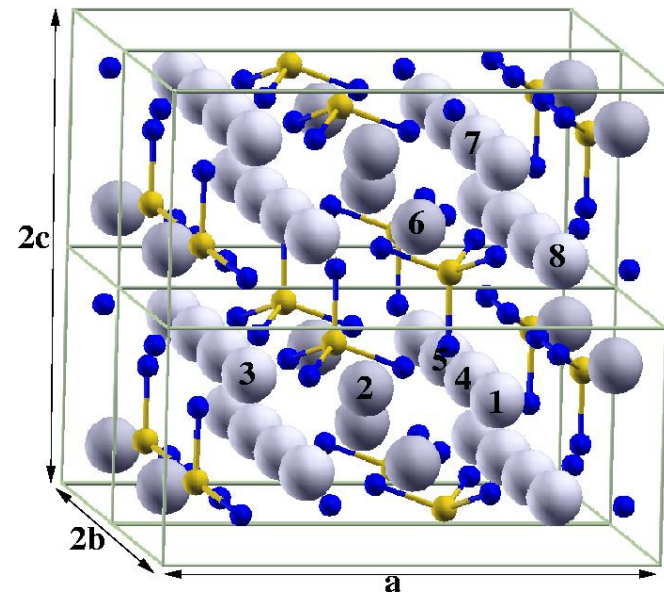
$$\sigma \cdot T \sim e^{-E_m/kT}$$

$\text{Li}_{2.88}\text{PO}_{3.73}\text{N}_{0.14}$ with 12%vacancy as doped.

-
- Method.
 - Vacancy mechanism of Li ion.
 - Interstitial mechanism of Li ion.
 - Formation of vacancy-interstitial pair.
 - Conclusion.

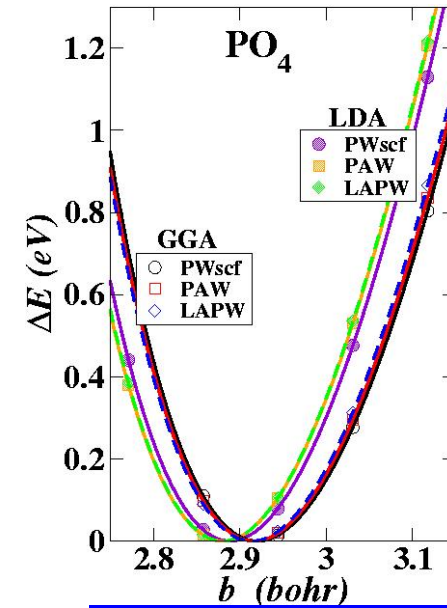
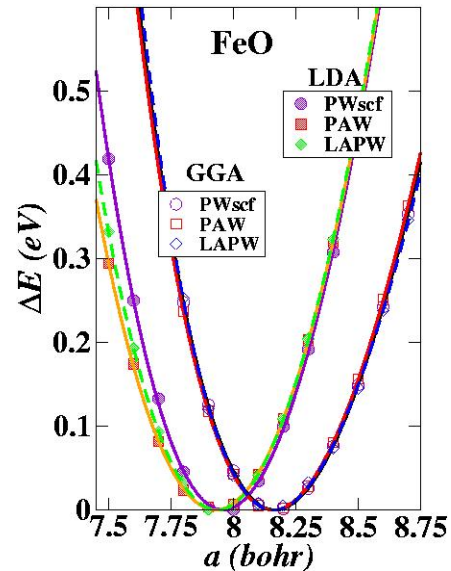
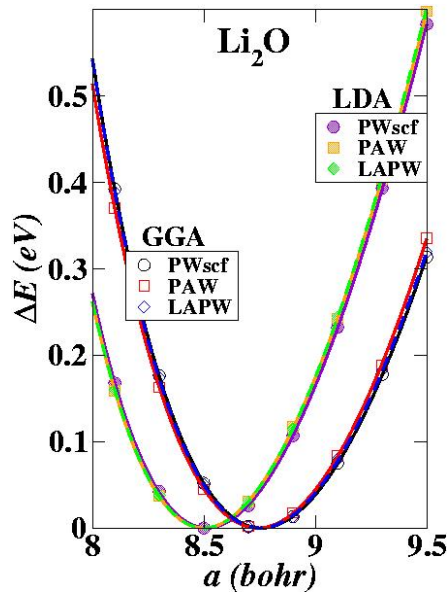
1. A. R. West, *Basic Solid state Chemistry*, 2nd ed; John Wiley & Sons: Chichester, U.K., 1999, p.217-218.

$\gamma\text{-Li}_3\text{PO}_4$ (Pnma)



Methods

Quantum ESPRESSO (*PWscf*)¹ package and ultra-soft pseudopotential formalism of Vanderbilt using GGA and LDA.

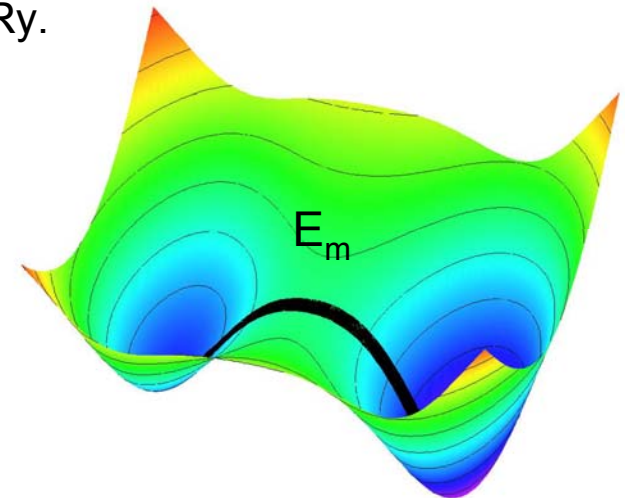


Single L-point k-mesh sampling, cutoff of planewave is 30 Ry.

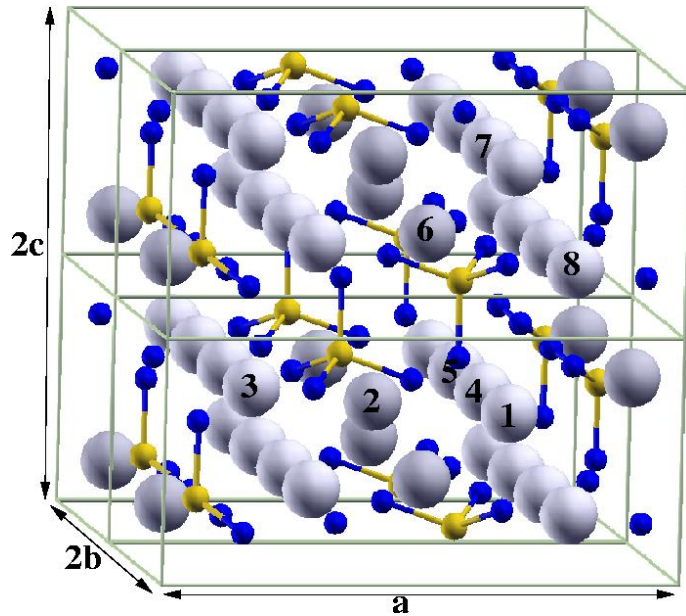
Nudged elastic band¹ method determines the minimal energy path connecting two adjacent local minima

1. www.pwscf.org

2. H. Jónsson *et al.*, in *Classical and Quantum Dynamics in Condensed Phase Simulations*, edited by B. J. Berne, G. Ciccotti, and D. F. Coker (World Scientific, Singapore, 1998), P. 385. G. Henkelman *et al.*, *J. Chem. Phys.* **113**, 9901 (2000).



Vacancy diffusion mechanism

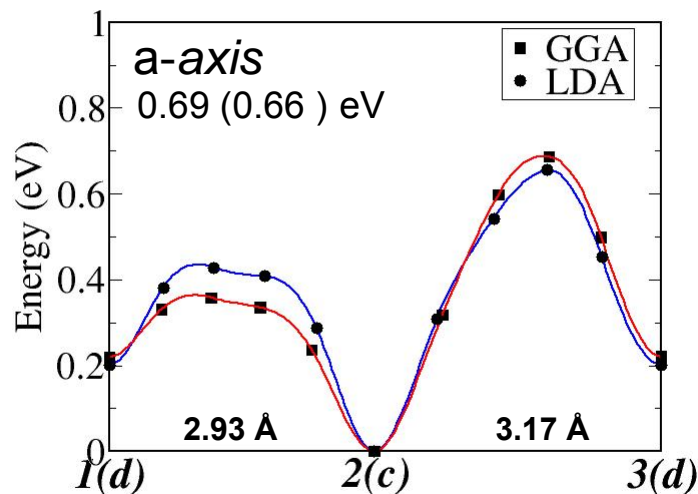


Volume optimized by Parrinello-Rahman scheme

	Experiment ¹	GGA	LDA
a (Å)	10.490	10.58	10.32
b (Å)	6.120	6.17	6.01
c (Å)	4.9266	4.99	4.84

Two types of Li (*d* and *c*) result in two types of Li ion vacancy:

$$E(\text{Li}_{v(d)}) - E(\text{Li}_{v(c)}) = 0.22 \text{ (0.20) eV}$$



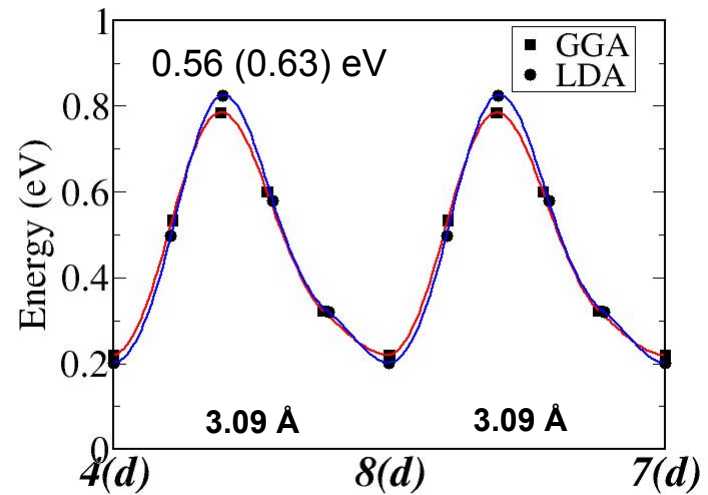
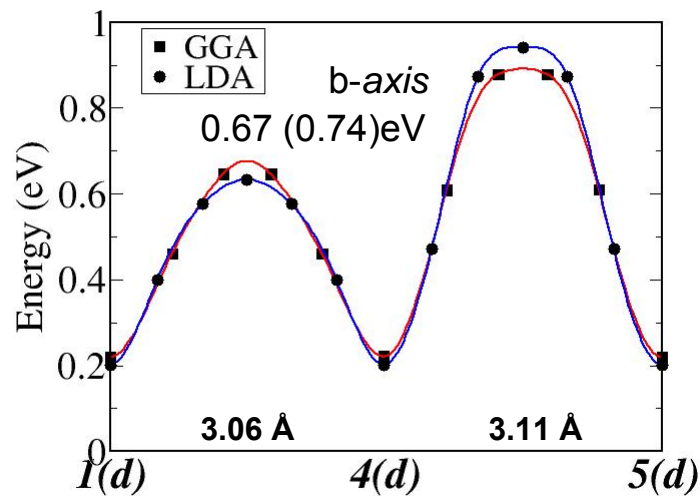
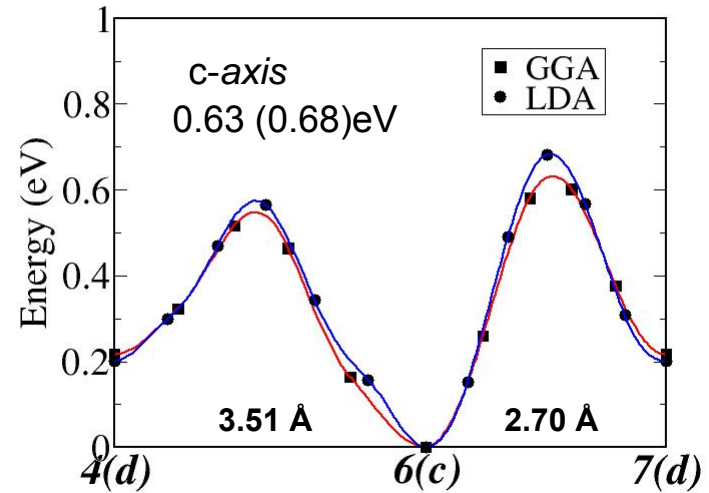
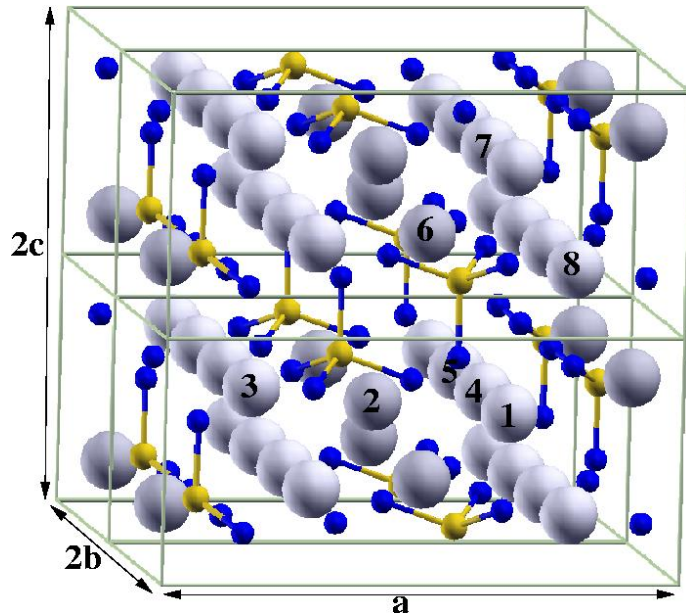
X coordinate is defined as

$$x_{il} = \Delta X_{if} \frac{u_{il}}{u_{if}} \quad \text{where}$$

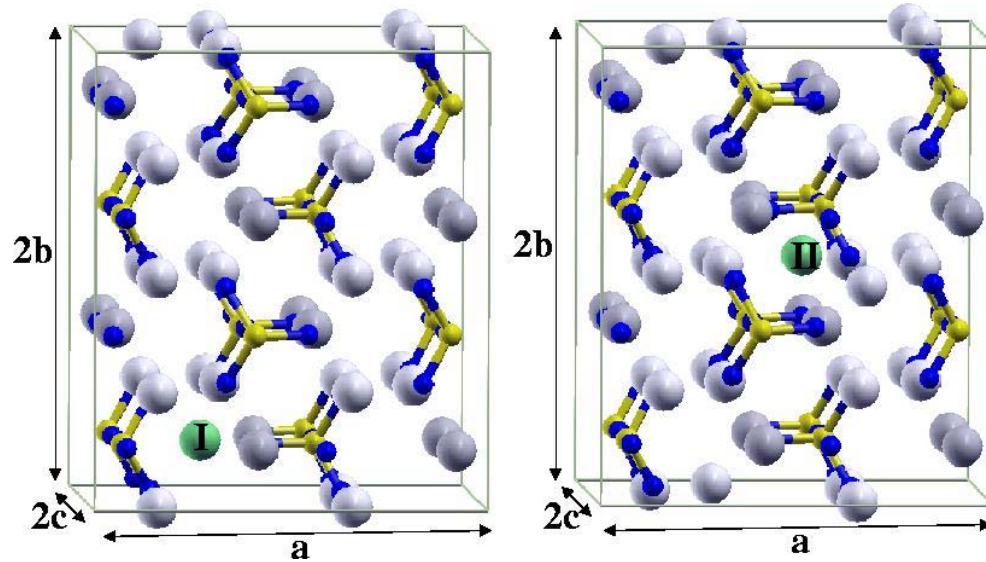
$$u_{il} \equiv \sum_{J=i+1}^I d_{J,J-1} \quad \text{and} \quad d_{J,J-1} \equiv \left| \sum_a (\mathbf{R}_J^a - \mathbf{R}_{J-1}^a) \right|$$

1. O. V. Yakubovich and V. S. Urusov, *Crystallography Reports* **42**, 261 (1997).

Vacancy diffusion mechanism



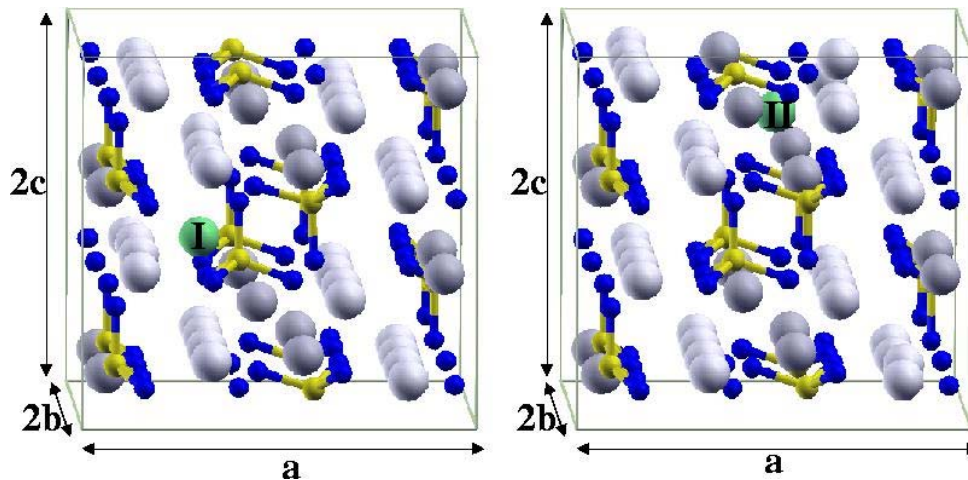
The configuration of Li ion interstitial



The crystal can be divided into two distinct voids channel along the c-axis, which, in turn, provides a general scan of possible interstitial sites.

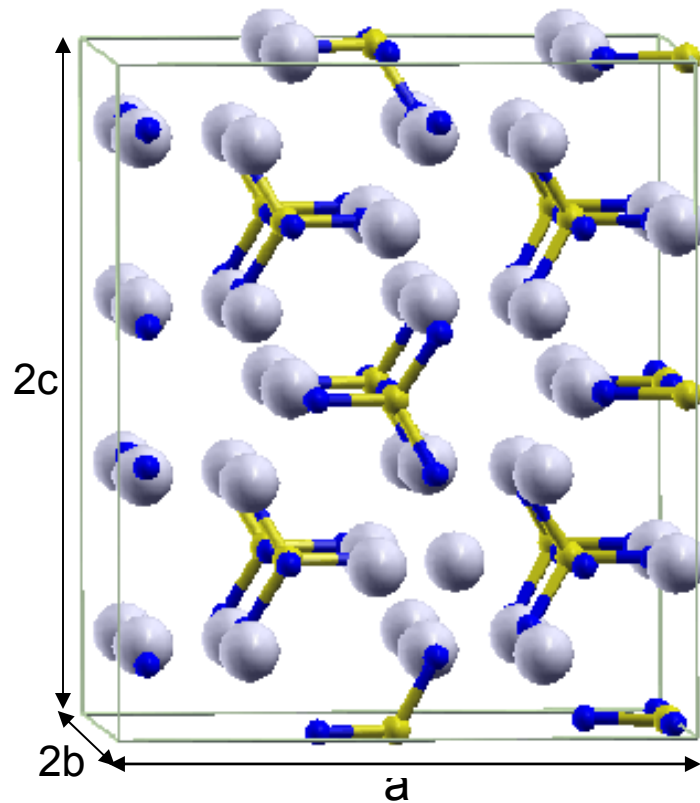
	Energy	X	y	z
I_0	0.00	0.30	0.25	0.00
I_1	0.78	0.28	0.25	0.59
II_0	0.18	0.52	0.07	0.57
II^*	0.35	0.50	0.00	0.50

Results are computed in GGA



The II_0 interstitial induces biggest distortion of a neighboring c-type Li ion

Interstitial diffusion mechanism along the b-c axis

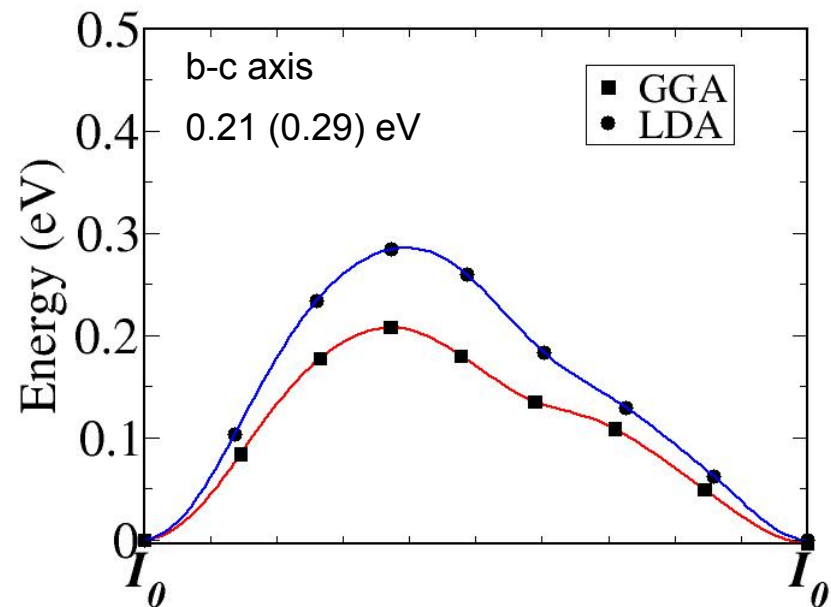


The I_0 kicks and replace a neighboring d-type Li-ion. The “kicked-out” d-type Li-ion becomes an I_0 . The whole process takes place between two adjacent I channel.

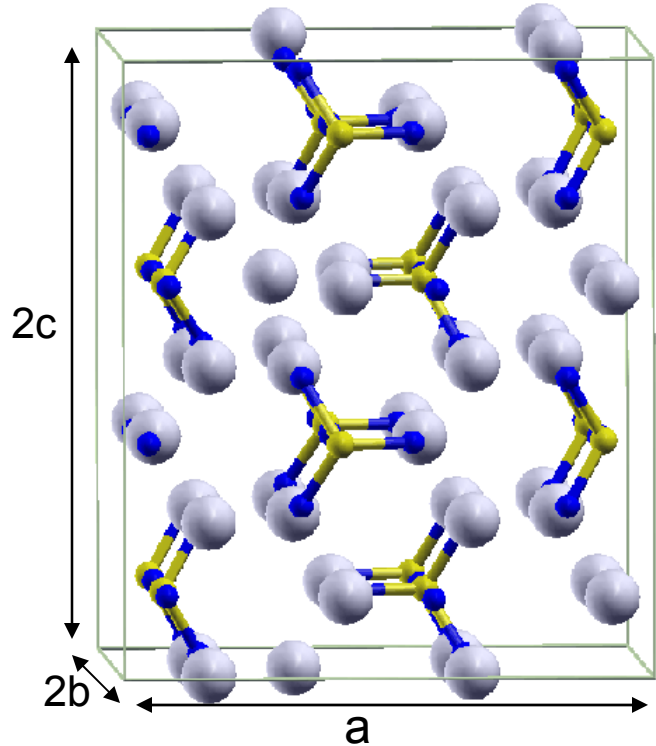
$$I_0(-0.30, 0.75, 1.00)$$



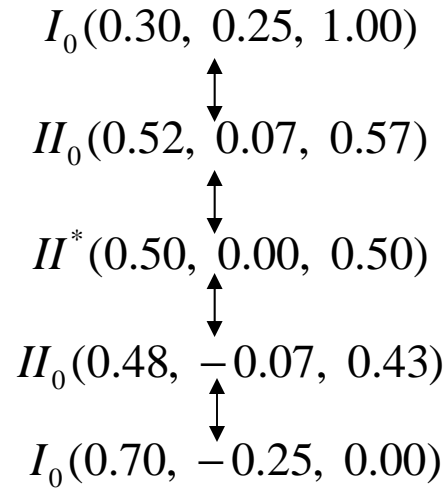
$$I_0(-0.20, 0.25, 0.50)$$



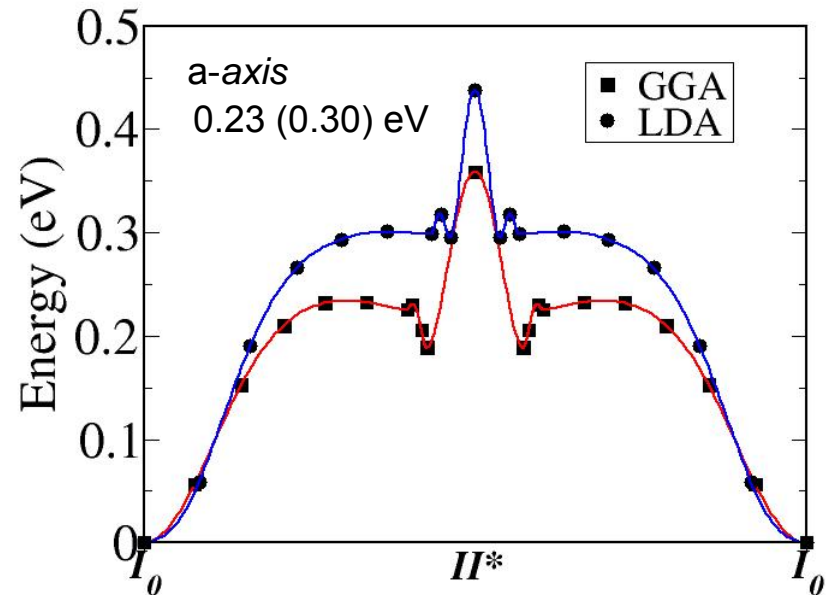
Interstitial diffusion mechanism along a-axis



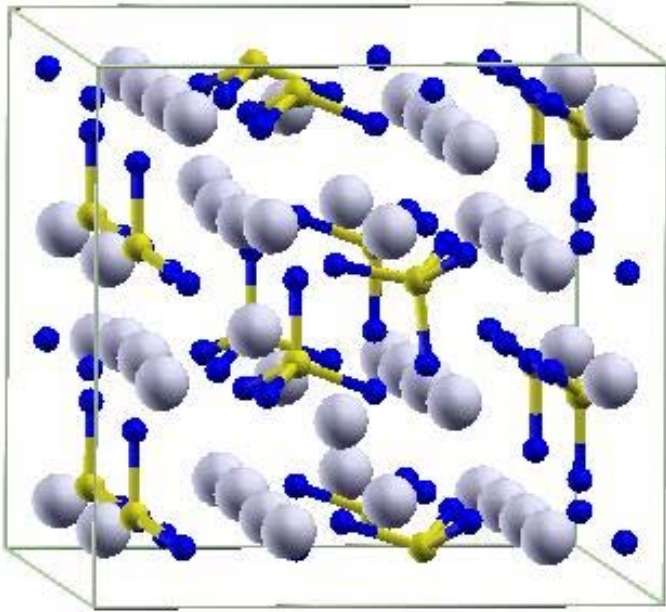
Diffusion occurs between two different void channels: *I* and *II*.



The whole process has an inversion symmetry centered at the saddle point configuration II^* at the site (0.5, 0.0, 0.5)



Formation of interstitial-vacancy pair



The interstitial-vacancy pair is constructed as I_0 interstitial and its next-neighbor c-type vacancy.

Formation energy: $E_f = 1.6$ (1.7) eV

Conductivity of $\gamma\text{-Li}_3\text{PO}_4$

$$\sigma \cdot T \sim e^{-(E_m + E_f / 2) / kT}$$

Interstitial diffusion of barrier of 0.2 eV dominates vacancy diffusion of 0.6-0.7 eV

	Experiment ¹ (eV)	GGA(eV)	LDA (eV)
a	1.23	1.0	1.1
b	1.14	1.0	1.1
c	1.14	1.0	1.1

1. A. K. Ivanov-Shitz, et al., *Crystallography Report* **46**, 864 (2001)

Future work

- The doped $\text{Li}_{2.88}\text{PO}_{3.73}\text{N}_{0.14}$ has a measured diffusion barrier of 0.97 compared to our computed 0.6 – 0.7 eV in GGA and 0.7 eV in LDA.
- The oxygen vacancy might provide traps for migrating Li ion.
- Interface between anode and electrolyte may also have a significant effect on the diffusion.
- The role of N dopants has yet to be investigated.
- The diffusion within $\beta\text{-Li}_3\text{PO}_4$ is currently under study. Preliminary results shows it has comparable barriers as $\gamma\text{-Li}_3\text{PO}_4$.

Conclusion

- Li ion can migrate in Li_3PO_4 via both vacancy and interstitial mechanisms.
- For the vacancy mechanism, Li ion diffuses along three crystallographic directions with a slight anisotropy of 0.6 – 0.7 eV.
- The interstitial mechanism involves a “kick-out” process, and provides the lowest migration barrier of 0.21 (0.29) eV along the b and c axes and 0.23 (0.30) eV along the a axis.
- The formation energy of interstitial-vacancy pair is 1.6 (1.7) eV. Hence the intrinsic defects can diffuse along three crystallographic directions with a slight anisotropy of 1.0 – 1.1 eV consistent with experimental results.