Wake Forest University

Simulated electrolyte-metal interfaces -- γ-Li_3PO_4 and Li

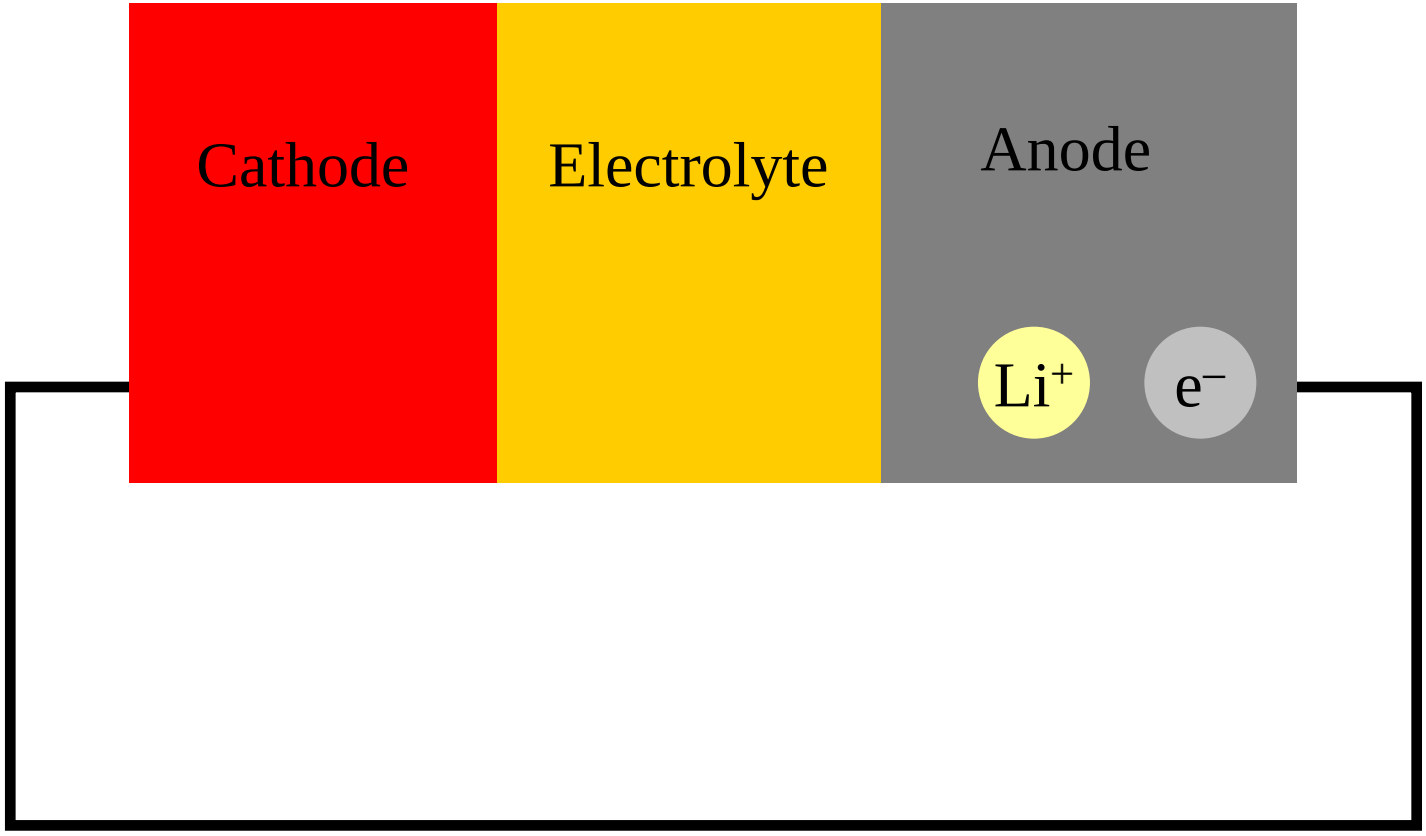
Xiao Xu , Yaojun Du and N.A.W. Holzwarth

- Introduction to Li-ion Batteries
- Project Motivation
- Model and Method of Calculation
- Results for geometry optimization and densities of states
- Conclusions and future work

Supported by NSF grants DMR-0465456 + 0427055

Wake Forest University

Discharge operation of Li ion battery



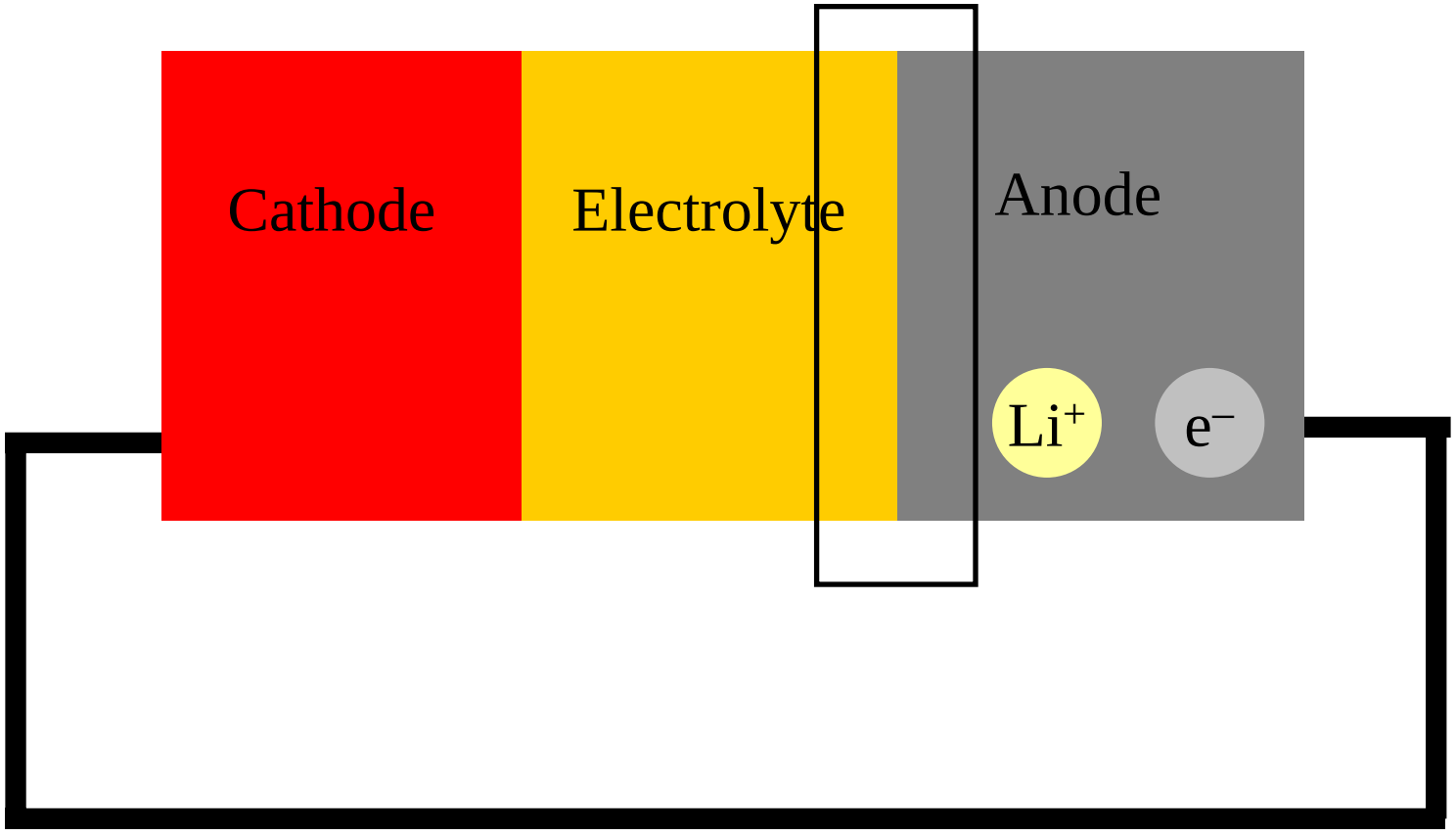
Wake Forest University

Li ion battery components

Cathode materials	Old technology: $LiCoO_2$ $LiMn_2O_4$ $LiNiO_2$ New technology : LiFePO4	Store Li^+ ions and electrons in discharge mode
Electrolyte materials	Liquid solvent , gel, polymer And $LiPF_6$ or $LiClO_4$ Solid : **LiPON , γ-Li_3PO_4**	Transport Li^+ ions Exclude electrons
Anode materials	Li Al alloy Li intercalated graphite **Metal Li**	provide source of Li+ ions Make stable interface and electrons in discharge mode.

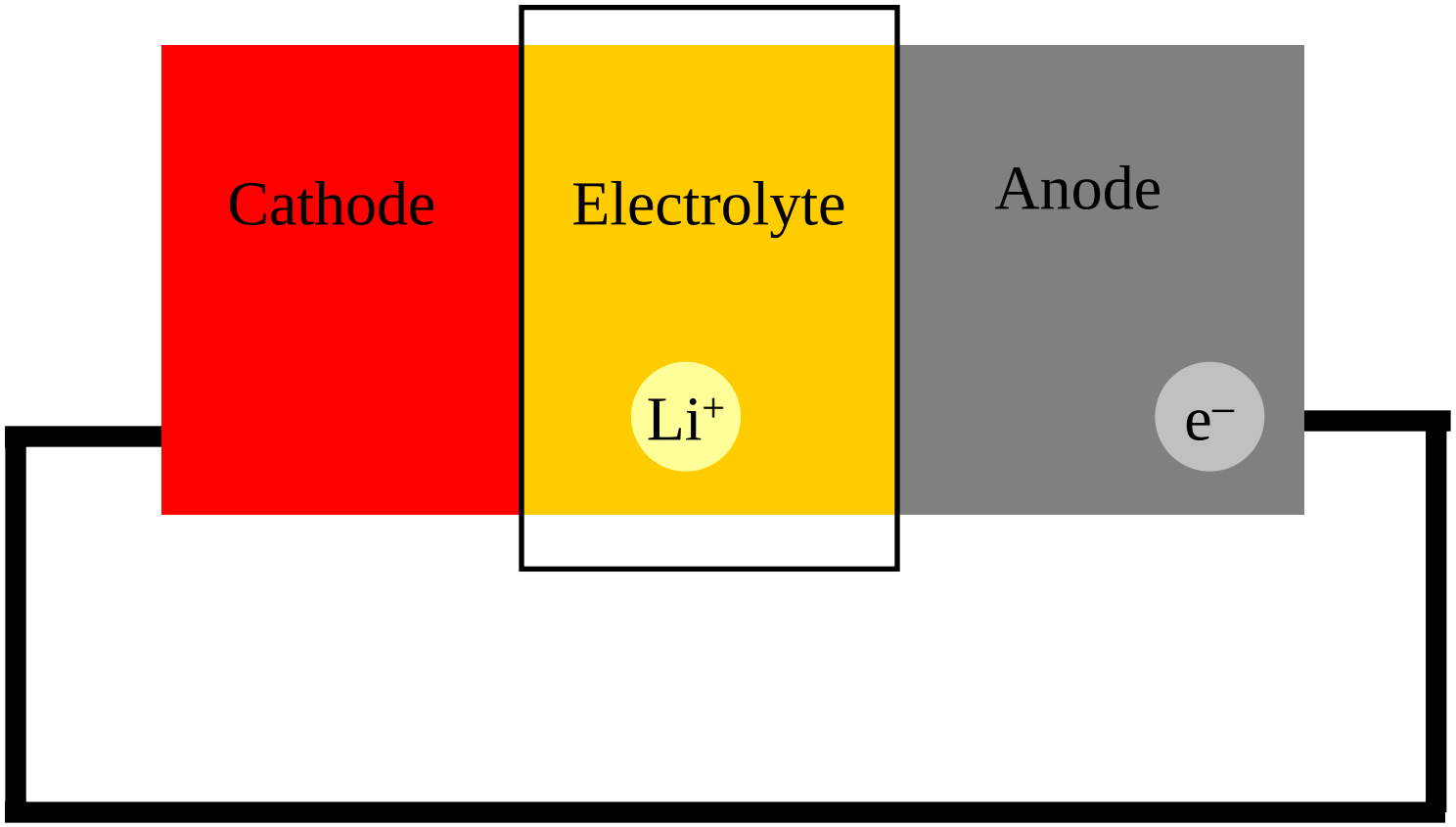
Wake Forest University

This talk : What the interface would look like ?



Wake Forest University

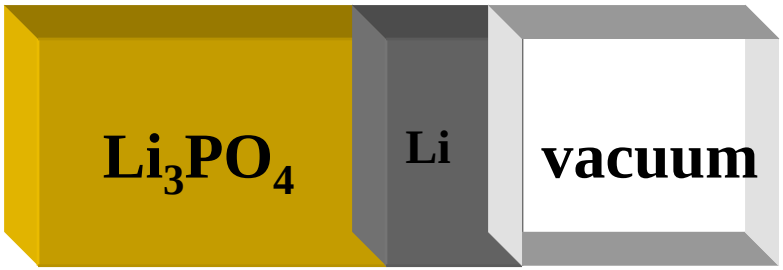
Next talk : How Li would migrate with in the electrolyte



Wake Forest University

Motivation & Questions

- **Motivation**
  - LiPON[1] And Li_3PO_4
  - Why crystal ?



- **Questions**
  - What are the possible structures of an ideal Li_3PO_4 – Li metal interface
  - Are the interfaces physically and chemically stable ?

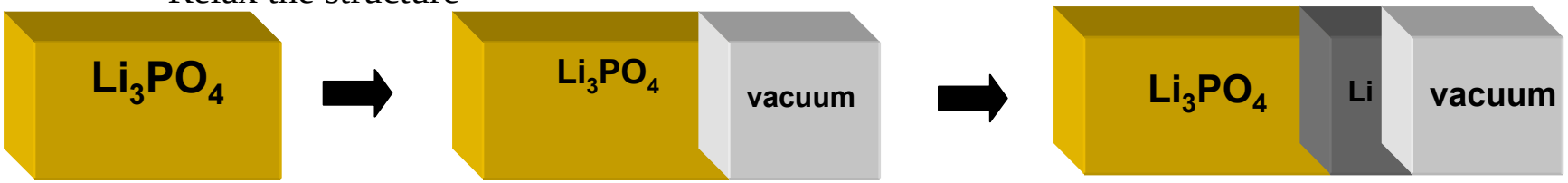
1 LiPON materials are developed at Oak Ridge National Lab

Wake Forest University

Model & Method Of Calculation

Model

- Started with ideal γ-Li_3PO_4 crystal
- Constructed an ideal surface plane, assuming charge neutrality and keep all PO_4 bonds.
- Relax surface in vacuum
- Deposit a few layers of Li between electrolyte surface and vacuum
- Relax the structure



Method of Caculation

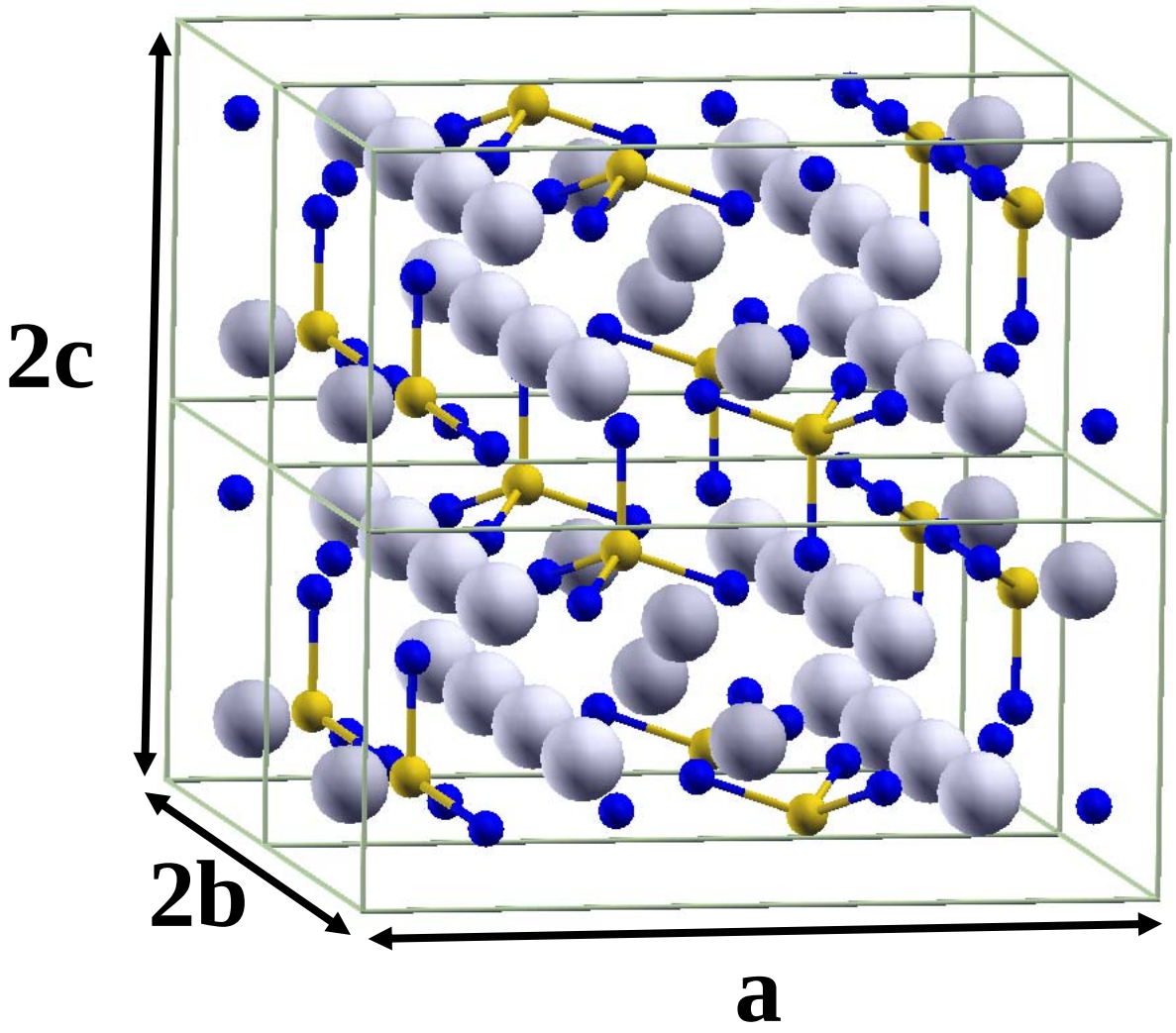
- Plan wave basis with soft pseudo potentials and PAW (PWscf[1] code and PWPAW[2] code)
- $|k + K|^2 \leqq$ 30 Ryd
- Atomic positions relaxed until force components less than 3×10^{-4} Ry/Bohr

1 www.pwscf.org

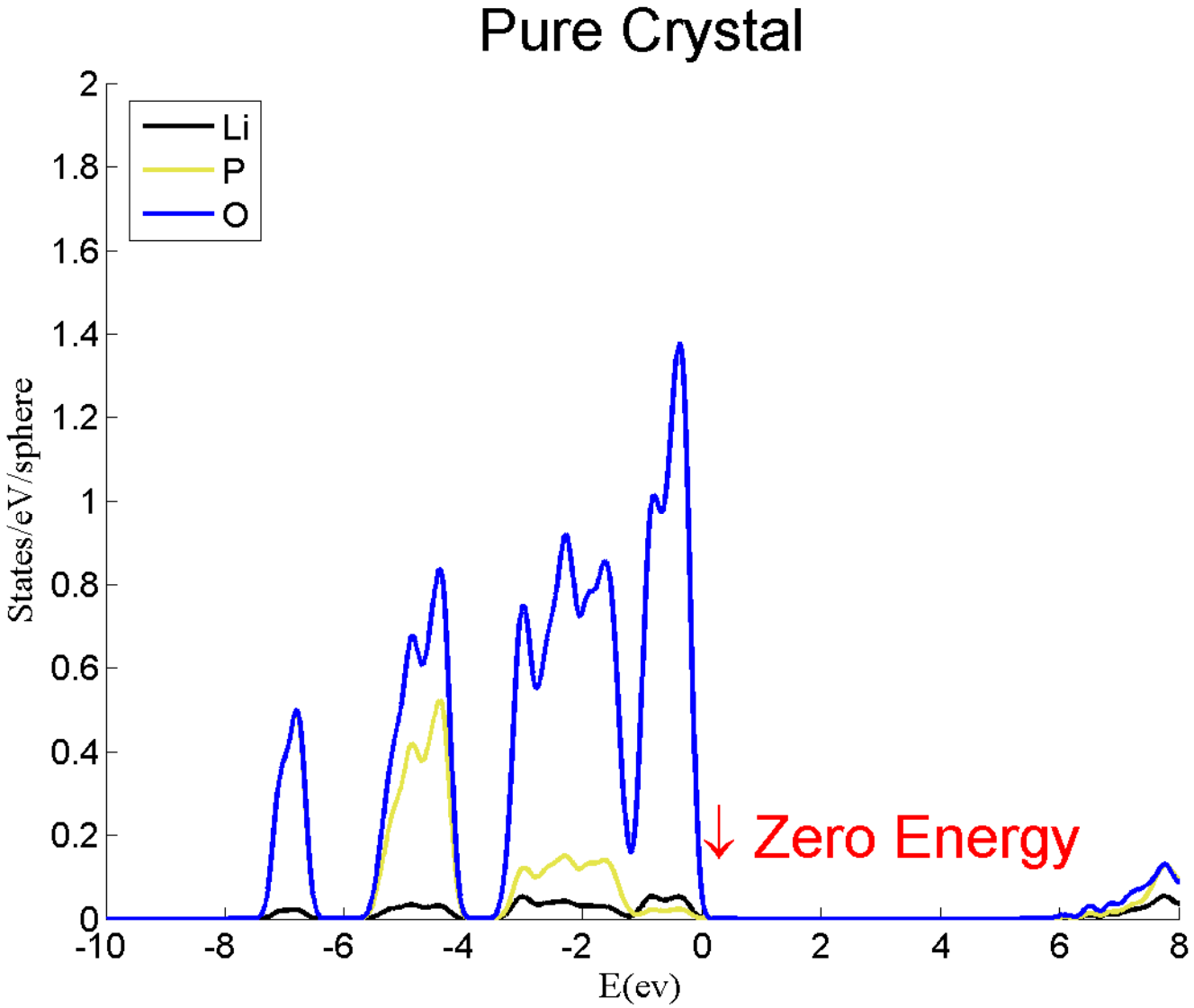
2 pwpaw.wfu.edu

Wake Forest University

Crystal structure of γ-Li_3PO_4 (Pnma)



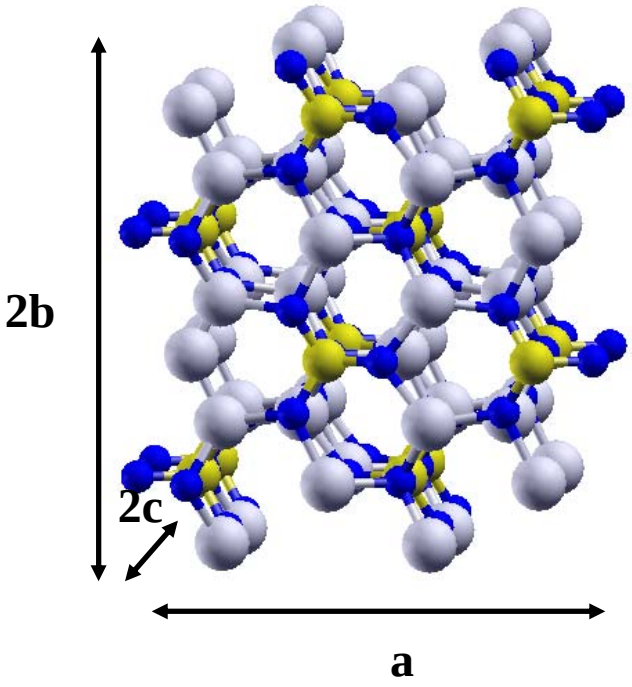
Pure Crystal Partial DOS



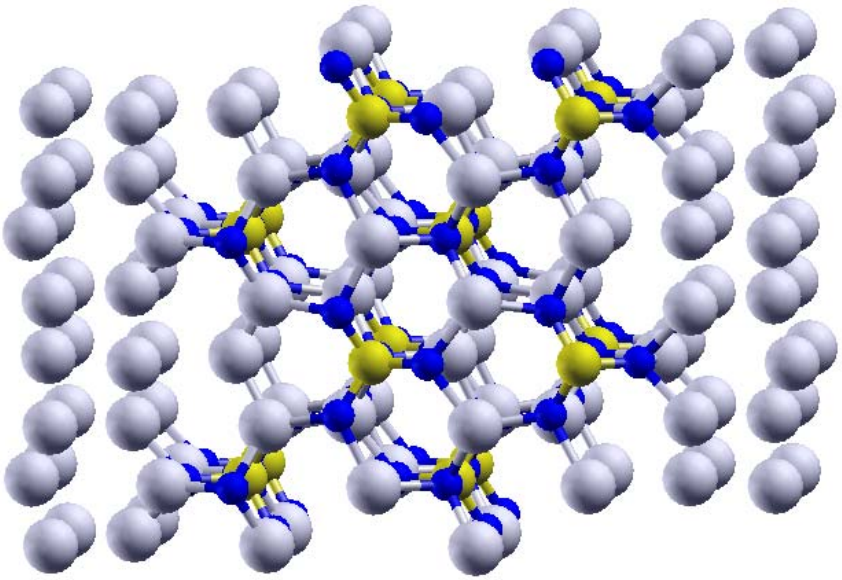
Wake Forest University

Li γ-Li_3PO_4 interface a-direction

Relaxed Structure of γ-Li_3PO_4 with vacuum

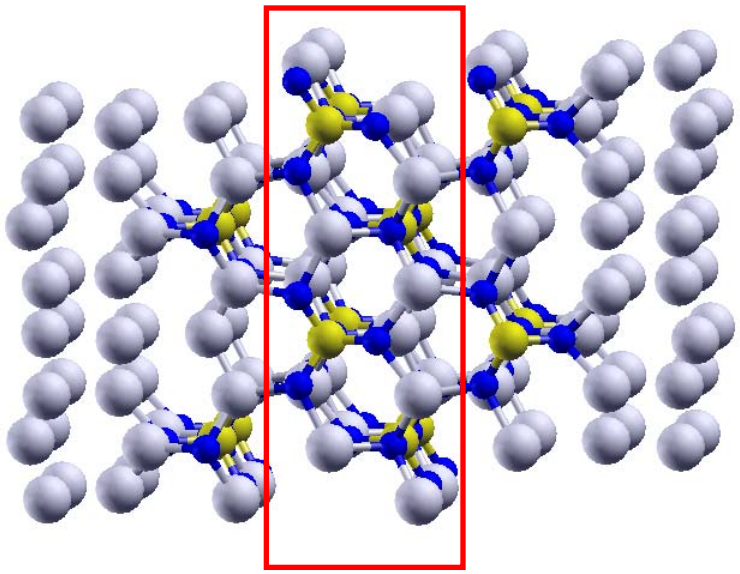


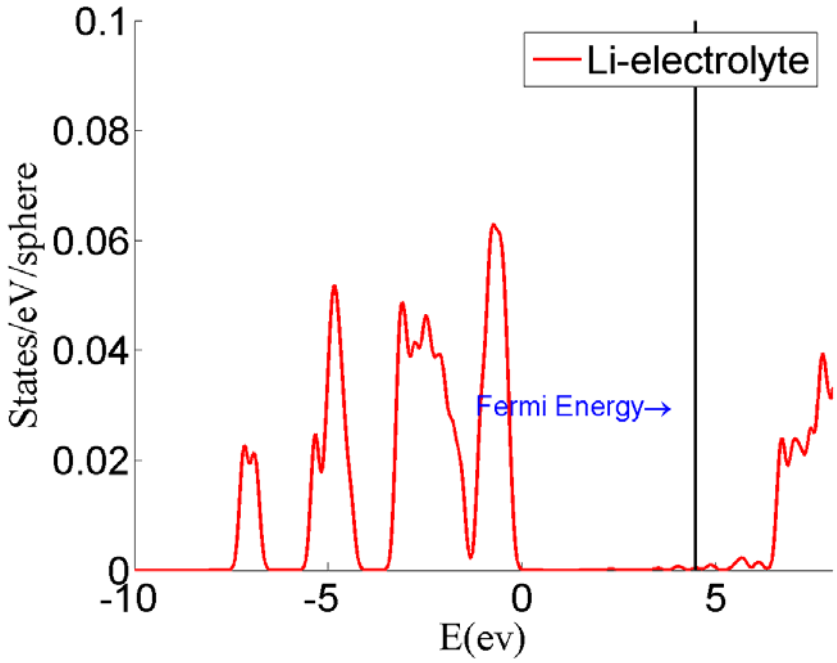
Converged structure of Li- γ-Li_3PO_4 interface



Wake Forest University

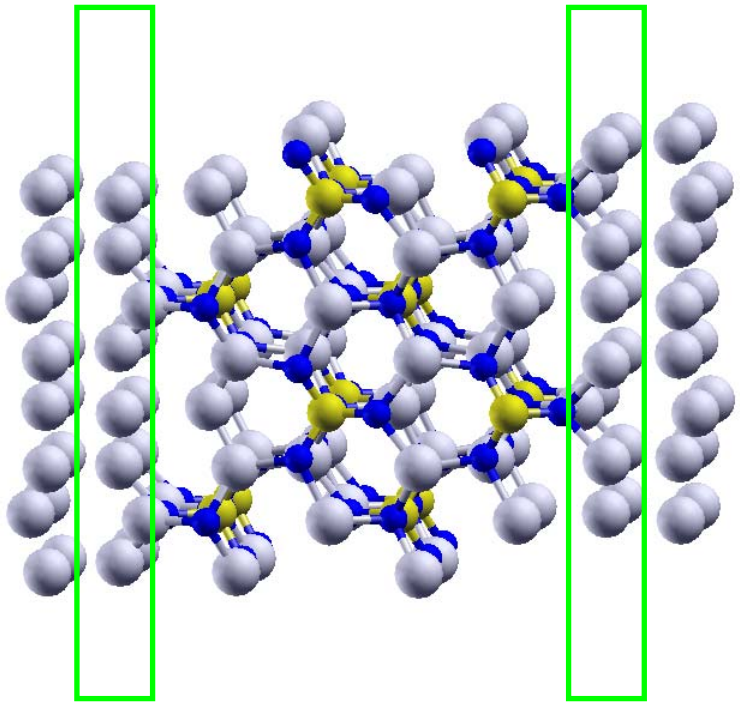
Interface a-direction Partial Density Of States

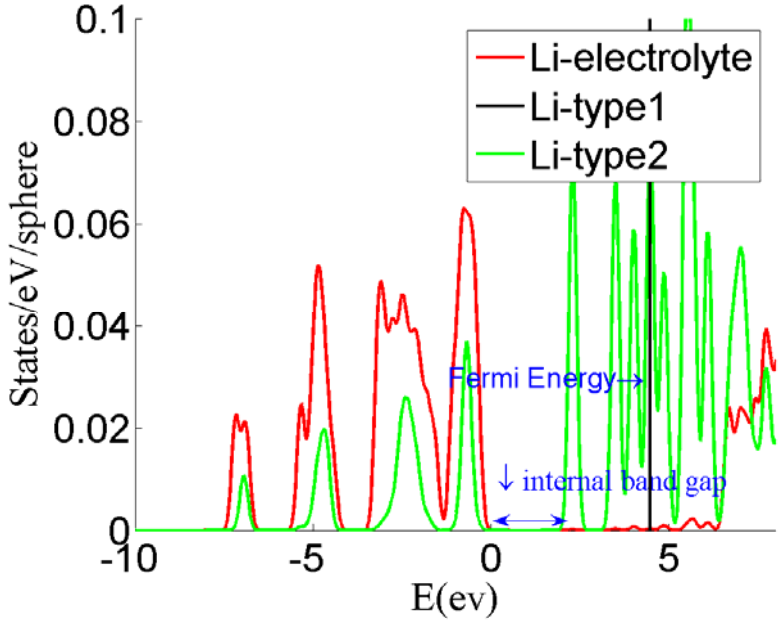




Wake Forest University

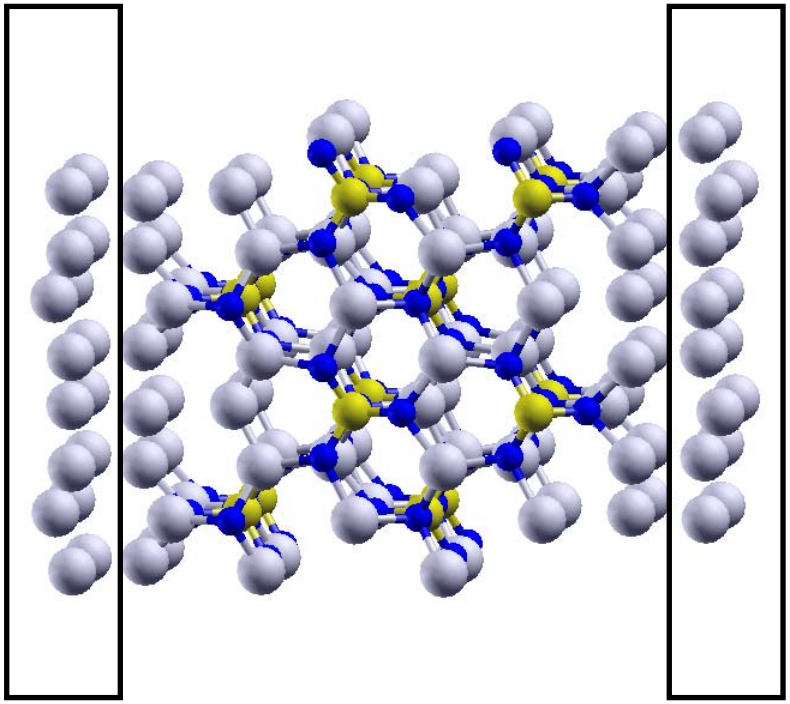
Interface a-direction Partial Density Of States

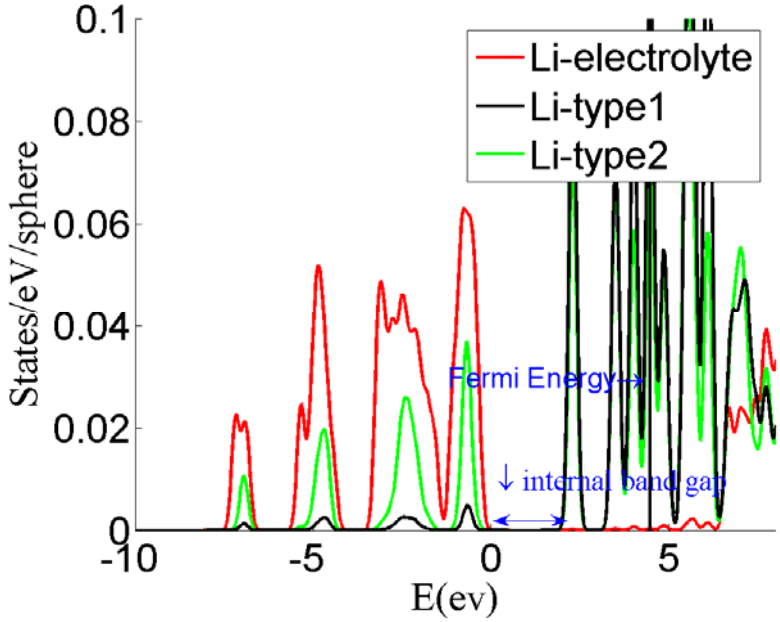




Wake Forest University

Interface a-direction Partial Density Of States

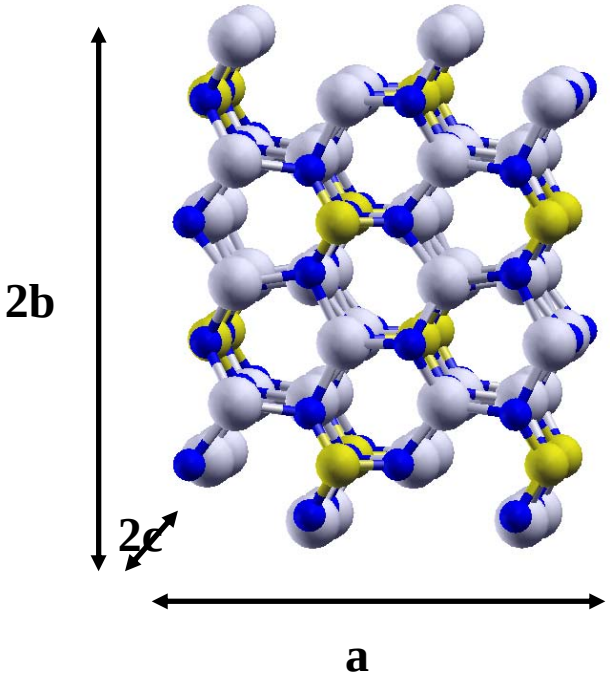


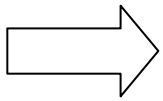


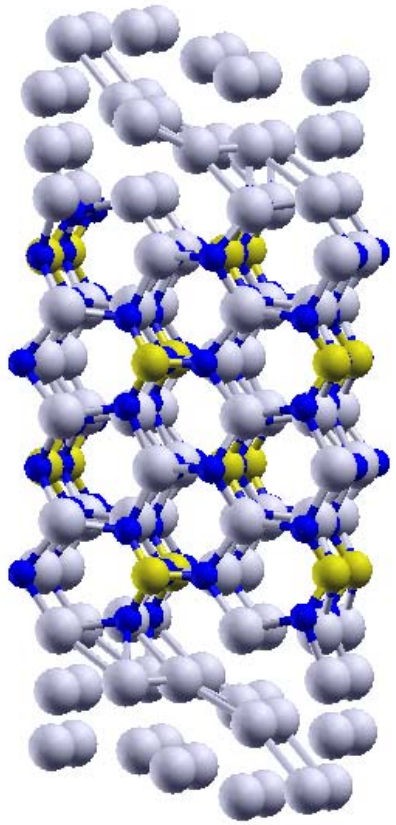
Wake Forest University

Li-Li_3PO_4 interface b-direction

Relaxed Structure of γ-Li_3PO_4 with vacuum

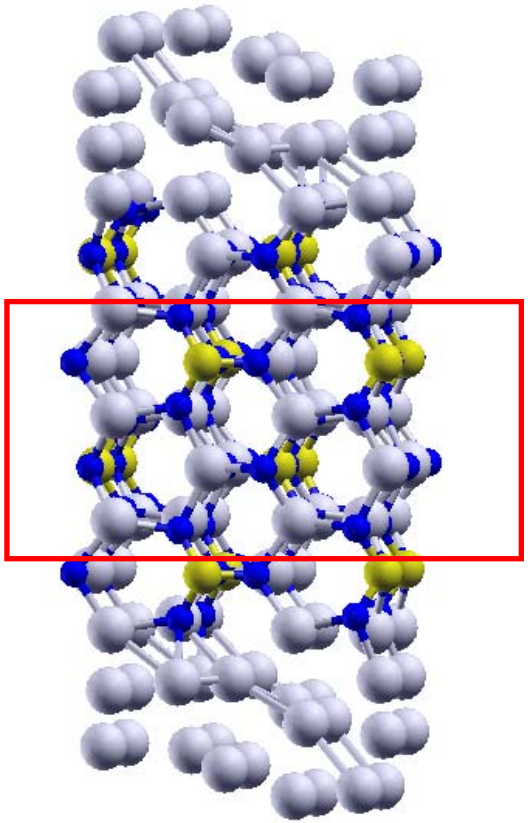


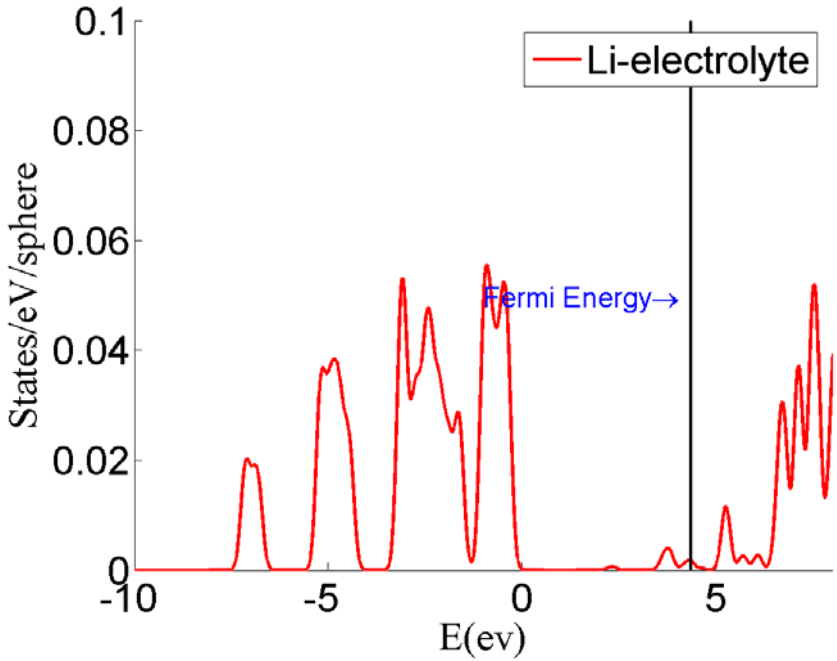




Wake Forest University

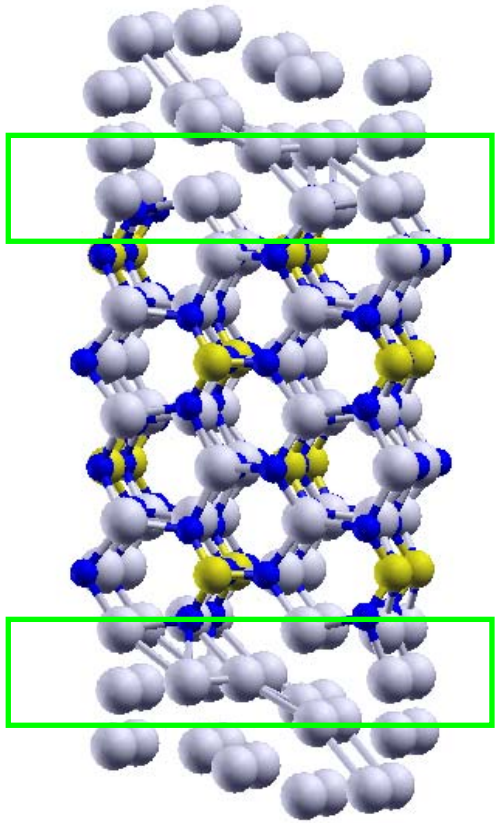
Interface b-direction Partial Density Of States

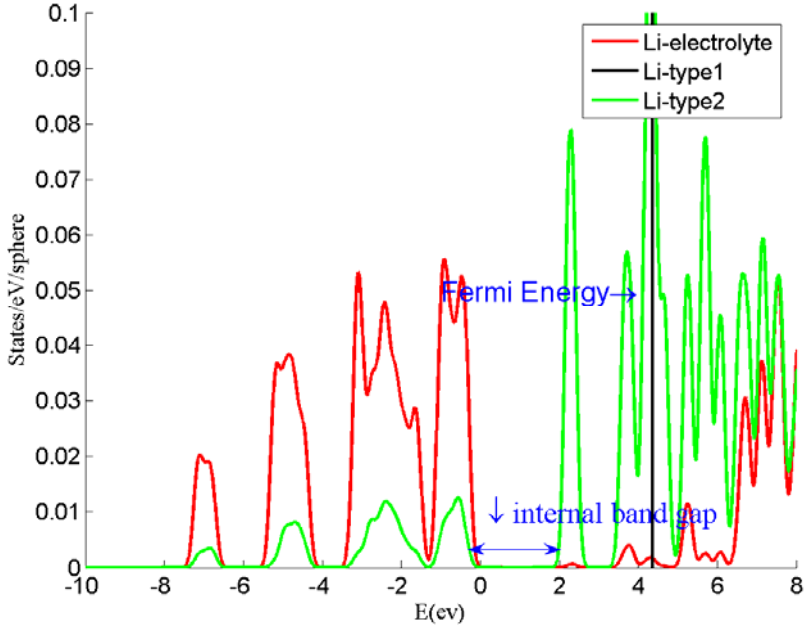




Wake Forest University

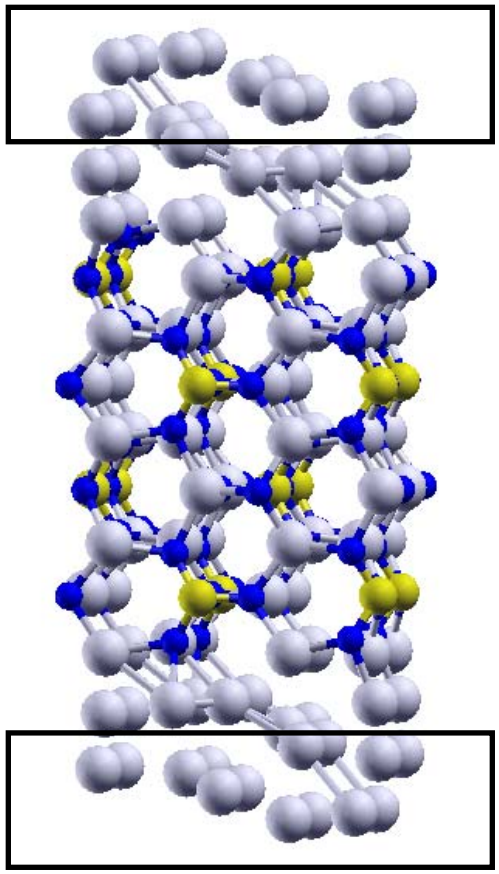
Interface b-direction Partial Density Of States

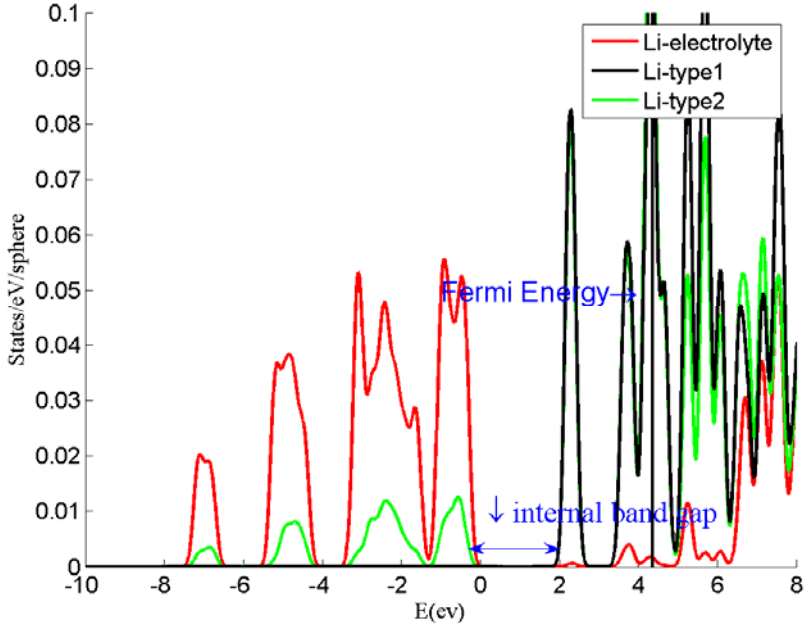




Wake Forest University

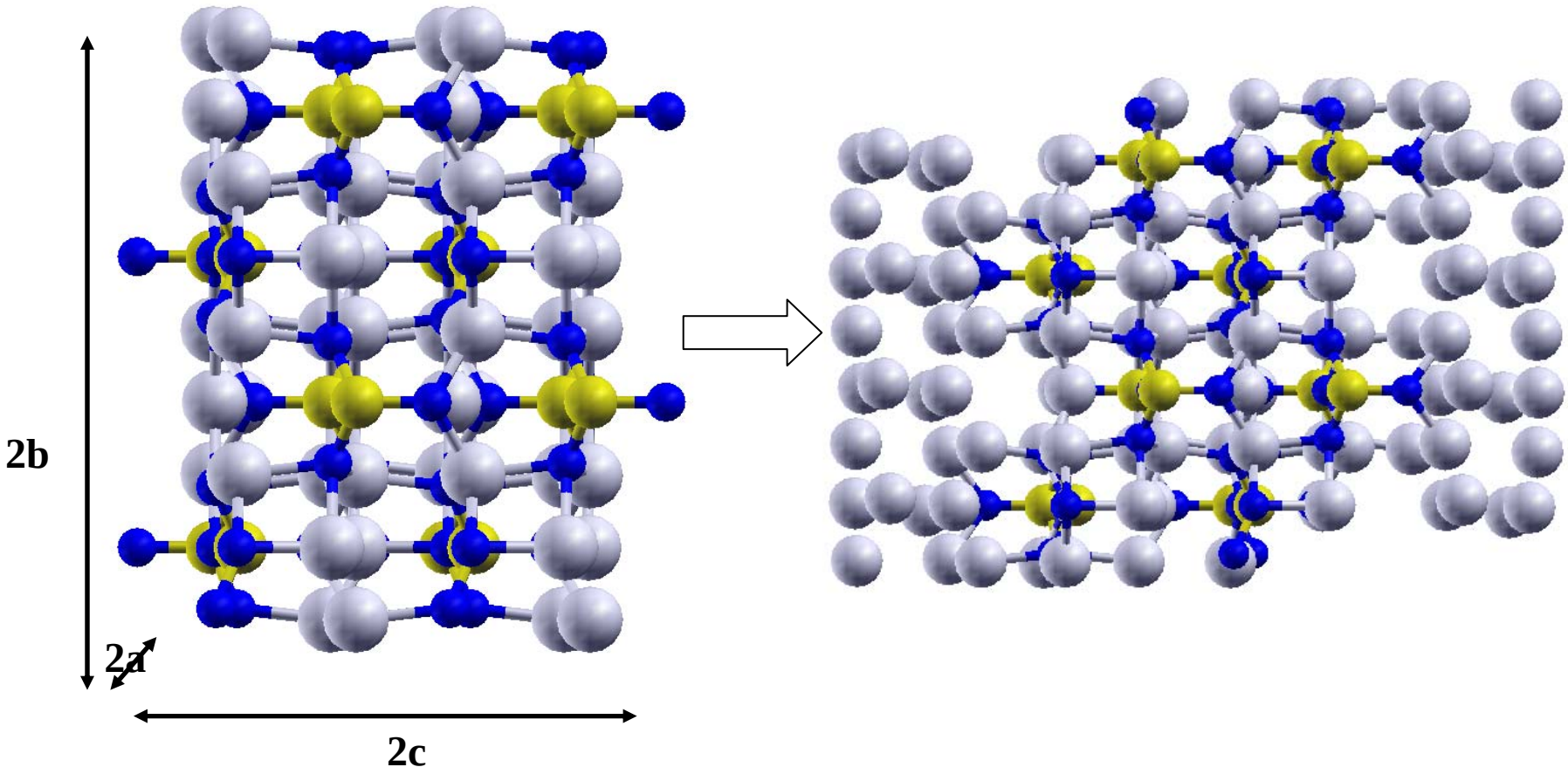
Interface b-direction Partial Density Of States





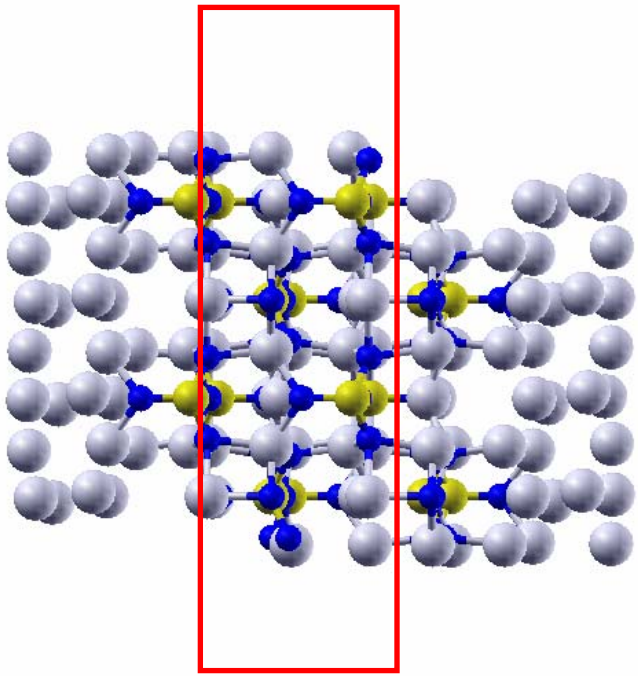
Wake Forest University

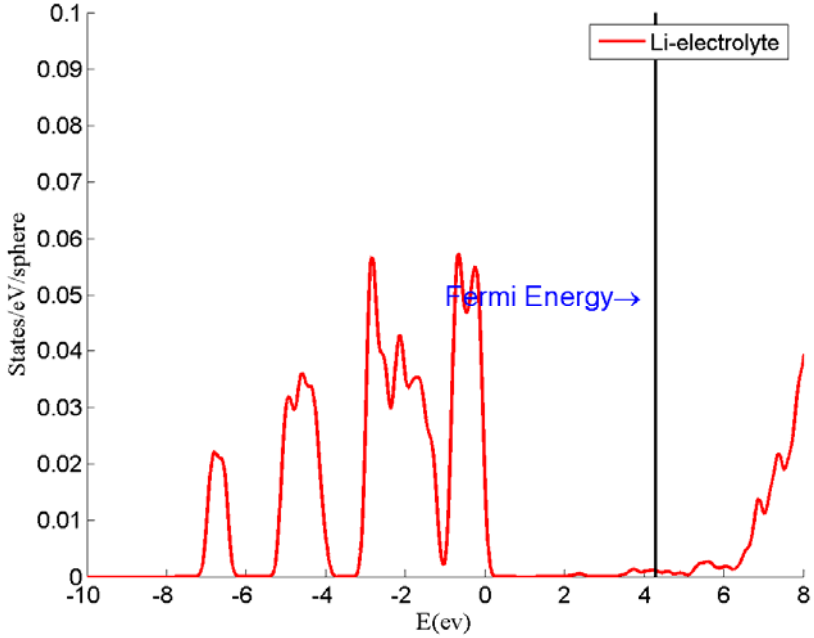
Li-Li_3PO_4 interface c-direction



Wake Forest University

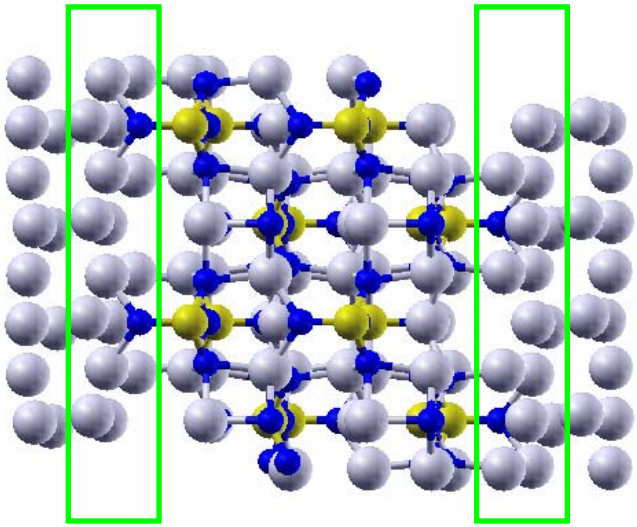
Interface c-direction Partial Density Of States

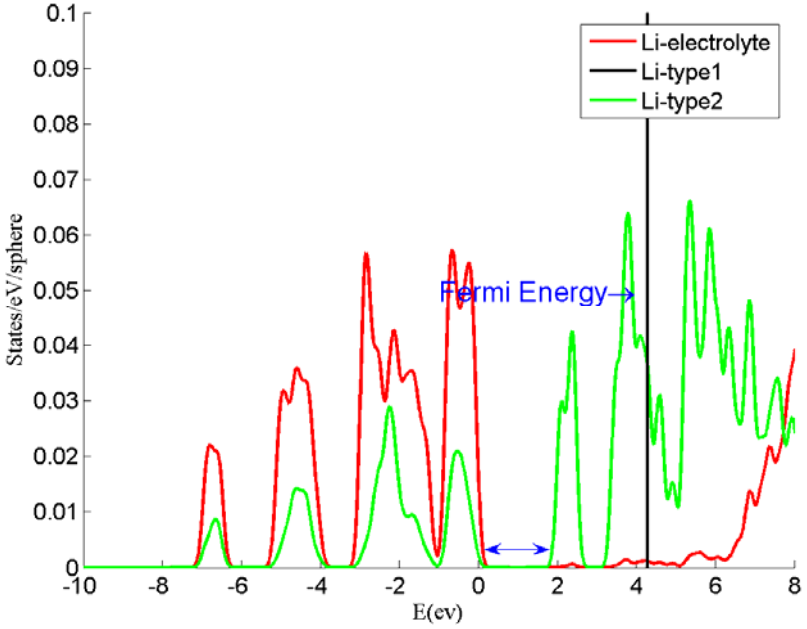




Wake Forest University

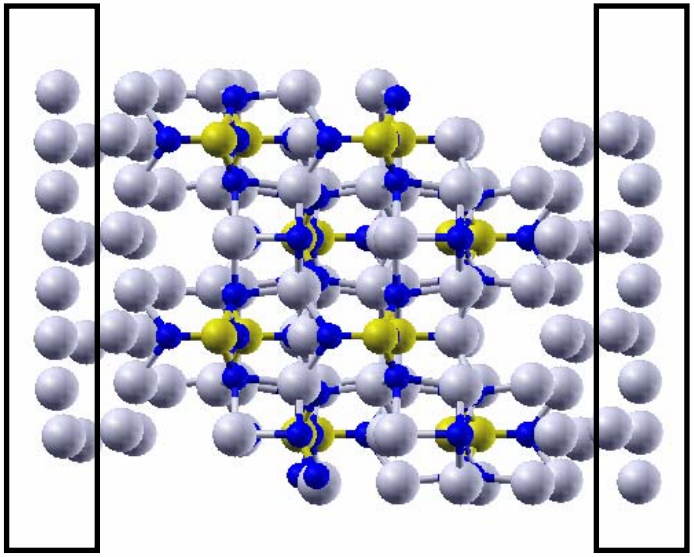
Interface c-direction Partial Density Of States

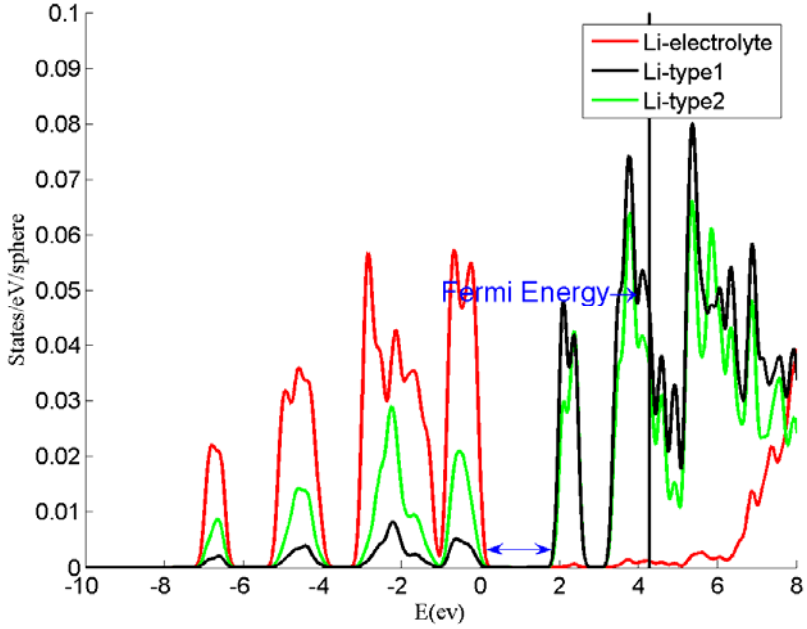




Wake Forest University

Interface c-direction Partial Density Of States

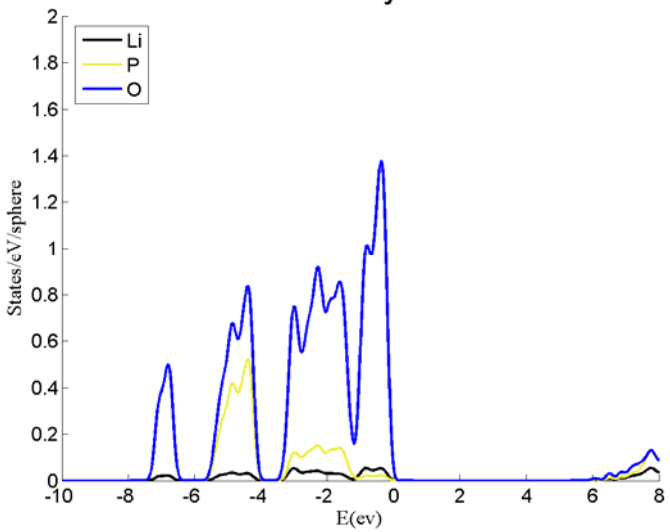




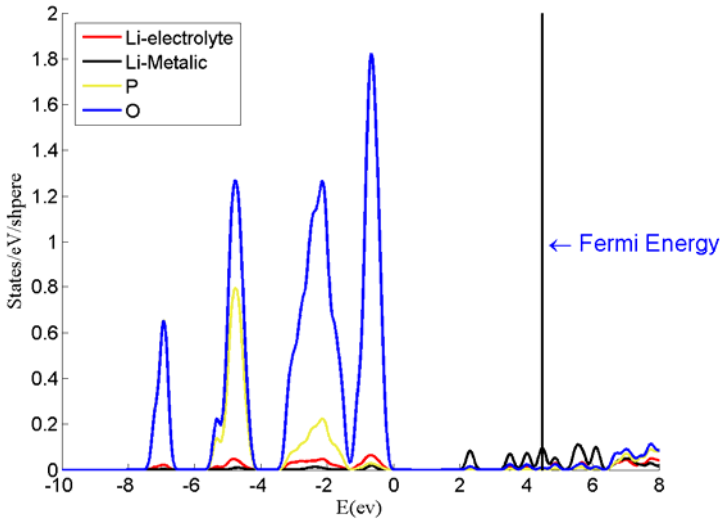
Wake Forest University

Comparing Pure Crystal with Interface

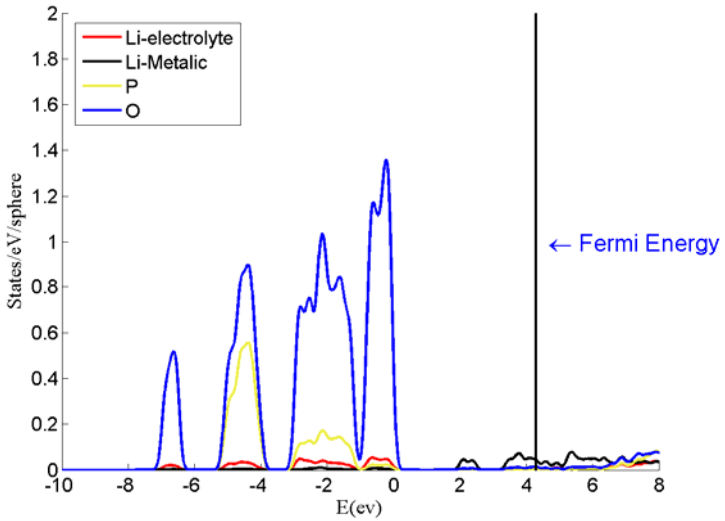
Pure Crystal



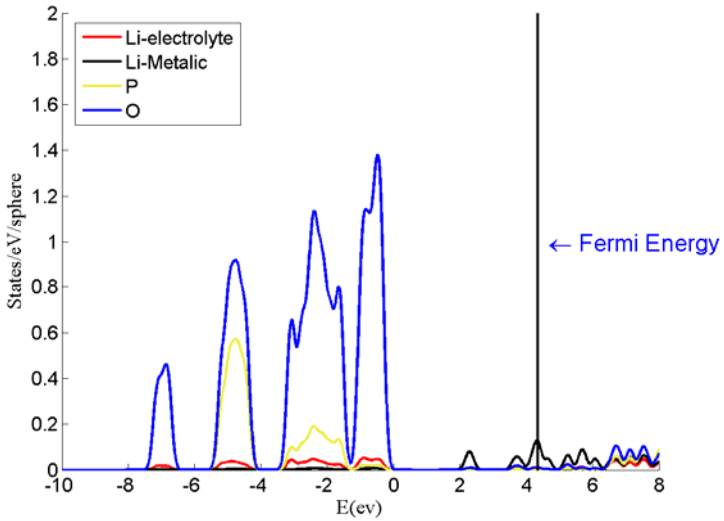
a-direction inteface



c-direction inteface

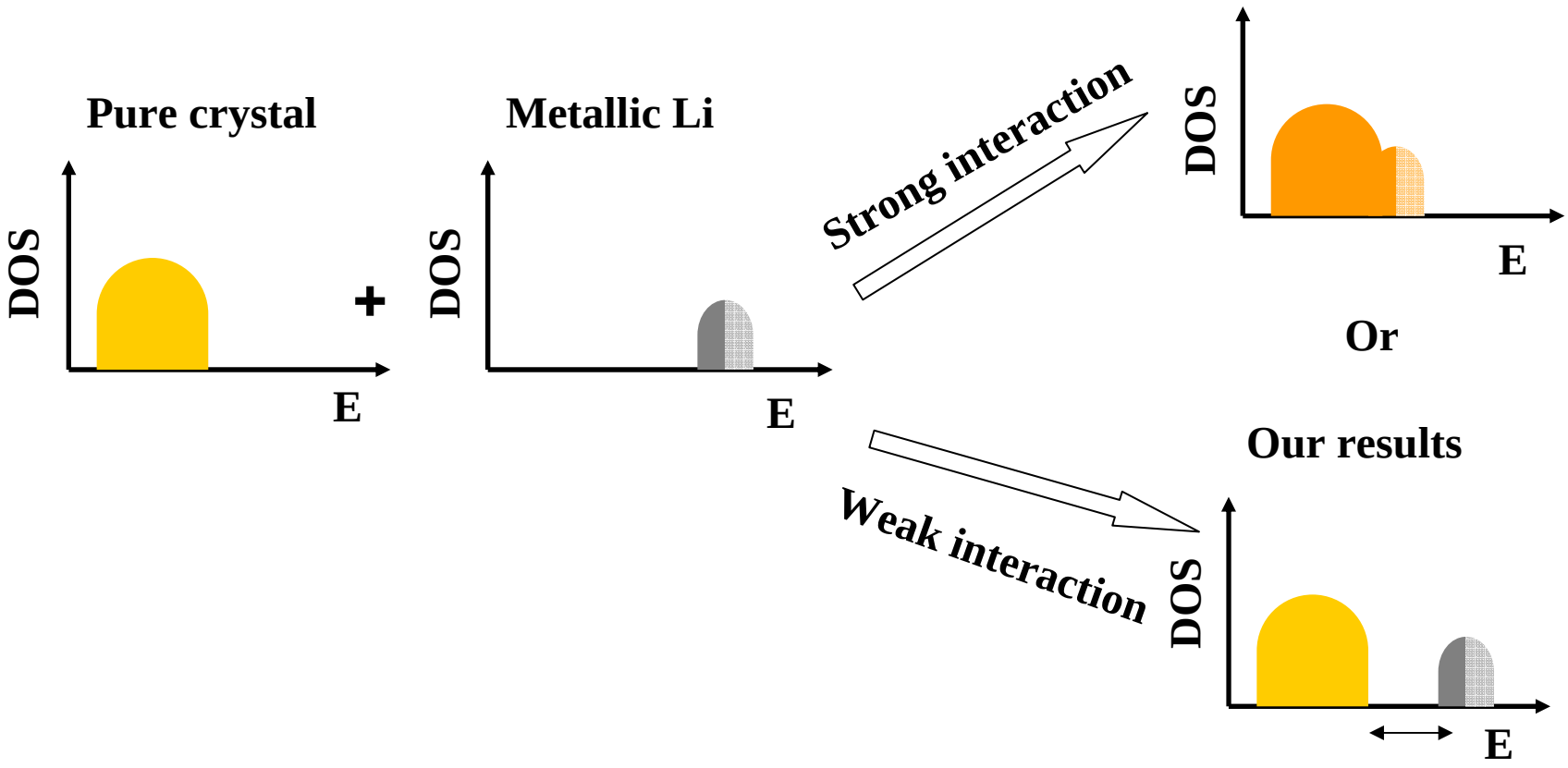


b-direction inteface



Wake Forest University

Simplified DOS model



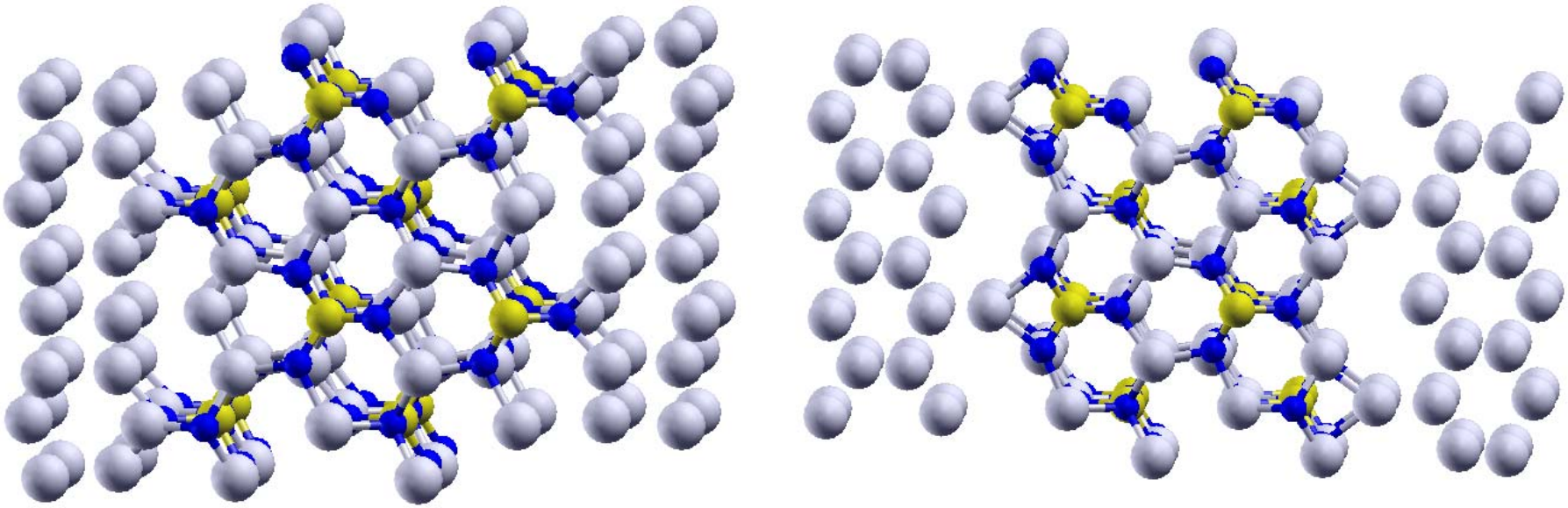
Wake Forest University

Conclusion and future work

- We constructed 3 different interfaces on a , b and c planes, with Li metal on Li_3PO_4
- We found plausible structures with well-defined electrolyte boundary
- From the Partial DOS plots, we found an energy gap between electrolyte and metal states.
- On the presence of Li metal, electrolyte is physically and chemically stable.
- We plan to study Li-ion diffusion across these interfaces

Wake Forest University

Other possible structures
two a-direction interfaces



Wake Forest University

Other possible structures
two b-direction interfaces