Electrolyte properties of $Li_4P_2S_6$ -- Simulations and comparison with experiment; Contrast with simulations of Na analog*

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*Supported by NSF Grants DMR-1105485 and 1507942. Computations were performed on WFU's DEAC cluster. Helpful discussion with Chengdu Liang, Gayatri Sahu, Hui Wang, Jong Keum, and E. Andrew Payzant at ORNL and William C. Kerr, Cameron Kates, Shiba Adikari, Keerthi Senevirathne, Michael Gross, Cynthia Day, and Abdessadek Lachgar at WFU are gratefully acknowledged.

$Li_4P_2S_6$/ $Na_4P_2S_6$

Why--

- Search for ideal solid electrolyte materials for all-solid state batteries
- **$Li_4P_2S_6$** reported by Mercier et al., J. Solid State Chem. **43,** 151-164 (1982); hexagonal structure with disorder on the P sites
- **$Li_4P_2S_6$** frequently identified as unintended constituent of solid electrolyte preparations; relatively stable in air
- **$Na_4P_2S_6$** recently report by Kuhn et al., ZAAC **640**, 689-692 (2014); related ordered structure

What--

Experimental results for **$Li_4P_2S_6$** and computation results for **$Li_4P_2S_6$** and **$Na_4P_2S_6$**:

- Structural analysis
- Transport properties
- Interfaces with Li or Na metal

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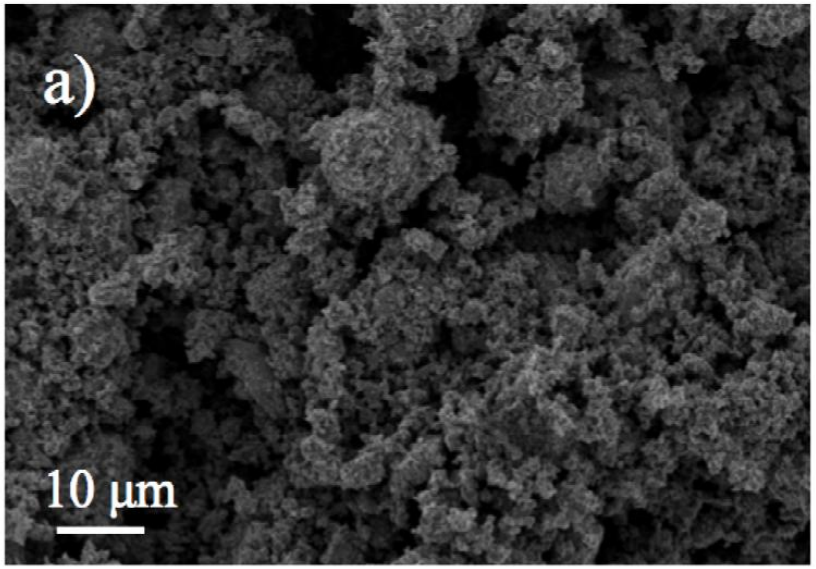
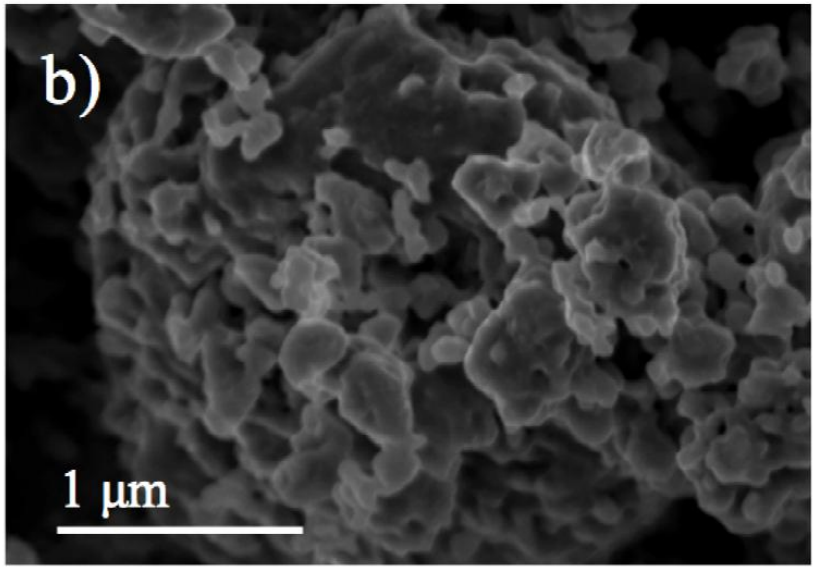
Synthesis:

$$2Li_2S + P_2S_5 \xrightarrow[750-900^{o}\,C]{} Li_4P_2S_6 + S$$

Sulfur removed by treatment with solvent; powder sample prepared for electrochemical applications using ball milling.

Scanning Electron Micrograph of prepared sample:





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Computational methods

- Density functional theory with LDA
- PAW formalism using datasets generated with ***ATOMPAW*** code (Holzwarth et al. *CPC* **135**, 329 (2001)) http://pwpaw.wfu.edu
- Electronic structure calculations performed using ***QUANTUM ESPRESSO*** and ***ABINIT*** codes**.** (Giannozzi et al. *JPCM* **21,** 394402 (2009); http://www.quantum-espresso.org, Gonze et al., *CPC* **180***,* 2582 (2009)); http://www.abinit.org
- Plane wave expansion for wave functions with $|\mathbf{k}+\mathbf{G}|^2 \leq 64\ \mathrm{Ry}$
- Brillouin zone integration mesh of 0.003 bohr^{-3}
- Ion migration energies estimated with Nudged Elastic Band (NEB) method. (Hinkleman et al. *JCP* **113**, 9901 & 9978 (2000))
- Visualization software: ***Xcrysden, VESTA***, and ***CrystalMaker***
- X-ray powder diffraction simulated using ***Mercury***
- Neutron powder diffraction simulated using ***GSAS***

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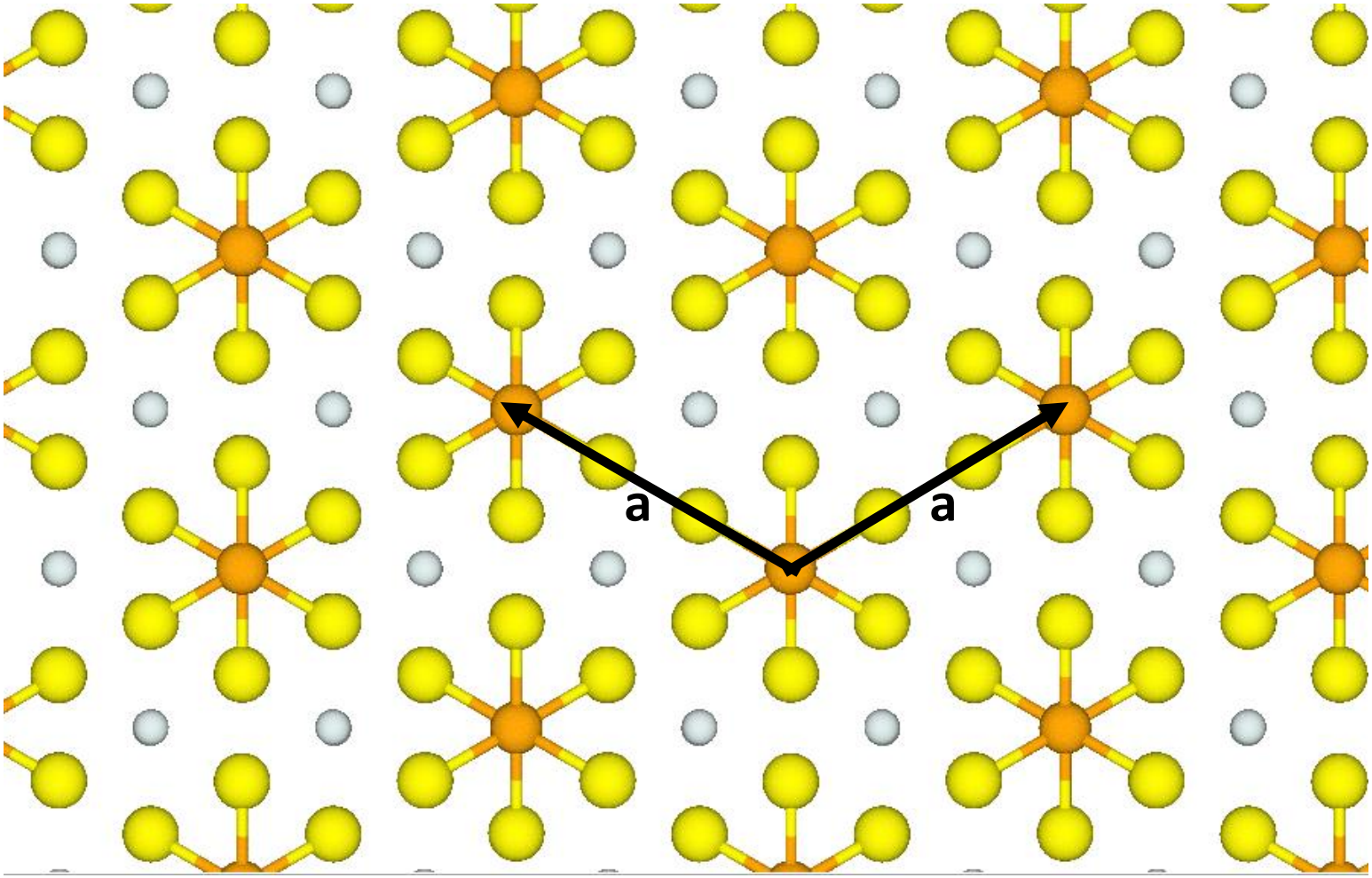
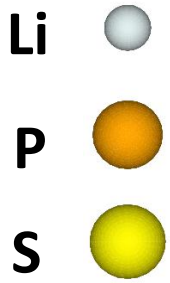
Crystal structure of $Li_4P_2S_6$: Space Group *P6$_3$/mcm* (#193)

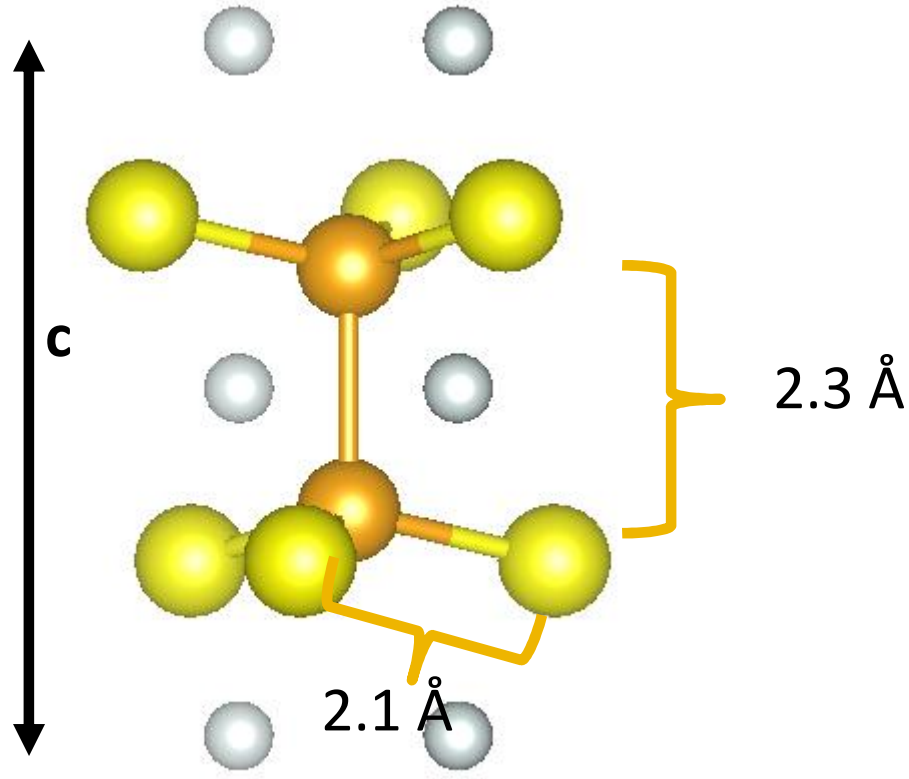
Projection on to hexagonal plane:

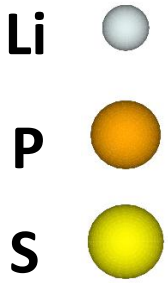




Crystal structure of $Li_4P_2S_6$: Space Group *P6$_3$/mcm* (#193)

$Li_4P_2S_6$ units:





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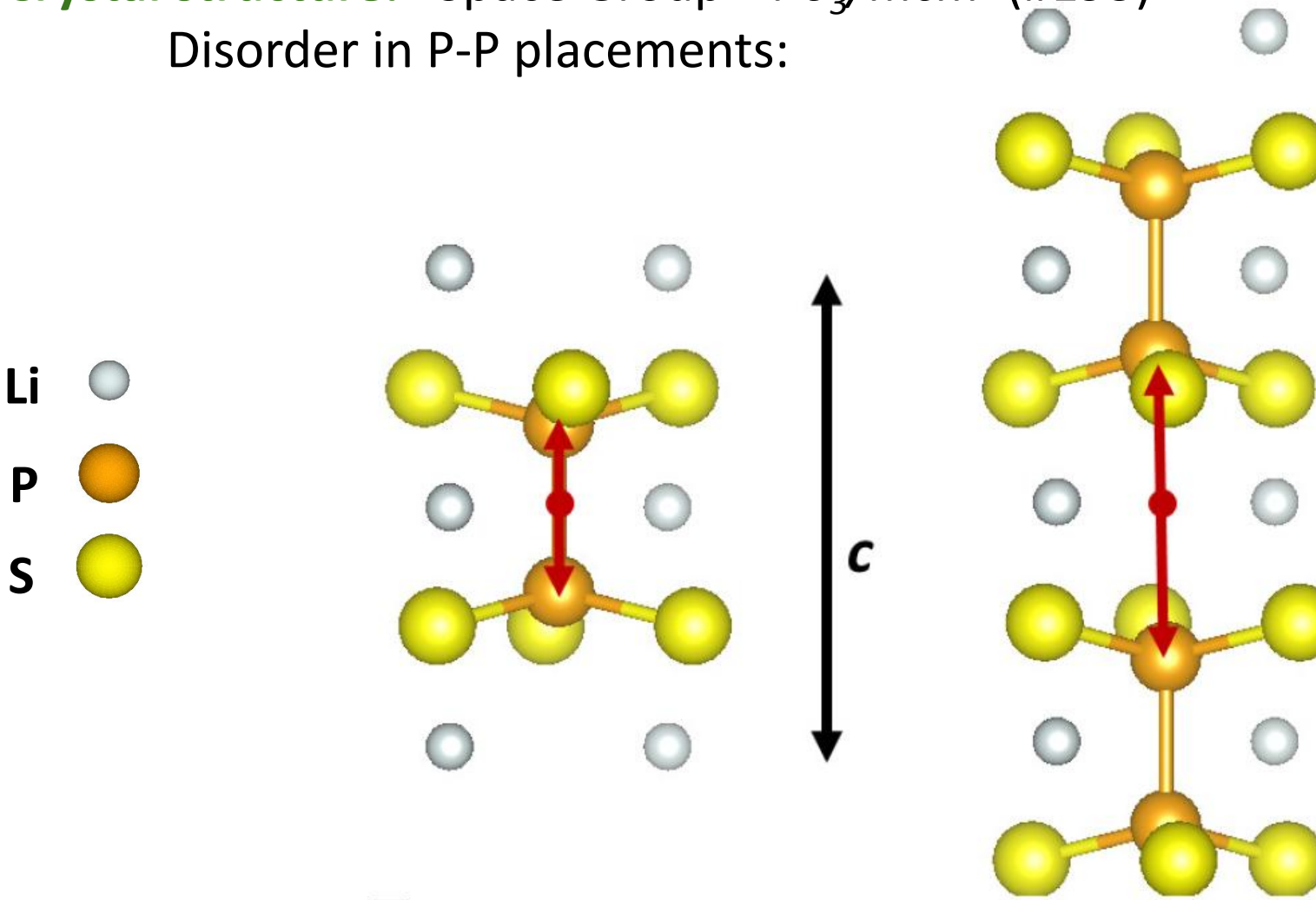
Crystal structure: Space Group $P6_3/mcm$ (#193)

Disorder in P-P placements:



$$P_{\uparrow} \equiv \pm z_P c \qquad P_{\downarrow} \equiv \pm\left(\frac{1}{2} - z_P\right)c$$

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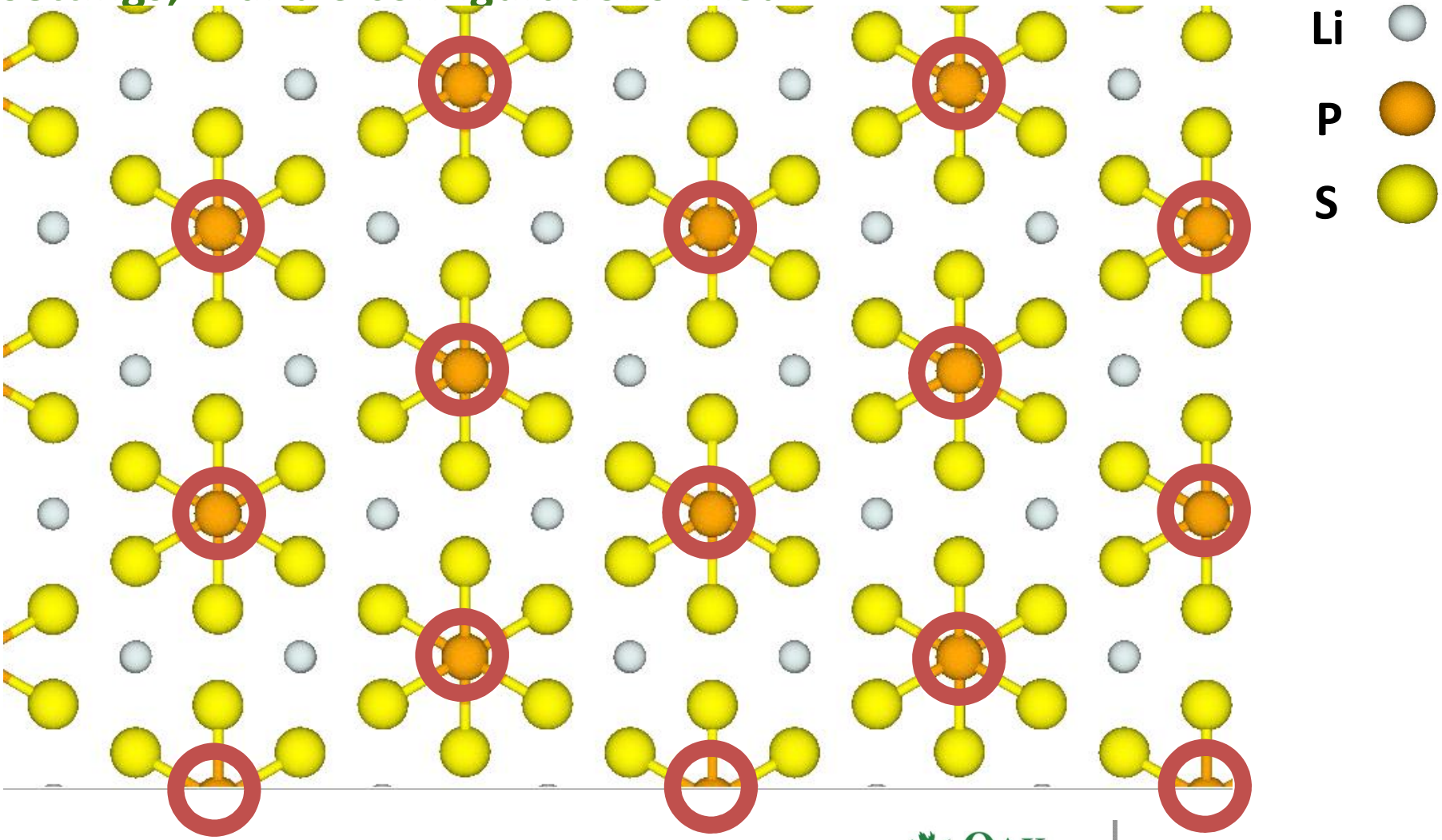
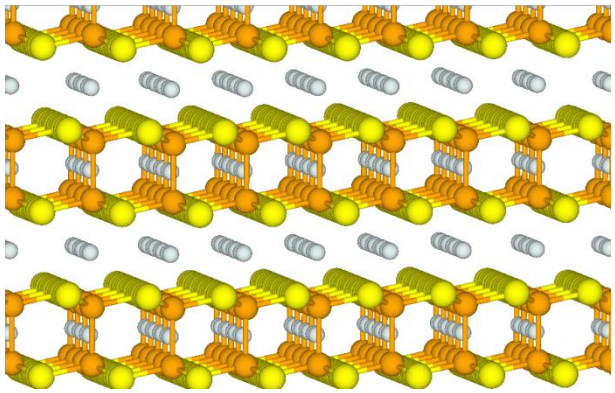
Structural variation can be mapped on to a two-dimensional hexagonal lattice with each P configuration taking P↑ or P↓ settings; Li and S configurations fixed



Examples:

Structure “b”

$P\bar{3}1m$



$\Delta E = 0.03$ eV

100% P↑

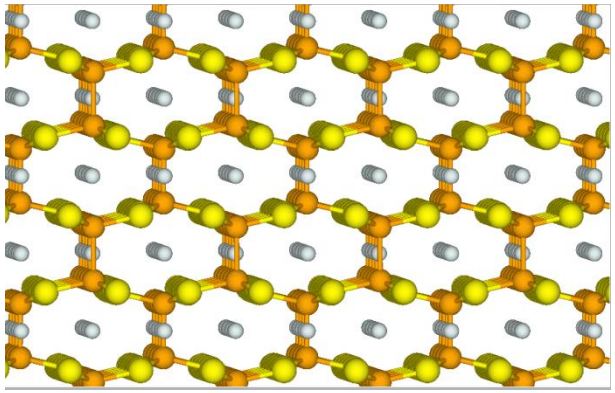
Li

P

S

Structure “c”

$Pnnm$



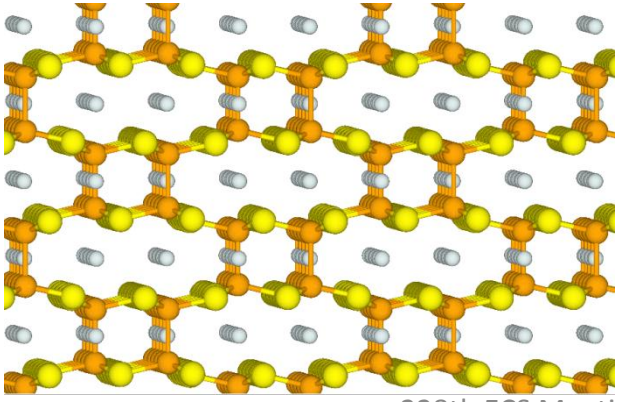
$\Delta E = 0$

50% P↑

50% P↓

Structure “d”

$Pnma$



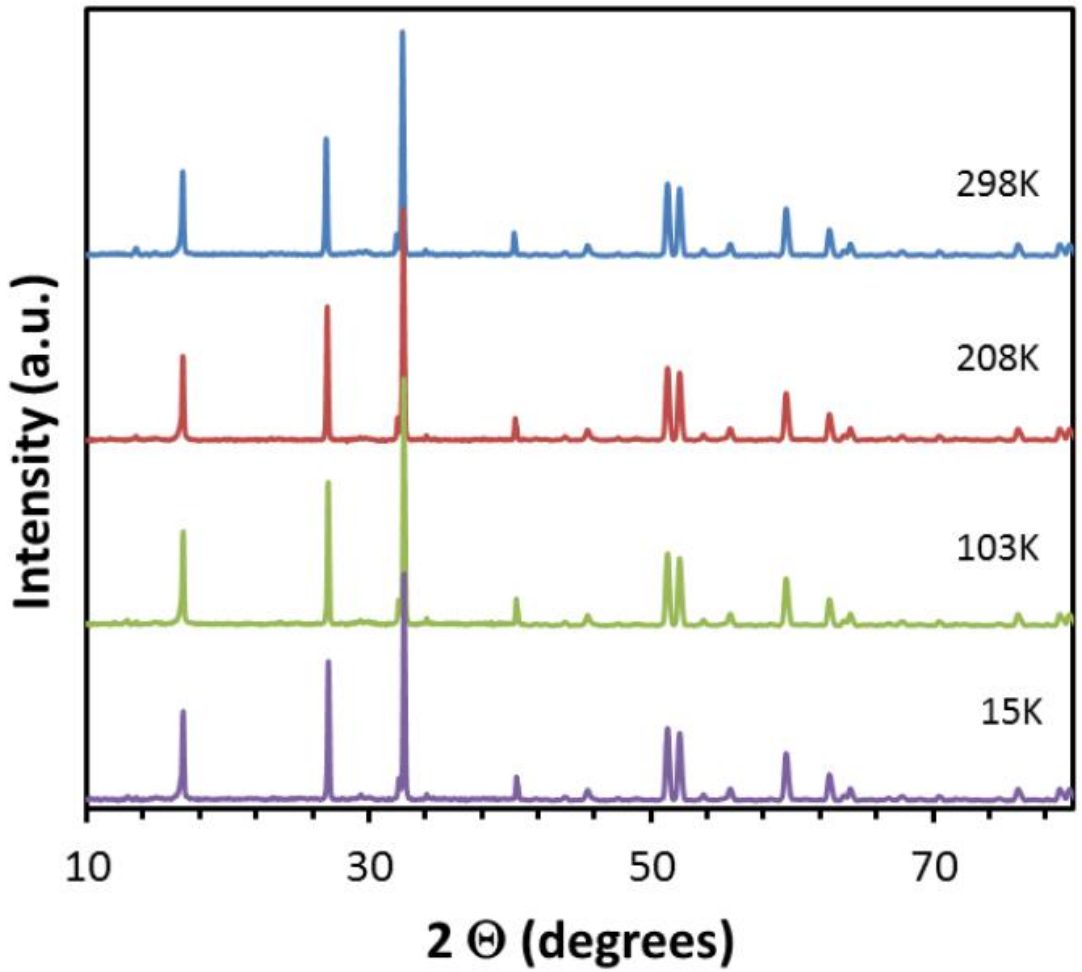
$\Delta E = 0$

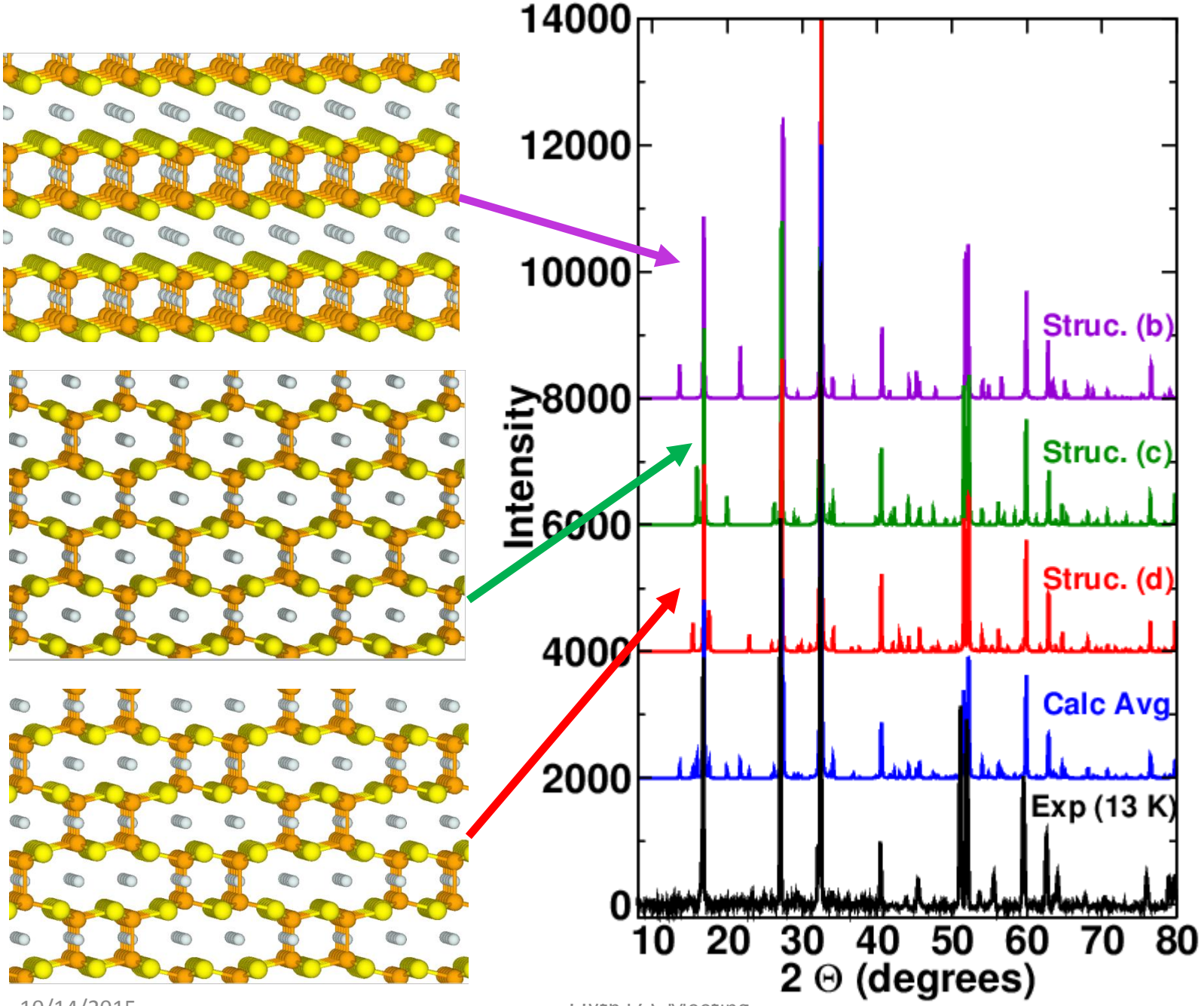
50% P↑

50% P↓

Two model configurations of disordered ground state structure

Temperature in^dependence of X-ray powder diffraction

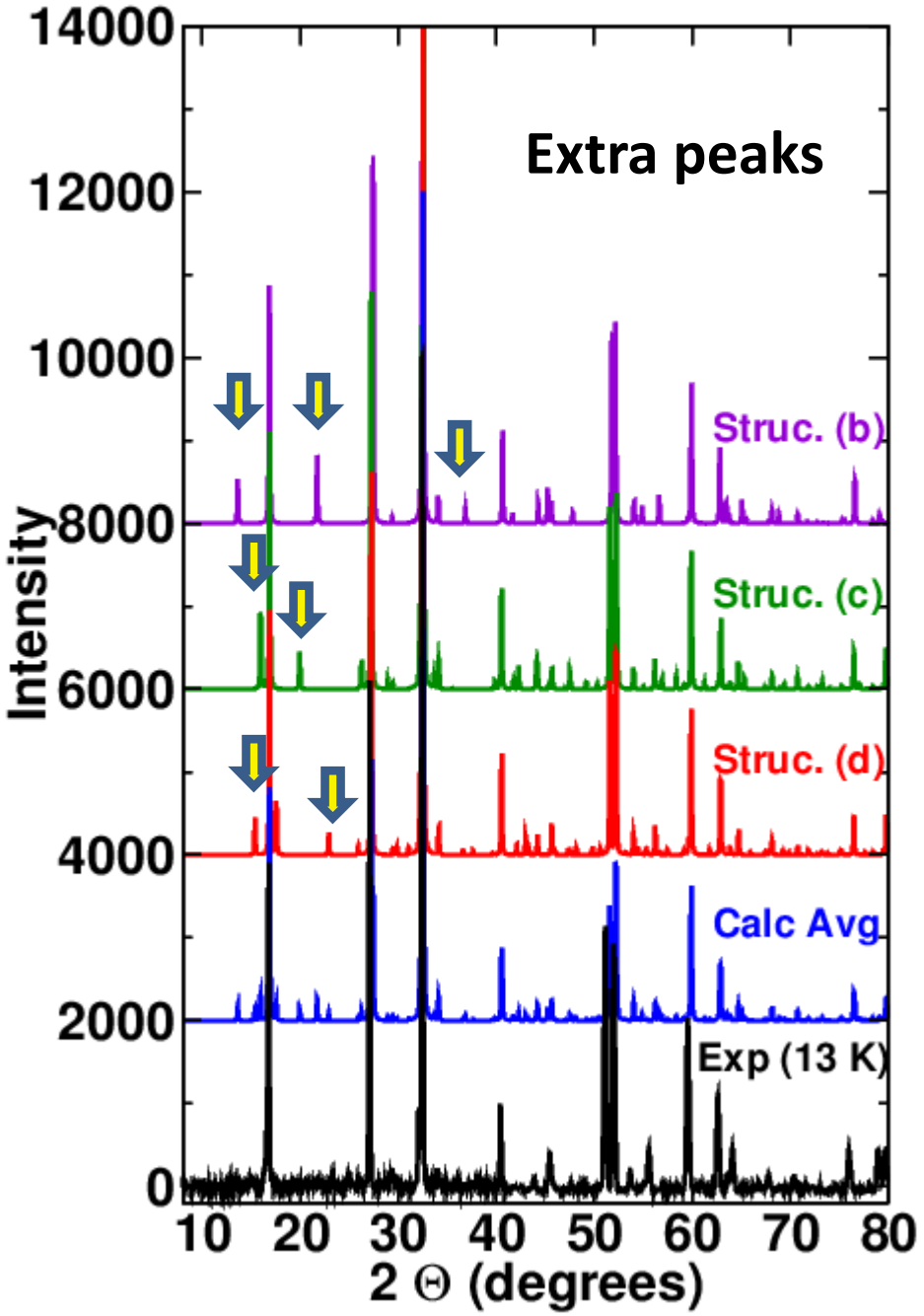



14000
12000
10000
8000
6000
4000
2000
0
Intensity
10
20
30
40
50
60
70
80
2 Θ (degrees)
Struc. (b)
Struc. (c)
Struc. (d)
Calc Avg
Exp (13 K)

Comparison of 15 K X-ray data with simulation

Note: simulations scaled by 102% to compensate for systematic LDA error.

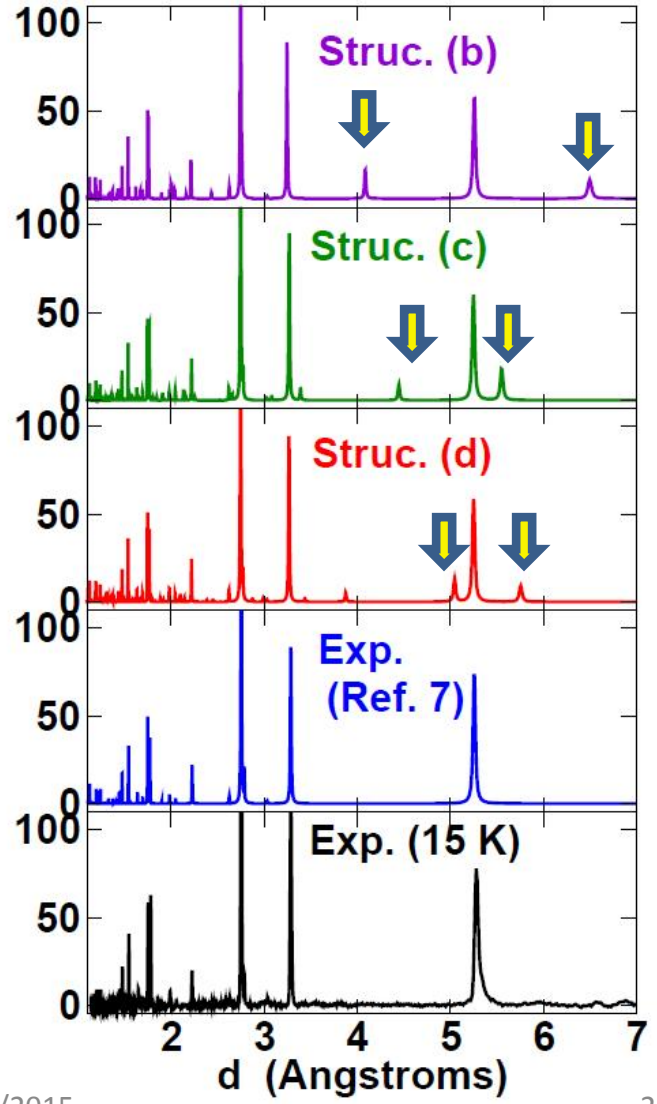
Simulations consistent with incoherent average over all P↑ and P↓ configurations



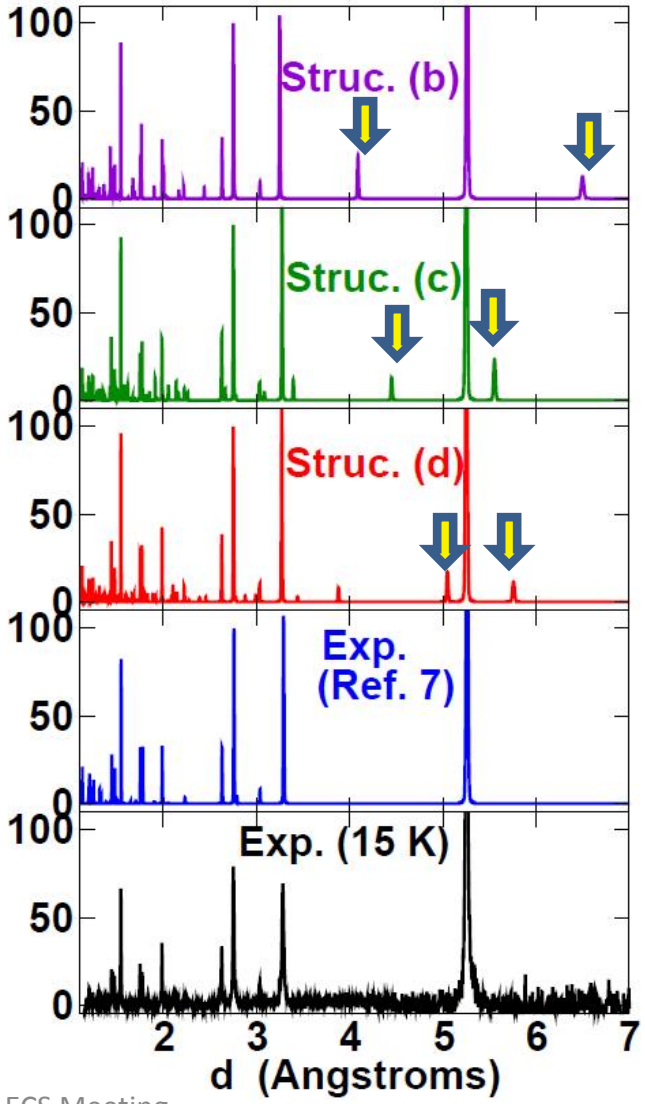
In terms of diffracting plane spacing:

$$d = \lambda / (2\sin\Theta)$$

X-ray spectrum



Neutron spectrum



Structural parameters

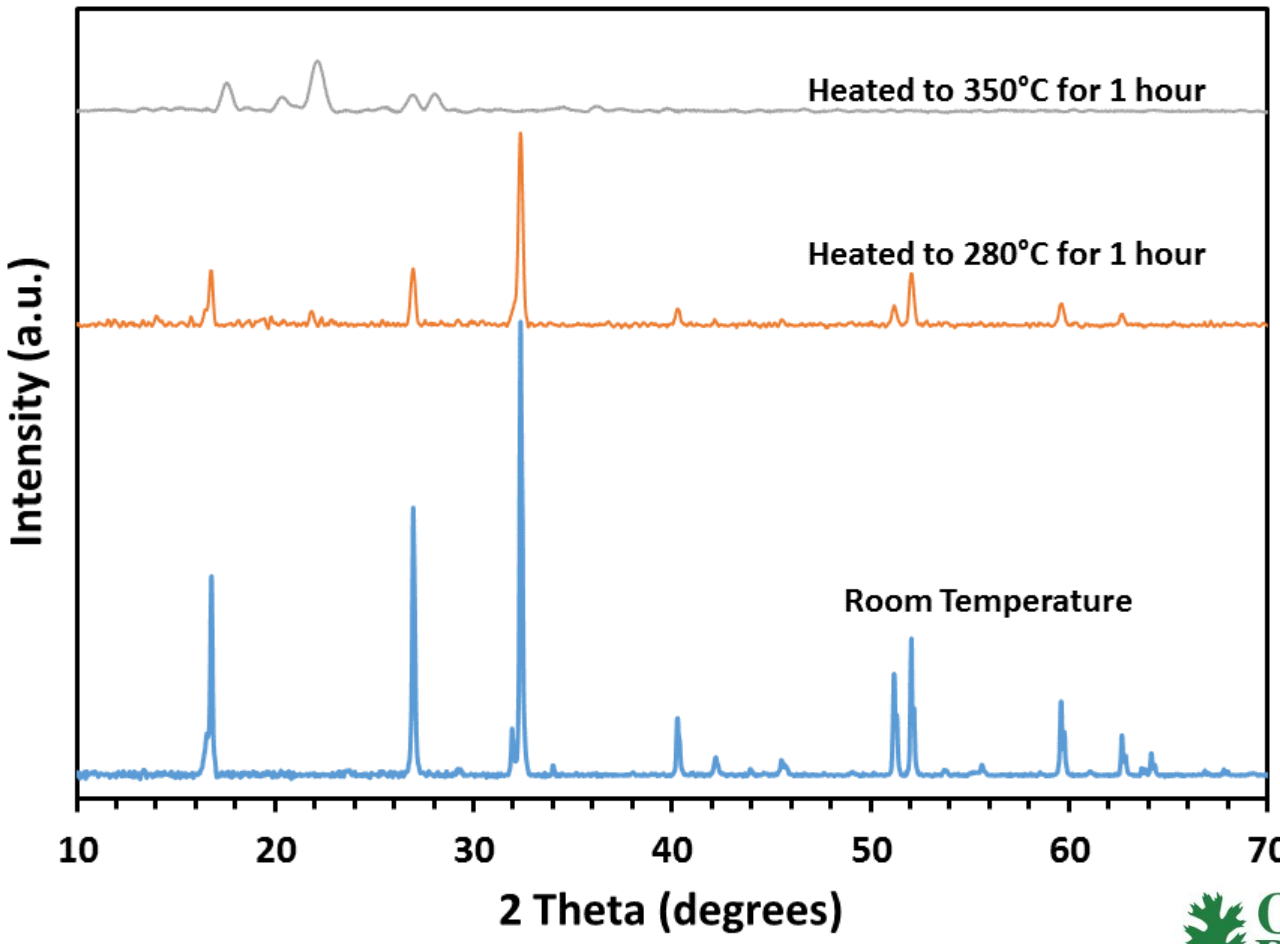
	a (Å)	c (Å)	z_P	z_S
Exp. 293K (X-ray)*	6.070	6.557	0.1715	0.3237
Exp. 300K (X-ray)	6.075	6.597	0.172	0.324
Exp. 300K (neutron)	6.075	6.595	0.173	0.326
Exp. 15K (X-ray)	6.051	6.548	0.172	0.324
Exp. 15K (neutron)	6.055	6.553	0.172	0.326
Calc. structure "b"	6.07	6.50	0.18	0.33
Calc. structure "c"	6.06	6.54	0.17	0.33
Calc. structure "d"	6.06	6.54	0.17	0.33

Hood *et al.*** with 102% LDA corr.

*Mercier *et al.*, J. Solid State Chem. 43, 151 (1982)

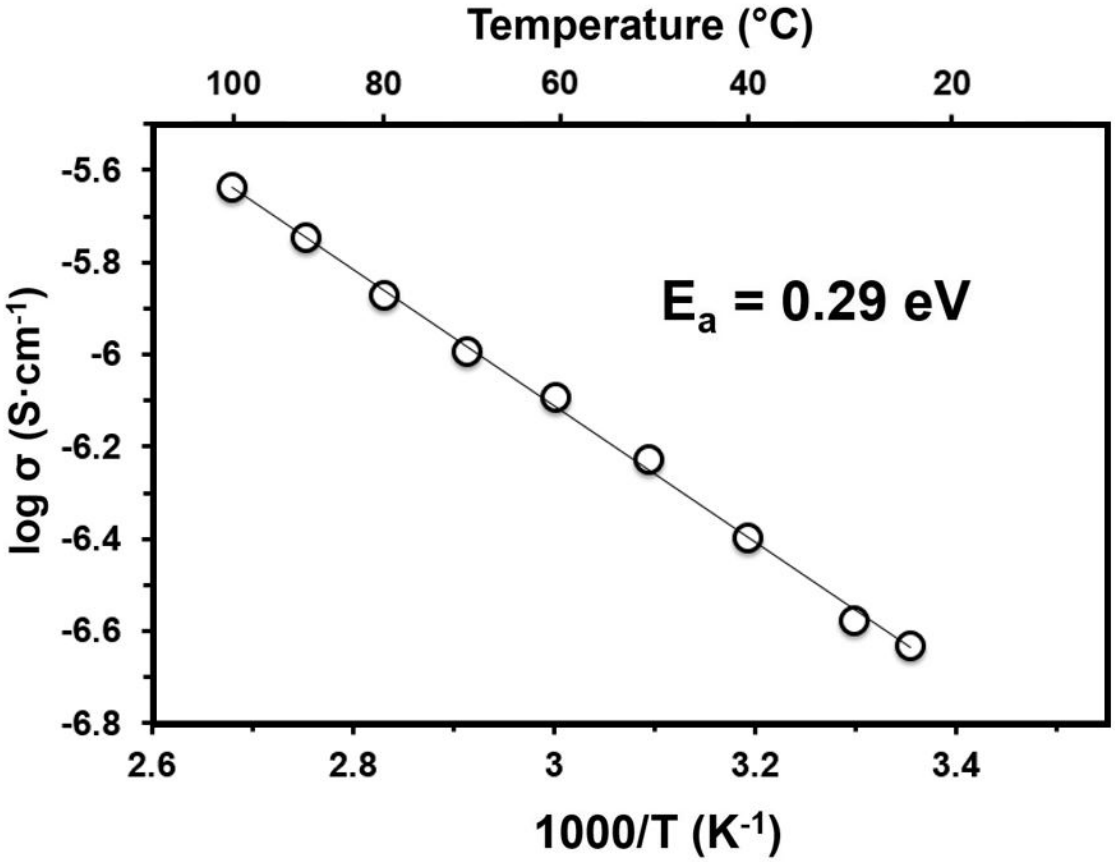
**Hood *et al.*, submitted to SSI (2015)

Stability: $Li_4P_2S_6$ is much less reactive than other lithium thio-phosphates, but it decomposes in air, especially at higher temperature



Decomposition products:
P_2O_5
$Li_4P_2O_7$
Li_2SO_4

Ionic conductivity and Activation Energy



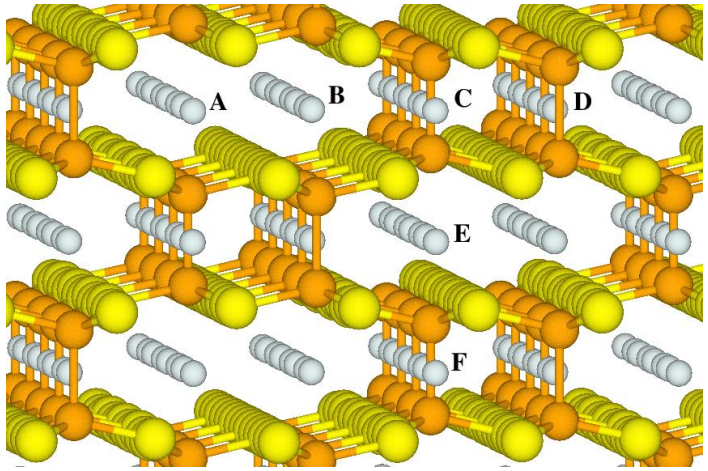
2.38 x 10^{-7} S/cm at 25˚C and 2.33 x 10^{-6} S/cm at 100˚C
$Li_4P_2S_6$ pressed pellets with blocking (Al/C) electrodes

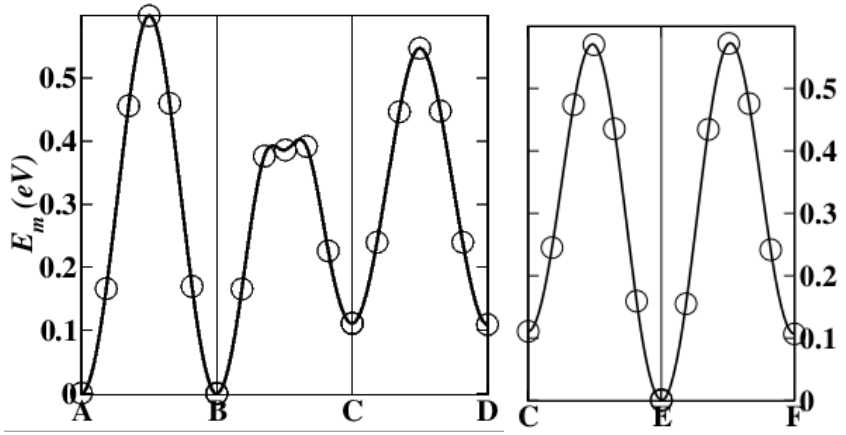
Li/ $Li_4P_2S_6$ /Li cells could not be cycled

Simulations of ion mobility using Nudged Elastic Band Model

Vacancy mechanism:
ΔE>0.6 eV

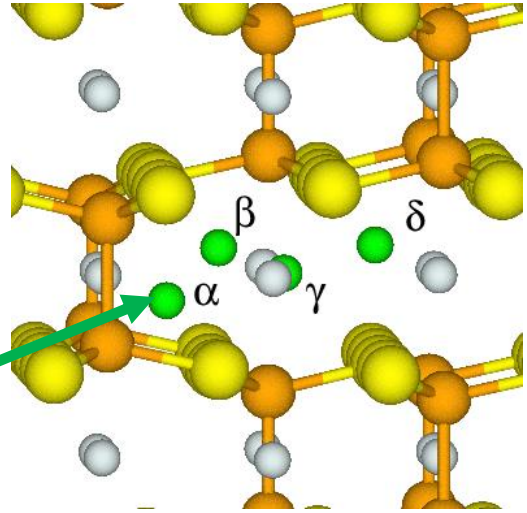
Li
P
S

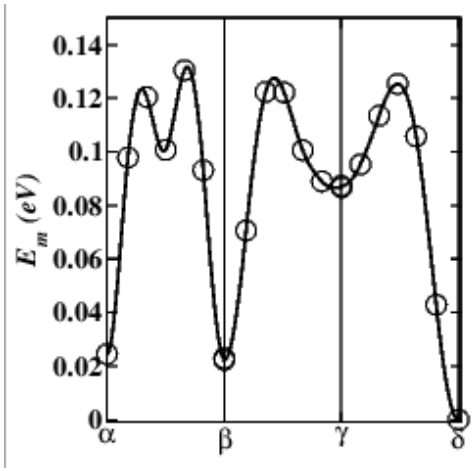




Interstitial mechanism:
ΔE>0.1 eV

Possible interstitial sites





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Models of $Li_4P_2S_6$/Li interfaces -- Surface parallel to P-P bonds:

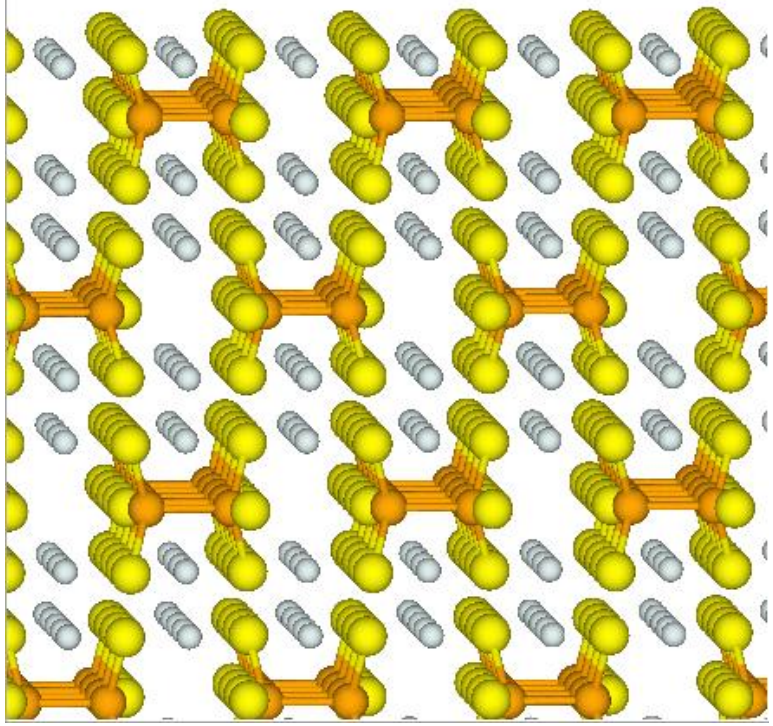
Surface with vacuum

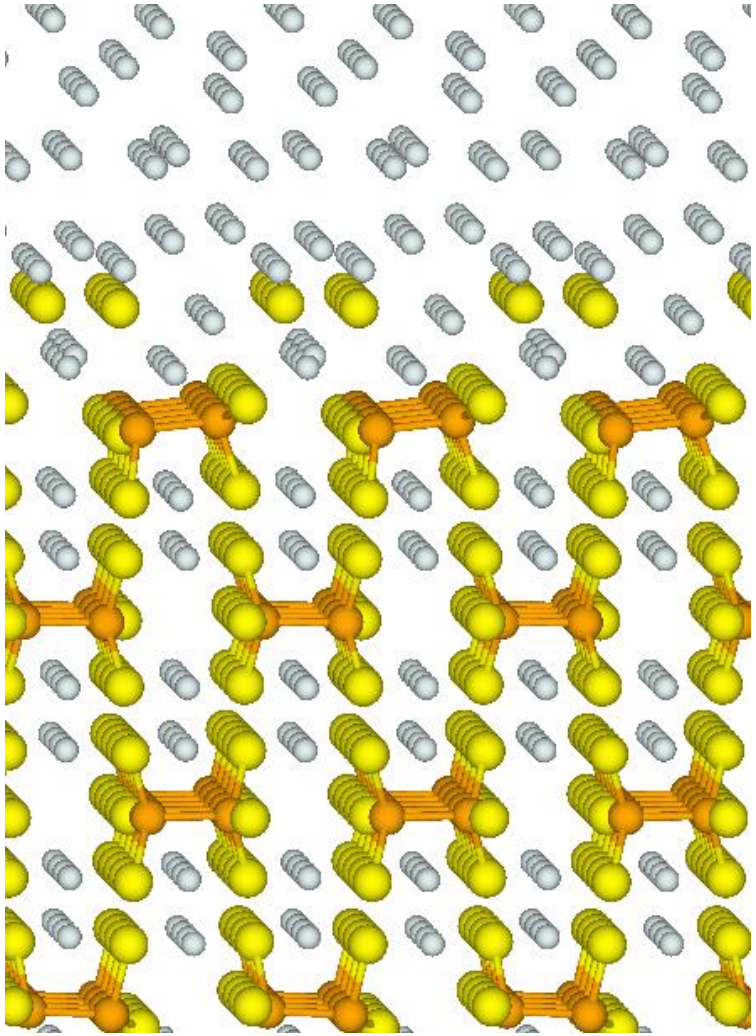
Surface with lithium

Li

P

S





Models of $Li_4P_2S_6$/Li interfaces -- Surface perpendicular to P-P bonds:

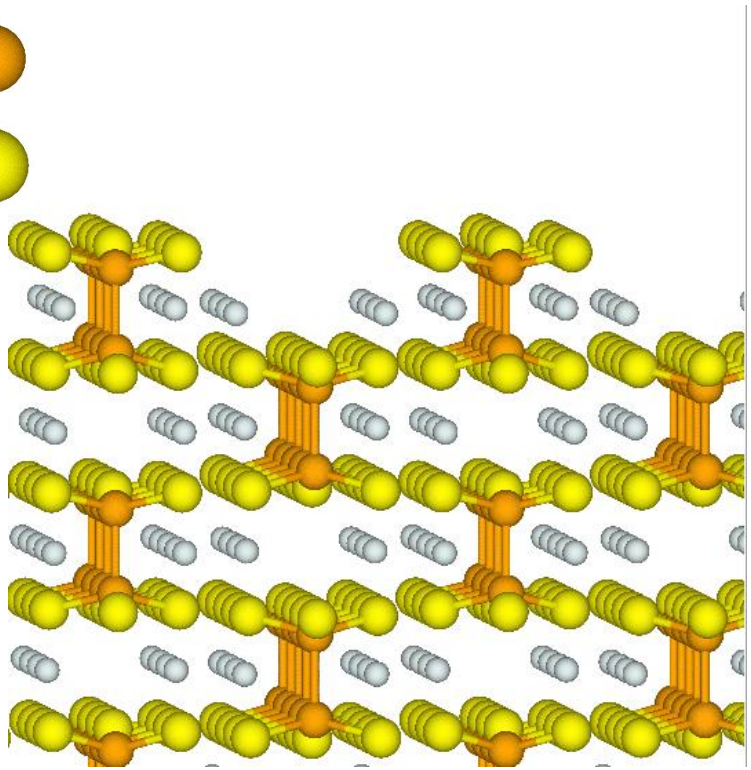
Surface with vacuum

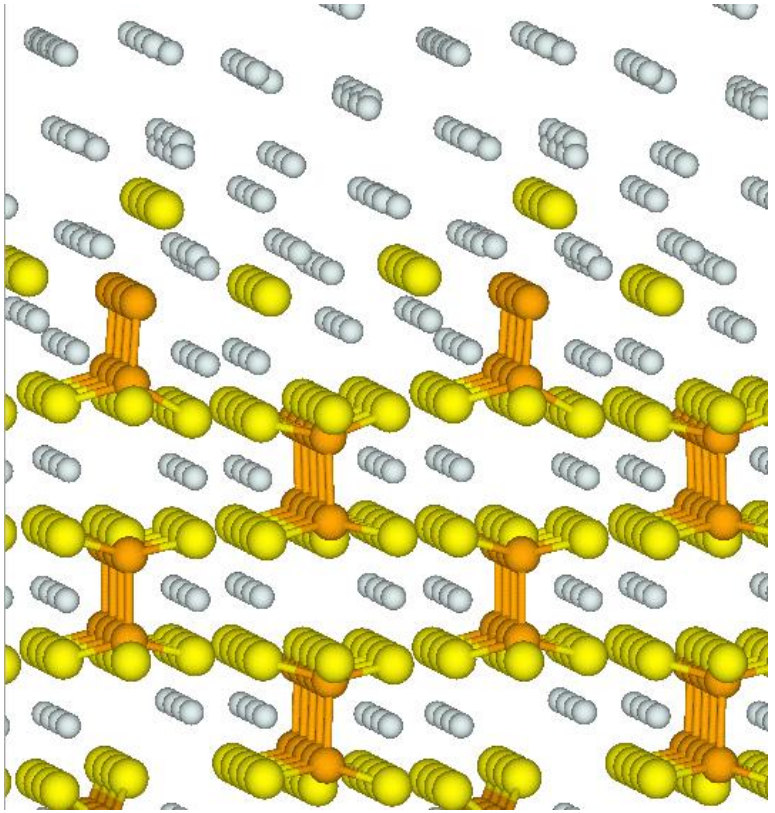
Surface with lithium

Li

P

S





Reactivity of Li/$Li_4P_2S_6$ interface models consistent with experimental observation that Li/ $Li_4P_2S_6$ /Li cells could not be cycled

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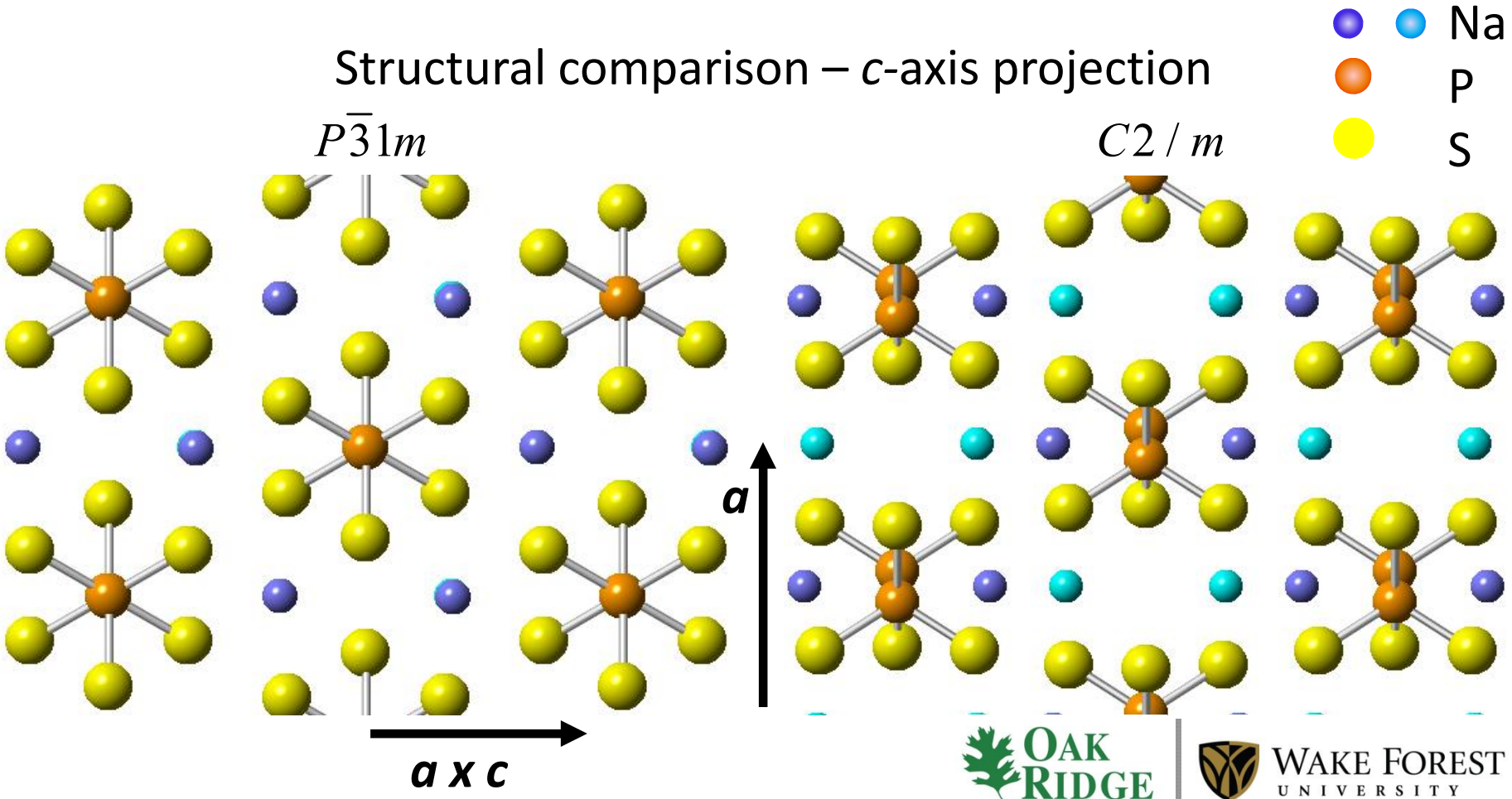
Preliminary results for $Na_4P_2S_6$:

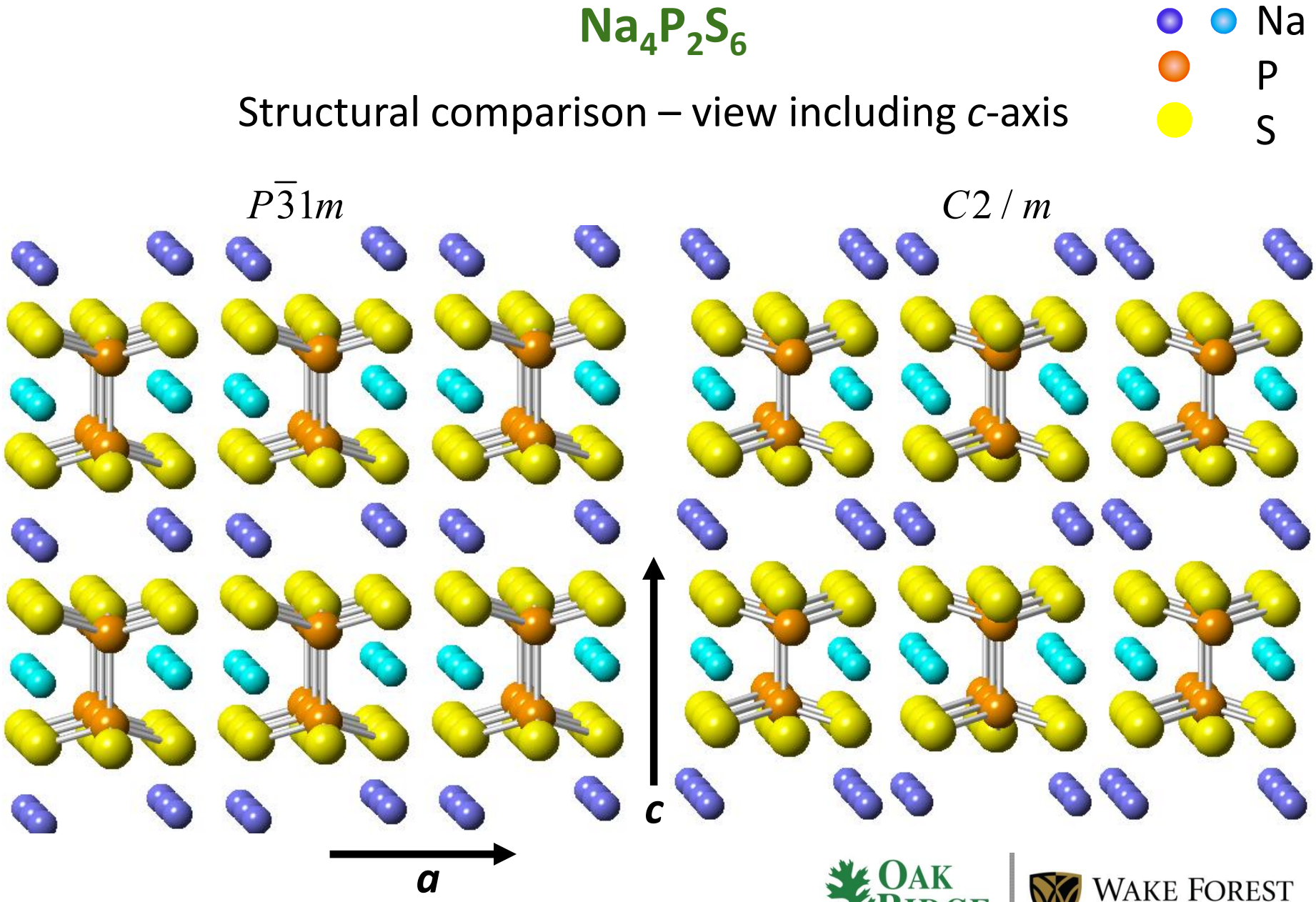
Kuhn et al., ZAAC **640**, 689-692 (2014) synthesized single crystals with a monoclinc structure having space group *C2/m* with similarities to the trigonal structure with $P\bar{3}1m$ space group

Structural comparison – *c*-axis projection



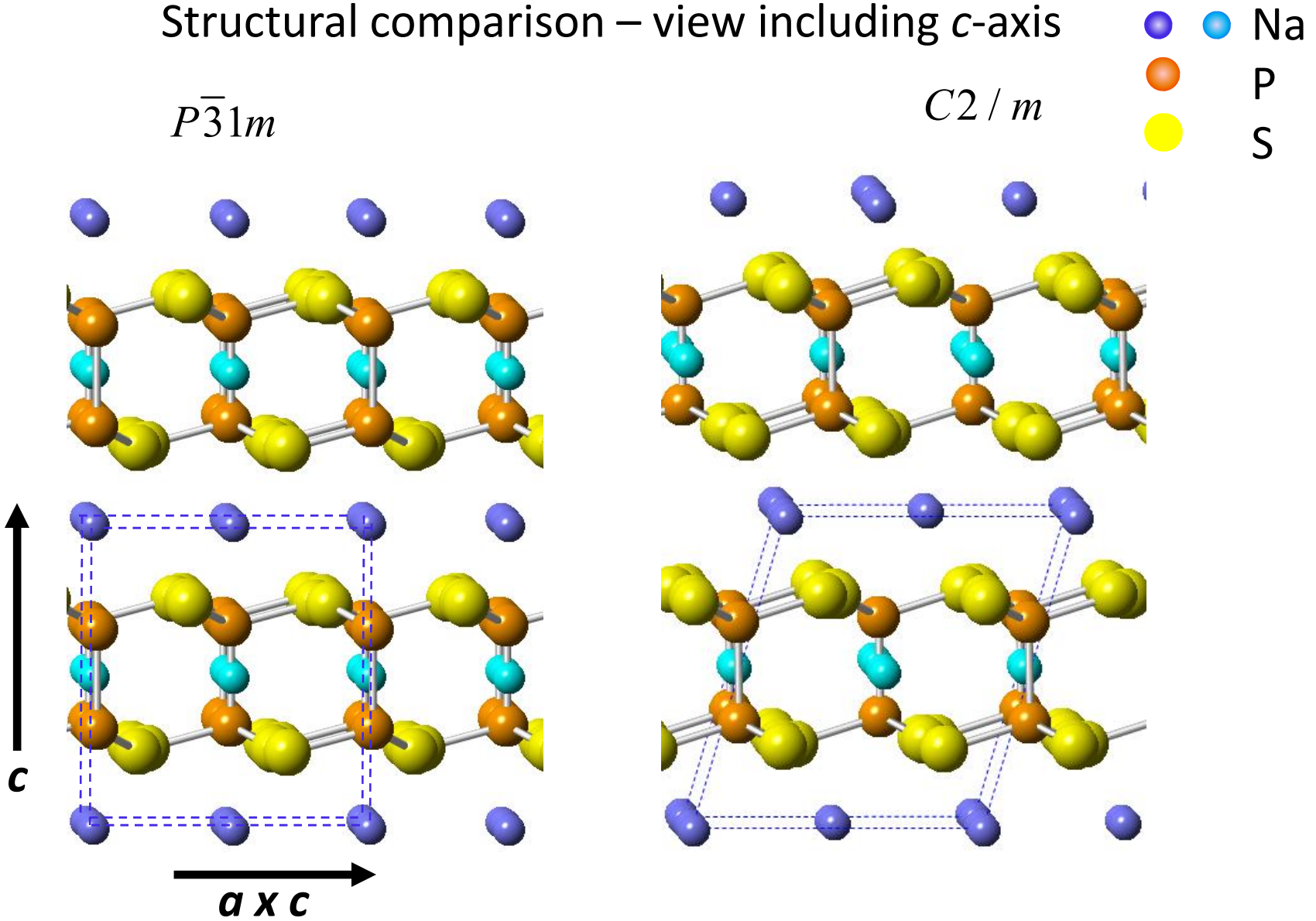
$Na_4P_2S_6$

Structural comparison – view including *c*-axis



$Na_4P_2S_6$

Structural comparison – view including *c*-axis



Preliminary results for $Na_4P_2S_6$:

Calculated heats of formation (eV per formula unit) for $Na_4P_2S_6$ and $Li_4P_2S_6$ in 4 structural models

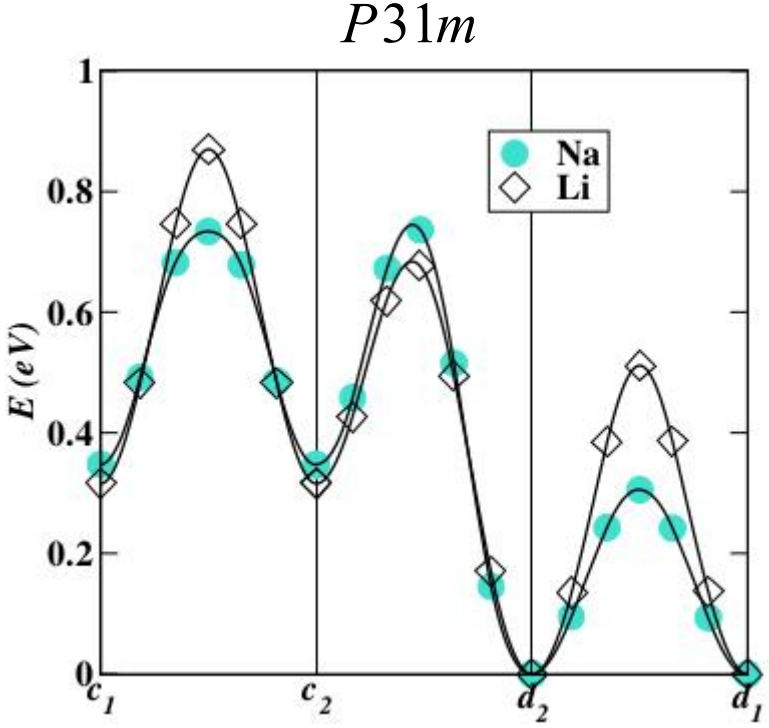
	$Na_4P_2S_6$	$Li_4P_2S_6$
Kuhn structure	-11.47 eV	-12.07 eV
Structure "b"	-11.47 eV	-12.42 eV
Structure "c"	-11.56 eV	-12.46 eV
Structure "d"	-11.56 eV	-12.46 eV

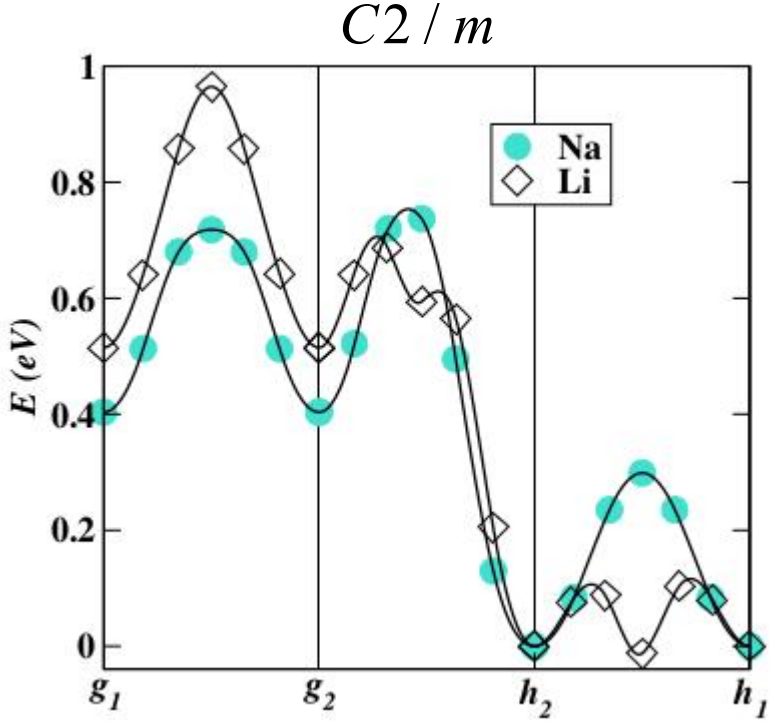
} Models of disordered Mercier structure

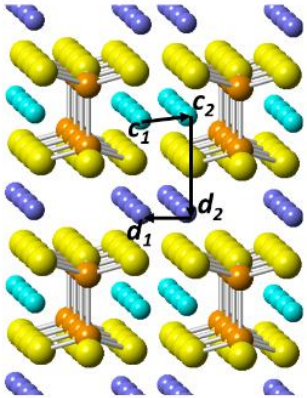
➔ Calculations find the most stable structure for both $Na_4P_2S_6$ and $Li_4P_2S_6$ to be the disordered Mercier structure, suggesting that the Kuhn structure is meta-stable.

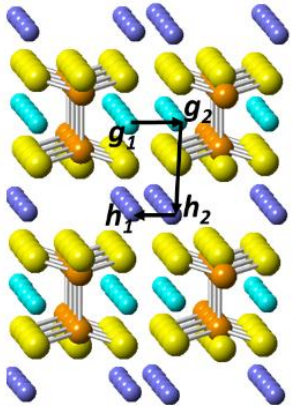
$Na_4P_2S_6$

Comparison of vacancy migration of $Na_4P_2S_6$ and $Li_4P_2S_6$



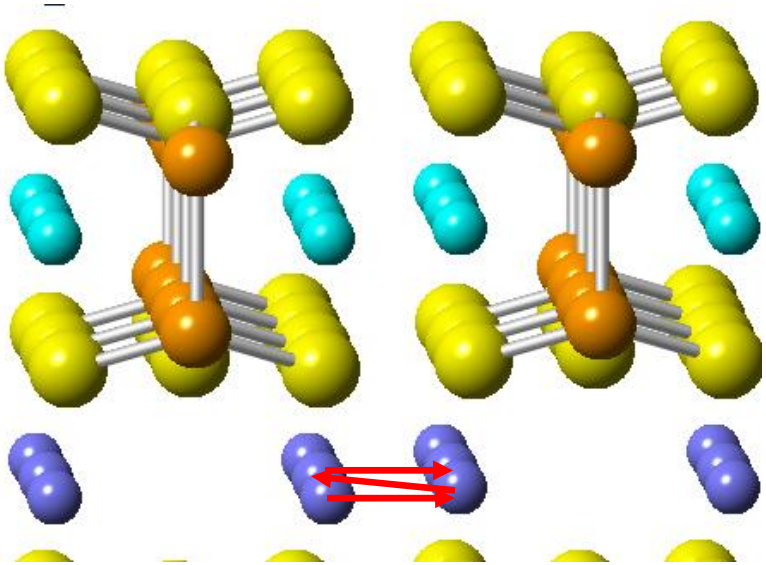




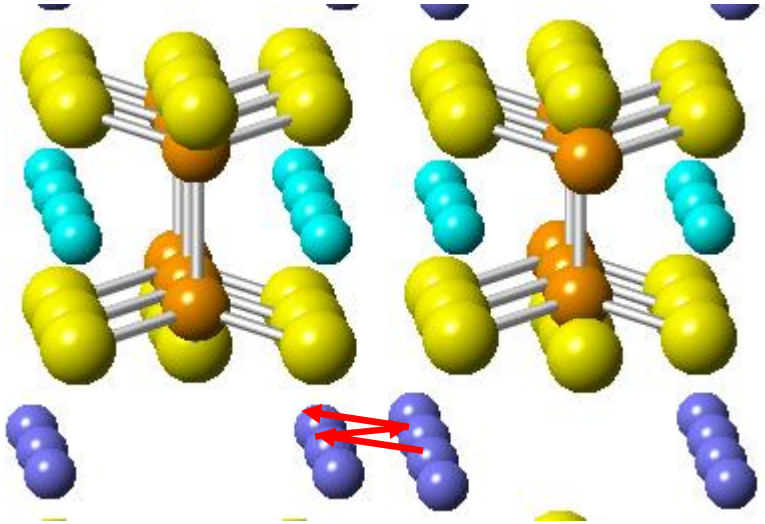


Na
P
S

$P\bar{3}1m$



$C2/m$



Na
P
S

Minimum ion vacancy migration energies

	$P\bar{3}1m$	$C2/m$
$Na_4P_2S_6$	0.3 eV	0.3 eV
$Li_4P_2S_6$	0.5 eV	0.1 eV

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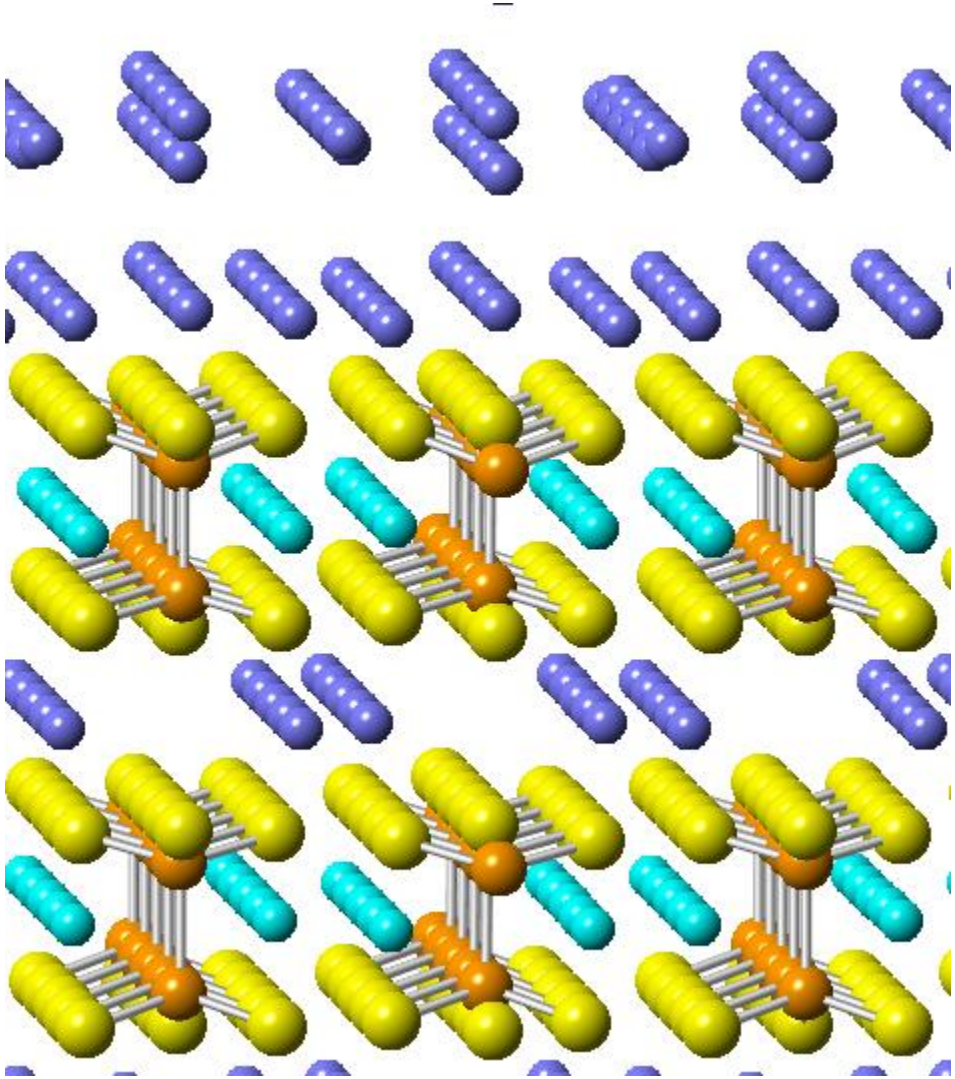
Model of $Na_4P_2S_6$/Na interface in Kuhn structure

Na
P
S



meta-stable
ideal interface

Conclusions:

- $Li_4P_2S_6$ and $Na_4P_2S_6$ have interesting structural properties; simulations find the most stable structure for both to be the disordered Mercier structure, suggesting that the Kuhn structure is meta-stable.
- Experimental structural studies for $Li_4P_2S_6$ agree with the simulations; material is found to be remarkably temperature independent and thermally stable relative to other thio-phosphates.
- Measurements find $Li_4P_2S_6$ to have low ionic conductivity; simulations suggest that $Na_4P_2S_6$ may have more favorable ionic conductivity.
- Models of ideal $Li_4P_2S_6$/Li interfaces find broken P—S bonds; $Na_4P_2S_6$/Na interfaces in the Kuhn structure may be slightly more stable

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