Computational Study of the Solid Electrolyte Li_4PS_4I and related materials

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Outline:

- What are probable crystal structures?
- What stabilizes these structures?
- Electrolyte/Li interface stability

Computational methods:

- PAW formalism using Quantum Espresso (http://www.quantum-espresso.org) & Abinit (https://www.abinit.org)
- LDA XC functional with 1.02 scaling of lattice parameters

X-ray diffraction patterns

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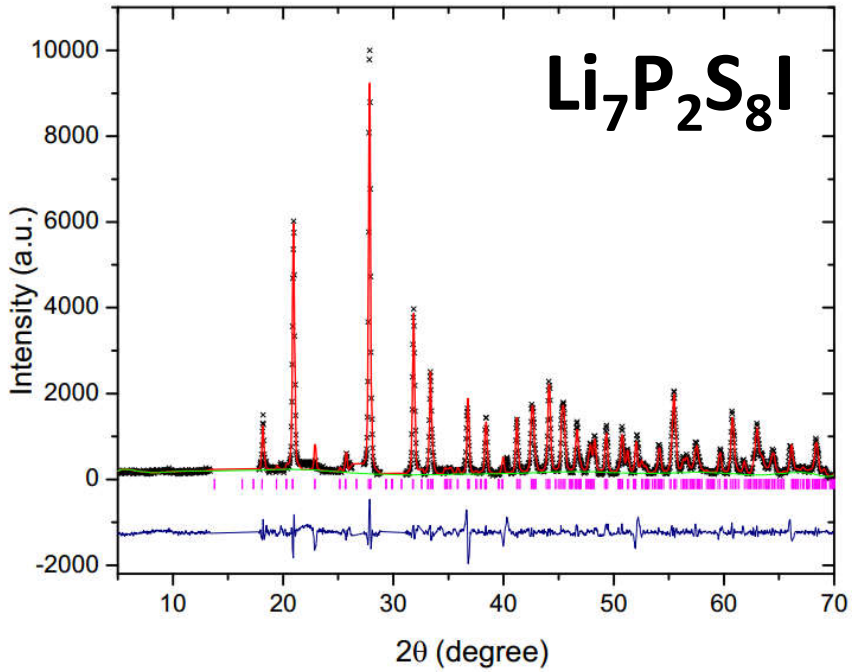
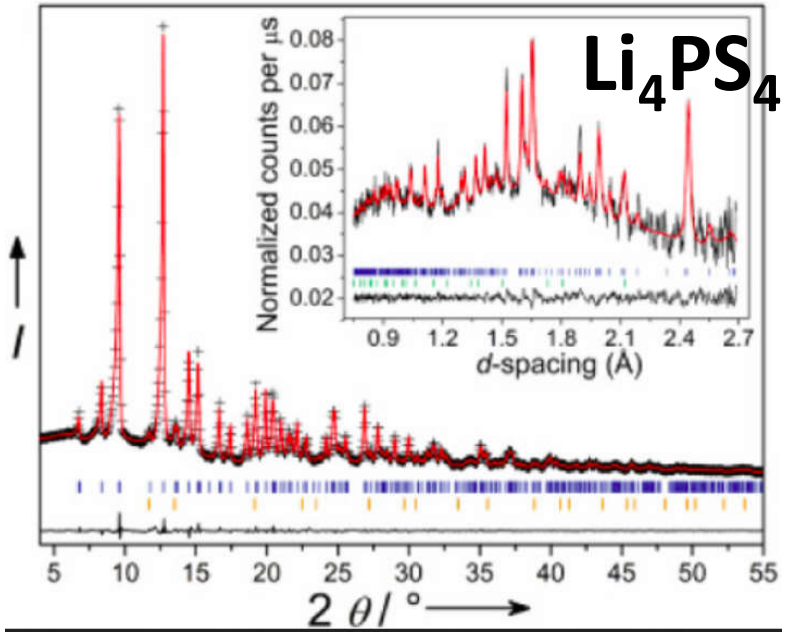
$2Li_3PS_4+LiI$ → solvents+processing



Li_3PS_4+LiI → solvents+processing

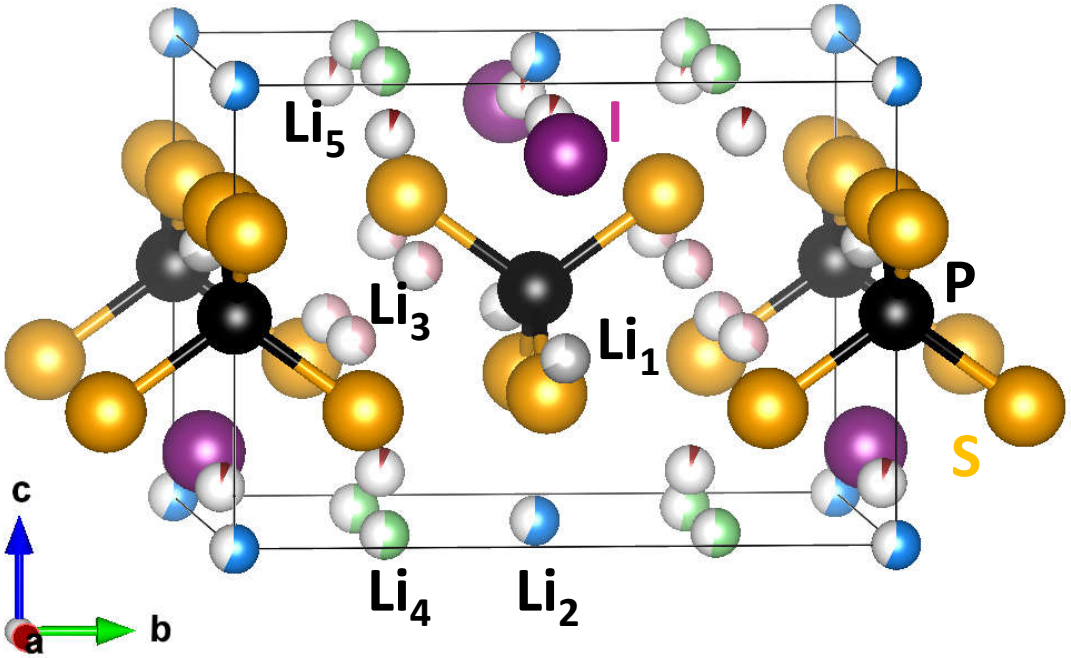


$Li_7P_2S_8I$ diffraction from λ=1.5406 Å X-rays reported by E. Rangasamy *et al.*, ***JASC* 137** 1384-1387 (2015)

Li_4PS_4I diffraction from λ=0.7093 Å X-rays reported by S. Sedlmaier *et al.*, ***CM* 29** 1830-1835 (2017)

Structural analysis of Li_4PS_4I

S. Sedlmaier *et al.*, ***CM* 29** 1830-1835 (2017) and
S. Sicolo *et al.*, ***SSI* 319** 83-91 (2018)

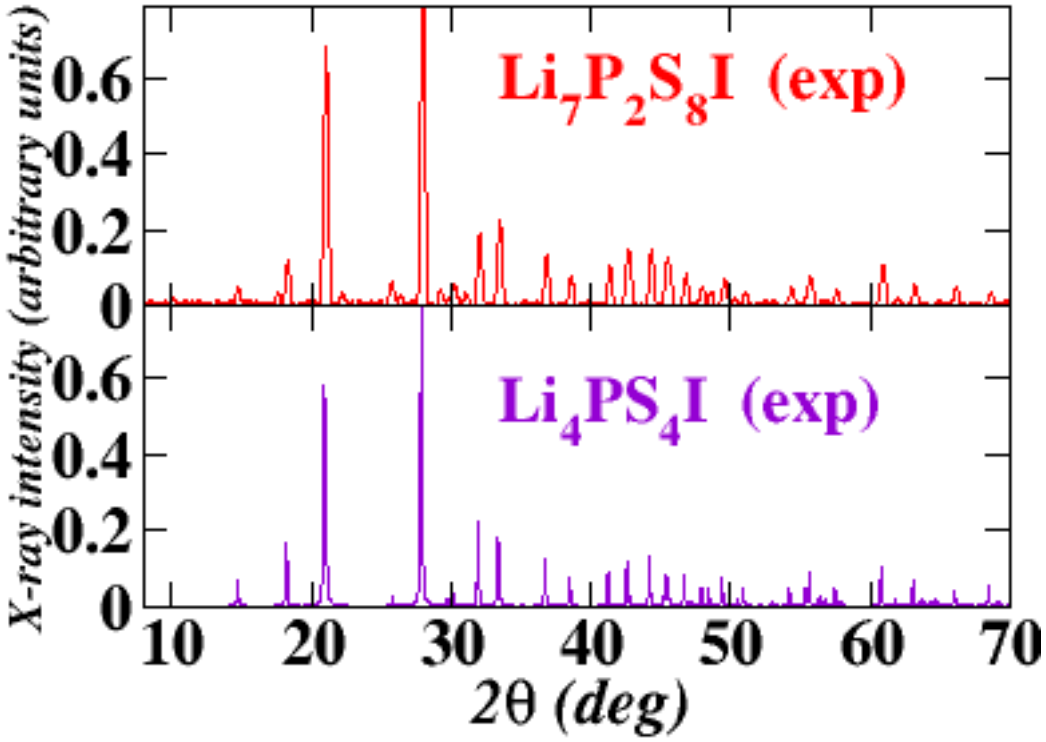


Tetragonal structure with SG P4/mmm (#129)

Disordered Li sublattice with 5 fractionally occupied sites:

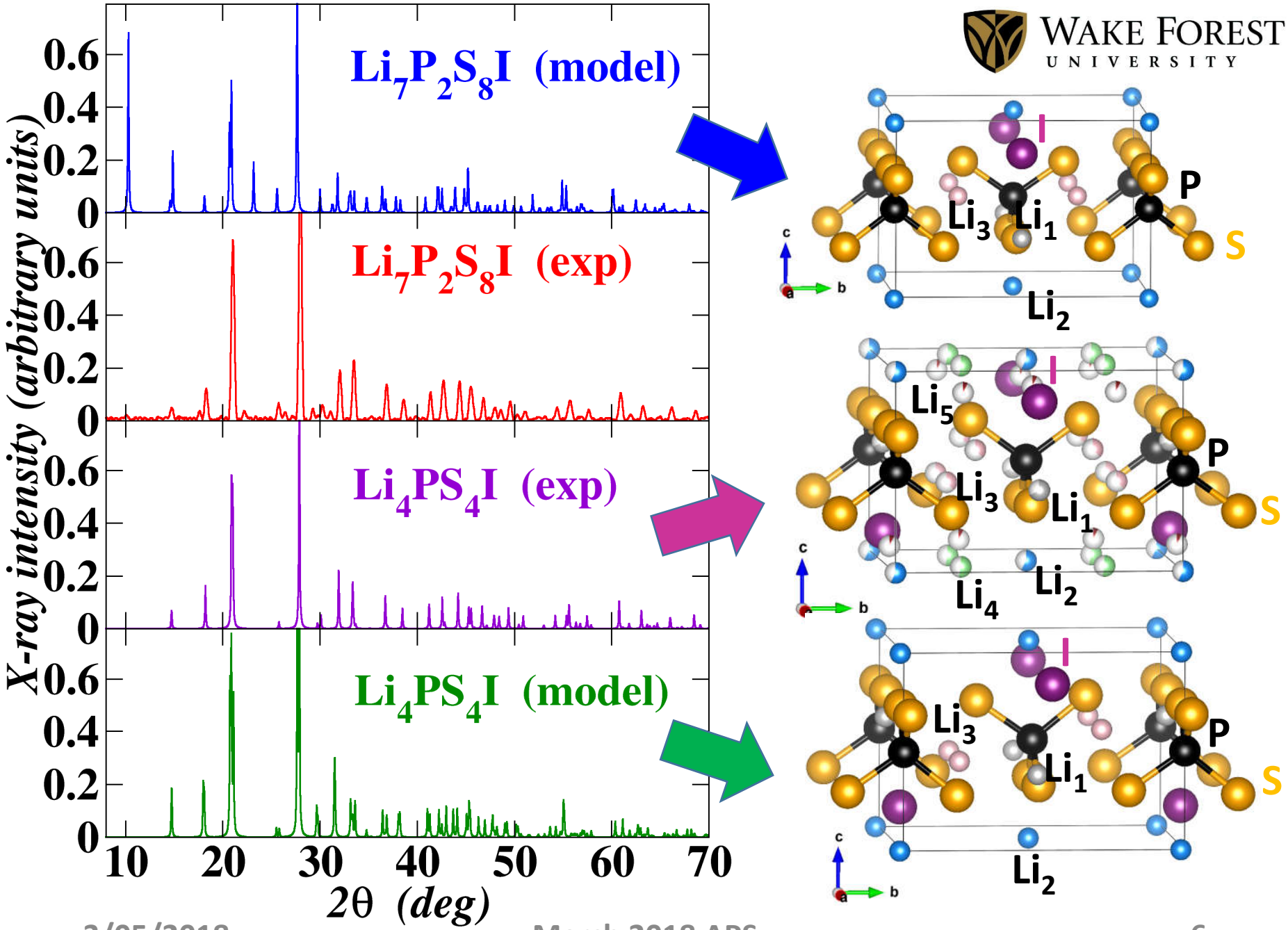
	Wyck.	degen.	av. occ.
Li_1	c	2	1.4
Li_2	a	2	1.2
Li_3	j	8	3.0
Li_4	d	4	2.1
Li_5	i	8	0.6

Comparing X-ray diffraction patterns at λ=1.5406 Å



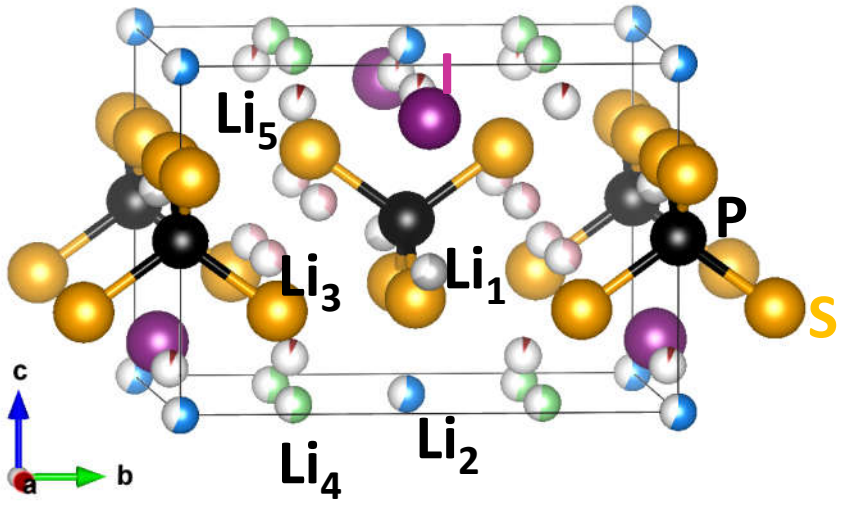
From data of E. Rangasamy *et al.*, ***JASC* 137** 1384-1387 (2015)

Generated diffraction from analysis of S. Sedlmaier *et al.*, ***CM* 29** 1830-1835 (2017)

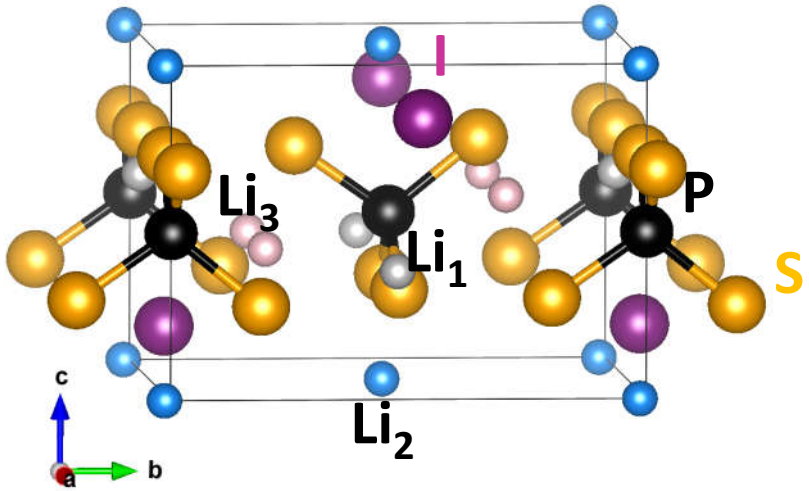

Li7P2S8I (model)
Li7P2S8I (exp)
Li4PS4I (exp)
Li4PS4I (model)
X-ray intensity (arbitrary units)
0.6
0.4
0.2
0
10
20
30
40
50
60
70
2θ (deg)
WAKE FOREST
UNIVERSITY
I
P
S
Li3
Li1
Li2
Li5
Li4
c
b
a

Structure details

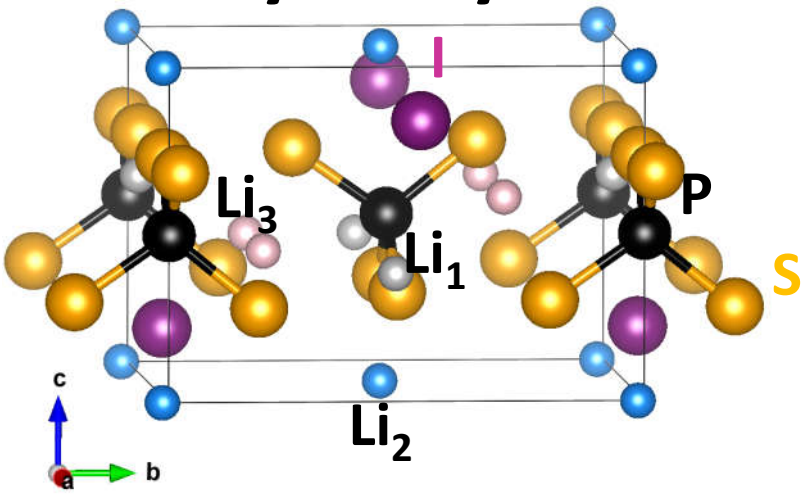
Sedlmaier structure: *P4/mmm*
a=*b*=8.48 Å, *c*=5.93 Å
5 fractionally occupied Li sites

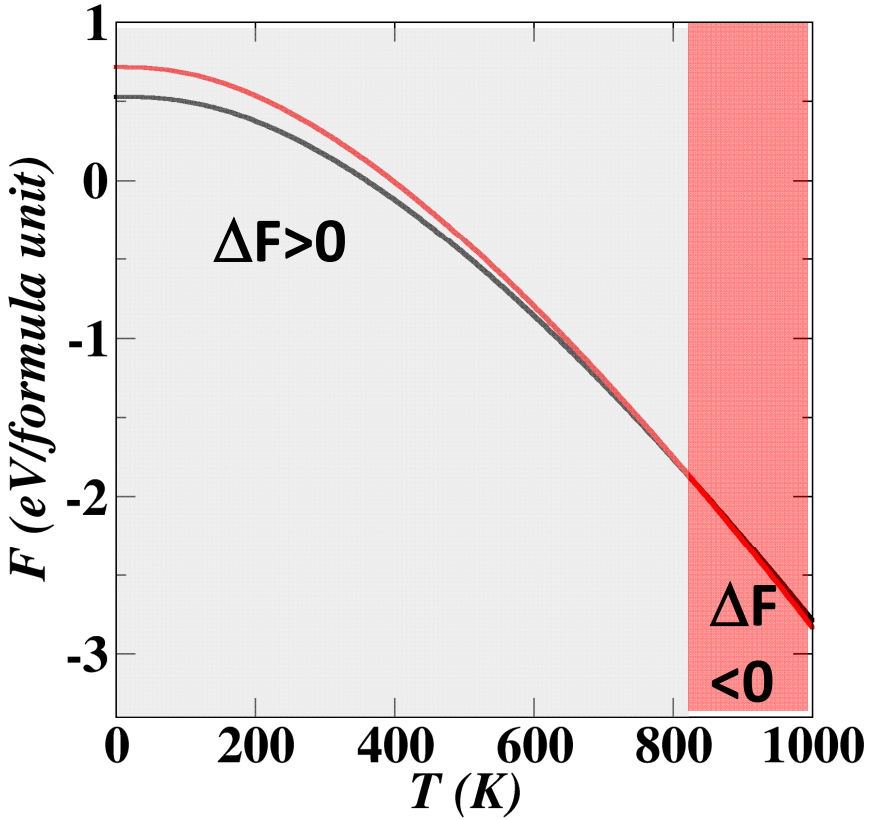


Possible low temperature phase from optimization: *Pmn2*$_1$
a=8.41 Å, b=8.55 Å, c=6.02 Å
3 fully occupied Li sites



Stability analysis





At T=0 K, Li_4PS_4I is unstable relative to γ-Li_3PS_4+LiI.

Li_4PS_4I → γ-Li_3PS_4+LiI+ΔF

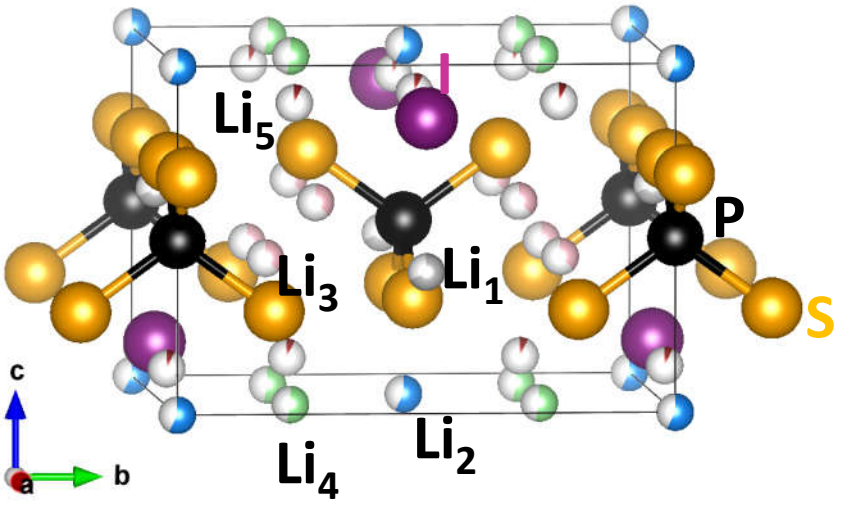
Helmholz free energy:

$F=U_{SL}+F_{vib}$

Static lattice internal energy

phonon free energy in harmonic approximation

Stability analysis



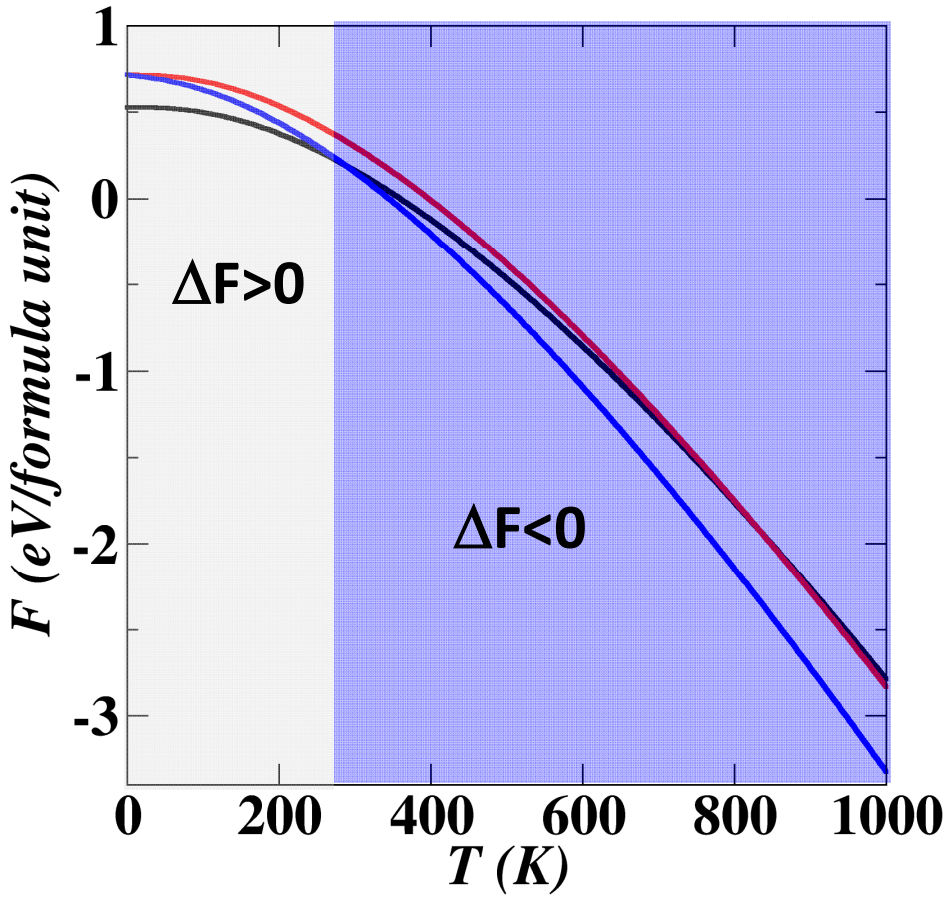
At T=0 K, Li_4PS_4I is unstable relative to γ-Li_3PS_4+LiI.

$Li_4PS_4I \rightarrow \gamma$-$Li_3PS_4$+LiI+$\Delta F$

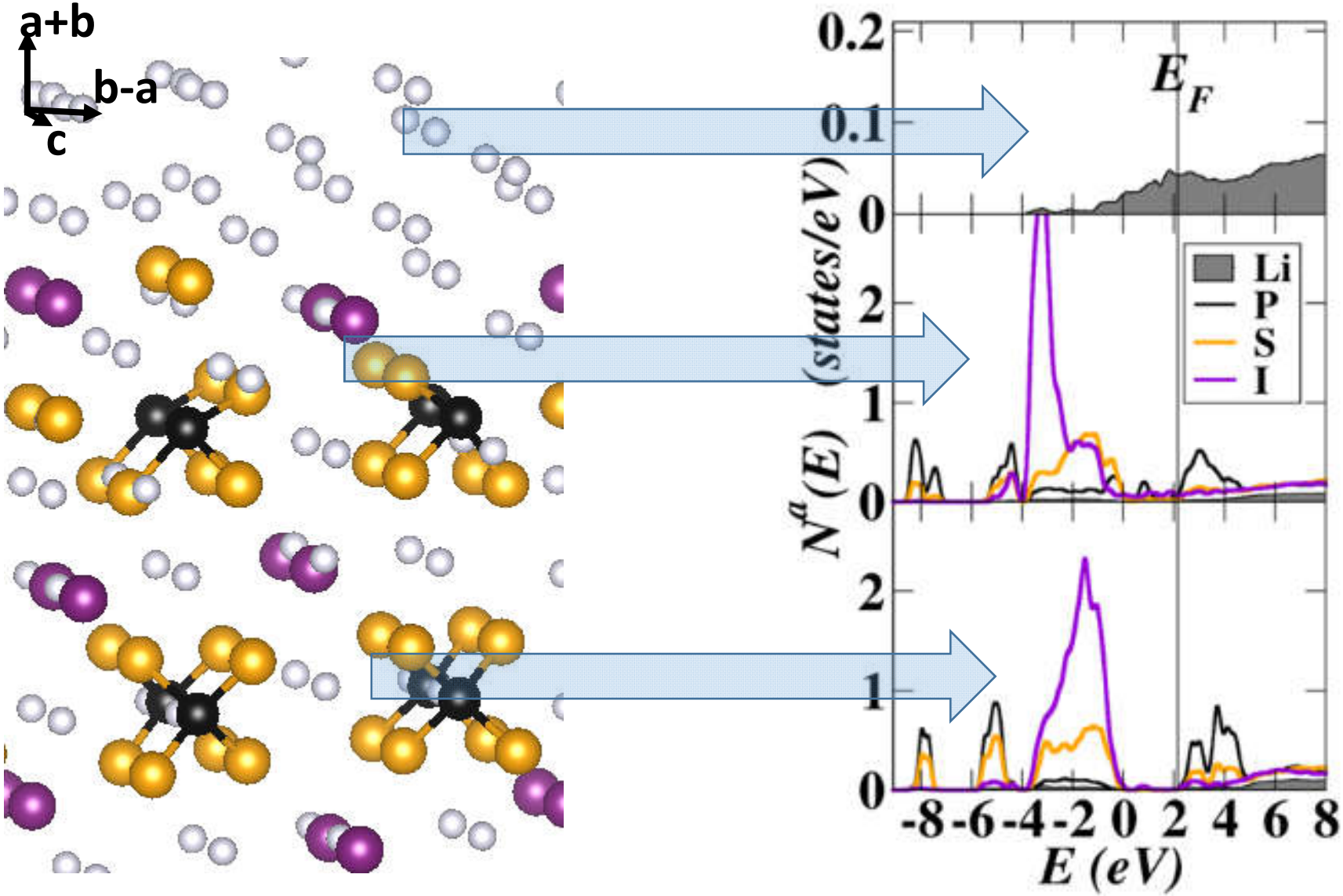
Helmholz free energy:

$F=U_{SL}+F_{vib}-TS_{config}$

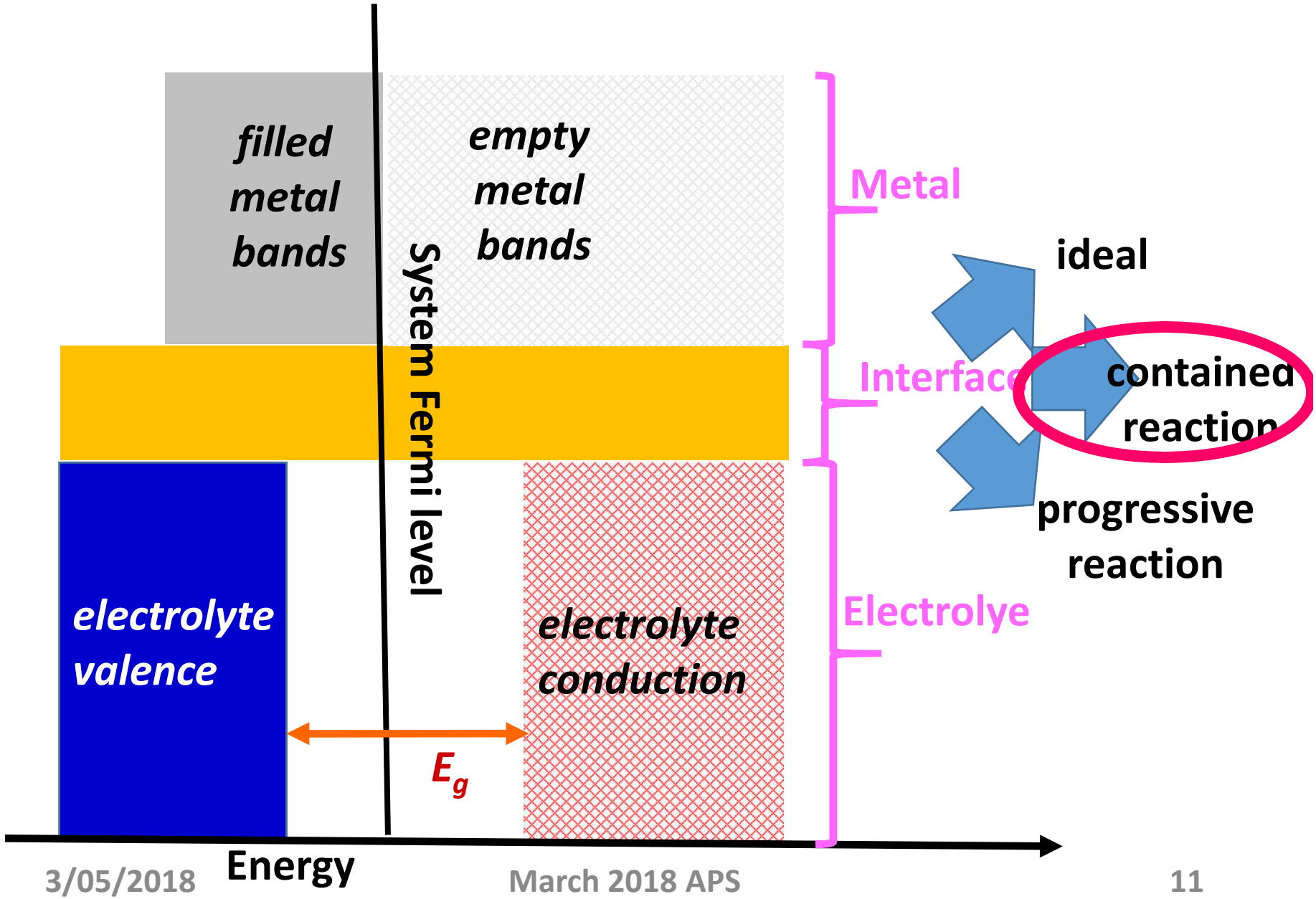
configurational entropy



Interface model: Li4PS4I[110]/Li



Possible interface configurations



Summary:

- Predicted a metastable ground state structure of Li_4PS_4I having orthorhombic $Pmn2_1$ structure
- Free energy estimates suggest that the Sedlmaier tetragonal *P4/mmm* structure of Li_4PS_4I is stabilized by configurational entropy
- X-ray patterns suggests that $Li_7P_2S_8I$ is based on the same structure as Li_4PS_4I with random LiI vacancies
- Electrolyte/Li model shows contained interface reaction within ~ one-two layers