Computational and experimental investigation of $Na_4P_2S_6$ as a promising solid electrolyte material for sodium metal batteries

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Motivation

- Kuhn et al.[1] observed that $Na_4P_2S_6$ crystallizes to form monoclinic space group **C2/m (#12)**
- Computational results of Rush et al.[2]: **Kuhn structure is meta-stable**
- Recent experimental results of Hood et al.[3] also find the **C2/m** structure

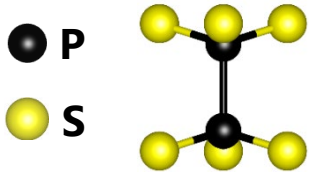
→ **Reexamine previous calculations to understand the stability of the Kuhn structure**

- Theoretically, $Na_4P_2S_6$ and $Li_4P_2S_6$ are chemically and structurally related
- Using combined approach of NMR and X-ray, the new experimental analysis[4] on $Li_4P_2S_6$ concludes the structure to be ordered with space group **P321 (#150)**

→ **Property similarities (discrepancies) between $Na_4P_2S_6$ and $Li_4P_2S_6$**

- Compared to $Li_4P_2S_6$, $Na_4P_2S_6$ is a competitive electrolyte candidate[3]

→ **Conductivity mechanism**



$(P_2S_6)^{4-}$ with D_{3d} symmetry

[1]Kuhn et al., *Z. Anorg. Allg. Chem*. 640, 689-692 (2014).
[2]Rush et al., *Solid State Phys*. 286, 45-50 (2016).
[3]Hood et al., Manuscript in preparation.
[4]Neuberger et al., *Dalton Trans*. 47, 11691-11695 (2018).

Computational Methods

- Density Functional Theory (DFT) and Density Functional Perturbation Theory (DFPT) with the modified Perdew-Burke-Ernzerhof generalized gradient approximation **(PBEsol GGA)**

  *PRB **79** 1551107 (2019)*

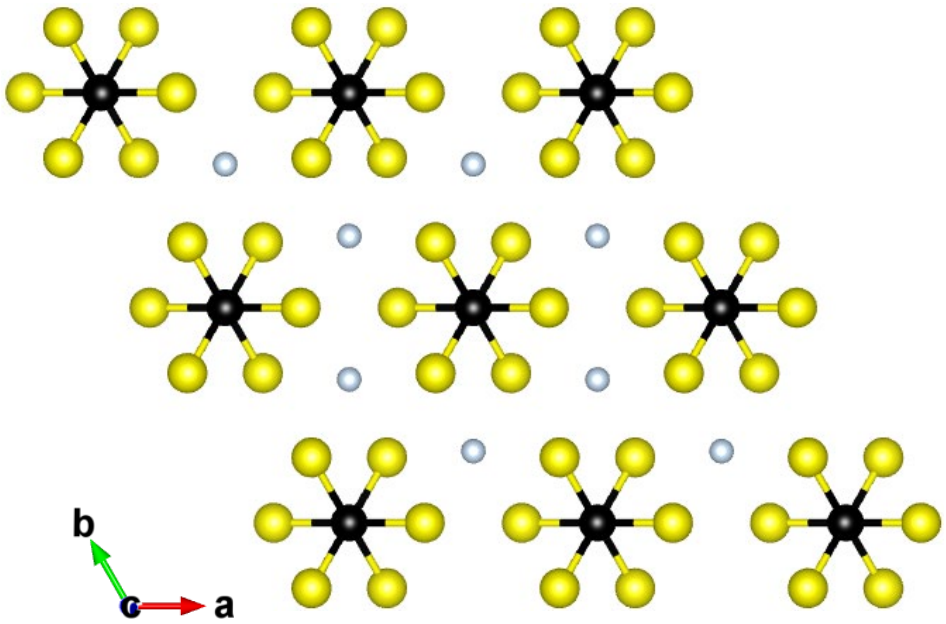
- The projector augmented wave (PAW) formalism using ABINIT (https://www.abinit.org) & Quantum ESPRESSO (http://www.quantum-espresso.org)
- Datasets generated by ATOMPAW code available at http://pwpaw.wfu.edu
- Visualization software: XCrySDen, VESTA
- Space-group analysis: FINDSYM
- X-ray powder diffraction: Mercury

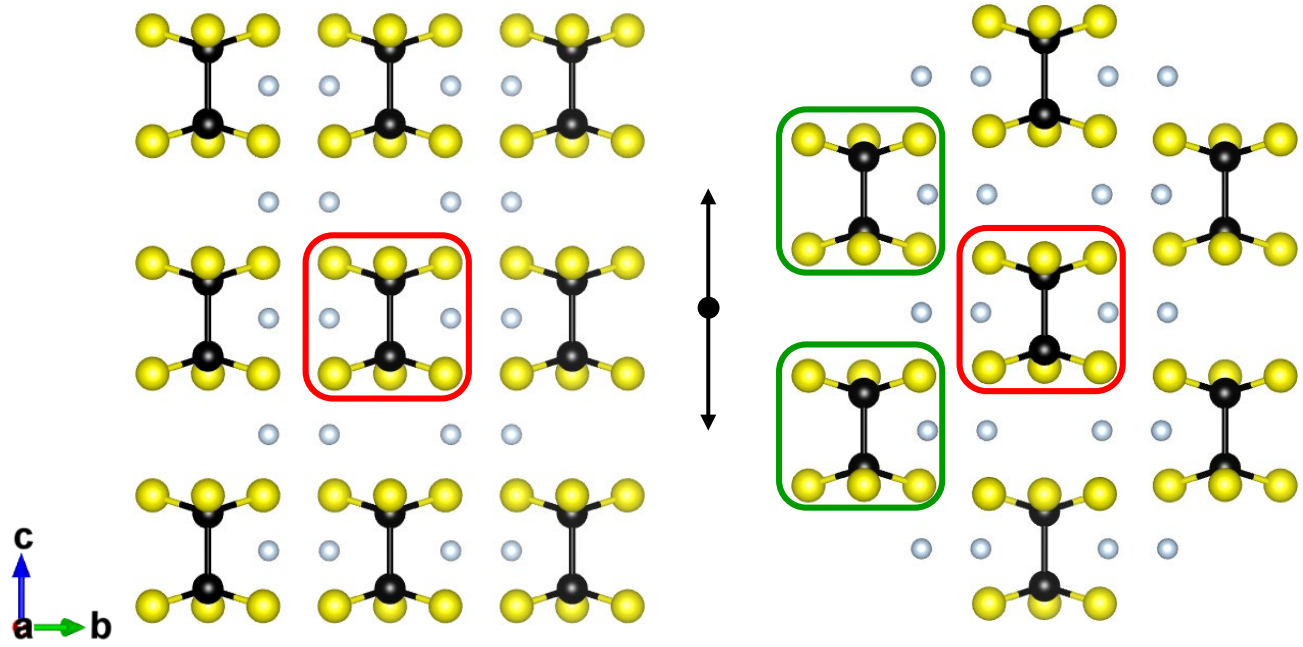
Previously reported results[1] obtained using (Local-density approximation) LDA

[1]Rush et al., *Solid State Phys*. 286, 45-50 (2016).

Structure Analysis

P S





Projection of the basic structure

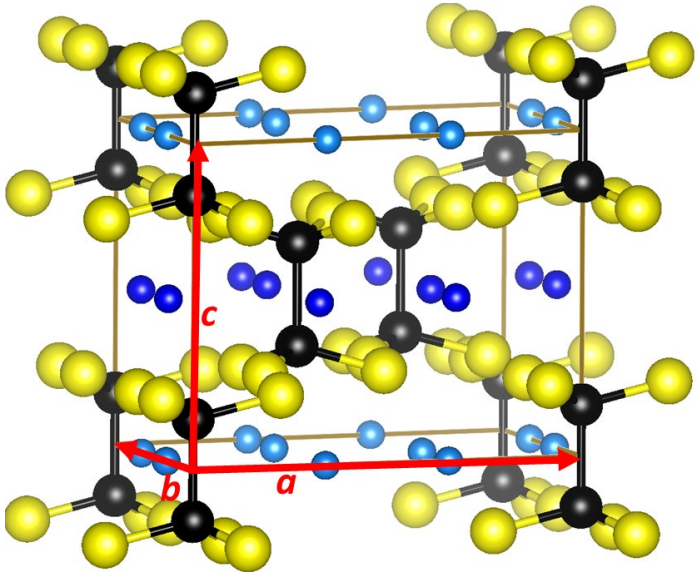
$$\mathbf{P}_{\uparrow} = \pm Z_P \vec{c}$$

$$\mathbf{P}_{\downarrow} = \pm \left(\frac{1}{2} - Z_P\right) \vec{c}$$

Hood et al., *J. Solid State Ionics* 284, 61 (2016).

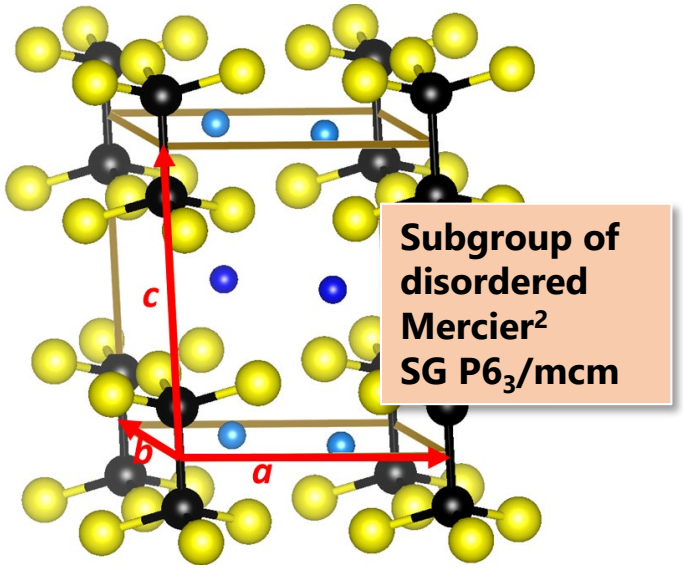
Model Structures Considered

Inequiv. Na(Li) P S



Hexagonal **P321** (#150)[1]
3 formula units / unit cell

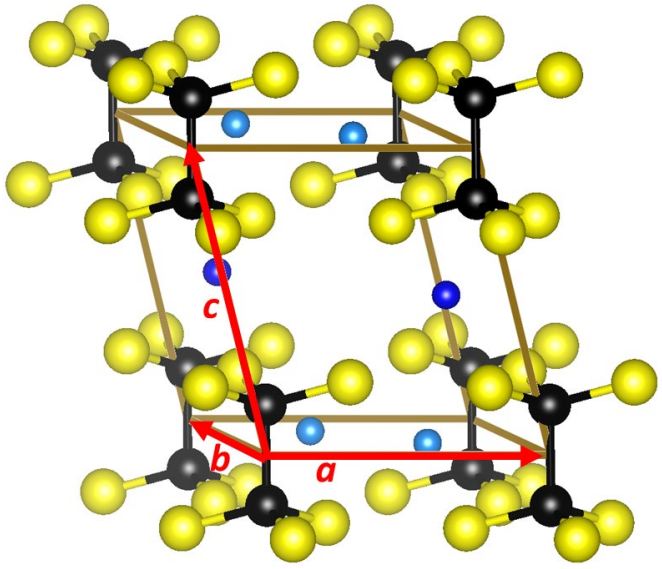
$\frac{1}{3}$ **P**$_{\uparrow}$ $\frac{2}{3}$ **P**$_{\downarrow}$



Subgroup of disordered Mercier[2] SG P6$_3$/mcm

Hexagonal **P$\bar{3}$1m** (#162)[3]
1 formula unit / primitive unit cell

100% P$_{\uparrow}$

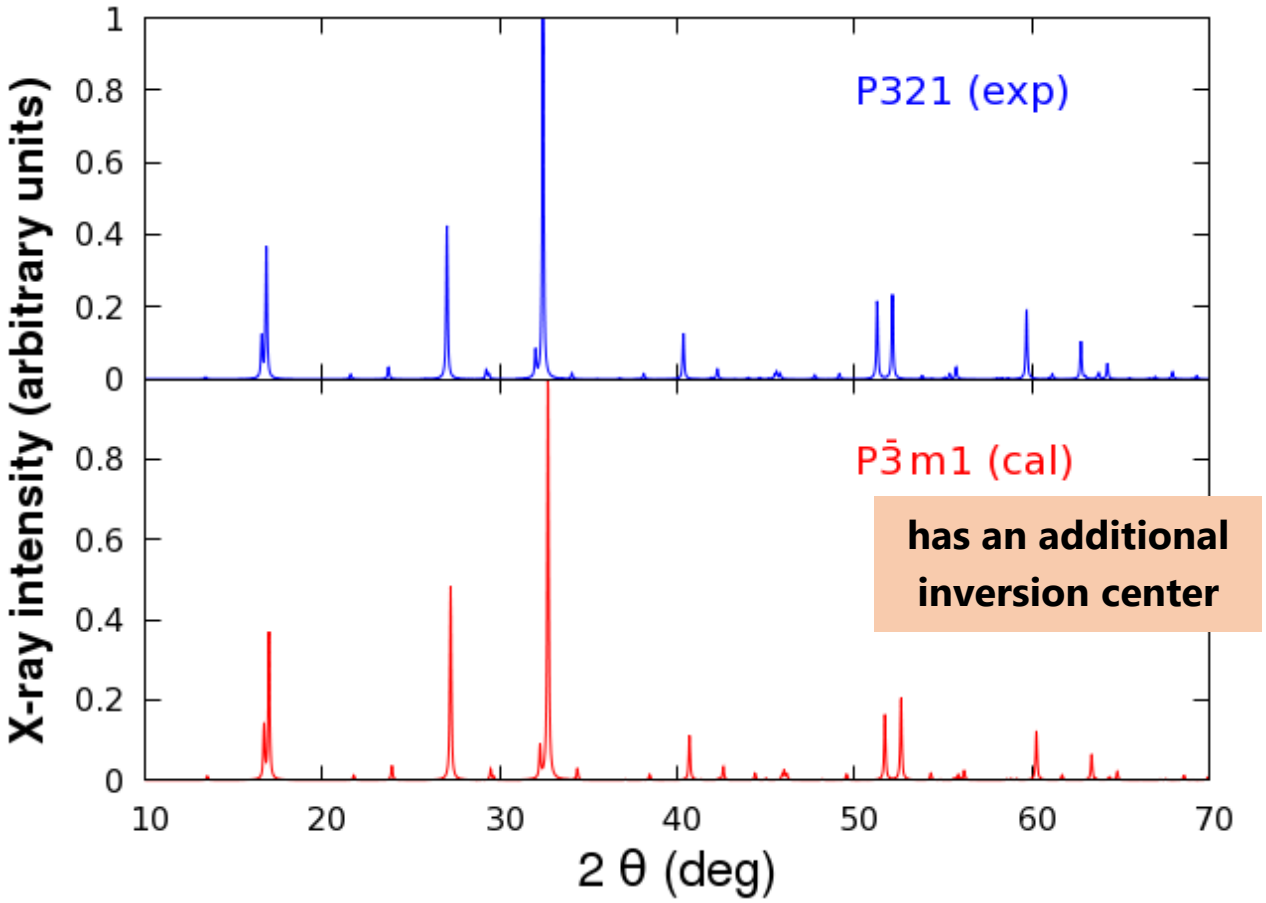


Monoclinic **C2/m** (#12)[4]
1 formula unit / primitive unit cell

100% P$_{\uparrow}$

[1]Neuberger et al., *Dalton Trans*. 47, 11691-11695 (2018).
[2]Mercier et al., J. *Solid State Chem*. 43, 151–162 (1982).
[3]Hood et al., *J. Solid State Ionics*, 284, 61 (2016).
[4]Kuhn et al., *Z. Anorg. Allg. Chem*. 640, 689-692 (2014).

More about the P321 Structure



has an additional inversion center

Comparing X-ray diffraction patterns at λ = 1.54056 Å

Comparison of the fractional coordinates of $Li_4P_2S_6$ and $Na_4P_2S_6$ based on the Neuberger structure[1].

$Li_4P_2S_6$		Calculated			Experiment			
Atom	Wyck	x	y	z	Wyck	x	y	z
Li	6 g	0.666	0.000	0.000	3 e	0.625/0.683	0.000	0.0000
Li	6 h	0.667	0.000	$\frac{1}{2}$	3 f	0.631/0.671	0.000	$\frac{1}{2}$
P	2 c	0.000	0.000	0.171	2 c	0.000	0.000	0.170
P	2 d	$\frac{1}{3}$	$\frac{2}{3}$	0.663	2 d	$\frac{1}{3}$	$\frac{2}{3}$	0.668
P	2 d	$\frac{1}{3}$	$\frac{2}{3}$	0.324	2 d	$\frac{1}{3}$	$\frac{2}{3}$	0.335
S	6 i	0.110	0.220	0.242	6 g	0.108	0.217	0.241
S	6 i	0.114	0.557	0.254	6 g	0.122	0.561	0.250
S	6 i	0.447	0.224	0.259	6 g	0.452	0.226	0.255

$Na_4P_2S_6$		Calculated		
Atom	Wyck	x	y	z
Na	6 g	0.659	0.000	0.000
Na	6 h	0.676	0.000	$\frac{1}{2}$
P	2 c	0.000	0.000	0.157
P	2 d	$\frac{1}{3}$	$\frac{2}{3}$	0.660
P	2 d	$\frac{1}{3}$	$\frac{2}{3}$	0.342
S	6 i	0.102	0.205	0.229
S	6 i	0.129	0.564	0.271
S	6 i	0.463	0.231	0.264

[1]Neuberger et al. *Dalton Trans*. 47, 11691-11695 (2018).

Static Lattice Results

Summary of static lattice results calculated with PBEsol GGA formalism. Lattice constants for the primitive unit cells are listed in units of Å and angles in degrees. The energies ΔE are listed as eV/(formula unit) referenced to the energy of the P$\bar{3}$m1 structure.

$Li_4P_2S_6$	*a*	*b*	*c*	*α*	*β*	*γ*	*ΔE*
P$\bar{3}$1m (#162)	6.03	6.03	6.48	90.0	90.0	120.0	0.04
C2/m (#12)	6.08	6.08	6.89	97.9	97.9	119.1	0.31
P$\bar{3}$m1 (#164)[a]	10.42	10.42	6.54	90.0	90.0	120.0	0.00
$Na_4P_2S_6$	*a*	*b*	*c*	*α*	*β*	*γ*	*ΔE*
P$\bar{3}$1m (#162)	6.45	6.45	7.13	90.0	90.0	120.0	0.09
C2/m (#12)[b]	6.51	6.51	7.52	98.5	98.5	117.6	0.00
P$\bar{3}$m1 (#164)	11.10	11.10	7.25	90.0	90.0	120.0	0.00

LDA results suggest that C2/m structure is meta-stable

static and vibrational

[a] Corresponding experimental values quoted from Neuberger et al., *Dalton Trans.* 47, 11691-11695 (2018) are $a = b = 10.51$ Å, $c = 6.59$ Å

[b] Corresponding experimental values deduced from Kuhn et al., *Z. Anorg. Allg. Chem.* 640, 689-692 (2014) are $a = b = 6.54$ Å, c = 7.54 Å, $\alpha = \beta = 98.7$ deg, $\gamma = 118.1$ deg.

Phonon Spectrum of $Na_4P_2S_6$ in the C2/m Structure

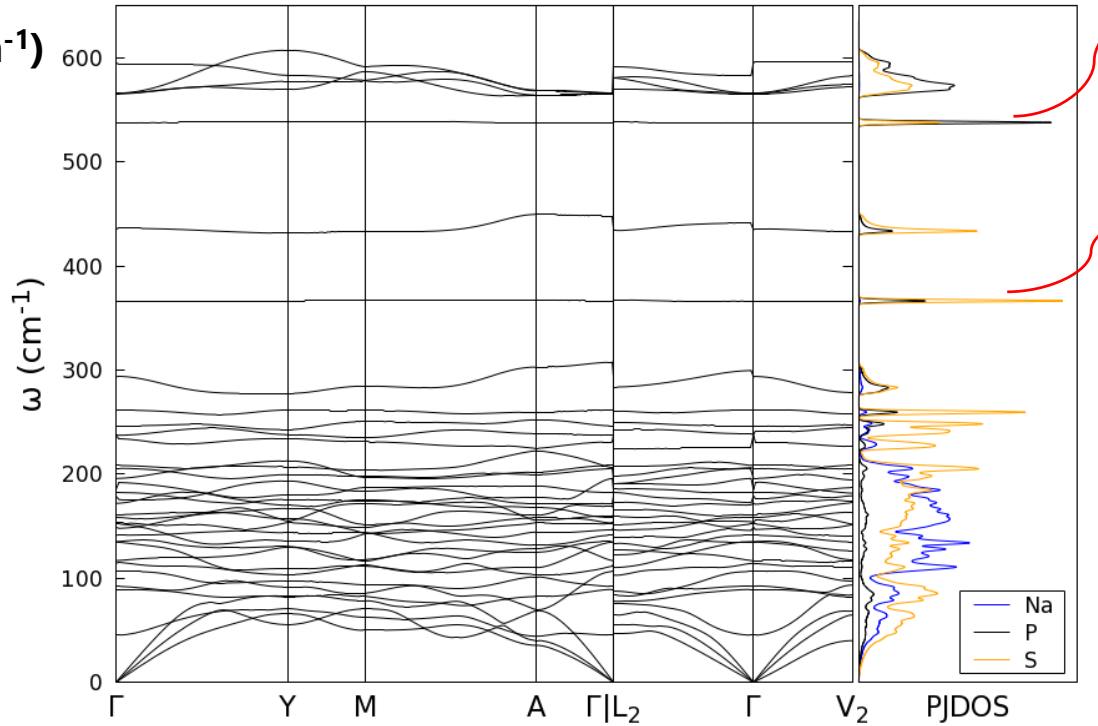
Inequiv. Na P S

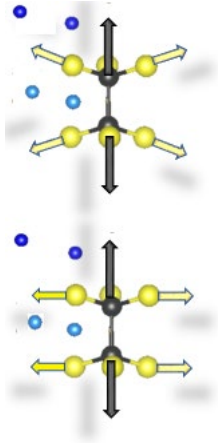
Density Functional Perturbation Theory (DFPT)[1]: $\left(H_{SCF}-\varepsilon_n\right)|\Delta\psi_n\rangle=-\left(\Delta V_{SCF}-\Delta\varepsilon_n\right)|\psi_n\rangle$

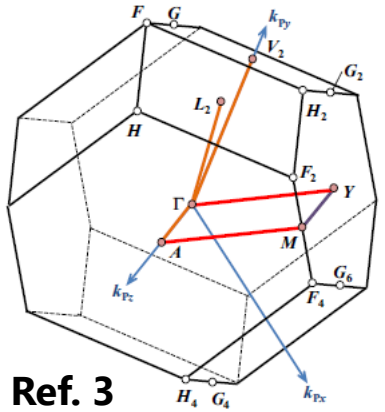
$$\sum_{t,\beta}\left(\tilde{D}_{st}^{\alpha\beta}\left(\vec{q}\right)-\omega^2\left(\vec{q}\right)\delta_{st}\delta_{\alpha\beta}\right)u_t^{\beta}\left(\vec{q}\right)=0 \quad \Rightarrow \quad \text{Eigenvalues and Eigenvectors } (\omega(q),\ \{u_i\})$$

Comparisons of main Raman active modes (cm^{-1})

Cal.	Exp.[2]
149	152
196	203
261	273
366	383
537	560
565	577







Ref. 3

mC (*b*>*a*sinβ elongated dodecahedron):
Γ–*Y*–*M*–*A*–Γ | L_2–Γ–V_2

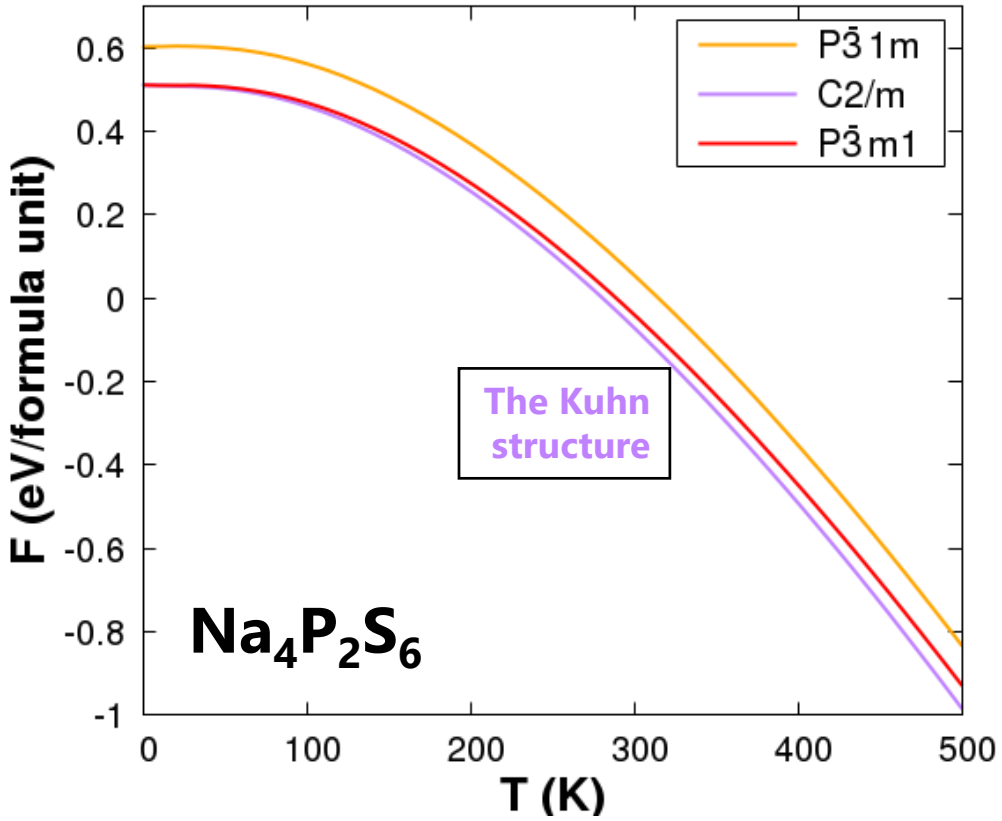
12 atoms/cell × 3 dimensions
⇒ 36 phonons (vibrational modes)

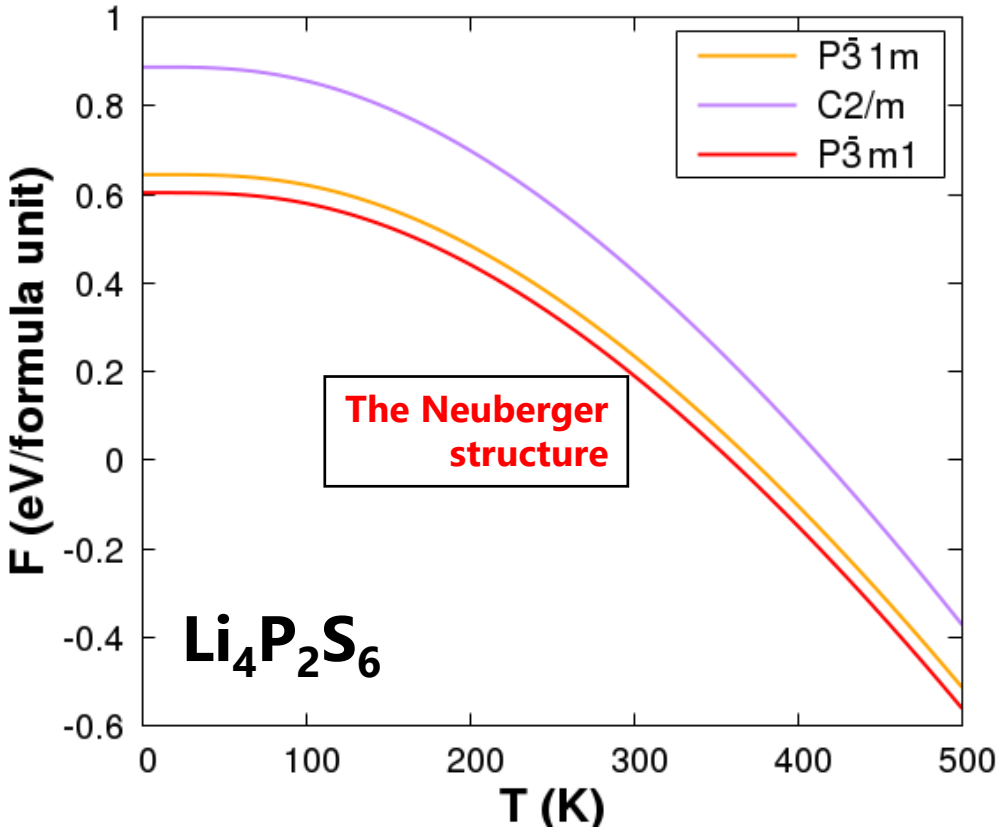
[1]Baroni et al., *Rev. Mod. Phys*. 73, 515-562 (2001).
[2]Hood et al., Manuscript in preparation.
[3]Hinuma et al., *Comp. Mat. Sci.* 128, 140-184 (2017).

Stability Analysis

Helmholtz free energy: $\mathbf{F = U_{SL} + F_{vib}}$

Where U_{sL} is the static lattice internal energy and F_{vib} is the phonon free energy in harmonic approximation





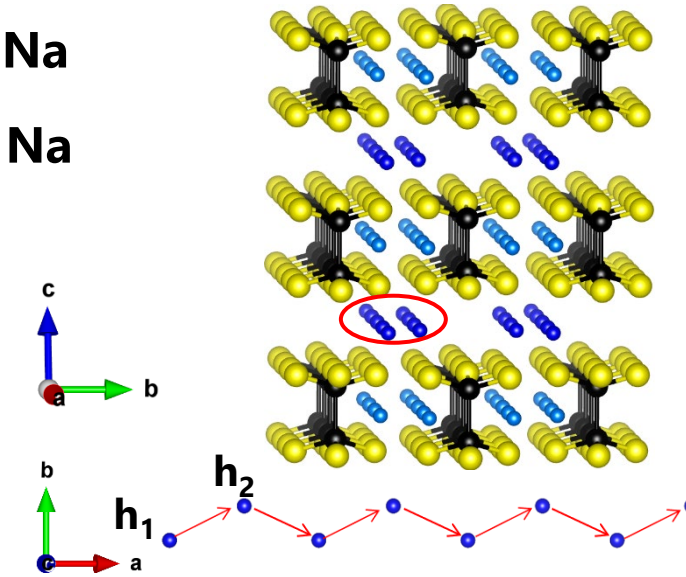
Ion Migration of $Na_4P_2S_6$ in the C2/m Structure

***g* site Na**

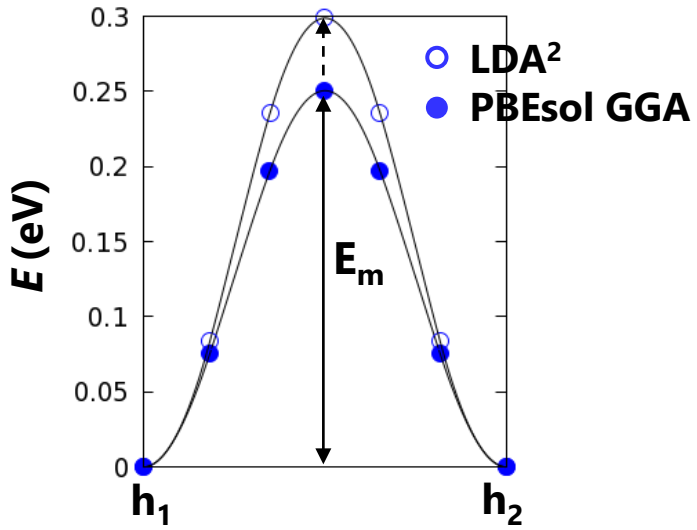
***h* site Na**

P

S



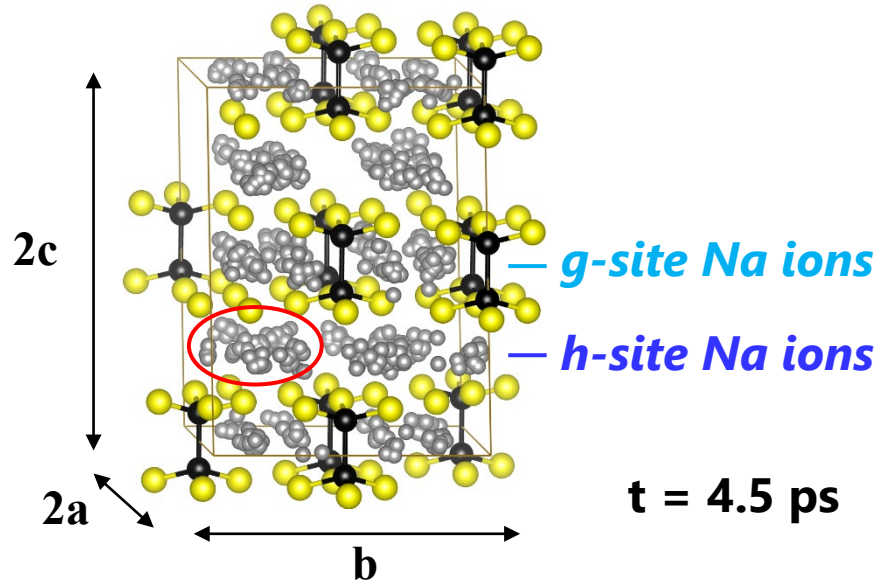
Nudged Elastic Band Method[1]



$$E_A^{NEB} = E_m + \frac{1}{2}E_f\,, \quad \sigma(T) = \frac{\mathrm{K}}{\mathrm{T}}\, e^{-E_A/k_BT}$$

Comparing activation energies E_A (eV) for Na ion conductivity

PBEsol GGA	LDA[2]	Exp[3]
0.34	0.42	0.39



Ab-initio Molecular Dynamics with T = 1000 K

[1]Henkleman et al., *J. Chem. Phys.* 113, 9901-9904 (2000).
[2]Rush et al., *Solid State Phys.* 286, 45-50 (2016).
[3]Hood et al., Manuscript in preparation.

Summary

- According to PBEsol GGA results, $Na_4P_2S_6$ is to be stabilized in the C2/m structure and $Li_4P_2S_6$ is to be stabilized in the $P\bar{3}m1$ structure
- PBEsol GGA and LDA results of activation energy for Na ion migration reasonably agree with the experimental measurements which suggest a viable solid electrolyte
- MD simulations are expected to provide more information on understanding the conductivity mechanisms
- Calculations will be performed to investigate the stability of $Na_4P_2S_6$/Na interface

Acknowledgements

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- Thank my advisor Prof. Natalie A. W. Holzwarth and our experimental collaborator Dr. Zachary D. Hood