Computational (re)investigation of the structural and electrolyte properties of $Li_4P_2S_6$, $Na_4P_2S_6$, and $Li_2Na_2P_2S_6$

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Outline

- Motivations
- Computational methods
- Structures and stabilities of $Na_4P_2S_6$ and $Li_4P_2S_6$
- Structures and stabilities of predicted $Li_2Na_2P_2S_6$
- Comparison of electrolyte properties
- Summary and conclusions

Motivations

- 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**

- 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)**
- Theoretically, $Na_4P_2S_6$ and $Li_4P_2S_6$ are chemically and structurally related

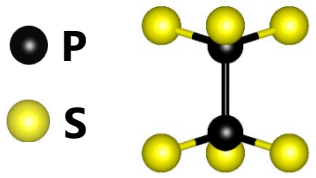
→ **Property similarities (discrepancies) between $Na_4P_2S_6$ and $Li_4P_2S_6$**

- Structure and stability of the mixed ion material $Li_2Na_2P_2S_6$

→ **Material prediction**

- Performance of $Li_2Na_2P_2S_6$ in comparison with $Na_4P_2S_6$ as solid electrolytes

→ **Conductivity studies**



$(P_2S_6)^{4-}$ 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)

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Summary of Computational methods

- Density Functional Theory (DFT) and Density Functional Perturbation Theory (DFPT) with the modified Perdew-Burke-Ernzerhof generalized gradient approximation[1] **(PBEsol GGA)**

  **Previously reported results[2] obtained using Local-density approximation (LDA)*

- 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

[1]Perdew et al., *Phys. Rev. L.* **100**, 136406 (2008)
[2]Rush et al., *Solid State Phys*. **286**, 45-50 (2016)

Outputs of DFT and DFPT

Born-Oppenheimer approximation

DFT

At equilibrium: $\mathbf{F}_I = -\frac{\partial U(\{\mathbf{R}_I\})}{\partial \mathbf{R}_I} = 0$

- Optimized structural parameters
- Static lattice energy: $U_{\mathrm{SL}} = \min U(\{\mathrm{R_I}\})$
- Kohn-Sham orbitals and energies
- Migration related energies

DFPT

Near equilibrium: $M_s(\omega^\nu)^2 u^\nu_{s\alpha}(\mathbf{q}) = \sum_{t\beta} \tilde{C}^{\alpha\beta}_{st}(\mathbf{q}) u^\nu_{t\beta}(\mathbf{q})$ and $\tilde{C}^{\alpha\beta}_{st}(\mathbf{q}) \rightleftharpoons C^{\alpha\beta}_{st}(\mathbf{R})$

- Phonon frequencies and eigenvectors at any wavevector
- Phonon dispersions: $\omega^\nu \sim \mathbf{q}$
- Phonon density of states (PDOS): $g(\omega) = \frac{V}{(2\pi)^3} \int d^3q \sum_{\nu=1}^{3N} \delta(\omega - \omega^\nu(\mathbf{q}))$
- Thermodynamic properties such as the vibrational energy: $F_{vib}(T) = k_B T \int_0^\infty d\omega \ln\left(2\sinh\left(\frac{\hbar\omega}{2k_BT}\right)\right) g(\omega)$

The Helmholtz free energy:

$$F(T) = F_{SL}(T) + F_{vib}(T) \approx U_{SL} + F_{vib}(T)$$

Stable and metastable structures

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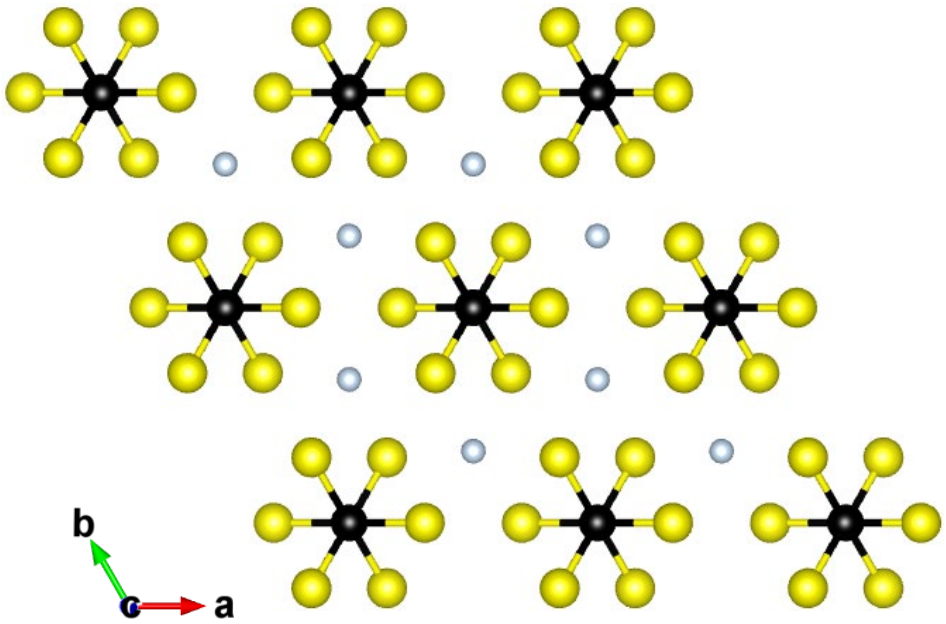
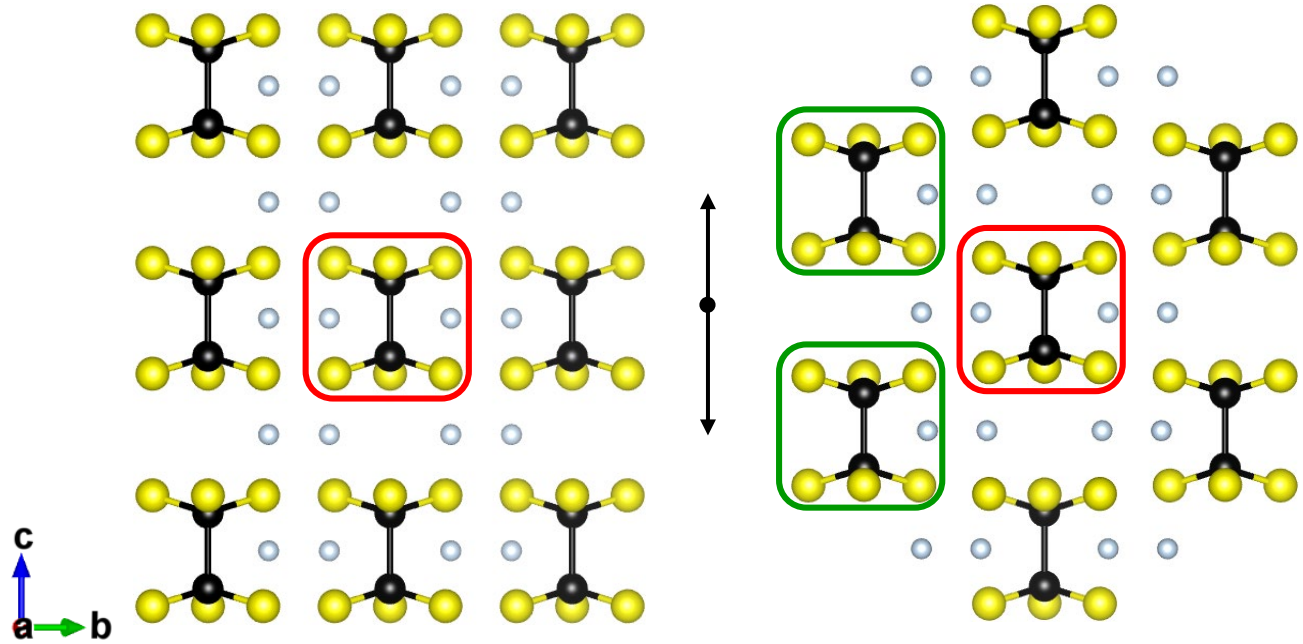
Structure analysis

P S





Projection of the basic structure

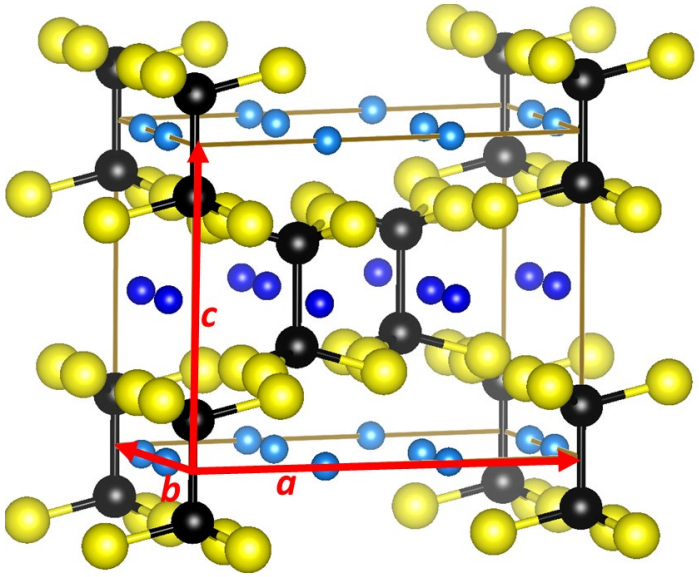
$$\mathbf{P}_{\uparrow} = \pm Z_P \vec{c}$$

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

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

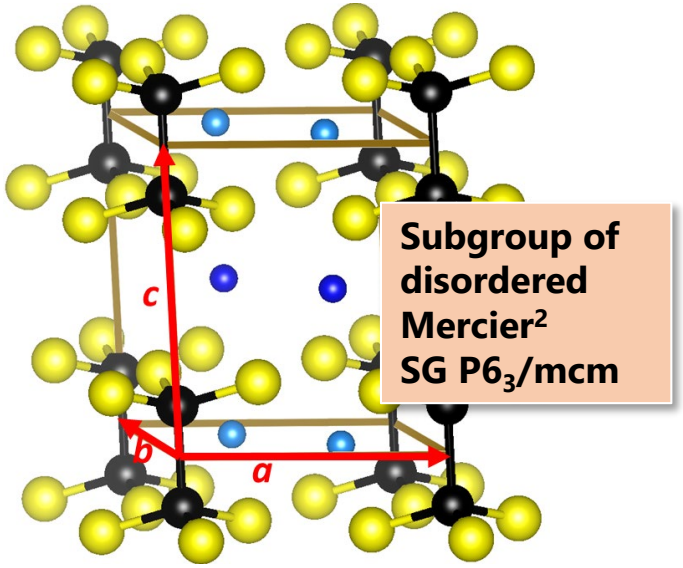
Model structures considered

Inequiv. Na(Li) P S



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

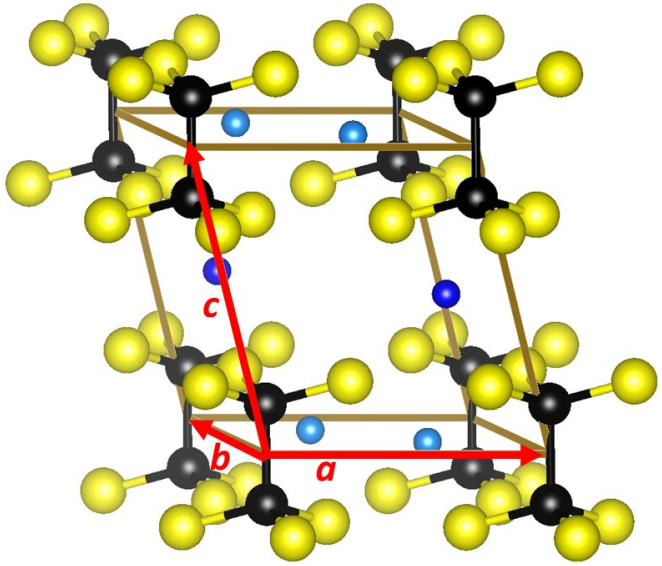
$\frac{1}{3}$ **P**$_{\uparrow}$ $\frac{2}{3}$ **P**$_{\downarrow}$



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

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

100% P$_{\uparrow}$

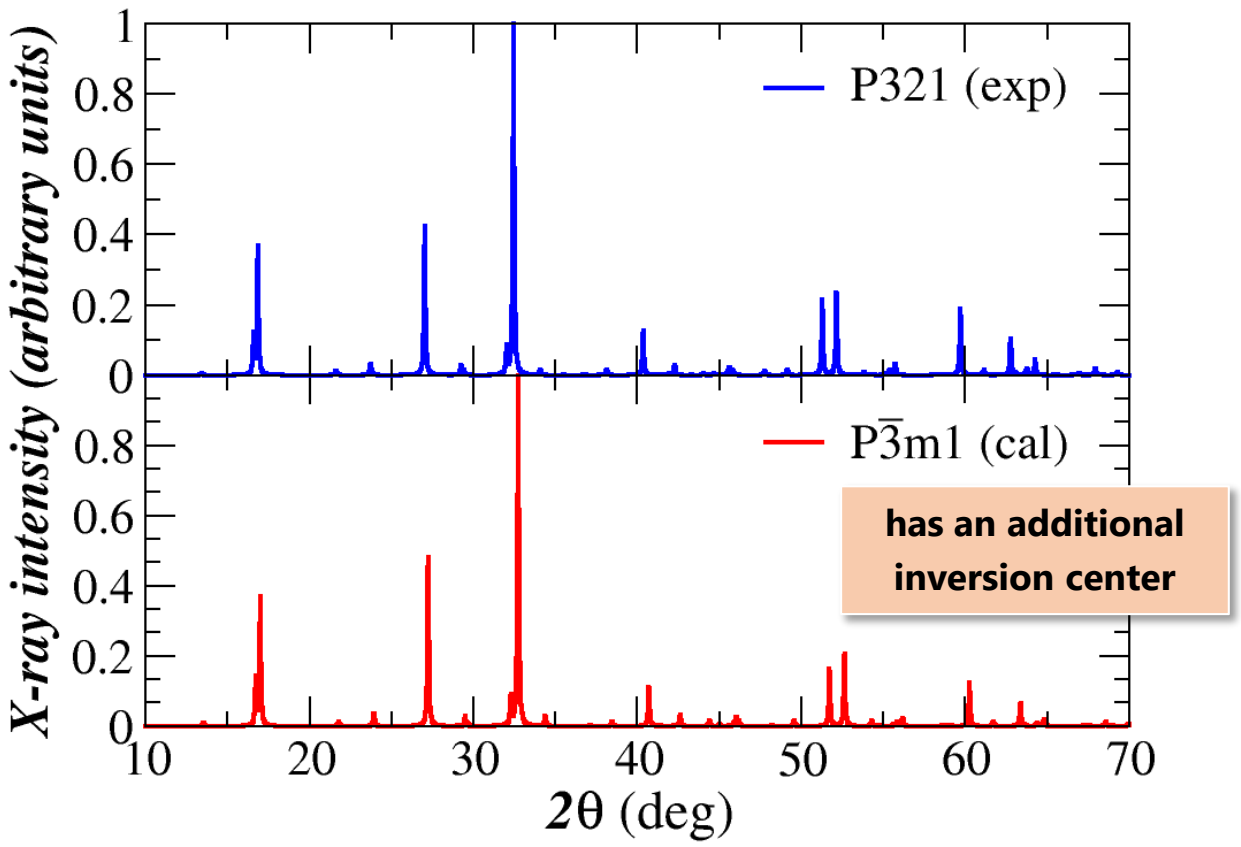


Monoclinic **C2/m** (#12)[4]
1 formula unit / primitive unit cell

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



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

TABLE: 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 static lattice energy differences ΔU_{SL} 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*	ΔU_{SL}
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*	ΔU_{SL}
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

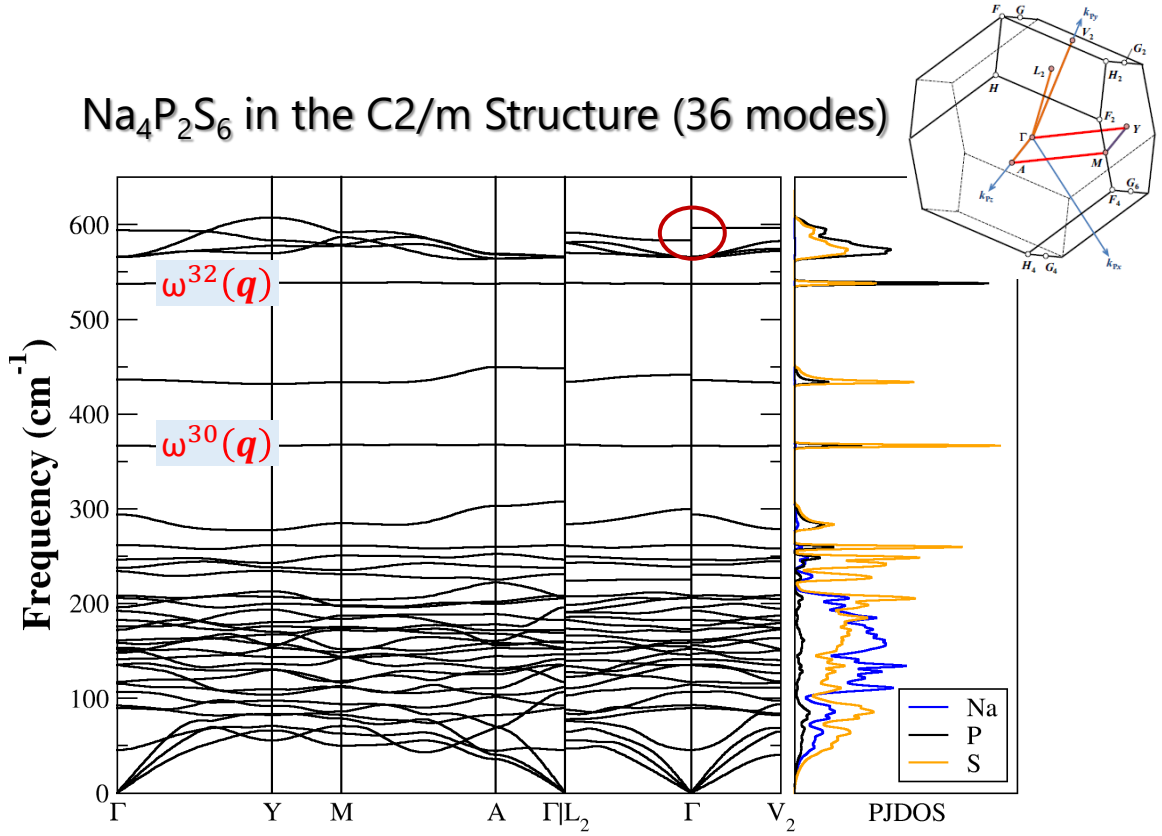
static and vibrational

[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

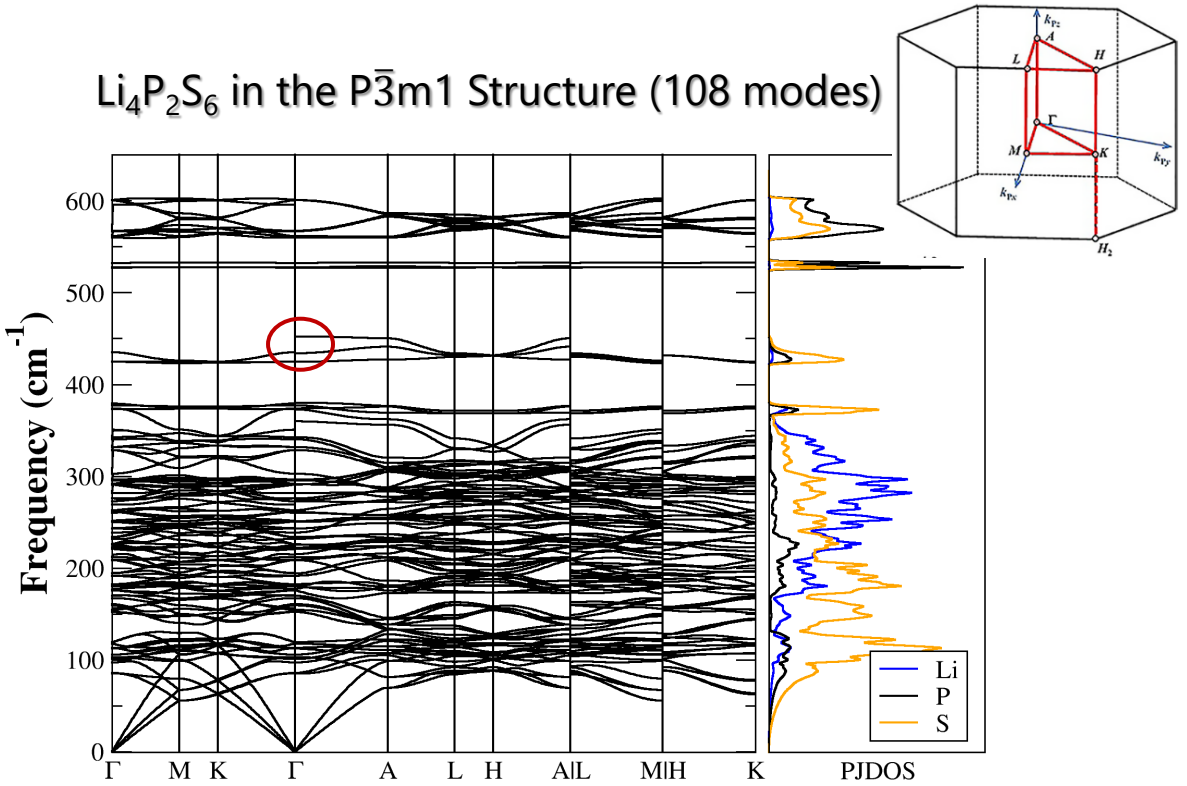
$Na_4P_2S_6$ in the C2/m Structure (36 modes)



Na^+ 0~300 cm^{-1}

$(P_2S_6)^{4-}$ 300~600 cm^{-1}

$Li_4P_2S_6$ in the P$\bar{3}$m1 Structure (108 modes)



Li^+ 0~370 cm^{-1}

$(P_2S_6)^{4-}$ 370~600 cm^{-1}

PJDOS: $g^a(\omega) \equiv \frac{V}{(2\pi)^3} \int d^3q \sum_{\nu=1}^{3N} (\delta(\omega - \omega_\nu(\mathbf{q}))W_a^\nu(\mathbf{q}))$

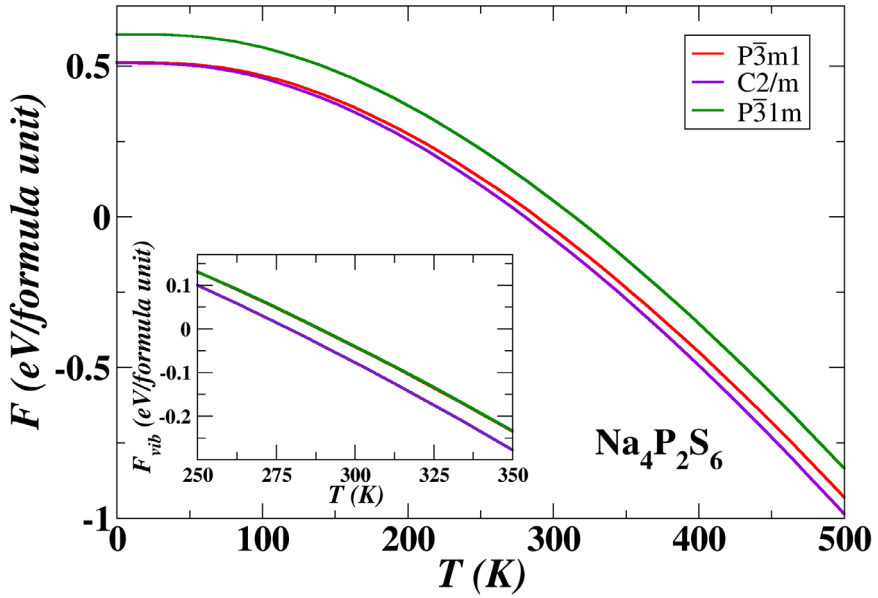
Discontinuous branches at Γ: coupling between photon and photon[2]

[1]Suggested path: Hinuma et al., *Comp. Mat. Sci.* **128**, 140-184 (2017)

[2]Li et al., *J. Phys. Condens. Matter, accepted*

Stability analysis

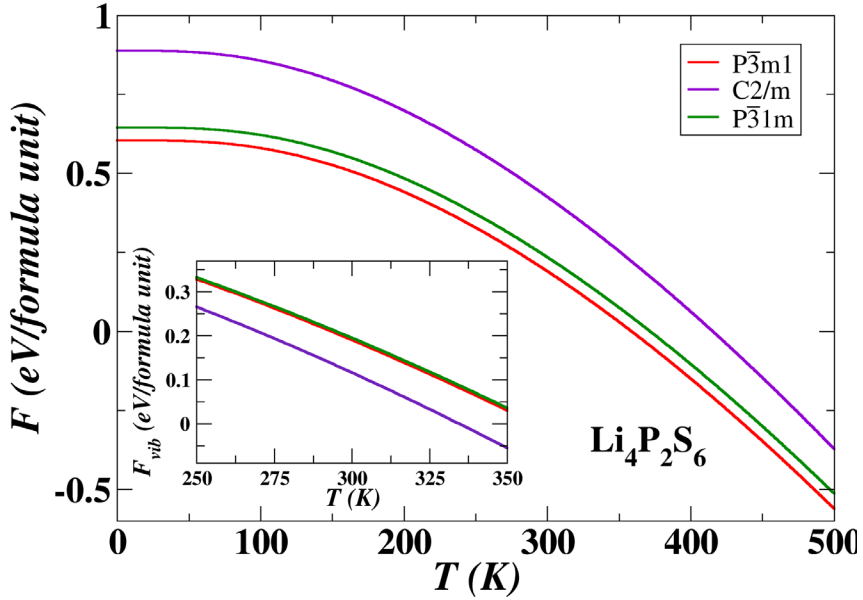
Helmholtz free energy: $F = U_{SL} + F_{vib}$



U_{SL}: P$\bar{3}$m1 = C2/m < P$\bar{3}$1m

F_{vib}: C2/m < P$\bar{3}$m1 = P$\bar{3}$1m

➡ **F_{lowest}: C2/m (expt.[1,2])**



U_{SL}: P$\bar{3}$m1 < P$\bar{3}$1m < C2/m

F_{vib}: C2/m < P$\bar{3}$m1 = P$\bar{3}$1m

➡ **F_{lowest}: P$\bar{3}$m1 (expt.[3])**

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

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Structures of the predicted material: $Li_2Na_2P_2S_6$

Replace the (a) *g*-type or (b) *h*-type Na ions in the monoclinic $Na_4P_2S_6$ with Li ions

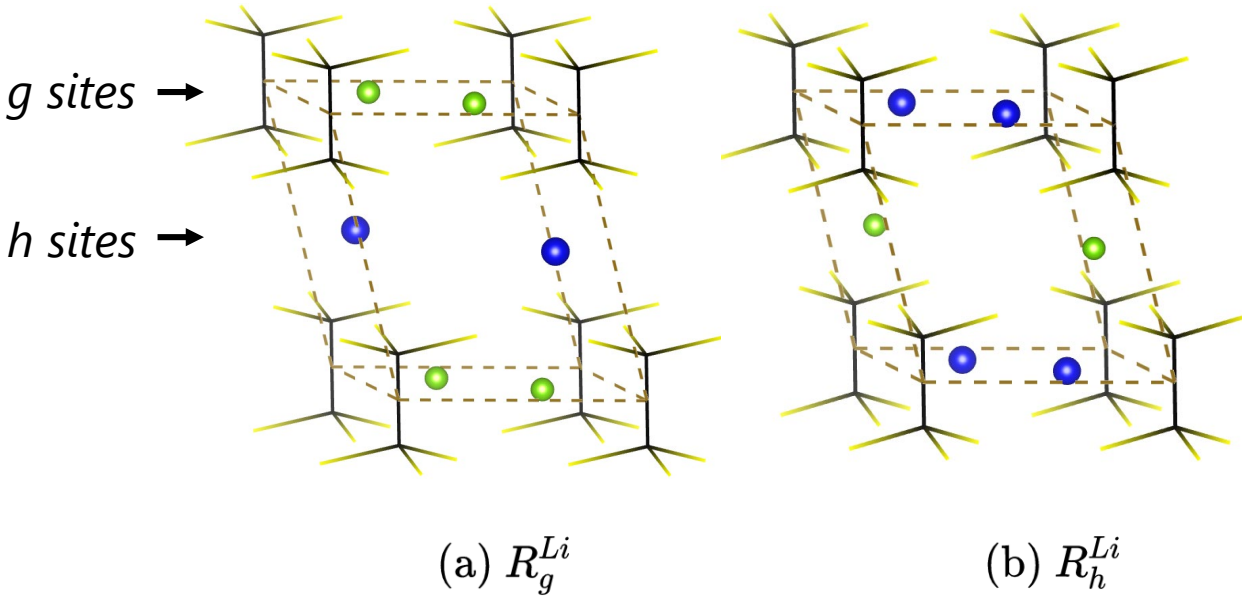


TABLE: Comparison of the optimized lattice parameters for $Li_2Na_2P_2S_6$ in the R_g^{Li} and R_h^{Li} structures. Also listed is the static lattice energy differences U_{SL} referenced to the energy of the R_h^{Li} structure in units of eV/formula unit.

		R_g^{Li}	R_h^{Li}
Primitive cell:	$a = b$ (Å)	6.18	6.46
	c (Å)	7.50	7.01
	$\alpha = \beta$ (deg)	97.77	97.88
	γ (deg)	119.21	118.43
Conventional cell:	a_c (Å)	6.26	6.61
	b_c (Å)	10.67	11.10
	c_c (Å)	7.50	7.01
	β_c (deg)	105.50	105.54
	ΔU_{SL} (eV/FU)	-0.16	0.00

Stability of the predicted material: $Li_2Na_2P_2S_6$

The possible reaction pathway:

$$Na_4P_2S_6 + 2Li \rightarrow Li_2Na_2P_2S_6 + 2Na$$

$$\Delta F(T) = \Delta U_{SL} + \Delta F_{vib}(T) + \Delta F_{\text{elec}}^{\text{metal}}(T)$$

trivial contribution (10^{-3} eV)

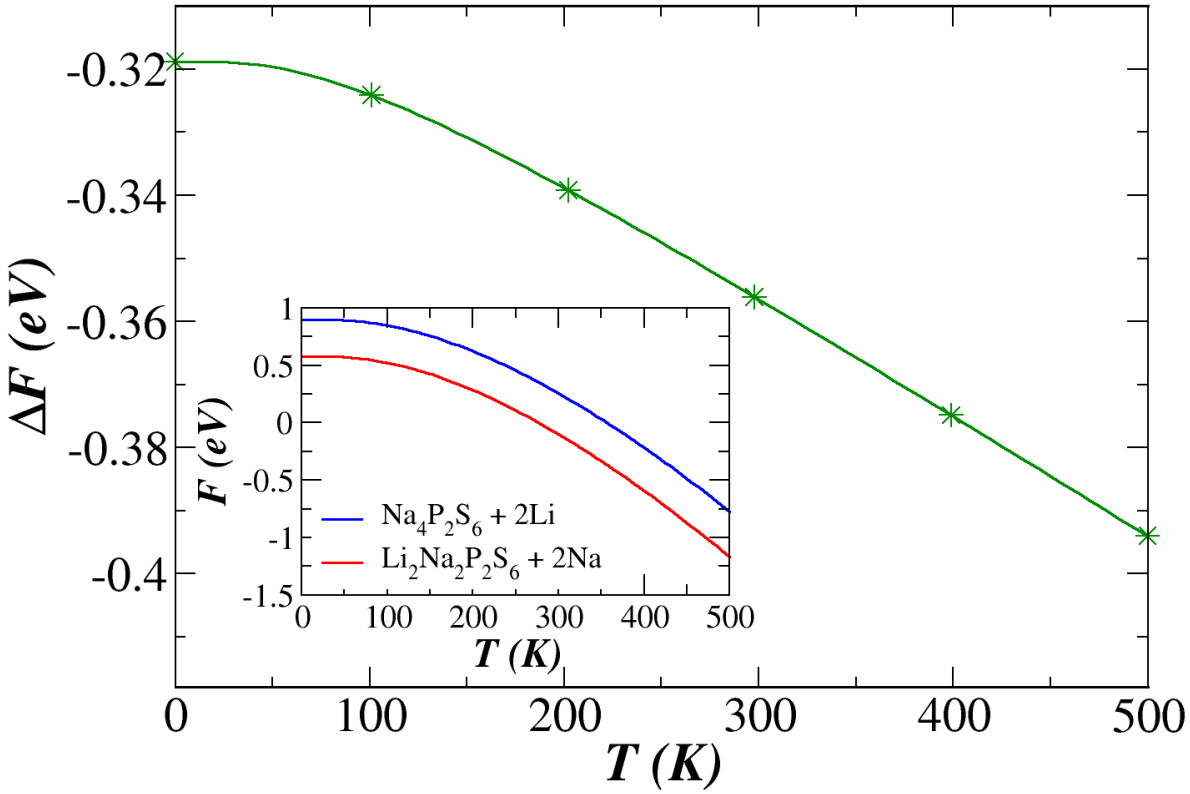
$$\Delta = \Delta^{Products} - \Delta^{Reactants}$$

Energy changes at T = 300 K in eV:

$$\Delta U_{SL} = -0.29$$

$$\Delta F_{vib} = -0.06$$

$$\Rightarrow \quad \Delta F = -0.35$$



Negative energies (net released energies) imply that the structure of $Li_2Na_2P_2S_6$ is stable with respect to the possible exothermic process.

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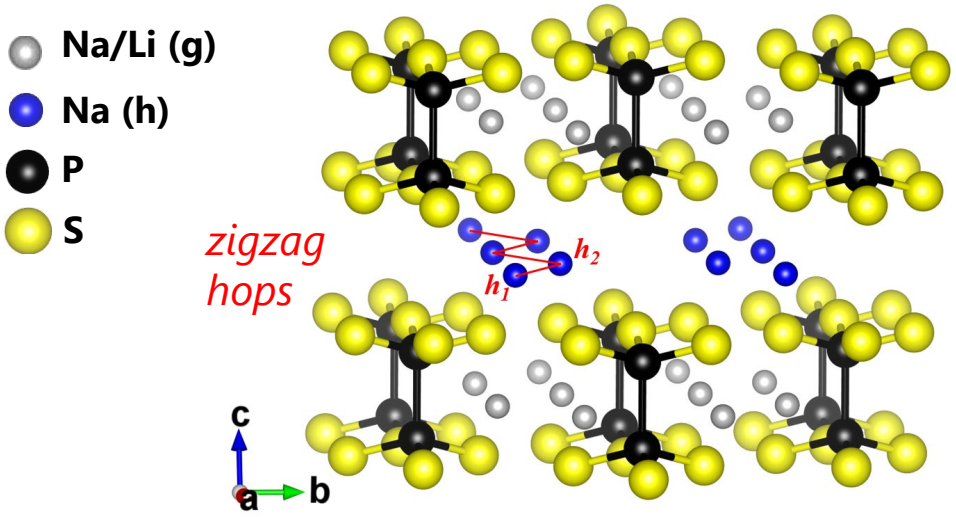
Ion migration of vacancy mechanisms



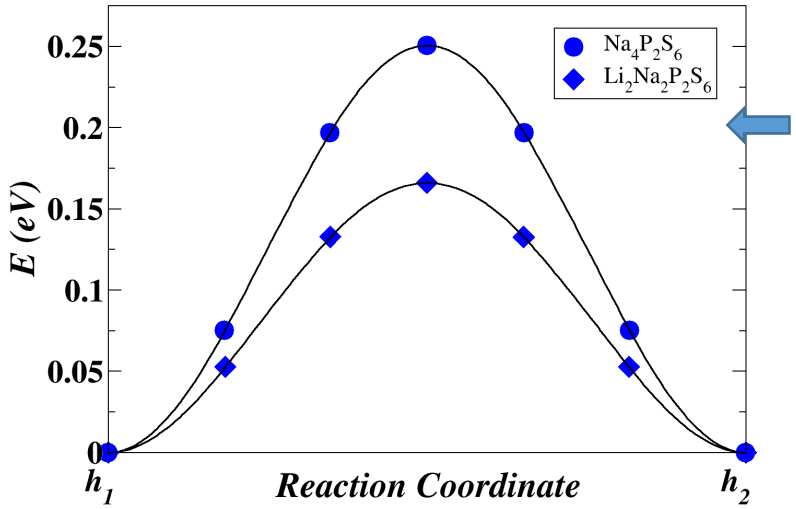


Diagram of energy path for Na ion vacancy diffusions, estimated using "Nudged Elastic Band" (NEB) algorithm[1]

E_m^{NEB}

Activation energy:

$$E_a^{cal} = E_m^{NEB} + \frac{1}{2}E_f$$

Conductivity:

$$\sigma \cdot \mathrm{T} = K\, e^{-E_a^{exp}/k_B T}$$

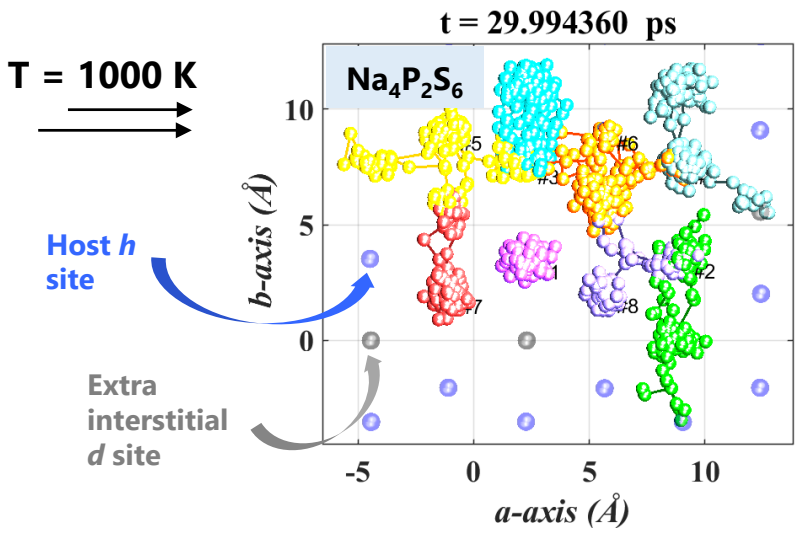
Summary of vacancy diffusion results

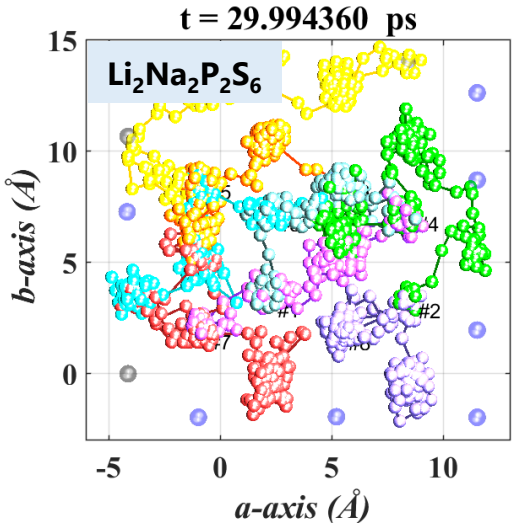
Material	Functional	Step	Distance	E_m^{cal}	E_f^{cal}	E_a^{cal}	E_a^{exp}
$Na_4P_2S_6$	PBEsol GGA	$h_1 \rightarrow h_2$	3.67	0.25	0.18	0.34	0.39[3]
	LDA	$h_1 \rightarrow h_2$	3.59	0.30	0.24	0.42[2]	
$Li_2Na_2P_2S_6$	PBEsol GGA	$h_1 \rightarrow h_2$	3.44	0.16	0.13	0.23	--

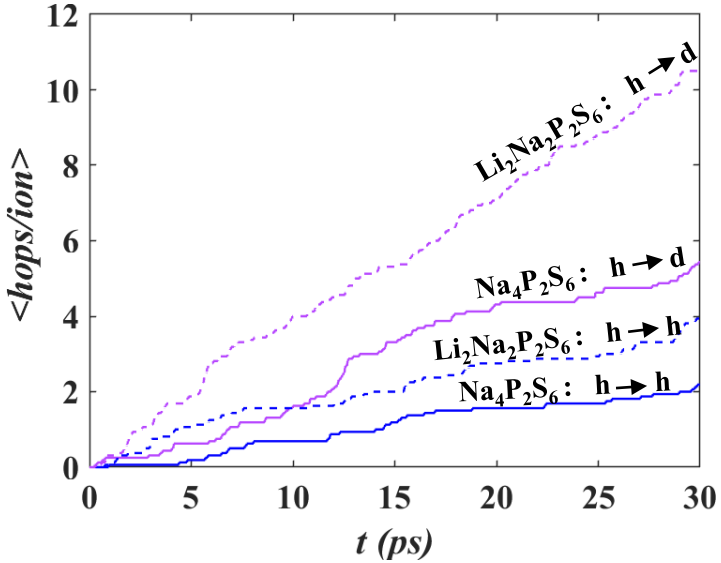
The distance in units of Å, and all energies are given in eV units

[1]Henkelman 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.

Migration study using molecular dynamics simulations

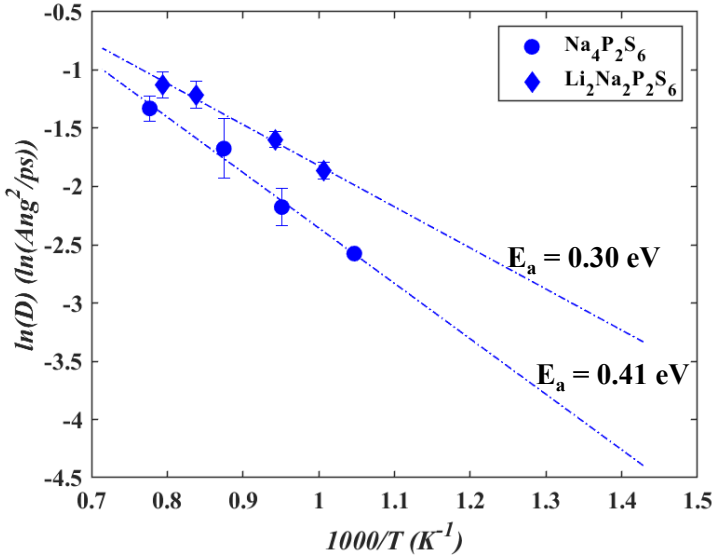






- No g → h and g → g hopping
- All migrations occur within layer of h sites
- Direct h → h vacancy migration is consistent with NEB analysis
- Indirect h → d → h vacancy migration is prevalent
- No interstitial d → d migration
- Calculate E_a from $D(\mathrm{T}) = D_0\, e^{-E_a/k_B T}$

$$\text{where } D = \frac{1}{6}\lim_{t\to\infty}\left(\frac{1}{t}\,MSD(t)\right)$$



**AIMD simulations were carried out using supercells composed of 2x1x2 conventional units (96 atoms)*

*** E_a was obtained from runs of 50-70 ps*

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Summary and conclusions

- 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
- The predicted crystal $Li_2Na_2P_2S_6$ has a stable structure. Compared to $Na_4P_2S_6$, the mixed alkali electrolyte can substantially enhances Na ion conductivity
- Both NEB and MD simulations reveal that the Na ion diffusions in both $Na_4P_2S_6$ and $Li_2Na_2P_2S_6$ are via vacancy mechanisms, and MD simulations provide more information on understanding the conductivity mechanisms