

Computational investigation of the structural and electrolyte properties of $\text{Li}_4\text{P}_2\text{S}_6$, $\text{Na}_4\text{P}_2\text{S}_6$, and $\text{Li}_2\text{Na}_2\text{P}_2\text{S}_6$

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WFU effort supported by NSF Grant DMR-1507942.

Contributions from previous students including Larry Rush and Cameron Kates are also gratefully acknowledged.

Zach, Natalie, and Yan posing at 256th Meeting of the Electrochemical Society in Atlanta, GA Oct. 12-17, 2019

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Outline

- **Motivation**
- **Experimental story**
- **Computational story**
- **Outlook**

- **Motivation**
 - **Research on battery materials**
 - **The case for all solid state batteries**
 - **Challenges for realistic (idealistic??) computer modeling**

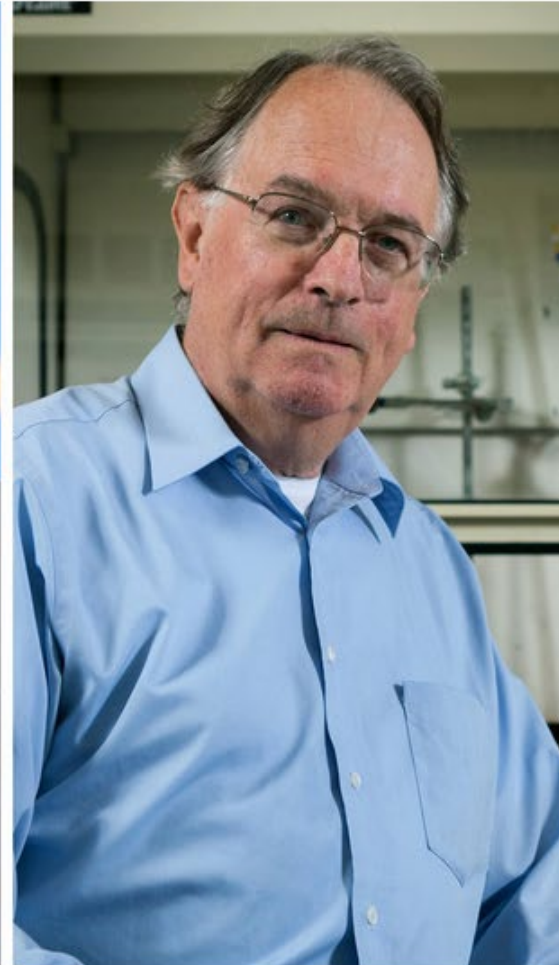
➤ **Motivation**

➤ **Research on battery materials**

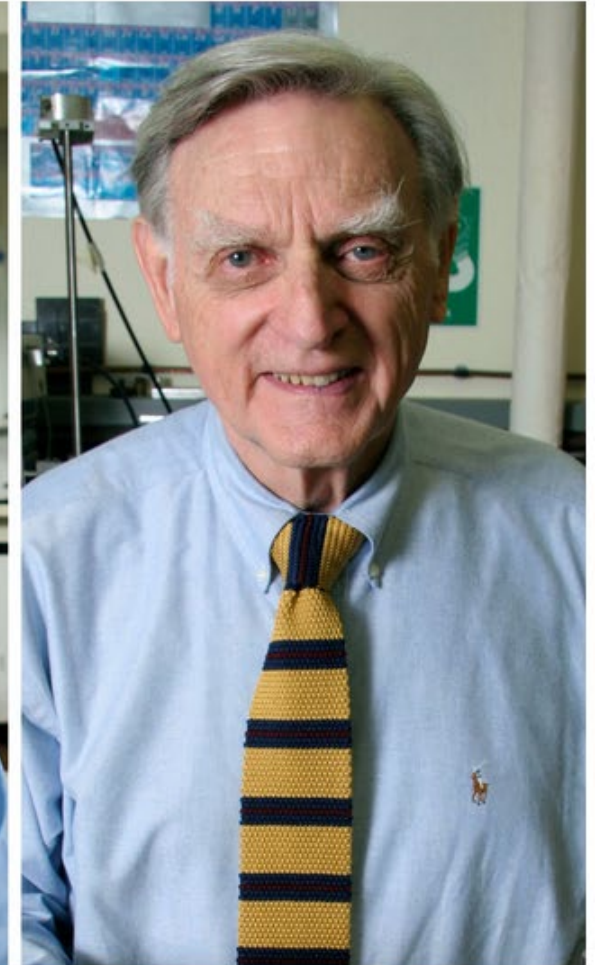
**2019 Nobel Prize
in Chemistry – for
development of
the Li ion battery**



Akira Yoshino



M. Stanley Whittingham



John B. Goodenough

From NY Times

11/6/2019

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➤ Motivation

➤ Research on battery materials

2019 Nobel Prize in Chemistry – for development of the Li ion battery

“Lithium-ion batteries have revolutionized our lives and are used in everything from mobile phones to laptops and electric vehicles,” the Nobel Committee said. “Through their work, this year's Chemistry Laureates have laid the foundation of a wireless, fossil fuel-free society.”

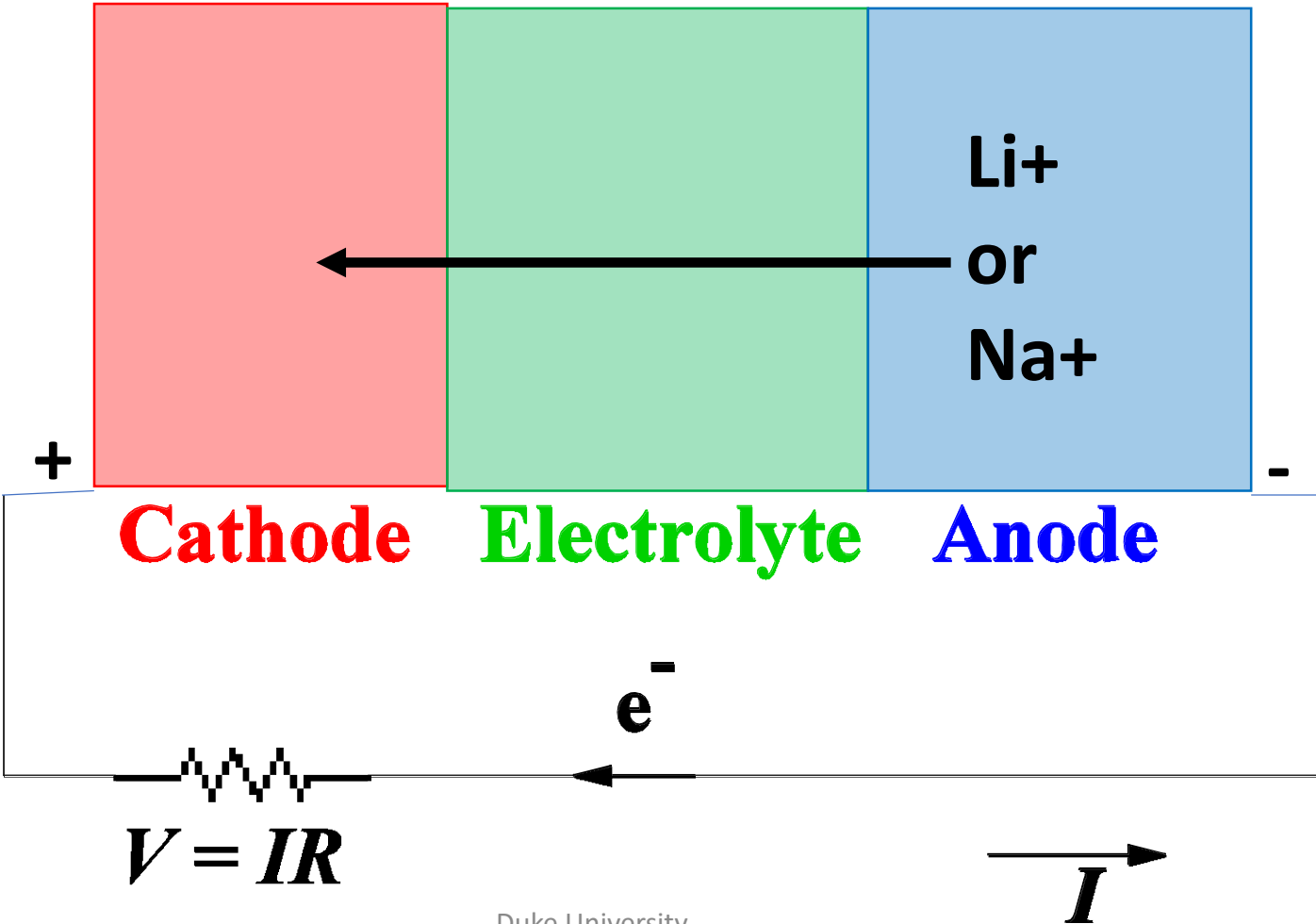
In the early 1970s, Whittingham developed the first functional lithium-ion battery, and in the following decade, Goodenough found a way to double the battery's potential. Yoshino made the battery safer by eliminating the need for pure lithium, a highly reactive metal.

From NY Times

- **Motivation**
- **Research on battery materials**

Materials components of a Li or Na ion battery

Role of the electrolyte is to allow for the transport of Li^+ or Na^+ ions, excluding electrons from the battery and forcing them through the external circuit.



Illustrating discharge mode

➤ Motivation

➤ The case for all solid state batteries

Development of LiPON electrolyte films at Oak Ridge National Laboratory

Solid State Ionics 53–56 (1992) 655–661
North-Holland

**SOLID
STATE
IONICS**

Sputtering of lithium compounds for preparation of electrolyte thin films

N.J. Dudney, J.B. Bates, R.A. Zuhr and C.F. Luck

Solid State Division, Oak Ridge National Laboratory, P O Box 2008, Oak Ridge, TN 37831-6030, USA

and

J.D. Robertson

Department of Chemistry, University of Kentucky, 800 Rose St , Lexington, KY 40506-0055, USA

➤ Motivation -- The case for all solid state batteries

Materials
Views

www.MaterialsViews.com

Adv. Energy Mater. 2015, 5, 1401408

DOI: 10.1002/aenm.201401408

ADVANCED
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www.advenerymat.de

Solid Electrolyte: the Key for High-Voltage Lithium Batteries

Juchuan Li,* Cheng Ma, Miaofang Chi, Chengdu Liang, and Nancy J. Dudney* ORNL

Advantages

- Compatible and stable with high voltage cathodes
- Compatible and stable with Li metal anodes

Disadvantages

- Relatively low ionic conductivity (Compensated with the use of less electrolyte material?)
- Lower total capacity compared with liquid electrolytes

Demonstrated for $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4/\text{LiPON}/\text{Li}$

- 10^{-6} m LiPON electrolyte layer achieved adequate conductivity
- 10,000 cycles* with 90% capacity retention

*1 cycle per day for 27 years

- **Motivation**
- **Challenges for realistic (idealistic??) computer modeling**
 - **Technological challenges –**
 - **Improving the ionic conductivity**
 - **Stabilizing the electrolyte material in battery conditions**
 - **Stabilizing the cathode/electrolyte and anode/electrolyte interfaces**
 - **Checking accuracy of computational models in terms of physical and numerical approximations, comparing with real materials**

➤ **Experimental story – $\text{Li}_4\text{P}_2\text{S}_6$ and $\text{Na}_4\text{P}_2\text{S}_6$ as examples of interesting electrolyte systems**

$\text{Li}_4\text{P}_2\text{S}_6$ has been identified as a low conductivity decomposition product in the formation of lithium thiophosphate electrolytes.

Journal of the Ceramic Society of Japan 118 [4] 305-308 2010

Paper

Preparation and characterization of superionic conducting $\text{Li}_7\text{P}_3\text{S}_{11}$ crystal from glassy liquids

Keiichi MINAMI, Akitoshi HAYASHI and Masahiro TATSUMISAGO[†]

**Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University,
1-1 Gakuen-cho, Naka-ku, Sakai, Osaka, 599-8531**

Minami et al. 2010, continued

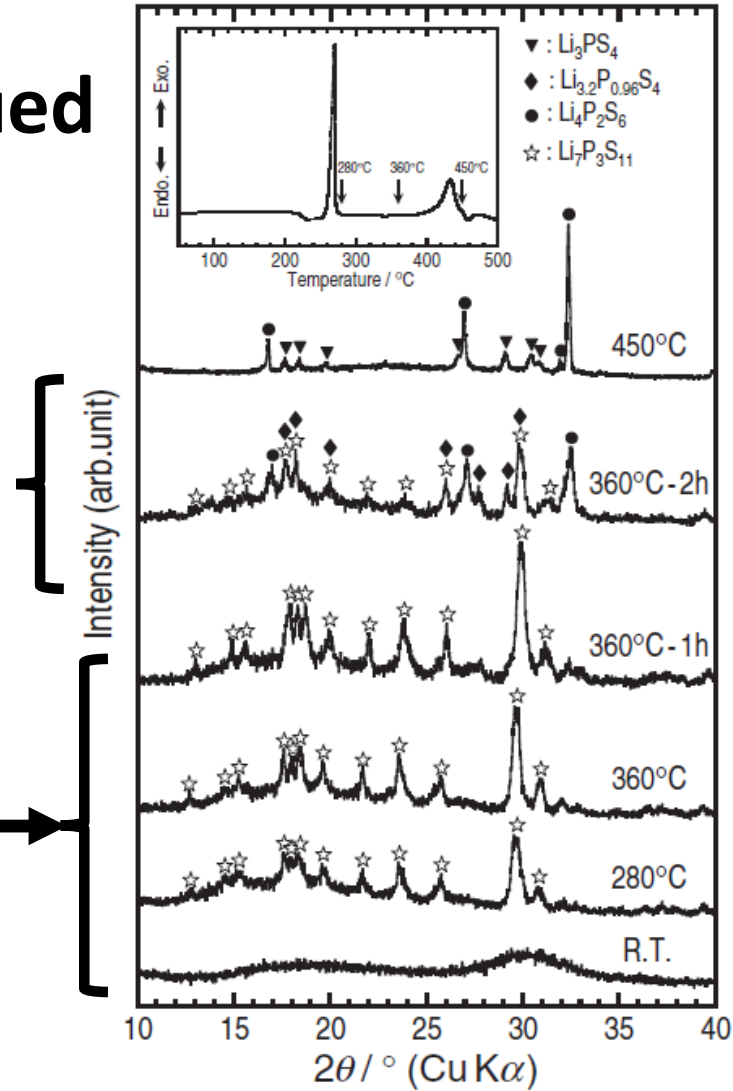
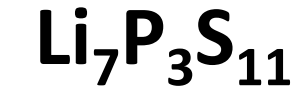
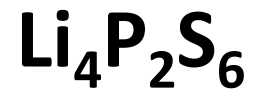


Fig. 1. XRD patterns of the glass and crystallized samples prepared from the glass by heat treatment at various temperatures and holding periods of time.

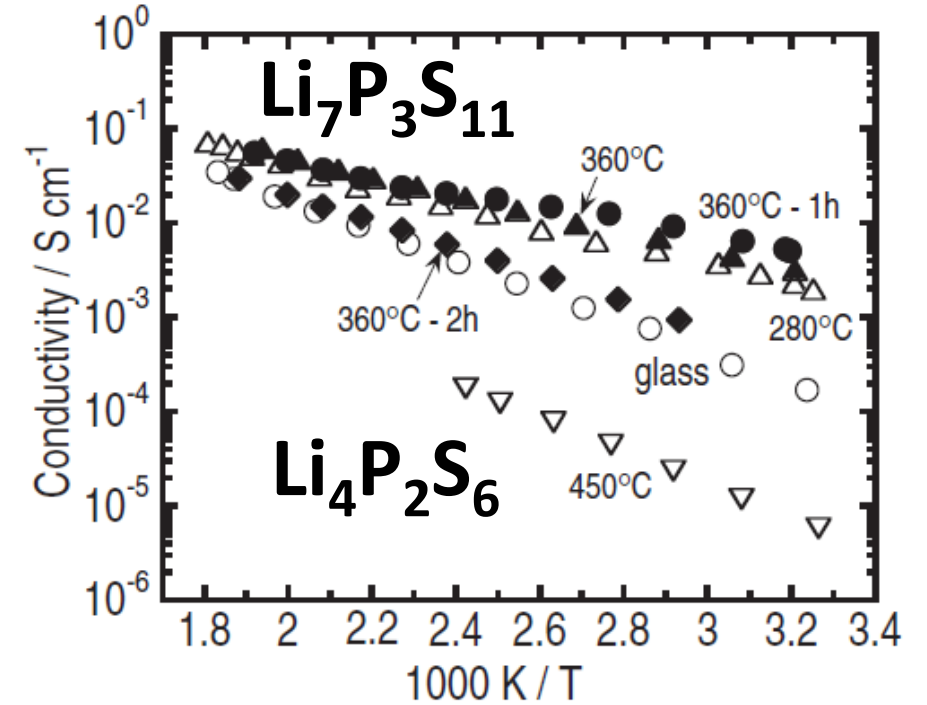


Fig. 2. Temperature dependence of conductivities for the crystallized samples prepared from the glass by heat treatment at various temperatures and holding periods of time.

➤ Experimental story – $\text{Li}_4\text{P}_2\text{S}_6$ continued --

JOURNAL OF SOLID STATE CHEMISTRY **43**, 151–162 (1982)

Synthese, structure cristalline et analyse vibrationnelle de l'hexathiohypodiphosphate de lithium $\text{Li}_4\text{P}_2\text{S}_6$

R. MERCIER, J. P. MALUGANI, B. FAHYS, J. DOUGLADE,* ET
G. ROBERT

*Laboratoire d'Electrochimie des Solides, ERA 810, et *Laboratoire de
Chimie Physique, Université de Franche-Comté, 25030 Besancon Cedex,
France*

**Structure analyzed as a disordered hexagonal structure with space group
 $P6_3/mcm$ (#193)**

➤ Experimental story – $\text{Li}_4\text{P}_2\text{S}_6$ continued --

Solid State Ionics 284 (2016) 61–70



Contents lists available at ScienceDirect

Solid State Ionics

journal homepage: www.elsevier.com/locate/ssi



Structural and electrolyte properties of $\text{Li}_4\text{P}_2\text{S}_6$



Zachary D. Hood ^{a,1}, Cameron Kates ^{b,2}, Melanie Kirkham ^c, Shiba Adhikari ^d,
Chengdu Liang ^{a,3}, N.A.W. Holzwarth ^{b,*}

^a Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

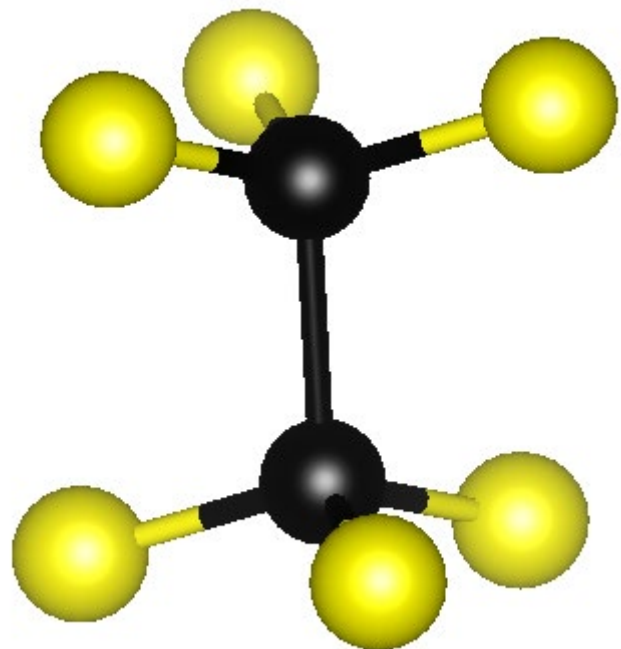
^b Department of Physics, Wake Forest University, Winston-Salem, NC 27109-7507, USA

^c Spallation Neutron Source, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

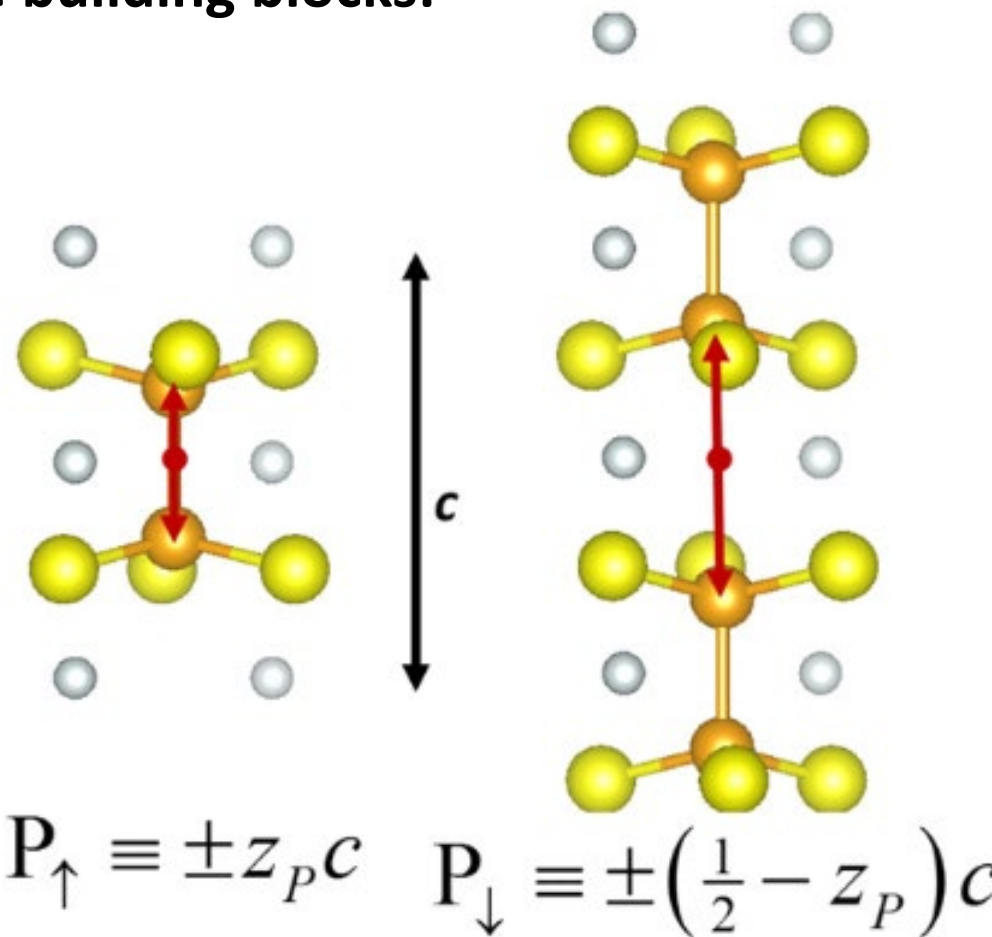
^d Department of Chemistry, Wake Forest University, Winston-Salem, NC 27109-7486, USA

➤ Experimental story – $\text{Li}_4\text{P}_2\text{S}_6$ continued --

P_2S_6 building blocks:

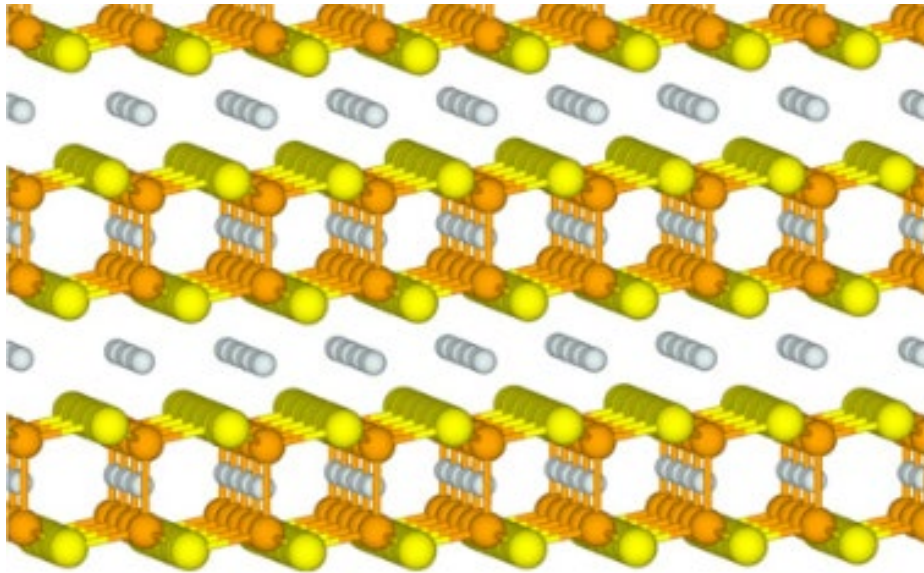


Mercier's disordered structure can be described in terms of the alternative stacking patterns of the building blocks:



➤ Experimental story – $\text{Li}_4\text{P}_2\text{S}_6$ continued --

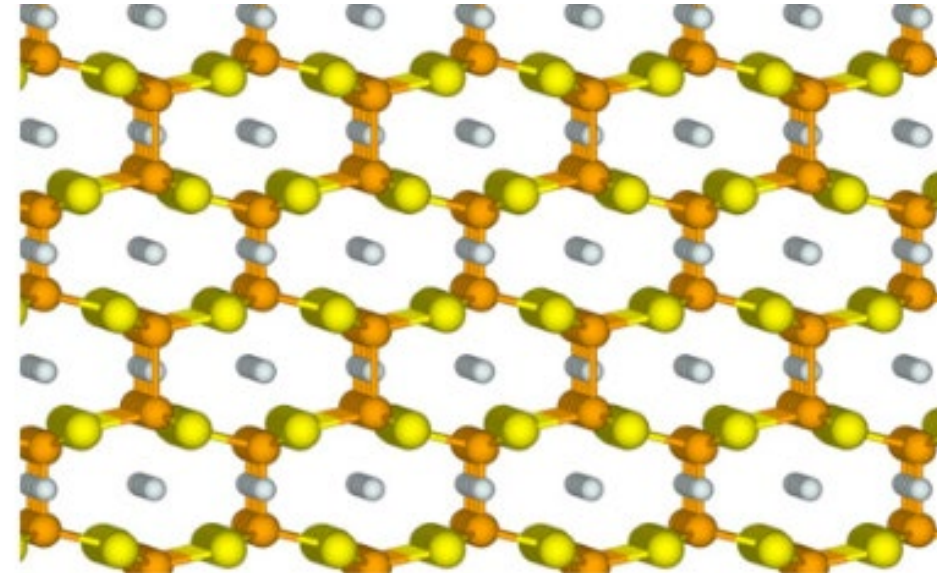
Possible stacking structures



100% P↑

Space group $P\bar{3}1m$

Energetically less favored
according to simulations



50% P↑

50% P↓

Consistent with Mercier's analysis;
energetically favored; not sensitive to
detailed structure according to simulations

➤ Experimental story – $\text{Li}_4\text{P}_2\text{S}_6$ continued --

Dalton Transactions

PAPER

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Refinement of the crystal structure of $\text{Li}_4\text{P}_2\text{S}_6$ using NMR crystallography†

Cite this: *Dalton Trans.*, 2018, 47, 11691

Sven Neuberger, ^a Sean P. Culver,^b Hellmut Eckert, ^{c,d} Wolfgang G. Zeier ^b
and Jörn Schmedt auf der Günne ^{*a}

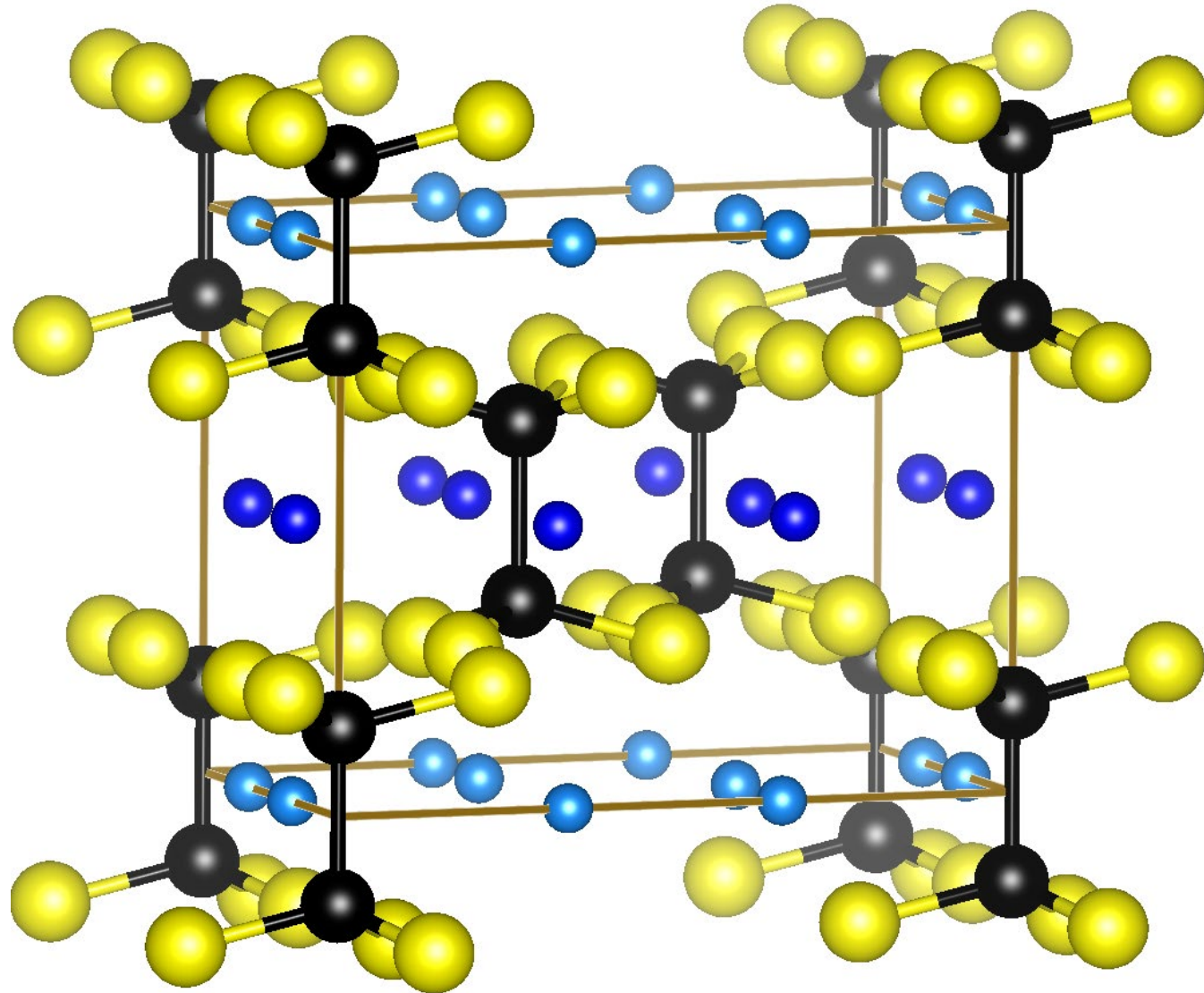
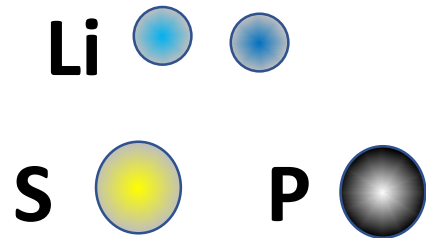
Prepare more highly crystalline samples; combine NMR and X-ray analysis to show that there are two inequivalent P sites

➤ Experimental story – $\text{Li}_4\text{P}_2\text{S}_6$ continued --

Neuberger structure

67% $\text{P}\uparrow$ 33% $\text{P}\downarrow$

Space group
 $P321 \rightarrow P\bar{3}m1$



➤ **Experimental story – Na₄P₂S₆ continued --**

DOI: 10.1002/zaac.201300575

Z. Anorg. Allg. Chem. **2014**, *640*, (5), 689–692

**Synthesis and Structural Characterization of the Alkali Thiophosphates
Na₂P₂S₆, Na₄P₂S₆, K₄P₂S₆, and Rb₄P₂S₆**

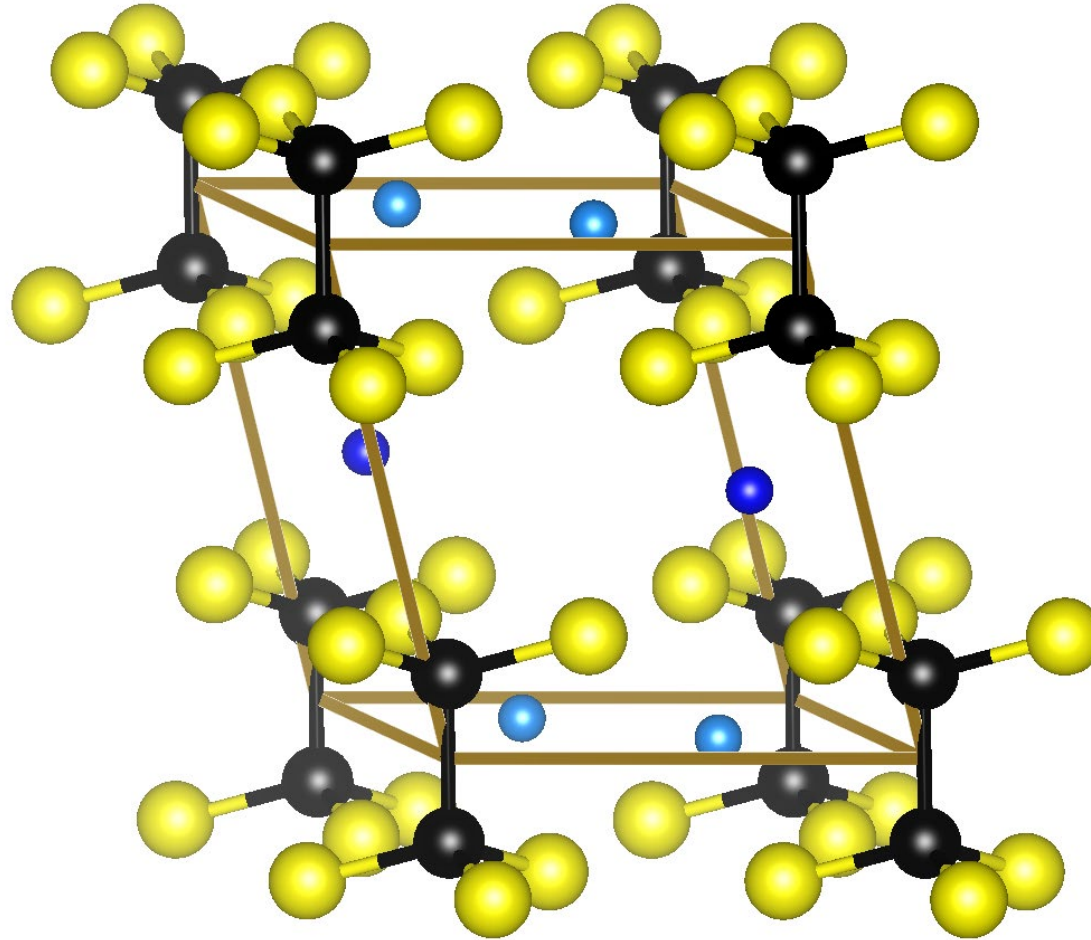
Alexander Kuhn,^[a] Roland Eger,^[a] Jürgen Nuss,^[a] and Bettina V. Lotsch*^[a,b]

Na₄P₂S₆ found to crystallize in a base centered monoclinic structure with space group *C2/m* (#12); result verified by Zachary Hood and colleagues who also found the material to have appreciable Na ion conductivity.

➤ Experimental story – $\text{Na}_4\text{P}_2\text{S}_6$ continued --

Primitive cell of the
Kuhn structure

Space group $C2/m$



Na  

S  P 

- **Computational challenges –**
 - **Can computer modeling explain the structural stability patterns found by experiment?**
 - **What about possible new related materials?**
 - **What does computer modeling say about the mechanisms of ionic conductivity?**

➤ Simulation of structural stability patterns

Computational details –

Formalism: Born-Oppenheimer approximation + Density functional theory
(Hohenberg and Kohn, *Phys. Rev.* 136 B864 (1964); Kohn and Sham, *Phys. Rev.* 140 A1133 (1965))

Method: Projector Augmented Wave (P. Blöchl, *Phys. Rev. B* 50 17953 (1994))

Exchange correlation function: PBEsol (Perdew et al., *PRL* 100 136406 (2008))

Codes used for calculations


Function	Code	Website
Generate atomic datasets	ATOMPAW	http://pwpaw.wfu.edu
DFT; optimize structure; vibrational analysis	PWscf abinit	http://www.quantum-espresso.org http://www.abinit.org
Structural visualization	XCrySDen VESTA	http://www.xcrysden.org http://jp-minerals.org/vesta/en/

Stability approximated in terms of the Helmholtz free energy

as a function of temperature T :


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


**Static
lattice
approx**

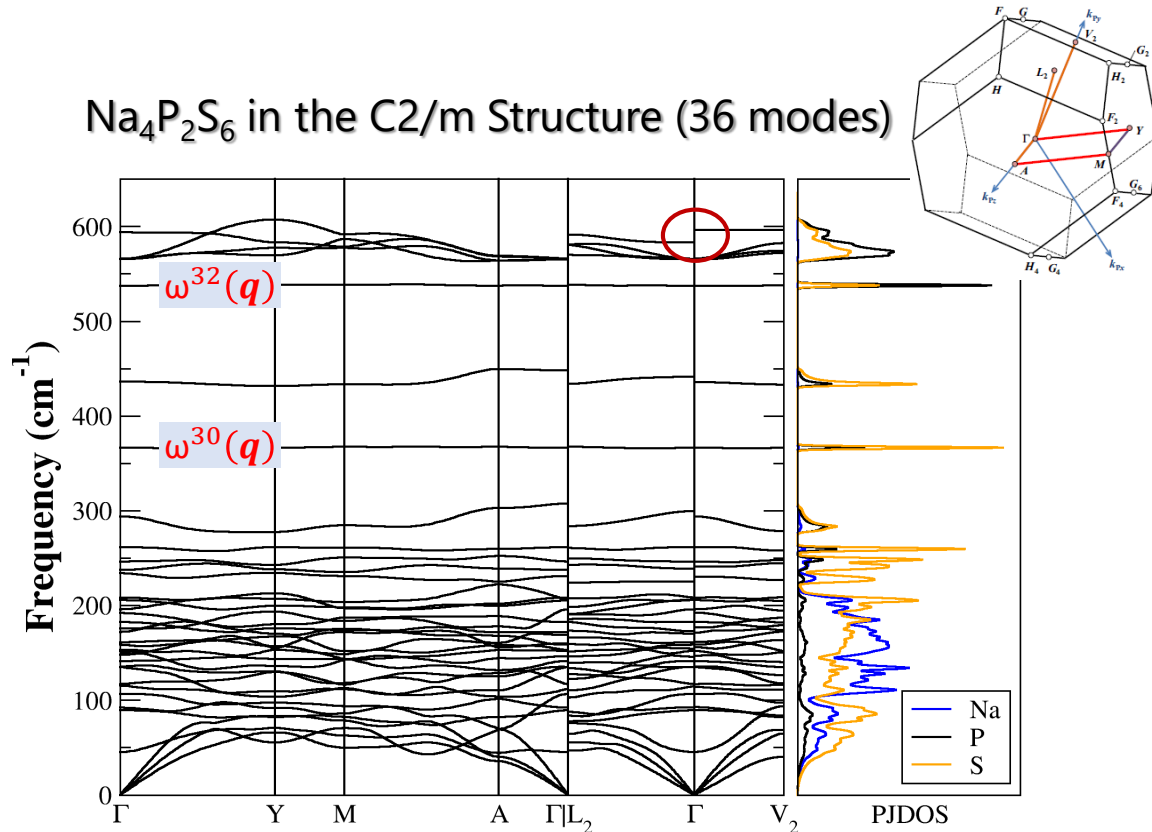

**Harmonic
phonon
approx**


**Internal
energy
from DFT**

$$F_{vib}(T) = k_B T \int_0^{\infty} d\omega \ln \left(2 \sinh \left(\frac{\hbar \omega}{2k_B T} \right) \right) g(\omega)$$

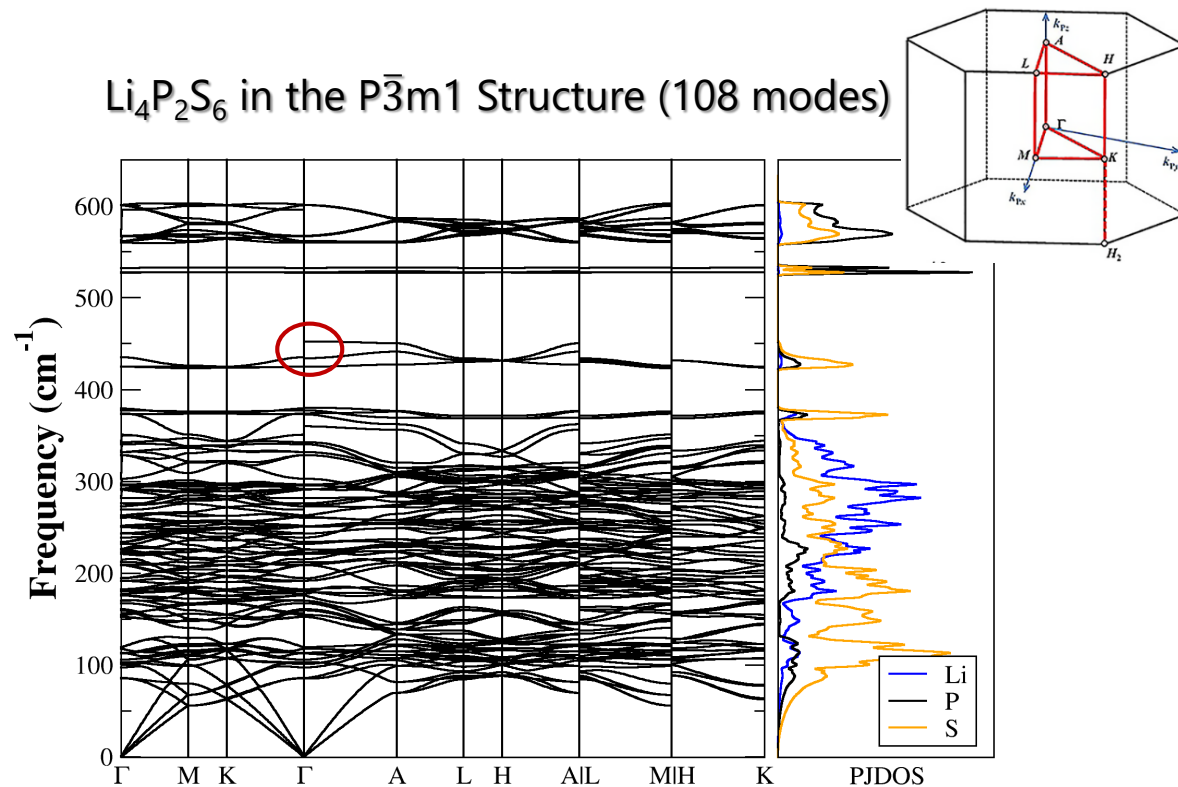
 **Phonon DOS**

Na₄P₂S₆ in the C2/m Structure (36 modes)



Na⁺ 0~300 cm⁻¹
(P₂S₆)⁴⁻ 300~600 cm⁻¹

Li₄P₂S₆ in the P3m1 Structure (108 modes)



Li⁺ 0~370 cm⁻¹
(P₂S₆)⁴⁻ 370~600 cm⁻¹

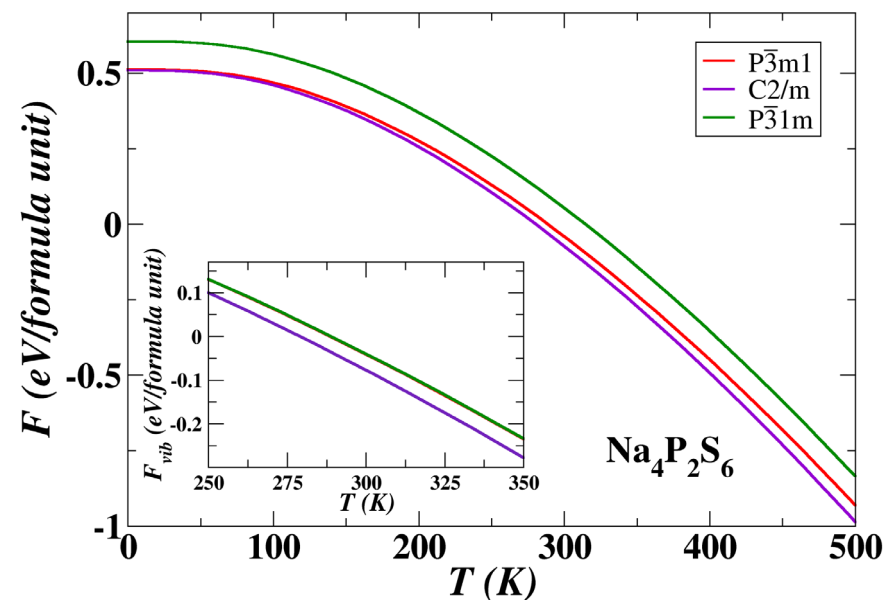
¹Suggested path: Hinuma et al., *Comp. Mat. Sci.* **128**, 140-184 (2017)

²Li et al., *J. Phys. Condens. Matter*, **32**, 055402 (2020)

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 photon²

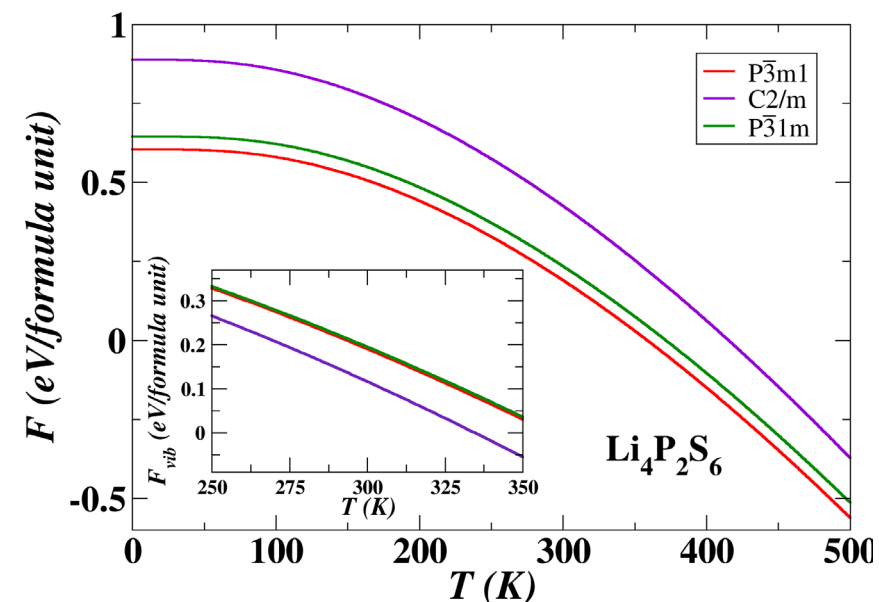
Helmholtz free energy: $F = U_{\text{SL}} + F_{\text{vib}}$



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)**

¹Kuhn et al., *Z. Anorg. Allg. Chem.* **640**, 689-692 (2014)

²Hood et al., *J. Solid State Ionics* **284**, 61 (2016)

³Neuberger et al., *Dalton Trans.* **47**, 11691-11695 (2018)

Summary of simulation energies

$\text{Na}_4\text{P}_2\text{S}_6$	$\Delta U_{SL}(\text{eV})$	$F_{vib}(300\text{K})(\text{eV})$	$F(300\text{K})(\text{eV})$
Neuberger structure ($P\bar{3}m1$)	0.00	-0.04	-0.04
Kuhn structure ($C2/m$)	0.00	-0.08	-0.08
Simple hex structure ($P\bar{3}1m$)	0.09	-0.04	0.05
$\text{Li}_4\text{P}_2\text{S}_6$	$\Delta U_{SL}(\text{eV})$	$F_{vib}(300\text{K})(\text{eV})$	$F(300\text{K})(\text{eV})$
Neuberger structure ($P\bar{3}m1$)	0.00	0.19	0.19
Kuhn structure ($C2/m$)	0.31	0.12	0.43
Simple hex structure ($P\bar{3}1m$)	0.04	0.20	0.24

Energies given in units of eV/formula unit with zero set at the static lattice energy for the Neuberger structure.

➤ Some details of the vibrational stabilization

Vibrational Helmholtz free energy expression:

$$F_{vib}(T) = k_B T \int_0^{\infty} d\omega \ln \left(2 \sinh \left(\frac{\hbar \omega}{2k_B T} \right) \right) g(\omega)$$

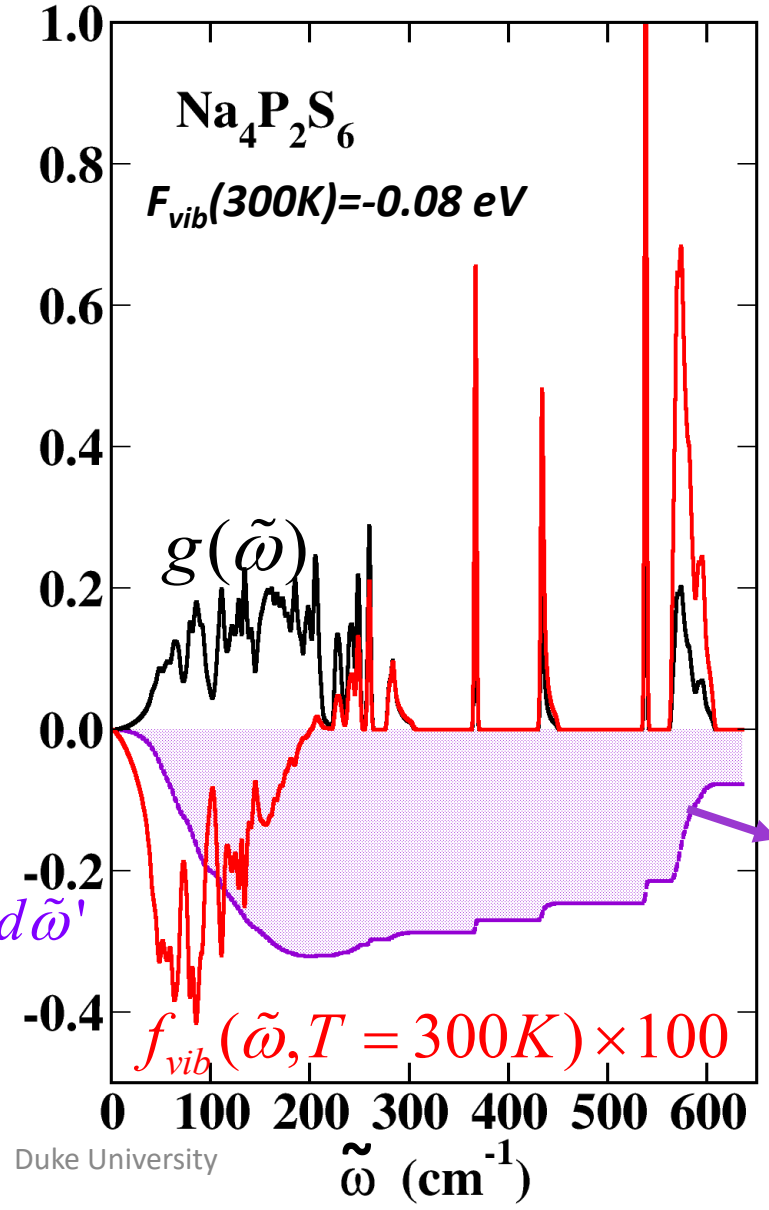
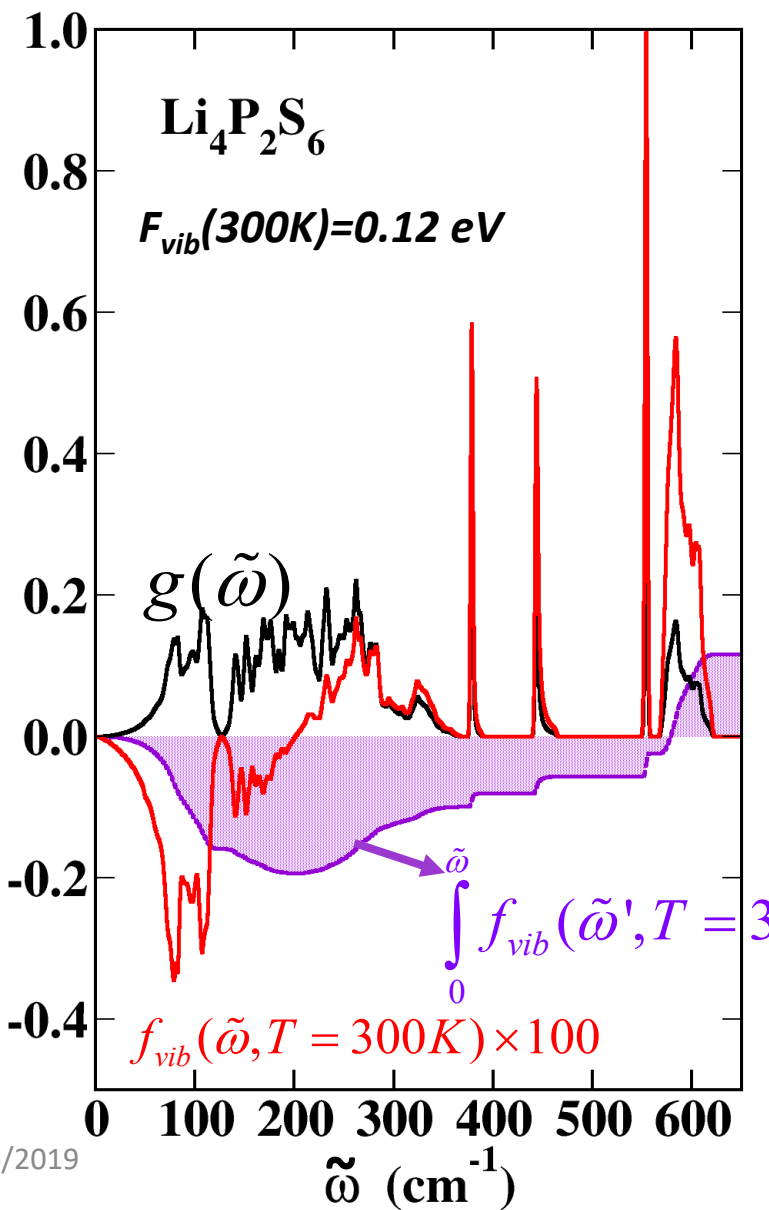
In practice, it is convenient to express frequencies in wavenumbers:

$$\tilde{\omega} = \frac{\omega}{2\pi c} \text{ (cm}^{-1}\text{)} \quad \text{with} \quad F_{vib}(T) = \int_0^{\infty} d\tilde{\omega} f_{vib}(\tilde{\omega}, T)$$

where the weighted phonon DOS factor is

$$f_{vib}(\tilde{\omega}, T) \equiv k_B T \ln \left(2 \sinh \left(\frac{hc\tilde{\omega}}{2k_B T} \right) \right) g(\tilde{\omega})$$

➤ Some details of the vibrational stabilization at $T=300\text{K}$ for $\text{Li}_4\text{P}_2\text{S}_6$ and $\text{Na}_4\text{P}_2\text{S}_6$ in C2/m structure



➤ What about possible new related materials?

Consider the possible alloy $\text{Li}_2\text{Na}_2\text{P}_2\text{S}_6$ in the $C2/m$ structure

Replace the (a) g -type or (b) h -type Na ions in the monoclinic $\text{Na}_4\text{P}_2\text{S}_6$ with Li ions

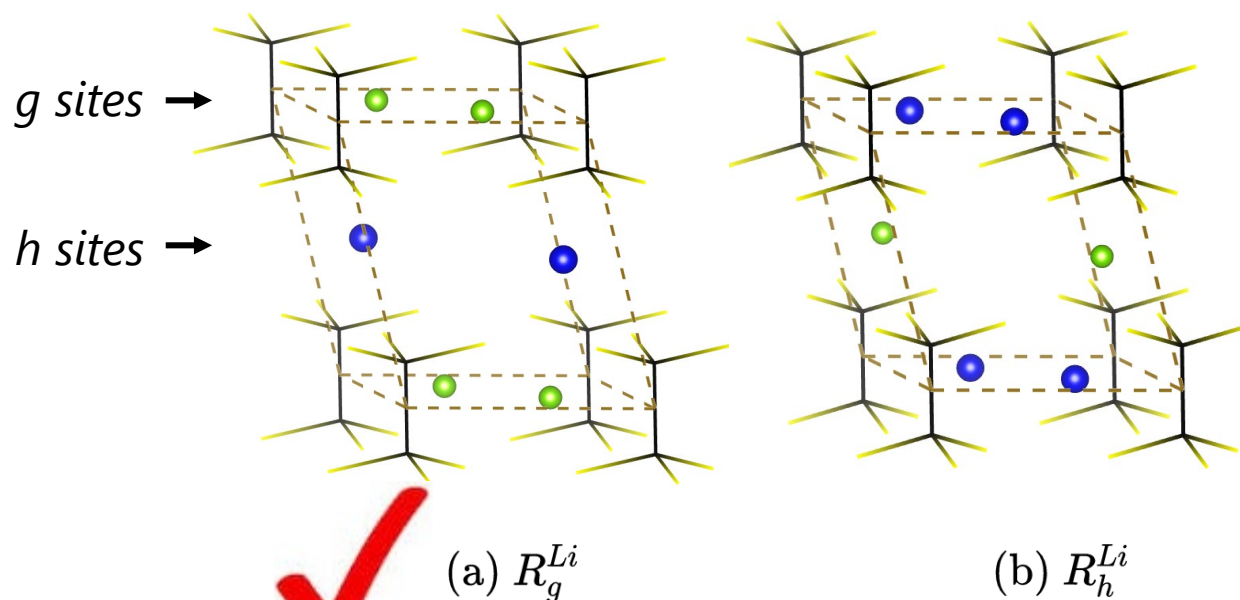
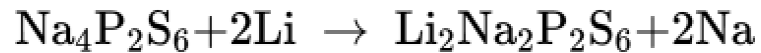


TABLE: Comparison of the optimized lattice parameters for $\text{Li}_2\text{Na}_2\text{P}_2\text{S}_6$ in the R_g^{Li} and R_h^{Li} structures. Also listed is the static lattice energy differences U_{SL} referenced to the energy of the R_h^{Li} structure in units of eV/formula unit.

		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

➤ What about the possible new related material – $\text{Li}_2\text{Na}_2\text{P}_2\text{S}_6$ -- is it stable/useful?

The possible reaction pathway:



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

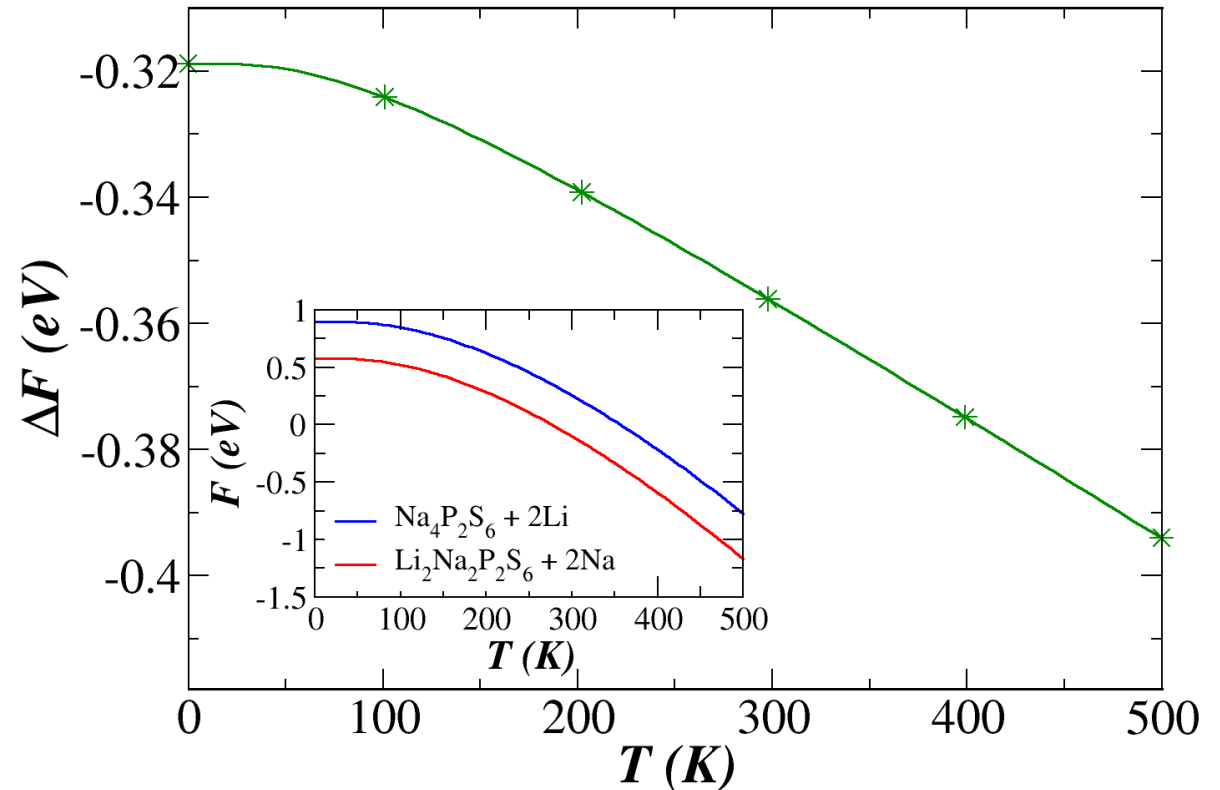
trivial contribution
(10^{-3} eV)

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

Energy changes at $T = 300$ K in eV:

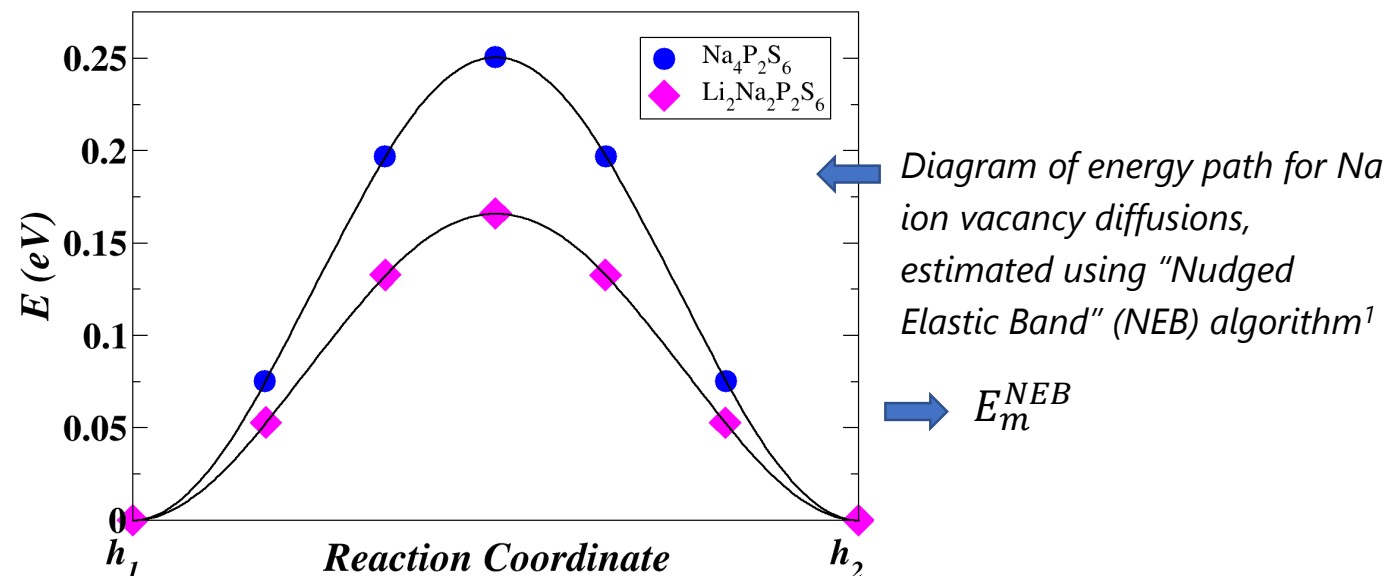
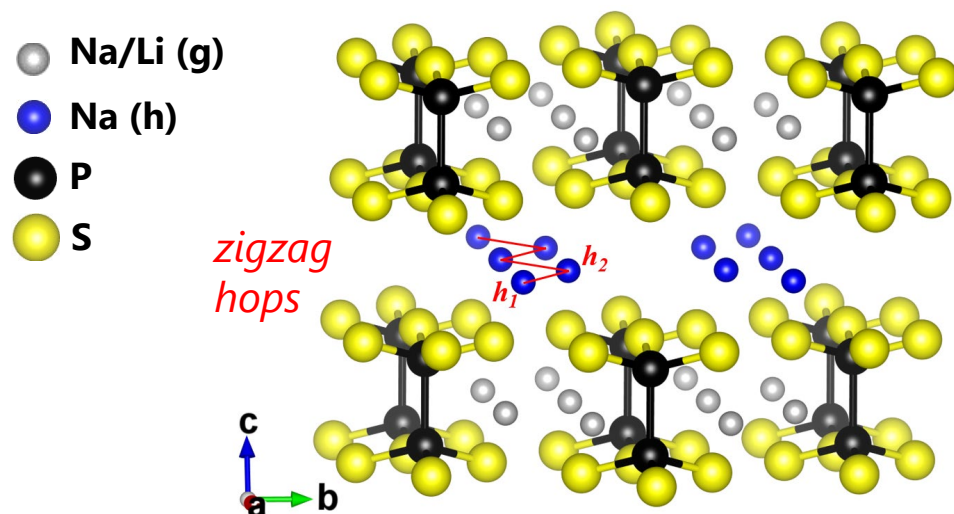
$$\Delta U_{SL} = -0.29 \quad \rightarrow \quad \Delta F = -0.35$$

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



Negative energy implies that the product $\text{Li}_2\text{Na}_2\text{P}_2\text{S}_6 + 2\text{Na}$ is stable with respect to the reactants $\text{Na}_4\text{P}_2\text{S}_6 + 2\text{Li}$.

Computer modeling of mechanisms of ionic conductivity; comparing $\text{Na}_4\text{P}_2\text{S}_6$ and $\text{Li}_2\text{Na}_2\text{P}_2\text{S}_6$ --



Activation energy:

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

Conductivity:

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

Summary of vacancy diffusion results

Material	Functional	Step	Distance	E_m^{cal}	E_f^{cal}	E_a^{cal}	E_a^{exp}
$\text{Na}_4\text{P}_2\text{S}_6$	PBESol GGA	$h_1 \rightarrow h_2$	3.67	0.25	0.18	0.34	0.39
	LDA	$h_1 \rightarrow h_2$	3.59	0.30	0.24	0.42	
$\text{Li}_2\text{Na}_2\text{P}_2\text{S}_6$	PBESol GGA	$h_1 \rightarrow h_2$	3.44	0.16	0.13	0.23	—

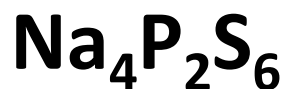
¹Henkelman et al., *J. Chem. Phys.* **113**, 9901-9904 (2000)

²Rush et al., *Solid State Phys.* **286**, 45-50 (2016)

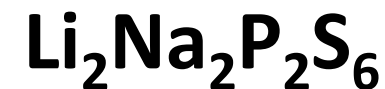
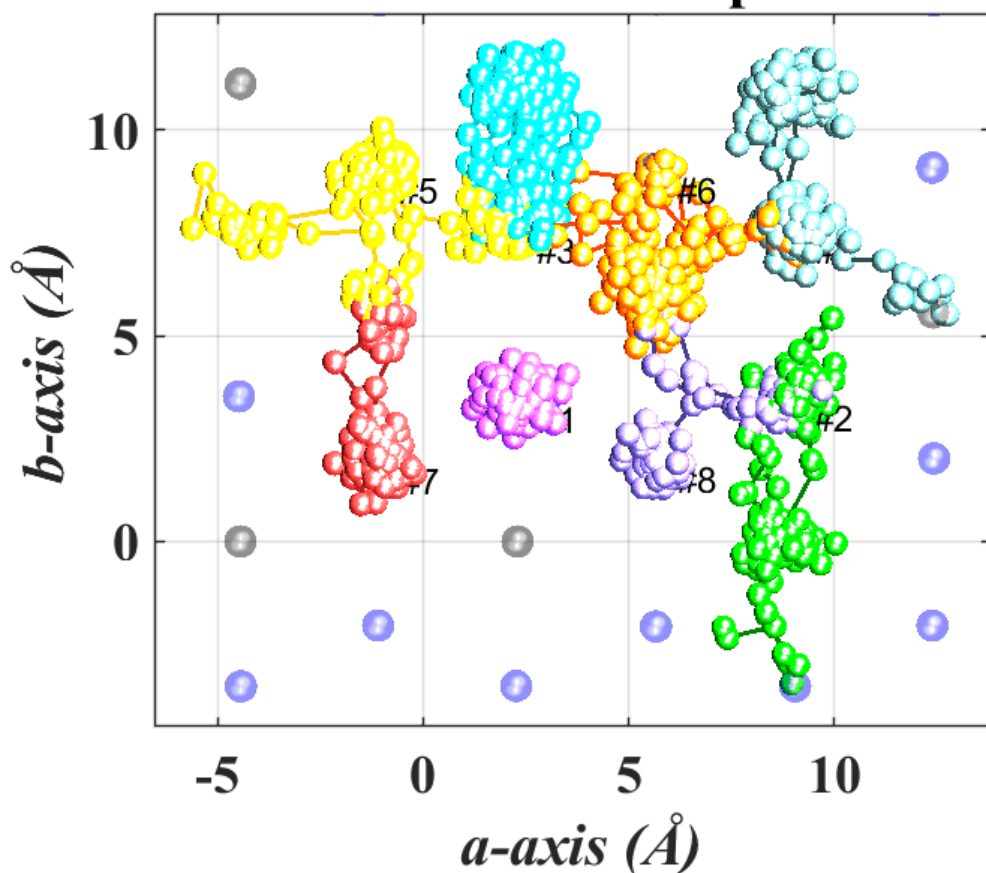
³Hood et al., Manuscript in preparation.



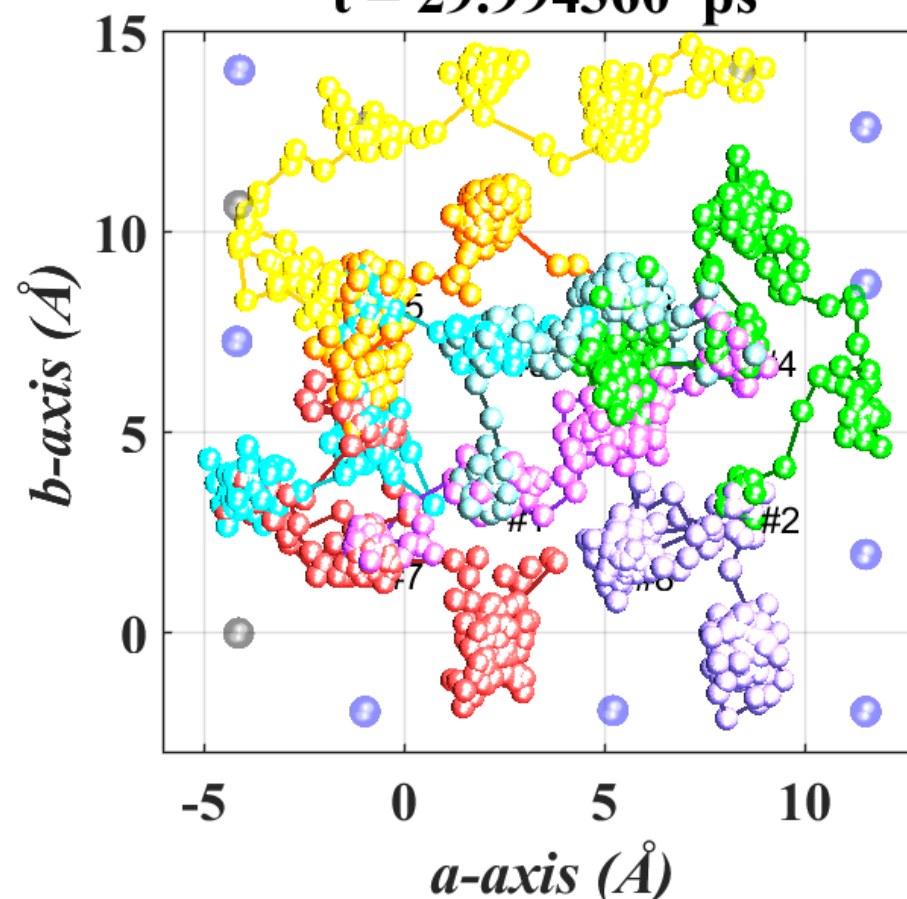
Computer modeling of mechanisms of ionic conductivity; comparing $\text{Na}_4\text{P}_2\text{S}_6$ and $\text{Li}_2\text{Na}_2\text{P}_2\text{S}_6$ -- MD simulations at $\langle T \rangle = 1000\text{K}$; Na ion motion in h planes --



$t = 29.994360$ ps



$t = 29.994360$ ps



➤ Outlook

- ❑ DFT with PBEsol+harmonic phonon simulations agree with the experimental structures of $\text{Na}_4\text{P}_2\text{S}_6$ (space group $C2/m$ found by Kuhn and Hood) and $\text{Li}_4\text{P}_2\text{S}_6$ (space group $P\bar{3}m1$, close to that found by Neuberger).
- ❑ For $\text{Na}_4\text{P}_2\text{S}_6$ find Na+ migration to take place in planes with the h -sites via a vacancy mechanism, involving interstitial d -sites. Both simulations and experiment suggest that $\text{Na}_4\text{P}_2\text{S}_6$ may be a viable solid electrolyte.
- ❑ Simulations predict $\text{Li}_2\text{Na}_2\text{P}_2\text{S}_6$ to crystallize with the $C2/m$ structure and to be stable relative to $\text{Na}_4\text{P}_2\text{S}_6+2\text{Li}-2\text{Na}$. The mixed alkali electrolyte is predicted to substantially enhance Na ion conductivity.
- ❑ In addition to experimental verification (or otherwise) of the predictions for $\text{Li}_2\text{Na}_2\text{P}_2\text{S}_6$, further MD simulations for both $\text{Na}_4\text{P}_2\text{S}_6$ and $\text{Li}_2\text{Na}_2\text{P}_2\text{S}_6$ will help us better understand Na ion conductivity mechanisms.