First principles simulations of electrolyte materials with a view toward all solid-state battery technology -- $Li_4P_2S_6$, $Na_4P_2S_6$, and possible alloys

Yan Li[1], Zachary Hood[2], and Natalie Holzwarth[1]
[1]Department of Physics, Wake Forest University
[2]Electrochemical Materials Laboratory, MIT; now at Argonne National Labs

WFU effort supported by Deac Cluster and NSF Grants DMR-1507942 and 1940324.

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

Ref: PRM 4, 045406 (2020)

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

Outline

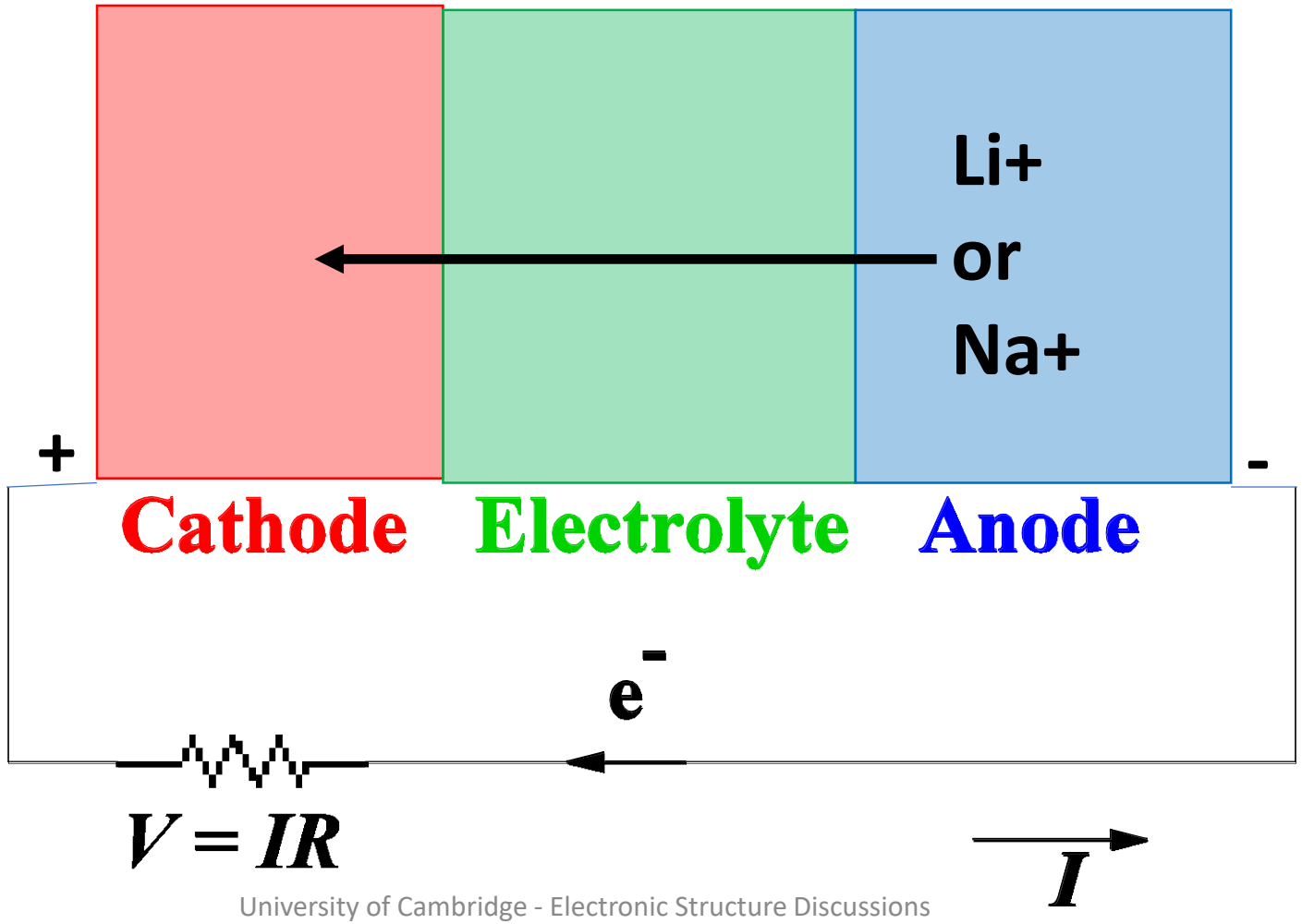
- Motivation
- Experimental story
- Computational story
- Outlook

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

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

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 ENERGY MATERIALS
www.advenergymat.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
- Can be effective in thin formats

Disadvantages

- Relatively low ionic conductivity
- Lower total capacity compared with liquid electrolytes
- Possible physical and chemical interface issues

Demonstrated for $LiNi_{0.5}Mn_{1.5}O_4$/LiPON/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 – $Li_4P_2S_6$ and $Na_4P_2S_6$ as examples of interesting electrolyte systems

$Li_4P_2S_6$ 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 $Li_7P_3S_{11}$ 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

$Li_4P_2S_6$ →

$Li_7P_3S_{11}$ →

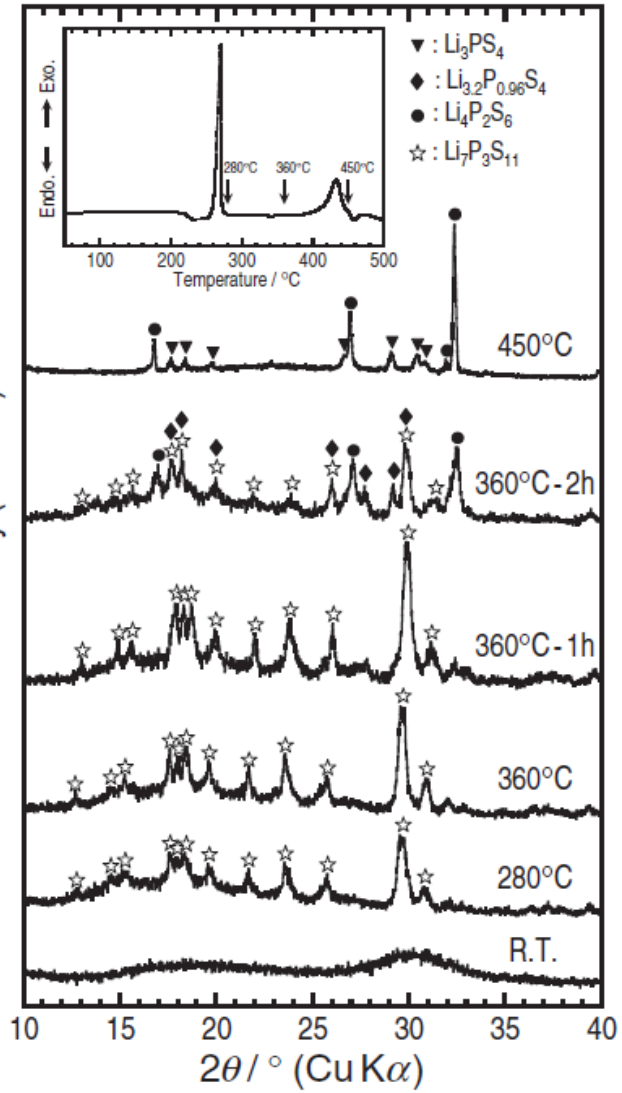


Fig. 1. XRD patterns of the glass and crystallized samples prepared from the glass by heat treatment at various temperatures and holding periods of time.

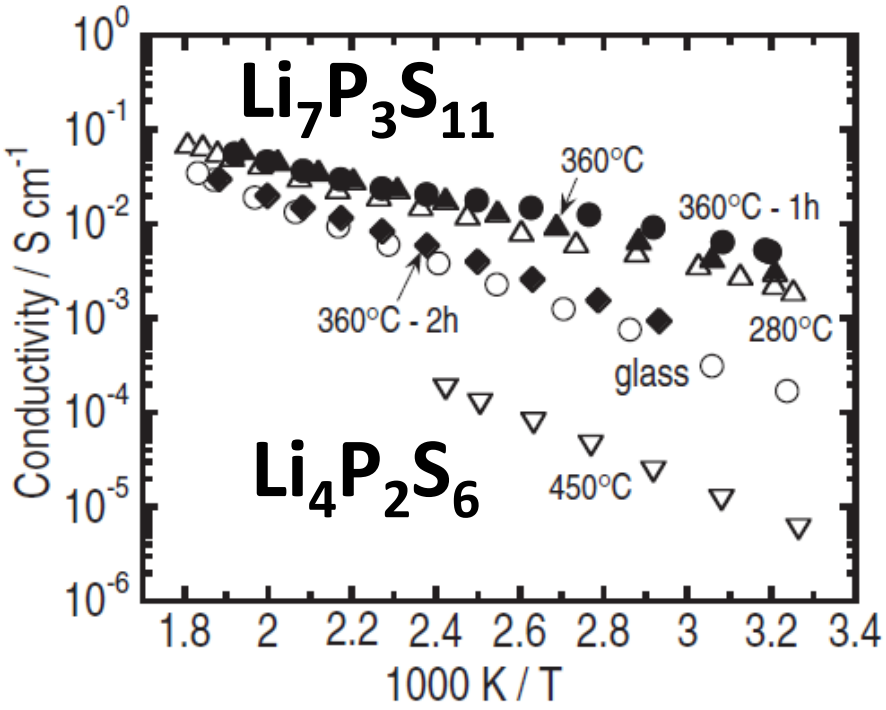


Fig. 2. Temperature dependence of conductivities for the crystallized samples prepared from the glass by heat treatment at various temperatures and holding periods of time.

➢ Experimental story – $Li_4P_2S_6$ continued --

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

Synthese, structure cristalline et analyse vibrationnelle de l'hexathiohypodiphosphate de lithium $Li_4P_2S_6$

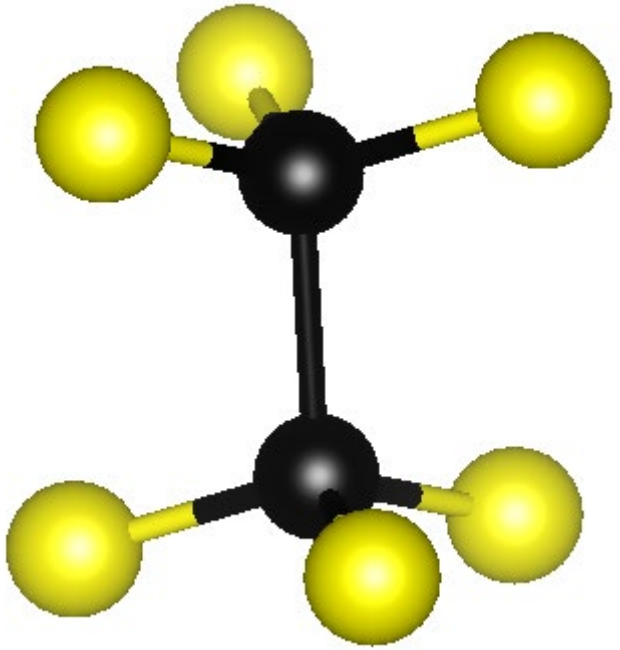
R. MERCIER, J. P. MALUGANI, B. FAHYS, J. DOUGLADE,* ET G. ROBERT

*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 – $Li_4P_2S_6$ continued --

$P_2S_6^{4-}$ building blocks:



hexathiohypodiphosphate

S P

Mercier's disordered structure ascribed to placement of the building blocks and the corresponding arrangement of Li ions.

➢ Experimental story – $Li_4P_2S_6$ continued --

Dalton Transactions

PAPER

View Article Online
View Journal | View Issue

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

Refinement of the crystal structure of $Li_4P_2S_6$ using NMR crystallography†

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

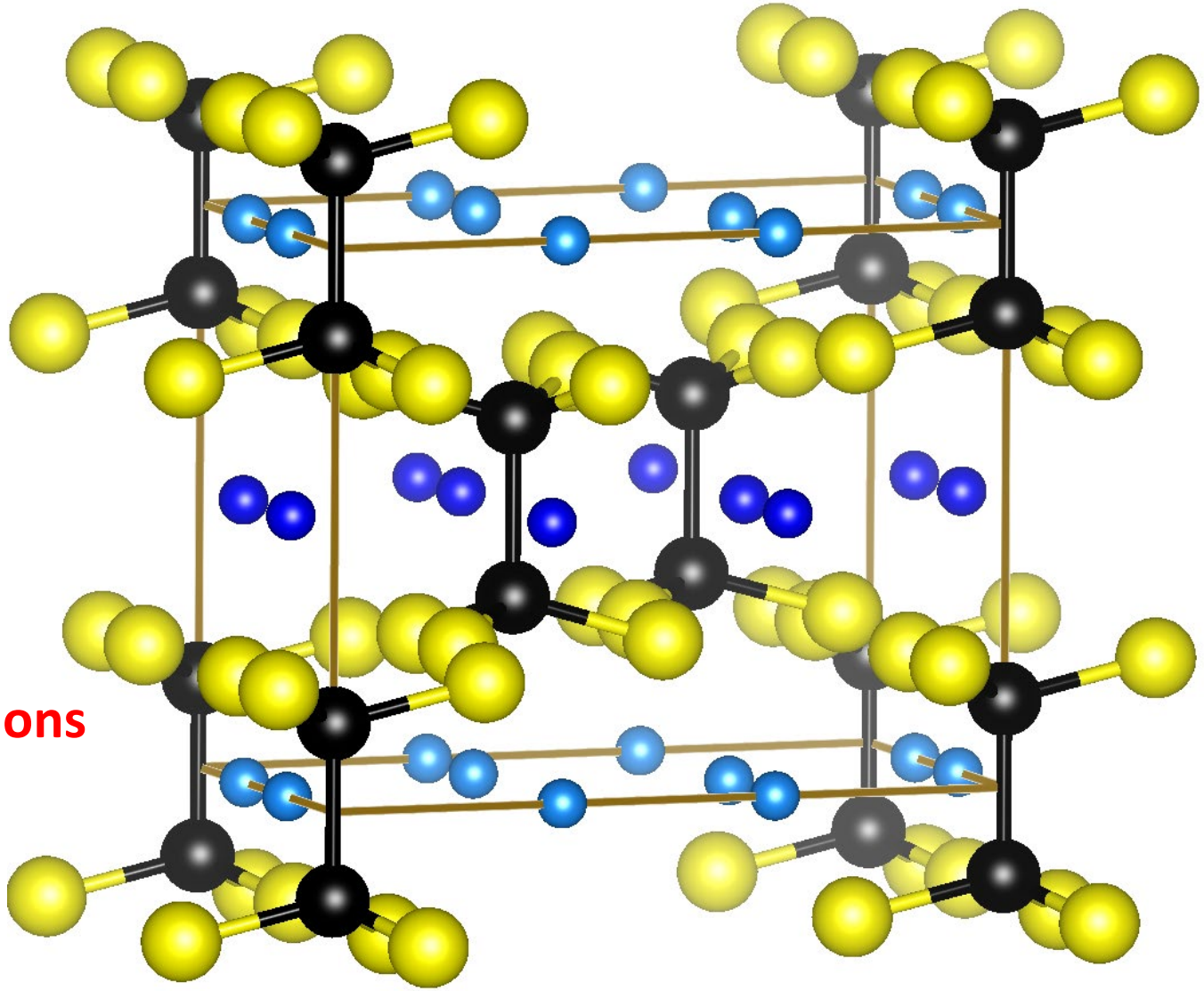
Prepared more highly crystalline samples; combined NMR and X-ray analysis to show that there are two inequivalent P sites

➢ Experimental story – $Li_4P_2S_6$ continued --

Neuberger structure
➔ordered structure reported as P321

Space group
P321 → $P\bar{3}m1$

our simulations



Li

S **P**

➢ Experimental story – $Na_4P_2S_6$ continued --

DOI: 10.1002/zaac.201300575

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

Synthesis and Structural Characterization of the Alkali Thiophosphates $Na_2P_2S_6$, $Na_4P_2S_6$, $K_4P_2S_6$, and $Rb_4P_2S_6$

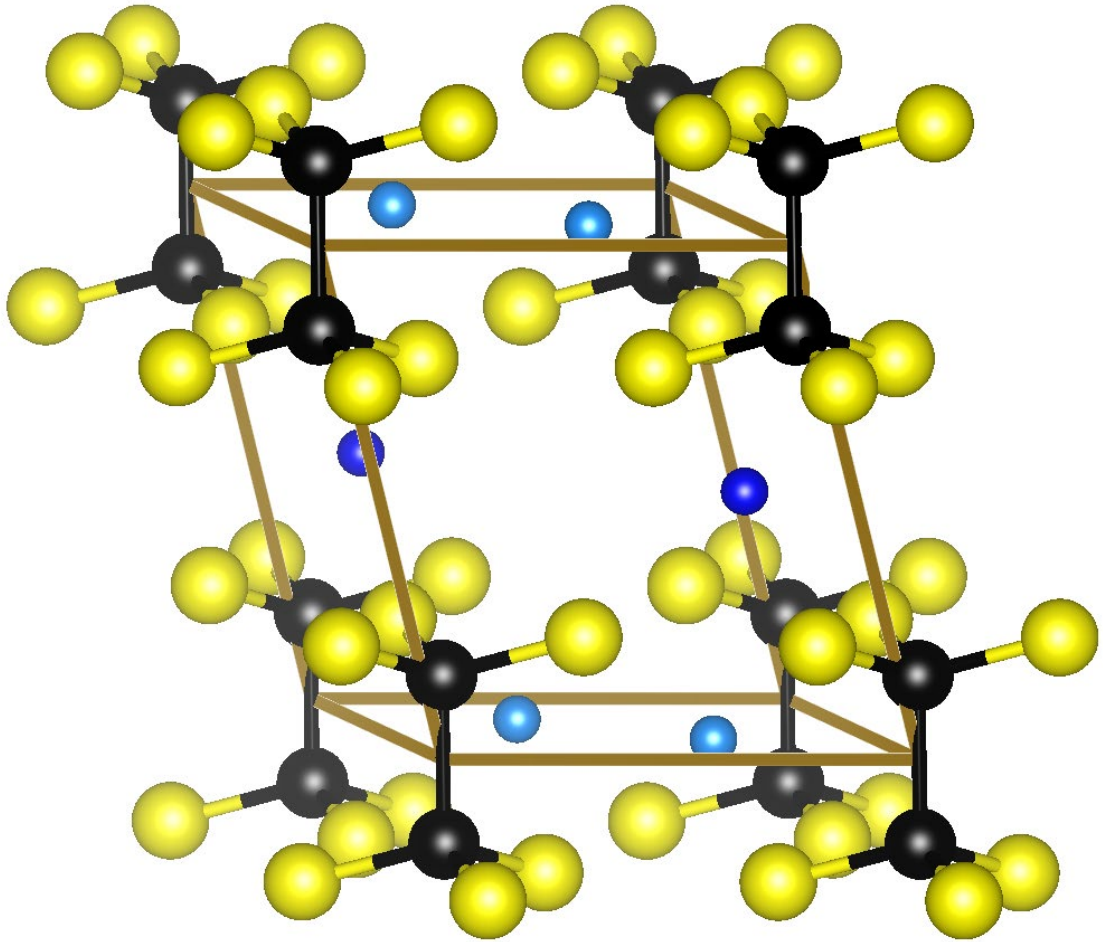
Alexander Kuhn,[a] Roland Eger,[a] Jürgen Nuss,[a] and Bettina V. Lotsch*[a,b]

$Na_4P_2S_6$ 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 – $Na_4P_2S_6$ 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/

➢ Simulation of structural stability patterns -- continued

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

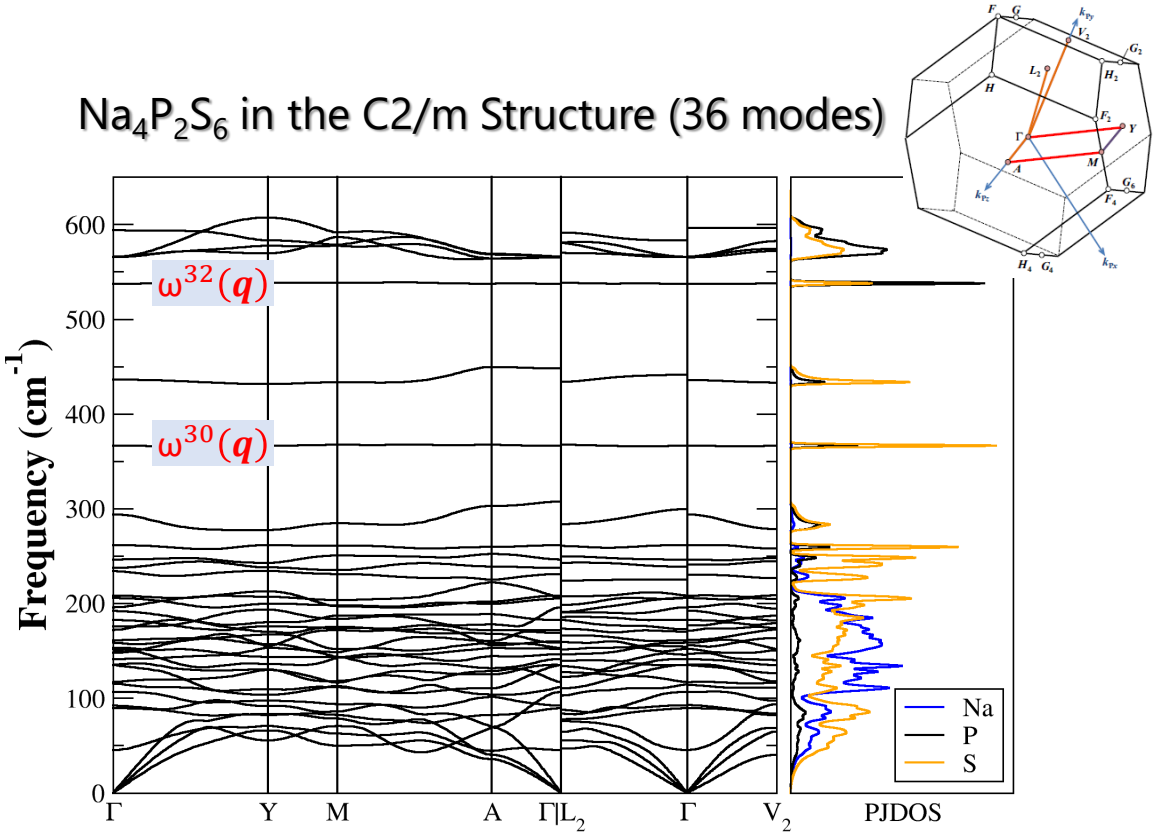
$$F_{vib}(T) = k_B T \int_0^\infty d\omega \ \ln\left(2\sinh\left(\frac{\hbar\omega}{2k_B T}\right)\right) g(\omega)$$

phonon DOS

Simulation of structural stability patterns -- continued

WAKE FOREST UNIVERSITY

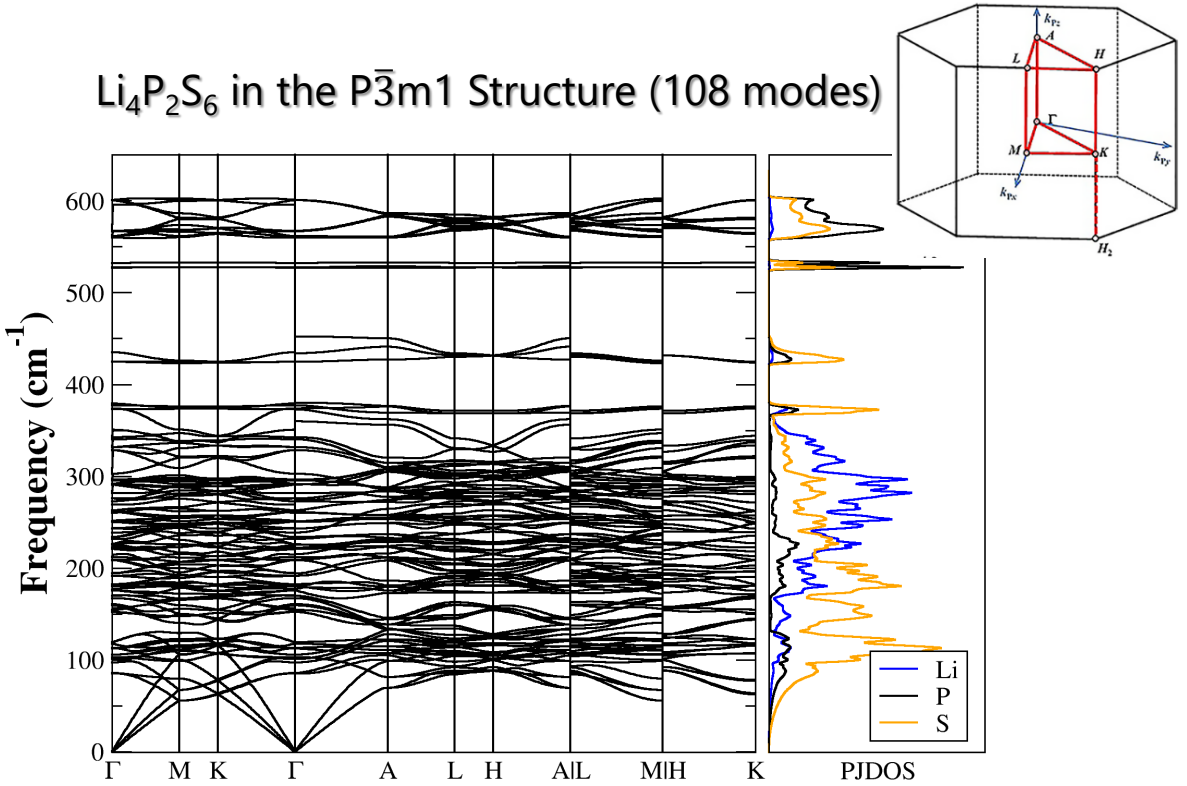
$Na_4P_2S_6$ in the C2/m Structure (36 modes)



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

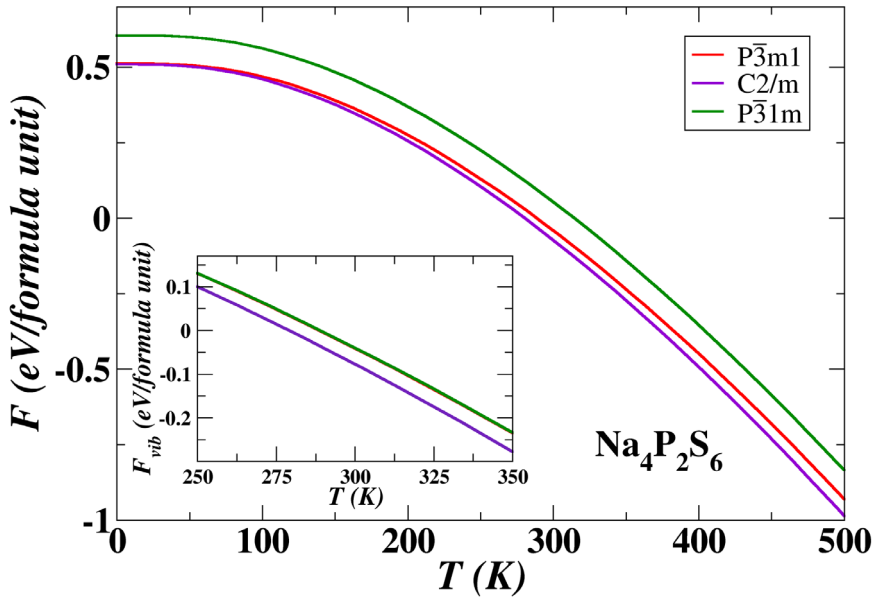
Discontinuous branches at Γ: coupling between photon and photon[2]

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

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

Simulation of structural stability patterns -- continued

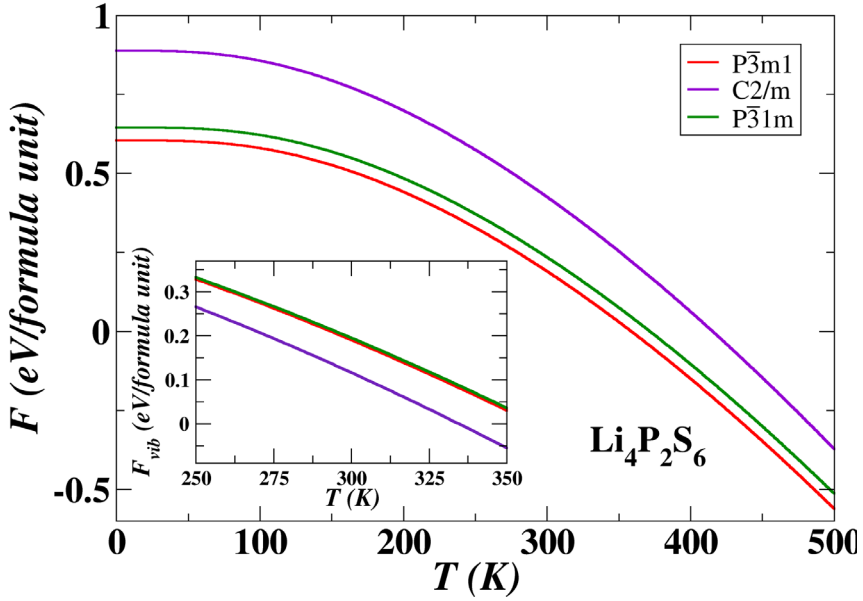
Helmholtz free energy: $F = U_{SL} + F_{vib}$



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)

Simulation of structural stability patterns -- continued

Summary of simulation energies

$Na_4P_2S_6$	ΔU_{SL}(eV)	$F_{vib}(300K)$(eV)	$F(300K)$(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
$Li_4P_2S_6$	ΔU_{SL}(eV)	$F_{vib}(300K)$(eV)	$F(300K)$(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:

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

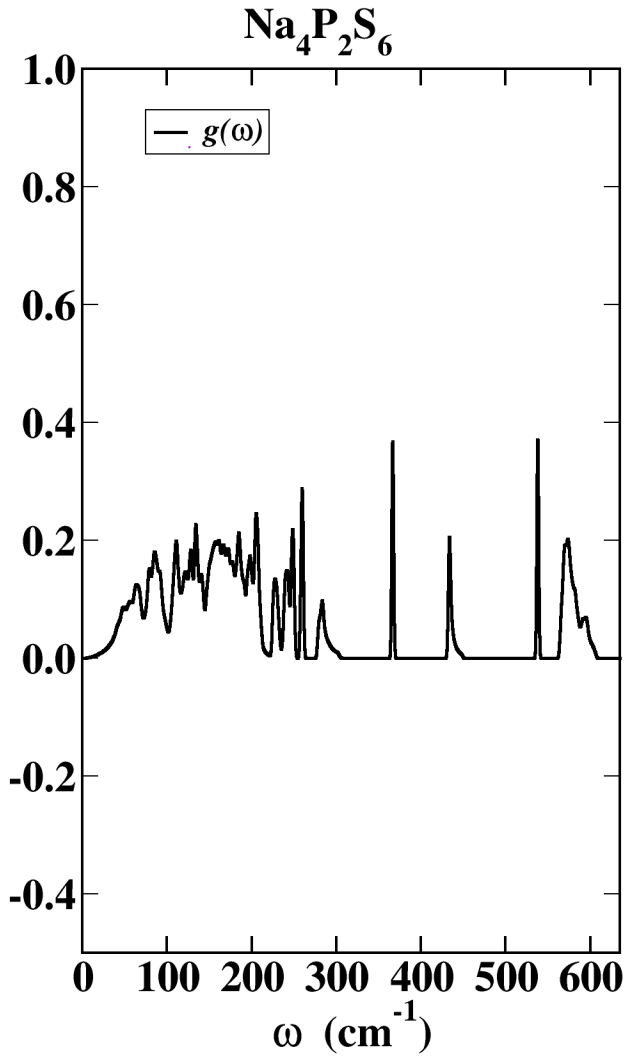
In practice, it is convenient to express frequencies in wavenumbers:

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

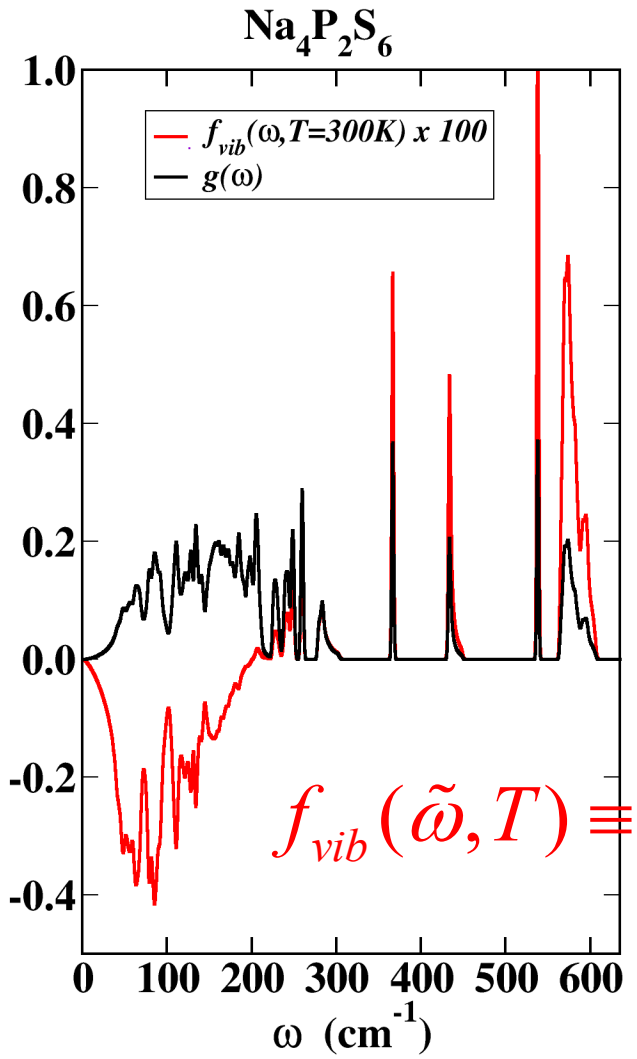
where the weighted phonon DOS factor is

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

Some details of the vibrational stabilization

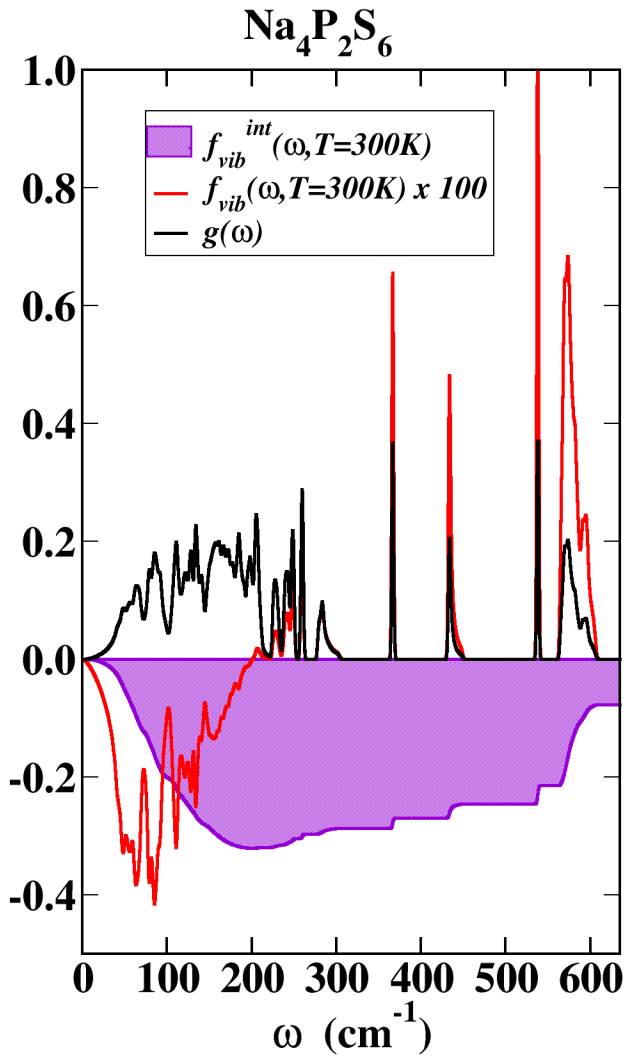


Some details of the vibrational stabilization



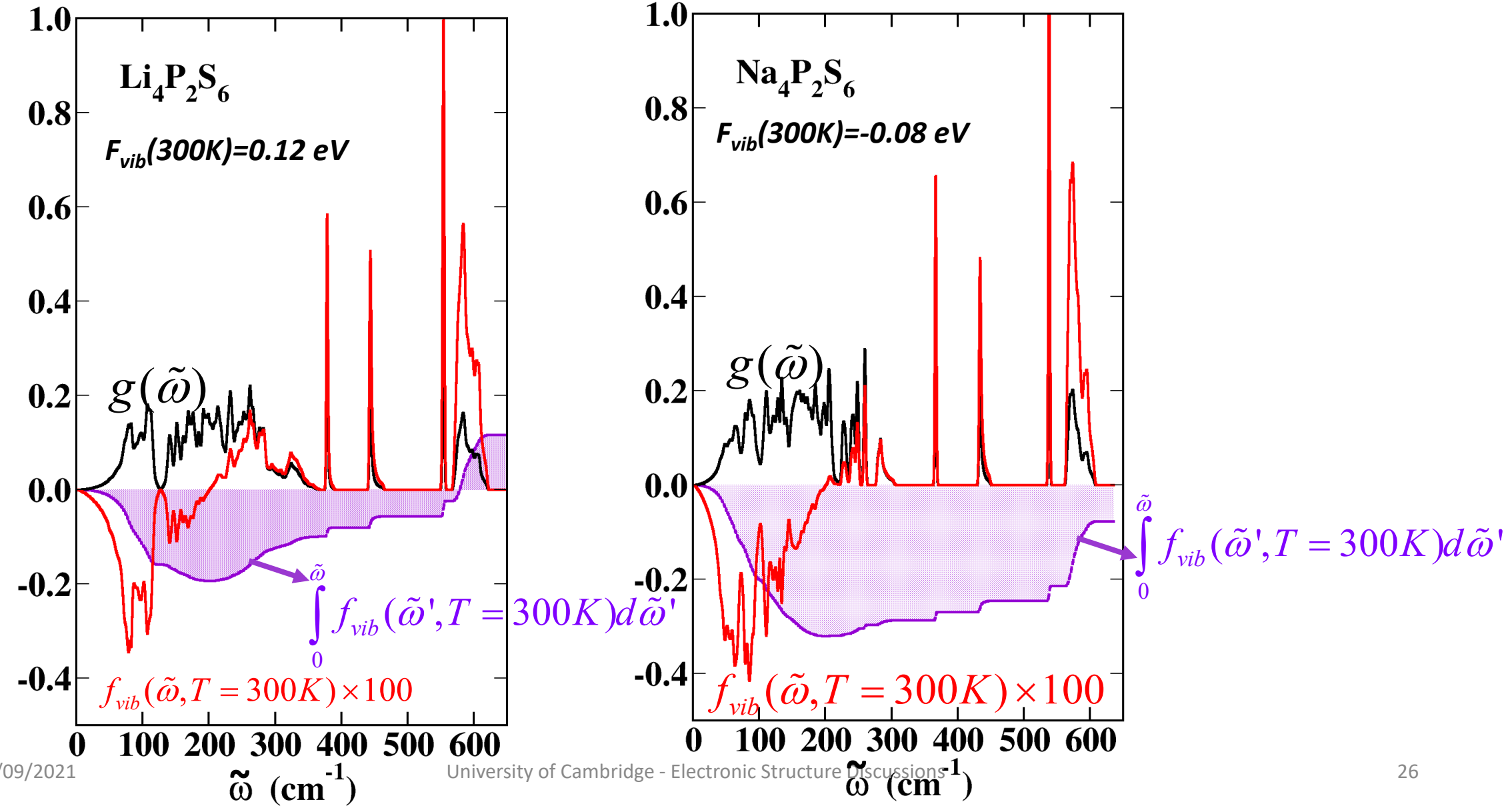
$$f_{vib}(\tilde{\omega},T) \equiv k_B T \ln\left(2\sinh\left(\frac{hc\tilde{\omega}}{2k_B T}\right)\right) g(\tilde{\omega})$$

Some details of the vibrational stabilization

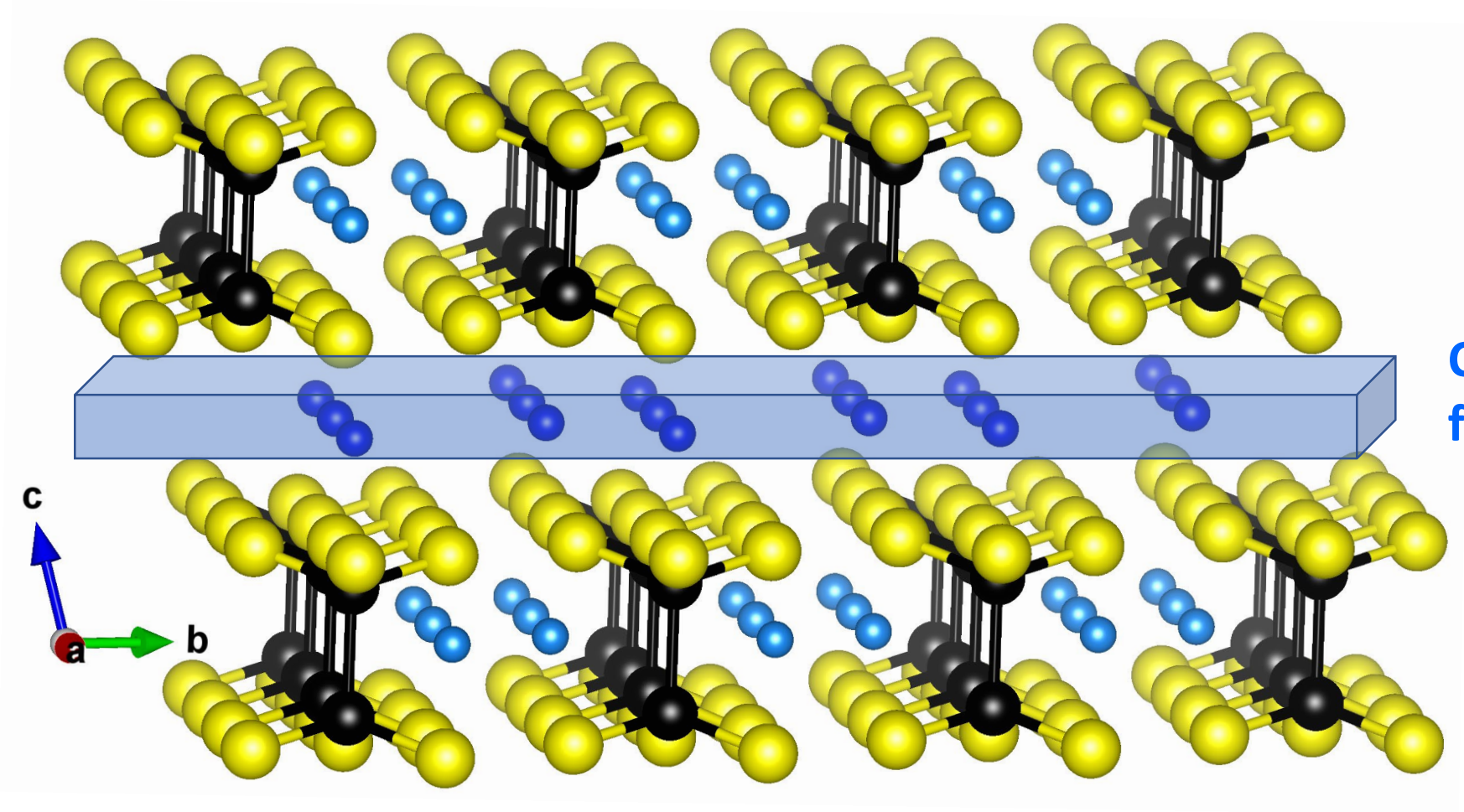


$$\int_0^{\tilde{\omega}} d\tilde{\omega}' f_{vib}(\tilde{\omega}',T)$$

Some details of the vibrational stabilization at T=300K for $Li_4P_2S_6$ and $Na_4P_2S_6$ in C2/m structure



➢ Na ion conductivity of $Na_4P_2S_6$ and $Li_2Na_2P_2S_6$ in the C2/m structure



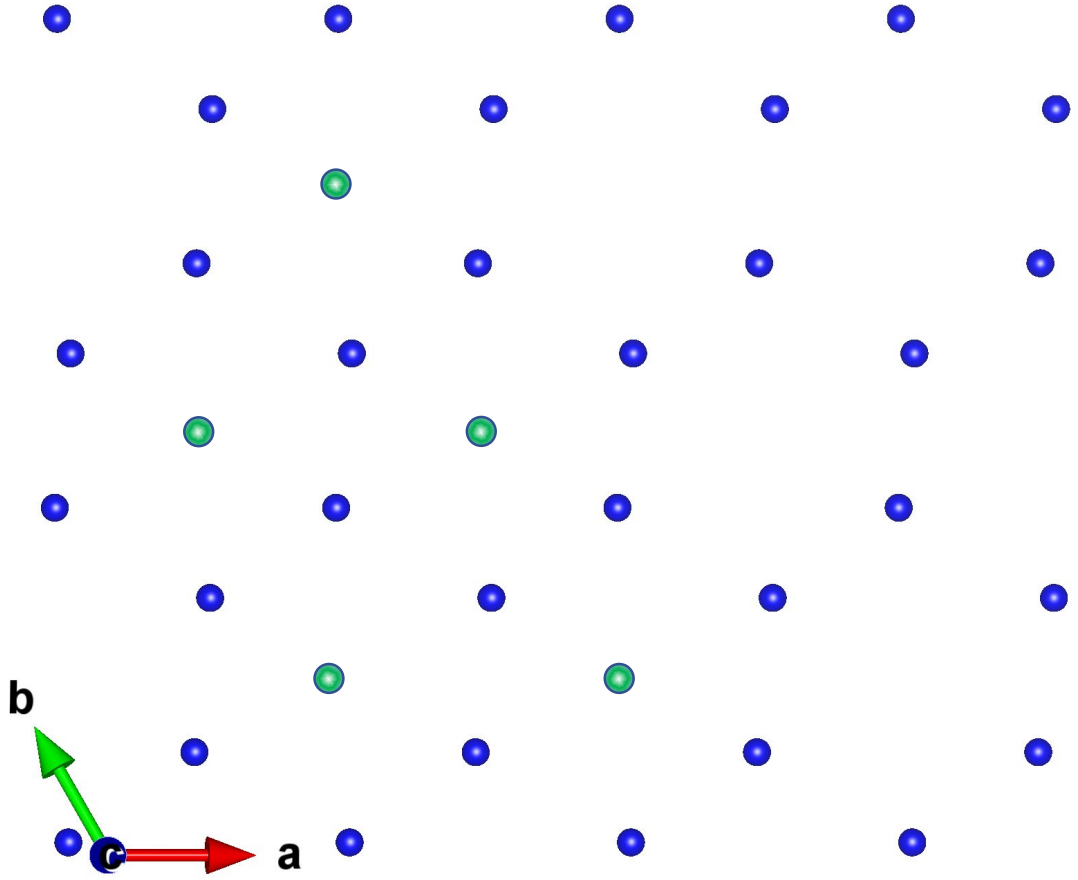
Conducting plane for Na ions

Predicted $Li_2Na_2P_2S_6$ has Li ions at these g sites.

Na ion conductivity of $Na_4P_2S_6$ and $Li_2Na_2P_2S_6$ in the C2/m structure

View of mobile Na ion plane (h plane)

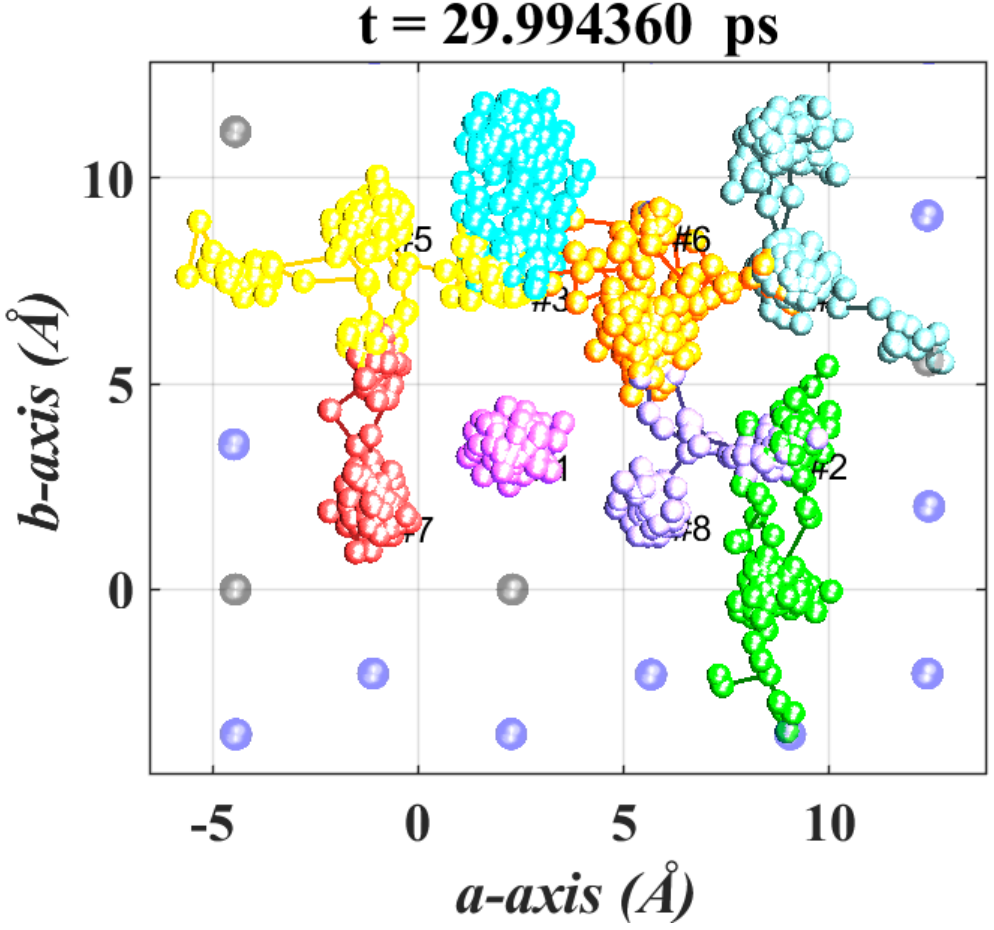
- **host Na site**
- **interstitial Na site**



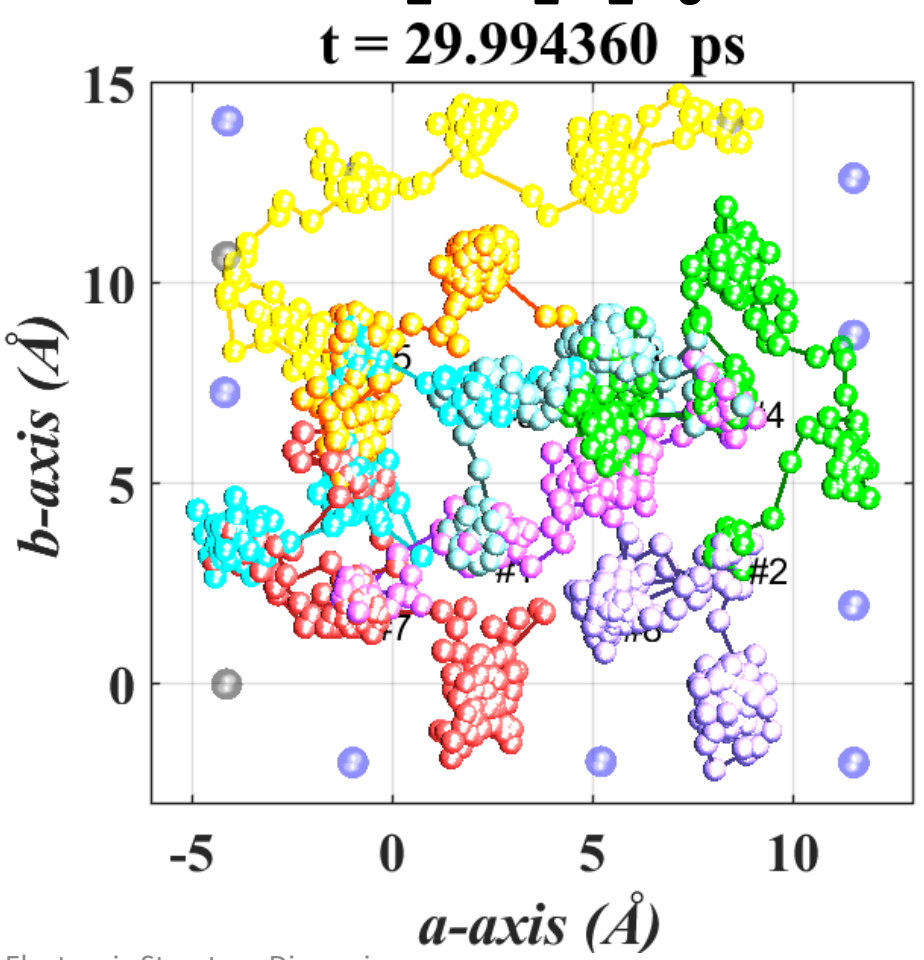
Computer modeling of mechanisms of ionic conductivity; comparing $Na_4P_2S_6$ and $Li_2Na_2P_2S_6$ --

MD simulations at <T>=1000K; Na ion motion in *h* planes --

$Na_4P_2S_6$



$Li_2Na_2P_2S_6$



Ionic conductivity

Some equations

Self ("tracer") diffusion as a function of temperature (T) of MD trajectories:

$$D_{tr}(T) = \frac{1}{2dN_{\mathrm{Na}}} \lim_{t \to \infty} \left(\frac{1}{t} \left\langle \sum_{i=1}^{N_{\mathrm{Na}}} \left| \mathbf{r}_i(t) - \mathbf{r}_i(0) \right|^2 \right\rangle_T \right)$$

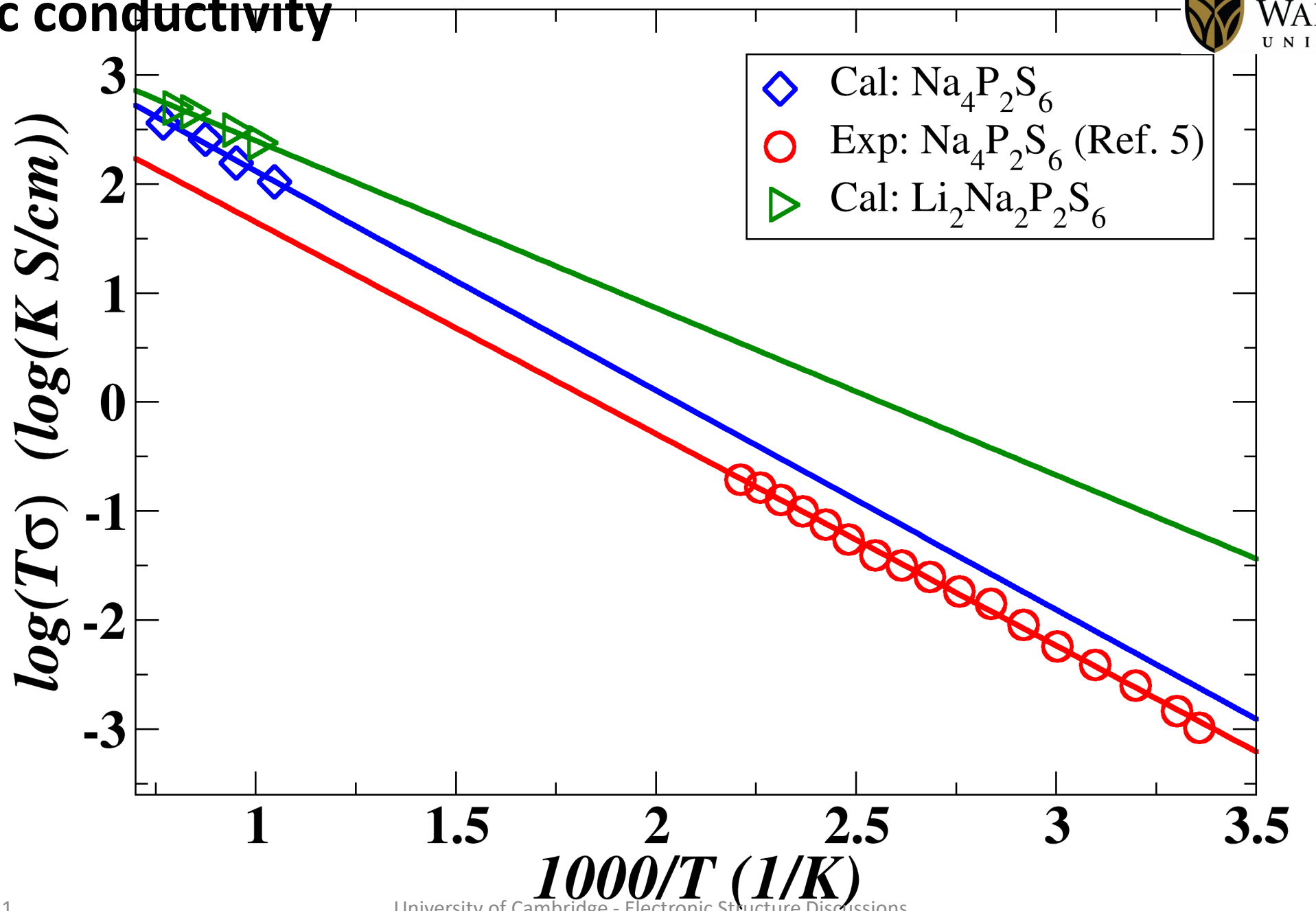
$$\sigma(T) = \frac{N_{\mathrm{Na}}}{V} \frac{e^2 D_{tr}(T)}{k_B T H_r}$$

$N_{\mathrm{Na}} \equiv$ number of mobile Na ions

$V \equiv$ volume

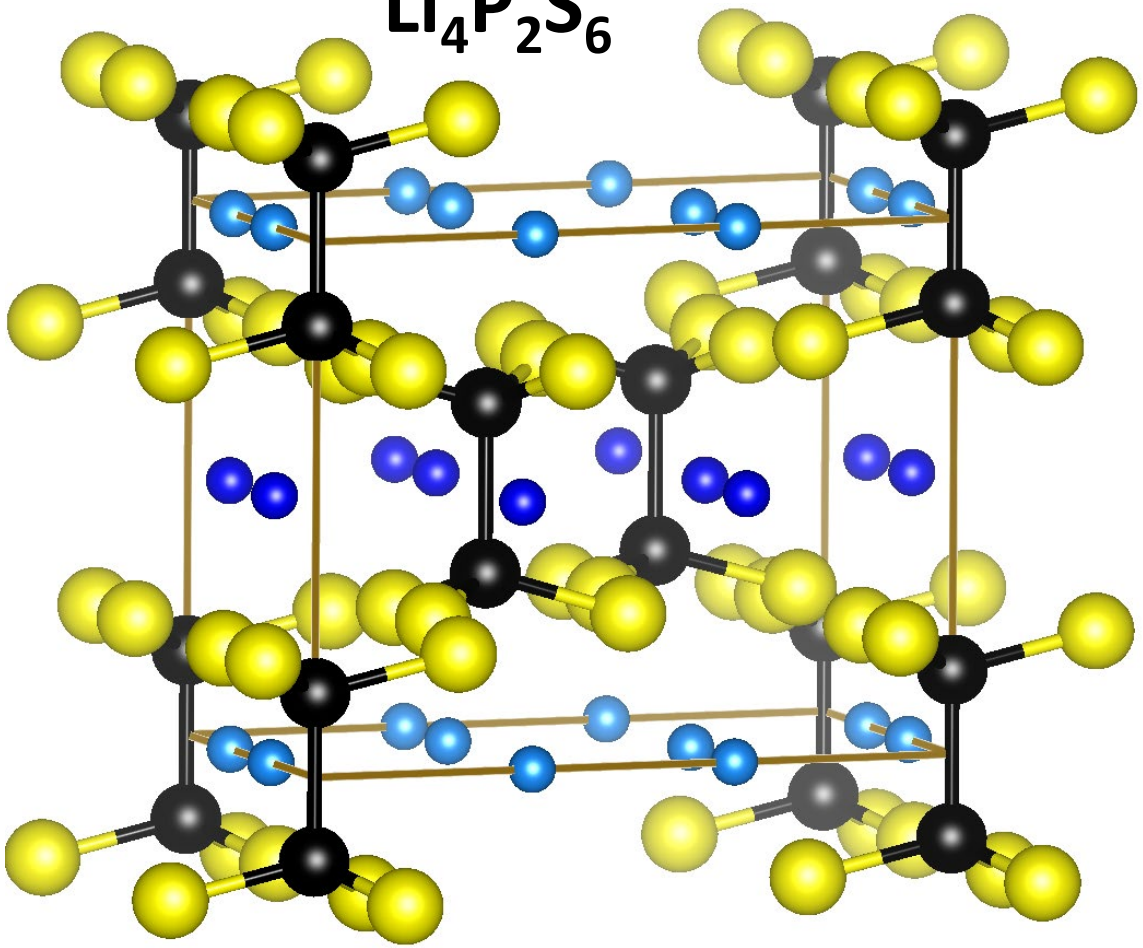
$H_r \equiv$ Haven ratio (estimated as 1)

Ionic conductivity



Summary

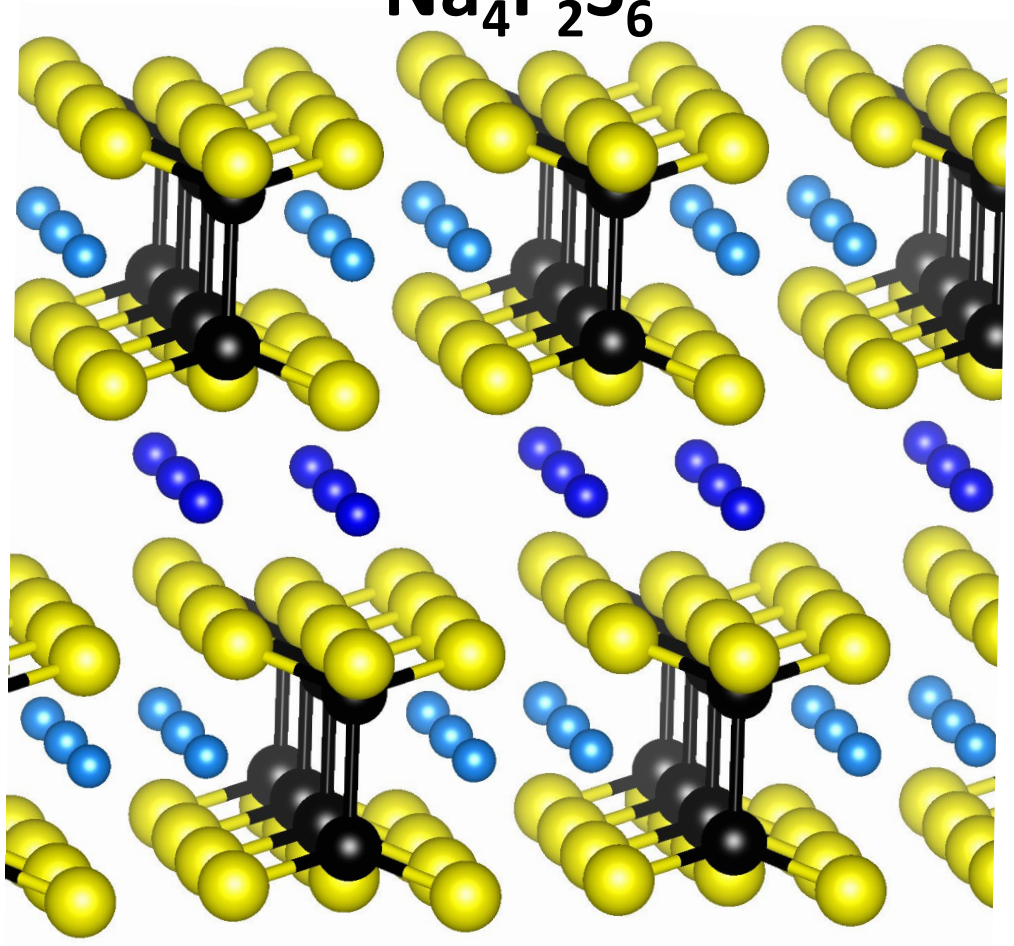
$Li_4P_2S_6$



Poor ionic conductor

Structure stabilized by static lattice energy

$Na_4P_2S_6$



Good ionic conductor within plane

Structure stabilized by vibrational energy

➢ More thoughts

- DFT with PBEsol+harmonic phonon simulations agree with the experimental structures of $Na_4P_2S_6$ (space group *C2/m* found by Kuhn and Hood) and $Li_4P_2S_6$ (space group $P\bar{3}m1$, close to that found by Neuberger).
- For $Na_4P_2S_6$ 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 $Na_4P_2S_6$ may be a viable solid electrolyte.
- Simulations predict $Li_2Na_2P_2S_6$ to crystallize with the *C2/m* structure and to be stable relative to $Na_4P_2S_6$+2Li-2Na. The mixed alkali electrolyte is predicted to substantially enhance Na ion conductivity.
- In addition to experimental verification (or otherwise) of the predictions for $Li_2Na_2P_2S_6$, further MD simulations for both $Na_4P_2S_6$ and $Li_2Na_2P_2S_6$ will help us better understand Na ion conductivity mechanisms.