First principles simulations of idealized known and unknown crystalline materials

Natalie Holzwarth, Department of Physics WFU

Reported work supported by NSF Grant DMR-1507942 and earlier NSF grants.

Collaborators for reported work include Yan Li (WFU), William C. Kerr (WFU), Zachary D. Hood (soon to be at ANL), Keerthi Senevirathne (now at FAMU), Cynthia S. Day (WFU), Michael D. Gross (WFU), Abdessadek Lachgar (WFU), Yaojun Du (now in China)

Outline --

Main question: What is the most productive way for computational/theoretical scientists to collaborate with their experimental colleagues?

Argument for "first principles" perspective: Control of physical and numerical accuracy extended by extrapolation to properties measured at the macroscopic scale

Example studies: Li_2PO_2N; $Li_4P_2S_6$ and $Na_4P_2S_6$

Main question: What is the most productive way for computational/theoretical scientists to collaborate with their experimental colleagues?

- Human factors; interdisciplinary conflicts and misinterpretations of terminologies

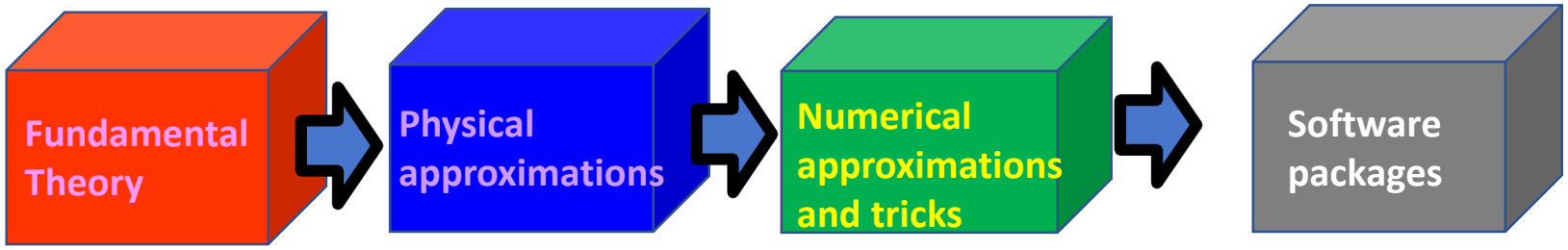
- State of the art of computational and experimental methods

  What is accurately calculated is not necessarily accurately measurable.

  What is accurately measured is not necessarily accurately calculatable.

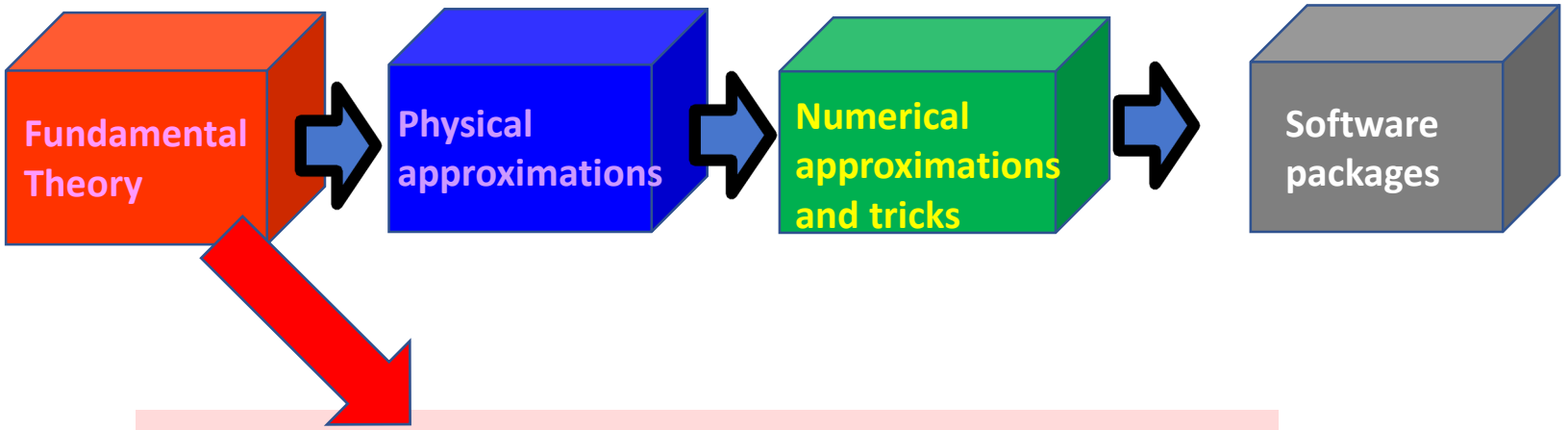
Argument for “first principles” perspective:

Perspectives on Materials Simulations



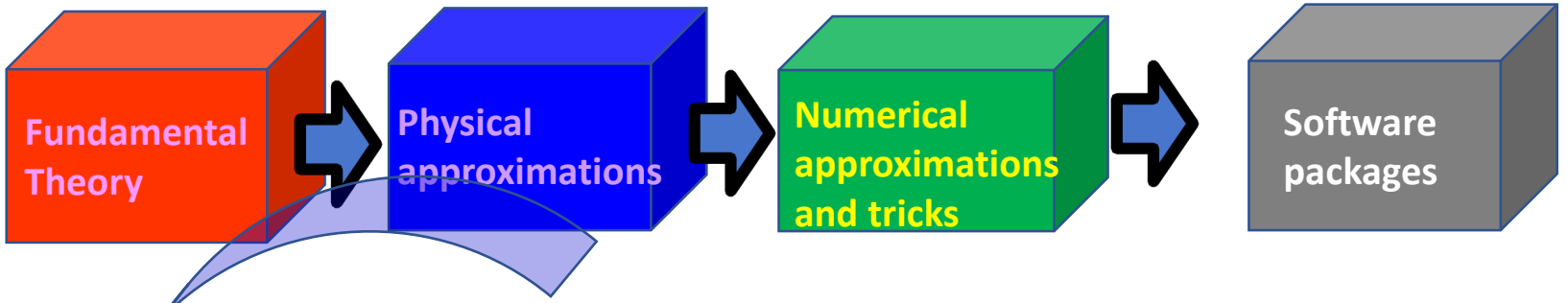
It is important to know what is inside the box!

Argument for “first principles” perspective:



Quantum mechanics and electrodynamics as it applies to many particle systems

Argument for "first principles" perspective:

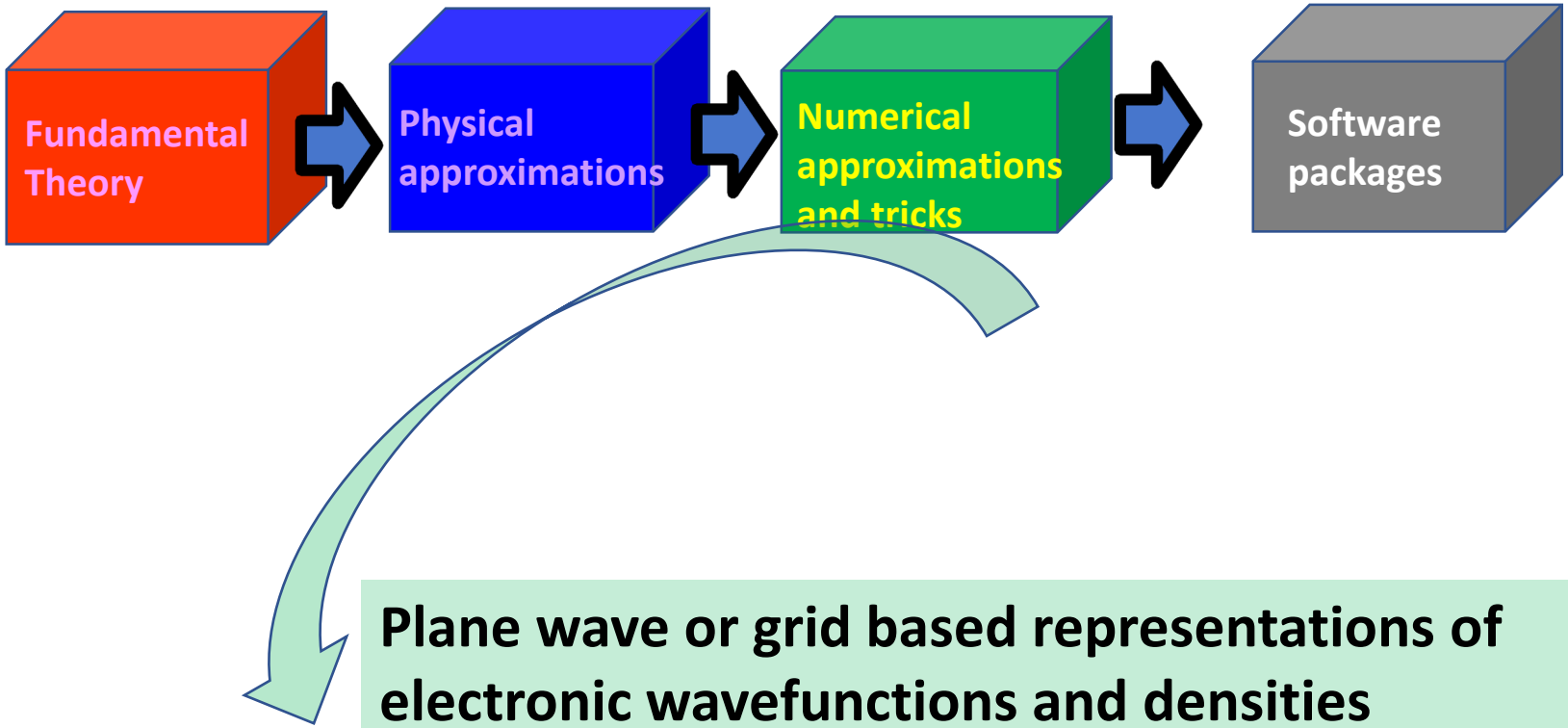


Born-Oppenheimer approximation [*Born & Huang, Dynamical Theory of Crystal Lattices , Oxford (1954)*]: Nuclear motions treated classically while electronic motions treated quantum mechanically because $M_N >> m_e$

Density functional theory [*Kohn, Hohenberg, Sham, PR 136, B864 (1964), PR 140, A1133 (1965)*]: Many electron system approximated by single particle approximation using a self-consistent mean field.

Frozen core approximation[*von Barth, Gelatt, PRB 21, 2222 (1980)*]: Core electrons assumed to be "frozen" at their atomic values; valence electrons evaluated variationally.

Argument for “first principles” perspective:



Plane wave or grid based representations of electronic wavefunctions and densities

Pseudopotential formulations

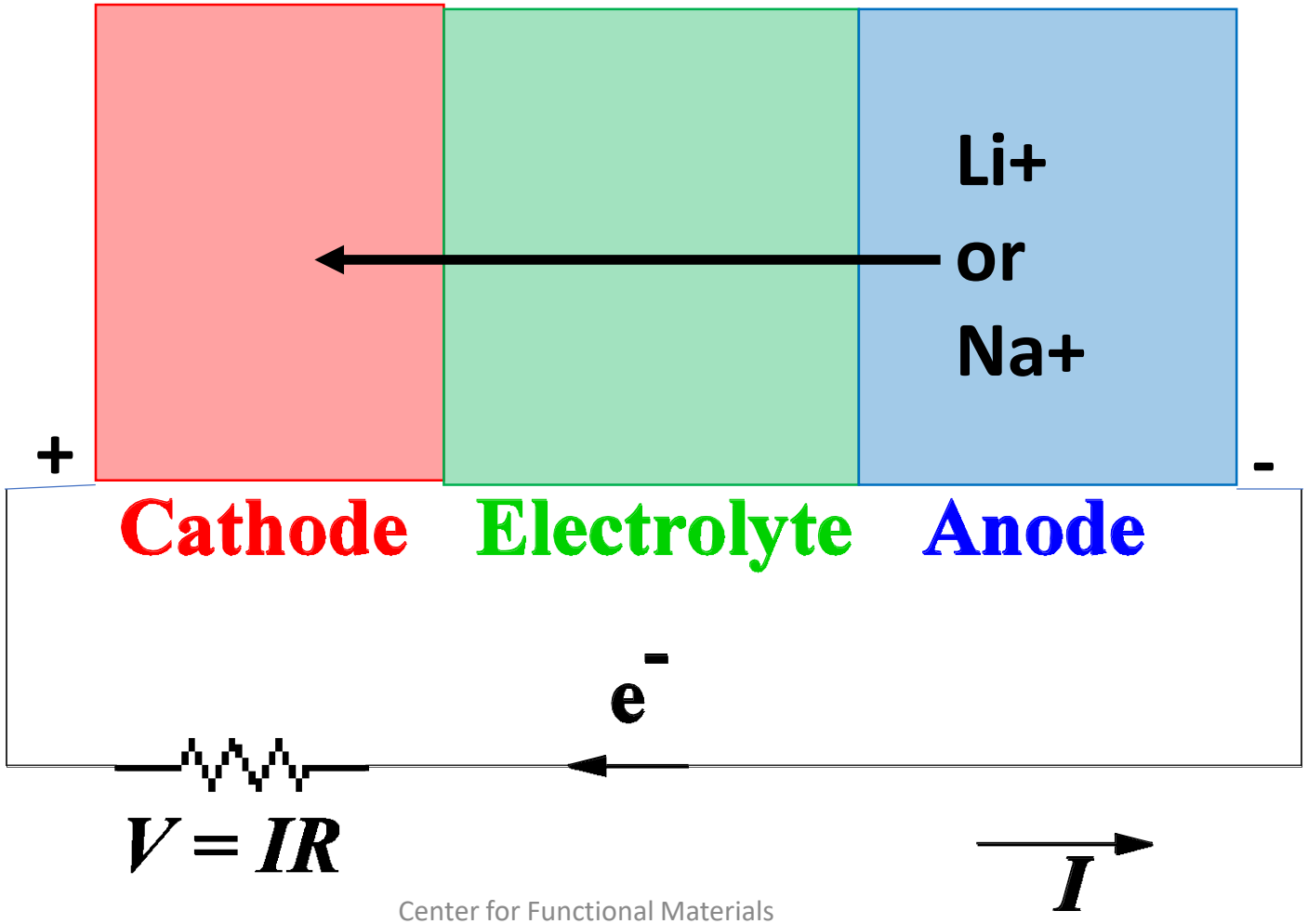
Classical or harmonic phonon approximation for nuclear motion

Example studies:

- **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 inside the battery and forcing them through the external circuit.



Example studies: (continued)

- **The case for all solid state batteries**

Development of the LiPON thin film

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

Example studies: (continued)

Validation of the LiPON thin film

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**

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

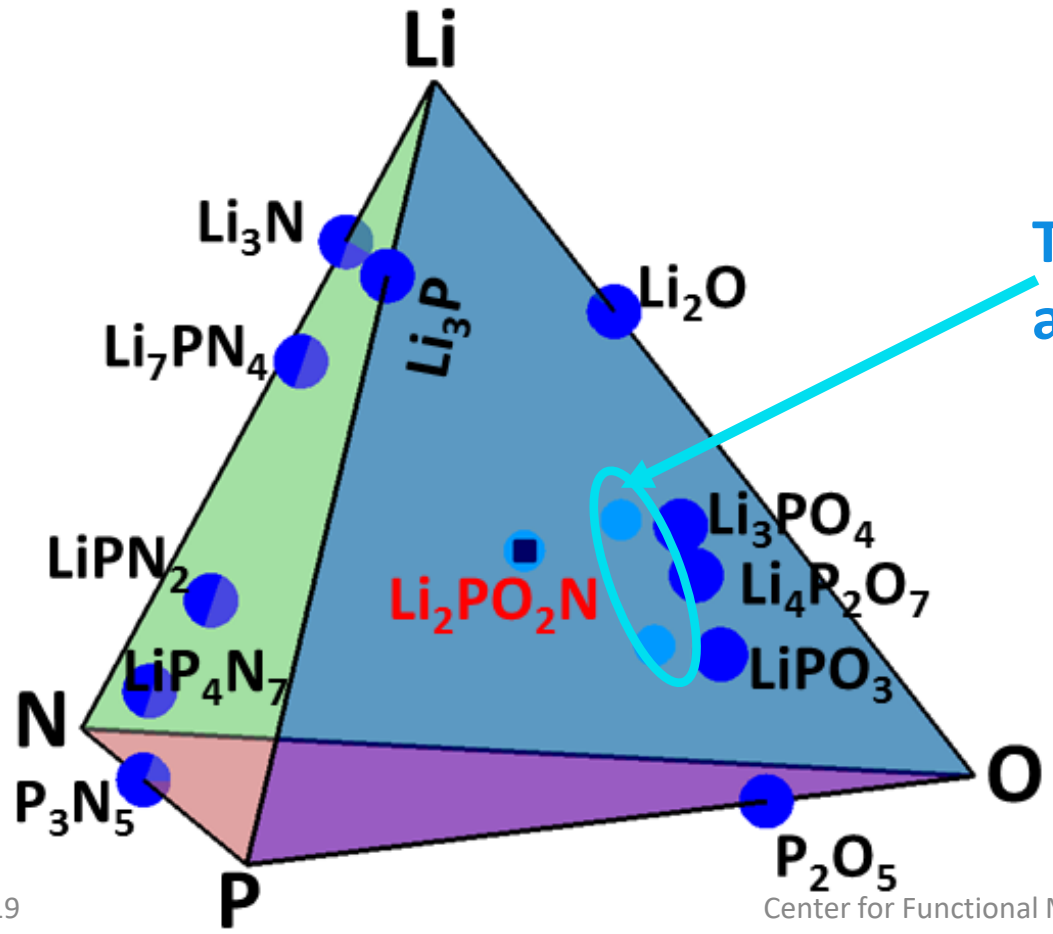
Demonstrated for $LiNi_{0.5}Mn_{1.5}O_4$/LiPON/Li

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

*1 cycle per day for 27 years

Example studies: (continued)

Systematic study of LiPON materials – $Li_xPO_yN_z$ –
(Yaojun A. Du and N. A. W. Holzwarth, Phys. Rev. B 81, 184106 (2010))



Typical composition of amorphous LiPON films

Example studies: (continued)

Experimentally known structure

$LiPO_3$

Computationally predicted structure

s_1-Li_2PO_2N

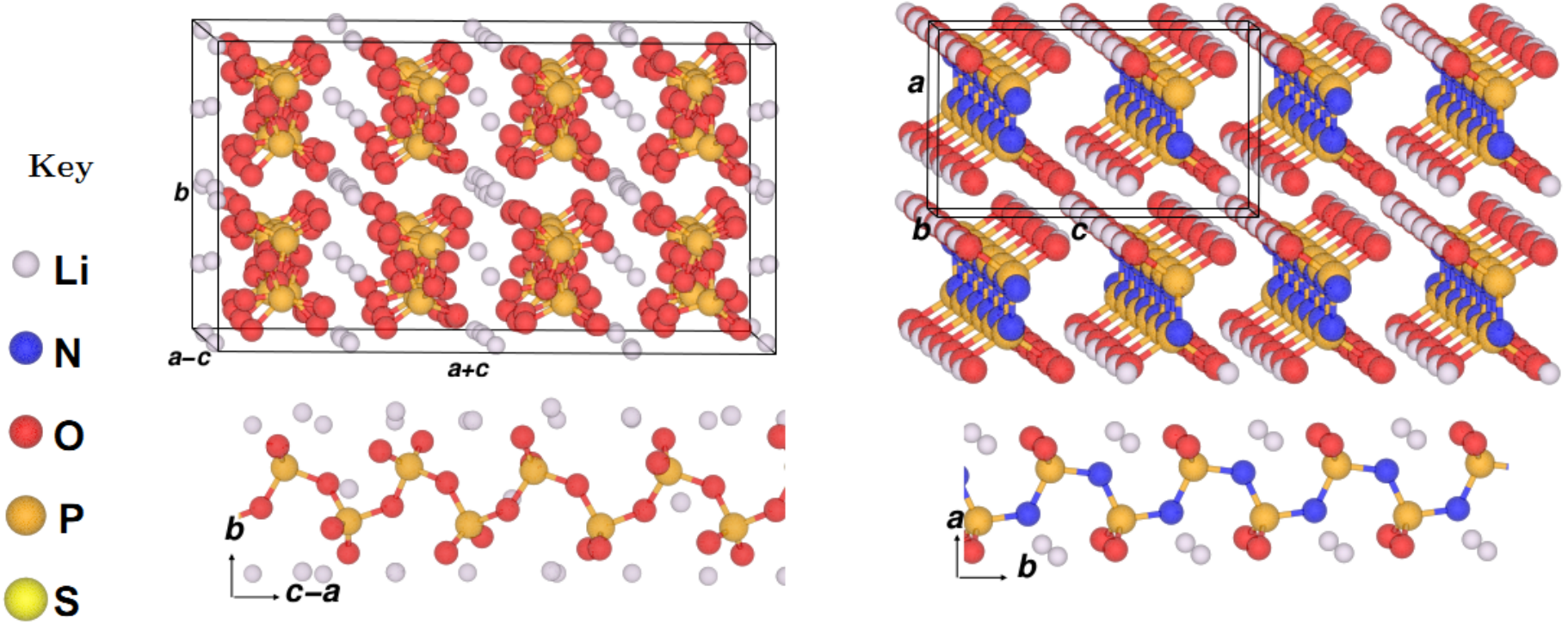
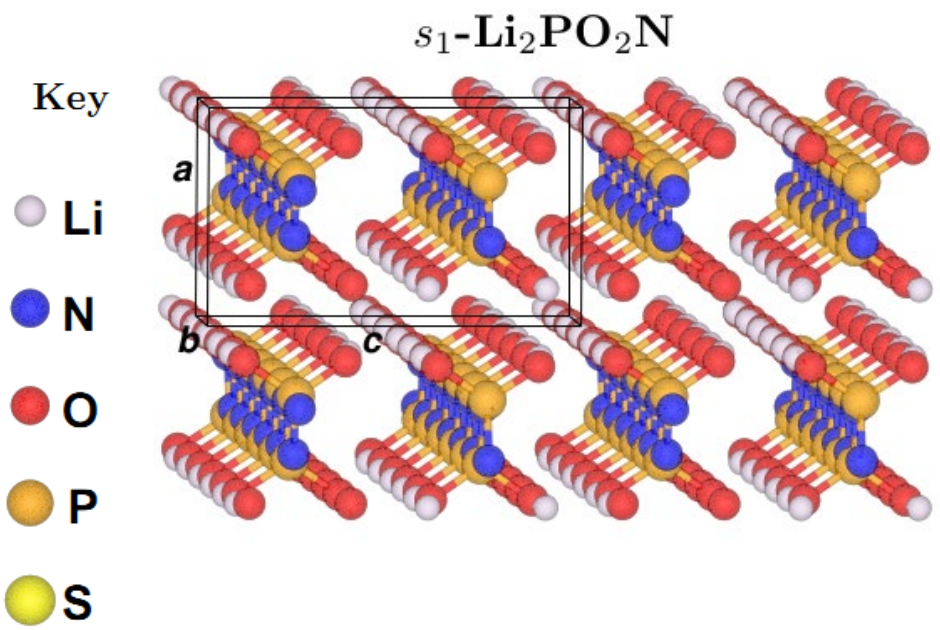


Fig. 7. Ball and stick diagrams for $LiPO_3$ in the $P2/c$ structure (20 formula units per unit cell) and $s1$-Li_2PO_2N in the $Pbcm$ structure (4 formula units per unit cell) from the calculated results. For each crystal diagram, a view of a horizontal chain axis is also provided for a single phosphate or phospho-nitride chain.

Example studies: (continued)

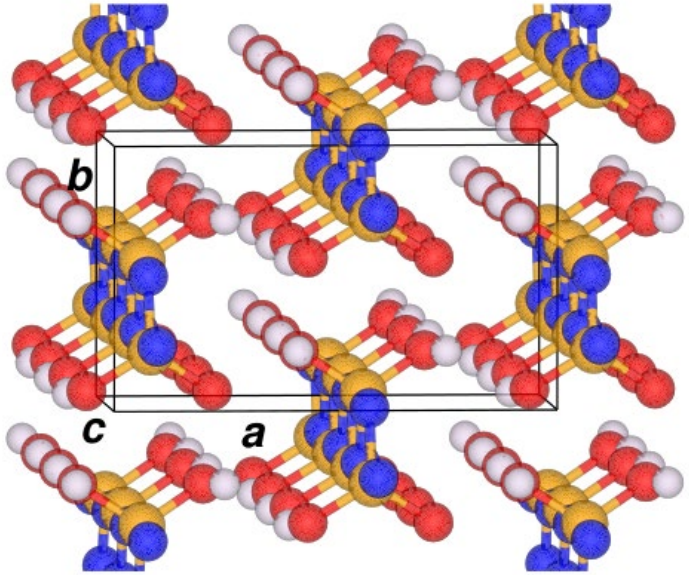
Computationally predicted structure



Pbcm

Experimentally realized structure

***SD*-Li_2PO_2N**



$Cmc2_1$

Example studies: (continued)

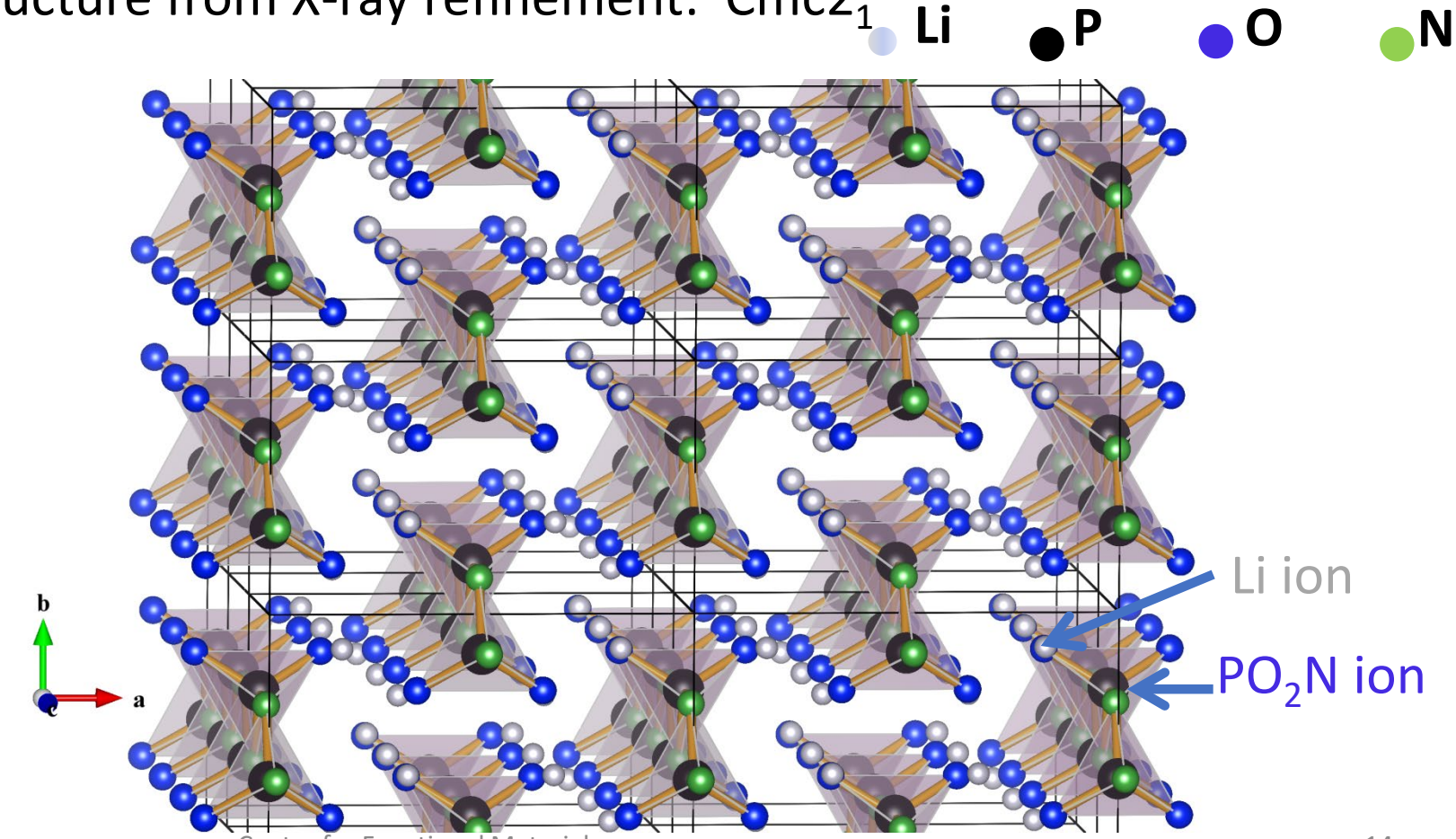
Synthesis of Li_2PO_2N by Keerthi Senevirathne, Cynthia Day, Michael Gross, and Abdessadek Lachgar

Solid State Ionics **233**, 95-101 (2013)

Method: High temperature solid state synthesis based on reaction

$$Li_2O + \tfrac{1}{5}P_2O_5 + \tfrac{1}{5}P_3N_5 \rightarrow Li_2PO_2N$$

Structure from X-ray refinement: $Cmc2_1$



Was this a success?

- Not a good ionic conductor; not a good model for glassy LiPON
- Paper cited 59 times
- Found in some LiPON processing as a stable by-product

Example studies: (continued)

- **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

Example studies: (continued)

Minami et al. 2010, continued

$Li_4P_2S_6$ →

$Li_7P_3S_{11}$ →

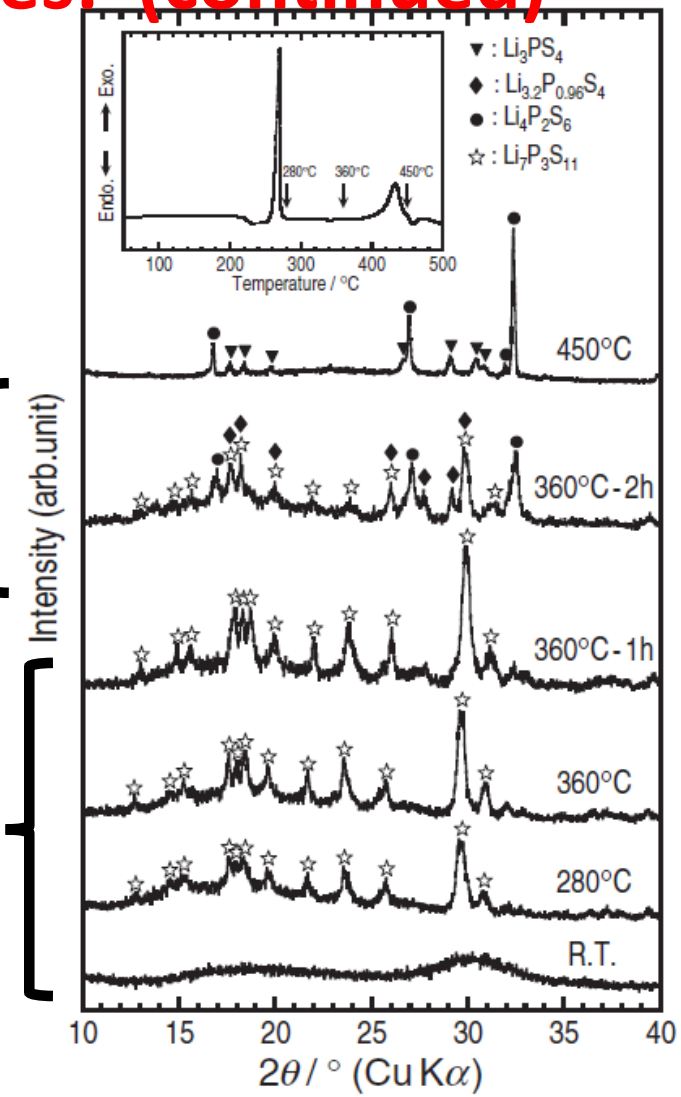


Fig. 1. XRD patterns of the glass and crystallized samples prepared from the glass by heat treatment at various temperatures and holding periods of time.

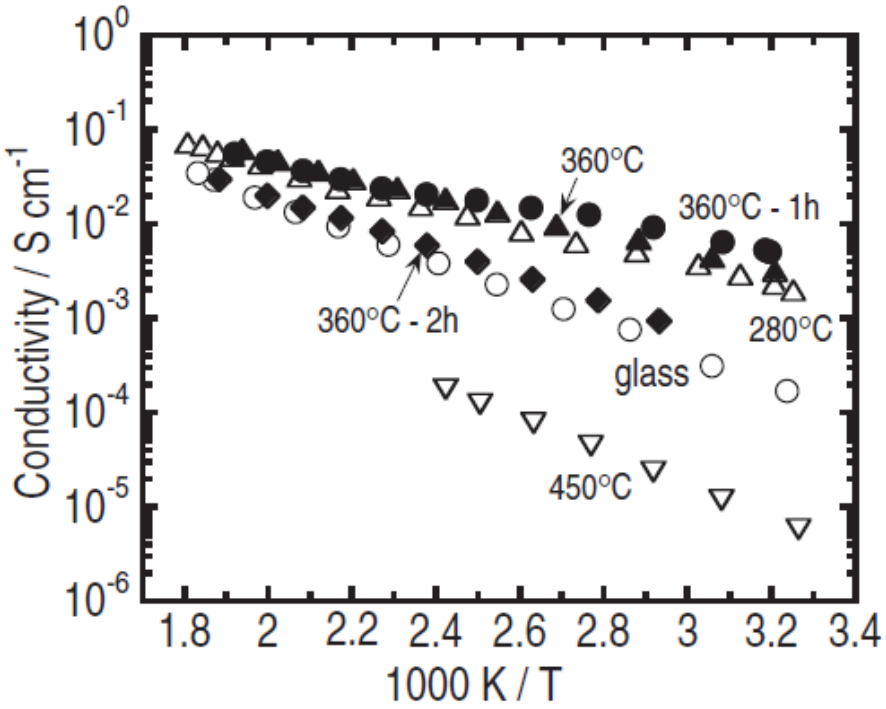


Fig. 2. Temperature dependence of conductivities for the crystallized samples prepared from the glass by heat treatment at various temperatures and holding periods of time.

Example studies: (continued)

Previously determined structure of $Li_4P_2S_6$

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)

Example studies: (continued)

Solid State Ionics 284 (2016) 61–70

Contents lists available at ScienceDirect

Solid State Ionics

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

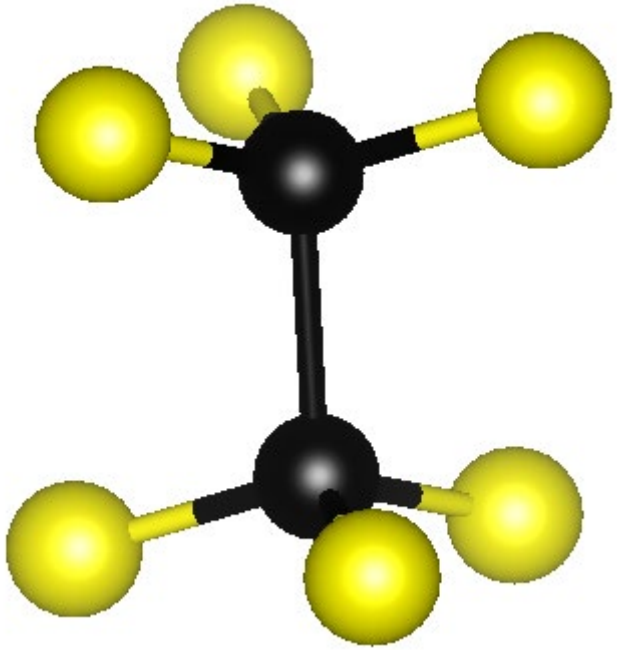
Structural and electrolyte properties of $Li_4P_2S_6$

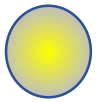
Zachary D. Hood [a,1], Cameron Kates [b,2], Melanie Kirkham [c], Shiba Adhikari [d], Chengdu Liang [a,3], N.A.W. Holzwarth [b,*]

[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

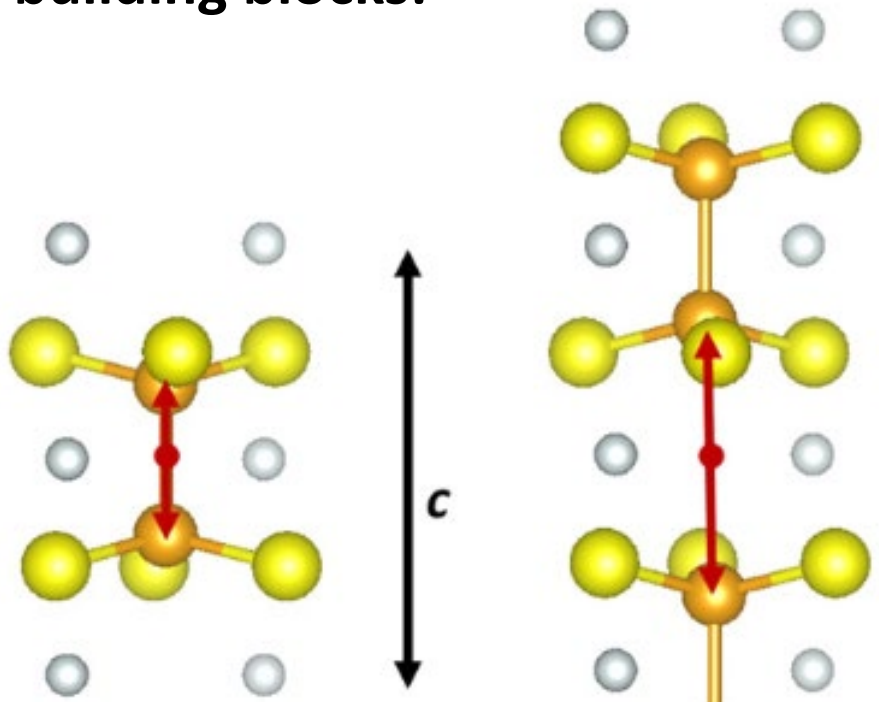
Example studies: (continued)

P_2S_6 building blocks:



S  P  or 

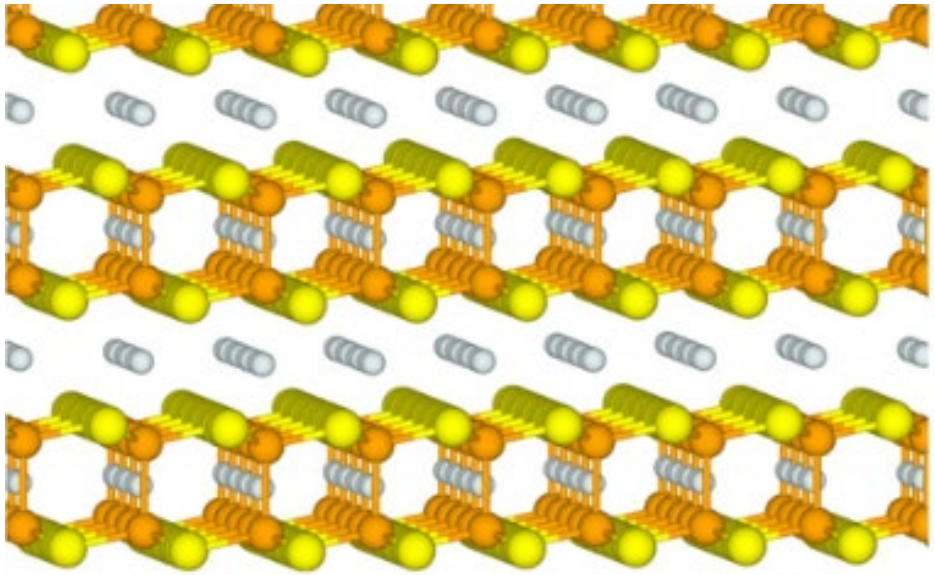
Mercier's disordered structure can be described in terms of the alternative stacking patterns of the building blocks:



$$P_{\uparrow} \equiv \pm z_P c \qquad P_{\downarrow} \equiv \pm\left(\frac{1}{2} - z_P\right)c$$

Example studies: (continued)

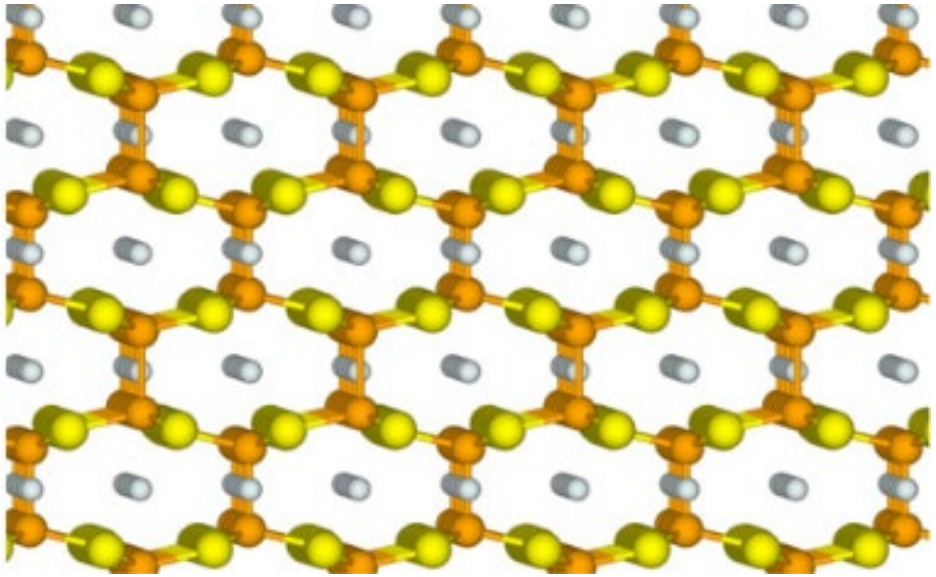
Possible stacking structures



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 stacking according to simulations

Example studies: (continued)

Dalton Transactions

PAPER

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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]

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

Example studies: (continued)

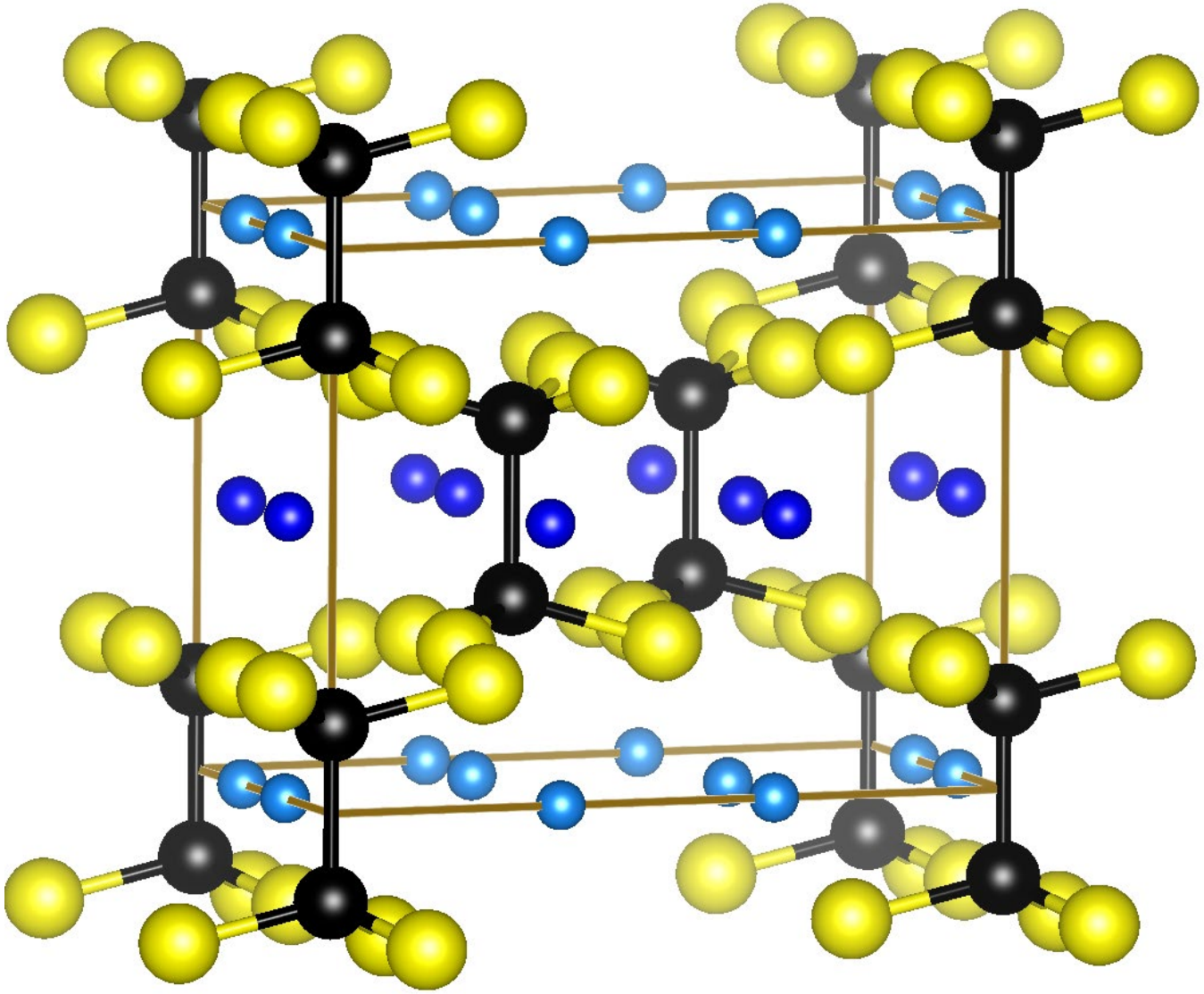
Neuberger structure

67% P↑ 33% P↓

Space group
P321 → P$\bar{3}$m1

Li

S **P**



Example studies: (continued)

DOI: 10.1002/zaac.201300575

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

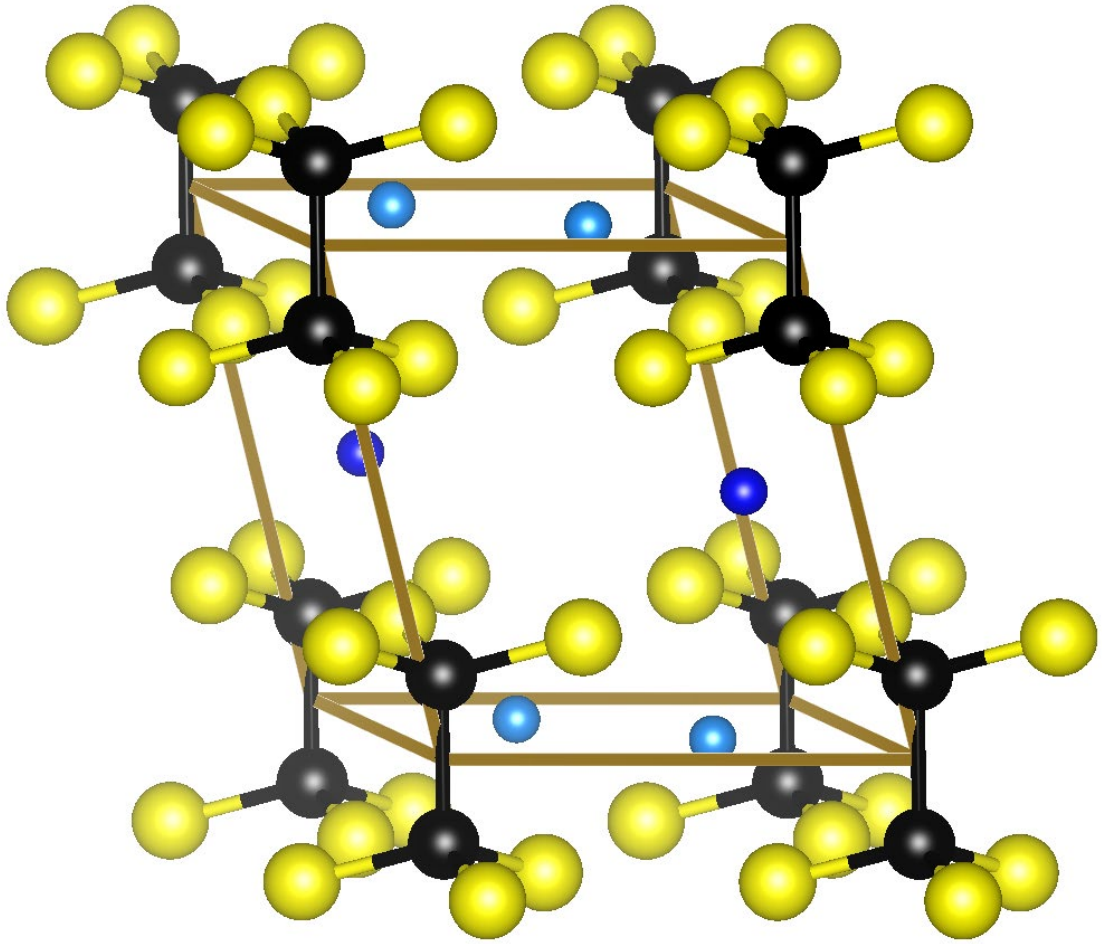
Alexander Kuhn,[a] Roland Eger,[a] Jürgen Nuss,[a] and Bettina V. Lotsch*[a,b]

$Na_4P_2S_6$ 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.

Example studies: (continued)

Primitive cell of the Kuhn structure

Space group *C2/m*



Na

S **P**

Example studies: (continued)

Can the observed structural stability patterns be understood from first principles?

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

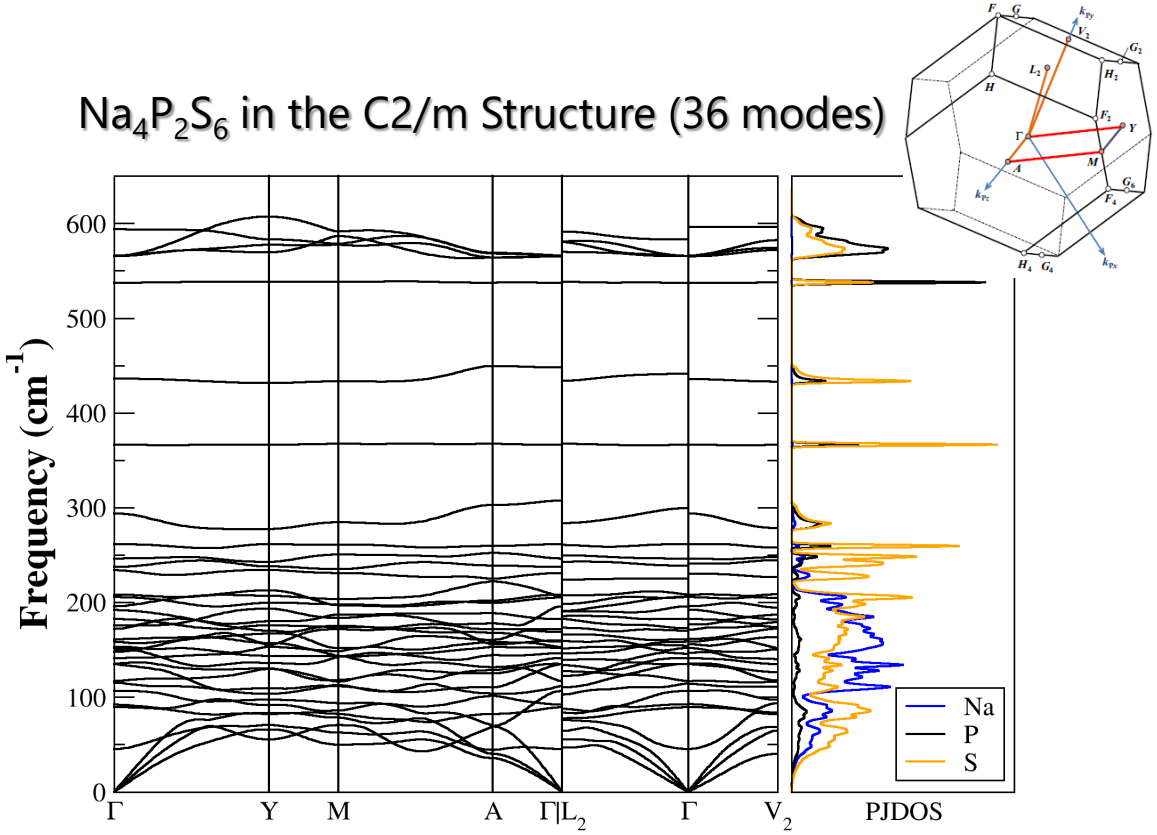
$$F_{vib}(T) = k_B T \int_0^\infty d\omega \ \ln\left(2\sinh\left(\frac{\hbar\omega}{2k_B T}\right)\right) g(\omega)$$

Phonon DOS computed from DFPT

Example studies: (continued)

Phonon dispersion curves prepared by Yan Li

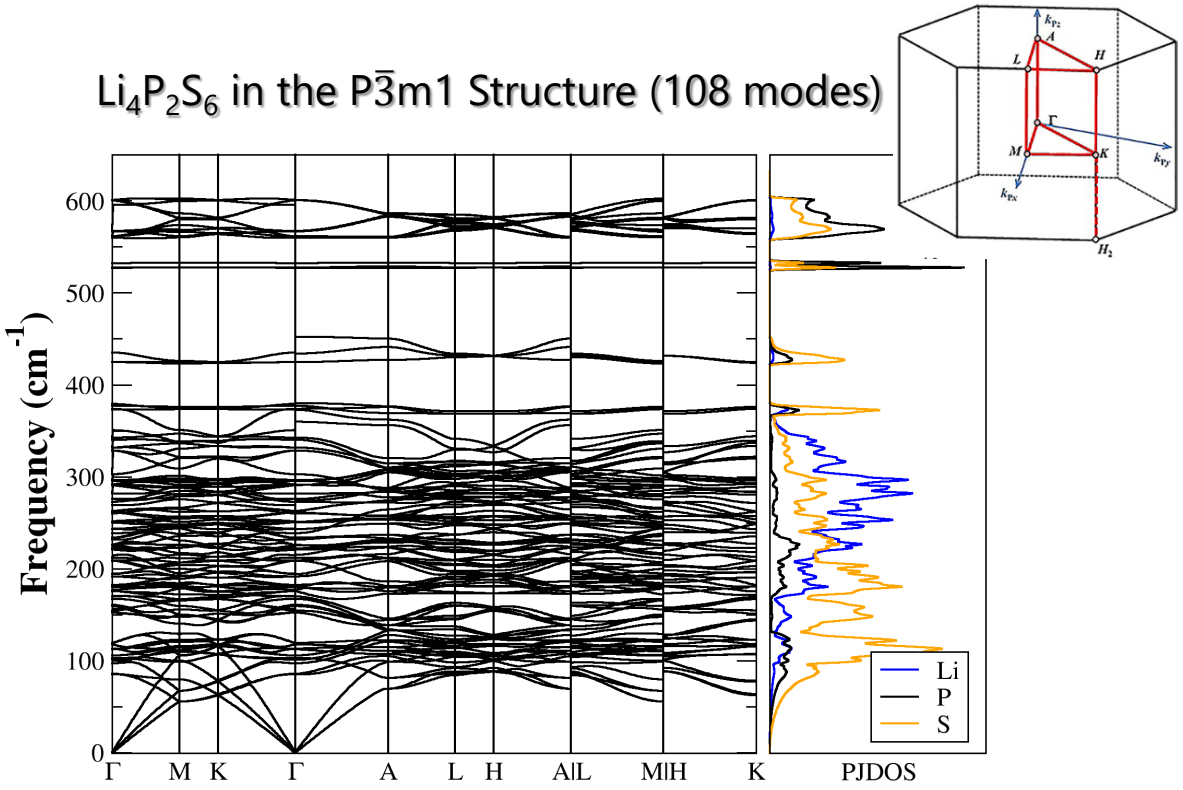
$Na_4P_2S_6$ in the C2/m Structure (36 modes)



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]

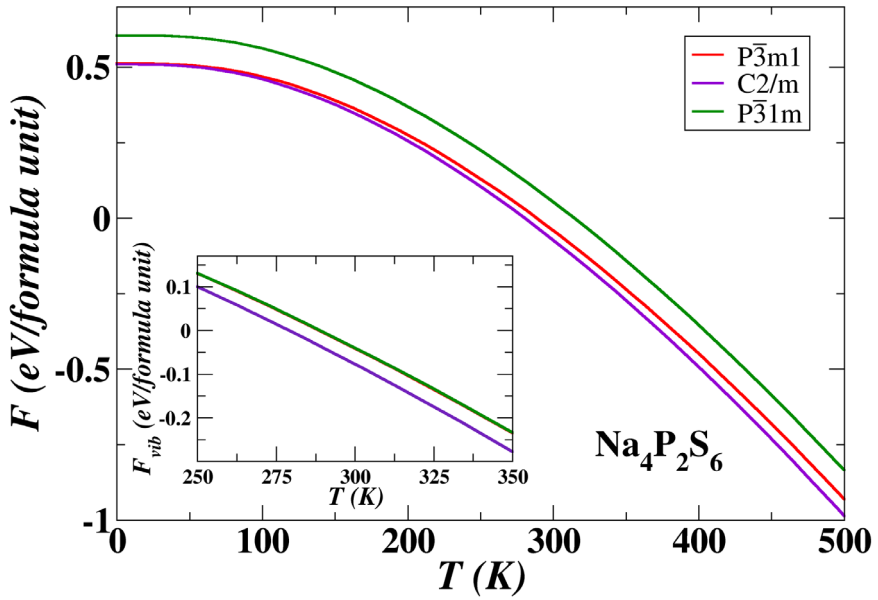
[1]Suggested path: Hinuma et al., *Comp. Mat. Sci.* **128**, 140-184 (2017)

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

Example studies: (continued)

Helmholtz free energy analysis by Yan Li

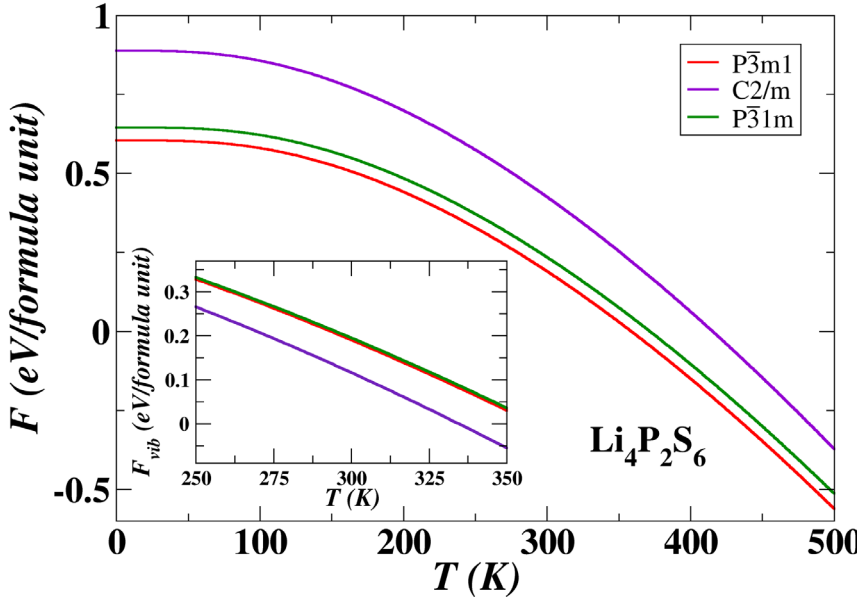
Helmholtz free energy: $F = U_{SL} + F_{vib}$



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)

Example studies: (continued)

Summary of simulation energies

$Na_4P_2S_6$	ΔU_{SL}(eV)	$F_{vib}(300K)$(eV)	$F(300K)$(eV)
Neuberger structure (*P3m1*)	0.00	-0.04	-0.04
Kuhn structure (*C2/m*)	0.00	-0.08	-0.08
Simple hex structure (*P31m*)	0.09	-0.04	0.05
$Li_4P_2S_6$	ΔU_{SL}(eV)	$F_{vib}(300K)$(eV)	$F(300K)$(eV)
Neuberger structure (*P3m1*)	0.00	0.19	0.19
Kuhn structure (*C2/m*)	0.31	0.12	0.43
Simple hex structure (*P31m*)	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.

Example studies: (continued)

➢ 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:

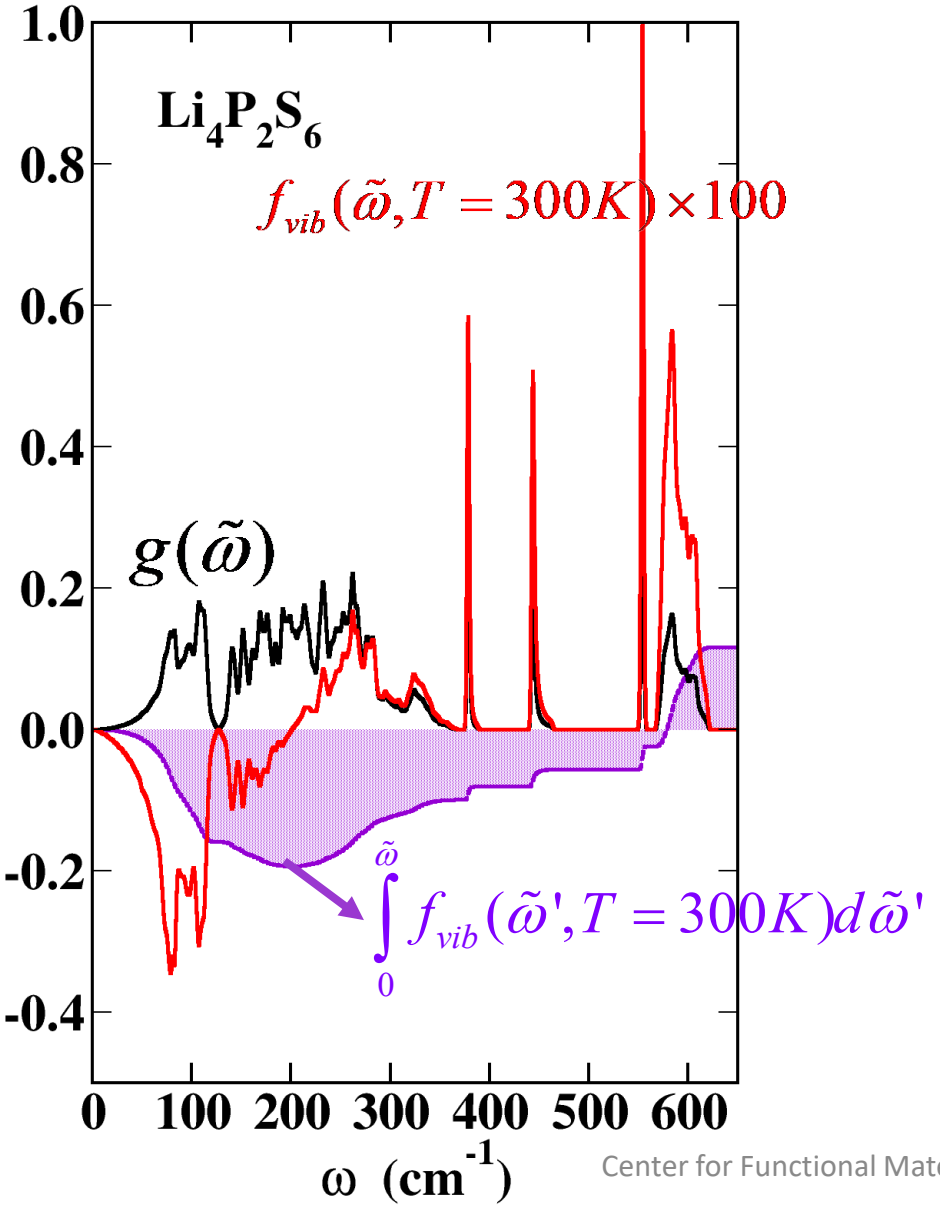
$$\tilde{\omega} = \frac{\omega}{2\pi c} \ (\mathrm{cm}^{-1}) \quad \text{with} \quad F_{vib}(T) = \int_0^\infty d\tilde{\omega} \, f_{vib}(\tilde{\omega}, T)$$

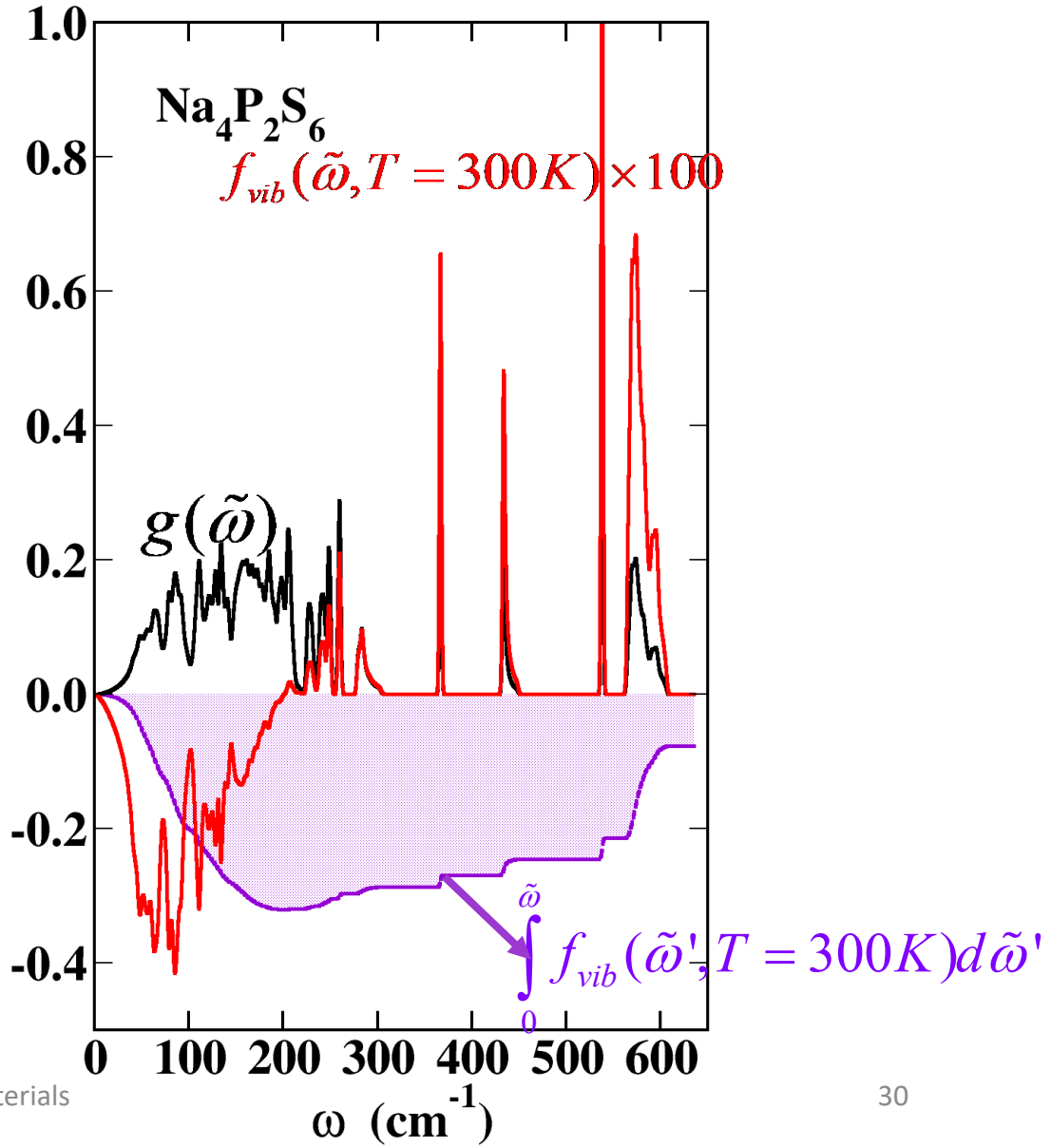
where the weighted phonon DOS factor is

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

Example studies: (continued)

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





Outlook –

- **From the perspective of computational/theoretical scientist, it is highly desirable to collaborate with experimental colleagues**

Short list --

What can be well modeled/calculated from "first principles" –

- **Ordered crystalline materials, electronically insulating in their structural ground state**
- **Computed heats of formation and reactions among the crystalline materials in their ground states**

Corresponding real materials and their experimental measurements –

- **Stoichiometrically well-defined materials; not necessarily single crystals but with significant bulk/surface ratios.**
- **Calorimetry measurements of heats of formation and reactions among the crystalline materials referenced to STP**

Outlook –

- **From the perspective of computational/theoretical scientist, it is highly desirable to collaborate with experimental colleagues**

Extensions beyond simple first principles calculations

- Metallic materials; ➔ may need to consider electronic correlation effects
- Isolated defects in crystalline materials; ➔loss of periodicity may need some numerical tricks
- Crystalline materials with partial disorder; ➔need to develop sampling techniques in order to average over likely configurations of sample
- Materials in electronically excited states; ➔ additional levels of theory/computation
- Many others ---