Modeling Crystalline Electrolytes: $Li_7P_3S_{11}$ and Analogous Phosphates

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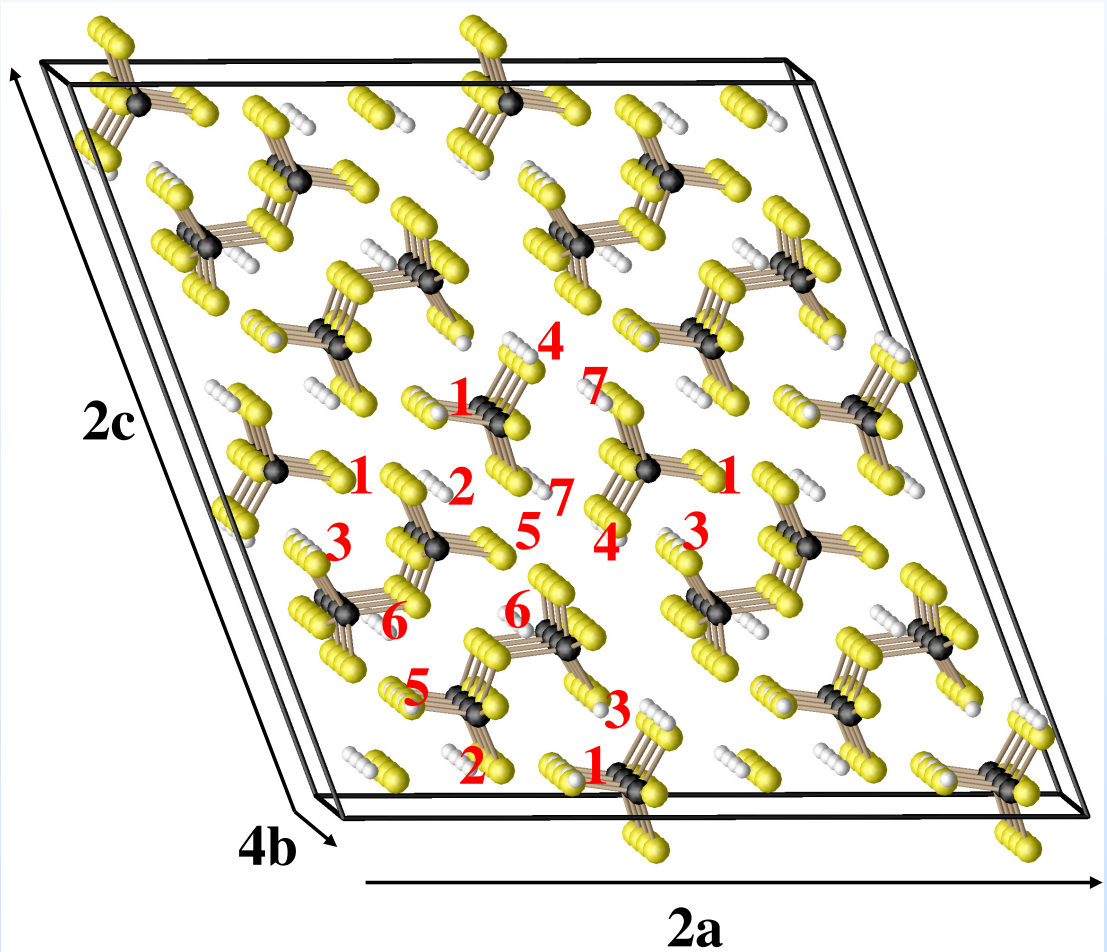
Why Study Thiophosphate Solid Electrolytes

- Many solid electrolytes have safety advantages over traditional organic liquid electrolytes
- Electrochemical stability window for solids allows new battery chemistries
- Lithium thiophosphates have high conductivities relative to LiPON and many other solid electrolyte materials
- Conductivity increase associated with crystallization

$Li_7P_3S_{11}$



- 42 atoms (2 formula units)/unit cell
- Triclinic ($P\bar{1}$ symmetry)
- Mixture of PS_4 tetrahedra and P_2S_7 dimers
- No fractional occupancy

Summary of Experimental Findings

- Synthesis
  - Heated glass precursor
  - Water quenched melt
- Metastable with respect to $Li_4P_2S_6$ and Li_3PS_4

From:K. Minami, A. Hayashi, M. Tatsumisago, Journal of the Ceramic Society of Japan 118, 305 (2010).

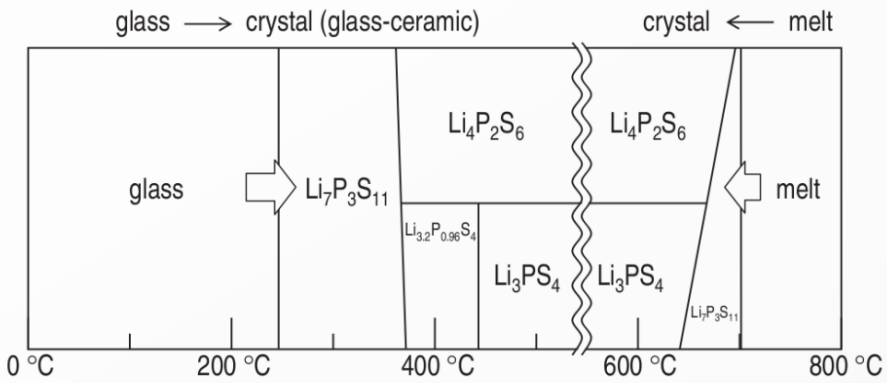


Fig. 6. Simple phase diagram of the $70Li_2S{\cdot}30P_2S_5$ (mol %) composition based on the XRD results of crystals precipitated from the glass and the melt.

From: M. Tatsumisago and A. Hayashi, J. Non-Cryst. Solids 354 1411-1417 (2008)

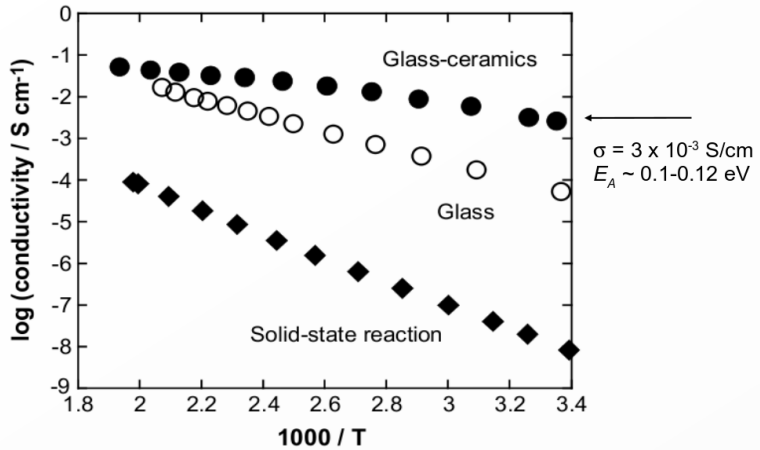


Fig. 5. Temperature dependences of the conductivities for the $70Li_2S \cdot 30P_2S_5$ glass and glass–ceramics. The conductivity data for the sample prepared by solid-state reaction are also shown.

- Conductivity of 3×10^{-3}S/cm
- Activation energy of 0.12 eV per formula unit
- Described as "superionic conductor"

Goals for this theoretical study

Understanding Structures and Stability

- Calculate heats of formation

Exploring Detailed Mechanisms for Conductivity

- Evaluate vacancy and interstitial defect migration mechanisms
- Energy cost for migration (E_m)
- Energy cost for defect pair formation (E_f)

Conductivity relations

1. $\sigma(T) = (\frac{C}{T})e^{-E_A/k_B T}$
2. $E_A = {}^{E_f}/_2 + E_m$

Methods

Calculational Methods

- Density functional theory
- LDA approximation
- USPP
- Quantum Espresso(PWscf)

Exploring Detailed Mechanisms for Conductivity

- Defect calculations were carried out in 84 atom supercell
- Add/remove ion and compensate with a uniform charge of the opposite sign
- Nudged Elastic Band(NEB) method used to estimate migration barriers

Structures and Stability

$Li_7P_3S_{11}$

- Metastable
- $Li_7P_3S_{11} \rightarrow Li_3PS_4 + Li_4P_2S_6 + S - 0.78$ eV
- Corresponds to exothermic decomposition seen in experiment
- Crystal is stable at room temperature

$Li_7P_3O_{11}$

- Metastable
- $Li_7P_3O_{11} \rightarrow Li_3PO_4 + Li_4P_2O_7 - 0.35$ eV
- Structure has not been experimentally realized

$Li_8P_3O_{10}N$

- Metastable
- $Li_8P_3O_{10}N \rightarrow Li_3PO_4 + Li_5P_2O_6N - 0.06$ eV
- Structure has not been experimentally realized

Understanding Conductivity: $Li_7P_3S_{11}$ Interstitial Sites

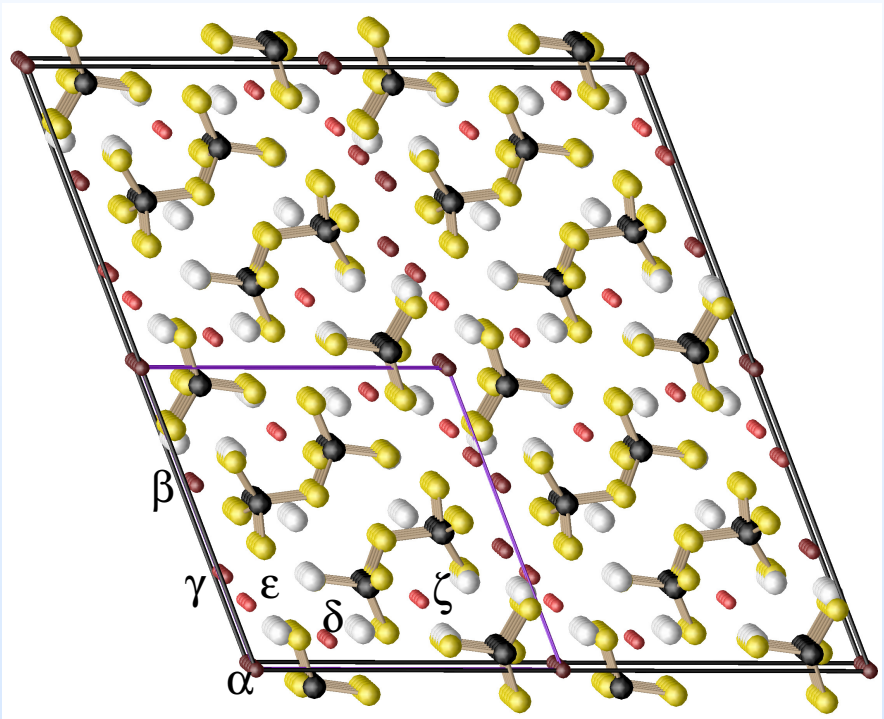
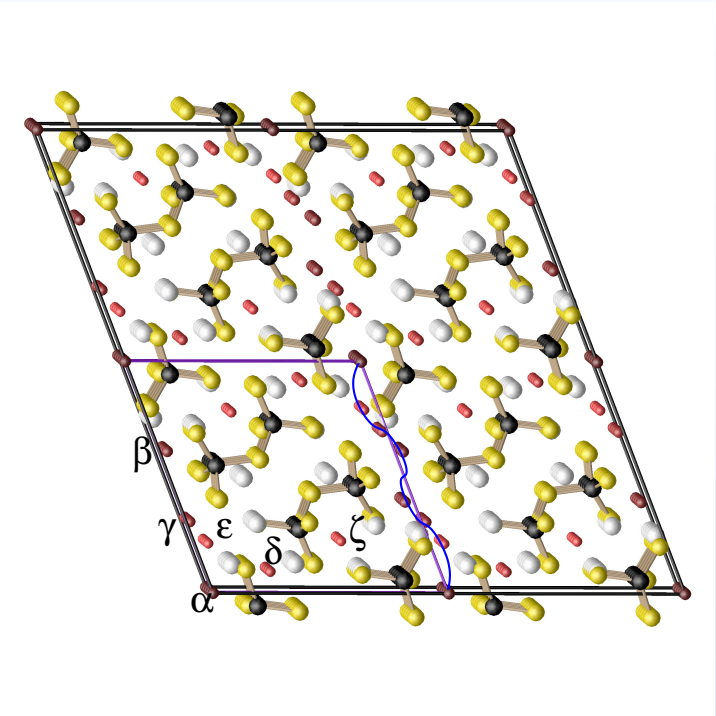


Table: $Li_7P_3S_{11}$ interstitial energies relative to α

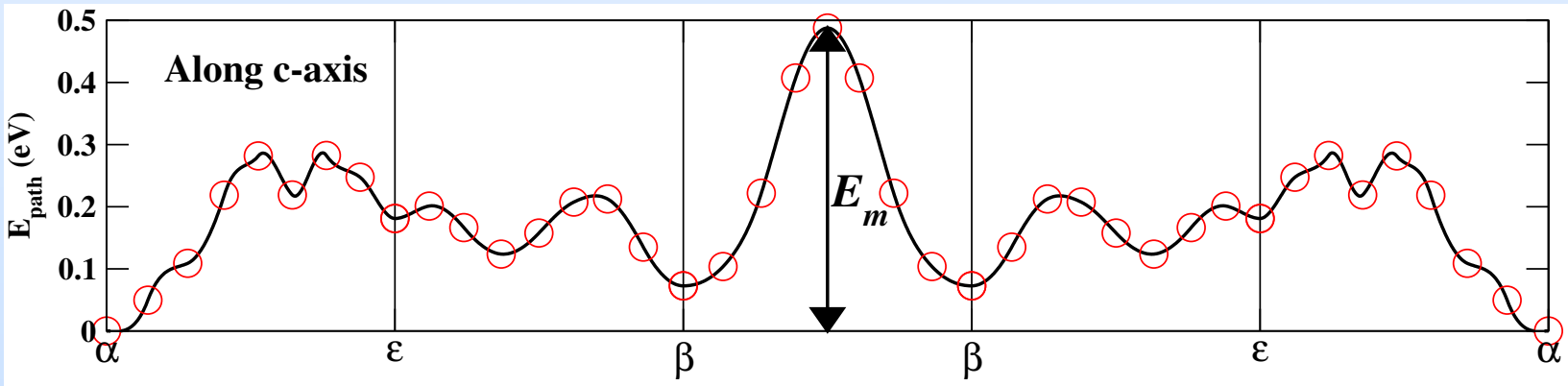
Label	E_i(eV)
α	0.00
β	0.07
γ	0.11
δ	0.11
ϵ	0.18
ζ	0.19

- Found via grid search
- 6 inequivalent interstitial positions
- 7 perfect crystal Li positions

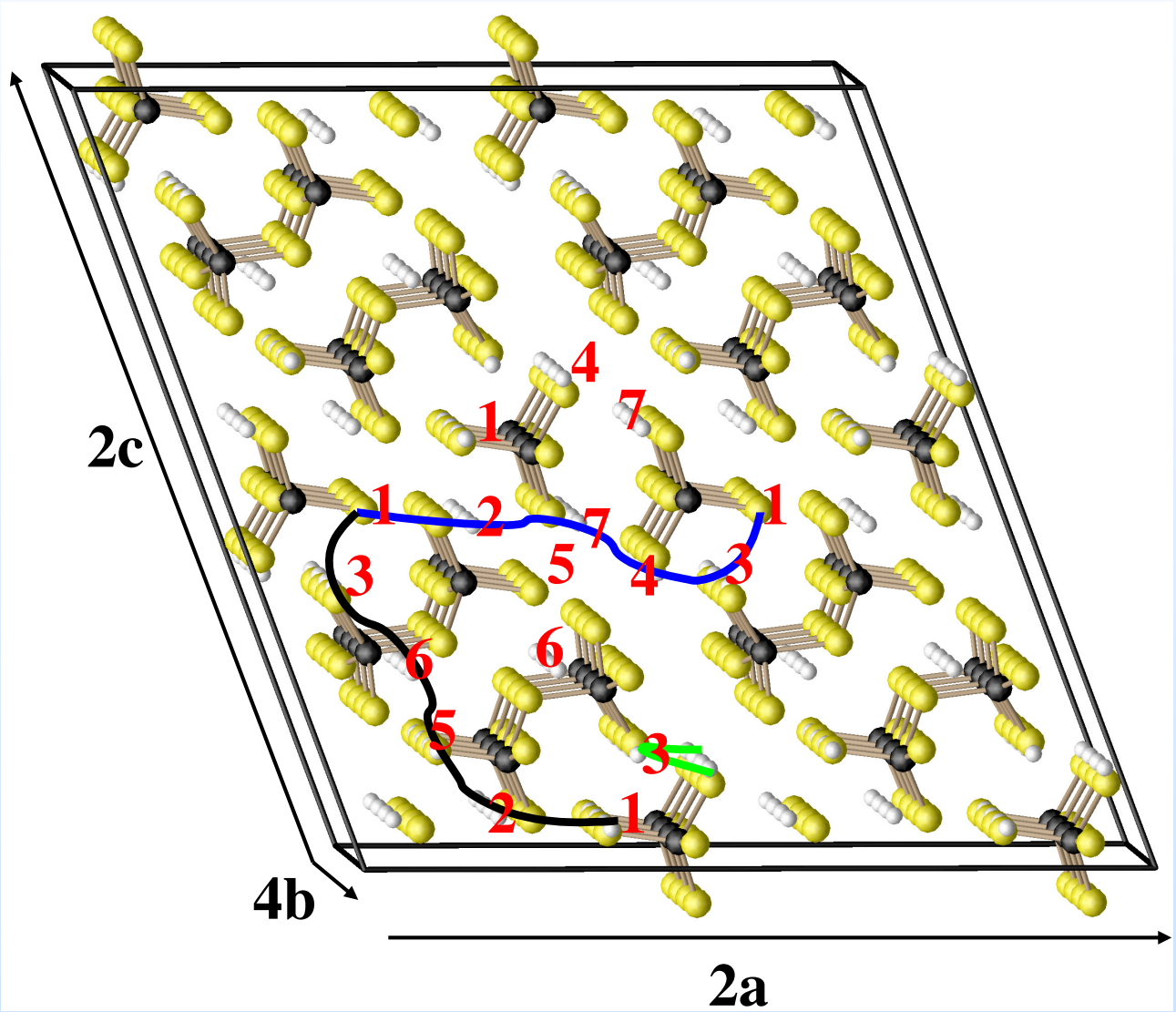
Understanding Conductivity: $Li_7P_3S_{11}$ Interstitial Migration



- Not evenly distributed
- Pure interstitial E_m=0.49 eV

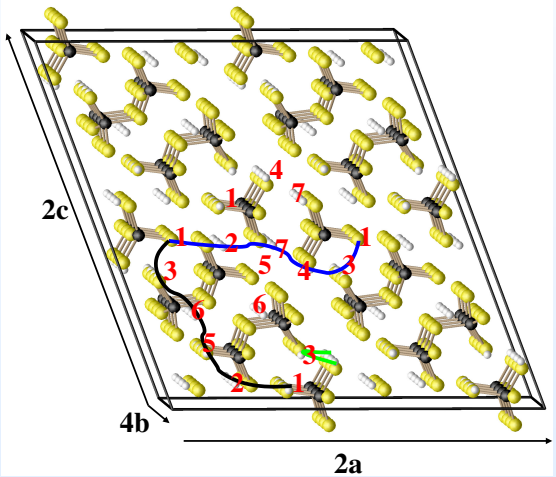


Understanding Conductivity: $Li_7P_3S_{11}$ Vacancy Migration

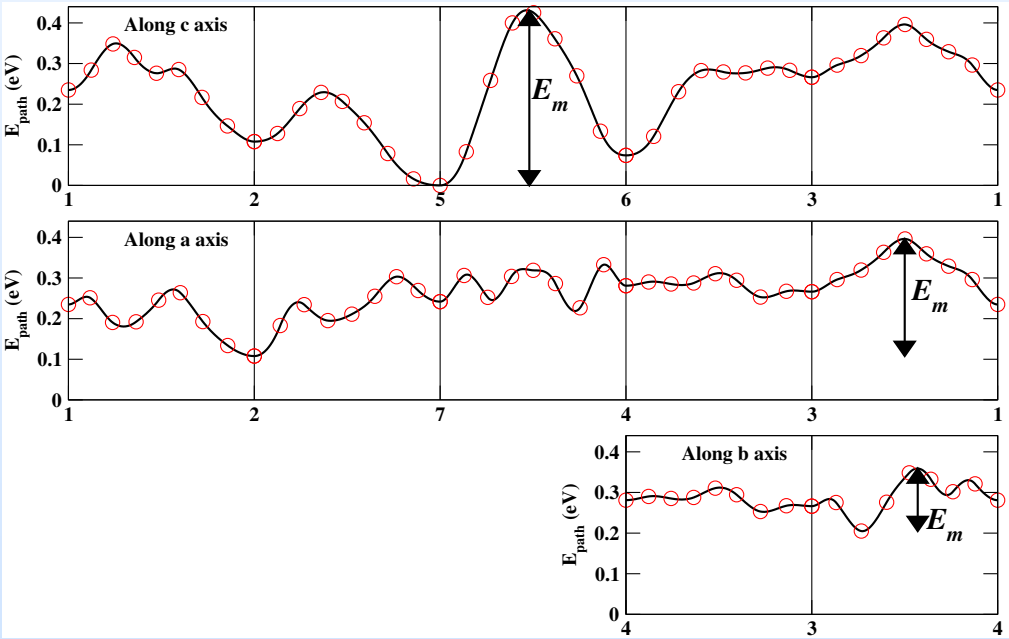


- Energy range of vacancies is 0.28 eV
- Large number of possibilities
- Pairwise steps
- "Shortest path problem" with E_m as weight

Understanding Conductivity: $Li_7P_3S_{11}$ Vacancy Migration

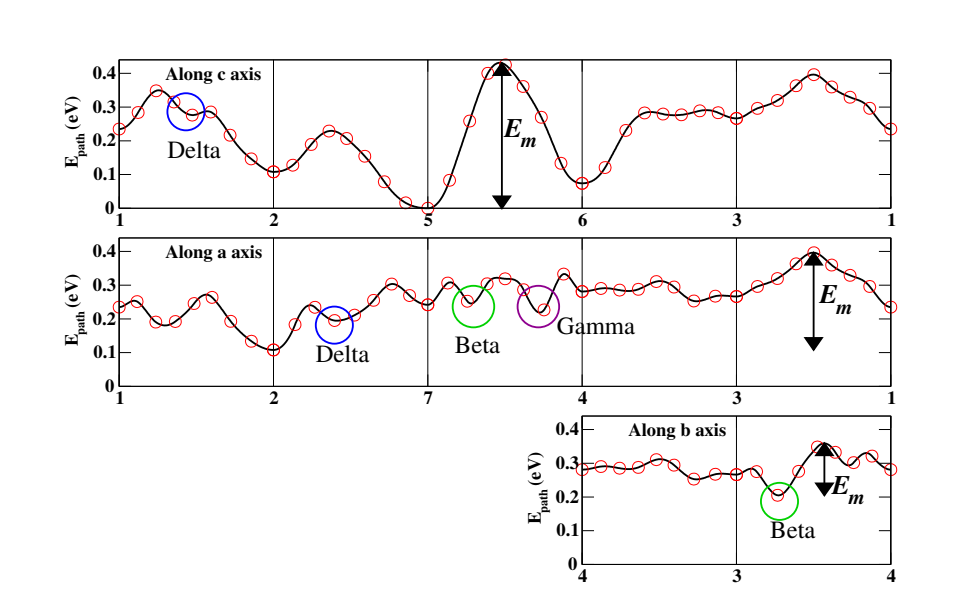


- Lowest energy complete path along a,b,c
- Paths contain significant structure



- Energy barriers (E_m)
  - $\vec{c} \rightarrow$ 0.42 eV
  - $\vec{a} \rightarrow$ 0.29 eV
  - $\vec{b} \rightarrow$ 0.15 eV
- Calculated value agrees with experiment: $0.15eV \approx 0.12eV$

Understanding Conductivity: $Li_7P_3S_{11}$ Vacancy Migration

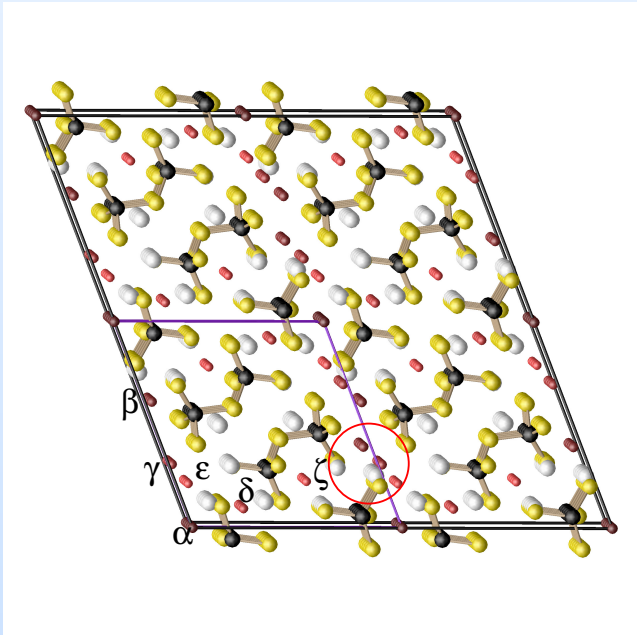


- Structure in paths can be related to locations of interstitial sites
- Vacancy only mechanism involves interstitial locations
- Many interstitial locations near lowest energy vacancy path

Purple→ γ

Blue→ δ

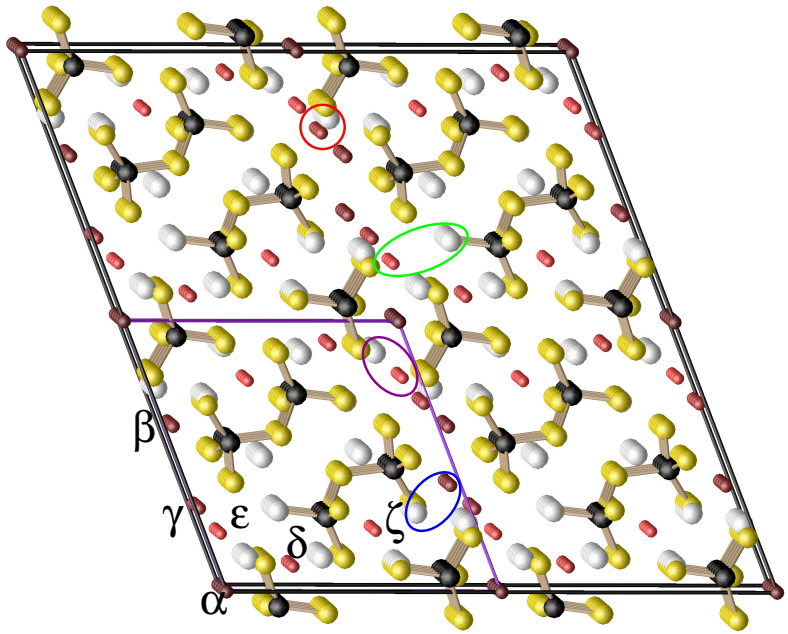
Green→ β



Understanding Conductivity: $Li_7P_3S_{11}$ Defect Pair Formation

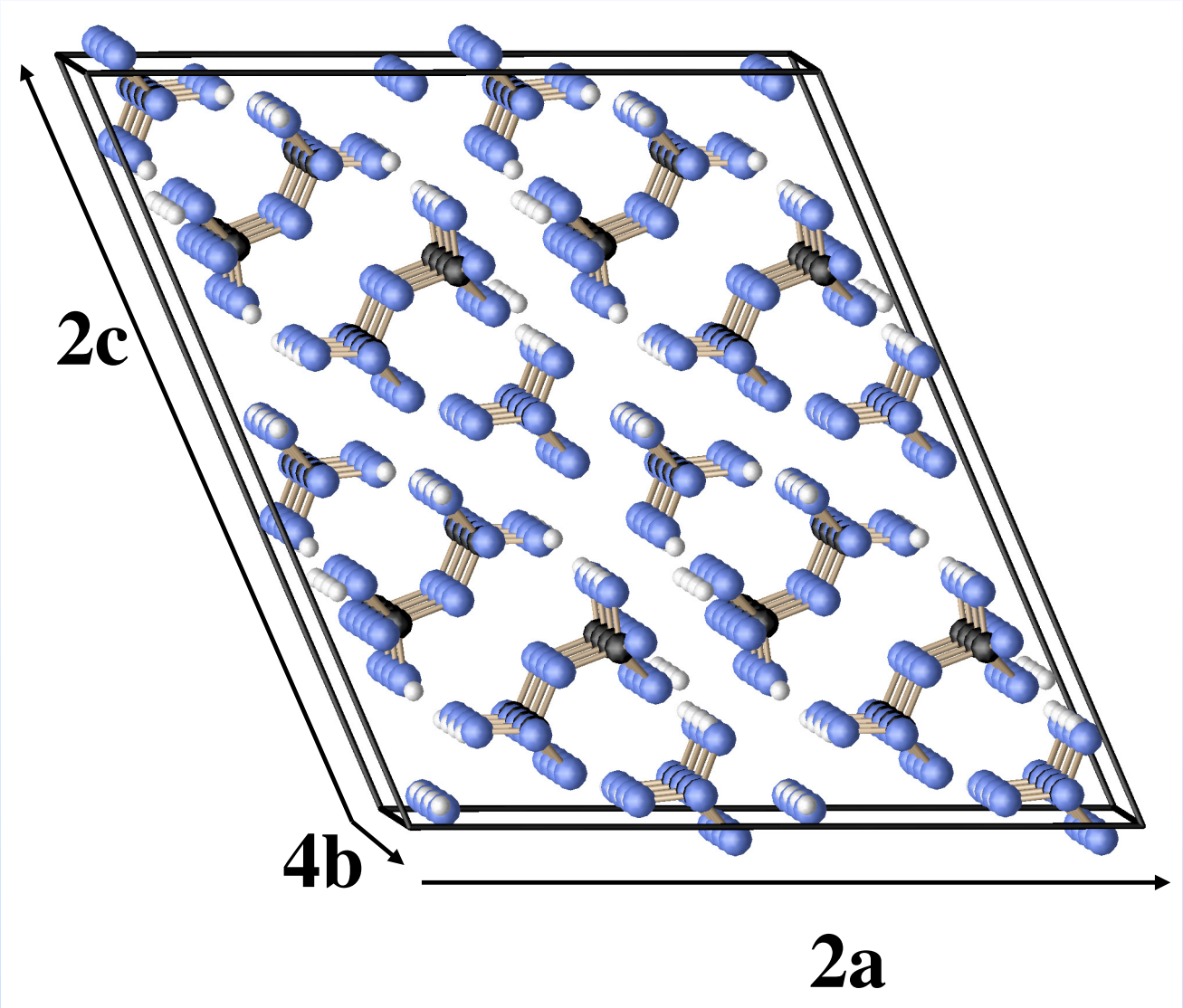
Table: $Li_7P_3S_{11}$ interstitial energies

Label	E_f(eV)	E_{fm}(eV)
5ϵ	-0.03	0.13
4γ	0.02	0.08
3β	0.05	0.09
7ϵ	0.07	0.11



- Several E_f values near zero
- E_{fm} is the barrier height for pair formation
- Negative value is within error due to limited supercell
- Low energy interstitials are similar to fractional occupancy

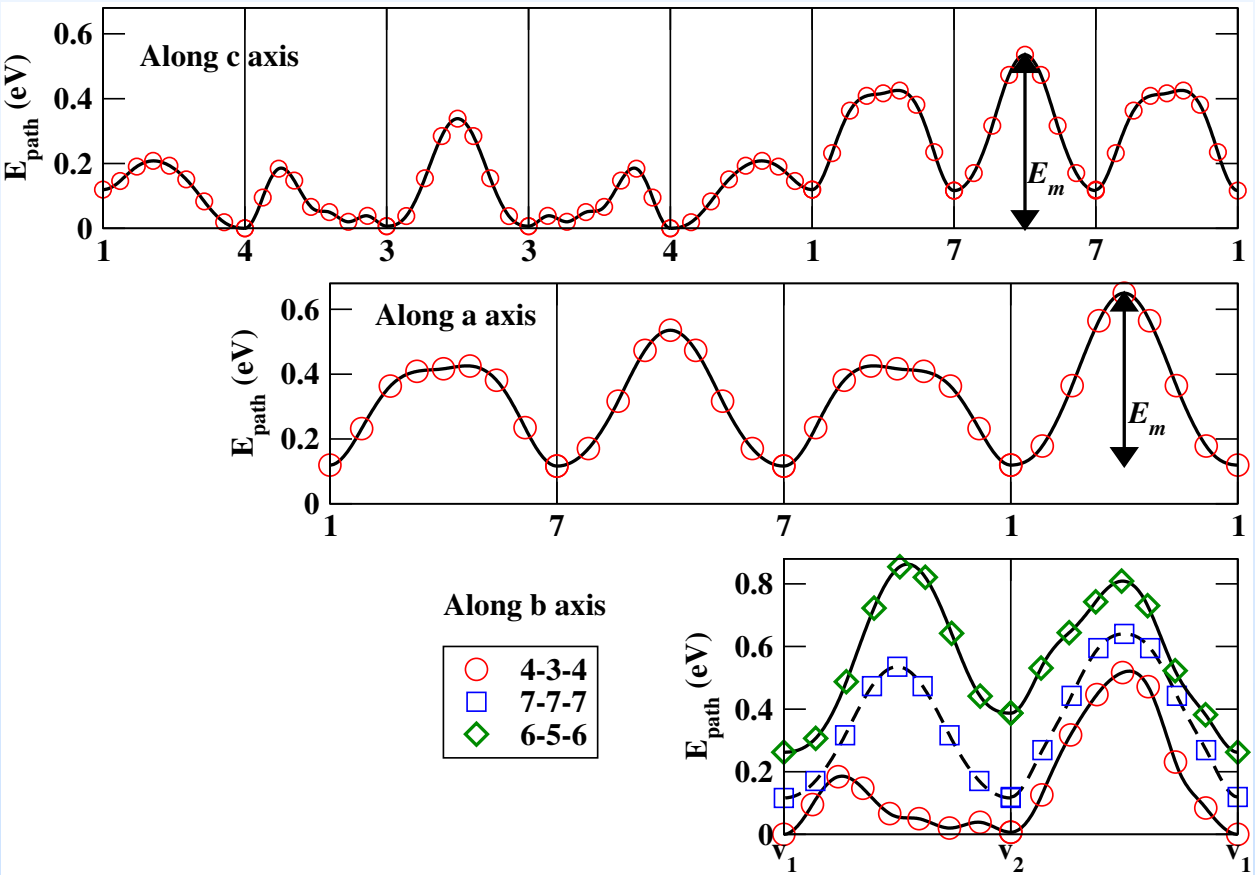
$Li_7P_3O_{11}$ and $Li_8P_3O_{10}N$



- Neither structure has been synthesized
- Insight into possible local structures in LiPON

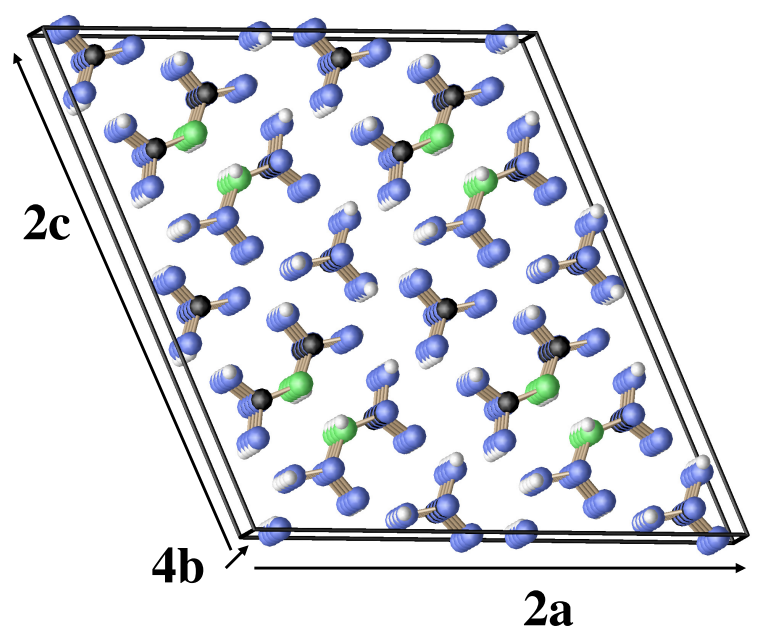
$Li_7P_3O_{11}$ Conductivity

The activation energy for $Li_7P_3O_{11}$ was found in the same manner as its thiophosphate analogue.



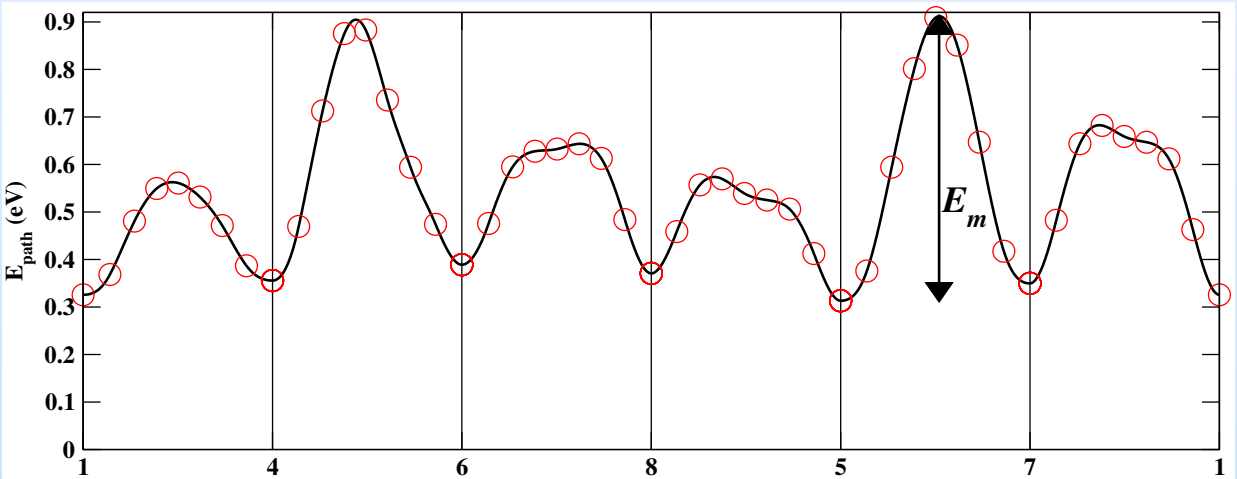
- E_m=0.52 eV
- No structure corresponding to low energy metastable sites
- Typical $E_f \approx 0.8$
- Close to experimental values for similar materials

$Li_8P_3O_{10}N$ Conductivity



Conductivity in $Li_8P_3O_{10}N$ was evaluated in a similar way.

- E_m=0.60 eV
- $E_f \approx 1.2$
- Close to experimental values for similar materials



Conclusions

- Stabilized crystal structure approximately corresponds to experiment
- Calculated metastability agrees with experiment
- Calculated E_A (0.16 eV) agrees well with experiment (0.12eV)
- Vacancy mechanism dominant
- Low energy interstitial sites appear to play an important role in conductivity
- Nitrogen addition increased stability, not conductivity

Acknowledgements

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Crystalline Electrolytes – Lithium Thiophosphates and Phosphates
N. D. Lepley and N. A. W. Holzwarth, J. Electrochem. Soc. 159, A538-A547 (2012)