

Atomic interaction at the solid interface between $\text{Li}_6\text{PS}_5\text{Cl}$ (solid electrolyte) and Li metal (anode)



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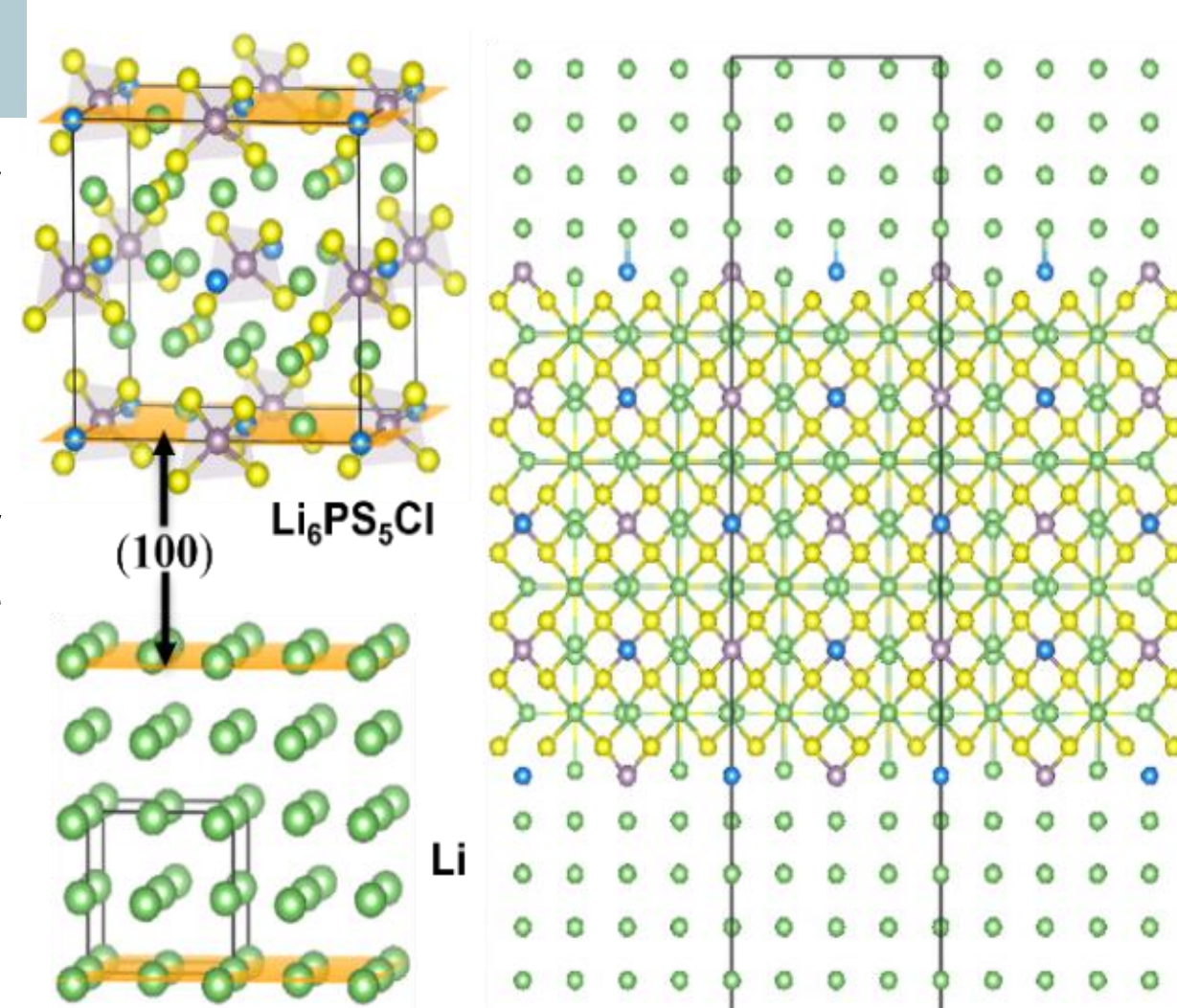
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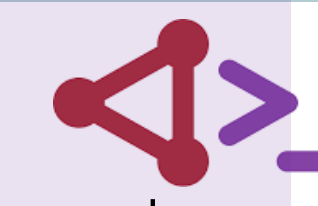
MOTIVATION

Solid-state batteries offer higher energy density and improved safety than conventional lithium-ion cells with flammable liquid electrolytes,¹ but poor interfacial compatibility at the solid-electrolyte (SE)|electrode interface, especially with lithium metal anodes, remains a major challenge.² In this study, we examine the structural and chemical factors governing the formation of interface between $\text{Li}_6\text{PS}_5\text{Cl}$ (SE) and Li metal anode.



METHOD

- Ab-initio molecular dynamics combined with machine-learning potentials (MLPs).
- Temperatures (T): 200-400 K.
- Interface and bulk structures relaxed using density functional theory (DFT).



VASP



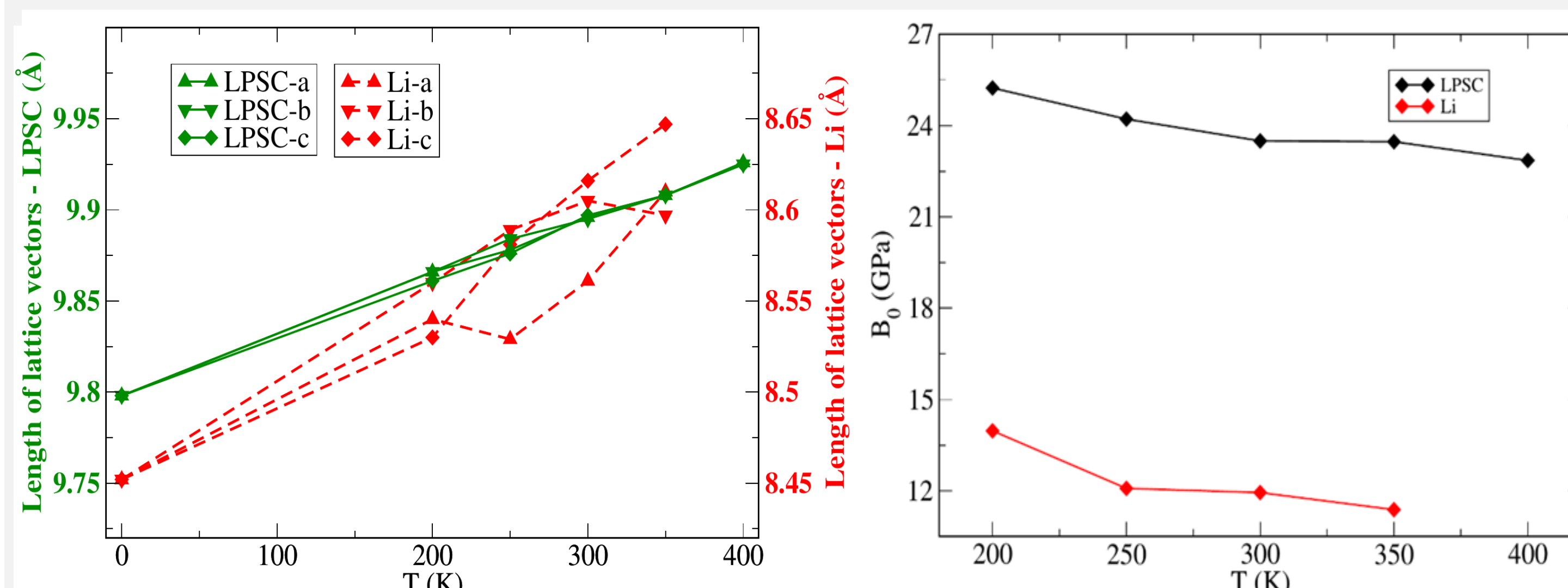
Properties:

- Structural parameters and bulk moduli as thermal averages from ML_MD.
- Radial distribution functions (RDF) of interatomic distances.
- COHP/COBI

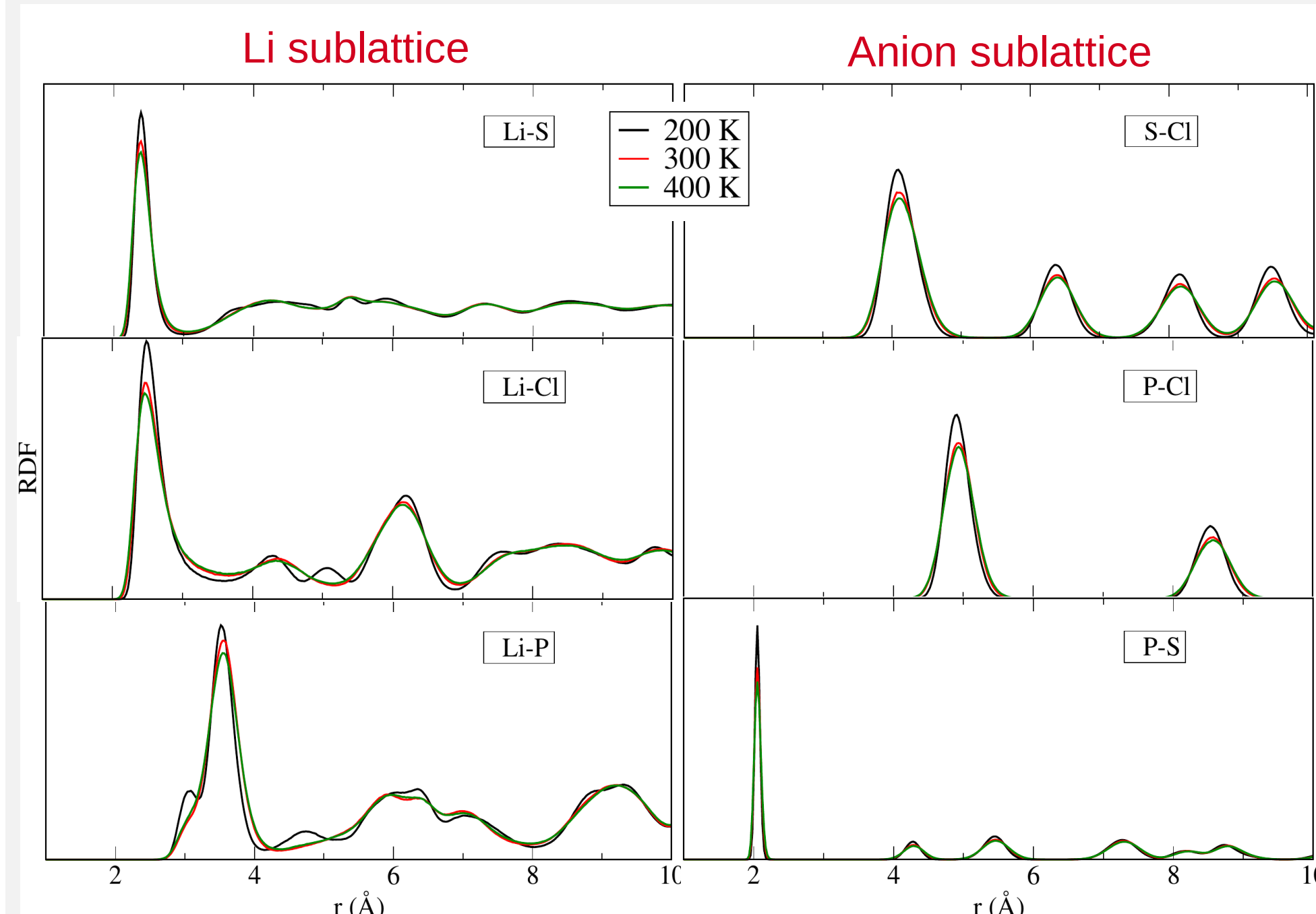
Bonding analysis using Crystal Orbital Hamilton Population³ analysis via LOBSTER.⁴

RESULTS AND CONCLUSIONS

Bulk structure

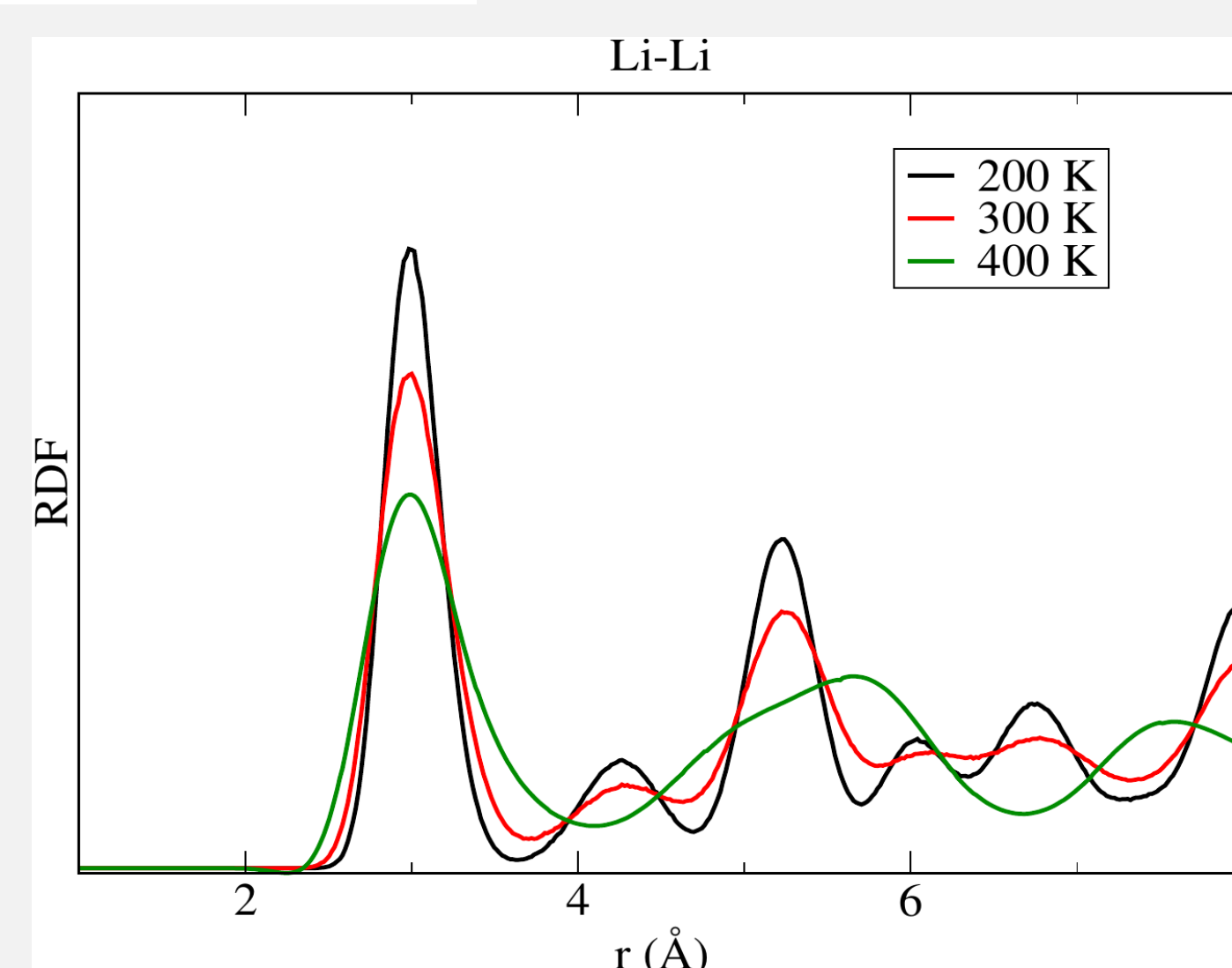


- Isotropic thermal expansion in $\text{Li}_6\text{PS}_5\text{Cl}$ and retains cubic symmetry up to 400 K. In contrast, Li shows irregular changes in its lattice vectors with T , reflecting a softer ($\alpha_{\text{Li}} > \alpha_{\text{LPSC}}$) and dynamically distorted pseudo-cubic structure.
- The absolute lattice mismatch between $\text{Li}_6\text{PS}_5\text{Cl}$ and Li remains constant (~ 1.7 Å), suggesting interfacial misfit strain does not strongly depend on temperature.
- Bulk modulus (B_0) of $\text{Li} \ll \text{Li}_6\text{PS}_5\text{Cl}$, $\rightarrow$ Li is softer, more compressible than SE.

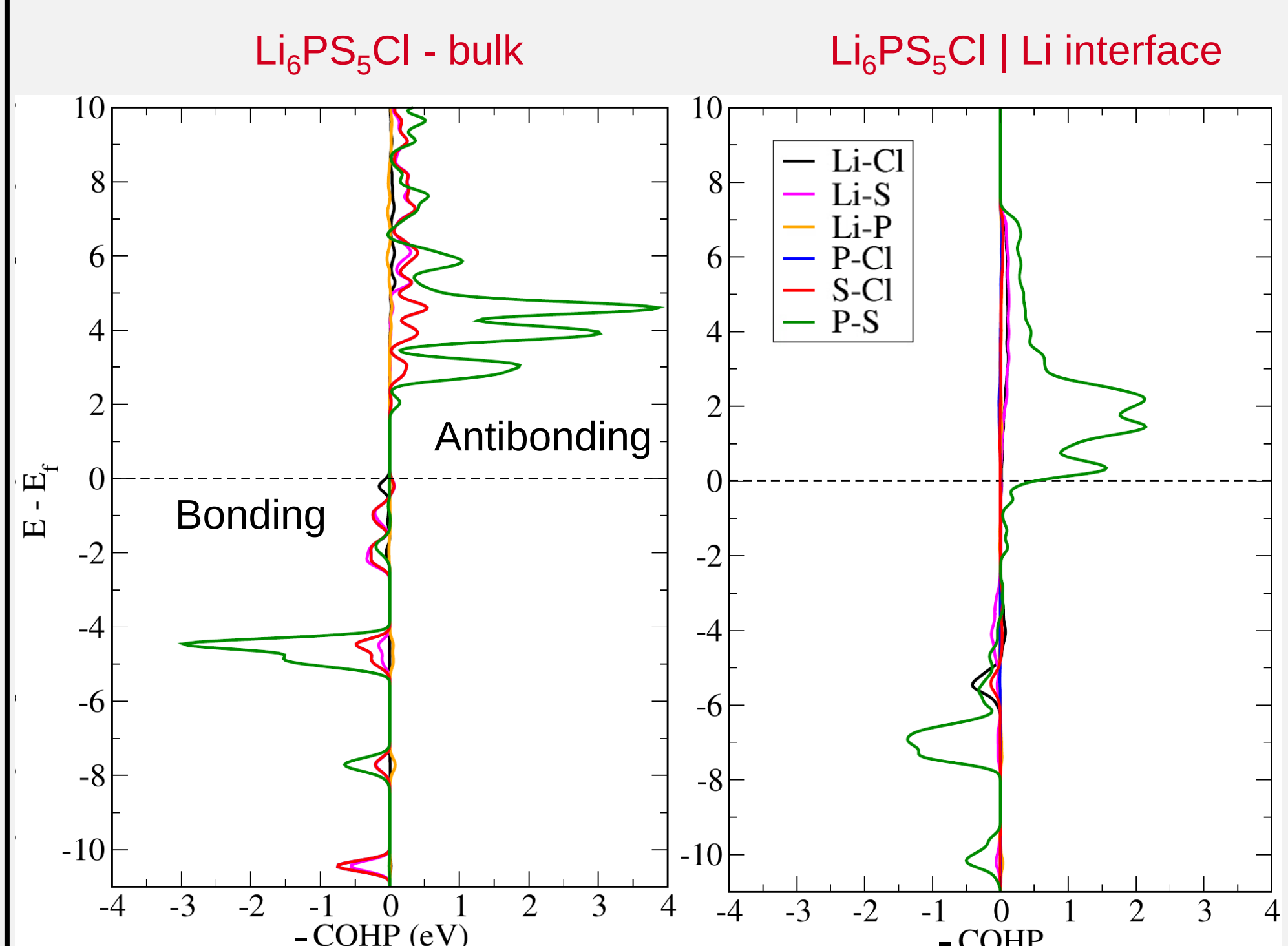


- In $\text{Li}_6\text{PS}_5\text{Cl}$: Li sublattice disorder is evident from broadening and losing intensity of the Li-S, Li-Cl, Li-P peaks with increasing T , due to highly mobile Li^+ ions. While all the P-S, S-Cl and P-Cl RDFs show sharp peaks implying a robust anion sublattice.

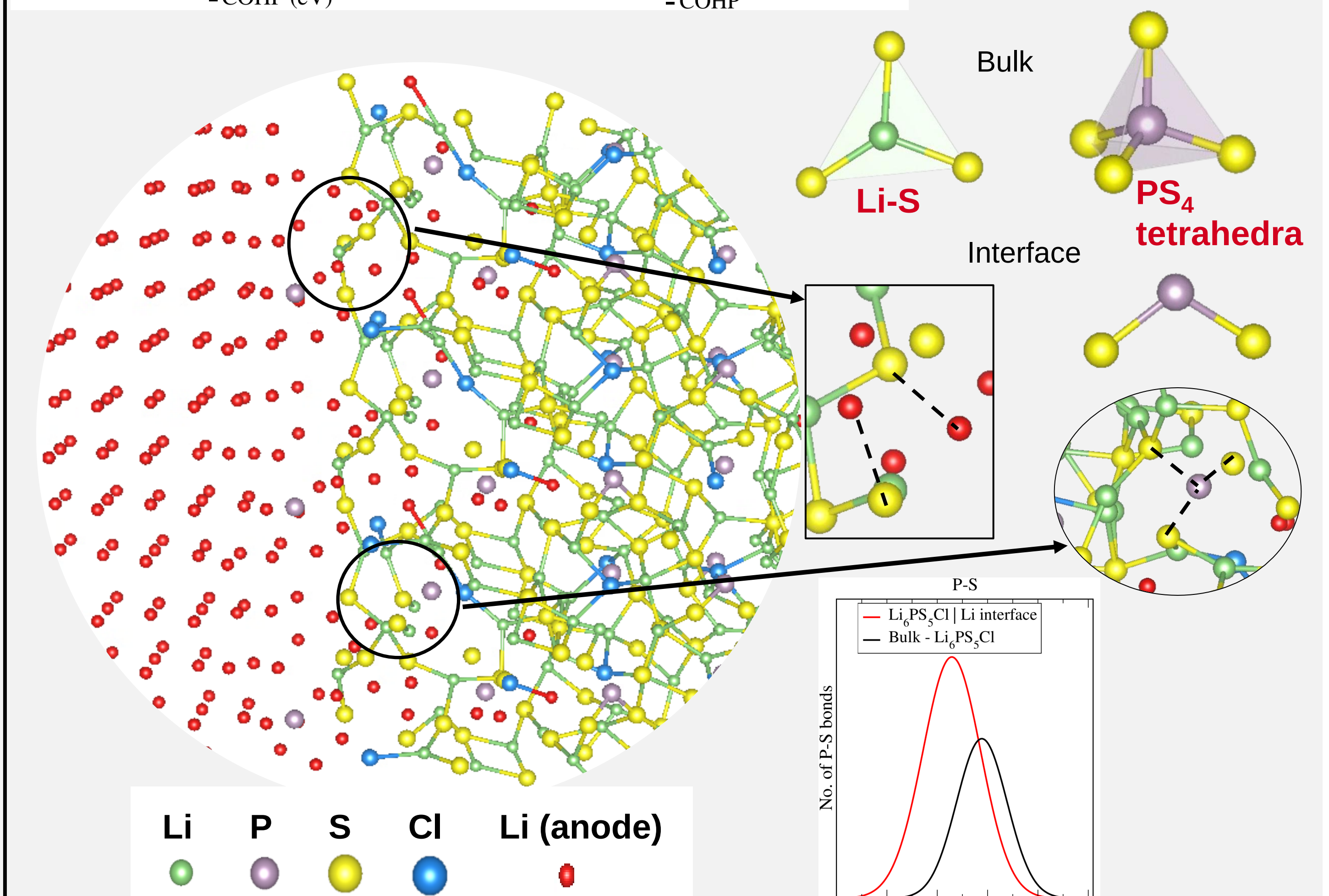
- In Li anode, the broadening and merging of RDF peaks (4 Å onwards) at 400 K indicate increased atomic disorder, consistent with Li approaching a pre-melting regime (also evidenced by the pronounced fluctuations in its lattice parameters at 400 K). Note that the melting point of Li is 453.7 K.



Comparing bonding behaviour at the interface v/s bulk



- In $\text{Li}_6\text{PS}_5\text{Cl}$ bulk, the P-S bonds dominate the bonding states, due to strong covalent PS_4^{3-} units. Li-S and S-Cl interactions show shallow bonding peaks near -5 and -2 eV implying weaker ionic bonds. The electronic structure has clear bonding-antibonding separation implying a chemically stable bulk.



NOTE: The simulations on the interface structure is still work in progress. Presented here are just some preliminary results.

- In $\text{Li}_6\text{PS}_5\text{Cl}|$ Li interface, the reduced P-S peak intensity in the valence region reflects weakened P-S bonding. Near E_F , a tail of weak antibonding states from P-S in the valence region indicates partial reduction of interfacial species. The antibonding P-S states above E_F are shifted and less pronounced, due to distorted or partially decomposed PS_4^{3-} units by Li contact. A reduced ICOBI value for the P-S bond indicate partial loss of covalent character.

References

- [1] C. Lin et al.: "Thermal runaway and gas production characteristics of semi-solid electrolyte and liquid electrolyte lithium-ion batteries: A comparative study", *Process Saf. and Environ. Prot.* 189, 2024, 577-586.
- [2] A. C. Radjendirane et al.: "Overview of Inorganic Electrolytes for All-Solid-State Sodium Batteries", *Langmuir* 40 (32), 2024, 16690-16712.
- [3] R. Nelson et al.: "LOBSTER: Local orbital projections, atomic charges, and chemical-bonding analysis from projector-augmented-wave-based density-functional theory" *J. Comp. Chem.*, 41, 2020, 1931-1940.
- [4] A. Naik et al.: "LobsterPy: A package to automatically analyze LOBSTER runs", *J. open source softw.* 9 (94), 2024, 6286.

PLAN AHEAD

- T -dependent analysis of atomic environments and bonding characteristics at the interface.
- Compare ionic conductivities at the interface v/s bulk.
- Determine rate of ion transport at the interface.
- Develop a robust, transferable, and fully integrated automated workflow that leverages MLPs trained on first-principles computations (primarily DFT), to perform high-throughput screening of various SE-anode compositions in future.

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