

Stacking-Fault Defects Modulate Ion Transport in Ternary Halide Solid Electrolytes

Yan Li¹, Wei-Fan Huang², Zeyu Deng¹, Lars Grabow^{2,3}, Pieremanuele Canepa^{4,3}

1. Department of Materials Science and Engineering, National University of Singapore

2. Department of Chemical and Biomolecular Engineering, University of Houston

3. Texas Center for Superconductivity, University of Houston

4. Department of Electrical and Computer Engineering, University of Houston

Abstract

Despite the prevalence of stacking faults (SFs) as planar defects in crystalline materials used for energy applications, their thermodynamic stability and influence on Li-ion transport in ternary halide solid electrolytes (SEs) for all-solid-state batteries (ASSBs) remain poorly understood. Here, we combine firstprinciples-trained cluster-expansion Hamiltonians and Monte Carlo simulations with machinelearned interatomic potentials to investigate SFs in trigonal Li_3YCl_6 (LYC) and monoclinic Li_3YBr_6 (LYB), two promising SEs compatible with high-voltage positive-electrode materials. SFs in LYC are metastable. In LYB, SFs are nearly energetically degenerate with the pristine phase. Nanosecond-scale molecular dynamics simulations of thermodynamically accessible faulted structures show that SFs increase Li-ion conductivity in LYC by an order of magnitude while lowering the Li-ion migration activation energy from 0.33 (in the bulk) to 0.21 eV. The analysis suggests that this enhancement arises from the disruption of the rigid Li sublattice ordering and the activation of threedimensional diffusion pathways by SFs at low temperatures. Our approach provides a general protocol for screening SFs in layered materials, including ion conductors. We show that defecttransport coupling is strongly framework dependent, highlighting synthesis-controlled defect engineering as a route to tune ionic conductivity in halide SEs and potentially other ion conductors.

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Yan Li,[†] Wei-Fan Huang,[‡] Zeyu Deng,[†] Lars Grabow,^{‡,§} and Pieremanuele Canepa^{*,¶,§}

[†]*Department of Materials Science and Engineering, National University of Singapore, 9 Engineering Drive 1, 117575, Singapore*

[‡]*Department of Chemical and Biomolecular Engineering, University of Houston, Houston, Texas, 77204, United States*

[¶]*Department of Electrical and Computer Engineering, University of Houston, Houston, Texas, 77204, United States*

[§]*Texas Center for Superconductivity, University of Houston, Houston, Texas, 77204, United States*

E-mail: pcanepa@uh.edu

Despite the prevalence of stacking faults (SFs) as planar defects in crystalline materials used for energy applications, their thermodynamic stability and influence on Li-ion transport in ternary halide solid electrolytes (SEs) for all-solid-state batteries (ASSBs) remain poorly understood. Here, we combine first-principles-trained cluster-expansion Hamiltonians and Monte Carlo simulations with machine-learned interatomic potentials to investigate SFs in trigonal Li_3YCl_6 (LYC) and monoclinic Li_3YBr_6 (LYB), two promising SEs compatible with high-voltage positive-electrode materials. SFs in LYC are metastable. In LYB, SFs are nearly energetically degenerate with the pristine phase. Nanosecond-scale molecular dynamics simulations of thermodynamically accessible faulted structures show that SFs increase Li-ion conductivity in LYC by an order of magnitude while lowering the Li-ion migration activation energy from 0.33 (in the bulk) to 0.21 eV. The analysis suggests that this enhancement arises from the disruption of the rigid Li sublattice ordering and the activation of three-dimensional diffusion pathways by SFs at low temperatures. Our approach provides a general protocol for screening SFs in layered materials,

including ion conductors. We show that defect-transport coupling is strongly framework dependent, highlighting synthesis-controlled defect engineering as a route to tune ionic conductivity in halide SEs and potentially other ion conductors.

Introduction: All-solid-state batteries (ASSBs) promise higher energy and power densities and improved safety owing to the non-flammability of solid electrolyte (SEs) materials.^{1–4} Among various SE candidates explored, ternary lithium metal halides (*e.g.*, Li_3MX_6 , where $\text{M} = \text{Y}, \text{Sc}, \text{In}, \text{Er}, \text{Yb}, \text{and Ho}$; and $\text{X} = \text{F}, \text{Cl}, \text{and Br}$) exhibit pronounced compatibility with high-voltage oxide positive electrode (cathode) materials, favorable processability, and tunable ionic conductivities on the order of mS/cm.^{5–9} Previous studies have shown that ionic transport in these halides is strongly influenced by the synthesis route, underscoring the roles of local structural environments and defect chemistry in ionic conduction.^{10–13}

Halide solid electrolytes feature a close-packed anion sublattice, adopting either hexagonal close-packed (hcp) or cubic close-packed

(ccp) arrangements, with cations occupying octahedral sites to form layered honeycomb structures.^{14–16} Adjacent tetrahedral interstitial sites create a three-dimensional network of diffusion pathways that enables fast Li-ion migration.^{17–19}

As is typical of layered structures, the multiple equivalent stacking vectors in these materials make them susceptible to random layer shifts. Consequently, high-energy ball milling—a common low-temperature synthesis route for halide and sulfide SEs—often introduces a high density of planar defects, known as stacking faults (SFs).^{11,20–23}

Although SFs are known to induce electrochemo-mechanical degradation and cracking in layered oxide positive electrode materials,²³ recent studies suggest that they can instead play a beneficial role in SEs by modulating, and in some cases enhancing, lithium-ion transport.^{11,22,24} In mechanochemically synthesized Li_3YCl_6 (LYC), for example, SFs introduce face-sharing YCl_6^{3-} octahedra and alter the local coordination environments.¹¹ These structural changes lower Li-ion migration barriers and create interconnected inter-layer pathways that facilitate bulk ionic conduction.^{11,25} Similar planar defects and associated effects on ion transport have been reported in other halide SEs, including $\text{Li}_3\text{HoBr}_{6-x}\text{I}_x$ and Li_3ScCl_6 .^{9,21,22,24}

Despite their relevance to Li-ion conduction in halide SEs, the thermodynamic origins of SFs and their atomistic effects on ion transport remain elusive. Macroscopic characterization techniques, such as powder X-ray and neutron diffraction, typically yield spatially averaged structural descriptions of material specimens that obscure local atomic configurations within faulted domains.^{21,26,27} Thus, quantifying SF concentrations in real samples remains challenging because of instrumental sensitivity limitations.

Computational modeling of these extended planar defects presents comparable challenges. *Ab initio* molecular dynamics (AIMD) simulations face practical time- and length-scale constraints, which limit the direct observation of long-range Li-ion transport across such defect

networks.¹¹ Furthermore, evaluating the finite-temperature thermodynamic stability of large ensembles of structurally disordered configurations requires advanced statistical-mechanics treatments beyond conventional 0 K density functional theory (DFT)²⁸ calculations.^{29,30} As a result, it remains unclear which SF motifs are thermodynamically accessible and how they contribute to Li-ion connectivity and transport in halide SEs.

In this Letter, we investigate the thermodynamic stability of stacking faults (SFs) and their impact on Li-ion transport in LYC and Li_3YBr_6 (LYB). These materials possess hcp and ccp anion frameworks, respectively, and each exhibits a room-temperature ionic conductivity of approximately 1 mS/cm.³¹ First, we identify all possible gliding SF models in Li_3YCl_6 and Li_3YBr_6 to capture their distinct planar-defect chemistries. This approach avoids relying on the empirical models pre-selected in experimental studies to match specific X-ray powder diffraction patterns.^{11,21,22}

Using these SF models, we develop a multi-scale model based on cluster expansion (CE) and Monte Carlo (MC) simulations to evaluate the finite-temperature stability of these faulted configurations.^{32,33} Then, we train machine learning interatomic potentials (MLIPs) within the atomic cluster expansion (ACE) framework to perform nanosecond-scale molecular dynamics (MD) simulations of Li-ion transport in large cells containing SFs.^{34–36}

Through this integrated approach, we reveal that thermodynamically accessible SFs modify the local coordination environments and redirect Li-ion migration pathways, resulting in increased ionic conductivity. These findings demonstrate that carefully selected synthesis strategies can control the concentration of extended defects, including SF, and thereby tune targeted properties in ionic conductors.

Pristine and Faulted Structural Models of Li_3YX_6 : Li_3YCl_6 adopts two primary polymorphs: a ground-state hcp trigonal phase (hcp-t, $P\bar{3}m1$, No. 164) and a metastable orthorhombic structure (hcp-o,

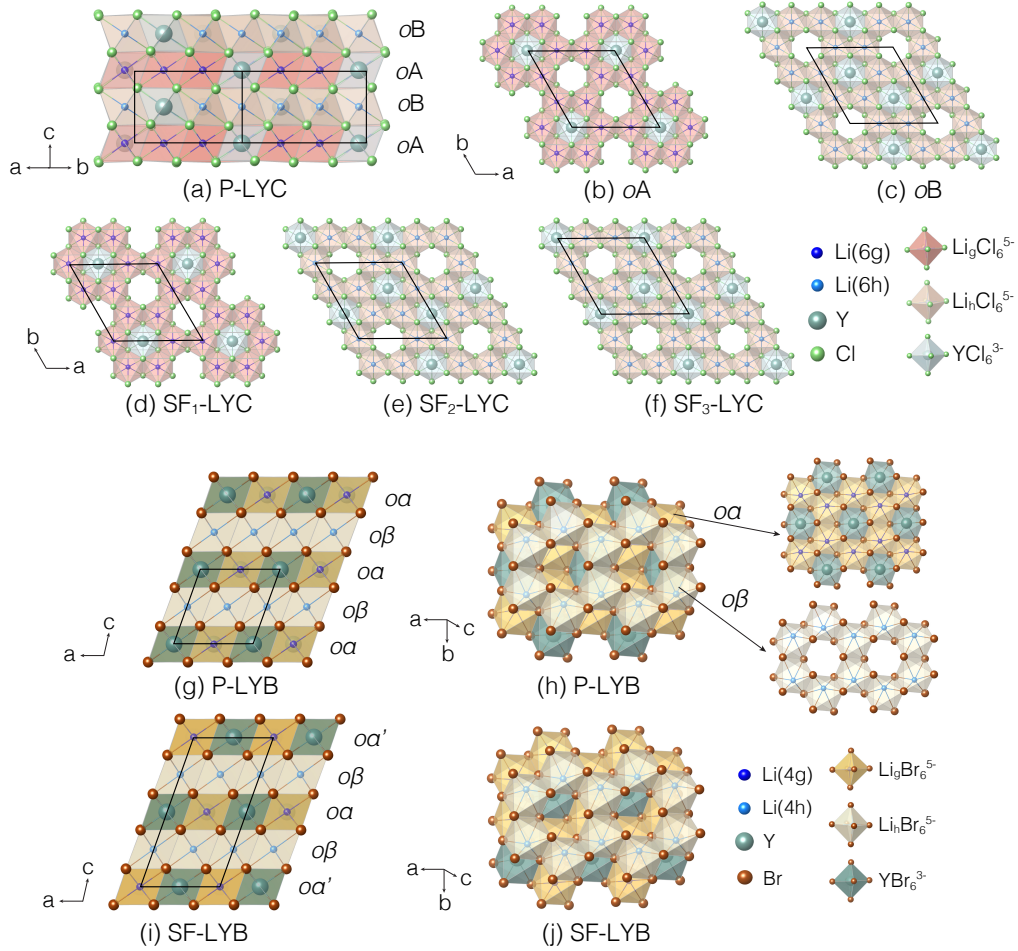


Figure 1: Structural models and layer stacking sequences for the LYC and LYB phases. (a) Polyhedral side-view representation of P-LYC, illustrating the alternating stacking of oA and oB anion layers along the c -axis. (b, c) Top-down views of the individual oA and oB layers. (d–f) Topologies of three relevant SF configurations in LYC: (d) SF₁-LYC, (e) SF₂-LYC, and (f) SF₃-LYC. These SF models arise from rigid crystallographic translations of the anion layers (indicated by black cell boundaries). (g, h) The P-LYB structure displaying the monoclinic $o\alpha/o\beta$ stacking sequence, shown in (g) layer-by-layer and (h) polyhedral views. (i, j) The faulted SF-LYB configuration, generated by a lateral displacement of the basal layer, is shown in (i) layer-by-layer and (j) polyhedral representations. In all panels, black parallelograms mark the projected conventional unit cells or supercells.

$Pnma$, No. 62).^{14,15,37} We focus exclusively on the hcp-t phase, which contains three formula units (30 atoms) per unit cell and displays occupational disorder on the Li and Y sublattices. In this structure, Li ions are fractionally distributed over the $6g$ ($z \approx 0$) and $6h$ ($z \approx 0.5$) sites. Y^{3+} fully occupies the $1a$ site at $(0, 0, 0)$ (Y1) and partially occupies two $2d$ sites at $(1/3, 2/3, 1/2)$ and $(1/3, 2/3, 0)$ (Y2 and Y3).

To resolve the occupational disorder, pristine LYC (P-LYC) models were subjected to a preliminary Li/Y ordering, and their energetics were evaluated with DFT (Figure S1 in Supporting Information, SI). DFT calcula-

tions identify the M1-M2 arrangement (Figure 1a, and Figures S1a and S1c in SI, with Y1 and Y2 sites occupied, and Y3 vacant) as the ground state, lying ~ 42.31 meV/atom below the lowest-energy M1-M3 configuration (Figure S1b and S1d in SI, Y1 and Y3 sites occupied, Y2 vacant). This thermodynamic preference for the M1-M2 arrangement agrees with existing literature^{11,12} and justifies selecting this model to define the Y sublattice for all subsequent analyses.

Structurally, the M1-M2 model (Figure 1a) comprises an alternating sequence of two edge-sharing octahedral layers stacked along the c -

axis: the *oA* layer at $z = 0$ (Figure 1b) and the *oB* layer at $z = 0.5$ (Figure 1c). The *oA* layer consists of edge-sharing $[\text{Li}(6g)\text{Cl}_6]$ and $[\text{Y}(1a)\text{Cl}_6]$ octahedra, while the *oB* layer contains $[\text{Li}(6h)\text{Cl}_6]$ and $[\text{Y}(2d)\text{Cl}_6]$ building blocks.

SF models were constructed by introducing a single *oA* or *oB* layer shift into the pristine P-LYC structure using a $1 \times 1 \times 2$ supercell model, which yields a defect periodicity of one faulted layer per four octahedral layers along the *c*-axis. To maintain the local Li and Y coordination within the chloride framework, we translated the shifted layer within the *ab* plane along vectors connecting neighboring octahedral sites. This constraint reduces the possible translations to two symmetrically unique shift vectors, $\mathbf{v}_1 = (1/3, 0, 0)$ and $\mathbf{v}_2 = (1/3, 2/3, 0)$.

Shifting the *oA* layer by $\mathbf{v}_1$ forms the SF₁-LYC configuration (Figure 1d). The $\mathbf{v}_2$ shift of *oA* was excluded, as this translation displaces yttrium species from Y1 into vacant Y3 positions, resulting in energetically unfavorable cation arrangements rather than a distinct stacking sequence. By comparison, translating the *oB* layer by $\mathbf{v}_1$ and $\mathbf{v}_2$ generates two distinct fault models: SF₂-LYC (Figure 1e) and SF₃-LYC (Figure 1f). Due to the symmetry-related registry of the cation sites, each layer shift locally introduces an effective Li-Y antisite disorder that modifies the cation coordination environment relative to neighboring layers.

The pristine Li_3YBr_6 (P-LYB) structure crystallizes in monoclinic $C2/m$ (No. 12) symmetry with two formula units (20 atoms) per conventional cell. LYB is isostructural with Li_3ErBr_6 ,¹⁶ where Y^{3+} cations fully occupy the $2a$ (0, 0, 0) sites, and Li^+ ions fractionally distribute the intralayer $4g$ ($z \approx 0$) and interlayer $4h$ ($z \approx 0.5$) sites. Reports revealed discernible yet distinct Li-Y anti-site disorder patterns.^{10,31} Asano et al.³¹ identified $\sim 8\%$ Y substitution on the Li $4g$ sites, while Ref. 10 reported a more complex arrangement with $\sim 12\%$ Y occupying the Li $4h$ sites and $\sim 4\%$ Li, displacing Y at the $2a$ sites. A unified structural model reconciling these two descriptions remains to be established.

We used the lattice constants and atomic co-

ordinates from Ref. 10 as the reference structure for SF generation, with Y and Li restricted to the $2a$ and $4g/4h$ sites, respectively (Figure 1g). The P-LYB structure comprises two alternating octahedral layers, *oα* and *oβ*, stacked along the *c*-axis (Figure 1g). The *oα* layer contains edge-sharing $[\text{Li}(4g)\text{Br}_6]$ and $[\text{Y}(2a)\text{Br}_6]$ octahedra arranged in a honeycomb sublattice, where each $[\text{YBr}_6]$ unit is coordinated by six edge-sharing $[\text{Li}(4g)\text{Br}_6]$ octahedra. In contrast, the *oβ* layer consists entirely of equivalent $[\text{Li}(4h)\text{Br}_6]$ octahedra that form a honeycomb motif enclosing interlayer voids. These layers interconnect in three dimensions through corner- and edge-sharing Br atoms. The honeycomb lattices in the *oα* and *oβ* layers exhibit a lateral offset relative to one another (Figure 1h), resulting in a staggered stacking arrangement characteristic of the LYB monoclinic phase.

LYB SFs were examined within the *oα* layer. Through a systematic exploration of potential slip directions, we identified a representative SF model (SF-LYB in Figure 1i). This fault is generated by displacing the *oα* layer (at $z = 0$ in a $1 \times 1 \times 2$ P-LYB supercell) by $\sim (1/2, 3/4, 0)$, mimicking the partial Li-Y exchange between the $2a$ and $4g$ sites reported previously.^{10,31} The translation transforms the parent *oα* layer into a shifted variant *oα'*, modifying the stacking sequence along the *c*-axis from *oα-oβ-oα-oβ* to *oα'-oβ-oα-oβ-oα'*. This stacking rearrangement results in a distinct zigzag ordering of the Y sublattice along the *c*-direction. Figure 1j reveals the altered coordination environment arising from the superposition of the *oβ* layer onto the shifted *oα'* layer, contrasting with the pristine *oα-oβ* alignment of Figure 1h.

Although this Letter focuses on gliding SFs, the proposed generation model is also consistent with structural models reported for other monoclinic halide SEs. For example, rotational SFs in Li_3ScCl_6 ⁹ involve shifting the transition-metal-rich layers (*oα* $\rightarrow$ *oα'*) while leaving the intervening Li-rich layers (*oβ*) unchanged. This shift modifies the stacking vectors between consecutive layers, yet preserves the crystallographic equivalence of each adjacent pair of transition-metal-rich layers.

First-Principles Insights into Stability and Structural Distortions of Li_3YX_6 : To account for fractional Li-site occupancy in pristine and faulted LYC and LYB structures, we systematically enumerated ordered configurations. Evaluating Li ordering in the P-LYC M1-M2 model yielded 24 and 362 symmetry-inequivalent configurations within the conventional cell (3 f.u.) and a $1 \times 1 \times 2$ supercell (6 f.u.), respectively. For the LYC SFs (SF_1 , SF_2 , and SF_3), 422, 396, and 467 unique orderings were also sampled. In P-LYB, 10 and 160 unique configurations were found using the conventional cell (2 f.u.) and a $1 \times 1 \times 2$ supercell (4 f.u.), respectively, while enumeration of the SF-LYB model ($1 \times 1 \times 2$, with 4 f.u.) generated 420 distinct ordered arrangements.

Structural optimizations of pristine and SF models were performed using the $r^2\text{SCAN}$ meta-GGA functional³⁸ with lattice constants fixed to experimental values,¹⁰ while the atomic coordinates were optimized. This constraint is validated by our benchmark data (Figure S3 in SI), which shows a negligible energy difference (< 2 meV/atom) compared to the fully relaxed structures, where coordinates and lattice parameters are relaxed. A similar approach was adopted in Ref. 39. All energy values reported herein represent the DFT internal energy at 0 K, which disregards zero-point, entropic, and pV effects.

Figure 2a shows the $r^2\text{SCAN}$ energy distribution of all enumerated configurations for the pristine and faulted LYC models. For P-LYC, the sampled (ordering) configurations span a narrow energy range of ~ 15 meV/atom above the ground-state ordering (Figure S2a).

All evaluated SF models (SF_1 , SF_2 , and SF_3) appear thermodynamically metastable (Figure 2a), with the most stable configuration for each fault shown in Figure S2b–c. Specifically, the SF_1 , SF_2 , and SF_3 models exhibit energies of 16.81, 20.19, and 36.63 meV/atom, respectively, relative to the pristine ground state. These values agree well with the ~ 20 meV/atom energy difference reported for the most stable SF models in Ref. 11, which were derived from refinements of synchrotron X-ray diffraction data. This agreement with

the experimental observations,¹¹ further supports the use of these models to represent SFs in LYC.

The thermodynamic metastability of the SF models is structurally corroborated by an increase in atomic site distortion (Figure 2b), quantified by larger values of the parameter $\bar{D}$ (Eq. S1). Pristine P-LYC structures exhibit minimal $\bar{D}$ values, with $0 < \bar{D} \leq 0.17$ Å. The faulted configurations display a baseline shift to higher $\bar{D}$ values, with the lower bound rising to ~ 0.20 Å for the SF_1 and SF_2 models, and exceeding ~ 0.32 Å for SF_3 . Further analysis shows that the heavier YCl_6^{3-} octahedra remain relatively rigid, whereas the more flexible Li sublattice undergoes substantial positional rearrangements to accommodate SFs, leading to greater site distortions in the faulted structures.

Figures 3a and 3b analyze the thermodynamic and structural characteristics of the P-LYB and SF-LYB models. In contrast to its LYC analog, LYB incurs a negligible energy penalty for stacking disorder. Indeed, the relative energy distributions of the P-LYB and SF-LYB ensembles closely resemble each other (Figure 3a), yielding ground state model structures that are energetically degenerate ($\Delta E < 0.01$ meV/atom). Unlike the distinct distortion baseline shift observed in LYC, the $\bar{D}$ profiles for both LYB phases are highly similar and center around 0.23–0.25 Å (Figure 3b). For LYB, the similar energy profiles and structural distributions indicate an intrinsic tolerance for crystallographic slip that exceeds that of LYC (Figure 2).

The identified ground states for the P-LYB and SF-LYB models (Figures 3c and 3d) possess distinct symmetries: the P-LYB ground state adopts the $C2$ (No. 5) space group, whereas the SF-LYB state exhibits $C2/c$ (No. 15) symmetry, characterized by an additional c -glide plane (Table S2 in SI). Although both ground states were identified through independent Li/vacancy enumerations, their resulting configurations are highly similar. Aside from structural deviations confined to the basal layer ($z = 0$), where the fault-generation vector laterally displaces the Li and Y atoms, the other

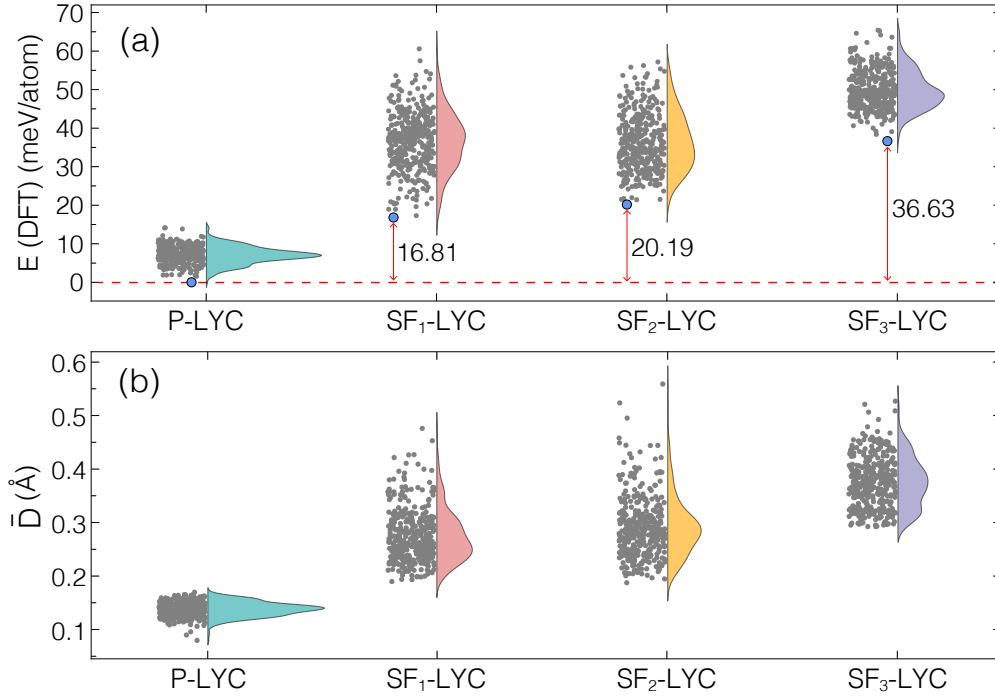


Figure 2: Energy distributions and geometrical distortions of P-LYC and three SF-LYC structures. (a) DFT-calculated relative energies (E) with respect to the P-LYC ground state, indicated by the red dashed line. Blue markers denote the energy minima within each set of configurations. (b) Average distortion parameters ($\bar{D}$) for each enumerated configuration. Probability density plots show the data distributions (shaded curves).

atomic positions are nearly identical. The inter-layer Li ions (light blue, $4h$ sites) and mid-plane intralayer Li ions ($z \approx 0.5$, dark blue, $4g$ sites) map directly between the two configurations.

Statistically relevant Li₃YX₆ stacking fault models: To extend our analysis to finite-temperature conditions, we employed CE Hamiltonians with MC simulations to assess temperature-dependent thermodynamic functions (and related quantities) in LYC, LYB, and their faulted structures.^{33,40,41}

With yttrium positions constrained within each reference lattice, the CE is developed on the Li/vacancy configurational space, in which the energy $E[\vec{\sigma}]$ of a given Li/vacancy arrangement is expressed as a polynomial expansion of site occupation variables: $E(\vec{\sigma}) = V_0 + \sum_i V_i \sigma_i + \sum_{i,j} V_{i,j} \sigma_i \sigma_j + \sum_{i,j,k} V_{i,j,k} \sigma_i \sigma_j \sigma_k + \dots$, where $\vec{\sigma}$ denotes the atomic configuration, and σ_i specifies the occupation of site i as either a Li-ion ($\sigma_i = 1$) or a vacancy ($\sigma_i = 0$). The CE is parameterized by coefficients V_0 , V_i , $V_{i,j}$,

and $V_{i,j,k}$, which are the reference energy, point terms (i.e., the chemical potentials), and the pair and triplet effective cluster interactions (ECIs), respectively. The crystallographic parameters defining the lattices used to train the CEs for pristine LYC and LYB are listed in Tables S3 and S4 in SI. Reference structures for the faulted systems were generated as described in the previous section. For LYC, the relatively stable SF₁ configuration was chosen as the representative faulted framework for CE training and is referred to hereafter as SF-LYC. Additional on CE-related details are provided in the SI.

The CE Hamiltonians accurately reproduce the DFT energies, as shown by the close agreement in Figures 4a,d. The cross-validation scores are 0.69 and 1.12 meV/atom for pristine and stacking-faulted LYC, respectively, and 0.48 and 0.75 meV/atom for the corresponding LYB models. Additional error distributions and ECI terms are provided in Figures S4 and S5 in SI. Using the fitted CEs, finite-temperature properties were obtained from MC simulations

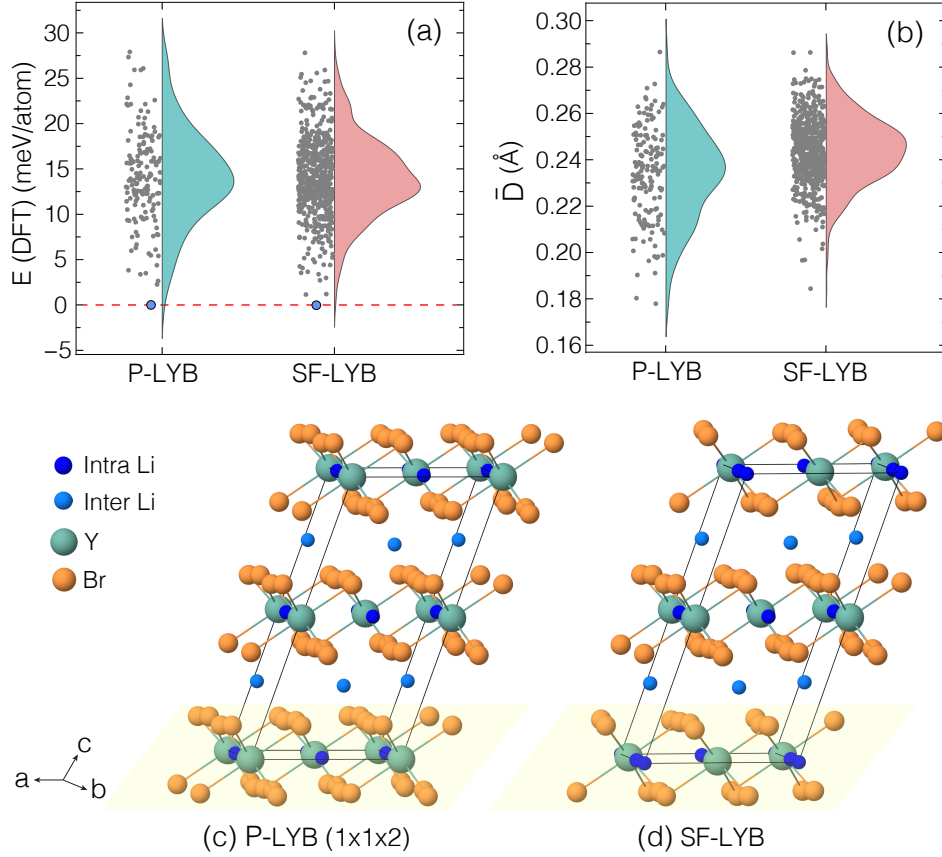


Figure 3: Energy profile, geometrical distortions, and ground-state structures of P-LYB and SF-LYB. (a) DFT-calculated relative energies (E , meV/atom) with respect to the pristine ground state, indicated by the red dashed line. Blue markers denote the energy minima within each configuration set. (b) Average distortion parameters ($\bar{D}$) for each enumerated configuration. The data are shown as hybrid plots combining individual configurations (gray points) with probability density distributions (shaded curves). (c, d) Lowest-energy structures of (c) P-LYB, shown in a $1 \times 1 \times 2$ supercell, and (d) SF-LYB. The highlighted basal layer illustrates the distinct cation arrangements associated with the P-LYB and SF-LYB configurations.

on large supercells to minimize finite-size effects. LYC simulations used $12 \times 12 \times 24$ (pristine) and $12 \times 12 \times 12$ (faulted) supercells with 103,680 atoms, whereas LYB used $24 \times 12 \times 24$ (pristine) and $24 \times 12 \times 12$ (faulted) supercells with 138,240 atoms.

The temperature-dependent configurational energy, $\Phi(T)$, and heat capacity, $C_v(T)$, defined in Eqs. S3 and S4 of the SI, reveal the thermodynamic effects of SFs in LYC and LYB (Figure 4b–f).

For LYC, the configurational energy curves (Figure 4b) show that SF₁-LYC (orange) remains higher in energy than the pristine phase (green) across the full temperature range (0–2,000 K). At low temperature, the penalty is ~ 16 meV/atom relative to the pristine ground

state, indicating that SFs are thermodynamically unfavorable in the trigonal chloride framework.

The disruption of long-range crystalline order is further reflected in the corresponding heat-capacity (C_v) curves (Figure 4c). Pristine LYC exhibits a sharp λ -type peak centered at ~ 480 K, characteristic of a well-defined order-disorder (2nd order) phase transition of the Li/vacancy sublattice.^{42,43} Configurational entropy drives this transition: thermal energy flattens the local potential landscape, allowing Li ions to leave their ordered positions and form a dynamically disordered network.

In contrast, the stacking-faulted LYC structure (SF₁-LYC) exhibits a broad, weak thermal response spanning a wide temperature

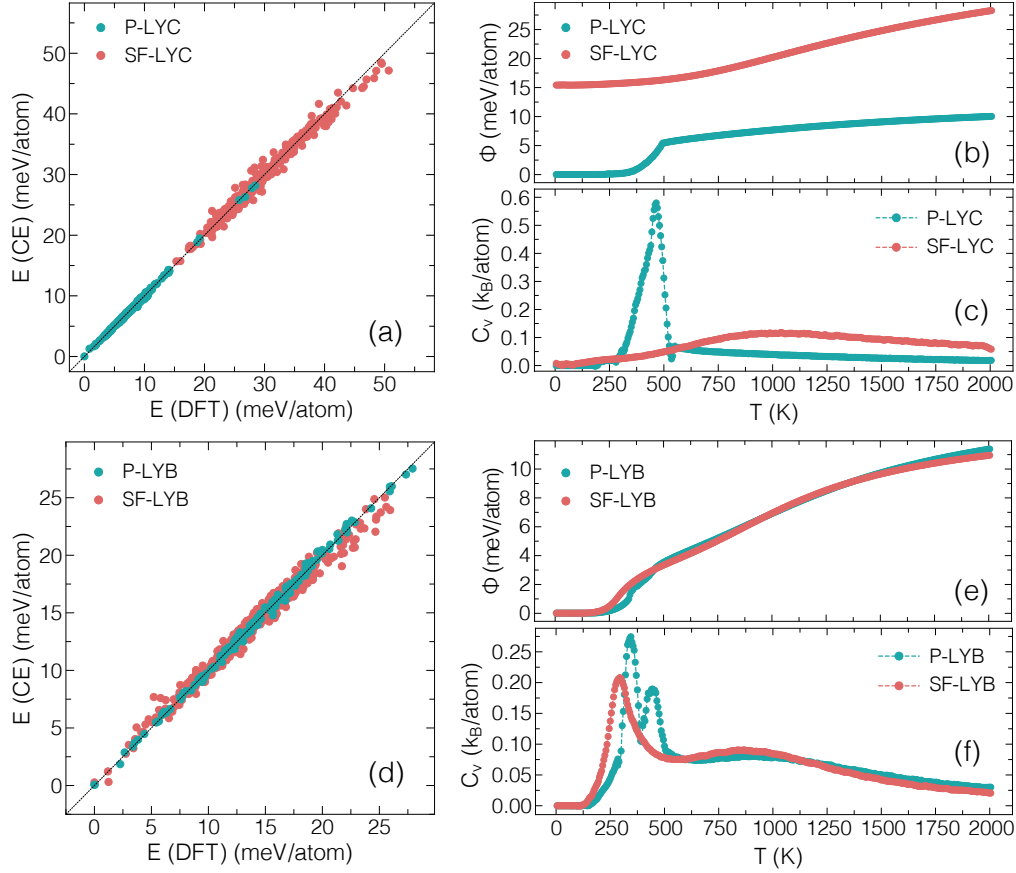


Figure 4: Thermodynamic properties of pristine (green) and stacking-faulted (orange) models. Results for LYC (a–c, top) and LYB (d–f, bottom) were derived from CE fitting and canonical MC simulations. (a, d) Parity plots of fitted (E_{CE}) vs. calculated (E_{DFT}) energies, referenced to the DFT ground states. (b, e) Configurational energy Φ as a function of temperature. (c, f) Heat capacity, C_V , profiles illustrating phase-transition behavior.

range. This broadening can be attributed to the symmetry-breaking nature of the planar defects, which creates a heterogeneous distribution of thermodynamic site energies, thereby smearing the transition into a continuous, progressive randomization of the Li-vacancy sublattice.

By comparison with LYC, the Φ curves for LYB (Figure 4e) show that the pristine and faulted phases remain nearly degenerate over the full temperature range (0–2,000 K), with minimal energy differences. This result confirms that the monoclinic bromide framework accommodates SFs more readily than trigonal LYC, resulting in a negligible thermodynamic penalty for planar-defect formation. The heat-capacity profiles of LYB (Figure 4f) demonstrate that SFs alter the Li-sublattice disordering behavior. While the pristine LYB lat-

tice exhibits a bimodal thermal response (two peaks between ~ 350 – 450 K), the faulted phase displays a single dominant peak shifted to a lower temperature (~ 300 K). Although planar defects suppress the discrete ordering state of pristine, defect-free LYB by merging the bimodal transition into a single disordering event, the overall thermodynamic behavior remains analogous: in both LYB and SF-LYB, thermal excitation drives an entropy-driven transition toward comparably dynamically disordered states. This resulting thermodynamic similarity may explain experimental observations that SFs negligibly influence Li-ion transport in other monoclinic halide frameworks, such as Li_3ScCl_6 and $\text{Li}_{3+x}\text{Sc}_{1-x}(\text{Zr/Mg})_x\text{Cl}_6$.^{9,22,24}

Effect of Stacking-fault Disorder on Li-ion Conductivity in LYC:

Building upon the established pristine and SF models, we next examine the influence of stacking faults on ionic transport. This analysis focuses on LYC, for which the structural effects of these defects are pronounced. Because our thermodynamic analysis indicates that the SF-LYC phase preserves the characteristic Li-vacancy disorder of the pristine model, we restrict the following analysis to LYC, where their effects are more pronounced.

While the pristine arrangement with exclusive Li/vacancy ordering in the M1-M2 framework provides the expanded interlayer spacing and continuous diffusion networks essential for high Li-ion conductivity,¹² our comparative assessment evaluates how planar defects, driven by rigid-layer shifts that mimic localized Li/Y site exchange, affect these diffusion pathways. To enable nanosecond sampling of extended faulted domains beyond *ab initio* timescales, we developed high-fidelity ACE-based machine-learning potentials.^{34–36}

For a systematic evaluation of defect concentration, we constructed two representative faulted models: 1/2 SF-LYC and 1/3 SF-LYC. The former corresponds to the previously discussed SF₁-LYC configuration, generated by introducing a single faulted layer into a $1 \times 1 \times 2$ pristine supercell (which comprises four octahedral layers). The latter was constructed by incorporating a single faulted layer into a larger $1 \times 1 \times 3$ pristine supercell (comprising six octahedral layers). These different defect periodicities manifest locally as varying degrees of effective Li–Y site exchange.

Building on previous work,⁴⁴ we developed an ACE potential in five iterations of active learning (Figure 5a).

Although r²SCAN was used for phase stability and cluster-expansion analysis, we trained the ACE potential for Li-ion transport using optB88-vdW. Unlike r²SCAN and PBEsol, optB88-vdW captures the two-regime Arrhenius behavior reported in Ref. 44, likely because it better describes interlayer dispersion in layered LYC. The initial ACE model was trained on optB88-vdW AIMD trajectories from 60-atom supercells and static DFT calculations of the pristine and SF models.

During ACE-driven MD, reliability was monitored using the extrapolation grade, γ , which measures the degree of extrapolation relative to the training domain.^{45,46} Configurations falling into the range $2 < \gamma < 10$ (Figure 5a) were classified as extrapolative, re-evaluated using DFT, and incorporated into the training set for the subsequent iteration. As depicted in the γ histograms (Figure 5b), the active test set for the initial model contained a substantial fraction of high- γ configurations, demonstrating that the MD trajectories frequently sampled structures outside the initial training distribution (see Section S6 in SI). Following five active-learning iterations, the γ distributions for both the standard and active test sets shifted predominantly below the selection threshold of $\gamma = 2$. This confirms that the final model operates in a highly interpolative regime across these sampled trajectories. Furthermore, the final ACE potential quantitatively agrees with the DFT references, yielding mean absolute errors of ~ 0.48 meV/atom and ~ 14.76 meV/Å for energies and forces, respectively, on the test set.

Temperature-dependent Li-ion transport kinetics in pristine and faulted Li₃YCl₆ were quantified using the validated ACE model. Long-timescale production MD simulations were performed in LAMMPS^{47,48} in the *NVT* ensemble with a Nosé–Hoover thermostat.^{49,50} Following an initial equilibration period of 2 ns, 10 ns production simulations were conducted with a 1 fs timestep. Figure 5c presents the Arrhenius plots of the predicted Li⁺ tracer diffusivity (D , as defined in the methodology) for pristine P-LYC, as well as the 1/3 SF-LYC and 1/2 SF-LYC SF models. The quantitative room-temperature ionic conductivities (σ) and activation energies (E_a) summarized in Table 1.

For P-LYC, the diffusivity curve exhibits an inflection point at $T_c = 425$ K, corresponding to an order-disorder 2nd-order phase transition. Below T_c , the activation energy is 0.33 eV, which decreases to 0.28 eV above T_c . Introducing planar SFs alters this Li-ion transport behavior. Both the 1/3 SF-LYC and 1/2 SF-LYC models show higher diffusivities than P-LYC across the measured temperature range and lack a phase-transition inflection. The dif-

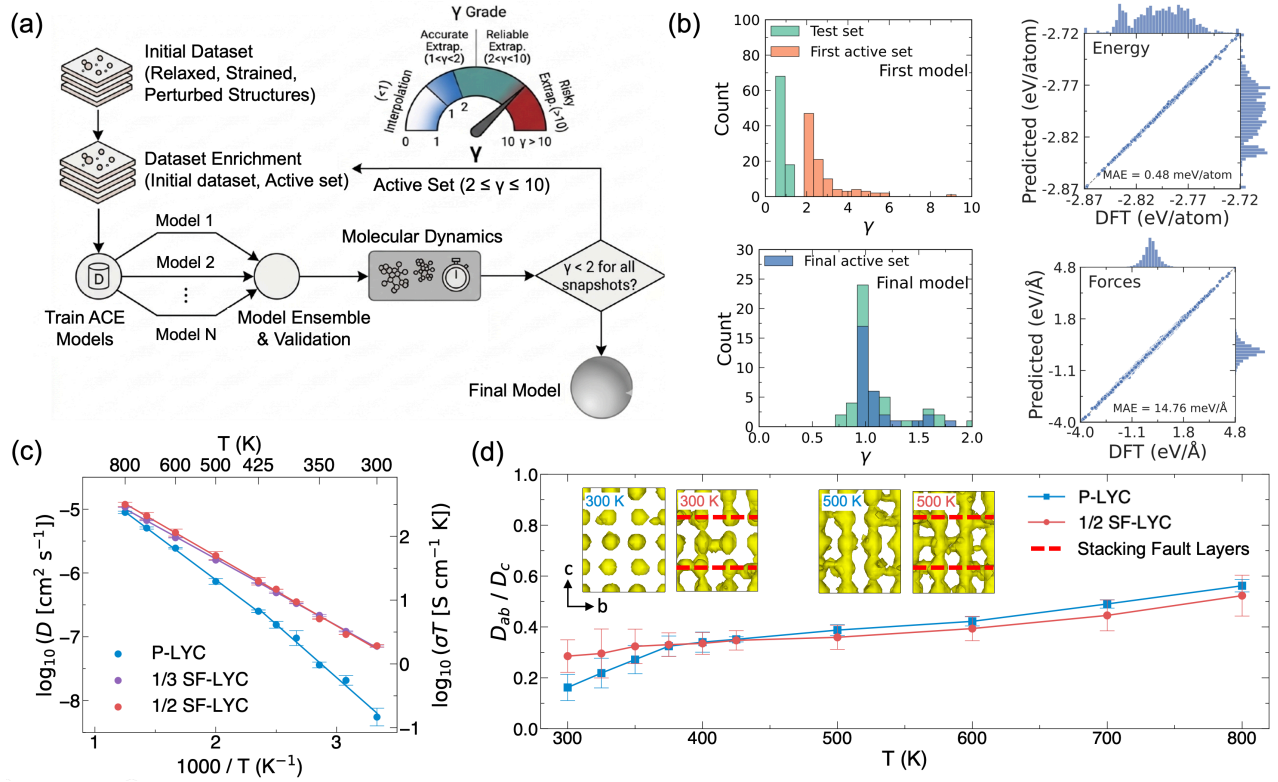


Figure 5: Simulated Li-ion transport in P-LYC and SF-LYC. (a) Active learning workflow for ACE model development. (b) ACE model validation via extrapolation grade (γ) histograms and parity plots of predicted versus DFT reference energies and forces. (c) Arrhenius plot of Li⁺ diffusivity (D) for pristine (P-LYC) and faulted (1/3 SF-LYC and 1/2 SF-LYC) structures. (d) Temperature-dependent diffusivity ratio of the Oct–Tet–Oct (D_{ab}) to Oct–Oct (D_c) pathways. Insets display Li-ion probability density plots in the b – c plane.

fusivity profiles for 1/3 SF-LYC and 1/2 SF-LYC nearly overlap, yielding a lower activation energy of 0.21 eV. The similar Li-ion conductivities across the SF models suggest that the stacking-fault-induced enhancement saturates above a critical fault concentration. Notably, a planar-defect concentration of only $\sim 17\%$ (1/3 SF-LYC) appears sufficient to fully activate the high-diffusivity pathways.

As in Table 1, the MLIP-predicted ionic conductivity (σ) at 300 K for P-LYC aligns closely with reported experimental benchmarks. According to Asano et al.³¹ experimental Li-ion conductivities primarily reflect bulk transport because grain-boundary contributions are negligible. Furthermore, our MD simulations indicate that SFs increase the room-temperature conductivity to over 6 mS/cm. This value is an order of magnitude higher than that of pristine LYC, suggesting that planar defects facilitate fast ion transport in these materials. In con-

trast, experimental data (Table 1) show no significant enhancement in Li-ion transport, even in samples reported to contain SFs,¹¹ indicating that the overall ionic conductivity is governed by the dominant pristine phase.

To uncover the structural origin of the lowered activation barriers and higher Li-ion diffusivities in the faulted models, we analyzed the Li⁺ diffusion pathways. In the hcp anion framework of LYC, Li⁺ migration proceeds via two mechanisms: (i) a direct octahedral-to-octahedral (Oct–Oct) hop along the c -axis, and (ii) a cooperative octahedral-tetrahedral-octahedral (Oct–Tet–Oct) route through interstitial tetrahedral sites (Figure S9 in SI).⁴⁴

To evaluate how SFs modulate directional ion transport, we decomposed the total diffusivity into components parallel (D_{ab}) and perpendicular (D_c) to the fault plane, with a , b , and c the principal crystallographic directions. Figure 5d shows the temperature depen-

Table 1: Machine-learning predicted and experimentally reported Li-ion conductivity σ (in mS/cm at the indicated temperatures) and activation energy E_a (in eV) in LYC bulk (pristine) and its SF models. The computed phase transition temperature $T_c = 425$ K for $P\bar{3}m1$ (Figure 5), and relative E_a s are reported separately for the low-temperature ($T < T_c$) and high-temperature ($T > T_c$) regimes. Synthesis method shows the synthesis protocol: high-temperature solid-state (SS), and chemo-mechanical ball milling (BM) syntheses.

LYC	σ	$E_a(T < T_c)$	$E_a(T > T_c)$	Synthesis Method
Bulk ³¹	0.510 @298 K	0.40	–	BM
Bulk ¹⁰	0.404 @303 K	0.41	–	BM
Bulk ¹⁰	0.090 @303 K	0.45	–	BM + Annealing
Bulk ¹⁰	0.045 @303 K	0.49	–	SS
Bulk ¹¹	0.067 @295 K	0.47	–	SS
Bulk+SF ^{11, a}	0.490 @295 K	0.41	–	BM
Bulk ^b	0.490 @300 K	0.33	0.28	–
1/3 SF ^b	6.330 @300 K	0.21	0.21	–
1/2 SF ^b	6.420 @300 K	0.22	0.22	–

^aSynchrotron X-ray diffraction modeling indicated 15% layer-1 Y faults, 30% Li-defect layers, and 20% fully occupied Y layers.¹¹ However, the concentration of SFs was not deliberately controlled by Sebti et al.¹¹

^bThis work: ACE machine learning MD simulations.

dence of the anisotropy ratio (D_{ab}/D_c) alongside the spatial Li-ion probability density profiles. In P-LYC at low temperatures ($T < T_c$), the high formation energy of interstitial tetrahedral sites makes these sites energetically inaccessible. This confines Li-ion transport primarily to high-barrier, one-dimensional (1D) Oct–Oct migration along the c -axis. Tetrahedral interstitial sites become accessible only above T_c . This accessibility establishes the 3D Oct–Tet–Oct percolation network and causes D_{ab}/D_c to increase steadily with temperature. SF in LYC remove this restriction at low temperatures ($T < 400$ K). The faulted structures therefore display higher D_{ab}/D_c ratios at 300 K compared to P-LYC. The Li⁺ probability density plots shown as an inset in Figure 5 illustrate that SFs alter local coordination environments. This alteration lowers the Oct–Tet–Oct barrier and facilitates in-plane (ab -plane) cross-channel hopping without requiring thermal transition across T_c . By enabling this interconnected 3D diffusion network at lower temperatures, SFs bypass the high-barrier 1D c -axis migration, explaining the lower overall activation energy.

Understanding how extended defects, such as two-dimensional stacking faults, affect ion

transport in energy materials, in particular, solid electrolytes is critical to developing commercially viable all-solid-state batteries.

This Letter establishes a rigorous protocol for screening stacking faults and demonstrates that they are thermodynamically accessible in trigonal Li₃YCl₆ and monoclinic Li₃YBr₆ (Figures 2–4). Stacking faults in Li₃YCl₆ are metastable (~ 16.81 meV/atom above the bulk ground state), whereas those in Li₃YBr₆ are nearly degenerate with the bulk.

Our simulations show that high fault concentrations enhance bulk ion transport in Li₃YCl₆. However, the experimental data (Table 1) do not exhibit comparable increase in Li-ion transport, as the bulk Li₃YCl₆ phase limits the overall conductivity.

At the structural level, our study indicates that this enhancement in Li-ion conductivity arises from stacking-fault-induced changes in Li sublattice ordering. Heat-capacity profiles (Figure 4c) reveal a sharp peak near 480 K for bulk Li₃YCl₆, consistent with a discrete phase transition in which the Li-ion sublattice adopts a rigid, low-mobility ordered state at lower temperatures. In contrast, stacking faults in Li₃YCl₆ exhibit a broad, continuous ther-

mal response without a phase transition. As indicated by relatively large atomic distortions (Figure 2b) in stacking-faulted Li_3YCl_6 , these defects force Li-ions into a disordered network, providing low-barrier pathways increasing Li-ion conductivity (Figures 5b and c).

The defect-transport coupling observed in Li_3YCl_6 is not universal among ternary halide solid electrolytes. In monoclinic Li_3YBr_6 , pristine and stacking-faulted structures exhibit comparable atomic-site distortions (Figure 3b) and similar thermodynamic behavior (Figure 4d-f). Their principal distinction lies in the Li-sublattice disordering pathway: pristine Li_3YBr_6 shows two heat-capacity peaks near 300 K, whereas the faulted material exhibits a single peak (Figure 4f). This close correspondence is consistent with reports for other monoclinic halides, in which stacking faults have limited effects on long-range Li-ion migration.^{22,24}

Because the faulted states in Li_3YCl_6 are metastable, moderate thermal annealing readily eliminates these planar defects, as previously demonstrated by Sebti et al.¹¹ Consequently, high concentrations of stacking faults are expected only under non-equilibrium processing conditions, such as mechanochemical milling¹¹ or rapid quenching from high-temperature synthesis,^{9,21,24} which kinetically trap defect populations before they relax to the ordered ground state.

In summary, this work highlights extended defects, particularly stacking faults, as critical structural features that can govern the functional properties of solid electrolytes and disordered materials more broadly. Controlling stacking-fault populations through targeted synthesis strategies offers a pathway toward the deliberate tuning of transport and other technologically relevant properties.

Computational Method: First-principles DFT²⁸ calculations were performed to generate the reference energies and atomic forces required for the multiscale simulations. These datasets were specifically used to parameterize cluster expansion Hamiltonian for finite-temperature thermodynamic sampling and to

train atomic cluster expansion potentials for large-scale molecular dynamics simulations.

All DFT calculations were carried out using the Vienna *ab initio* Simulation Package.^{51,52} The exchange-correlation energy was evaluated using the regularized strongly constrained and appropriately normed (r²SCAN) meta-generalized gradient approximation.³⁸ The ion-electron interactions were described using the projector augmented-wave (PAW) formalism.⁵³ The specific PAW potentials employed in this study include Li_{sv} (10Sep2004, $1s^22s^1$), Y_{sv} (25May2007, $4s^24p^64d^15s^2$), Cl (06Sep2000, $3s^23p^5$), and Br (06Sep2000, $4s^24p^5$). The electronic wave functions were expanded in a plane-wave basis set with a kinetic energy cutoff of 520 eV. Brillouin zone integration was performed using a Γ -centered k -point mesh with a uniform reciprocal space spacing of less than $0.3/\text{\AA}$. Lattice parameters were fixed to their experimental values,¹⁰ while internal atomic coordinates were fully relaxed until the maximum residual force acting on any atom fell below $0.01 \text{ eV}/\text{\AA}$.

Details of the CE Hamiltonian parameterization and active-learning training of the ACE potentials are provided in the Supporting Information (SI). Specifically, to generate the ACE training datasets, we employed the optB88-vdW functional⁵⁴ to capture long-range van der Waals interactions. A comparative evaluation of these functionals is detailed in the SI. The validated ACE potentials were then used for MD simulations of Li-ion transport in 1,620-atom cells for all LYC models. To construct these configurations, the 60-atom ground-state P-LYC and 1/2 SF-LYC base models were expanded by $3 \times 3 \times 3$, while the 90-atom 1/3 SF-LYC base model was expanded by $3 \times 3 \times 2$. Additionally, $P\bar{3}m1$ -based $3 \times 3 \times 6$ supercell models (1,620 atoms) were used for both pristine and faulted LYC.

The tracer diffusion coefficient D was obtained from the slope of the Li-ion mean squared displacement via $D = \frac{1}{2dNt} \sum_{i=1}^N \langle |\mathbf{r}_i(t) - \mathbf{r}_i(0)|^2 \rangle$,⁵⁵ where N is the number of mobile ions, $d = 3$ represents the system dimensionality, and $\mathbf{r}_i(t)$ denotes the position vector of ion i at time t . Assuming un-

correlated ion migration, the ionic conductivity σ was estimated using the Nernst–Einstein equation $\sigma = \frac{N}{V} \frac{q^2}{k_B T} D$,⁵⁶ where q is the charge of the Li-ion carriers, V is the volume of the simulation cell, k_B is the Boltzmann constant, and T is the temperature.

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Supporting Information Available

The Supporting Information is available free of charge at xxxxxxxx. This document provides further details on the structural models, cluster-expansion and Monte Carlo simulations, ACE validation, and analyses of Li-ion transport and defect effects.

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Supporting Information:

Stacking-Fault Defects Modulate Ion Transport in Ternary Halide Solid Electrolytes

Yan Li,[†] Wei-Fan Huang,[‡] Zeyu Deng,[†] Lars Grabow,^{‡,§} and Pieremanuele
Canepa^{*,¶,§}

[†]*Department of Materials Science and Engineering, National University of Singapore, 9
Engineering Drive 1, 117575, Singapore*

[‡]*Department of Chemical and Biomolecular Engineering, University of Houston, Houston,
Texas, 77204, United States*

[¶]*Department of Electrical and Computer Engineering, University of Houston, Houston,
Texas, 77204, United States*

[§]*Texas Center for Superconductivity, University of Houston, Houston, Texas, 77204, United
States*

E-mail: pcanepa@uh.edu

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S1 Optimized Li_3YX_6 ($\text{X} = \text{Cl}, \text{Br}$) Crystal Structures

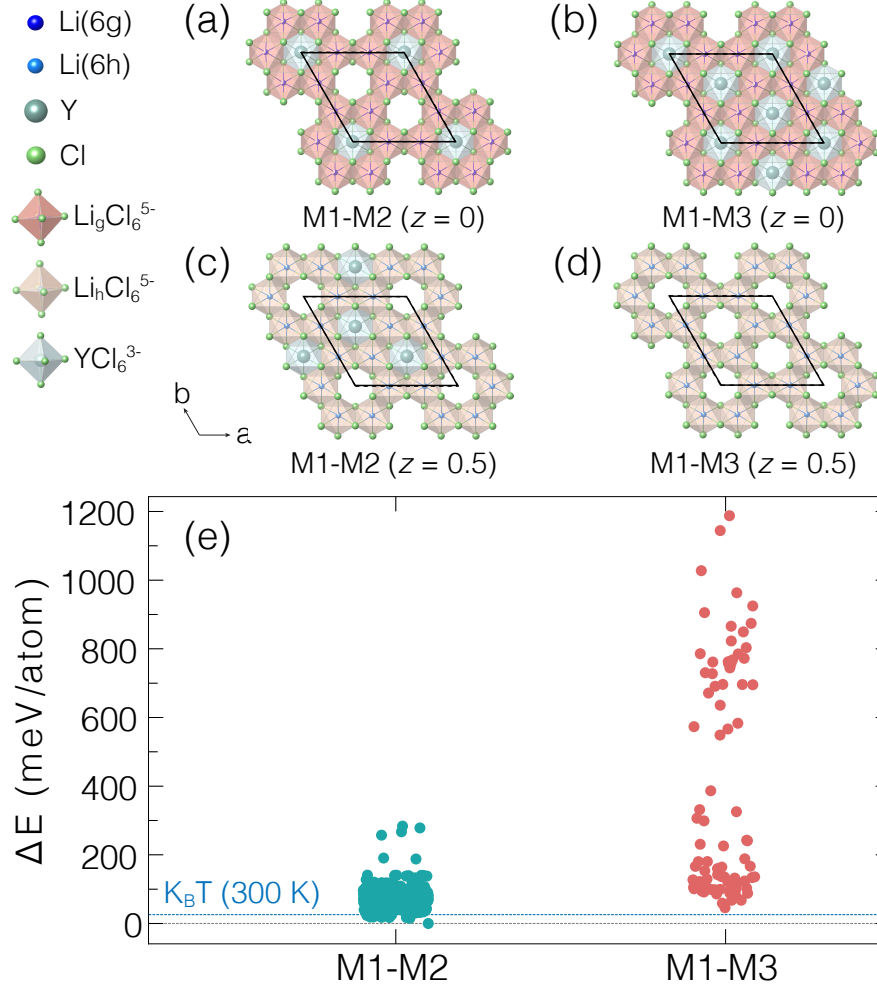


Figure S1: Thermodynamic preference for the M1-M2 structural framework in Li_3YCl_6 (LYC). (a–d), Atomic projections along the c -axis at $z = 0$ and $z = 0.5$ illustrating the distinct YCl_6^{3-} polyhedral networks of the experimentally reported $P\bar{3}m1$ phase.^{S1} The structural frameworks are defined by their specific Y-site occupancies: the Y1 site at $(0, 0, 0)$ is fully occupied in both, while the secondary Y atom fractionally occupies the Y2 site at $(1/3, 2/3, 0.5)$ to form the M1-M2 model (a, c), and the Y3 site at $(1/3, 2/3, 0)$ to form the M1-M3 model (b, d). (e) Relative energies (ΔE) of ~ 460 enumerated configurational ensembles within the conventional cell and the $1 \times 1 \times 2$ supercell of LYC. The M1-M2 framework constitutes the thermodynamically stable phase, exhibiting a dense cluster of ordered configurations below the room-temperature thermal fluctuation threshold ($k_B T \approx 26$ meV/atom, blue dashed line) relative to the global ground state (gray dashed line).

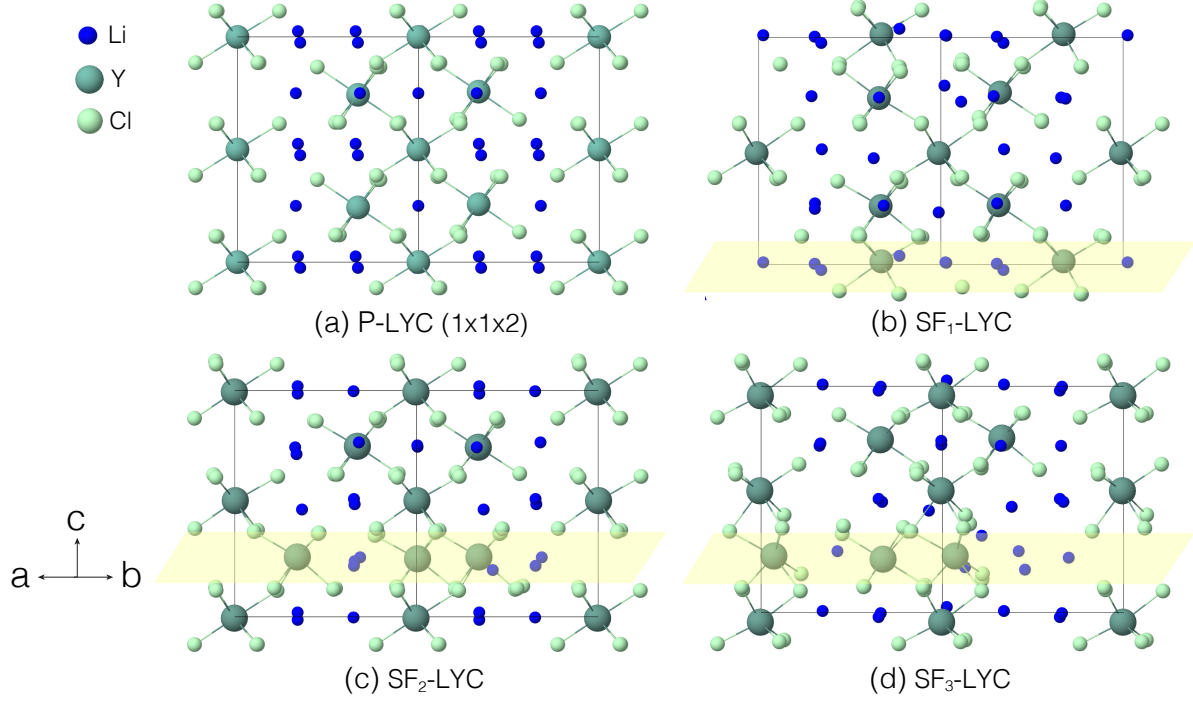


Figure S2: Optimized crystal structures of pristine and faulted LYC. Ball and stick representations of the lowest-energy configurations identified for (a) the pristine LYC (P-LYC) supercell ($1 \times 1 \times 2$) and (b–d) the stacking fault (SF) models: (b) SF₁-LYC, (c) SF₂-LYC, and (d) SF₃-LYC. The yellow planes highlight the crystallographic layers where the rigid translations (stacking faults) were applied.

To quantify the atomic rearrangements associated with structural relaxation, specifically those induced by stacking faults, we defined an average lattice distortion parameter, $\bar{D}$:

$$\bar{D} = \frac{1}{N_{\text{tot}}} \sum_a N_a \bar{u}_a \quad (\text{S1})$$

where the mean atomic site distortion ($\bar{u}_a$) for species a is given by:

$$\bar{u}_a = \frac{1}{N_a} \sum_{i=1}^{N_a} |(\mathbf{R}_i^a - \mathbf{P}_{j^*(i)}^a) - \mathbf{d}_{\text{drift}}| \quad (\text{S2})$$

In Eqs. S1 and S2, N_{tot} denotes the total number of ions in the simulation cell, and N_a is the number of atoms of species a . The vector $\mathbf{R}_i^a$ represents the relaxed position of the i -th atom of species a , while $\mathbf{P}_{j^*(i)}^a$ corresponds to the nearest-neighbor site in the corresponding

Table S1: Calculated lowest-energy ordered configuration ($P\bar{3}c1$ symmetry) of P-LYC, derived from the experimental disordered $P\bar{3}m1$ parent phase.^{S1} The table lists the optimized lattice constants (in Å and degrees), fractional coordinates (x, y, z), and the corresponding Wyckoff multiplicities.

	$a = b$	c	$\alpha = \beta$	γ
Cal.	11.209	12.094	90.000	120.000
Atom	Wyck	x	y	z
Li1	12 g	0.347	0.013	0.974
Li2	6 f	0.322	0.000	0.250
Y1	2 b	0.000	0.000	0.000
Y2	4 d	0.333	0.667	0.257
Cl1	12 g	0.120	0.888	0.386
Cl2	12 g	0.229	0.788	0.134
Cl3	12 g	0.457	0.564	0.380

Table S2: Calculated lowest-energy ordered configuration ($C2$ symmetry) of pristine Li_3YBr_6 (P-LYB), derived from the experimental disordered $C2/m$ parent phase.^{S1} The table lists the optimized lattice constants (in Å and degrees), fractional coordinates (x, y, z), and the corresponding Wyckoff multiplicities.

	a	b	c	$\alpha = \gamma$	β
Cal.	6.919	11.974	6.864	90.000	109.781
Atom	Wyck	x	y	z	
Li1	2 a	0.000	0.331	0.000	
Li2	2 a	0.500	0.174	0.000	
Li3	2 b	0.000	0.164	0.500	
Y1	2 a	0.000	0.003	0.000	
Br1	4 c	0.255	0.013	0.760	
Br2	4 c	0.235	0.172	0.252	
Br3	4 c	0.265	0.672	0.748	

unrelaxed reference lattice (defined as the experimental structure for pristine models, or the idealized faulted framework constructed for SF models), mapped *via* periodic boundary conditions. The vector $\mathbf{d}_{\text{drift}}$ corrects for the global center-of-mass translation of the simulation cell during relaxation, and $\|\cdot\|$ denotes the Euclidean norm.

S2 Validation of the Fixed-lattice Approximation of Li_3YCl_6

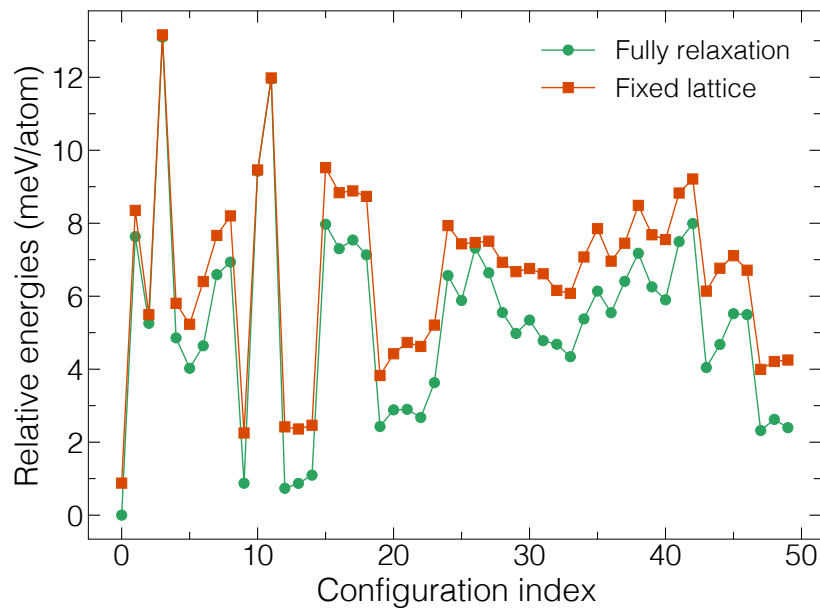


Figure S3: Comparison of relative energies for 50 representative P-LYC configurations. Configurations were obtained via full structural relaxation (lattice vectors and atomic positions relaxed; green circles) vs. a constrained approach (lattice fixed, atomic positions relaxed; orange squares). The negligible energy discrepancy (< 2 meV/atom) and strictly preserved energetic trend justify using the fixed-lattice scheme for all structural optimizations performed in this study.

S3 Cluster Expansion Construction and Validation

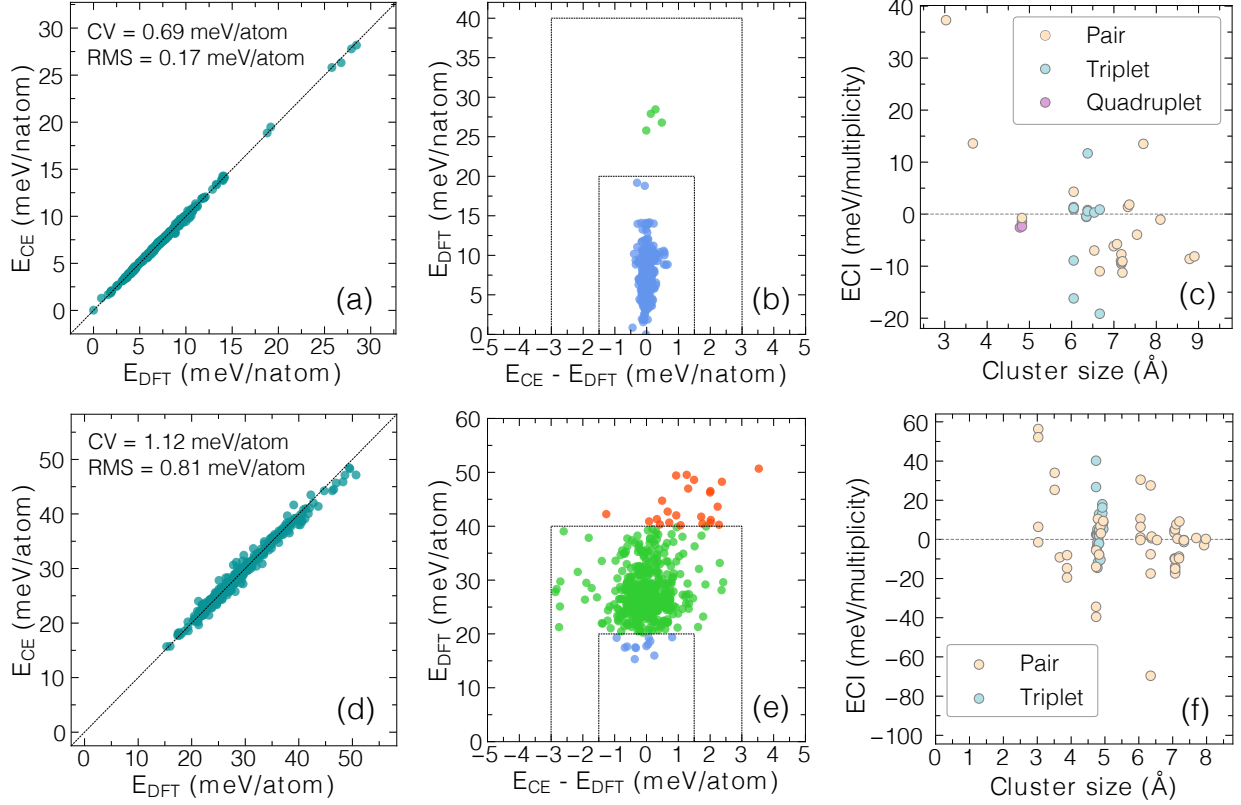


Figure S4: Validation of the Cluster Expansion (CE) models for the pristine and stacking-faulted LYC systems. (a–c) Fitting results for the pristine LYC system. (d–f) Fitting results for the stacking-faulted SF_1 -LYC system. Panels (a) and (d) show the parity plots comparing the CE-predicted energies (E_{CE}) with the DFT-calculated energies (E_{DFT}), referenced to the lowest-energy DFT configuration. Both models demonstrate reasonable predictive accuracy, achieving low Cross-Validation (CV) scores of 0.69 meV/atom for the pristine phase and 1.12 meV/atom for the faulted phase. Panels (b) and (e) depict the energy residuals ($E_{CE} - E_{DFT}$). The errors for the pristine system are tightly confined within a narrow range ($\approx \pm 1$ meV/atom), while the SF_1 -LYC system exhibits a slightly broader error distribution, due to the increased structural complexity introduced by the stacking faults. Panels (c) and (f) present the effective cluster interactions (ECIs) as a function of cluster size. The pristine model was fitted using interaction cutoffs of 9 Å, 7 Å, and 5 Å for pair, triplet, and quadruplet clusters, respectively. For the faulted models, smaller cutoffs of 8, 6, and 4 Å were used because the reduced lattice symmetry rapidly increases the number of distinct cluster orbits. This procedure yielded 38 and 95 nonzero terms for pristine LYC and SF_1 -LYC, respectively.

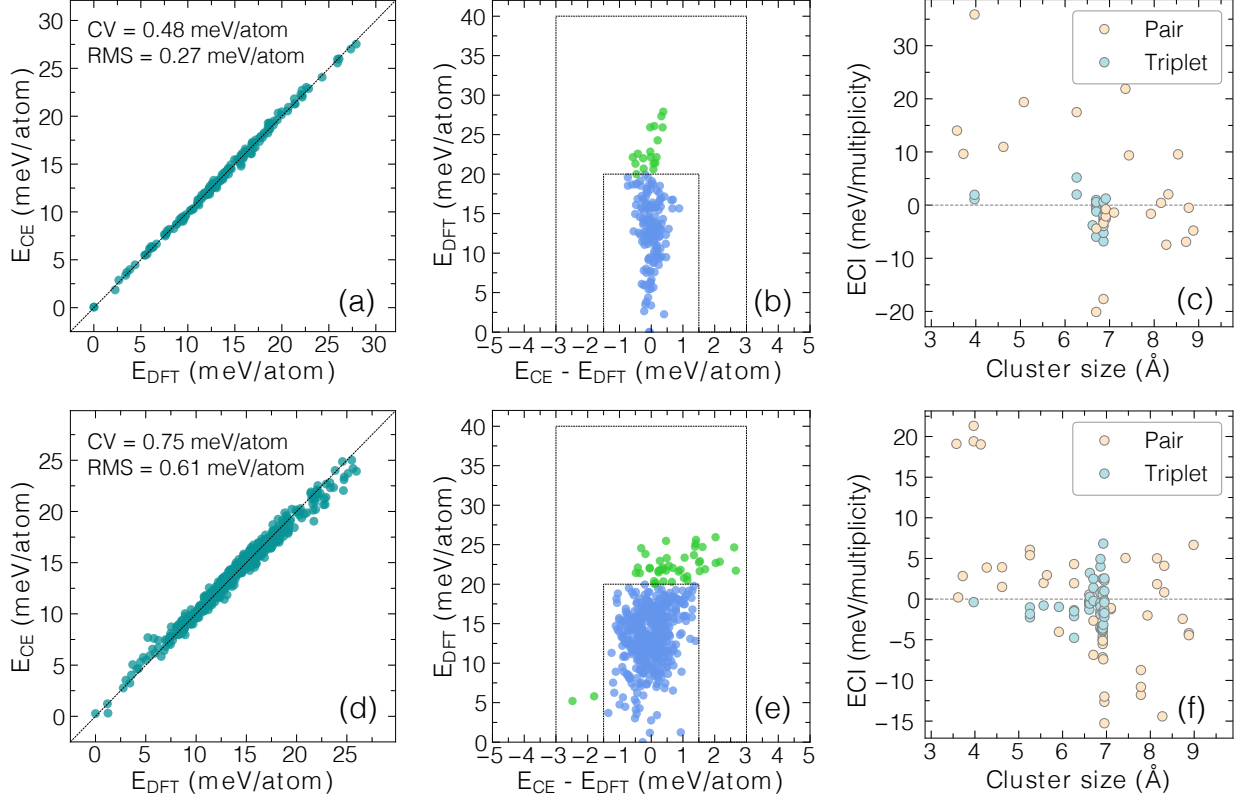


Figure S5: Validation of the Cluster Expansion (CE) models for the pristine and stacking-faulted LYB systems. (a–c) Fitting results for the pristine LYB system. (d–f) Fitting results for the stacking-faulted SF-LYB system. Panels (a) and (d) show the parity plots comparing the CE-predicted energies (E_{CE}) with the DFT-calculated energies (E_{DFT}), referenced to the lowest-energy DFT configuration. The low Cross-Validation (CV) and Root Mean Square (RMS) errors (< 1 meV/atom) indicate high predictive accuracy for both models. Panels (b) and (e) display the distribution of fitting errors (residuals, $E_{CE} - E_{DFT}$) as a function of energy, demonstrating that errors are tightly confined within ± 3 meV/atom range relative to the DFT ground states. Panels (c) and (f) present the Effective Cluster Interactions (ECIs) as a function of cluster size. Both models were fitted using interaction cutoffs of 9 Å, 7 Å, and 5 Å for pair, triplet, and quadruplet clusters, respectively, resulting in the selection of 50 (pristine LYB) and 92 (SF-LYB) non-zero terms.

Table S3: Crystallographic parameters of the P-LYC reference lattice used in the cluster expansion analysis. The structural data were derived from the experimental work of Ref. S1. Lattice constants are in Å and degrees. The fractional coordinates and Wyckoff labels correspond to the trigonal $P\bar{3}m1$ space group. The notation “Li/Va” indicates the sublattice sites where binary occupancy (Li atom or Vacancy) is enabled in the configurational modeling.

Space group	a = b	c	$\alpha = \beta$	γ
$P\bar{3}m1$	11.209	6.047	90.000	120.000

Index	Atomic species	Wyckoff label	Fractional coordinate		
			x	y	z
0	Li/Va	$6g$	0.343	0.000	0.000
1	Li/Va		0.657	0.000	0.000
2	Li/Va		0.000	0.343	0.000
3	Li/Va		0.000	0.657	0.000
4	Li/Va		0.657	0.657	0.000
5	Li/Va		0.343	0.343	0.000
6	Li/Va	$6h$	0.327	0.000	0.500
7	Li/Va		0.673	0.000	0.500
8	Li/Va		0.000	0.327	0.500
9	Li/Va		0.000	0.673	0.500
10	Li/Va		0.673	0.673	0.500
11	Li/Va		0.327	0.327	0.500
12	Y	$1a$	0.000	0.000	0.000
13	Y	$2d$	0.333	0.667	0.500
14	Y		0.667	0.333	0.500
15	Cl	$6i$	0.113	0.887	0.765
16	Cl		0.887	0.113	0.235
17	Cl		0.113	0.226	0.765
18	Cl		0.887	0.774	0.235
19	Cl		0.774	0.887	0.765
20	Cl		0.226	0.113	0.235
21	Cl	$6i$	0.221	0.779	0.263
22	Cl		0.779	0.221	0.737
23	Cl		0.221	0.441	0.263
24	Cl		0.779	0.559	0.737
25	Cl		0.559	0.779	0.263
26	Cl		0.441	0.221	0.737
27	Cl	$6i$	0.446	0.554	0.753
28	Cl		0.554	0.446	0.247
29	Cl		0.446	0.892	0.753
30	Cl		0.554	0.108	0.247
31	Cl		0.108	0.554	0.753
32	Cl		0.892	0.446	0.247

Table S4: Crystallographic parameters of the P-LYB reference lattice used in the cluster expansion analysis. The structural data were derived from the experimental work of Ref.^{S1} Lattice constants are provided in Å and degrees. The fractional coordinates and Wyckoff labels correspond to the monoclinic $C2/m$ space group. The notation “Li/Va” indicates the sublattice sites where binary occupancy (Li atom or Vacancy) is enabled in the configurational modeling.

Space group	a	b	c	$\alpha = \gamma$	β
$C2/m$	6.919	11.974	6.864	90.000	109.780

Index	Atomic species	Wyckoff label	Fractional coordinate		
			x	y	z
0	Li/Va	$4g$	0.500	0.193	0.000
1	Li/Va		0.500	0.807	0.000
2	Li/Va		0.000	0.693	0.000
3	Li/Va		0.000	0.307	0.000
4	Li/Va	$4h$	0.000	0.212	0.500
5	Li/Va		0.000	0.788	0.500
6	Li/Va		0.500	0.712	0.500
8	Li/Va		0.500	0.288	0.500
8	Y	$2a$	0.000	0.000	0.000
9	Y		0.500	0.500	0.000
10	Br	$4i$	0.244	0.000	0.757
11	Br		0.756	0.000	0.243
12	Br		0.744	0.500	0.757
13	Br		0.256	0.500	0.243
14	Br	$8j$	0.252	0.171	0.237
15	Br		0.748	0.829	0.763
16	Br		0.748	0.171	0.763
17	Br		0.252	0.829	0.237
18	Br		0.752	0.671	0.237
19	Br		0.248	0.329	0.763
20	Br		0.248	0.671	0.763
21	Br		0.752	0.329	0.237

S4 Monte Carlo Simulation Convergence

The configurational energy, $\Phi(T)$, and constant-volume heat capacity, $C_v(T)$, were derived from canonical ensemble averages over microscopic configurations sampled by the CE Hamiltonian:

$$\Phi(T) = \langle E(\vec{\sigma}) \rangle \quad (\text{S3})$$

and

$$C_v(T) = \frac{\langle E(\vec{\sigma})^2 \rangle - \langle E(\vec{\sigma}) \rangle^2}{k_B T^2} \quad (\text{S4})$$

where $\langle \dots \rangle$ denotes the thermal average at temperature T , and k_B is the Boltzmann constant.

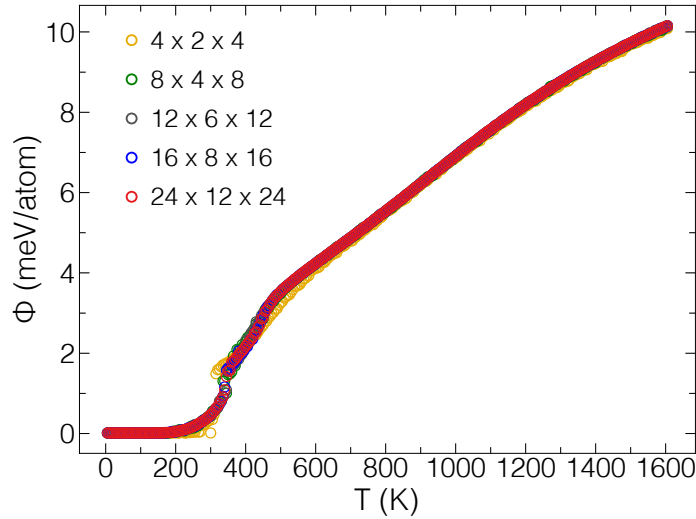


Figure S6: Convergence of the configurational energy (Φ) with respect to simulation cell size for the P-LYB system. Canonical Monte Carlo (CMC) simulations were performed during the heating scan at fixed composition on supercells of increasing dimensions, ranging from $4 \times 2 \times 4$ to $24 \times 12 \times 24$ expansions of the reference(primitive) unit cell (2 f.u., 20 atoms), using the effective Hamiltonian fitted *via* the CASM code.^{S2} The energy profiles exhibit negligible variation for system sizes larger than the $12 \times 6 \times 12$ supercell.

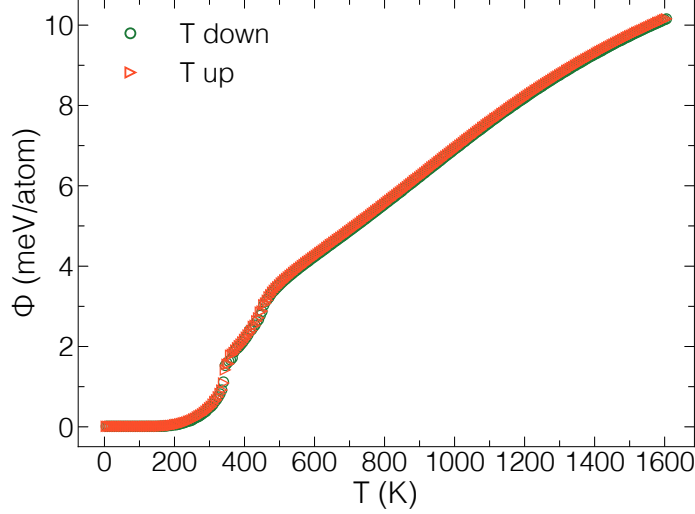


Figure S7: Assessment of thermodynamic reversibility for the P-LYB system. Configurational energy (Φ) profiles were calculated using CMC simulations during heating (orange triangles, T up) and cooling (green circles, T down) sequences on a $24 \times 12 \times 24$ supercell of the reference unit cell. The heating and cooling branches exhibit negligible hysteresis, suggesting that the system achieves thermodynamic equilibrium at each temperature step over the entire simulated range.

S5 Atomic Cluster Expansion Methodology

The atomic cluster expansion (ACE) framework^{S3-S5} provides a complete, symmetry-adapted basis for describing local atomic environments and constructing interatomic potential energy surfaces. By construction, ACE satisfies fundamental physical symmetries, including invariance under spatial translation, rotation, and inversion, as well as permutation covariance among identical atomic species.

Within the ACE formalism, the potential energy E of a system of N -atoms is decomposed into local atomic contributions ϵ_i :

$$E = \sum_{i=1}^N \epsilon_i. \quad (\text{S5})$$

A linear expansion of symmetry-adapted basis functions $B_{i\nu}$ characterizes the local environment of atom i :

$$\varphi_i = \sum_{\nu} c_{\nu} B_{i\nu}, \quad (\text{S6})$$

where φ_i describes the local environment of atom i , and the expansion coefficients c_ν are adjustable parameters optimized during potential fitting.

To capture the many-body interactions governing chemical bonding, the local atomic energy ϵ_i is expressed as a nonlinear functional, $\mathcal{F}$, of P atomic properties:

$$\epsilon_i = \mathcal{F}(\varphi_i^1, \varphi_i^2, \dots, \varphi_i^P). \quad (\text{S7})$$

Inspired by the Embedded Atom Method (EAM),^{S6,S7} a standard approach uses an EAM-like form that retains the first two property terms in Eq. S7:

$$\epsilon_i = \varphi_i^1 + \sqrt{\varphi_i^2}. \quad (\text{S8})$$

By systematically expanding the basis set, ACE converges rigorously toward the reference first-principles ground-truth potential energy surface. This provides a physically meaningful and computationally efficient approach for atomistic simulations. Ref. S5 provides the detailed parameterization and extended discussion of this framework.

S6 ACE Development for Li_3YCl_6

As Figure 5a in the main text outlines, an active learning protocol generated the ACE potentials used to simulate Li-ion transport in LYC solid electrolytes. This protocol ensures accurate reproduction of the DFT reference energies and forces. To initialize this process, we generated a training set of LYC configurations comprising two primary structural categories: (i) perturbed configurations of relaxed and strained lattices with atomic positions stochastically displaced by 0 to 0.3 Å; and (ii) dynamical snapshots from *ab initio* molecular dynamics (AIMD) trajectories. We ran these simulations from 300 to 700 K under strains ranging from -3% to +3% to capture lattice deformations and thermal fluctuations.

This process generated two initial datasets of 2,400 structures each, complete with DFT-computed energies and forces. We developed two training sets using different DFT exchange-correlation functionals to evaluate the potential against experimental benchmarks. The first set applies the meta-generalized gradient approximation r²SCAN of the exchange and correlation functional^{S8} to pristine LYC structures to establish a baseline. The second set employs the optB88-vdW functional^{S9} and combines faulted and pristine LYC structures in a 3:2 ratio. The optB88-vdW functional captures van der Waals interactions known to stabilize layered LYC structures.^{S10}

For each DFT dataset, we trained an initial ACE potential using an 8:1:1 ratio for training, validation, and test subsets to prevent overfitting. Minimizing a loss function over the predicted and reference energies and forces optimized the model parameters. The resulting r²SCAN potential achieved training (validation) root-mean-square errors of 0.66 (0.66) meV/atom for energies and 19.65 (19.80) meV/Å for forces. Similarly, the optB88-vdW potential yielded training (validation) errors of 0.64 (0.67) meV/atom and 19.16 (19.23) meV/Å.

An active learning loop subsequently refined the first-generation ACE model. First, we performed MD simulations for up to 100,000 steps using the current ACE potential. We evaluated the extrapolation grade γ at each step using the D-optimality criterion.^{S11} Configurations with $\gamma < \gamma_{\text{select}} = 2$ were considered well-interpolated. Those exceeding $\gamma_{\text{break}} = 10$ triggered immediate simulation termination. Intermediate configurations ($\gamma_{\text{select}} \leq \gamma \leq \gamma_{\text{break}}$) augmented the training set.^{S11} We performed DFT single-point calculations on the selected structures and retrained the model on the expanded dataset. This loop was repeated until all MD snapshots satisfy $\gamma < \gamma_{\text{select}}$, ensuring the robustness of the final ACE potential.

S7 Effect of DFT Functionals on Predicted Diffusivity

Figure S8 evaluates how the choice of DFT exchange-correlation functional (PBEsol, optB88-vdW, or r²SCAN) affects the predicted Li-ion diffusivity in pristine LYC (P-LYC) across a broad temperature range.

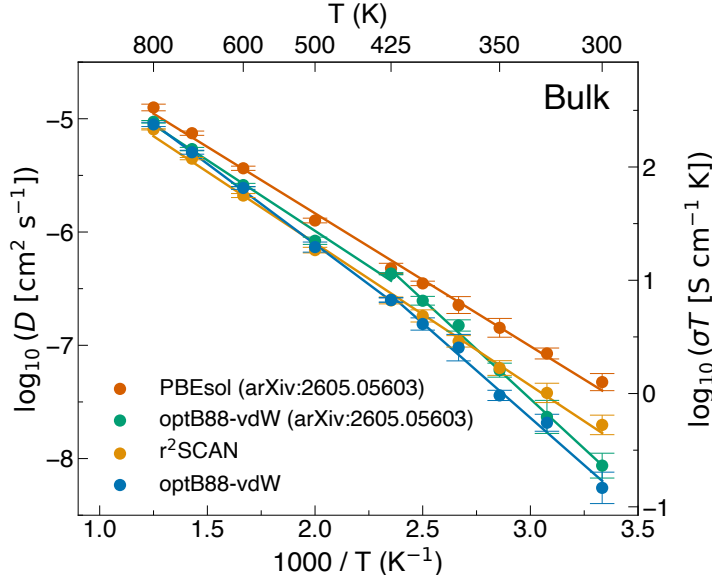


Figure S8: Effect of DFT functionals on predicted Li-ion diffusivity in P-LYC. Reference data (labeled as arXiv:2605.05603) is extracted from Ref. S10.

Consistent with previous findings by Huang et al.,^{S10} only the optB88-vdW functional describes the structural phase transition, which is evidenced by a distinct change in the Arrhenius slope at the transition temperature (~ 425 K). In contrast, the PBEsol and r²SCAN functionals yield a single linear Arrhenius relationship and fail to reproduce the phase transition.

S8 Li-ion Migration Pathways in Li₃YCl₆

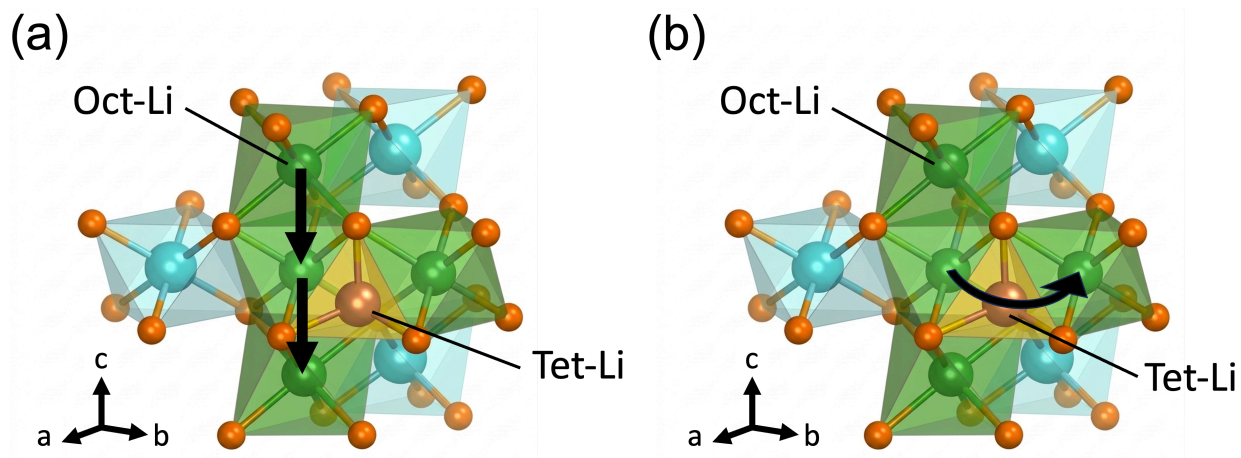


Figure S9: Schematic illustration of the Li-ion migration pathways in Li_3YCl_6 : (a) Octahedral (Oct)–Oct sites and (b) Oct–Tetrahedral (Tet)–Oct mechanisms.

S9 Impact of Lithium Vacancy on Transport

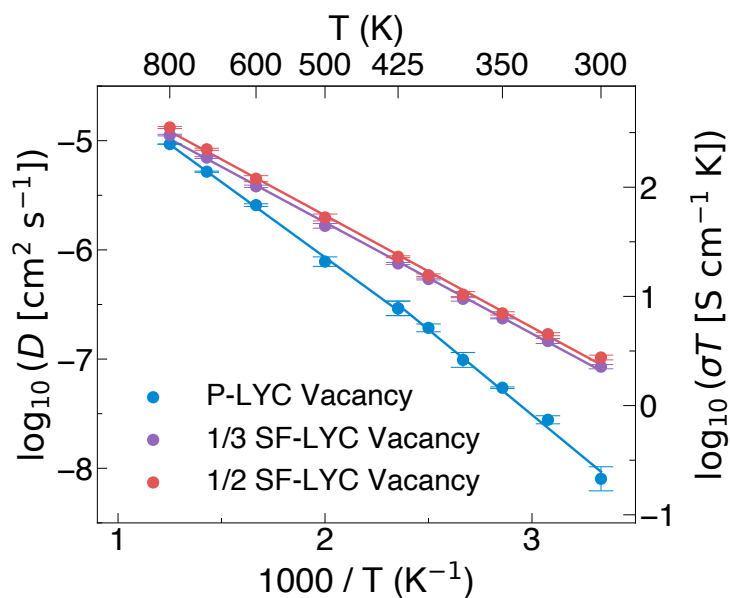


Figure S10: Arrhenius plots of Li-ion diffusivity, D , and conductivity, σ , for Li-vacancy-containing pristine (P-LYC) and two faulted (1/3 SF-LYC and 1/2 SF-LYC) structural models.

In stoichiometric LYC, without added Li vacancies, Li-ion migration is strongly suppressed by site blocking,^{S10} requiring higher-energy interstitialcy mechanisms involving highly corre-

lated hopping sequences. Introducing Li vacancies therefore relieves this kinetic bottleneck by providing accessible destination sites for neighboring ions. These Li vacancies reduce local electrostatic repulsion and transition-state relaxation penalties, favoring direct, low-barrier vacancy hopping that increases both hopping frequency and ionic conductivity.

As shown in Figure S10 and Table S5, the deliberate introduction of Li vacancies enhances the ionic conductivity across all structural configurations compared to their pristine bulk structure. Notably, while the activation energy exhibits only a slight reduction or remains essentially unchanged, the increased availability of destination sites leads to substantially boosted diffusion kinetics. Specifically, for P-LYC, introducing vacancies increases σ from 0.49 mS/cm to 0.71 mS/cm at 300 K, with E_a slightly dropping from 0.33 eV to 0.31 eV ($T < T_c$). In the presence of stacking faults, vacancy-containing structures deliver even higher conductivities, reaching 8.45 mS/cm for the partially faulted (1/3 SF) and 5.03 mS/cm for the fully faulted (1/2 SF) models, while maintaining low activation energies that are nearly identical to their vacancy-free equivalents.

Table S5: Li vacancy effect on ionic conductivity σ (in mS/cm) at 300 K and activation energy E_a (in eV). The critical temperature is $T_c = 425$ K for $P\bar{3}m1$, and the activation energies (in eV) E_a are reported separately for the low-temperature ($T < T_c$) and high-temperature ($T > T_c$) regimes.

Structure	σ @300 K	$E_a(T < T_c)$	$E_a(T > T_c)$
Pristine	0.71	0.31	0.27
Partially Faulted – 1/3 SF	8.45	0.20	0.20
Faulted – 1/2 SF	5.03	0.22	0.22

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