Strain Sensitivity of Li-ion Conductivity in β-Li$_3$PS$_4$ Solid Electrolyte

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(Received 22 December 2021; revised 27 May 2022; accepted 1 June 2022; published 21 July 2022)

Strain is present at the interfaces of solid electrolytes with the cathode and the anode in solid-state batteries due to interfacial reactions and due to volumetric expansion and contraction of the electrodes during battery charging and discharging cycles. This work quantifies the effect of elastic strain on Li-ion diffusion in a model solid electrolyte, β-Li$_3$PS$_4$, by using ab initio molecular dynamics (AIMD). We find that the strain tensors which compress the c axis (+2% a-b, −2% a-c, −2% b-c, −2% isotropic) increase the Li-ion diffusivity, and the strain tensors which stretch the c axis (−2% a-b, +2% a-c, +2% b-c, +2% isotropic) reduce it. Ionic conductivity increases by 2–14-fold with a reduction in activation energy for c-axis compressive strains and decreases by 1–14-fold with an increase in activation energy for c-axis tensile strains at room temperature. The c-axis compression increases disorder in the lattice and promotes jumps along all migration pathways. In particular, the Li 4$c$ site occupancy increases from about 3% to 6% (at 500 K), thus creating more vacancies at otherwise fully occupied and bottleneck 8$d$ and 4$b$ sites. The c-axis compression also reduces the distance between the 8$d$ and 4$b$ sites, thus increasing Coulomb repulsion between these sites. Increased Coulomb repulsion can destabilize Li at the 8$d$ and 4$b$ sites, promoting reduced occupancy and increased diffusivity associated with these sites. The results show that elastic strain can promote Li disorder and superionic conductivity, with an effect on Li-ion diffusion comparable to that of chemical substitution, and is important to consider for an accurate understanding and prediction of the solid-state Li-ion battery interface properties.

DOI: 10.1103/PRXEnergy.1.023003

I. INTRODUCTION

Fast ionic conductivity is important for efficient operation of solid-state ionic devices, including all-solid-state lithium-ion batteries [1], solid-oxide fuel cells [2], proton-conducting programmable resistors [3], and electrochemical analog programmable resistors [4]. While solid-state batteries offer better safety and higher energy density, the Li-ion conductivity of solid electrolytes remains lower than that of liquid organic electrolytes, limiting their charging rate and power density. The ionic conductivity of known lithium-ion-conducting solid-state electrolytes lies within 10$^{-9}$–10$^{-2}$ S/cm at room temperature [5], with conductivities above 10$^{-3}$ S/cm being desirable to enable practical applications. Solid electrolytes must also satisfy chemical, electrochemical, mechanical, and thermal stability [6], which narrows down the set of viable electrolytes. The ionic conductivity of known electrolytes is tuned by chemical substitution and new materials are being explored for their ability to conduct Li ions [7–9].

Strain engineering presents new ways of tuning ionic conductivity in solids. Elastic strain is known to alter the mobility of holes and electrons in semiconductors [10] and to reduce band gaps [11,12]. Elastic strain can also facilitate ion transport in oxides through an increase in migration volume and decrease in metal-oxygen bond strengths [13–15]. In principle, the desired strain can be achieved through epitaxial growth of thin films on a substrate with a particular lattice mismatch [16,17], through generating electrostrictive strain in a substrate material [18], or by nanomechanical manipulation [12,19]. Accurate modulation of strain is far from trivial for practical applications of ion conductors.

Importantly, the battery charging (discharging) process often leads to volumetric expansion (contraction) of the cathode and anode materials, thus introducing mechanical strain at the interface [20–24]. Interface strains also arise as a result of interfacial reactions between the solid
electrolyte and the cathode or anode [22,25–28]. Interface-induced stresses extending into the solid electrolyte have been detected and quantified in several systems. Although stress decreases with distance from the interface, stress experienced by the electrolyte can be substantial [22,25,29]. Continuum modeling of the stress distribution in the LiCoO2/LiPON/Si solid-state battery shows that (i) stress can reach about 1 GPa at the electrode-electrolyte interfaces during the charging process [25], with about 0.1–1 GPa stress extending into the LiPON electrolyte within at least a few nm [25]; and (ii) electrolyte decomposition can cause severe stress profiles in the order of about 10 GPa at the interface, with about 1 GPa stress extending into the electrolyte within about 100 nm [25]. Similarly, about 1 GPa stress extending into about 1 µm was reported for the Li1.3Ti1.7Al0.3(PO4)3 solid electrolyte during the charging process in a composite cathode [29]. Likewise, continuum modeling of the Li1+xAl2O3 (PO4)3/Li interphase growth shows about 0.1 GPa stress extending within about 100 µm into the electrolyte region [22]. In addition, compressive strains as large as 5%–10% were observed in Li0.33La0.56TiO3 electrolyte at the vicinity of the epitaxial interface with a Li-rich layered electrode [30]. The anode and cathode layers also sustain large stress levels during charging and discharging processes. For example, compressive stress as high as 1.5 GPa was reported in Si thin films during galvanostatic cycling (0.01–1.5 V vs Li/Li+ at 50 µA cm−2) [31]. Similarly, about 0.4 GPa compressive stress was reported for V2O5 thick films (4.0–2.8 V vs Li/Li+ at 6 µA cm−2) [32]. With such high levels of stress, and respective strains in the order of about 1% (assuming ~30 GPa bulk modulus of a sulfide electrolyte [33] at a hydrostatic stress of 1 GPa for simplicity), it is reasonable to expect changes in the ionic conductivity of the electrolyte and electrode materials near their interface, as well as of the solid-electrolyte interphases (SEIs) [34,35]. To determine whether the effect of strain is beneficial or detrimental, it is important to quantify its impact on Li-ion conductivity and the underlying mechanism.

A simplified understanding of the way strain affects ionic conductivity, as deduced from the literature, is that a small tensile strain usually facilitates ion transport, while compressive strain impedes it. Tensile strain was found to accelerate ion conduction in archetypical lithium- and oxygen-ion conductors, such as Li10GeP2S12 (LGPS) [36,37], Y-ZrO2 [13], CeO2 [14,38], and perovskite oxides [39]. In oxides, such a beneficial effect of tensile strain is rationalized in terms of increased volume along the migration path and decreased metal-oxygen bonding strength, which together facilitate migration [13].

However, in some materials, ionic conductivity increases upon compression not tension. Specifically, one should consider the activation enthalpy of ion diffusion: \( \Delta H_a = \Delta E_a + p \Delta V_a \), where \( \Delta E_a \) is the activation energy (without strain) and \( \Delta V_a \) is the activation volume [14]. Materials with a negative activation volume increase diffusivity under compression (and decrease diffusivity under tension). Negative activation volumes are found in Li-β-Al2O3 [40], Al-doped Li1-xLaxZrO12 (Al-LLZO) [41], and many Ag-ion electrolytes (β-AgI, γ-AgI, Ag,AgI, Ag,AgBr) [42]. Compressive strain may lead to cation-disordered super-ion-conducting phases in Cu2Se and Li2Se through slight stabilization of high-energy sites [43]. Although positive activation volumes are reported more frequently [42], the activation volume of many materials is still unknown [42]. In general, activation volume depends on the material, composition, and even the migrating ion. Thus, the ionic conductivity of Li-, Na-, and K-β-Al2O3, respectively, decreases, remains unchanged, and increases under hydrostatic compression (\( \Delta V_a = -0.7, \sim 0, +1.3 \text{ cm}^3/\text{mol} \), respectively) [40].

In the most general form, one should consider activation enthalpy as a function of stress: \( \Delta H_a = \Delta E_a - \Delta V_a = -tr(\sigma \cdot \Delta V_a) = -(\sigma_{xx} \Delta V_{xx} + \sigma_{yy} \Delta V_{yy} + \sigma_{zz} \Delta V_{zz}) \), where \( \sigma_{ii} \) and \( \Delta V_{ii} \) are the elements of, respectively, stress and activation volume tensors [44]. Therefore, not only isotropic (or hydrostatic) strain should be considered, but also biaxial and uniaxial strains, both compressive and tensile, and shear strains, as they all influence ionic conductivity, which is not trivial to foresee quantitatively.

Atomistic simulations are useful in the characterization of the intrinsic strain effect, by “isolating” the role of strain from other factors affecting conductivity in an experimental setup [45]. For example, biaxial and uniaxial strain were shown to substantially change Li-migration barriers in LiCoO2 [46,47], LiFePO4 [48], and LiMnSiO4 [49] cathode materials: up to ±0.1 eV changes for a given migration path were reported at 1% strain [we further use (eV/%) units]. Such a large change in a barrier corresponds to 50-fold increase (\( e^{0.1 \text{ eV/F}} \)) of diffusion at room temperature. However, one has to be careful in assessing the relative change in Li-ion diffusivity quantitatively, since multiple different types of migration paths can be affected differently by strain [50], and so, direct simulations of diffusivity from molecular dynamics simulations would be more accurate [48].

The assessment of the strain effect on Li-ion conductivity may be challenging due to the complexity of Li diffusion. Superionic conductors often have a large concentration of diffusing entities (Li ions), which interact strongly in a confined lattice framework (“frustration”) [51]. They often have multiple Li sites (which may be partially occupied, i.e., disordered) and migration pathways, display correlated ion motion [52–57], and coupling of Li migration with the anion sublattice (e.g., rotation of polyatomic groups [58,59]). These features are typical for superionic conductors in general: Na [60], Ag [61], and F [62]. Therefore, collective simulations, for example, by \textit{ab initio} molecular dynamics (AIMD), is more suitable than
calculating the migration barrier for a given migration path to assess the effect of elastic strain on ion conductivity in superionic conductors.

AIMD simulations of Li-ion conduction under strain were reported for LGPS [36,37,41] and Al-LLZO [41] (Table I). For LGPS, conductivity increases under isotropic tension, while for Al-LLZO it increases under isotropic compression. The activation enthalpy change is larger under compression, reaching −0.06 eV/% (LGPS) and +0.09 eV/% (Al-LLZO). This corresponds to, respectively, an 8-fold decrease and 13-fold increase of conductivity at room temperature (ε = −1%). The effect of anisotropic uniaxial strain was also reported (LGPS [37]) but was less pronounced than that of the isotropic one. The opposite behavior of LGPS and LLZO under strain was attributed to the fact that Li–S bonds tend to increase at the transition state (LLZO) [41]. The selected model material, β-Li3PS4, meets the above-mentioned criteria. It has a simple structure, good Li-ion conductivity at room temperature (∼10−4 S/cm), and represents the sulfide-based electrolyte family with known correlated Li-ion motion [63]. Its ionic conductivity (without strain) is well studied. The crystal structure of orthorhombic β-Li3PS4 is shown in Fig. 1. The conventional cell contains 4 formula units (4Li3PS4), with 12 Li-ions distributed over a total of 16 Li sites (8

| Electrolyte | Strain    | ΔE/|σ| (eV/%) | σ/σo | Refs. |
|-------------|-----------|-----------------|--------|-------|-------|
| LGPS        | iso., −1% | −0.05, −0.06    | 0.13, 0.58 | [36,41] |
|             | iso., +2% | −0.02, −0.02    | 3.4, 4.8  | [36,41] |
|             | uniax. c, +4% | −0.005 (a-b plane) | 3 (a-b plane) | [37] |
|             |           | −0.03 (c axis)  | 14 (c axis) | [37] |
|             |           |                 | 3 (total)  | [37] |
| Al-LLZO     | iso., −1% | +0.09           | 13       | [41] |
|             | iso., +1% | +0.02           | 0.7      | [41] |

The selected model material, β-Li3PS4, meets the above-mentioned criteria. It has a simple structure, good Li-ion conductivity at room temperature (∼10−4 S/cm), and represents the sulfide-based electrolyte family with known correlated Li-ion motion [63]. Its ionic conductivity (without strain) is well studied. The crystal structure of orthorhombic β-Li3PS4 is shown in Fig. 1. The conventional cell contains 4 formula units (4Li3PS4), with 12 Li-ions distributed over a total of 16 Li sites (8d, 4b, 4c). The 8d and 4b sites are almost fully occupied and the 4c site is nearly empty [63]. Various migration pathways are active and contribute to Li transport [63]; connections between the neighboring 4b-4c, 8d-4c, and 8d-4b sites are especially facile, while the 8d-8d jumps along the a axis are less frequent [63]. Diffusion can be enhanced by Li off-stoichiometry achieved through chemical substitution [63,66,67].

Here, by means of AIMD simulations, we show that elastic biaxial strain has a significant effect on diffusivity. We find that strains which compress the c axis (+2% a-b, −2% a-c, −2% b-c) increase diffusivity, while strains which stretch the c axis (−2% a-b, +2% a-c, +2% b-c) decrease it. The increase or decrease of diffusivity is about twofold at 500 K. Diffusivity enhancement arises from an increase of disorder and nearly even acceleration of all migration pathways. Due to compression of the c axis, Li at 4c sites becomes more stable, increasing the occupancy from about 3% to 6%, and the corresponding concentration of Li vacancies at the 8d and 4b sites increases from about 1% to 2%. The doubling of the Li vacancies at the 8d and 4b sites increases the diffusion coefficient by about
twofold. For strains that stretch the c axis and reduce the Li-ion diffusivity, the concentration of Li vacancies at the 8d and 4b sites, and occupancy of Li at the 4c site, generally decrease. Extrapolations down to room temperature show that under ambient conditions strain can increase diffusivity by up to 1 order of magnitude for detrimental strains (±2% a-b, ±2% a-c, ±2% b-c) and decrease diffusivity by up to 1 order of magnitude for detrimental strains (±2% a-b, ±2% a-c, ±2% b-c). We observe that the magnitude of the strain effect on conductivity is comparable to the effect of chemical substitution in this material [63]. The creation of vacancies at stable sites (8d, 4b) and increase of Li occupancy at the high-energy sites by strain is similar to variation of the Li stoichiometry achieved by chemical substitution [63]. The enhancement of ionic conductivity by strain through increased disorder can also be compared with other materials, where population of the high-energy sites leads to superionic conductivity (Li$_2$Se, Cu$_2$Se, AgI) [43,68].

We suggest the following explanation for strain enhancement. We observe that beneficial strains shorten the Li-Li distance between the 8d and 4b sites, thus leading to stronger Coulomb repulsion, which, in turn, slightly destabilizes Li occupancy at these sites. Destabilization of Li at the 8d and 4b sites increases disorder and decreases the migration energy, thus enhancing diffusivity. In principle, the effect of Coulomb repulsion and geometric frustration are well-known signatures of superionicity [51,55,60,62], and here we highlight the connection between strain, separation distance between Li sites, diffusivity, and disorder.

### II. COMPUTATIONAL METHODS

Density functional theory (DFT) calculations were carried out using the projector augmented wave method [69] and the Perdew-Burke-Ernzerhof (PBE) [70,71] exchange-correlation functional, as implemented in the Vienna *ab initio* simulation package (VASP) code [72–76]. Li 2s, P 3s3p, and S 3s3p electrons were treated as valence and calculations were non-spin-polarized. The plane-wave cutoff was set to 340 eV, ensuring a small Pulay stress in strained supercell calculations (∼−0.2 kbar). To model β-Li$_3$PS$_4$, a $1 \times 2 \times 2$ supercell was used for all calculations (128 atoms; $\sim 13 \times 16 \times 12$ Å$^3$). The experimental crystal structure (Pnma space group) was used for initial lattice relaxations [77], and Li ions were placed onto the 8d and 4b sites (4c site was empty). The convergence criterion for lattice relaxation was set to 0.01 eV/Å for forces. Brillouin zone integration was performed on the Γ-centered $2 \times 2 \times 2$ k-point mesh for static calculations, and Γ'-point sampling for molecular dynamics runs.

Li-ion diffusion was quantified by means of AIMD simulations in the isothermal-isochoric (NVT) ensemble with the Nosé-Hoover thermostat [78,79], in the 650–500 K range. At each temperature, equilibrium lattice parameters were first determined in the isothermal-isobaric (NPT) simulations using the Parrinello-Rahman thermostat [80,81]: friction coefficients were set to 2 fs$^{-1}$ for atoms and 10 fs$^{-1}$ for lattice degrees of freedom; the fictitious supercell mass was set to 5 amu. In all AIMD simulations, 2 fs time steps were used. Equilibration runs were 20 ps long for NPT simulations and at least 10 ps long for NVT simulations. NPT production runs were about 200 ps long. The crystal structure was orthorhombic with all cell angles equal to 90°. The NPT converged lattice parameters were further used in NVT simulations. NVT production runs were about 200 ps at 650 K and about 1000 ps at 500 K, to acquire sufficient diffusion events (simulation of Li diffusion at 450 K or lower temperatures was found to be impractical due to poor statistics). For a complete list of performed AIMD simulations and respective Li diffusivities, see the Supplemental Material (Table S3) [82].

Biaxial strain, $\varepsilon$, was applied in NVT simulations as follows. At each temperature, the respective equilibrium lattice parameters, $L_0$, were strained, i.e., set to $(1 + \varepsilon)L_0$, while the strain-free lattice parameter was adjusted in steps until the NVT time-averaged stress was close to zero. In all production runs, residual stress was within ±0.3 kbar. Calculation of errors was carried out using the blocking method [83].
Li-ion diffusivity was calculated as follows. Tracer diffusivity, \(D_t\), was calculated as

\[
D_t \equiv \lim_{t \to \infty} \frac{\langle |\Delta r(t)|^2 \rangle}{6t} = \frac{1}{3} \int_0^\infty \langle \mathbf{v}(0) \mathbf{v}(t) \rangle dt,
\]

were \(\mathbf{r}(t)\) and \(\mathbf{v}(t)\) are, respectively, the single-particle coordinate and the velocity at time \(t\). The charge diffusion coefficient, \(D_{ch}\) (Li center of mass diffusion coefficient), was calculated as

\[
D_{ch} = \frac{N_{Li}}{3} \int_0^\infty \langle \mathbf{V}_c(0) \mathbf{V}_c(t) \rangle dt,
\]

where \(\mathbf{V}_c = (1/N_{Li}) \sum_{i=1}^{N_{Li}} \mathbf{v}_i\) is the average velocity of all Li ions [84]. \(D_t\) and \(D_{ch}\) were calculated from the integration of the velocity autocorrelation functions (Green-Kubo method), and error estimates were performed using the block average method [85]. Li-ion conductivity, \(\sigma\), was calculated from the Nernst-Einstein equation,

\[
\sigma = \frac{N_{Li} e^2 (Z^2 c^2 C_{Li})/k_B T}{V}
\]

where \(C_{Li} = N_{Li}/V\) is the number of Li ions per volume, and \(D\) is either tracer \((D_t)\) or charge \((D_{ch})\) diffusivity. Ionic conductivity calculated from the charge diffusivity explicitly accounts for ionic correlations and is more rigorous than that conventionally estimated from the tracer diffusivity [84]. However, charge diffusivities converge much slower with the length of trajectory as compared with tracer diffusivities [84,86]. Therefore, we discuss charge diffusivity only in a limited number of cases, and mostly we use tracer diffusivity results throughout the paper. The room-temperature conductivity was calculated from the \(D_t\) extrapolated down to room temperature.

To calculate Li-site occupancies, we performed Bader charge analysis [87,88] on the AIMD calculated Li-ion density. Bader analysis is commonly used to assign ionic charges by partitioning the electron density of molecules and solids [87]. The advantage of Bader analysis is that it does not assume any particular form or symmetry of charge density and is therefore suitable for partitioning Li-ion density, which is highly anisotropic (see Fig. 2). Partitioning was done by finding zero-flux surfaces between atoms, with density taking a minimum on the surface and increasing along the normal [87,88]. Integration of the density within Bader volume of an atom (space enclosed within zero-flux surfaces surrounding atom) yielded atomic charge, and this gave the Li-site occupancy in our case. To calculate the number of Li-ion jumps between sites, we followed the approach outlined by de Klerk et al. [63], with improvements to account for strong anisotropy of Li thermal ellipsoids.

For further details regarding AIMD calculations, analysis, and result details, see the Supplemental Material (Secs. A–K) [82].

**FIG. 2.** Three-dimensional (3D) Li-ion density of \(\beta\)-Li3PS4 obtained from AIMD simulations at 500 K: \(a-c\) (left) and \(b-c\) (right) plane views. PS4 groups are shown as black-and-yellow sticks. 8d and 4b sites are stable, with typical residence times of 80 and 30 ps, respectively. 4c is a transient site with a short 1 ps residence time. 8d-4b, 4c sites form two-dimensional continuous layers (\(b-c\) layers), which are highlighted with dashed lines. Within the \(b-c\) layer, diffusion happens mainly via 8d-4c, 8d-4b, and 8d-8d nearest-neighbor jumps. Between \(b-c\) layers, diffusion happens mainly via 8d-8d interlayer jumps.

### III. RESULTS AND DISCUSSION

#### A. Crystal structure and site occupancies

**1. \(\beta\)-Li3PS4 crystal structure**

We start with a comparison of the calculated lattice parameters, unit cell volume, and thermal expansion coefficient with available experimental data. Our results are summarized in Table II. The static lattice parameters calculated by DFT are overestimated by 0.2%–1.8% and the unit cell volume by 3.6%, as compared to the experimental values at room temperature. We note that such an overestimation is typical for the PBE functional [91].

AIMD simulations in the NPT ensemble show that \(\beta\)-Li3PS4 retains an orthorhombic shape (all interaxial angles are 90°). The room-temperature lattice parameters are overestimated by 0.4%–2.9% and the unit cell volume

<table>
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<th></th>
<th>Expt.</th>
<th>DFT (static)</th>
<th>AIMD (300 K)</th>
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<td>13.02</td>
<td>13.05</td>
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<tr>
<td>(b) (Å)</td>
<td>8.04</td>
<td>8.17</td>
<td>8.28</td>
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<tr>
<td>(c) (Å)</td>
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<td>6.25</td>
<td>6.30</td>
</tr>
<tr>
<td>(V) (Å³)</td>
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<td>664.6</td>
<td>680.4</td>
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<tr>
<td>(\alpha) (10⁻⁵ K⁻¹)</td>
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<td>not applicable</td>
<td>1.2</td>
</tr>
<tr>
<td>(\beta) (10⁻⁵ K⁻¹)</td>
<td>5.2</td>
<td>not applicable</td>
<td>4.8</td>
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<tr>
<td>(\gamma) (10⁻⁵ K⁻¹)</td>
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<td>2.5</td>
</tr>
<tr>
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<td>8.1</td>
<td>not applicable</td>
<td>8.2</td>
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by 6%. The calculated thermal expansions coefficients are in good agreement with experiments, showing most pronounced expansion for the b axis, a smaller expansion along the c axis, and minor expansion along the a axis. The volumetric thermal expansion coefficient is $8.2 \times 10^{-5}$ K$^{-1}$ at room temperature, which is in excellent agreement with the experimentally determined value (see Table II).

We note that a negative thermal expansion along the a axis was reported from 50 to 350°C [92]. We also note that the reported experimental lattice parameters are somewhat scattered (agree within $\sim 1\%$ [89,93,94]) and differences might be attributed to different synthesis methods, resulting structures ("nanoporous" or bulk) [95], or impurities [90].

2. Li-site occupancy and disorder

Fast ion transport is mainly possible via disorder, as is known for archetypal superionic conductors PbF$_2$ [96, 97], AgI [61,98,99], Bi$_2$O$_3$ [100,101], and others (see Ref. [102] for a review). Therefore, assessment of the Li sublattice disorder (site occupancy) and its change upon strain is central to this work.

In $\beta$-Li$_3$PS$_4$, three Li sites are commonly distinguished: 8d (tet), 4b (oct), and 4c (tet) [64]. Li-site occupancies of $\beta$-Li$_3$PS$_4$ were previously reported; however, the values were inconsistent between studies [63,64,77,89,90,92,103]. The occupancies in experimental studies were obtained with Rietveld refinement of x-ray and neutron diffraction data [64,77,89,90,92], and the reported values for the 8d, 4b, and 4c sites were 1, 0.7, and 0.3 [64,77,90,92] [These refs. include a single-crystal x-ray diffraction study [64], x-ray powder diffraction (XPD) [77], neutron powder diffraction (NPD) [92], and simultaneous refinement of XPD and NPD at two neutron wavelengths [90].] Occupancies of 1, 0.4, and 0.6 were also reported in one NPD study [89]. The reported Rietveld refinements show that 4b and 4c sites are partially occupied, which points to substantial disorder on these sites. By contrast, our AIMD simulations yielded practically integer occupancies (0.99, 0.99, 0.03), which means that the Li sublattice is ordered [104,105]. The discrepancy could have arisen from the fact that the reported Rietveld refinements of $\beta$-Li$_3$PS$_4$ [64,77,89,90,92] failed to address the anisotropy of Li thermal ellipsoids, which was critical for determination of the occupancies (cf. [106,107]). Li thermal ellipsoids of superionic conductors are highly anisotropic, according to nuclear density maps from AIMD [57,108] and neutron diffraction [90,106,109]. Numerous examples include LLZO [57,106,108], LGPS [57], $\beta$-Li$_3$PS$_4$ [57,90], and other compounds [57]. To restore the anisotropy of thermal ellipsoids from the Rietveld refinement a high-quality diffraction signal [106] or advanced fitting methods, such as reverse Monte Carlo, are required [107].

Anisotropy of Li thermal ellipsoids in $\beta$-Li$_3$PS$_4$ is seen from AIMD [Fig. 2 (cf. [57,90])]. The 8d, 4b, and 4c ellipsoids have complex shapes of Li-ion density, which require a delicate analysis to assign site occupancies; a crude integration “in spheres” would lead to oversimplification. In this work, we determine occupancies by Bader analysis [87,110], which is commonly used to partition the arbitrary electron density of molecules and solids and assign ionic charges [87] and is thus suitable to partition highly anisotropic Li-ion density (Fig. 2) and assign site occupancies. As seen in Fig. 2, Li-ion density at the 4c site is much lower than that at the 8d and 4b sites. Thus, the 4c site is the least stable and respective ion residency time is much shorter than those at the 8d and 4b sites.

Isotropic Li ellipsoids used in the reported Rietveld refinements [64,77,89,90,92] could lead to a high occupancy (0.3). The 4b thermal ellipsoids are elongated towards the 4c site (Fig. 2), thus part of the 4b site Li-ion density is wrongly assigned to the 4c site. Similar inaccuracy can be produced by a crude analysis of AIMD: in Ref. [103], integration of the Li density within site-centered spheres yields 0.34 occupancy of the 4c site (700 K), assuming the 4c sphere radius is 2.5 Å [103], which clearly overlaps with two neighboring 4b ellipsoids. Integration within a smaller sphere radius of about 1 Å yields about 0.08 occupancy at most (750 K) [63].

To reconcile the reported Rietveld occupancies [64,77,90,92] and our AIMD results, we note that $\beta$-Li$_3$PS$_4$ has both configurational and “directional” Li disorder (i.e., occupancies and anisotropy of thermal ellipsoids). As discussed in the literature, occupancy and anisotropy estimated with Rietveld refinements are correlated [106,107], and our abovementioned analysis confirms this understanding. Reported Rietveld refinements impose directional isotropy [64,77,89,90,92]; therefore, the resultant occupancies display apparent disorder (0.7 of 4b and 0.3 of 4c). The Bader analysis of AIMD Li density imposes no restrictions on anisotropy, and hence, the obtained occupancies reflect the order (0.995 of 4b and 0.025 of 4c). We thus believe that $\beta$-Li$_3$PS$_4$ has (1) strongly anisotropic Li thermal ellipsoids, and (2) an ordered Li sublattice with virtually full 8d and 4b sites and an almost empty 4c site. This is valid at the temperatures of our AIMD simulations and at room temperature (for further discussion, see the Supplemental Material, Sec. D [82], and Refs. [63,93] about the order and disorder in $\beta$-Li$_3$PS$_4$).

B. Li-ion diffusion

1. Diffusion without strain

Li diffusion in $\beta$-Li$_3$PS$_4$ was investigated with AIMD simulations at 500–650 K; the calculated tracer diffusivity is shown in the Arrhenius plot of Fig. 3. We obtained an activation energy of 0.49 ± 0.02 eV, and extrapolation
to lower temperatures yielded \(D_\text{u} = 4.9 \times 10^{-10} \ \text{cm}^2/\text{s} \) (\( \sigma = 0.06 \ \text{mS/cm} \)) at room temperature.

Our calculated activation energy and conductivity fell within the range reported by experiments, which showed significant variability (0.22–0.49 eV, \(10^{-4}–10^{-1} \ \text{mS/cm} \)) [90,93,95,112]. However, our calculated values did not match both quantities simultaneously reported in a single experiment. The scatter in experimental literature could arise from different synthesis methods and resulting variabilities in the microstructure, such as the inclusion of glassy regions and grain boundaries [95]. Scatter also stems from different measurement techniques being used, which probe Li-ion motion on different time and length scales (see Table S1 within the Supplemental Material [82]). Previous AIMD reports showed scatter in the quantified activation energy and conductivity as well (Fig. 3). This could be attributed to short trajectories [111], different simulation temperatures [59], and excessive disorder affecting the activation energies [103].

We see that both experimental and computational studies have their own limitations, making straightforward agreement between them, so far, elusive. (For further discussion, see the Supplemental Material, Sec. F [82]). Instead, we focused on getting as accurate as possible results within our simulation model and assessed the effect of strain consistently with respect to the unstrained state in our simulations. For a proper analysis of strain effect on conductivity, we carefully converged the AIMD diffusivities and estimated errors of the Arrhenius fit (see the Supplemental Material, Sec. G [82]). In what follows, we set the reference state to be strain-free \(\beta\)-Li\(_3\)PS\(_4\) with an activation energy of 0.49 eV and Li-ion conductivity of 0.06 mS/cm.

![Graph of Li-ion diffusivity in \(\beta\)-Li\(_3\)PS\(_4\) (without strain, \(\varepsilon = 0\%\)) calculated with AIMD. AIMD simulations of diffusivity from the literature are shown for comparison: Yang and Tse et al. [111], Phani Dathar et al. [103], de Klerk et al. [63].](image)

**2. Diffusion under strain**

Here, we present and discuss the effect of strain on Li-ion diffusion in \(\beta\)-Li\(_3\)PS\(_4\). We investigated the +2% and −2% biaxial strains in the \(a\)-, \(a\)-, and \(b\)- crystallographic plains, as well as ±2% isotropic strain, and compared these to the unstrained case.

An Arrhenius plot of the Li-ion diffusivities calculated at 650–500 K is shown in Fig. 4(a). We see that the +2% \(a\)-, −2% \(a\)-, and −2% \(b\)- biaxial strains, and −2% isotropic strain, increased Li-ion diffusivity compared with the unstrained case. Interestingly, all these strains decreased the \(c\) lattice parameter by about 2% [Fig. 4(b)]. Conversely, the −2% \(a\)-, +2% \(a\)-, and +2% \(b\)- biaxial strains, and +2% isotropic strain, decreased the diffusivity and increased the \(c\) lattice parameter [Fig. 4(b)]. Thus, the strains that compressed the lattice along the \(c\) axis increased the Li-ion diffusivity, and those that expanded along the \(c\) axis decreased the Li-ion diffusivity in \(\beta\)-Li\(_3\)PS\(_4\).

The effect of strain on diffusivity was more pronounced at 500 K compared with that at higher temperatures (see also Fig. S17 within the Supplemental Material [82]). Diffusivity increased by a factor of 1.7–2.6 for strains that compressed the \(c\) axis (+2% \(a\)-, −2% \(a\)-, −2% \(b\)-, −2% isotropic), and decreased by a factor of 0.5−0.9 for strains that stretched the \(c\) axis (−2% \(a\)-, +2% \(a\)-, +2% \(b\)-, +2% isotropic). Extrapolation down to room temperature showed an even more pronounced effect, especially for the \(a\)- and \(a\)- strains [Fig. 4(c); note that the error bars are large; see also the Supplemental Material, Sec. G [82]; cf. Ref. [113]]. Li-ion conductivity could change by up to 1 order of magnitude with respect to the unstrained case: for +2% \(a\)-, −2% \(a\)-, −2% \(b\)-, and −2% isotropic strain, diffusivity increased by up to \(10^1\) times; for the −2% \(a\)-, +2% \(a\)-, +2% \(b\)-, and +2% isotropic strain, diffusivity decreased by up to \(10^{-1}\) times.

The activation energy varied linearly with strain from −2% to +2% [Fig. 5(a)], and the gradients were about [0.06], [0.03], and [0.00] eV/% for, respectively, \(a\)-, \(a\)-, and \(b\)- strains ([0.01] eV/% for isotropic strain). The variation of the pre-exponential factor was likewise linear [Fig. 5(b)].

Remarkably, the isotropic strain effect was less pronounced than that of the \(a\)- and \(a\)- biaxial strains (strain effect decreased as follows: \(a\)- > \(a\)- > isotropic > \(b\)-). While the figures here show only the biaxial strain effects, the effect of isotropic strain on Li-ion diffusivities are shown in the Supplemental Material, Sec. G [82].

The impact of small strain, at room temperature, could be interpolated from the Arrhenius fit in Fig. 5. Thus, 0.2% \(a\)-, \(a\)-, \(b\)-, or isotropic strain caused about 10–30% change in Li-ion conductivity and 0.5% strain caused about 10–80% change. Notably, 0.2% strain corresponded to about 60 MPa biaxial stress in \(\beta\)-Li\(_3\)PS\(_4\), which was comparable to the stack pressure [114,115] applied in
all-solid-state Li-ion batteries. Interestingly, about 0.2% strain could appear also because of the synthesis conditions, as recently reported for ball-milled Na3PS4 solid electrolyte [42]. Furthermore, 0.5% strain corresponded to about 150 MPa biaxial stress in β-Li3PS4, and, as discussed in Sec. I, such (interfacial) stress could penetrate deep into the solid electrolyte.

Furthermore, the activation volume tensor ($\Delta V_{ii}$) could be deduced from our calculations. We fit three unknown diagonal elements, $\Delta V_{ii}$, to the following eight equations (one for each strain): 

$$\Delta H_a - \Delta E_a = -\tau (\sigma \cdot \Delta V_{ii}) = -(\sigma_{xx} \Delta V_{xx} + \sigma_{yy} \Delta V_{yy} + \sigma_{zz} \Delta V_{zz}),$$

where $\Delta H_a$ and $\sigma_{ii}$ are, respectively, the activation enthalpy and stress at a given strain, and $\Delta E_a$ is the activation energy. We thus estimated that $\Delta V_{xx} = 2 \pm 4$ cm$^3$/mol, $\Delta V_{yy} = 13 \pm 5$ cm$^3$/mol, and $\Delta V_{zz} = -18 \pm 5$ cm$^3$/mol. The magnitudes of $\Delta V_{ii}$ reflected the response of diffusivity to strain along each crystallographic direction. Diffusivity was most sensitive to strain along the $c$ and $b$ axes and was least sensitive to strain along the $a$ axis. For example, +2% $a$-$b$ strain had the most pronounced effect: both the $b$ tension and the $c$ compression were beneficial, while the $a$ compression had little impact ($|\Delta V_{xx}| < |\Delta V_{yy}| < |\Delta V_{zz}|$). The average activation volume was estimated to be $\Delta V_a = -2 \pm 3$ cm$^3$/mol, which placed β-Li3PS4 among the few superionic conductors.

FIG. 4. Li-ion diffusivity under ±2% biaxial strain on the $a$-$b$, $a$-$c$, and $b$-$c$ planes of β-Li3PS4, deduced from AIMD simulations. (a) Arrhenius plot (650–500 K). Dashed line shows strain-free diffusivity ($\varepsilon = 0\%$) as a reference state. (Isotropic strain diffusivities are shown in the Supplemental Material, Sec. G [82].) (b) Relative change in $c$ lattice parameter under biaxial strain at 500 K. (c) Li-ion conductivity extrapolated to room temperature; one standard deviation confidence intervals are highlighted; $\varepsilon = -2\%$ and $\varepsilon = +2\%$ label conductivities under isotropic compressive and tensile strain, respectively; text label of each marker provides the relative change in Li-ion conductivity with respect to the unstrained state ($\sigma_{ii}/\sigma_{ii0}$ ratio).

FIG. 5. (a) Activation energy, $E_a$, and (b) logarithm of the pre-exponential factor ($\log_{10} A$) of Li-ion diffusivity under ±2% isotropic and biaxial strain on the $a$-$b$, $a$-$c$, and $b$-$c$ planes of β-Li3PS4 deduced by AIMD simulations at 500–650 K, presented as a function of the relative change in the $c$ parameter.
with a negative activation volume known to date (e.g., \(\beta\)-AgI, Ag\(_3\)S\(_4\), and Li-\(\beta\)-Al\(_2\)O\(_3\) having activation volumes of \(-5.9\), \(-2.3\), and \(-0.7\) cm\(^3\)/mol, respectively) [42].

### C. Mechanism of strain-enhanced Li-ion diffusivity

To resolve the mechanism by which elastic strain affected Li-ion diffusivity in \(\beta\)-Li\(_3\)PS\(_4\), we calculated the Li-site occupancies, analyzed Li jumps in AIMD, and calculated typical Li-ion residence times for each site. We also analyzed structural changes induced by strain.

#### 1. Site occupancies and ion jumps

Recall that the 8\(d\) and 4\(b\) sites are almost fully occupied, and the 4\(c\) site is almost empty. In fact, fully occupied or completely empty sites can impede diffusion, since they impede the exchange of charge carriers (Li ions or vacancies). In a simplified picture of (vacancy-mediated) single-ion hop diffusion, what matters for facile transport is the concentration of vacancies at the 8\(d\) and 4\(b\) sites and the concentration of Li ions at the 4\(c\) site. The highest conductivity is expected for a fully disordered Li sublattice (cf. Ref. [103]). Remember that beneficial strains are those that increase Li-ion diffusivity (and compress the \(c\) axis: +2\% \(a-b\), −2\% \(a-c\), −2\% \(b-c\)), while detrimental strains are those that decrease diffusivity (and stretch the \(c\) axis: −2\% \(a-b\), +2\% \(a-c\), +2\% \(b-c\)).

In \(\beta\)-Li\(_3\)PS\(_4\), various migration pathways are active and contribute to Li transport [63] (Fig. 2). In agreement with a previous study [63], we saw that jumps were most frequent between 4\(b\)-4\(c\), 8\(d\)-4\(c\), and 8\(d\)-4\(b\) neighboring sites. These jumps provided transport within the \(b-c\) layers and were often back-and-forth hops. Less frequent were 8\(d\)-8\(d\) jumps between neighboring sites (within \(b-c\) layers) and 8\(d\)-8\(d\) jumps between \(b-c\) layers, which contributed to long-range diffusion along the \(a\) axis. Overall, Li diffusion was facile in all three dimensions, although somewhat faster in the \(b-c\) plane and somewhat slower along the \(a\) axis. There are also other types of jumps, which are rare, and we do not consider them here for simplicity.

Remarkably, the beneficial strains that compressed the \(c\) axis promoted all these “main” jumps (4\(b\)-4\(c\), 8\(d\)-4\(c\), 8\(d\)-4\(b\), 8\(d\)-8\(d\)) (Fig. 6). An average increase in jump rate was 1.8 times at 500 K (from 1.2 times to 3.2 times), as

![FIG. 6. Number of jumps observed during AIMD runs (500 K, 1 ns). Number of jumps in the strain-free case is shown in the first column (\(\varepsilon = 0\%\)). Next three columns show detrimental strains (−2\% \(a-b\), +2\% \(a-c\), +2\% \(b-c\)), which stretch the \(c\) axis. Last three columns show beneficial strains (+2\% \(a-b\), −2\% \(a-c\), −2\% \(b-c\)), which compress the \(c\) axis. Dashed lines show number of jumps in the strain-free case as a reference. Types of jumps are as described in the main text (“8\(d\)-8\(d\) short” are jumps between nearest-neighbor sites; “8\(d\)-8\(d\) long” are jumps between \(b-c\) layers). For jumps between different sites (4\(b\)-4\(c\), 8\(d\)-4\(c\), 8\(d\)-4\(b\)), the number of backward jumps (4\(c\)-4\(b\), 4\(c\)-8\(d\), 4\(b\)-8\(d\)) is not shown (it is almost equal to the number of forward jumps, as expected in equilibrium [63]). For jumps between the same sites (8\(d\)-8\(d\)), the total number of jumps is shown (forward and backward). We also note that only a portion of jumps contribute to a net displacement of Li ions (see the Supplemental Material, Sec. H [82]; cf. Refs. [116,117]).]
calculated for beneficial strains (+2% $a$-$b$, $-2% a$-$c$, $-2% b$-$c$). For detrimental strains, an average change in jump rates was 0.8 times at 500 K (from 0.4 times to 1.3 times). This naïve averaging over different jump and strain types correlated rather well with the overall diffusivity increase presented in the previous section (2.2 times and 0.7 times for, respectively, beneficial and detrimental biaxial strains at 500 K). We also noted that the three-dimensional character of Li-ion diffusion was retained, regardless of biaxial strain type.

The acceleration of Li ion diffusion, associated with an increased number of jumps, could also be rationalized in terms of the Li-site disorder (site occupancies, Fig. 7). The beneficial strains increased the 4$c$ site occupancy and increased the number of 8$d$ and 4$b$ site vacancies (decrease in Li occupancy). This increase in Li occupancy at 4$c$ sites and in Li vacancies at 8$d$ and 4$b$ sites was about twofold at 500 K, which was consistent with the almost 2 times increase in the Li-ion diffusion coefficient. Detrimental strains influenced the site occupancies somewhat less markedly. For $+2% a$-$c$ strain, the increase in 4$c$ site occupation and increase in 8$d$ and 4$b$ vacancy concentrations was minor. For $-2% a$-$b$ and $+2% b$-$c$ strains, the 4$c$ site occupation and 8$d$ and 4$b$ vacancy concentrations somewhat decreased (Fig. 7).

To assess the role of disorder on Li-ion conduction, i.e., increase in the 8$d$ and 4$b$ Li vacancy concentrations and the 4$c$ Li-site occupation, we estimated the change in jump rates based only on site occupancies. In the single-ion hop picture of (vacancy-mediated) diffusion, the jump rate from site $i$ to $j$ was proportional to $p_i(1 - p_j)$, where $p_i$ and $p_j$ were respective site occupancies. For beneficial strains that compressed the $c$ axis, the thus calculated average increase in Li-ion diffusion was 2.3 times at 500 K (from 1.0 to 6.6 times). For detrimental strains, the average change was 0.6 times at 500 K (from 0.0 to 1.5 times). These simple estimates of how much the Li-ion conductivity should change based on site occupancies were largely consistent with the changes in Li-ion conductivity calculated from AIMD, as presented above.

## 2. Site energy and stability

The changes in the Li-site occupancies could be justified by calculating the effect of strain on the site energies for Li in β-Li$_3$PS$_4$. We created a defect pair by placing one Li ion from the 8$d$ site into the neighboring 4$c$ site. This defect pair was associated with a site occupancy increase at 4$c$ and decrease at 8$d$. The placement of one 8$d$ Li ion on the 4$c$ site cost about 0.29 eV from static DFT.
calculations in the strain-free case. The formation energy of such \(8d-4c\) defect pairs decreased by about 0.026 eV (on average) for strains that increased Li-ion conductivity (those that compressed along \(c\)) and increased by 0.014 eV (on average) for detrimental strains. The relative change in the 4c site occupation at 500 K could thus be estimated using a Boltzmann distribution, \(\exp(-\Delta E/k_B T)\), and this gave 1.8 and 0.7 times relative changes on 4c site occupancy, respectively, for beneficial and detrimental strains. This was largely in agreement with the changes in the 4c site occupancies as a function of strain calculated from AIMD simulations presented above (Fig. 7). We also analyzed lattice relaxation after Li migration from the 8d to the 4c site. The \(a\) and \(b\) lattice parameters expanded by, respectively, +0.018 and +0.012 Å, while the \(c\) lattice parameter changed by −0.023 Å, and the total supercell volume change was positive, +0.5 Å\(^3\). This was consistent with our finding that compression along the \(c\) axis favored an increase in Li occupancy at the 4c sites (Fig. 7).

The change in site energy (stability) was also evaluated from AIMD simulations. We calculated the ion residency time (how long the Li ion stayed at a given site) and further assessed the escape barriers of Li-ion migration from a given site to another site. For strains that increased conductivity (\(c\)-axis compressive), the 8d and 4b escape barriers decreased by about 0.02 eV (on average), while the 4c escape barrier increased by about +0.01 eV (on average). Thus, the relative stability of the 4c site was increased by \(\Delta E = (−0.02 + 0.01) = 0.01\) eV, consistent with the static calculations. Although the stability of the 4c site for Li increased, it was still much less stable than 8d and 4b and remained a transient site with a short residency time of about 1 ps, as opposed to about 80 ps for 8d and about 30 ps for 4b (see the Supplemental Material, Sec. J [82], for further details).

3. Structure: Li-Li distances
We analyzed the structural changes upon strain in \(\beta\)-Li\(_3\)PS\(_4\) by first looking at the radial distribution function (RDF). The analysis was complicated by the fact that each RDF peak was affected by biaxial strain, causing slight shifts of peaks, broadening or stiffening of peaks, or peak splitting. We could identify two RDF features that were common to all the strains that compressed the \(c\) axis and accelerated Li-ion conduction.

The first feature concerned the second P-P peak shown in Figs. 8(a) and 8(b); this peak was a superposition of several crystallographic distances in the 6–7 Å range, which formed a 3D framework. First, compression of the \(c\) axis reduced the P-P distances parallel to \(c\); therefore, the component at the left of this peak (separated as a shoulder) shifted to the left. Second, the whole second P-P peak was broadened [Fig. 8(a)]. In contrast, detrimental strains that expanded the \(c\) axis sharpened this peak [Fig. 8(b)]. Peak broadening implied that, overall, the P framework was becoming more “geometrically disordered.” Such an increased “disorder” of P–P bond population might be associated with a more flexible structure, and therefore, facilitated Li diffusion. The flexibility of the lattice is known to enhance ion diffusion in solids [118,119]. We note that these P-P distances (6–7 Å) are not necessarily
tribute to their slight destabilization (as seen in Fig. 7). In β-Li3PS4, the shortest Li-Li separation was between 8d and 4b sites: the average distance was about 3.4 Å and the tail spanned to about 2.5 Å. An increase of the short-bond population was consistent with c-axis compression, as it brought the 8d and 4b sites closer to each other (the average separation decreased by 1%-2%). The presence of such short Li-Li distances should increase Coulomb repulsion between the 8d and 4b sites as a result, the Li-site energy at 8d and 4b sites increased (as presented above) and should contribute to their slight destabilization (as seen in Fig. 7). This increase in site energy should reduce the energy barrier to ion migration, assuming no change in the transition state. Thus, this shortened Li-Li distance could promote Li-ion diffusion and conduction.

An increase of ionic conductivity under compression was reported for several superionic conductors, including Li and Ag conductors [42]. We note that Coulomb repulsion and geometric frustration between ions are the signatures of superionicity [51,55,60,62], and many superionic conductors are reported to have short Li-Li distances [108]. Therefore, it is plausible that compressive strain can increase ionic repulsions and promote diffusion in a variety of superionic conductors (cf. Ref. [120]). Of course, other factors, such as initial occupancies of sites and their connectivity, as well as the mutual orientation of thermal ellipsoids might be important to delineate why some superionic conductors do benefit from compressive strain (e.g., LLZO [41]) and some others do not (e.g., LGPS [36,41]).

4. Strain versus chemical substitution

The magnitude of the strain effect found in this work on Li-ion diffusivity was comparable to that of chemical substitution in β-Li3PS4 [63,66,67]. Previous AIMD simulations showed that a nonstoichiometric composition of β-Li3PS4 (namely, Li2.75PS4 or Li3.25PS4) yielded faster diffusivity, by 1 order of magnitude at 450 K, and better site connectivity due to vacancies or interstitials. In these cases, the degree of correlated motion also increased [63]. Similarly, β-Li1.94PS4 doped with Br and O also showed faster diffusivity, ca. 1 order of magnitude at 450 K for β-Li3PS3.75O0.25 and β-Li2.75PS3.75Br0.25. The Br and O substitution effect was similar to that of the Li nonstoichiometric composition. Near O, a locally lower concentration of Li was established, thus creating a higher concentration of Li ions elsewhere [63]. A twofold conductivity increase was experimentally achieved by Sb2O5 substitution of β-Li1.94PS4 [66] and ZnO substitution of Li3PS4 glass [67] at room temperature.

The strain-induced disorder and substitution-induced Li nonstoichiometry had similar effects on the site occupancy, both in terms of the magnitude of the effect and in terms of the mechanism underlying the effect. They both created vacancies at the 8d and 4b sites (strain and Li deficiency, e.g., Li2.75PS4 [63]) or populated the 4c site (strain and Li surplus, e.g., Li3.25PS4 [63]), thus increasing the concentration of these active charge carriers and promoting diffusion. Notably, in Ref. [63], variation of the stoichiometry was ±0.25 Li per formula unit; this corresponded to +25% increase of the 4c site occupancy, assuming all Li surplus populated the 4c site; in our biaxially strained supercells, the increase in Li 4c occupancy was +3% at most, and the respective change of diffusivity was smaller, too.

Since practical solid electrolytes are often nonstoichiometric (i.e., chemically substituted), it is further interesting to assess the effect of strain on diffusivity in nonstoichiometric compositions. We investigated this effect of: isotropic strain on the ionic conductivity of Li-deficient and Li-excess compositions, β-Li2.94PS4 and β-Li3.06PS4. We intentionally avoided substituted ions to isolate the effect of strain alone, since substitutions could introduce other effects, such as defect association (see the Supplemental Material, Sec. K [82], for further details). Overall, the β-Li2.94PS4 case was similar to that of β-Li3PS4, namely, isotropic compression promoted diffusivity. In β-Li2.94PS4, the combined effect of a vacancy and compressive strain on diffusivity was 1.79±0.28 times, which was similar to that of strain alone in the stoichiometric case (1.74±0.20 times at 600 K for ε = −2%). In detail, the introduction of one vacancy sped up diffusivity by 1.36±0.25 times, while subsequent isotropic compression sped up diffusivity further by 1.33±0.25 times. We thus concluded that the net effect of strain was somewhat smaller in the nonstoichiometric case compared with that in the purely stoichiometric compound. This was reasonable, since nonstoichiometry already introduced charge carriers (vacancies), which promoted diffusion. Nevertheless, the effect of strain on the Li-ion diffusivity of β-Li2.94PS4 was pronounced, and it was as large as the effect of introducing a vacancy alone. Our test calculations on strained β-Li3.06PS4 showed that the effect of strain on diffusivity was somewhat less perceptible for interstitials (see the Supplemental Material, Sec. K [82]). We note that the investigation of nonstoichiometric compositions under strain is technically complicated, as one must either introduce substituting ions or carry out calculations with charged supercells, which both complicate the analysis. We believe that this analysis can be refined with higher accuracy in future studies, but this level of analysis already indicates that the role of strain can be as important as nonstoichiometry obtained by chemical substitution.

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IV. SUMMARY AND REMARKS

We found that elastic strain (biaxial and isotropic) which resulted in c-axis compression in $\beta$-Li$_3$PS$_4$ facilitated Li-ion conduction, while c-axis tension slowed down Li-ion conduction. The diffusivity increase or decrease with respect to the unstrained state was about twofold at 500 K and was up to about tenfold when extrapolated to room temperature. Overall, $\beta$-Li$_3$PS$_4$ had a negative activation volume, $\Delta V_a = -2$ cm$^3$/mol, which was comparable to that in other superionic conductors like $\beta$-AgI, Ag$_3$SI, and Li-$\beta$-Al$_2$O$_3$ [42]. The magnitude of the strain effect on the activation energy and diffusion was comparable to that in other Li-ion superionic conductors, namely, LGPS [36] and Al-LLZO [41]. The mechanism and the magnitude of the effect of elastic strain on Li-ion diffusion was also comparable to that of chemical substitution in this material [63,66,67].

Compression of the c axis facilitated Li-ion diffusion through increased disorder (higher Li occupancy of the 4c site and higher concentration of Li vacancies at the 8d and 4b sites) in $\beta$-Li$_3$PS$_4$. The relative increase in conductivity correlated closely with the relative increase in disorder at these sites. The mechanism behind the increased disorder, resulting in increased conductivity with c-axis compression, could be deduced from the decrease of the shortest Li-Li distance (8d-4b) seen in the RDF. This increased the Coulomb repulsion between the 8d and 4b sites and destabilized Li at these sites, thus reducing Li occupancy, resulting in more frequent ion hops. In principle, the short Li-Li distance is a characteristic for many superionic Li-ion conductors [108], while Coulomb repulsion and geometric frustration are well-known signatures of superionicity [51,55,60,62]. These findings indicated that manipulation of Li-Li distances by strain could be used to promote Li disorder and superionic conductivity.

ACKNOWLEDGMENTS

We are grateful to K.J. Van Vliet, Y.-M. Chiang, J. Li, H. Tuller, Y.-T. Chi, R. Park, K. Klyukin, V. Somjit, Y. Dong, and U. Kudu for helpful discussions and suggestions. This work was supported by the Department of Energy, Basic Energy Sciences, under Award No. DE-SC0002633 (Chemomechanics of Far-From-Equilibrium Interfaces). P.Z. thanks Knut and Alice Wallenberg Foundation scholarship program for supporting his postdoctoral studies at Massachusetts Institute of Technology. Part of the DFT calculations were carried out using (i) the Extreme Science and Engineering Discovery Environment (XSEDE), which is supported by the National Science Foundation (Grant No. ACI-1321548562), and (ii) resources of the National Energy Research Scientific Computing Center (NERSC), a U.S. Department of Energy Office of Science User Facility located at the Lawrence Berkeley National Laboratory, operated under Contract No. DE-AC02-05CH11231.


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