



Lattice Compatibility and Energy Barriers in Intercalation Compounds

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We present a continuum model for symmetry-breaking phase transformations in intercalation compounds, based on Ericksen’s multiwell energy formulation. The model predicts the nucleation and growth of crystallographic microstructures in $\text{Li}_2\text{Mn}_2\text{O}_4$ —a representative intercalation compound—with twin boundary orientations and volume fractions that closely match experimental observations. Our chemo-mechanically coupled model not only generates geometrically accurate microstructures through energy minimization, but also reveals a subtle interplay between twinned domains and electrochemomechanical behavior. A key finding is that intercalation compounds satisfying specific compatibility conditions (e.g., $\lambda_2 = 1$ or $|\det \mathbf{U} - 1| = 0$) show lower elastic energy barriers, require smaller driving forces, and display narrower voltage hysteresis loops. Furthermore, we show that twinned domains act as conduits for fast Li diffusion. These results establish quantitative design guidelines for intercalation compounds, which focuses on tailoring lattice deformations (rather than suppressing them) and reducing energy barriers to mitigate structural degradation and enhance the electrochemical performance of battery electrodes.

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I. INTRODUCTION

Intercalation compounds are a class of phase-change materials in which guest species, such as ions, atoms, or molecules, are reversibly inserted into host lattices [1]. This reversible insertion makes intercalation compounds ideal for use as electrodes in batteries, supercapacitors, catalysts, and energy harvesters [2]. Many of these applications require these compounds to be cycled reversibly and repeatedly over a single lifespan. However, inserting a guest species into a host compound commonly induces an abrupt and large deformation of its lattices. This deformation generates significant internal stresses and volume changes in the material, leading to capacity fade, voltage hysteresis, and shortening their lifespans [3–7]. To address these issues, current material design strategies focus on minimizing and eliminating changes in lattice geometries during intercalation.

Researchers employ advanced techniques to minimize lattice geometry changes, such as site-selective doping of intercalation compounds [8,9], multilayering

of heterostructures [10], pillaring of layered materials [11], and designing mechanical constraints (e.g., epitaxial strains, electrode coating, engineering coherent precipitates) [12–14]. These zero-strain strategies suppress lattice distortions during intercalation and facilitate the reversible cycling of compounds. For example, the doping efforts by Zhang *et al.* [8] have resulted in a high-entropy Ni-based layered compound that shows nearly zero-volume changes during intercalation, greatly reducing cracking during the charge and discharge cycles. Another intercalation compound $\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4$, undergoes near zero lattice distortions [i.e., cubic symmetry in both reference ($a_0 = 8.365 \text{ \AA}$) and transformed ($a = 8.370 \text{ \AA}$) phases], which in turn contributes to its improved cyclability (>100 cycles with 94% capacity retention) [15]. Other strategies, such as engineering coherent precipitates in NMC cathodes and suppressing structural transformations through a pinning effect [14], or synthesizing nanosized disordered spinel-like domains separated by antiphase boundaries, have contributed to improved cyclability of electrodes [16]. Similarly, in our previous work, we showed that epitaxial strains can be designed to suppress phase transformations with large lattice deformations in $\text{Li}_x\text{V}_2\text{O}_5$ [12]. In doing so, we demonstrated reversible structural transformations in $\text{Li}_x\text{V}_2\text{O}_5$ despite operating in a wide voltage window [12]. These strategies have identified new material compositions and innovative boundary constraints and have initiated a “zero-strain” approach

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to designing intercalation compounds with improved lifespans [17–20].

In contrast to the “zero-strain” design strategy that aims to suppress or eliminate lattice geometry changes, we draw inspiration from ferroelastic materials, in which lattices undergo finite deformations but still generate microstructures with stress-free interfaces and volume-preserving macroscopic changes [7,21]. The lattice geometry changes in these ferroelastic materials (e.g., shape-memory alloys) satisfy specific compatibility criteria, deform along defined habit planes, and collectively generate crystallographic microstructures at the continuum scale [22]. This relationship between lattice deformations and continuum microstructures is well established for ferroelastic materials and other functional materials, including ferroelectrics, and ferromagnets [23–25]. Researchers have extensively used this lattice-continuum link as a design guideline and carefully engineered lattice geometries in phase-transformation materials to achieve remarkable reversibility and enhanced material lifespans.

A lattice compatibility criterion known as the middle eigenvalue condition ($\lambda_2 = 1$) has emerged as an important guideline in materials design [26]. This criterion signifies an “unstretched” edge between the lattices of reference and transformed regions during phase transformation. Materials satisfying this criterion generate two-phase microstructures with phase boundaries that are compatible and stress-free. Theoretically, these interfaces have zero elastic energy and offer minimal energy barriers for phase transformation. Other lattice geometry relationships, such as the cofactor conditions [26] and self-accommodation (or volume-preserving) conditions [27], also significantly reduce the elastic energy built in the material during phase transformations. These special lattice deformations have had a significant impact in mitigating structural decay in materials and enhancing reversible phase transformations. For example, shape-memory alloys satisfying the compatibility criteria are shown to have ultralow fatigue [28], reduced thermal hysteresis [29], and enhanced reversibility [30]. These lattice geometry relations have also informed the design of several functional materials with improved lifespans, such as ferroelectrics, semiconductors, and ferromagnets [31–34].

Phase transformations in intercalation compounds are analogous to the first-order phase transformations observed in structural and functional materials [7], see Fig. 1. The host lattices in intercalation compounds such as $\text{Li}_2\text{Mn}_2\text{O}_4$, LiCoO_2 , and LiFePO_4 , undergo abrupt and displacive transformations during Li-intercalation [35–38]. The scalar Li-composition field driving phase transformations in intercalation compounds is similar to the thermal-field driving phase change in shape-memory alloys. Additionally, intercalation compounds with Jahn-Teller active elements, such as $\text{Li}_2\text{Mn}_2\text{O}_4$ and NaMnO_2 , undergo symmetry-breaking lattice deformations characteristic of

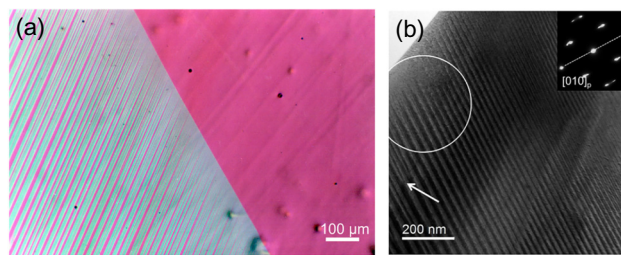


FIG. 1. Phase-transformation microstructures in shape-memory alloys and intercalation compounds bear similarities in that they generate a mixture of finely twinned domains. (a) An austenite-martensite interface showing the finely twinned martensitic domains in the Cu-14.0%Al-3.9%Ni shape-memory alloy. Image courtesy of Chu and James [23]. (b) A bright field image of a partially transformed $\text{Li}_2\text{Mn}_2\text{O}_4$ showing the twinned tetragonal variants. (Reproduced with permission from American Chemical Society [35].)

shape-memory alloys [35,38,39]. The symmetry-breaking transformations in intercalation compounds generate finely twinned microstructures that are quantitatively consistent with the crystallographic theory of martensites (see Fig. 1 and Refs. [23,40,41]). While there are a few exceptions between intercalation compounds and ferroelastics, such as the anisotropy of Li diffusion in select compounds [42] and cation migration or dissolution in disordered cathodes [43,44], we will initially focus on intercalation compounds in which the host lattices undergo exclusively displacive structural transformations.

The crystallographic microstructures not only minimize the elastic energy during phase change but also are reported to alter the ion-transport properties in intercalation compounds. For example, a first-principles study in LiCoO_2 demonstrates faster diffusion of lithium along twin boundaries when compared to Li diffusion across twin interfaces [45]. Similar coherent interfaces with low interfacial energy have been reported in other intercalation compounds such as NaMnO_2 [39]. These twinned microstructures were imaged in large concentrations and were found to be thermodynamically stable at equilibrium voltages [39]. These findings reveal the common occurrence and stability of twin boundaries in intercalation compounds and highlight the potential for crystallographically designing twin interfaces to serve as conduits for fast charge and discharge conditions.

More recently, we developed algorithms to screen intercalation compounds ($n > 5000$ pairs from open-source material databases) that undergo displacive phase transformations and identified candidate materials that approximately satisfy the lattice compatibility criteria for stress-free interfaces and volume-preserving microstructures [40]. Our results showed that intercalation compounds such as $\text{Li}_x\text{Mn}_2\text{O}_4$ (spinel structure) and $\text{Li}_x\text{Ti}_2(\text{PO}_4)_3$ (NASICON structure) typically undergo

symmetry-breaking lattice deformations and are suitable to generate energy-minimizing crystallographic microstructures [35,40,46]. Other symmetry-breaking transformations are reported in Prussian blue analogues [47,48] during alkali-ion (e.g., Na^+ and Li^+) insertion and extraction. To predict these crystallographic microstructures, we develop a multivariant continuum model using an energy landscape that is informed by lattice symmetry with $\text{Li}_2\text{Mn}_2\text{O}_4$ as a representative example [41]. A key feature of our model is that we not only distinguish between the phases in terms of Li compositions (e.g., Li rich or Li poor), but also differentiate between the various tetragonal lattice variants formed during the symmetry-breaking transformation. By minimizing the total energy across a multiwell energy landscape, we demonstrate the nucleation and growth of crystallographic microstructures in an electrochemical environment.

In this work, we propose a material design approach that emphasizes *compatibility*, i.e., the fitting together of phases during transformation. Using our multivariant continuum model, we predict microstructures in $\text{Li}_2\text{Mn}_2\text{O}_4$ that are geometrically accurate, consistent with experimental observations, and arise naturally from elastic energy minimization. We demonstrate that allowing certain lattice deformations in intercalation compounds—provided they satisfy specific compatibility criteria—can minimize internal stresses and net volume changes. In this approach, lattice deformations are carefully engineered to mitigate interfacial stresses at phase boundaries and to accommodate volume changes that accompany phase change in intercalation compounds. In doing so, we show how precise lattice geometries can substantially lower the elastic energy barriers that emerge during phase transformation, thereby reducing voltage hysteresis and enhancing material reversibility. These energy barriers and energy-minimizing microstructures, characteristic of first-order phase transformations, are difficult to estimate using first-principles calculations, but are effectively captured by our continuum approach. Furthermore, we find that crystallographic microstructures facilitate faster Li diffusion along twin boundaries and can be intentionally designed in intercalation compounds to enable rapid charge and discharge cycles. Our theoretical results reveal lattice geometry relationships—beyond the conventional “zero-strain” condition—that provide new guidelines for designing intercalation compounds with improved lifespans.

II. CONTINUUM THEORY OF CRYSTALLINE SOLIDS

In this section, we describe the continuum theory of crystalline solids that undergo a first-order phase transformation and highlight its application to intercalation compounds. We begin with the Cauchy-Born rule that relates

the displacive movement of atoms to the overall deformation of the material [49]. During phase transformation, the lattices undergo an abrupt and displacive deformation and collectively form energy-minimizing continuum microstructures. The kinematic conditions for compatibility use the lattice deformation gradient to precisely construct the crystallographic microstructures formed during phase change. This theory is general and applicable to all first-order phase-transformation materials, and we demonstrate its significance to predict continuum microstructures in intercalation compounds.

A. Cauchy-Born rule

Let us consider a crystalline solid Ω in a three-dimensional space \mathbb{R}^3 . In the reference configuration, each point in the solid is defined by a position vector \mathbf{x} . During phase transformation, part of this solid deforms by $\mathbf{y}(\mathbf{x})$ and the deformation gradient is defined by a tensor $\mathbf{F} = \nabla \mathbf{y}$. The Cauchy-Born rule states that this overall deformation gradient of the macroscopic body maps onto the deformation gradient of individual lattices at the atomic scale. This lattice-continuum link plays an important role in predicting microstructures that emerge during phase change [49]. Understanding the structural deformation of lattices during intercalation is important in the crystallographic designing of materials with enhanced lifespans.

The deformation gradient can be decomposed into a unique rotation and a stretch tensor $\mathbf{F} = \mathbf{Q}\mathbf{U}$. The stretch tensor \mathbf{U} is a positive-definite symmetric matrix and describes the displacive distortions of lattices between the reference and transformed phases. We construct this stretch tensor using lattice geometries of the crystalline solid, and it is an important input to predict the geometric features of microstructures, such as the orientation of twin interfaces and phase boundaries.

The stretch tensor \mathbf{U} for a given material can have multiple solutions based on the choice of lattice vectors used to describe the Bravais lattices of the reference and transformed phases. For example, consider the structural transformation of the lattices accompanying the LiMn_2O_4 to $\text{Li}_2\text{Mn}_2\text{O}_4$ intercalation process. Assume a cubic unit cell for the reference LiMn_2O_4 phase described by lattice vectors \mathbf{e}_{Ri} , see Fig. 2. The unit cells of the transformed $\text{Li}_2\text{Mn}_2\text{O}_4$ can be defined in multiple ways, such as \mathbf{e}_{Ti} for a primitive cell, \mathbf{e}_{Ti}^A or \mathbf{e}_{Ti}^B for conventional cells, see Fig. 2. The stretch tensors mapping the reference to the transformed lattices can therefore have multiple solutions. Determining the optimal stretch tensor for a given phase transformation is important to developing our continuum theory.

To determine an optimal stretch tensor, we use a structural transformation algorithm developed in recent works [40,50]. In this algorithm, a distance function is introduced to identify the minimal lattice distortion between all

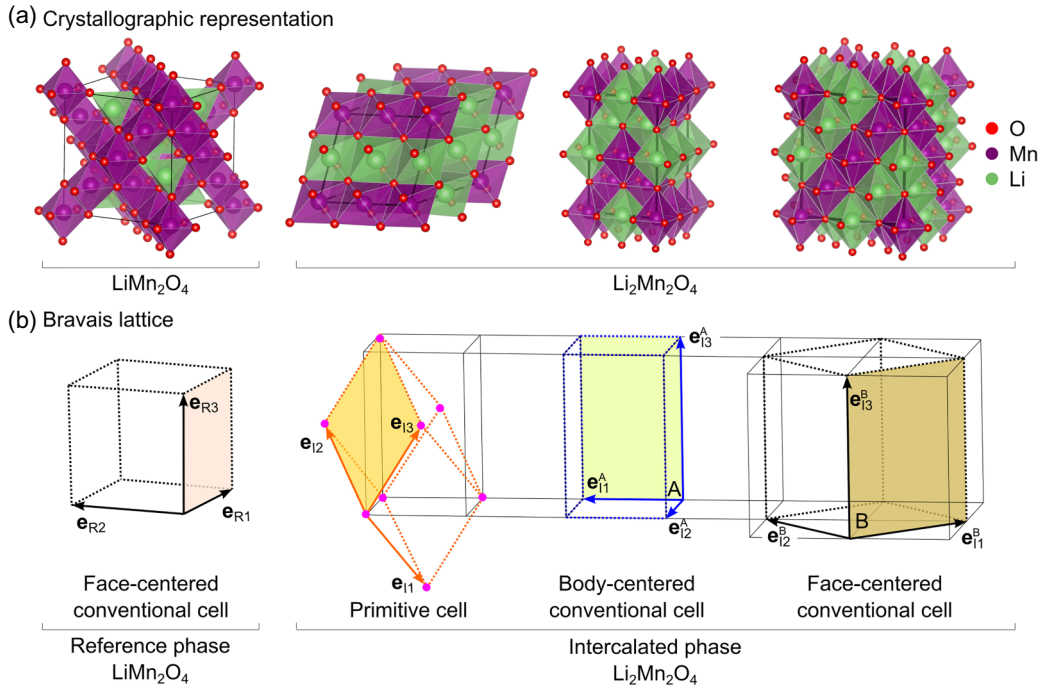


FIG. 2. (a) Crystallographic and (b) Bravais lattice representations of unit cells of LiMn_2O_4 (reference phase) and $\text{Li}_2\text{Mn}_2\text{O}_4$ (intercalated phase). The vectors $\{\mathbf{e}_{R1}, \mathbf{e}_{R2}, \mathbf{e}_{R3}\}$ span the unit cell of LiMn_2O_4 ($Fd3m$, $a_0 = 8.24 \text{ \AA}$). Similarly, vectors $\{\mathbf{e}_{I1}, \mathbf{e}_{I2}, \mathbf{e}_{I3}\}$ enclose the primitive unit cell of the intercalated phase $\text{Li}_2\text{Mn}_2\text{O}_4$. Representative examples of conventional unit cells are identified by vectors with superscripts “A” and “B.” On minimizing the distance function Eq. (1) across the three stretch tensors mapping LiMn_2O_4 to primitive, body-centered, and face-centered $\text{Li}_2\text{Mn}_2\text{O}_4$, respectively, we identify that the stretch tensor corresponding to the face-centered conventional cell of $\text{Li}_2\text{Mn}_2\text{O}_4$ ($F4_1/d\bar{d}m$, $a = 8.0 \text{ \AA}$, $c = 9.3 \text{ \AA}$) has the smallest structural distortion. We use this stretch tensor as an input for our model.

combinations of reference and transformed lattices:

$$\text{dist}(\mathbf{U}) = \|\mathbf{U}^{-2} - \mathbf{I}\|^2. \quad (1)$$

The stretch tensor that minimizes the distance function in Eq. (1) is chosen as the optimal stretch tensor to construct continuum microstructures. This approach of identifying the stretch tensor has seen recent success in the context of shape-memory alloys [50], and more recently, in our work on intercalation compounds [40]. By applying this algorithm to $\text{Li}_2\text{Mn}_2\text{O}_4$ we identify the cubic ($a_0 = 8.24 \text{ \AA}$) to tetragonal ($a = 8.0 \text{ \AA}$, $c = 9.3 \text{ \AA}$) deformation as the distance-minimizing stretch tensor. This transformation pathway is consistent with experimental results [35,38] and generates three crystallographically equivalent lattice variants. (Note that the number of lattice variants is determined by the group-subgroup relationships between the parent and product phases. For example, the cubic LiMn_2O_4 has 24 symmetry equivalent rotations in its point group, and the tetragonal $\text{Li}_2\text{Mn}_2\text{O}_4$ has eight rotations. The cubic-to-tetragonal transformation generates $24/8 = 3$ lattice variants.) We follow this approach to determine the stretch tensors and lattice variants for other representative intercalation compounds, including NaMnO_2 [39]

and $\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4$ [15], see Tables S3 and S4 within the Supplemental Material [51].

B. Kinematic compatibility conditions

Intercalation compounds that undergo a symmetry-breaking transformation generate continuum microstructures with fine platelike crystallographic features, see Fig. 3(b). We show that these twinned microstructures in intercalation compounds form as a consequence of elastic energy minimization and satisfy the kinematic compatibility conditions [22].

The compatibility conditions predict the orientation of the twin plane along which lattices with different deformation gradients (or, equivalently, the stretch tensors) align to form a compatible interface. Consider any two tetragonal lattices, \mathbf{U}_I , \mathbf{U}_J , generated during the cubic-to-tetragonal transformation in $\text{Li}_2\text{Mn}_2\text{O}_4$. These lattices rotate and fit together to form a compatible interface:

$$\mathbf{Q}\mathbf{U}_J - \mathbf{U}_I = \mathbf{a} \otimes \hat{\mathbf{n}}. \quad (2)$$

The solutions to the compatibility condition in Eq. (2) are vectors \mathbf{a} , $\hat{\mathbf{n}}$ that describe the orientation of twin planes. These twin planes are special interfaces along which lattices with distinct deformation gradients meet and share

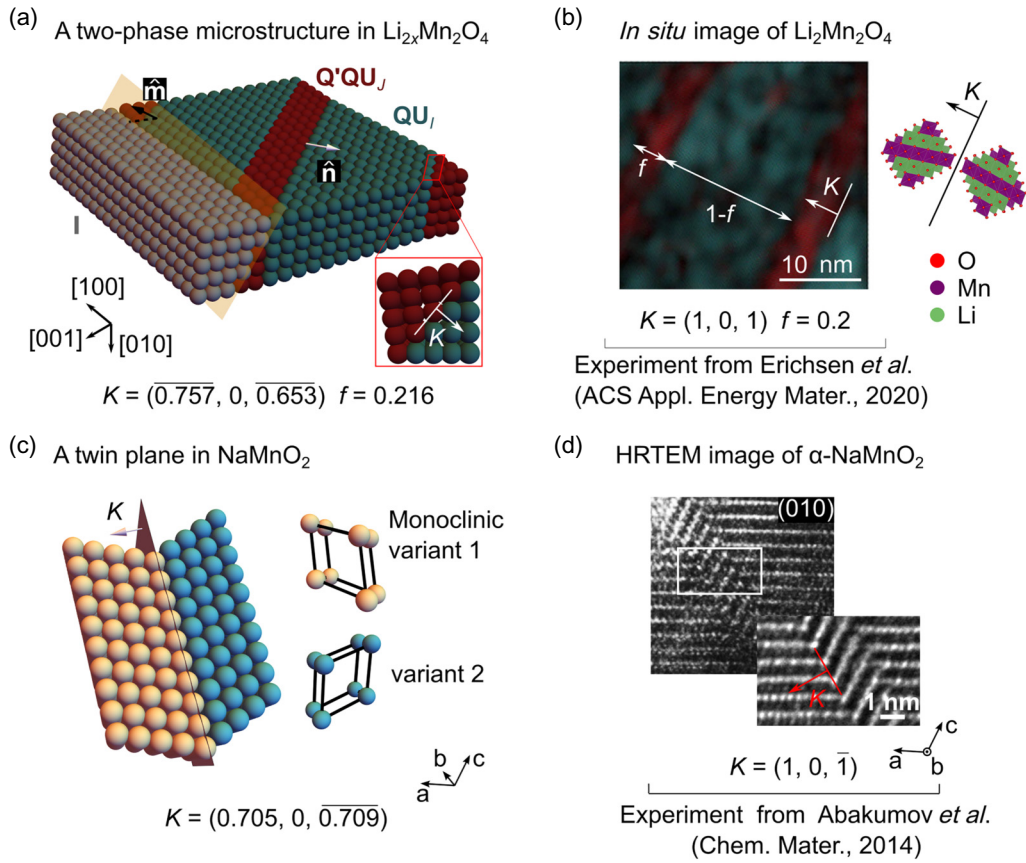


FIG. 3. A comparison between theoretical and experimental microstructures in representative intercalation compounds. Using the lattice geometries of $\text{Li}_2\text{Mn}_2\text{O}_4$ and NaMnO_2 as inputs, we analytically derive the twin solutions as shown in Tables S2 and S3 within the Supplemental Material [51]. We use these solutions to geometrically construct the microstructures shown in (a),(c), respectively. (a) The twinned microstructure in spinel $\text{Li}_{2x}\text{Mn}_2\text{O}_4$, with vectors $\hat{\mathbf{m}}$ and $\hat{\mathbf{n}}$ representing the orientations of the phase boundary and the twin plane, respectively. Our calculations predict a volume fraction of the twinned mixture to be $f = 0.216$, in agreement with experimental measurements [35]. (b) Bragg-filtered HRTEM image of the lamellar microstructures from Erichsen *et al.* [35], showing a twin plane of $(1, 0, 1)$ orientation and a volume fraction of $f = 0.2$. (c) Geometric construction of a twin interface between two monoclinic variants of NaMnO_2 , with an orientation given by $K = (0.705, 0, 0.709)$. (d) Our geometric construction matches previously reported HRTEM imaging of a NaMnO_2 sample by Abakumov *et al.* [39], which shows the $(1, 0, \bar{1})$ direction of the twins in the monoclinic phase. (Reprinted with permission from American Chemical Society [39].)

an edge that is relatively unstretched. This compatible fit between neighboring lattices results in coherent twin interfaces and allows several twins to form in a material with no (or minimal) energy penalty. However, twin interfaces are rarely found in isolation; instead, several parallel twins appear as fine mixtures during phase transformation [see Figs. 1 and 3(a)].

The finely twinned mixtures form an interface with a uniform domain, see Fig. 3(a). This interface, commonly referred to as the austenite-martensite interface (terminology used in shape-memory alloys), forms as a consequence of energy minimization and satisfies the compatibility condition:

$$\mathbf{Q}'(f\mathbf{Q}\mathbf{U}_J + (1-f)\mathbf{U}_I) = \mathbf{I} + \mathbf{b} \otimes \hat{\mathbf{m}}. \quad (3)$$

In Eq. (3) the uniform reference phase with a single-crystal structure is represented by an identity stretch tensor \mathbf{I} , and the finely twinned transformed phase consists of parallel twins between the tetragonal variants \mathbf{U}_J and \mathbf{U}_J . The interface between any single tetragonal variant and the reference phase is elastically stressed because of the lattice mismatch. To minimize this interfacial energy, the tetragonal lattices form a finely twinned mixture that is nearly compatible with the reference phase. The volume fraction of the twins $0 \leq f \leq 1$ is a sophisticated averaging of the tetragonal variants that minimizes the elastic energy stored at the austenite-martensite interface. The vectors \mathbf{b} , $\hat{\mathbf{m}}$ describe the orientation of this interface, and the rotation tensors are given by \mathbf{Q}' , \mathbf{Q} [22].

C. Crystallographic microstructures in intercalation compounds

The kinematic compatibility conditions are general and applicable to all ferroelastic materials. For our purposes, we note that several intercalation compounds undergoing a symmetry-breaking phase transformation generate energy-minimizing microstructures that satisfy these compatibility conditions in Eqs. (2) and (3) [35,38,39]. We next analyze the geometric features of crystallographic microstructures in representative intercalation compounds and establish the first-order phase-transformation characteristics in these materials.

Figures 3(a)–3(d) show the theoretical and experimental comparison of the twinned domains in two representative intercalation compounds, namely $\text{Li}_2\text{Mn}_2\text{O}_4$ and NaMnO_2 . These compounds undergo a symmetry-breaking transformation on intercalation, i.e., cubic-to-tetragonal in $\text{Li}_2\text{Mn}_2\text{O}_4$ and orthorhombic-to-monoclinic in NaMnO_2 , which generates multiple lattice variants. Using the stretch tensor for $\text{Li}_2\text{Mn}_2\text{O}_4$ [see Figs. 3(a)–3(b)], we calculate a volume fraction of $f = 0.216$ for the twinned domains and analytically derive the normal vector of the twin plane to be $K = \mathbf{U}_T^{-1} \hat{\mathbf{n}} / |\mathbf{U}_T^{-1} \hat{\mathbf{n}}| = (0.757, 0, 0.653)$. These theoretical results align favorably with the experimental Bragg-filtered high-resolution transmission electron microscopy (HRTEM) measurements of the twin-plane orientation $(1, 0, 1)$ and the volume fraction $f = 0.2$ in Ref. [35]. Similarly, using the stretch tensor for NaMnO_2 [see Figs. 3(c)–3(d)], we geometrically construct a twin interface between two monoclinic variants of NaMnO_2 . We calculate a twin-plane orientation of $K = (0.705, 0, 0.709)$ that matches the previously reported $(1, 0, \bar{1})$ direction shown in the HRTEM image of NaMnO_2 by Abakumov *et al.* [39].

The austenite-martensite type of microstructures in intercalation compounds is three dimensional in nature and inherently complex to visualize; specifically, the surface normal of the twin interface in the martensite phase, $\hat{\mathbf{n}}$, does not lie in the same plane as the surface normal of the austenite-martensite interface, $\hat{\mathbf{m}}$. However, there exists a plane in \mathbb{R}^3 that is orthogonal to both the twin interface and the austenite-martensite phase boundary—namely the vector $\hat{\mathbf{m}} \times \hat{\mathbf{n}}$ —on which two-dimensional (2D) projections of the microstructural features can be geometrically represented. We note that the experimental images in Fig. 3(b) are projected on the $(0, 1, 0)$ 2D plane [35], which introduces geometric inaccuracies in the crystallographic features, see Figs. 3(b) and 6(e). These errors in twin-plane orientations ($\Delta\theta \approx 0.89^\circ$) and volume fractions ($\Delta f \approx 0.01$) are small in the case of $\text{Li}_2\text{Mn}_2\text{O}_4$, due to its small out-of-plane strain components. With these differences in mind, we note that the compatibility conditions developed for ferroelastic materials are applicable to twinned microstructures in intercalation compounds. Our analytical calculations, compared with the experimental images,

support the use of the Cauchy-Born rule in predicting microstructures in intercalation compounds.

D. Special microstructures

A notable impact of the compatibility conditions on material performance has been in enhancing material lifespans. With the recent advances in energy-barrier analysis, researchers have identified special combinations of lattice geometries that generate stress-free interfaces and volume-preserving (or self-accommodating) microstructures [27, 52,53]. These microstructures, when engineered to form in ferroelastic materials (e.g., shape-memory alloys, ferroelectric, ferromagnets, semiconductors) [32,34,54–56], have significantly improved the structural reversibility of these materials during phase change.

In this section, we outline the theory underlying these special microstructures and identify combinations of lattice geometries necessary to form (a) stress-free interfaces (or $\lambda_2 = 1$) and (b) volume-preserving microstructures (or $|\det \mathbf{U} - 1| = 0$) [57]. These parameters will serve as inputs for our multivariant continuum model and Sec. IV D in the Results.

A phase boundary is *stress-free* when the lattices undergo a finite deformation but share an edge that remains relatively unstretched between the two phases (i.e., satisfying the $\lambda_2 = 1$ criterion). This condition corresponds to an exact interface (without misfit strains) between the reference and transformed lattices and is associated with enhanced reversibility and low fatigue in phase-transformation materials [26,28,30]. The compatibility condition for this exact interface is given by

$$\mathbf{Q}\mathbf{U} - \mathbf{I} = \mathbf{a} \otimes \hat{\mathbf{n}}. \quad (4)$$

The change in lattice geometry between the reference and transformed phases is described by the stretch tensor \mathbf{U} and the rotation tensor \mathbf{Q} . The transformed lattices form a compatible interface with the reference phase \mathbf{I} if the eigenvalues of the stretch tensor \mathbf{U} satisfy $\lambda_1 \leq \lambda_2 = 1 \leq \lambda_3$. The middle eigenvalue criterion $\lambda_2 = 1$ corresponds to the common lattice edge between the reference and transformed phases that remains relatively unstretched. In other words, this interface satisfies the invariant-plane strain condition well established in the crystallographic theory of martensites, in which the plane is undistorted or unrotated during transformation.

Symmetry-breaking phase transformations involve changes in lattice geometries, and under certain conditions, these changes can result in a *volume-preserving* deformation. In such materials, the stretch tensor \mathbf{U} satisfies the condition $|\det \mathbf{U} - 1| = 0$. The determinant of \mathbf{U} represents the volume ratio between the transformed and reference lattices, and $|\det \mathbf{U} - 1| = 0$ indicates that the transformation occurs without a net volume change of the unit cells. This condition is one of the important criteria

necessary to form self-accommodating microstructures in shape-memory alloys.

The compatibility conditions, namely the $\lambda_2 = 1$ condition to form stress-free interfaces and the $|\det \mathbf{U} - 1| = 0$ condition for volume-preserving microstructures, are more general than the zero-strain condition that is widely used in designing intercalation compounds [5,9,58,59]. For example, both the $\lambda_2 = 1$ and $|\det \mathbf{U} - 1| = 0$ conditions can be satisfied by *multiple* combinations of lattice geometries and symmetry-breaking transformation pathways. Figure 8(a) shows several combinations of lattice geometries undergoing a cubic-to-tetragonal transformation that satisfy the $\lambda_2 = 1$ and/or $|\det \mathbf{U} - 1| = 0$ conditions. These multiple combinations of lattice geometries provide several routes to engineer lattice deformations—beyond the zero-strain condition—by doping intercalation compounds, and thus offer greater flexibility to chemists in designing material compositions. Moreover, the zero-strain condition is a special case of the compatibility condition in Eq. (4), where the eigenvalues satisfy $\lambda_1 = \lambda_2 = \lambda_3 = 1$. This condition is met when the host lattices are rigid and do not distort, corresponding to the $\alpha = \beta = 1$ in Fig. 8(a), and results in zero volume change during phase transformation. By contrast, the solutions to Eq. (4) and $|\det \mathbf{U} - 1| = 0$ are more general and allow a wider range of lattice deformations satisfying $\lambda_1 \leq \lambda_2 = 1 \leq \lambda_3$. In our study, we use representative lattice geometries identified as “A” and “B” in Fig. 8(a) that satisfy the $\lambda_2 = 1$ and $\det \mathbf{U} = 1$ conditions, respectively, and analyze the energy barriers associated with these microstructures during phase change (see Results Sec. IV D).

The crystallographic microstructures emerge phenomenologically in the material during phase transformations. In intercalation compounds, the electrochemical driving forces—in addition to elastic energy minimization—affect the pathways of microstructural evolution. For example, anisotropic Li diffusion, thermodynamic and kinetic energy barriers, and galvanostatic and potentiostatic surface conditions, all affect microstructural evolution. These factors are not accounted for in the crystallographic theory of martensites (a sharp-interface theory), and the energy-minimizing sequences given by Eqs. (2), (3), and (4) are purely analytical solutions used to derive continuum microstructures. Therefore, it is important to analyze the nucleation and growth of the crystallographic microstructures in an electrochemical environment, and to investigate the collective energy barriers and driving forces that shape continuum microstructures.

III. MULTIVARIANT CONTINUUM MODEL

We present a continuum theory for intercalation compounds undergoing symmetry-breaking phase transformations. Unlike existing phase-field models [42,60–62], which use Li composition as the primary order parameter

and typically homogenize and linearize lattice deformations, our approach accounts for individual lattice variants that emerge during symmetry-breaking transformations. We formulate the free energy landscape as a multiwell potential that is frame indifferent and takes into account the symmetry of the crystal lattices [22,49]. This formulation has been referred to as Ericksen’s multiwell energy landscape in the martensitic literature [21,22,49,63]. By minimizing the total energy across this multiwell landscape with flux boundary conditions, our continuum model predicts the nucleation and growth of crystallographic microstructures. This symmetry-related continuum theory is general and applicable to all symmetry-breaking intercalation compounds [64]. For a detailed derivation and formulation of our continuum model, please refer to our previous work [41].

We begin by formulating the continuum theory in three dimensions and then reduce it to a two-dimensional framework. This dimensional reduction is achieved by assuming in-plane lattice deformations and selecting appropriate 2D projections based on the orientations of compatible interfaces. The well-characterized compound $\text{Li}_2\text{Mn}_2\text{O}_4$ serves as a representative material for this study. Our findings provide quantitative insight into the internal stresses and volume changes that accompany phase transformations in $\text{Li}_2\text{Mn}_2\text{O}_4$. Moreover, our multivariant continuum model serves as a computational tool for crystallographically designing stress-free interfaces and volume-preserving microstructures in intercalation compounds. These theoretical results potentially suggest new ways for designing intercalation compounds with enhanced reversibility.

A. Free energy

We construct a multiwell free-energy landscape for $\text{Li}_2\text{Mn}_2\text{O}_4$ using two order parameters, namely the normalized Li composition \bar{c} and a strain measurement vector $\mathbf{e} = \{e_1, e_2, e_3, \dots, e_6\}^\top$. The Li composition distinguishes between the reference and intercalated phases, while the components of the strain measurement vector (e.g., e_2, e_3) distinguish between lattice variants in the transformed phase. The strain measurements are linear combinations of the components of the Green-Lagrange strain tensor \mathbf{E} , and are given by [65]

$$\begin{aligned} e_1 &= \frac{1}{\sqrt{3}}(E_{11} + E_{22} + E_{33}), \\ e_2 &= \frac{1}{\sqrt{2}}(E_{11} - E_{22}), \\ e_3 &= \frac{1}{\sqrt{6}}(E_{11} + E_{22} - 2E_{33}), \\ e_4 &= \sqrt{2}E_{23} = \sqrt{2}E_{32}, \\ e_5 &= \sqrt{2}E_{13} = \sqrt{2}E_{31}, \\ e_6 &= \sqrt{2}E_{12} = \sqrt{2}E_{21}. \end{aligned} \quad (5)$$

The Green-Lagrange strain is a symmetric tensor related to the host-lattice deformation gradient as $\mathbf{E} = \frac{1}{2}(\mathbf{F}^T \mathbf{F} - \mathbf{I})$.

We formulate the total free-energy density of an intercalation compound that undergoes a symmetry-breaking transformation in 3D as

$$\begin{aligned} \Psi(\mathbf{e}, \nabla \mathbf{e}, \bar{c}, \nabla \bar{c}) = & \int_{\Omega} \underbrace{RT_0 c_0 \left(\frac{T}{T_0} [\bar{c} \ln \bar{c} + (1 - \bar{c}) \ln (1 - \bar{c})] + \mu_0 \bar{c} + \bar{c} (1 - \bar{c}) \sum_{i=1}^n \alpha_i (1 - 2\bar{c})^{i-1} \right)}_{\psi_{\text{ther}}(\bar{c})} \\ & + \frac{3}{2} K \left(e_1 - \frac{\bar{c} - 0.5}{1.0 - 0.5} \Delta V \right)^2 + G(e_4^2 + e_5^2 + e_6^2) \\ & + \underbrace{C \frac{\bar{c} - 0.75}{0.5 - 0.75} (e_2^2 + e_3^2) + \beta_0 \frac{\bar{c} - 0.75}{1.0 - 0.75} e_3 (e_3^2 - 3e_2^2) + \beta_1 (e_2^2 + e_3^2)^2}_{\psi_{\text{elas}}(\mathbf{e}, \bar{c})} \\ & + \underbrace{\frac{RT_0 c_0}{2} (\nabla \bar{c} \cdot \lambda \nabla \bar{c} + \nabla e_2 \cdot \kappa \nabla e_2 + \nabla e_3 \cdot \theta \nabla e_3)}_{\psi_{\text{grad}}(\nabla \bar{c}, \nabla e_2, \nabla e_3)} \, d\mathbf{x}. \end{aligned} \quad (6)$$

Figure 4(a) shows a three-dimensional plot of the free energy, corresponding to Eq. (6), as a function of the strain measure components e_2 , e_3 and the normalized concentration \bar{c} . At $(e_2, e_3, \bar{c}) = (0, 0, 0.5)$, there exists an energy well corresponding to the higher-symmetry cubic phase.

This cubic phase is represented by the identity tensor \mathbf{I} . Three additional energy wells are located at (e_2, e_3, \bar{c}) with $(0.1, 0.07, 1.0)$, $(-0.1, 0.07, 1.0)$, and $(0, -0.11, 1.0)$. These wells correspond to the tetragonal variants in the lower symmetry phase. The tetragonal variants are

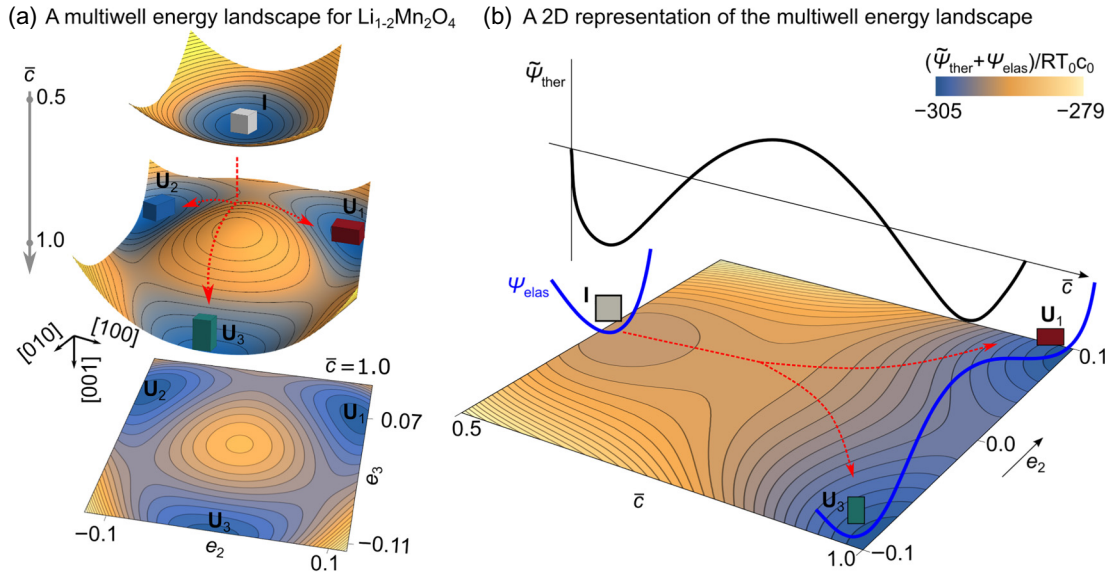


FIG. 4. The multiwell energy landscape describing the symmetry-breaking phase transformation in $\text{Li}_{2x}\text{Mn}_2\text{O}_4$ ($0.5 \leq x \leq 1$). (a) Contour plots of the free energy as a function of the order parameters: Li composition \bar{c} and strain variants (e_2, e_3) . The single well at $\bar{c} = 0.5$ corresponds to the high-symmetry cubic phase (LiMn_2O_4), and the three equivalent energy wells at $\bar{c} = 1.0$ correspond to the three tetragonal variants of $\text{Li}_2\text{Mn}_2\text{O}_4$. (b) In 2D, we represent the cubic-to-tetragonal transformation with a square unit cell for the reference phase at $(\bar{c}, e_2) = (0.5, 0)$ and rectangular unit cells for the transformed phase at $(\bar{c}, e_2) = (1.0, \pm 0.1)$. The double-well potential describes the thermodynamic energy $\tilde{\psi}_{\text{ther}}$, with minima at $\bar{c} = 0.5$ and $\bar{c} = 1.0$, respectively.

represented by the stretch tensors \mathbf{U}_1 , \mathbf{U}_2 , and \mathbf{U}_3 , respectively. We note that the free energy density in Eq. (6) satisfies both frame-indifference and material-symmetry conditions $\psi(\mathbf{R}\mathbf{e}, \mathbf{R}\nabla(\mathbf{e})\mathbf{R}^\top, c, \mathbf{R}\nabla c) = \psi(\mathbf{e}, \nabla\mathbf{e}, c, \nabla c)$ for all rotations \mathbf{R} in the finite point group of the undistorted crystalline lattice $\mathcal{P}(\mathbf{e}_i^\circ)$ [41].

We assume a two-dimensional form of the model with $E_{13} = E_{23} = E_{33} = 0$, and reduce the strain measures in Eq. (5) to $e_1 = \frac{1}{\sqrt{2}}(E_{11} + E_{22})$, $e_2 = \frac{1}{\sqrt{2}}(E_{11} - E_{22})$, and $e_6 = \sqrt{2}E_{12} = \sqrt{2}E_{21}$. Using these strain measurements, we construct the free energy in 2D as a function of e_1 , e_2 , and e_6 :

$$\begin{aligned} \Psi(\mathbf{e}, \nabla\mathbf{e}, \bar{c}, \nabla\bar{c}) = & \int_{\Omega} \underbrace{\text{RT}_0c_0 \left(\frac{T}{T_0} [\bar{c} \ln \bar{c} + (1 - \bar{c}) \ln (1 - \bar{c})] + \mu_0\bar{c} + \bar{c}(1 - \bar{c}) \sum_{i=1}^n \alpha_i (1 - 2\bar{c})^{i-1} \right)}_{\psi_{\text{ther}}(\bar{c})} \\ & + \underbrace{K(e_1 - \frac{\bar{c} - 0.5}{1.0 - 0.5} \Delta V)^2 + C \frac{\bar{c} - 0.75}{0.5 - 0.75} e_2^2 + \beta_1 e_2^4 + G e_6^2}_{\psi_{\text{elas}}(\mathbf{e}, \bar{c})} \\ & + \underbrace{\frac{\text{RT}_0c_0}{2} (\nabla\bar{c} \cdot \lambda \nabla\bar{c} + \nabla e_2 \cdot \kappa \nabla e_2)}_{\psi_{\text{grad}}(\nabla\bar{c}, \nabla e_2)} \, dx. \end{aligned} \quad (7)$$

Equation (7) describes a multiwell free-energy landscape that not only differentiates between the reference and intercalated phases—located at $\bar{c} = 0.5$ and $\bar{c} = 1.0$, respectively—but also distinguishes between the two tetragonal lattice variants at $e_2 = \pm 0.1$ and the cubic lattice at $e_2 = 0$. Figure 4(b) shows this multiwell energy landscape, calibrated for $\text{Li}_{1-2}\text{Mn}_2\text{O}_4$, in two dimensions.

The total free energy accounts for thermodynamic, elastic, and gradient energy contributions. In Eqs. (6) and (7), we use the Redlich-Kister polynomial series to construct the thermodynamic energy of the intercalation compound [66], and we fit the coefficients μ_0 and α_i to the open-circuit voltage (OCV) curve of $\text{Li}_2\text{Mn}_2\text{O}_4$ [67]. The Legendre transformation of $\psi_{\text{ther}}(\bar{c})$ results in a double-well potential with minima at $\bar{c} = 0.5$ and $\bar{c} = 0.99$ [see Fig. 4(b)]:

$$\tilde{\psi}_{\text{ther}}(\bar{c}) = \psi_{\text{ther}}(\bar{c}) - \frac{\partial \psi_{\text{ther}}(\bar{c} = 0.99)}{\partial \bar{c}} \bar{c}. \quad (8)$$

In Eq. (7), the polynomial constructed using the strain measurement order parameters (e_1 , e_2 , and e_6) describes a multiwell energy landscape that distinguishes between the individual lattice variants resulting from the symmetry-breaking phase transformation. For small deformations, the e_1 parameter governs dilatational changes of the cubic phase, the e_2 parameter breaks the 90° rotational symmetry of the cubic phase, generating the multiwell structure characteristic of the tetragonal phase, and the e_6 parameter controls shearing of the cubic phase. The bulk modulus K , shear modulus G , and deviatoric modulus C correspond to

the elastic constants of LiMn_2O_4 , and are fitted as $K = (c_{11} + c_{12})/2$, $G = c_{44}$, and $C = (c_{11} - c_{12})/2$, respectively. The coefficients β_0 , β_1 and the constant ΔV are calibrated to satisfy the equilibrium condition (with \mathbf{e}_0 corresponding to the spontaneous strain value for $\text{Li}_2\text{Mn}_2\text{O}_4$ derived in Sec. II A):

$$\left. \frac{\partial \psi_{\text{elas}}(\mathbf{e}, \bar{c})}{\partial e_i} \right|_{\bar{c}=1.0, \mathbf{e}=\mathbf{e}_0} = 0. \quad (9)$$

The anisotropic elasticity tensor, used to derive the bulk K , shear G , and deviatoric C moduli above, is calibrated with the cubic LiMn_2O_4 phase. An elasticity tensor defined in the cubic basis contains three independent entries, namely c_{11}, c_{12}, c_{44} (see Table S5 in the Supplemental Material [51]), which for LiMn_2O_4 are widely measured in experiments and predicted by density-functional theory (DFT) calculations [68–71]. The transformed phase $\text{Li}_2\text{Mn}_2\text{O}_4$, however, corresponds to lattices with tetragonal symmetry, and an elasticity tensor in the tetragonal basis would contain six independent entries. Experimental characterization of the elasticity tensor for the $\text{Li}_2\text{Mn}_2\text{O}_4$ phase remains limited, however a few DFT studies estimate that the elastic moduli (K, G, C) of $\text{Li}_x\text{Mn}_2\text{O}_4$ across the Li-composition range are comparable in magnitude [70]. The DFT calculations predict a mean deviation of less than 10% for the bulk modulus of $\text{Li}_x\text{Mn}_2\text{O}_4$ across the Li-composition range $0 < x < 2$ [70]. Based on these findings and previous work on spinel compounds [68,69,71], we assume in our calculations that the bulk, shear, and deviatoric moduli are independent of the composition field.

We note that assuming an elasticity tensor defined on a cubic basis introduces a minor approximation in the local stress fields, however, given that the elastic moduli for the two phases $\text{Li}_{1-2}\text{Mn}_2\text{O}_4$ do not differ significantly, the effect of composition-independent moduli on our results is negligible.

Finally, we model isotropic gradient energy terms to penalize changes in Li composition and strain. The corresponding gradient energy coefficients, λ , κ , and θ , are numerically calibrated to describe the diffuse phase boundaries between the reference and transformed phases, and the compatible twin boundaries between lattice variants, respectively.

B. Governing equations

We compute the evolution of Li composition following the law of mass conservation:

$$\frac{\partial c}{\partial t} + \nabla \cdot \mathbf{j} = 0. \quad (10)$$

In Eq. (10), \mathbf{j} is the diffusive flux, defined by the Onsager relation $\mathbf{j} = -\mathbf{M}(c)\nabla\mu$. This flux depends on the mobility tensor $\mathbf{M}(c)$ and the gradient of the chemical potential μ . Li diffusion in $\text{Li}_2\text{Mn}_2\text{O}_4$ is isotropic [35], and we formulate the mobility tensor as $\mathbf{M}(c) = \frac{D_0 c(c_0 - c)}{RT_0 c_0} \mathbf{I}$, in which D_0 is the Li-diffusion coefficient. The chemical potential μ is defined as the variational derivative of the free energy:

$$\mu = \frac{1}{c_0} \frac{\partial \psi_{\text{ther}}}{\partial \bar{c}} + \frac{1}{c_0} \frac{\partial \psi_{\text{elas}}}{\partial \bar{c}} - RT_0 (\nabla \cdot \lambda \nabla \bar{c}). \quad (11)$$

The individual terms in Eq. (11) represent the thermodynamic, elastic, and gradient energy contributions to the chemical potential. These contributions vary across space and time, and we analyze their effects on phase-transformation kinetics in Sec. IV B. In particular, we find that the elastic-energy-driven component of the chemical potential contributes anisotropically to Li diffusion along and across twin boundaries—a feature not previously captured in phase-field models for intercalation compounds.

We neglect surface wetting on the electrode particle (i.e., $\nabla c \cdot \hat{\mathbf{n}} = 0$) and model a constant Li flux on all surfaces as

$$\mathbf{j} \cdot \hat{\mathbf{n}} = -\frac{C c_0 L}{3600}. \quad (12)$$

In Eq. (12) C represents the C rate and L corresponds to the computational domain size.

In our calculations, we assume that mechanical relaxation occurs instantaneously compared to the timescale of Li diffusion. In the absence of external mechanical loads on the electrode, we solve for the mechanical equilibrium

conditions as

$$\nabla \cdot \mathbf{T}_R^\top - \nabla \cdot (\nabla \cdot \mathbf{Y}^\top)^\top = 0. \quad (13)$$

In Eq. (13) \mathbf{T}_R and \mathbf{Y} denote the first Piola-Kirchhoff stress tensor and the higher-order stress tensor, respectively. These stress tensors are related to the variational derivatives of the free energy as

$$\mathbf{T}_R = \sum_i \left(\frac{\partial \psi_{\text{elas}}}{\partial e_i} \frac{\partial e_i}{\partial \mathbf{F}} + \frac{\partial \psi_{\text{grad}}}{\partial \nabla e_i} \frac{\partial \nabla e_i}{\partial \mathbf{F}} \right), \quad (14)$$

$$\mathbf{Y} = \sum_i \frac{\partial \psi_{\text{grad}}}{\partial \nabla e_i} \frac{\partial \nabla e_i}{\partial \nabla \mathbf{F}}. \quad (15)$$

The first Piola-Kirchhoff stress tensor \mathbf{T}_R is defined in the reference configuration. For our analysis, we convert it to the classical Cauchy stress tensor $\boldsymbol{\sigma}$, which is defined in the deformed configuration, as follows:

$$\mathbf{T}_R = J \boldsymbol{\sigma} \mathbf{F}^{-\top}. \quad (16)$$

In Eq. (16), the Jacobian determinant is given by $J = \det \mathbf{F}$. Detailed derivations of the constitutive equations for Li diffusion and the finite deformation of host lattices are described in our recent work [41]. We implement our multivariant continuum model within a finite-element framework. We use QUAD elements for 2D simulations and HEX elements for 3D simulations. We use the Galerkin weak forms of the dimensionless Eqs. (10), (11), and (13) in the open-source, parallel finite-element framework (MOOSE). These fourth-order partial differential equations (e.g., mechanical equilibrium with high-order stress gradients and the Cahn-Hilliard diffusion) require C^1 -continuous finite elements, making the C^0 -continuous Lagrange basis functions insufficient. Following Ref. [72], we develop a mixed-type finite-element formulation, introducing deformation gradient and chemical potential as additional degrees of freedom to solve the coupled higher-order diffusion and nonlinear strain gradient elasticity problem. We solve the system of nonlinear equations using the preconditioned Jacobian-free Newton-Krylov method, and compute time integration using the implicit Backward-Euler method. Further details on the numerical implementation of our model are provided in Ref. [41] and outlined in Appendix C of the Supplemental Material [51].

IV. RESULTS

We apply our continuum model to investigate the evolution of crystallographic microstructures in intercalation compounds and to analyze the energy barriers accompanying phase transformations. In our computations, we predict geometrically accurate microstructures in $\text{Li}_2\text{Mn}_2\text{O}_4$ that forms as a consequence of energy minimization,

and provide quantitative insights into stress concentrations along phase boundaries and anisotropic Li diffusion along twin interfaces. Our continuum model serves as a crystallographic design tool that we use to engineer special combinations of lattice geometries and study the phenomenological evolution of stress-free interfaces and self-accommodating microstructures in intercalation compounds. Broadly, our analysis provides insights into the relations between energy barriers, crystallographic microstructures, and macroscopic material responses (e.g., voltage curves, structural reversibility).

In our computations, we model a domain of length $L = 500$ nm, with periodic boundary conditions applied to the surfaces $x_1 = 0$ and $x_1 = L$ (and a thickness of 40 nm for three-dimensional calculations). We apply a Li flux on all surfaces with a constant $0.5C$ rate, and we solve for mechanical equilibrium at each step of the microstructural evolution. In all calculations below, we initialize the computational domain in the uniform reference LiMn_2O_4 phase.

A. Geometric microstructures in $\text{Li}_2\text{Mn}_2\text{O}_4$

Figure 5 shows the nucleation and growth of crystallographic microstructures in $\text{Li}_2\text{Mn}_2\text{O}_4$ during a discharge half-cycle at $0.5C$ rate in 3D. Lithiating the reference phase LiMn_2O_4 induces an abrupt cubic-to-tetragonal transformation of the host lattices. The order parameters e_2 and e_3 collectively describe the lattice deformation and the three tetragonal variants $\mathbf{U}_1, \mathbf{U}_2, \mathbf{U}_3$ are positioned equidistant

from the reference energy well **I**, see Fig. 4(a). The lattice misfit between the cubic phase and any single variant of the tetragonal phase is significant approximately 13% and contributes to the elastic energy at the phase boundary. To minimize this energy, the tetragonal variants form a fine mixture [e.g., \mathbf{U}_1 and \mathbf{U}_2 in Fig. 5(a)] with an average deformation that is compatible with the cubic phase. These finely twinned microstructures (also referred to as the classic austenite-martensite microstructure) minimize coherency stresses at the phase boundary, and are formed as a consequence of elastic energy minimization.

Figures 5(a)–5(b) shows two examples of crystallographic microstructures that evolve in platelet-shaped 3D computational domains. These calculations predict the volume fraction of the twinned mixture as $f = 0.208$ and a twin-plane orientation of 45° . These results compare favorably with the experiments by Erichsen *et al.* [35], in which the bright field imaging of $\text{Li}_2\text{Mn}_2\text{O}_4$ microstructure shows a volume fraction of $f = 0.2$ and a twin orientation of 45° . These crystallographic microstructures are necessarily three-dimensional; however, their geometric features can be accurately captured on specific 2D planes [e.g., $\hat{\mathbf{m}} \times \hat{\mathbf{n}}$ in Fig. 6(e)]. This dimensionality reduction would benefit numerical calculations, which are expensive in 3D because of the higher-order PDEs involved and the challenges associated with stabilizing finite element calculations (see the Methods section). For $\text{Li}_2\text{Mn}_2\text{O}_4$, the out-of-plane strain component is small ($(a - a_0)/a_0 = -0.03$) when compared to its in-plane strain component ($(c - c_0)/c_0 = 0.13$). This small out-of-plane distortion explains the $\sim 2\%$ error in twin plane orientation ($\Delta\theta \approx 0.89^\circ$) and volume fractions ($\Delta f \approx 0.01$) reported in experiments (i.e., Erichsen *et al.* [35] imaged $\text{Li}_2\text{Mn}_2\text{O}_4$ microstructures on the (010) plane). With these differences in mind, we proceed to characterize and investigate these on a representative 2D plane.

Figures 6(a)–6(d) show the nucleation and growth of the 2D $\text{Li}_2\text{Mn}_2\text{O}_4$ microstructures with increasing state-of-charge (SOC = $\int_{\Omega} \bar{c} dV/V$). The geometric features of the twinned domains satisfy kinematic compatibility criteria, and the volume fraction of twins, twin-plane orientation, and phase boundaries emerge phenomenologically (without any *a priori* assumptions) in our computations. In Fig. 6(b), the volume fraction of the martensite twins in the $\text{Li}_2\text{Mn}_2\text{O}_4$ phase is $f \approx 0.2$, which closely matches our analytical solution of $f = 0.216$ for $\text{Li}_2\text{Mn}_2\text{O}_4$ in Eq. (3) and is within approximately 4% error of our 3D calculations. The twin interfaces are oriented at about 45° , which is consistent with the solution of the twinning equation with $\hat{\mathbf{n}} = (\overline{0.707}, 0, \overline{0.707})$. The volume fraction and orientation of the twinned domains are a consequence of the averaging of tetragonal variants (to maintain compatibility with the reference phase) and emerge in the early stages of phase transformation. The microstructural evolution in Fig. 6 was computed at $0.5C$ rate, which is sufficiently

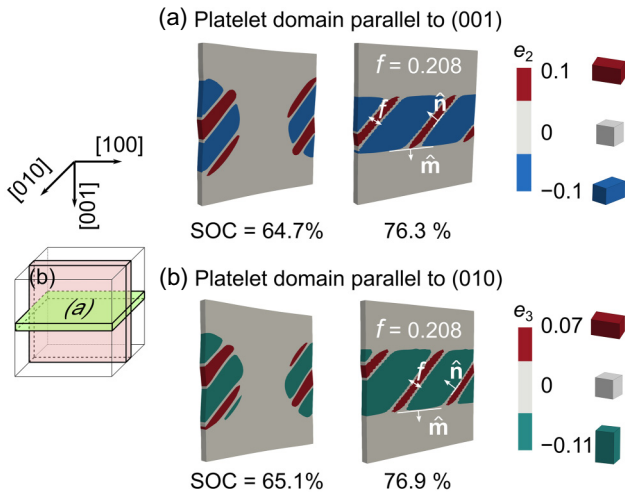


FIG. 5. The nucleation and growth of twinned microstructures in $\text{Li}_2\text{Mn}_2\text{O}_4$ on platelet-shaped 3D computational domains. In both (a),(b), our multivariant continuum model predicts crystallographic microstructures with a volume fraction $f = 0.208$ for the twinned domains. These results are consistent with the bright-field imaging of $\text{Li}_2\text{Mn}_2\text{O}_4$, which shows $f = 0.2$ [35], and with our analytical calculations in Table S2 of the Supplemental Material [51].

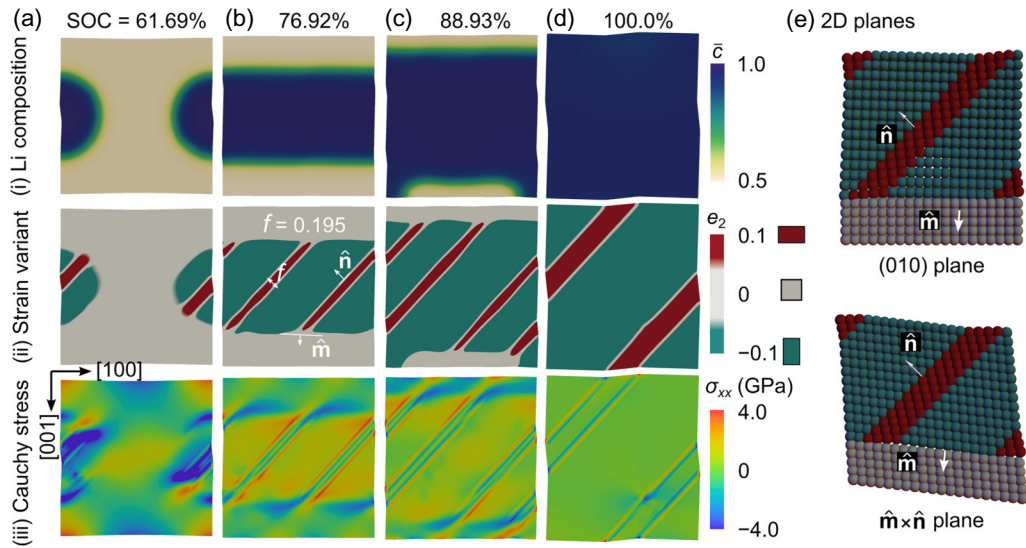


FIG. 6. The nucleation and growth of twinned microstructures in $\text{Li}_{2x}\text{Mn}_2\text{O}_4$ during a discharge half-cycle at 0.5C rate. (a)–(d) The images on the top (i) and middle (ii) rows, respectively, illustrate the evolution of Li composition \bar{c} , and the strain variant e_2 as a function of the SOC. The geometric features of the twinned microstructures, such as the twin-plane orientation \hat{n} , volume fraction f , and the approximate orientation of the phase boundary \hat{m} , are highlighted. The images on the bottom row (iii) show the Cauchy stresses σ_{xx} with compressive stresses of up to -4 GPa across the phase boundary. (e) We project microstructures onto the (010) and $\hat{m} \times \hat{n}$ planes, respectively. The twin-plane orientations and the volume fraction are geometrically accurate on the $\hat{m} \times \hat{n}$ plane; however, have minor errors ($\pm 5\%$) on the (0, 1, 0) plane because of negligible out-of-plane distortions in $\text{Li}_2\text{Mn}_2\text{O}_4$.

slow for instantaneous relaxation of the elastic energy. This explains why the volume fraction and twin boundary orientation correspond to the energy-minimizing solutions in the initial stage of the discharge cycle.

In Fig. 6(b), the phase boundary separating the uniform LiMn_2O_4 and the finely twinned $\text{Li}_2\text{Mn}_2\text{O}_4$ is planar with orientation (0, 0, 1). This orientation of the phase boundary closely matches the analytical solution of the austenite-martensite interface in Fig. 3(a). With continued lithiation, the phase boundary propagates through the computational domain. This phase boundary motion is driven not only by elastic energy minimization, but also by the anisotropic Li diffusion (see Sec. IV B) and surface boundary conditions. Consequently, the orientations of the phase boundary in Fig. 6(c) form in a collective response to energy minimization and the applied flux boundary condition.

Figure 6(bottom row) shows the Cauchy stress distribution during phase change. Although twin boundaries are exactly compatible according to sharp interface theory [22], our simulations predict finite stresses at these interfaces. In our multivariant continuum model, based on diffuse-interface theory, we penalize changes in the deformation gradient (i.e., $\nabla \mathbf{e}$). This penalty manifests as higher-order stresses of approximately equal to ± 2 GPa localized along the twin interfaces. Furthermore, the interfacial stress at the phase boundary—although minimized by fine twinning—is not entirely eliminated [see Fig. 6(bottom row)]. This interfacial penalty, along with the stress penalty at the twin boundaries, is necessary for

solving the elastic energy minimization problem. Without it, the transformed martensitic phase (i.e., $\text{Li}_2\text{Mn}_2\text{O}_4$ phase) would generate twins of infinitesimal thickness. By accounting for the strain gradient energy terms we limit this infinite twinning to finite domains with a characteristic thickness of $f = 0.195$. These results are geometrically consistent with the experimental measurements of microstructures observed in $\text{Li}_2\text{Mn}_2\text{O}_4$ [35]. At the phase boundary, the Cauchy stresses $\sigma_{xx} \approx 4$ GPa accumulate with repeated cycling and nucleate microcracks in the material [38]. The cubic-to-tetragonal transformation in $\text{Li}_2\text{Mn}_2\text{O}_4$ is not a volume-preserving deformation (i.e., $|\det \mathbf{U} - 1| = 6.4\%$), which in turn builds interfacial stresses between neighboring electrode particles or between an electrode and solid-electrolyte interface. These chemomechanical challenges accelerate the decay of intercalation compounds.

B. Anisotropic diffusion along twin interfaces

The finite stresses along twin interfaces and phase boundaries act as additional driving forces for Li diffusion. These driving forces are nonhomogeneous on the computational domain and introduce anisotropy in the evolution of Li composition in electrode particles. For example, in Eq. (7) of the Methods section, the moduli $C = (c_{11} - c_{12})/2$, $K = (c_{11} + c_{12})/2$, and $G = c_{44}$ are linear combinations of the elastic stiffness components c_{11} , c_{12} , and c_{44} of LiMn_2O_4 . The term related to deviatoric modulus

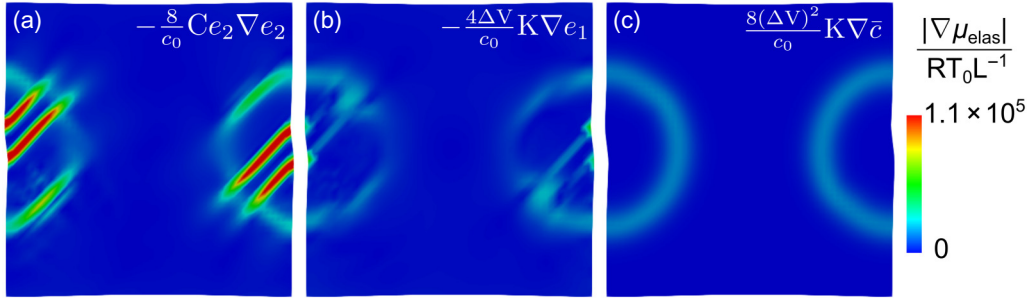


FIG. 7. Anisotropic driving forces for Li diffusion arising from the twinned domains in $\text{Li}_2\text{Mn}_2\text{O}_4$. (a) The gradient term with ∇e_2 in Eq. (18) facilitates faster Li diffusion along twin boundaries. (b) The effect of ∇e_1 on Li diffusion is negligible when the dilatational changes to the lattice geometry are small. (c) The gradient of composition $\nabla \bar{c}$ drives Li diffusion across the phase boundary. Overall, the driving force arising from the $-(8/c_0)C e_2 \nabla e_2$ term is dominant and is primarily present along the twin boundaries; this driving force is absent across the twins.

$C((\bar{c} - 0.75)/(0.5 - 0.75))e_2^2$) and the term related to bulk modulus $K(e_1 - ((\bar{c} - 0.5)/(1.0 - 0.5))\Delta V)^2$ are functions of the chemical composition and affect the stress chemical potential as follows:

$$\begin{aligned} \mu_{\text{elas}} &= \frac{1}{c_0} \frac{\partial \psi_{\text{elas}}}{\partial \bar{c}} \\ &= -\frac{4}{c_0} C e_2^2 - \frac{4\Delta V}{c_0} K \left(e_1 - \frac{\bar{c} - 0.5}{1.0 - 0.5} \Delta V \right), \end{aligned} \quad (17)$$

The driving force for diffusion (arising explicitly from the elastic energy component) is given by

$$\nabla \mu_{\text{elas}} = -\frac{8}{c_0} C e_2 \nabla e_2 - \frac{4\Delta V}{c_0} K \nabla e_1 + \frac{8(\Delta V)^2}{c_0} K \nabla \bar{c}. \quad (18)$$

Figure 7 shows the driving-force contributions from individual terms in Eq. (18). We note that these driving forces are primarily active along the twin boundaries (arising from ∇e_2 term) but not across the twins. Likewise, the contributions in Figs. 7(b)–7(c) are finite along, but not across, the phase boundary (arising from $\nabla \bar{c}$ and ∇e_1 terms). These stress-induced contributions to the chemical potential are in addition to the thermodynamic and gradient energy contributions described in Eq. (7).

The driving forces in Eq. (18) originate from the crystallographic features in $\text{Li}_2\text{Mn}_2\text{O}_4$ and promote enhanced Li diffusion along twin boundaries. For example, the strain measure e_2 distinguishes between the tetragonal lattice variants in the transformed $\text{Li}_2\text{Mn}_2\text{O}_4$ phase, and the strain gradient term ∇e_2 penalizes the elastic energy localized at the twin boundary. This energy penalty contributes to anisotropy in the chemical potential gradient, thereby facilitating relatively faster Li diffusion along the twin interfaces compared to the surrounding bulk. In contrast, the contribution of other strain gradient terms, such as ∇e_1 , is relatively minor on Li diffusion. This is because

the volumetric changes, quantified by e_1 , between tetragonal variants (and between tetragonal and cubic phases) are negligible. These effects are captured in our continuum calculations, see Fig. 7, which show that the higher-order strain gradient terms assist Li diffusion along the twin boundaries. Figure 7 also highlights the broader potential of engineering crystallographic microstructures in intercalation compounds to facilitate rapid charging and discharging of electrodes during phase transformation.

It is important to note that prior experimental and first-principles studies have also reported anisotropic Li-ion mobility near twin boundaries [45,73–75]. For instance, enhanced Li diffusion along twin boundaries has been observed in LiCoO_2 [45], SnO_2 [75], and LiMn_2O_4 [73, 74]. These studies consistently show that the activation energy for Li migration is lower along twin boundaries and higher across them. This difference in activation energy values E_a is strongly linked to the twin-boundary defect structures in the crystal, and leads to spatial variations in the local diffusion coefficient D_0 . Likewise in the vicinity of antiphase boundaries the local cation environment and the distribution of the zero transition metal channels affect Li-diffusion coefficient [76]. In the present work, however, we simplify this behavior and assume a constant, homogeneous diffusion coefficient D_0 for lithium in our continuum model. Consequently, the anisotropy in Li diffusion shown in Fig. 7 arises primarily from the chemical potential gradient terms in Eq. (18).

Our multivariant continuum model effectively predicts the crystallographic microstructures that nucleate and grow in $\text{Li}_2\text{Mn}_2\text{O}_4$. Using lattice geometries of this intercalation compound as the primary input, our continuum model predicts geometrically accurate microstructures that form during electrochemical cycling. These results are consistent with the existing experimental literature [35], and build on these reports by providing quantitative insights into the stress and its contributions in accelerating phase-transformation kinetics. The predictive capabilities of the model offer fundamental insights into the microstructural

effects on material properties, and open up new possibilities to crystallographically design intercalation compounds.

C. Crystallographic designing

We use our multivariant continuum model as a crystallographic design tool to engineer special microstructures with stress-free interfaces $\lambda_2 = 1$ and volume-preserving deformations $|\det \mathbf{U} - 1| = 0$ during phase change; by doing so, we demonstrate a proof-of-concept for designing materials with enhanced lifespans beyond the zero-strain criterion. These special crystallographic microstructures would help address common structural failure issues such as cracking and delamination, which limit the lifetime of solid-state batteries. It is important to note that both these microstructures are more general than the zero-strain condition, in that they allow individual lattices to distort and/or undergo symmetry change during phase transformation, but satisfy specific compatibility criteria.

Figure 8(a) shows combinations of the lattice geometries that satisfy the compatibility criteria for stress-free interfaces and volume-preserving microstructures. For materials undergoing a cubic-to-tetragonal transformation, two independent stretch parameters describe the lattice geometry changes: $\alpha = a/a_0$ and $\beta = c/a_0$. The hatched region in Fig. 8(a) identifies combinations of lattice geometries that can form the characteristic twinned domains (i.e., austenite-martensite microstructure) during phase change. The lattice geometries of $\text{Li}_{2x}\text{Mn}_2\text{O}_4$ (LMO) satisfy this constraint. To achieve stress-free interfaces, the middle

eigenvalue of the stretch tensor must satisfy $\lambda_2 = 1$. This condition can be met in two ways: either $\alpha = 1$ for any value of β , or $\beta = 1$ for any value of α . This is shown as vertical ($\alpha = 1$) and horizontal ($\beta = 1$) lines, respectively, in Fig. 8(a) and identified by a representative example “A.” A volume-preserving deformation requires the stretch tensor to satisfy $\det \mathbf{U} = 1$, which implies $\alpha^2\beta = 1$. This stretch tensor should also satisfy the inequalities ($\alpha < 1 < \beta$ and $1/\alpha^2 + 1/\beta^2 < 2$, or $\beta < 1 < \alpha$ and $\alpha^2 + \beta^2 < 2$) to form cubic and twinned-tetragonal interfaces (identified by the hatched region) [21,22]. The solid line inside the hatched region, therefore, represents combinations of lattice geometries that satisfy the volume-preserving deformation with a representative example identified by “B” in Fig. 8(a). These compatibility conditions offer multiple solutions to design lattice geometries of intercalation compounds when compared to the ‘zero-strain’ approach that requires $\alpha = \beta = 1$ as the only solution [77].

Using two representative lattice geometries “A” and “B” in Fig. 8(a)—which satisfy the $\lambda_2 = 1$ and $|\det \mathbf{U} - 1| = 0$ conditions, respectively—we derive the multiwell energy landscapes for our continuum calculations, see Figs. 8(b)–8(c). These energy landscapes have three minima located at $(\bar{c}, e_2) = (0.5, 0)$, corresponding to the Li-poor phase, and at $(\bar{c}, e_2) = (1.0, \pm 0.065)$ or $(\bar{c}, e_2) = (1.0, \pm 0.1)$, corresponding to individual lattice variants in the Li-rich phase. The thermodynamic energy barriers governing the phase change in Figs. 8(b)–8(c) are constant and correspond to that of $\text{Li}_{2x}\text{Mn}_2\text{O}_4$ ($0.5 \leq x \leq 1$). We calibrate the reference phase at $(\bar{c}, e_2) = (0.5, 0)$ with the cubic lattice geometry of LiMn_2O_4 and derive the

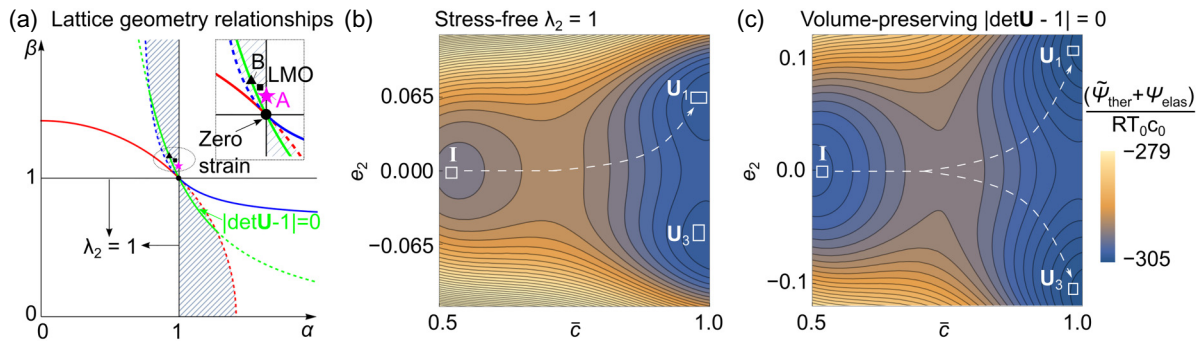


FIG. 8. (a) Lattice geometry relationships to form crystallographic microstructures in materials undergoing a cubic-to-tetragonal ($\mathbf{I} \rightarrow \mathbf{U}$) symmetry-breaking transformation. The stretch tensor \mathbf{U} is a diagonal matrix with two independent parameters $\alpha = a/a_0$ and $\beta = c/a_0$. The hatched regions show lattice geometries necessary to form the characteristic austenite-martensite interface; the solid-green line inside the hatched region (see inset) corresponds to the volume-preserving ($|\det \mathbf{U} - 1| = 0$) deformation. The vertical black lines correspond to the $\lambda_2 = 1$ criterion necessary for stress-free interfaces. The stretch tensor of $\text{Li}_2\text{Mn}_2\text{O}_4$ is highlighted by “LMO” and we identify two representative lattice geometry relations “A” and “B” that, respectively, satisfy the $\lambda_2 = 1$ and $|\det \mathbf{U} - 1| = 0$ criteria. The “zero-strain” criterion is satisfied only when $\alpha = \beta = 1$. (b) Using the representative lattice geometry relations at “A,” we derive a multiwell energy landscape as a function of Li composition \bar{c} and strain order parameter e_2 . By minimizing the total free energy across this landscape, stress-free interfaces emerge as the energy minimizer during phase change. (c) Similarly, using the lattice geometry relation at “B,” we construct a multiwell energy landscape that generates volume-preserving microstructures during phase change. We use the energy landscapes in (b),(c) to compute the nucleation and growth of special microstructures during intercalation-induced phase transformation.

position of energy wells in Figs. 8(b)–8(c) using the lattice deformation gradients of “A” and “B” (see Appendix C.3 of the Supplemental Material [51] for further details). Note that by tuning the lattice geometries of the transformed phase, we change the separation between energy wells; however, the thermodynamic energy barriers governing $\mathbf{I} \leftrightarrow \mathbf{U}_i$ transformation are not affected. In the next section, we will show that the position of these energy wells plays a crucial role in generating energy minimizers (i.e., twinned domains or compatible microstructures) that collectively lower the elastic energy barrier during phase change. The elastic energy barrier is not explicitly defined in the continuum energy landscape; however, it emerges during phase transformation (e.g., lattice misfit strains at phase boundaries, volume changes in constrained electrodes). This elastic energy barrier is associated with the dissipation of useful electrochemical work and contributes to the structural decay of electrodes; this energy barrier can be minimized for specific combinations of lattice geometries.

By minimizing the total energy of the system in the stress-free energy landscape [Fig. 8(b)] and under constant flux boundary conditions, stress-free interfaces form in a 500-nm electrode particle. Figure 9 shows the sequence of microstructural evolution in an electrode particle satisfying the $\lambda_2 = 1$ constraint [i.e., point “A” in Fig. 8(a)]. On Li-intercalation into the electrode, a Li-rich phase nucleates at SOC = 61.94%, and with continued lithiation, grows through the electrode, forming a planar phase boundary.

At the initial nucleation stage, both the tetragonal variants with $e_2 = \pm 0.065$ appear in the lithiated phase, see Fig. 8(middle row). This twinned microstructure is transient and a single lattice variant with $e_2 = -0.065$ stabilizes and grows to form a planar interface at SOC = $\sim 77\%$ [78].

The phase boundary between the reference cubic and transformed tetragonal phase has a normal along $\hat{\mathbf{n}} = (0, 0, 1)$, see Fig. 9(c). This interface orientation predicted by our continuum calculations is consistent with the analytical solution to the compatibility condition in Eq. (4) with $\hat{\mathbf{n}} = (0, 0, 1)$. The analytical construction of the 3D microstructure in Fig. 9(d) shows a planar interface between the cubic-reference phase and a single variant of the tetragonal-transformed phase. This interface is exactly compatible and stress-free according to the sharp interface theory, however our numerical calculations (based on diffuse interface theory) show small interfacial stress of $\sigma_{xx} = -0.3$ GPa, see Fig. 9(bottom row). We note that these finite interfacial stresses arise in our continuum calculations because of the nonzero gradient energy terms in Eq. (7). These interfacial stresses, however, are negligible when compared to those observed at the $\text{LiMn}_2\text{O}_4/\text{Li}_2\text{Mn}_2\text{O}_4$ phase boundary, see Fig. 11(b) for comparison. The compatible and relatively unstressed phase boundary in the crystallographically designed intercalation compound offers the potential to minimize internal stresses during phase transformation and potentially mitigate microcracking [79]. These stress-free interfaces also

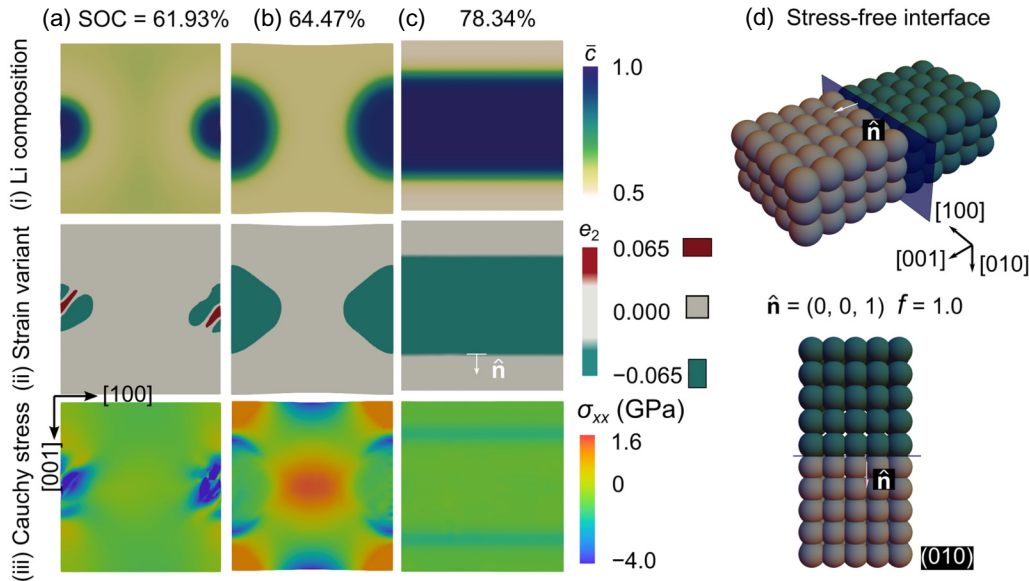


FIG. 9. A microstructural evolution pathway for stress-free interfaces, predicted by our multivariant continuum model. Rows (i)–(iii) show the evolution of Li-composition \bar{c} , strain variant e_2 , and the Cauchy stress component σ_{xx} , respectively, as a function of the SOC. The phase-boundary orientation $\hat{\mathbf{n}}$ of the single variant matches the analytical prediction for a stress-free interface in subfigure (d). The peak stress reaches $\sigma_{xx} = 1.6$ GPa due to volume changes during nucleation, while the two-phase microstructure generates only negligible stresses of $\sigma_{xx} = -0.3$ GPa across the phase boundary [see subfigure (c)].

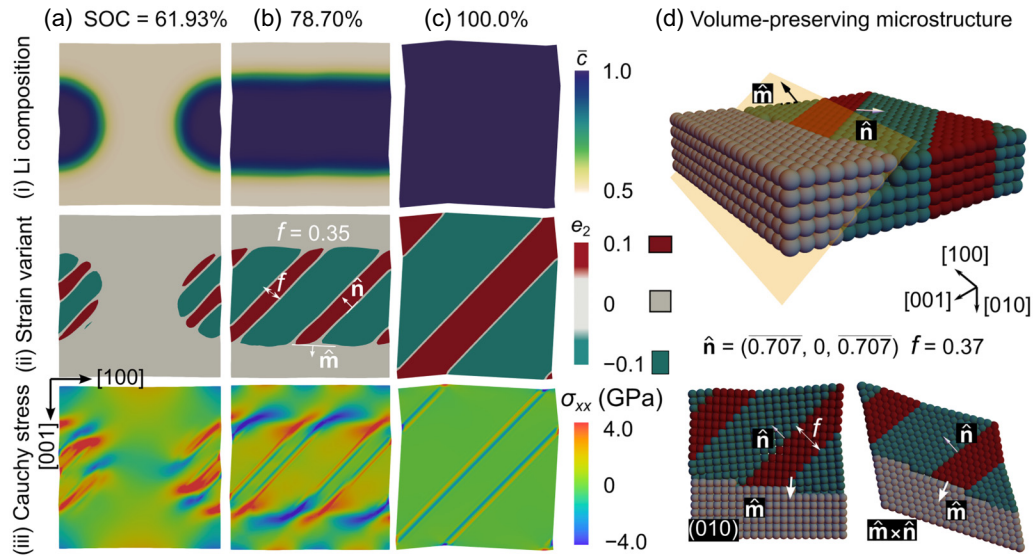


FIG. 10. Nucleation and growth of volume-preserving microstructures during a discharge half cycle. (a)–(c) The top (i) and middle (ii) rows show the evolution of Li-composition \bar{c} and strain variant e_2 with increasing SOC. Twinned microstructural features, including the twin-plane orientation $\hat{\mathbf{n}}$, volume fraction $f = 0.35$, and phase-boundary orientation $\hat{\mathbf{m}}$, are highlighted. Row (iii) shows the Cauchy stress distribution σ_{xx} with tensile stresses reaching up to ± 4 GPa across the phase boundary. (d) Analytical construction of 3D microstructures satisfying the volume-preserving ($|\det \mathbf{U} - 1| = 0$) deformation. The 2D projections of these microstructures onto the (010) and $\hat{\mathbf{m}} \times \hat{\mathbf{n}}$ planes are shown. We note that the geometric features from our continuum simulations deviate by no more than $\pm 5.4\%$ from the crystallographic theory.

lower the energy barriers for reversible transformation, and we discuss this in detail in Sec. IV D.

In contrast, intercalation electrodes with lattice geometries satisfying the condition $|\det \mathbf{U} - 1| = 0$ form twinned microstructures during phase transformation. These microstructures form in materials with symmetry-breaking lattice deformations but can self-accommodate within an electrode, resulting in minimal volume changes. Figure 10 shows the nucleation and growth of volume-preserving microstructures in a representative intercalation compound with lattice geometries corresponding to point “B” in Fig. 8(a). These microstructures form as a consequence of minimizing the elastic energy across the volume-preserving energy landscape in Fig. 8(c). A finely twinned Li-rich phase nucleates at SOC = 61.93%, and with continued lithiation, the Li-rich nucleus grows into a planar microstructure with a twinned volume fraction of $f = 0.35$.

Individual tetragonal lattices satisfy the volume-preserving deformation $|\det \mathbf{U}_i - 1| = 0$ for $i = 1$ and 3 in Figs. 10(a)–10(c); however, the transformed phase is a finely twinned mixture comprising both the variants \mathbf{U}_1 and \mathbf{U}_3 . Although individual lattice variants generate zero-volume changes, the lattice misfit between the reference and transformed phases is significant, which contributes to interfacial stresses at the phase boundary. Minimizing this elastic energy across the multiwell energy landscape in Fig. 8(c) generates the finely twinned domains. We note that these microstructures are three dimensional, and their

(010) planar projection introduces errors in the orientation of the phase boundary $\hat{\mathbf{m}}$ and the volume fraction f of the twins, see Fig. 10. With these reservations in mind, the geometric features of the microstructures predicted by our continuum simulations, such as the volume fraction f , are within 5.4% error with the crystallographic theory.

Figure 10(bottom row) shows the Cauchy stress in the electrode during the nucleation and growth of volume-preserving microstructures. The interfacial stresses are considerable in the volume-preserving microstructure compared to the microstructures satisfying the $\lambda_2 = 1$ condition; however, the hydrostatic stresses T_H (mean of normal stresses) in Fig. 11(a) that correspond to the internal pressure arising from the net volume changes are a minimum in the volume-preserving microstructures compared to both the $\text{Li}_{2x}\text{Mn}_2\text{O}_4$ and $\lambda_2 = 1$ interface. These hydrostatic stresses characterize the collective volume expansion of the electrode during phase change, which is minimized by forming volume-preserving microstructures [80]. These microstructures offer the potential to mitigate the challenges associated with electrode cracking and delamination failures in solid-state batteries.

Figure 11(b) shows the Cauchy stress distribution σ_{xx} along the phase boundary (path 2). These planar interfaces separate the twinned tetragonal variants of the lithiated phase from the uniform cubic lattices of the reference phase (e.g., in spinel LMO and volume-preserving microstructures). Although these twinned domains are

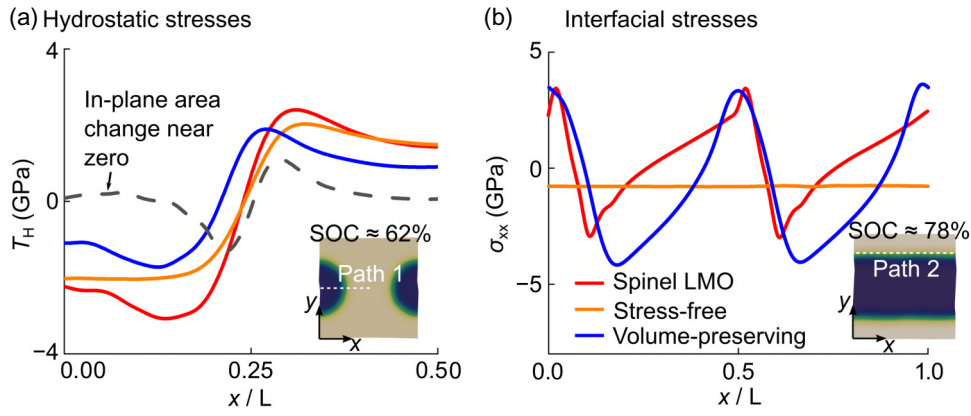


FIG. 11. Stress distributions in $\text{Li}_{2x}\text{Mn}_2\text{O}_4$, stress-free, and volume-preserving microstructures at selected SOC. (a) We compute the hydrostatic stress distribution T_H , across a Li-rich nucleus at SOC $\approx 62\%$. Along path 1, T_H is small in the volume-preserving microstructure (approximately equal to 2 GPa) compared to the spinel LMO and the stress-free interface. The dashed line represents a hypothetical case with zero area change on the $(0, 1, 0)$ plane, and is associated with much smaller hydrostatic stresses of $T_H = 0.9$ GPa. (b) The Cauchy stress, σ_{xx} , along the planar phase boundary (path 2) at SOC $\approx 78\%$. Significant lattice misfits at phase boundaries in $\text{Li}_{2x}\text{Mn}_2\text{O}_4$ and volume-preserving microstructures generate stresses of up to $\sigma_{xx} \approx \pm 4$ GPa. In contrast, the stress-free interface, which satisfies the compatibility condition, has minimum stresses of approximately -0.3 GPa.

formed to reduce the elastic energy stored at the phase boundary, there is a finite elastic stress along these interfaces as shown in Fig. 11(b). The alternating stresses of ± 4 GPa correspond to the misfit between the cubic lattice and the tetragonal lattices. In contrast, the stress-free interface forms an exactly compatible phase boundary between the cubic phase and a single tetragonal lattice variant and thus generates significantly lower stresses of approximately -0.3 GPa.

D. Energy barrier analysis

The stresses shown in Figs. 6, 9, and 10 are primarily concentrated at the interfaces or phase boundaries. These stresses contribute to the finite elastic energy stored in the system and are a function of both the lattice compatibility (i.e., the fitting together of two phases) and the *emergent* microstructural patterns that form during phase change. These elastic energy contributions at the continuum scale are not captured in the energy barrier of the free energy function (which are calibrated with the material's thermodynamic and elastic constants) but instead emerge during phase transformation. In this section, we show that this elastic energy contribution can be reduced by energy-minimizing sequences, such as twins and stress-free interfaces ($\lambda_2 = 1$), and doing so has a direct impact on the chemical potential (related to voltage hysteresis) and driving forces (related to material reversibility) in intercalation compounds. In these analyses, we do not assume a pre-existing nucleus of the transformed phases, but instead compute the energy barriers and analyze the stability of a two-phase microstructural pattern that phenomenologically forms during charge and discharge processes.

Figure 12 shows the free energy landscape governing phase change in three representative materials, namely $\text{Li}_{1-2}\text{Mn}_2\text{O}_4$, and two crystallographically designed compounds satisfying the stress-free ($\lambda_2 = 1$) interface and volume-preserving ($|\det \mathbf{U} - 1| = 0$) deformation, respectively. To compare energy barriers across the three representative materials, we construct the energy landscape using identical thermodynamic and elastic constants (corresponding to those of LiMn_2O_4). For example, in Fig. 12(a) the dashed line corresponds to the thermodynamic energy barrier governing the phase change ($\bar{c} = 0.5 \rightarrow 1.0$) is calibrated with the open-circuit voltage of $\text{Li}_{1-2}\text{Mn}_2\text{O}_4$ [67] and is held constant across the three cases. Likewise, the elastic constants including the bulk modulus ($K = (c_{11} + c_{12})/2$), deviatoric modulus ($C = (c_{11} - c_{12})/2$) and shear modulus ($G = c_{44}$) are fitted with those of LiMn_2O_4 . This enables us to compare the differences in elastic energy barriers that emerge during phase change across the three representative materials.

Figure 12(a) shows the total energy ($\Psi_{\text{avg}} = \int_{\Omega} (\tilde{\psi}_{\text{ther}} + \psi_{\text{elas}} + \psi_{\text{grad}}) dV/V$) of the system for the three cases as a function of the intercalant composition \bar{c} . In all cases, the total energy increases until the spinodal point, beyond which the domain decomposes into a two-phase microstructure separated by a phase boundary. The lattice compatibility across these phase boundaries differs among the three cases (governed by the deformation gradient) and manifests as distinct interfacial stresses in our calculations (see Cauchy stress plots in Figs. 6, 9, and 10). These stresses contribute to the finite elastic energy in the respective materials, which, in turn, generates additional energy barriers that hinder phase separation.

The collective energy barriers for each of the three representative materials are shown in Fig. 12(b). The positive

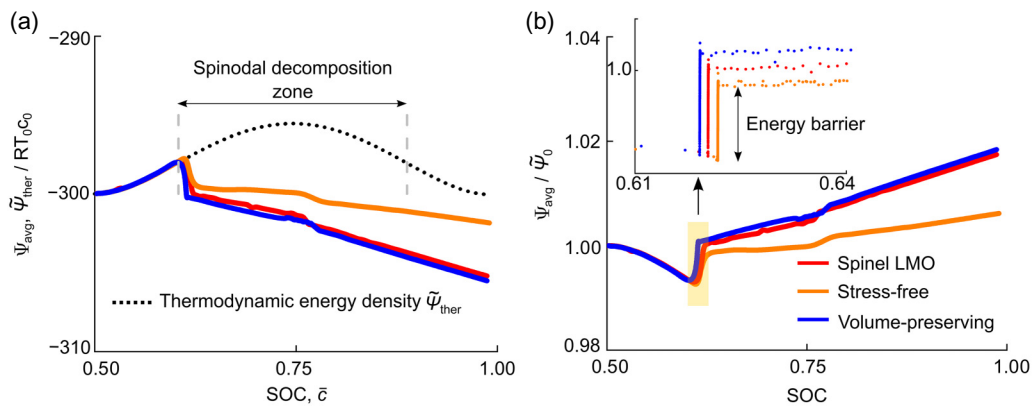


FIG. 12. (a) We compute the total free energy of the system Ψ_{avg} as a function of the SOC. This energy Ψ_{avg} increases up to the first spinodal point, after which the system phase separates and is marked by an abrupt drop in the total energy. This drop in energy is different for each of the three cases, namely $\text{Li}_2\text{Mn}_2\text{O}_4$, stress-free interface, and volume-preserving microstructure, and is a consequence of the collective elastic energy barriers that emerge during phase change. (b) Normalized energy barriers during phase change in the three microstructures ($\tilde{\psi}_0$ is the average energy of the Li-poor phase). The inset plot shows that the stress-free interface offers the lowest nucleation energy barrier during phase change (because of the exactly compatible phase boundaries) when compared to the energy barriers that emerge in $\text{Li}_2\text{Mn}_2\text{O}_4$ and volume-preserving $|\det \mathbf{U} - 1| = 0$ microstructures.

slope of these curves corresponds to the finite elastic energy accumulated in the system during the phase change. This elastic energy in $\text{Li}_2\text{Mn}_2\text{O}_4$ and the volume-preserving microstructure corresponds to the interfacial stresses at the phase boundary. The twinned domains relieve the lattice misfit at the phase boundary and lower the interfacial stresses; however, the resulting phase boundary is still not exactly compatible. These small but finite stresses contribute to elastic energy in the system that manifests in the form of a positive slope in the energy-barrier curves for $\text{Li}_2\text{Mn}_2\text{O}_4$ and the volume-preserving microstructure, see Fig. 12(b). In contrast, the elastic energy barrier is the smallest for the stress-free ($\lambda_2 = 1$) interface. In this case, a single variant of the transformed phase forms an exactly compatible interface with the reference phase. This interface is associated with theoretically zero stresses, which lowers the elastic energy stored in the system [81]. Therefore, given that all other thermodynamic and elastic constants are identical in the three representative materials, the elastic energy barriers emerging during phase change are the lowest for the $\lambda_2 = 1$ interface [82].

These energy barriers accompanying phase change have a direct impact on the chemomechanical performance of intercalation compounds. For example, the elastic energy barriers alter the chemical potential values (governing the two-phase separation) and thus affect the width of the voltage hysteresis loops, see Figs. 13(a)–13(b). For reference, the dashed line Fig. 13(a) shows the thermodynamic potential of $\text{Li}_{2x}\text{Mn}_2\text{O}_4$ ($0.5 \leq x \leq 1$), and the dashed line in Fig. 13(b) corresponds to the open-circuit voltage measurement [67]. The chemical potential curves for the three cases deviate with a positive slope from the voltage plateau in Fig. 13(a). This deviation is significant in $\text{Li}_2\text{Mn}_2\text{O}_4$

and the volume-preserving microstructure, when compared to the $\lambda_2 = 1$ interface. We attribute this difference in the slopes to the larger elastic energy stored at the phase boundaries in $\text{Li}_2\text{Mn}_2\text{O}_4$ and volume-preserving material systems. The near-zero interfacial stresses in the $\lambda_2 = 1$ interface generate a relatively small elastic energy that governs the phase change. This behavior mirrors that of other intercalation compounds (e.g., LiFePO_4 [83] and LiCoO_2 [60]), which form solid solutions at high C rate, resulting in flatter curves as the coherency strain becomes less influential. Our key finding from Fig. 13 is that fine tuning the lattice compatibility of individual lattices to achieve the stress-free interface during phase transformation—in addition to the thermodynamic and kinetic driving forces—lowers the energy barrier and internal stress, thereby improving the performance of intercalation compounds.

Figure 13(b) shows the voltage hysteresis loops for the three representative materials. In deriving these loops, we assume symmetric energy barriers that govern the charge and discharge processes. The area enclosed by the voltage hysteresis loops quantifies the energy lost during an electrochemical cycle [4]. Among the three cases, the voltage hysteresis loop is the narrowest for the $\lambda_2 = 1$ interface. This suggests that the phase change in the $\lambda_2 = 1$ interface is driven by relatively small differences in voltage values and is associated with a minimum energy dissipation. In contrast, the voltage hysteresis loops for $\text{Li}_2\text{Mn}_2\text{O}_4$ and the volume-preserving microstructure are wider, indicating that larger voltage drops are necessary to induce a phase change.

The voltage hysteresis calculation for $\text{Li}_2\text{Mn}_2\text{O}_4$ aligns with the 2–4 V voltage window reported in the

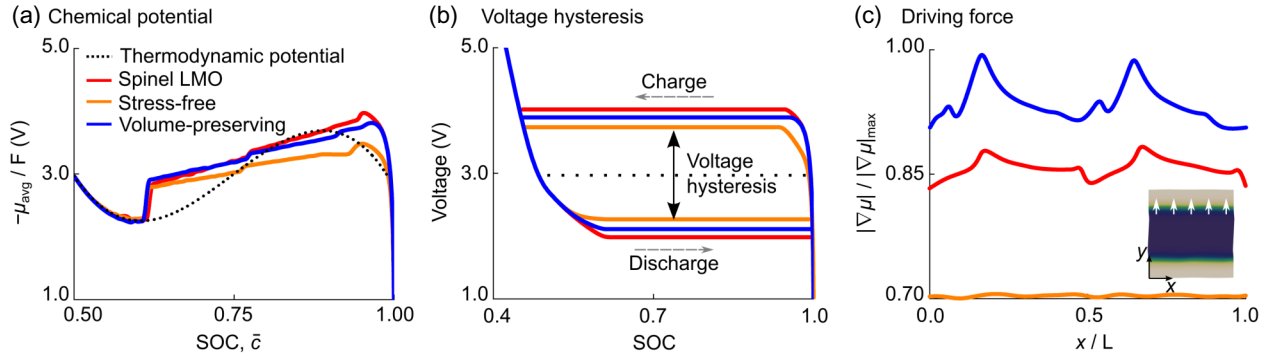


FIG. 13. (a) Chemical potential curves from our continuum calculations for the three representative materials (namely $\text{Li}_{1-2}\text{Mn}_2\text{O}_4$ and two crystallographically designed compounds satisfying the stress-free $\lambda_2 = 1$ interface and volume-preserving $|\det \mathbf{U} - 1| = 0$ deformation). All curves show a positive slope, indicating a finite elastic energy stored at the phase boundaries. This slope is the smallest in the $\lambda_2 = 1$ interface because of near-zero interfacial stresses, but is noticeably larger in the other two materials. (b) We derive voltage hysteresis loops from our continuum calculations for the three representative materials. The width of the voltage hysteresis loop is the smallest for the $\lambda_2 = 1$ interface, and shows relatively wider loops for $\text{Li}_2\text{Mn}_2\text{O}_4$ and the $|\det \mathbf{U} - 1| = 0$ deformation. We attribute the narrow hysteresis loop in the $\lambda_2 = 1$ interface to the smaller elastic energy stored at the phase boundaries. These results offer preliminary insights into the advantages of crystallographically designing intercalation compounds to lower-energy barriers that govern phase transformation. (c) We calculate the driving forces across the phase boundary during phase change. These forces are 30% lower for the $\lambda_2 = 1$ interface when compared to $\text{Li}_2\text{Mn}_2\text{O}_4$. Smaller driving forces reduce energy dissipation and promote structurally reversible phase transformations.

experiments by Erichsen *et al.* [35]. The width of this voltage hysteresis loop can be further reduced by minimizing the thermodynamic energy barrier associated with ψ_{ther} in Eqs. (6) and (7), see Appendix C.4 of the Supplemental Material [51]. This thermodynamic energy barrier $\Delta\psi$ is a function of temperature (that is, $\Delta\psi \propto -T$) and the enthalpy of mixing coefficients α_i . Increasing the temperature, or equivalently decreasing α_1 reduces the barrier height and contributes to narrower voltage hysteresis loops; see Fig. S1 of the Supplemental Material [51]. This is analogous to the regular solution model, where reducing the enthalpy of the mixing parameter Ω or increasing the temperature T proportionally lowers the thermodynamic energy barrier. We detail this analysis in Appendix C.4 of the Supplemental Material [51].

Figure 13(c) shows the maximum driving forces acting across the phase boundaries in the three representative materials at $\text{SOC} \approx 78\%$. The total driving force for phase change $\nabla\mu$ is calculated from Eq. (11), in which the total free energy of the system, including the elastic energy effects in Eq. (18), is accounted for. A small driving force demonstrates that the phase boundary moves back and forth in the material for the smallest perturbation (or energy changes) during charge and discharge processes. At $\text{SOC} \approx 78\%$, the morphology of the phase boundary in all three cases is a planar interface [see inset Fig. 13(c) showing the direction of the driving force]. The magnitude of the driving force acting across the phase boundary is highest in the volume-preserving microstructure (with $|\det \mathbf{U} - 1| = 0$) and lowest in the stress-free interface (with $\lambda_2 = 1$). The driving force in $\text{Li}_2\text{Mn}_2\text{O}_4$

[with $|\det \mathbf{U} - 1| \approx 0.064$ and satisfying the average compatibility condition in Eq. (3)] is intermediate between the three cases. Their magnitude corresponds to the energy required to drive the phase transformation. In other words, the lower driving force in the $\lambda_2 = 1$ case suggests that phase boundaries can be moved with minimal energy input, leading to reduced energy dissipation and enhanced reversibility during phase change.

V. DISCUSSION

Our multivariant continuum model extends existing phase-field methodologies by predicting crystallographic microstructures that form during phase transformations in intercalation compounds. A distinguishing feature of our approach is that we construct a multiwell energy landscape that is a function of not only the Li composition but also individual lattice variants of a given phase. By minimizing the total free energy (for $\text{Li}_2\text{Mn}_2\text{O}_4$), we predict geometrically accurate microstructural patterns, such as twin-plane orientations, volume fractions, and compatible phase boundaries that emerge during phase transformation. These energy-minimizing deformations were not previously captured by phase-field models for intercalation compounds, and offer new routes to design materials with improved structural reversibility.

Our key finding is that by designing lattice compatibility in intercalation compounds, we can significantly reduce the energy barriers governing phase transformations. These barriers manifest primarily as elastic energy stored as interfacial stresses in microstructural patterns,

which can be minimized in materials with special combinations of lattice geometries (e.g., $\lambda_2 = 1$ microstructure reduces interfacial stresses from ± 4 GPa to -0.3 GPa, and the $|\det \mathbf{U} - 1| = 0$ microstructure reduces hydrostatic stresses to near-zero values). These crystallographically designed materials have small energy barriers; therefore, they require substantially lower driving forces (by 30%) to move phase boundaries and are associated with narrower voltage hysteresis loops. These elastic energy barriers accompanying phase transformations are difficult to estimate using atomistic or first-principles calculations, but are effectively captured in our continuum approach.

Additionally, we show that the twin boundaries that form during phase change serve as conduits for fast Li-ion transport. The finite stresses along the twin interfaces and the phase boundaries act as additional driving forces for Li-diffusion. These driving forces are anisotropic, facilitating faster diffusion along the twin interfaces when compared to the diffusion across the twins. This finding highlights another potential of crystallographically designing intercalation compounds in which twin interfaces are engineered radially outward in electrode particles to facilitate rapid charging/discharging.

Our ability to predict accurate elastic energy barriers and their effects on macroscopic material properties is limited. This limitation arises from the lack of experimental characterization of interfacial energy constants and the strain energy landscape, as well as the computational costs associated with 3D calculations. These factors are likely to affect the elastic transition layer (i.e., the phase boundary) predicted by our model. With ongoing efforts to characterize interfacial constants [84,85] and the use of first-principles calculations to derive free-energy landscapes [86], we expect to gain quantitative insights into these coefficients and improve the accuracy of our predictions. Additionally, by optimizing our numerical algorithms and/or porting to GPUs to efficiently solve higher-order PDEs, our continuum model will enable us to compute larger domain sizes and to investigate the interplay between lattice compatibility and nonlinearities (e.g., defects such as grain boundaries and dislocations) during phase change.

We formulate our multivariant continuum model using the Cauchy-Born rule, which relates the movement of atoms to the overall deformation of a solid. This rule works well for simple crystals with Bravais lattices (e.g., $\text{Li}_2\text{Mn}_2\text{O}_4$, NaMnO_2 , and $\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4$ [15,35,39]) but may fail for compounds with multilattices (e.g., perovskite Li_xReO_3 [87]), and for materials in which lattice planes slip (or glide) and undergo reconstructive transformations (e.g., layered oxides LiCoO_2 [79,88]). For example, applying our framework to intercalation compounds containing two or more constituent Bravais lattices, such as the perovskite Li_xReO_3 , [87] requires careful consideration. Li insertion into perovskite ReO_3 induces internal rotations of

the individual Re octahedra making lattice mapping based solely on the deformation gradient insufficient. In these multilattices, atoms may shift and/or shuffle during displacive phase transformations, and these movements may not be fully captured by the deformation gradient alone. Under dynamic or high-rate loading conditions, atomic shuffling may affect material response (e.g., hysteresis, reversibility, or diffusion). In such cases, we need to investigate whether the relative shifts between Bravais lattices are congruent and whether the microstructural evolution can be modeled under quasiequilibrium conditions.

Similarly, our multivariant continuum model is applicable to predict martensitic microstructures in intercalation compounds that undergo pure displacive transformations. For example, in LiMn_2O_4 host lattices deform displacively on lithiation and return to their original state without any change in near-neighbor host atoms on delithiation. These displacive transformations of the host lattices satisfy the Cauchy-Born rule and are mathematically defined to operate in an Ericksen-Pitteri neighborhood [63]. Our model cannot describe phase transformations in which the lattice planes slip and the host atoms rearrange into a new configuration. For example, in layered compounds such as LiCoO_2 host lattices undergo reconstructive transformations, in which the network of oxygen polyhedra rearranges on delithiation. These transformations lie outside the Ericksen-Pitteri neighborhood and do not satisfy the Cauchy-Born rule. Currently, we are extending our theoretical framework to account for both martensitic and reconstructive phase transformations, and the results will be presented in a future study.

Despite these challenges, our computations remain valuable for understanding symmetry-breaking phase transformations at the continuum scale. The model quantitatively captures the interplay between individual lattice deformations and Li flux during phase change. By constructing a multiwell energy landscape, we allow for individual lattices to deform into symmetry-related variants and predict energy-minimizing sequences (e.g., twins, compatible phase boundary). In intercalation compounds, these microstructures evolve under dynamic loading conditions, making them a nonlinear problem that is difficult to solve analytically. Our multivariant continuum model not only investigates this nonlinear behavior, but also predicts quantitative elastic energy barriers that manifest during phase change (e.g., decrease in interfacial stresses for compatible microstructures in comparison to $\text{Li}_2\text{Mn}_2\text{O}_4$) and their impact on driving forces and hysteresis in an electrochemical environment. These predictions of crystallographic microstructures are phenomenological, made without *a priori* assumptions about the critical Li-rich nucleus or explicit boundary conditions on moving interfaces. The equilibrated microstructures from our continuum model are geometrically accurate and are remarkably close (within $\pm 5\%$ error) to experimental observations

of crystallographic microstructures in intercalation compounds. This ability to make quantitative predictions under dynamic electrochemical loads enables us to use our continuum model as both an exploratory tool to investigate fundamental microstructural mechanisms in symmetry-breaking phase transformations and as a design tool to crystallographically engineer intercalation compounds with improved reversibility.

The proof of concept of our crystallographically designed materials (e.g., satisfying the conditions $\lambda_2 = 1$, $|\det \mathbf{U} - 1| = 0$) expands the design parameter space beyond the existing zero-strain design rule for intercalation compounds. Unlike the zero-strain condition $\mathbf{F} = \mathbf{I}$ commonly used in the literature [17–20], our compatibility design rules do not restrict lattices from deforming but instead impose less stringent constraints on lattice deformation to satisfy interfacial and volume compatibility [7,40,41]. In doing so, we find multiple solutions for lattice geometries, see Fig. 8(a), which enable chemists and material scientists to synthesize intercalation compounds (e.g., site-selective doping) over a wider composition space. This expanded composition space identifies potential electrodes with extended lifespans. For example, Shin and Manthiram [46] demonstrated that systematic doping of spinel compounds reduces intercalation-induced volume changes to less than 0.2%, directly improving cycling stability. Similarly, Schofield *et al.* [9] achieved up to 0.8% reduction in lattice misfit strains through site-selective molybdenum doping in V_2O_5 electrodes, enhancing phase-transformation reversibility.

Furthermore, our multivariant continuum model can be extended to other symmetry-lowering transformations in intercalation cathodes such as NaMnO_2 [39], Prussian blue analogs [47,48], and perovskite solid electrolytes ($\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$) [89]. To describe other symmetry-lowering transformations (e.g., orthorhombic to monoclinic in NaMnO_2 [39]), our model can be further generalized by incorporating shear strain order parameters (e.g., e_4 , e_5 , and e_6) in addition to e_2 and e_3 . Our computations predict the length scales and electrochemical boundary conditions under which the crystallographic microstructures nucleate and grow steadily in these materials. These continuum findings provide insights into identifying potential electrode particle sizes and morphologies. Our findings on the impact of crystallographic microstructures on electrochemical performance (e.g., voltage hysteresis loops, driving forces) further demonstrate that lattice compatibility, in addition to the thermodynamic and kinetic barriers, plays an important role in the performance and reversibility of intercalation compounds.

Beyond intercalation compounds, our theoretical and computational framework will serve as an investigatory tool to study the nucleation of martensitic microstructures in shape-memory alloys [90], understand ferroelastic toughening in ceramics [91], and to investigate

the deformation-microstructure-property relations in other phase-transformation materials (e.g., ferroelectrics [24], magnets [25,34,92], molecular crystals [93]). Previous analytical research on these materials has led to remarkable progress in reducing fatigue and improving reversibility [28–30,56], but has relied on assumptions of specific nucleus geometries in equilibrium [26,27,52]. In our framework, we allow for these crystallographic features to evolve *in situ* and without *a priori* assumptions, and thus establish a framework to quantitatively probe the energy barriers emerging during phase change. These continuum techniques could be powerful in investigating the origins of irreversibility in phase-transformation materials.

VI. CONCLUSION

In summary, we present a materials design strategy centered on lattice compatibility and reducing energy barriers to enhance the lifespan and electrochemical performance of intercalation compounds. Using $\text{Li}_2\text{Mn}_2\text{O}_4$ as a representative material, we develop a multivariant continuum model that directly links lattice deformations with the crystallographic microstructures formed during phase change. Our continuum model not only predicts geometrically accurate microstructures in $\text{Li}_2\text{Mn}_2\text{O}_4$, but also demonstrates the beneficial role of twin interfaces in promoting faster Li-ion transport and minimizing interfacial stresses. Our energy-barrier analysis shows that compatible interfaces lower the elastic energy barriers, resulting in smaller driving forces for phase transformation and narrower voltage hysteresis loops. As a proof of concept, we use the model to design intercalation compounds with stress-free interfaces and volume-preserving microstructures, which, in turn, enable easier phase transformations and narrower voltage hysteresis. These results suggest that tailoring lattice deformations to meet special compatibility conditions—rather than suppressing them entirely—can result in compounds that maintain structural integrity and electrochemical performance over extended use.

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DATA AVAILABILITY

The data supporting this study's findings are available within the article. All codes developed in this study are open-source and available on the OSF repository at [OSF|Solids & Materials Group \(UCSB\)](https://osf.io/8v3kz/).

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