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The exploration of nonlinear elasticity and its efficient parameterization for crystalline materials

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ABSTRACT

Conventional approaches to analyzing the very large coherency strains that can occur during solid-state phase transformations are founded in linear elasticity and rely on infinitesimal strain metrics. Despite this, there are many technologically important examples where misfit strains of multi-phase mixtures are very large during their synthesis and/or application. In this paper, we present a framework for constructing strain-energy expressions and stress-strain relationships beyond the linear-elastic limit for crystalline solids. This approach utilizes group theoretical concepts to minimize both the number of free parameters in the strain-energy expression and amount of first-principles training data required to parameterize strain-energy models that are invariant to all crystal symmetries. Within this framework, the strain-energy and elastic stiffness can be described to high accuracy in terms of a set of conventional symmetry-adapted finite strain metrics that we define independent of crystal symmetry. As an illustration, we use first-principles electronic structure data to parameterize strain energy polynomials and employ them to explore the strain-energy surfaces of HCP Zr and Mg, as well as several important Zr-H and Mg-Nd phases that are known to precipitate coherently within the HCP matrices of Zr and Mg.

1. Introduction

Most multi-component crystalline solids undergo several phase transformations as a function of temperature, composition, and deformation that result in changes in crystal structure and ordering. It is common practice to attempt to guide the thermodynamic path that a material takes between two or more phases in order to optimize the microstructure or nanostructure of a material during synthesis. For example, quenching a homogeneous solid solution to a temperature where ordered phases are stable can create a multi-phase coexistence consisting of ordered precipitates coherently embedded within a matrix phase. The formation of such multi-phase mixtures typically produce strain fields that can affect the properties of the material in a multitude of ways, such as the well-known ability of coherent multi-phase mixtures to strengthen materials and increase their resistance to plastic deformation (Strudel, 1996). Multi-phase mixtures recently have also been exploited as a means of scattering long-wave-length phonons to reduce thermal conductivity in materials for thermoelectric applications (Vineis et al., 2010).

Multi-phase mixtures may also present hurdles to the optimal performance of functional materials. The electrode materials of rechargeable Li and Na batteries undergo phase transformations during electrochemical Li insertion and removal

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that proceed through a coherent multi-phase coexistence (Ravnsbaek et al., 2014). While coherency is desirable during such phase transformations to avoid pulverization of the electrode particles, the large misfit strains between coexisting phases can be accompanied by a sizable strain energy penalty that causes hysteresis in the voltage curve between charge and discharge of the battery (Van der Ven et al., 2009).

The usual approach of analyzing coherency strains in solid-state phase transformations employs linear elasticity and infinitesimal strain metrics. However, there are many technologically important examples where misfit strains are very large. For example, Metastable ordered precipitates in the Mg–Nd binary alloy form coherently within a Mg-rich HCP matrix phase, in spite of a 10% misfit strain along one of the orthorhombic axes of the precipitate (Natarajan et al., 2016). The misfit strain between $LiFePO_4$ and $FePO_4$, an important electrode material for Li ion batteries, can be as large as 5.2% (Chen et al., 2006). There are also theoretical descriptions of martensitic transformations (Barsch and Krumhansl, 1984) and mechano-chemical spinodal decomposition (Rudraraju et al., 2016) that rely on strain not only to measure strain energy, but also to serve as order parameters for symmetry breaking distortions of the crystallographic unit cell of the high symmetry phase.

Strains of even several percent usually cannot be described with infinitesimal strain metrics as they lack rotation invariance. Furthermore, since most solids become less stiff at large elastic strains, linear-elastic treatments, which assume that elastic moduli are independent of strain, tend to overestimate the strain-energy penalty. As such, linear elasticity certainly breaks down in theories of martensitic transformations that rely on Landau free energies in terms of strain order parameters measured relative to a high symmetry reference crystal. The free energies of these treatments exhibit not only multiple local minima, but also regions of negative curvature where elastic moduli become negative. An essential component of any model that describes either the static morphology or dynamical evolution of precipitates is a strain-energy model that meets two main requirements. First, it must be able to unambiguously describe very large deformations of the crystal and its corresponding energy, and, secondly, it must be invariant to all relevant symmetries of the high-symmetry reference crystal.

In this paper, we present a framework for constructing strain-energy expressions and stress-strain relationships beyond the linear-elastic limit. First, we define and examine strain metrics that are well-adapted for both large elastic deformations and for the symmetry of a crystallographic point group. Then, we build a polynomial expression from these strain metrics that obeys all symmetry of the undeformed crystal. As an illustration, we use first-principles electronic structure data to parameterize these polynomials and use them to explore the strain-energy surfaces of HCP Zr and Mg, as well as several important Zr-H and Mg-Nd phases that are known to precipitate coherently within the HCP matrices of Zr and Mg.

2. Metrics of deformation for crystal lattices

We wish to express the strain energy of a crystal as a function of variables that measure the degree to which the crystal is deformed relative to some reference state. To this end it is first necessary to review a number of metrics that describe the shape (or deformation) of the crystal in an unambiguous way and to determine how the underlying symmetry of the reference crystal affects these metrics.

A common representation of a crystal is in terms of positional data. The periodicity of a crystal is determined by the primitive-cell lattice vectors $\vec{l}_i$ such that translation of the crystal by the vector

$$\vec{R} = n_1\vec{l}_1 + n_2\vec{l}_2 + n_3\vec{l}_3, \tag{1}$$

for integer n_i, maps each atom of the crystal onto an equivalent atom. It is useful to introduce the matrix $\mathbf{L}$ having the lattice vectors as its columns, such that

$$\mathbf{L} = \left(\vec{l}_1\middle|\vec{l}_2\middle|\vec{l}_3\right). \tag{2}$$

The lattice vectors define the unit cell as a parallelepiped with respect to a set of Cartesian coordinate axes x, y, and z. The unit cell has volume $\mathcal{V}_0 = |\det(\mathbf{L})|$, and if no unit cell of smaller volume that periodically tiles the crystal can be found, then $\mathbf{L}$ defines a primitive cell, which wholly specifies the Bravais lattice of the crystal.

A homogeneous deformation of the crystal can be described by a 3 × 3 matrix, $\mathbf{F}$, which linearly transforms the initial, or reference, state of the crystal, whose lattice vectors are given by the matrix $\mathbf{L}_0$, to a deformed state, whose lattice vectors are given by $\mathbf{L}_1 = \mathbf{F}\mathbf{L}_0$. $\mathbf{F}$ describes a deformation in Cartesian space, and can be decomposed as a symmetric pure stretch matrix $\mathbf{U}$ followed by an orthogonal rotation matrix $\mathbf{S}$ as $\mathbf{F} = \mathbf{S}\mathbf{U}$. Thus, $\mathbf{F}$ is not uniquely defined, since two deformation tensors $\mathbf{F}$ and $\mathbf{F}' = \mathbf{S}'\mathbf{F}$ that differ only by a post-rotation result in the same final shape and energy of the crystal, even though the final orientation is different.

We may construct alternative metrics of deformation that are unique and invariant to rotation in terms of the matrix product $\mathbf{F}^\top\mathbf{F}$. Since rotation matrices are orthogonal, satisfying $\mathbf{S}^\top = \mathbf{S}^{-1}$, it is easy to verify the invariance relation $\mathbf{F}^\top\mathbf{S}^\top\mathbf{S}\mathbf{F} = \mathbf{F}^\top\mathbf{F}$. Any monotonic and analytic function of the deformation tensor $\mathbf{F}^\top\mathbf{F}$ is thus a valid descriptor of finite crystal deformation, including the family of strain tensors proposed by Seth (1964) and Hill (1968), which are defined as

$$\mathbf{E}(\mu) = \left[(\mathbf{F}^\top\mathbf{F})^\mu - \mathbf{I}_3\right]/2\mu, \tag{3}$$

where μ is a parameter that specifies a particular strain metric. $\mathbf{E}(\mu)$ is zero at the reference lattice $\mathbf{L}_0$ and it is rotation invariant, making it suitable for describing finite strains. $\mathbf{E}(1/2)$ is commonly referred to as the Biot strain, while $\mathbf{E}(1)$ is the Green–Lagrange strain. By convention, $\mu = 0$ is used to denote the Hencky strain, which has the form $\mathbf{E}(0) = \ln(\mathbf{F}^\top\mathbf{F})/2 =$