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A universal symmetry criterion for the design of high performance ferroic materials

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ABSTRACT

The symmetry of a crystal has profound effects on its physical properties and so does symmetry-breaking on the characteristics of a phase transition from one crystal structure to another. For an important class of smart materials, the ferroics, their functionality and performance are associated with *cycles of transitions from multiple structural states of one phase to those of the other*. Using group and graph theories, we construct phase transition graph (PTG) and show that both the functionality and performance of ferroics are dictated by the *topology of their PTGs*. In particular, we demonstrate how the giant piezoelectricity in ferroelectrics and the functional fatigue in shape memory alloys (SMAs) are related to their unique PTG topological features. Using PTG topology as a guide, we evaluate systematically new systems potentially having giant piezoelectricities and giant electro- and magneto-strictions and discuss the design strategies for high performance SMAs with much improved functional fatigue resistance.

1. Introduction

Crystal structural changes in response to external fields (temperature, pressure/stress, electrical or magnetic, etc.) underpin the functionality of an important class of smart materials, the ferroics. Because of the symmetry-breaking associated with a structure change, there are multiple crystallographically equivalent and energetically degenerate ways to transform from one crystal structure to another (will be referred to as *phase transition pathways* (PTPs) hereafter), generating multiple crystallographically equivalent and energetically degenerate structural states of the product phase called transformation variants [1–4]. These variants arrange themselves into self-accommodating domain patterns and can switch from one to another by an external field, thus sensing and actuation can be realized simultaneously. The ferroics have found critical applications in many fields [5–9] and extensive efforts have been made in recent years to develop advanced ferroics with much enhanced performance, such as giant piezoelectricity, giant electro- and magneto-striction and giant super-elastic response.

It has yet to be recognized, however, that the properties of ferroics are dictated not only by the symmetry of individual crystal structures involved in and the symmetry-breaking during the phase transition, but also by the interconnection of the multiple structural states through the multiple PTPs, which yields a PTP network or *phase transition graph* (PTG). PTG is a new theoretical construct capturing the sequential changes of crystal structures during multiple forward and backward phase transitions (will be referred to as *phase transition cycles* hereafter), and it can be utilized to analyze systematically the symmetry breaking during the transition cycles as well as the associated defect structures. In the following sections, we first provide a rigorous mathematical definition of PTG by using group and graph theories and then demonstrate how its graph features (e.g., connectivity, topology, symmetry, etc.) dictate the properties of ferroics such as the giant piezoelectricity in ferroelectrics and functional fatigue in shape memory alloys (SMAs). In contrast to crystal physics [10] that studies the relationship between physical properties and the structure and symmetry of each individual phase, and to Landau theory [11] that studies properties of one-way structural phase transitions with symmetry-breaking, this PTG analysis studies the characteristics and physical properties of *transition cycling from multiple structural states of one phase to those of the other*.

In Landau theory [11] of structural phase transitions, the free energy of a low-symmetry product phase is approximated by a power series expansion with respect to the high-symmetry parent phase. However, there are two inherent deficiencies in this approach: (1) it requires a unique high-symmetry phase that has all the symmetry elements of the low symmetry phase (i.e., a group-

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subgroup relationship); (2) only local pathway connectivity within the vicinity of the high-symmetry phase is captured. Consider, for example, the body-centered cubic (BCC, space group $Im\bar{3}m$) structure to hexagonal-close-packed (HCP, space group $P6_3/mmc$) structure transition through the Burgers path [12]. The four-fold symmetry breaks during the BCC→HCP transition while the six-fold symmetry breaks during the HCP→BCC transition, leading to 12 and 3 crystallographic equivalent PTPs and structural states, respectively. Since a crystalline state having both four-fold and six-fold symmetry is theoretically impossible, a high-symmetry state that has all the symmetry elements of these two structures does not exist and the pathway connectivity among the multiple BCC and HCP states cannot be localized and limited within the vicinity of any of these states (infinite and interconnected pathway network as will be shown later). The same is true for the face-centered-cubic (FCC) to BCC structural phase transition through the Bain path [13], another commonly observed structural change. Thus Landau theory is limited in a *local* description and cannot capture the *global connectivity* of structural states and PTPs as well as the topology of PTG during multiple transition cycles, which is critical for the operation of ferroics. Even though some specific forms of the free energy have been proposed to deal with certain phase transitions (e.g., BCC to HCP) in the literature [14], a general way to capture the global connectivity is unavailable. Obviously a new theoretical framework is required to construct PTGs and study their topological features.

Below we formulate a general theoretical framework based on group and graph theories to construct PTGs. Through the construction of PTGs, a fundamental connection among crystal symmetry, topology of PTG and behavior of structural phase transition cycling is established. As examples of applications, typical structural phase transitions found in experiments that offer giant piezoelectricity and giant electro- and magneto-strictions are analyzed and a unique topological feature shared by their PTGs is identified, which reveals the crystallographic requirements of the exceptional functionalities discovered around the so-called morphotropic phase boundaries (MPBs) in these systems [15–23]. Furthermore, we investigated the physical origin of functional fatigue characterized by the irrecoverable strain accumulated during repeated actuation of SMAs [24,25]. We show that the functional fatigue is attributed to the change in PTG topology by the activation of symmetry dictated non-PTPs (NPTP), which leads to the construction of generalized-PTG (GPTG). In particular, crystalline defects generated in NiTi because of such a PTG topology change are analyzed and the special grain boundaries and dislocations predicted through the PTG analysis are shown to be consistent with experimental observations. Using PTG topology as a new design criterion, ferroic systems potentially having giant piezoelectricity and giant electro- and magneto-strictions are predicted, and strategies to improve functional fatigue resistance are proposed. Thus PTGs can be used in combination with phase diagrams to motivate and guide the design of ferroic smart materials and other advanced material systems whose properties are controlled by structural phase transition cycling.

2. Construction of phase transition graph

Mathematically, a phase transition between two structural states can be interpreted as a pairwise relation and represented conveniently by a graph. Taking advantage of the well-established study of topology (e.g., circular vs. tree, see Fig. 1) and symmetry of a graph in graph theory [26], the topology and symmetry of PTG can be investigated systematically. In particular, the symmetry of a PTG can be defined as the automorphism group of the graph, including all operations that map the PTG onto itself while preserving its connectivity. Note the similarity and difference between crystal symmetry and PTG symmetry; the crystal symmetry is described through space and point groups consisting of all symmetry operations that map a crystal structure onto itself, while the PTG symmetry is described by the automorphism group consisting of all symmetry operations that map the graph onto itself. In fact, a crystal lattice can also be considered as a "lattice graph" with the lattice sites as vertices and the "bonds" between nearest neighboring sites as edges. Then all the operations in the space group of the crystal lattice belong to the automorphism group of the "lattice graph". In graph theory, both the topology and symmetry of a graph are important features characterizing its connectivity. They are utilized fully in the current study to analyze and classify PTGs and the associated physical properties of the corresponding phase transition cycling, as will be shown in Section 3.

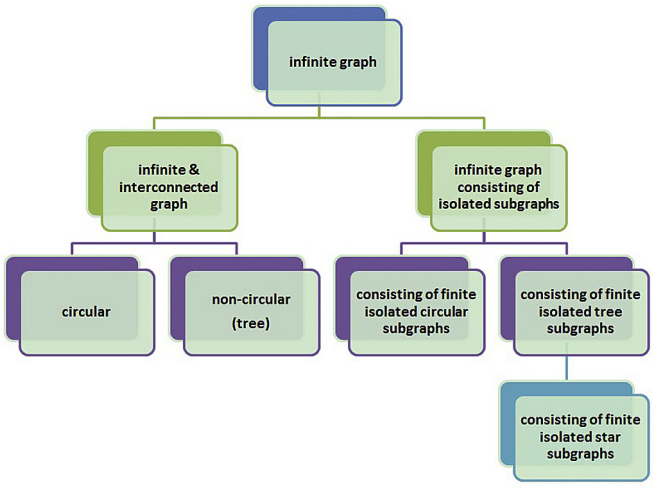

Fig. 1. Topological classification of infinite graphs.

For a PTG, $G(V, E)$, $V = \{v_{\alpha 1}, v_{\alpha 2}, \ldots, v_{\beta 1}, v_{\beta 2}, \ldots\}$ is a set of vertices that correspond to the multiple structural states of α, β, … phases mentioned earlier and E is a set of edges that connect the vertices and represent the PTPs among the structural states. Since an edge describes a transition process, edges connecting a vertex to itself are excluded. Consider, for example, the PTG for an α ↔ β transition where there are only one structural state for each phase and there is only one PTP between the two structural state. Then the PTG includes two vertices and one edge connecting them. In this case, the order of both α vertex and β vertex (i.e., the number of edges connecting to them) is 1, which can be noted as $(N_\alpha, N_\beta) = (1,1)$. In general, (N_α, N_β) depends on the number PTPs of the forward (N_α) α→β transition and backward (N_β) β→α transition and can be determined by using group theory [4,27]. When (N_α, N_β) equals $(1,n)$ or $(n,1)$, a "n-star" graph will be generated (n is an integer larger than 1). However, if both N_α and N_β are larger than 1 for a given (N_α, N_β), diverse types of PTGs could be generated, including finite or infinite tree graph, and circular graphs with different length, as will be demonstrated below. The global connectivity and topological features of these PTGs depend on the nature of the structural phase transitions. In Fig. 1, different types of graphs are classified based to their topology, some of which will be utilized in the following pathway analysis.

To illustrate the PTG at an intuitive level, we first consider several typical martensitic phase transitions in 2D (Fig. 2). For the square ↔ hexagon transition with the lattice correspondence (LC) shown in Fig. 2(a), the vertex order can be determined as (2,3) [4,27]. By choosing a reference state (e.g., the square state in the