Acta Materialia 147 (2018) 296–303

Contents lists available at ScienceDirect

Acta Materialia

journal homepage: www.elsevier.com/locate/actamat

Full length article

# First-principles calculations of thermal properties of the mechanically unstable phases of the PtTi and NiTi shape memory alloys

Sara Kadkhodaei*, Axel van de Walle

*School of Engineering, Brown University, Providence, RI 02912, USA*

ARTICLE INFO

*Article history:*
Received 23 October 2017
Received in revised form
21 December 2017
Accepted 16 January 2018
Available online 3 February 2018

*Keywords:*
Ab initio calculation
Shape memory alloys
Thermodynamic modeling
Phonon instability

ABSTRACT

The design of shape memory alloys (SMA) demands detailed knowledge of their thermodynamic properties and of the underlying atomic-level mechanisms governing their shape-memory behavior. This knowledge is traditionally obtained via atomistic simulations, but these systems have so far resisted such efforts due to the presence of phonon instabilities and associated spontaneous symmetry breaking. In this study, we investigate the thermodynamics of PtTi, a novel and promising SMA (and of the related better-known NiTi SMA, for comparison purposes) using recently developed first-principles computational method specifically designed to tackle this issue. The method efficiently explores the system's potential energy surface by discrete sampling of local minima, combined with a continuous sampling of the vicinity of these local minima via a constrained harmonic lattice dynamic approach. Our calculations provide a complete and atomic-level-based model for these compounds' free energy and shed some light on the ongoing search for the precise structure of dynamically stabilized high temperature phases in SMAs.

## 1. Introduction

There has been an ongoing effort to devise a thermodynamic framework for the mechanically unstable phases that can get stabilized due to lattice dynamics at high-enough temperatures. These mechanical instabilities are common among a number of solid-state systems, such as many transition metals [1], shape-memory alloys [2], refractory oxides [3] and ferroelectric materials [4]. The ongoing challenge in describing such material phases is that they lack a single representative stable crystal structure. We have addressed this challenge by developing a method called Piecewise Polynomial Potential Partitioning or $P^4$ method [5], which enables the free energy calculation of such phases. In the $P^4$ method, we describe the material's structure by dynamic fluctuations between the "local low-symmetry distortions" of the"high-symmetry structure", which provides stabilizing entropy contributions. Our method divides the problem of anharmonic energy model into simpler piecewise harmonic models by partitioning the phase space into relevant subregions. Introducing an augmented lattice implicitly splits phase space into corresponding subregions and enables the use of coarse-graining of the partition function along with a cluster expansion approach. Here, we present the thermodynamic properties for NiTi and PtTi, which represent two examples of mechanically unstable system with different anharmonicity strengths. The agreement of the thermodynamic properties obtained in this study with experimental measurements confirms the validity of our method and sheds some light on the ongoing search for the austenite phase of NiTi.

When considering the phase stability and thermodynamics of crystalline systems, finite-temperature lattice vibrations become crucial. The standard lattice dynamics frameworks, such as (quasi) harmonic approximation, provide an accurate description of lattice dynamics for studying harmonic vibrations in a solid [6]. However, these frameworks become less valid as the system deviates from an ideal harmonic solid, specially for mechanically unstable systems. This is due to the unavailability of a single representative mechanically stable crystal structure. In this case, the energy surface becomes non-convex along unstable modes and introduces nonphysical divergence in the calculation of the harmonic free energy.

A number of solutions have been devised so far in order to tackle the issue of lattice dynamics of anharmonic solids, (and the related problem of mechanically unstable phases [7–9]). Some of these solutions include self-consistent lattice dynamics approaches

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* Corresponding author.
*E-mail address:* sara_kadkhodaei@brown.edu (S. Kadkhodaei).

https://doi.org/10.1016/j.actamat.2018.01.025

[10,11], thermodynamic integration approaches [12,13], and effective Hamiltonian approaches [14–17]. While these approaches have proven promising to handle anharmonic vibrations and are widely used, they are not devoid of drawbacks. Self-consistent lattice dynamics methods rely on the assumption of the existence of an effective harmonic model, and hence the accuracy of these models cannot be systematically improved for strong anharmonic systems. Thermodynamic integration approaches employ brute-force *ab intio* molecular dynamics to calculate the anharmonic free energy using (quasi)harmonic calculations as a reference. As a result, they become computationally demanding when the anharmonicity is strong, especially so strong that it creates multiple local minima around a local high-symmetry maximum [18]. In effective Hamiltonian methods, constructing a parameterized Hamiltonian to the energy surface can becomes demanding for strongly anharmonic degrees of freedom, or for systems with complex unit cells. A detailed comparison of the $P^4$ method with other existing approaches is provided in Section 3.

Shape memory alloys have a lot of technologically important applications, including mechanical actuator devices and medical stents [19]. The underlying mechanism of the so-called “shape-memory” effect behavior is the martensitic transformation between a high-temperature austenite phase and a low-temperature martensite phase [20]. The existence of soft modes and instabilities in the austenite phase in SMAs initiates the martensitic transformation. NiTi (nitinol) is the most widely used material among many practical applications of SMAs, with martensitic transformation temperature of about 366.15 K [21]. On the other hand, PtTi has attracted considerable attention as a promising potential candidate for the basis of high temperature SMAs [22–24], due to its higher transformation temperature of about 1273 K [22]. Both PtTi and NiTi exhibit a high-temperature austenite phase with cubic B2 structure (CsCl structure with space group $Pm\bar{3}m$) [25–27], transformed to a low-temperature martensite phase with orthorhombic B19 (space group Pmma) [22], and monoclinic B19′ structure (space group $P2_1/m$) [28], respectively.

The experimental observation of (i) a set of radial diffuse streaks (i.e. a continuum of scattered X-rays that fall between the Bragg peaks) and (ii) a set of discrete reflection spots at 1/3 position of the regular B2 reciprocal lattice, for the X-ray diffraction of single-crystal NiTi [29,30], caused an ongoing dispute over the structure of the austenite phase for ordered NiTi. These observations led Wang et al. to assume that the austenite structure is basically a statistical distribution of lower-symmetry $3 \times 3 \times 3$ superlattice of ordinary B2 lattice [space group $P\bar{3}m1$], which on average appears as CsCl structure [29]. Later, Sandrock et al. attributed the observed radial streaks to lattice vibrations present in the ordinary B2 structure, reflecting incipient instability of the lattice [30]. Recently, Zarkevich et al. proposed a mechanically stable austenite phase that is described by a hexagonal lattice [31], which appears B2 on average in diffraction, while it has large atomic displacements from the ideal B2 sites. In this paper, we illustrate in detail that how the description of the mechanically unstable austenite NiTi by dynamic fluctuations among local distortions provides a better insight about the structure of the austenite phase and explains the reversible appearance and disappearance of radial streaks and discrete 1/3 reflections observed experimentally upon cooling and heating around the martensitic transformation temperature.

## 2. Results

### 2.1. Piecewise polynomial potential partitioning

The “dynamical stabilization” of the high symmetry phase with mechanical instabilities at high enough temperatures is due to entropy contributions arising from constant hopping among low-symmetry distortions of the high symmetry structure. From this perspective, the high symmetry structure is only one of the possible configurational states that the system can access, along with multiple low-symmetry configurational states that are accessible to the system. In order to take these states into account in the free energy calculation, an augmented lattice, denoted by $L_{aug}$, is constructed including the high symmetry point and low-symmetry distortions as the basis. Introducing the augmented lattice partitions the configuration space into different configurations, denoted by $\sigma$.

A coarse-grained form of the Helmholtz free energy associated with the augmented lattice, $F_{L_{aug}}$, is considered as the following [32].

$$F_{L_{aug}} = -k_B T \ln \sum_{\sigma \in L_{aug}} e^{-\beta F^*_\sigma}, \tag{1}$$

where

$$F^*_\sigma = -k_B T \ln \int_{\mathbf{x} \in \zeta_\sigma} e^{-\beta V(\mathbf{x})} d\mathbf{x}, \tag{2}$$

where $\beta = 1/k_B$, T is temperature, $k_B$ is Boltzmann's constant, $\mathbf{x}$ is a $3N$ vector of all atomic positions, $N$ is the number of atoms in the system, $\zeta_\sigma$ is the proximity of configuration $\sigma$, and $V(\mathbf{x})$ is the potential energy of the system at a state represented by the position vector $\mathbf{x}$.

The constrained vibrational free energy, denoted by $F^*_\sigma$ in equation (2), takes into account the entropy contributions arising from local vibrations in the vicinity of each distortion, while the entropy contributions due to the hopping of the system among local distortions is accounted for in the “outer” level integration of equation (1). We use a local constrained harmonic model of potential energy $V(\mathbf{x})$ expanded about $x^r_\sigma$, defined as the location of the minimum within $\zeta_\sigma$, for the calculation of the “inner” level free energy contributions in equation (2) and a lattice gas model for the calculation of the free energy in equation (1).

In the lattice gas model, we use the cluster expansion formalism in order to represent the constrained vibrational free energy as a polynomial series in terms of the occupation variable of each lattice site i, denoted by $\sigma_i$. For an ordered compound (and not a solid solution), there is no permutation of different atomic species, thus the same occupation variable can be used for all atom types. Therefore, $\sigma_i = +1$ if site i is occupied and $\sigma_i = -1$ if site i is empty, and cluster expansion formalism is represented as the following.

$$\frac{F^*(T,\sigma)}{N_s} = \sum_\alpha m_\alpha J_\alpha(T) \left\langle \prod_{i \in \alpha} \sigma_i \right\rangle_{\alpha'} \tag{3}$$

The above sum is over symmetrically distinct clusters $\alpha$, while the average is over clusters $\alpha'$, which are symmetrically equivalent to $\alpha$. $N_s$ is the number of sites in the augmented lattice, $m_\alpha$ is the multiplicity of cluster $\alpha$ and $J_\alpha(T)$ is the effective cluster interaction (ECI) of cluster $\alpha$ at temperature T [33]. The ECIs, which are the polynomial coefficients, are determined via the fitting of the above series to the *ab initio* calculated $F^*_\sigma$ at different temperatures.

Thermodynamic integration is used to obtain the Helmholtz free energy difference between the high temperature limit and a desired temperature T. Here, ensemble-averaged constrained vibrational free energy ($F^*$) changes is integrated over instead of ensemble-averaged enthalpy changes, in order to incorporate the local vibration contributions to entropy. The closed-form expansion of Eq. (3) is used to calculate the ensemble-averaged constrained vibrational free energy in the thermodynamic integration, utilizing