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# Thermomechanical lattice instability and phase field theory of martensitic phase transformations, twinning and dislocations at large strains

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## Abstract

Using the second law of thermodynamics, a criterion for the instability of a crystal lattice with respect to a change in order parameters is derived for finite strains and lattice rotations. An explicit relation for lattice rotation is derived. A Gibbs (Landau) potential describing martensitic phase transformations, twinning, and dislocation nucleation is derived for a prescribed nonsymmetric nominal stress tensor and small elastic strain, but finite transformation strain and rotations. The equilibrium and transformation conditions are obtained. Martensitic phase transformations in NiAl, BN and C are analyzed and the importance of finite-strain corrections is demonstrated.

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## 1. Introduction

Phase field or Landau–Ginzburg theory of phase transformations (PTs) and dislocations is widely used to estimate interface energies and the energies of critical nuclei, to model microstructure evolution, and to study heterogeneous nucleation at various defects [1,2]. We have developed several polynomial Gibbs (Landau) potentials for the description of multivariant stress- and temperature-induced martensitic PT in 3D [2]. Our approach was a phenomenological one, that is, the potentials were constructed by requiring that they respect the experimentally observed features of martensitic PT in shape memory alloys and steels, specifically, constant (stress-independent)

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transformation strain (TS) tensor, weakly temperature dependent, or constant, stress hysteresis, and transformation at nonzero elastic moduli. The models can incorporate all temperature-dependent thermomechanical properties of both phases for arbitrary crystal symmetries, including higher-order elastic constants. The same approach was applied to the phase field theory of twinning and dislocations. The main drawback of [2] and all other Landau models is their limitation to small TS,  $\epsilon_t < 0.1$ . TS shear is 0.2 for PTs in steels and shape memory alloys, the volumetric TS for the graphite–diamond and BN rhombohedral-cubic PTs is 0.54, the TS shear for twinning in bcc and fcc lattices is 0.71, and for dislocations it is  $|\mathbf{b}|/d \sim 1$ , where  $\mathbf{b}$  is the Burgers vector and  $d$  is the distance between the glide planes. Moreover, finite rotations of the crystal lattice, which can even occur at small TS, can crucially affect the PT conditions.

PT conditions in phase field theory are conditions for instability of the crystal lattice. Recent research on lattice instabilities at finite strain has focused on the ideal strength of crystals and solid–solid, amorphization, and melting PTs [3–8]. A general approach to stability at finite strain has been developed on the basis of the Lagrange–Dirichlet criterion for conservative systems [3–5]. Nonconservative loading was considered by Wang et al. [6] who postulated an alternative criterion. Most stability studies have addressed only intrinsic stability, where the applied stress “follows” the material during deformation. However, intrinsic stability may differ significantly from stability in laboratory experiments, where finite rotation of the specimen is involved [3,4]. Hill [3] investigated stability under fixed loads, accounting for finite rotations. Strong limitations on stability were obtained by assuming that the rotation can be varied arbitrary, but as we will see, rotation under a prescribed load is a function of the strain, which invalidates Hill’s conclusions.

It is impossible to describe all of the experimentally observed features of strong martensitic PT using a polynomial potential in total strain [2], but these features can be encoded in a Gibbs (Landau) potential in order parameters related to the TS. For small strains, the total strain is simply the sum of the elastic and TS:  $\epsilon = \epsilon_e + \epsilon_t$ . However, at finite strain this additive decomposition breaks down and one must resort to multiplicative decomposition of the deformation gradient into elastic and transformational parts and take into account finite rotations [9]. This nonlinearity and strong coupling between strains and rotations pose significant challenges to constructing a proper Gibbs potential and studying PTs. Another basic point is that a change in order parameter is a dissipative process, so none of the existing criteria for the stability of conservative systems can be applied. Also, the required invariance of the Gibbs potential and the instability criteria under changes in the stress and strain measures is nontrivial to realize in practice.

In this Letter, we derive a thermomechanical lattice instability criterion with respect to change in order parameters using the second law of thermodynamics. It accounts for *finite elastic and transformation strains and lattice rotations*. Invariance of the instability criterion and Gibbs potential under changes in stress and strain measures is proved. The Gibbs potential, criteria for PT, twinning, and dislocation nucleation, and equilibrium conditions are derived for a prescribed nonsymmetric Piola–Kirchhoff (nominal) stress tensor  $\mathbf{P}$ , i.e., the force per unit area in the undeformed state, and small elastic strains but *finite transformation strains and rotations*. In contrast to other formulations, it is not necessarily the case that the instability occurs at a stationary value of some stress measure. PTs in NiAl, BN and C are analyzed and significant differences between the small- and finite-strain Gibbs potentials are found. All of these results are obtained for the first time.

Contractions of tensors  $\mathbf{A} = \{A_{ij}\}$  and  $\mathbf{B} = \{B_{ji}\}$  over one and two indices are denoted  $\mathbf{A} \cdot \mathbf{B} = \{A_{ij} B_{jk}\}$  and  $\mathbf{A} : \mathbf{B} = A_{ij} B_{ji}$ . The transpose of  $\mathbf{A}$  is  $\mathbf{A}^T$ , and  $\mathbf{I}$  is the unit tensor.

## 2. Instability criterion

A PT between austenite (A) and martensitic variant  $M_i$ ,  $i = 1, 2, \dots, n$ , is characterized by the constant transformation deformation gradient  $\mathbf{F}_{ti}$ , which is considered to be an irrotational deformation of the crystal lattice [9]. For example,  $\mathbf{F}_{ti}$  reduces to the symmetric Bain strain  $\mathbf{U}_{ti}$  for PT between two lattices. The nonsymmetric transformation deformation gradient for an invariant-plane-strain (IPS) variant, a mixture of two twin-related Bain

strain variants, is  $\mathbf{F}_{ti} = \mathbf{I} + \varepsilon \mathbf{n}_i \mathbf{n}_i + \gamma \mathbf{m}_i \mathbf{n}_i$ , a simple shear  $\gamma$  in direction  $\mathbf{m}_i$  in the habit plane with normal  $\mathbf{n}_i$  and a strain  $\varepsilon$  normal to the habit plane. When the order parameters  $\tilde{\eta} = (\eta_1, \dots, \eta_i, \dots, \eta_n)$  vary from  $\hat{\eta}_0 = (0, \dots, 0)$  to  $\hat{\eta}_i = (0, \dots, \eta_i = 1, \dots, 0)$  the TS gradient varies from  $\mathbf{I}$  to its final value  $\mathbf{F}_{ti}$ ; see Eq. (8).

The rate of entropy production per unit undeformed volume,  $\dot{s}_\mu$ , due to the PT at fixed temperature  $\theta$  is, according to the second law of thermodynamics, nonnegative

$$\theta \dot{s}_\mu = \mathbf{P}^T : \dot{\mathbf{F}} - \dot{\psi} \geq 0. \quad (1)$$

The total deformation gradient,  $\mathbf{F} = \partial \mathbf{r} / \partial \mathbf{r}_0$ , where  $\mathbf{r} = \mathbf{r}(\mathbf{r}_0, t)$  is the location of a material point at time  $t$  and  $\mathbf{r}(\mathbf{r}_0, 0) = \mathbf{r}_0$ , can be multiplicatively decomposed into elastic and transformational parts,  $\mathbf{F} = \mathbf{F}_e \cdot \mathbf{F}_t$  [9], and  $\psi(\mathbf{F}_e, \theta, \tilde{\eta})$  is the Helmholtz free energy. For  $d\tilde{\eta}/dt = 0$ , the rate of entropy production is zero and one obtains the elasticity law  $\mathbf{P} \cdot \mathbf{F}_t^T = \partial \psi / \partial \mathbf{F}_e$ , which leads to the dissipative inequality

$$\theta \dot{s}_\mu = X_i \dot{\eta}_i \geq 0, \quad X_i := \mathbf{P}^T \cdot \mathbf{F}_e : \frac{\partial \mathbf{F}_t}{\partial \eta_i} - \frac{\partial \psi}{\partial \eta_i}, \quad (2)$$

where  $X_i$  is the driving force for PT leading to the  $i$ th variant. The corresponding Ginzburg–Landau equation is  $\partial \eta_k / \partial t = \sum_{i=1}^n L_{ki} (X_i + \beta_p : \nabla \nabla \eta_i)$ , where  $\beta_i$  is the second-rank gradient energy tensor and  $L_{kp}$  are kinetic coefficients.

Equilibrium and its stability can only be analyzed for prescribed boundary conditions (BC) for stresses  $\mathbf{T}$  and temperature. We consider only isothermal processes and homogeneous stress states. For example,  $\mathbf{T}$  is biaxial tension in  $\mathbf{P}$  for the loading device used in [10]; alternatively,  $\mathbf{T}$  may be the prescribed Cauchy stress  $\boldsymbol{\sigma} = J^{-1} \mathbf{P} \cdot \mathbf{F}^T$  (true stress, i.e., force per unit deformed area) [6], where  $J = \det \mathbf{F}$ . In general,  $\mathbf{P} = \bar{q}(\mathbf{T}, \mathbf{F}) = q(\mathbf{T}, \mathbf{F}_e, \tilde{\eta})$ , and  $X_i = X_i(\mathbf{T}, \mathbf{F}_e, \tilde{\eta})$ . The thermodynamic equilibrium conditions  $X_i(\mathbf{T}, \mathbf{F}_e, \tilde{\eta}) = 0$  define the equilibrium values of the order parameters:  $\tilde{\eta}^{\text{eq}} = \hat{\eta}_i$ ,  $i = 0, 1, \dots, n$ . If a spontaneous deviation of  $\tilde{\eta}$  from  $\tilde{\eta}^{\text{eq}}$  is thermodynamically admissible under prescribed BC, that is,  $\dot{s}_\mu \geq 0$ , then the equilibrium is unstable:

$$X_i(\mathbf{T}, \mathbf{F}_e + \Delta \mathbf{F}_e, \tilde{\eta}^{\text{eq}} + \Delta \tilde{\eta}) \dot{\eta}_i \geq 0 \rightarrow \text{equilibrium is unstable.} \quad (3)$$

Eq. (3) leads to the instability condition

$$\left. \frac{\partial X_i}{\partial \eta_j} \right|_{\mathbf{T}} \dot{\eta}_i \dot{\eta}_j = \left( \frac{\partial X_i}{\partial \mathbf{F}_e^T} : \frac{\partial \mathbf{F}_e}{\partial \eta_j} + \frac{\partial X_i}{\partial \eta_j} \right) \dot{\eta}_i \dot{\eta}_j \geq 0, \quad (4)$$

thus the instability occurs when  $\partial X_i / \partial \eta_j |_{\mathbf{T}}$  first becomes positive definite. Let  $\mathbf{H}$  be the strain measure work-conjugate to  $\mathbf{T}$ , i.e., the rate of transformation work is  $\mathbf{P}^T : \dot{\mathbf{F}} = \mathbf{T} : \dot{\mathbf{H}}$ . Introducing the Gibbs potential  $G(\mathbf{T}, \theta, \tilde{\eta}) = \psi - \mathbf{T} : \mathbf{H}$ , one obtains  $X_i = -\partial G / \partial \eta_i |_{\mathbf{T}}$  and  $\partial X_i / \partial \eta_j |_{\mathbf{T}} = -\partial^2 G / \partial \eta_i \partial \eta_j |_{\mathbf{T}}$ . Hence, if the Gibbs potential is expressed in terms of  $\mathbf{T}$  then lattice instability corresponds to the first nonconvexity of  $G$  in order parameter space. Since  $\mathbf{T}$  can be expressed in terms of any other stress measure and  $\mathbf{F}$ , the Gibbs potential can also be expressed in terms of other stress measures. However, differentiation with respect to  $\eta_j$  in Eq. (4) is performed for constant  $\mathbf{T}$ , so the instability criterion is unchanged.

### 3. Instability and potential under prescribed nominal stress

Fig. 1 exhibits the deformation and rotation of a sample after a PT under fixed components of the nominal stress tensor  $\mathbf{P}$ . The magnitude and direction of all forces are the same before and after the PT. Using Eq. (2) and the elasticity rule, which results in the cancellation of two terms involving the derivative  $\partial \mathbf{F}_e / \partial \eta_j$ , one obtains

$$\left. \frac{\partial X_i}{\partial \eta_j} \right|_{\mathbf{P}} = \mathbf{P}^T \cdot \mathbf{F}_e : \frac{\partial^2 \mathbf{F}_t}{\partial \eta_i \partial \eta_j} - \frac{\partial^2 \psi(\mathbf{F}_e, \eta_i)}{\partial \eta_i \partial \eta_j} \Big|_{\mathbf{F}_e}. \quad (5)$$

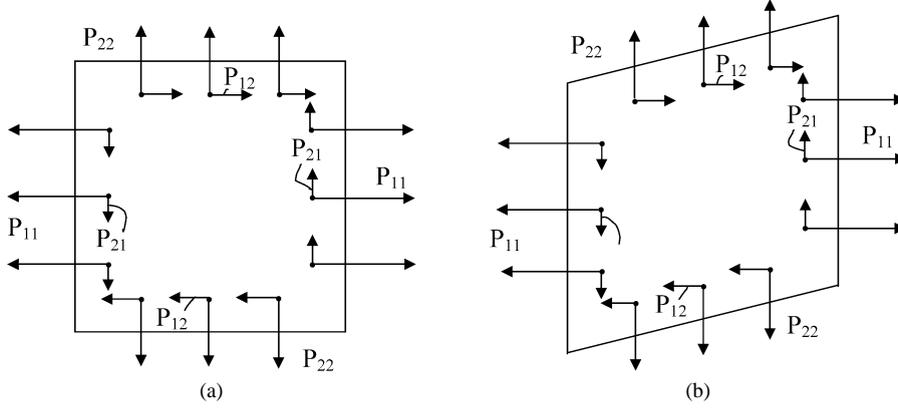


Fig. 1. Deformation and rotation of a sample after PT under fixed components of nominal stress tensor  $\mathbf{P}$ : (a) before PT; (b) after PT.

Invoking polar decomposition  $\mathbf{F}_e = \mathbf{R} \cdot \mathbf{U}_e$ , where  $\mathbf{R} \in SO(3)$  characterizes the rigid-body rotation of the crystal lattice and  $\mathbf{U}_e$  is the symmetric elastic stretch tensor, one obtains  $\mathbf{F}^T = \mathbf{F}_t^T \cdot \mathbf{U}_e \cdot \mathbf{R}^T$ . Substituting  $\mathbf{F}^T$  in the equation  $\boldsymbol{\sigma} = \mathbf{J}^{-1} \mathbf{P} \cdot \mathbf{F}^T$  and designating  $\mathbf{N} := \mathbf{P} \cdot \mathbf{F}_t^T \cdot \mathbf{U}_e$ , one obtains  $\mathbf{N} = \mathbf{J} \boldsymbol{\sigma} \cdot \mathbf{R}$ , that is, the polar decomposition of  $\mathbf{N}$  into symmetric  $\mathbf{J} \boldsymbol{\sigma}$  and orthogonal parts,  $\mathbf{N} \cdot \mathbf{N}^T = \mathbf{J}^2 \boldsymbol{\sigma} \cdot \boldsymbol{\sigma}$ , and finally

$$\mathbf{N} = (\mathbf{N} \cdot \mathbf{N}^T)^{1/2} \cdot \mathbf{R}. \quad (6)$$

Thus the PT-induced rotation cannot be varied arbitrary, as was done by Hill for  $\mathbf{F}_t = \mathbf{I}$  [3], because it is determined from Eq. (6).

Analytical expressions for  $\mathbf{F}_e$ , and consequently, for the Gibbs potential in terms of  $\mathbf{P}$  cannot be obtained for even the simplest realistic elasticity law. However, an analytical expression for  $G(\mathbf{P})$  can be derived for the case when the changes in the elastic strains accompanying the PT are small but  $\mathbf{F}_t$  and  $\mathbf{R}$  are finite; the change in elastic energy is negligible. Deviatoric elastic strains are always small because  $|\text{dev } \mathbf{U}_e - \mathbf{I}| \leq \tau_y / \mu$ , and the ratio of the yield stress in shear,  $\tau_y$ , to the shear modulus  $\mu$  is of order  $10^{-3}$  for steels and  $10^{-2}$  for shape memory alloys. The assumption of small elastic volumetric strain is valid for pressures  $p \leq 0.1 \Delta S$ , where  $\Delta S$  is the jump in the bulk compliance.

In the case of a single martensitic variant we have  $G = -\mathbf{P}^T : \mathbf{F} + f(\theta, \eta_i)$ , where  $f$  is the thermal (chemical) part of the free energy. Generalizing to  $n$  martensitic variants by following the procedure in [2], one obtains the Gibbs potential for small elastic strains but finite transformation strains and lattice rotations

$$\begin{aligned} G &= -\mathbf{P}^T \cdot \mathbf{R}(\mathbf{P}, \tilde{\eta}) : \left( \mathbf{I} + \sum_{k=1}^n \boldsymbol{\varepsilon}_{tk} \varphi(\eta_k) \right) + \sum_{k=1}^n f(\theta, \eta_k) + \sum_{i=1}^{n-1} \sum_{j=i+1}^n F_{ij}(\eta_i, \eta_j), \\ \varphi(\eta_k) &= \frac{a \eta_k^2}{2} + (3-a) \eta_k^4 + \frac{(a-4) \eta_k^6}{2}, \quad 0 \leq a \leq 6, \\ f(\theta, \eta_k) &= \frac{A \eta_k^2}{2} + (3 \Delta G^\theta - A) \eta_k^4 + \frac{(A - 4 \Delta G^\theta) \eta_k^6}{2}, \\ F_{ij}(\eta_i, \eta_j) &= B \eta_i^2 \eta_j^2 + (Z_{ij} - B) \eta_i^4 \eta_j^2 + C \eta_i^3 \eta_j^3 + (Z_{ji} - B) \eta_i^2 \eta_j^4, \\ 2Z_{ij} &= \mathbf{P}^T \cdot \mathbf{R}(\mathbf{P}, \tilde{\eta}) : [a \boldsymbol{\varepsilon}_{ij} - 3(\boldsymbol{\varepsilon}_{ij} - \boldsymbol{\varepsilon}_{ii})] + \bar{A} - A, \quad \boldsymbol{\varepsilon}_{ij} := \mathbf{F}_{ij} - \mathbf{I}. \end{aligned} \quad (7)$$

Here  $\Delta G^\theta$  is the difference between the thermal parts of the Gibbs free energies of M and A. The parameters  $A$  and  $\bar{A}$  characterize the thresholds for  $A \leftrightarrow M_i$  and  $M_j \leftrightarrow M_i$  transformations,  $a$  governs the variation of  $\boldsymbol{\varepsilon}_{ii}$  between the

A and  $M_i$  minima, and  $B$  and  $C$  control the Gibbs energy away from both the A and  $M_i$  minima and the minimum-energy paths between the minima. The rotation  $\mathbf{R}(\mathbf{P}, \tilde{\eta})$  is determined from Eq. (6) with  $\mathbf{N} = \mathbf{P} \cdot \mathbf{F}_t^T(\tilde{\eta})$  and  $\mathbf{F}_t(\tilde{\eta})$  determined from Eq. (8).

Eq. (7) formally coincide with the corresponding equations in [2] if one substitutes  $\sigma_e = \mathbf{P}^T \cdot \mathbf{R}(\mathbf{P}, \tilde{\eta})$  for  $\sigma$  and allows for nonsymmetric  $\boldsymbol{\varepsilon}_{ti}$  and  $\sigma$ . There is, nevertheless, a significant difference between the small and large TS cases because of the strong coupling between the TS and lattice rotation (Eq. (6)), which introduces an  $\tilde{\eta}$  dependence into  $\sigma_e$  for large strains. The remaining difference is that all phase equilibrium and PT conditions depend on the rotation tensor at  $\tilde{\eta} = \hat{\eta}_i$ . From  $\mathbf{R}(\mathbf{P}, \tilde{\eta}) \cdot \mathbf{F}_t(\tilde{\eta}) = -\partial G/\partial \mathbf{P}$  we obtain

$$\mathbf{F}_t(\tilde{\eta}) = \mathbf{I} + \sum_{k=1}^n \boldsymbol{\varepsilon}_{tk} \varphi(a, \eta_k) - \frac{1}{2} \sum_{i=1}^{n-1} \sum_{j=i+1}^n \eta_i^2 \eta_j^2 \{ [a\boldsymbol{\varepsilon}_{ij} - 3(\boldsymbol{\varepsilon}_{tj} - \boldsymbol{\varepsilon}_{ti})] \eta_i^2 + [a\boldsymbol{\varepsilon}_{ti} - 3(\boldsymbol{\varepsilon}_{ti} - \boldsymbol{\varepsilon}_{ij})] \eta_j^2 \}. \quad (8)$$

It is easily verified that  $\boldsymbol{\varepsilon}_t(\tilde{\eta}) = \mathbf{F}_t(\tilde{\eta}) - \mathbf{I}$  satisfies all requirements:  $\boldsymbol{\varepsilon}_t(\hat{\eta}_0) = \mathbf{0}$ ,  $\boldsymbol{\varepsilon}_t(\hat{\eta}_i) = \boldsymbol{\varepsilon}_{ti}$ ,  $\boldsymbol{\varepsilon}_t(\eta_i \hat{\eta}_i) = \boldsymbol{\varepsilon}_{ti} \varphi(\eta_i)$ .

The potential (7) can be trivially modified to describe twinning and dislocation nucleation. In each case,  $\Delta G^\theta = 0$  and  $a = 3$ . The TS for twinning is  $\boldsymbol{\varepsilon}_{ti} = \gamma \mathbf{m}_i \mathbf{n}_i$ , and for dislocations it is  $\boldsymbol{\varepsilon}_{ti} = \mathbf{b}_i \mathbf{n}_i / d$ , where  $\mathbf{n}_i$  is the normal to the glide plane. For dislocations, each of the order parameters must be replaced by  $\tilde{\eta}_i = \eta_i - \text{Int}(\eta_i) \in [0, 1]$ , where the integer part  $\text{Int}(\eta_i)$  accounts for the presence of  $n$  dislocations in the slip plane. The function  $\varphi(\eta_i)$  is likewise replaced by  $\varphi(\tilde{\eta}_i) + \text{Int}(\eta_i)$ , as for small strains [2]. For 2–3–4 quartic polynomials, the expressions for  $\varphi$ ,  $f$  and  $F_{ij}$  are the same as for the small strain case in [2].

The thermodynamic driving forces for the  $A \rightarrow M_i$  and  $M_i \rightarrow M_j$  PTs are

$$\begin{aligned} G(\mathbf{P}, \hat{\eta}_0) - G(\mathbf{P}, \hat{\eta}_i) &= \mathbf{P}^T : [\mathbf{F}(\hat{\eta}_i) - \mathbf{F}(\hat{\eta}_0)] - \Delta G^\theta \\ &= \mathbf{P}^T : [\mathbf{R}(\mathbf{P}, \hat{\eta}_i) - \mathbf{R}(\mathbf{P}, \hat{\eta}_0) + \mathbf{R}(\mathbf{P}, \hat{\eta}_i) \cdot \boldsymbol{\varepsilon}_{ti}] - \Delta G^\theta, \end{aligned} \quad (9)$$

$$G(\mathbf{P}, \hat{\eta}_i) - G(\mathbf{P}, \hat{\eta}_j) = \mathbf{P}^T : [\mathbf{F}(\hat{\eta}_j) - \mathbf{F}(\hat{\eta}_i)] = \mathbf{P}^T : [\mathbf{R}(\hat{\eta}_j) - \mathbf{R}(\hat{\eta}_i) + \mathbf{R}(\hat{\eta}_j) \cdot \boldsymbol{\varepsilon}_{tj} - \mathbf{R}(\hat{\eta}_i) \cdot \boldsymbol{\varepsilon}_{ti}]. \quad (10)$$

The phases are in thermodynamic equilibrium when these driving forces vanish. The potential (7) was designed to satisfy the condition that the local thermodynamic equilibrium conditions,  $\partial G/\partial \eta_i = 0$ , for any  $\mathbf{P}$  and  $\theta$  have  $n + 1$  solutions corresponding to A and the  $M_i$ :  $\tilde{\eta} = \hat{\eta}_i$ . In other words, the locations of the A and M extrema in order parameter space are independent of the stress and temperature. Consequently, the TS and Burgers vector are independent of the stress and temperature, in contrast to all previous phase field theories, but in agreement with experiments on shape memory alloys and traditional (not phase field) dislocation theory. The PT conditions are as follows:

$$\begin{aligned} A \rightarrow M_i: \quad & \frac{\partial^2 G(\mathbf{P}, \hat{\eta}_0)}{\partial \eta_i^2} \leq 0 \Rightarrow \mathbf{P}^T \cdot \mathbf{R}(\mathbf{P}, \hat{\eta}_0) : \boldsymbol{\varepsilon}_{ti} \geq \frac{A}{a}; \\ M_i \rightarrow A: \quad & \frac{\partial^2 G(\mathbf{P}, \hat{\eta}_i)}{\partial \eta_i^2} \leq 0 \Rightarrow \mathbf{P}^T \cdot \mathbf{R}(\mathbf{P}, \hat{\eta}_i) : \boldsymbol{\varepsilon}_{ti} \leq \frac{A - 6\Delta G^\theta}{a - 6}; \\ M_i \rightarrow M_j: \quad & \frac{\partial^2 G(\mathbf{P}, \hat{\eta}_i)}{\partial \eta_j^2} = -6\mathbf{P}^T \cdot \mathbf{R}(\mathbf{P}, \hat{\eta}_i) : (\boldsymbol{\varepsilon}_{tj} - \boldsymbol{\varepsilon}_{ti}) + 2\bar{A} \leq 0. \end{aligned} \quad (11)$$

The simplicity of (11), despite the strong coupling between rotation and  $\eta_i$ , is a consequence of the fact that  $\partial \mathbf{R}/\partial \eta_j = 0$  at the points  $\hat{\eta}_0$  and  $\hat{\eta}_i$  for the potential (7). For small TS and rotations, one can substitute  $\sigma$  for all  $\mathbf{P}^T \cdot \mathbf{R}$  and use symmetric  $\boldsymbol{\varepsilon}_{ti}$ . Note that in contrast to all known instability criteria [3–6] the instability conditions (11) are consistent with experiments on steels, which show that the transformations occur at nonzero corresponding tangent moduli  $\partial \mathbf{P}/\partial \mathbf{F}$ .

#### 4. Application to NiAl alloy, BN and C

We now turn to a comparison of the small and finite strain theories. The PTs of interest are the cubic-tetragonal in NiAl and the rhombohedral-cubic in BN and C (graphite–diamond PT). The cubic phase is taken to be the A in each case.

All parameters for the potential (7) can be found by comparing to atomistic calculations of  $G$  or stress-strain curves, as was done in [2] using the results of [11,12] for the cubic to tetragonal PT in NiAl. The tensors  $\epsilon_{ti}$  are known from crystallography, and  $\Delta G^\theta$  from thermodynamics. Parameters  $A$ ,  $\bar{A}$ , and  $a$  can be determined at each  $\theta$  from Eq. (11) when stresses are determined from atomistic calculations (see, e.g., [5,8]). Parameters  $B$  and  $C$  do not affect the PT and phase equilibrium conditions and can be determined either from the condition that  $G$  has no spurious minima or by fitting to the  $G$  function calculated atomistically at points away from the  $A$  and  $M_i$  minima. Note that there are no additional material parameters associated with rotations, thus it is sufficient to perform atomistic calculations for the rotation-free case and uniaxial loading. While the parameters  $A$  and  $a$  have been found for a number of PT using stress-strain curves for the  $A - M_i$  PT [5,8], all material parameters (including  $\bar{A}$ ) have been determined only for NiAl [11].

A polynomial approximation to the energy  $\Phi$  in Lagrangian strains, which were not explicitly defined, was presented in [11]. At the minimum of  $\Phi$  the elastic strain vanishes and the TSs were found to have the diagonal components  $\epsilon_{t1} = \{0.215, -0.078, -0.078\}$ , etc. In order to obtain  $U_t$  we must first determine whether the TS in [11] was defined as  $E_t = (U_t : U_t - I)/2$ , the usual definition of Lagrangian strain, or as  $\epsilon_t = U_t - I$ . In the first case,  $U_t = (2E_t + I)^{1/2} = \{1.196, 0.919, 0.919\}$ ,  $c/a = 1.196/0.919 = 1.302$ , and the volumetric TS is  $\det U_t - 1 = 0.009$ . In the second case,  $U_t = \{1.215, 0.922, 0.922\}$ ,  $c/a = 1.318$ , and the volumetric TS is 0.033. The  $c/a$  ratios are both close to the value 1.32 given in [11]. Their MD simulations gave a volumetric strain of 0.025, and it was mentioned that this must be accurately reflected in the Landau potential. Other MD simulations give a minimum volumetric TS of 0.04 for several NiAl alloys [12]. We conclude that  $\epsilon_t = U_t - I$  was used in [11,12]. Note that the volumetric TS for NiAl is  $\epsilon_t : I = 0.059$  for the small strain theory, almost twice the finite-strain value. This difference between the TSs will result in a difference of the same order in the internal stresses obtained by solution of the coupled Ginzburg–Landau and elasticity equations. The difference in internal stresses will change the microstructure itself.

We consider the uniaxial loading of single crystals of NiAl, BN and C by a stress  $P$  in direction 1, and only account for two martensitic variants,  $M_1$  and  $M_2$ ; see Fig. 2 inset. Axes  $1'$  and  $2'$  are the cubic axes. Note

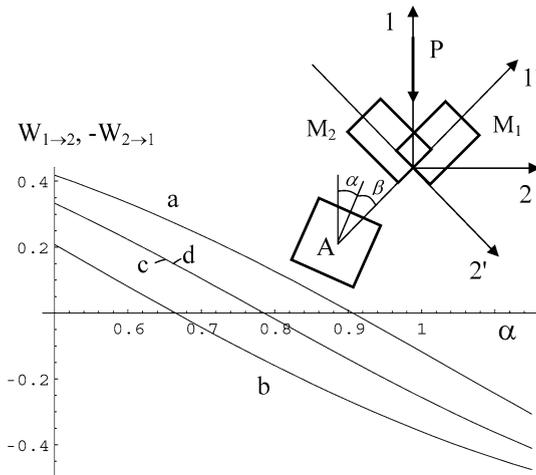


Fig. 2. Normalized transformation work  $W_{1 \rightarrow 2}$  (a, c), and  $-W_{2 \rightarrow 1}$  (b, d) for BN for finite (a, b) and small strain (c, d) theories.

that the  $c$ -axis of  $M_i$  is directed along the axis  $i'$  before rotation. Representing the two-dimensional tensor  $\mathbf{a}$  as  $\{a_{11}, a_{12}, a_{21}, a_{22}\}$ , the TSs for  $M_1$  and  $M_2$  in the  $1' - 2'$  coordinates are  $\boldsymbol{\varepsilon}_{i1} = \{\varepsilon_1, 0, 0, \varepsilon_2\}$  and  $\boldsymbol{\varepsilon}_{i2} = \{\varepsilon_2, 0, 0, \varepsilon_1\}$ , where  $\varepsilon_1 = 0.215$  and  $\varepsilon_2 = -0.078$  for NiAl, and  $\varepsilon_1 = 0.596$  and  $\varepsilon_2 = -0.02$  for the layer puckering mechanism [13] in BN and C. The lattice rotation tensor is defined as  $\mathbf{R} = \{\cos \beta, \sin \beta, -\sin \beta, \cos \beta\}$ . Solution of Eq. (6) gives  $\beta(\hat{\eta}_0) = 0$  and  $\cos \beta(\hat{\eta}_k) = F_{i11}/(F_{i11}^2 + F_{i12}^2)^{1/2}$ , where  $F_{tij}$  is obtained by transforming  $\mathbf{F}_i(\hat{\eta}_k) = \mathbf{I} + \boldsymbol{\varepsilon}_{ik}$  to the 1–2 coordinates. The maximum value of  $\beta$  for NiAl is  $8^\circ$  and for BN it is  $14^\circ$ , both for  $\alpha \simeq 0.9$ ;  $\beta$  can be much larger for other PTs, e.g., if  $F_{i11} = F_{i12}$ , then  $\beta = 45^\circ$ . The normalized transformation work is defined by  $W_{i \rightarrow j} := \mathbf{P}^T \cdot \mathbf{R}(\hat{\eta}_i) : (\boldsymbol{\varepsilon}_{ij} - \boldsymbol{\varepsilon}_{ii})/P$  and represents the TS along 1 axis; the transformation work  $W_{i \rightarrow j}$  appears in the PT criteria (10). The finite-strain value of  $W_{1 \rightarrow 0}$  exceeds the small strain approximation by about 0.06 for BN and 0.015 for NiAl, and the difference is weakly dependent on  $\alpha$ . This difference is of course most significant near the zeroes of  $W_{1 \rightarrow 0}$ . In Fig. 2 we plot  $W_{1 \rightarrow 2}$ , and  $-W_{2 \rightarrow 1}$  versus  $\alpha$  for C and BN for both finite and small strain theories. The maximum value of  $W_{1 \rightarrow 2} + W_{2 \rightarrow 1}$  reaches 0.285 for BN and 0.09 for NiAl; it is zero in small strain theory. The above deviations demonstrate the importance of finite strain corrections.

The results of numerous finite strain atomistic calculations [4–8,11] could not be presented in a practical analytical form and used in continuum microscale studies of nucleation and microstructure formation because of the lack of continuum finite strain models for PTs. The explicit expression for  $G$ , Eq. (7), will bridge this gap.

Note that the crystallographic theory of martensitic PTs has long been based on finite strain kinematics (for neglected elastic strains), and the necessity of accounting for finite strain and rotations has been proven [14]. Since a Ginzburg–Landau model of martensitic microstructure must reproduce the results of crystallographic theory when it is applicable (e.g., the orientation of the interfaces between martensitic variants and between austenite and twinned martensite, and the volume fraction of martensitic variants inside the martensitic plate), it must also be a finite strain theory.

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