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ORIGINAL REPORT



Elastic model for stress–tensor-induced martensitic transformation and lattice instability in silicon under large strains

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ABSTRACT

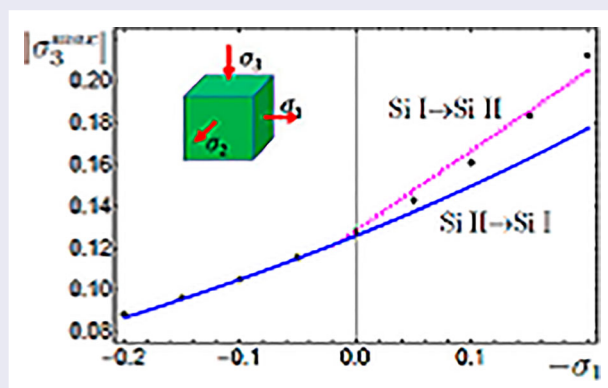
Recent molecular dynamics simulations for phase transformations (PTs) $\text{Si I} \leftrightarrow \text{Si II}$ under multiaxial loading revealed that lattice instability criteria for $\text{Si I} \leftrightarrow \text{Si II}$ PTs are linear in the stresses σ_i normal to the cubic faces; instability stress σ_3 depends on $\sigma_2 + \sigma_1$ and is independent of shears; for some stresses $\sigma_2 = \sigma_1$, the instability stresses σ_3 are the same for direct and reverse PTs; at critical stress $\sigma_2 = \sigma_1$, the first-order PTs are substituted with the second-order PT. We demonstrated that these features can be qualitatively reproduced using the simplest model with quadratic elastic energy in terms of Lagrangian strain.

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KEYWORDS

Martensitic phase transformation; crystal lattice instability; multiaxial loading; geometrically nonlinear elasticity



IMPACT STATEMENT

Various nontrivial features of the martensitic transformation and lattice instability under complex loading in silicon are reproduced using the simplest model with quadratic elastic energy in terms of Lagrangian strain.

Introduction

Displacive stress-induced phase transformations (PTs) under both normal and high pressures are broadly studied from both fundamental and applied points of view. They are important for understanding and improvement of behavior of shape memory alloys and caloric materials [1–4] and for quantifying the effects of non-hydrostatic stresses on high-pressure PTs [5–9], which can be utilized for the synthesis of new phases. The starting point in studying PTs at low temperature is finding stresses at which the crystal lattice loses its instability. There are several approaches that describe

lattice instability under stresses. In the most traditional approach [10–15] (named below as the zero-moduli condition), lattice instability occurs when some elastic moduli or their combinations reduce to zero. For complex lattices, intracell displacements (shuffles) are included in the instability criteria [13–16]. A lattice instability criterion with respect to change in the order parameters within a Landau-type theory was developed in [17–19] and was coined as the modified transformation work criterion. Also, phonon stability (soft-mode) criteria [13–16] were applied, which offer additional conditions for short wavelengths.

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In [19,20], molecular dynamics (MD) simulations for cubic-tetragonal PTs Si I (diamond-cubic) $\leftrightarrow$ Si II (β -Sn) under general multiaxial loading revealed various nontrivial results and phenomena.

(a) While the instability stress for Si I $\rightarrow$ Si II PT is described by both zero-moduli and the modified transformation work criteria, the reverse Si II $\rightarrow$ Si I PT is described by the modified transformation work criterion only.

(b) Instability criteria for both Si I $\leftrightarrow$ Si II PTs are linear in the true (Cauchy) stresses σ_1 , σ_2 , and σ_3 normal to the cubic faces of Si I; i.e. they represent two planes in the stress space σ_i ($i = 1, 2, 3$).

(c) The effect of the shear stresses within the considered range ≤ 3 GPa is negligible.

(d) The instability stress σ_3 along the c direction of the tetragonal phase or direction in a cubic lattice, which transforms to the c direction, depends on $\sigma_2 + \sigma_1$ rather than on σ_1 and σ_2 separately.

(e) Instability points for Si I $\rightarrow$ Si II and Si II $\rightarrow$ Si I PTs correspond to the maximum $|\sigma_3^{\max}|$ and minimum $|\sigma_3^{\min}|$ stresses, respectively, in the stress – Lagrangian strain E_3 curves for different fixed σ_1 and σ_2 .

(f) For some tensile stress $\sigma_1 = \sigma_2$, the instability line for the direct $\sigma_3^{\max}(\sigma_1)$ PT and reverse $\sigma_3^{\min}(\sigma_1)$ PT intersects. For larger tensile stresses, while the straight line $\sigma_3^{\min}(\sigma_1)$ remains the same, the line $\sigma_3^{\max}(\sigma_1)$ bends toward and then coincides with $\sigma_3^{\min}(\sigma_1)$. In this region, the stresses for the instability of the crystal lattice are the same for direct and reverse PTs, which leads to a number of interesting and important phenomena [20].

(g) The magnitude of the strain in the c direction, at which instability starts, $|E_3^{\max}|$, increases with increasing tensile stresses $\sigma_1 = \sigma_2$ (and reduces with the growing magnitude of the compressive stresses $|\sigma_1| = |\sigma_2|$), and jump in strain from the parent to the product phase decreases as well. At some $\sigma_1 = \sigma_2$ the jump becomes zero, which means that the first-order PT is substituted with the second-order PT.

All the above results create the impression of a very sophisticated nonlinear elastic material behavior for large strains at the edge of lattice instability under multiaxial loading. In particular, the coincidence for the Si I $\rightarrow$ Si II PT of two completely independent criteria, the zero-moduli condition and the modified transformation work criterion, may impose very strict constraints on nonlinear elasticity equations. Even without intending to describe the above features and constraints, the elastic energy for a cubic to tetragonal PT is considered to be a fourth-degree polynomial in terms of the Lagrangian strain tensor E [21].

In this letter, we demonstrate that all the enumerated features of Si I $\rightarrow$ Si II PT can be qualitatively reproduced using the simplest finite-strain model with quadratic elastic energy in terms of Lagrangian strain E . This results in a linear relationship between the second Piola–Kirchhoff stress T and E . However, under compression, e.g. along axis 3, it produces curves for the first Piola–Kirchhoff (nominal) stress P_3 (force per unit reference area) and the Cauchy (true) stress σ_3 (force per unit actual area) vs E_3 with the maximum (see Figure 1, similar to figures in [19,20]). The maximum of the Cauchy stress corresponds to the lattice instability point and the initiation of the direct PT Si I $\rightarrow$ Si II [19,20]. The reverse PT is also described in the simplest way, yet still consistent with MD results in [19,20]. Such a surprisingly simple description of multiple complex phenomena in PTs and lattice instabilities reveals that the main reason for all of them is geometric rather than physical nonlinearities.

Below, we designate contractions of tensors $A = \{A_{ij}\}$ and $B = \{B_{ji}\}$ over one and two indices as $A \cdot B = \{A_{ij}B_{jk}\}$ and $A : B = A_{ij}B_{ji}$, respectively. The superscript T designates transposition and I is the unit tensor. Because tensile (compressive) stresses and strains are positive (negative) and our main interest is in compression, we use the magnitude $|\dots|$ and in many cases change the sign of stresses and strains, similar to [19,20].

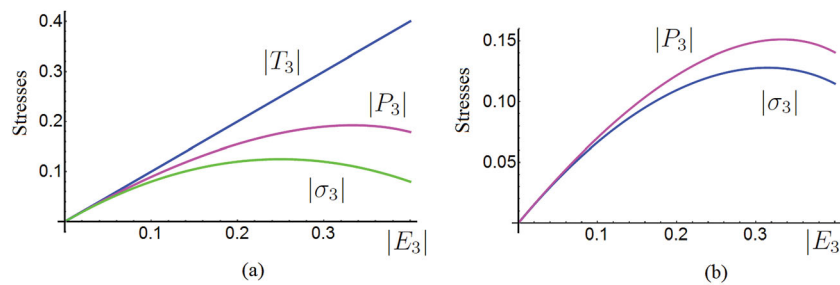


Figure 1. Normalized stress—Lagrangian strain $|E_3|$ curves for uniaxial compression for the Cauchy $|\sigma_3|$, the first $|P_3|$ and the second Piola–Kirchhoff $|T_3|$ stress. (a) For weakly compressible material with $J \simeq 1$ and (b) for compressible material and $C = 0.3855$.

Model

Let the deformation gradient $\mathbf{F}$ represent the linear mapping of the undeformed (stress-free) cubic crystal lattice in the deformed state, in particular, into a deformed tetragonal lattice, and the Lagrangian strain is $\mathbf{E} = 0.5(\mathbf{F}^T \cdot \mathbf{F} - \mathbf{I})$. The Jacobian determinant describes the ratio of volumes V in the deformed and the undeformed configurations, $J = dV/dV_0 = \det \mathbf{F}$. We will accept the simplest finite-strain model with quadratic elastic energy per unit undeformed volume

$$\psi(\mathbf{E}) = 0.5\mathbf{E} : \mathbf{C} : \mathbf{E}, \quad (1)$$

where $\mathbf{C}$ is the fourth-rank elasticity tensor for the cubic lattice. Relationships between the second Piola–Kirchhoff stress $\mathbf{T}$, the first Piola–Kirchhoff (nominal) stress $\mathbf{P}$ and the Cauchy (true) stress $\boldsymbol{\sigma}$ and $\mathbf{E}$ and $\mathbf{F}$ in nonlinear elasticity are defined as [22]

$$\begin{aligned} \mathbf{T} &= \frac{\partial \psi}{\partial \mathbf{E}} = \mathbf{C} : \mathbf{E}; \quad \mathbf{P} = \mathbf{F} \cdot \mathbf{T} = \mathbf{F} \cdot \mathbf{C} : \mathbf{E}; \\ \boldsymbol{\sigma} &= J^{-1} \mathbf{F} \cdot \mathbf{T} \cdot \mathbf{F}^T = J^{-1} \mathbf{F} \cdot \mathbf{C} : \mathbf{E} \cdot \mathbf{F}^T. \end{aligned} \quad (2)$$

It is clear that the relationship between $\mathbf{T}$ and $\mathbf{E}$ is linear, i.e. this is indeed the simplest model in nonlinear elasticity. However, expressions for $\mathbf{P}$ and $\boldsymbol{\sigma}$ are nonlinear and for large strains, they will reproduce all of the above features related to lattice instability and PTs.

The reverse PT in [19,20] is not related to the elastic instability, but rather is described within a Landau-type theory by the modified transformation work criterion. In order to avoid a complex formulation based on an order parameter [19,20] which is not necessary for this paper, we will utilize some results from [19,20] to develop the simplest description. According to Figure 3 in [20], the elastic behavior of Si II is linear with very large elastic moduli, and stress–strain curves for Si II for several $\sigma_1 = \sigma_2$ represent the single (almost) vertical line. Thus, elastic deformations of Si II are negligible in comparison

with deformations of Si I, and we will neglect them. Then strains in Si II are constant and equal to the strains of the stress-free Si II. According to Levitas et al. [19,20], deformation gradient $\mathbf{F}^r$ for the stress-free Si II has components $F_1^r = F_2^r = 1.175$ and $F_3^r = 0.553$, which correspond to the Lagrangian strain $\mathbf{E}^r$ with components $E_1^r = E_2^r = 0.19$ and $E_3^r = -0.35$. Thus, we will assume that PT Si I $\rightarrow$ Si II completes and that the reverse PT Si II $\rightarrow$ Si I starts at fixed strain $\mathbf{E}^r$, and that the product phase has infinite elastic moduli (Figure 2). Despite the simplicity, this corresponds well with the MD results in [19,20] and is fully sufficient for our objectives here.

Stress–strain curves and lattice instability under three stresses normal to the cubic faces

General equations

We will focus on the loading of a crystal of cubic symmetry by three stresses normal to the cubic faces. In this case, tensors $\mathbf{F}$, $\mathbf{E}$, $\mathbf{T}$, $\mathbf{P}$, and $\boldsymbol{\sigma}$ are coaxial and diagonal and Equation (2) for the Cauchy stress simplifies to

$$\boldsymbol{\sigma} = J^{-1} \mathbf{F}^2 \cdot \mathbf{C} : \mathbf{E} \quad (3)$$

or in component form for $\boldsymbol{\sigma}$ and $\mathbf{P}$:

$$\sigma_i = (F_1 F_2 F_3)^{-1} F_i^2 \frac{\partial \psi}{\partial E_i}; \quad P_i = F_i \frac{\partial \psi}{\partial E_i}. \quad (4)$$

Explicit expressions for the cubic symmetry are

$$\begin{aligned} \sigma_1 &= (F_1 F_2 F_3)^{-1} F_1^2 (C_{11} E_1 + C_{12} (E_2 + E_3)); \\ \sigma_2 &= (F_1 F_2 F_3)^{-1} F_2^2 (C_{11} E_2 + C_{12} (E_1 + E_3)); \\ \sigma_3 &= (F_1 F_2 F_3)^{-1} F_3^2 (C_{11} E_3 + C_{12} (E_2 + E_3)), \end{aligned} \quad (5)$$

where C_{11} and C_{12} are elastic constants for the cubic crystal. All stresses and C_{12} can be normalized by C_{11} . To avoid additional notations, we just set $C_{11} = 1$ and

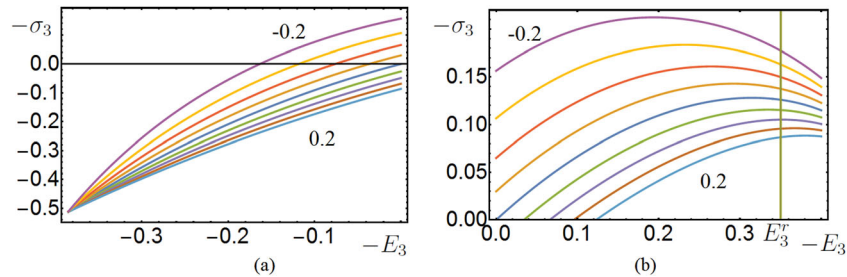


Figure 2. Effect of different fixed stresses $\sigma_1 = \sigma_2$ on the stress σ_3 —strain E_3 curve for tensile (a) and compressive (b) strain E_3 . The vertical line $E_3^r = -0.35$ represents idealized rigid behavior of Si II, curves for $-E_3^r > 0.35$ do not have physical meaning. The values of σ_1 for the upper and lower curves are -0.2 and 0.2 , respectively. The values of σ_1 for the intermediate curves are between these numbers with the step of 0.05 .

designate $C = C_{12}/C_{11}$. In addition, we express all $F_i = \sqrt{1 + 2E_i}$, and obtain from Equation (5):

$$\begin{aligned}\sigma_1 &= \frac{\sqrt{1 + 2E_1}}{\sqrt{1 + 2E_2}\sqrt{1 + 2E_3}}(E_1 + C(E_2 + E_3)); \\ \sigma_2 &= \frac{\sqrt{1 + 2E_2}}{\sqrt{1 + 2E_1}\sqrt{1 + 2E_3}}(E_2 + C(E_1 + E_3)); \\ \sigma_3 &= \frac{\sqrt{1 + 2E_3}}{\sqrt{1 + 2E_1}\sqrt{1 + 2E_2}}(E_3 + C(E_1 + E_2)).\end{aligned}\quad (6)$$

We will also need

$$P_3 = \sqrt{1 + 2E_3}(E_3 + C(E_1 + E_2)). \quad (7)$$

Uniaxial loading of a weakly compressible material

To obtain simple results independent of the material parameters, we assume that $J - 1$ is small and that the volumetric part of geometric nonlinearity can be neglected. Thus, we set $J \simeq 1$, and consider uniaxial tension-compression along axis 3 at $\sigma_1 = \sigma_2 = 0$. Then it follows from Equations (5) and (7)

$$\begin{aligned}E_1 &= E_2 = -E_3 \frac{C}{1 + C}; \\ \sigma_3 &= BE_3(1 + 2E_3); \quad B = 1 - \frac{2C^2}{1 + C}, \\ P_3 &= BE_3\sqrt{1 + 2E_3}; \quad T_3 = BE_3.\end{aligned}\quad (8)$$

A plot of all three stresses normalized by B is shown in Figure 1(a). It is evident, that even the simplest quadratic expression for the energy vs. E and the corresponding linear relationship between T and E result in the stress-strain curves for $|\sigma_3|$ and $|P_3|$ under compression with the maximum attributable to pure geometric nonlinearity. These curves are qualitatively similar to those obtained in MD simulations (Figure 3 in [20]). The maximum of the Cauchy stress, $|\sigma_3^{\max}| = 0.125$, corresponds to $E_3^{\text{Cmax}} = -1/4$ and for the nominal stress is $|P_3^{\max}| = 0.192$ at $E_3^{\text{Nmax}} = -1/3$. For comparison, MD results for Si I in [19] exhibit $E_3^{\text{Cmax}} = -0.2293$ and $E_3^{\text{Nmax}} = -0.2610$; i.e. the simplest model gives quite reasonable results. Note that for $C = 0.3855$ (the value for Si I [23] used in this paper) and $E_3^{\text{Cmax}} = -1/4$, one has $J \simeq 0.93$, i.e. neglecting geometric nonlinearity in J leads to an error of 7%.

In [19,20], lattice instability was identified at the maximum of the Cauchy stress, independent of which stress or strain was prescribed. This was proven analytically [18] for the Landau-type description of a PT in terms of the order parameter. If the prescribed Cauchy stress $|\sigma_3|$ is greater than $|\sigma_3^{\max}|$, then the system cannot be equilibrated and the magnitude of strain will increase toward

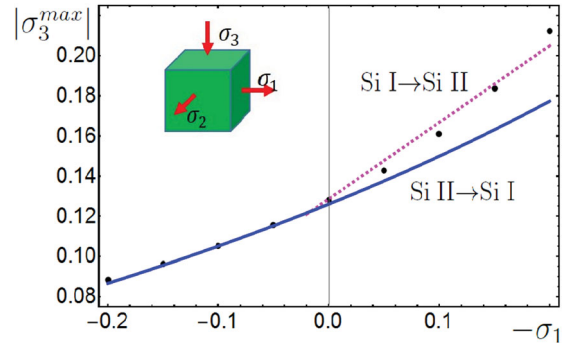


Figure 3. Instability stress $|\sigma_3^{\max}|$ vs. σ_1 for direct Si I $\rightarrow$ Si II phase transformation (dots) and reverse Si II $\rightarrow$ Si I phase transformation (lower line) vs. $\sigma_1 = \sigma_2$. The dashed line is the linear interpolation of points for direct transformation for $\sigma_1 \in [-0.05, 0.2]$.

$E_3^r = -0.35$, i.e. the product phase. For the elastic instability considered here, results depend on which stress is prescribed. Thus, if the prescribed $|P_3| < |P_3^{\max}|$, the system under homogeneous strains can be equilibrated for $|E_3^{\text{Cmax}}| < |E_3| < |E_3^{\text{Nmax}}|$. In terms of the order parameter η , which is 0 in the parent phase and 1 in the product phase [19], the parent phase loses its stability and PT starts for $|E_3| > |E_3^{\text{Cmax}}|$. Equilibration for $|E_3^{\text{Cmax}}| < |E_3| < |E_3^{\text{Nmax}}|$ under prescribed P_3 means that this state is an equilibrium intermediate homogeneous state with $0 < \eta < 1$. However, for heterogeneous perturbations, e.g. in MD simulations, multiple two-phase stationary solutions can be observed for $|E_3^{\text{Cmax}}| < |E_3| < |E_3^{\text{Nmax}}|$ and prescribed P_3 . Thus, the maximum Cauchy stress $|\sigma_3^{\max}|$ will be considered as the stress for lattice instability and initiation of direct PT. The same criterion was used in most of previous publications for uniaxial loading, e.g. in [11,12].

3D loading with $\sigma_1 = \sigma_2$

In this case, also $E_1 = E_2$ and analytical solution can be obtained as well. Equation (6) simplifies to

$$\sigma_1 = \frac{1}{\sqrt{1 + 2E_3}}(E_1 + C(E_1 + E_3)); \quad (9)$$

$$\sigma_3 = \frac{\sqrt{1 + 2E_3}}{1 + 2E_1}(E_3 + 2CE_1); \quad (10)$$

$$P_3 = \sqrt{1 + 2E_3}(E_3 + 2CE_1). \quad (11)$$

Solving Equation (9) for E_1 ,

$$E_1 = \frac{\sigma_1\sqrt{1 + 2E_3} - CE_3}{1 + C}, \quad (12)$$

and substituting Equation (12) in Equations (10) and (11), we obtain

$$\sigma_3 = \sqrt{1 + 2E_3} \frac{E_3(1 + C - 2C^2) + 2C\sigma_1\sqrt{1 + 2E_3}}{1 + C(1 - 2E_3) + 2\sigma_1\sqrt{1 + 2E_3}}; \quad (13)$$

$$P_3 = \sqrt{1 + 2E_3} \left(E_3 + 2C \frac{\sigma_1\sqrt{1 + 2E_3} - CE_3}{1 + C} \right). \quad (14)$$

Plots of the stresses σ_3 and P_3 vs. strain E_3 for stress $\sigma_1 = 0$ and $C = 0.3855$ are shown in Figure 1(b). Although compression magnitude of both stresses possess maxima, tensile curves are monotonous (similar to MD simulations in [19,20]). The maximum of the true stress, $|\sigma_3^{\max}| = 0.128$, is reached at $E_3^{\text{Cmax}} = -0.315$. Since Equation (14) for the first Piola–Kirchhoff stress is independent of J , for $\sigma_1 = 0$ it coincides with Equation (8) and $E_3^{\text{Nmax}} = -1/3$, which corresponds to $|P_3^{\max}| = 0.151$ (different than in Figure 1(a) due to different normalization). While $|E_3^{\text{Cmax}}| = 0.315$ is significantly larger than 0.23 in MD simulations [20], the small difference between E_3^{Cmax} and E_3^{Nmax} is similar to the MD results.

The effect of different fixed stresses σ_1 on the stress σ_3 — strain E_3 curves is shown in Figure 2. Qualitatively, it is similar to what is found in MD simulations (see item (g) in the Introduction). Thus, tensile stresses σ_1 increase the instability strain $|E_3^{\text{Cmax}}|$ and decrease the instability stress $|\sigma_3^{\max}|$, lowering stress–strain curves. Compressive σ_1 acts in the opposite way. For the tensile E_3 , stress–strain curves are monotonous for all σ_1 . One of the interesting features of Equation (13) is that for $E_3 = C$, the stress $\sigma_3 = E_3\sqrt{1 + 2E_3}$ is independent of σ_1 and all curves for different σ_1 pass through this point (Figure 2(a)).

The instability stress $|\sigma_3^{\max}|$ for direct PT vs. σ_1 is shown in Figure 3. It is well described by the parabolic function $|\sigma_3^{\max}| = 0.128 - 0.299\sigma_1 + 0.559\sigma_1^2$ in the entire range under consideration $\sigma_1 \in [-0.2, 0.2]$. The instability stress $|\sigma_3^r|(-\sigma_1)$ for the reverse PT is obtained by substituting in the stress σ_3 —strain E_3 curves for different σ_1 the value $E_3 = E_3^r = -0.35$. It is also included in Figure 3. This dependence is practically linear in the range $\sigma_1 \in [-0.2, 0.2]$, and in the broad range $\sigma_1 \in [-0.2, 0.02]$ it practically coincides with the instability curve $|\sigma_3^{\max}|(-\sigma_1)$ for the direct PT. Points $|\sigma_3^{\max}|$ vs. σ_1 deviate for $\sigma_1 \in [-0.05, 0.2]$ from the linear approximation $|\sigma_3^{\max}| = 0.129 - 0.382\sigma_1$ by less than 3%. Thus, Figure 3 is qualitatively the same as Figure 1 in MD simulations in [20]:

(i) both instability lines are straight lines, for reverse PT in the whole range of σ_1 , for the direct PT

for $-\sigma_1 \in [-0.05, 0.2]$ (see items (b) and (f) in the Introduction);

(ii) The curve $|\sigma_3^{\max}|(-\sigma_1)$ bends toward the intersection point of the straight lines for the direct and reverse PTs, and then there is a significant region $\sigma_1 \in [-0.2, 0.02]$, where both curves practically coincide (item (f)). In this region, the stresses for the instability of the crystal lattice are the same for direct and reverse PTs, i.e. the energy barrier between phases disappears and the Gibbs energy possesses a flat portion. This leads to unique homogeneous, hysteresis-free and dissipation-free first-order PTs, for which each intermediate lattice along the transformation path is in indifferent thermodynamic equilibrium and can be arrested and studied at fixed strain [20]. The above properties are of great interest from the fundamental and applied points of view, especially for various PT-related applications [1–4].

Figure 4 exhibits the dependence of the strain $|E_3^{\text{Cmax}}|$, corresponding to initiation of the Si I $\rightarrow$ Si II PT vs. σ_1 . It can be approximated by the quadratic equation $|E_3^{\text{Cmax}}| = 0.3156 + 0.4542\sigma_1 - 0.6948\sigma_1^2$. The difference between E_3^{Cmax} and E_3^r represents jump in the strain during Si I $\rightarrow$ Si II PT. With increasing tensile stress σ_1 , this jump reduces (similar to MD results; see Figure 3 in [20] and item (g) above) to zero at $\sigma_1 = 0.088$. At this point, the first-order PT is substituted with the second-order PT, as reported in [20] and item (g).

3D loading with $\sigma_1 = -\sigma_2$

MD results in [19] demonstrated that $|\sigma_3^{\max}|$ depends on $\sigma_2 + \sigma_1$ rather than on σ_1 and σ_2 separately, see item (d) above. Since generally $|\sigma_3^{\max}| = f(\sigma_2 + \sigma_1, \sigma_2 - \sigma_1)$, where f is some function (even in $\sigma_2 - \sigma_1$ due to symmetry with respect to exchange of directions 1 and 2), this means that f is independent of $\sigma_2 - \sigma_1$. Similar to

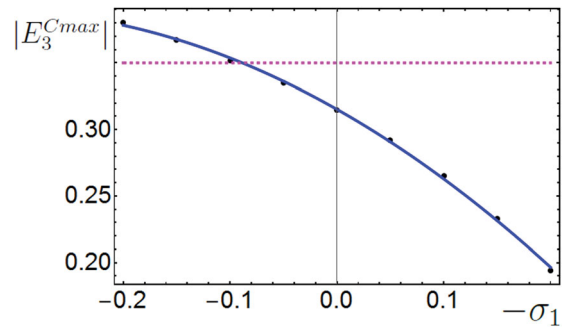


Figure 4. Strain $|E_3^{\text{Cmax}}|$ corresponding to initiation of the Si I $\rightarrow$ Si II PT vs. σ_1 . The horizontal line $E_3 = E_3^r = -0.35$ corresponds to Si II. The intersection point determines stress σ_1 at which the first-order PT is substituted with the second-order PT.

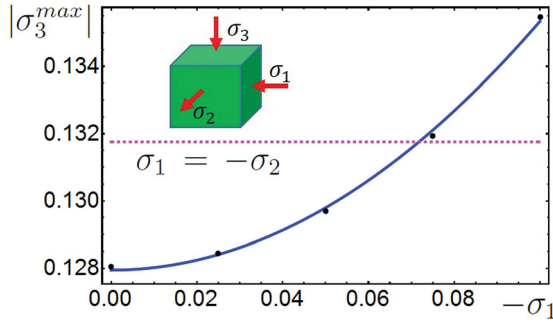


Figure 5. Instability stress $|\sigma_3^{\max}|$ versus $\sigma_1 = -\sigma_2$, results (dots) and approximation with quadratic function (line). The horizontal line $|\sigma_3^{\max}| = 0.1317$ corresponds to the middle value of the instability stress in this range. Deviation of the data from the middle value is smaller than $\pm 2.8\%$.

[19], we will check whether f is independent of $\sigma_2 - \sigma_1$ for the particular case $\sigma_2 + \sigma_1 = 0$. Thus, we consider the effect on the instability condition of stresses σ_1 and σ_2 for the particular case of $\sigma_1 = -\sigma_2$. Prescribing different values of $\sigma_1 = -\sigma_2$ in Equation (6), we find numerically strain E_3^{Cmax} and corresponding maximum stresses $|\sigma_3^{\max}|$ (Figure 5). Results are described well by parabolic approximation $|\sigma_3^{\max}| = 0.128 + 0.740\sigma_1^2$. Deviation of these data from the middle value $|\sigma_3^{\max}| = 0.1317$ in the range $|\sigma_1| < 0.1$ does not exceed $\pm 2.8\%$. This is in agreement with the results of MD simulations [19], in which the deviation is within $\pm 2\%$, i.e. within an error of simulations. Thus, $|\sigma_3^{\max}|$ is independent of $\sigma_2 - \sigma_1$ (at least for $\sigma_1 = -\sigma_2$), which is consistent with the statement that $|\sigma_3^{\max}|$ depends on $\sigma_2 + \sigma_1$ rather than on σ_1 and σ_2 separately, see item (d) above.

Effect of shear stress

In addition to the normal stresses, shear stress $\tau = \sigma_{13}$ can be applied. To exclude rigid-body rotation, we accept that the components $F_{31} = 0$. Then the deformation gradient and Lagrangian strain have the following form:

$$\mathbf{F} = \begin{pmatrix} F_1 & 0 & F_{13} \\ 0 & F_2 & 0 \\ 0 & 0 & F_3 \end{pmatrix};$$

$$\mathbf{E} = 0.5 \begin{pmatrix} F_1^2 - 1 & 0 & F_{13}F_1 \\ 0 & F_2^2 - 1 & 0 \\ F_{13}F_1 & 0 & F_3^2 - 1 + F_{13}^2 \end{pmatrix}. \quad (15)$$

Such an expression for $\mathbf{F}$ (even if we additionally include F_{12} and F_{23}) does not change $J = \det \mathbf{F}$. In the MD simulations [19,20], the effect of the shear stress $\sigma_{13} = 3$ GPa on the lattice instability did not exceed ± 2 . Since for Si I shear modulus $C_{44} = 80$ GPa [23], an estimate for the

shear strain is $E_{13} = \sigma_{13}/(2C_{44}) = 0.01875 \ll 1$. Then, Equation (2) for the Cauchy stress has the following form:

$$\boldsymbol{\sigma} = J^{-1} \mathbf{F} \cdot \mathbf{T} \cdot \mathbf{F}^T$$

$$= J^{-1} \begin{pmatrix} F_1(F_1 T_1 + F_{13} T_{13}) & 0 & F_3(F_1 T_{13} + F_{13} T_3) \\ +F_{13}(F_1 T_{13} + F_{13} T_3) & F_2^2 T_2 & 0 \\ 0 & 0 & F_3^2 T_3 \end{pmatrix}$$

$$\simeq J^{-1} \begin{pmatrix} F_1^2 T_1 & 0 & F_3(F_1 T_{13} + F_{13} T_3) \\ 0 & F_2^2 T_2 & 0 \\ F_3(F_1 T_{13} + F_{13} T_3) & 0 & F_3^2 T_3 \end{pmatrix}. \quad (16)$$

We kept the term with F_{13} in the expression for σ_{13} because $T_3 \gg T_{13}$. To estimate E_{12} for the geometrically nonlinear formulation, we express T_{13} from Equation (16), i.e. from $\sigma_{13} = J^{-1} F_3(F_1 T_{13} + F_{13} T_3)$, while allowing for $T_3 = \sigma_3/JF_3^2$ and $F_{13} = 2E_{13}/F_1 = T_{13}/(C_{44}F_1)$ (see Equation (15)):

$$T_{13} = \frac{JC_{44}F_1F_3\sigma_{13}}{C_{44}F_1^2F_3^2 + J\sigma_3} = 2C_{44}E_{13}. \quad (17)$$

For uniaxial compression ($\sigma_1 = 0$) at instability point, $F_3 = \sqrt{1 - 2 \times 0.32} = 0.60$, $F_1 = \sqrt{1 + 2 \times 0.09} = 1.086$, $J = 0.708$, $\sigma_3 = -0.13 \times C_{11} = -21.58$ GPa, and, according to Equation (17), $T_{13} = 5.92$ GPa, which is significantly larger than $\sigma_{13} = 3$ GPa used in the linearized theory. Still $E_{13} = T_{13}/(2C_{44}) = 0.037 \ll 1$ and $F_{13} = 2E_{13}/F_1 = 0.068 \ll 1$, and we will see that their effect on the critical stress $|\sigma_3^{\max}|$ can be neglected. Indeed, an exact expression for σ_3 in Equation (16) is independent of F_{13} . An exact equation for σ_1 in Equation (16) differs from the approximate by three terms equal to 0.004 (normalized by C_{11}). According to the expression $|\sigma_3^{\max}| = 0.128 - 0.382\sigma_1$, this changes $|\sigma_3^{\max}|$ by 0.0016, i.e. by 1.2%, which is negligible. Also, in expression for E_3 in Equation (15), the term due to shear $F_{13}^2 = 0.0046$ is also just 1.5% of the value 0.31 without shear.

Thus, the effect of shear stresses of 3 GPa on the instability stress for uniaxial compression is negligible in the current model, similar to the MD simulation results in [19] (item (c)).

Concluding remarks

In the letter, we demonstrated that all numerous non-trivial features found in MD simulations [19,20] for cubic-tetragonal PTs Si I $\leftrightarrow$ Si II under general multiaxial loading can be qualitatively reproduced using the simplest model with quadratic elastic energy in terms of a Lagrangian strain. These phenomena include: (a) lattice instability criteria for both Si I $\leftrightarrow$ Si II PTs are linear in the Cauchy stresses σ_i ($i = 1, 2, 3$); (b) the instability

stress σ_3 depends on $\sigma_2 + \sigma_1$ rather than on σ_1 and σ_2 separately; (c) the negligible effect of the shear stresses; (d) coincidence of the instability stresses σ_3 for direct and reverse PTs for some range of tensile stresses $\sigma_2 = \sigma_1$, which results in a variety of interesting phenomena [20]; (e) a jump in strain E_3 from the parent to the product phase reduces with growing tensile stresses $\sigma_2 = \sigma_1$ until it approaches zero, which substitutes the first-order PT with the second-order PT.

Such a success in a description means that all of the enumerated phenomena result from geometric nonlinearity rather than any physical mechanisms or effects. This model can be included in the phase field simulation of stress-induced PTs and microstructure evolution, as well as analyses of the effect of nonhydrostatic stresses on high-pressure PTs.

The results obtained allow us to answer the question raised in [19,20]: why two different lattice instability criteria, one based on the elastic instability and another one that is derived within Landau theory, coincide for direct Si I to Si II PT and both are linear in terms of the components of the Cauchy stress? MD simulations in [19,20] show that instability for direct Si I to Si II PT occurs at zero elastic modulus and the corresponding criterion is linear in the components of the Cauchy stress. When applying the Landau approach, we eliminated terms that give nonlinear contribution; two material parameters in the remaining linear criterion were calibrated utilizing MD results. Here, we obtained the linear in stress instability criterion based on elastic instability and the simplest finite-strain elastic model.

Introducing the third degree contribution to the energy in terms of E may be sufficient for the quantitative description of the elastic behavior observed in MD simulations; this will result in quantitative coincidence with MD results on instability stresses and, consequently, with results based on Landau theory. Similar approaches can be developed for other materials that experience large strains during stress-induced transformations.

Disclosure statement

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References

- [1] Cui J, Chu YS, Famodu OO. Combinatorial search of thermoelastic shape-memory alloys with extremely small hysteresis width. *Nat Mater*. 2006;5:286–290.
- [2] Chluba C, Ge W, Lima de Miranda R. Ultralow-fatigue shape memory alloy films. *Science*. 2015;348:1004–1007.
- [3] Song Y, Chen X, Dabade V, et al. Enhanced reversibility and unusual microstructure of a phase-transforming material. *Nature*. 2013;502:85–88.
- [4] Takeuchi I, Sandeman K. Solid-state cooling with caloric materials. *Phys Today*. 2015;68:48–54.
- [5] Levitas VI, Shvedov LK. Low pressure phase transformation from rhombohedral to cubic BN: experiment and theory. *Phys Rev B*. 2002;65:104109.
- [6] Ji C, Levitas VI, Zhu H, et al. Shear-induced phase transition of nanocrystalline hexagonal boron nitride to wurtzitic structure at room temperature and lower pressure. *Proc Natl Acad Sci USA*. 2012;109:19108–19112.
- [7] Levitas VI, Ma Y, Hashemi J, et al. Strain-induced disorder, phase transformations and transformation induced plasticity in hexagonal boron nitride under compression and shear in a rotational diamond anvil cell: in-situ X-ray diffraction study and modeling. *J Chem Phys*. 2006;125:044507.
- [8] Blank VD, Estrin EI. Phase transitions in solids under high pressure. Boca Raton, FL: CRC Press; 2014. p. 382–423.
- [9] Ma Y, Selvi E, Levitas VI, et al. Effect of shear strain on the $\alpha - \epsilon$ phase transition of iron: a new approach in the rotational diamond anvil cell. *J Phys Cond Matter*. 2006;18:1075–1082.
- [10] Hill R, Milstein F. Principles of stability analysis of ideal crystals. *Phys Rev B*. 1977;15:3087–3096.
- [11] Milstein F, Marschall J, Fang HE. Theoretical bcc $\rightarrow$ fcc transitions in metals via bifurcations under uniaxial load. *Phys Rev Lett*. 1995;74:2977–2980.
- [12] Wang J, Yip S, Phillpot SR, et al. Crystal instabilities at finite strain. *Phys Rev Lett*. 1993;71:4182–4185.
- [13] Dove MT. Introduction to lattice dynamics. Cambridge: Cambridge University Press; 1993.
- [14] Grimvall G, Blanka M-K, Ozolins V, et al. Lattice instabilities in metallic elements. *Rev Mod Phys*. 2012;84:945–986.
- [15] Pokluda J, Cerny M, Sob M, et al. Ab initio calculations of mechanical properties: methods and applications. *Prog Mater Sci*. 2015;73:127–158.
- [16] Elliott RS, Triantafyllidis N, Shaw JA. Reversible stress-induced martensitic phase transformations in a bi-atomic crystal. *J Mech Phys Solids*. 2011;59:216–236.
- [17] Levitas VI, Preston DL. Three-dimensional Landau theory for multivariant stress-induced martensitic phase transformations. Part II. *Phys Rev B*. 2002;74:134206.
- [18] Levitas VI. Phase-field theory for martensitic phase transformations at large strains. *Int J Plast*. 2013;49:85–118.
- [19] Levitas VI, Chen H, Xiong L. Lattice instability during phase transformations under multiaxial stress: modified transformation work criterion. *Phys Rev B*. 2017. (submitted).
- [20] Levitas VI, Chen H, Xiong L. Triaxial-stress-induced homogeneous hysteresis-free first-order phase transformations with stable intermediate phases. *Phys Rev Lett*. 2017;118:025701.
- [21] Clapp PC, Becquart CS, Shao Y, et al. Transformation toughening explored via molecular-dynamics and

- Monte-Carlo simulations. *Model Simul Mater Sci Eng.* [1994](#);2:551–558.
- [22] Lurie AI. *Nonlinear theory of elasticity*. Amsterdam: North-Holland; [1990](#).
- [23] Gaal-Nagy K, Schmitt M, Pavone P, et al. Ab initio study of the high-pressure phase transition from the cubic-diamond to the beta-tin structure of Si. *Comp Mater Sci.* [2001](#);22:49–55.