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We propose the possibility of a spinodal mechanism for deformation twinning in addition to the nucleation and growth mechanism assumed in all existing studies of twinning, using the thermodynamic stability analysis of a homogeneously deformed crystal by examining its energy landscape as a function of strain along the twinning direction obtained from first-principles calculations. Twinning occurs continuously owing to thermodynamic instability with respect to twinning at large shear strains, whereas it can only take place through the nucleation and growth mechanism at small shear strains.

Keywords: deformation twinning; thermodynamic instability; spinodal mechanism

Twinning is a phenomenon commonly observed in crystalline solids ranging from simple face-centred cubic (fcc), hexagonal close-packed (hcp) and body-centred cubic metals to minerals with complex crystal structures. Twinning may take place during crystal growth, phase transformations with a point-group symmetry reduction or mechanical deformation. While twinning is to be avoided in some applications such as single-crystal growth, it can be utilized to improve the properties of materials. For example, deformation twinning, which is one of the major plastic deformation modes of crystalline solids operating to release the strain energy when the strain exceeds the elastic regime [1], has been exploited to dramatically improve the ductility of alloys such as Mg-alloys and steels.

The effects of temperature, strain rate and composition on deformation twinning have been extensively studied experimentally [1]. Despite the extensive efforts in uncovering new mechanisms [2–4], exploring the conditions, for example, grain size [5–8] or crystal size [9], for the twinning, and studying the twin growth behaviour, for example, growth speed [10,11], the physical mechanisms of deformation twinning have not been completely understood. Existing theoretical efforts on deformation twinning include the phenomenological modelling of twin nucleation associated with the dislocation reaction [12,13], estimation of the stress required for twin nucleation and the analysis of the criteria for twin growth using a simple model [14], the computation of twinning energy landscape to determine the critical layer thickness [15,16] and the investigation of generalized planar fault energy as well as the critical twinning stress for twin nucleation in pure metals or metallic alloys using density functional theory

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[17–20], molecular dynamics (MD) simulations demonstrating or capturing the twin nucleation process in fcc or hcp metals [5,21–24], and the energetic approach to predicting the formation of twins [25]. It is widely known that spontaneous materials processes such as phase separation and ordering are classified into two mechanisms, nucleation and growth or spinodal, based on the thermodynamics of the initial state. However, all the existing studies of deformation twinning either assumed or showed that it takes place through only a nucleation and growth mechanism [13,14], for example, at existing grain boundaries in a polycrystalline solid or other structural defects where the dissociation of dislocations into stacking faults or the emission of Shockley partials [22,26–28] occurs. The classical theory of homogeneous twinning also assumed a nucleation mechanism through thermal fluctuations [1], which requires extremely high stress. Recently, homogeneous twinning was explained by mechanical instability of a crystal lattice [29,30]. The main purpose of this work is to demonstrate that twinning in a severely deformed crystalline solid may take place through a *spinodal mechanism* at large shear deformation while twinning at smaller shear deformation occurs via the classical nucleation and growth mechanism.

We use fcc copper (Cu) as an example, in which twinning takes place on $\{1\,1\,1\}$ twinning planes along $\langle 1\,1\,\bar{2}\rangle$ directions with a total of 12 possible twinning modes. Therefore, the deformation energy of a crystal under homogeneous shear can be expressed in terms of 12 deformation strains corresponding to each of the 12 modes. This energy landscape can, in principle, be directly computed using first-principles methods [31,32]. However, to generate such a deformation energy function in a 12-dimensional space is cumbersome and hence to simplify the discussion without losing the essential physics, we computed the deformation energy (or stored strain energy) on the (1 1 1) plane using the following deformation matrix which represents the relationship between the reference lattice vectors ($R = \begin{pmatrix} \vec{a} \\ \vec{b} \\ \vec{c} \end{pmatrix}$) of the original crystal and the lattice vectors ($R' = \begin{pmatrix} \vec{a}' \\ \vec{b}' \\ \vec{c}' \end{pmatrix}$) of the deformed crystal [33,34]:

$$\mathbf{X} = \begin{bmatrix} 1 + t/2 + s/2 & t/2 & -t - s/2 \\ t/2 + s/2 & 1 + t/2 & -t - s/2 \\ t/2 + s/2 & t/2 & 1 - t - s/2 \end{bmatrix}, \tag{1}$$

where t and s represent the amount of deformation along the twinning direction $[1\,1\,\bar{2}]$ and the slipping direction $[1\,0\,\bar{1}]$, respectively. The energies were calculated in a 51×51 mesh in the $t \times s$ space using the first-principles method. We employed the projector-augmented wave method [31,32] implemented in the Vienna *ab initio* simulation package (version 4.6). The exchange-correlation functional according to Perdew–Burke–Ernzerhof [35] was employed with a $20 \times 20 \times 20$ Γ-centred k-mesh and an energy cut-off of 300 eV. Figure 1(a) shows the computed deformation energy landscape in the $t \times s$ space of a deformed crystal under a homogeneous shear along possible all directions on the (1 1 1) plane. For the case of pure twinning without slipping, we may neglect s and represent the deformation energy function as a function of t only (as indicated by an arrow in Figure 1(a)). We then convert the variable t to the corresponding shear strain ($\gamma_{(1\,1\,1)[1\,1\,\bar{2}]}$) using the interplanar spacing of (1 1 1) plane ($d_{1\,1\,1}$) as

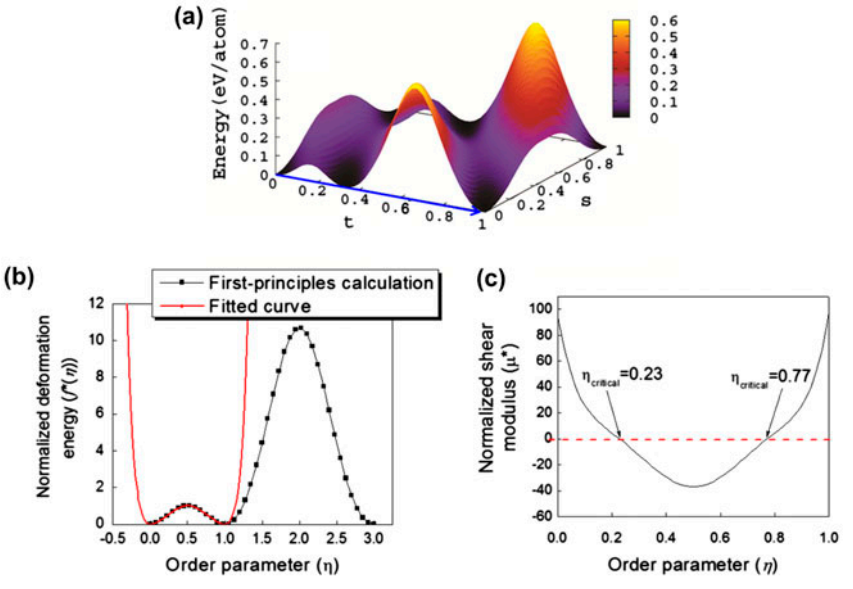

Figure 1. (colour online) (a) Deformation energy landscape of a deformed Cu crystal along all directions on a (1 1 1) plane computed by the first-principles method. (b) normalized deformation energy landscape and (c) normalized tangent modulus as a function of an order parameter (normalized shear strain) along a $[1\,1\,\bar{2}]$ direction on a (1 1 1) plane of a deformed Cu crystal.

$$\gamma_{(1\,1\,1)[1\,1\,\bar{2}]} = \frac{tL_{[1\,1\,\bar{2}]}}{d_{1\,1\,1}} = \frac{t(\sqrt{6}a_0/2)}{\sqrt{3}a_0/3} = \frac{3}{\sqrt{2}}t, \tag{2}$$

where $L_{[1\,1\,\bar{2}]}$ is the length of t path we scanned along the $[1\,1\,\bar{2}]$ direction for the calculation and a_0 is the lattice parameter.

Within the context of diffuse-interface approach, we define a phase-field order parameter η to distinguish the original undeformed crystal ($\eta = 0$) and the twinned state ($\eta = 1$), i.e. the order parameter is basically the shear strain along $[1\,1\,\bar{2}]$ direction on the (1 1 1) plane normalized by the magnitude of twinning strain $\gamma^{twin}_{(1\,1\,1)[1\,1\,\bar{2}]}$ ($= 1/\sqrt{2}$ [25]) of a fully twinned state as $\eta = \gamma_{(1\,1\,1)[1\,1\,\bar{2}]}/\gamma^{twin}_{(1\,1\,1)[1\,1\,\bar{2}]} = \sqrt{2}\gamma_{(1\,1\,1)[1\,1\,\bar{2}]}$ where $\gamma_{(1\,1\,1)[1\,1\,\bar{2}]}$ is the shear strain along $[1\,1\,\bar{2}]$ direction on the (1 1 1) plane. We normalize the deformation energy f using $|\Delta f_{\max}|$ which is the difference between the maximum deformation energy (between the original crystal state and the twin state) along the twinning direction and the energy of the original crystal or the twin state, i.e. $f^* = f/|\Delta f_{\max}|$ as shown in Figure 1(b). The deformation energy at the twin state is exactly the same (=0) as that of the original crystal. If the crystal is enforced to be deformed further along $[1\,1\,\bar{2}]$ direction on the (1 1 1) plane even after the twin state established, i.e. $\eta > 1$, the planar stacking highly deviates from the regular fcc stacking. It causes the high deformation energy within the regime corresponding to $1 < \eta \leq 3$ as shown in Figure 1(b). In addition, the calculation result confirms that deformation twinning occurs only within the regime corresponding to $0 \leq \eta \leq 1$. Further, when η reaches 3, the normal fcc stacking is established again, which results in zero deformation energy (ground state) when $\eta = 3$.

As one can see from the figure, the deformation energy landscape displays a double-well type function within the regime corresponding to $0 \le \eta \le 1$, which is associated with the twinning process. For convenience, the energy profile of that regime ($0 \le \eta \le 1$) is fitted to the eighth-order polynomial (See Equation (S4) in the Supplemental Material for the explicit form of the polynomial).

Deformation twinning can be understood as a rapid transformation process from a homogeneously deformed crystal to a twinned structure under a fixed macroscopic deformation driven by deformation energy dissipation as described in Figure 2. The stability of the homogeneously deformed crystal can be examined by considering the variation of the total free energy of the system with infinitesimal fluctuations of an order parameter under the fixed macroscopic strain constraint. The total Helmholtz free energy F of an inhomogeneous system in the diffuse-interface description [36] is given by the following functional form:

$$F = \int_{\Omega} \left[f(\eta) + \frac{\kappa_{ij}}{2} \nabla_i \eta \nabla_j \eta \right] dV + E_{\text{coh}}, \tag{3}$$

where κ_{ij} is the gradient energy coefficient tensor, Ω represents the entire system, and E_{coh} represents the coherency strain energy arising from the lattice distortion between the matrix and deformed regions during the twinning process. Essentially, the deformation energy f represents the stored strain energy density of a local domain participating in the deformation process. Following Khachaturyan [37], the coherency strain energy is expressed by:

$$E_{\text{coh}} = \frac{1}{2} V_{\Omega} \cdot C_{ijkl} \bar{\varepsilon}_{ij} \bar{\varepsilon}_{kl} - C_{ijkl} \bar{\varepsilon}_{ij} \int_{\Omega} \varepsilon^0_{kl} dV + \frac{1}{2} \iiint \frac{d^3k}{(2\pi)^3} B(\vec{n}) |\theta(\vec{k})|^2, \tag{4}$$

where V_{Ω} denotes the volume of the entire system, $\bar{\varepsilon}_{ij}$ is the homogeneous strain representing the macroscopic shape deformation, ε^0_{ij} is the eigenstrain, $\theta(\vec{k})$is the Fourier

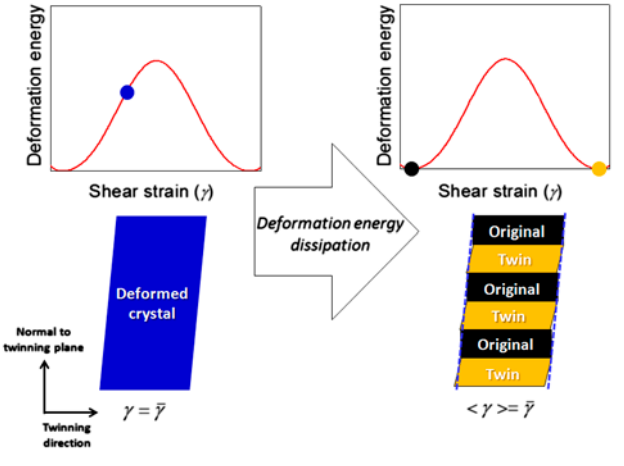

Figure 2. (colour online) Schematic diagram of the deformation twinning process from a homogeneously deformed crystal to a twinned structure driven by deformation energy dissipation.

transform of the shape function representing the domains such as deformation twins in a microstructure, and $B(\vec{n}) = C_{ijkl}\varepsilon^0_{ij}\varepsilon^0_{kl} - n_i\sigma^0_{ij}\Omega_{jl}(\vec{n})\sigma^0_{lm}n_m$ where $\sigma^0_{ij} = C_{ijkl}\varepsilon^0_{kl}$, $\Omega^{-1}_{jl} = C_{jilm}n_in_m$, and n_i denotes the unit wave vector in Fourier space. For simplicity, the elastic modulus C_{ijkl} for the coherency strain energy calculation is assumed to be homogeneous within an entire system. The deformation twinning involves simple shearing with the magnitude of γ. The eigenstrain is expressed as $\varepsilon^0_{ij} = \gamma(l_in^0_j)$ where $\vec{l}$ is the unit vector along shear direction, and $\vec{n}^0$ is the unit vector normal to the twinning plane. Plugging ε^0_{ij} into $B(\vec{n})$ and assuming that a deformation twin is an infinite platelet of infinitesimal thickness (i.e. $B(\vec{n})$ in Equation (4) becomes $B(\vec{n}^0)$), we conclude that the third term in Equation (4) is equal to zero [37]. In addition, the second term becomes constant with the constraint of the fixed deformation, i.e. $\int_\Omega \varepsilon^0_{ij}dV = V_\Omega\bar{\varepsilon}_{ij}$. This means that the contribution of the coherency strain energy to the thermodynamic stability is not significant. Therefore, the variation of the total free energy with small fluctuations is given by the following:

$$\Delta F = \int_\Omega \left[f(\eta) + \frac{\kappa_{ij}}{2}\nabla_i\eta\nabla_j\eta\right]dV - \int_\Omega f(\bar{\eta})dV. \tag{5}$$

The deformation energy can be expanded with respect to $\bar{\eta}$ up to the second-order term for the small fluctuations as $f(\eta) = f(\bar{\eta}) + (\eta-\bar{\eta})\frac{\partial f}{\partial\eta}\Big|_{\eta=\bar{\eta}} + \frac{1}{2}(\eta-\bar{\eta})^2\frac{\partial^2 f}{\partial\eta^2}\Big|_{\eta=\bar{\eta}}$. The difference in free energy per volume between the initial homogeneously deformed crystal and one with a fluctuating order parameter given by $\eta - \bar{\eta} = A\cos(\beta_i r_i)$ where A is the amplitude of the fluctuation, β_i is the components of the wave vector $\vec{k}$, and r_i is the component of the position vector $\vec{r}$ under the fixed deformation condition (or $\int_\Omega(\eta-\bar{\eta})dV = 0$ where $\bar{\eta}$ is the fixed normalized shear strain) as in [38–40] becomes

$$\frac{\Delta F}{V_\Omega} = \frac{1}{4}A^2\left[\frac{\partial^2 f}{\partial\eta^2}\Big|_{\eta=\bar{\eta}} + \kappa_{ij}\beta_i\beta_j\right], \tag{6}$$

where the second term in the bracket is positive. Therefore, the stability of the homogeneously deformed crystal can be simply determined by the second derivative of the deformation energy with respect to the order parameter (or the deformation shear strain along twinning direction on the twinning plane).

It should be noted that the second derivative of the deformation energy with respect to deformation shear strain is essentially the tangent modulus μ corresponding to the twinning direction on the twinning plane, i.e. $\mu(\eta) = \frac{\partial^2 f}{\partial\gamma^2_{(1\,1\,1)[1\,1\,\bar{2}]}} = 2\frac{\partial^2 f}{\partial\eta^2}$. The normalized tangent modulus μ^* as a function of the order parameter (normalized shear strain) is plotted in Figure 1(c). The values of tangent modulus are zero at two-order parameter values (~0.23 and ~0.77) corresponding to the inflection points of f and are negative in between. A negative tangent modulus implies the thermodynamic instability of a deformed state. Therefore, for an initial severely deformed state described by any of the order parameter values between the two inflection points are thermodynamically unstable. Using the analogy to thermodynamic instability of a binary solution with respect to composition, such a severely deformed state is unstable with respect to infinitesimal order parameter fluctuations, and the corresponding twinning process is called "spinodal twinning" analogous to "spinodal decomposition" [38–41]. The spinodal twinning concept would provide a natural explanation of spontaneous and/or homogeneous

twinning in single crystals or grain interiors observed in MD simulations [5,21,23] or experiments [42,43].

For order parameter values outside the spinodal regime, the tangent modulus is positive and an initial deformed state described by those order parameter values is metastable, i.e. it is stable with respect to small fluctuations in order parameter, but unstable with respect to large fluctuations in order parameter. Therefore, deformation twinning of such a deformed state takes place through the classical nucleation and growth mechanism.

To demonstrate the spinodal twinning mechanism or the classical nucleation and growth mechanism, we designed 'computational experiments' using the phase-field method [44–47] for deformation twinning (see Ref. [34] and Supplemental Material for details). We considered a simple controlled configuration of the computational system where other deformation modes are not allowed than twinning in order to be able to clearly show the differences in operating twinning mechanisms depending on the magnitudes of the applied shear strain. For simplicity, we performed computer simulations of twinning processes in two dimensions on the $(1\,\bar{1}\,0)$ plane with the computational cell outlined in dashed lines in Figure 3(b). In this case, there are two possible modes of twinning; one is along the $[1\,1\,\bar{2}]$ direction on the $(1\,1\,1)$ twinning plane (variant 1), and the other is along the $[\bar{1}\,\bar{1}\,\bar{2}]$ direction on the $(\bar{1}\,\bar{1}\,1)$ habit plane (variant 2). To reduce the possible discretization grid effect, we define new coordinate axes (x', y', z') along the $[0\,0\,\bar{1}]$, $[1\,1\,0]$ and $[1\,\bar{1}\,0]$ directions, respectively. Therefore, we use two-order parameter fields, η_1 and η_2, to describe the twinning process. $(\eta_1, \eta_2) = (0, 0)$, $(1, 0)$ and $(0, 1)$ represent the original crystal, twin variant 1 and twin variant 2, respectively.

Since the interfacial energy along the twin boundaries is much smaller than interfaces along other orientations, the interfacial energy between twin and original crystal is strongly anisotropic. We fitted the gradient energy coefficient using the twin boundary energy (25.4 mJ/m^2 (calculated in this work)) and the dislocation core energy ($E_{\text{core}} = 4.8 \times 10^{-7}$ mJ/m) [48–50].

We use the deformation strain tensor **D** along a twin direction on a twinning plane as the eigenstrain (ε_{ij}^0), which is directly obtained from the deformation matrix **X** in Equation (1). The symmetrized deformation strain tensor in (x, y, z) (see Figure 3(b) for the coordinate setting and Supplemental Material for the derivation) is given by $\begin{bmatrix} 0 & \gamma/2 & 0 \\ \gamma/2 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$, which can be expressed in terms of the order parameter as $\eta \cdot \begin{bmatrix} 0 & \gamma^{twin}/2 & 0 \\ \gamma^{twin}/2 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} = \eta \cdot [\varepsilon_{ij}^{twin,ref}]$ where $\varepsilon_{ij}^{twin,ref}$ is the twinning strain tensor [25] in (x, y, z) reference frame. The twinning strain tensors of variant 1 ($\varepsilon_{ij}^{twin,1}$) and 2 ($\varepsilon_{ij}^{twin,2}$) in ($x'$, y', z') are obtained by the axis transformation from (x, y, z) to (x', y', z'). Thus, the eigenstrain tensor is given by $\varepsilon_{ij}^0 = \sum_p \varepsilon_{ij}^{twin,p} H(\eta_p)$ where H is the interpolation function [34]. Elastic constants for the calculation of coherency strain energy were chosen to be $C_{11} = 176.20$ GPa, $C_{12} = 124.94$ GPa and $C_{44} = 81.77$ GPa [51].

The evolution of order parameters is assumed to be governed by the time-dependent Ginzburg–Landau (TDGL) equation [52]. In particular, the deformation twinning

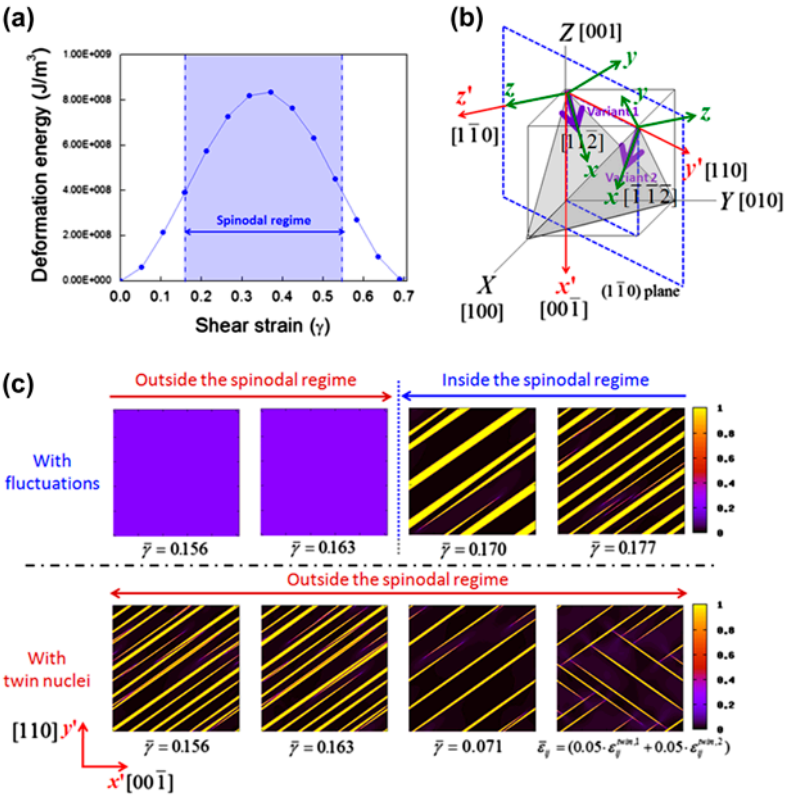

Figure 3. (colour online) (a) Spinodal twinning regimes of Cu where γ represents the shear strain along a $[1\,1\,\bar{2}]$ direction on a (1 1 1) plane. (b) system configuration for phase-field simulations and (c) order parameter profiles by phase-field simulations of deformation twinning in Cu with initial small fluctuations or randomly distributed twin nuclei where $\bar{\gamma}$ represents magnitude of the fixed macroscopic shear strain along a $[1\,1\,\bar{2}]$ direction on a (1 1 1) plane.

process was simulated under a fixed macroscopic deformation, i.e. the volume average of the eigenstrain during the entire process should be equal to the fixed homogeneous strain ($\bar{\varepsilon}_{ij}$): $\frac{1}{V}\int_\Omega \varepsilon^0_{ij} dV = \bar{\varepsilon}_{ij}$. The TDGL equation with the constraint was numerically solved by adding a penalty term [53], $\frac{1}{2}\sum_{i,j} M_{ij}(\frac{1}{V_\Omega}\int_\Omega \varepsilon^0_{ij} dV - \bar{\varepsilon}_{ij})^2$ where M_{ij} are the penalty constants to the free energy (see Ref. [34] and Supplemental Material). Following Khachaturyan's elasticity theory [37], we solved the mechanical equilibrium equation, $\nabla_j \sigma_{ij} = 0$, using Fourier spectral method [37] to obtain the elastic solution. Our current model assumes the linear and homogeneous elasticity for solving the mechanical equilibrium equation. The assumption can be relaxed by applying the nonlinear elasticity [54] and the inhomogeneous elasticity [55]. In addition, it should be noted that the model does not take into account the possible thermal effects and does not consider the possibility of dislocation slip to focus on the deformation twinning.

All the simulations were conducted in a square domain with $512\Delta x \times 512\Delta x$ grids where Δx is the grid size and was chosen as 0.2 nm with a periodic boundary condition. We normalized the parameters in the simulations: $\Delta x^* = \frac{\Delta x}{l}$, $t^* = L|\Delta f_{\max}|t$, $\kappa^*_{11} = \frac{\kappa_{11}}{l^2|\Delta f_{\max}|}$,

$\kappa_{22}^* = \frac{\kappa_{22}}{l^2|\Delta f_{\max}|}$, $C_{11}^* = \frac{C_{11}}{|\Delta f_{\max}|}$, $C_{12}^* = \frac{C_{12}}{|\Delta f_{\max}|}$ and $C_{44}^* = \frac{C_{44}}{|\Delta f_{\max}|}$. The characteristic length (l) is chosen to be the same as Δx, the maximum driving force ($|\Delta f_{\max}|$) is obtained from the deformation energy, and L is the kinetic coefficient of the TDGL equation.

The simulations started with a homogeneously deformed state ($\forall(\eta_1, \eta_2) = (\alpha, \beta)$), and the applied macroscopic strain ($\bar{\varepsilon}_{ij}$) as a mechanical boundary condition is equal to $(\alpha \cdot \varepsilon_{ij}^{twin,1} + \beta \cdot \varepsilon_{ij}^{twin,2})$ where $\varepsilon_{ij}^{twin,1}$ and $\varepsilon_{ij}^{twin,2}$ are the twinning strain tensors of twin variant 1 and 2 as defined in Supplemental Material. The α and β can be any value between 0 and 1 to describe the initial deformation state. First of all, we chose several magnitudes of macroscopic shear strain ($\bar{\gamma}$) along $[1\,1\,\bar{2}]$ direction on a (1 1 1) plane, i.e. the initial condition of order parameter was $\forall(\eta_1, \eta_2) = (\alpha, 0)$ with small order parameter fluctuations (−0.0025~0.0025).

The first row of Figure 3(c) shows the simulation results with shear strain magnitudes near the twining spinodal in Figure 3(a). It should be noted that such large shear strains can be experimentally achieved. For instance, the equal channel angular pressing technique enables quite large shear strains (~1.0) of Cu [56]. Therefore, shear strain magnitudes within the range can be applicable to the shear deformation of fcc Cu. For shear strains inside the spinodal ($\bar{\gamma} = 0.170$ ($\bar{\eta} = 0.24$), or 0.177 ($\bar{\eta} = 0.25$)), deformation twinning occurs spontaneously with initial, small order parameter fluctuations. However, outside the spinodal regime ($\bar{\gamma} = 0.156$ ($\bar{\eta} = 0.22$) or 0.163 ($\bar{\eta} = 0.23$)), the homogeneous deformed state is maintained under the small order parameter fluctuations owing to its metastability, i.e. twinning requires explicit nucleation and growth.

To model the nucleation and growth mechanism at smaller deformation, we randomly distributed twin nuclei. We assumed a nucleus to be a stack of a few planar faults with very large aspect ratio (length/thickness) [16,19,25], i.e. we chose a layer with thickness $3\Delta x$ as a nucleus. The second row of Figure 3(c) shows examples of twin structure formation via the nucleation and growth mechanism. Lengthening and thickening of twins take place under small macroscopic strains outside the spinodal regime, which results in a twinned structure that is close metastable equilibrium as additional simulation steps did not significantly change the twin microstructure. Our simulation results convincingly show that deformation twins may be formed by completely different mechanisms, i.e. spinodal or nucleation and growth, depending on the deformation strain state of a crystal.

In summary, we proposed the possibility of spinodal mechanism with respect to a shear strain for deformation twinning analogous to spinodal decomposition of a binary solution with respect to a composition through the thermodynamic analysis of the deformation energy landscape of a homogeneously deformed crystal computed by first-principles calculations. The twinning process occurs continuously without having to overcome a nucleation barrier due to thermodynamic instability of a deformed state with respect to twinning at large shear deformation inside the spinodal regime ($\frac{\partial^2 f}{\partial \eta^2} < 0$). On the other hand, twining can only take place through the nucleation and growth mechanism, which requires overcoming a nucleation barrier at small shear deformation outside the spinodal regime ($\frac{\partial^2 f}{\partial \eta^2} > 0$). The proposed mechanism was demonstrated using phase-field simulations. The spinodal twinning mechanism provides a more plausible interpretation of twinning in a severely deformed crystal. We show that the thermodynamics of spinodal twinning, with deformation strain as a globally conserved order parameter, bears a strong similarity to classical spinodal decomposition described by a composition that is both locally and globally conserved. Therefore, spinodal

mechanism is a much more common mechanism that may be responsible for a wide variety of physical processes in nonequilibrium systems in addition to spinodal phase separation.

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Supplemental material

Supplemental material for this article can be accessed here http://dx.doi.10.1080/14786435.2013.868946.

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