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# Pretransitional Effects at Structural Phase Transitions

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Heterogeneous coexistence of high- and low-temperature phases has been observed around structural phase transitions. We find that such intermediate states result from a cubic coupling term of the form $e_1\psi^2$ in the free energy, with which the dilation strain $e_1$ can modify the effective temperature for the order parameter (tetragonal strain) $\psi$. We show that $e_1$ is asymmetrically induced in the high- and low-temperature phases, leading to elastic stabilization of tetragonally strained domains coherently embedded in the disordered matrix.

KEYWORDS: structural phase transition, martensitic transition, pretransitional effects, pattern formation in solids

## §1. Introduction

In a number of metallic alloys near structural phase transitions, distinct domains (or *embryos*) with low-temperature tetragonal symmetry have been detected in a high-temperature cubic phase.[1-6] They have been observed as *tweed patterns* by electron microscopy, anomalous increase of internal friction, or the central peak by neutron scattering. These pretransitional (or premartensitic) effects are very unusual, but ubiquitous and can sometimes be seen hundreds of degrees above the transition temperature at which the cubic phase disappears. On the other hand, in usual fluid systems, droplets of a new phase cannot emerge above their first-order transition temperature and those below it continuously grow once their sizes exceed the critical radius. Kartha *et al.*[7] have ascribed the origin of the tweed patterns to quenched disorder imposed by the compositional randomness, which is considered to strongly perturb the order parameter fluctuations. However, impurity mechanisms can only lead to fuzzy inhomogeneous lattice distortions above the nominal transition temperature. On the other hand, to explain distinctly discernible tetragonal embryos, Yamada and coworkers[5,8] sought an intrinsic mechanism stemming from anharmonic elasticity. However, their analysis was based on one-dimensional space dependence and provided only limited results.

In this letter we will further examine whether or not anharmonic elasticity can produce and freeze tetragonal domains in a disordered matrix. We will present some analytic and numerical results in two dimensions (2D), where we consider a square-rectangle structural phase transition. The low temperature phase, which will be called the tetragonal phase, consists of two variants elongated in the $x$ and $y$ directions.

## §2. Cubic Interaction at the Square-Rectangle Transition

We consider martensitic materials in which the elastic constant $C' = (C_{11} - C_{12})/2$ against [110] sounds becomes small towards the transition as[4,6]

$$C' = A_T(T - T_0). \tag{1}$$

With this softening effect in mind, some authors developed a Ginzburg-Landau theory in which the order parameter is the strain field,[7,9,10]

$$\psi = \nabla_x u_x - \nabla_y u_y. \tag{2}$$

Hereafter, $\nabla_x \equiv \partial/\partial x$ and $\nabla_y \equiv \partial/\partial y$. In 2D the other strain fields are expressed by

$$e_1 = \nabla_x u_x + \nabla_y u_y, \quad e_3 = \nabla_y u_x + \nabla_x u_y. \tag{3}$$

In a dimensionless form the elastic free energy density may be assumed to be given by

$$f = \frac{\gamma_1}{2}e_1^2 + \frac{\gamma_3}{2}e_3^2 + \frac{\tau}{2}\psi^2 - \frac{1}{4}\psi^4 + \frac{1}{6}\psi^6 + |\nabla\psi|^2. \tag{4}$$

Here we measure the lengths, the strains, and the free energy density in appropriate units of $\ell_0$, $e_0$, and $f_0$. Then $C' = \tau f_0/e_0^2$, while $B = \gamma_1 f_0/e_0^2$ and $C_{44} = \gamma_3 f_0/e_0^2$ are the bulk and shear moduli assumed to be constants. To describe the first-order phase transition we have added the 4-th and 6-th order terms and the gradient free energy in (4). Without the first two terms in (4) we have a disordered phase ($\psi = 0$) for $\tau > \tau_{c0} = 3/16$ and an ordered phase for $\tau < \tau_{c0}$ in equilibrium. At $\tau = \tau_{c0}$ the free energy takes the same value in the disordered and ordered ($\psi = \pm(3/4)^{1/2}$) phases. The unit strain $e_0$ is then the typical strain in the ordered phase just below the transition. The role of the first two terms in (4) is to stabilize a *twin structure* for $\tau < \tau_{c0}$ in which the two variants of the ordered phase appear alternately in the [1, 1] or [1, $\bar{1}$] direction. This can be understood if the elastic field is expressed in terms of the order parameter fluctuations.[7,11] See also the sentence below (14).

In the literature, however, no adequate examination has yet been made on the possible effect of a cubic term $\sim e_1\psi^2$, although its presence is obvious. Fuchizaki and Yamada[8] included this term in their theory, but they incorrectly treated $e_1$ and $\psi$ as independent variables. This term can arise from the fact that $C' = C'(T, \rho)$ should sensitively depend on the lattice constant or the density $\rho$. Because the density deviation $\delta\rho$ is related to $e_1$ as $\delta\rho/\rho = -e_1$ we obtain

$$C' = A_T(T - T_0) - C_1' e_1. \quad (5)$$

Hence there arises a cubic coupling term in the free energy,

$$f_3 = -\alpha e_1 \psi^2, \quad (6)$$

where $\alpha = C_1' e_0^3/2f_0 = \gamma_1 e_0 C_1'/2B$ in dimensionless units. We may assume $\alpha > 0$ without loss of generality because the total free energy density $f + f_3$ is invariant with respect to the changes $\alpha \to -\alpha$ and $\boldsymbol{u} \to -\boldsymbol{u}$. The stress tensor $\sigma_{ij}$ is written as

$$\begin{aligned} \sigma_{xx} &= \gamma_1 e_1 - \alpha\psi^2 + \mu, \\ \sigma_{yy} &= \gamma_1 e_1 - \alpha\psi^2 - \mu, \\ \sigma_{xy} &= \gamma_3 e_3, \end{aligned} \quad (7)$$

where

$$\mu = (\tau - 2\alpha e_1 - 2\nabla^2)\psi - \psi^3 + \psi^5. \quad (8)$$

In the tetragonal phase, we thus have $e_1 = (\alpha/\gamma_1)\psi^2$ and $\mu = 0$ under the stress-free boundary condition. The former condition becomes $\nabla_x u_x + \nabla_y u_y = (\alpha/\gamma_1)e_0\psi^2$ in the original units and may be used to determine the magnitude of $\alpha$. The dilation strain is smaller than $e_0$ under most conditions, so we will assume $\alpha/\gamma_1 \lesssim 1$.

In the following we will investigate the effect of this cubic term. Because $u_x$ and $u_y$ are fundamental variables, the three fields $e_1$, $e_3$, and $\psi$ are related by

$$\nabla^2 e_1 - 2\nabla_x\nabla_y e_3 = (\nabla_x^2 - \nabla_y^2)\psi, \quad (9)$$

which readily follows from definitions (2) and (3). To obtain the equilibrium state, we then eliminate the subsidiary fields $e_1$ and $e_3$ by minimizing the space integral of

$$\bar{f} = f + f_3 + \lambda\left[\nabla^2 e_1 - 2\nabla_x\nabla_y e_3 - (\nabla_x^2 - \nabla_y^2)e_2\right], \quad (10)$$

with $\psi$ held fixed and $\lambda = \lambda(x, y)$ being a Lagrange multiplier.[7] Then $\partial(f + f_3)/\partial e_1 = -\nabla^2\lambda$ and $\partial(f + f_3)/\partial e_3 = 2\nabla_x\nabla_y\lambda$. Using the operator,

$$\mathcal{L} = \nabla^4 + 4(\gamma_1/\gamma_3)\nabla_x^2\nabla_y^2, \quad (11)$$

we eliminate $\lambda$ to obtain

$$\mathcal{L}e_1 = \nabla^2(\nabla_x^2 - \nabla_y^2)\psi - (4\alpha/\gamma_3)\nabla_x^2\nabla_y^2\psi^2, \quad (12)$$

$$\mathcal{L}e_3 = -(2/\gamma_3)[\gamma_1(\nabla_x^2 - \nabla_y^2)\psi + \alpha\nabla^2\psi^2]. \quad (13)$$

The free energy contribution

$$\Delta F = \int d\boldsymbol{r}\left[\frac{1}{2}(\gamma_1 e_1^2 + \gamma_3 e_3^2) - \alpha e_1\psi^2\right], \quad (14)$$

can then be expressed in terms of $\psi$, but in a very complicated form. Note that if $\alpha = 0$, $\Delta F$ is nonnegative-definite and vanishes for inhomogeneities satisfying $(\nabla_x^2 - \nabla_y^2)\psi = 0$ or varying in the $[1, 1]$ and $[1, \bar{1}]$ directions. A twin structure is thus selected.

If $\alpha > 0$, $\Delta F$ can be negative with appearance of domains. To illustrate the essence of the problem in the simplest manner, we write the expression in the limit $\gamma_3 \gg \gamma_1$ as

$$\Delta F = \int d\boldsymbol{r}\left[\frac{1}{2}\gamma_1\tilde{e}_1^2 - \alpha\tilde{e}_1\psi^2\right], \quad (15)$$

where $\tilde{e}_1$ is the solution of the equation,

$$\nabla^2\tilde{e}_1 = (\nabla_x^2 - \nabla_y^2)\psi. \quad (16)$$

In this limit (11)–(13) give $e_3 = O(\gamma_1/\gamma_3) \cong 0$ and $e_1 = \tilde{e}_1 + O(\gamma_1/\gamma_3)$. We can see that $\tilde{e}_1 \cong \pm\psi$ if $\psi$ varies in the $x$ or $y$ direction much more rapidly than in the other direction. As an example, we consider an ellipse making an angle of $\varphi$ with respect to the $x$ axis. It is represented by $x'^2/a^2 + y'^2/b^2 = 1$ with $x' = x\cos\varphi - y\sin\varphi$ and $y' = x\sin\varphi + y\cos\varphi$. If $\psi = \psi_e = const.$ inside it and $\psi = 0$ outside it, solving (16) is a problem of electrostatics.[12] We simply obtain $\nabla^{-2}\psi = (bx'^2 + ay'^2)\psi_e/2(a + b)$ and $\tilde{e}_1 = g\psi_e$ within the ellipse. Here $g$ is a geometrical factor given by

$$g = \frac{b - a}{a + b}\cos(2\varphi), \quad (17)$$

which is in the region $-1 \le g \le 1$. Thus, the free energy arising from the deformation of $e_1$ is

$$\Delta F = (\pi ab)\psi_e^2(\frac{1}{2}\gamma_1 g^2 - \alpha g\psi_e). \quad (18)$$

We first vary $g$ with the area $\pi ab$ and $\psi_e$ held fixed. Then, for $\alpha|\psi_e| < \gamma_1$, the minimum of $\Delta F$ is negative as

$$(\Delta F)_{min} = -(\pi ab)\frac{\alpha^2}{2\gamma_1}\psi_e^4 < 0, \quad (19)$$

at $g = \alpha\psi_e/\gamma_1 < 1$. Furthermore, to decrease the surface energy arising from the gradient term in $f$, we should require the smallest perimeter length at a fixed area to obtain $\theta = 0$ and

$$(b - a)/(a + b) = \alpha\psi_e/\gamma_1. \quad (20)$$

Thus, for $\psi_e > 0$ the domain is elongated in the $y$ direction, while for $\psi_e < 0$ it is elongated in the $x$ direction. On the other hand, for $\alpha|\psi_e| > \gamma_1$, $\Delta F$ decreases as $g \to 1$ (for which $b \gg a$ and $\theta = 0$) and

$$(\Delta F)_{min} = (\pi ab)\psi_e^2(\frac{1}{2}\gamma_1 - \alpha\psi_e) < 0. \quad (21)$$

Here, the elastic deformations outside the ellpse are neglected, but they trigger birth of other tetragonal domains as evidenced in our simulation below. Thus the assumption of a single domain is very insufficient.

Nevertheless, the above results indicate that tetragonal regions and disordered regions can coexist (or be mixed) even for $\tau > \tau_c$, if volume changes are induced such that $\alpha e_1 > 0$ within the domains and $\alpha e_1 < 0$ in the matrix. In this way the effective reduced temperature $\tau - 2\alpha e_1$ in (10) (or the elastic constant $C'$ in (5)) is decreased within the tetragonal regions. Here, if $\alpha/\gamma_1 \lesssim 1$, $e_1$ can be at most on the order of $\alpha/\gamma_1$ as suggested by the example of elliptic domains, where we assume $\psi \sim 1$ in the ordered phase. Thus, for $\alpha/\gamma^1 \lesssim 1$ the width of the temperature region in which the intermediate states are stable is estimated as

$$\Delta\tau \sim \alpha^2/\gamma_1 \quad \text{or} \quad \Delta T \sim (e_0 C_1')^2/A_T B, \tag{22}$$

where $B$ is the bulk modulus and $A_T$ and $C_1'$ are defined in (5). The effects of the cubic coupling on the first-order phase transition become drastic for $\alpha^2 \gtrsim \gamma_1$ under $\alpha \lesssim \gamma_1$.

## §3. Computer Simulation

Elastic disturbances are propagated on the acoustic time scale throughout the system. The proper dynamic equation then becomes[13)]

$$\frac{\partial^2}{\partial t^2}\boldsymbol{u} - \zeta\nabla^2\frac{\partial}{\partial t}\boldsymbol{u} = -\frac{\delta}{\delta\boldsymbol{u}}F = \nabla\cdot\overleftrightarrow{\boldsymbol{\sigma}}, \tag{23}$$

where $\zeta$ is the bulk viscosity and is assumed to be isotropic, and $F$ is the total elastic free energy or the space integral of the free energy density $f + f_3$. In this letter, we instead solve a simpler dynamic equation,

$$\frac{\partial}{\partial t}\boldsymbol{u} = -L\frac{\delta}{\delta\boldsymbol{u}}F. \tag{24}$$

This is allowable at least if we are interested in nearly steady states in which the system is in equilibrium or metastable. For simplicity, we set $\gamma_1 = \gamma_3 = 1/L$ to obtain

$$\frac{\partial}{\partial t}u_x = \nabla_x[e_1 - (\alpha/\gamma_1)\psi^2] + \nabla_y e_3 + \gamma_1^{-1}\nabla_x\mu, \tag{25}$$

$$\frac{\partial}{\partial t}u_y = \nabla_y[e_1 - (\alpha/\gamma_1)\psi^2] + \nabla_x e_3 - \gamma_1^{-1}\nabla_y\mu, \tag{26}$$

where $\mu$ is given by (8). These equations are integrated with the Euler scheme on a $128 \times 128$ lattice with the mesh sizes $\Delta t = 0.05$ and $\Delta x = 1$. In the following we preent some representative results.

First, at $t = 0$, we prepare a spherical domain with radius 15 within which $\psi \cong 1$ and outside of which $\psi \cong 0$. Here $\gamma_1 = 4$, $\alpha = 2$, and $\tau = 0.25 > \tau_c$. Subsequent time evolutions of $\psi$ and $e_1$ are shown in Fig. 1 at $t = 363$ in (a), $t = 824$ in (b), and $t = 15383$ in (c). The domain is soon deformed into an ellipse and elastically expanded ($e_1 > 0$ since $\alpha > 0$). Then the neighborhoods of the tips of the ellipse also become elastically expanded, which generates new elliptical domains with the opposite sign of $\psi$. This successive generation of domains proceeds eventually resulting in a nearly frozen configuration given in (c), where the tetragonal regions are lozenges.

Second, nearly steady patterns of $\psi$ and $e_1$ are displayed in Fig. 2. As the initial condition, $u_x$ and $u_y$ are random numbers in the range $[-0.05, 0.05]$ at each lattice point. Rounded ellipses appear for $\gamma_1 \sim 1$, as shown in (a) at $t = 3957$ with $\gamma_1 = 2$, $\alpha = 1$, and $\tau = 0$. However, with increasing $\gamma_1$, tetragonal regions tend to become lozenges with edges. In (b) a tweed pattern can be seen where $t = 13000$ at $\tau = 0$, $\gamma_1 = 8$, and $\alpha = 2$. In (c) even small lozenges have long life times where $t = 21933$ with $\gamma_1 = 8$, $\alpha = 4$, and $\tau = -1$. For large $\gamma_1$ (large bulk modulus) lozenges are under strong elastic constraints and their sizes are not equalized even after long times. See the top figures of Fig. 3 for another nearly steady situation.

Third, we follow a transformation process of a tweed pattern into a twin structure in Fig. 3, where $\tau = 0.3$,

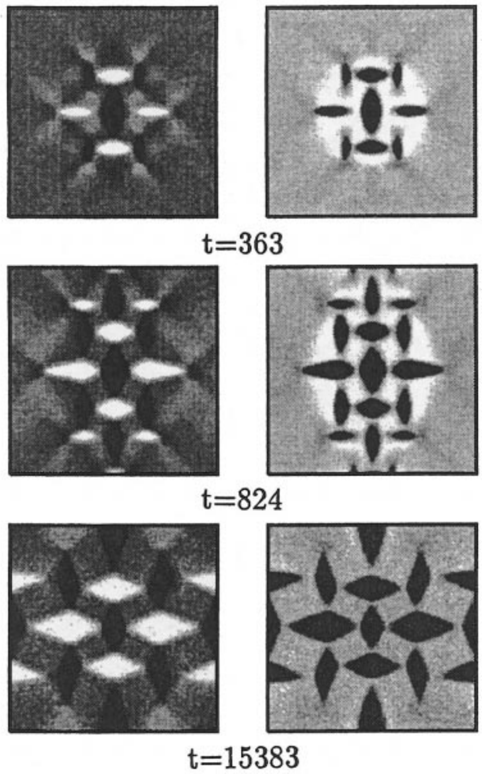


Fig. 1. Time evolution of $\psi$ on the left and $e_1$ on the right starting with a spherical droplet at $t = 0$. Elliptical domains (in black at $\psi \sim 1.5$ and in white at $\psi \sim -1.5$) are then successively created, while the gray regions remain in the disordered phase ($\psi \sim 0$). Note that $e_1$ is positive (in black) in the two variants of the tetragonal regions.

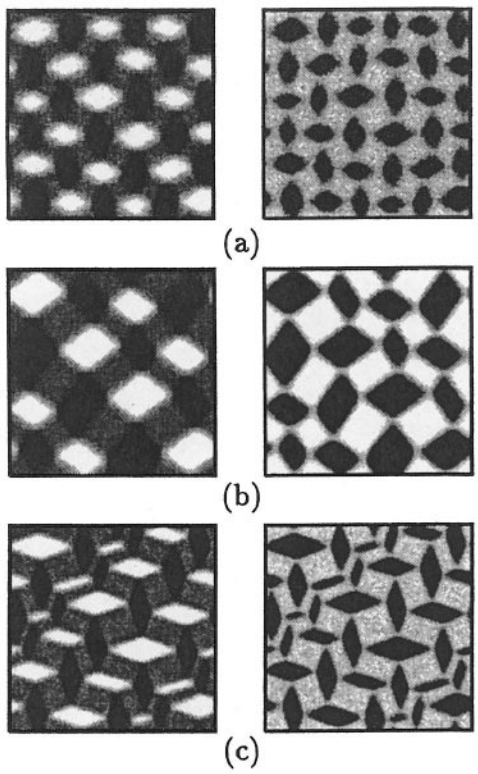


Fig. 2. Nearly steady patterns of $\psi$ on the left and $e_1$ on the right exhibiting coexistence of the two tetragonal variants (in black and white on the left) and the disordered regions (in gray). (a) $t = 3957$, $\tau = 0$, $\gamma_1 = 2$, and $\alpha = 1$. (b) $t = 13000$, $\tau = 0$, $\gamma_1 = 8$, and $\alpha = 2$. (c) $t = 21933$, $\tau = -1$, $\gamma_1 = 8$, and $\alpha = 4$.

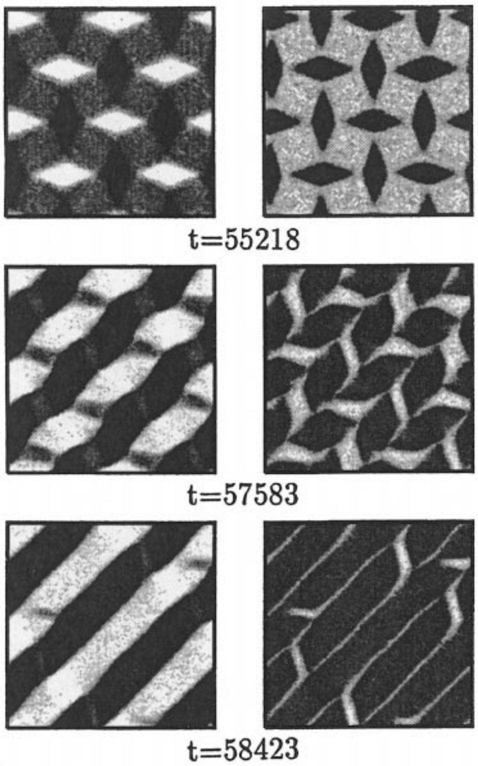


Fig. 3. Formation of a twin structure from an intermediate state at $\gamma_1 = 4$ and $\alpha = 2$. The $\psi$ patterns are on the left and those of $e_1$ are on the right. At $t = 55218$ (the top figures) $\tau$ is changed from 0.3 to $-2$. The middle figures show transient patterns at $t = 57583$. The bottom figures represent a twin structure at $t = 58423$.

$\gamma_1 = 4$, and $\alpha = 2$. The upper patterns have been stable until $t = 55218$, at which $\tau$ is suddenly decreased to $-2$. Then the intermediate state is destabilized. Subsequent snapshots are shown at $t = 57583$ in (b) and $t = 58423$ in (c).

We have numerically realized three kinds of states: disordered states with $\psi \cong 0$, intermediate states illustrated in Fig. 2, and ordered states with twin structures. With varying $\tau$ these states become either stable, metastable, or unstable. In particular, metastability effects are conspicuous because elasticity prefers special morphologies. For example, if we start with a disordered phase, we can realize intermediate states with $\tau > 0$ first by decreasing $\tau$ to a negative value to create considerable fluctuations and then by raising $\tau$ to a positive value.

## §4. Remarks

1) We have shown that the cubic coupling $\sim e_1\psi^2$ can lead to a vast variety of patterns depending on $\tau$, $\gamma_1$, $\alpha$, and the initial conditions. We can see that there can be numerous metastable configurations in which domains of the low-temperature phase are coherently embedded in the disordered phase. Here, volume changes are asymmetric between the high- and low-temperature phases and are highly cooperative.

2) The domain pinning here is very similar to pinning in phase-separating binary alloys in which the order parameter is the composition $c$ and the shear modulus depends on $c$ (the elastic misfit effect).[14,15] In the latter case the free energy has a cubic coupling term of the form $\sim \delta c e_3^2 \sim e_1 e_3^2$, where the dilation strain $e_1$ is linearly related to the composition deviation $\delta c$, and $e_3$ is the shear strain (3). Due to this coupling, shear deformation is asymmetrically induced in softer and harder regions, which serves to pin the domain structure.

3) Elastic deformations in 2D and 3D can be very different. In the 3D cubic-tetragonal transition we have two equivalent strain fields, $u_2 \equiv (\partial u_x/\partial x - \partial u_y/\partial y)/\sqrt{2}$ and $u_3 \equiv (2\partial u_z/\partial z - \partial u_x/\partial x - \partial u_y/\partial y)/\sqrt{6}$. They give rise to a cubic form $\sim u_3^3 - 3u_2^2 u_3$ in the free energy.[5,9] We should examine the role of this cubic term in the transition as well as the role of the cubic coupling $\sim (\nabla \cdot \boldsymbol{u})(u_2^2 + u_3^2)$. Thus, 3D simulations with various elastic couplings are strongly needed and very promising.

4) In this letter the tetragonal strain is taken as the order parameter, but in other Ginzburg-Landau schemes, another variable such as electric polarization, has been chosen as the order parameter $\psi$. In the latter cases, we need the proper coupling $e_2\psi$ to induce the phonon softening and $e_1\psi^2$ to achieve the intermediate state reported in this paper.


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