Antiphase structures of an improper ferroelastic phase transition driven by an M$_5^+$ zone boundary phonon in RAg$_{1-x}$In$_x$

Wenwu Cao, 1,* Avadh Saxena, 2,† and Dorian M. Hatch 3,‡

1Materials Research Laboratory, The Pennsylvania State University, University Park, Pennsylvania 16802
2Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545
3Department of Physics, Brigham Young University, Provo, Utah 84602

(Received 12 October 1999; revised manuscript received 21 February 2001; published 21 June 2001)

Rare-earth alloys RAg$_{1-x}$In$_x$ (where R = La, Ce, and Pr) are improper ferroelastic materials with the CsCl structure. A weakly first-order phase transition occurs with the softening of a zone-edge M$_5^+$ mode that drives the material from a cubic phase to a tetragonal phase. Based on Ginzburg-Landau theory, we utilize the complete free-energy density, constructed from a six-dimensional primary order parameter (shuffle) that couples to strain, to study domain formation. The model allows the study of complex antiphase structures that appear in this cubic-to-tetragonal phase transition. With the help of numerical techniques, the order-parameter profiles across antiphase boundaries of different orientations and their temperature dependence are calculated. We find a single set of two coupled dimensionless governing equations, which are applicable to order-parameter profiles across all antiphase boundaries for this transition.

DOI: 10.1103/PhysRevB.64.024106 PACS number(s): 64.70.Kb, 02.20.-a, 61.50.Ah, 61.50.Ks

I. INTRODUCTION

Landau theory was originally developed for a second-order phase transition for which the amplitude of the soft-mode phonon becomes dominant near the phase-transition temperature. 1 This expansion method of using only the amplitude of the dominant mode is also applicable to the case of a weakly first-order phase transition. 2,3 To account for the inhomogeneous structures that occur as a result of the phase transition, an energy term associated with order-parameter (OP) gradients was introduced, which is often called the Ginzburg term. 4 The simple formulation of Ginzburg-Landau (GL) theory has proven to be successful for the description of many phase transitions and inhomogeneous structures, such as domains, domain walls, and interfaces. 5 In most of the cases reported in the literature, simplified one- or two-dimensional models are often used that, although easy to solve mathematically, often miss many interesting physical phenomena associated with the phase transition, such as possible lower symmetry phases and antiphase structures, which are of particular interest here.

As a general rule, the formulation of the GL free energy should be based on the symmetry relations between the parent and product phases. There are two routes of constructing the GL theory and they differ in the method of selection of the basis for the order parameter. The lattice-dynamical approach follows the idea of using the modes obtained from the diagonalization of the dynamical matrix. The amplitudes or phase angles of the relevant modes are chosen as the order parameter to describe the phase transition. 6–11 Another equivalent and convenient approach is to generate the free energy and the displacement modes from the basis vectors of irreducible representations of the space group of the parent phase. The OP then has its foundation in the symmetry relationship between the parent and product phases and the associated representation that induces the symmetry change. 12,13 It has been shown that the two formulations are equivalent and can be converted from one to the other by a rotation of basis within OP space. 14 In this paper, we use the lattice-dynamical formulation, which was also checked against the group-theoretical approach using the program ISOTROPY. 15

The soft phonon mode in La(AG$_{1-x}$In$_x$) ($x = 0.2$) has been measured by several groups. 16–18 Specifically, the transverse acoustic (TA) phonon mode of the parent phase with wave vector $k = [1,1,0]$ ($\pi/a$) and polarization in the $[110]$ direction softens as the transition temperature is approached from above. This TA mode is degenerate with the longitudinal acoustic (LA) mode with wave vector $k = [1,1,0]$ ($\pi/a$) and polarization in $[110]$. By comparing the softening of the shear modulus $C' = (C_{11} - C_{12})/2$ and temperature dependence of other elastic constants with the TA mode softening, the conclusion is reached that the atomic shuffles are the primary cause for the transformation and the strains play a secondary role. Any softening of elastic moduli is a result of anharmonic coupling of the primary OP to the strains.

In the next section, we present the details of the free energy in terms of a six-component shuffle order parameter. We incorporate coupling of the primary OP with the strain as well as the Ginzburg (nonlocal gradient) terms. Section III describes the homogeneous solutions. In Sec. IV, the general procedure is developed for using a phonon mode order parameter in more than three dimensions (a six-component “vector”) to describe antiphase microstructures. We present the various antiphase boundary solutions. A single set of coupled nonlinear equations that provide OP profiles for all possible antiphase domain relationships for this transition are obtained. Section V contains a brief discussion and connection to experimental data in order to determine the parameters of the Ginzburg-Landau model. Finally, we summarize the main results in Sec. VI.
II. GINZBURG-LANDAU FREE ENERGY

The materials of interest here, $R\text{Ag}_{1-x}\text{In}_x$ ($R=$La, Ce, Pr), have the CsCl structure (space group $O_h^1, Pm\overline{3}m$) with two atoms per unit cell in the cubic phase and undergo an improper ferroelastic transition to a tetragonally distorted phase (space group $D_{4h}^{17}, I4/mmm$) with primitive cell quadrupling. Using lattice dynamics, one can derive the six degenerate eigenvectors which correspond to the $M^5$ mode.\(^{14}\)

We denote the equilibrium atomic positions by $x(1\kappa) = x(l) + x(\kappa)$, where $x(l) = l_a, l_b, l_c$ and $x(\kappa) = (1/2)(\kappa - 1)(a + b + c)$. Here, $l_a = \text{integer} (\alpha = x, y, z)$, and labels the origin of the $l$th unit cell in multiples of the lattice constant $a$; $\kappa = 1, 2$ denotes the two sublattices of the CsCl structure; $a = a\hat{x}, b = a\hat{y},$ and $c = a\hat{z}$ are the crystallographic axes of the primitive cubic lattice. For periodic boundary conditions, all atomic displacements $u(\kappa | k)$ from the equilibrium positions may be expanded in a Fourier series with respect to the normal coordinates $Q(k\lambda)$ according to

$$u_\alpha(1\kappa) = \frac{1}{\sqrt{N M_\kappa}} \sum_{k\lambda} e_\alpha(\kappa | k\lambda) e^{i k \cdot x(l)} Q(k\lambda),$$

where $M_\kappa (\kappa = 1, 2)$ denotes the masses of the two types of atoms and the sum is extended over all wave vectors $k$ of the first Brillouin zone and over all branches $\lambda (= 1, 2, \ldots, 6)$ for the CsCl structure (of the associated phonon-dispersion curves. The expansion coefficients $e_\alpha(\kappa | k\lambda)$ are the eigenvectors of the dynamical matrix. Thus, from the orthonormality of $e_\alpha(\kappa | k\lambda)$,

$$Q(k\lambda) = \frac{1}{\sqrt{N}} \sum_{\alpha l \kappa} \sqrt{M_\kappa} e_\alpha(\kappa | k\lambda) u_\alpha(1\kappa) e^{-i k \cdot x(l)}.$$

The primary OP driving the transition here is a softening $M^5$ phonon mode and consists of the set of normal mode coordinates $Q = (Q_1, Q_2, Q_3, Q_4, Q_5, Q_6)$ that belong to the star of the wave vector $k$ at the $M$ point. The $k_M$ star has three arms and the mode corresponding to each arm of the star has twofold degeneracy. The $Q_j$’s are given by

$$Q_1 = \sum_{L=1}^{8} [u_0 u_y(L) + v_0 v_z(L)] (-1)^{i_1 + i_2},$$

$$Q_2 = \sum_{L=1}^{8} [u_0 u_y(L) + v_0 v_z(L)] (-1)^{i_2 + i_3},$$

$$Q_3 = \sum_{L=1}^{8} [u_0 u_y(L) + v_0 v_z(L)] (-1)^{i_3 + i_4},$$

$$Q_4 = \sum_{L=1}^{8} [u_0 u_y(L) + v_0 v_z(L)] (-1)^{i_4 + i_5},$$

$$Q_5 = \sum_{L=1}^{8} [u_0 u_y(L) + v_0 v_z(L)] (-1)^{i_5 + i_6},$$

$$Q_6 = \sum_{L=1}^{8} [u_0 u_y(L) + v_0 v_z(L)] (-1)^{i_6 + i_1},$$

where the parameter $\zeta$ depends on the interatomic force constants of the relevant mode, and $M_1$ and $M_2$ denote the masses of the two types of atoms (In$_{1-x}$Ag$_x$ and La, respectively, and the summation is over eight parent primitive unit cells $2 \times 2 \times 2$ labeled by $L$ which make up the supercell required by $M^5$ (see Fig. 1). Furthermore,

$$u_0 = \sqrt{\frac{M_1}{8}} u_1, \quad v_0 = \sqrt{\frac{M_2}{8}} v_1;$$

$$u_1 = -\sqrt{\frac{M_1}{M_1 + \zeta^2 M_2}}, \quad v_1 = \sqrt{\frac{\zeta^2 M_2}{M_1 + \zeta^2 M_2}},$$

where the parameter $\zeta$ depends on the interatomic force constants of the relevant mode, and $M_1$ and $M_2$ denote the masses of the two types of atoms (In$_{1-x}$Ag$_x$ and La) in the unit cell (see Fig. 1). The quantities $u_1$ and $v_1$ appear in Eq. (10) below (Sec. III) where atomic displacements are expressed in terms of the normal mode amplitudes $Q_j$.

Using the above six eigenvectors and the $O_h^1$ space group symmetry operations, the total GL free-energy density can be written in the following form:\(^{15}\)

$$F = F_L + F_e + F_G,$$

where the Landau free energy, $F_L$, contains the primary OP contributions from the $M^5$ normal mode coordinates,
The gradient $F_o$ contains the secondary OP elastic contribution [see the definitions of the strains in Eqs. (4a)–(4f) below],

$$F_{el} = \frac{\hat{c}_{11}}{2} e_{11}^2 + \frac{\hat{c}_{22}}{2} (e_{22}^2 + e_{55}^2) + \frac{\hat{c}_{44}}{2} (e_{11}^2 + e_{22}^2 + e_{55}^2). \tag{3b}$$

$F_c$ contains terms that couple the phonon modes with the elastic strains,

$$F_c = D_1 e_1 (Q_1^2 + Q_2^2 + Q_3^2 + Q_4^2 + Q_5^2 + Q_6^2)
+ D_2 \sqrt{3} e_2 (Q_1^2 + Q_6^2 - Q_3^2 - Q_4^2)
+ e_3 (Q_1^2 + Q_2^2 + Q_3^2 + Q_4^2 - 2Q_1^2 - 2Q_5^2)
+ D_3 \sqrt{3} e_3 (Q_1^2 - Q_5^2 - Q_2^2)
+ D_4 (e_4 Q_4 Q_6 + e_5 Q_3 Q_4 + e_6 Q_1 Q_2). \tag{3c}$$

The gradient (or Ginzburg) energy $F_G$, with a subscript preceding by a comma denoting partial differentiation, is given by $^{19}$

$$F_G = g_1 (Q_{4x}^2 + Q_{3z}^2 + Q_{1x}^2 + Q_{2y}^2 + Q_{3y}^2 + Q_{5z}^2)
+ g_2 (Q_{4x}^2 + Q_{4z}^2 + Q_{2x}^2 + Q_{4y}^2 + Q_{6y}^2 + Q_{5z}^2)
+ g_3 (Q_{4x}^2 + Q_{5z}^2 + Q_{3y}^2 + Q_{5x}^2 + Q_{6x}^2)
+ g_4 (Q_{3x} Q_{4z} + Q_{2y} Q_{6y} + Q_{5x} Q_{6z})
+ g_5 (Q_{3x} Q_{4z} + Q_{1y} Q_{6y} + Q_{5x} Q_{6z}). \tag{3d}$$

The OP gradient terms describe the generalized “exchange” interaction between neighboring domains in a material with spatially varying OP.

The symmetry-adapted strain tensor components $e_i$ are defined in terms of the conventional (geometrically linear) strain $e_{ij} = \frac{1}{2} [(\partial u_i / \partial x_j) + (\partial u_j / \partial x_i)]$ by the following relations:

$$e_1 = \frac{1}{\sqrt{3}} (e_{xx} + e_{yy} + e_{zz}), \tag{4a}$$
$$e_2 = \frac{1}{\sqrt{2}} (e_{xx} - e_{yy}), \tag{4b}$$
$$e_3 = \frac{1}{\sqrt{6}} (e_{xx} + e_{yy} - 2e_{zz}), \tag{4c}$$
$$e_4 = e_{xy}, \tag{4d}$$
$$e_5 = e_{yz}, \tag{4e}$$
$$e_6 = e_{zx}. \tag{4f}$$

The elastic constants $\hat{c}_{ij}$ are given by

$$\hat{c}_{11} = c_{11} + 2c_{12}, \tag{4g}$$
$$\hat{c}_{22} = c_{11} - c_{12}, \tag{4h}$$
$$\hat{c}_{44} = 4c_{44}. \tag{4i}$$
TABLE I. Homogeneous solutions corresponding to the tetragonal product phase.

<table>
<thead>
<tr>
<th>Tetragonal axis</th>
<th>Domain No.</th>
<th>Tetragonal state</th>
<th>Order parameter</th>
<th>Displacement direction of the atom at $x(\kappa)=[0,0,0]\alpha$</th>
<th>$x(\kappa)=1/2[1,1,1]\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x$</td>
<td>3</td>
<td>I$_x$</td>
<td>(0, $Q_0$, 0,0,0)</td>
<td>[011]</td>
<td>[100]</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>II$_x$</td>
<td>(0, $Q_0$, 0,0,0)</td>
<td>[010]</td>
<td>Not moving</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>III$_x$</td>
<td>(0, $Q_0$, 0,0,0)</td>
<td>[011]</td>
<td>Not moving</td>
</tr>
<tr>
<td>$y$</td>
<td>12</td>
<td>IV$_x$</td>
<td>(0,0,0,0,0,$Q_0$)</td>
<td>[001]</td>
<td>[010]</td>
</tr>
<tr>
<td>$z$</td>
<td>1</td>
<td>I$_z$</td>
<td>(0,0,0,0,0,$Q_0$)</td>
<td>[001]</td>
<td>[010]</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>II$_z$</td>
<td>(0,0,0,0,0,$Q_0$)</td>
<td>[010]</td>
<td>Not moving</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>III$_z$</td>
<td>(0,0,0,0,0,$Q_0$)</td>
<td>[110]</td>
<td>Not moving</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>IV$_z$</td>
<td>(0,0,0,0,0,$Q_0$)</td>
<td>[101]</td>
<td>[100]</td>
</tr>
</tbody>
</table>

Note that the shear strains $\epsilon_4=\epsilon_5=\epsilon_6=0$ for the cubic-to-tetragonal transition. Only the gradient energy of the primary OP is considered here and the elastic energy is kept only up to the second order in strain. All energy expansion coefficients are assumed to be temperature-independent except $A_0=\alpha_0(T-T_c)$. Here $T_c$ is the (fictitious) temperature at which the mode frequency would become zero. The Landau coefficients are taken as temperature-independent everywhere.

In a homogeneous phase, the stress is zero everywhere, i.e., $\sigma_\lambda=0$, therefore, for equilibrium single domain states, the six strain components $\epsilon_i$ can be expressed in terms of the six order-parameter components $Q_i$. These expressions for strain are then substituted back into $F_L$ and $F_G$. As a result, we obtain an effective free energy just of the form $F_L$ in Eq. (3a) with “renormalized” coefficients. Minima of this effective free energy yield lower symmetry domain states.

There are twelve single domain states for our tetragonal phase. These are given in Table I in terms of the OP vector $Q=(Q_1, Q_2, Q_3, Q_4, Q_5, Q_6)$. As shown in Table I, four degenerate states exist for each of the three principal tetragonal axes. We label these solutions by a domain number from 1 to 4 and a capital Roman numeral letter with a subscript indicating the corresponding tetragonal axis.

For a first-order transition the expansion must be at least to sixth degree in the absence of third order invariants. The transition temperature $T_0$ and the spontaneous OP value $Q_c$ (at $T_0$) are given by

$$ T_0 = T_c + \frac{b^2}{16a_0(4C_1 + C_4 - C_7 - C_9)}, $$

for a first-order transition.
\[ Q^2_c = \frac{b}{4(4C_4 + C_4 - C_y - C_y)} \] (7b)

where
\[ b = 4B_1 + B_4 - \frac{4D_1^2}{c_{11}} + \frac{4}{c_{22}}(D_2 + \sqrt{3}D_3)^2 \]. (8)

For other temperatures below \( T_0 \), the amplitude of the OP, \( Q_0 \), in a single tetragonal domain state can be related to \( Q_c \) through the following relation:
\[ Q_0 = Q_c \sqrt{\frac{2}{3} \left( 1 + \sqrt{\frac{3}{4} - \tau} \right)} \] (9a)
\[ \tau = \frac{T - T_c}{T_0 - T_c} \] (9b)

The normal mode amplitude \( Q_0 \) is linked to the atomic displacement of the two atoms through Eq. (1). Since we are working in the \( Q \) space, it is useful to invert Eq. (1),
\[ u^{(L)}_x = (u_1 / \sqrt{8M_1})[(-1)^{l_x+1}Q_1 + (-1)^{l_x+1}Q_4], \] (10a)
\[ u^{(L)}_y = (u_1 / \sqrt{8M_1})[(-1)^{l_y+1}Q_2 + (-1)^{l_y+1}Q_3], \] (10b)
\[ u^{(L)}_z = (u_1 / \sqrt{8M_1})[(-1)^{l_z+1}Q_3 + (-1)^{l_z+1}Q_6], \] (10c)
\[ v^{(L)}_x = (v_1 / \sqrt{8M_2})[(-1)^{l_x+1}Q_2 + (-1)^{l_x+1}Q_3], \] (10d)
\[ v^{(L)}_y = (v_1 / \sqrt{8M_2})[(-1)^{l_y+1}Q_1 + (-1)^{l_y+1}Q_6], \] (10e)
\[ v^{(L)}_z = (v_1 / \sqrt{8M_2})[(-1)^{l_z+1}Q_4 + (-1)^{l_z+1}Q_5]. \] (10f)

Here \( u^{(L)}_i \) and \( v^{(L)}_i \) are displacement components of the two sublattices at \([0,0,0]\) and \([a/2,a/2,a/2]\), respectively. The superscript, \( L = 1, 2, \ldots, 8 \), represents labeling of the unit cells which make up our expanded supercell (see Fig. 1).

The last two columns of Table I give the lattice displacement direction for the two atoms in the unit cell that is located at the origin of our coordinate system. One can easily generate the lattice displacement pattern for the supercell from the pattern of the first cell together with Eq. (10). For example, for domain state \( I_x \), the three-dimensional lattice displacement pattern is shown in Fig. 1 and the pattern for \( I_x \) was given in Fig. 1 of Ref. 14.

Since the three-dimensional representation is difficult to plot unambiguously, it is useful to use the 2D projection of these states. Shown in Fig. 2(a) is the projection plot on the \( z = 0 \) plane for the domain state \( I_x \). There are four such domain states having the tetragonal axis in the \( x \) direction. The dot (cross) in the center of a lattice circle represents that the lattice point also moves up (down) at the same time as it moves along the arrow direction in the plane in the low-temperature phase. The shaded lattice in the center of the unit cell is half a unit higher above the base plane, i.e., at the \( z = a/2 \) plane. The displacement patterns for \( II_x, III_x \), and \( IV_x \) can be obtained by a translation of the coordinate system by a vector of \([0,a,0] \), \([a,a,0]\), and \([a,a,0]\), respectively. Figures 2(b) and 2(c) correspond to domain states \( I_y \) and \( I_z \), respectively, with other patterns \((II_y,III_y,IV_y,II_z,III_z,IV_z)\) obtained via translation by appropriate vectors.

**IV. ANTIPHASE BOUNDARY SOLUTIONS**

The existence of four variants for each tetragonal orientation, related by a fractional translation (which is not a body center point, i.e., \([1/2,1/2,1/2]\)) of the new structure, will create antiphase variant structures. An antiphase boundary (APB) is the (planar or curved) surface where two such domain states meet. We choose the first group of solutions in Table I as examples for the analysis. Antiphase structures allow different domain relationships to form, distinct from ferroelastic domains, since the requirement of strain compatibility is automatically satisfied. A few special orientations of the APBs are studied here to illustrate the associated richness of the atomic structure and the corresponding continuum description of the antiphase boundaries. For mathematical simplicity, we will only study planar APBs so that the problem can be rendered quasi-one-dimensional for each given antiphase structure.
along the quantum quantities are a function of space variable $x$ while for the case of the $I_{\perp x}$ antiphase boundary, the $I_{\perp x}$ atom shifts along the $y$ direction. APBs can orient in many directions, for example with normals, $\{010\}$, $\{100\}$, $\{210\}$, $\{111\}$, etc. Any two of the four states can be paired up with an APB along these orientations. For simplicity, let us first study the case of the APB oriented along $[010]$. A few combinations of antiphase structures are $I_{\perp x}, I_{\perp \parallel x}$, and $I_{\perp \perp x}$ as shown in Figs. 3(a)–3(c). At the $I_{\perp \parallel x}$ antiphase boundary, the $Ag_{1-x}$ atoms shift along the $z$ direction; for the case of the $I_{\perp \perp x}$ antiphase boundary, the $Ag_{1-x}$ atoms shift along the $y$ direction; while for the case of the $I_{\parallel x}$ antiphase boundary, the $Ag_{1-x}$ atoms stay put.

Under the quasi-1D (Q1D) approximation, the physical quantities are a function of space variable $y$ only and only two components $Q_2$ and $Q_3$ are nonzero. Therefore, $Q = (0, Q_2(y), Q_3(y), 0, 0, 0)$. From Eq. (5a), we have

\begin{align*}
8_1 Q_{2,yy} &= A Q_2 + 2B_1 Q_2 (Q_2^2 + Q_3^2) + B_3 Q_2 Q_3^2 + 3C_1 Q_2 (Q_2^2 + Q_3^2)^2 + (C_4 - C_7 - C_9) (2Q_2^2 + Q_3^2) Q_2^2 + D_1 e_1 Q_2 \\
&\quad - 2D_2 e_3 Q_2 + D_3 (e_3 - \sqrt{3}e_2) Q_2 \quad (11a)
\end{align*}

\begin{align*}
8_2 Q_{3,yy} &= A Q_3 + 2B_1 Q_3 (Q_2^2 + Q_3^2) + B_3 Q_2 Q_3^2 + 3C_1 Q_3 (Q_2^2 + Q_3^2)^2 + (C_4 - C_7 - C_9) (2Q_2^2 + Q_3^2) Q_2^2 + D_1 e_1 Q_3 \\
&\quad - 2D_3 e_3 Q_3 + D_2 (e_3 - \sqrt{3}e_2) Q_3 \quad (11b)
\end{align*}

The boundary conditions determine which particular APB pair of the four domain states is described by the solutions of Eq. (11). For the $II_{\perp x}$ antiphase structure,

$$\lim_{y \to \pm \infty} (Q_2, Q_3) = (\pm Q_0, Q_0)$$

(12a)

for the $II_{\parallel x}$ antiphase structure,

$$\lim_{y \to \pm \infty} (Q_2, Q_3) = (Q_0, \pm Q_0)$$

(12b)

and for the $IV_{\perp x}$ antiphase structure,

$$\lim_{y \to \pm \infty} (Q_2, Q_3) = (\pm Q_0, \pm Q_0)$$

(12c)

In order to solve for a general case, we follow the procedure of Refs. 10, 11 and 20 to normalize the order parameter and define

\begin{align*}
A' &= D_1 e_1^2 - 2(D_2 + \sqrt{3}D_3) e_3^2 \\
&\quad + \left[ (\sqrt{2}D_1 - 2(D_2 - \sqrt{3}D_3)) (\sqrt{2}D_1 + D_2 + \sqrt{3}D_3) \right] Q_0^2 \\
&\quad \frac{1}{\tilde{c}_{11} + 2\tilde{c}_{22}} \quad (13a)
\end{align*}

\begin{align*}
B_1' &= - \frac{4(\sqrt{2}D_1 - 2D_2 + \sqrt{3}D_3)^2}{4(\tilde{c}_{11} + 2\tilde{c}_{22})} \quad (13b)
\end{align*}

\begin{align*}
B_3' &= \frac{2(D_3 - 2(D_2 - \sqrt{3}D_3))^2}{2(\tilde{c}_{11} + 2\tilde{c}_{22})} \quad (13c)
\end{align*}

\begin{align*}
A'' &= D_1 e_1^2 - 2(D_2 + \sqrt{3}D_3) e_3^2 \\
&\quad + \left[ (\sqrt{2}D_1 + 4D_2) (\sqrt{2}D_1 + D_2 + \sqrt{3}D_3) \right] Q_0^2 \\
&\quad \frac{1}{\tilde{c}_{11} + 2\tilde{c}_{22}} \quad (14a)
\end{align*}

\begin{align*}
B_2'' &= \frac{(\sqrt{2}D_1 + 4D_2)^2}{4(\tilde{c}_{11} + 2\tilde{c}_{22})} \quad (14b)
\end{align*}

\begin{align*}
B''_3 &= B_2'' \quad (14c)
\end{align*}
Using these definitions, the equilibrium conditions of Eq. (11) become

\[ g_1Q_{2,y} = (A + A')Q_2 + 2(B_1 + B_1')Q_2^3 + (2B_1 + B_4 + B_4')Q_2Q_3^2 + 3C_1Q_2(Q_2^2 + Q_3^2)^2 + (C_4 - C_7 - C_9)(2Q_3^2Q_3^2 + Q_2^2Q_3^2), \]

(15a)

\[ g_3Q_{3,y} = (A + A'')Q_3 + 2(B_1 + B_1'')Q_3^3 + (2B_1 + B_4 + B_4'')Q_3Q_2^2 + 3C_1Q_3(Q_2^2 + Q_3^2)^2 + (C_4 - C_7 - C_9)(2Q_3^2Q_2^2 + Q_3^2Q_2^2), \]

(15b)

Now, we define dimensionless functions \( q_1, q_2 \) and space variable \( \xi \) as the following:

\[ (Q_2, Q_3) = Q_1(q_2, q_3), \]

(16a)

\[ y = \gamma \xi, \]

(16b)

\[ \gamma^2 = \frac{g_1g_3}{A_c}, \]

(16c)

where \( A_c = \alpha_0(T_0 - T_c) \).

The final dimensionless equations are

\[ dq_{2,\xi} = \tau_2q_2 - \alpha_2q_2^3 - \alpha_2'q_2q_3^2 + \beta q_2^5 + \left(1 - \frac{\beta}{3}\right)(2q_2^2q_3^2 + q_2^2q_3^2), \]

(17a)

\[ dq_{3,\xi} = \tau_3q_3 - \alpha_3q_3^3 - \alpha_3'q_3q_2^2 + \beta q_3^5 + \left(1 - \frac{\beta}{3}\right)(2q_3^2q_2^2 + q_3^2q_2^2). \]

(17b)

Similarly, one can normalize the boundary conditions, Eq. (12). The dimensionless parameters in Eq. (17) are given by

\[ \tau_2 = \tau + \frac{A'}{A_c}, \]

(18a)

\[ \alpha_2 = \frac{8(B_1 + B_1')}{b}, \]

(18b)

\[ \alpha_2' = \frac{4(2B_1 + B_4 + B_4')}{b}, \]

(18c)

\[ \tau_3 = \tau + \frac{A''}{A_c}, \]

(18d)

\[ \alpha_3 = \frac{8(B_1 + B_1'')}{b}, \]

(18e)

\[ \alpha_3' = \frac{4(2B_1 + B_4 + B_4'')}{b}, \]

(18f)

We find that Eq. (17) becomes identical to the case solved in Ref. 11. Solving Eq. (17) under different boundary conditions, given by Eq. (12), gives us three different antiphase structures for \( I_x - II_x, I_y - II_y, \) and \( I_z - IV_z \) with the APB oriented in [010]. The solutions for the choice of \( d = 1, \tau = -4, \alpha_2 = \alpha_3 = 2.1, \alpha_2' = \alpha_3' = 1.8, \) and \( \beta = 10 \) are given in Figs. 4–6.

In Fig. 4, we depict the antiphase boundary solutions in terms of \( (q_2, q_3) \) for the three different boundary conditions. Figure 4(a) shows that \( q_2 \) is a kinklike and \( q_3 \) is a bell-like soliton for the \( I_x - II_x \) antiphase structure. For the \( I_y - II_y \) antiphase structure [Fig. 4(b)] the roles are reversed, i.e., \( q_2 \) is a bell-like and \( q_3 \) is a kink-like soliton. In Figs. 4(c) and 4(d), both \( q_2 \) and \( q_3 \) profiles are kinklike for the \( I_z - IV_z \) antiphase structure. The difference depicted in these figures is that in Fig. 4(c), the two solutions overlap because we assumed no coupling between \( q_2 \) and \( q_3 \), i.e., \( \alpha_2 = \alpha_3 = 0 \) and \( \beta = 0 \). In general, the two kinks do not overlap as shown in Fig. 4(d) due to the cross coupling between \( q_2 \) and \( q_3 \).

Figure 5 shows the influence of the gradient coefficient, \( d \), on the order-parameter profiles for the \( I_x - II_x \) antiphase structure. In general, domain-wall thickness monotonically increases with \( d \). Figure 6 depicts the effect of the variation in the sixth-order coefficient \( \beta \). An APB becomes narrower with increasing \( \beta \). In addition, the bell-like order-parameter profile flips to a hump shape at a critical value of \( \beta \). Figure 7 shows the effect of temperature, \( \tau \), on the shape and amplitude of \( I_x - II_x \) APB. It reveals that as temperature decreases, the amplitude of the order parameter increases while the thickness of the APB decreases.

The discontinuous atomic displacement patterns corresponding to the three different boundary conditions, Eqs. (12a)–(12c), are given in Fig. 3. Because of the constraints of the gradient energy, the actual displacement pattern changes continuously as shown by the continuum profiles of \( q_2 \) and \( q_3 \) in Figs. 4–7.

B. Antiphase boundaries of other orientations

Because the elastic strains are compatible in antiphase structures, there are several possible orientations for the antiphase boundary corresponding to certain lattice planes. The discontinuous lattice displacement patterns for antiphase structures with APBs on the (011) and (101) lattice planes are illustrated in Fig. 8.

For antiphase structures consisting of domain states with the \( x \) direction as the tetragonal axis, the order-parameter
The profile is governed by two coupled differential equations for $Q_2$ and $Q_3$ as in Eqs. (15a) and (15b). The only difference is in the parameters $A_8, A_9, B_{18}, B_{19}, B_{48},$ and $B_{49}$. These parameters are given in Table II for different APB orientations and are determined by material properties.

After normalization, all equations have the identical dimensionless form of Eqs. (17a) and (17b). Therefore, Eqs. (17a) and (17b) are universal equations for antiphase boundaries in this transition. One point that must be emphasized is that the Q1D treatment should always choose the independent space variable to be perpendicular to the APB plane. For example, while calculating the antiphase structures with APB oriented in [011] and [101], the system must be rotated 45 degrees around [100] and [010], respectively, so that the problem can be rendered Q1D.

In general, the existence of several allowed orientations for APB in a variety of materials and their relatively small energy makes it difficult to maintain the APB on one of the lattice planes through an entire sample. Instead, APBs are often observed as curved or jointed boundaries resulting from several differently oriented APBs joining together. Moreover, the thickness of the domain wall can be on the...
order of a fraction of a unit cell to several unit cells. In simulations for lead phosphate, the trace of the APB was on the same order as the "W" wall.

V. DETERMINATION OF THE EXPANSION COEFFICIENTS

The coefficients of the Landau portion of the free energy can be determined from the available lattice parameter data measured by x-ray and neutron scattering as a function of temperature. The coefficients of the Ginzburg (i.e., gradient) terms are obtained from the phonon-dispersion data near the soft mode $M_5$ as described below. There is only a limited amount of data for this transition, primarily contained in Refs. 17 and 18.

A. Coefficients for the Landau energy

For the cubic-to-tetragonal transition, we have expanded the free energy to the sixth degree. The form for the effective free energy is $F = \alpha_0 (T - T_c)^2 + \beta_0 Q^4 + C Q^6$, where $\alpha_0 = m \omega_M^2$ and $m = 923.39 \text{ kg/m}^3$ is the mass density. The coefficients $\alpha_0$ and $T_c$ can be determined from the temperature dependence of the soft phonon mode (Fig. 6 in Ref. 17). $T_c$ is the temperature at which the frequency of the softening phonon would go to zero and $\alpha_0$ is the slope of the linear approach to zero. $T_0$ is the temperature at which the first-order transition takes place. For LaAg$_{1-x}$In$_x$ ($x = 0.2$), the cubic lattice parameter (at 300 K) is $a_c = 7.65$ Å, and the tetragonal lattice parameters (at 100 K) are $a_t = 7.56$ Å and $c_t = 7.75$ Å. In the tetragonal phase at 100 K, the shuffle (in units of the cubic lattice parameter) of La atoms is $\epsilon = 0.0285$ and the shuffle of Ag$_{1-x}$In$_x$ atoms is $\delta = 0.0139$ (Fig. 4 in Ref. 17). We find the slope of the soft mode $S = 8.294 \times 10^{20}/\text{K (sec)}^2$. Since $\alpha_0 = mS$, we obtain the following values for these three constants:

$T_c = 120$ K, $T_0 = 125$ K, $\alpha_0 = 7.6587 \times 10^{21} \frac{J}{\text{m}^3 \text{kg} \text{K}^2}$.

Specifically, by comparing with the atomic displacements measured for the tetragonal phase, the two model parameters $(Q_c, \xi)$ may be determined from the two atomic displacements $\epsilon$ and $\delta$ for La and Ag$_{1-x}$In$_x$, respectively, according to

$Q_c = \sqrt{2} \sqrt{M_1 (2 \alpha_0 \delta)^2 + M_2 (\xi \epsilon)^2}$, $\quad \xi = \frac{c_t \epsilon}{2 \alpha_0 \delta}$.

We find the following values:

$Q_c^2 = 3.8823 \times 10^{-46}$ kg m$^2$, $\quad \xi = 1.01045$, and

$B = 3.9455 \times 10^{70} \frac{J}{\text{m}^7 (\text{kg})^2}$, $\quad C = 7.622 \times 10^{115} \frac{J}{\text{m}^9 (\text{kg})^3}$.

Note that the units of $\alpha_0$, $B$, and $C$ contain mass (kg) in the denominator since the order parameter, $Q$ in Eq. (1), has units of (kg)$^{1/2}$ m.
TABLE II. Coefficients $A'$, $A''$, $B'_1$, $B''_1$, $B'_2$, and $B''_2$ for antiphase boundary between $I_x$ and $H_x$. Here $e_1^- = -(2D_1/c_{11})Q_0^2$, $e_2^- = -(\sqrt{3}(D_2 + \sqrt{3}D_3)/c_{22})Q_0^2$, and $e_3^- = [(D_2 + \sqrt{3}D_3)/c_{22}]Q_0^2$.

<table>
<thead>
<tr>
<th>Wall orientation</th>
<th>$A'$</th>
<th>$A''$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[100]</td>
<td>$D_1e_1^- - 2(D_2 + \sqrt{3}D_3)e_3^- + \frac{[\sqrt{2}D_1 - 2(D_2 - \sqrt{3}D_3)]^2}{c_{11} + 2c_{22}}$</td>
<td>$\frac{2(\sqrt{2}D_1 - 2(D_2 - \sqrt{3}D_3)]}{2c_{11} + 2c_{22}}$</td>
</tr>
<tr>
<td>[010]</td>
<td>$D_1e_1^- - 2(D_2 + \sqrt{3}D_3)e_3^- + \frac{[\sqrt{2}D_1 - 2(D_2 + \sqrt{3}D_3)]^2}{c_{11} + 2c_{22}}$</td>
<td>$\frac{2(\sqrt{2}D_1 + D_3 + \sqrt{3}D_3)}{2c_{11} + 2c_{22} + 6c_{44}}Q_0^2$</td>
</tr>
<tr>
<td>[011]</td>
<td>$D_1e_1^- - 2(D_2 + \sqrt{3}D_3)e_3^- + \frac{2(\sqrt{2}D_1 + D_3 + \sqrt{3}D_3)}{2c_{11} + c_{22} + 6c_{44}}Q_0^2$</td>
<td>$\frac{D_1^2}{2c_{11} + 3c_{44}} + \frac{(D_2 + \sqrt{3}D_3)^2}{2c_{22}}$</td>
</tr>
<tr>
<td>[101]</td>
<td>$D_1e_1^- + \frac{2D_1^2}{c_{11} + 3c_{44}}Q_0^2$</td>
<td>$\frac{D_1^2}{2c_{11} + 3c_{44}} + \frac{(D_2 + \sqrt{3}D_3)^2}{2c_{22}}$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Wall orientation</th>
<th>$B'_1$</th>
<th>$B''_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[010]</td>
<td>$-\frac{2(\sqrt{2}D_1 - 2D_2 + 2\sqrt{3}D_3)^2}{4(c_{11} + 2c_{22})}$</td>
<td>$\frac{[\sqrt{2}D_1 - 2(D_2 - \sqrt{3}D_3)](\sqrt{2}D_1 + 4D_2)}{2c_{11} + 2c_{22}}$</td>
</tr>
<tr>
<td>[100]</td>
<td>$-\frac{[(\sqrt{2}D_1 - 2D_2 + 2\sqrt{3}D_3)^2]}{4(c_{11} + 2c_{22})}$</td>
<td>$\frac{2(\sqrt{2}D_1 - 2(D_2 - \sqrt{3}D_3)]}{2c_{11} + 2c_{22}}$</td>
</tr>
<tr>
<td>[011]</td>
<td>$\frac{2(\sqrt{2}D_1 + D_2 + \sqrt{3}D_3)}{2c_{11} + c_{22} + 6c_{44}}Q_0^2$</td>
<td>$\frac{2(\sqrt{2}D_1 + D_2 + \sqrt{3}D_3)}{2c_{11} + c_{22} + 6c_{44}}Q_0^2 + \frac{(\sqrt{3}D_2 - D_3)^2}{c_{22}}$</td>
</tr>
<tr>
<td>[101]</td>
<td>$\frac{D_1^2}{2c_{11} + 3c_{44}} + \frac{(D_2 + \sqrt{3}D_3)^2}{2c_{22}}$</td>
<td>$\frac{D_1^2}{2c_{11} + 3c_{44}} + \frac{(D_2 + \sqrt{3}D_3)^2}{2c_{22}}$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Wall orientation</th>
<th>$B'_2$</th>
<th>$B''_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[010]</td>
<td>$\frac{(\sqrt{2}D_1 + 4D_2)^2}{4(c_{11} + 2c_{22})}$</td>
<td>$\frac{D_1^2}{2c_{11} + 3c_{44}} + \frac{(D_2 + \sqrt{3}D_3)^2}{2c_{22}}$</td>
</tr>
<tr>
<td>[100]</td>
<td>$B'_1$</td>
<td>$B''_1$</td>
</tr>
<tr>
<td>[011]</td>
<td>$B'_1$</td>
<td>$B''_1$</td>
</tr>
<tr>
<td>[101]</td>
<td>$B'_1$</td>
<td>$B''_1$</td>
</tr>
</tbody>
</table>

B. Gradient terms and phonon dispersion

The gradient coefficients are related to the curvature of the dispersion surface near the soft mode and the dispersion relation can be measured by inelastic neutron-scattering experiments.

Starting with the Euler-Lagrange equation with explicit time dependence,

$$m \ddot{Q}_\lambda + \frac{\partial (F_L + F_G)}{\partial Q_\lambda} - \sum_j \frac{\partial}{\partial x_j} \left( \frac{\partial F}{\partial Q_{\lambda,j}} \right) = 0$$

$(\lambda = 1 - 6)$, $j = 1 - 3$, (20)}

where $m$ is the effective-mass density of atoms associated with the $M_5$ mode. For small amplitude oscillations, we can
ignore the nonlinear terms by keeping only the lowest-order terms in the order parameter. Thus, the above six linearized equations have the following harmonic solutions: \( Q_\lambda = Q_0^\lambda \exp[i(k_M \cdot \hat{x} - \omega t)] \), where \( k_M \) is one of the arms of the star \( k_M \). The \( M_5 \) mode is sixfold-degenerate and it splits into several distinct modes if the \( k \) value deviates from that at the first Brillouin-zone edge. For example, if \( k = -k_M - q \), then Eq. (20) results in the following eigenvalue problem:

\[
G_1 = \begin{pmatrix}
2A + 2g_1q_1^2 + 2g_2q_2^2 + 2g_3q_3^2 & (g_2 + g_5)q_1q_2 \\
(g_4 + g_5)q_1q_2 & 2A + 2g_2q_1^2 + 2g_1q_2^2 + 2g_3q_3^2
\end{pmatrix},
\]

\[
G_2 = \begin{pmatrix}
2A + 2g_2q_1^2 + 2g_5q_2^2 + 2g_1q_3^2 & (g_4 + g_5)q_1q_3 \\
(g_4 + g_5)q_1q_3 & 2A + 2g_1q_1^2 + 2g_2q_2^2 + 2g_2q_3^2
\end{pmatrix},
\]

\[
G_3 = \begin{pmatrix}
2A + 2g_3q_1^2 + 2g_1q_2^2 + 2g_2q_3^2 & (g_4 + g_5)q_2q_3 \\
(g_4 + g_5)q_2q_3 & 2A + 2g_3q_1^2 + 2g_2q_2^2 + 2g_1q_3^2
\end{pmatrix}.
\]

The matrix \( G \) is in block-diagonal form and the three blocks are equivalent when we choose different arms of the star \( k_M \). The gradient energy causes the two coupled modes of a given \( k \) value to split when moving away from the \( M \) point. We can use one of the blocks in \( G \) to derive the dispersion relations by introducing a small perturbation to the wave vector along the high-symmetry directions in the first Brillouin zone. Let us choose the first block \( G_1 \), which involves the order-parameter components \( Q_1 \) and \( Q_2 \) and the wave vector \( k = 2\pi/a[110] \).

In the \( M^-I \) direction, the perturbation is \( q = q[1.1.0] \) with the amplitude \( q \ll 2\pi/a \). The perturbation causes mode splitting:

\[
m\omega_1^2 = 2A + (2g_1 + 2g_2 + 4g_3 + 5g_5)q^2, \quad (23a)
\]

\[
m\omega_2^2 = 2A + (2g_1 + 2g_2 - 2g_4 + 3g_5)q^2. \quad (23b)
\]

In the \( M^-X \) direction of the Brillouin zone, \( q = q[010] \) and we can get two more relations:

\[
m\omega_1^2 = 2A + 2g_2q_2^2, \quad (24a)
\]

\[
m\omega_2^2 = 2A + 2g_1q_1^2. \quad (24b)
\]

Finally, in the \( M^-R \) direction, \( q = q[001] \), we get

\[
m\omega_1^2 = 2A + 2g_3q_3^2. \quad (24c)
\]

Since below the transition temperature \( T < 0 \), phonon stability requires that the slopes of the above five dispersion curves be positive. These five equations give us enough combinations to derive all five independent gradient coefficients \( g_i \) in Eq. (3d). However, the phonon dispersions along the \( M^-X \) and \( M^-R \) directions have not been measured for \( \text{LaAg}_2 \). Therefore, we can obtain only the two combinations \( g_1 + g_2 \) and \( g_4 + g_5 \) by fitting the 300-K data in the \( M^-I \) direction [Fig. 4 (left column, middle panel)] for the longitudinal acoustic (LA) mode for \( \text{LaAg} \) in Ref. 18 to Eq. (23a) and Fig. 5 for the second transverse acoustic mode (TA) for \( \text{LaAg}_2 \) in Ref. 18 to Eq. (23b). If we denote the slopes for these two dispersions, respectively, by

\[
S_1 = 2(g_1 + g_2) + (g_4 + g_5), \quad S_2 = 2(g_1 + g_2) - (g_4 + g_5),
\]

we find \( S_1 = 2.2539 \times 10^6 \text{ J/m}^3 \) and \( S_2 = 2.1747 \times 10^9 \text{ J/m}^3 \). Thus, the two combinations of gradient coefficients are

\[
g_1 + g_2 = \frac{1}{2}(S_1 + S_2) = 1.107 \times 10^9 \text{ J/m}^3,
\]

\[
g_4 + g_5 = \frac{1}{2}(S_1 - S_2) = 3.96 \times 10^7 \text{ J/m}^3.
\]

Note that we can determine the temperature dependence of \( S_2 \), since the temperature dependence of phonon dispersion for the TA branch of \( \Sigma_2 \) symmetry has also been measured (Fig. 5 in Ref. 18). As discussed above and depicted in Fig. 5, the thickness of the antiphase boundaries is proportional to the square root of the gradient coefficients. The thickness can be on the order of a fraction of a unit cell to several unit-cell dimensions. Unfortunately, there are insufficient data to determine each gradient coefficient and thus the value for parameter \( d \) in Eq. (18g), which determines the domain-wall thickness.

VI. SUMMARY AND CONCLUSIONS

Using a Ginzburg-Landau model with a six-dimensional phonon order parameter, we provide a general formulation of the antiphase structures of \( \text{RAg}_2 \) (where \( \text{R} = \text{La}, \text{Ce}, \text{Pr} \)).
and Pr) that can form in a cubic ($O_h^1, Pm\overline{3}m$) to tetragonal ($D_{17}^h, 14\text{mmm}$) improper ferroelastic phase transition driven by the $M_h^*$ zone boundary mode of the CsCl structure. There are four independent domain states for each of the three possible tetragonal axes in the low-temperature phase, constituting 12 domain states in total.

Antiphase boundaries are formed between any two domain states of the same tetragonal axis. Using the quasi-1D approximation, we treated four differently oriented APBs and found that equilibrium conditions for the OP profiles can be related to a single set of two dimensionless coupled differential equations involving two components of the OP. The relationships between the parameters in the common set of equations [Eq. (17)] and the free-energy expansion coefficients in Eq. (3) were derived for the case of the tetragonal axis along the $x$ direction. These results are also applicable to the cases with the tetragonal axis along the $y$ and $z$ directions.

It is interesting to note that all of the final differential equations reduce to the same universal set of equations with proper normalization constants. This is also true for other systems that can be described by a Ginzburg-Landau model, although the order parameter may be different. As shown previously for a first-order ferroelectric phase transition, the order parameter is only a three-dimensional vector; the APB solution in that case can also be described by the same set of equations as given in Eq. (17). It is speculative but these equations may be a representative form for all APB domain walls in other transitions.

Some of the expansion coefficients in the GL model, Eq. (3), can be extracted from experimental measurements. In particular, we derived the coefficients of the effective Landau free energy and the relationships between the gradient coefficients and the phonon-dispersion curves near the $M_h^*$ soft mode. Note that the analysis presented here is applicable to the cubic to orthorhombic ($D_3^h, Pmm\overline{2}$) transition (see second entry in Table 7 of Ref. 14) in AuCd and NiTi-$M$ ($M = \text{Fe, Al, Cu}$) shape memory alloys.

**ACKNOWLEDGMENTS**

We are grateful to Professor G. R. Barsch for numerous insightful discussions and suggestions. This work was supported in part by NSF Grant No. DMS9704714 and in part by the U.S. Department of Energy under Contract No. W-7405-ENG-36.

*Electronic address: cao@math.psu.edu
†Electronic address: avadh@lanl.gov
15*ISOTROPY* is a computer program by H. T. Stokes and D. M. Hatch based upon space group representations and parametric distortions which lead to a symmetry reduction. It was used to obtain the data in the tables of Ref. 14. It has been extended to calculate data pertaining to transitions in solids, e.g., domains and their orientations, tensorial properties, gradient invariants, etc.