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Determination of Domain and Domain Wall Formation at Ferroic Transitions

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Through the example of the $Pm\overline{3}m - I4/mmm$ structural phase transition in $LaAg_{1-x}In_x$ (x–0.2), a general procedure is given in this paper to model and predict the domain pair and domain wall formation using a group theoretical approach and a Landau-Ginzburg type continuum theory. The heterogeneous order parameter profile can then be calculated by using an initial value scan method based on the equilibrium conditions of the order parameter and the minimization of the total elastic energy. The dependence of the domain wall profile on different expansion coefficients of the free energy is demonstrated numerically in several examples.

Keywords: Group theory; Domains; Domain walls; Phase transitions; Ferroelastic; Landau-Ginzburg theory

INTRODUCTION

Group theoretical methods provide the tools to obtain a great deal of information about phase transitions and the resulting domain structures. The symmetry change at a transition allows us to obtain the following: (1) the Landau-Ginzburg free energy, including gradient and secondary order-parameter (OP) invariants, (2) the number and the physical properties of possible homogeneous domains,

(3) the classification of equivalent domain and twin pairs and their symmetry, (4) the sets of non-linear equations which define the domain wall profiles in the heterogeneous structures, (5) the criteria for stability, and (6) the merging and splitting of domain walls.

In this paper we use the improper ferroelastic phase transition in a CsCl structure to illustrate the methodology of the symmetry approach. The transition is from a $Pm\bar{3}m$ to $I4/mmm$ structure[1] and is induced by an M_5^- mode softening in the pseudo- binary rare earth alloy $LaAg_{1-x}In_x$ (x~0.2). Structural details of the transition in CsCl are given in Ref. 1. We use the software program *ISOTROPY*[2] by Stokes and Hatch to quickly obtain some of the pertinent details of the invariants and domain twins.

THE LANDAU -GINZBURG FREE ENERGY

The symmetry of the $I4/mmm$ distorted phase with cell quadrupling initially gives two possible choices[2] for this symmetry change from $Pm\bar{3}m$. However, comparison with the observed displacements leads uniquely to the realization that the transition is induced by the soft mode of the M_5^- irreducible representation, corresponding to a six-component OP $\eta = (\eta_1,\eta_2,\eta_3,\eta_4,\eta_5,\eta_6)$, with the direction[1] of P_{10} = (a, a, 0, 0, a, -a). The Landau-Ginzburg free energy is constructed by forming polynomials which are invariant under the complete set of transformations of the higher symmetry group $Pm\bar{3}m$. The invariants obtained from *ISOTROPY* can be collected into two parts. The first, the Landau energy part, is composed of invariant polynomials of the primary and secondary OPs. These terms are indicated in the following manner $F_L(\eta)=F_{primary} + F_{secondary} + F_{coupled}$, with invariants up to sixth order in the primary and fourth order in secondary OPs, and terms coupling these two sets of parameters[1]. As far as the space group symmetry change is concerned, the first order vs second order nature of a transition does not play a prominent role, therefore, we take the expansion for the primary OP only up to fourth order in this paper, which allows us to obtain some simple analytic and numerical solutions. The Ginzburg portion, F_G, is an invariant combination of spatial derivatives of the primary OP. The free

$$
\begin{aligned}
F_G = {} & b_1\Big(\tfrac{5}{6}(\eta_{1,x})^2 - \tfrac{1}{\sqrt{3}}(\eta_{1,x})(\eta_{1,y}) + \tfrac{1}{2}(\eta_{1,y})^2 + \tfrac{1}{3}(\eta_{2,x})^2 + (\eta_{2,y})^2 \\
& + \tfrac{5}{6}(\eta_{3,x})^2 + \tfrac{1}{\sqrt{3}}(\eta_{3,x})(\eta_{3,y}) + \tfrac{1}{2}(\eta_{3,y})^2\Big) \\
& + b_2\Big(-\tfrac{1}{2\sqrt{3}}(\eta_{1,x})^2 + (\eta_{1,x})(\eta_{1,y}) + \tfrac{1}{2\sqrt{3}}(\eta_{1,y})^2 + \tfrac{1}{\sqrt{3}}(\eta_{2,x})^2 - \tfrac{1}{\sqrt{3}}(\eta_{2,y})^2 \\
& - \tfrac{1}{2\sqrt{3}}(\eta_{3},x)^2 - (\eta_{3},x)(\eta_{3},y) + \tfrac{1}{2\sqrt{3}}(\eta_{3,y})^2\Big) \\
& + b_3\Big(\tfrac{1}{2}(\eta_{1,x})(\eta_{1,z}) + \tfrac{\sqrt{3}}{2}(\eta_{1,y})(\eta_{1,z}) - (\eta_{2,x})(\eta_{2,z}) \\
& + \tfrac{1}{2}(\eta_{3,x})(\eta_{3,z}) - \tfrac{\sqrt{3}}{2}(\eta_{3,y})(\eta_{3,z})\Big) + b_4\big((\eta_{1,z})^2 + (\eta_{2,z})^2 + (\eta_{3,z})^2\big)
\end{aligned} \tag{1}
$$

energy form for this portion is given in Eq. (1). Euler's equations then lead to six coupled partial differential equations in η and three equations in stress as shown in Eq. (2),

$$
\begin{aligned}
\sum\nolimits_m \frac{\partial}{\partial x_j}\left[\frac{\partial F}{\partial \eta_{i,j}}\right] - \frac{\partial F}{\partial \eta_i} = 0, \quad (j=1,2,3;\ i=1,\ldots.6), \\
\sum\nolimits_m \sigma_{nm,m} = 0, \quad (m,n=1,2,3).
\end{aligned} \tag{2}
$$

DOMAIN TWINS

The transition from $Pm\bar{3}m$ to $I4/mmm$ produces twelve homogeneous single domain states, labeled $S_1, S_2, \ldots, S_{12}$. The set of all elements of the parent group that do not change S_1 comprise the isotropy group $I4/mmm$ of the first domain. We label this group F_1, which is a subgroup with basis vectors (2,0,0), (0,2,0), (0,0,2) and origin (½, ½, 0) with respect the parent group. Those elements of the parent group that transform S_1 into the particular domain S_i will form a left coset with respect to F_1 and the cosets can be used to write the parent group, denoted as G, in the form $G = F_1 + g_{2,1}F_1 + g_{3,1} + ... g_{12,1}F_1$, where $g_{i,1}$ is an element that transforms S_1 to domain S_i. The isotropy group of S_i is $g_{i,1} F_1 g_{i,1}^{-1} = F_i$.

A domain pair is of the form (S_i,S_j) and is made up of two domains which simultaneously exist in space without being combined and without interacting. Two domain pairs are said to be equivalent if there is some element g of the parent group G for which $g(S_i,S_j)=(gS_i,gS_j)=(S_k,S_l)$. This procedure allows all possible domain pairs for the $LaAg_{(1-x)}In_x$ transition to be grouped into four classes. The identity class (S_i,S_i), two antiphase classes exemplified by the domain pairs (S_1,S_{10}) and (S_1,S_4), and an orientation class exemplified by the pair (S_1,S_2). Equivalent domain pairs are indicated in Table I. We will not

Table I Equivalent domain pairs. *k, m, n* are positive integers; $k+3m$, $k+3n+1$, $k+3n+2$ are smaller than 12.

Domain Pair	**Equivalent Pairs**
(1,10)	(2,11), (3,12), (4,7), (5,8), (6,9)
(1,4)	(k, $k+3m$) without pairs in type (1,10)
(1,2)	(k, $k+3n+1$), (k, $k+3n+2$)

discuss here the case of the identity class. The study of domain walls will then be reduced to studying one representative from each of three classes.

A domain twin is defined as two semi-infinite single domain regions separated by a thin planar wall, with normal **n**, and containing the point **p**. Following Janovec's notation[3], this twin will be labeled (S_i/**n**,**p**/S_j). Its symmetry group (hereafter called its twin group) consists of four parts:

$$J_{ij} = \hat{F}_{ij} + \underline{t}'_{ij}\hat{F}_{ij} + \underline{r}_{ij}\hat{F}_{ij} + s'_{ij}\hat{F}_{ij}. \quad (3)$$

Here, $\hat{F}_{ij}$ contains those elements that leave S_i, S_j, and **n** invariant; $\underline{t}'_{ij}\hat{F}_{ij}$ contains those elements that interchange S_i and S_j, and reverse **n**; $\underline{r}_{ij}\hat{F}_{ij}$ contains those elements that leave S_i and S_j invariant and reverse **n**; and $s'_{ij}\hat{F}_{ij}$ contains those elements that interchange S_i and S_j, and leave **n** invariant; while all of the above leave **p** invariant. Representative twin groups are indicated in Table II.

Table II Representative Twin Groups in LaAgIn
(in terms of the parent cubic setting)

Twin, Group, Basis, Origin	$\hat{F}_{ij}$	$\underline{t}'_{ij}\hat{F}_{ij}$	$s'_{ij}\hat{F}_{ij}$	$\underline{r}_{ij}\hat{F}_{ij}$
(1/(0,0,1),(0,0,0)/10) **P4/m2/m2/m** (1,-1,0),(-1,-1,0) (1/2,1/2,0)	**P4mm**	(C2b|0,0,0)	(E|-1,1,0)	(C2b|-1,1,0)
(1/(0,0,1),(0,0,0)/4) **P2/m2/m2/m** (0,2,0),(-1,0,0) (0,1/2,0)	**P2mm**	(C2y|0,0,0)	(E|-1,0,0)	(C2y|-1,0,0)
(2/(1,1,0),(0,0,0)/3) **C2mm** (0,0,2),(2,-2,0) (0,0,-1/2)	**C11m**	none	(C2a|0,0,1)	none
(2/(-1,1,0),(0,0,0)/3) **Cmm2** (-2,2,0),(2,2,0) (0,-1,0)	**C11m**	none	none	(C2a|0,0,1)

DOMAIN WALL SOLUTIONS

(I) The (1,10) antiphase boundary (APB) is formed between $P_1(\eta') = (\sqrt{2}\,a, 0,0,0,0, \sqrt{2}\,a)$ and $P_{10}(\eta') = (-\sqrt{2}\,a, 0,0,0,0, -\sqrt{2}\,a)$. For convenience new OP components have been defined where $\eta'_i = \sqrt{2}\,(\eta_i + \eta_{i+1})$ or $\eta'_i = \sqrt{2}\,(\eta_i - \eta_{i-1})$ for i even or odd, respectively. The APB is formed by half a lattice constant

translation of the lower symmetry phase along the z direction. The single domain states serve as boundary conditions for heterogeneous solutions, and we consider the *inverse* boundary value problem based on the assumption that both the primary and the secondary OP depend only on the position coordinate z perpendicular to the domain wall, thus $\eta' = \eta'(z)$. The strains are subjected to

$$-(2D_4 - D_1)\frac{d^2\eta'}{dz^2} + k^*\eta' + (A_6^* + A_{1,6}^*)\eta'^3 = 0. \qquad (4)$$

compatibility relations[4]. Assuming $\eta'_2 = \eta'_3 = \eta'_4 = \eta'_5 = 0$, the Euler equations reduce to two non-linear coupled second-order ordinary differential equations for $\eta'_1(z)$ and $\eta'_6(z)$. Both order parameter components satisfy the same equation, The solutions are $\eta'_1 = \eta'_6 = \mathrm{a}\tanh(z/\xi_{APB})$, where $\xi_{APB} = [-2(2D_4 - D_1)/k^*]^{1/2}$ is the half width of the APB and k^- is a renormalized second-order coefficient.

(II) The (1,4) antiphase boundary is formed between $P_1(\eta') = (\sqrt{2}\,\mathrm{a},0,0,0,0,$

$$-(2D_4 + D_1)\frac{d^2\eta_1'}{dx^2} + k_1^*\eta_1' + A_1^*\eta_1'^3 + A_{1,6}^*\eta_1'\eta_6'^2 = 0,$$
$$-2D_3\frac{d^2\eta_6'}{dx^2} + k_6^-\eta_6' + A_6^*\eta_6'^3 + A_{6,1}^*\eta_6'\eta_1'^2 = 0. \qquad (5)$$

$\sqrt{2}\,\mathrm{a})$ and $P_4(\eta') = (-\sqrt{2}\,\mathrm{a},0,0,0,0,\sqrt{2}\,\mathrm{a})$. This APB is formed by half a lattice constant translation of the lower symmetry phase along the x direction . We assume $\eta'_2 = \eta'_3 = \eta'_4 = \eta'_5 = 0$ and a domain wall perpendicular to x. The set of coupled nonlinear equations are given in Eq. (5). If we take no coupling, i.e., $A^*_{1,6} = 4A'_1 + 2A'_3 = 0$, we can find the following solution: $\eta'_1 = \sqrt{2}\,\mathrm{a}\tanh(x/\xi_{APB})$, $\eta'_6 = \sqrt{2}\,\mathrm{a}$, and $\xi_{APB} = [-2(2D_4 + D_1/k_1^*]^{1/2}$. In addition, the strain components e_2, e_3 are constant and $\sigma_{12} = \sigma_{23} = \sigma_{13} = \sigma_{11} = 0$.

(III) The (2,3) orientation twin boundary (OTB) is formed between $P_2(\eta') = (0,0,0,\sqrt{2}\,\mathrm{a},\sqrt{2}\,\mathrm{a},0)$ and $P_3(\eta') = (0,\sqrt{2}\,\mathrm{a},\sqrt{2}\,\mathrm{a},0,0,0)$. The domains 2 and 3 are related by a three-fold rotation along the [111] direction of the $Pm3m$ structure. Note that the (2,3) OTB is equivalent to the (1,2) OTB. In contrast to

the antiphase domains, orientation twin domains are distinguished by their ferroic properties, i.e., the two twin domains have *different* strains which can be detected optically or with x rays. The order-parameter profile representing the twin boundary has the following form: $\eta' = (0, \eta'_2, \eta'_3, \eta'_4, \eta'_5, 0)$ and contains the x = y plane. For the special case $Q_1 = \eta_2' = \eta_3'$, $\eta_4' = \eta_5' = Q_2$ we get the two coupled differential equations:

$$D^+ \frac{d^2 Q_1}{ds^2} + 2k_1^+ Q_1 + 4A_1^+ Q_1^3 + 2A_{1,2}^+ Q_1 Q_2^2 = 0,$$
$$D^- \frac{d^2 Q_2}{ds^2} + 2k_2^+ Q_2 + 4A_2^+ Q_2^3 + 2A_{1,2}^+ Q_2 Q_1^2 = 0. \qquad (6)$$

Assuming $A_{1,2}^+ = 0$ and by defining $\xi_{TB} = \sqrt{D^- / k_2^+}$, we get $Q_1 = 1/\sqrt{2}a\left[1 + \tanh(s/\xi_{TB})\right]$, and $Q_2 = 1/\sqrt{2}a[1 - \tanh(s/\xi_{TB})]$. The domain wall energy is $E = -\xi_{TB}(\frac{10}{3}k_2^+ a^2 + \frac{8}{3}A_1^+ a^4 + 2A_{1,2}^+ a^4)$. The strains e_r', e_3' are constant and $\sigma_{ss} = 0$, where *r* and *s* denote the [110] and $[1,\bar{1},0]$ directions, respectively.

(IV) Numerical Solutions: General solutions for both the antiphase and twin boundaries can be obtained by numerically solving the nonlinear coupled differential Eqs. (4), (5), and (6). From the mathematical formulations, the differential equations for the OTB (2,3) is the same as that for the AP twin boundary (1,4); therefore, we will analyze the equations for (1,4) using normalized variables and the normalized equations can also apply to the OTB case. The differential equations for a (1,4) AP boundary were given in Eq. (5). This set of coupled nonlinear differential equations can be solved by using the initial value scan method[5], and the solutions are expected to be similar to the solutions of Cao and Barsch[6].

The solutions for $A_{1,6}^+ = 0$ were given in our discussion after Eq. (5). For the more general case, $A_{1,6}^+ \neq 0$, we must solve Eq. (5) numerically. To simplify the mathematical problem, the following substitutions are introduced:

$$q_1 = \frac{\eta_1'}{\sqrt{2a}}, \quad q_2 = \frac{\eta_2'}{\sqrt{2a}}, \tag{7a,b}$$

$$\alpha = \sqrt{\frac{2D_3 k_1^*}{k_6^*(2D_4 + D_1)}}, \quad \beta_1 = \frac{A_{1,6}^*}{A_1^* + A_{1,6}^*}, \quad \beta_2 = \frac{A_{1,6}^*}{A_6^* + A_{1,6}^*}, \tag{7c,d,e}$$

$$x = \gamma\xi, \qquad \gamma = \sqrt{\frac{(2D_4 + D_1)D_3}{k_1^* k_6^*}}. \tag{7f,g}$$

With these substitutions, Eqs. (6a,b) becomes dimension-less, i.e.,

$$\begin{aligned} \frac{1}{\alpha}\frac{d^2 q_1}{d\xi^2} &= q_1 + (1-\beta_1)q_1^3 + \beta_1 q_1 q_2^2, \\ \alpha\frac{d^2 q_1}{d\xi^2} &= q_1 + (1-\beta_2)q_2^3 + \beta_2 q_2 q_1, \end{aligned} \tag{8a,b}$$

and the boundary conditions become

$$\lim_{x\to\pm\infty} q_1 = \pm 1, \quad \lim_{x\to\pm\infty} q_2 = 1. \tag{9a,b}$$

From Eqs. (8) and (9), the function $q_1(\xi)$ should be an odd function, $q_2(\xi)$ should be an even function, and the following conditions hold:

$$q_1(0) = 0, \quad \frac{dq_2(0)}{d\xi}. \tag{10a,b}$$

One integral exists for Eqs. (8a,b), and is shown in Eq. (11),

$$\begin{aligned} &\beta_2^2\left(\frac{dq_1}{d\xi}\right)^2 + \alpha^2\beta_1\left(\frac{dq_2}{d\xi}\right)^2 + \alpha\beta_2(q_1^2 - 1) - \frac{\alpha}{2}\beta_2(1-\beta_1)(q_1^4 - 1) \\ &+ \alpha\beta_1(q_2^2 - 1) - \frac{\alpha}{2}\beta_1(1-\beta_2)(q_2^4 - 1) - \alpha\beta_1\beta_2(q_1^2 q_2^2 - 1) = 0. \end{aligned} \tag{11}$$

Analyzing Eqs. (8a,b), one finds that stability requires $\beta_2 < 1$, which means that the coefficients A_6^* and A_{16}^* must have the same sign. The coefficient α should be on the order of one and positive. There are three independent parameters in Eqs. (8a,b), β_1, β_2 and α, which control the variation of the order parameter across a domain wall or an AP boundary. Fig. 1 shows the influence of β_1 while the parameters α and β_2 are fixed. One can see that the anti-symmetric component q_1 of the order parameter changes the most while q_2, the symmetric component, shows little change. In

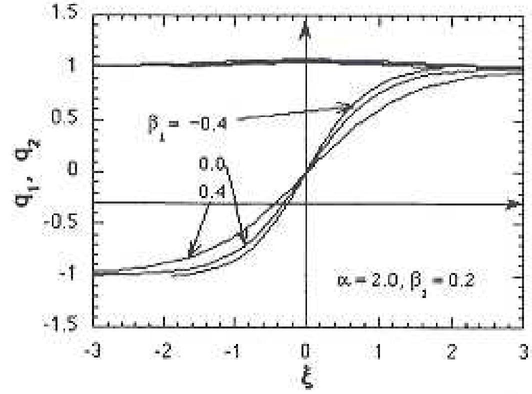

Figure 1 Numerical solutions for Eq. (8 a,b) with the coefficients $\alpha = 2.0$, $\beta_2 = 0.2$ and $\beta_1 = -0.4$, 0.0 and 0.4, respectively.

Fig. 2, α and β_1 are fixed and β_2 changes from -0.4 to 0.2. For this case, only the symmetric component of the OP q_2 changes its amplitude while q_1 is practically un-changed. For both cases, only the amplitude of the OP varies but the thickness of the transition region is almost unchanged by the variation of β_1 and β_2. In Fig. 3, both β_1 and β_2 are fixed but changes in α go from -0.4 to 0.4. As we can see the wall thickness increases with α. The OP amplitude variation across a domain wall is determined by the nonlinear coefficients in the free energy expansion while the domain wall thickness is mainly controlled by the gradient coefficients.

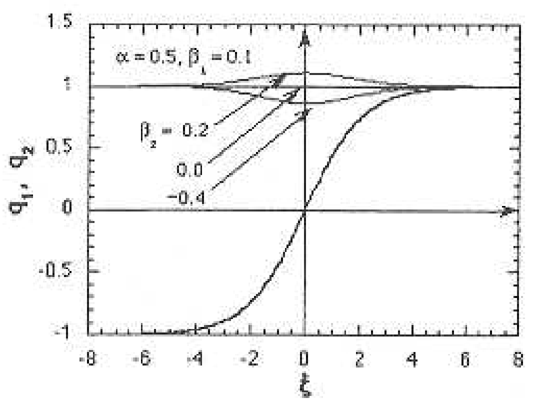

Figure 2 Numerical solutions for Eq. (8 a,b) with the coefficients $\alpha = 0.5$, $\beta_1 = 0.1$ and $\beta_2 = -0.4$, 0.0 and 0.2, respectively.

Stronger non-local coupling (large gradient coefficients) results in broader domain walls.

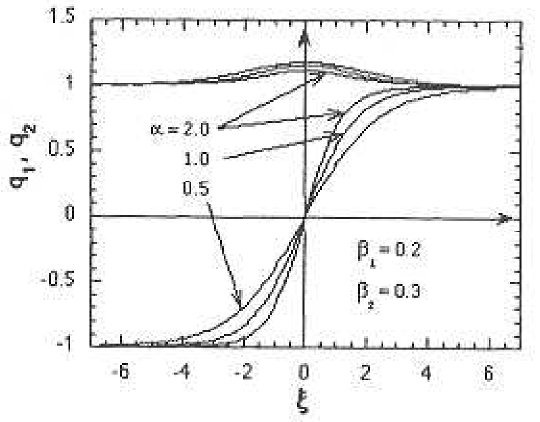

Figure 3: Numerical solutions for Eq. (8 a,b) with the coefficients $\alpha = 2.0$, $\beta_2 = 0.2$ and $\beta_1 = -0.4$, 0.0 and 0.4, respectively.

CONCLUSION

We have described a systematic method for studying the domains and also domain walls that occur in ferroic phase transitions. Use of the continually expanding ISOTROPY program gives information about primary and secondary order parameters and their invariants, gradient invariants, domain pairs and domain twins, as well as symmetry determined physical properties. Numerical solutions for the domain walls provided additional insight into the detailed OP variation in the spatial transition region and the influence of different physical parameters in the free energy.

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