

A symmetry comparison of orientation-twin and antiphase domain walls in $\text{Pb}_3(\text{VO}_4)_2$

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2001 J. Phys.: Condens. Matter 13 3111

(<http://iopscience.iop.org/0953-8984/13/13/320>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.226

The article was downloaded on 16/05/2010 at 11:46

Please note that [terms and conditions apply](#).

A symmetry comparison of orientation-twin and antiphase domain walls in $\text{Pb}_3(\text{VO}_4)_2$

R A Hatt¹ and D M Hatch

Department of Physics and Astronomy, N283 ESC, Brigham Young University, Provo, UT 84602, USA

E-mail: hatt@sou.edu and hatchd@wigner.byu.edu

Received 18 January 2000, in final form 18 January 2001

Abstract

A group-theoretical comparison of domain walls in orientation twins and antiphase structures is presented for the improper ferroelastic transition in lead orthovanadate, $\text{Pb}_3(\text{VO}_4)_2$. Six possible domains arise in the daughter state: three orientation states and three translation-related antiphase states. The transition is driven by a three-component primary order parameter belonging to the F_2^+ irrep, with secondary order parameters consisting of elements of the spontaneous strain tensor. Order-parameter profiles across domain walls which arise in structures composed of pairs of the allowed daughter states can be calculated by constructing the Landau–Ginzburg free energy and applying the Euler–Lagrange equations. We present some solutions of the resulting differential equations, and note some interesting features in the symmetries of the profiles described by these solutions. In particular, the antiphase wall is described by the same diperiodic group as the domains on either side of it, whereas the orientation-twin wall is described by a different diperiodic group to either of the two domains bordering it.

1. Introduction

Phase transitions in solids frequently result in multi-domain structures, which necessarily contain boundaries between domains, i.e., domain walls. These domain walls represent regions where the values of the order parameters are changing. Such changes in order parameters can affect the macroscopic properties of the material, and therefore are of theoretical and experimental interest. The mathematical description of how an order parameter changes across a wall is contained in its *profile*. In this work, we will focus on a symmetry description of the domains and order-parameter profiles that arise in the ferroelastic transition in lead orthovanadate, $\text{Pb}_3(\text{VO}_4)_2$.

¹ Current address: Department of Physics and Engineering, Southern Oregon University, 1250 Siskiyou Boulevard, Ashland, OR 97520, USA.

At high temperatures, lead orthovanadate has the structure [1] shown schematically in figure 1(a). The structural units shown are repeated along a hexagonal lattice and are described by the hexagonal space group $R\bar{3}m$ (here, we follow the convention of the *International Tables* [2], and take the c -axis to be parallel to the $\bar{3}$ axis). In this phase, the lead and vanadium atoms align along the c -axis. The oxygen atoms form tetrahedra around the vanadium atoms, with successive tetrahedra along the c -axis rotated by 60° with respect to each other. Upon cooling through $T_c \approx 120^\circ\text{C}$, the material undergoes a structural phase transition to a monoclinic phase depicted in figures 1(b) and 1(c), and described by the space group $P2_1/c$. This monoclinic phase arises as a result of atomic displacements as depicted in figure 1(c), with two of the lead and both of the vanadium atoms displacing perpendicular to the c -axis (the central lead atom does not displace), and accompanied by the appearance of a spontaneous strain. The oxygen tetrahedra also rotate around an axis perpendicular to the displacements of the lead and vanadium atoms. These distortions define the transition as being driven by F-point distortions (order parameter), specifically belonging to the F_2^+ irreducible representation of the parent $R\bar{3}m$ space group. This irreducible representation carries a three-component primary order parameter, (η_1, η_2, η_3) , that describes the displacements of the atoms from their parent hexagonal positions. For example, atoms at Wyckoff c positions (such as the V atoms and two of the Pb atoms) will distort off the c -axis along the hexagonal a -direction (corresponding to η_1), b -direction (corresponding to η_2) or $-a - b$ -direction (corresponding to η_3), thus breaking the threefold symmetry of the parent structure.

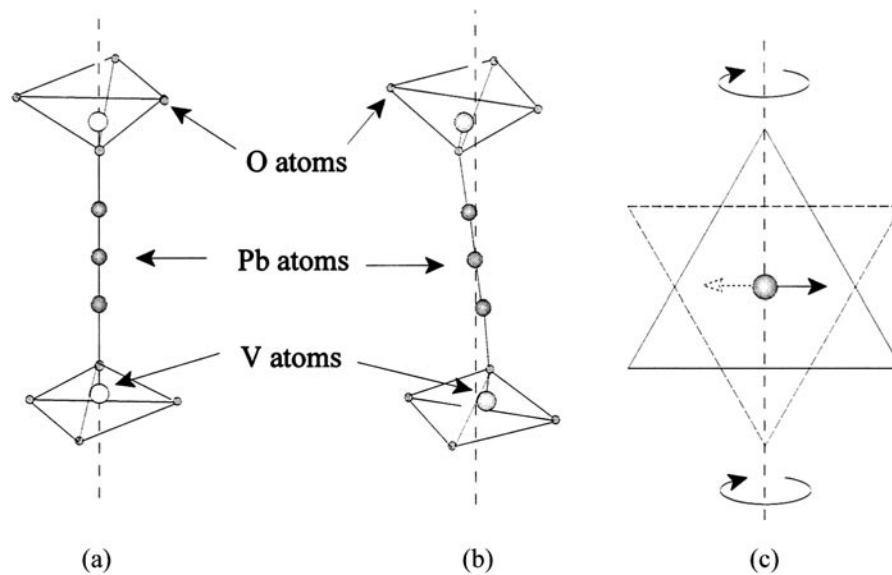


Figure 1. Structure of a formula unit of $\text{Pb}_3(\text{VO}_4)_2$: (a) parent phase, (b) monoclinic phase and (c) symmetry-breaking distortions at Wyckoff c positions.

F_2^+ distortions simultaneously allow Γ_1^+ and Γ_3^+ distortions to appear (since no further symmetry change is introduced by these distortions). These distortions correspond to the secondary order parameters, which in this case are components of the spontaneous strain tensor, as indicated below:

$$\begin{aligned} \Gamma_1^+: v &= e_{11} + e_{22} \\ \Gamma_3^+: (u_1, u_2) &= (e_{11} - e_{22}, 2e_{12}). \end{aligned} \quad (1)$$

2. Relationships between domains

The atomic displacements shown in figures 1(b) and 1(c) result in the loss of the threefold symmetry axis of the parent phase. This means that there will be three orientation states in the monoclinic daughter phase, which will be labelled S_1 , S_2 and S_3 . Furthermore, the transition results in a cell doubling [3], meaning the loss of half of the parent translation subgroup, which gives rise to three more states, labelled S_4 , S_5 and S_6 , in the daughter phase. These three states are related to the three orientation states by simple translations, S_4 being related to S_1 , S_5 being related to S_2 and S_6 being related to S_3 . Thus, there are six possible domains in the daughter phase [4–6]. The values of the primary order parameter for each of the six possible domains are given in table 1.

Table 1. Primary-order-parameter values.

Domain	OP	Domain	OP
S_1	$(a, 0, 0)$	S_4	$(-a, 0, 0)$
S_2	$(0, a, 0)$	S_5	$(0, -a, 0)$
S_3	$(0, 0, a)$	S_6	$(0, 0, -a)$

Since there is more than one state in the daughter phase, there will be some elements in the parent group, G , that are not in the daughter group, F . For example, in lead orthovanadate, the threefold axis present in the parent phase is lost in the ferroelastic transition, as are half of the pure translations (due to the cell doubling). These lost symmetry elements transform the possible domains into each other. For example, the lost threefold axis, upon successive applications, transforms S_1 into S_2 and then S_3 . The set of lost elements, $\{g_{21}\}$, that transform the domain S_1 into the domain S_2 , is the right coset of the symmetry group, F_1 , of the domain S_1 :

$$\{g_{21}\} = g_{21}F_1 \quad (2)$$

where the g_{21} on the right-hand side is any one element that transforms domain S_1 into domain S_2 . Similar cosets can be calculated for the remaining domains.

The value of calculating the cosets, and thus listing the elements that transform domains into each other, is in the constructing of twin groups, which describe the symmetry of a structure composed of two juxtaposed semi-infinite domains with their separating planar domain wall (figure 2). For the purposes of this discussion, such a structure has two types of symmetry element: operations that leave each domain and the direction normal to the wall unchanged; and operations that interchange the two domains and reverse the direction normal to the domain wall. (The symmetry elements can be further classified into four types [7], but such detail is not necessary here.) Additionally, the operations must leave the position of the domain wall and its orientation (aside from the direction reversal just mentioned) unchanged, so the twin group has, in general, fewer elements than the symmetry groups describing either domain. The symmetry elements which leave each domain unchanged are found in the intersection of the symmetry groups of the two domains, while the symmetry elements that interchange the two domains are found in the intersection of the two cosets, each of which transforms one domain into the other. The usefulness of the elements of the twin group, particularly the elements which interchange the domains, will be emphasized below.

Since there are six possible single-domain states, there are $6 \times 6 = 36$ possible twin configurations (each of which has a number of possible wall orientations). For the specific transition we are considering, this number can be reduced to three distinct classes of twins: the degenerate ‘twins’ class where the same domain state is on each side of the wall, the

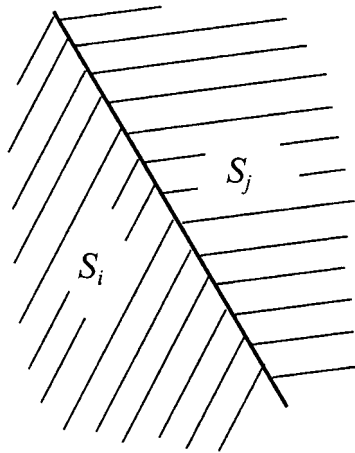


Figure 2. A sample domain twin.

orientation-twin class and the class of antiphase structures. The degenerate case will not be considered further, and one orientation twin and one antiphase structure can be considered as representative of each class of twins.

3. Equations describing the order-parameter profiles

Calculation of order-parameter profiles makes use of the Landau–Ginzburg free energy. This free energy is constructed as an expansion in invariant polynomials of the primary and secondary order parameters. Such invariant polynomials are left unchanged by the actions of the elements of the parent space group, and so reflect the symmetry of the parent structure. These invariant polynomials can be calculated by computer [8, 9], and included to arbitrary order. However, in practice, the expansion is typically kept only to fourth order in the primary order parameter, and to second order in the secondary order parameters (the expansion may need to be carried to higher order for stability concerns or to model first-order transitions). The specific form of the invariants, especially those involving derivatives, can depend on the coordinate system chosen; in particular, the strain components e_{ij} depend on the coordinate system, since they involve differentiation of displacement-vector components with respect to the defined coordinate directions. The invariant polynomials of the primary order parameter for the ferroelastic transition in lead orthovanadate are listed in table 2, for the coordinate system defined as in figure 3 with the Cartesian y - and z -axes chosen parallel to the hexagonal b - and c -axes. Gradient terms with second derivatives are included. This generality is unnecessary in systems where the order parameter varies slowly enough in space that only first-derivative terms are needed, but is necessary for cases of very thin walls where contributions from higher-order derivatives cannot be ignored. Because we are performing a second-order variation below, we have included such terms in table 2.

In general, the orientation of the domain wall will not contain a coordinate axis. However, since the domains on either side of the wall are semi-infinite, all quantities associated with the structure are variables in the distance from the wall only. That is, changes in position parallel to the wall will not result in changes in local properties of the crystal. So, it is useful to rotate to a new coordinate system, (x', y', z') where the x' -direction is normal to the domain wall. For example, if the domain wall is parallel to the σ_{v3} mirror plane (a case that will occur below),

Table 2. Invariant polynomials for the F_2^+ irreducible representation of $R\bar{3}m$.

Primary order parameter
$\varphi_1 = \eta_1^2 + \eta_2^2 + \eta_3^2$
$\varphi_2 = (\eta_1^2 + \eta_2^2 + \eta_3^2)^2$
$\varphi_3 = \eta_1^4 + \eta_2^4 + \eta_3^4$
Secondary order parameters
$\psi_1 = v$
$\psi_2 = v^2$
$\psi_3 = u_1^2 + u_2^2$
Coupling terms
$\zeta_1 = v(\eta_1^2 + \eta_2^2 + \eta_3^2)$
$\zeta_2 = \frac{1}{2}u_1(\eta_1^2 - 2\eta_2^2 + \eta_3^2) + \frac{\sqrt{3}}{2}u_2(\eta_1^2 - \eta_3^2)$
Gradient terms
$\delta_1 = \frac{5}{6}\eta_1 \frac{\partial^2 \eta_1}{\partial x^2} - \frac{1}{\sqrt{3}}\eta_1 \frac{\partial^2 \eta_1}{\partial x \partial y} + \frac{1}{2}\eta_1 \frac{\partial^2 \eta_1}{\partial y^2} + \frac{1}{3}\eta_2 \frac{\partial^2 \eta_2}{\partial x^2} + \eta_2 \frac{\partial^2 \eta_2}{\partial y^2} + \frac{5}{6}\eta_3 \frac{\partial^2 \eta_3}{\partial x^2} + \frac{1}{\sqrt{3}}\eta_3 \frac{\partial^2 \eta_3}{\partial x \partial y} + \frac{1}{2}\eta_3 \frac{\partial^2 \eta_3}{\partial y^2}$
$\delta_2 = -\frac{1}{2\sqrt{3}}\eta_1 \frac{\partial^2 \eta_1}{\partial x^2} + \eta_1 \frac{\partial^2 \eta_1}{\partial x \partial y} + \frac{1}{2\sqrt{3}}\eta_1 \frac{\partial^2 \eta_1}{\partial y^2} + \frac{1}{\sqrt{3}}\eta_2 \frac{\partial^2 \eta_2}{\partial x^2} - \frac{1}{\sqrt{3}}\eta_2 \frac{\partial^2 \eta_2}{\partial y^2} - \frac{1}{2\sqrt{3}}\eta_3 \frac{\partial^2 \eta_3}{\partial x^2} - \eta_3 \frac{\partial^2 \eta_3}{\partial x \partial y} + \frac{1}{2\sqrt{3}}\eta_3 \frac{\partial^2 \eta_3}{\partial y^2}$
$\delta_3 = \frac{1}{2}\eta_1 \frac{\partial^2 \eta_1}{\partial x \partial z} + \frac{\sqrt{3}}{2}\eta_1 \frac{\partial^2 \eta_1}{\partial y \partial z} - \eta_2 \frac{\partial^2 \eta_2}{\partial x \partial z} + \frac{1}{2}\eta_3 \frac{\partial^2 \eta_3}{\partial x \partial z} - \frac{\sqrt{3}}{2}\eta_3 \frac{\partial^2 \eta_3}{\partial y \partial z}$
$\delta_4 = \eta_1 \frac{\partial^2 \eta_1}{\partial z^2} + \eta_2 \frac{\partial^2 \eta_2}{\partial z^2} + \eta_3 \frac{\partial^2 \eta_3}{\partial z^2}$
$\delta_5 = \frac{5}{6} \left(\frac{\partial \eta_1}{\partial x} \right)^2 - \frac{1}{\sqrt{3}} \left(\frac{\partial \eta_1}{\partial x} \right) \left(\frac{\partial \eta_1}{\partial y} \right) + \frac{1}{2} \left(\frac{\partial \eta_1}{\partial y} \right)^2 + \frac{1}{3} \left(\frac{\partial \eta_2}{\partial x} \right)^2 + \left(\frac{\partial \eta_2}{\partial y} \right)^2 + \frac{5}{6} \left(\frac{\partial \eta_3}{\partial x} \right)^2 + \frac{1}{\sqrt{3}} \left(\frac{\partial \eta_3}{\partial x} \right) \left(\frac{\partial \eta_3}{\partial y} \right) + \frac{1}{2} \left(\frac{\partial \eta_3}{\partial y} \right)^2$
$\delta_6 = -\frac{1}{2\sqrt{3}} \left(\frac{\partial \eta_1}{\partial x} \right)^2 - \left(\frac{\partial \eta_1}{\partial x} \right) \left(\frac{\partial \eta_1}{\partial y} \right) + \frac{1}{2\sqrt{3}} \left(\frac{\partial \eta_1}{\partial y} \right)^2 + \frac{1}{\sqrt{3}} \left(\frac{\partial \eta_2}{\partial x} \right)^2 - \frac{1}{\sqrt{3}} \left(\frac{\partial \eta_2}{\partial y} \right)^2 - \frac{1}{2\sqrt{3}} \left(\frac{\partial \eta_3}{\partial x} \right)^2 - \left(\frac{\partial \eta_3}{\partial x} \right) \left(\frac{\partial \eta_3}{\partial y} \right) + \frac{1}{2\sqrt{3}} \left(\frac{\partial \eta_3}{\partial y} \right)^2$
$\delta_7 = \frac{1}{2} \left(\frac{\partial \eta_1}{\partial x} \right) \left(\frac{\partial \eta_1}{\partial z} \right) + \frac{\sqrt{3}}{2} \left(\frac{\partial \eta_1}{\partial x} \right) \left(\frac{\partial \eta_1}{\partial z} \right) - \left(\frac{\partial \eta_2}{\partial x} \right) \left(\frac{\partial \eta_2}{\partial z} \right) + \frac{1}{2} \left(\frac{\partial \eta_3}{\partial x} \right) \left(\frac{\partial \eta_3}{\partial z} \right) - \frac{\sqrt{3}}{2} \left(\frac{\partial \eta_3}{\partial y} \right) \left(\frac{\partial \eta_3}{\partial z} \right)$
$\delta_8 = \left(\frac{\partial \eta_1}{\partial z} \right)^2 + \left(\frac{\partial \eta_2}{\partial z} \right)^2 + \left(\frac{\partial \eta_3}{\partial z} \right)^2$

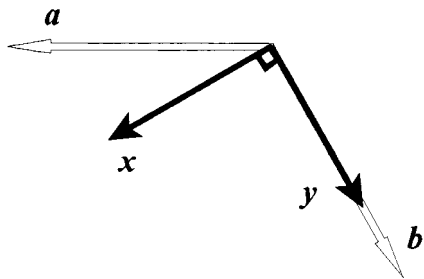


Figure 3. Cartesian x - and y -axes in relationship to the parent hexagonal axes.

the transformation is an anticlockwise rotation of 30° around the z -axis:

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}. \quad (3)$$

In making such a coordinate transformation, care must be taken that all quantities which depend on the coordinate system are transformed, including vector components and derivatives.

After this coordinate transformation has been applied, the second-order variational Euler-Lagrange equations are used:

$$\frac{\partial}{\partial x'_j} \frac{\partial}{\partial x'_k} \left[\frac{\partial \mathcal{F}}{\partial \eta_{i,jk}} \right] - \frac{\partial}{\partial x'_j} \left[\frac{\partial \mathcal{F}}{\partial \eta_{i,j}} \right] + \frac{\partial \mathcal{F}}{\partial \eta_i} = 0 \quad (4)$$

$$\sigma_{ij,j} = 0. \quad (5)$$

Here, a comma denotes partial differentiation; i.e., $\eta_{i,j} = \partial\eta_i/\partial x'_j$, and σ_{ij} denotes the stress tensor, which is related to the strain tensor by

$$\sigma_{ij} = \frac{\partial \mathcal{F}}{\partial e_{ij}}. \quad (6)$$

Equation (5), together with the compatibility relations among the second derivatives of the strain tensor components,

$$\varepsilon_{pks} \frac{\partial}{\partial x'_k} \left(\frac{\partial e_{sj}}{\partial x'_i} - \frac{\partial e_{si}}{\partial x'_j} \right) = 0 \quad (7)$$

(where ε_{pks} denotes the totally antisymmetric third-rank Levi-Civita tensor), puts constraints on the strain components, allowing the secondary order parameters to be written (after some straightforward but tedious algebra) as functions of the primary order parameters. This means the free energy can be rewritten as a function of only the primary order parameter. Then, the variation shown in equation (4) yields a set of three coupled ordinary differential equations which describe the primary-order-parameter profiles. We obtained sets of coupled equations for several domain wall orientations and for several antiphase and orientation-twin walls. For our considerations with $\text{Pb}_3(\text{VO}_4)_2$, the most general form of these equations is

$$\begin{aligned} \frac{d^2 \eta_1}{dx'^2} &= \alpha_1 \eta_1 + \beta_1 \eta_1^3 + \gamma_1 \eta_1 \eta_2^2 + \varepsilon_1 \eta_1 \eta_3^2 \\ \frac{d^2 \eta_2}{dx'^2} &= \alpha_2 \eta_2 + \beta_2 \eta_2^3 + \gamma_2 \eta_1^2 \eta_2 + \varepsilon_2 \eta_2 \eta_3^2 \\ \frac{d^2 \eta_3}{dx'^2} &= \alpha_3 \eta_3 + \beta_3 \eta_3^3 + \gamma_3 \eta_1^2 \eta_3 + \varepsilon_3 \eta_2^2 \eta_3 \end{aligned} \quad (8)$$

where the coefficients depend on the orientation of the domain wall, and the expansion coefficients in the Landau–Ginzburg free energy. The boundary conditions for these equations are the values for the primary order parameter as listed in table 1.

For numerical simplicity, the primary order parameter will be rescaled to ± 1 :

$$(\eta_1, \eta_2, \eta_3) \rightarrow a(\eta_1, \eta_2, \eta_3). \quad (9)$$

For example, in S_1 , the order parameter will be $(1, 0, 0)$. This rescaling does not affect the form of the equations (8), but simply rescales the coefficients, so that each $\beta_i, \gamma_i, \varepsilon_i$ is multiplied by a^2 . For simplicity of notation, the a^2 will be dropped.

4. The antiphase case

As a representative example of an antiphase structure, consider the structure composed of domains S_1 and S_4 , which are related by a simple translation. We will take x' to be positive on the S_4 side of the wall (the origin, $x' = 0$, is taken to be at the centre of the wall). Referring to table 1 and equation (9), the order parameter changes across the wall and matches the boundary condition

$$\lim_{x \rightarrow \pm\infty} (\eta_1, \eta_2, \eta_3) = (\pm 1, 0, 0). \quad (10)$$

Since the boundary conditions require both η_2 and η_3 to be zero far from the domain wall, it is natural, at first, to make the simplifying assumption that these two components are identically zero:

$$\eta_2 \equiv 0 \quad \eta_3 \equiv 0. \quad (11)$$

This reduces the set of three coupled equations to a single equation,

$$\frac{d^2\eta_1}{dx'^2} = \alpha\eta_1 + \beta\eta_1^3. \quad (12)$$

Far from the wall, the order parameter reaches the constant value it has in the corresponding domain. Additionally, this means that all of its derivatives approach zero. Examining equation (12), this leads to the conclusion that

$$\alpha + \beta = 0. \quad (13)$$

Thus, the boundary condition puts the strong restriction on the coefficients that if $\alpha \neq -\beta$ no real solution to equation (12) that matches the boundary conditions (10) exists. Under this condition, rescaling the x' -axis,

$$x'' = \sqrt{\beta}x' \quad (14)$$

further simplifies the equation to

$$\frac{d^2\eta_1}{dx''^2} = -\eta_1 + \eta_1^3. \quad (15)$$

This equation has the analytical solution

$$\eta_1 = \tanh(x''/\sqrt{2}). \quad (16)$$

Rewriting this in terms of x' ,

$$\eta_1 = \tanh(x'\sqrt{\beta/2}) \quad (17)$$

expresses the general solutions that occur. Furthermore, it is easily seen from equation (17) that in order for the solution to be real, β must be positive; that is,

$$\beta > 0. \quad (18)$$

The solutions for several values of β are shown in figure 4. Note that the solution converges to its final value *faster* for *larger* values of β .

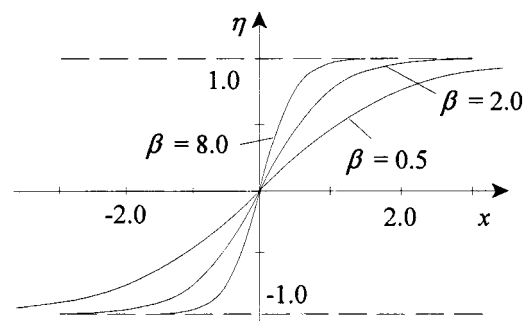


Figure 4. Solutions for three values of β in the antiphase case, with $\eta_2 = 0$, $\eta_3 = 0$.

The more general case of the antiphase twin allows *all three* components of the order parameter to be nonzero. A simplified case will be examined: orientations of the wall for which there is an element in the twin group that interchanges η_2 and η_3 , and reverses the direction normal to the wall. In the present case, such elements are either twofold axes, parallel to C_{21}'' , or mirror planes, parallel to σ_{v1} (following the notation of Bradley and Cracknell [10]). For one of these elements to be in the twin group, the wall must be oriented so that it is either parallel to σ_{v1} , or parallel to the C_{21}'' -axis. For any other wall orientation, the action of C_{21}'' or

σ_{v1} will rotate the wall into some other orientation, and so such elements will not be in the twin group.

If either C''_{21} or σ_{v1} is present in the twin group as described above, the matrix representation of these elements in the F_2^+ irrep can be used to gain some insight. These two elements have the same matrix representation,

$$\Gamma(C''_{21}) = \Gamma(\sigma_{v1}) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & -1 & 0 \end{pmatrix}. \quad (19)$$

The action of this element has two effects: a rotation in the space spanned by (η_1, η_2, η_3) , which interchanges η_2 and η_3 with a sign change in accordance with equation (19), and a rotation in the (x', y', z') Cartesian space. The rotation in Cartesian space is not represented by equation (19), but the rotation, C''_{21} or σ_{v1} , does switch x' to $-x'$. Overall,

$$\begin{aligned} \eta_1(x') &\leftrightarrow -\eta_1(-x') \\ \eta_2(x') &\leftrightarrow -\eta_3(-x'). \end{aligned} \quad (20)$$

This immediately means that η_1 is odd. Further, if η_2 is odd (even) then η_3 must also be odd (even), as in figure 5.

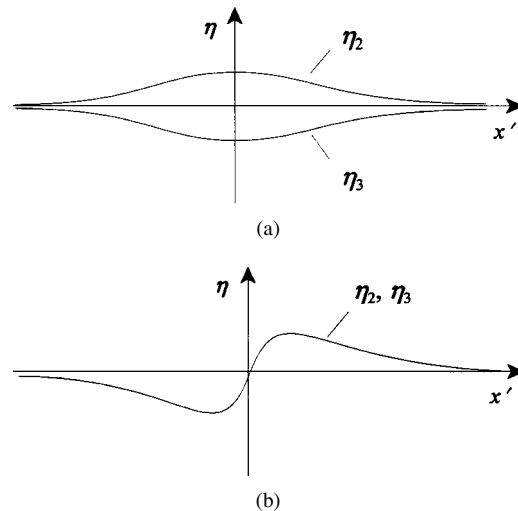


Figure 5. Relationship between η_2 and η_3 , with (a) η_2 and η_3 both even and (b) η_2 and η_3 both odd.

The interchangeability of η_2 and η_3 requires that their coefficients in the differential equations (8) be equal. This allows a first integral to be computed, relating the values of the order-parameter components to their first derivatives. Since η_1 must be odd, its value at the origin is zero. If η_2 and η_3 are also odd, their values must also be zero at the origin. In this case, the first integral is expressed in terms of values of the derivatives of η_1 and η_2 at the origin,

$$\eta_1'(0)^2 + 2 \frac{\gamma_1}{\gamma_2} \eta_2'(0)^2 = \frac{1}{2} \quad (21)$$

where the prime indicates differentiation with respect to x' . On the other hand, if η_2 and η_3 are even, their first derivatives at the origin are both zero, so the first integral is expressed in

terms of the derivative of η_1 and the value of η_2 at the origin,

$$\eta_1'(0)^2 = 2\left(\frac{\alpha_2}{\beta_1}\right)\left(\frac{\gamma_1}{\gamma_2}\right)\eta_2(0)^2 + \frac{1}{2}\left(\frac{\beta_2 + \varepsilon_2}{\beta_1}\right)\left(\frac{\gamma_1}{\gamma_2}\right)\eta_2(0)^4 + \frac{1}{2}. \quad (22)$$

In either case, there are two unknowns at the origin: the derivative of η_1 , and either the value of, or the derivative of, η_2 and η_3 (the interchangeability of η_2 and η_3 requires their values and derivatives at the origin to be equal, to within a sign change).

At this point, simple shooting methods can be employed to numerically solve the system of differential equations. When this is done, however, the only solutions found which match the boundary conditions are those in which η_2 and η_3 both remain identically zero. From a symmetry standpoint, this means that the form of the order parameter does not change across the wall; i.e., it is always of the form $(a, 0, 0)$. This means that the wall and the domains on either side of it are all described by the same diperiodic space group.

5. The orientation-twin case

The twin formed by domains S_1 and S_2 will be studied as a representative example for the orientation-twin case, with S_1 on the $x' < 0$ side of the wall. For this case, the order parameter changes across the wall as

$$\lim_{x' \rightarrow \mp\infty} (\eta_1, \eta_2, \eta_3) = \begin{cases} (1, 0, 0) & x' \rightarrow -\infty \\ (0, 1, 0) & x' \rightarrow +\infty. \end{cases} \quad (23)$$

Now, two of the components have a nonzero boundary condition.

Since the phase transition studied here is ferroelastic, the orientation of allowed domain walls is specified by Sapriel's result [11], which is that allowed domain walls are either parallel to lost mirror planes (W walls) or contain lost twofold axes (W' walls) which transform the two domains into each other. For the orientation twin considered here, formed by domains S_1 and S_2 , the lost twofold axis is the C''_{23} -axis, and the lost mirror plane is the σ_{v3} -plane. For walls parallel or perpendicular to this axis, the twin group contains an element that interchanges η_1 and η_2 while reversing the direction normal to the wall. This is either the C''_{23} -axis or the σ_{v3} -plane. The F_2^+ matrix representation of this element is

$$\Gamma(C''_{22}) = \Gamma(\sigma_{v2}) = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}. \quad (24)$$

For either W or W' walls, then, the action of this twin-group element on the order parameter is (recall that this element also switches x' to $-x'$)

$$\begin{aligned} \eta_1(x') &= \eta_2(-x') \\ \eta_3(x') &= -\eta_3(-x'). \end{aligned} \quad (25)$$

This means that the coefficients of η_1 and η_2 in the differential equations must be equal. Since the boundary conditions that must be met are not even or odd, it must be concluded that η_1 and η_2 are both neither even nor odd. However, their interchangeability ensures that their values are equal at the origin, and that their first derivatives at the origin differ only in sign. Further, it is seen that η_3 is odd. These observations allow the system of differential equations to be simplified in a manner analogous to what was done with the antiphase case.

Since the derivatives must all vanish far from the wall, the condition must be met that

$$\alpha_1 + \beta_1 = 0. \quad (26)$$

This allows the differential equations to be written:

$$\begin{aligned}\frac{d^2\eta_1}{dx'^2} &= -\beta_1\eta_1 + \beta_1\eta_1^3 + \gamma_1\eta_1\eta_2^2 + \varepsilon_1\eta_1\eta_3^2 \\ \frac{d^2\eta_2}{dx'^2} &= -\beta_1\eta_2 + \beta_1\eta_2^3 + \gamma_1\eta_1^2\eta_2 + \varepsilon_1\eta_2\eta_3^2 \\ \frac{d^2\eta_3}{dx'^2} &= \alpha_3\eta_3 + \beta_3\eta_3^3 + \gamma_3(\eta_1^2 + \eta_2^2)\eta_3.\end{aligned}\quad (27)$$

In the numerical analysis of this system of equations, a similar result is obtained, in that, in order to match the boundary conditions on all three components, η_3 must remain identically zero, while only η_1 and η_2 vary. So, in what follows it will be assumed that $\eta_3 \equiv 0$. The system of differential equations then reduces to

$$\begin{aligned}\eta_1'' &= -\eta_1 + \eta_1^3 + \gamma\eta_1\eta_2^2 \\ \eta_2'' &= -\eta_2 + \eta_2^3 + \gamma\eta_1^2\eta_2\end{aligned}\quad (28)$$

where the x' -axis has been rescaled by $\sqrt{\beta_1}$, and the prime indicates differentiation with respect to this rescaled axis. These equations have an associated first integral whose value at the origin is

$$\eta_1'(0)^2 = -\eta_1(0)^2 + \frac{1}{2}(\gamma + 1)\eta_1(0)^4 + \frac{1}{2}. \quad (29)$$

Again, using this result, simple shooting methods allow solutions to be calculated. Representative solutions to these equations are shown in figures 6 and 7. Figure 6 shows both η_1 and η_2 for a typical solution, while figure 7 shows how one component depends on the

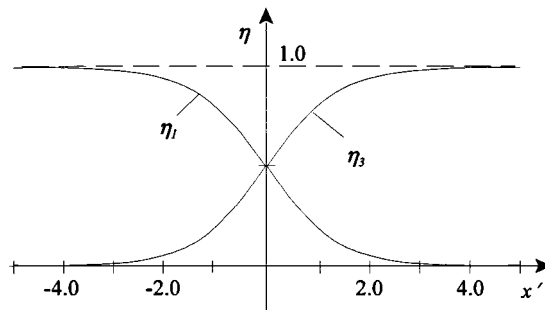


Figure 6. Graph of the solution for $\gamma = 3.0$.

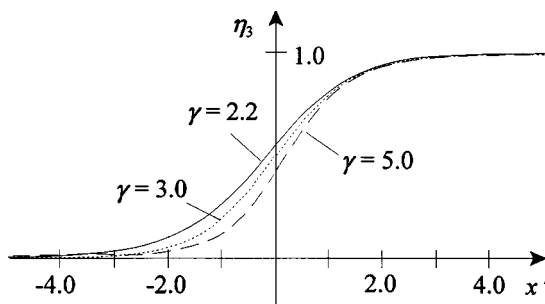


Figure 7. Solutions for different values of γ .

value of the parameter γ . Here it is seen that the solution converges more rapidly for larger values of γ .

The symmetry implication here is markedly different to that for the antiphase case. In the orientation-twin case, the wall has a primary-order-parameter form of $(a, b, 0)$, which means that the diperiodic group describing the wall is different from the two (different) diperiodic groups describing the two domains comprising the twin.

6. Summary

A numerical and analytical study of the symmetries of antiphase and orientation-twin structures in lead orthovanadate has been presented. The forms of the primary order parameter in the six allowed domain states in the low-temperature phase are given, and the Landau–Ginzburg free energy for the transition has been constructed. From this information, profiles for the order parameters as they change across the domain walls in two-domain structures have been calculated. Two types of two-domain structure have been considered: orientation twins and antiphase structures. The symmetries of the two structures are shown to be markedly different. In particular, the domain wall has the same form for the order parameter as the translationally related domains on either side of the wall, while the orientation-twin wall has an order parameter that is distinct from those of the domains on either side of it. We also find, for both the antiphase and orientation twins, if an order-parameter component is zero far from the domain wall on both sides it remains zero across the wall. We suspect, but have not proven, that the result for the antiphase case might be quite general for translationally related domains which share the same space group, where the order parameter should see at most a change in sign across an antiphase wall. For the orientation case, generalization presents some difficulties, because the relationship between the two domains has more possibilities. In the present example of lead orthovanadate, there is only one nonzero order-parameter component, and so the possible relationship is simple. However, a more general case might have two nonzero components in the order parameter, and the possible relationships would be richer. Therefore, it is not known at this point how general the results presented here are for orientation twins. However, the methodology can be applied to a wide variety of phase transitions, so further study in these directions to determine the generality of these conclusions is to be carried out.

References

- [1] 1948 *Struct. Rep.* **11** 388
1970 *Struct. Rep. A* **35** 363
1984 *Struct. Rep. A* **51** 213
- [2] Hahn T (ed) 1983 *International Tables for X-Ray Crystallography* (Dordrecht: Reidel)
- [3] Kasatani H, Umeki T and Terauchi H 1992 *J. Phys. Soc. Japan* **61** 2309
- [4] Manolikas C and Amelinckx S 1980 *Phys. Status Solidi a* **60** 607
- [5] Manolikas C, Van Tendeloo G and Amelinckx S 1986 *Solid State Commun.* **58** 851
- [6] Hatt R A and Hatch D M 1999 *Ferroelectrics* **226** 61
- [7] Janovec V, Schranz W, Warhanek H and Zikmund Z 1989 *Ferroelectrics* **98** 171
- [8] Stokes H T and Hatch D M 1988 *Isotropy Subgroups of the 230 Crystallographic Space Groups* (Singapore: World Scientific)
- [9] Stokes H T and Hatch D M *ISOTROPY Software* Internet and PC (DOS) versions available at <http://www.physics.byu.edu/~stokesh/isotropy.html>
- [10] Bradley C J and Cracknell A P 1972 *The Mathematical Theory of Symmetry in Solids* (Oxford: Clarendon)
- [11] Sapriel J 1975 *Phys. Rev. B* **12** 5128