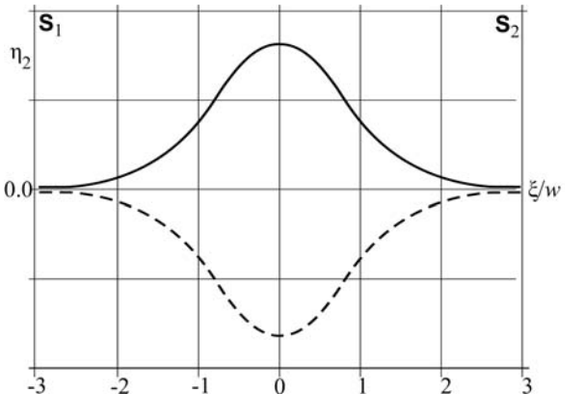

Fig. 3.4.4.10. A profile of the second order parameter component in a degenerate domain wall.

Example 3.4.4.4. In our illustrative phase transition $4_z/m_z m_x m_{xy} \supset 2_x m_y m_z$, the order parameter has two components η_1, η_2 that can be associated with the x and y components P_1 and P_2 of the spontaneous polarization (see Table 3.1.3.1 and Fig. 3.4.2.2). We have seen that the domain wall $[\mathbf{S}_1[010]\mathbf{S}_2]$ of zero thickness has the symmetry $\mathsf{T}_{12} = \underline{2}^\star_z/m_z$. If one lets $\eta_1(y)$ relax and keeps $\eta_2(y) = 0$ (a so-called *linear structure*), then $\mathsf{T}_{12}(\eta_1) = \underline{2}^\star_z/m_z$ (see Fig. 3.4.4.2 with $\xi = y$). If the last condition is lifted, a possible profile of a relaxed $\eta_2(y)$ is depicted by the full curve in Fig. 3.4.4.10. If both components $\eta_1(y)$ and $\eta_2(y)$ are nonzero within the wall, one speaks about a *rotational structure* of domain wall. In this relaxed domain wall the spontaneous polarization rotates in the plane (001), resembling thus a Néel wall in magnetic materials. The even profile $\eta_2(-y) = \eta_2(y)$ has the symmetry $\mathsf{T}_{12}(\eta_2) = m^\star_x 2^\star_y m_z$. Hence, according to (3.4.4.34), the symmetry of a relaxed wall with a rotational structure is $\mathsf{T}_{12}(\eta) = \underline{2}^\star_z/m_z \cap m^\star_x 2^\star_y m_z = \{1, m_z\}$. This is an asymmetric state-reversible (AR*) wall with two chiral variants [see equation (3.4.4.33)] that are related by $\underline{\bar{1}}^\star$ and $\underline{2}^\star_z$; the profile $\eta_2(y)$ of the second variant is depicted in Fig. 3.4.4.10 by a dashed curve.

Similarly, one gets for a zero-thickness domain wall $[\mathbf{S}_1[001]\mathbf{S}_2]$ perpendicular to z the symmetry $\mathsf{T}_{12} = \underline{2}^\star_y/m_y$. For a relaxed domain wall with profiles $\eta_1(z)$ and $\eta_2(z)$, displayed in Figs. 3.4.4.6 and 3.4.4.10 with $\xi = z$, one gets $\mathsf{T}_{12}(\eta_1) = \underline{2}^\star_y/m_y$, $\mathsf{T}_{12}(\eta_2) = m^\star_x \underline{2}^\star_y m_z$ and $\mathsf{T}_{12}(\eta) = \{1, \underline{2}^\star_y\}$. The relaxed domain wall with rotational structure has lower symmetry than the zero-thickness wall or the wall with linear structure, but remains a symmetric and reversible (SR) domain wall in which spontaneous polarization rotates in a plane (001), resembling thus a Bloch wall in magnetic materials. Two chiral right-handed and left-handed variants are related by operations m_z and $\underline{\bar{1}}^\star$. This example illustrates that the structure of domain walls may differ with the wall orientation.

We note that the stability of a domain wall with a rotational structure and with a linear structure depends on the values of the coefficients in the Landau free energy, on temperature and on external fields. In favourable cases, a phase transition from a symmetric linear structure to a less symmetric rotational structure can occur. Such phase transitions in domain walls have been studied theoretically by Bul'bich & Gufan (1989*a*,*b*) and by Sonin & Tagancev (1989).

3.4.4.7. *Microscopic structure and symmetry of domain walls*

The thermodynamic theory of domain walls outlined above is efficient in providing quantitative results (wall thickness, energy) in any specific material. However, since this is a continuum theory, it is not able to treat local structural changes on a microscopic level and, moreover, owing to the small thickness of domain walls (several lattice constants), the reliability of its conclusions is to some extent uncertain.

Discrete theories either use simplified models [*e.g.* pseudospin ANNNI (axial next nearest neighbour Ising) model] that yield quantitative results on profiles, energies and interaction energies of walls but do not consider real crystal structures, or calculate numerically for a certain structure the atomic positions within a wall from interatomic potentials.

Symmetry analysis of domain walls provides useful qualitative conclusions about the microscopic structure of walls. Layer groups with discrete two-dimensional translations impose, *via* the site symmetries, restrictions on possible displacements and/or ordering of atoms or molecules. From these conclusions, combined with a reasonable assumption that these shifts or ordering vary continuously within a wall, one gets *topological constraints on the field of local displacements and/or ordering of atoms or molecules in the wall*. The advantage of this treatment is its simplicity and general validity, since no approximations or simplified models are needed. The analysis can also be applied to domain walls of zero thickness, where thermodynamic theory fails. However, this method does not yield any quantitative results, such as values of displacements, wall thickness, energy *etc*.

The procedure is similar to that in the continuum description. The main relations equations (3.4.4.12)–(3.4.4.17) and the classification given in Table 3.4.4.3 hold for a microscopic description as well; one has only to replace point groups by space groups.

A significant difference is that the sectional layer groups and the wall symmetry depend on the location of the plane p in the crystal lattice. This position can by expressed by a vector $s\mathbf{d}$, where $\mathbf{d}$ is the *scanning vector* (see *IT* E, 2010 and the example below) and s is a non-negative number smaller than 1, $0 \leq s < 1$. An extended symbol of a twin in the microscopic description, corresponding to the symbol (3.4.4.1) in the continuum description, is

$$(\mathsf{S}_1|\mathbf{n}; s\mathbf{d}|\mathsf{S}_2) \equiv (\mathsf{S}_2|-\mathbf{n}; s\mathbf{d}|\mathsf{S}_1). \qquad (3.4.4.35)$$

The main features of the analysis are demonstrated on the following example.

Example 3.4.4.5. Ferroelastic domain wall in calomel. We examine a ferroelastic compatible domain wall in a calomel crystal (Janovec & Zikmund, 1993; *IT* E, 2010, Chapter 5.2). In Section 3.4.2.5, Example 3.4.2.7, we found the microscopic domain states (see Fig. 3.4.2.5) and, in Section 3.4.3.7, the corresponding ordered domain pair $(\mathsf{S}_1, \mathsf{S}_3)$ and unordered domain pair $\{\mathsf{S}_1, \mathsf{S}_3\}$ (depicted in Fig. 3.4.3.10). These pairs have symmetry groups $\mathcal{F}_{13} = Pn_{x\bar{y}}n_{xy}m_z$ and $\mathcal{J}_{13} = P4^\star_{2z}/m_z n_{xy} m^\star_x$, respectively. Both groups have an orthorhombic basis $\mathbf{a}^o = \mathbf{a}^t - \mathbf{b}^t$, $\mathbf{b}^o = \mathbf{a}^t + \mathbf{b}^t$, $\mathbf{c}^o = \mathbf{c}^t$, with a shift of origin $\mathbf{b}^t/2$ for both groups.

Compatible domain walls in this ferroelastic domain pair have orientations (100) and (010) in the tetragonal coordinate system (see Table 3.4.3.6). We shall examine the former case – the latter is crystallographically equivalent. Sectional layer groups of this plane in groups $\mathcal{F}_{13}$ and $\mathcal{J}_{13}$ have a two-dimensional translation group (net) with basic vectors $\mathbf{a}^s = 2\mathbf{b}^t$ and $\mathbf{b}^s = \mathbf{c}^t$, and the scanning vector $\mathbf{d} = 2\mathbf{a}^t$ expresses the repetition period of the layer structure (*cf.* Fig. 3.4.3.10*a*). From the diagram of symmetry elements of the group $\mathcal{F}_{13}$ and $\mathcal{J}_{13}$, available in *IT* A (2005), one can deduce the sectional layer groups at any location $s\mathbf{d}$, $0 \leq s < 1$. These sectional layer groups are listed explicitly in *IT* E (2010) in the *scanning tables* of the respective space groups.

The resulting sectional layer groups $\overline{\mathcal{F}}_{13}$ and $\overline{\mathcal{J}}_{13}$ are given in Table 3.4.4.7 in two notations, in which the letter p signifies a two-dimensional net with the basic translations $\mathbf{a}^s$, $\mathbf{b}^s$ introduced above. Standard symbols are related to the basis $\mathbf{a}^s$, $\mathbf{b}^s$, $\mathbf{c}^s = \mathbf{d}$. Subscripts in non-coordinate notation specify the orientation of symmetry elements in the reference Cartesian coordinate system of the tetragonal phase, the partial translation in the glide plane a and in the screw axis 2_1 is equal to $\frac{1}{2}\mathbf{a}^s = \mathbf{b}^t$, *i.e.* the symbols a and 2_1 are also related to the basis $\mathbf{a}^s$, $\mathbf{b}^s$, $\mathbf{c}^s$. At special locations $s\mathbf{d} = 0\mathbf{d}$, $\frac{1}{2}\mathbf{d}$ and $s\mathbf{d} = \frac{1}{4}\mathbf{d}$, $\frac{3}{4}\mathbf{d}$, sectional groups contain both side-