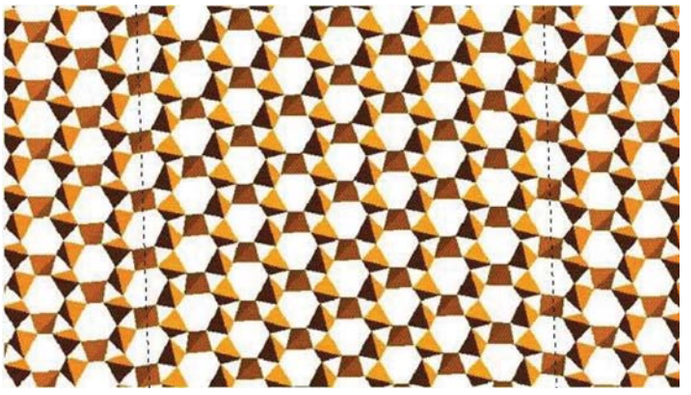

Fig. 3.4.4.4. Microscopic structure of two domain states and two parallel mutually reversed domain walls in the α phase of quartz. The left-hand vertical dotted line represents the domain wall W_{12}, the right-hand line is the reversed domain wall W_{12}. To the left of the left-hand line and to the right of the right-hand line are domains with domain state $\mathbf{S}_1$, the domain between the lines has domain state $\mathbf{S}_2$. For more details see text. Courtesy of M. Calleja, University of Cambridge.

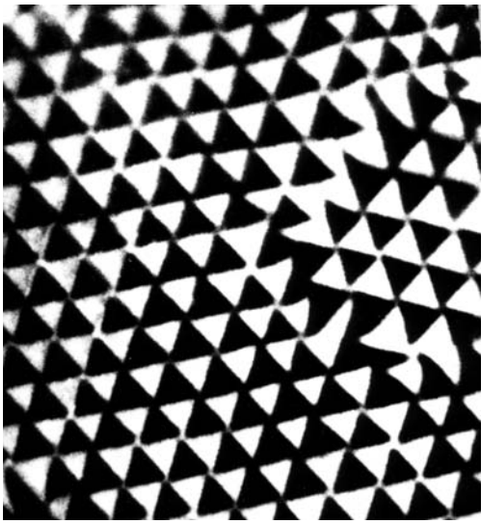

Fig. 3.4.4.5. Transmission electron microscopy (TEM) image of the incommensurate triangular ($3-q$ modulated) phase of quartz. The black and white triangles correspond to domains with domain states $\mathbf{S}_1$ and $\mathbf{S}_2$, and the transition regions between black and white areas to domain walls (discommensurations). For a domain wall of a certain orientation there are no reversed domain walls with the same orientation but reversed order of black and white; the walls are, therefore, non-reversible. Domain walls in regions with regular triangular structures are related by 120 and 240° rotations about the z direction and carry parallel spontaneous polarizations (see text). Triangular structures in two regions (blocks) with different orientations of the triangles are related *e.g.* by 2_x and carry, therefore, antiparallel spontaneous polarizations and behave macroscopically as two ferroelectric domains with antiparallel spontaneous polarization. Courtesy of E. Snoeck, CEMES, Toulouse and P. Saint-Grégoire, Université de Toulon.

al., 1998). An example of such an *engineered domain structure* is presented in Fig. 3.4.4.3.

Anisotropic domain walls can also appear if the Landau free energy contains a so-called Lifshitz invariant (see Section 3.1.3.3), which lowers the energy of walls with certain orientations and can be responsible for the appearance of an incommensurate phase (see *e.g.* Dolino, 1985; Tolédano & Tolédano, 1987; Tolédano & Dmitriev, 1996; Strukov & Levanyuk, 1998). The irreversible character of domain walls in a commensurate phase of crystals also containing (at least theoretically) an incommensurate phase has been confirmed in the frame of phenomenological theory by Ishibashi (1992). The incommensurate structure in quartz that demonstrates such an anisotropy is discussed at the end of the next example.

Example 3.4.4.2. Domain walls in α-phase of quartz. Quartz (SiO_2) undergoes a structural phase transition from the parent β phase (symmetry group $6_z2_x2_y$) to the ferroic α phase (symmetry 3_z2_x). The α phase can appear in two domain states $\mathbf{S}_1$ and $\mathbf{S}_2$, which have the same symmetry $F_1 = F_2 = 3_z2_x$. The symmetry J_{12} of the unordered domain pair $\{\mathbf{S}_1, \mathbf{S}_2\}$ is given by $J_{12}^\star = 3_z2_x \cup 2_y^*\{3_z2_x\} = 6_z^*2_x2_y^*$.

Table 3.4.4.5 summarizes the results of the symmetry analysis of domain walls (twins). Each row of the table contains data for one representative domain wall $\mathbf{W}_{12}(\mathbf{n}_{12})$ from one orbit $G\mathbf{W}_{12}(\mathbf{n}_{12})$. The first column of the table specifies the normal $\mathbf{n}$ of the wall plane p, further columns list the layer groups $\widehat{\mathsf{F}}_{12}$, T_{12} and $\overline{\mathsf{J}}_{12}$ that describe the symmetry properties and classification of the wall (defined in Table 3.4.4.3), and n_W is the number of symmetrically equivalent domain walls [*cf.* equation (3.4.4.21)].

The last two columns give possible components of the spontaneous polarization $\mathbf{P}$ of the wall $\mathbf{W}_{12}(\mathbf{n})$ and the reversed wall $\mathbf{W}_{21}(\mathbf{n})$. Except for walls with normals [001] and [100], all walls are polar, *i.e.* they can be spontaneously polarized. The reversal of the polarization in reversible domain walls requires the reversal of domain states. In irreversible domain walls, the reversal of $\mathbf{W}_{12}$ into $\mathbf{W}_{21}$ is accompanied by a change of the polarization $\mathbf{P}$ into $\mathbf{P}'$, which may have a different absolute value and direction different to that of $\mathbf{P}$.

The structure of two domain states and two mutually reversed domain walls obtained by molecular dynamics calculations are depicted in Fig. 3.4.4.4 (Calleja *et al.*, 2001). This shows a projection on the *ab* plane of the structure represented by SiO_4 tetrahedra, in which each tetrahedron shares four corners. The threefold symmetry axes in the centres of distorted hexagonal channels and three twofold symmetry axes (one with vertical orientation) perpendicular to the threefold axes can be easily seen. The two vertical dotted lines are the wall planes p of two mutually reversed walls $[\mathbf{S}_1[010]\mathbf{S}_2] = \mathbf{W}_{12}[010]$ and $[\mathbf{S}_2[010]\mathbf{S}_1] = \mathbf{W}_{21}[010]$. In Table 3.4.4.5 we find that these walls have the symmetry $\mathsf{T}_{12}[010] = \mathsf{T}_{21}[010] = \underline{2}_x2_y^\star\underline{2}_z^\star$, and in Fig. 3.4.4.4 we can verify that the operation $\underline{2}_x$ is a 'side-reversing' operation $\underline{s}_{12}$ of the wall (and the whole twin as wall), operation $2_y^\star$ is a 'state-exchanging operation' $r_{12}^\star$ and the operation $\underline{2}_z^\star$ is a non-trivial 'side-and-state reversing' operation $\underline{t}_{12}^\star$ of the wall. The walls

Table 3.4.4.5. *Symmetry properties of domain walls in quartz*

$|\mathbf{P}| \neq |\mathbf{P}'|,\ P'_\alpha \neq -P_\alpha,\ \alpha = x, y, z.$

$\mathbf{n}$	$\widehat{\mathsf{F}}_{12}$	T_{12}	$\overline{\mathsf{J}}_{12}$	Classification	n_W	$\mathbf{P}(\mathbf{W}_{12})$	$\mathbf{P}(\mathbf{W}_{21})$
[001]	3_z	$3_z\underline{2}_y^*$	$6_z^*\underline{2}_x\underline{2}_y^*$	SR	2		
[100]	2_x	$2_x\underline{2}_y^*2_z^*$	$2_x\underline{2}_y^*\underline{2}_z^*$	SI	3		
[010]	1	$\underline{2}_z^*$	$\underline{2}_x2_y^*\underline{2}_z^*$	SR	6	$0, 0, P_z$	$0, 0, -P_z$
[0vw]	1	1	$\underline{2}_x$	A$\underline{\mathrm{R}}$	12	P_x, P_y, P_z	$P_x, -P_y, -P_z$
[u0w]	1	$\underline{2}_y^*$	$\underline{2}_y^*$	SI	6	$0, P_y, 0$	$0, -P'_y, 0$
[uv0]	1	$\underline{2}_z^*$	$\underline{2}_z^*$	SI	6	$0, 0, P_z$	$0, 0, P'_z$
[uvw]	1	1	1	AI	12	P_x, P_y, P_z	P'_x, P'_y, P'_z

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