

## 3. PHASE TRANSITIONS, TWINNING AND DOMAIN STRUCTURES

tions involving a spontaneous distortion of the crystal lattice that entails a change of shape of the crystallographic or conventional unit cell (Wadhawan, 2000). Such a transformation is accompanied by a change in the number of independent nonzero components of a symmetric second-rank tensor  $u$  that describes spontaneous strain.

In discussing ferroelastic and non-ferroelastic domain structures, the concepts of crystal family and holohedry of a point group are useful (IT A, 2002). Crystallographic point groups (and space groups as well) can be divided into seven crystal systems and six *crystal families* (see Table 3.4.2.2). A symmetry descent within a crystal family does not entail a qualitative change of the spontaneous strain – the number of independent nonzero tensor components of the strain tensor  $u$  remains unchanged.

We shall denote the crystal family of a group  $M$  by the symbol  $\text{Fam}M$ . Then a simple criterion for a ferroic phase transition with symmetry descent  $G \subset F$  to be a *non-ferroelastic phase transition* is

$$F \subset G, \quad \text{Fam}F = \text{Fam}G. \quad (3.4.2.25)$$

A necessary and sufficient condition for a *ferroelastic phase transition* is

$$F \subset G, \quad \text{Fam}F \neq \text{Fam}G. \quad (3.4.2.26)$$

A *ferroelastic domain state*  $\mathbf{R}_i$  is defined as a state with a homogeneous spontaneous strain  $u^{(i)}$ . [We drop the suffix ‘s’ or ‘(s)’ if the serial number of the domain state is given as the superscript (i).] The definition of spontaneous strain is given in Section 3.4.3.6.1.] Different ferroelastic domain states differ in spontaneous strain. The symmetry of a ferroelastic domain state  $\mathbf{R}_i$  is specified by the stabilizer  $I_G(u^{(i)})$  of the spontaneous strain  $u^{(i)}$  of the principal domain state  $\mathbf{S}_i$  [see (3.4.2.16)]. This stabilizer, which we shall denote by  $A_i$ , can be expressed as an intersection of the parent group  $G$  and the holohedry of group  $F_i$ , which we shall denote  $\text{Hol}F_i$  (see Table 3.4.2.2):

$$A_i \equiv I_G(u^{(i)}) = G \cap \text{Hol}F_i. \quad (3.4.2.27)$$

This equation indicates that the ferroelastic domain state  $\mathbf{R}_i$  has a prominent single-domain orientation. Further on, the term ‘ferroelastic domain state’ will mean a ‘ferroelastic domain state in single-domain orientation’.

In our illustrative example,

$$\begin{aligned} A_1 &= I_{4_z/m_z m_x m_{xy}}(u_{11} - u_{22}) \\ &= \text{Hol}(2_x m_y m_z) \cap m4_z/m_z m_x m_{xy} \\ &= m_x m_y m_z \cap 4_z/m_z m_x m_{xy} = m_x m_y m_z. \end{aligned}$$

The number  $n_a$  of ferroelastic domain states is given by

$$n_a = [G : A_1] = |G| : |A_1|. \quad (3.4.2.28)$$

In our example,  $n_a = |4_z/m_z m_x m_{xy}| : |m_x m_y m_z| = 16 : 8 = 2$ . In Table 3.4.2.7, last column, the number  $n_a$  of ferroelastic domain states is given for all possible ferroic phase transitions.

The number  $d_a$  of principal domain states compatible with one ferroelastic domain state (degeneracy of ferroelastic domain states) is given by

$$d_a = [A_1 : F_1] = |A_1| : |F_1|. \quad (3.4.2.29)$$

In our example,  $d_a = |m_x m_y m_z| : |2_x m_y m_z| = 8 : 4 = 2$ , i.e. two non-ferroelastic principal domain states are compatible with each of the two ferroelastic domain states (*cf.* Fig. 3.4.2.2).

The product of  $n_a$  and  $d_a$  is equal to the number  $n$  of all principal domain states [see equation (3.4.2.19)],

$$n_a d_a = [G : A_1][A_1 : F_1] = [G : F_1] = n. \quad (3.4.2.30)$$

The number  $d_a$  of principal domain states in one ferroelastic domain state can be calculated for all ferroic phase transitions from the ratio of numbers  $n$  and  $n_a$  that are given in Table 3.4.2.7.

According to Aizu (1969), we can recognize three possible cases:

(i) *Full ferroelastics*: All principal domain states differ in spontaneous strain. In this case,  $n_a = n$ , i.e.  $A_1 = F_1$ , ferroelastic domain states are identical with principal domain states.

(ii) *Partial ferroelastics*: Some but not all principal domain states differ in spontaneous strain. A necessary and sufficient condition is  $1 < n_a < n$ , or, equivalently,  $F_1 \subset A_1 \subset G$ . In this case, ferroelastic domain states are degenerate secondary domain states with degeneracy  $n > d_a = |A_1| : |F_1| > 1$ . In this case, the phase transition  $G \supset F_1$  can also be classified as an *improper ferroelastic* one (see Section 3.1.3.2).

(iii) *Non-ferroelastics*: All principal domain states have the same spontaneous strain. The criterion is  $n_a = 1$ , i.e.  $A_1 = G$ .

A similar classification for ferroelectric domain states is given below. Both classifications are summarized in Table 3.4.2.3.

*Example 3.4.2.1. Domain states in leucite.* Leucite ( $\text{KAlSi}_2\text{O}_6$ ) (see e.g. Hatch *et al.*, 1990) undergoes at about 938 K a ferroelastic phase transition from cubic symmetry  $G = m\bar{3}m$  to tetragonal symmetry  $L = 4/mmm$ . This phase can appear in  $|G = m\bar{3}m| : |4/mmm| = 3$  single-domain states, which we denote  $\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3$ . The symmetry group of the first domain state  $\mathbf{R}_1$  is  $L_1 = 4_x/m_x m_y m_z$ . This group equals the stabilizer  $I_G(u^{(1)})$  of the spontaneous strain  $u^{(1)}$  of  $\mathbf{R}_1$  since  $\text{Hol}(4_x/m_x m_y m_z) = 4_x/m_x m_y m_z$  (see Table 3.4.2.2), hence this phase is a full ferroelastic one.

At about 903 K, another phase transition reduces the symmetry  $4/mmm$  to  $F = 4/m$ . Let us suppose that this transition has taken place in a domain state  $\mathbf{R}_1$  with symmetry  $L_1 = 4_x/m_x m_y m_z$ ; then the room-temperature ferroic phase has symmetry  $F_1 = 4_x/m_x$ . The  $4_x/m_x m_y m_z \supset 4_x/m_x$  phase transition is a non-ferroelastic one [ $\text{Hol}(4_x/m_x) = \text{Hol}(4_x/m_x m_y m_z) = 4_x/m_x m_y m_z$ ] with  $|4_x/m_x m_y m_z| : |4_x/m_x| = 8 : 4 = 2$  non-ferroelastic domain states, which we denote  $\mathbf{S}_1$  and  $\mathbf{S}_2$ . Similar

Table 3.4.2.2. Crystal systems, holohedries, crystal families and number of spontaneous strain components

Point group $M$	Crystal system	Holohedry $\text{Hol}M$	Spontaneous strain components		Crystal family $\text{Fam}M$
			Independent	Nonzero	
$23, m\bar{3}, 432, \bar{4}3m, m\bar{3}m$	Cubic	$m\bar{3}m$	1	3	Cubic
$6, \bar{6}, 6/m, 622, 6mm, \bar{6}2m, 6/mmmm$	Hexagonal	$6/mmm$	2	3	Hexagonal
$3, \bar{3}, 32, 3m, \bar{3}m$	Trigonal	$\bar{3}m$	2	3	
$4, \bar{4}, 4/m, 422, 4mm, \bar{4}2m, 4/mmm$	Tetragonal	$4/mmm$	2	3	Tetragonal
$222, mm2, mmm$	Orthorhombic	$mmm$	3	3	Orthorhombic
$2, m, 2/m$	Monoclinic	$2/m$	4	4	Monoclinic
$1, \bar{1}$	Triclinic	$\bar{1}$	6	6	Triclinic