principal tensors are: $\kappa_2^{(1)} = (g_4, 0)$, $\kappa_3^{(1)} = (d_{11}, 0)$, $\kappa_4^{(1)} = (d_{12}, 0)$, $\kappa_5^{(1)} = (d_{13}, 0)$, $\kappa_6^{(1)} = (d_{26}, 0)$, $\kappa_7^{(1)} = (d_{35}, 0)$ (the physical meaning of the components is explained in Table 3.4.3.5). In the domain state $\mathbf{S}_3$ they keep their absolute value but appear as the second nonzero components, as with spontaneous polarization.

There is an intermediate group $L_{13} = m_x m_y m_z$ between $F_1 = 2_x m_y m_z$ and $K_{13} = 4_z/m_z m_x m_{xy}$, since $L_{13} = m_x m_y m_z$ does not contain $g_{13} = 2_{xy}$. The one-dimensional secondary tensor parameters for the symmetry descent $K_{13} = 4_z/m_z m_x m_{xy} \supset L_{13} = m_x m_y m_z$ was also found in Example 3.4.2.4: $\lambda_1^{(1)} = u_1 - u_2$; $\lambda_2^{(1)} = A_{14} + A_{25}, A_{36}$; $\lambda_3^{(1)} = s_{11} - s_{22},\ s_{13} - s_{23},\ s_{44} - s_{55}$; $\lambda_4^{(1)} = Q_{11} - Q_{22},\ Q_{12} - Q_{21},\ Q_{13} - Q_{23},\ Q_{31} - Q_{32},\ Q_{44} - Q_{55}$. All these parameters have the opposite sign in $\mathbf{S}_3$.

The tensor distinction of two domain states $\mathbf{S}_1$ and $\mathbf{S}_j$ in a domain pair $(\mathbf{S}_1, \mathbf{S}_j)$ provides a useful *classification of domain pairs* given in the second and the third columns of Table 3.4.3.1. This classification can be extended to ferroic phases which are named according to domain pairs that exist in this phase. Thus, for example, if a ferroic phase contains ferroelectric (ferroelastic) domain pair(s), then this phase is a ferroelectric (ferroelastic) phase. Finer division into full and partial ferroelectric (ferroelastic) phases specifies whether all or only some of the possible domain pairs in this phase are ferroelectric (ferroelastic) ones. Another approach to this classification uses the notions of principal and secondary tensor parameters, and was explained in Section 3.4.2.2.

A discussion of and many examples of secondary ferroic phases are available in papers by Newnham & Cross (1974*a*,*b*) and Newnham & Skinner (1976), and tertiary ferroic phases are discussed by Amin & Newnham (1980).

We shall now show that the tensor distinction of domain states is closely related to the switching of domain states by external fields.

3.4.3.3. *Switching of ferroic domain states*

We saw in Section 3.4.2.1 that all domain states of the orbit $G\mathbf{S}_1$ have the same chance of appearing. This implies that they have the same free energy, *i.e.* they are degenerate. The same conclusion follows from thermodynamic theory, where domain states appear as equivalent solutions of equilibrium values of the order parameter, *i.e.* all domain states exhibit the same free energy Ψ (see Section 3.1.2). These statements hold under a tacit assumption of absent external electric and mechanical fields. If these fields are nonzero, the degeneracy of domain states can be partially or completely lifted.

The free energy $\Psi^{(k)}$ per unit volume of a ferroic domain state $\mathbf{S}_k$, $k = 1, 2, \ldots, n$, with spontaneous polarization $\mathbf{P}_0^{(k)}$ with components $P_{0i}^{(k)}$, $i = 1, 2, 3$, and with spontaneous strain components $u_{0\mu}^{(k)}$, $\mu = 1, 2, \ldots, 6$, is (Aizu, 1972)

$$\Psi^{(k)} = \Psi_0 - P_{0i}^{(k)} E_i - u_{0\mu}^{(k)} \sigma_\mu - d_{i\mu}^{(k)} E_i \sigma_\mu - \tfrac{1}{2}\varepsilon_0 \kappa_{ik}^{(k)} E_i E_k - \tfrac{1}{2} s_{\mu\nu}^{(k)} \sigma_\mu \sigma_\nu - \tfrac{1}{2} Q_{ik\mu} E_i E_k \sigma_\mu - \ldots, \quad (3.4.3.32)$$

where the Einstein summation convention (summation with respect to suffixes that occur twice in the same term) is used with $i, j = 1, 2, 3$ and $\mu, \nu = 1, 2, \ldots, 6$. The symbols in equation (3.4.3.32) have the following meaning: E_i and u_μ are components of the external electric field and of the mechanical stress, respectively, $d_{i\mu}^{(k)}$ are components of the piezoelectric tensor, $\varepsilon_0 \kappa_{ij}^{(k)}$ are components of the electric susceptibility, $s_{\mu\nu}^{(k)}$ are compliance components, and $Q_{ij\mu}^{(k)}$ are components of electrostriction (components with Greek indices are expressed in matrix notation) [see Section 3.4.5 (Glossary), Chapter 1.1 or Nye (1985); Sirotin & Shaskolskaya (1982)].

We shall examine two domain states $\mathbf{S}_1$ and $\mathbf{S}_j$, *i.e.* a domain pair $(\mathbf{S}_1, \mathbf{S}_j)$, in electric and mechanical fields. The difference of their free energies is given by

$$\begin{aligned}\Psi^{(j)} - \Psi^{(1)} = {}& -(P_{0i}^{(j)} - P_{0i}^{(1)}) E_i - (u_{0\mu}^{(j)} - u_{0\mu}^{(1)}) \sigma_\mu - (d_{i\mu}^{(j)} - d_{i\mu}^{(1)}) E_i \sigma_\mu \\ & - \tfrac{1}{2}\varepsilon_0 (\kappa_{ik}^{(j)} - \kappa_{ik}^{(1)}) E_i E_k - \tfrac{1}{2} (s_{\mu\nu}^{(j)} - s_{\mu\nu}^{(1)}) \sigma_\mu \sigma_\nu \\ & - \tfrac{1}{2} (Q_{ik\mu}^{(j)} - Q_{ik\mu}^{(1)}) E_i E_k \sigma_\mu - \ldots. \end{aligned} \quad (3.4.3.33)$$

For a domain pair $(\mathbf{S}_1, \mathbf{S}_j)$ and given external fields, there are three possibilities:

(1) $\Psi^{(j)} = \Psi^{(1)}$. Domain states $\mathbf{S}_1$ and $\mathbf{S}_j$ can coexist in equilibrium in given external fields.

(2) $\Psi^{(j)} < \Psi^{(1)}$. In given external fields, domain state $\mathbf{S}_j$ is more stable than $\mathbf{S}_1$; for large enough fields (higher than the coercive ones), the state $\mathbf{S}_1$ switches into the state $\mathbf{S}_j$.

(3) $\Psi^{(j)} > \Psi^{(1)}$. In given external fields, domain state $\mathbf{S}_j$ is less stable than $\mathbf{S}_1$; for large enough fields (higher than the coercive ones), the state $\mathbf{S}_j$ switches into the state $\mathbf{S}_1$.

A typical dependence of applied stress and corresponding strain in ferroelastic materials has a form of a elastic hysteresis loop (see Fig. 3.4.1.3). Similar dielectric hysteresis loops are observed in ferroelectric materials; examples can be found in books on ferroelectric crystals (*e.g.* Jona & Shirane, 1962).

A classification of switching (state shifts in Aizu's terminology) based on equation (3.4.3.33) was put forward by Aizu (1972, 1973) and is summarized in the second and fourth columns of Table 3.4.3.1. The order of the state shifts specifies the switching fields that are necessary for switching one domain state of a domain pair into the second state of the pair.

Another distinction related to switching distinguishes between *actual* and *potential* ferroelectric (ferroelastic) phases, depending on whether or not it is possible to switch the spontaneous polarization (spontaneous strain) by applying an electric field (mechanical stress) lower than the electrical (mechanical) breakdown limit under reasonable experimental conditions

Table 3.4.3.1. *Classification of domain pairs, ferroic phases and of switching (state shifts)*

$P_{0i}^{(k)}$ and $u_{0\mu}^{(k)}$ are components of the spontaneous polarization and spontaneous strain in the domain state $\mathbf{S}_k$, where $k = 1$ or $k = j$; similarly, $d_{i\mu}^{(k)}$ are components of the piezoelectric tensor, $\varepsilon_0\kappa_{ij}^{(k)}$ are components of electric susceptibility, $s_{\mu\nu}^{(k)}$ are compliance components and $Q_{ij\mu}^{(k)}$ are components of electrostriction (components with Greek indices are expressed in matrix notation) [see Chapter 1.1 or *e.g.* Nye (1985) and Sirotin & Shaskolskaya (1982)]. Text in italics concerns the classification of ferroic phases. $\mathbf{E}$ is the electric field and σ is the mechanical stress.

Ferroic class	Domain pair – *at least in one pair*	Domain pair – *phase*	Switching (state shift)	Switching field
Primary	At least one $P_{0i}^{(j)} - P_{0i}^{(1)} \neq 0$	Ferroelectric	Electrically first order	$\mathbf{E}$
	At least one $u_{0\mu}^{(j)} - u_{0\mu}^{(1)} \neq 0$	Ferroelastic	Mechanically first order	σ
Secondary	At least one $P_{0i}^{(j)} - P_{0i}^{(1)} \neq 0$ and at least one $u_{0\mu}^{(j)} - u_{0\mu}^{(1)} \neq 0$	Ferroelastoelectric	Electromechanically first order	$\mathbf{E}\sigma$
	All $P_{0i}^{(j)} - P_{0i}^{(1)} = 0$ and at least one $\varepsilon_0(\kappa_{ik}^{(j)} - \kappa_{ik}^{(1)}) \neq 0$	Ferrobielectric	Electrically second order	$\mathbf{EE}$
	All $u_{0\mu}^{(j)} - u_{0\mu}^{(1)} = 0$ and at least one $s_{\mu\nu}^{(j)} - s_{\mu\nu}^{(1)} \neq 0$	Ferrobielastic	Mechanically second order	$\sigma\sigma$
...	...	...	...	...

$i, j = 1, 2, 3$; $\mu, \nu = 1, 2, \ldots, 6$.

references