

3.1. STRUCTURAL PHASE TRANSITIONS

alters the chemical bond lengths (by less than *e.g.* 0.1 Å) and their relative orientations (by less than *e.g.* a few degrees).

Experimentally, such transitions are characterized by small values of the heat of transformation (less than a few calories per gram), weak discontinuities in the relevant physical quantities (*e.g.* lattice parameters) and *the occurrence of a symmetry relationship between the two phases surrounding the transition.*

In the simplest case, this relationship consists of the fact that the space group of one of the phases is a *subgroup* of the space group of the other phase, and that there is specific correspondence between the symmetry elements of the two phases. For example, for the phase transition occurring at 322 K in triglycine sulfate (Lines & Glass, 1977), the same binary axis can be found in the two phases. Likewise, the vector defining one of the primitive translations in one phase can be a multiple of the vector defining a primitive translation in the other phase.

In a more general way, the crystal structures of the two phases considered are both slight distortions of a *reference* structure, termed the *prototype* (or *parent*) structure. In this case, the space groups of the two phases are both subgroups of the space group of the prototype structure, with, as in the simple case above, a specific correspondence between the symmetry elements of the two phases and of the prototype structure. A well documented example of this situation is provided by two of the three transitions occurring in barium titanate (Lines & Glass, 1977).

A subclassification of *structural* transitions into *ferroic classes* is of interest (Aizu, 1969; Tolédano & Tolédano, 1987, and references therein). Indeed the distinction of ferroic classes allows one to establish a relationship between the point symmetries of the two phases surrounding a phase transition, the observed twinning, and the nature of the physical properties mainly affected by the phase transition.

The group–subgroup relationship that exists, in the standard situation, between the *space groups* of the two phases adjacent to a structural transition implies that the *point group* of one phase is either a *subgroup* of the point group of the other phase or is *identical* to it.

If the two point groups are *identical*, the corresponding transition is classified as *non-ferroic*.

In the general case, the point group of one phase (the *ferroic phase*) is a strict subgroup of the point group of the other phase (the *prototype phase*). The transition is then classified as *ferroic*. Originally, a somewhat more abstract definition was given (Aizu, 1969): a crystal was said to be ferroic if it can exist in two or more *orientation states* having equal stabilities in the absence of external forces, and when the various orientation states have crystal structures that only differ in their global spatial orientations. The latter definition, which focuses on the situation of the *ferroic phase*, derives from the former one: the *lowering of point symmetry* that accompanies the transition between the prototype phase and the ferroic phase results in the existence of various *variants* or twin orientations having the same structures within a

global reorientation (see also Sections 3.2.1, 3.2.3, 3.3.7, 3.3.10 and 3.4.1).

The various orientation states can coexist in a given sample and then determine a *twinning pattern*. Geometrical and physical considerations pertaining to twinned structures are developed in Chapters 3.2 and 3.3 of this volume. In particular, it can be shown that the structure of one orientation state can be brought to coincide with the structure of another orientation state by means of a set of geometrical transformations *R* which all belong to the space group of the *prototype phase*.

If we adopt a common frame of reference for all the orientation states of the ferroic phase, the tensors representing certain macroscopic quantities (see Chapter 1.1) will have different values in the different states (*e.g.* distinct nonzero components). If a certain macroscopic tensor has components differing in two states, *a* and *b*, these components are thus modified by the action of the geometrical transformations *R* which transforms (reorients) one structure into the other. Hence they are *not invariant* by geometrical operations belonging to the group of symmetry of the *prototype phase*: their value is necessarily zero in this phase.

Ferroic transitions therefore possess three characteristics:

(i) They are associated with a lowering of crystallographic point symmetry.

(ii) Components of certain macroscopic tensors acquire nonzero values below T_c .

(iii) The same tensors allow one to distinguish, at a macroscopic level, the various orientation states arising in the ferroic phase.

The subclassification of ferroics into *ferroic classes* has a crystallographic and a physical content. The crystallographic aspect is based on the type of point-symmetry lowering occurring at the transition, while the physical aspect focuses on the *rank of the tensor* (necessarily traceless) characterizing the different orientation states of the crystal in the ferroic phase and on the nature of the physical quantity (electrical, mechanical, ...) related to the relevant tensor (see Chapter 1.1). Table 3.1.1.1 specifies this twofold classification.

Note that a given transition related to a class defined by a tensor of rank *n* can belong to several classes defined by tensors of higher rank: *e.g.* a ferroelectric transition can also be ferroelastic and will also display characteristics of a higher-order ferroic.

The point-symmetry changes defining each class have been enumerated in various works (see for instance Aizu, 1973, and references therein).

The interest of the above classification is that it provides a guiding framework for the experimental investigations. Hence, the recognition that a transition is ferroelectric (respectively, ferroelastic) directs the investigation of the transition towards the examination of the dielectric (respectively, mechanical) properties of the system in the expectation that these will be the quantities mainly affected by the transition. This expectation is

Table 3.1.1.1. *Ferroic classification of structural parameters*

	Class		
	Ferroelectric	Ferroelastic	Higher-order ferroic
Symmetry change	(1) Non-polar to polar crystal point group (reference situation) or (2) polar to polar group with additional polar axes	Change of crystal system (syngony) (except from hexagonal to rhombohedral)	Change of point group not complying with the two preceding classes
Examples	(1) $2/m \Rightarrow 2$ (2) $mm2 \Rightarrow m$	$mmm \Rightarrow 2/m$ (orthorhombic \Rightarrow monoclinic)	$622 \Rightarrow 32$ $4/mmm \Rightarrow 4/m$
Rank of relevant tensor	1 (vector)	2	≥ 3
Physical nature of the tensorial quantity	Dielectric polarization	Strain	Component of the piezoelectric or elastic tensor
Main physical properties affected by the transition	Dielectric, optical	Mechanical, elastic	Piezoelectric
Prototype example (temperature of transition)	Triglycine sulfate (322 K)	Lanthanum pentaphosphate, $\text{LaP}_5\text{O}_{14}$ (420 K)	Quartz, SiO_2 (846 K); niobium dioxide, NbO_2 (1080 K)