

3.1. Structural phase transitions

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This chapter contains six contributions describing aspects of phase transitions in crystals that are of interest to crystallographers. The first contribution (Section 3.1.1) is a brief introduction aimed at defining the field of *structural transitions*. This restricted field constitutes, at present, the background of the clearest set of experimental and theoretical considerations. In this section, the terminology is specified. The second section (Section 3.1.2) describes the ideas and methods of the *theory of structural phase transitions*. This theory relates the symmetry characteristics of the transitions to their physical characteristics. The application of the symmetry principles that derive from this theory is illustrated by the results contained in Tables 3.1.3.1 and 3.1.4.1. The first of these two tables concerns the simple but experimentally widespread situation in which a structural transition is not accompanied by a change in the number of atoms per *primitive* crystal cell. The second table concerns the general case, in which the number of atoms changes, and which corresponds to the onset of superlattice reflections at the phase transition. This table provides, for a set of hypothetical transformations, the various symmetry-based predictions of the theory. Section 3.1.5 is devoted to the important topic of *soft modes*, which is related to the microscopic mechanism of a structural transition. Finally, Section 3.1.6 is an introduction to the accompanying software package *Group Informatics*.

3.1.1. Introduction

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Phase transformations (the term *transitions* can be considered as a synonym) are experimentally recognized to exist in a large variety of systems submitted to a change in temperature or pressure: fluids, solids or mesophases, crystalline or disordered solids, metals or insulators.

This recognition is sometimes based on very obvious effects. This is, for instance, the case for the boiling or the freezing of a liquid, because the different *phases*, vapour, liquid, solid, differ greatly in their physical properties (*e.g.* the difference of density between the two fluids, or the difference of mechanical hardness between the liquid and the solid). In these cases, a phase transformation appears as an abrupt and major change of the physical properties.

In other systems, solids in particular, the existence of a phase transformation is generally revealed by more subtle effects only. The nature of these effects differs from one system to another: minor discontinuities in the lattice parameters of a crystalline phase; occurrence over a narrow temperature range of anomalies in certain specific physical properties; onset of a definite pattern of crystal twins *etc.*

Systems undergoing phase transitions constitute an important field of interest for crystallographers. This is due to the fact that, at the microscopic level, a phase transformation is generally accompanied by a change of the global or local atomic configuration. The structural data, *i.e.* the specification of the differences in atomic configurations between the two phases, or the study of the local ordering precursor to a transition, are thus essential, or at least important, clues to the understanding of the mechanism of the transition considered.

Conversely, the investigation of phase transitions has stimulated new developments in the techniques and concepts used by

crystallographers. For instance, it has been necessary to improve the precision of goniometric measurements and the control of temperature in order to detect accurately anomalies affecting the lattice parameters across a phase transition or to study the asymmetry of diffraction spots caused by the domain structure in a ‘low-symmetry’ phase. On the other hand, new methods of structural determination, relying on concepts of *n*-dimensional crystallography, had to be developed in order to study transitions to incommensurate phases.

Standard crystallographic considerations, based on the determination of the characteristics of a lattice and of a basis, appear to be most useful in the study of phase transformations between crystalline phases, due to the fact that, at a microscopic level, each phase is entirely described by its periodic crystal structure. There are a wide variety of such transformations and the task of classifying them has been attempted from several standpoints.

The most important distinction is that made between *reconstructive* and *non-reconstructive* transitions. This distinction stems from a comparison of the crystal structures of the two phases. In a *reconstructive transition*, the distances between certain atoms change by amounts similar to the dimension of the unit cell, and certain chemical bonds between neighbouring atoms are then necessarily broken (see Tolédano & Dmitriev, 1996, and references therein). The graphite–diamond transformation and many transformations in metals and alloys are examples of reconstructive transitions. If, instead, a transition preserves approximately the configuration of the chemical bonds between constituents, the transition is *non-reconstructive*.

Other classifications, which partly overlap with the preceding one, involve distinctions between *diffusionless* and *diffusion-assisted* transitions (*i.e.* those that require random hopping of atoms to achieve the change of atomic configuration) or between *displacive* and *order–disorder* transitions. Likewise, a number of transformations in metals or alloys are assigned to the class of *martensitic* transformations that is defined by a set of specific experimental observations (twinning behaviour, mechanical properties *etc.*). Finally, the distinction between *ferroic* and *non-ferroic* transitions has been progressively adopted in the recent years.

Owing to an insufficient understanding of the observations, the relationships between these various classifications is not fully clear at present. It is not even clear whether the same definitions and concepts can be applied to the description of all phase transformations between solid phases. For instance, one observes in certain solids (*e.g.* mixed lead magnesium niobates with an average perovskite structure) very broad anomalies of the physical properties (*i.e.* extending over a wide range of temperatures). These systems, which have stimulated many studies in recent years, are known to be chemically and structurally heterogeneous *simultaneously at several length scales*. The relevance to these systems of standard concepts defined for phase transitions in homogeneous systems, in which the anomalies of the physical properties are sharp, is uncertain.

It is therefore reasonable to restrict a review of basic concepts and theories to the simple reference case of *structural phase transitions*. We consider this terminology, in its *restricted* meaning, as pertaining to the situation of only a fraction of the phase transitions that take place in solids and imply a modification of the crystal structure. These are part of *non-reconstructive* transitions between homogeneous crystalline phases. It is customary to specify that a structural transition only *slightly*

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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)

3. PHASE TRANSITIONS, TWINNING AND DOMAIN STRUCTURES

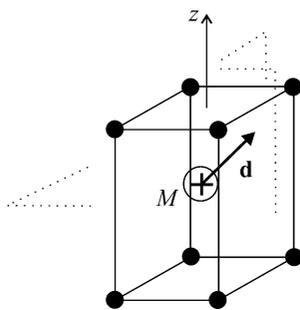


Fig. 3.1.2.1. Model of a structural transition. The filled circles at the vertices of the cell are singly charged negative ions and the empty circle at the centre is a singly charged positive ion. \mathbf{d} is an arbitrary displacement of the central ion.

based on the fact that the dielectric polarization (respectively, the thermal strain tensor) acquires spontaneous components across the transition.

Conversely, if neither of these two classes of ferroics is involved in the transition considered, one knows that one must focus the study on components of higher-rank macroscopic tensors in order to reveal the characteristic anomalies associated with the transition. Also, the knowledge of the ferroic class of a transition specifies the nature of the macroscopic tensorial quantity that must be measured in order to reveal the domain structure. For instance, ferroelastic domains correspond to different values of symmetric second-rank tensors. Aside from the spontaneous strain tensor, we can consider the dielectric permittivity tensor at optical frequencies. The latter tensor determines the optical indicatrix, which will be differently oriented in space for the distinct domains. Consequently, with suitably polarized light one should always be able to ‘visualize’ ferroelastic domains. Conversely, such visualization will never be possible by the same method for a non-ferroelastic system.

3.1.2. Thermodynamics of structural transitions

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3.1.2.1. Introduction

In the study of structural phase transitions, the crystallographer is often confronted by an ambiguous situation. Small changes in atomic positions determine structures having different space groups, and the data are generally compatible with several possible symmetry assignments. In order to make a choice, the crystallographer must be able to rely on some theoretical substrate, which will allow him to discard certain of the possible assignments.

The relevant theoretical framework in this field is the thermodynamical and symmetry considerations that form the *Landau theory of phase transitions*. In this chapter, we describe the ideas and results of this theory.

In the next section, we give an introduction to the main ideas of the theory by using an example consisting of a simple speculative type of structural phase transition. In Section 3.1.2.3, we discuss various situations of experimental interest relative to the thermodynamical aspect of the theory: first and second order of the transition, metastable states and thermal hysteresis. In Section 3.1.2.4, we provide a brief description, in two steps, of the general arguments constituting the foundation of the theory. In Section 3.1.2.5, we discuss the case of a structural transition actually occurring in nature and having a greater complexity than the speculative case considered in Section 3.1.2.2. In this section we also analyse the relationship between the *ferroic* character of a transition (see Section 3.1.1) and its order-parameter symmetry.

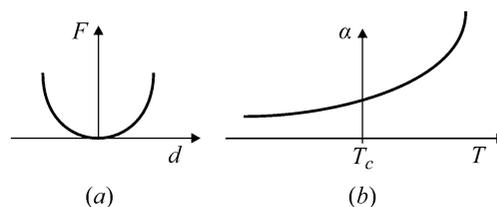


Fig. 3.1.2.2. (a) Variation of the free energy as function of the amplitude of the displacement of the central ion in Fig. 3.1.2.1. (b) Typical temperature dependence in the vicinity of T_c of the coefficient of a second-degree term in the Landau expansion (3.1.2.1) whenever this coefficient is strictly positive at T_c : one can see that this positivity is also valid slightly above and below T_c .

3.1.2.2. Basic ideas of Landau’s theory of phase transitions

The Landau theory of phase transitions is a phenomenological theory. It does not aim to establish that a phase transition exists in a given system. The existence of a transition is an experimental fact considered as a starting point of the theory. The explanatory power of the theory is to establish the overall consistency of the microscopic characteristics of the transition (space symmetry and structural changes, anomalies in the phonon spectrum *etc.*) and the results of the measurement of various relevant macroscopic quantities of thermal, dielectric, optical or mechanical nature.

The continuous (‘second-order’) character of the transition plays an essential role in working out the general foundations of the theory. However, though its strict field of validity is that of continuous transitions, the theory also satisfactorily applies to a large fraction of discontinuous transitions.

The Landau theory defines two basic concepts: the *order parameter* (OP) and the transition free energy (LFE). It is worth pointing out that these concepts keep their usefulness in the modern statistical theory of critical phenomena, even though these phenomena do not generally comply with the results of Landau’s theory. From the symmetry properties of the *order parameter* and of the *Landau free energy*, it is possible to infer, on the one hand, a certain number of observable symmetry characteristics of the system: degeneracy of the ‘low-symmetry’ phase (*i.e.* number of energetically equivalent domain orientations in this phase), enumeration of the possible symmetries of the ‘low-symmetry’ phase for a given symmetry of the ‘high-symmetry’ phase. On the other hand, macroscopic physical quantities can be classified as functions of their symmetries with respect to the order parameter. This classification leads to that of the various types of anomalous behaviours that can be induced by the occurrence of a phase transition.

In order to give an intuitive approach to the basic arguments of the Landau theory, and to its use, we first analyse an artificially simplified example of a crystalline phase transition.

3.1.2.2.1. Description of a prototype example

Fig. 3.1.2.1 represents a unit cell of a speculative crystalline structure with a simple tetragonal Bravais lattice, in which a phase transition is assumed to take place. Negative ions (filled circles) occupy the vertices of the tetragonal cell (lattice constants $a = b \neq c$). A positive ion M^+ is at the centre of the cell.

This configuration is assumed to be the equilibrium state of the system above the temperature T_c of the transition (see Fig. 3.1.2.2). Below T_c , equilibrium is assumed to correspond to a structure that only differs from the high-temperature structure by the fact that M^+ lies out of the centre of the cell in an unspecified direction. Hence the latter equilibrium is characterized by the magnitude and direction of the displacement $\mathbf{d}_0 = (d_x, d_y, d_z)$ of the central ion. At high temperature, the equilibrium corresponds to $\mathbf{d}_0 = 0$.