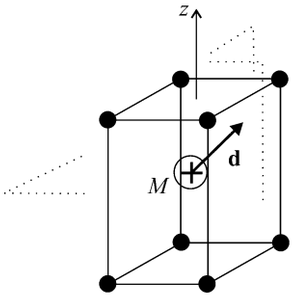

Fig. 3.1.2.1. Model of a structural transition. The filled circles at the vertices of the cell are singly charged negative ions and the empty circle at the centre is a singly charged positive ion. **d** is an arbitrary displacement of the central ion.

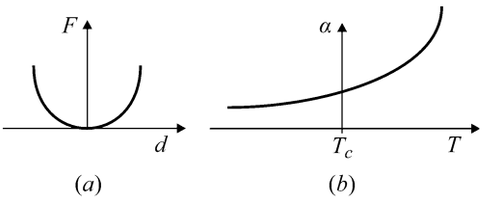

Fig. 3.1.2.2. (*a*) Variation of the free energy as function of the amplitude of the displacement of the central ion in Fig. 3.1.2.1. (*b*) Typical temperature dependence in the vicinity of T_c of the coefficient of a second-degree term in the Landau expansion (3.1.2.1) whenever this coefficient is strictly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

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

By J.-C. Tolédano

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.

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 $\mathbf{d}_0 = 0$.