

## 3. SYMMETRY ASPECTS OF PHASE TRANSITIONS, TWINNING AND DOMAIN STRUCTURES

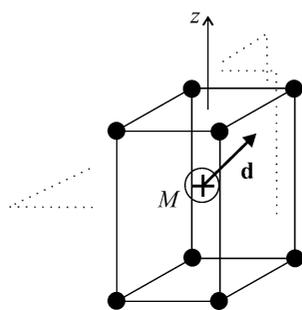


Fig. 3.1.2.1. Model of a structural transition. The filled circles at the vertices of the cell are singly charged negative ions and the empty circle at the centre is a singly charged positive ion.  $\mathbf{d}$  is an arbitrary displacement of the central ion.

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.

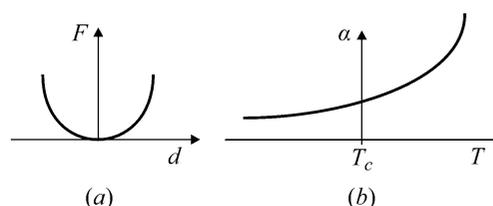


Fig. 3.1.2.2. (a) Variation of the free energy as function of the amplitude of the displacement of the central ion in Fig. 3.1.2.1. (b) Typical temperature dependence in the vicinity of  $T_c$  of the coefficient of a second-degree term in the Landau expansion (3.1.2.1) whenever this coefficient is strictly 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  $\mathbf{d}_0 = 0$ .

### 3.1. STRUCTURAL PHASE TRANSITIONS

#### 3.1.2.2.2. Basic assumptions and strategy

Our aim is to determine the above displacement as a function of temperature. Landau's strategy is to determine  $\mathbf{d}_0$  by a *variational method*. One considers an arbitrary displacement  $\mathbf{d}$  of the  $M^+$  ion. For given temperature  $T$  and pressure  $p$  (or volume  $V$ ), and specified values of the components of  $\mathbf{d}$ , there is, in principle, a definite value  $F(T, p, d_x, d_y, d_z)$  for the free energy  $F$  of the system. This function is a *variational free energy* since it is calculated for an arbitrary displacement. The equilibrium displacement  $\mathbf{d}_0(T, p)$  is defined as the displacement that minimizes the variational free energy  $F$ . The equilibrium free energy of the system is  $F_{\text{eq}}(T, p) = F(T, p, \mathbf{d}_0)$ . Note that, strictly speaking, in the case of a given pressure, one would have to consider a variational Gibbs function ( $F + pV$ ) in order to determine the equilibrium of the system. We will respect the current use in the framework of Landau's theory of denoting this function  $F$  and call it a *free energy*, though this function might actually be a Gibbs potential.

The former strategy is not very useful as long as one does not know the form of the variational free energy as a function of the components of the displacement. The second step of Landau's theory is to show that, given general assumptions, one is able to determine simply the form of  $F(T, p, \mathbf{d})$  in the required range of values of the functions' arguments.

The basic assumption is that of *continuity of the phase transition*. It is in fact a dual assumption. On the one hand, one assumes that the equilibrium displacement  $\mathbf{d}_0(T, p)$  has components varying continuously across the transition at  $T_c$ . On the other hand, one assumes that  $F$  is a continuous and derivable function of  $(T, p, \mathbf{d})$ , which can be expanded in the form of a *Taylor expansion* as function of these arguments.

Invoking the continuity leads to the observation that, on either side of  $T_c$ ,  $|\mathbf{d}_0|$  is small, and that, accordingly, one can restrict the determination of the functional form of  $F(T, p, \mathbf{d})$  to small values of  $(d_x, d_y, d_z)$  and of  $|T - T_c|$ .  $F$  will then be equal to the sum of the first relevant terms of a Taylor series in the preceding variables.

#### 3.1.2.2.3. Symmetry constraints and form of the free energy

The central property of the variational free energy which allows one to specify its form is a symmetry property.  $F$  is a function of  $(d_x, d_y, d_z)$  which is *invariant by the symmetry transformations of the high-temperature equilibrium structure*. In other terms, an arbitrary displacement  $\mathbf{d}$  and the displacement  $\mathbf{d}'$  obtained by applying to  $\mathbf{d}$  one of the latter symmetry transformations correspond to the same value of the free energy.

Indeed, both displacements determine an identical set of mutual distances between the positive and negative ions of the system and the free energy only depends on this 'internal' configuration of the ions.

Note that, in the case considered here (Fig. 3.1.2.1), the set of symmetry transformations comprises, aside from the lattice translations, fourfold rotations around the  $z$  axis, mirror symmetries into planes and the products of these transformations. The set of rotations and reflections forms a *group*  $G$  of order 16, which is the crystallographic point group  $4/mmm$  (or  $D_{4h}$ ).

Also note that this symmetry property of the free energy also holds for each degree of the Taylor expansion of  $F$  since the geometrical transformations of  $G$  act linearly on the components of  $\mathbf{d}$ . Hence, terms of different degrees belonging to the expansion of  $F$  will not 'mix', and must be separately invariant.

Let us implement these remarks in the case in Fig. 3.1.2.1. It is easy to check that by successive application to the components of  $\mathbf{d}$  of the mirror symmetries perpendicular to the three axes, no linear combination of these components is invariant by  $G$ : each of the three former symmetry transformations reverses one

component of  $\mathbf{d}$  and preserves the two others. *Linear terms are therefore absent from the expansion.*

As for second-degree terms, the same symmetry transformations preclude the existence of combinations of bilinear products of the type  $d_x d_y$ . Actually, one finds that the fourfold symmetry imposes that the most general form of the second-degree contribution to the variational free energy is a linear combination of  $d_z^2$  and of  $(d_x^2 + d_y^2)$ . Hence the Taylor expansion of  $F$ , restricted to its lowest-degree terms, is

$$F = F_0(T, p) + \frac{\alpha_1(T, p)}{2} d_z^2 + \frac{\alpha_2(T, p)}{2} (d_x^2 + d_y^2). \quad (3.1.2.1)$$

#### 3.1.2.2.4. Reduction of the number of relevant degrees of freedom: order parameter

Let us now derive the *key result of the theory*, namely, that either the component  $d_z$  or the pair of components  $(d_x, d_y)$  will take nonzero values below  $T_c$  (but not both). The meaning of this result will be clarified by symmetry considerations.

The derivation of this result relies on the fact that one, and one only, of the two coefficients  $\alpha_i$  in equation (3.1.2.1) must vanish and change sign at  $T_c$ , and that the other coefficient must remain positive in the neighbourhood of  $T_c$ .

(a) Before establishing the latter property in (b) hereunder, let us show that its validity implies the stated key result of the theory. Indeed, if one  $\alpha_i$  coefficient is strictly positive (e.g.  $\alpha_1 > 0$ ), then the minimum of  $F$  with respect to the components of  $\mathbf{d}$  (e.g.  $d_z$ ) multiplying this coefficient in (3.1.2.1) occurs for zero equilibrium values of these components (e.g.  $d_z^0 = 0$ ) in the vicinity of  $T_c$ , *above and below this temperature*. Hence, depending on the coefficient  $\alpha_i$  which remains positive, either  $d_z$  or the pair  $(d_x, d_y)$  can be omitted, in the first place, from the free-energy expansion. *The remaining set of components is called the order parameter of the transition*. At this stage, this fundamental quantity is defined as the set of degrees of freedom, the coefficient of which in the second-degree contribution to  $F$  vanishes and changes sign at  $T_c$ . The number of independent components of the order parameter (one in the case of  $d_z$ , two in the case of the pair  $d_x, d_y$ ) is called the dimension of the order parameter.

Note that the preceding result means that the displacement of the  $M^+$  ion below  $T_c$  cannot occur in an arbitrary direction of space. It is either directed along the  $z$  axis, or in the  $(x, y)$  plane.

(b) Let us now establish the property of the  $\alpha_i$  postulated above.

At  $T_c$ , the equilibrium values of the components of  $\mathbf{d}$  are zero. Therefore, at this temperature, the variational free energy (3.1.2.1) is minimum for  $d_x, d_y, d_z = 0$ . Considering the form (3.1.2.1) of  $F$ , this property implies that we have (Fig. 3.1.2.2)  $\alpha_i(T_c) \geq 0$  ( $i = 1, 2$ ).

Note that these inequalities cannot be strict for both coefficients  $\alpha_i$ , because their positiveness would hold on either side of  $T_c$  in the vicinity of this temperature. Consequently, the minimum of  $F$  would correspond to  $\mathbf{d} = 0$  on either side of the transition while the situation assumed is only compatible with this result *above*  $T_c$ . Using the converse argument that the equilibrium values of the components of  $\mathbf{d}$  are not *all* equal to zero below  $T_c$  leads easily to the conclusion that one, at least, of the two coefficients  $\alpha_i$  must vanish at  $T_c$  and become negative below this temperature.

Let us now show that the two coefficients  $\alpha_i$  cannot vanish simultaneously at  $T_c$ . This result relies on the 'reasonable' assumption that the two coefficients  $\alpha_i$  are *different* functions of temperature and pressure (or volume), no constraint in this respect being imposed by the symmetry of the system.

Fig. 3.1.2.3 shows, in the  $(T, p)$  plane, the two lines corresponding to the vanishing of the two functions  $\alpha_i$ . The simultaneous vanishing of the two coefficients occurs at an isolated point

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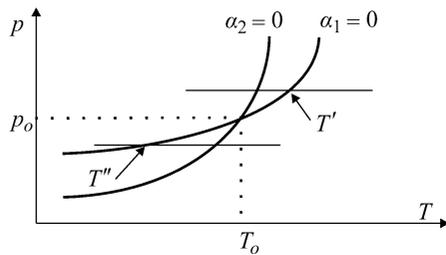


Fig. 3.1.2.3. Plots representative of the equations  $\alpha_1(p, T) = 0$  and  $\alpha_2(p, T) = 0$ . The simultaneous vanishing of these coefficients occurs for a single couple of temperature and pressure  $(p_0, T_0)$ .

$(T_0, p_0)$ . Let us consider, for instance, the situation depicted in Fig. 3.1.2.3. For  $p > p_0$ , on lowering the temperature,  $\alpha_1$  vanishes at  $T'$  and  $\alpha_2$  remains positive in the neighbourhood of  $T'$ . Hence, the equilibrium value of the set  $(d_x, d_y)$  remains equal to zero on either side of  $T'$ . A transition at this temperature will only concern a possible change in  $d_z^0$ .

Likewise for  $p$  below  $p_0$ , a transition at  $T''$  will only concern a possible change of the set of components  $(d_x^0, d_y^0)$ , the third component  $d_z$  remaining equal to zero on either sides of  $T''$ . Hence an infinitesimal change of the pressure (for instance a small fluctuation of the atmospheric pressure) from above  $p_0$  to below  $p_0$  will *modify qualitatively the nature of the phase transformation* with the direction of the displacement changing abruptly from  $z$  to the  $(x, y)$  plane. As will be seen below, the crystalline symmetries of the phases stable below  $T'$  and  $T''$  are different. This is a singular situation, of *instability*, of the type of phase transition, not encountered in real systems. Rather, the standard situation corresponds to pressures away from  $p_0$ , for which a slight change of the pressure does not modify significantly the direction of the displacement. In this case, one coefficient  $\alpha_i$  only vanishes and changes sign at the transition temperature, as stated above.

#### 3.1.2.2.5. Stable state below $T_c$ and physical anomalies induced by the transition

We have seen that either  $d_z$  or the couple  $(d_x, d_y)$  of components of the displacement constitute the order parameter of the transition and that the free energy needs only to be expanded as a function of the components of the order parameter. Below the transition, the corresponding coefficient  $\alpha_i$  is negative and, accordingly, the free energy, limited to its second-degree terms, has a maximum for  $\mathbf{d} = 0$  and no minimum. Such a truncated expansion is not sufficient to determine the equilibrium state of the system. The stable state of the system must be determined by positive terms of higher degrees. Let us examine first the simplest case, for which the order parameter coincides with the  $d_z$  component.

The same symmetry argument used to establish the form (3.1.2.1) of the Landau free energy allows one straightforwardly to assert the absence of a third-degree term in the expansion of  $F$  as a function of the order parameter  $d_z$ , and to check the effective occurrence of a fourth-degree term. If we assume that this simplest form of expansion is sufficient to determine the equilibrium state of the system, the coefficient of the fourth-degree term must be positive in the neighbourhood of  $T_c$ . Up to the latter degree, the form of the relevant contributions to the free energy is therefore

$$F = F_0(T, p) + \frac{\alpha(T - T_c)}{2} d_z^2 + \frac{\beta}{4} d_z^4. \quad (3.1.2.2)$$

In this expression,  $\alpha_1$ , which is an odd function of  $(T - T_c)$  since it vanishes and changes sign at  $T_c$ , has been expanded linearly. Likewise, the lowest-degree expansion of the function  $\beta(T - T_c)$  is a *positive constant* in the vicinity of  $T_c$ . The function  $F_0$ , which is the zeroth-degree term in the expansion, represents

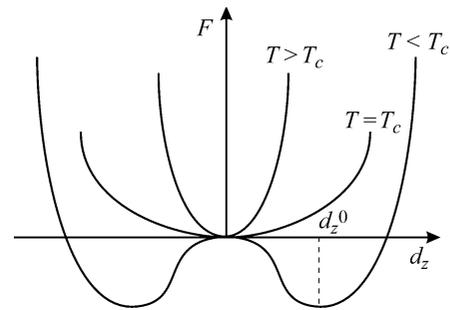


Fig. 3.1.2.4. Plots of the Landau free energy as a function of the order parameter, for values of the temperature above or below  $T_c$  or coincident with  $T_c$ . The shape of the plot changes qualitatively from a one-minimum plot to a two-minimum plot.

the normal 'background' part of the free energy. It behaves smoothly since it does not depend on the order parameter. A plot of  $[F(d_z) - F_0]$  for three characteristic temperatures is shown in Fig. 3.1.2.4.

The minima of  $F$ , determined by the set of conditions

$$\frac{\partial F}{\partial d_z} = 0; \quad \frac{\partial^2 F}{\partial d_z^2} > 0, \quad (3.1.2.3)$$

occur above  $T_c$  for  $d_z = 0$ , as expected. For  $T < T_c$  they occur for

$$d_z^0 = \pm \sqrt{\alpha \frac{(T_c - T)}{\beta}}. \quad (3.1.2.4)$$

This behaviour has a general validity: the order parameter of a transition is expected, in the framework of Landau's theory, to possess a square-root dependence as a function of the deviation of the temperature from  $T_c$ .

Note that one finds two minima corresponding to the same value of the free energy and opposite values of  $d_z^0$ . The corresponding upward and downward displacements of the  $M^+$  ion (Fig. 3.1.2.1) are distinct states of the system possessing the same stability.

Other physical consequences of the form (3.1.2.2) of the free energy can be drawn: absence of latent heat associated with the crossing of the transition, anomalous behaviour of the specific heat, anomalous behaviour of the *dielectric susceptibility* related to the order parameter.

The *latent heat* is  $L = T\Delta S$ , where  $\Delta S$  is the difference in entropy between the two phases at  $T_c$ . We can derive  $S$  in each phase from the equilibrium free energy  $F(T, p, d_z^0(T, p))$  using the expression

$$S = -\frac{dF}{dT} \Big|_{d_z^0} = -\left[ \frac{\partial F}{\partial T} \Big|_{d_z^0} + \frac{\partial F}{\partial d_z} \frac{d(d_z^0)}{dT} \Big|_{d_z^0} \right]. \quad (3.1.2.5)$$

However, since  $F$  is a minimum for  $d_z = d_z^0$ , the second contribution vanishes. Hence

$$S = -\frac{\alpha}{2} (d_z^0)^2 - \frac{\partial F_0}{\partial T}. \quad (3.1.2.6)$$

Since both  $d_z^0$  and  $(\partial F_0/\partial T)$  are continuous at  $T_c$ , there is no entropy jump  $\Delta S = 0$ , and *no latent heat at the transition*.

Several values of the specific heat can be considered for a system, depending on the quantity that is maintained constant. In the above example, the displacement  $\mathbf{d}$  of a positive ion determines the occurrence of an electric dipole (or of a macroscopic polarization  $\mathbf{P}$ ). The quantity  $\epsilon$ , which is thermodynamically conjugated to  $d_z$ , is therefore proportional to an electric field (the conjugation between quantities  $\eta$  and  $\zeta$  is expressed by the fact that infinitesimal work on the system has the form  $\zeta d\eta - cf$ .

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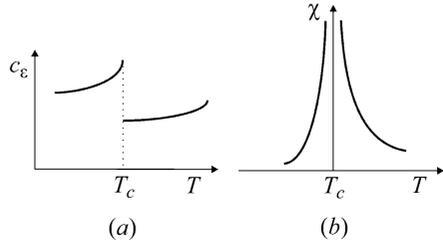


Fig. 3.1.2.5. (a) Qualitative temperature dependence of the specific heat at a continuous transition. (b) Temperature dependence of the susceptibility at a continuous transition.

Sections 1.1.1.4 and 1.1.5). Let us show that the specific heat at *constant electric field* has a specific type of anomaly.

This specific heat is expressed by

$$c_\varepsilon = T \left. \frac{\partial S}{\partial T} \right| \varepsilon. \quad (3.1.2.7)$$

Using (3.1.2.6), we find

$$T > T_c: \quad c_\varepsilon^0 = -\frac{\partial^2 F_0(T, p)}{\partial T^2}, \quad (3.1.2.8)$$

$$T < T_c: \quad c_\varepsilon = -\frac{\partial^2 F_0(T, p)}{\partial T^2} - \frac{\alpha}{2} \frac{d(d_z^0)^2}{dT} T = c_\varepsilon^0 + \frac{\alpha^2}{2\beta}. \quad (3.1.2.8a)$$

Hence above and below  $T_c$  the specific heat is a different, smoothly varying function of temperature, determined by the background free energy  $F_0(T, p)$  and by the smooth variation of the  $\beta$  coefficient. Fig. 3.1.2.5(a) reproduces the anomaly of the specific heat, which, on cooling through  $T_c$ , has the form of an upward step.

Finally, let us consider the anomaly of the susceptibility  $\chi$ , which, in the case considered, is proportional to the dielectric susceptibility of the material. It is defined as

$$\chi = \lim_{\varepsilon \rightarrow 0} \left. \frac{\partial d_z}{\partial \varepsilon} \right| d_z^0. \quad (3.1.2.9)$$

In order to calculate  $\chi$ , it is necessary to examine the behaviour of the system in the presence of a small field,  $\varepsilon$ , conjugated to the order parameter. In this case, the appropriate thermodynamical potential whose minimum determines the equilibrium of the system is not  $F$  but  $G = F - d_z \varepsilon$ . Minimizing  $G$  with respect to  $d_z$  leads to

$$d_z \{ \alpha(T - T_c) + \beta d_z^2 \} = \varepsilon. \quad (3.1.2.10)$$

For small values of  $\varepsilon$ , the solution of this equation must tend towards the equilibrium values  $d_z = 0$ . Deriving these solutions with respect to  $\varepsilon$ , we obtain

$$\chi(T > T_c) = \frac{1}{\alpha(T - T_c)}; \quad \chi(T < T_c) = \frac{1}{2\alpha(T - T_c)}. \quad (3.1.2.11)$$

The susceptibility goes to infinity when  $T \rightarrow T_c$  from either side of the transition (Fig. 3.1.2.5b). The set of anomalies in  $c_\varepsilon$  and  $\chi$  described in this paragraph represents the basic effects of temperature on quantities that are affected by a phase transition. They constitute the ‘canonical signature’ of a phase transition of the *continuous* type.

Certain complications arise in the cases where the transition is not strictly continuous, where the order parameter is coupled to other degrees of freedom, and where the order parameter is not

one-dimensional. We consider one of these complications in Section 3.1.2.3.

#### 3.1.2.2.6. Symmetry considerations

##### 3.1.2.2.6.1. Order-parameter symmetry

Up to now, we have defined the order parameter as a set of degrees of freedom determining a second-degree contribution to the free energy, the coefficient of which has a specific temperature dependence proportional to  $(T - T_c)$ . Actually, the order parameter can also be defined on the basis of its specific symmetry characteristics.

Let us consider the manner by which the components  $(d_x, d_y, d_z)$  transform when we apply to the crystal each of the 16 symmetry operations of the group  $G = 4/mmm$ . Table 3.1.2.1 specifies the results of these transformations.

In the first place, we note that  $d_z$  is transformed either into itself or into  $(-d_z)$ . If we consider this coordinate as the basis vector of a one-dimensional vector space, we can conclude that this *vector space* (i.e. the space formed by the set of vectors that are linear combinations of the basis) is *invariant* by all the transformations of the group  $G$ . Such a space, containing obviously no space of smaller dimension, is, according to the definitions given in Chapter 1.2, a *one-dimensional irreducible invariant space with respect to the group G*.

Each of the components  $(d_x, d_y)$  is not transformed into a proportional component by *all* the elements of  $G$ . Certain of these elements transform  $d_x$  into  $\pm d_y$ , and conversely. Hence  $d_x$  and  $d_y$  are not, separately, bases for one-dimensional irreducible invariant spaces. However, their set generates a two-dimensional vector space that has the property to be invariant and irreducible by all the transformations of  $G$ .

Note that the set of the three components  $(d_x, d_y, d_z)$  carries a three-dimensional vector space which, obviously, has the property to be invariant by all the transformations of  $G$ . However, this vector space *contains* the two invariant spaces carried respectively by  $d_z$  and by  $(d_x, d_y)$ . Hence it is not irreducible.

In conclusion, from a symmetry standpoint, the order parameter of a phase transition is a set of degrees of freedom that carries an irreducible vector space (an irreducible representation) with respect to the action of the group  $G$ , the latter group being the symmetry group of the high-symmetry phase.

##### 3.1.2.2.6.2. Degeneracy of the low-symmetry phase

We had noted above that the structure is invariant by  $G$  in the stable state of the system above  $T_c$ . When  $\mathbf{d} \neq 0$ , the structure becomes invariant by a smaller set of transformations. Let us enumerate these transformations for each possible stable state of the system below  $T_c$ .

When the order parameter coincides with  $d_z$ , we determined, below  $T_c$ , two stable states,  $d_z^0 = \pm[\alpha(T_c - T)/\beta]^{1/2}$ . The crystalline structures determined by these displacements of the  $M^+$  ion parallel to the  $z$  axis are both invariant by the same set of eight symmetry transformations. These comprise the cyclic group of order 4 generated by the fourfold rotation around  $z$ , and by the reflections in planes containing this axis. This set is the group

Table 3.1.2.1. Transformation of the components of  $\mathbf{d}$  under the symmetry operations of group  $G = 4/mmm$

$G$	$E$	$C_4$	$C_2$	$C_4^3$	$\sigma_x$	$\sigma_y$	$\sigma_{xy}$	$\sigma_{xy'}$
$d_z$	$d_z$	$d_z$	$d_z$	$d_z$	$d_z$	$d_z$	$d_z$	$d_z$
$d_x$	$d_x$	$d_y$	$-d_x$	$-d_y$	$-d_x$	$d_x$	$-d_y$	$d_y$
$d_y$	$d_y$	$-d_x$	$-d_y$	$d_x$	$d_y$	$-d_y$	$-d_x$	$d_x$
$G$	$I$	$S_4^3$	$\sigma_z$	$S_4$	$U_x$	$U_y$	$U_{xy}$	$U_{xy'}$
$d_z$	$-d_z$	$-d_z$	$-d_z$	$-d_z$	$-d_z$	$-d_z$	$-d_z$	$-d_z$
$d_x$	$-d_x$	$-d_y$	$d_x$	$d_y$	$d_x$	$-d_x$	$-d_y$	$d_y$
$d_y$	$-d_y$	$d_x$	$d_y$	$-d_x$	$-d_y$	$d_y$	$d_x$	$-d_x$

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$C_{4v} = 4mm$ , a subgroup  $F$  of  $G$ . The transition is thus accompanied by a lowering of the symmetry of the system.

Also note that the two states  $\pm d_z^z$  are transformed into each other by certain of the symmetry operations such as the mirror symmetry  $\sigma_z$  'lost' below  $T_c$ . These two states correspond to the same value of the free energy [the minimum value determined in equation (3.1.2.3)]: they are equally stable. This can also be checked by applying to the system the mirror symmetry  $\sigma_z$ . This transformation keeps unchanged the value of  $F$  since the free energy is invariant by all the transformations belonging to  $G$  (to which  $\sigma_z$  belongs). The state  $d_z$  is, however, not preserved, and is transformed into  $(-d_z)$ .

We have not determined explicitly the stable states of the system in the case of a two-dimensional order parameter  $(d_x, d_y)$ . A simple discussion along the line developed for the one-dimensional order parameter  $d_z$  would show that the relevant form of the free energy is

$$F = F_0 + \frac{\alpha(T - T_c)}{2} (d_x^2 + d_y^2) + \beta_1 (d_x^4 + d_y^4) + \beta_2 d_x^2 d_y^2 \quad (3.1.2.12)$$

and that the possible stable states below  $T_c$  are:

- (i)  $d_x^0 = \pm[\alpha(T_c - T)/\beta_1]^{1/2}$ ,  $d_y = 0$ ;
- (ii)  $d_y^0 = \pm[\alpha(T_c - T)/\beta_2]^{1/2}$ ,  $d_x = 0$ ;
- (iii) and (iv)  $d_x^0 = \pm d_y^0 = \pm[\alpha(T_c - T)/(\beta_1 + \beta_2)]^{1/2}$ .

Like the case of  $d_z$ , there is a lowering of the crystal symmetry below  $T_c$ . In the four cases, one finds that the respective symmetry groups of the structure are (i)  $F = C_{2v} = mm2_x$ ; (ii)  $F' = C_{2v} = mm2_y$ ; (iii)  $F = C_{2v} = mm2_{xy}$ ; (iv)  $F' = C_{2v} = mm2_{xy}$ .

States (i) and (ii) correspond to each other through one of the 'lost' transformations of  $G$  (the rotations by  $\pi/2$ ). They therefore possess the same free energy and stability. The second set of states (iii) and (iv) also constitute, for the same reason, a pair of states with the same value of the equilibrium free energy.

Note that the symmetry groups associated with equally stable states are conjugate relative to  $G$ , that is they satisfy the relationship  $F' = gFg^{-1}$ , with  $g$  belonging to  $G$ .

#### 3.1.2.3. Free-energy models for discontinuous transitions

Expression (3.1.2.2) for the free energy, discussed in the preceding section, only contains terms of even degrees as a function of the order parameter. We have stressed that this property derives from symmetry considerations. Let us provisionally ignore the symmetry constraints and assume that the phase transition in a given system is described by a free energy containing a term of degree three as a function of the order parameter.

$$F = F_0 + \frac{\alpha(T - T_0)}{2} \eta^2 + \frac{\delta}{3} \eta^3 + \frac{\beta}{4} \eta^4. \quad (3.1.2.13)$$

The stable state of this system at each temperature is determined by the minimum of  $F$ . The extrema of this function are provided by

$$\frac{\partial F}{\partial \eta} = \eta[\alpha(T - T_0) + \delta\eta + \beta\eta^2] = 0, \quad (3.1.2.14)$$

the solutions of which are

$$\eta = 0 \quad \text{and} \quad \eta = \frac{1}{2\beta} \left[ -\delta \pm \sqrt{\delta^2 + 4\alpha\beta(T_0 - T)} \right]. \quad (3.1.2.15)$$

A straightforward analysis based on (3.1.2.13) and (3.1.2.15) shows that, depending on the range of temperatures, the free energy has one of the forms schematically represented in Fig. 3.1.2.6(a). This form changes at three characteristic temperatures.

(i) Above  $T_1 = (T_0 + \delta^2/4\alpha\beta)$ , the free energy has one extremum (a minimum) for  $\eta = 0$ . The stable state of the system corresponds to a zero value of the order parameter.

(ii) For  $T_0 < T < T_1$ , the free energy has two minima, one for  $\eta = 0$  and the other one for  $\eta = (1/2\beta)\{-\delta \pm [\delta^2 + 4\alpha\beta(T_1 - T)]^{1/2}\}$ . These minima define one stable state (the deepest minimum) and one metastable state. Note that the zero value of the order parameter constitutes the stable state in the range  $T_c < T < T_1$  with  $T_c = T_0 + \delta^2/9\beta\alpha$ . Hence, the observed phase transition corresponding to a change from a zero value to a nonzero value of the order parameter occurs at  $T_c$ . Below this temperature, and down to  $T_0$ , the system has a stable state at  $\eta \neq 0$  and a metastable state at  $\eta = 0$ .

(iii) Finally, below  $T_0$ , the free energy has two minima both corresponding to  $\eta \neq 0$ , the value  $\eta = 0$  being a relative maximum.

The remarkable physical consequences of this sequence of shapes are the following.

In the first place, it appears that the equilibrium value of the order parameter changes discontinuously at  $T_c$ . The free energy (3.1.2.13) therefore provides us with a model of discontinuous phase transitions. Referring to equation (3.1.2.6), we can see that a discontinuity of the order parameter is necessarily associated with a nonzero latent heat (or entropy) for the transition. More precisely, the downward jump experienced, on heating, by the equilibrium value of the order parameter corresponds to an endothermal transition. Such a transition is also termed (following Ehrenfest's classification) a *first-order transition*, since the entropy, which is a *first derivative* of the free energy, is discontinuous.

On the other hand, the occurrence of metastable states, in certain temperature ranges, generates *thermal hysteresis*. Indeed, on cooling from above  $T_1$ , the system is likely to remain in the state  $\eta = 0$  down to the temperature  $T_0$ , even though between  $T_1$  and  $T_0$  this state is not the stable state of the system. Conversely, on heating, the system will remain in a state  $\eta \neq 0$  up to  $T_1$ , even though this state does not constitute the stable state of the system between  $T_c$  and  $T_1$ . Hence, the variations of the order parameter will schematically vary as in Fig. 3.1.2.6(b), the temperature dependence below the discontinuity being determined by equation (3.1.2.15). Likewise, the susceptibility will vary as in Fig. 3.1.2.6(c).

The form (3.1.2.13) of the free energy is not the only model form for discontinuous transitions. Another canonical form is

$$F = F_0 + \frac{\alpha(T - T_0)}{2} \eta^2 - \frac{\beta}{4} \eta^4 + \frac{\gamma}{6} \eta^6, \quad (3.1.2.16)$$

where  $\eta$ ,  $\beta$  and  $\gamma$  are positive coefficients. The negative coefficient of the fourth-degree term has the effect of introducing more than one minimum in a certain temperature range. Fig. 3.1.2.7 shows the different shapes of the plot of  $F(\eta)$  over different temperature ranges. The situation is similar to the one already discussed in the presence of a third-degree contribution to the free energy. It corresponds to a discontinuous transition associated with a latent heat as well as to the existence of a range of thermal hysteresis.

Two relevant questions arise from consideration of the above models of first-order transitions.

In the first place, one can object to the use of a polynomial expansion of the free energy in cases involving a discontinuity of the order parameter while the assumption of continuity of the phase transition has been used as an essential substrate of the argument developed. However, the approach will clearly keep its validity if a transition, though discontinuous, involves 'small' discontinuities. The criterion for estimating if a discontinuity is small relies on the comparison between the atomic displacements involved by the transition and the distances between atoms in the structure. If the displacements are a small fraction of the distances between atoms, then the method used can be consid-

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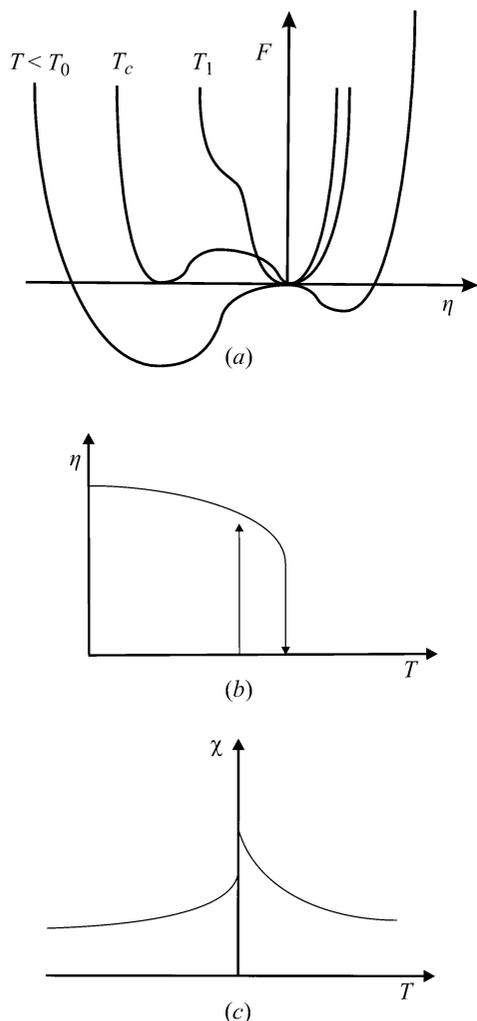


Fig. 3.1.2.6. (a) Plots of the free energy as a function of the order parameter for various temperature values in the framework of the model of a discontinuous transition associated with equation (3.1.2.13). (b) Temperature dependence of the equilibrium value of the order parameter, as determined by the model of a discontinuous transition. (c) Temperature dependence of the susceptibility in this model.

ered as valid. Indeed, the total free energy of the system depends on the distance between atoms, because this distance controls the strength of the interaction energy within the system. Hence, the transition only changes in a minor way the value of the system's free energy.

On the other hand, one has to check that there are systems of physical interest for which the crystallographic symmetry allows free-energy forms of the type (3.1.2.13), (3.1.2.16). Indeed, the crystallographic symmetry relative to the example in Section 3.1.2.2 was such that the presence of a third-degree term in the Landau free energy was excluded.

Such verification is not necessary for the free energy of type (3.1.2.16). This free energy is only characterized by a *specific sign* of the coefficient of the fourth-degree term, a circumstance that is not defined by symmetry considerations.

By contrast, an actual crystallographic model of a transition described by (3.1.2.13), which involves a term of degree three, is required to support the relevance of the corresponding model. Such a model is provided, for instance, by a crystal the high-temperature phase of which has a rhombohedral symmetry (e.g.  $R3m$ ), and which undergoes a transition corresponding to an atomic displacement  $\mathbf{d}$  perpendicular to the ternary axis (Fig. 3.1.2.8).

If we refer the components to a rectangular frame of coordinates, the matrices representing the mode of transformation of the components  $(d_x, d_y)$  under application of the generating

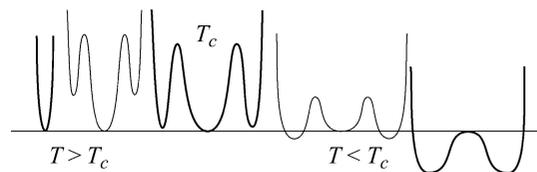


Fig. 3.1.2.7. Plots of the free energy as a function of the order parameter for various temperatures in the framework of the model of a discontinuous transition associated with equation (3.1.2.16). The temperature decreases from right to left, the transition being reached for the temperature corresponding to the third plot.

elements of the group  $R3m$  have a form reproduced in existing tables. It is easy to check that the form of the Landau free energy resulting from a search of invariant polynomials of successive degrees is

$$F = F_0 + \frac{\alpha(T - T_0)}{2}(d_x^2 + d_y^2) + \frac{\delta}{3}(d_x^2 - 3d_y^2) + \frac{\beta}{4}(d_x^2 + d_y^2)^2. \quad (3.1.2.17)$$

We note that the form of the free energy of this system, determined by its symmetry, involves a third-degree term. Let us show that the thermodynamic properties corresponding to this form are qualitatively identical to the ones derived from the canonical free energy (3.1.2.13). In this view, let us put  $d_x = \eta \cos \theta$  and  $d_y = \eta \sin \theta$ . The free energy takes the form

$$F = F_0 + \frac{\alpha(T - T_0)}{2}\eta^2 + \frac{\delta}{3}\eta^3 \cos \theta (\cos^2 \theta - 3 \sin^2 \theta) + \frac{\beta}{4}\eta^4. \quad (3.1.2.18)$$

For such a free energy, it is remarkable that for  $\eta \neq 0$  the directions  $\theta$  of the extrema, which are determined by  $\partial F / \partial \theta = 0$ , are independent of the value of  $\eta$ . These directions form two sets which we denote  $A$  ( $\theta = 0, 2\pi/3, 4\pi/3$ ) and  $B$  ( $\pi/3, \pi, -\pi/3$ ). If we replace in equation (3.1.2.18)  $\eta$  by one of these values, we obtain

$$F = F_0 + \frac{\alpha(T - T_0)}{2}\eta^2 \pm \frac{\delta}{3}\eta^3 + \frac{\beta}{4}\eta^4, \quad (3.1.2.19)$$

the sign in front of the  $\delta$  coefficient being  $+$  for the  $A$  set of  $\theta$  angles and  $-$  for the  $B$  set. We are therefore brought back to a form close to the canonical one [equation (3.1.2.13)]. Note that for  $\delta > 0$ , the stable second minimum of the free energy [equation (3.1.2.15)] corresponded to  $\eta < 0$ , i.e. to  $\delta\eta < 0$ . Hence in (3.1.2.19),  $\eta$  being a positive modulus, the second stable minimum will correspond to a negative coefficient for  $\eta^3$ . Depending on the sign of  $\delta$ , the direction  $\theta$  of this minimum will either be the set  $A$  or the set  $B$  of  $\theta$  values.

#### 3.1.2.4. Generalization of the approach

Let us summarize the results obtained in the study of the specific models described in the preceding sections. We have shown that an order parameter (e.g.  $d_z$  or  $d_x, d_y$ ) is a set of scalar degrees of freedom that allows the description of the symmetry and physical changes accompanying the phase transition in a system. The equilibrium values of the  $n$  components of the order parameter are zero for  $T \geq T_c$  and *not all zero* for  $T < T_c$ . The  $n$  components define a vector space that is an irreducible invariant

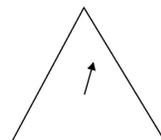


Fig. 3.1.2.8. Schematic representation of the displacement associated with the order parameter in a crystal having trigonal (rhombohedral) symmetry.

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space by the group  $G$ , which is the crystallographic symmetry group of the high-temperature phase. A variational free energy  $F$  associated with the transition, and termed the Landau free energy, can be expanded as a function of the components of the order parameter. The second-degree term of this expansion has a coefficient that vanishes and changes sign at the transition temperature. The form of  $F$  is determined by the symmetry properties of the order parameter, *i.e.* by the mode of transformation of the components of the order parameter into each other when the operations of  $G$  are applied to them. The specific form of  $F$  determines the symmetries of the potentially stable phases below  $T_c$ , the degeneracy of these phases, the temperature dependencies of relevant physical quantities and, in certain cases, the thermodynamic order of the phase transition.

In this section, let us briefly outline the arguments used in order to formulate the theory in a general framework.

These arguments rely in part on the properties of the irreducible representations of a group. The reader can refer to Chapter 1.2 for a comprehensive presentation of irreducible representations. We will consider here representations of a group  $G$  carried by a set of degrees of freedom  $(\eta_1, \eta_2, \eta_3, \dots)$ , and use essentially the following properties.

(a) If the set is irreducible and non-totally symmetric (trivial), there is no linear combination  $f_1(\eta_i) = \alpha_1\eta_1 + \alpha_2\eta_2 + \dots$  of the  $\eta_i$  that is invariant by all the elements of  $G$ .

(b) If the set is irreducible, there is a single homogeneous polynomial of degree two that is invariant by the group  $G$ . Its form is  $f_2 = \sum \eta_i^2$ .

(c) If  $g(\mathbf{r})$  is an arbitrary function of the space coordinates  $[\mathbf{r} = (x, y, z)]$ , one can always write

$$g(\mathbf{r}) = \sum_{\gamma} \sum_j \varphi_{\gamma,j}(\mathbf{r}), \quad (3.1.2.20)$$

where each set of functions  $\varphi_{\gamma,j}$  ( $j = 1, 2, \dots, p$ ) defines a space generated by the  $p$  functions which is invariant and irreducible by the group  $G$  and corresponds to the irreducible representation labelled  $\tau_{\gamma}$  of  $G$ .

#### 3.1.2.4.1. Description of the phase transition

In order to generalize the considerations developed in the preceding sections, we have to define, independently from any specific structure, the basic ingredients of the theory: definition of a variational set of degrees of freedom; construction of a free energy; determination of the stable states on either side of a transition temperature.

In a first step, we describe an arbitrary atomic configuration of a system by the set of densities  $\rho_i(\mathbf{r})$  of the particles of type  $(i)$ . This set constitutes variational degrees of freedom, which can be used to construct the variational free energy of the system  $F[T, \rho_i(\mathbf{r})]$ . The equilibrium of the system is defined by the set of functions  $\rho_i^{\text{eq}}(T, \mathbf{r})$  that minimize the free energy.

The symmetry of the system at a given temperature is defined as the set of geometrical transformations that leave invariant all the  $\rho_i^{\text{eq}}$ . This set forms a group.

We are then in a position to define a *continuous transition* at  $T_c$  by two conditions:

(i) The  $\rho_i^{\text{eq}}(T, \mathbf{r})$  are functions whose forms change continuously across  $T_c$ .

(ii) The symmetry group of the system just above  $T_c$  is different to the symmetry just below  $T_c$ .

Hence the phase transition, though associated with a *continuous* change of the spatial configuration of the atoms, is associated with a *sudden* change of the symmetry.

#### 3.1.2.4.2. Order parameter

As compared with the set  $(d_x, d_y, d_z)$  used in the example of Section 3.1.2.2, the variational functions  $\rho_i(\mathbf{r})$  have the drawback

of not being *small and scalar* quantities, thus making an expansion of the free energy more complicated.

Without loss of generality, let us restrict ourselves to a single type of  $(i)$  particles. In order to remove the difficulty mentioned above we put

$$\rho(\mathbf{r}) = \rho_0(\mathbf{r}) + \sum \sum \eta_{\gamma,j} \varphi_{\gamma,j}(\mathbf{r}), \quad (3.1.2.21)$$

where  $\rho_0 = \rho^{\text{eq}}(T_c, \mathbf{r})$  is the equilibrium density at  $T_c$ . Let us denote by  $G$  the symmetry group of this equilibrium density. The sum in the second part of (3.1.2.21) is a small increment since the transition is continuous. This increment has been expanded, as in (3.1.2.20), as a function of irreducible functions with respect to the group  $G$ . Moreover, each function has been expressed as the product of a normalized function  $\varphi_{\gamma,j}$  and of small scalar parameters  $\eta_{\gamma,j}$ . It is easy to convince oneself that it is possible to consider that under the action of  $G$  either the  $\varphi_{\gamma,j}$  transform into each other, the  $\eta_{\gamma,j}$  being fixed coefficients, or the  $\eta_{\gamma,j}$  transform into each other, the functions  $\varphi_{\gamma,j}$  being fixed. *We shall adopt the second convention.* The variational free energy can then be written in the form

$$F = F[T, \eta_{\gamma,j}, \varphi_{\gamma,j}(\mathbf{r})]. \quad (3.1.2.22)$$

At each temperature, the characteristics of the system are specified by the following conditions:

(i) The equilibrium corresponds to the values  $\eta_{\gamma,j}$  that make the free energy a minimum. These values define through (3.1.2.21) the equilibrium density of particles in the system.

(ii) The symmetry of the system is defined as the group of invariance of the determined equilibrium density.

Note that, in  $(\rho - \rho_0)$ , the contribution of the degrees of freedom  $\eta_{\gamma,j}$  spanning a *totally symmetric representation* can be ignored in the first place. One can show that such a contribution would have the same symmetry on either side of the transition. Therefore it is not crucially associated with the symmetry change defining the phase transition.

Following the ideas introduced in Section 3.1.2.2, the free-energy form is obtained as a Taylor expansion as a function of the small parameters  $\eta_{\gamma,j}$ . Besides, each polynomial term of a given degree of this expansion is invariant by  $G$ . Indeed,  $F$ , being a scalar, is unchanged by any rotation or reflection. Among the transformations, those belonging to  $G$  have the additional property of leaving invariant the density  $\rho_0$  which is, besides  $T$  and the  $\eta_{\gamma,j}$ , an argument of the function  $F$ .

It is easy to check that the group-theoretical rules recalled at the beginning of this section determine the absence of an invariant linear term in the expansion. Moreover, these rules specify the form of the second-degree contribution. We have

$$F = F_0(T) + \sum \alpha_{\gamma} (\sum \eta_{\gamma,j}^2). \quad (3.1.2.23)$$

On the other hand, the equilibrium density is

$$\rho^{\text{eq}} - \rho_0 = \sum \sum \eta_{\gamma,j}^0 \varphi_{\gamma,j}(\mathbf{r}). \quad (3.1.2.24)$$

Let us first consider the system at  $T_c$ . The equilibrium values of all the  $\eta_{\gamma,j}$  are zero. Hence, on the basis of (3.1.2.23), we conclude that all the  $\alpha_{\gamma}$  satisfy the condition  $\alpha_{\gamma} > 0$  (since the second-degree expansion must be minimum at the origin). Note that this condition *cannot be strict for all  $\gamma$* . Otherwise, these coefficients would also be positive in the vicinity of  $T_c$ , on either side of this temperature. As a consequence, the equilibrium values  $\eta_{\gamma,j}^0$  would all be zero and the symmetry would be unchanged. *Hence, one at least of the  $\alpha_{\gamma}$  has to vanish and to change sign at  $T_c$ .* An argument already invoked in Section 3.1.2.2 allows one to assert that one  $\alpha_{\gamma}$  coefficient only has this property. The  $\eta_{\gamma,j}$  corresponding to the other indices  $\gamma$  keep zero equilibrium values in the vicinity of  $T_c$  and can be ignored in the first place. We can therefore drop in (3.1.2.23) all degrees of freedom except the ones associated with

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the  $\alpha_\gamma$  coefficient that vanishes at  $T_c$ . The set  $\eta_{\gamma,j}$  ( $j = 1, 2, \dots, m$ ) constitutes the  $m$ -dimensional order parameter of the transition considered. As this set comprises all the degrees of freedom contributing to a single second-degree term in the free energy, it necessarily constitutes a basis for an irreducible vector space with respect to  $G$ , according to the group-theoretical rules recalled above.

#### 3.1.2.4.3. Stable states and symmetry in the vicinity of $T_c$

Above  $T_c$ , due to the positivity of  $\alpha$  (we can drop the  $\gamma$  index), the equilibrium values of the  $\eta_j$  are zero and the symmetry is  $G$ , identical to the symmetry at  $T_c$ . Below  $T_c$ ,  $\alpha$  is negative and the minimum of  $F$  occurs away from the origin in the  $\{\eta_j\}$  space. The symmetry of the system is defined by all the transformations leaving invariant the density:

$$\rho^{\text{eq}} = \rho_0 + \sum \eta_j^0 \varphi_j(\mathbf{r}). \quad (3.1.2.25)$$

Since the  $\eta_j^0$  contribution to the second member is small, these transformations have to be selected among those belonging to the invariance group of  $\rho_0$ . The space  $\{\eta_j\}$  defines a *non-trivial representation* of the latter group since the linear combination of the order-parameter components present in  $\rho^{\text{eq}}$  cannot be invariant by all the transformations of  $G$ . The symmetry group of the system below  $T_c$  is therefore a subgroup  $F$  of  $G$ .

As pointed out in Section 3.1.2.2, in order to determine the minimum of  $F$  below  $T_c$ , it is necessary to expand the free energy to degrees higher than two. The relevant expression of the free energy is then

$$F = F_0(T, \rho_0) + \frac{1}{2}\alpha(T - T_c)(\sum \eta_j^2) + f_3(\eta_j) + f_4(\eta_j) + \dots, \quad (3.1.2.26)$$

where we have developed the coefficient  $\alpha$ , which is an odd function of  $(T - T_c)$  to the lowest degree in  $(T - T_c)$ . It can be shown that the existence of a third-degree term  $f_3(\eta_j)$  depends exclusively on the nature of the representation  $\tau_\gamma$  associated with the order parameter. If the symmetry of the order parameter is such that a third-degree term is not symmetry forbidden, the transition will be of the type analysed in Section 3.1.2.3: it will be discontinuous.

For any symmetry of the order parameter, fourth-degree terms  $f_4(\eta_j)$  will always be present in the free-energy expansion (there will be at least one such term that is the square of the second-degree term). No further general statement can be made. Depending on the form and coefficients of this term, a continuous or discontinuous transition will be possible towards one or several distinct low-symmetry phases. The form of the  $f_4(\eta_j)$  term can be determined by searching the most general fourth-degree polynomial that is invariant by the set of transformations belonging to  $G$ .

In summary, in the light of the preceding considerations, the study of a phase transition according to the Landau scheme can be developed along the following lines:

(a) Search, as a starting information on the system, the symmetry group  $G$  of the more symmetric phase surrounding the transition and the nature of the irreducible representation  $\tau_\gamma$  associated with the order parameter. Both can be obtained from a crystallographic investigation as illustrated by the example in the next section.

(b) Check the possibility of a third-degree invariant on symmetry grounds.

(c) Construct the free energy by determining the form of the invariant polynomials of the required degrees.

(d) Determine, as a function of the coefficients of the free-energy expansion, the absolute minimum of  $F$ .

(e) For each minimum, determine the invariance group of the density  $\rho^{\text{eq}}$ , *i.e.* the ‘low-symmetry’ group of the system.

(f) Derive the temperature dependence of the quantities related to the order parameter component  $\eta_j$ .

(g) Consider (as discussed in the next section) the coupling of the order parameter to other relevant ‘secondary’ degrees of freedom, and derive the temperature dependence of these quantities.

#### 3.1.2.5. Application to the structural transformation in a real system

Let us examine the particular ingredients needed to apply Landau’s theory to an example of *structural* transitions, *i.e.* a transition between crystalline phases.

##### 3.1.2.5.1. Nature of the groups and of their irreducible representations

The phases considered being crystalline, their invariance groups,  $G$  or  $F$ , coincide with *crystallographic space groups*. Let us only recall here that each of these groups of infinite order is constituted by elements of the form  $\{R|\mathbf{t}\}$  where  $R$  is a point-symmetry operation and  $\mathbf{t}$  a translation. The symmetry operations  $R$  generate the point group of the crystal. On the other hand, among the translations  $\mathbf{t}$  there is a subset forming an infinite group of ‘primitive’ translations  $\mathbf{T}$  generating the three-dimensional Bravais lattice of the crystal.

For a space group  $G$ , there is an infinite set of unequivalent irreducible representations. An introduction to their properties can be found in Chapter 1.2 as well as in a number of textbooks. They cannot be tabulated in a synthetic manner as the better-known representations of finite groups. They have to be constructed starting from simpler representations. Namely, each representation is labelled by a double index.

(i) The first index is a  $\mathbf{k}$  vector in reciprocal space, belonging to the first Brillouin zone of this space. The former vector defines a subgroup  $G(\mathbf{k})$  of  $G$ . This group is the set of elements  $\{R|\mathbf{t}\}$  of  $G$  whose component  $R$  leaves  $\mathbf{k}$  unmoved, or transforms it into an ‘equivalent’ vector (*i.e.* differing from  $\mathbf{k}$  by a reciprocal-lattice vector). The group  $G(\mathbf{k})$  has irreducible representations labelled  $\tau_m(\mathbf{k})$  of dimension  $n_m$  which are defined in available tables.

(ii) A representation of  $G$  can be denoted  $\Gamma_{\mathbf{k},m}$ . It can be constructed according to systematic rules on the basis of the knowledge of  $\tau_m(\mathbf{k})$ . Its dimension is  $n_m r$  where  $r$  is the number of vectors in the ‘star’ of  $\mathbf{k}$ . This star is the set of vectors, unequivalent to  $\mathbf{k}$ , having the same modulus as  $\mathbf{k}$  and obtained from  $\mathbf{k}$  by application of all the point-symmetry elements  $R$  of  $G$ .

##### 3.1.2.5.2. The example of gadolinium molybdate, $Gd_2(MoO_4)_3$

Gadolinium molybdate (GMO) is a substance showing one complication with respect to the example in Section 3.1.2.2. Like the prototype example already studied, it possesses below its phase transition an electric dipole (and a spontaneous polarization) resulting from the displacement of ions. However, one does not observe the expected divergence of the associated susceptibility (Fig. 3.1.2.5).

##### 3.1.2.5.2.1. Experimental identification of the order-parameter symmetry

The high-temperature space group  $G$  is known for GMO from X-ray diffraction experiments. It is the tetragonal space group  $P4_2/m$ . The corresponding point group  $4_2m$  has eight elements, represented in Fig. 3.1.2.9.

The  $\mathbf{k}$  vector labelling the irreducible representation associated with the order parameter can be directly deduced from a comparison of the diffraction spectra above and below  $T_c$ . We have seen that the difference of the two stable structures surrounding the transition is specified by the equilibrium density:

$$\rho(T, \mathbf{r}) - \rho(T_c, \mathbf{r}) = \sum \eta_{\mathbf{k},m} \varphi_{\mathbf{k},m}(\mathbf{r}). \quad (3.1.2.27)$$

### 3. SYMMETRY ASPECTS OF PHASE TRANSITIONS, TWINNING AND DOMAIN STRUCTURES

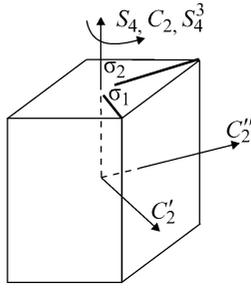


Fig. 3.1.2.9. Rotations/reflections belonging to the point group of gadolinium molybdate.

One can show, using the properties of the irreducible representations of the space groups, that the Fourier transform of the difference of densities given above is proportional to  $\delta(\mathbf{K} - \mathbf{k})$ , i.e. this Fourier transform is nonzero only for a  $\mathbf{K}$  vector equal to the  $\mathbf{k}$  vector indexing the order parameter. The implication of this property is that below  $T_c$ , the X-ray spectrum of the system will contain additional reflections whose locations in reciprocal space are defined by the vector of the order parameter. Experimentally, the vectors joining the Bragg spots existing in both phases to the closest superlattice spots only appearing below  $T_c$  are the vectors  $\mathbf{k}$  defining partly the irreducible representation  $\Gamma_{\mathbf{k},m}$  that specifies the symmetry properties of the order parameter.

In GMO, X-ray diffraction measurements show that superlattice spots appear below  $T_c$  at one of the four equivalent  $\mathbf{k}$  vectors

$$\pm \frac{\mathbf{a}_1^* \pm \mathbf{a}_2^*}{2}. \quad (3.1.2.28)$$

The operations of the point group  $\bar{4}2m$  transform these vectors into each other. The star of  $\mathbf{k}$  is therefore reduced to a single vector. On the other hand, consultation of available tables provides us with the possible representations  $\tau_{\mathbf{k},m}$  necessary to construct the representation  $\Gamma_{\mathbf{k},m}$  of the order parameter (the entries of the tables being the  $\mathbf{k}$  vector determined and the space group  $G$ ). There are three unequivalent  $\tau_{\mathbf{k},m}$ , which are reproduced in Table 3.1.2.2.

The ambiguity in the symmetry of the order parameter has now to be lifted. In this approach, the method is to work out for each  $\tau_m$  the symmetries  $G$  of the phases that are possibly stable below  $T_c$ . One then compares the results with the observed space group below  $T_c$ , which, for GMO, is the orthorhombic space group  $Pba2$ .

The group  $F$  of interest is the invariance group of the density difference [equation (3.1.2.27)]. Note that this difference can be considered as a 'vector' with components  $\eta_i$  in the irreducible space of the order parameter. In each irreducible space, the action of the elements of  $G$  on a vector is represented by the set

of matrices reproduced in Table 3.1.2.2. Let us first examine  $\tau_1$  in this table. Clearly, the matrices relative to  $\{S_4|0\}$ ,  $\{S_4^3|0\}$ ,  $\{C_2|\mathbf{t}\}$  and  $\{C_2'|\mathbf{t}\}$  rotate by  $\pi/2$  any vector of the two-dimensional space carrying the representation. These elements will not leave any direction unmoved and consequently they will not belong to  $F$ . The other elements either preserve any vector (and they then obviously belong to  $F$ ) or they reverse any direction. However, in the latter case, the product of any two of these elements belongs to  $F$ .

Summarizing these remarks, we obtain a single possible group  $F$  consisting of the elements  $\{E|0\}$ ,  $\{C_2|\mathbf{a}_1\}$ ,  $\{\sigma_1|\mathbf{t}\}$ ,  $\{\sigma_2|\mathbf{t} + \mathbf{a}_1\}$  and by the infinite translation group generated by the vectors  $(\mathbf{a}_1 \pm \mathbf{a}_2)$  and  $\mathbf{a}_3$ . The symbol for this space group is  $Pmm2$ .

A similar inspection yields for the representation  $\tau_2$  the group  $Pba2$  and for  $\tau_3$  three possible groups ( $P4$ ,  $Pbm2$  and  $P2$ ). Comparison with the experimental observation, recalled above, allows one to identify unambiguously the appropriate representation as  $\tau_2$ . In conclusion, the irreducible representation associated with the order parameter of the transition in GMO can be denoted  $\Gamma_{\mathbf{k},m}$ . Its  $\mathbf{k}$  vector is  $\mathbf{k} = \pm(\mathbf{a}_1^* \pm \mathbf{a}_2^*)/2$ , and its 'small representation' is  $\tau_2(\mathbf{k})$ . The number of components of the order parameter is two, equal to the dimension of  $\Gamma_{\mathbf{k},m}$ , which itself is equal to the product of the number of vectors in the star of  $\mathbf{k}$  (one) and of the dimension of  $\tau_2$  (two).

#### 3.1.2.5.2.2. Construction of the free energy and stable states

Denote by  $(\eta_1, \eta_2)$  the two components of the order parameter. The Landau free energy can be constructed by selecting the homogeneous polynomials of different degrees that are invariant by the *distinct* matrices of  $\tau_2$ . There are four such matrices. It is easy to check that the most general form of fourth-degree polynomial invariant by the action of these four matrices is

$$F = F_0 + \frac{\alpha(T - T_c)}{2}(\eta_1^2 + \eta_2^2) + \frac{\beta_1}{4}(\eta_1^4 + \eta_2^4) + \frac{\beta_2}{2}\eta_1^2\eta_2^2 + \frac{\beta_3}{2}\eta_1\eta_2(\eta_1^2 - \eta_2^2). \quad (3.1.2.29)$$

A discussion of the minima of this free energy can be made according to the same method as in Section 3.1.2.3, by putting  $\eta_1 = \rho \cos \theta$ ,  $\eta_2 = \rho \sin \theta$ . One then finds that, in accordance with the symmetry considerations developed in Section 3.1.2.5.2.1, there is a single possible symmetry below  $T_c$ . The equilibrium state of the system corresponds to an angle  $\theta$  whose value depends on the values of the coefficients in the expansion. The modulus  $\rho$  has the standard temperature dependence  $\rho \propto (T_c - T)^{1/2}$ .

As in the model/example described in Section 3.1.2.2, below  $T_c$  there are several stable states having the same free energy. Indeed, one can easily check in expression (3.1.2.29) that if  $(\eta_1^0, \eta_2^0)$  is an absolute minimum of the free energy (3.1.2.29), the states  $(-\eta_1^0, \eta_1^0)$ ,  $(-\eta_1^0, \eta_2^0)$ ,  $(-\eta_1^0, -\eta_2^0)$  are symmetry-related

Table 3.1.2.2. Matrices defining the irreducible representations of  $Pba2$  for  $\mathbf{k} = \mathbf{a}_1^* + \mathbf{a}_2^*$

	$G$										
	$\{E 0\}$	$\{S_4 0\}$	$\{C_2 0\}$	$\{S_4^3 0\}$	$\{\sigma_1 \mathbf{t}\}$	$\{\sigma_2 \mathbf{t}\}$	$\{C_2' \mathbf{t}\}$	$\{C_2'' \mathbf{t}\}$	$\mathbf{a}_1$	$\mathbf{a}_2$	$\mathbf{a}_3$
$\tau_1$	1 0 0 1	0 1 -1 0	-1 0 0 -1	0 -1 1 0	1 0 0 1	-1 0 0 -1	0 1 -1 0	0 -1 1 0	-1 0 0 -1	-1 0 0 -1	1 0 0 1
$\tau_2$	1 0 0 1	0 1 -1 0	-1 0 0 -1	0 -1 1 0	-1 0 0 -1	1 0 0 1	0 -1 1 0	0 1 -1 0	-1 0 0 -1	-1 0 0 -1	1 0 0 1
$\tau_3$	1 0 0 1	1 0 0 -1	1 0 0 1	1 0 0 -1	0 1 1 0	0 1 1 0	0 -1 1 0	0 -1 1 0	-1 0 0 -1	-1 0 0 -1	1 0 0 1

### 3.1. STRUCTURAL PHASE TRANSITIONS

minima corresponding to the same value of the equilibrium free energy.

The intensities of the diffraction ‘superlattice’ spots, being proportional to the square of the atomic displacement  $\rho$ , vary linearly as a function of temperature. On the other hand, the diverging susceptibility associated with the order parameter is related to a rapid increase of the diffuse scattering of X-rays or neutrons at the location of the superlattice spots in reciprocal space. Hence, consistent with the macroscopic measurements, it is not related to a divergence of the dielectric susceptibility.

#### 3.1.2.5.2.3. Macroscopic behaviour of GMO

In GMO, macroscopic quantities are degrees of freedom that are distinct from the order parameter. Indeed, their symmetry properties are different, since any lattice translation will leave them invariant, while this is not the case for the order parameter (see Section 3.1.2.5.2.1). Nevertheless, certain of the macroscopic quantities behave singularly at the transition. These degrees of freedom can be decomposed, as shown in Section 3.1.2.4, as the sum of irreducible degrees of freedom. Having a symmetry different from that of the order parameter, they were neglected in the first step of the description of the phase transition. In a more detailed description, they have to be taken into account.

Let us, for instance, consider the  $P_z$  component of the dielectric polarization of GMO, as well as the  $\varepsilon$  component of the strain tensor which represents a shear in the  $xy$  plane of the crystal. The matrices in Table 3.1.2.3 recall the mode of transformation of the order-parameter components as well as those of these two quantities under the action of the  $G$  group.

We can complete the expression of the free energy of the system by adding to  $F$  in (3.1.2.29) the contributions of the preceding degrees of freedom up to the second degree (which, as will be seen, is comparable to the fourth degree used for the order parameter). The resulting expression is provided by (3.1.2.30) below, in which we have neglected a bilinear term in  $P_z$  and  $\varepsilon$  as this term does not change the qualitative result we want to establish.

$$F_1 = F + \frac{b}{2}P_z^2 + \frac{c}{2}\varepsilon^2 + \delta_1 P_z(\eta_1^2 - \eta_2^2) + \delta_2 \varepsilon(\eta_1^2 - \eta_2^2), \quad (3.1.2.30)$$

where  $F$  is provided by equation (3.1.2.29). At equilibrium, the derivatives of  $F_1$  with respect to  $P_z$  and  $\varepsilon$  vanish. These conditions yield

$$P_z = -\frac{\delta_1}{b}(\eta_1^2 - \eta_2^2); \quad \varepsilon = -\frac{\delta_2}{c}(\eta_1^2 - \eta_2^2). \quad (3.1.2.31)$$

As stressed in Section 3.1.2.5.2.2, the equilibrium direction in the order-parameter space corresponds to the trivial  $\theta = 0$  angle. Hence  $(\eta_1^2 - \eta_2^2) \neq 0$  below  $T_c$ , resulting in the fact that nonzero values of  $P_z$  and  $\varepsilon$  will onset below the transition temperature. Besides, the form (3.1.2.31) indicates that the two macroscopic quantities considered, which are proportional to the square of the order parameter, are expected to vary linearly as a function of temperature below  $T_c$ . Note that terms such as  $P_z^2$  are of the same order of magnitude as fourth-degree terms of the order parameter.

We can also determine the behaviour of the dielectric susceptibility  $\chi$ , by calculating the variations of the equilibrium

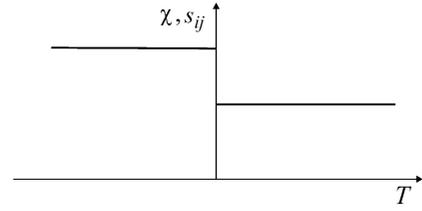


Fig. 3.1.2.10. Temperature dependence of the macroscopic susceptibility (or elastic compliance,  $s_{ij}$ ) in gadolinium molybdate. Compare with the ‘normal’ behaviour in Fig. 3.1.2.5(b).

value of  $P_z$  as a function of an applied electric field  $\mathbf{E}$  parallel to the polarization. We proceed as in Section 3.1.2.2, and minimize the potential  $G_1 = (F_1 - P_z E)$  with respect to the order parameter and to the polarization. In order to obtain the qualitative behaviour of  $\chi$ , we simplify the free energy by considering a single component of the order parameter. We also neglect the shear strain component  $\varepsilon$ . The set of simplified equations

$$\chi = \frac{\partial P_z}{\partial E} \Big|_{E=0}; \quad bP_z + \delta\eta^2 = E \quad (3.1.2.32)$$

$$\frac{\partial F_1}{\partial E} = \eta \left\{ \alpha(T - T_c) + \left( \beta - \frac{2\delta_1^2}{b} \right) \eta^2 + \frac{2\delta_1}{b} E \right\}$$

yields the following expression of the susceptibility:

$$\chi = \frac{1}{b} \quad \text{for } T > T_c \quad \text{and} \quad \chi = \frac{1}{b} + \frac{2\delta_1^2}{b(\beta - 2\delta_1^2/b)} \quad \text{for } T < T_c. \quad (3.1.2.33)$$

We find an upward step of the dielectric susceptibility on cooling. Likewise, consideration of the ‘elastic’ susceptibility relative to the shear strain component  $\varepsilon$  would determine an upward step of the elastic compliance (Fig. 3.1.2.10). The more usually measured elastic constant, which is the inverse of the compliance, undergoes a downward step on cooling.

We have seen in the preceding paragraph that the low-symmetry phase of gadolinium molybdate possesses four equally stable states differing by the values of the order-parameter components. Equation (3.1.2.31) shows that two of the states are associated with the same sign of the polarization  $P_z$  or of the shear strain  $\varepsilon$ , while the two other states possess opposite values of  $P_z$  and  $\varepsilon$ . According to the definitions given in Section 3.1.1, gadolinium molybdate belongs to the category of ferroelectrics as well as to that of ferroelastics.

The example of GMO clearly shows that the ferroic classification is less informative than the one based on the order-parameter symmetry. The latter determines the full symmetry change (orientational and translational), while the former only specifies the orientational symmetry change. On the other hand, the ferroic classification is not informative about the physical behaviour as a function of temperature. Thus, the model ferroelectric in Section 3.1.2.2 has a diverging dielectric susceptibility at  $T_c$ , while a GMO-type ferroelectric keeps a finite susceptibility. The ferroic classification has nevertheless the advantage of specifying the nature of the macroscopic quantities that are expected to behave anomalously at the transition, and are therefore worth measuring.

Table 3.1.2.3. Action of the generators of  $P6_3/m2$  on the order parameter and on the polarization and strain components

	$E$	$S_4$	$\sigma_1$	$\mathbf{a}_1$	$\mathbf{a}_2$	$\mathbf{a}_3$
$\eta_1$	1 0	0 1	-1 0	-1 0	-1 0	1 0
$\eta_2$	0 1	-1 0	0 -1	0 -1	0 -1	0 1
$P_z$	1	-1	1	1	1	1
$\varepsilon$	1	-1	1	1	1	1