

3. PHASE TRANSITIONS, TWINNING AND DOMAIN STRUCTURES

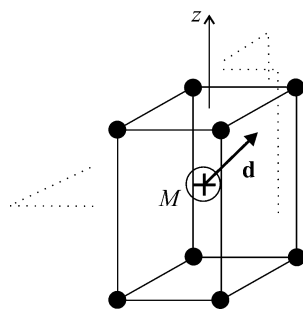


Fig. 3.1.2.1. Model of a structural transition. The filled circles at the vertices of the cell are singly charged negative ions and the empty circle at the centre is a singly charged positive ion. \mathbf{d} is an arbitrary displacement of the central ion.

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.

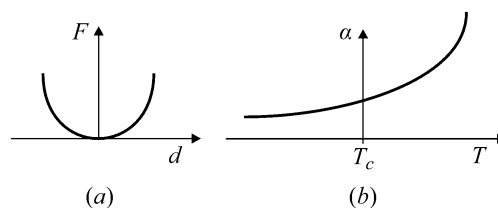


Fig. 3.1.2.2. (a) Variation of the free energy as function of the amplitude of the displacement of the central ion in Fig. 3.1.2.1. (b) Typical temperature dependence in the vicinity of T_c of the coefficient of a second-degree term in the Landau expansion (3.1.2.1) whenever this coefficient is strictly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

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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 α_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 α_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 α_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 α_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 α_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 α_i must vanish at T_c and become negative below this temperature.

Let us now show that the two coefficients α_i cannot vanish simultaneously at T_c . This result relies on the 'reasonable' assumption that the two coefficients α_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 α_i . The simultaneous vanishing of the two coefficients occurs at an isolated point

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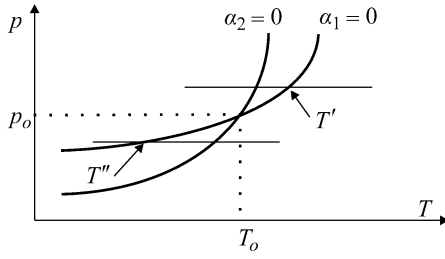


Fig. 3.1.2.3. Plots representative of the equations $\alpha_1(p, T) = 0$ and $\alpha_2(p, T) = 0$. The simultaneous vanishing of these coefficients occurs for a single couple of temperature and pressure (p_0, T_0) .

(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, α_1 vanishes at T' and α_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 α_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 α_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, α_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

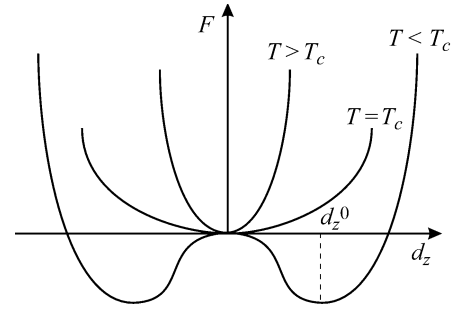


Fig. 3.1.2.4. Plots of the Landau free energy as a function of the order parameter, for values of the temperature above or below T_c or coincident with T_c . The shape of the plot changes qualitatively from a one-minimum plot to a two-minimum plot.

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 ΔS 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 ϵ , which is thermodynamically conjugated to d_z , is therefore proportional to an electric field (the conjugation between quantities η and ζ is expressed by the fact that infinitesimal work on the system has the form $\zeta d\eta - cf$.

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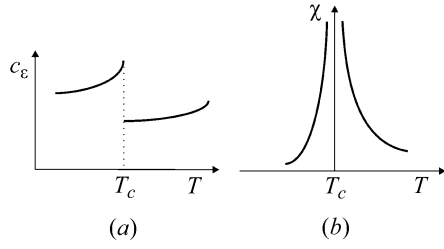


Fig. 3.1.2.5. (a) Qualitative temperature dependence of the specific heat at a continuous transition. (b) Temperature dependence of the susceptibility at a continuous transition.

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 β 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 χ , 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 χ , it is necessary to examine the behaviour of the system in the presence of a small field, ε , 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 ε , the solution of this equation must tend towards the equilibrium values $d_z = 0$. Deriving these solutions with respect to ε , 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_ε and χ 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	σ_x	σ_y	σ_{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	σ_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 $\pm d_z^2$ are transformed into each other by certain of the symmetry operations such as the mirror symmetry σ_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 σ_z . This transformation keeps unchanged the value of F since the free energy is invariant by all the transformations belonging to G (to which σ_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) $d_x^0 = \pm d_y = \pm[\alpha(T_c - T)/(\beta_1 + \beta_2)]^{1/2}$.

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 η , β and γ 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-