

3. PHASE TRANSITIONS, TWINNING AND DOMAIN STRUCTURES

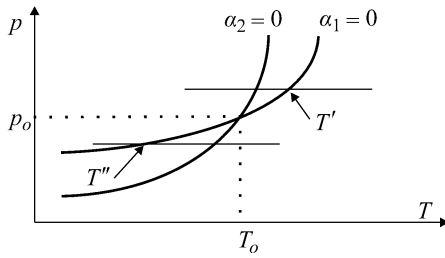


Fig. 3.1.2.3. Plots representative of the equations $\alpha_1(p, T) = 0$ and $\alpha_2(p, T) = 0$. The simultaneous vanishing of these coefficients occurs for a single couple of temperature and pressure (p_0, T_0) .

(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

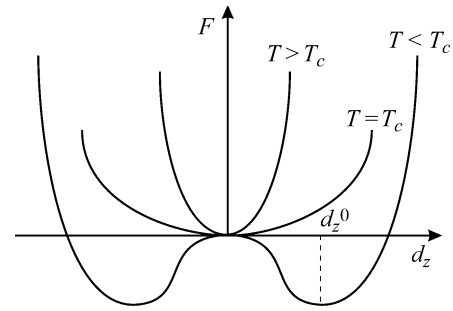


Fig. 3.1.2.4. Plots of the Landau free energy as a function of the order parameter, for values of the temperature above or below T_c or coincident with T_c . The shape of the plot changes qualitatively from a one-minimum plot to a two-minimum plot.

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 $\zeta d\eta - cf$.

3.1. STRUCTURAL PHASE TRANSITIONS

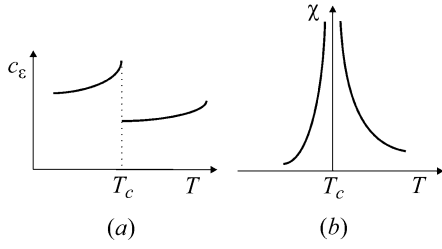


Fig. 3.1.2.5. (a) Qualitative temperature dependence of the specific heat at a continuous transition. (b) Temperature dependence of the susceptibility at a continuous transition.

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	$-d_x$