

3. PHASE TRANSITIONS, TWINNING AND DOMAIN STRUCTURES

$C_{4v} = 4mm$, 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-

3.1. STRUCTURAL PHASE TRANSITIONS

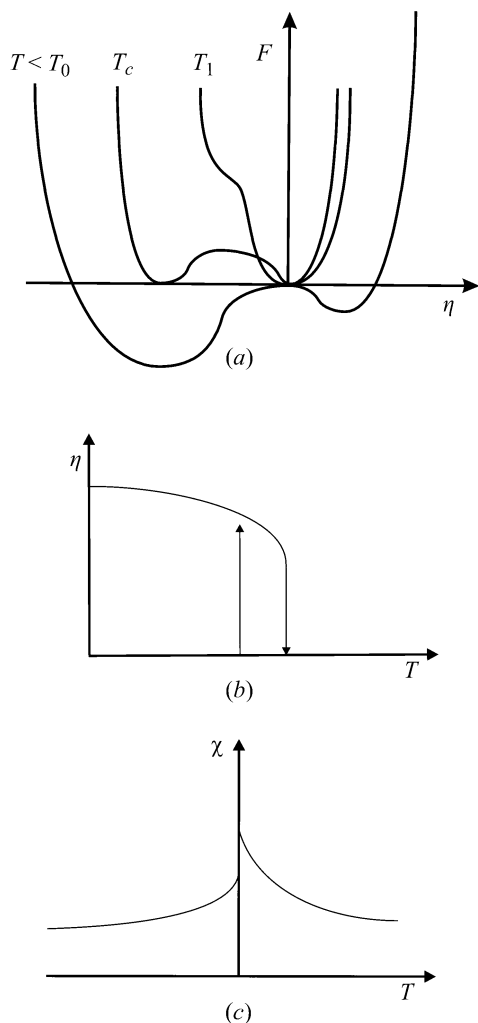


Fig. 3.1.2.6. (a) Plots of the free energy as a function of the order parameter for various temperature values in the framework of the model of a discontinuous transition associated with equation (3.1.2.13). (b) Temperature dependence of the equilibrium value of the order parameter, as determined by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

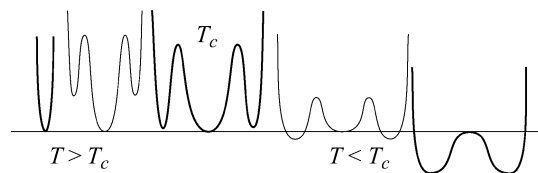


Fig. 3.1.2.7. Plots of the free energy as a function of the order parameter for various temperatures in the framework of the model of a discontinuous transition associated with equation (3.1.2.16). The temperature decreases from right to left, the transition being reached for the temperature corresponding 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 θ of the extrema, which are determined by $\partial F / \partial \theta = 0$, are independent of the value of η . These directions form two sets which we denote A ($\theta = 0, 2\pi/3, 4\pi/3$) and B ($\theta = \pi/3, \pi, -\pi/3$). If we replace in equation (3.1.2.18) η 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 δ coefficient being $+$ for the A set of θ 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), η being a positive modulus, the second stable minimum will correspond to a negative coefficient for η^3 . Depending on the sign of δ , the direction θ of this minimum will either be the set A or the set B of θ 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

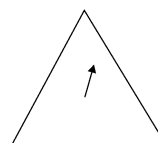


Fig. 3.1.2.8. Schematic representation of the displacement associated with the order parameter in a crystal having trigonal (rhombohedral) symmetry.