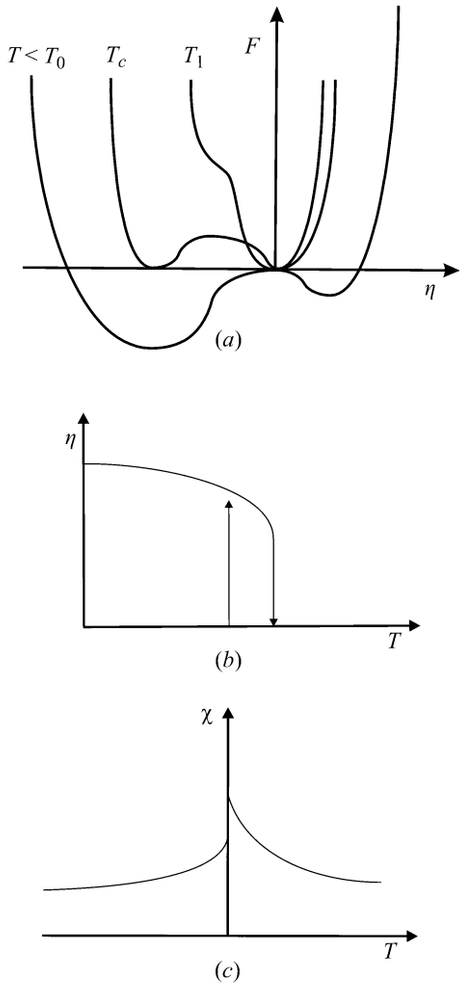

Fig. 3.1.2.6. (*a*) Plots of the free energy as a function of the order parameter for various temperature values in the framework of the model of a discontinuous transition associated with equation (3.1.2.13). (*b*) Temperature dependence of the equilibrium value of the order parameter, as determined 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.* *R*3*m*), and which undergoes a transition corresponding to an atomic displacement **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

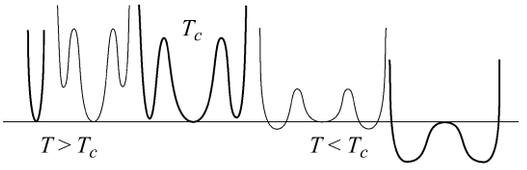

Fig. 3.1.2.7. Plots of the free energy as a function of the order parameter for various temperatures in the framework of the model of a discontinuous transition associated with equation (3.1.2.16). The temperature decreases from right to left, the transition being reached for the temperature corresponding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

elements of the group *R*3*m* 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

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

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

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

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 ($\pi/3, \pi, -\pi/3$). If we replace in equation (3.1.2.18) η by one of these values, we obtain

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

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

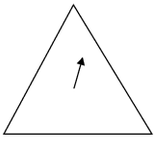

Fig. 3.1.2.8. Schematic representation of the displacement associated with the order parameter in a crystal having trigonal (rhombohedral) symmetry.