the α_γ coefficient that vanishes at T_c. The set $\eta_{\gamma,j}$ ($j = 1, 2, \ldots, m$) 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 α (we can drop the γ index), the equilibrium values of the η_j are zero and the symmetry is G, identical to the symmetry at T_c. Below T_c, α 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:

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

Since the η_j^0 contribution to the second member is small, these transformations have to be selected among those belonging to the invariance group of ρ_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 $\rho^{\rm eq}$ 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

$$F = F_0(T, \rho_0) + \tfrac{1}{2}\alpha(T - T_c)\left(\sum \eta_j^2\right) + f_3(\eta_j) + f_4(\eta_j) + \ldots, \qquad (3.1.2.26)$$

where we have developed the coefficient α, 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 τ_γ 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 τ_γ 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 $\rho^{\rm eq}$, *i.e.* the 'low-symmetry' group of the system.

(*f*) Derive the temperature dependence of the quantities related to the order parameter component η_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 $P\bar{4}2_1m$. The corresponding point group $\bar{4}2m$ 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:

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