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:

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

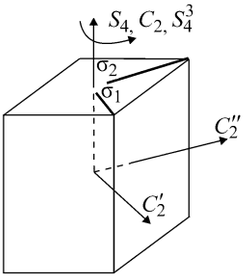

Fig. 3.1.2.9. Rotations/reflections belonging to the point group of gadolinium molybdate.

One can show, using the properties of the irreducible representations of the space groups, that the Fourier transform of the difference of densities given above is proportional to $\delta(\mathbf{K}-\mathbf{k})$, *i.e.* this Fourier transform is nonzero only for a $\mathbf{K}$ vector equal to the $\mathbf{k}$ vector indexing the order parameter. The implication of this property is that below T_c, the X-ray spectrum of the system will contain additional reflections whose locations in reciprocal space are defined by the vector of the order parameter. Experimentally, the vectors joining the Bragg spots existing in both phases to the *closest superlattice spots only appearing below* T_c are the vectors $\mathbf{k}$ defining partly the irreducible representation $\Gamma_{\mathbf{k},m}$ that specifies the symmetry properties of the order parameter.

In GMO, X-ray diffraction measurements show that superlattice spots appear below T_c at one of the four equivalent $\mathbf{k}$ vectors

$$\pm\frac{\mathbf{a}_1^* \pm \mathbf{a}_2^*}{2}. \qquad (3.1.2.28)$$

The operations of the point group $\bar{4}2m$ transform these vectors into each other. The star of $\mathbf{k}$ is therefore reduced to a single vector. On the other hand, consultation of available tables provides us with the possible representations $\tau_{\mathbf{k},m}$ necessary to construct the representation $\Gamma_{\mathbf{k},m}$ of the order parameter (the entries of the tables being the $\mathbf{k}$ vector determined and the space group G). There are three unequivalent $\tau_{\mathbf{k},m}$, which are reproduced in Table 3.1.2.2.

The ambiguity in the symmetry of the order parameter has now to be lifted. In this approach, the method is to work out for each τ_m the symmetries G of the phases that are possibly stable below T_c. One then compares the results with the observed space group below T_c, which, for GMO, is the orthorhombic space group *Pba*2.

The group F of interest is the invariance group of the density difference [equation (3.1.2.27)]. Note that this difference can be considered as a 'vector' with components η_i in the irreducible space of the order parameter. In each irreducible space, the action of the elements of G on a vector is represented by the set of matrices reproduced in Table 3.1.2.2. Let us first examine τ_1 in this table. Clearly, the matrices relative to $\{S_4|0\}$, $\{S_4^3|0\}$, $\{C_2'|\mathbf{t}\}$ and $\{C_2''|\mathbf{t}\}$ rotate by $\pi/2$ any vector of the two-dimensional space carrying the representation. These elements will not leave any direction unmoved and consequently they will not belong to F. The other elements either preserve any vector (and they then obviously belong to F) or they reverse any direction. However, in the latter case, the product of any two of these elements belongs to F.

Summarizing these remarks, we obtain a single possible group F consisting of the elements $\{E|0\}$, $\{C_2|\mathbf{a}_1\}$, $\{\sigma_1|\mathbf{t}\}$, $\{\sigma_2|\mathbf{t}+\mathbf{a}_1\}$ and by the infinite translation group generated by the vectors $(\mathbf{a}_1 \pm \mathbf{a}_2)$ and $\mathbf{a}_3$. The symbol for this space group is *Pmm*2.

A similar inspection yields for the representation τ_2 the group *Pba*2 and for τ_3 three possible groups (*P*4, *Pbm*2 and *P*2). Comparison with the experimental observation, recalled above, allows one to identify unambiguously the appropriate representation as τ_2. In conclusion, the irreducible representation associated with the order parameter of the transition in GMO can be denoted $\Gamma_{\mathbf{k},m}$. Its $\mathbf{k}$ vector is $\mathbf{k} = \pm(\mathbf{a}_1^* \pm \mathbf{a}_2^*)/2$, and its 'small representation' is $\tau_2(\mathbf{k})$. The number of components of the order parameter is two, equal to the dimension of $\Gamma_{\mathbf{k},m}$, which itself is equal to the product of the number of vectors in the star of $\mathbf{k}$ (one) and of the dimension of τ_2 (two).

3.1.2.5.2.2. *Construction of the free energy and stable states*

Denote by (η_1, η_2) the two components of the order parameter. The Landau free energy can be constructed by selecting the homogeneous polynomials of different degrees that are invariant by the *distinct* matrices of τ_2. There are four such matrices. It is easy to check that the most general form of fourth-degree polynomial invariant by the action of these four matrices is

$$F = F_0 + \frac{\alpha(T-T_c)}{2}\left(\eta_1^2+\eta_2^2\right) + \frac{\beta_1}{4}\left(\eta_1^4+\eta_2^4\right) + \frac{\beta_2}{2}\eta_1^2\eta_2^2 + \frac{\beta_3}{2}\eta_1\eta_2\left(\eta_1^2-\eta_2^2\right). \qquad (3.1.2.29)$$

A discussion of the minima of this free energy can be made according to the same method as in Section 3.1.2.3, by putting $\eta_1 = \rho\cos\theta$, $\eta_2 = \rho\sin\theta$. One then finds that, in accordance with the symmetry considerations developed in Section 3.1.2.5.2.1, there is a single possible symmetry below T_c. The equilibrium state of the system corresponds to an angle θ whose value depends on the values of the coefficients in the expansion. The modulus ρ has the standard temperature dependence $\rho \propto (T_c - T)^{1/2}$.

As in the model/example described in Section 3.1.2.2, below T_c there are several stable states having the same free energy. Indeed, one can easily check in expression (3.1.2.29) that if (η_1^0, η_2^0) is an absolute minimum of the free energy (3.1.2.29), the states $(-\eta_2^0, \eta_1^0)$, $(-\eta_1^0, \eta_2^0)$, $(-\eta_1^0, -\eta_2^0)$ are symmetry-related

Table 3.1.2.2. *Matrices defining the irreducible representations of Pba*2 *for* $\mathbf{k} = \mathbf{a}_1^* + \mathbf{a}_2^*$

	G										
	$\{E\|0\}$	$\{S_4\|0\}$	$\{C_2\|0\}$	$\{S_4^3\|0\}$	$\{\sigma_1\|\mathbf{t}\}$	$\{\sigma_2\|\mathbf{t}\}$	$\{C_2'\|\mathbf{t}\}$	$\{C_2''\|\mathbf{t}\}$	$\mathbf{a}_1$	$\mathbf{a}_2$	$\mathbf{a}_3$
τ_1	$\begin{matrix}1&0\\0&1\end{matrix}$	$\begin{matrix}0&1\\-1&0\end{matrix}$	$\begin{matrix}-1&0\\0&-1\end{matrix}$	$\begin{matrix}0&-1\\1&0\end{matrix}$	$\begin{matrix}1&0\\0&1\end{matrix}$	$\begin{matrix}-1&0\\0&-1\end{matrix}$	$\begin{matrix}0&1\\-1&0\end{matrix}$	$\begin{matrix}0&-1\\1&0\end{matrix}$	$\begin{matrix}-1&0\\0&-1\end{matrix}$	$\begin{matrix}-1&0\\0&-1\end{matrix}$	$\begin{matrix}1&0\\0&1\end{matrix}$
τ_2	$\begin{matrix}1&0\\0&1\end{matrix}$	$\begin{matrix}0&1\\-1&0\end{matrix}$	$\begin{matrix}-1&0\\0&-1\end{matrix}$	$\begin{matrix}0&-1\\1&0\end{matrix}$	$\begin{matrix}-1&0\\0&-1\end{matrix}$	$\begin{matrix}1&0\\0&1\end{matrix}$	$\begin{matrix}0&-1\\1&0\end{matrix}$	$\begin{matrix}0&1\\-1&0\end{matrix}$	$\begin{matrix}-1&0\\0&-1\end{matrix}$	$\begin{matrix}-1&0\\0&-1\end{matrix}$	$\begin{matrix}1&0\\0&1\end{matrix}$
τ_3	$\begin{matrix}1&0\\0&1\end{matrix}$	$\begin{matrix}1&0\\0&-1\end{matrix}$	$\begin{matrix}1&0\\0&1\end{matrix}$	$\begin{matrix}1&0\\0&-1\end{matrix}$	$\begin{matrix}0&1\\1&0\end{matrix}$	$\begin{matrix}0&1\\1&0\end{matrix}$	$\begin{matrix}0&-1\\1&0\end{matrix}$	$\begin{matrix}0&-1\\1&0\end{matrix}$	$\begin{matrix}-1&0\\0&-1\end{matrix}$	$\begin{matrix}-1&0\\0&-1\end{matrix}$	$\begin{matrix}1&0\\0&1\end{matrix}$