

3.1. STRUCTURAL PHASE TRANSITIONS

the α_γ coefficient that vanishes at T_c . The set $\eta_{\gamma,j}$ ($j = 1, 2, \dots, m$) 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:

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

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 ρ^{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

$$F = F_0(T, \rho_0) + \frac{1}{2}\alpha(T - T_c)(\sum \eta_j^2) + f_3(\eta_j) + f_4(\eta_j) + \dots, \quad (3.1.2.26)$$

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 ρ^{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 $P4_2/m$. The corresponding point group 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:

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