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3.1.2.2.2. *Basic assumptions and strategy*

Our aim is to determine the above displacement as a function of temperature. Landau's strategy is to determine $\mathbf{d}_0$ by a *variational method*. One considers an arbitrary displacement $\mathbf{d}$ of the M^+ ion. For given temperature T and pressure p (or volume V), and specified values of the components of $\mathbf{d}$, there is, in principle, a definite value $F(T, p, d_x, d_y, d_z)$ for the free energy F of the system. This function is a *variational free energy* since it is calculated for an arbitrary displacement. The equilibrium displacement $\mathbf{d}_0(T, p)$ is defined as the displacement that minimizes the variational free energy F. The equilibrium free energy of the system is $F_{\rm eq}(T, p) = F(T, p, \mathbf{d}_0)$. Note that, strictly speaking, in the case of a given pressure, one would have to consider a variational Gibbs function $(F + pV)$ in order to determine the equilibrium of the system. We will respect the current use in the framework of Landau's theory of denoting this function F and call it a *free energy*, though this function might actually be a Gibbs potential.

The former strategy is not very useful as long as one does not know the form of the variational free energy as a function of the components of the displacement. The second step of Landau's theory is to show that, given general assumptions, one is able to determine simply the form of $F(T, p, \mathbf{d})$ in the required range of values of the functions' arguments.

The basic assumption is that of *continuity of the phase transition*. It is in fact a dual assumption. On the one hand, one assumes that the equilibrium displacement $\mathbf{d}_0(T, p)$ has components varying continuously across the transition at T_c. On the other hand, one assumes that F is a continuous and derivable function of $(T, p, \mathbf{d})$, which can be expanded in the form of a *Taylor expansion* as function of these arguments.

Invoking the continuity leads to the observation that, on either side of T_c, $|\mathbf{d}_0|$ is small, and that, accordingly, one can restrict the determination of the functional form of $F(T, p, \mathbf{d})$ to small values of (d_x, d_y, d_z) and of $|T - T_c|$. F will then be equal to the sum of the first relevant terms of a Taylor series in the preceding variables.

3.1.2.2.3. *Symmetry constraints and form of the free energy*

The central property of the variational free energy which allows one to specify its form is a symmetry property. F is a function of (d_x, d_y, d_z) which is *invariant by the symmetry transformations of the high-temperature equilibrium structure*. In other terms, an arbitrary displacement $\mathbf{d}$ and the displacement $\mathbf{d}'$ obtained by applying to $\mathbf{d}$ one of the latter symmetry transformations correspond to the same value of the free energy.

Indeed, both displacements determine an identical set of mutual distances between the positive and negative ions of the system and the free energy only depends on this 'internal' configuration of the ions.

Note that, in the case considered here (Fig. 3.1.2.1), the set of symmetry transformations comprises, aside from the lattice translations, fourfold rotations around the z axis, mirror symmetries into planes and the products of these transformations. The set of rotations and reflections forms a *group G* of order 16, which is the crystallographic point group $4/mmm$ (or D_{4h}).

Also note that this symmetry property of the free energy also holds for each degree of the Taylor expansion of F since the geometrical transformations of G act linearly on the components of $\mathbf{d}$. Hence, terms of different degrees belonging to the expansion of F will not 'mix', and must be separately invariant.

Let us implement these remarks in the case in Fig. 3.1.2.1. It is easy to check that by successive application to the components of $\mathbf{d}$ of the mirror symmetries perpendicular to the three axes, no linear combination of these components is invariant by G: each of the three former symmetry transformations reverses one component of $\mathbf{d}$ and preserves the two others. *Linear terms are therefore absent from the expansion*.

As for second-degree terms, the same symmetry transformations preclude the existence of combinations of bilinear products of the type $d_x d_y$. Actually, one finds that the fourfold symmetry imposes that the most general form of the second-degree contribution to the variational free energy is a linear combination of d_z^2 and of $(d_x^2 + d_y^2)$. Hence the Taylor expansion of F, restricted to its lowest-degree terms, is

$$F = F_o(T, p) + \frac{\alpha_1(T, p)}{2} d_z^2 + \frac{\alpha_2(T, p)}{2}\left(d_x^2 + d_y^2\right). \qquad (3.1.2.1)$$

3.1.2.2.4. *Reduction of the number of relevant degrees of freedom: order parameter*

Let us now derive the *key result of the theory*, namely, that either the component d_z or the pair of components (d_x, d_y) will take nonzero values below T_c (but not both). The meaning of this result will be clarified by symmetry considerations.

The derivation of this result relies on the fact that one, and one only, of the two coefficients α_i in equation (3.1.2.1) must vanish and change sign at T_c, and that the other coefficient must remain positive in the neighbourhood of T_c.

(*a*) Before establishing the latter property in (*b*) hereunder, let us show that its validity implies the stated key result of the theory. Indeed, if one α_i coefficient is strictly positive (*e.g.* $\alpha_1 > 0$), then the minimum of F with respect to the components of $\mathbf{d}$ (*e.g.* d_z) multiplying this coefficient in (3.1.2.1) occurs for zero equilibrium values of these components (*e.g.* $d_z^0 = 0$) in the vicinity of T_c, *above and below this temperature*. Hence, depending on the coefficient α_i which remains positive, either d_z or the pair (d_x, d_y) can be omitted, in the first place, from the free-energy expansion. *The remaining set of components is called the order parameter of the transition*. At this stage, this fundamental quantity is defined as the set of degrees of freedom, the coefficient of which in the second-degree contribution to F vanishes and changes sign at T_c. The number of independent components of the order parameter (one in the case of d_z, two in the case of the pair d_x, d_y) is called the dimension of the order parameter.

Note that the preceding result means that the displacement of the M^+ ion below T_c cannot occur in an arbitrary direction of space. It is either directed along the z axis, or in the (x, y) plane.

(*b*) Let us now establish the property of the α_i postulated above.

At T_c, the equilibrium values of the components of $\mathbf{d}$ are zero. Therefore, at this temperature, the variational free energy (3.1.2.1) is minimum for $d_x, d_y, d_z = 0$. Considering the form (3.1.2.1) of F, this property implies that we have (Fig. 3.1.2.2) $\alpha_i(T_c) \geq 0$ $(i = 1, 2)$.

Note that these inequalities cannot be strict for both coefficients α_i, because their positiveness would hold on either side of T_c in the vicinity of this temperature. Consequently, the minimum of F would correspond to $\mathbf{d} = 0$ on either side of the transition while the situation assumed is only compatible with this result *above* T_c. Using the converse argument that the equilibrium values of the components of $\mathbf{d}$ are not *all* equal to zero below T_c leads easily to the conclusion that one, at least, of the two coefficients α_i must vanish at T_c and become negative below this temperature.

Let us now show that the two coefficients α_i cannot vanish simultaneously at T_c. This result relies on the 'reasonable' assumption that the two coefficients α_i are *different* functions of temperature and pressure (or volume), no constraint in this respect being imposed by the symmetry of the system.

Fig. 3.1.2.3 shows, in the (T, p) plane, the two lines corresponding to the vanishing of the two functions α_i. The simultaneous vanishing of the two coefficients occurs at an isolated point

  references