3.1. STRUCTURAL PHASE TRANSITIONS
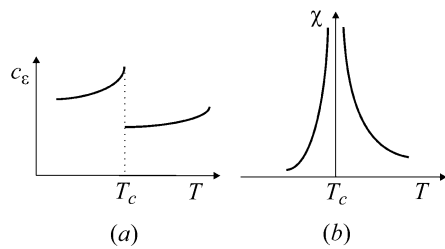

Fig. 3.1.2.5. (*a*) Qualitative temperature dependence of the specific heat at a continuous transition. (*b*) Temperature dependence of the susceptibility at a continuous transition.

Sections 1.1.1.4 and 1.1.5). Let us show that the specific heat at *constant electric field* has a specific type of anomaly.

This specific heat is expressed by

$$c_\varepsilon = T \left.\frac{\partial S}{\partial T}\right|\varepsilon. \qquad (3.1.2.7)$$

Using (3.1.2.6), we find

$$T > T_c: \quad c_\varepsilon^0 = -\frac{\partial^2 F_0(T, p)}{\partial T^2}, \qquad (3.1.2.8)$$

$$T < T_c: \quad c_\varepsilon = -\frac{\partial^2 F_0(T, p)}{\partial T^2} - \frac{\alpha}{2}\frac{\mathrm{d}(d_z^0)^2}{\mathrm{d}T} T = c_\varepsilon^0 + \frac{\alpha^2}{2\beta}. \qquad (3.1.2.8a)$$

Hence above and below T_c the specific heat is a different, smoothly varying function of temperature, determined by the background free energy $F_0(T, p)$ and by the smooth variation of the β coefficient. Fig. 3.1.2.5(*a*) reproduces the anomaly of the specific heat, which, on cooling through T_c, has the form of an upward step.

Finally, let us consider the anomaly of the susceptibility χ, which, in the case considered, is proportional to the dielectric susceptibility of the material. It is defined as

$$\chi = \lim_{\varepsilon \to 0} \left.\frac{\partial d_z}{\partial \varepsilon}\right| d_z^0. \qquad (3.1.2.9)$$

In order to calculate χ, it is necessary to examine the behaviour of the system in the presence of a small field, ε, conjugated to the order parameter. In this case, the appropriate thermodynamical potential whose minimum determines the equilibrium of the system is not F but $G = F - d_z\varepsilon$. Minimizing G with respect to d_z leads to

$$d_z\{\alpha(T - T_c) + \beta d_z^2\} = \varepsilon. \qquad (3.1.2.10)$$

For small values of ε, the solution of this equation must tend towards the equilibrium values $d_z = 0$. Deriving these solutions with respect to ε, we obtain

$$\chi(T > T_c) = \frac{1}{\alpha(T - T_c)}; \quad \chi(T < T_c) = \frac{1}{2\alpha(T - T_c)}. \qquad (3.1.2.11)$$

The susceptibility goes to infinity when $T \to T_c$ from either side of the transition (Fig. 3.1.2.5*b*). The set of anomalies in c_ε and χ described in this paragraph represents the basic effects of temperature on quantities that are affected by a phase transition. They constitute the 'canonical signature' of a phase transition of the *continuous* type.

Certain complications arise in the cases where the transition is not strictly continuous, where the order parameter is coupled to other degrees of freedom, and where the order parameter is not

one-dimensional. We consider one of these complications in Section 3.1.2.3.

3.1.2.2.6. *Symmetry considerations*

3.1.2.2.6.1. *Order-parameter symmetry*

Up to now, we have defined the order parameter as a set of degrees of freedom determining a second-degree contribution to the free energy, the coefficient of which has a specific temperature dependence proportional to $(T - T_c)$. Actually, the order parameter can also be defined on the basis of its specific symmetry characteristics.

Let us consider the manner by which the components (d_x, d_y, d_z) transform when we apply to the crystal each of the 16 symmetry operations of the group $G = 4/mmm$. Table 3.1.2.1 specifies the results of these transformations.

In the first place, we note that d_z is transformed either into itself or into $(-d_z)$. If we consider this coordinate as the basis vector of a one-dimensional vector space, we can conclude that this *vector space* (*i.e.* the space formed by the set of vectors that are linear combinations of the basis) is *invariant* by all the transformations of the group G. Such a space, containing obviously no space of smaller dimension, is, according to the definitions given in Chapter 1.2, *a one-dimensional irreducible invariant space with respect to the group G.*

Each of the components (d_x, d_y) is not transformed into a proportional component by *all* the elements of G. Certain of these elements transform d_x into $\pm d_y$, and conversely. Hence d_x and d_y are not, separately, bases for one-dimensional irreducible invariant spaces. However, their set generates a two-dimensional vector space that has the property to be invariant and irreducible by all the transformations of G.

Note that the set of the three components (d_x, d_y, d_z) carries a three-dimensional vector space which, obviously, has the property to be invariant by all the transformations of G. However, this vector space *contains* the two invariant spaces carried respectively by d_z and by (d_x, d_y). Hence it is not irreducible.

In conclusion, from a symmetry standpoint, the order parameter of a phase transition is a set of degrees of freedom that carries an irreducible vector space (an irreducible representation) with respect to the action of the group G, the latter group being the symmetry group of the high-symmetry phase.

3.1.2.2.6.2. *Degeneracy of the low-symmetry phase*

We had noted above that the structure is invariant by G in the stable state of the system above T_c. When $\mathbf{d} \neq 0$, the structure becomes invariant by a smaller set of transformations. Let us enumerate these transformations for each possible stable state of the system below T_c.

When the order parameter coincides with d_z, we determined, below T_c, two stable states, $d_z^0 = \pm[\alpha(T_c - T)/\beta]^{1/2}$. The crystalline structures determined by these displacements of the M^+ ion parallel to the z axis are both invariant by the same set of eight symmetry transformations. These comprise the cyclic group of order 4 generated by the fourfold rotation around z, and by the reflections in planes containing this axis. This set is the group

Table 3.1.2.1. *Transformation of the components of* $\mathbf{d}$ *under the symmetry operations of group* $G = 4/mmm$

G	E	C_4	C_2	C_4^3	σ_x	σ_y	σ_{xy}	$\sigma_{xy'}$
d_z	d_z	d_z	d_z	d_z	d_z	d_z	d_z	d_z
d_x	d_x	d_y	$-d_x$	$-d_y$	$-d_x$	d_x	$-d_y$	d_y
d_y	d_y	$-d_x$	$-d_y$	d_x	d_y	$-d_y$	$-d_x$	d_x

G	I	S_4^3	σ_z	S_4	U_x	U_y	U_{xy}	$U_{xy'}$
d_z	$-d_z$	$-d_z$	$-d_z$	$-d_z$	$-d_z$	$-d_z$	$-d_z$	$-d_z$
d_x	$-d_x$	$-d_y$	d_x	d_y	d_x	$-d_x$	d_y	$-d_y$
d_y	$-d_y$	d_x	d_y	$-d_x$	$-d_y$	d_y	d_x	$-d_x$

references