

## 3.1. STRUCTURAL PHASE TRANSITIONS

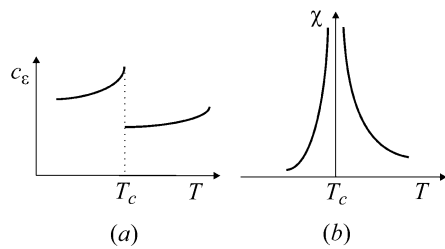


Fig. 3.1.2.5. (a) Qualitative temperature dependence of the specific heat at a continuous transition. (b) Temperature dependence of the susceptibility at a continuous transition.

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

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

Using (3.1.2.6), we find

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

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

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  $\beta$  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  $\chi$ , which, in the case considered, is proportional to the dielectric susceptibility of the material. It is defined as

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

In order to calculate  $\chi$ , it is necessary to examine the behaviour of the system in the presence of a small field,  $\varepsilon$ , 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

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

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

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

The susceptibility goes to infinity when  $T \rightarrow T_c$  from either side of the transition (Fig. 3.1.2.5b). The set of anomalies in  $c_\varepsilon$  and  $\chi$  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  $G = 4/mmm$

| $G$   | $E$    | $C_4$   | $C_2$      | $C_4^3$ | $\sigma_x$ | $\sigma_y$ | $\sigma_{xy}$ | $\sigma_{xy'}$ |
|-------|--------|---------|------------|---------|------------|------------|---------------|----------------|
| $d_z$ | $d_z$  | $d_z$   | $d_z$      | $d_z$   | $d_z$      | $d_z$      | $d_z$         | $d_z$          |
| $d_x$ | $d_x$  | $d_y$   | $-d_x$     | $-d_y$  | $-d_x$     | $d_x$      | $-d_y$        | $d_y$          |
| $d_y$ | $d_y$  | $-d_x$  | $-d_y$     | $d_x$   | $d_y$      | $-d_y$     | $-d_x$        | $d_x$          |
| $G$   | $I$    | $S_4^3$ | $\sigma_z$ | $S_4$   | $U_x$      | $U_y$      | $U_{xy}$      | $U_{xy'}$      |
| $d_z$ | $-d_z$ | $-d_z$  | $-d_z$     | $-d_z$  | $-d_z$     | $-d_z$     | $-d_z$        | $-d_z$         |
| $d_x$ | $-d_x$ | $-d_y$  | $d_x$      | $d_y$   | $d_x$      | $-d_x$     | $-d_y$        | $d_y$          |
| $d_y$ | $-d_y$ | $d_x$   | $d_y$      | $-d_x$  | $-d_y$     | $d_y$      | $d_x$         | $-d_x$         |

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$C_{4v} = 4mm$ , a subgroup  $F$  of  $G$ . The transition is thus accompanied by a lowering of the symmetry of the system.

Also note that the two states  $\pm d_z^2$  are transformed into each other by certain of the symmetry operations such as the mirror symmetry  $\sigma_z$  'lost' below  $T_c$ . These two states correspond to the same value of the free energy [the minimum value determined in equation (3.1.2.3)]: they are equally stable. This can also be checked by applying to the system the mirror symmetry  $\sigma_z$ . This transformation keeps unchanged the value of  $F$  since the free energy is invariant by all the transformations belonging to  $G$  (to which  $\sigma_z$  belongs). The state  $d_z$  is, however, not preserved, and is transformed into  $(-d_z)$ .

We have not determined explicitly the stable states of the system in the case of a two-dimensional order parameter  $(d_x, d_y)$ . A simple discussion along the line developed for the one-dimensional order parameter  $d_z$  would show that the relevant form of the free energy is

$$F = F_0 + \frac{\alpha(T - T_c)}{2} (d_x^2 + d_y^2) + \beta_1 (d_x^4 + d_y^4) + \beta_2 d_x^2 d_y^2 \quad (3.1.2.12)$$

and that the possible stable states below  $T_c$  are:

- (i)  $d_x^0 = \pm[\alpha(T_c - T)/\beta_1]^{1/2}$ ,  $d_y = 0$ ;
- (ii)  $d_y^0 = \pm[\alpha(T_c - T)/\beta_2]^{1/2}$ ,  $d_x = 0$ ;
- (iii) and (iv)  $d_x^0 = \pm d_y = \pm[\alpha(T_c - T)/(\beta_1 + \beta_2)]^{1/2}$ .

Like the case of  $d_z$ , there is a lowering of the crystal symmetry below  $T_c$ . In the four cases, one finds that the respective symmetry groups of the structure are (i)  $F = C_{2v} = mm2_x$ ; (ii)  $F' = C_{2v} = mm2_y$ ; (iii)  $F = C_{2v} = mm2_{xy}$ ; (iv)  $F' = C_{2v} = mm2_{xy}$ .

States (i) and (ii) correspond to each other through one of the 'lost' transformations of  $G$  (the rotations by  $\pi/2$ ). They therefore possess the same free energy and stability. The second set of states (iii) and (iv) also constitute, for the same reason, a pair of states with the same value of the equilibrium free energy.

Note that the symmetry groups associated with equally stable states are conjugate relative to  $G$ , that is they satisfy the relationship  $F' = gFg^{-1}$ , with  $g$  belonging to  $G$ .

#### 3.1.2.3. Free-energy models for discontinuous transitions

Expression (3.1.2.2) for the free energy, discussed in the preceding section, only contains terms of even degrees as a function of the order parameter. We have stressed that this property derives from symmetry considerations. Let us provisionally ignore the symmetry constraints and assume that the phase transition in a given system is described by a free energy containing a term of degree three as a function of the order parameter.

$$F = F_0 + \frac{\alpha(T - T_0)}{2} \eta^2 + \frac{\delta}{3} \eta^3 + \frac{\beta}{4} \eta^4. \quad (3.1.2.13)$$

The stable state of this system at each temperature is determined by the minimum of  $F$ . The extrema of this function are provided by

$$\frac{\partial F}{\partial \eta} = \eta[\alpha(T - T_0) + \delta\eta + \beta\eta^2] = 0, \quad (3.1.2.14)$$

the solutions of which are

$$\eta = 0 \quad \text{and} \quad \eta = \frac{1}{2\beta} \left[ -\delta \pm \sqrt{\delta^2 + 4\alpha\beta(T_0 - T)} \right]. \quad (3.1.2.15)$$

A straightforward analysis based on (3.1.2.13) and (3.1.2.15) shows that, depending on the range of temperatures, the free energy has one of the forms schematically represented in Fig. 3.1.2.6(a). This form changes at three characteristic temperatures.

(i) Above  $T_1 = (T_0 + \delta^2/4\alpha\beta)$ , the free energy has one extremum (a minimum) for  $\eta = 0$ . The stable state of the system corresponds to a zero value of the order parameter.

(ii) For  $T_0 < T < T_1$ , the free energy has two minima, one for  $\eta = 0$  and the other one for  $\eta = (1/2\beta)\{-\delta \pm [\delta^2 + 4\alpha\beta(T_1 - T)]^{1/2}\}$ . These minima define one stable state (the deepest minimum) and one metastable state. Note that the zero value of the order parameter constitutes the stable state in the range  $T_c < T < T_1$  with  $T_c = T_0 + \delta^2/9\beta\alpha$ . Hence, the observed phase transition corresponding to a change from a zero value to a nonzero value of the order parameter occurs at  $T_c$ . Below this temperature, and down to  $T_0$ , the system has a stable state at  $\eta \neq 0$  and a metastable state at  $\eta = 0$ .

(iii) Finally, below  $T_0$ , the free energy has two minima both corresponding to  $\eta \neq 0$ , the value  $\eta = 0$  being a relative maximum.

The remarkable physical consequences of this sequence of shapes are the following.

In the first place, it appears that the equilibrium value of the order parameter changes discontinuously at  $T_c$ . The free energy (3.1.2.13) therefore provides us with a model of discontinuous phase transitions. Referring to equation (3.1.2.6), we can see that a discontinuity of the order parameter is necessarily associated with a nonzero latent heat (or entropy) for the transition. More precisely, the downward jump experienced, on heating, by the equilibrium value of the order parameter corresponds to an endothermal transition. Such a transition is also termed (following Ehrenfest's classification) a *first-order transition*, since the entropy, which is a *first derivative* of the free energy, is discontinuous.

On the other hand, the occurrence of metastable states, in certain temperature ranges, generates *thermal hysteresis*. Indeed, on cooling from above  $T_1$ , the system is likely to remain in the state  $\eta = 0$  down to the temperature  $T_0$ , even though between  $T_1$  and  $T_0$  this state is not the stable state of the system. Conversely, on heating, the system will remain in a state  $\eta \neq 0$  up to  $T_1$ , even though this state does not constitute the stable state of the system between  $T_c$  and  $T_1$ . Hence, the variations of the order parameter will schematically vary as in Fig. 3.1.2.6(b), the temperature dependence below the discontinuity being determined by equation (3.1.2.15). Likewise, the susceptibility will vary as in Fig. 3.1.2.6(c).

The form (3.1.2.13) of the free energy is not the only model form for discontinuous transitions. Another canonical form is

$$F = F_0 + \frac{\alpha(T - T_0)}{2} \eta^2 - \frac{\beta}{4} \eta^4 + \frac{\gamma}{6} \eta^6, \quad (3.1.2.16)$$

where  $\eta$ ,  $\beta$  and  $\gamma$  are positive coefficients. The negative coefficient of the fourth-degree term has the effect of introducing more than one minimum in a certain temperature range. Fig. 3.1.2.7 shows the different shapes of the plot of  $F(\eta)$  over different temperature ranges. The situation is similar to the one already discussed in the presence of a third-degree contribution to the free energy. It corresponds to a discontinuous transition associated with a latent heat as well as to the existence of a range of thermal hysteresis.

Two relevant questions arise from consideration of the above models of first-order transitions.

In the first place, one can object to the use of a polynomial expansion of the free energy in cases involving a discontinuity of the order parameter while the assumption of continuity of the phase transition has been used as an essential substrate of the argument developed. However, the approach will clearly keep its validity if a transition, though discontinuous, involves 'small' discontinuities. The criterion for estimating if a discontinuity is small relies on the comparison between the atomic displacements involved by the transition and the distances between atoms in the structure. If the displacements are a small fraction of the distances between atoms, then the method used can be consid-