CHAPTER I

INTUITIVE APPROACH TO THE BASIC IDEAS OF LANDAU'S THEORY

1. INTRODUCTION

The occurence of a phase transition at a certain temperature and pressure can be easily perceived in certain physical systems. This is, for instance, the case of the evaporation, or the melting of a substance, for which the two phases differ greatly in some of their physical properties (e.g. mechanical, optical,...) and, in consequence, can be straightforwardly distinguished by visual inspection. In many other systems, the existence of a phase transition can only be infered from observation of subtle changes in physical quantities whose measurement require sophisticated equipment (e.g. neutron scattering). Generally speaking, the detection of a phase transition implies that, at least one specific physical quantity differs in the two phases. The identification of this property is an important step in the description and understanding of the considered transition.

In the case of the liquid-vapour transition, a relevant property is the fluid's density (or the specific volume) the value of which changes by several orders of magnitude between the two phases. However, it is to be noted that this quantity does not only change between the two phases, but also in each phase when the temperature or pressure is modified. The transition point is singled out by the fact that a discontinuous (finite) change of the density will occur as opposed to its continuous variations in either phases. In fluids, the presence of a discontinuity appears as a requirement for revealing the transition through the variations of the relevant physical quantity. Such a requirement does not hold necessarily for other types of systems. In the liquid-vapour transition, it derives from the fact that the two phases adjacent to the transition can be considered as "quantitatively distinct" but "qualitatively identical". Indeed ,beyond the critical point (which is the end-point of the line of discontinuous transitions in the pressure-temperature plane) the two phases are essentially undistinguishable. The concept of a "qualitative difference" between phases can be precisely defined as their <u>difference of symmetry</u>.

We can provisionally define the symmetry of a given phase (this point will be further discussed in chapter II) as the set of geometrical transformations which leave unchanged the equilibrium spatial configuration of the particles (atoms) constituting the system, in the considered phase. In both the liquid, and the vapour phase, the distribution of atoms in space is "isotropic" and "homogeneous". The former property ensures that these phases are invariant by all rotations and reflexions about any point of the medium, while the latter implies the invariance by any translation. The two phases have the same symmetry, defined by the set of the enumerated geometrical transformations.

A different situation arises when the two phases have different symmetries and thus differ "qualitatively". In this case, whatever the temperature and the pressure, the two phases can be distinguished by their symmetries, and, accordingly, there can be no "end-point" as in fluids. Besides, the transition point can be defined, independently from the discontinuous jump of a physical parameter, by the point of occurence of a symmetry change.

The Landau theory of phase transitions pertains to the latter category of transitions. It is a phenomenological theory : it assumes the existence of a phase transition in the considered system, as well as the occurence of a symmetry change across the transition point. Its aim is to establish the mutual compatibility of the symmetry characteristics, and of the physical characteristics of the transition : relationship between the symmetries of the two phases, consistency between the nature of the symmetry change and the nature of the physical quantities behaving anomalously across the transition. It achieves this aim by means of introducing two basic concepts, the order-parameter (OP) and the Landau-free-energy.

The working out of the theory will be performed in chapter II, and its application to various types of systems will be described in chapters III-VII. In the present chapter, we rely on an elementary example , taken in the class of "crystalline" phase transitions, in order to provide an inductive introduction to the basic arguments used in the theory.

2. MODEL EXAMPLE OF PHASE TRANSITION IN A CRYSTAL.

2.1. The system and its degrees of freedom

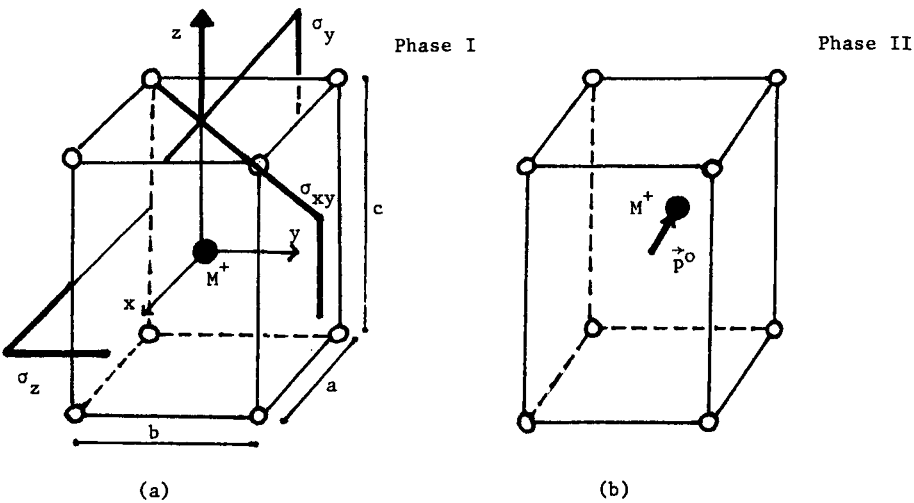


Fig.1

We consider a crystalline substance in which a phase transition is assumed to take place at a given temperature and pressure (T_c,P_c). In one of the phases (denoted phase I, and assumed to be stable for $T > T_c$), the substance consists in the juxtaposition of unit-cells all identical to the one represented on figure 1a). This "tetragonal" cell is a regular prism with a square basis ($a = b \neq c$). Its vertices and its center are respectively occupied by negative ions and by a positive ion M^+. We assume, on the other hand, that the other phase (denoted II, and stable for $T < T_c$) is also constituted by the juxtaposition of identical tetragonal unit-cells, only differing from the ionic configuration of phase I by the fact that the M^+ ion is displaced out of the center of the cell, in an unspecified direction. The displacement is assumed to be the same in all the unit-cells of the crystal. The relevant degree of freedom allowing to distinguish one phase from the other is the set of coordinates of the off-center displacement of the M^+ ion. As this displacement generates, in each cell, an electric dipole $\vec{p}_o = (p^o_x, p^o_y, p^o_z)$, we can also characterize phases I and II, respectively by $\vec{p}_o = 0$ and $\vec{p}_o \neq 0$ [in an equivalent way we can also use the resultant of the dipoles per macroscopic unit volume, i.e. the dielectric polarisation $\vec{P}_o$].

2.2. Symmetry of the two phases

Given the assumed identity of the different unit-cells of the crystal, in the two phases, let us consider that the structure of the crystal is entirely represented by the ionic configuration of one unit-cell. In each phase, this configuration is left unchanged by a set of rotations and reflexions, refered to the center of the cell, whose elements are easily enumerated.

As apparent on figure 1a), phase I is left invariant by fourfold ($\pi/2$) rotations around the z-axis, by reflexions about planes σ_y, σ_z, or σ_{xy} perpendicular to the coordinate axes, or to the diagonals of the square basis of the unit-cell. It is also unchanged by the inversion I about the center of the cell. Clearly the product of any two of the preceding geometrical transformations will also leave the structure unchanged : the set of "symmetry" transformations is a group G_o which contains 16 elements (Its crystallographic label in either of the two currently used conventions is 4/mmm or D_{4h}. Cf. chapter III §2).

The set of transformations leaving invariant phase II is a group G which depends of the direction of the displacement of M^+. If the dipole $\vec{p}_o$ associated to this displacement is along the z-direction, G contains the fourfold rotations around z as well as the various reflexions σ_x, σ_{xy}, in planes containing the z-axis. It does not include other elements of G_o such as the inversion I or the reflexion σ_z since these transformations reverse the sense of $\vec{p}_o$, and accordingly do not preserve the displaced position of M^+. In this case G is a group of 8 elements (whose standard label is 4 mm or C_{4v}) all belonging to G_o : G is a subgroup of G_o.

It is easy to check (figure 1b) , in the cases where $\vec{p}_o$ belongs to the (x,y) plane, that, depending on the direction of $\vec{p}_o$

in this plane, the structure is invariant by sets of transformations G forming subgroups of G_o of various orders. For instance if $\vec{p}_o$ is along the x-axis, G is a group of 4 elements generated by the 2 reflexions in the planes σ_z and σ_y (labelled $mm2_x$ or C_{2v}). Table 1 lists the symmetry groups of phase II for the other possible directions of $\vec{p}_o$, within the (x,y) plane or inclined on this plane.

Table 1

Direction	Symmetry-group	Direction	Symmetry-group
(0,0, p)	4mm	$(p_x,0,p_z)$	(E,σ_y)
(p,0,0)	$mm2_{\pm x}$	$(0,p_y,p_z)$	(E,σ_x)
(0, p,0)	$mm2_{\pm y}$	(p,p,p_z)	(E,σ_{xy})
(p,p,0)	$mm2_{\pm\bar{x}y}$	$(-p,p,p_z)$	(E,σ_{xy})
(-p,p,0)	$mm2_{\pm xy}$	$(p_x,p_y \neq p_x,p_z)$	E
$(p_x,p_y \neq p_x,0)$	(E,σ_z)		

2.3. Variational free-energy associated to the system

A basic idea of Landau's theory is to consider an arbitrary displacement of M^+, specified by the dipole $\vec{p}$, as a variational degree of freedom of the system, and to note that the equilibrium value $\vec{p}_o(T,P)$, at any temperature and pressure, can be determined by minimizing with respect to the components of $\vec{p}$, a variational "free-energy" $F(T,P, p_x, p_y, p_z)$, referred, for instance ,to one unit-cell of the system. (F is not necessarily a free-energy in the strict sense. It is rather the thermodynamic potential whose minimum, in the given external conditions imposed to the system, determines the equilibrium state of the system. We will use, nevertheless the term "free-energy" for it).

The next step is to show that, given certain general assumptions, a form of F, valid in the neighborhood of T_c, can be determined. We assume, first, that the transition is continuous, i.e. that the components of $\vec{p}_o(P,T)$ vary continuously across T_c. On the other hand, we assume that the regularity of the function F is such that a Taylor expansion of F can be performed nearby $(T_c, P_c, \vec{p}_o)$.

Invoking the continuity, we note that in the vicinity of the transition, $|\vec{p}_o|$ is zero, or small. Accordingly, the determination of the functional form of F can be restricted to small $|\vec{p}|$, $|T-T_c|$ and $|P-P_c|$. F is then equal to the sum of the first relevant terms of its Taylor expansion as a function of $\vec{p}$, $(T-T_c)$ and $(P - P_c)$.

2.4. Symmetry property of F and form of its 2nd degree Taylor expansion

The important symmetry argument which allows to specify the form of F is that F is a function of $\vec{p}$, invariant by all the geometrical transformations constituting the group G_o of phase I. Indeed, an arbitrary displacement ($\vec{p}$) and the displacement ($\vec{p}'$) transformed from ($\vec{p}$) by any element of G_o (e.g. a fourfold rotation) correspond to identical relative positions of the negative and positive ions in the system. Only the global orientation of this configuration is changed. As the free-energy F only depends of the "internal" state of the system, and not of its absolute orientation (or, equivalently, of the coordinate framework adopted), F has to be invariant when the transformations $\vec{p} \rightarrow \vec{p}'$ are performed.

This invariance with respect to G_o also holds for the terms of each degree belonging to the Taylor expansion of F.

Indeed, any element of G_o will transform the components (p_x, p_y, p_z) into linear combinations of the same components. The degree of each term of the Taylor expansion will be preserved, and accordingly terms of different degrees will not "mix" in the transformation (A less general argument could also be invoked relying on the fact that, for small $|\vec{p}|$, the terms of different degrees have different orders of magnitude, and have to be separately invariant by G_o).

Up to second degree terms in the p_i, the expansion of F can be written as :

$$F(T,P,\vec{p}) = F_o(T,P) + \Sigma a_i(T,P).p_i + \Sigma b_{ij}(T,P).p_i.p_j \qquad (2.1)$$

As T and P are scalar quantities the coefficients a_i and b_{ij} do not change under the application of a geometrical transformation.

a) Absence of a linear term

Consider the 3 reflexions σ_x, σ_y and σ_z belonging to G_o. Each σ_i reverses the corresponding component p_i and leaves unchanged the two other components. The action of these transformations shows that the linear term in (2.1) cannot be invariant by all the transformations of G_o, as required, unless the coefficients $a_i(T,P)$ are identically zero. The invariance of F with respect to G_o therefore implies that its Taylor expansion does not contain a linear term in the p_i.

b) Form of the second-degree term

The action of the σ_i also precludes the existence in (2.1) of any "cross"-term $p_i.p_j$ ($i \neq j$). On the other hand, the action of a fourfold rotation around $\hat{z}$ exchanges p_x^2 and p_y^2. This implies $b_{11}=b_{22}$. The latter condition completes the restrictions set by the requirement of invariance of the second-degree term in (2.1) with respect to G_o. Indeed, any element of G_o is a product of the elements already considered. Hence a term invariant by these elements will be invariant by their successive, or repeated application : it is sufficient to check the invariance by the "generators" of the group (in the present case G_o can be generated by a fourfold rotation and by the two reflexions σ_x and σ_z). Relabelling the coefficients b_{ii}, we can write the form of (2.1), up to the second degree terms (which are the relevant terms of lowest degree of the expansion):

$$F(T,P,\vec{p}) = F_o(T,P) + \frac{\alpha_2(T,P)}{2}(p_x^2 + p_y^2) + \frac{\alpha_1(T,P)}{2} p_z^2 \qquad (2.2)$$

2.5. Decoupling of the (p_x, p_y) and p_z degrees of freedom. Order-parameter

Let us now describe an important step of the method, and show that either p_z, or (p_x, p_y) can take non-zero values below T_c, but not both sets of components. The meaning of this result will be clarified by the symmetry considerations developed in §.2.8. Its derivation relies on the proof that one only of the two coefficients α_i in eq.(2.2) vanishes at (T_c, P_c) while the other one remains strictly positive in the neighbourhood of the phase transition. In turn, this proof is deduced from the "reasonable" assumption that these two coefficients are different (independent) functions of T and P. Indeed, the symmetry of the considered structure, which is the starting information of the model, does not impose any relation between α_1 and α_2. Consequently, in the phenomenological framework adopted here, α_1 and α_2 must be considered as unrelated.

a) positiveness of the α_i for $T > T_c$

For $T > T_c$, the equilibrium state has been assumed to be $\vec{p}_o(T,P) = 0$. This state corresponds to the minimum of F with respect to p_x, p_y, p_z. For vanishingly small $\vec{p}$, the expression of F is provided by (2.2) which will have $\vec{p}_o = 0$ as its minimum if, and only if, $\alpha_1 \geqslant 0$, $\alpha_2 \geqslant 0$.

b) vanishing of at least one α_i for $T = T_c$

The positiveness of the α_i (in a broad sense) holds for $T = T_c$. However, for the latter temperature this positiveness cannot be strict for all the α_i. Indeed, if $\alpha_i > 0$ $(i = 1,2)$ for $T = T_c$, then, due to the regularity of F and of its coefficients, the same strict inequality would be fulfilled slightly below T_c. In the range $T < T_c$, the minimum of the free-energy (2.2) would again correspond to $\vec{p}_o = 0$, in contradiction with the basic assumption (§.2.1) that for $T < T_c$, $\vec{p}_o(T,P_c) \neq 0$. Hence, one at least of the $\alpha_i(T,P)$ vanishes for (T_c, P_c).

c) vanishing of a single α_i, and exclusion of "singular" transitions

The different temperature and pressure dependence of α_1 and α_2, discussed above, implies that their simultaneous vanishing can only occur at certain isolated points of the (T,P) plane. Consider, for instance, the situation depicted on figure 2. For P above P_1, on lowering the temperature, α_1 vanishes at T'_c and α_2 remains positive in the neighbourhood of T'_c. Hence the equilibrium value of the set (p_x, p_y) remains equal to zero on either sides

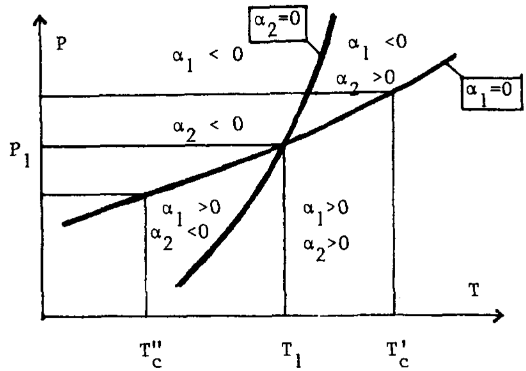


Fig.2

of T'_c. A transition at T'_c only concerns a possible change in p_z^o. Likewise, for P below P_1, a transition at T''_c only concerns a possible change in the set (p_x^o, p_y^o), the third component p_z^o remaining equal to zero on either sides of T''_c. Finally, for $P = P_1$, the transition at T_1 [where $\alpha_1 = \alpha_2 = 0$] can concern a change in the equilibrium value of all 3 components.

Hence, a small change of the pressure above or below P_1 modifies the direction of $\vec{p}_o$ in such a way (table 1) that the symmetry of phase II will change. We can qualify this situation by saying that, at the point (T_1,P_1) a slight change of pressure modifies "qualitatively" the nature of the transition (i.e. its symmetry characteristics). By contrast, away from (T_1,P_1) a slight shift of the pressure does not change the symmetry characteristics of the transition.

The Landau theory considers those "non-singular" transitions which exist with preserved symmetry characteristics in a portion of line in the pressure-temperature plane, i.e. it excludes the transition points of the type (T_1,P_1).

We will assume that the transition at (T_c, P_c) discussed here is not singular from the symmetry point of view. This implies that one only of the two α_i coefficients vanishes at T_c for the pressure P_c imposed to the system.

d) reduction of the number of relevant degrees of freedom. Order parameter

As emphasized above, if $\alpha_1(T_c,P_c) = 0$, and $\alpha_2(T_c,P_c) > 0$, the transition concerns a possible change in p_z^o, while in the converse case the change will only concern (p_x^o,p_y^o). The two sets of components (p_z) and (p_x,p_y) pertain to two disjoint types of transitions. For each type, one set of p-components remains equal to zero across T_c, and can be neglected in the description of the transition (at least in a first approximation : Cf.§ 2.9).

The remaining set, whose equilibrium value is modified by the transition, is the order-parameter of the transition.

2.6. Need for an expansion of degree higher than 2, below T_c

The vanishing at T_c of one α_i necessarily occurs with a change of sign across the transition. A positive sign above and below T_c would imply $\vec{p}_o = 0$ below T_c. Thus α_i becomes negative below T_c. The first term of the Taylor expansion of $\alpha_i(T,P_c)$ as a function of $(T-T_c)$ is :

$$\alpha_i = a(P_c).(T-T_c) \quad \text{with} \quad a(P_c) > 0 \tag{2.3}$$

(A first term of any odd-degree would also satisfy the stated requirement of sign-change of α_i ; however as no characteristic of the system imposes the vanishing of the linear term, assuming the absence of this term would be an unjustified complication of the theory).

The condition $\alpha_i < 0$ below T_c ensures that $\vec{p}_o = 0$ is not a minimum of F below T_c. Reduced to the second degree terms in the order-parameter components (either p_z, or (p_x,p_y), the free-energy becomes infinitely negative for $|\vec{p}| \to \infty$. In order to determine the possible existence of a minimum of F for finite OP values, and locate the position of this minimum, it is necessary to expand F as a function of the OP components up to degrees higher than two.

Let us examine the situations respectively encountered when $p_z(\alpha_1(T_c,P_c) = 0)$, or $(p_x,p_y)(\alpha_2(T_c,P_c) = 0)$ are the OP of the system.

2.7. Simple physical consequences of the 4th degree order-parameter expansion

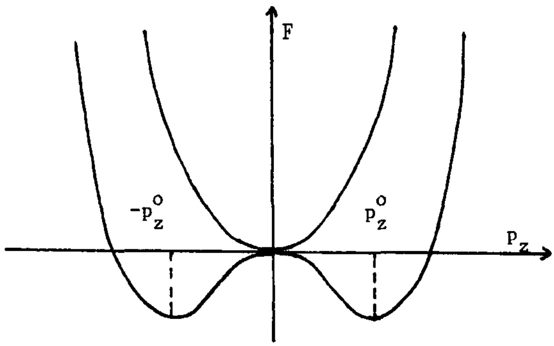
2.7.1. Order-parameter coinciding with p_z

The form of the successive powers of p_z in the Taylor expansion of F are straightforwardly obtained by using the property of invariance of the n^{th} degree term of the expansion by the group G_o. Due to the occurence in G_o of transformations reversing p_z (e.g. σ_z or I), no odd power of p_z is invariant by G_o : F only contains even powers of p_z. Up to the 4^{th} degree, the expression of F is, omitting the explicit dependence of the coefficients on pressure ,

$$F = F_o + \frac{a}{2} (T - T_c).p_z^2 + \frac{\beta(T)}{4} p_z^4 \tag{2.4}$$

Clearly, to ensure the existence of a minimum for finite values of p_z we must have $\beta(T) > 0$ for $T < T_c$. As no condition is imposed to $\beta(T)$ for $T > T_c$, the simplest function satisfying the preceding condition, in the vicinity of T_c, is a positive constant β .

If $\beta < 0$ for $T < T_c$, one should search for higher degree terms



to obtain a minimum for finite values of p_z. However, as will be shown in chapter IV, in this case, one necessarily has a discontinuous transition, which does not enter strictly the framework discussed here.

For $\beta > 0$, the variations of $F(p_z)$ above and below T_c, are sketched on figure 3. Below T_c, the minima of F occur at $\pm p_z^o$, with :

$$p_z^o = \sqrt{\frac{a(T_c - T)}{\beta}} \tag{2.5}$$

The OP has a "square-root" temperature dependence as function of (T_c-T). Note that one finds two minima corresponding to the same value of F (eq.2.4). The corresponding upward and downward displacements of the M^+ ion in fig. 1 are distinct states of the system possessing the same stability : there is a twofold degeneracy of states below the transition. Other physical consequences of the free-energy (2.4) can be drawn. They concern the absence of "latent heat" for the considered transition, and the existence of anomalies in the temperature dependence of the specific heat, and of the "susceptibility associated to the OP".

a) Absence of transition heat

The latent heat is $L = T_c \Delta S$, where ΔS is the difference of entropy between the two phases at T_c. We can derive S in each phase from the equilibrium free-energy F_{eq} [$T, P, p_z(T,P)$] : $S = -(\partial F_{eq}/\partial T)_P$. We also note that

$$\frac{\partial F_{eq}}{\partial T} = \frac{\partial F}{\partial T} + \frac{\partial F}{\partial p_z} \cdot \frac{dp_z}{dT} \tag{2.6}$$

However, as $[\partial F/\partial p_z|_{p_z^o} = 0]$ we can write :

$$S = -\frac{\partial F}{\partial T}(T,P,p_z)|_{p_z^o} = -\frac{a}{2}(p_z^o)^2 - \frac{\partial F_o(T,P)}{\partial T} \tag{2.7}$$

F_o (T,P) represents the "background" free-energy associated to degrees of freedom of the system not coupled to the OP. This function will be continuous at T_c. Moreover p_z^o is continuous at T_c. Thus $\Delta S = 0$, and, accordingly, there is no latent heat associated to the transition.

b) Anomaly of the specific heat at zero-field

As in the case of a fluid, two specific heats can be considered, depending of the quantity maintained constant, either p_z or the thermodynamically conjugated quantity which is proportional to the component ε_z of the electric field (since p_z is proportional to the macroscopic polarization component P_z). The specific heat can be derived from eq.(2.7) through the relation:

$$c_u = T\left(\frac{\partial S}{\partial T}\right)_u \qquad (2.8)$$

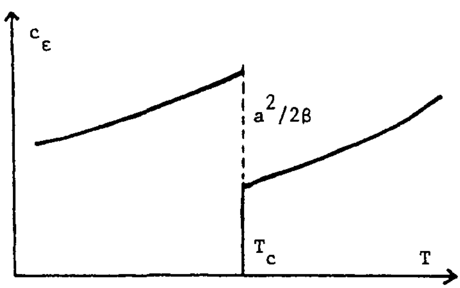
If p_z^o is maintained constant, eq.(2.7) clearly shows that c_p only depends of the derivative of F_o(T,P) which has no anomaly at T_c. The specific heat at constant value of the OP varies smoothly through the transition. By contrast, in zero field, p_z^o is a function of temperature (eq.2.5), and we have,

$$T > T_c \qquad c_\varepsilon^o = -\frac{\partial^2 F_o(T,P)}{\partial T^2}$$

$$T < T_c \qquad c_\varepsilon = -T\frac{\partial^2 F_o}{\partial T^2} - \frac{a}{2}\frac{d[(p_z^o)^2]}{dT} = c_\varepsilon^o + \frac{a^2}{2\beta} \qquad (2.9)$$

Above and below T_c, c_ε is a different, smoothly varying function of T, determined by the background free-energy F_o(T,P), and by the smooth variation of the coefficient β. The anomaly of c_ε is an upward step variation, on cooling through T_c (figure 4).

Fig.4



c) Anomaly of the susceptibility associated to the OP

The susceptibility χ is defined by :

$$\chi = \lim_{\varepsilon_z \to o} \left[\frac{\partial p_z}{\partial \varepsilon_z} \right] \Big|_{p_z^o} \qquad (2.10)$$

where ε_z is the field conjugate to p_z. χ is proportional to the dielectric susceptibility.

In order to calculate χ in (2.10), it is necessary to examine the behaviour of the system in the presence of the field ε_z.The appropriate variational thermodynamic potential to consider,in order to determine the equilibrium is not $F(T,P,\vec{p})$,but the potential $G = F - p_z . \varepsilon_z$. Minimizing with respect to p_z, and using the expression (2.4) of F, we obtain :

$$p_z \left[a(T - T_c) + \beta \, p_z^2 \right] = \varepsilon_z \qquad (2.11)$$

Deriving the two members of (2.11) with respect to ε_z and making ($\varepsilon_z \to 0$), we obtain :

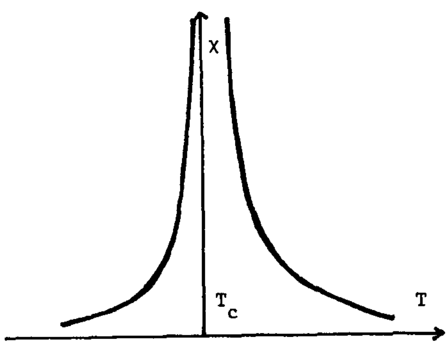
$$\chi[a(T - T_c) + 3\beta \, (p_z^o)^2] = 1 \qquad (2.12)$$

where p_z^o is the equilibrium value of p_z, at zero applied field. Replacing (p_z^o) by its values above ($p_z^o = 0$) and below (eq.2.5) T_c, we finally have :

$$\chi \; (T > T_c) = \frac{1}{a(T-T_c)} \quad ; \quad \chi(T < T_c) = \frac{1}{2a \; (T_c - T)} \qquad (2.13)$$

The susceptibility goes to infinity when $T \to T_c$ from either sides of the transition. Figure 5 shows the form of the corresponding anomaly.

Fig.5



2.7.2. Order-parameter coinciding with (p_x, p_y)

As in the preceding case, one has first to find the form of the expansion of $F(T,P,p_x,p_y)$ up to the terms of lowest degree ensuring the existence of a minimum of F for finite (p_x,p_y) values.

The same type of argument as used in §.2.4.b shows the absence of 3rd degree terms, and provides the form of the 4th-degree ones.

Thus, the occurence of operations of G_o which reverse one coordinate p_i and preserve the two others (i.e. $\sigma_x, \sigma_y, \sigma_z$), forbid the invariance either of the third degree monomials $(p_x^3, p_x^2 p_y, p_x p_y^2, p_y^3)$, or of their linear combinations.

This argument can also be used to predict the absence of fourth degree monomials containing odd powers of one coordinate p_i. Hence, the only possible invariants of 4th degree are linear combinations of the 3 monomials $(p_x^4, p_x^2 p_y^2, p_y^4)$. Clearly, the two combinations $(p_x^4 + p_y^4)$ and $(p_x^2 . p_y^2)$ are invariant by the generators of G_o indicated in §.2.4.b). Other 4th degree polynomials possess the same invariance (e.g. $(p_x^2+p_y^2)^2$) but they are linear combinations of the two former ones. Hence, the most general 4th degree polynomial of (p_x,p_y), invariant by G_o, is a linear combination, with arbitrary coefficients, of the two above polynomials : up to the 4th degree, the expansion of F can be written as :

$$F = F_o(T,P) + \frac{\alpha_2}{2} (p_x^2 - p_y^2) + \frac{\beta_1}{4} (p_x^4 + p_y^4) + \frac{\beta_2}{2} p_x^2 . p_y^2 \qquad (2.14)$$

where, again, we have $\alpha_2 = a(T - T_c)$ [the same notation for the coefficients a and β_1 is used, though the free-energies (2.14) and (2.4) are not related].

Unlike the situation in §.2.7.1, the signs or values of β_1 and β_2, ensuring the existence of a minimum of F for finite (p_x, p_y) values, are not obvious. They will be determined in the course of the minimization procedure of F.

For the two-variable function (2.14) a minimum is determined by the set of conditions :

$$\frac{\partial F}{\partial p_x} = 0 \quad ; \quad \frac{\partial F}{\partial p_y} = 0 \quad ; \quad \left[\frac{\partial^2 F}{\partial p_i \partial p_j}\right] > 0 \qquad (2.15)$$

where the third condition represents the positiveness of the eigenvalues of the matrix built from the second derivatives of F.

a) Possible extrema of F.

Using eq.(2.14), the vanishing of the first derivatives is expressed by :

$$\begin{aligned} p_x(\alpha_2 + \beta_1 . p_x^2 + \beta_2 . p_y^2) &= 0 \\ p_y(\alpha_2 + \beta_1 . p_y^2 + \beta_2 . p_x^2) &= 0 \end{aligned} \qquad (2.16)$$

Eqs; (2.16) have three sets of solutions:

i) $p_x = p_y = 0$

ii) $p_x = 0$ $p_y = \pm\sqrt{-\alpha/\beta_1}$; or $p_y = 0$, $p_x = \pm\sqrt{-\alpha/\beta_1}$. These 4 solutions correspond to the same value of the free-energy (2.14).

iii) $p_x \neq 0$ $p_y \neq 0$, p_x and p_y being determined by the vanishing of the two bracketted expressions in (2.16). Let us substract one of these expressions from the other. We obtain :

$$(\beta_1 - \beta_2)(p_x^2 - p_y^2) = 0 \qquad (2.17)$$

We can use an argument similar to the one in §.2.5.c) to show that the only acceptable solution of (2.17) is $p_x = \pm p_y$. Indeed, we can note that $(\beta_1 - \beta_2)$ is a function of temperature and pressure. For the considered pressure P_c, it cannot vanish in the entire temperature interval examined, above and below T_c. As a consequence (2.17) would yield $p_x = \pm p_y$ except at the discrete temperatures where $(\beta_1 - \beta_2)$ vanish (for which any direction of the $\vec{p}$ vector in the (p_x, p_y) plane is acceptable). Hence the symmetry of phase II would abruptly change in the vicinity of the vanishing points of $(\beta_1 - \beta_2)$. As in §.5.2.c) we exclude this "singular" type of behaviour and assume that $(\beta_1 - \beta_2) \neq 0$.

Reporting into (2.16) the condition $(p_x = \pm p_y)$ we obtain a third type of 4 solutions, all corresponding to the same value of F :

$$p_x = \pm p_y \qquad p_x = \pm\sqrt{-\alpha/(\beta_1 + \beta_2)}$$

We note that in phase II, the OP components vary as $(T_c - T)^{0.5}$, as in §.2.7.1.

b) conditions of stability of the solutions

The second derivatives of F are :

$$\frac{\partial^2 F}{\partial p_x^2} = \alpha_2 + 3\,\beta_1.p_x^2 + \beta_2.p_y^2$$

$$\frac{\partial^2 F}{\partial p_y^2} = \alpha_2 + 3\,\beta_1.p_y^2 + \beta_2.p_x^2 \qquad (2.18)$$

$$\frac{\partial^2 F}{\partial p_x \partial p_y} = 2\beta_2.p_x p_y$$

One can check straightforwardly that the positiveness of the values of the symmetric matrix of second derivatives determines the following conditions of stability for the various extrema listed above :

Solution i) corresponds to the absolute minimum of F for $\alpha_2 > 0$, i.e. $T > T_c$.

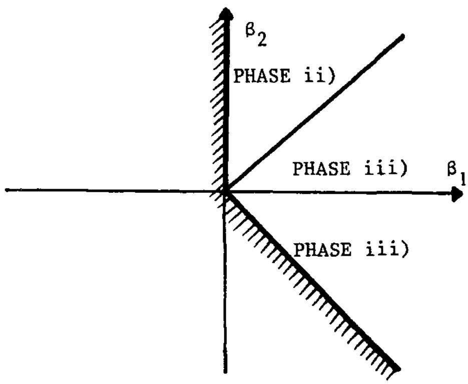
Solutions ii) are stable for $\alpha_2 < 0$ and $\beta_2 > \beta_1 > 0$.

Solutions iii) are stable for $\alpha_2 < 0$ and $\beta_1 > |\beta_2|$.

When for $T < T_c$ β_1 and β_2 do not comply with any of the former conditions (e.g. $\beta_1 < 0$), the absolute minimum of F occurs for infinite values of (p_x, p_y). Similarly to the case involved in §.2.7.1, the addition to F of even degree terms of degree higher than 4 can determine a minimum for finite (p_x, p_y). However, the transition between phases I and II will then be a discontinuous one (cf.Chap.IV)

The above results can be summarized, for $T < T_c$, by a "phase diagram" in the (β_1, β_2) plane (fig.6).

Fig.6



As in §.2.7.1, phase II displays a "degeneracy". Hence, for $\alpha_2 < 0$ and $\beta_2 > \beta_1 > 0$, the transition occuring at T_c will be towards one of four possible phases, corresponding to the 4 solutions ii) with the same free-energy : F has 4 minima possessing the same depth. The same situation occurs for solutions iii).

c) Physical anomalies at T_c

We will not repeat the derivation, performed in §.2.7.1, of the absence of latent heat at T_c, or of the shape of the specific heat anomaly induced by the transition.

By contrast, let us examine the behaviour of the susceptibility which is slightly more complex than §.2.7.1, since there are 3 components of the susceptibility tensor : $\chi_{xx} = (\partial p_x/\partial \varepsilon_x)$, $\chi_{yy} = (\partial p_y/\partial \varepsilon_y)$, and $\chi_{xy} = \chi_{yx} = (\partial p_x/\partial \varepsilon_y)$. Here again we form the potential $G = F - p_x\varepsilon_x - p_y\varepsilon_y$. Minimizing F with respect to p_x and p_y and applying the same method as in §.2.7.1.c), we obtain, in the case $\beta_2 > \beta_1 > 0$ (i.e. for a phase of type ii)) :

$$\chi_{xx} = \chi_{yy} = \frac{1}{a(T - T_c)} \; ; \quad \chi_{xy} = 0 \qquad \text{for } T > T_c \tag{2.19}$$

$$\chi_{xx} = \frac{1}{2a(T_c - T)} \; ; \; \chi_{yy} = \frac{\beta_1}{\beta_2 - \beta_1} \cdot \frac{1}{a(T_c - T)} \; ; \; \chi_{xy} = 0 \qquad \text{for } T < T_c$$

Both diagonal components diverge at T_c but their temperature dependence is different below T_c. This is due to the fact that the onset of a non-zero p_x^o value, below T_c, destroys the equivalence of the x and y directions : the "longitudinal" susceptibility χ_{xx} becomes different from the "transverse" one χ_{yy}.

2.8. Symmetry considerations

We have already stressed in §.2.2. that, for $\vec{p} \neq 0$, the group of invariance of the system is a subgroup of G_o, which is the invariance group of phase I. We can refer to table 1 to find the symmetry-groups corresponding to each of the possible phases II found in §.2.7.1. or 2.7.2.

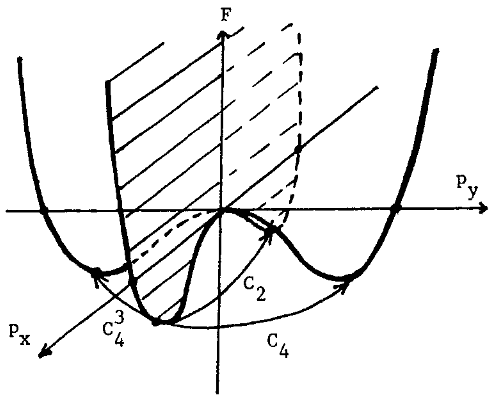
2.8.1. Relationship between equally-stable phases

The fact that each minimum of F is associated to a phase of lower symmetry than G_o (i.e. invariant by a subgroup G of G_o) is directly related to the existence of several minima with the same value of the free-energy.

Consider, for instance, in §.2.7.2. the minimum of (2.14) consisting in a solution $\vec{p}_o$ of type ii) ($p_x \neq 0, p_y = 0$). According to table 1, the symmetry-group of the corresponding phase is the group $G_1 = (mm2_x)$. Consider, on the other hand, the fourfold rotation C_4. This geometrical transformation belongs to G_o and therefore leaves F (eq.2.14) invariant. As it does not belong to G_1, $\vec{p}_o$ is not preserved by it. It is transformed into a perpendicular vector $\vec{p}_o'$, of same modulus, and necessarily corresponding to a minimum of F with the same depth, <u>due to the invariance of F.</u> As sketched on figure 7, the various operations of G_o not belonging to G_1 will transform $\vec{p}_o$ into one of the 4 equivalent minima found directly in §.2.7.2. by minimizing F.

This argument shows that the "symmetry breaking" associated to a given minimum of F is necessarily compensated by the occurence of several "equivalent" minima corresponding to each other through operations of G_o not belonging to the "low-symmetry group".

Fig.7



a) Conjugated character of the various "low-symmetry" groups

We note on table 1 that the symmetry groups relative to the 4 equivalent (symmetry related) minima of F ($\pm p_x^o$, 0) and (0, $\pm p_y^o$) are $mm2_x$ for the two first minima and $mm2_y$ for the two last ones. Thus the symmetry groups of symmetry related phases are not identical, in general. However, they are related to each other through a geometrical correspondance consisting in a conjugation with respect to the symmetry group G . G_1 and G_2 are said to be conjugated with respect to G_o if any element g_2^i of G_2 can be written as:

$$g_2^i = g.g_1^i.g^{-1} \tag{2.20}$$

where g is a given element of G_o (necessarily external to G_1 and G_2) and g_1^i an element of G_1. Eq. (2.20) shows that the role of G_1 and G_2 can be interchanged in this definition. It is easy to check that in the example considered the groups $mm2_x$= and $mm2_y$ are conjugated with respect to G_o. Indeed we have :

$$(mm2_y) = C_4.(mm2_x).(C_4)^{-1} \tag{2.21}$$

where the fourfold rotation C_4 belongs to G_o.

b) "Irreducibility" of the order-parameter

Table 2 hereunder indicates the manner $\vec{p} = (p_x, p_y, p_z)$ transforms under the action of the generators of G_o.

Table 2.

G_o	C_4	σ_x	I
p_x	p_y	$-p_x$	$-p_x$
p_y	$-p_x$	p_y	$-p_y$
p_z	p_z	p_z	$-p_z$

We note that p_z is transformed into itself or into its opposite. If we consider the direction p_z as a <u>vector space</u>, we can see that this vector space is globally invariant by the transformations belonging to G_o.

By contrast the direction p_x does not constitute an invariant vector space since p_x is transformed into ($\pm$ p_y) by certain elements of G_o. However the vector space constituted by the set of directions (p_x, p_y) is globally invariant by G_o.

Obviously the entire set (p_x, p_y, p_z) also carries a 3-dimensional vector space invariant by G_o. This invariant space differs on one point, crucial to our argumentation, from the two preceding ones. It contains smaller spaces possessing themselves the property of invariance by G_o i.e. the spaces carried by p_z and (p_x,p_y) . Clearly p_z being one-dimensional does not contain any smaller space invariant by G_o. It is easy to check that this is also the case of (p_x, p_y). Indeed, in this plane, the C_4 rotation does not leave any direction fixed (we restrict here to "real" directions, a more rigorous approach will be described in chapter II). Hence, (p_x, p_y) does not contain any one-dimensional space invariant by all the transformations of G_o (including C_4).

We characterize this situation by saying that (p_x, p_y, p_z) is a <u>reducible</u> invariant space with respect to G_o, while (p_z) and (p_x, p_y) are <u>irreducible</u> invariant spaces with respect to this group.

It is well known that if a vector space is invariant by a linear transformation g_o, this transformation can be <u>represented</u> by a <u>matrix</u> $M(g_o)$, expressing the action of g_o on the basic vectors of the space. Table 3 indicates the matrices representing the generators of G_o in each of the three vector spaces considered above.

<u>Table 3.</u>

G_o	C_4	σ_x	I
(p_x,p_y,p_z)	$\begin{vmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{vmatrix}$	$\begin{vmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{vmatrix}$	$\begin{vmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{vmatrix}$
(p_x,p_y)	$\begin{vmatrix} 0 & -1 \\ 1 & 0 \end{vmatrix}$	$\begin{vmatrix} -1 & 0 \\ 0 & 1 \end{vmatrix}$	$\begin{vmatrix} -1 & 0 \\ 0 & -1 \end{vmatrix}$
p_z	1	1	-1

The set of all the matrices of the group G_o (there are 16 such matrices) relative to one of the vector spaces constitute a representation of G_o in this vector space.

By definition, the set of 3-dimensional matrices relative to the space (p_x, p_y, p_z) constitutes a reducible representation of G_o, because the carrier space is itself a reducible invariant space. The two other sets constitute irreducible representations of G_o, since the corresponding spaces are irreducible invariant spaces by G_o.

On the basis of the preceding remarks, we are now able to formulate differently the result, obtained in §.2.5., showing that the OP of the considered transition can either coincide with p_z, or with (p_x,p_y) but not with the set (p_x, p_y, p_z) : the degrees of freedom constituting possible order-parameters are characterized, from the standpoint of symmetry, by the fact that the OP components span an irreducible representation of the group G_o of phase I (the more symmetric phase). We will see in chapter II that this property is the central symmetry property used in the Landau theory of phase transitions.

c) Groups G and invariant directions in the OP space

Consider the case (§.2.7.2) of the OP coinciding with the set (p_x, p_y), and one possible set of values of the OP component corresponding to phase II, e.g. ($p^\circ_x = \sqrt{-\alpha/\beta_1}$, $p^\circ_y = 0$). The symmetry group G of this phase has been determined (Table 1) by enumerating the elements of G_o preserving the structure of the unit cell (including the displacement p°_x of the central ion). Actually as the ions at the vertices of the cell are invariant by G_o, G is the subgroup of G_o which preserves the vector (p°_x,o). The action of G_o on (p°_x, p°_y) is entirely determined by the set of matrices representing G_o in the irreducible space (p_x, p_y). Therefore the determination of G can be performed by enumerating the matrices which leave invariant the first basis vector of the OP space. In practice, G will correspond to the set of matrices which have (+ 1) as their first diagonal element. Table 4 hereunder indicates the complete list of 16 matrices associated to the 16 elements of G_o. One checks directly that G_1 is, as already indicated by table 1, the group ($mm2_x$). The same method can be used for the other stables phases compatible with the OP(p_x, p_y) (e.g. $p^\circ_x = 0$, $p^\circ_y \neq 0$ or $p^\circ_x = \pm p^\circ_y$) : the symmetry-group of each phase can be obtained by selecting the set of matrices of the OP- representation leaving invariant the corresponding vector belonging to the OP space. Clearly, this group does not depend on the magnitude of the vector (i.e. $p_x = \sqrt{-\alpha/\beta_1}$) but only of its direction in the OP space.

We summarize this result by saying that the possible symmetries of phase II (stable below T_c) are constituted by the various invariance groups of certain directions in the OP space, these directions being associated to the minima of the free-energy.

Table 4.

G_o	E	C_4	C_2	C_4^3	σ_x	σ_y	σ_{xy}	$\sigma_{\bar{x}y}$
p_x p_y	$\begin{vmatrix} 1 & 0 \\ 0 & 1 \end{vmatrix}$	$\begin{vmatrix} 0 & -1 \\ 1 & 0 \end{vmatrix}$	$\begin{vmatrix} -1 & 0 \\ 0 & -1 \end{vmatrix}$	$\begin{vmatrix} 0 & 1 \\ -1 & 0 \end{vmatrix}$	$\begin{vmatrix} -1 & 0 \\ 0 & 1 \end{vmatrix}$	$\begin{vmatrix} 1 & 0 \\ 0 & -1 \end{vmatrix}$	$\begin{vmatrix} 0 & -1 \\ -1 & 0 \end{vmatrix}$	$\begin{vmatrix} 0 & 1 \\ 1 & 0 \end{vmatrix}$
G_o	I	S_4^3	σ_z	S_4	U_x	U_y	U_{xy}	$U_{\bar{x}y}$
p_x p_y	$\begin{vmatrix} -1 & 0 \\ 0 & -1 \end{vmatrix}$	$\begin{vmatrix} 0 & 1 \\ -1 & 0 \end{vmatrix}$	$\begin{vmatrix} 1 & 0 \\ 0 & 1 \end{vmatrix}$	$\begin{vmatrix} 0 & -1 \\ 1 & 0 \end{vmatrix}$	$\begin{vmatrix} 1 & 0 \\ 0 & -1 \end{vmatrix}$	$\begin{vmatrix} -1 & 0 \\ 0 & 1 \end{vmatrix}$	$\begin{vmatrix} 0 & 1 \\ 1 & 0 \end{vmatrix}$	$\begin{vmatrix} 0 & -1 \\ -1 & 0 \end{vmatrix}$

2.9. Secondary order-parameters

The only relevant degree of freedom considered up to now, in the above model, is the set of 3 components of $\vec{p}$. Let us allow the possibility that the c-parameter, equal to the distance along z between the planes of negative ions, can change with temperature and pressure. This change corresponds to a deformation of the unit-cell along z which can be represented by a component e' of a strain tensor.

In the same manner as for the components of $\vec{p}$, the equilibrium value of e' can be determined by minimizing a variational free-energy which will be a function of e', in addition to the variables already considered (cf. §.2.3) : $F = F(T,P,p_x,p_y,p_z,e')$. The form of F can be determined along the same symmetry principles used in §.2.4. and §.2.7 in order to find the 4th degree Taylor expansion of F as a function of (p_x, p_y, p_z). In this view, we note that e' (which is a component of a second rank symmetric tensor, left invariant by the inversion I) is invariant under the application of all the transformations of G_o. The part of the expansion of F depending exclusively on e' is therefore of the form :

$$\lambda e' + \frac{C'e'^2}{2} + \frac{De'^3}{3} + \ldots\ldots \qquad (2.22)$$

Terms of any degree depending on e', are allowed, by symmetry, to be present in F.

On the other hand, any power of e' multiplied by any invariant polynomial of (p_x, p_y, p_z) will be invariant by G_o, and will appear in the expression of F. The term of lowest degree of this type is :

$$e'[\delta_1\ (p_x^2 + p_y^2) + \delta_2\ p_z^2\ ] \qquad (2.23)$$

Let us examine the effect of the presence of the e'-dependent terms. The minimum of F with respect to e' yields :

$$\lambda + C'e' + De'^2 + \delta_1(p_x^2 + p_y^2) + \delta_2 p_z^2 = 0 \qquad (2.24)$$

a) Elimination of the thermal expansion

As $\lambda(T,P)$ is a parameter which, in general, will not be *vanishingly small, e' cannot either be vanishingly small.* The reason underlying this result is that λ is attached to the thermal expansion of the material along z, i.e. to a particular form of the strain e', which exists at any temperature and is not induced by the presence of a phase transition at T_c. We can eliminate the resulting "normal" component of e' by setting $e' = (e_o + e)$ where e_o is the non-zero value of e' at the transition temperature. e_o is defined by :

$$\lambda + C'e_o + De_o^2 + \ldots = 0 \qquad (2.25)$$

b) Secondary OP

Both λ and e_o will vary smoothly across the considered transition [actually (2.25) could be integrated into the background free-energy F_o (T,P)]. Eq. (2.24) can then be written as :

$$e = -\frac{1}{C}\,[\delta_1\ (p_x^2 + p_y^2) + \delta_2\ p_z^2\ ] \qquad (2.26)$$

where the C coefficient differs from C' by corrections depending on e_o through the presence in (2.24) of terms such as De'^2. The C coefficient being the effective coefficient of the quadratic contribution in e to the free-energy, we know that, if α_1 or α_2 vanish at T_c, C necessarily remains strictly positive in the neighborhood of T_c (cf. §2.5). We can then deduce from (2.26) that e vanishes above T_c and becomes non-zero below T_c.

Hence, the OP (which is either p_z or (p_x, p_y) is not the only quantity possessing the property of being non-zero for $T < T_c$ and zero for $T > T_c$. Quantities such as e also possess this property. e will be called a <u>secondary OP</u>, while the OP defined formerly can be termed a <u>primary OP</u>. The latter OP can be distinguished from the former by the fact that the α_i coefficient, associated to it vanishes at T_c while the coefficient C remains strictly positive nearby T_c. The onset of a non-zero value for e is related to the occurence of a <u>coupling term</u> in the free-energy . If the coefficient δ of this term is zero, eq.(2.26) shows that e will remain equal to zero).

c) Influence of e on the symmetry properties of the system

Let us assume that $\alpha_2\ (T_c, P_c) = 0$, i.e. that the primary OP of the transition is the set (p_x, p_y). Taking into account (2.26)(2.25) and (2.14) we can eliminate e from the free-energy and obtain an expression of F which only depends, as (2.14),of the components p_x and p_y. This expression is (omitting the background free-energy):

$$F = \frac{(\alpha_2 - 2e_o \cdot \delta_1)}{2}(p_x^2 + p_y^2) + \frac{[\beta_1 - \frac{2\delta_1^2}{C}]}{4}(p_x^4 + p_y^4) + \frac{[\beta_2 - \frac{2\delta_1^2}{C}]}{2} p_x^2 p_y^2 \quad (2.27)$$

We can see that F has the same functional form as (2.14) but different coefficients. The effect of the coupling between the primary and secondary OP is to modify the coefficients of the free-energy associated to the sole primary OP, by amounts increasing with the "strength" δ_1 of the coupling.

Eq.(2.27) establishes that none of the conclusions reached in §.2.7.2 is changed : the list of possible phases and the form of the anomalies associated to the transition, which only depend on the functional form of F, are the same as in the absence of coupling. Only the boundaries of these phases are displaced. For instance the temperature of the phase transition corresponds to the vanishing of $(\alpha_2 - 2.e_o.\delta_1)$. It will be shifted with respect to the temperature T_c appearing in α_2. However the latter point is not necessarily significant : one can consider that expression (2.14) is the free-energy obtained when the couplings to degrees of freedom such as e have been taken into account and already eliminated through procedures similar to the one leading to (2.27).

We also note that the symmetry of the various phases will be the ones worked out in table 1. Indeed, the onset of a non-zero deformation e preserves the symmetry G_o of the structure and thus the breaking of symmetry is imposed by the onset of (p_x, p_y).

In summary, the symmetry characteristics of the considered transition (possible phases and their symmetries) is exclusively determined by the primary OP.

Accordingly, the reduction of the number of relevant degrees of freedom performed in 2.5.d) though not strictly correct (since other quantities than the primary OP are affected by the transition) is entirely justified in the first place: the results obtained by limiting the description of the system to the primary OP are correct. In a further step of investigation of the transition, consideration of other degrees of freedom allows to study "secondary" anomalies. Still, the primary OP plays a central role in this second step, since the occurence of a coupling between the additional degrees of freedom and the primary OP is a necessary condition for the singular behaviour of the additional quantities.

d) Anomalies related to the secondary OP

Eq.(2.26) can be used to deduce the temperature dependence of e. As already stressed e = 0 above T_c (we use the same notation for the temperature of the transition renormalized by the coupling to e_o). Below T_c, for any of the minima of F considered in §.2.7.2, $(p_x^2 + p_y^2)$ is proportional to $(T_c - T)$. Inserting this temperature dependence in (2.26) yields :

$$e \propto (T_c - T) \qquad (2.28)$$

Let us now derive the behaviour of the "susceptibility" associated to e.

The quantity which is thermodynamically conjugated to e is a component σ of the stress tensor, since e is a component of the strain tensor. The susceptibility $[s = \lim (\partial e/\partial \sigma)$ when $e \to 0]$ has the meaning of an "elastic compliance".

In the presence of a non-zero stress we minimize the thermodynamic potential $[F - \sigma . e]$ and obtain first as a substitute to eq. (2.26)

$$e = \frac{\sigma}{C} - \frac{1}{C}\ \delta_1 \cdot (p_x^2 + p_y^2) \qquad (2.29)$$

Likewise, instead of (2.27), we obtain the following expression for $(F - \sigma . e)$

$$\frac{(\alpha_2 - 2\delta_1 \cdot e_o + \sigma\delta_1/C)}{2} \cdot \rho^2 + \frac{(\beta_1 - 2\ \delta_1^2/C)}{4} \cdot \rho^4 + \frac{(\beta_2 - \beta_1)}{2}\ \rho^4 \sin^2\theta\cos^2\theta \qquad (2.30)$$

where we have set $p_x = \rho \cdot \cos\theta$ and $p_y = \rho . \sin\theta$

If we assume that the "mechanical susceptibility" s corresponds to conditions of zero applied field (i.e. no field conjugate to (p_x, p_y) is applied), we can write the minimum of (2.30) with respect to ρ and θ :

$$\rho\{[\alpha_2 - 2\delta_1 e_o + \sigma\delta_1/C] + [\beta_1 - 2\delta_1^2/C]\ \rho^2 + 2[\beta_2 - \beta_1]\rho^2\ \sin^2\theta\cos^2\theta\} = 0$$

and (2.31)

$$\sin 4\theta = 0$$

From (2.29) we draw the expression of the susceptibility s :

$$s = \left(\frac{\partial e}{\partial \sigma}\right) = \frac{1}{C} - \frac{\delta_1}{C} \cdot \left(\frac{\partial \rho^2}{\partial \sigma}\right) \qquad (2.32)$$

In (2.31), the solution $\rho = 0$ corresponds to $T > T_c$ while the vanishing of the expression between brackets corresponds to $T < T_c$. In the latter case, we derive the bracket with respect to σ [θ is independent from σ] and obtain :

$$\frac{\partial \rho^2}{\partial \sigma} = \frac{-\ \delta_1/C}{\beta_1 - 2\ \delta_1^2/C + b} \qquad (2.33)$$

where $b = 0$ if $\theta = 0\ (\pi/2)$, i.e. if solution ii) in §.2.7.2 is considered, or $b = (\beta_2 - \beta_1)/2$ if $\theta = \pi/4\ (\pi/2)$, i.e. if solution iii) is retained below T_c.

Replacing (2.33) into (2.32) we finally obtain :

$$s = \frac{1}{C} \qquad \text{for} \qquad T > T_c$$

$$s = \frac{1}{C} + \frac{\delta_1^2/C^2}{\beta_1 - 2\delta_1^2/C} \quad \text{for } T < T_c \text{ and solution ii)}$$

$$s = \frac{1}{C} + \frac{\delta_1^2/C^2}{(\beta_1+\beta_2)/2 - 2\,\delta_1^2/C} \quad \text{for } T < T_c \text{ and solution iii)} \qquad (2.34)$$

Results which are summarized by fig. 8 . We see that the susceptibility experiences an upward jump at T_c similar to the jump of the specific heat sketched on fig. 4.

We can also note on eq.(2.31) that α_2 is modified by the stress σ : the transition temperature is shifted linearly by the application of the stress. This shift, as well as the magnitude of the anomalies (2.34) is controlled by the "strength" δ_1 of the coupling between e and the primary OP

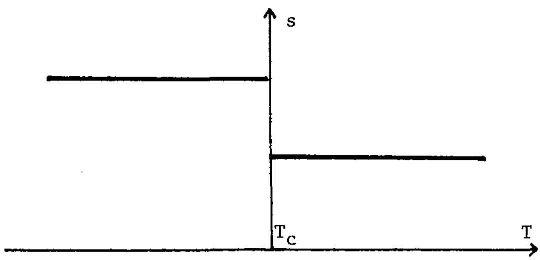


Fig.8

3. CONCLUSIONS

The analysis of the chosen type of "model" crystalline transition has illustrated the prominent features of the phenomenological theory of phase transitions.

1/ The description of the symmetry and physical characteristics of the transition is related to the identification of a specific set of degrees of freedom constituting the (primary) order-parameter of the transition. This set has well defined symmetry properties: its components span an irreducible representation of the group of transformations G_o leaving invariant the atomic structure of the "more symmetric" phase.

2/ The derivation of the physical anomalies accompanying the phase transition, and the enumeration of the possible stable phases of the system above and below T_c, rely on the form of the Landau free-energy , which is a variational thermodynamic potential. It is a polynomial expansion as a function of the components of the (primary) OP, and of the other degrees of freedom of the system which are coupled to the OP.

3/ The form of this polynomial expansion is entirely determined, on the one hand, by the fact that terms of a given degree are invariant by all the transformations belonging to G_o, and on the other hand, by the symmetry properties of the primary, and secondary order-parameters.

4/ The primary OP is particularized, with respect to other degrees of freedom, by the fact that the coefficient α of its quadratic contribution to the free-energy vanishes and changes sign at T_c.

As shown in chapter II, these features can be shown to possess a general validity. Their derivation constitutes the Landau theory of phase transitions.