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SIMULTANEOUS CONDENSATION OF SEVERAL MODES AT STRUCTURAL PHASE TRANSITIONS

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Abstract.

The structural transitions in a number of materials has been explained by the simultaneous condensation of several modes at the transition temperature. The various types of couplings between the order-parameters corresponding to this mechanism are discussed.

Most of the observed structural phase transitions have been related to the condensation of a single normal mode of the crystal. This confirms the basic assertion of the Landau theory\(^1\) which states that when the space-groups of two phases are group-subgroup related, the transition from one to another phase can be described by a single order-parameter (OP). In other words, the number of phenomenological variables that have to be introduced in the description of the transition is minimal and cannot be reduced. However, a small fraction of the materials undergoing structural transitions does not comply with the preceding scheme. This is, for example, the case of families of compounds such as the Boracites\(^2\), the Langbeinites\(^3\) and part of the Perovskites\(^4\); of isolated compounds such as Benzil\(^5\) or Bismuth titanate\(^6\); and also of incommensurate systems, such as Sodium nitrite and Thiourea\(^7\).

In these materials, the structural changes cannot be interpreted with a single OP and several modes related to distinct OP seem to be simultaneously involved. As each OP expresses a set of atomic displacements (a degree of freedom) associated to a certain normal mode of the system, the fact that several OP are involved signifies that the displacements related to one OP brings about an instability in parameters inducing other displacements. Due to the non-linear interaction between the various parameters, the modifications accompanying the transition (symmetry change, dielectric or elastic anomalies...) will require for their description an increasing number of thermodynamic variables. Thus, it can be asked to what extent a Landau-type theory involving several OP may still have a predictive value. In this paper we briefly discuss the case of transitions induced by two OP whose characteristics have been precised by a number of recent studies\(^7-13\).

As we have in mind a qualitative description, we can restrict to consider only single component OP's, namely p and q. The free-energy (FE) of the transition will contain, in addition to invariants of each OP, mixed invariants expressing the coupling between p and q. As it is the lowest degree coupling term which determines the essential features of the transition, we can therefore distinguish two main cases:
1) The FE is of the type:

\[ F = A_1 p^2 + A_2 p^4 + A_3 p^6 + B_1 q^2 + B_2 q^4 + B_3 q^6 + C p q^2 \]  \hspace{1cm} (1)

Such a case is encountered when lower couplings of the type \( p q \) or \( p^2 \) are forbidden by symmetry. It is realized, for instance, for two non-unit one dimensional real irreducible representations (IR) of the space-group \( G_0 \) describing the more symmetric (high temperature) phase.

When \( A_3 = B_3 = 0 \), (1) is related to an experimentally unrealistic set of two successive second order transitions. When only one of the sixth-degree coefficients (let say \( B_3 \)) is non-zero, we obtain an asymmetric FE which has been used by Holkovsky to describe the simultaneous onset of spontaneous values for \( p \) and \( q \) at a first order transition. More precisely, when one assumes a single temperature-dependent coefficient \( A_1 \), the softening of this coefficient triggers two phase transitions either at different or at the same temperature. In this latter case, which is realized for sufficient large values of the coupling coefficient \( C \), the spontaneous values of \( p \) change the coefficient at \( q^2 \) inducing a transition in \( q \). The soft vibrational mode of the high symmetry phase remains related to the "primary" CP, but the space group of the low symmetry phase is the intersection of the symmetries determined separately by \( p \) and \( q \). In addition to this remarkable property, other features allow the identification of "triggered" phase transitions, namely a complex domain structure depending on the possible orientation of two CP having different symmetry properties or the mixed behaviour of the dielectric constant (proper below the Curie point, improper above). Bismuth titanate has been proposed as an illustrative example of the preceding model though the available data are still incomplete for this material.

The phase diagram of (1) when \( A_3 \neq B_3 \neq 0 \) has been discussed by Gufan and Larin. It displays various sets of successive (and possibly simultaneous) transitions with intersecting lines of second and first order transitions.

2) The FE is of the type:

\[ F = A_1 p^2 + A_2 p^4 + A_3 p^6 + B_1 q^2 + B_2 q^4 + B_3 q^6 + C p q^2 \]  \hspace{1cm} (2)

with a linear-quadratic coupling term which can be formed if at least one of the two CP is spanned by a multidimensional IR. On the theoretical ground this FE has been shown to be connected to the simultaneous condensation of two modes. Besides, it has been used to describe accurately the experimental data of particular systems. In Boracites the low temperature phases and the dielectric anomaly have been explained by a mechanism in which the components of the polarization play the role of the primary CP triggering a six components CP associated to an IR of the cubic space group \( T_d^5 \) at the Brillouin zone boundary. In Benzil for which a detailed numerical model has been proposed, the primary and triggered CP possess respectively two and three components. In this material, the coupling to macroscopic quantities which are not symmetry breaking parameters has been considered. It has been shown that such a coupling does not affect the dynamical properties of the
crystal while the coupling between the OP p and q is likely to be active both in its static and dynamic behaviours. On the other hand quantitative values show that in Benzil, the triggering though essential to explain the symmetry characteristics of the transition influences only weakly the other physical properties.

The two FE considered in 1) and 2) summarize the qualitative situations which may be encountered for structural transitions induced by two OP. Numerical models should also take into account the actual symmetry of the OP and higher degree couplings. Besides when dealing with transitions towards incommensurate phases other type of coupling, involving the space derivatives of the OP, must be considered. This brings us to a third case.

3) The onset of intermediate incommensurate phases, such as in Sodium nitrite or Thiourea, has been attributed to the coupling of two distinct OP whose transformation properties allow an antisymmetric invariant of the type:

$$\frac{\partial \rho_{pq}}{\partial x} - \frac{\partial \rho_{qp}}{\partial x}$$

(3)

If we consider p and q as the amplitudes of two different normal modes of the crystal, (3) expresses the existence of a relative maximum in the lowest mode due to their interaction. This situation can be recognised when a commensurate phase, generally stable at lower temperature, is related to an IR of the high temperature commensurate phase which does not transform like (3). In Sodium nitrite and Thiourea the low temperature commensurate phase is connected to a one dimensional IR of the orthorhombic Brillouin zone center so that the construction of an invariant of type (3) needs to recourse to two distinct IR at that point. The preceding model is however far from being experimentally confirmed as it does not explain the complex set of phases which is for instance observed in Thiourea.

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