

Structural phase transitions

Group-Subgroup relationship
between space-groups of parent and daughter phases

No group-subgroup relationship

- Change in the structures with difference in energies much smaller than cohesive energy of each structure
 - No breaking of chemical bonds
 - Displacements $\sim 0.01 - 0.1 \text{ \AA}$
 - Latent heat $<$ few cal/g
 - Small discontinuities of lattice parameters at T_c
 - Tensorial classification (ferroelectrics, Ferroelastics, other ferroics, Non ferroics)
 - Microscopic classification (ferro - antiferro)
 - Many insulators
 - Well studied theoretically
- Temperature T

Reconstructive

Morphotropic

- Breaking of part of chemical bonds
 - Displacements of order of lattice-param.
 - Large discontinuity of lattice parameters at T_c .
 - Large latent heat and thermal hysteresis
 - Allotropic transitions in elements, Metallic alloys, Minerals (most)
 - Studied by metallurgists and recent Landau-type approach. (High-pressure structures)
- Temperature T
pressure P
- change in chemical composition
 - Different stoichiometries between adjacent homogeneous phases. separated by large biphasic regions (phase separation)
 - Minerals, Alloys
 - Recently studied theoretically
- Temperature
Concentration (T, c)

$$F = a_0(P, T) + a_2(P, T) p_z^2 + b_2(P, T) (p_x^2 + p_y^2) \quad (2)$$

$$\left. \begin{aligned} \frac{\partial F}{\partial p_z} = 2a_2 p_z = 0, \quad \frac{\partial^2 F}{\partial p_z^2} = 2a_2 > 0 \\ \frac{\partial F}{\partial p_x} = 2b_2 p_x = 0, \quad \frac{\partial^2 F}{\partial p_x^2} = 2b_2 > 0 \\ \frac{\partial F}{\partial p_y} = 2b_2 p_y = 0, \quad \frac{\partial^2 F}{\partial p_y^2} = 2b_2 > 0 \end{aligned} \right\} \begin{array}{l} \text{Equilibrium} \\ p_z = p_x = p_y = 0 \end{array} \quad \begin{array}{l} \text{Stability} \\ a_2 > 0 \\ b_2 > 0 \end{array}$$

Equilibrium $\vec{p} \neq 0$ requires that a_2 or b_2 change sign at T_c

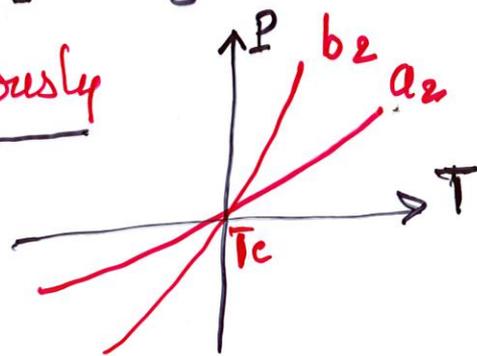
① a_2 and b_2 cannot vanish simultaneously

$a_2(P, T_c) = b_2(P, T_c) = 0$ only at an isolated point of (P, T) plane

\Rightarrow infinitesimal change of P or T would modify nature of the transition $p_z \leftrightarrow p_x, p_y$

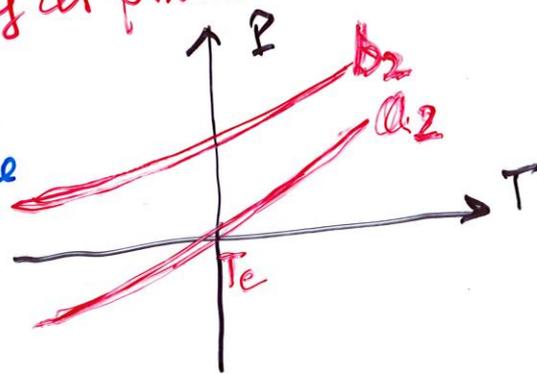
This is not observed experimentally at phase transitions

If $a_2(P, T_c) = 0 \Rightarrow b_2(P, T_c) > 0$



tion can move along z or in (x, y) plane but not in general direction

\Rightarrow Provisional definition of the transition order - parameter



"The set of degrees of freedom whose coefficient of the quadratic contribution to F changes sign at T_c "

\Rightarrow dimensionality of the OP \Rightarrow Number of independent components

($p_z \rightarrow 1, (p_x, p_y) \rightarrow 2$)

② $a_2 > 0$ for $T > T_c, a_2 < 0$ for $T < T_c \Rightarrow a_2$ odd function of $T - T_c: a_2 = a_{20}(T - T_c)$

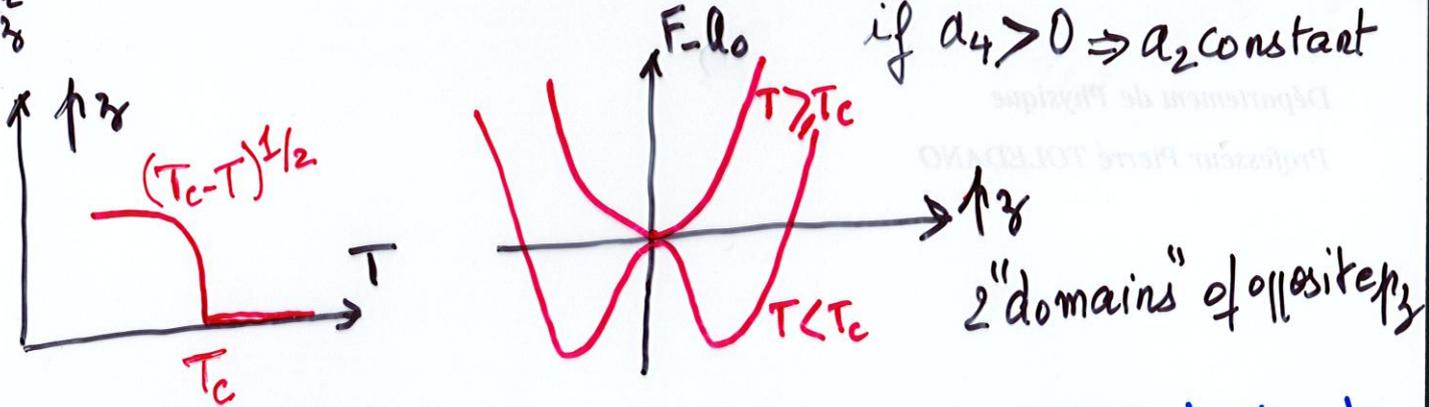
③ Second-degree expansion of F insufficient for $p_z \neq 0 \Rightarrow$ higher degree necessary

$$F = a_0(T, p) + a_{02}(T - T_c) p_z^2 + a_4 p_z^4 \quad (3)$$

$$\frac{\partial F}{\partial p_z} = 2 p_z [a_{02}(T - T_c) + 2 a_4 p_z^2] = 0 \Rightarrow \begin{cases} \text{State I } p_z = 0, T \geq T_c \\ \text{State II } p_z = \pm \left[\frac{a_{02}(T_c - T)}{2 a_4} \right]^{1/2} \end{cases}$$

$$\frac{\partial^2 F}{\partial p_z^2} = 2 a_{02}(T - T_c) + 12 a_4 p_z^2 \geq 0$$

if $a_4 > 0 \Rightarrow a_2$ constant



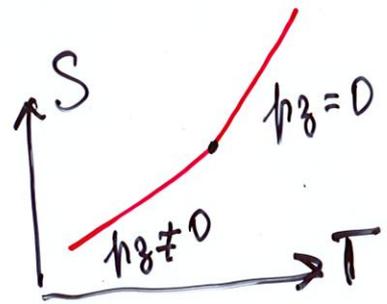
Fourth-degree sufficient for one-dimensional OP (p_z) but not for 2-component OP (p_x, p_y).

II Critical anomalies at T_c

1) No latent heat at T_c

$$S = - \left(\frac{\partial F_{eq}}{\partial T} \right) = - \frac{\partial a_0(T, p)}{\partial T} - a_{02} (p_z^{eq})^2$$

$$L = T_c \Delta S(T_c) = 0$$



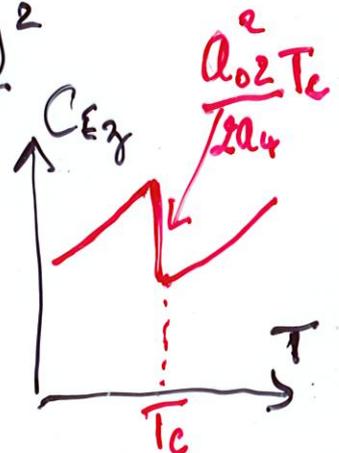
2) Upward discontinuity of specific heat on cooling

Electric field E_z conjugated quantity to p_z .

$$C_{E_z} = T \left(\frac{\partial S}{\partial T} \right)_{E_z} = - T \frac{\partial^2 a_0(T, p)}{\partial T^2} - a_{02} T \frac{\partial (p_z^{eq})^2}{\partial T}$$

$$(p_z^{eq})^2 = \frac{a_{02}}{2 a_4} (T_c - T) \Rightarrow C_{E_z}^0 = - T \frac{\partial^2 a_0(T, p)}{\partial T^2} (T \geq T_c)$$

$$C_{E_z} = C_{E_z}^0 + \frac{a_{02}^2 T}{2 a_4} (T < T_c)$$



3) Divergence of the dielectric Susceptibility at T_c

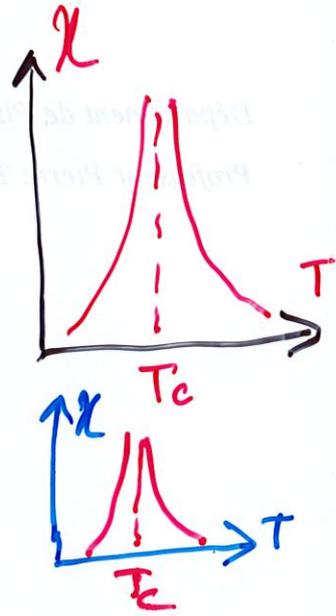
(4)

$$\chi = \lim_{E_z \rightarrow 0} \left(\frac{\partial p_z}{\partial E_z} \right)_{p_{eq}} \quad G = F - E_z p_z \quad (\text{free enthalpy})$$

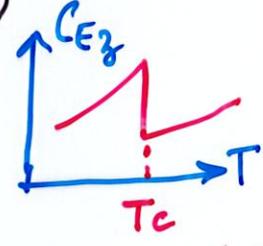
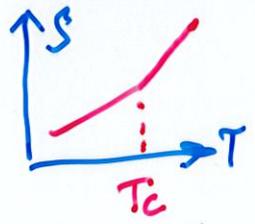
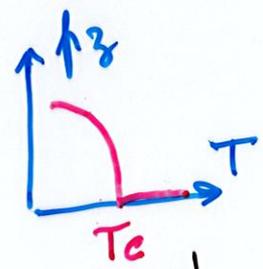
$$\frac{\partial G}{\partial p_z} = 2a_2 p_z (T - T_c) + 4a_4 p_z^3 = E_z$$

$$\frac{\partial^2 G}{\partial p_z^2} = 2a_2 (T - T_c) + 12a_4 p_z^2 = 1$$

$$\chi = \frac{1}{2a_2 (T - T_c) + 12a_4 p_z^2} = \begin{cases} \frac{1}{2a_2 (T - T_c)} & (T \geq T_c) \\ \frac{1}{4a_2 (T - T_c)} & (T < T_c) \end{cases}$$



In Summary



Ehrenfest \Rightarrow Second-order phase transitions
III order-parameter symmetry. Irreducibility-reducibility
Degeneracy of the low-symmetry phases.

- $G_0 = 4/mmm: p_z \rightarrow \pm p_z \Rightarrow p_z$ basic vector of a 1-dimensional vector-space invariant by G_0 and irreducible relatively to G_0 .
 - $(p_x, p_y) \rightarrow$ 2-dimensional vector-space invariant by G_0 and irreducible
 - $(p_x, p_y, p_z) \rightarrow$ 3-dimensional vector-space invariant by G_0 but reducible relatively to G_0 .
- \Rightarrow Order-parameter = Set of degrees of freedom spanning an irreducible vector-space (irreducible representation) of G_0 (parent symmetry group).

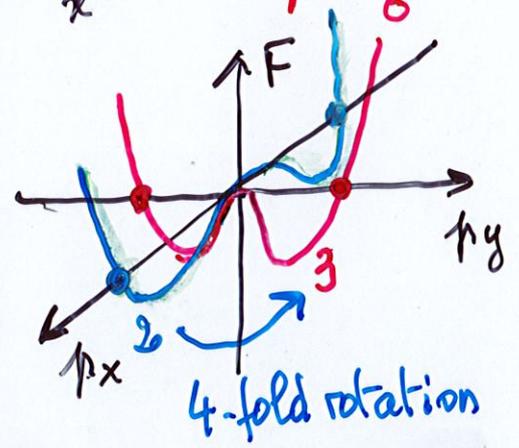
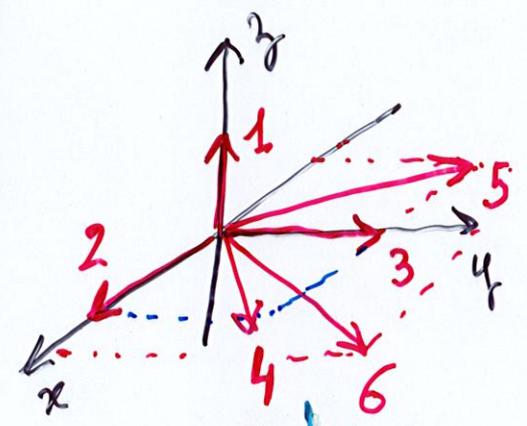
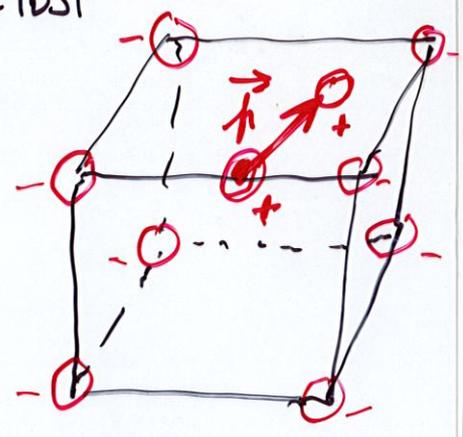
$\vec{P} = 0 \Rightarrow G_0 = 4/mmm, \vec{P} \neq 0$ symmetry operations are lost

Subgroup $G \subset G_0$

Degeneracy of low-symmetry states

Direction	G	Degeneracy
1 $(0, 0, \pm p_z)$	$4mm$	2 domains
2 $(p_x, 0, 0)$	$mm2_{\pm x}$	4 domains
3 $(0, p_y, 0)$	$mm2_{\pm y}$	
4 $(p_x, p_x, 0)$	$mm2_{\pm \bar{z}y}$	4 domains
5 $(-p_x, p_x, 0)$	$mm2_{\pm xy}$	
6 $(p_x, p_y \neq p_x, 0)$	m_z	8 domains
7 $(p_x, 0, p_z)$	mm_y	8 domains
8 $(0, p_y, p_z)$	m_x	8 domains
9 (p_x, p_x, p_z)	$m_{\bar{x}y}$	8 domains
10 $(-p_x, p_x, p_z)$	m_{xy}	8 domains
11 $(p_x, p_y \neq p_x, p_z)$	1	16 domains

Reducible or irreducible OP



\Rightarrow Several equivalent minima transforming into one another by symmetry operations of G_0 lost in the symmetry-breaking mechanism

\Rightarrow Direction 6 (m_z) requires 8-degree expansion $F(T, P, p_x, p_y)$

\Rightarrow Critical anomalies unchanged by (v_x, v_y) except χ .

$\chi_{xx}, \chi_{yy}, \chi_{xy} = \chi_{yx}$. χ_{xx} and χ_{yy} diverge but different below T_c because onset of p_x or p_y destroys equivalence of x and y directions.

IV Secondary order-parameters. (6)

μ_x or (μ_x, μ_y) are the "Primary" order-parameters because the structural mechanism is directly related to the onset of \vec{p} at T_c .

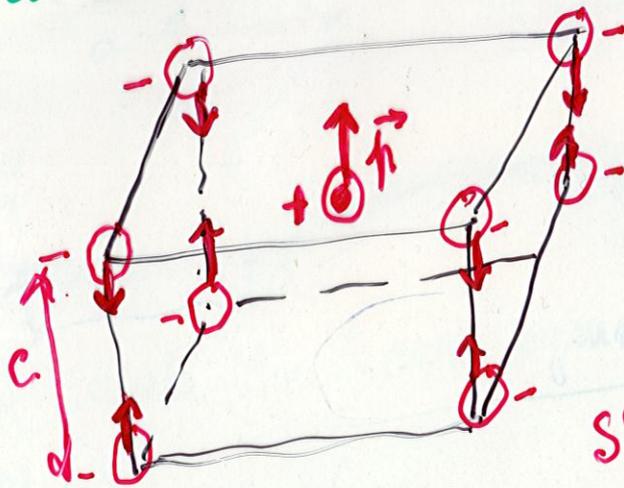
The primary order-parameter determines:

- the symmetry of the phases below T_c
- the domain pattern
- the critical anomalies

But other physical quantities appear spontaneously below T_c and show critical anomalies and domains.

However these "secondary" order-parameter:

- do not modify the symmetry and number of stable phases
- Influence only secondary aspects of the phase diagram (transition temperature, shape of transition curves...)



Deformation of the unit-cell due to displacement of - ions
 \Downarrow
 Strain component

$$\epsilon_{zz} = \frac{\Delta c}{c}$$

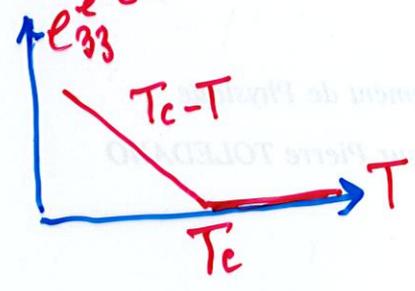
$$F(T, P, p_3, e_{33}) = a_0(T, P) + a_{02}(T - T_c) p_3^2 + a_4 p_3^4 + \delta e_{33} p_3^2 + \frac{C_{33}}{2} e_{33}^2$$

Coupling between e_{33} and OP

Elastic energy

$$\frac{\partial F}{\partial e_{33}} = \delta p_3^2 + C_{33} e_{33} = 0$$

$$e_{33}^e = -\frac{\delta}{C_{33}} p_3^2 = -\frac{\delta a_{02}(T_c - T)}{2a_4 C_{33}}$$



$$F(T, P, p_3) = a_0(T, P) + a_{02}(T - T_c) p_3^2 + \left(a_4 - \frac{\delta^2}{2C_{33}}\right) p_3^4$$

$\Rightarrow e_{33}$ renormalizes a_4 coefficient \Rightarrow change of limit of stability of the phases
 (2nd order \rightarrow 1st order) ($a_4 < 0$)

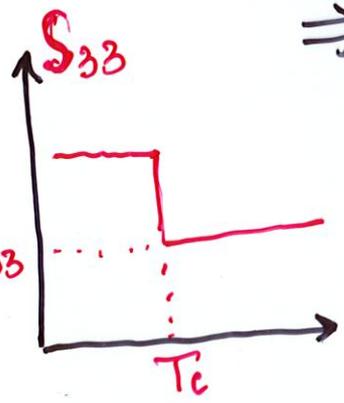
Elastic susceptibility $\chi_{\sigma_{33}} = \lim_{\sigma_{33} \rightarrow 0} \frac{\partial e_{33}}{\partial \sigma_{33}}$

$$G = F - \sigma_{33} e_{33} \Rightarrow \begin{cases} \frac{\partial G}{\partial e_{33}} = \delta p_3^2 + C_{33} e_{33} - \sigma_{33} = 0 \\ \frac{\partial G}{\partial p_3} [a_{02}(T - T_c) + 2a_4 p_3^2 + \delta e_{33}] = 0 \end{cases}$$

Second minimization with respect to σ_{33} :

$$\Rightarrow T \geq T_c (p_3 = 0) \Rightarrow \chi_{\sigma_{33}}^0 = \frac{1}{C_{33}} = S_{33}^0$$

$$T < T_c (p_3 \neq 0) \Rightarrow \chi_{\sigma_{33}} = \frac{1}{C_{33} - \frac{\delta^2}{2a_4}}$$



No divergence at T_c but small anomaly

\Rightarrow Secondary OP can be distinguished by critical anomalies (Also by domain pattern)

V First-order phase transitions

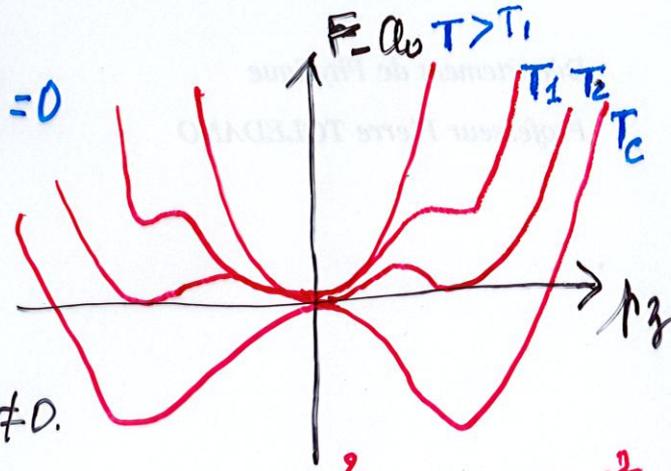
$$\rho_3^e = \pm \left[\frac{a_{02}(T_c - T)}{2a_4} \right]^{1/2} \Rightarrow a_4 > 0. \text{ If } a_4 < 0 \Rightarrow \rho_3^e \text{ unstable}$$

$$F(T, P, \rho_3) = a_0(T, P) + a_{02}(T - T_c)\rho_3^2 + a_4\rho_3^4 + a_6\rho_3^6$$

$a_4 < 0, a_6 > 0.$

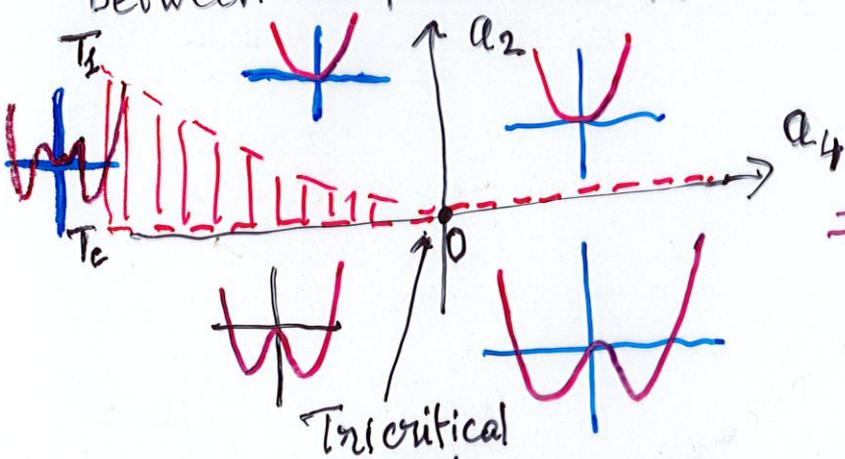
$$\frac{\partial F}{\partial \rho_3} = 2\rho_3 [a_{02}(T - T_c) + 2a_4\rho_3^2 + 3a_6\rho_3^4] = 0$$

$$\frac{\partial^2 F}{\partial \rho_3^2} = 2a_{02}(T - T_c) + 12a_4\rho_3^2 + 30a_6\rho_3^4 \geq 0$$



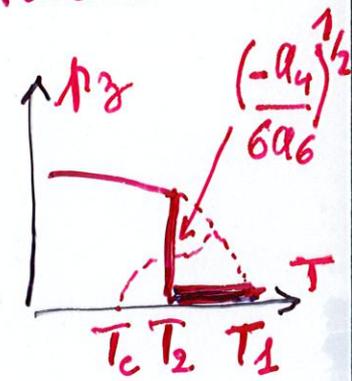
Between T_1 and T_c coexistence between the phases with $\rho_3 = 0$ and $\rho_3 \neq 0.$

$$T_1 = T_c + \frac{a_4^2}{3a_{02}a_6}, \quad T_2 = T_c + \frac{a_4^2}{4a_{02}a_6}$$

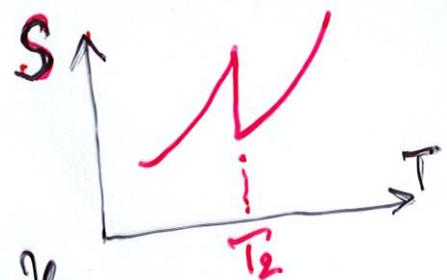


\Rightarrow Thermal hysteresis

$$T < T_1: \rho_3^e = \pm \left[\frac{-a_4 + (a_4^2 + 3a_{02}(T_c - T))^{1/2}}{3a_6} \right]^{1/2}$$

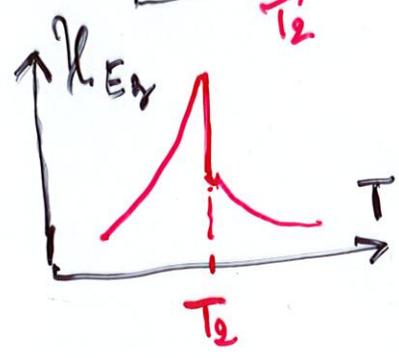


OP Discontinuous



Latent heat

$$L = T_2 \Delta S(T_2) = - \frac{a_{02} a_4 T_2}{6a_6}$$



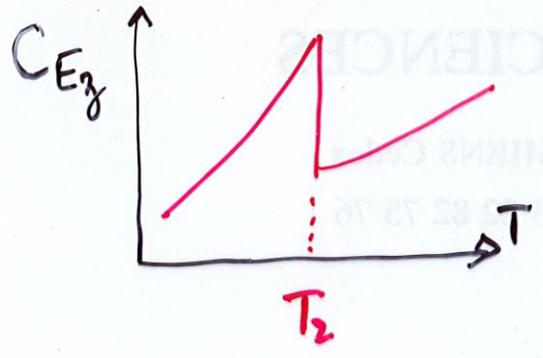
No divergence of χ

$$T > T_2 \quad \chi = \frac{1}{2a_{02}(T - T_c)}$$

$$T = T_2 \quad \chi(T_2) = \frac{2a_6}{a_4^2}$$

$$T < T_2 \quad \chi = \frac{1}{a_{02}(T - T_c) + 12a_4\rho_3^2 + 30a_6\rho_3^4}$$

Specific heat



$$C_{E3}^0 = -T \frac{\partial^2 a_0(T, P)}{\partial T^2} \quad T > T_2$$

$$C_{E3} = C_{E3}^0 + \frac{a_{02}^2}{[a_4^2 + 3a_6(T_2 - T)]^{1/2}} \quad T < T_2$$

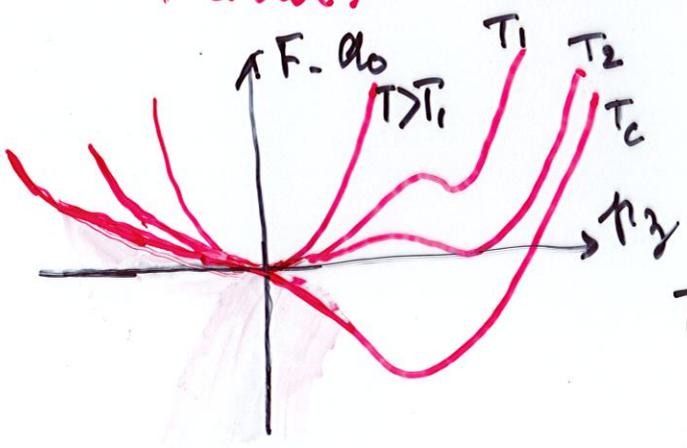
Sharp decrease below T_2

All derivatives of F discontinuous \Rightarrow First-order transition (Ehrenfest)

- Preceding example of first-order transition cannot be predicted by symmetry as it depends on the sign of the coefficients in F ($a_4 < 0, a_6 > 0$)
- Class of first-order transitions predicted by symmetry

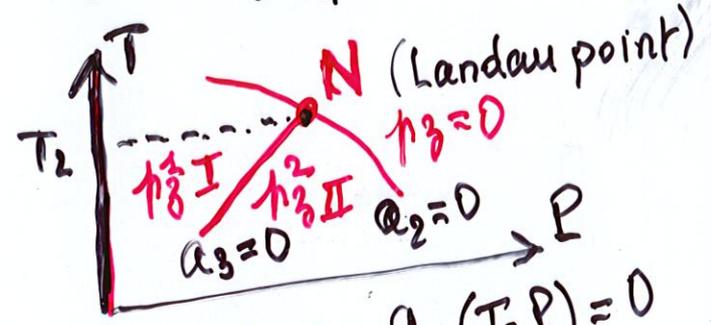
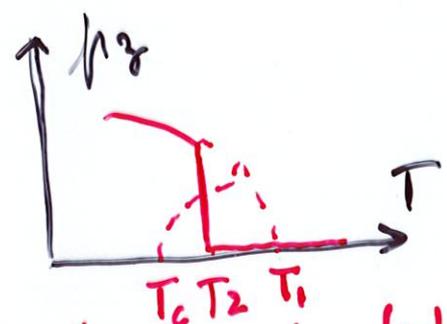
$$F = a_0(P, T) + a_{02}(T - T_c) \eta_3^2 + a_3 \eta_3^3 + a_4 \eta_3^4$$

cubic invariant of η_3



$$T > T_1 \quad \eta_3 = 0$$

$$T < T_1 \quad \eta_3 = \frac{-3a_3 + [9a_3^2 - 32a_{02}a_4(T - T_c)]^{1/2}}{8a_4}$$



η_3^1, η_3^2 antistructural phases
 $\eta_3^1 > 0 \quad \eta_3^2 < 0 \quad I, II$

N: $a_2(T_2, P) = 0, a_3(T_2, P) = 0$
 isolated point of continuous transition (3-phase point)

VI Useful rules for applying the Landau theory (10)

- At which degree F has to be truncated for determining all stable states associated with an OP?
- Can we predict the number of stable states for an OP?
- How to construct the phase diagram involving all stable states

Integrity basis

$$F(p_z) = a_0 + a_2 p_z^2 + a_4 p_z^4 + a_6 p_z^6$$

$$F(p_x, p_y) = a_0 + a_2 (p_x^2 + p_y^2) + a_4 (p_x^4 + p_y^4) + b_4 p_x^2 p_y^2$$

$$[p_x^4 + p_y^4 = (p_x^2 + p_y^2)^2 - 2 p_x^2 p_y^2]$$

Basic invariants

$$J = p_z^2$$

$$\begin{cases} J_1 = p_x^2 + p_y^2 \\ J_2 = p_x^2 p_y^2 \end{cases}$$

- The set of independent invariants (J_1, J_2, \dots) associated with an OP constitutes the integrity basis of the OP.
- Rule for truncating F in the integrity basis

If n is the degree of the highest-degree invariant, the determination of the full set of stable states requires to truncate F at the degree

$2n$ (second-order transition) or $2n+2$ (first-order transition).

$$F(p_z): n=2 \Rightarrow 2n=4 \text{ (2nd order)} \text{ or } 2n+2=6 \text{ (1st order)}$$

$$F(p_x, p_y): n=4 \Rightarrow 2n=8 \text{ (2nd order)} \text{ or } 2n+2=10 \text{ (1st order)}$$

Rules for determining the number of stable states

If m is the OP dimension and q the dimension of the integrity basis:

Case 1: If $m=q$ the number of stable states is 2^m .

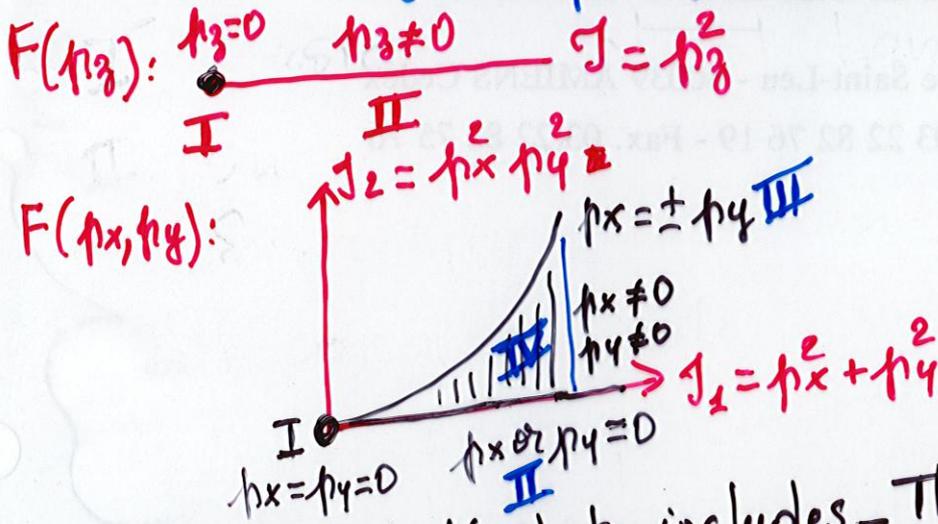
$$F(p_z): m=1, q=1 \Rightarrow 2^1 = 2 \text{ stable states } (p_z=0, p_z \neq 0)$$

$$F(p_x, p_y): m=2, q=2 \Rightarrow 2^2 = 4 \text{ stable states } \begin{cases} p_x = p_y = 0 \\ \pm p_x = \pm p_y \\ \pm p_x \text{ or } \pm p_y \\ p_x \neq p_y \end{cases}$$

$$p_x \neq p_y \Rightarrow 8^{\text{th}} \text{ degree}$$

Case 2: $m \neq q$. The number of stable states can be deduced from the integrity basis space (orbit space)

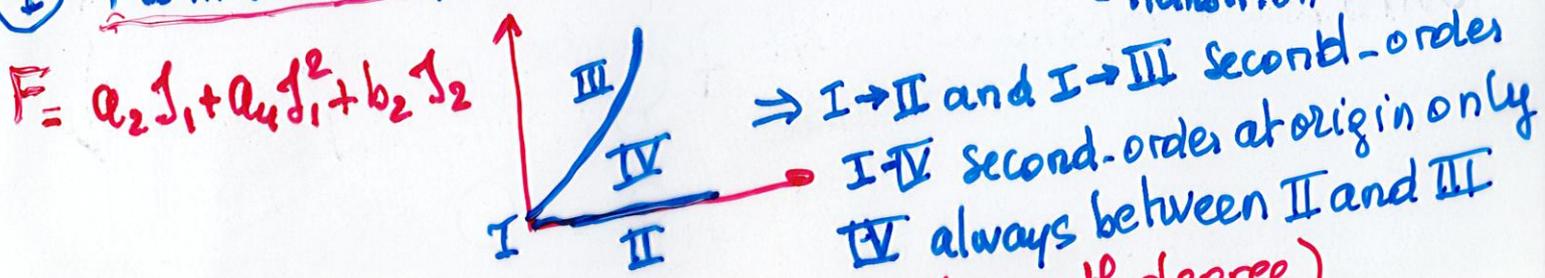
(11)



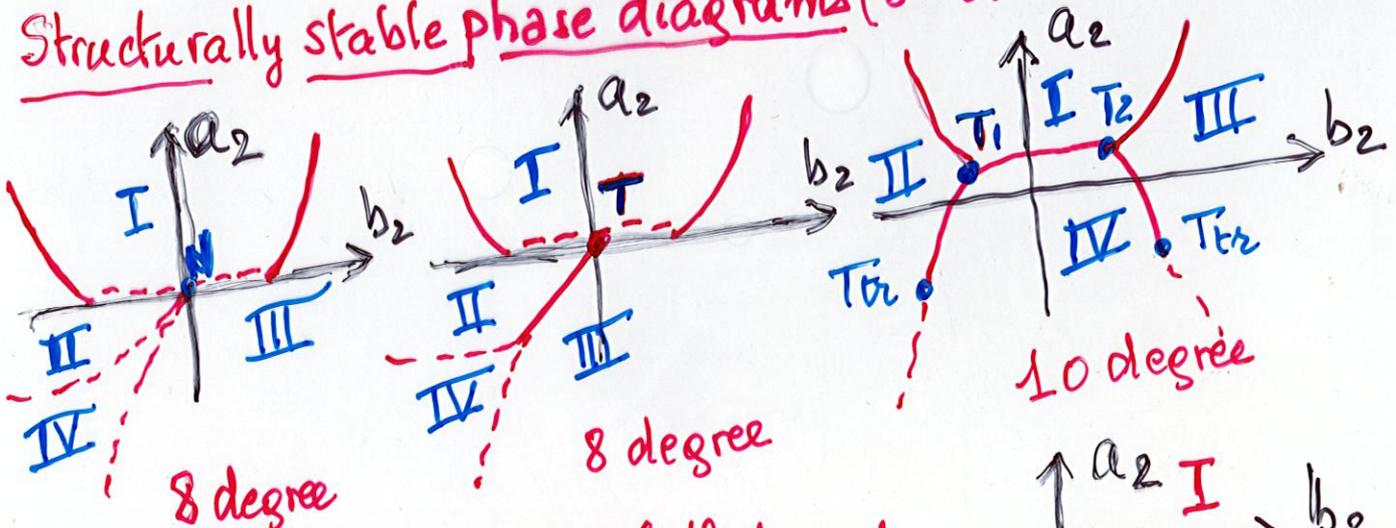
⇒ The number of stable states includes - The origin of the orbit space
 - The number of curves merging at the origin (2)
 - The number of surfaces located between the curves (1)
 - The volume contained in the surfaces (0)

Rules for constructing the phase diagrams

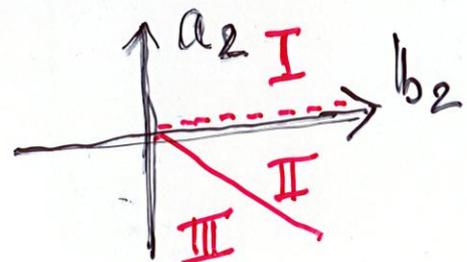
① From orbit space ⇒ topology of phases { contact neighboring Transition order



Structurally stable phase diagrams (8th or 10th degree)



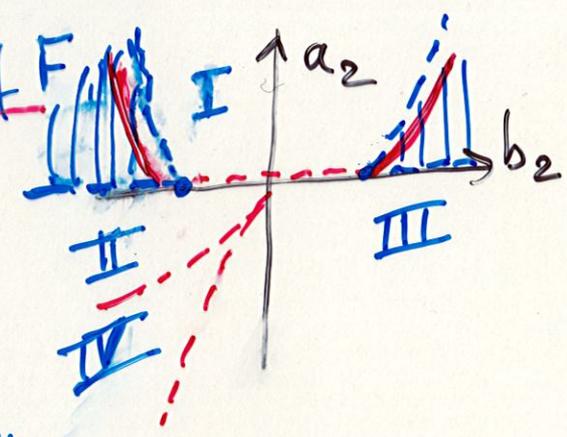
Structurally unstable (4th degree)
 (No phase IV)



② Standard minimization of F (12)

Limit of stability curves

$$\frac{\partial^2 F}{\partial \sigma_x^2 \partial \sigma_y^2} - \left(\frac{\partial^2 F}{\partial \sigma_x \partial \sigma_y} \right)^2 = 0$$



First-order transition curves

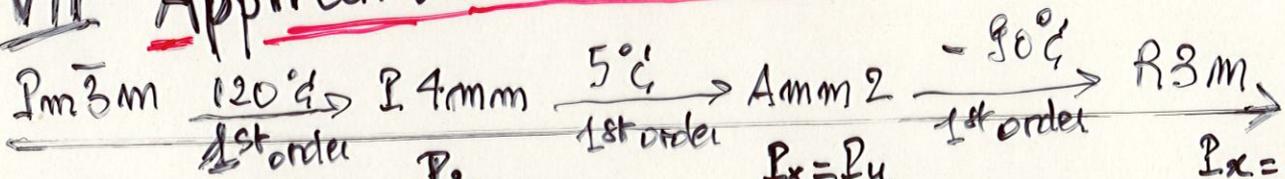
$$F(\sigma_1) = F(\sigma_2)$$

σ_1, σ_2 equilibrium values in phases 1 and 2

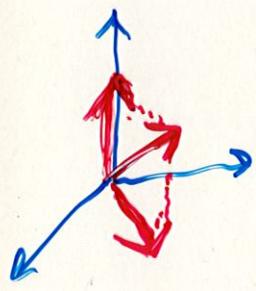
③ Dependence of phenomenological coefficients on external variables

- Number of varying coefficients depends on number of external variables and on dimension of integrity basis
- Varying coefficients correspond to basic invariants
- Linear dependence on T and P. Concentration more complicated.

VII Application to BaTiO₃



P_3	$P_x = P_y$	$P_x = P_y = P_z$
6 ferroelectric domains $\pm P_x, \pm P_y, \pm P_z$	12 ferroelectric domains $(\pm P_x, \pm P_y, 0)$	8 ferroelectric domains $\pm (P, P, P)$ $(-P, P, P)$
3 ferroelastic domains $2e_{33} - e_{xx} - e_{yy}$	6 ferroelastic domains $\begin{cases} e_{xy} \\ 2e_{33} - e_{xx} - e_{yy} \end{cases}$	4 ferroelastic domains $e_{xy} = e_{yz} = e_{zx}$
<u>Coupling</u> $P_3^2 (2e_{33} - e_{xx} - e_{yy})$	<u>Coupling</u> $P_x P_y P_z$	



\vec{P} proper ferroelectric primary OP \vec{e} proper ferroelastic secondary OP

$Pm\bar{3}m$: 48 matrices generated by (3dim representation) (13)

$$\begin{pmatrix} P_x \\ P_y \\ P_z \end{pmatrix} \begin{matrix} U_x \\ C_3^{2 \times 43} \\ C_3^{2 \times 43} \\ U_{xy} \\ I \\ \sigma_{xy} \end{matrix} \begin{bmatrix} 1 & & \\ & 1 & \\ & & -1 \end{bmatrix} \begin{bmatrix} 1 & & \\ & 1 & \\ & & -1 \end{bmatrix} \begin{bmatrix} -1 & & \\ & -1 & \\ & & -1 \end{bmatrix} \begin{bmatrix} -1 & & \\ & -1 & \\ & & -1 \end{bmatrix} \begin{bmatrix} -1 & & \\ & -1 & \\ & & -1 \end{bmatrix} \begin{bmatrix} 1 & & \\ & 1 & \\ & & 1 \end{bmatrix}$$

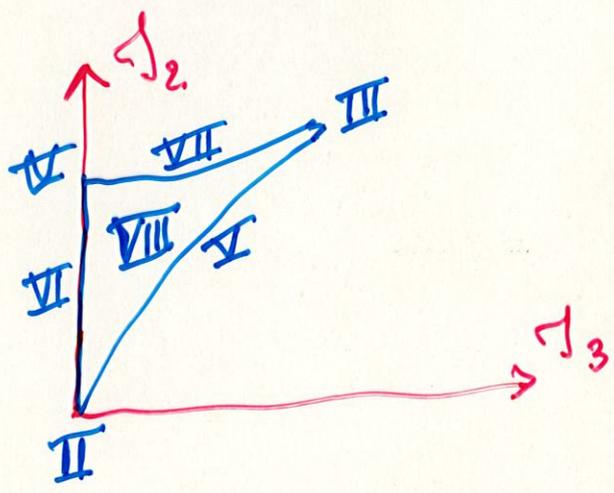
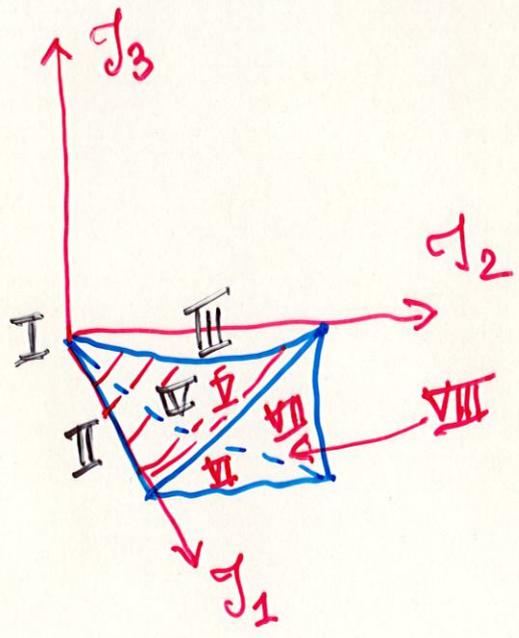
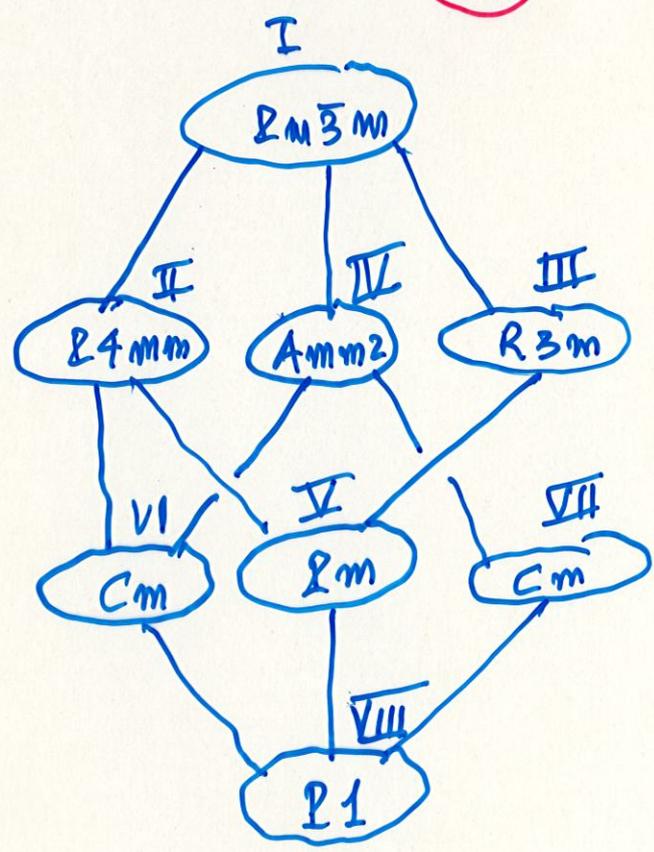
Basis of integrity: $J_1 = p_x^2 + p_y^2 + p_z^2$, $J_2 = p_x^4 + p_y^4 + p_z^4$, $J_3 = p_x^2 p_y^2 p_z^2$

Dimension of the OR: $m=3$, Dimension of integrity basis: $q=3$

$\Rightarrow 2^3 = 8$ possible stable states

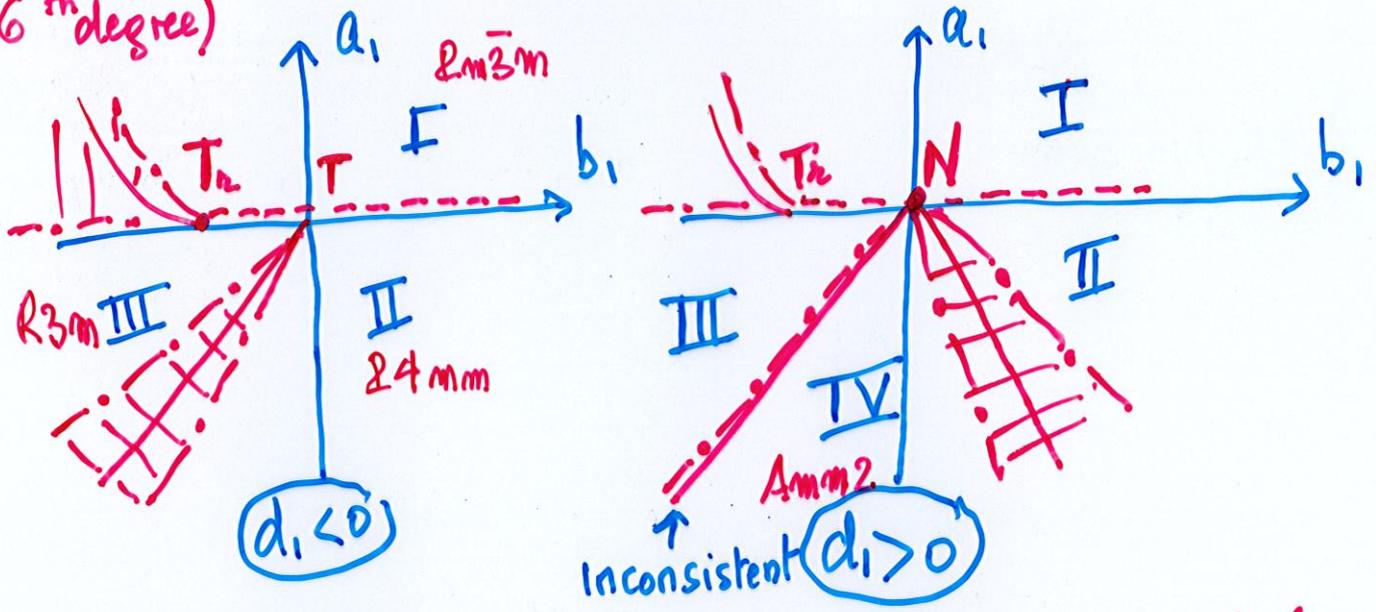
Structurally stable F truncated at degree $2n$ or $2n+2$
 with $n=6$

	p_x, p_y, p_z	
I	0 0 0	$Pm\bar{3}m$
II	0 0 p_z	$P4mm$
III	$p_x p_y p_z$	$R3m$
IV	$p_x p_x 0$	$Amm2$
V	$p_x p_x p_z$	Pm
VI	$p_x p_y 0$	Cm
VII	$p_z p_z p_x$	Cm
VIII	$p_x p_y p_z$	$P1$



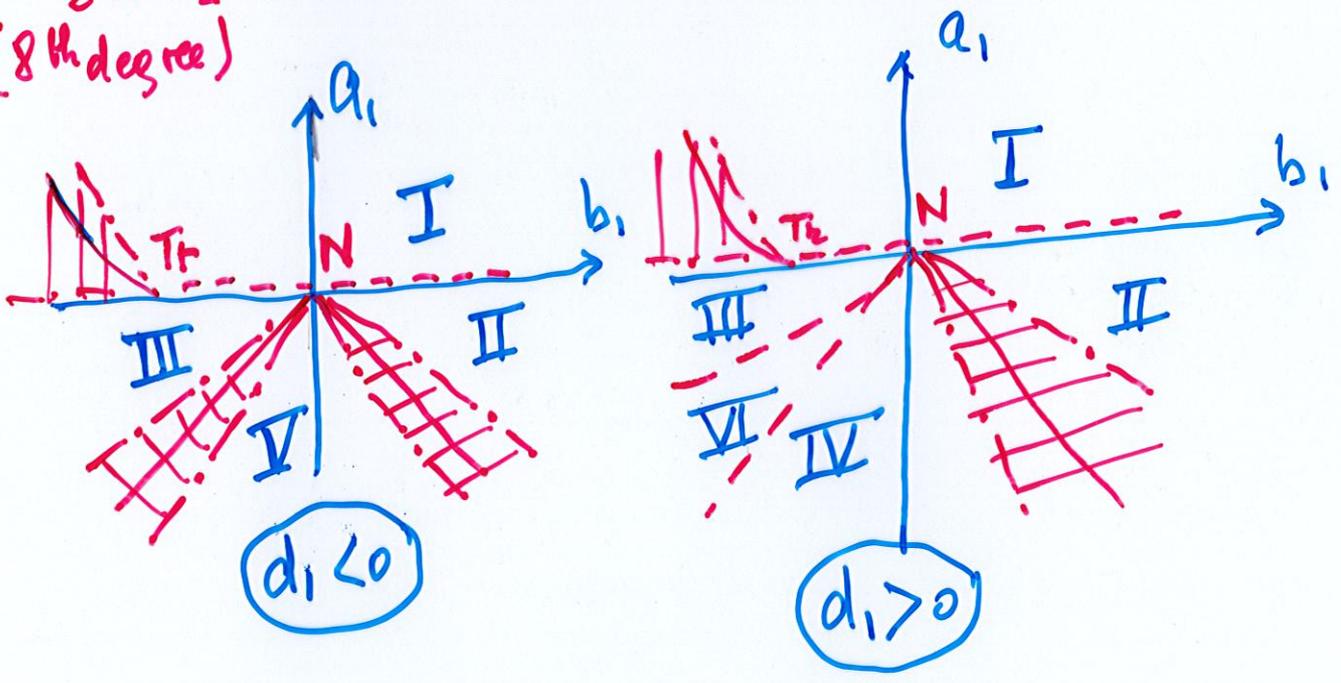
$$F_1 = a_1 J_1 + a_2 J_1^2 + a_3 J_1^3 + b_1 J_2 + c_{12} J_1 J_2 + d_1 J_3$$

(6th degree)



$$F_2 = F_1 + a_3 J_1^3 + a_4 J_1^4 + b_2 J_2^2 + c_{112} J_1^2 J_2 + c_{13} J_1 J_3$$

(8th degree)



VIII Images of a group: Determination of the free-energies.

● In $BaTiO_3$ the 48 matrices generated by:

$$\begin{pmatrix} 1 & & \\ & 1 & \\ & & 1 \end{pmatrix} \begin{matrix} U_x \\ C_3^{2 \times 43} \\ C_3^{2 \times 43} \\ U_{\bar{x}y} \\ I \\ m_{xy} \end{matrix} \begin{bmatrix} 1 & & \\ & 1 & \\ & & 1 \end{bmatrix} \begin{bmatrix} 1 & & \\ & 1 & \\ & & 1 \end{bmatrix} \begin{bmatrix} 1 & & \\ & 1 & \\ & & 1 \end{bmatrix} \begin{bmatrix} 1 & & \\ & 1 & \\ & & 1 \end{bmatrix} \begin{bmatrix} 1 & & \\ & 1 & \\ & & 1 \end{bmatrix} \begin{bmatrix} 1 & & \\ & 1 & \\ & & 1 \end{bmatrix}$$

are all different: one-to-one correspondence (isomorphism) between 48 matrices of the IR (Γ) of $m\bar{3}m = G_0$ and the 48 symmetry operations of G_0 . $\Rightarrow \Gamma$ is a faithful IR of G_0 .

● By contrast the 2 IR's of $G_0 = 4/mmm$ (Γ_1 and Γ_2)

$4/mmm$	C_4	C_2	C_4^3	m_x	m_y	m_{xy}	$m_{\bar{x}y}$	I	S_4	S_4^3	S_4	$2x$	$2y$	$2xy$	$2\bar{x}y$
Γ_1	1	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1	-1	-1
Γ_2	1	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1	-1	-1

are not faithful: homomorphism between 16 matrices and elements of $4/mmm$.

Image of G_0 : Set I_0 of distinct matrices of an IR of G_0

Image form a group I_0 isomorphous to Subgroup of G_0

Image-group of Γ of $m\bar{3}m$: I_0 isomorphous to $m\bar{3}m$

Image-group of Γ_1 of $4/mmm$ I_0 : $(1, -1)$ isomorphous to $(I, 2, m)$

Image-group of Γ_2 of $4/mmm$ I_0 : (8 matrices) isomorphous to $\begin{cases} 4mm \\ C2m \\ 422 \end{cases}$

● n-dimensional IR (Γ) of G_0 carried by n-component OP, $4/m$

Image-group I_0 of Γ isomorphous to irreducible subgroup

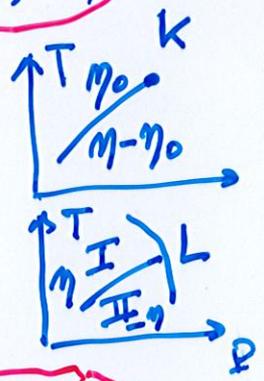
of orthogonal group $O(n)$: Determination of free-energies

F_n associated with ^{all} n-component OP consists in:

- Enumerating the irreducible subgroups of $O(n)$.
- For each subgroup, working out invariants of various degrees ^{involving} with OP components.

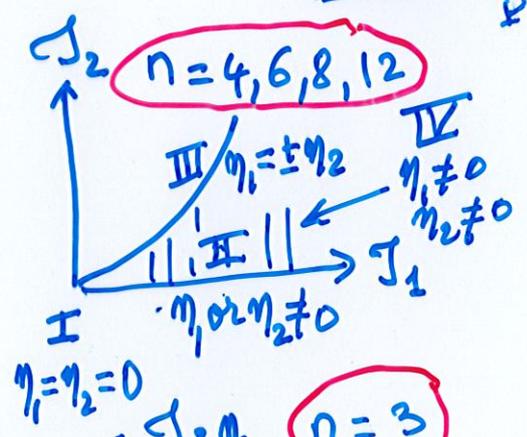
Enumeration of irreducible subgroups of $O(n)$ and free-energies
 \Rightarrow fully determined for $n \leq 4$ Partial for $n = 6, 8, 12$

$O(1) \Rightarrow I_0 = 1 \quad J = \eta \Rightarrow$ No symmetry change
 Isostructural transitions



$I_0 = (1, -1) \quad J = \eta^2$
 $I \quad \eta = 0$
 $II \quad \eta \neq 0$

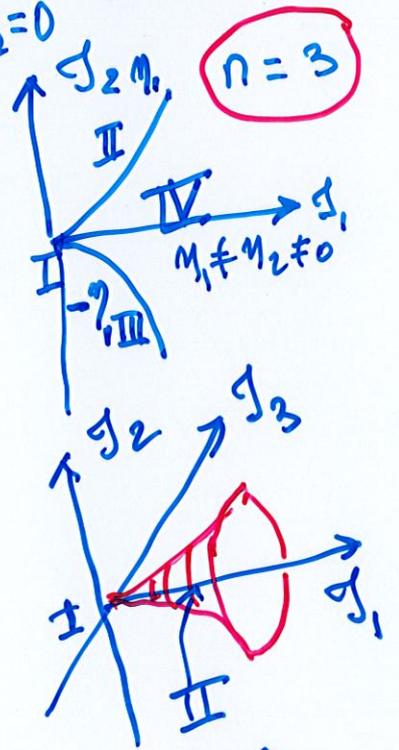
$O(2) \Rightarrow C_{nv} (n=3, 4, 6, 8, 12)$
 $\begin{cases} \eta_1 = \rho \cos \theta \\ \eta_2 = \rho \sin \theta \end{cases} \Rightarrow \begin{cases} J_1 = \rho^2 \\ J_2 = \rho^n \cos n\theta \end{cases}$



4 stable phases
 highest degree $2n$

$O(2) \Rightarrow C_n (n=4, 6, 8, 12)$
 $J_1 = \rho^2, J_2 = \rho^n \cos n\theta, J_3 = \rho^n \sin n\theta$
 but $J_2^2 + J_3^2 = J_1^n$

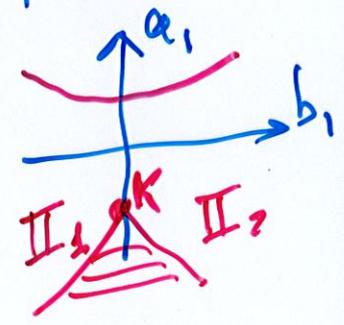
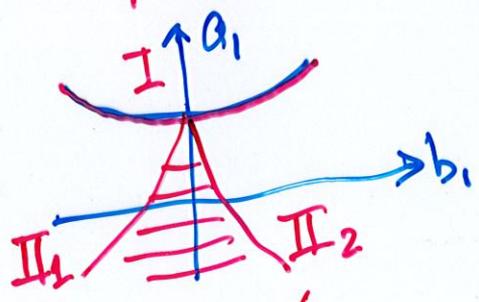
$n=3$
 II and III Antisometr.
 $J_1 \neq J_2 \neq 0$



2 stable states $I \quad \eta = 0$
 $II \quad \eta_1 \neq \eta_2 \neq 0$

$F = a_1 J_1 + a_2 J_1^2 + b_1 J_2$

$n=3 \quad C_3 \Rightarrow$



isostructural

• $O(3)$ Five irreducible subgroups with image groups isomorphic to cubic point-groups.

• $T_{23}(12)$ $\left\{ \begin{array}{l} J_1 = \eta_1^2 + \eta_2^2 + \eta_3^2 \\ J_2 = \eta_1 \eta_2 \eta_3 \\ J_3 = \eta_1^4 + \eta_2^4 + \eta_3^4 \\ J_4 = (\eta_1^2 - \eta_2^2)(\eta_2^2 - \eta_3^2)(\eta_3^2 - \eta_1^2) \end{array} \right.$ $2n=12$ 5 stable states

• $T_h(24)_{m3}$ $J_1, J_3, J_5 = \eta_1^2 \eta_2^2 \eta_3^2$ $2n=12$ 5 stable states

• $T_d(24)_{43m}$ J_1, J_2, J_3 $2n=8$ 8 stable states

• $O(24)_{432}$ $J_1, J_3, J_5, J_2 \times J_4$ $2n=12$ 5 stable states

• $O_h(48)_{m3m}$ J_1, J_3, J_5 $2n=12$ 8 stable states

• $O(4)$ 27 irreducible subgroups and free-energies (Michel et al 1985)

• $O(6)$ 32
 • $O(8)$ 12
 • $O(12)$ 8 } only for structural transitions

IX Space-groups and their irreducible representation (18)

Structural transitions between crystalline structures
Structures \Rightarrow 230 crystallographic space-groups

Space-group G : infinite order formed by symmetry operations

$\{R|E\}$ \bullet R point-symmetry operations
(rotations, reflections, inversion)
 \bullet E translations

Set of $R \Rightarrow$ point-group of crystal (finite group)
 T infinite subgroup of E generating
3-dimensional Bravais lattices

IR's of 32 point-groups tabulated (finite)
IR's of infinite space-groups \Rightarrow infinite, not tabulated
but can be constructed starting from IR's of point-group

IR's denoted $\Gamma_{\vec{k}, m}$ $\left\{ \begin{array}{l} \vec{k} \text{ vector of reciprocal space} \\ \text{belonging to first Brillouin-zone} \\ \text{of } G. \end{array} \right.$

2 indices

\vec{k} defines subgroup $G_{\vec{k}}$ of G
 $\Rightarrow G_{\vec{k}} =$ set of operations of $G = \{R|E\}$
whose rotational element R
leaves \vec{k} invariant or transform
in equivalent vector differing
by reciprocal lattice vector

$G_{\vec{k}}$ has irreducible
representations $\tau_m(\vec{k})$
of dimension n_m which are
tabulated (Kovalev, 1961)

$\Rightarrow \Gamma_{\vec{k}, m}$ of G (space-group) constructed using $\tau_m(\vec{k})$
dimension of $\Gamma_{\vec{k}, m}$ is $n_m \times \mathcal{N}$.
 $\mathcal{N} \equiv$ number of vectors of the star \vec{k}^* , which is
the set of vectors \vec{k} unequivalent to \vec{k} , obtained
by applying all point-symmetry elements R .

① The Lifshitz condition.

\vec{k} varies continuously in first-Brillouin-zone \Rightarrow Number of \vec{k} , m infinite.

Lifshitz (1941) \Rightarrow Absolute minima of $F(\eta_i)$ insufficient to test the stability of strictly periodic phases

$\Rightarrow F(\eta_i)$ has to be minimum with respect to small variations of η_i .

Discrete $F(\eta_i)$ replaced by continuous sum: $F = \int \varphi(\eta_i, \frac{\partial \eta_i}{\partial x_j}) dV$

$$\varphi(\eta_i, \frac{\partial \eta_i}{\partial x_j}) = f(\eta_i) + \delta \left(\eta_i \frac{\partial \eta_i}{\partial x_k} - \eta_j \frac{\partial \eta_j}{\partial x_k} \right) + \delta \left[\sum \left(\frac{\partial \eta_i}{\partial x_j} \right)^2 \right]$$

free-energy density \swarrow Landau polynomial \nearrow Lifshitz invariant \nearrow Ginzburg term \nearrow

• Antisymmetric invariant because symmetric invariant

$$\eta_i \frac{\partial \eta_j}{\partial x_k} + \eta_j \frac{\partial \eta_i}{\partial x_k} = \frac{\partial}{\partial x_k} (\eta_i \eta_j) \text{ do not affect stability.}$$

Lifshitz condition: No antisymmetric invariants of $(\eta_i, \frac{\partial \eta_i}{\partial x_k})$

Should be permitted for transitions to strictly periodic phase.

$\Rightarrow G_{\vec{k}}$ has to contain inversion or 3 intersecting 2-fold axes

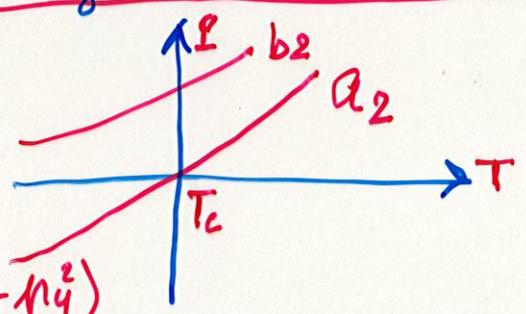
\Rightarrow Realized only at the centre of Brillouin-zone and for a few "high-symmetry" points on first Brillouin-zone surfaces

• Number of "active" IR's becomes finite (a few thousands)

\Rightarrow Symmetry changes associated to "active" IR's tabulated in the eighties (Stokes and Hatch 1988)

Phase transitions induced by several order-parameters

$4/mmm \Rightarrow \begin{cases} p_z, a_2 \Rightarrow 4mm \\ (p_x, p_y), b_2 \Rightarrow 2mm \end{cases}$

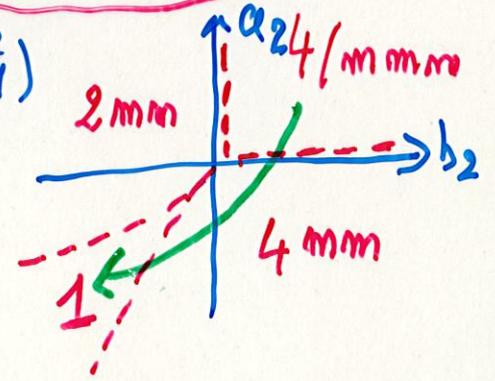


Case 1: Weak coupling: $\delta p_z^2 (p_x^2 + p_y^2)$

$a_2 = a_{02}(T - T_{c1}), b_2 = b_{02}(T - T_{c2})$: a_2 and b_2 change sign consecutively at T_{c1} and T_{c2} .
 Below T_{c1} $p_z, 4mm$
 Below T_{c2} $(p_x, p_y, p_z) 1$

$F(T, p, p_x, p_y, p_z) = F_1(p_z) + F_2(p_x, p_y) + \delta p_z^2 (p_x^2 + p_y^2)$

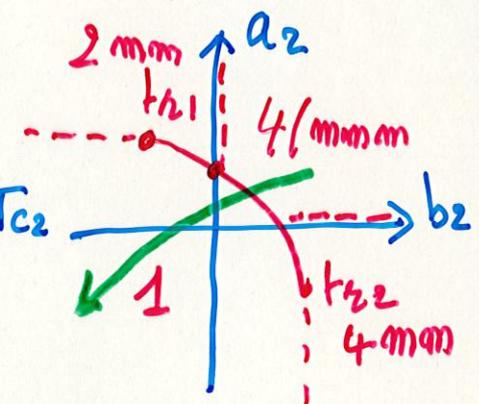
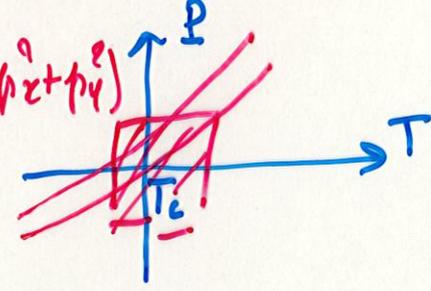
Integrity basis: $p_z^2, p_x^2 + p_y^2, p_x^2 p_y^2, p_z^2 (p_x^2 + p_y^2)$
 J_1, J_2, J_3, J_4



\Rightarrow phase 2mm absent from phase sequence.

Case 2: Strong coupling: $\delta p_z^2 (p_x^2 + p_y^2)$

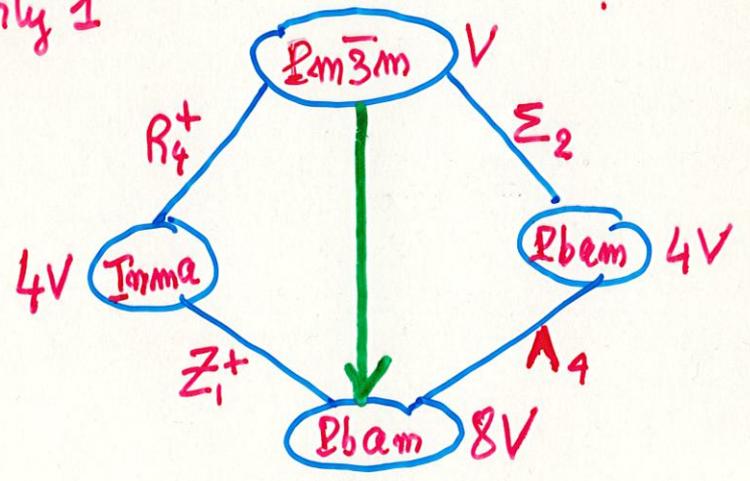
Triggering mechanism
 p_z triggers the onset of (p_x, p_y) at a temperature T_1 : $T_{c1} < T_1 < T_{c2}$



\Rightarrow First-order phase transition

\Rightarrow 4mm and 2mm absent. Only 1

Example: $PbZrO_3$:



The lowest degree coupling between 2 OP's determines their phase diagram.

⊙ Biquadratic coupling $\eta^2 \xi^2 \Rightarrow \xi$ and η have different symmetries (different IR's)

⊙ Linear quadratic coupling $\eta^2 \xi$

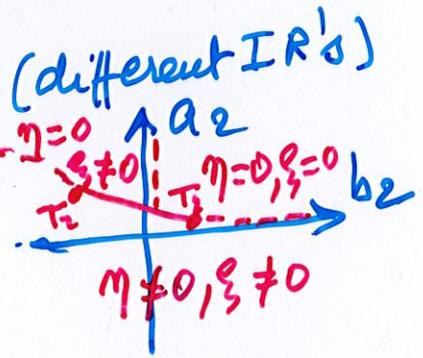
Case 1: improper coupling: η and ξ associated with the same IR
 η primary OP, ξ secondary OP

Examples: $\uparrow_z e_{zz}, (p_x^2 + p_y^2)(e_{xx} - e_{yy})$
 All ferroelectric - ferroelastics

Case 2: η and ξ have different symmetries (different IR's)

$$F(\eta, \xi) = a_2 \eta^2 + a_4 \eta^4 + b_2 \xi^2 + b_4 \xi^4 + \delta \eta^2 \xi$$

$\Rightarrow \xi$ destabilizes phase with $\eta \neq 0, \xi = 0$

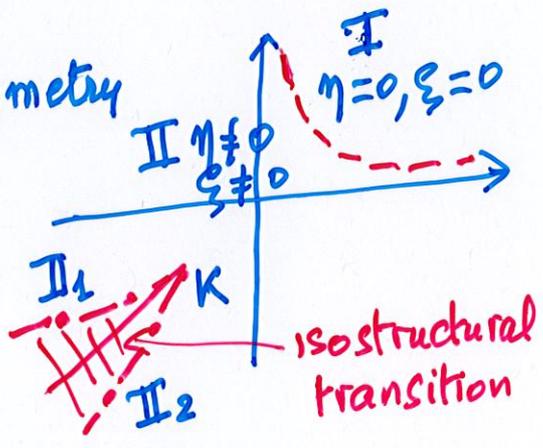


⊙ Bilinear coupling $\eta \xi$

$\Rightarrow \eta$ and ξ have the same symmetry

Example: $\text{KH}_2\text{PO}_4: I\bar{4}2d \rightarrow Fdd2$

$I\bar{4}2d$	1	2	S_4	S_4^3	C_2	C_2	$m \times 4$	$m \times 4$
$(p_z, e_{xy}) \Gamma$	1	1	-1	-1	-1	-1	1	1



XI Applicability of the theory to structural phase

transitions \Rightarrow Critical behaviour.

Landau Theory
 \downarrow

• Symmetry aspects rigorously verified by experimental results.

- Determination of low-symmetry phases associated with IR's of parent space-group
- Phase diagram from minimization of F.

• Verified qualitatively but not quantitatively

- Behaviour of physical quantities in the broken-symmetry phases in function of external variables (T, p) or fields (\vec{E} , \vec{H}).

• Why possible second-order transitions often first-order?

- Thermodynamic order of the transition

• Landau theory: same range of validity as mean field approximations

\Rightarrow Approximations modified when taking into account

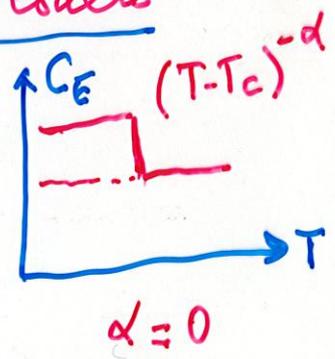
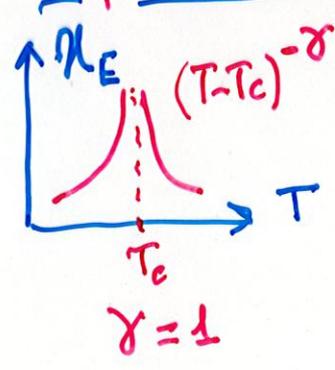
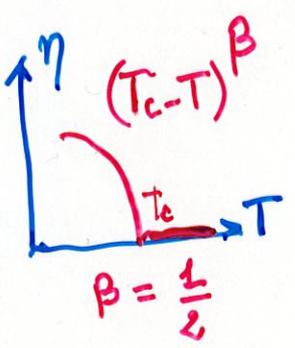
Critical fluctuations of order-parameter

\Rightarrow Renormalization Group approach to critical phenomena

\Rightarrow { Different power laws close to T_c
Thermodynamic order

(A) Critical exponents: theoretical predictions and experimental results

Landau \Rightarrow Prediction for 2nd order transitions



- In the RG approach the critical exponents ($|T-T_c|^{x_i}$) depend on
 - The spatial dimension d of the system (In general $d=3$ for structural transitions, but some reduction of the effective dimension can occur)
 - The number of OP components n
 - The anisotropies of the OP (Related to the anisotropies of the crystal, but in an indirect and complex way)
 - The range of the anisotropies of the interactions inducing the structural transitions.

● 4 classes of structural transitions have been mainly analyzed

- Elastic phase transitions (ferroelastics)
- Transitions with $d=3, n \leq 3$ with short-range forces
- uniaxial ferroelectrics
- Transitions with $n \geq 4$

1 Elastic transitions

It mainly includes "proper" ferroelastic transitions in which the spontaneous strain is the primary order-parameter.

- ⇒ Specific critical behaviour because:
- strong anisotropy of elastic instability
 - Divergence of fluctuations confined in limited regions of reciprocal space
 - Either in specific directions ($m=1$) or in planes ($m=2$)
- ⇒ For $m=1, d=3$ ⇒ "classical" Landau exponents
 $m=1, d < 5/2$ ⇒ non-classical
- ⇒ For $m=2, d=3$ ⇒ logarithmic correction to "classical" exponents

β and γ exponents measured for second-order transitions with $m=1$ and $m=2$.

Ferroelastics

	Material	Experimental Techniques	β	Relative extension of critical region $\frac{\Delta T}{T_c}$
Ferroelastics	LaP ₅ O ₁₄	{ γ -diffractometry birefringence	0.5 ± 0.007	3 · 10 ⁻²
			0.5	1 · 10 ⁻²
	TbVO ₄	{ γ -diffr. birefring.	0.5 ± 0.05	1 · 10 ⁻²
			0.5 ± 0.02	1 · 10 ⁻¹
	DyVO ₄	birefring.	0.5	1 · 10 ⁻³
	TmVO ₄	x-ray diffraction	0.5	?
	BiVO ₄	birefring.	0.5	4 · 10 ⁻¹
	KH ₂ (SeO ₃) ₂	{ birefring. x-ray diffrac.	0.5 ± 0.01	10 ⁻¹
			0.5	10 ⁻¹
	P ₂ AlO ₃	EPR	0.5	10 ⁻¹
TeO ₂	Neutron diffrac.	0.5	?	
Ferroferro	CsH ₁₈ NO	birefring	0.5 ± 0.01	5 · 10 ⁻³
			0.5	5 · 10 ⁻³
Ferroferro	RbH ₂ PO ₄	γ -diffr	0.5 ± 0.01	5 · 10 ⁻³
			0.5	5 · 10 ⁻³
Ferroferro	NaN ₃	NMR	0.27	?
			RbAg ₄ I ₅	birefring

Comments for m=1.

- Excellent agreement with "classical" exponents
- Reliable because: 2nd order character precisely known.
 - Coherent values for β and γ
 - Experimental techniques well adapted to elastic transitions (γ -diffrac. and birefring. for β Brillouin scatt. and ultrasound for γ)
 - power laws remain valid from 10⁻³ to 4 · 10⁻¹ ($\frac{\Delta T}{T_c}$).
- out of critical region:
 - Dependence of α and β well verified by Landau polynomial with degrees larger than 4.

	Material	Exp. Technique	γ	Relative extension $\Delta T/T_c$ of critical region
Ferroelastics	$m=1$ LaP ₅ O ₁₄	Brillouin Scattering	1 ± 0.02	$\pm 2 \cdot 10^{-2}$
	TbVO ₄	Ultrasound	1	10^{-1}
	DyVO ₄	{ Brillouin Scatt Ultrasound	$\neq 1$ $\neq 1$	$> 10^{-1}$
	TmVO ₄	Ultrasound	1	?
	BiVO ₄	Brillouin Scatt.	1	$5 \cdot 10^{-2}$
	KH ₂ (SeO ₃) ₂	{ Mecan. Reson. Brillouin Scatt	1 ± 0.02 1	10^{-1} $\pm 5 \cdot 10^{-3}$
		Y ₃ Si, Nb ₃ Sn	Ultrasound	1
	Ferro-ferro	C ₉ H ₁₈ NO	Electro-optical resp.	1 ± 0.02
KD ₂ PO ₄		Brillouin Scatt	1	10^{-2}
LiNH ₄ F ₄ H ₄ O ₆ ·H ₂ O		Brillouin Scatt	1	10^{-1}
$m=2$	KCN	Ultrasound	1	$5 \cdot 10^{-2}$
	RbAg ₄ I ₅	Ultrasound	Incomplete divergence	—

• But some exceptions to global (in and out) agreement.

Example: DyVO₄ • Classical exponents only for $\frac{\Delta T}{T_c} \leq 10^{-3}$

For $\frac{\Delta T}{T_c} > 10^{-3}$ non-classical power laws

- Adjustment requires Landau polynomial of degree 6-8
- To reconcile regimes dominated by fluctuations and without fluctuations \Rightarrow Elastic behaviour dominates in interval $\Delta T = \frac{W}{k}$ (W = elastic energy of one unit-cell - coincides with saturation value of spontaneous strain.)

- The extension of the "elastic" range varies from $\Delta T = 3K$ to $\Delta T = 528K$

Extension of the "elastic" domain

	$T_c(K)$	ΔT
$La_2S_3O_{14}$	400	240
$C_9H_{18}NO$	286	100
$TbVO_4$	33	35
$DyVO_4$	14	5
$BiVO_4$	528	200
$KH_2(SeO_3)_2$	212	350
KH_2PO_4	122	4
KCN	170	300
$RbAg_4I_5$	208	3

- ΔT is larger than 100° for most materials justifying a classical behaviour in the total interval of temperature.
- This is not true for $DyVO_4, KH_2PO_4, RbAg_4I_5$ which show a change in the critical regime.

① Comments for $m=2$. (Elastic anisotropy \Rightarrow Fluctuations along planes of reciprocal space)

- \Rightarrow Incomplete results for few examples ($KCN, NaN_3, RbAg_4I_5$) $\Rightarrow \beta$ differs (0.27, 0.56) but $\gamma=1$ for KCN .
- Cannot confirm logarithmic correction to classical values
- order of transitions shows contradictory results.

② Non classical structural transitions with $n \leq 3$

- Simple theoretical scheme because crystal anisotropies erased by fluctuations for transitions with short-range interactions \Rightarrow critical exponents depend exclusively on n .

They have been determined with precision (beyond precision of measurements)

	$n=1$	$n=2$	$n=3$
α	+0.110 (± 0.004)	-0.007 (± 0.006)	-0.115 (± 0.009)
β	+0.325 (± 0.0015)	+0.3455 (± 0.002)	+0.3645 (± 0.0025)
γ	1.241 (± 0.002)	1.316 (± 0.0025)	1.386 (± 0.004)

⊙ The results apply to improper ferroelastics and improper ferroelectrics, or structural transitions involving higher order tensors (piezoelectrics, ferroelastics, ...).

But many of the transitions are experimentally first-order, and no clear technique to measure γ (order-parameter is not of dielectric or elastic nature)

⇒ Results mainly obtained for some transitions of the perovskite family (α and β).

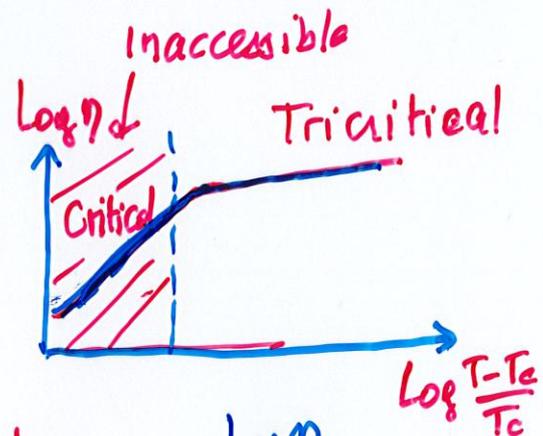
Material	α theory	α exp
K_2SeO_4	~ 0	+0.35
$TlCdF_3$	-0.11	+0.33
$RbCaF_3$	-0.11	+0.33
$CsRbCl_3$ I	-0.11	+0.5
II	~ 0	+0.4
$KMnF_3$	-0.11	+1.2
$BaMnF_4$	~ 0	0.54
$SrTiO_3$	-0.11	+0.14 \pm 0.4

Material	β theory	β exp
RbCaF ₃	0.325	0.18 ± 0.02
RbAlF ₄	0.345	0.28
NaNbO ₃	0.365	0.17 ± 0.02
SrTiO ₃	0.365	{ 0.33 ± 0.02 0.34 ± 0.02

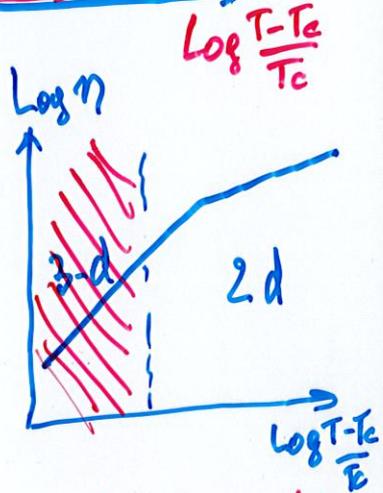
Comments

- α values systematically much higher than expected theoretical values ($0.14 < \alpha < 1.2$) which are close to 0.
- Except SrTiO₃, difference between measured β and theoretical β also obvious. β always smaller than theoretical value

- Proposed explanations for β
 - 1) System close to tricritical regime ($1/2 \rightarrow 1/4$)



2) Asymptotical regime assumed to be realized in narrow interval around T_c and not accessible to measurement.



3) Intermediate critical regime observed reflects a reduction of the effective dimension of the system $3d \rightarrow 2d$ due to secondary interactions competing with interactions determining the asymptotical regime \Rightarrow No explanation for α .

3) Uniaxial ferroelectrics

The subclass of uniaxial "proper" ferroelectric transitions contains many examples of confirmed second-order transitions and Larkin-Khmel'nitskii predicted logarithmic corrections for the mean-field approximations of their critical behaviour. The specific heat measured in TGS and the dielectric susceptibility of tri-sarcosine calcium chloride were adjusted with logarithmic corrections for their critical behaviour. However, the corrections are substantial and assume a change of critical regime close to T_c . A coherence is also lacking between the different physical quantities.

4) Critical exponents for $n \geq 4$.

For $n \geq 4$ crystalline anisotropies play essential role

⇒ Theoretical predictions less uniform and precise

⇒ Only a few measurements in structural transitions because difficulty to identify non-macroscopic order-parameter

- $n=4$ {
- $\text{NbO}_2 \Rightarrow 0.33 < \beta < 0.44$ (consistent with theory)
but also $\beta \approx 0.19 \pm 0.02$
 - Biphenyl $\text{C}_{12}\text{H}_{10} \Rightarrow \beta \approx 0.5$ in large interval ΔT
but not close to T_c

But for $n \geq 4$ possibility of forbidding second-order transitions.

B) Prediction of Thermodynamic Order.

- In Landau theory "Symmetry-Cube" criterion provides sufficient condition to the OP for first-order transition
- Secondary OP can transform second-order into first-order (and vice versa) by renormalizing sign of 4th degree coefficient.
- Similar result in Larkin-Bikin prediction of 2nd order \rightarrow 1st order under compressibility or interaction with acoustic phonons
- RG approach \Rightarrow fluctuation-induced first-order transition in absence of stable fixed point in the flow of Hamiltonians, or because the fixed point is inaccessible.
 - \Downarrow Problem of interest for $n \geq 4$. For $n \leq 3$ fixed point always exists (isotropic fixed point corresponding to isotropic 4th degree invariant)
- For $n \geq 4$ specific study required for each Hamiltonian form (anisotropic 4th degree invariants)
 - \Downarrow Existence or absence of stable fixed point calculated for $n=4$ (all) and $n=6,8$ (structural transitions)
 - \Rightarrow Possible comparison with experiments.

	Order-param. dimension n	order of transition	Stable fixed point	Active or not
VO_2	4	1	No	} Active
$CdSnAs_2$	6	1	Yes	
V_3Si	4	1	No	
Nb_3Sn	4	1	No	
$Ni_3B_7O_{13}I$	6	2	No	
NbO_2	4	2	Yes	Lifshitz
C_8CuCl_3	4	1	?	Lifshitz
$Cd(NO_3)_2$	6	1	Yes	Lifshitz
C_2N	6	1	No	Landau
K_2NaAlF_6	6	1	?	Landau
$C_{12}H_{10}$	4	2	Yes	Lifshitz
$BaMnF_4$	4	1	No	Lifshitz
$N_2H_6Cl_2$	6	1	?	Landau
$Ba_2NaNb_5O_{15}$	4	2	Yes	Lifshitz
$Al_{12}O_{24}(Cr_2O_4)_2$	6	1 \rightarrow 2	No	Active

Comments

- In VO_2, V_3Si, Nb_3Sn and $BaMnF_4$ the transitions are first-order, in agreement with the absence of stable fixed points in their Hamiltonians.
- Conversely $NbO_2, Ba_2NaNb_5O_{15}$ and $C_{12}H_{10}$ show a 2nd order consistent with presence of stable fixed point.

- But $Cd(NO_3)_2$ and $CdSnAs_2$ are first-order despite the presence of a stable fixed point.
- Conversely $Nb_3B_7O_{13}I$ has a second-order transition although its Hamiltonian has no stable fixed point.
- The cubic-orthorhombic ($I\bar{4}3m \rightarrow Abc2$) 6-dimensional order-parameter of the transition in Aluminate-Sodalites exhibits no stable fixed point, but its phase diagram shows curves of 1st and 2nd order transitions separated by a tricritical point.

Conclusion No definite rule can be inferred from the existence or absence of a stable fixed point with respect to the order of the transition.
 (presence of SFP does not exclude 1st order transition)
 Absence of SFP does not exclude 2nd order transition)

More general Conclusions

- Remarkable agreement of critical exponents with mean-field (Landau) predictions for elastic transitions.
- Systematic disagreement of experimental values with expected non-classical exponents: β smaller, α larger, as if fluctuations play more important role.
- Conjecture relating thermodynamic order with existence of stable fixed points partly contradicted for any n .
- At variance with second-order magnetic or liquid-crystal transitions, structural transitions more strongly influenced by marginal, uncontrollable factors: secondary order, Defects.