Landau theory in relation with the stability and symmetry of aperiodic crystals

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Materials that are periodic crystals:

- All types of materials
  - Minerals
  - Metals, alloys
  - Insulators
  - Inorganic Material
  - Organic materials
- In all types of conditions:

  - Some temperature interval or at all temperatures up to melting

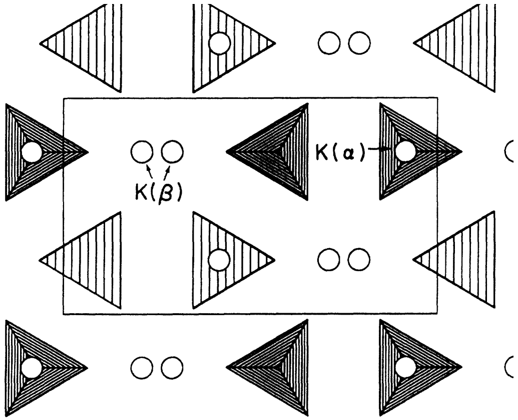
  - Some pressure interval….

  - at about 0K or at high temperatures ….

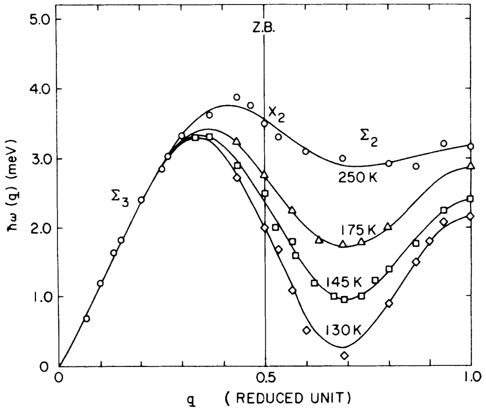
Incommensurate Modulated Structures - origin

K_2SeO_4 - (A_2BX_4)

Unstable mode



temperature dependent
soft-phonon branch:



Iizumi et al. Phys. Rev. B (1977)

Steric mechanism
calculation varying the “size” of K:

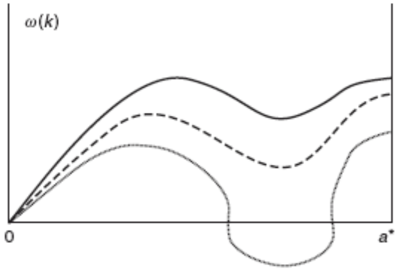
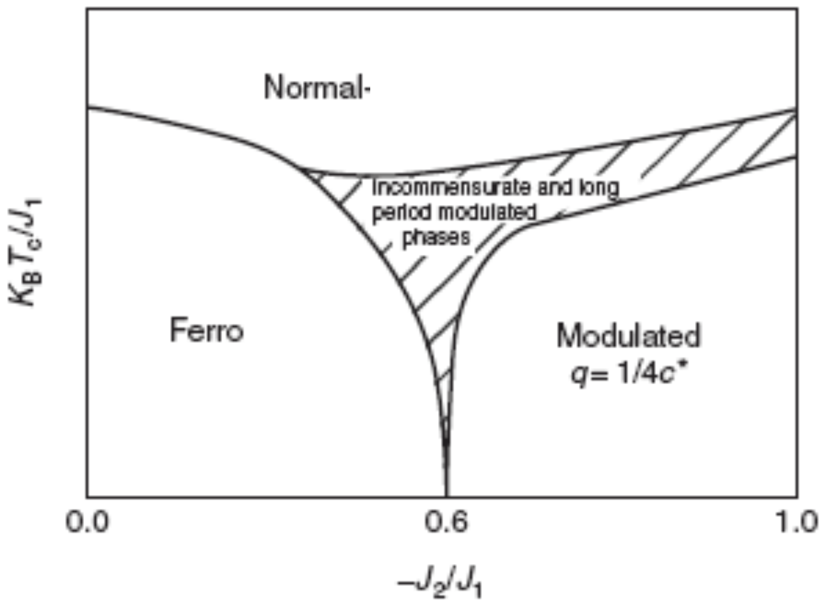


Figure 9 Scheme of the variation of the soft-mode branch in orthorhombic A_2BX_4 compounds as a function of the effective size of one of the independent A cations after the calculations in Etxebarria I, Perez-Mato JM, and Madariaga G (1992) *Physical Review B* 46: 2764. The branch lowers and becomes unstable at an incommensurate wave vector as the size increases. Imaginary frequency values are represented as negative.

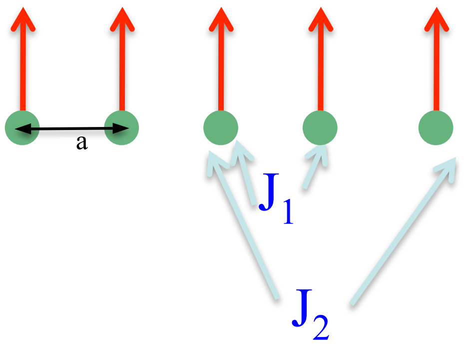
Incommensurate Modulated Structures - origin

“Competing interactions”

ANNNI Model
(Axial next nearest neighbour Ising model)



“fustration”



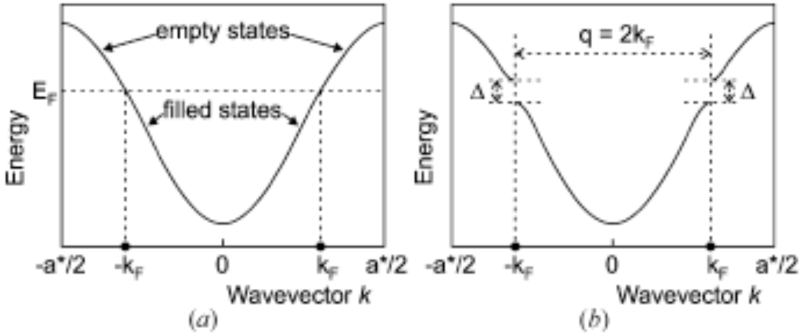
$\Delta E = -J.\ S_i.S_j$

$J_1>0,\ J_2<0$

Incommensurate Modulated Structures - origin

Charge density waves (CDW)
Peierls mechanism

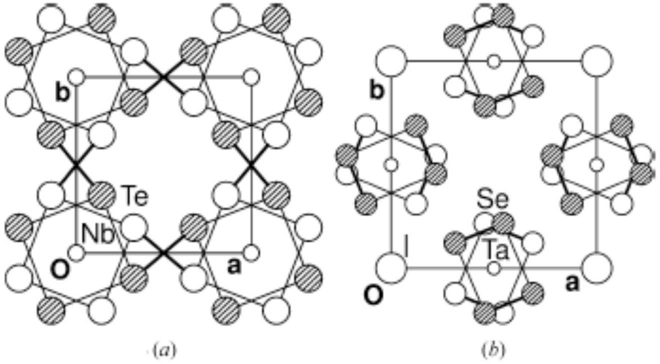
Transition metal-insulator



(a) (b)

Figure 1

Van Smaalen, Acta Cryst. (2005)



(a) (b)

Figure 10
Projections of the basic structures of (a) $NbTe_4$ and (b) $(TaSe_4)_2I$. Hatched and open circles are Te/Se atoms at $z = 0$ and 0.5, respectively. Nb/Ta are at $z = 0.25$ and 0.75, and I is at $z = \pm 0.15$.

Fermi surface nesting:

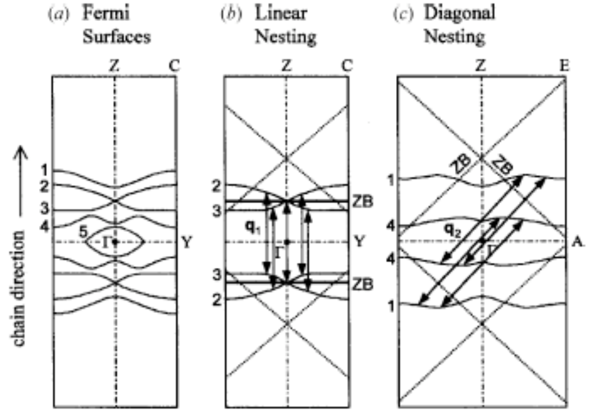
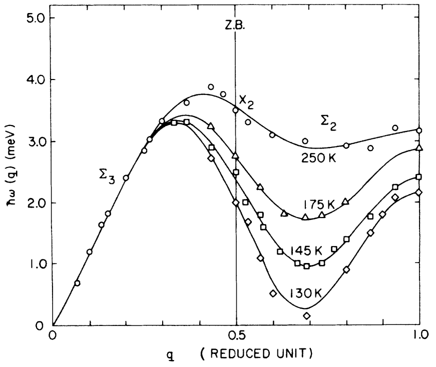


Figure 5
Sections of the Fermi surface of $NbSe_3$, showing the nesting of bands 2 and 3 with $\mathbf{q}^1 = (0, 0.241, 0)$ (responsible for the CDW at $T_{\mathrm{CDW}} = 145$K), and of bands 1 and 4 with $\mathbf{q}^1 = (1/2, 0.263, 1/2)$ (responsible for the second CDW at $T_{\mathrm{CDW}} = 59$ K). Reprinted figure with permission from Schafer *et al.* (2001). *Phys. Rev. Lett.* **87**, 196403. Copyright (2001) by the American Physical Society.

INCOMMENSURATE STRUCTURES AS RESULT OF A PHASE TRANSITION:

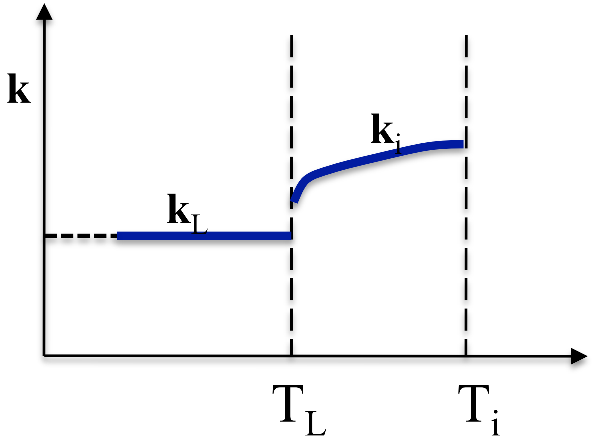
Simplest scenario

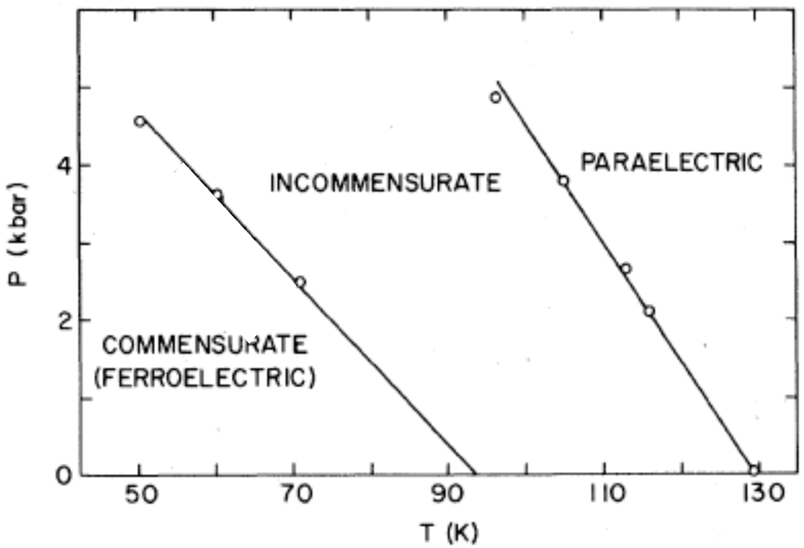
Example: K_2SeO_4



Lock-in phase $\overset{T_L}{\overline{\qquad\qquad}}$ INC phase $\overset{T_i}{\overline{\qquad\qquad}}$ Parent phase

wave vector T-dependence



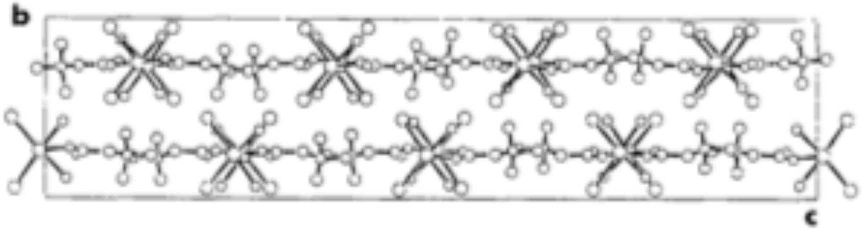


Press et al. 1980

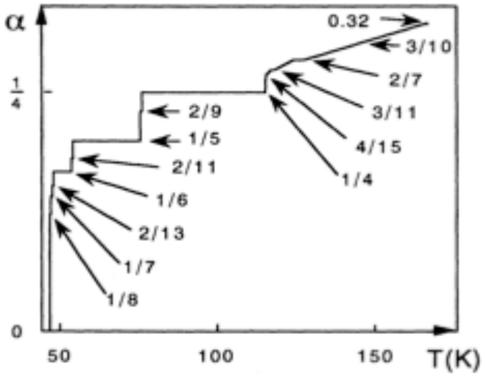
INCOMMENSURATE STRUCTURES AS RESULT OF A PHASE TRANSITION:

More complex situations:

$(CH_3)_3NCH_2$-$COOCaC_{12}.2H_20$ (**BCCD**)

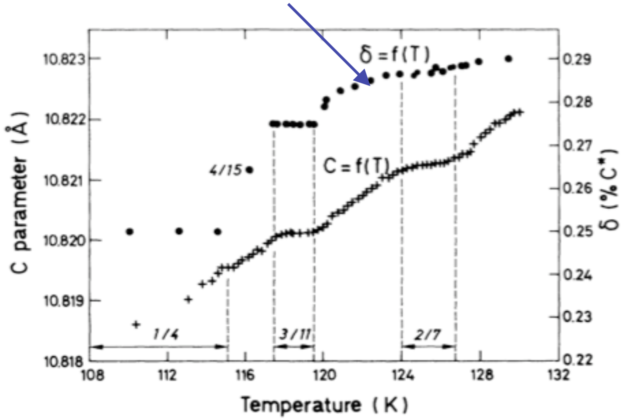


wave vector T-dependence



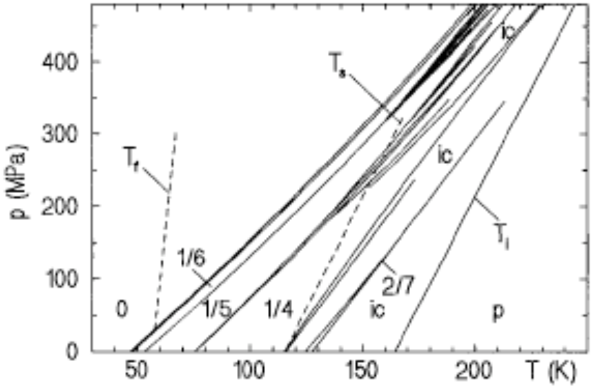
Kappler et al. 1993

wave vector T-dependence

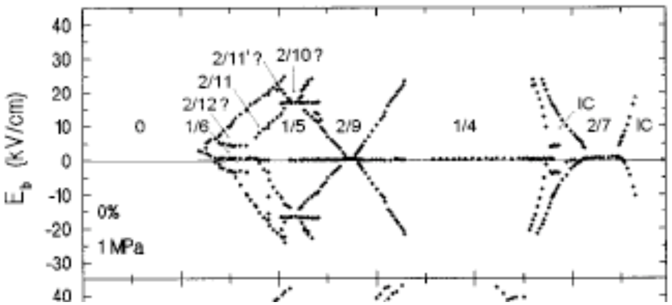


Kiat et al. 1997

Phase diagram with pressure



Phase diagram with electric field

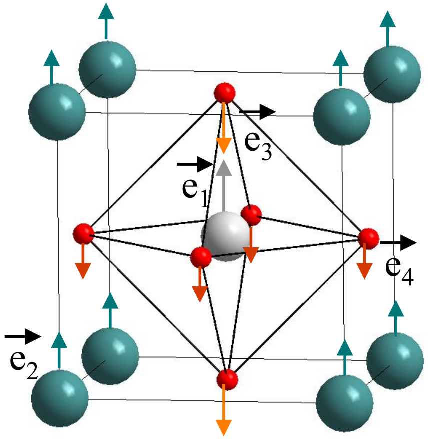


Le Maire et al. 1999

Phenomenological description of a structural phase transition – Landau Theory

<u>primary</u> distortion mode : order parameter = collective coordinate

distortion = Amplitude * polarization vector



Description of a displacive "mode":

$$\vec{u}(\text{atoms}) = Q\ \vec{e}$$

amplitude

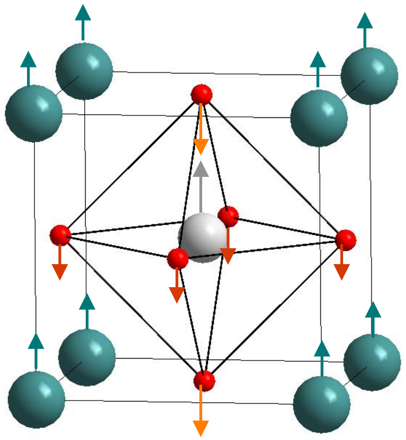
polarization vector

$$e = (\ \vec{e}_1\ , \vec{e}_2\ , \vec{e}_3\ , \vec{e}_4\ )$$

normalization: $|\vec{e}_1|^2 + |\vec{e}_2|^2 + |\vec{e}_3|^2 + 2\,|\vec{e}_4|^2 = 1$

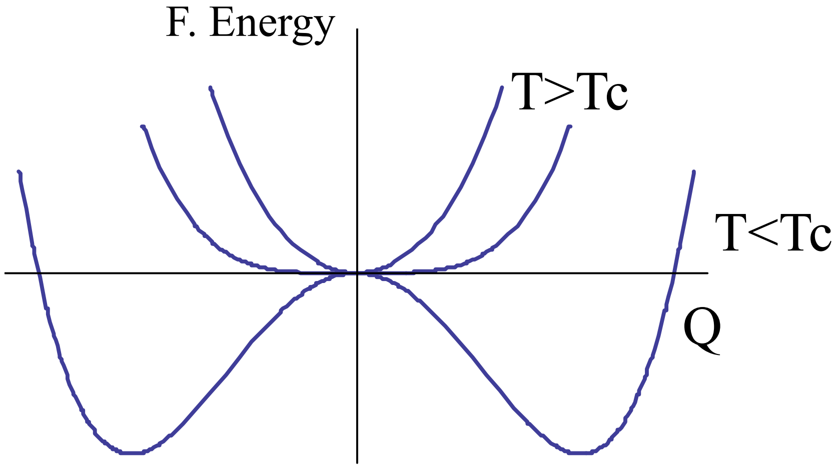
(within a unit cell)

Phenomenological description of a structural phase transition – Landau Theory



primary distortion mode : order parameter

Unstable collective degree of freedom:



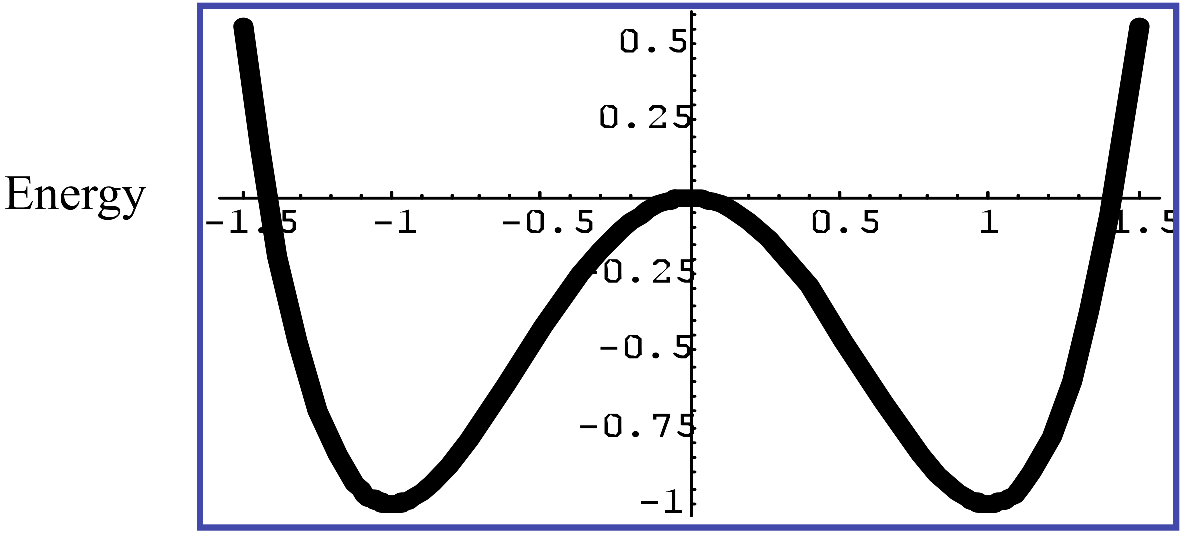
$$E = Eo + 1/2\ \kappa(T)\ Q^2 + \dots$$

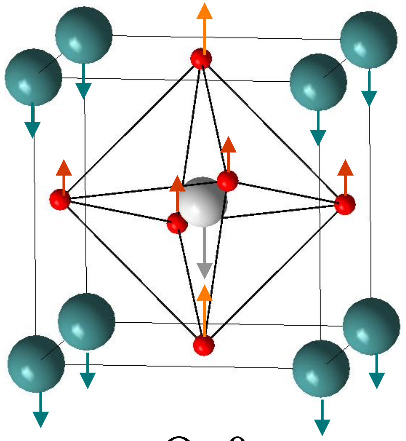
$\kappa(T)<0 \quad T<Tc$

distortion modes:

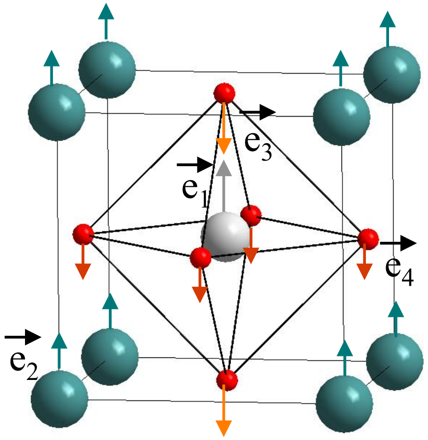
- displacive type: local variable =atomic displacements
- order-disorder type: local variable: site occupation probabilities
- magnetic type: local variable: atomic magnetic moments

Multistability:



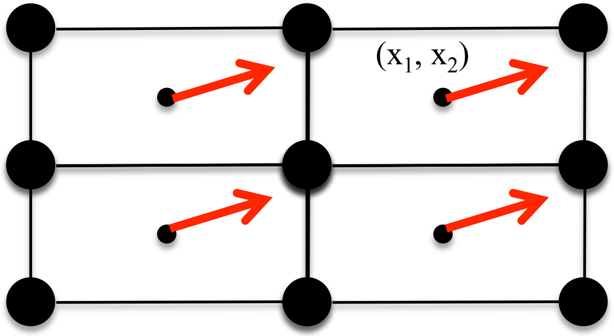


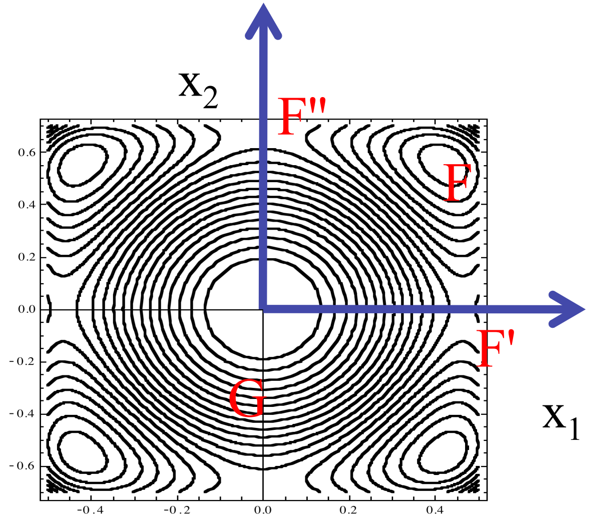
Q<0



Q >0

A mutidimensional energy map:





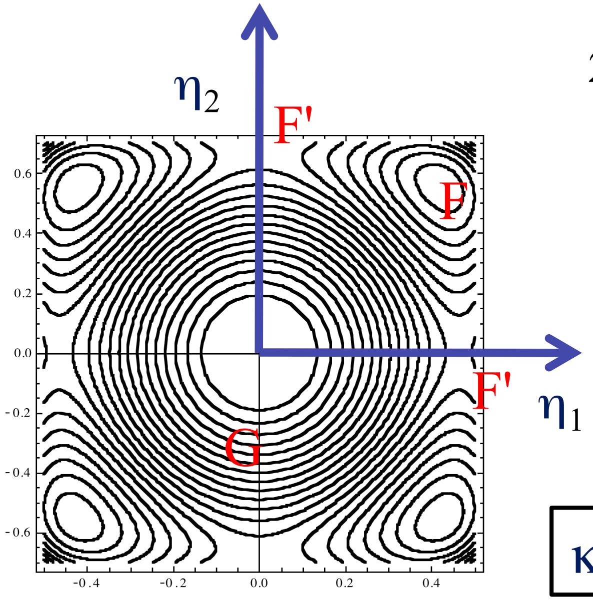
- Energy is extremal (maximum or minimum for symmetry breaking distortions)

- Taylor expansion of the energy (restricted by symmetry) :

invariants for all symmetry operations of G

$$E = Eo + \frac{1}{2}\ \kappa_1\ x_1^2 + \quad \frac{1}{2}\ \kappa_2\ x_2^2 + \quad \beta_1\ x_1^4 + \quad \beta_2\ x_2^4 + \quad \gamma\ x_1^2\ x_2^2 + \ldots.$$

The Landau potential: a temperature dependent (free) energy map

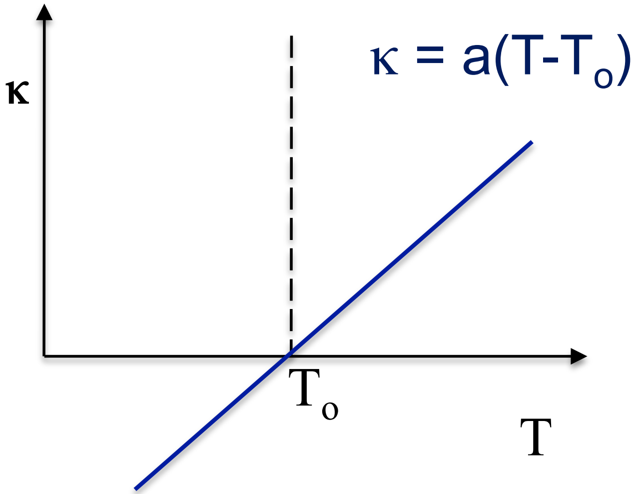


2dim order parameter

$\vec{Q} = (\eta_1 , \eta_2)$

collective coordinate

$\kappa < 0$



- Taylor expansion of the energy (restricted by symmetry) :

invariants for all symmetry operations of G

$$E = Eo + \tfrac{1}{2}\,\kappa\,(\eta_1^2+\eta_2^2) + \tfrac{1}{4}\,\beta\,(\eta_1^4 + \eta_2^4) + \gamma\,\eta_2^2\,\eta_2^2$$

- Multistability : energetically equivalent configurations/domains – switching properties
- Energy is extremal (maximum or minimum for symmetry breaking distortions)

Symmetry break in a commensurate-commensurate transition

High symmetry group G = {g}

Irreducible representation of G (irrep) (matrices)

$T(g)\vec{Q} = \vec{Q}$

g belongs to F

$T(g)\vec{Q} = \vec{Q}' \neq \vec{Q}$

g does not belong to F: $\vec{Q}'$ equivalent but distinguishable state

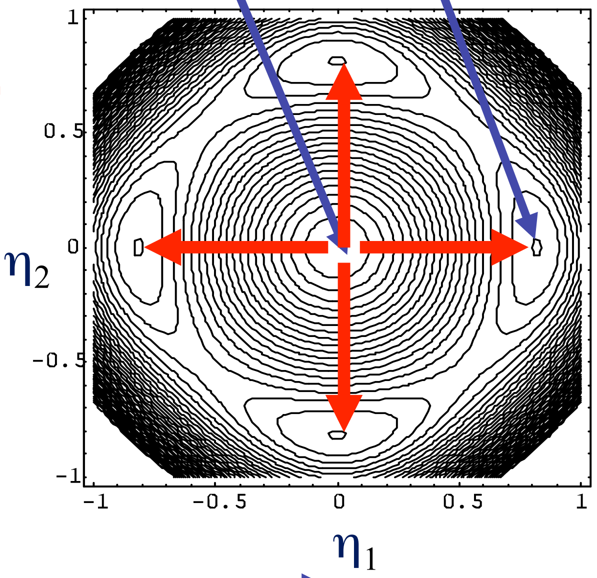
group-subgroup relation:

$G \rightarrow F$

F: isotropy subgroup

High symmetry

Low symmetry



Key concept of Landau Theory:
It defines the symmetry break

amplitude

→ Order parameter $\vec{Q} = (\eta_1, \eta_2) = \rho\,(a_1,a_2)$

$a_1^2+a_2^2 = 1$

Unstable modes in the description of the energy at 0K of a parent phase (ab-initio calculations):

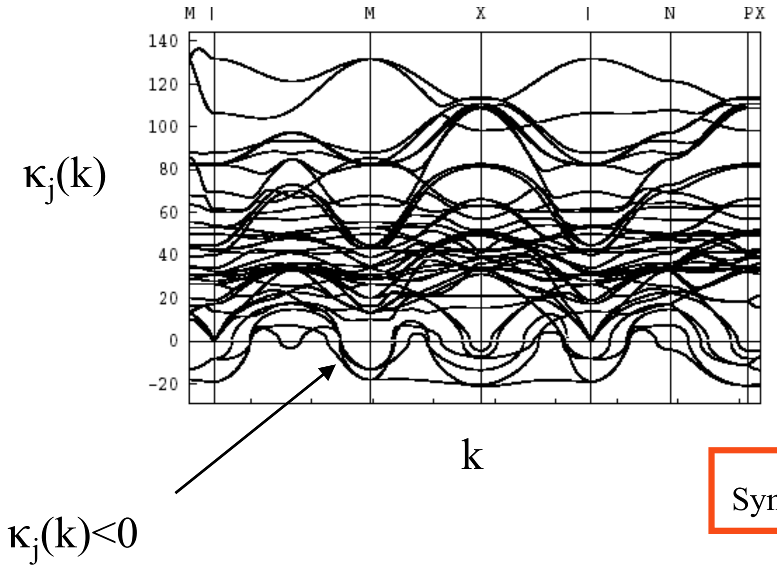
Energy around the high-symmetry non-distorted configuration:

$$E = Eo + 1/2 \sum\kappa_j(k)\ |Q_i(k)|^2\ + \ldots$$

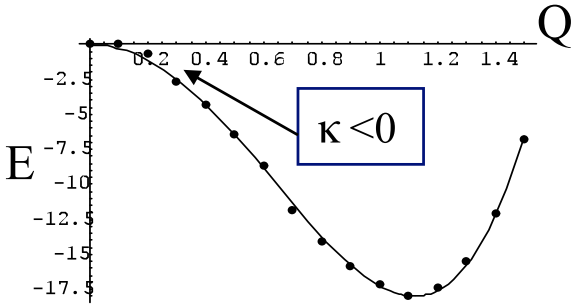
stiffness coefficients

Normal (static) coordinates

Ab-initio calculation of static normal modes in the high-symmetry configuration

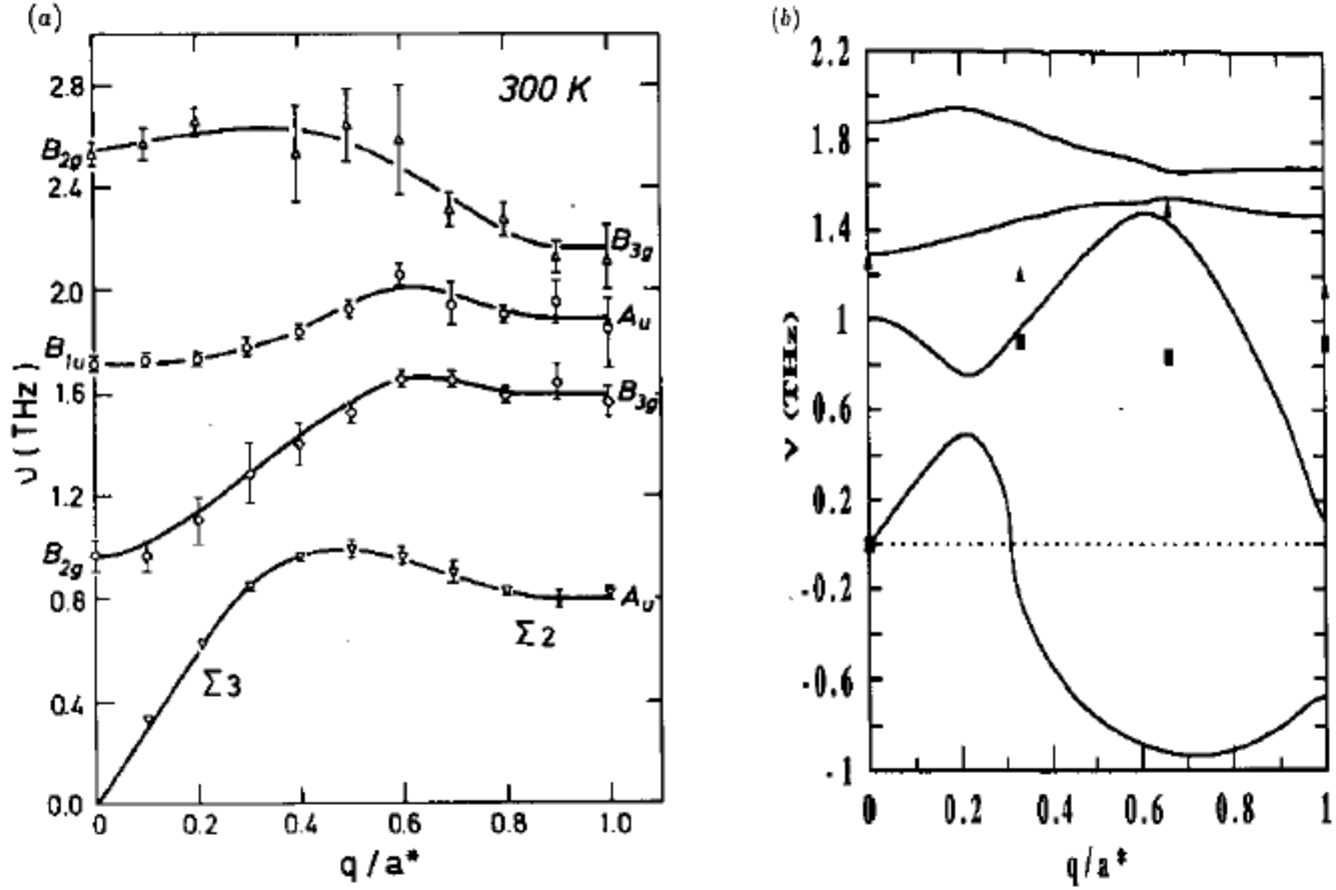


Energy as a function of the amplitude of an unstable Q:



Symmetry of distortion modes: irreducible representations (group theory)

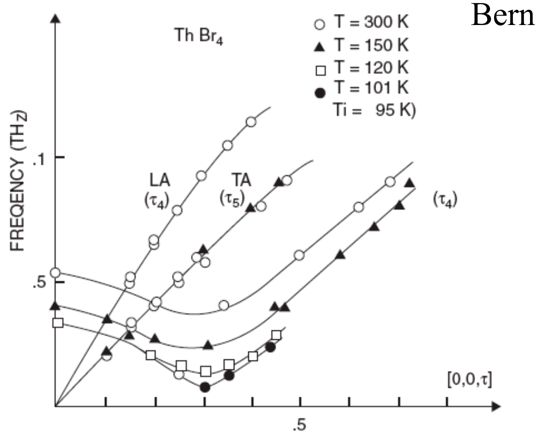
Thermal stabilization of unstable phonon branches



Etxebarria et al. 1992

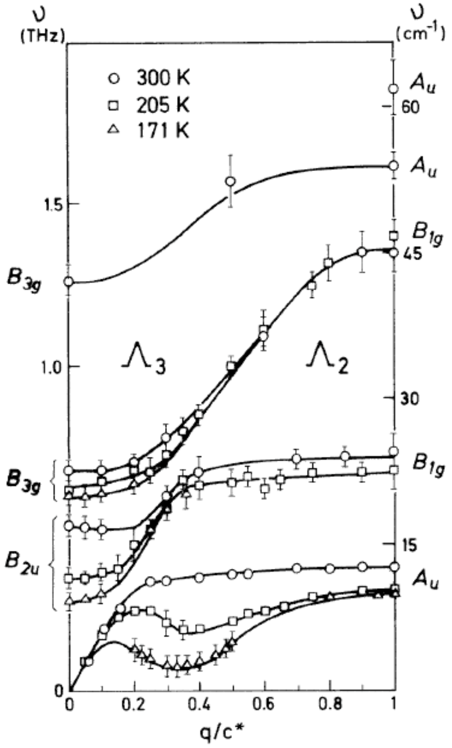
Landau assumption: $\kappa(k_o, T) = a(T-To)$

Soft-modes leading to incommensurate phases



Bernard et al. 1983

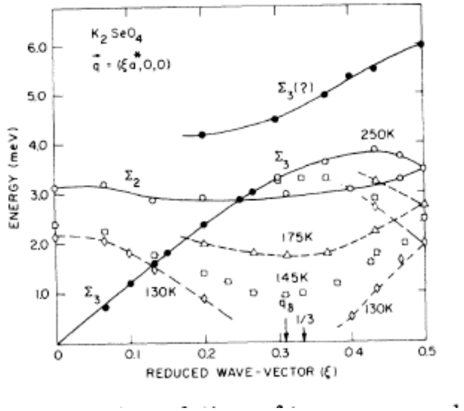
ThBr$_4$



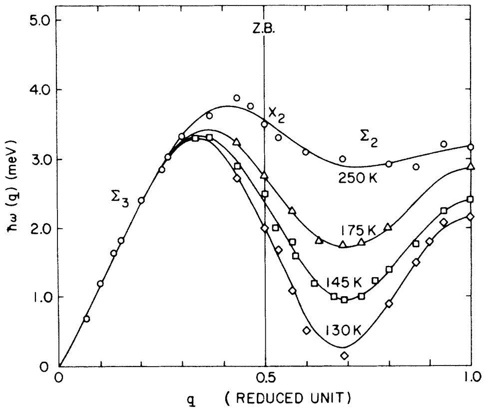
BCCD

Hlinka et al. 1996

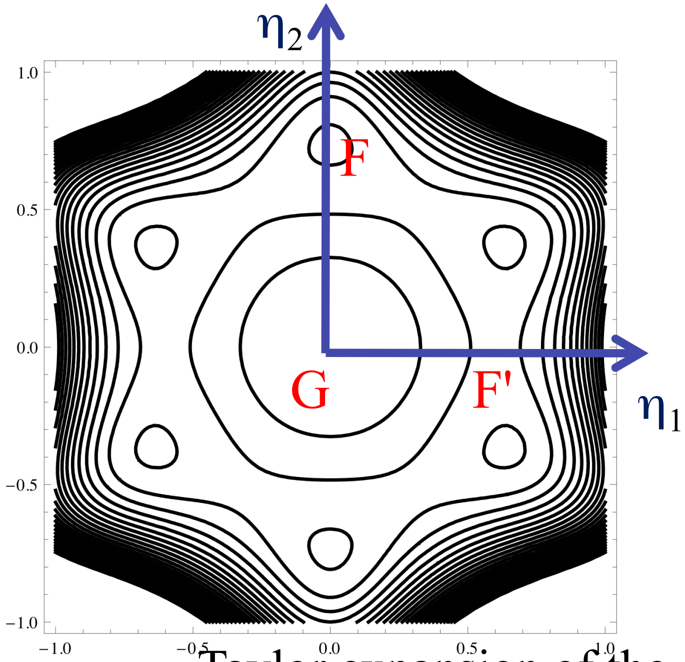
K$_2$SeO$_4$



Iizumi et al. 1977



Landau potential (T<Tc) of a commensurate structure with triplicated cell



$G \longrightarrow F$ (c'=3c) $\mathbf{k_L} = 1/3\ \mathbf{c^*}$

$$\boxed{\mathbf{u}(\text{atom},\mathbf{l}) = Q_k\, \mathbf{e}(\text{atom}) \exp[i\mathbf{k_L}.\mathbf{l}] + Q_{-k}\, \mathbf{e}^*(\text{atom}) \exp[-i\mathbf{k_L}.\mathbf{l}]}$$

2d order parameter $(Q_k, Q_{-k}) = (\eta_1, \eta_2)$

$Q_k = Q^*_{-k}$ $Q_k = \rho\, e^{\,i\,\theta}$

$\eta_1 = \rho\ \mathrm{Cos}(\theta)$

$\eta_2 = \rho\ \mathrm{Sin}(\theta)$

- Taylor expansion of the energy (restricted by symmetry) :

umklapp term

$$E = Eo + \tfrac{1}{2}\kappa\, Q_k Q_{-k} + \tfrac{1}{4}\beta_1 Q_k^2 Q_{-k}^2 + 1/6\,\gamma_1 Q_k^3 Q_{-k}^3 + 1/6\,\gamma_2 (Q_k^6 + Q_{-k}^6)$$

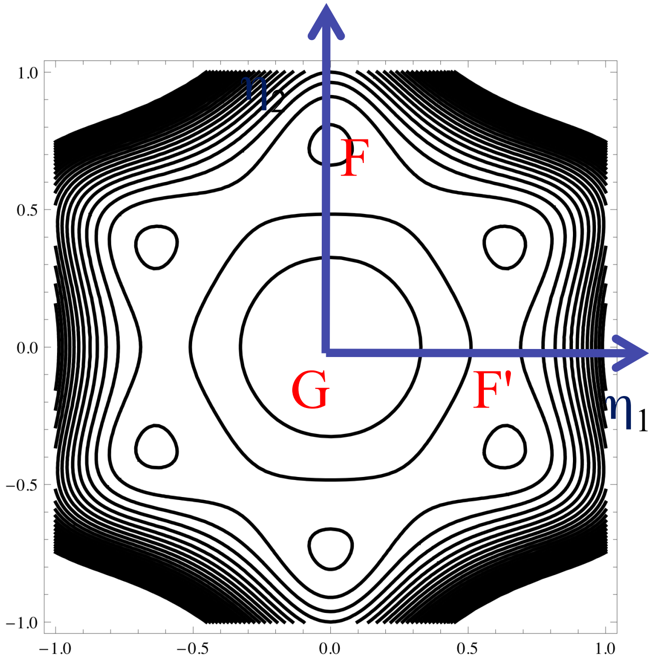
invariance for all symmetry operations of G:

$(Q_k^3 + Q_{-k}^3)$ – $\Sigma\, \mathbf{k}$ = r. lattice v. but not invariant for all G

$(Q_k^3 - Q_{-k}^3)$ – not invariant

$$E = Eo + \tfrac{1}{2}\kappa\, \rho^2 + \tfrac{1}{4}\beta_1 \rho^4 + 1/6\,\gamma_1 \rho^6 + 1/6\,\gamma_2\, \rho^6 \mathrm{Cos}(6\theta)$$

The Landau potential: a transition to a commensurate structure with triplicated cell



$G \longrightarrow F$ (c'=3c) $\mathbf{k}_L = 1/3\ \mathbf{c}^*$

$$\boxed{\mathbf{u}(\text{atom},\mathbf{l}) = Q_k\ \mathbf{e}(\text{atom}) \exp[i\mathbf{k}_L.\mathbf{l}] + Q_{-k}\ \mathbf{e}^*(\text{atom}) \exp[-i\mathbf{k}_L.\mathbf{l}]}$$

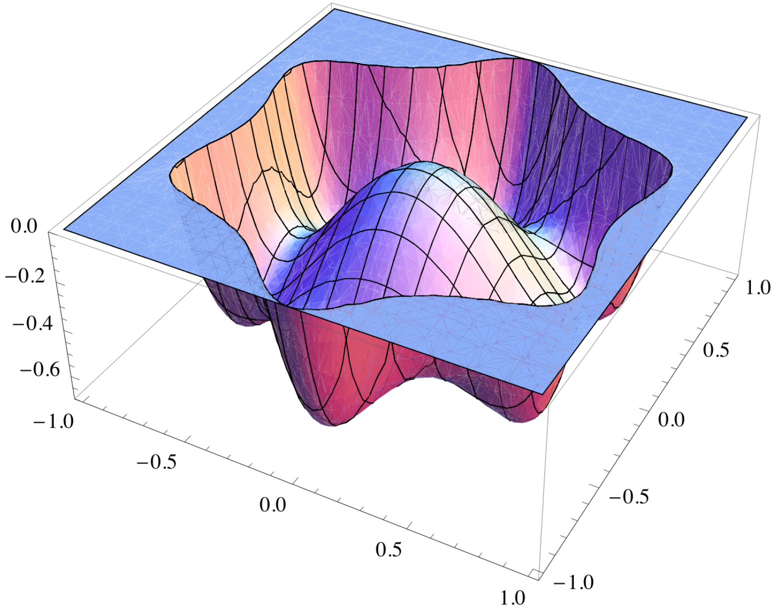
$$Q_k = \rho\ e^{i\theta}$$

$$E = Eo + \tfrac{1}{2}\kappa\rho^2 + \tfrac{1}{4}\beta_1\rho^4 + 1/6\ \gamma_1\rho^6 + 1/6\ \gamma_2\rho^6\mathrm{Cos}(6\theta)$$

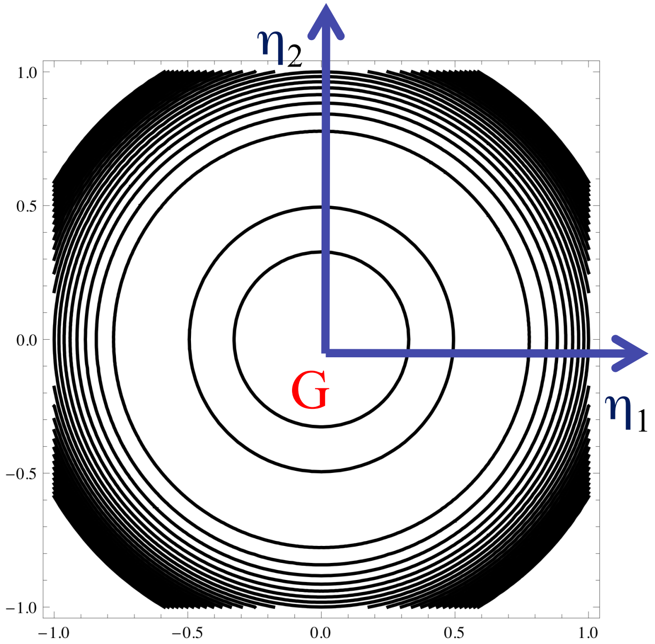
Number of energetic equivalent configurations (domains): 6

In general, number of domains:

superlattice factor*reduction factor of point group = 3*2



The Landau potential for a transition into an incommensurate structure



$$G \longrightarrow F \ (c' \approx 3c) \qquad \mathbf{k_i} \approx 1/3\ \mathbf{c^*}$$

$$\boxed{\mathbf{u}(\text{atom},\mathbf{l}) = Q_k\ \mathbf{e}(\text{atom})\ \exp[i\mathbf{k_i}.\mathbf{l}] + Q_{-k}\ \mathbf{e}^*(\text{atom})\ \exp[-i\mathbf{k_i}.\mathbf{l}]}$$

2d order parameter $(Q_k, Q_{-k}) = (\eta_1, \eta_2)$

$Q_k = Q^*_{-k}$ $\qquad Q_k = \rho\ e^{i\theta}$ $\qquad \eta_1 = \rho\ \mathrm{Cos}(\theta)$

$\eta_2 = \rho\ \mathrm{Sin}(\theta)$

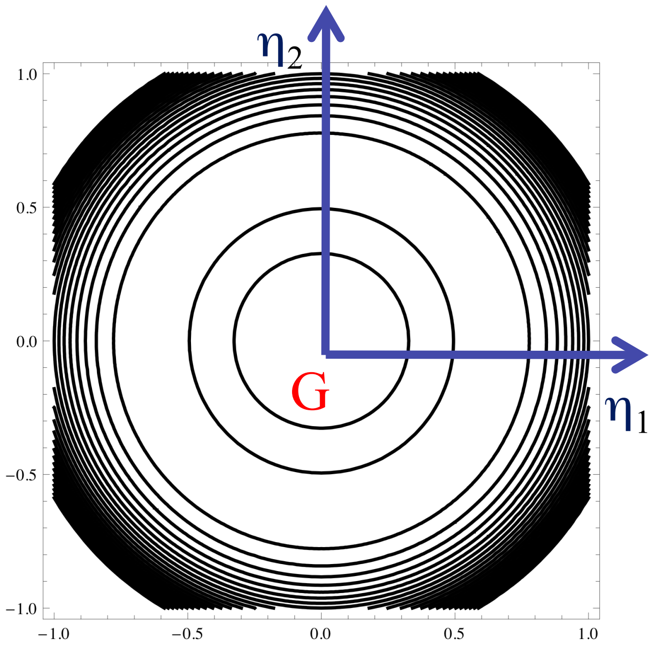
- Taylor expansion of the energy (restricted by symmetry) :

$$E = Eo + \tfrac{1}{2}\kappa\, Q_k Q_{-k} + \tfrac{1}{4}\beta_1 Q_k^2 Q_{-k}^2 + 1/6\,\gamma_1 Q_k^3 Q_{-k}^3 + 1/6\,\cancel{\gamma_2 (Q_k^6 + Q_{-k}^6)}$$

$$E = Eo + \tfrac{1}{2}\kappa\,\rho^2 + \tfrac{1}{4}\beta_1\rho^4 + 1/6\,\gamma_1\rho^6 + \cancel{1/6\,\gamma_2\,\rho^6 \mathrm{Cos}(6\theta)}$$

Σ **k** can never be a non-zero reciprocal lattice vector !

The Landau potential for a transition into an incommensurate structure



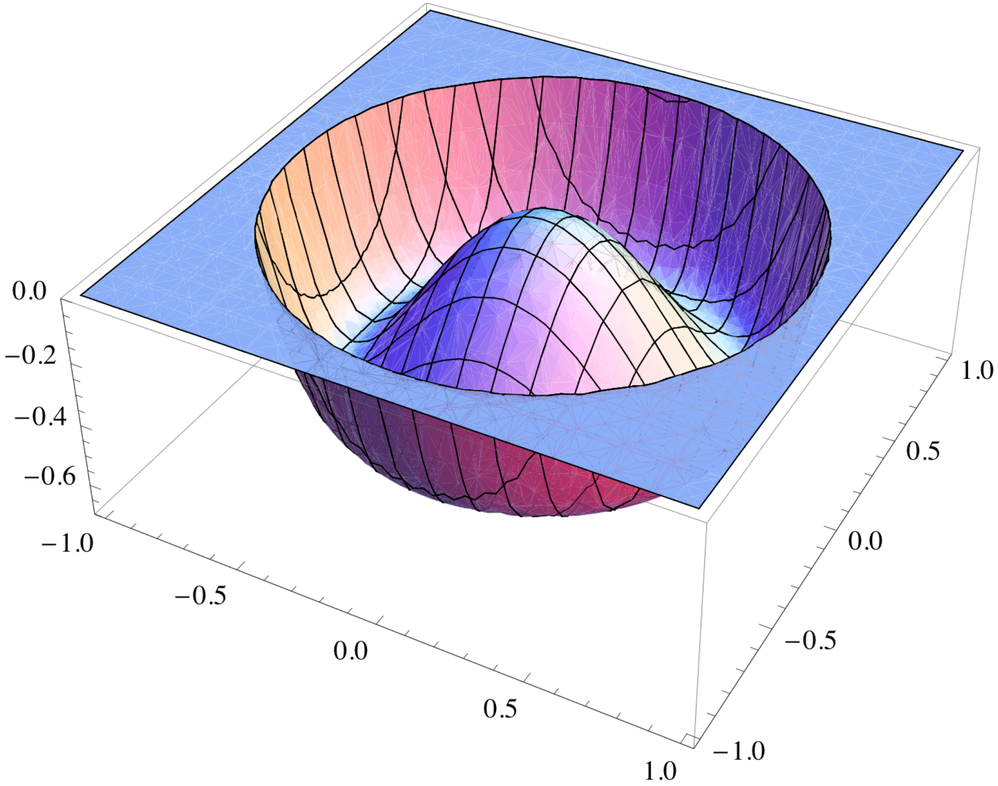
$$G \longrightarrow F \ (c'\approx 3c) \qquad \mathbf{k} \approx 1/3\ \mathbf{c}^*$$

$$\boxed{\mathbf{u}(\text{atom},\mathbf{l}) = Q_k\ \mathbf{e}(\text{atom})\ \exp[i\mathbf{k}.\mathbf{l}] + Q_{-k}\ \mathbf{e}^*(\text{atom})\ \exp[-i\mathbf{k}.\mathbf{l}]}$$

2d order parameter $(Q_k\,,\, Q_{-k})$ $Q_k = \rho\ e^{\,i\,\theta}$

$$E = Eo + \tfrac{1}{2}\,\kappa\,\rho^2 + \tfrac{1}{4}\,\beta_1\,\rho^4 + 1/6\ \gamma_1\,\rho^6$$

Number of energetic equivalent configurations (domains): infinite !



Energy is invariant for a change of the phase of the order parameter: **PHASONS**

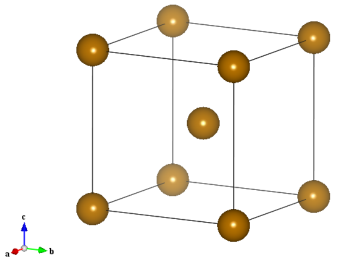
Symmetry and Physics

Symmetry break → Phase Transition

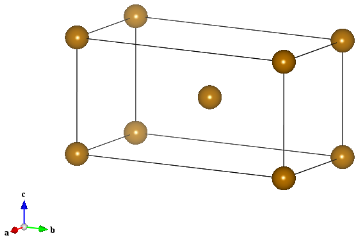
A symmetry property in a solid is NOT ONLY a certain geometric or transformation condition.

A well defined symmetry operation in a thermodynamic system must be maintained when scalar fields (temperature, pressure,…) are changed (except if a phase transition takes place).

The break of a symmetry condition (without external fields) necessarily implies a thermodynamic phase transition.



a=b=c symmetry property



a = c
b = 2a

"nice" but not a symmetry property

Symmetry in incommensurate crystals

A symmetry operation fullfills:

- the system is undistinguishable after the transformation
- the operation belongs to the set of transformations keeping the energy invariant

Symmetry operations in commensurate crystals:

Rotations, translations, space inversion, (time inversion)
and/or their combinations:

space group: $\{ \{R_i | t_i\} \}$

SUPERSPACE SYMMETRY IN INCOMMENSURATE CRYSTAL

•An INC phase has a well defined symmetry given by a superspace group.

Symmetry: no lattice → no space group

BUT there are additional zero-energy transformations:

arbitrary shifts of the modulation phase (phason)

“superspace” symmetry operations: $(R|t,\tau)$

Roto-inversion operation

translation

phase shift

Symmetry: superspace group = set of operations { $(R|t,\tau)$ } keeping the structure undistinguishable

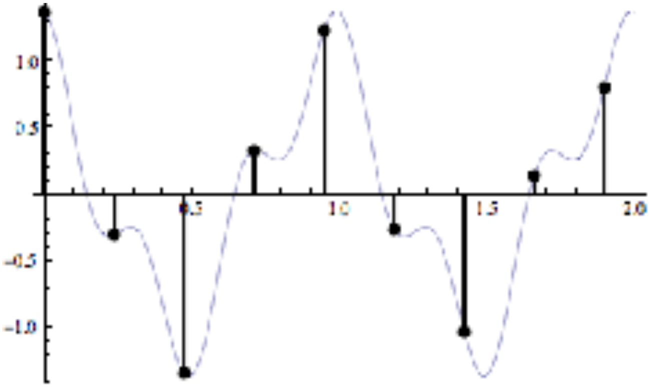
point group = set of operations { R }

Well defined symmetry operation: it is maintained when scalar fields are changed, except at a phase transition.
Why: because the symmetry operations are a subgroup of the continuous group of transformations keeping the energy, including the phason transformations.

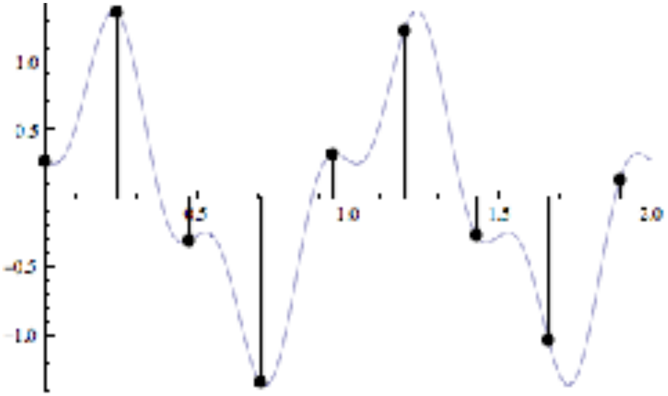
Superspace translational symmetry: {E|**T**, -**q**.**T**}
real spac. lat. translation + phase shift (internal space translation)

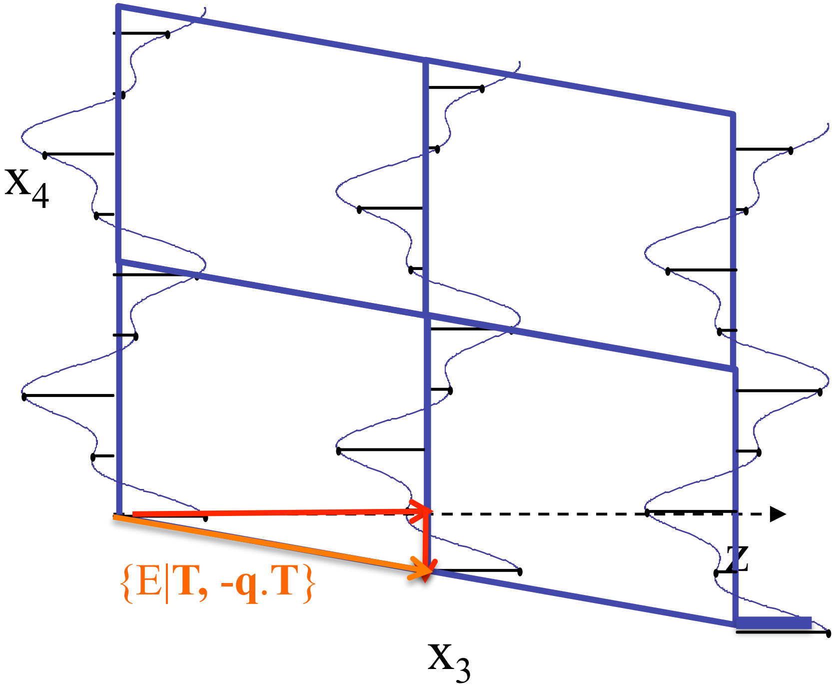
(combination of transformations that keep energy invariant)

“lost” real space translation translation:{E|T, 0}



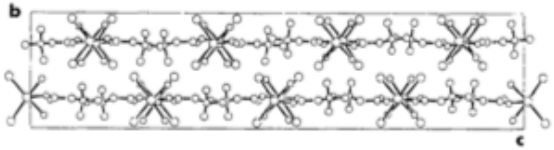
phase shift translation:{E|0, -q.T}





The old story of BCCD

$\mathrm{Pnma} \longrightarrow \mathrm{INC}$



How to calculate the superspace group of the INC phase from the knowledge of the symmetry of the order parameter:

$$\boxed{\mathbf{u}(\text{atom},\mathbf{l}) = Q_k\, \mathbf{e}(\text{atom}) \exp[i\mathbf{k_i}.\mathbf{l}] + Q_{-k}\, \mathbf{e}^*(\text{atom}) \exp[-i\mathbf{k_i}.\mathbf{l}]}$$

Generalization of invariance equation:

$(R|t,\tau)$ belongs to superspace group if :

$$\begin{pmatrix} e^{i2\pi\tau} & 0 \\ 0 & e^{-i2\pi\tau} \end{pmatrix} T[(R|t)] \begin{pmatrix} Q_k \\ Q_{-k} \end{pmatrix} = \begin{pmatrix} Q_k \\ Q_{-k} \end{pmatrix} \quad (Q_k = Q_{-k})$$

phase shift

operation of Pnma

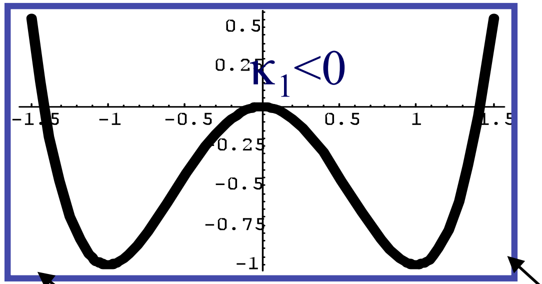
order parameter:
primary mode amplitude

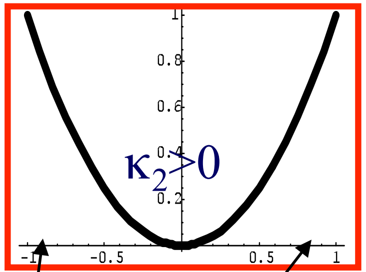
Additional term in an incommensurate phase

$$T[(m_y|0\ ½\ 0)] = \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix} \rightarrow (m_y|0\ ½\ 0,\ ½\ )$$

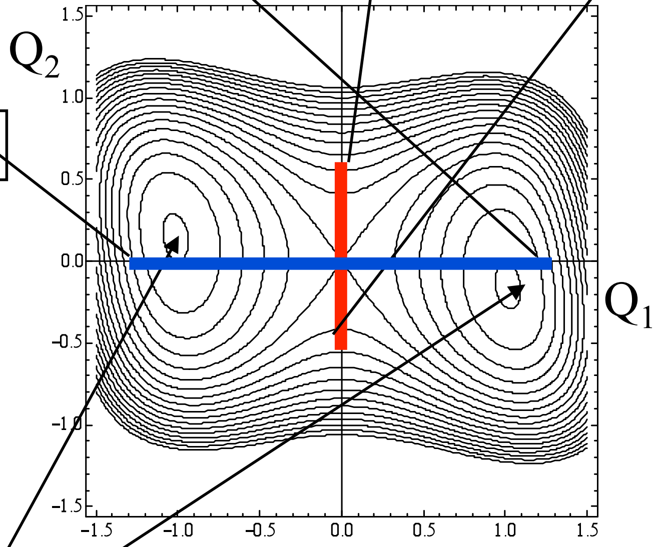
$$\mathrm{Pnma} \longrightarrow \mathrm{Pnma}(0\ 0\ \gamma)1s\text{-}1$$

Secondary weaker spontaneous variables





Example of a (free) energy map with primary order parameter (Q_1) and secondary spontaneous variable(Q_2):



faintness index

$\kappa_1<0$ $\kappa_2>0$

$$E = Eo + \tfrac{1}{2}\ \kappa_1 Q_1^2 + \tfrac{1}{2}\ \kappa_2 Q_2^2 + \gamma Q_1^3 Q_2 +$$

Anharmonic allowed coupling

$$Q_2{}^{\text{equil.}} = -(\gamma / k_2)\, Q_1{}^{3}$$

Equivalent structures of the same free energy

Universal/ubiquitous couplings

$\rho_X^2\ \rho^2$

ρ_X : amplitude of distortion mode of **any** wave vector **k**

ρ : amplitude of the order parameter distortion with a specific wave vector $\mathbf{k}_i$

Effect:

$$E = Eo + \tfrac{1}{2}\kappa\,\rho^2 + \tfrac{1}{2}\kappa_X\,\rho_X^2 \quad + \gamma\,\rho^2\,\rho_X^2 + \ldots$$

T<Tc $\rho = \rho_o$ – spontaneous

$$E = E(\rho_o) + \tfrac{1}{2}(\kappa_X + 2\gamma\,\rho_o^2)\,\rho_X^2 + \ldots$$

$\kappa_X + 2\gamma\,\rho_o^2$: effective stiffness of mode(s) X below Tc

If $k_X + 2\gamma\,\rho_o^2 < 0$: mode(s) X also spontaneous !

Fortunately γ >0 in most cases, otherwise Landau theory would be of not much use !

General rules for secondary spontaneous variables

for a given symmetry break $$G \longrightarrow F$$

secondary spontaneous variables X:

$\{Q_1,\ldots,Q_n\}$ – order parameter

Polynomial of order n (faintness index)

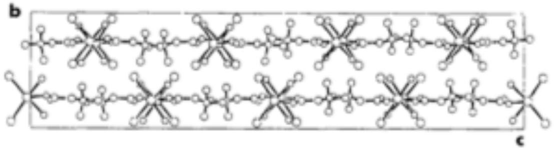
$$\boxed{X \sim F^{(n)}[Q_1,\ldots,Q_n]}$$

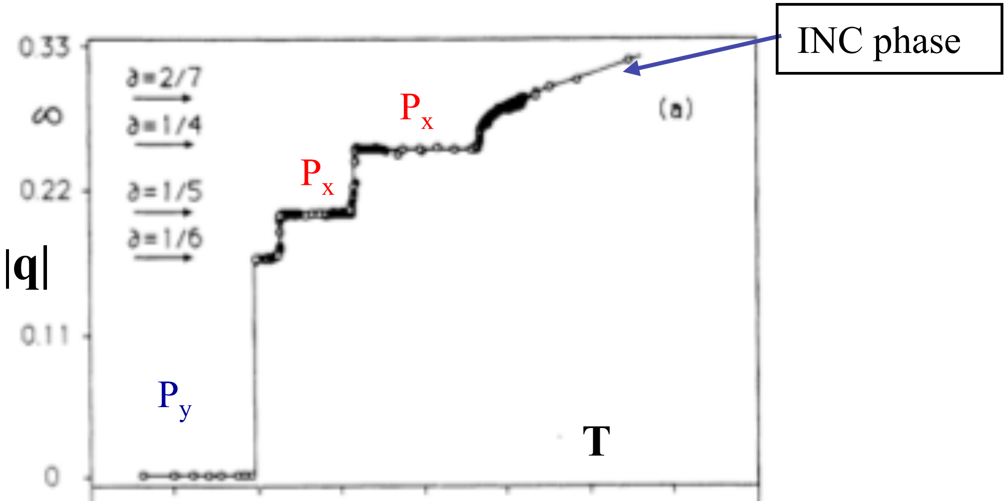
energy coupling: $X.F^{(n)}[Q_1,\ldots Q_n]$

secondary spontaneous variables X keep the symmetry defined by the order parameter

The old story of BCCD

Pnma ⟶ INC





$$u(atom,cell\ l))= Q(q)\ e(atom)\ exp[iq.l] + Q(-q)\ e^*(atom)\ exp[-iq.l]$$

An INC phase has a well defined symmetry, which is kept by all secondary variables/harmonics

Allowed energy coupling terms:

$$\underbrace{Q(q)Q(q)\ldots Q(q)}_{m}\ Q_{second}(-mq) \qquad (\sum q - mq=0)$$

Origin of **infinite** "spontaneous" secondary harmonics of wave vector mq mq
The symmetry constraints for this type of coupling equivalent to the one coming from the superspace group

In a commensurate phase:

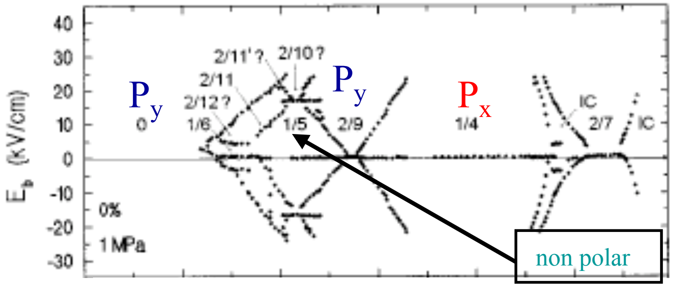
$$\underbrace{Q(q_c)Q(q_c)\ldots Q(q_c)}_{m}\ Q_{second}(-mq_c) \qquad (\sum q_c - mq_c=G)$$

reciprocal lattice vector

Number of inequivalent mq_c **finite**
Their symmetry contraints given by a space group

A well defined symmetry operation in a thermodynamic system must be maintained when scalar fields are changed, except at a phase transition….

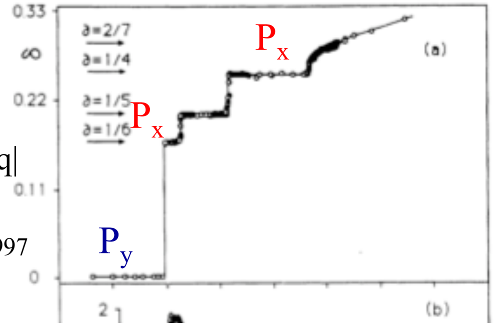
The old story of BCCD



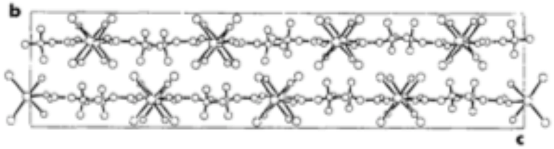
deuterated

|q|

Almeida et al. 1997



2d order parameter:



$$\vec{Q} = (Q, Q^*)$$

primary distortion mode/wave:

$$u(\text{atom}) = Q\, e(\text{atom}) \exp[iq.l] + Q^*\, e^*(\text{atom}) \exp[-iq.l]$$

irrep of the primary mode (order parameter) is changing ONLY its wave vector with temperature:

$$q = \frac{n}{m} c^* \quad \text{(m-fold supercell)}$$

spontaneous polarization is changing direction with the parity of the wave vector

$$\text{Pnma} \longrightarrow \text{F?}$$

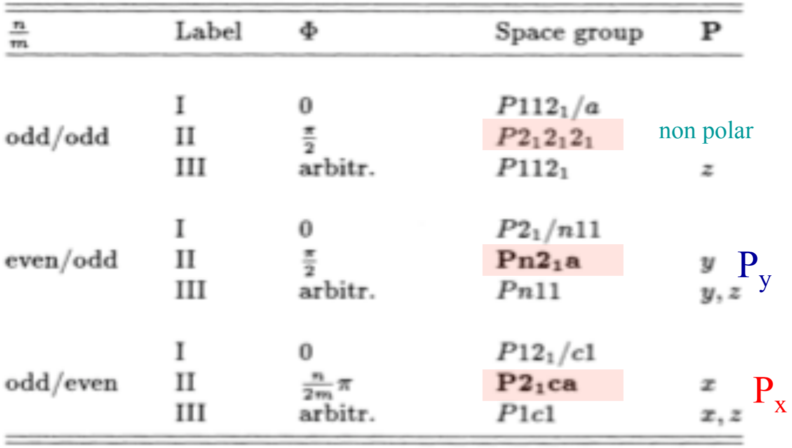
$$\boxed{T[g]\,\vec{Q} = \vec{Q}}$$

irrep matrices depend on the wave vector q

coupling primary mode – polarization:

(Q^m+Q^{*m}) P_y if n/m = even/odd

(Q^m+Q^{*m}) P_x if n/m = odd/even



$\frac{n}{m}$	Label	Φ	Space group	P	
	I	0	$P112_1/a$		
odd/odd	II	$\frac{\pi}{2}$	$P2_12_12_1$		non polar
	III	arbitr.	$P112_1$	z	
	I	0	$P2_1/n11$		
even/odd	II	$\frac{\pi}{2}$	$\mathbf{Pn2_1a}$	y	P_y
	III	arbitr.	$Pn11$	y, z	
	I	0	$P12_1/c1$		
odd/even	II	$\frac{n}{2m}\pi$	$\mathbf{P2_1ca}$	x	P_x
	III	arbitr.	$P1c1$	x, z	

Perez-Mato 1988

Secondary distortions in an incommensurate phase: Anharmonic modulations

Landau Potential – primary INC order parameter:

$$E_1 = Eo + \frac{1}{2}\kappa\, Q_k Q_{-k} + \frac{1}{4}\beta_1 Q_k Q_{-k} + 1/6\, \gamma_1 Q_k Q_{-k}$$

Landau Potential – Secondary INC modulations – higher harmonics:

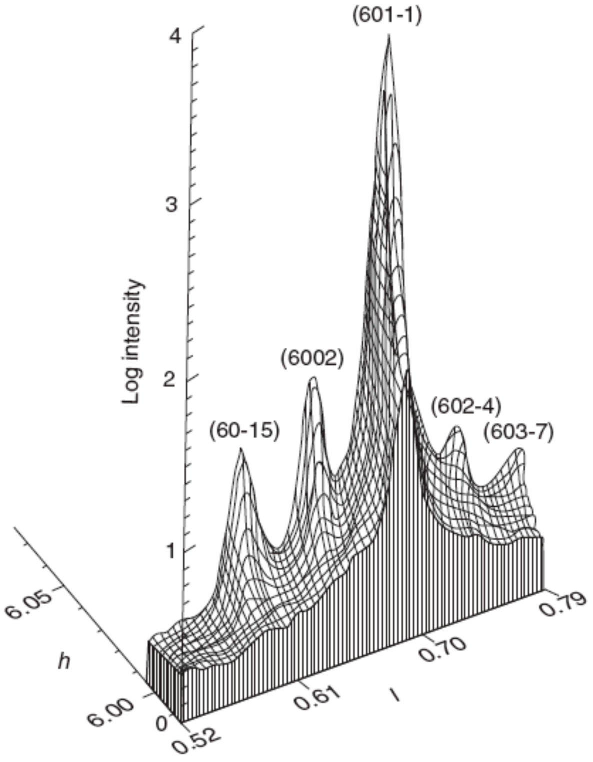
$$E_2 = \frac{1}{2}\kappa' Q'_{4k} Q'_{-4k} + \gamma' (Q'_{-4k} Q_k^4 + Q'_{4k} Q_{-k}^4) + \ldots$$

$\mathbf{3k_i} \approx 0\ \mathbf{c^*}$

$\mathbf{-2k_i} \approx 1/3\ \mathbf{c^*}$

$\mathbf{4k_i} \approx 1/3\ \mathbf{c^*}$

$\mathbf{-5k_i} \approx 1/3\ \mathbf{c^*}$



Describing the anharmonicity

(Type I)

$$\boxed{F = 1/L \int_L f(z)dz}$$

The Landau-Ginzburg free energy: Switching from Fourier space to direct space

$$(Q_k , Q_{-k}) \longrightarrow (Q_{kL}(z) , Q_{-kL}(z)) := (Q(z) , Q^*(z))$$

order parameter with
T-dependent inc.
wave vector k

local order parameter with commensurate
wave vector kL

$$Q(z) = \rho(z)\, e^{i\,\theta(z)} = \Sigma_k Q_k\, e^{i(k-k_L)z}$$

Example: $\mathbf{k_L} = 1/3\ \mathbf{c^*}$

$$f=\frac{\alpha}{2}QQ^*+\frac{\beta}{4}(QQ^*)^2+\frac{\gamma_1}{6}(QQ^*)^3+\frac{\gamma_2}{6}(Q^6+Q^{*6})+i\frac{\delta}{2}\left(Q^*\frac{dQ}{dz}-Q\frac{dQ^*}{dz}\right)+\frac{\kappa}{2}\frac{dQ}{dz}\frac{dQ^*}{dz}+\ldots$$

"lock-in term"
$\rho^6 Cos(6\theta)$

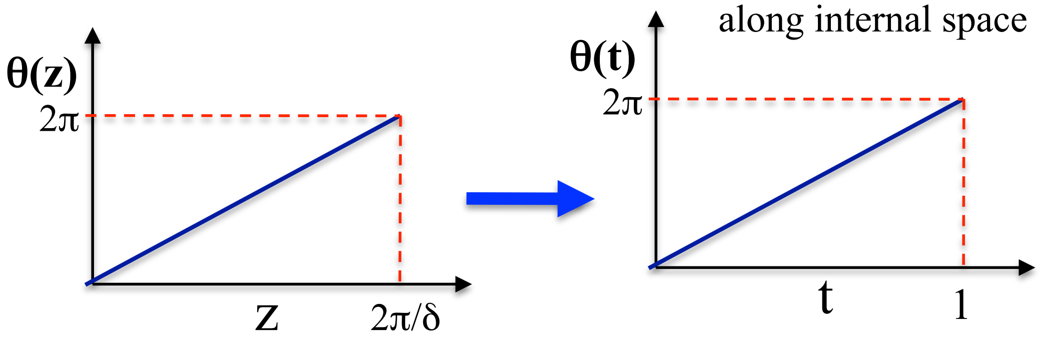
Lifshitz term

dispersion terms

Sinusoidal regime for T ≈Ti:

$$Q(z) = \rho(z)\, e^{i\,\theta(z)} \approx \rho\, e^{i\delta z}$$

$$k-k_L = \delta$$



Structural features within the Landau-Ginzburg approximation:

Aramburu et al. 1995

general expression for the atomic positions in a (3+1) INC phase:

$$\mathbf{u}(\mu, \mathbf{l}) = \sum_{n\geqslant 0} \mathbf{u}_n^\mu \exp(\mathrm{i}2\pi n \mathbf{q}_I \cdot \mathbf{l}) + \mathrm{cc.}$$

Restricted expression for the atomic positions assuming a local order parameter

$$\mathbf{u}(\mu, \mathbf{l}) = Q(\mathbf{l})\mathbf{e}^\mu \exp(\mathrm{i}2\pi \mathbf{q}_L \cdot \mathbf{l}) + \mathrm{cc.}$$

$q\text{-}q_L = \delta$

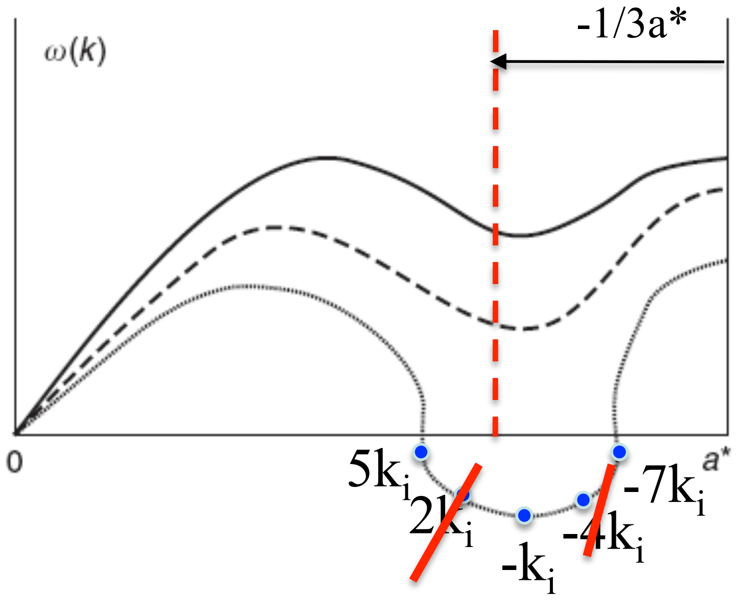
$$\mathbf{u}(\mu, \mathbf{l}) = \left({\sum_{n\mathbf{q}_L \equiv \mathbf{q}_L}}' \mathbf{u}_n^\mu \exp(\mathrm{i}2\pi n \boldsymbol{\delta} \cdot \mathbf{l}) \right) \exp(\mathrm{i}2\pi \mathbf{q}_L \cdot \mathbf{l}) + \mathrm{cc}$$

$$\mathbf{u}_n^\mu = b_n \mathbf{e}^\mu$$

$$Q(\mathbf{l}) \equiv \rho(\mathbf{l}) \exp(\mathrm{i}2\pi \theta(\mathbf{l})) = {\sum_n}' b_n \exp(\mathrm{i}2\pi n \boldsymbol{\delta} \cdot \mathbf{l})$$

all harmonics have same eigenvector, same symmetry !

Coupled high-harmonics within the Landau-Ginzburg approximation:



$$\frac{\gamma_2}{6}(Q^6+Q^{*6})$$

$$Q(z) = \Sigma_n Q_{nk}\, e^{in\delta z}$$

spontaneous secondary harmonics: (6n±1) 5, 7, 11, 13, ...

dependence on k of phonon eigenvector neglected:

$$\mathbf{e}(\mathbf{k}) \approx \mathbf{e} \qquad (u_n^{\mu} = b_n e^{\mu})$$

$(Q'_{-2k}\, Q^2_{k} + Q'_{2k}\, Q^2_{-k})$

$(Q'_{-4k}\, Q^4_{k} + Q'_{4k}\, Q^4_{-k})$

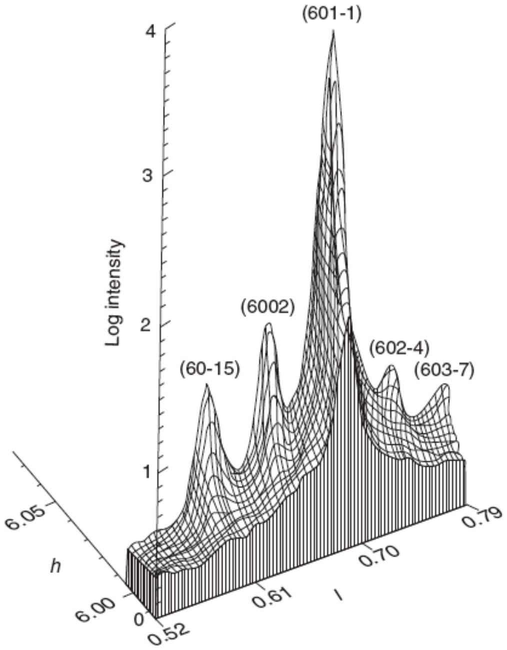
only with a (harder) branch of different symmetry!

$(Q_{-5k}\, Q^5_{k} + Q_{5k}\, Q^5_{-k})$

$(Q_{-7k}\, Q^7_{k} + Q_{7k}\, Q^7_{-k})$

lowest-order coupled harmonics within the same branch

……………………



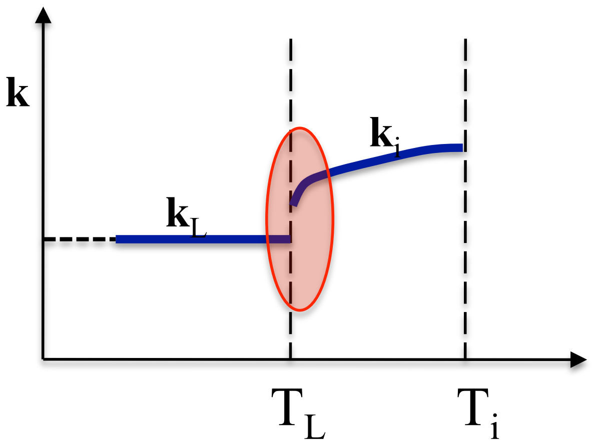
Example Landau-Ginzburg potential for an INC phase transition

polarization coupling

$$f=\frac{\alpha}{2}QQ^*+\frac{\beta}{4}(QQ^*)^2+\frac{\gamma_1}{6}(QQ^*)^3+\frac{\gamma_2}{6}(Q^6+Q^{*6})+\frac{P^2}{2\chi_0}+\xi_1P(Q^3+Q^{*3})+\zeta_1P^2QQ^*$$

$$+\frac{c_0}{2}u^2+i\xi_2u(Q^3-Q^{*3})+\zeta_2u^2QQ^*+i\frac{\delta}{2}\left(Q^*\frac{\mathrm{d}Q}{\mathrm{d}z}-Q\frac{\mathrm{d}Q^*}{\mathrm{d}z}\right)+\frac{\kappa}{2}\frac{\mathrm{d}Q}{\mathrm{d}z}\frac{\mathrm{d}Q^*}{\mathrm{d}z},$$

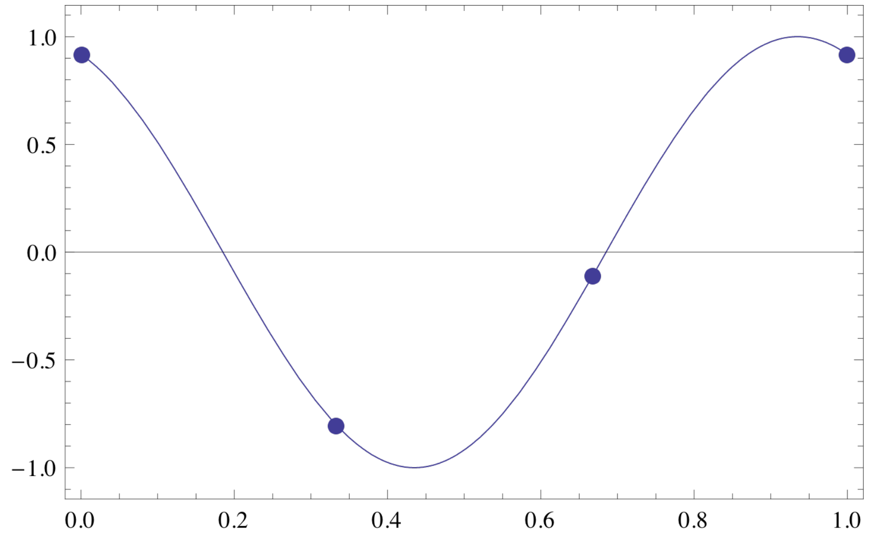
strain coupling



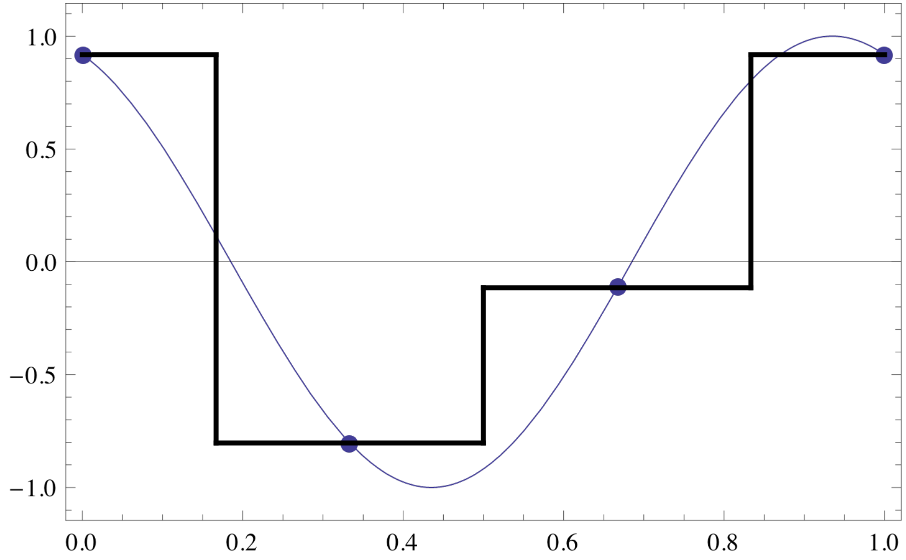
The system can get closer to the commensurate k_L configuration in two ways:

- Changing the wave vector k_i
- Changing the form the of atomic modutions (soliton regime – discommensurations)

Realization of a local commensurate configuration with discommensurations



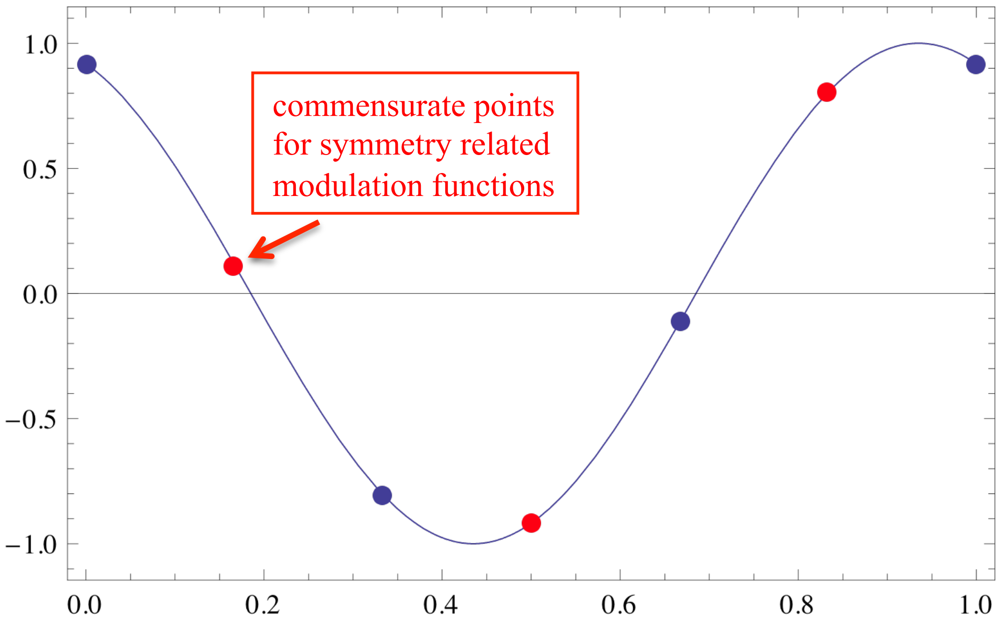
$k = k_L = 1/3\ c^*$



$k = k_i \approx 1/3\ c^*$

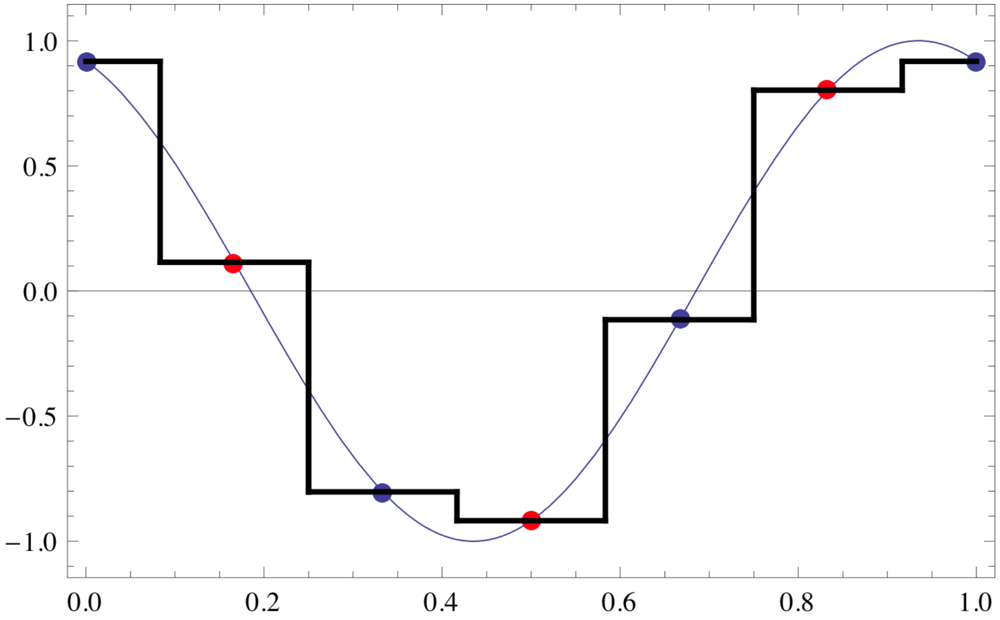
Same configuration except for periodic discommensurations/domain walls

Realization of a local commensurate configuration with discommensurations in a more realistic case, with decrease of the point group



commensurate points for symmetry related modulation functions

$k = k_L = 1/3\ c^*$



$k = k_i \approx 1/3\ c^*$

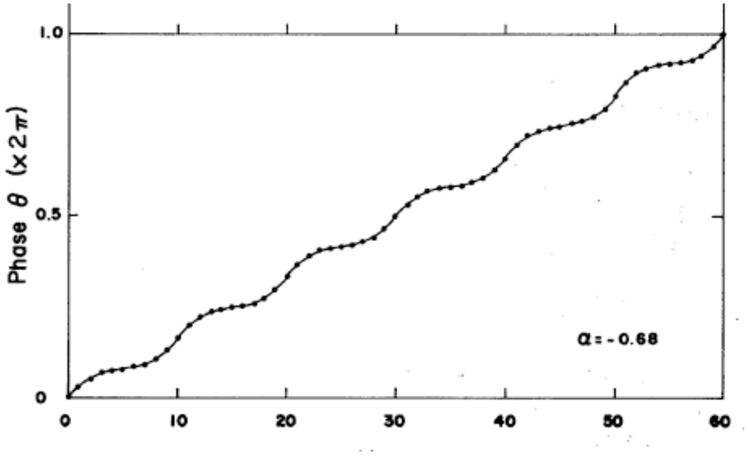
only harmonics 6n±1
(5, 7, 11, 13, ...) are present

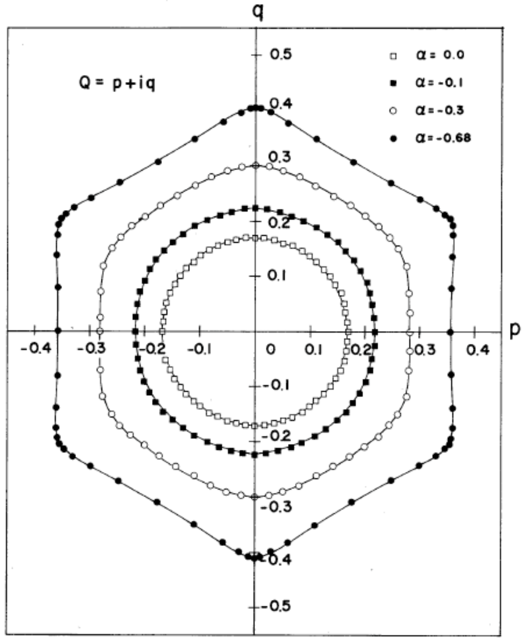
The soliton regime is predicted by the Landau-Ginzburg potential

$$f=\frac{\alpha}{2}QQ^*+\frac{\beta}{4}(QQ^*)^2+\frac{\gamma_1}{6}(QQ^*)^3+\frac{\gamma_2}{6}(Q^6+Q^{*6})+\frac{P^2}{2\chi_0}+\xi_1P(Q^3+Q^{*3})+\zeta_1P^2QQ^*$$
$$+\frac{c_0}{2}u^2+i\xi_2u(Q^3-Q^{*3})+\zeta_2u^2QQ^*+i\frac{\delta}{2}\left(Q^*\frac{\mathrm{d}Q}{\mathrm{d}z}-Q\frac{\mathrm{d}Q^*}{\mathrm{d}z}\right)+\frac{\kappa}{2}\frac{\mathrm{d}Q}{\mathrm{d}z}\frac{\mathrm{d}Q^*}{\mathrm{d}z},$$

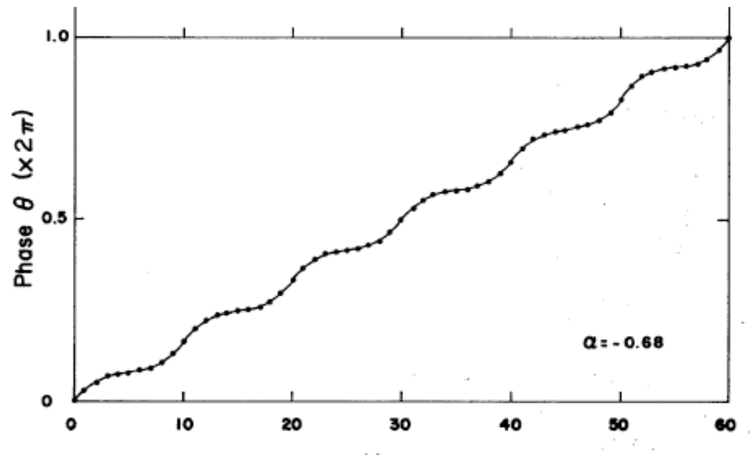
$$\bar{F}=\frac{1}{N}\sum_n\left\{\frac{\alpha}{2}(p_n^2+q_n^2)+\frac{\beta}{4}(p_n^2+q_n^2)^2+\frac{\gamma_1}{6}(p_n^2+q_n^2)^3+\frac{\gamma_2}{3}(p_n^6-15p_n^4q_n^2+15p_n^2q_n^4-q_n^6)\right.$$
$$+\frac{P_n^2}{2\chi_0}+\xi_1P_n(2p_n^3-6p_nq_n^2)+\zeta_1P_n^2(p_n^2+q_n^2)+\frac{c_0}{2}u_n^2+\xi_2u_n(2q_n^3-6q_np_n^2)+\zeta_2u_n^2(p_n^2+q_n^2)$$
$$\left.+\delta\left(q_n\cdot\frac{p_{n+1}-p_{n-1}}{2\Delta}+p_n\cdot\frac{q_{n+1}-q_{n-1}}{2\Delta}\right)+\frac{\kappa}{2}\left[\left(\frac{p_{n+1}-p_n}{\Delta}\right)^2+\left(\frac{q_{n+1}-q_n}{\Delta}\right)^2\right]\right\}$$

Numerical study Ishibashi et al. 1981

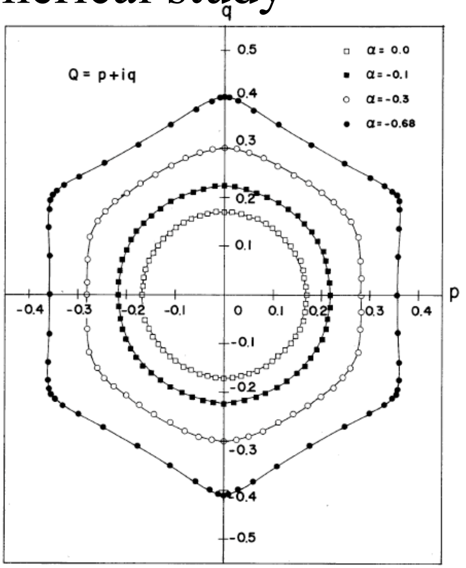




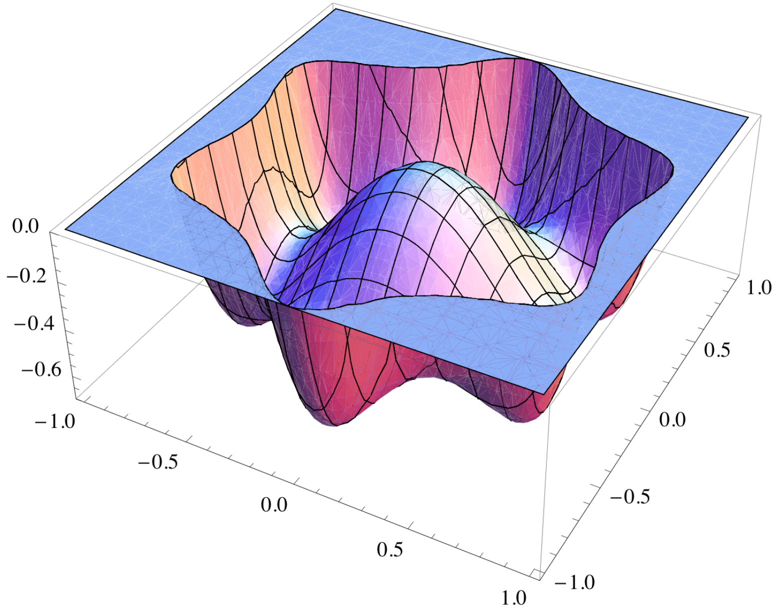
The soliton regime is predicted by the Landau-Ginzburg potential

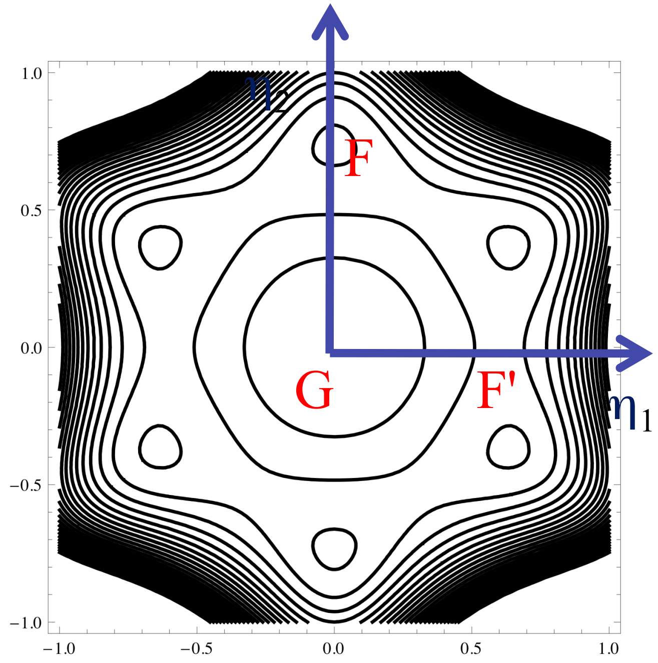


Numerical study Ishibashi et al. 1981



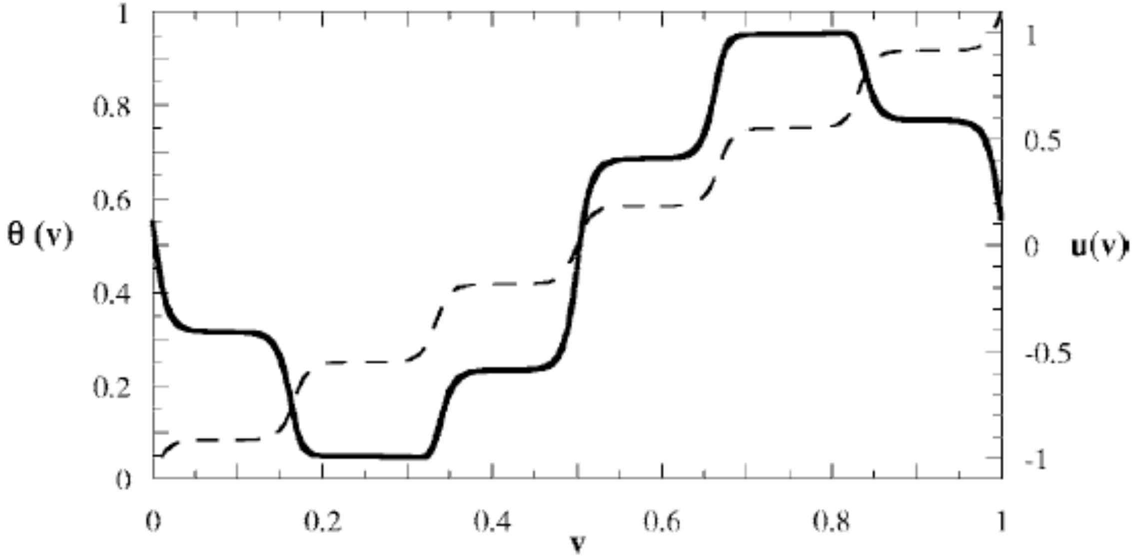
$$Q(z) = \rho(z)\, e^{i\,\theta(z)}$$





Phase of the order parameter and example of resulting atomic modulation Function (along the internal space) in a strong soliton regime for a system with 6 domains in the commensurate lock-in phase

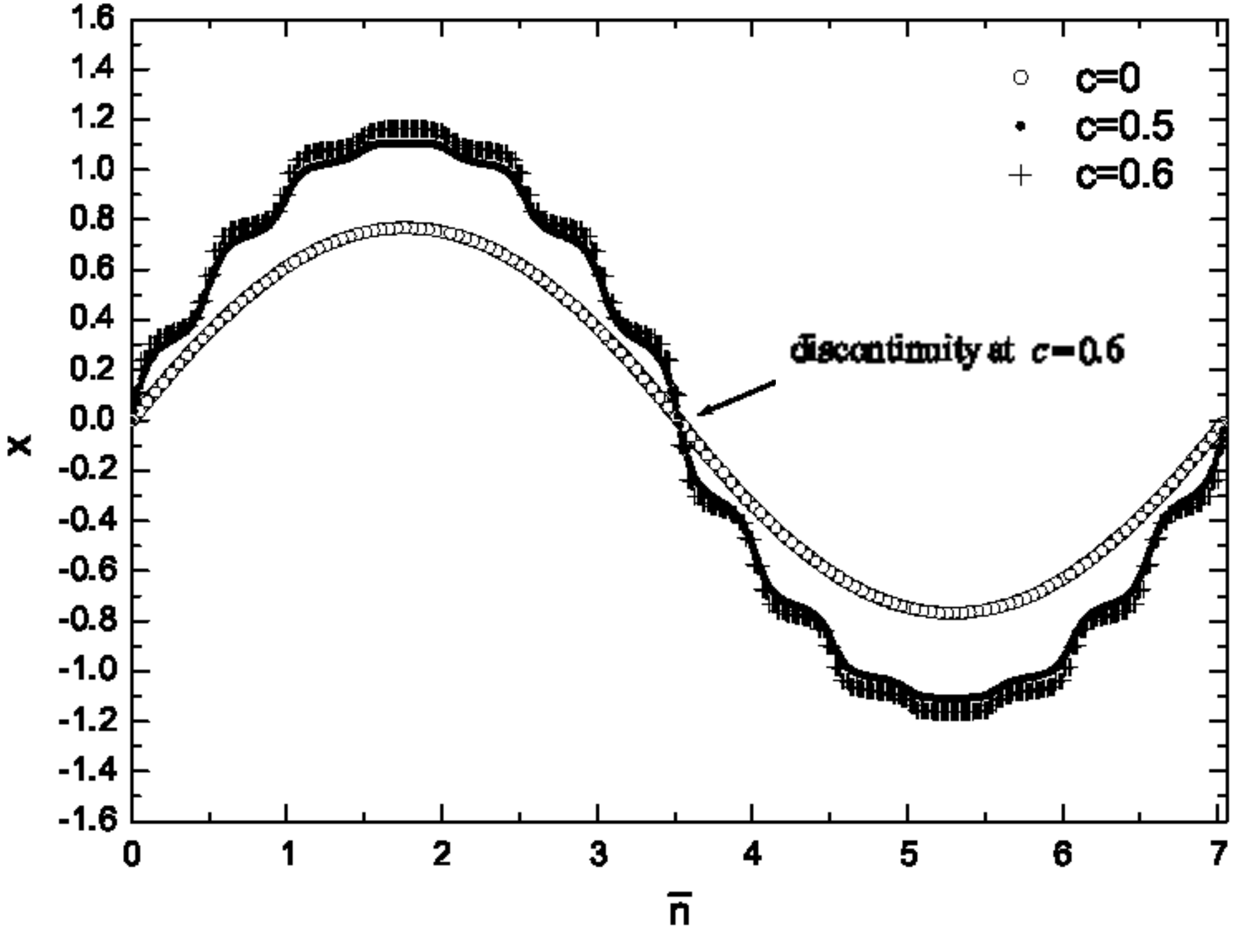
(secondary distortions/harmonics not related with the order parameter are not included)



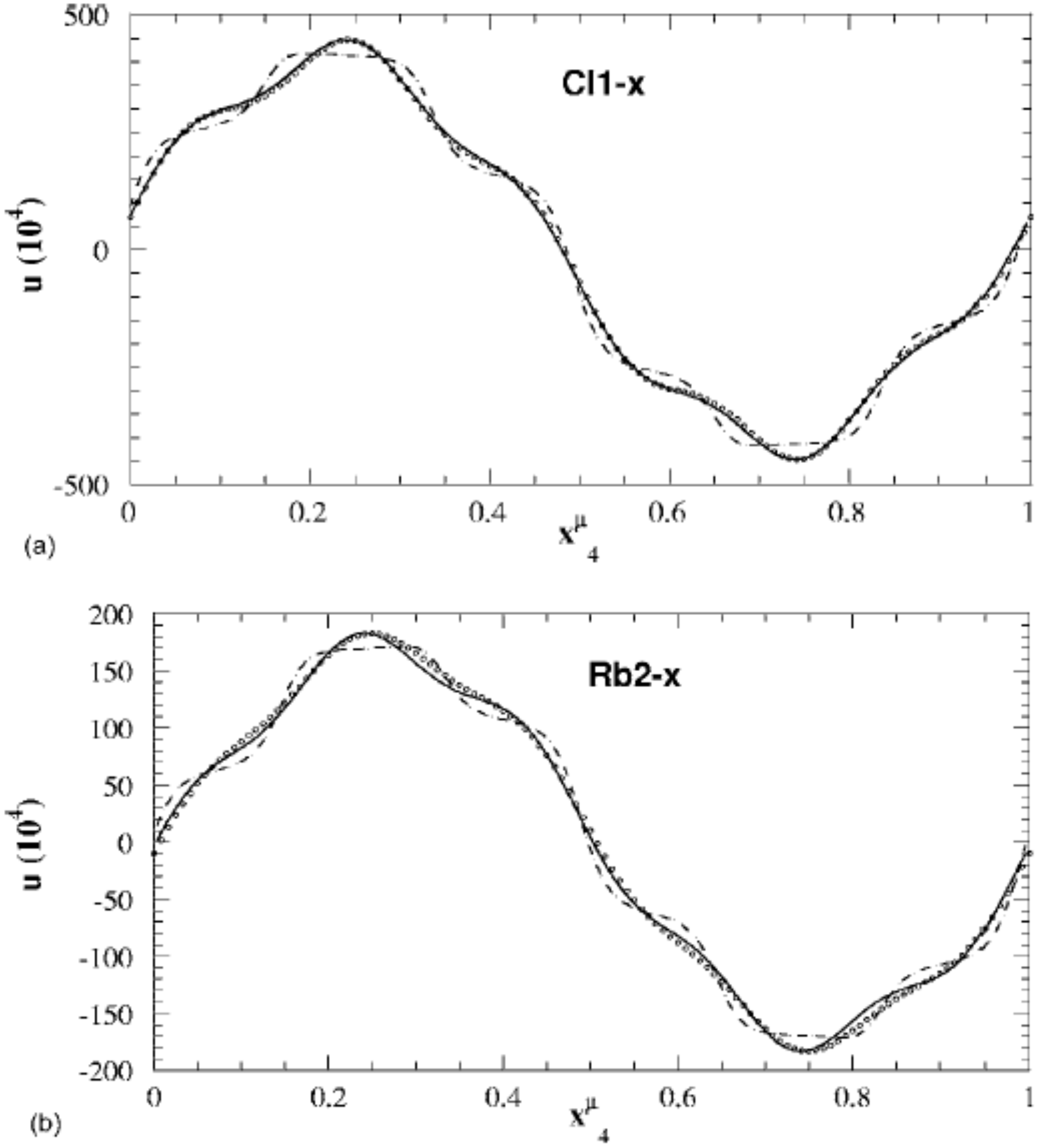
Break of analycity of a Modulated Phase

(as a function of temperature)

Diffour model – Janssen 2002



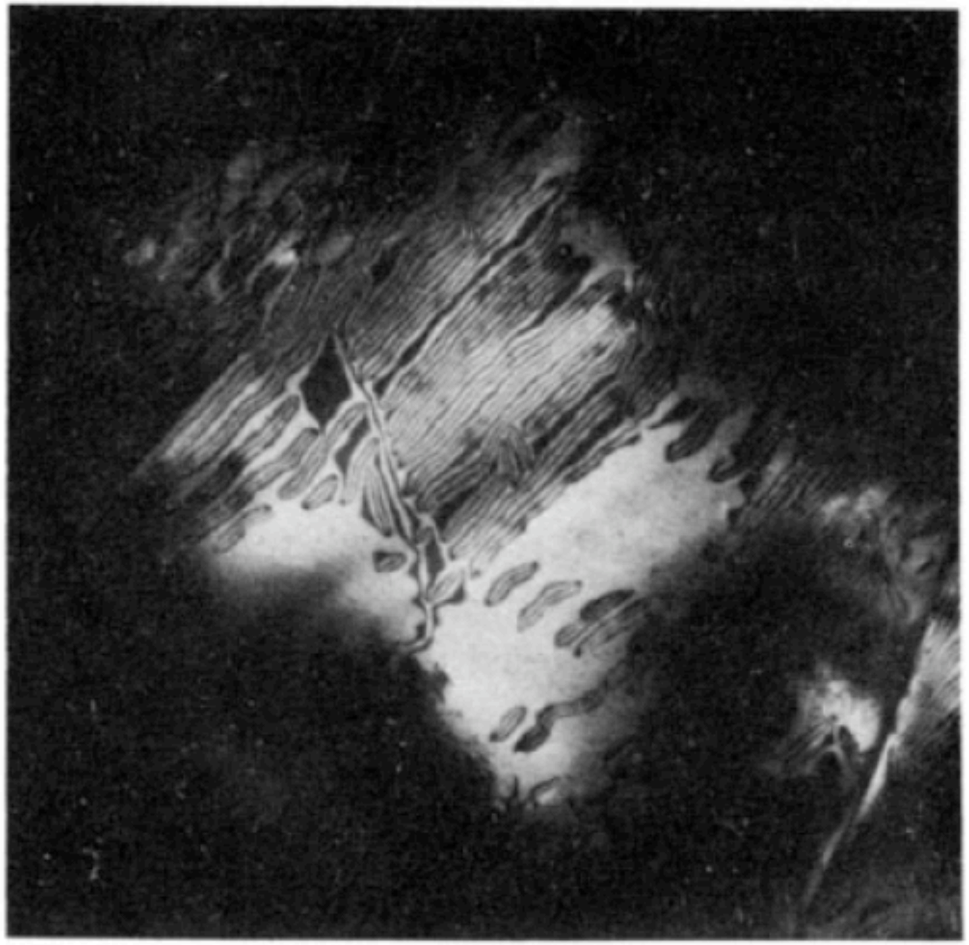
Structure of Rb_2ZnCl_4 in the soliton regime



Aramburu et al. PRB 73 (2006)

Underlying soliton like modulations and the experimentally determined Fourier truncated series

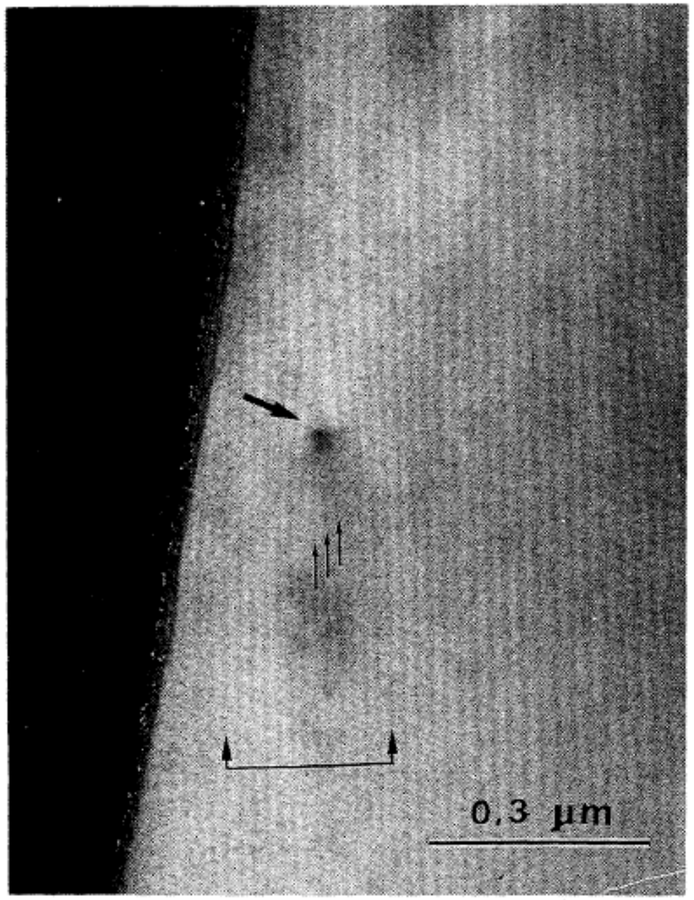
The soliton regime has been observed by different techniques:



Fung er a1 1981

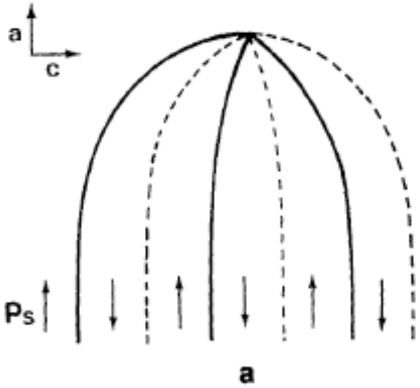
2H-TaSe2

The soliton regime has been observed by different techniques:



Rb_2ZnCl_4

Tsuda et al. 1988



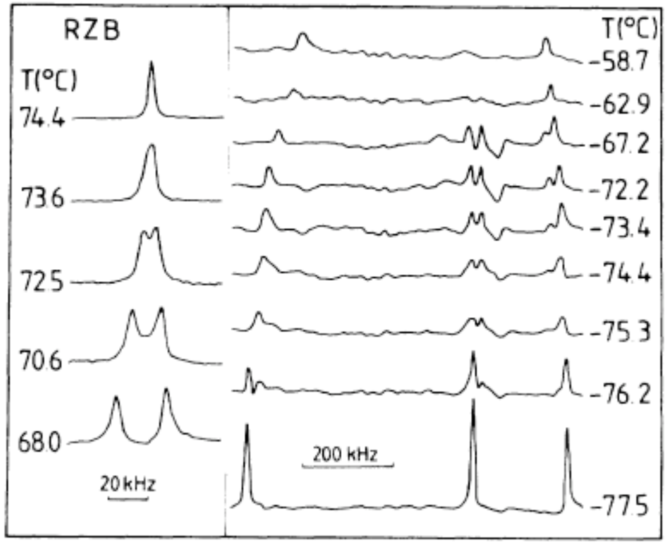
Bestgen 1986

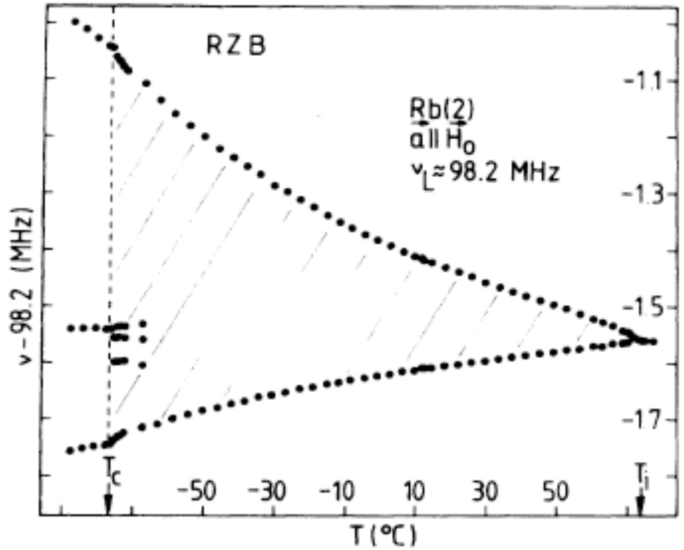
The soliton regime has been observed by different techniques:

NMR

Rb_2ZnBr_4

Walisch et al. 1987





The soliton regime without Lifshitz invariant

Zuñiga et al. Acta B 1989

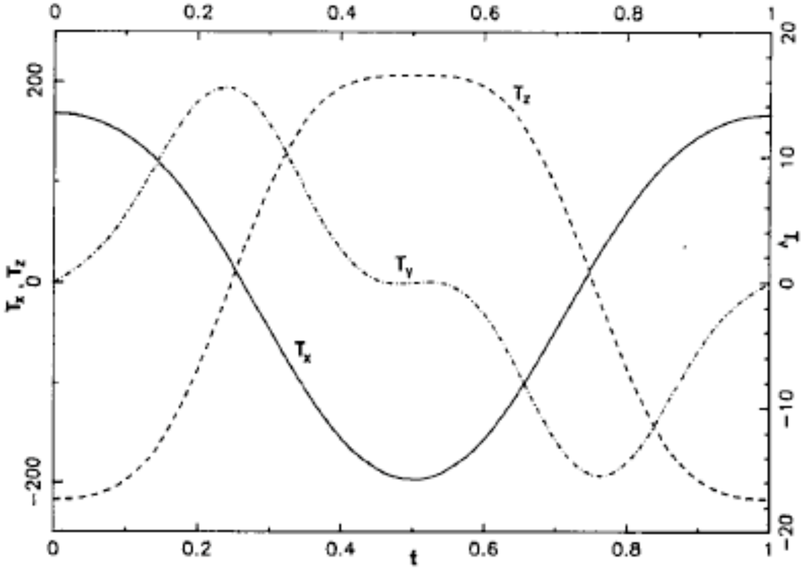
Thiourea $SC(NH_2)_2$

$P2_1ma\ (\mathbf{k}_L = 0)\ \overset{T_L}{\rule{2cm}{0.4pt}}\ \text{INC phase}\ \overset{T_i}{\rule{2cm}{0.4pt}}\ \text{Pnma}$

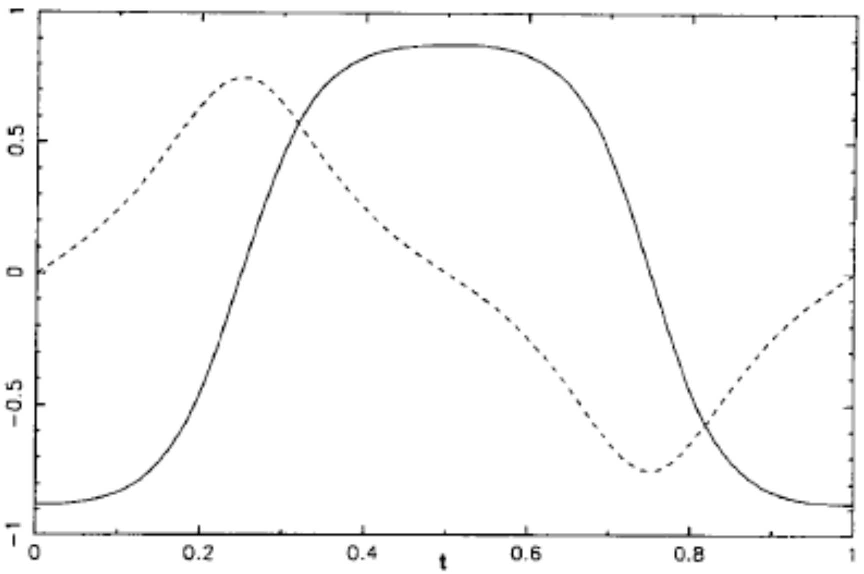
lock-in phase

Modulations of the molecular translations in the INC phase

experimental



simulated curves



The soliton regime without Lifshitz invariant

Aramburu et al. 1994

Thiourea $SC(NH_2)_2$

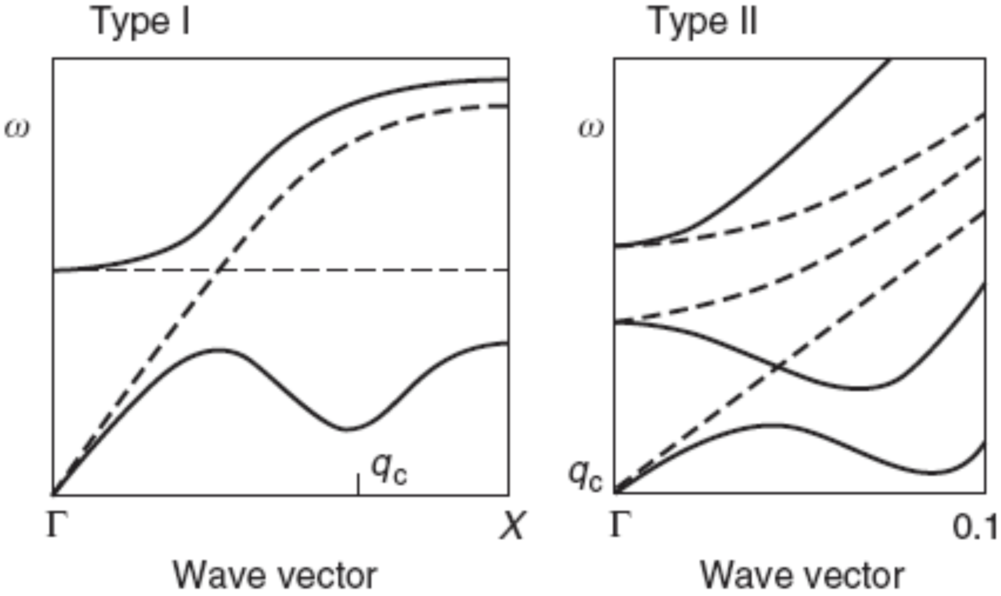
Type II INC systems

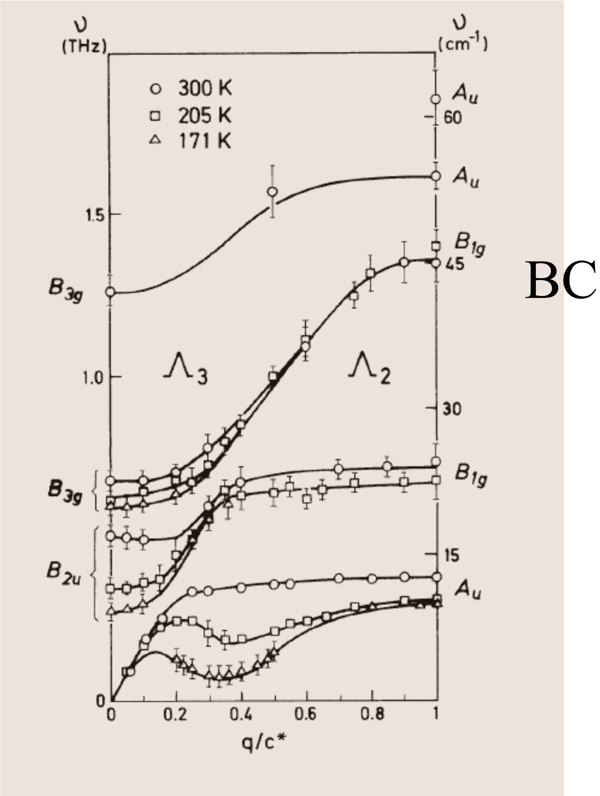
$$f(y)=\frac{\alpha}{2}\eta^2+\frac{\beta}{4}\eta^4-\frac{\gamma}{2}\left[\frac{d\eta}{dy}\right]^2+\frac{\delta}{2}\left[\frac{d^2\eta}{dy^2}\right]^2+\frac{\nu}{2}\eta^2\left[\frac{d\eta}{dy}\right]^2 ,$$

$$\beta,\gamma,\delta,\nu>0 .$$

Naive L-G potential

Order parameter at
the lock-in phase
one-dimensional





BCCD

The soliton regime without Lifshitz invariant

Aramburu et al. 1994

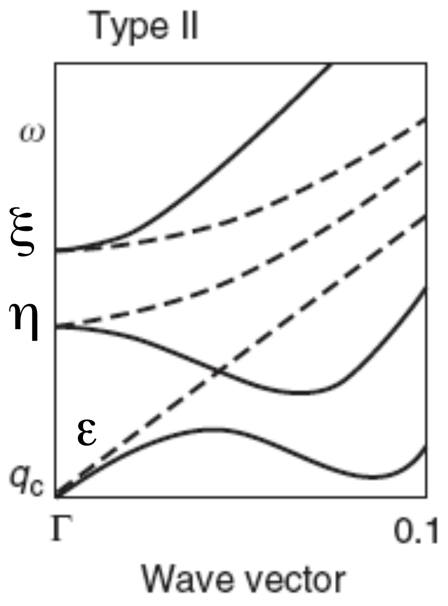
Thiourea $SC(NH_2)_2$

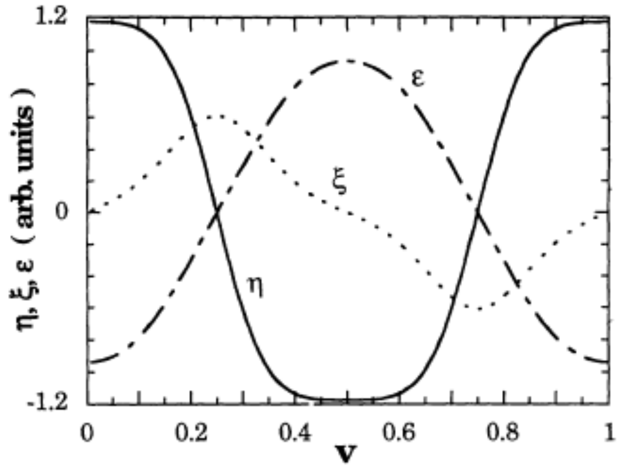
$$f(y)=\frac{\alpha}{2}\eta^2+\frac{\alpha'}{2}\xi^2+\frac{\beta}{4}\eta^4+\frac{\beta'}{4}\xi^4$$
$$+\frac{\beta''}{4}\eta^2\xi^2+\sigma(\dot{\eta}\xi-\eta\dot{\xi})+\frac{\delta}{2}\dot{\eta}^2+\frac{\delta'}{2}\dot{\xi}^2\,,$$
$$\dot{\eta}\equiv\frac{d\eta}{dy}\,,\quad \dot{\xi}\equiv\frac{d\xi}{dy}\,,\quad \alpha',\beta,\beta',\delta,\delta'>0\,,$$
$$\alpha=\alpha_T(T-T_0)\,,\quad F=\frac{1}{L}\int_0^L f(y)dy\,,$$

coupling with acoustic branch:

$$f_1=f+\frac{\lambda}{2}\dot{\eta}\,\dot{\varepsilon}+\frac{\mu}{2}\dot{\varepsilon}^2\quad(\mu>0)\,,$$
$$f_2=f_1+\varphi(\dot{\varepsilon}\,\xi-\dot{\xi}\,\varepsilon)\,.$$

Type II INC systems



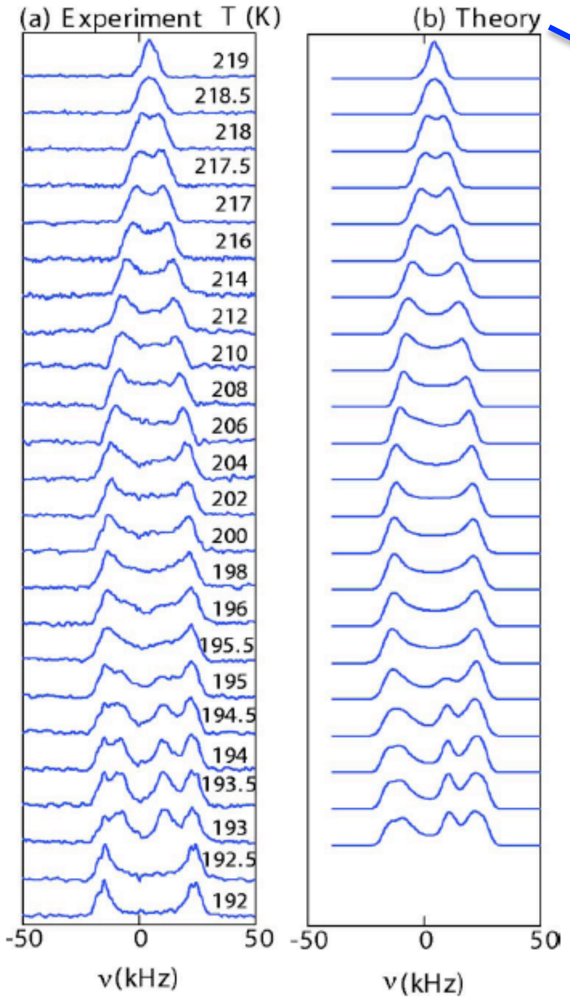


The eignvector of the distortion is strongly temperature dependent, in contrast with Type I

The soliton regime without Lifshitz invariant

Thiourea $SC(NH_2)_2$ Type II INC systems

NMR – Blinc et al. 2006



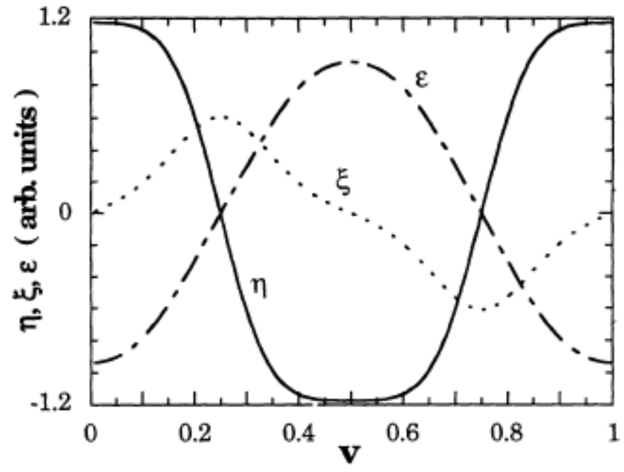
Aramburu et al. 1994

$$f(y)=\frac{\alpha}{2}\eta^2+\frac{\alpha'}{2}\xi^2+\frac{\beta}{4}\eta^4+\frac{\beta'}{4}\xi^4$$

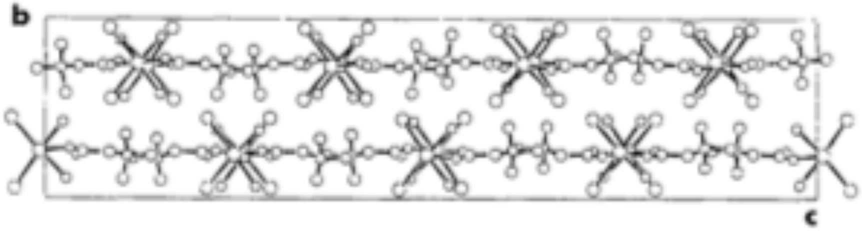
$$+\frac{\beta''}{4}\eta^2\xi^2+\sigma(\dot{\eta}\xi-\eta\dot{\xi})+\frac{\delta}{2}\dot{\eta}^2+\frac{\delta'}{2}\dot{\xi}^2 ,$$

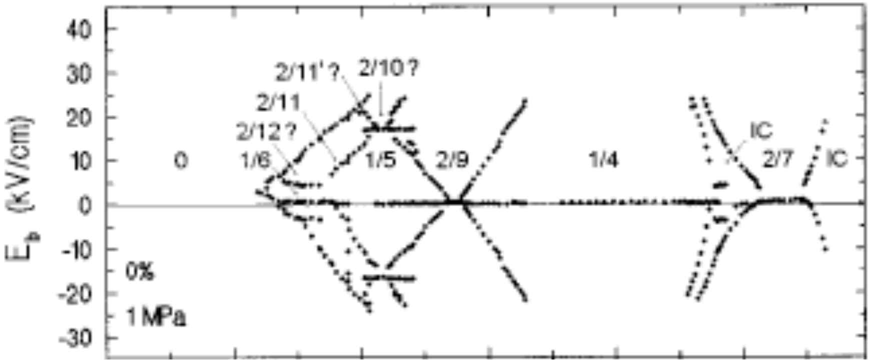
$$\dot{\eta}\equiv\frac{d\eta}{dy} , \quad \dot{\xi}\equiv\frac{d\xi}{dy} , \quad \alpha',\beta,\beta',\delta,\delta'>0 ,$$

$$\alpha=\alpha_T(T-T_0) , \quad F=\frac{1}{L}\int_0^L f(y)dy ,$$

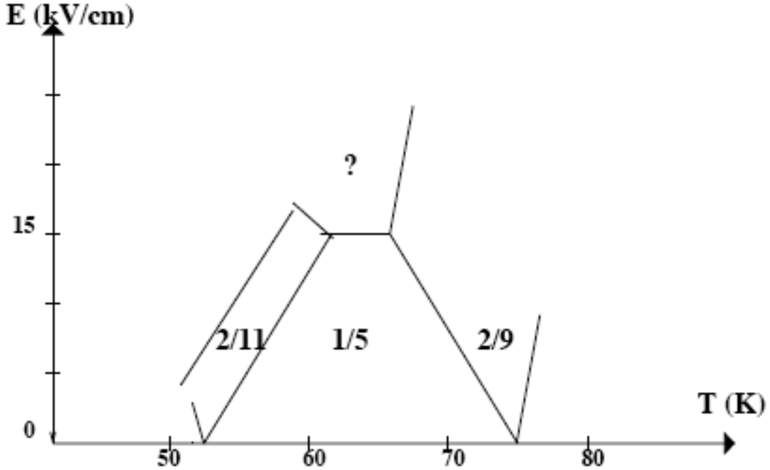


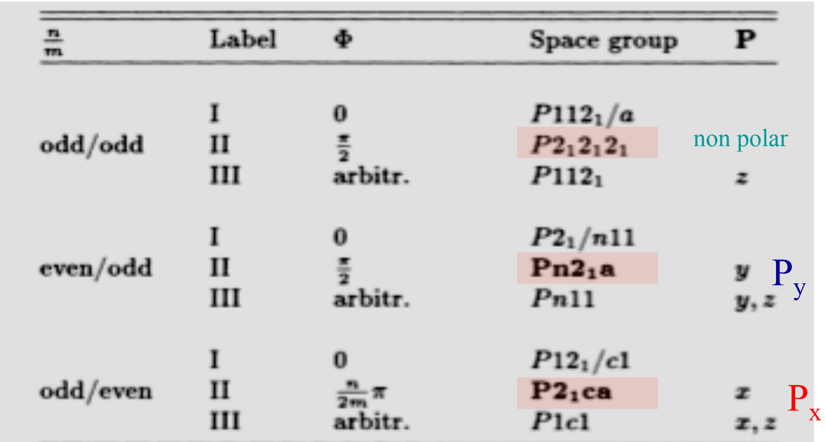
BCCD under electric field





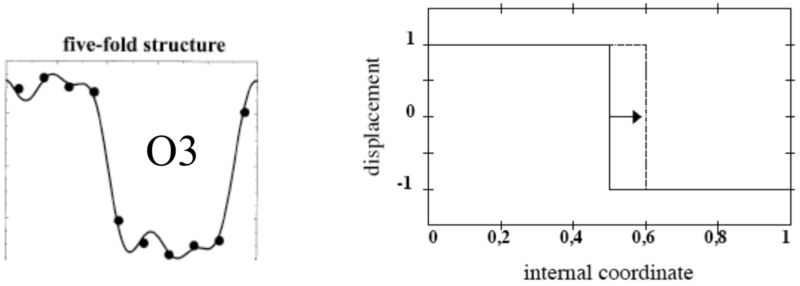
Le Maire et al. 1999





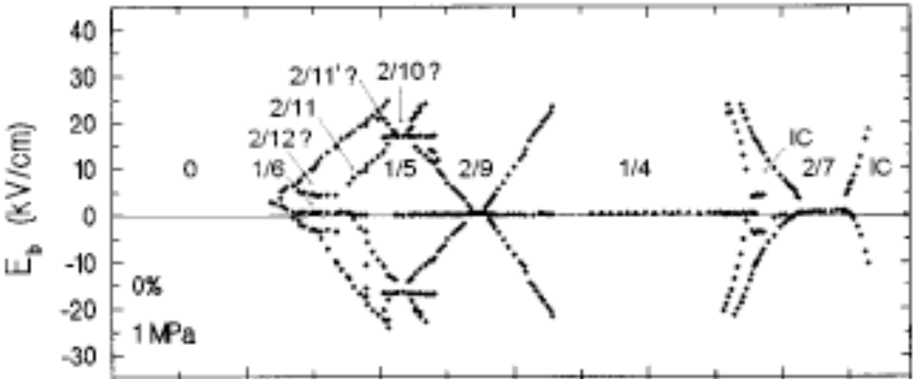
$\frac{n}{m}$	Label	Φ	Space group	P	
	I	0	$P112_1/a$		
odd/odd	II	$\frac{\pi}{2}$	$P2_12_12_1$		non polar
	III	arbitr.	$P112_1$	z	
	I	0	$P2_1/n11$		
even/odd	II	$\frac{\pi}{2}$	$Pn2_1a$	y	P_y
	III	arbitr.	$Pn11$	y, z	
	I	0	$P12_1/c1$		
odd/even	II	$\frac{n}{2m}\pi$	$P2_1ca$	x	P_x
	III	arbitr.	$P1c1$	x, z	

Perez-Mato 1988



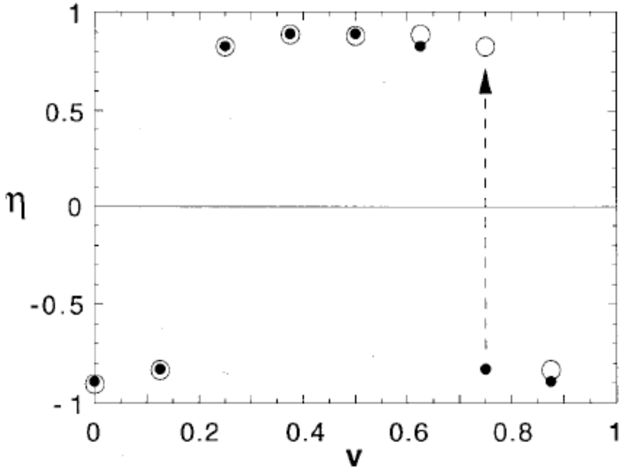
Hernandez et al. PRB 1998

BCCD under electric field



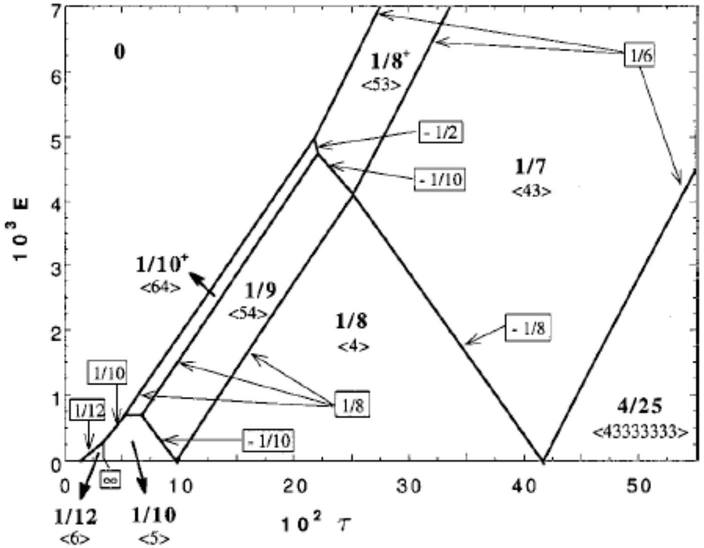
Le Maire et al. 1999

Perez-Mato PRB 2000



Landau potential = efective hamiltonian for the modulation functions

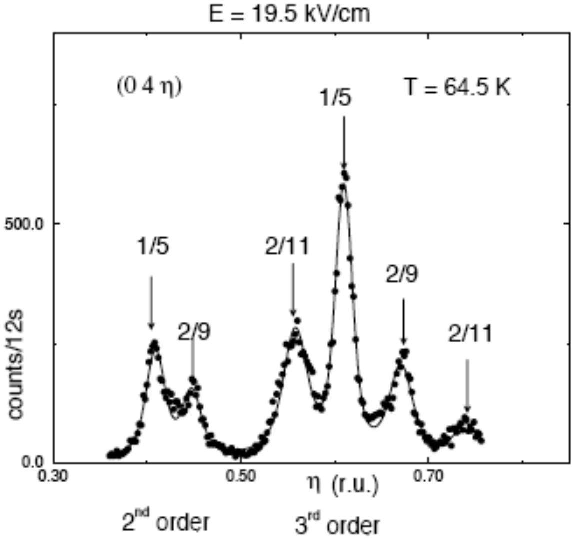
$$
\begin{aligned}
F = \frac{1}{N}\sum_{n} \Phi(\gamma, v_n) = \frac{1}{N}\sum_{n} \Biggl\{ & 2(\tau-1)\,\eta(v_n)^2 + \eta(v_n)^4 \\
& + \xi(v_n)^2 + \frac{\beta'}{4}\xi(v_n)^4 + \sigma\{[\eta(v_n+\gamma)-\eta(v_n)]\xi(v_n) \\
& - \eta(v_n)[\xi(v_n+\gamma)-\xi(v_n)]\} + \frac{\delta}{2}[\eta(v_n+\gamma)-\eta(v_n)]^2 \\
& + \frac{\delta'}{2}[\xi(v_n+\gamma)-\xi(v_n)]^2 - E\,\eta(v_n) \Biggr\},
\end{aligned}
$$

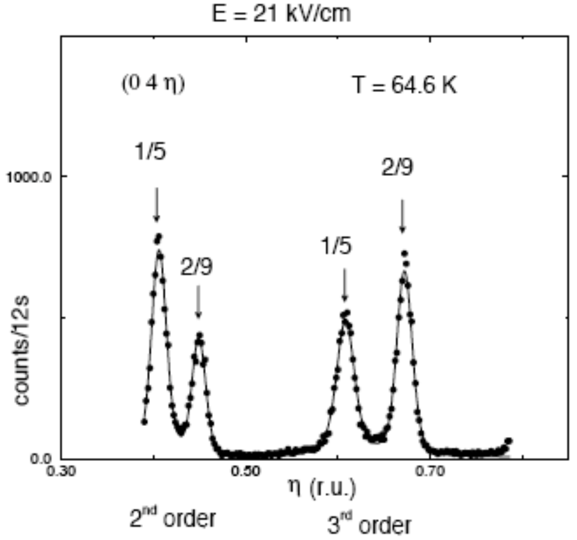


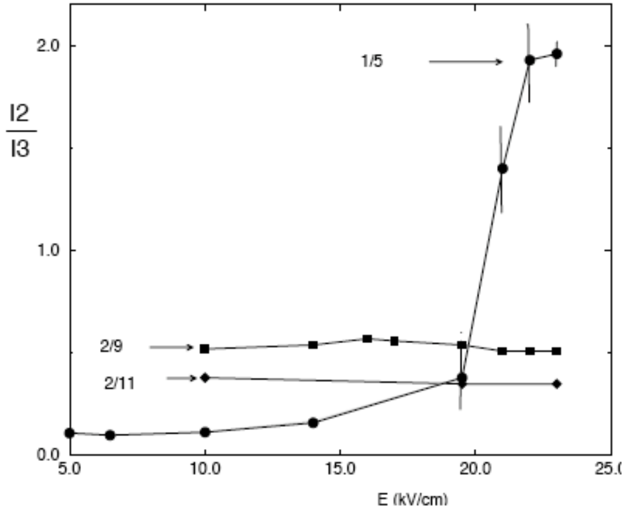
local coordinate → internal coordinate

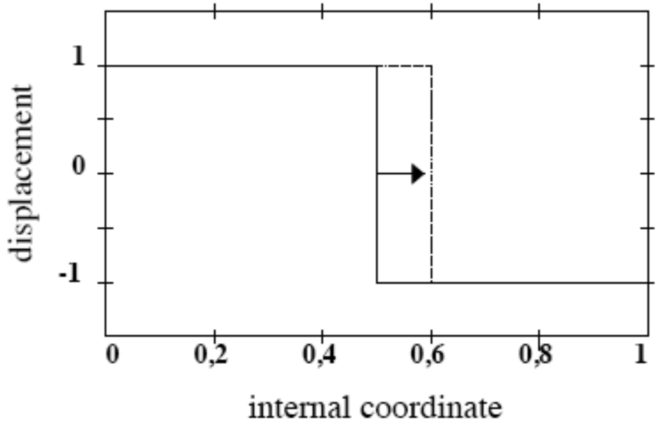
BCCD under electric field – neutron scattering

Quilichini et al 2002









Conclusion

Modulated INC structures and their phase transitions can be modelized
with Landau potentials, that become in practice temperature
effective hamiltonians, conveniently symmetry-adapted to specific systems