Phase Transitions in Aperiodic Crystals and Tilings

Description of Phase Transitions
Superspace Description
Modulated Phases
Incommensurate Composites
Quasicrystals
Magnetic Symmetry Changes

Katholieke Universiteit Nijmegen

School ‘Aperiodic Crystals’
Carqueiranne 2010

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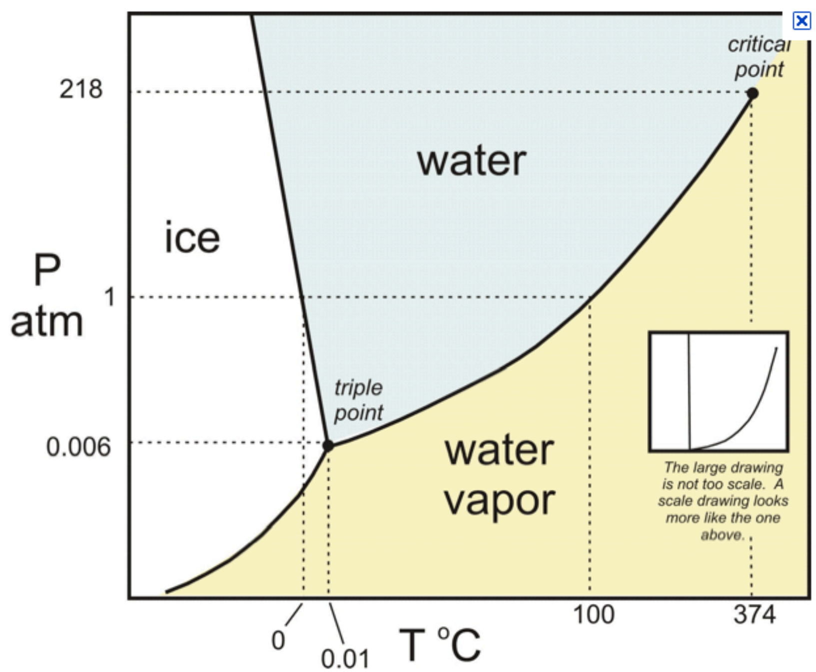
Phase transitions in commensurate and incommensurate crystals

Modulated crystals

Incommensurate composites

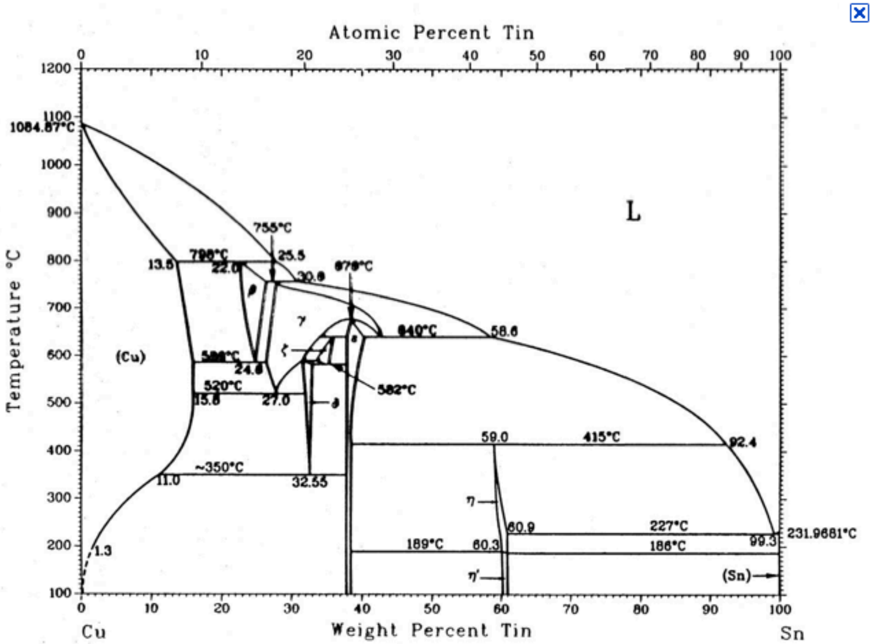
Quasicrystals and tilings

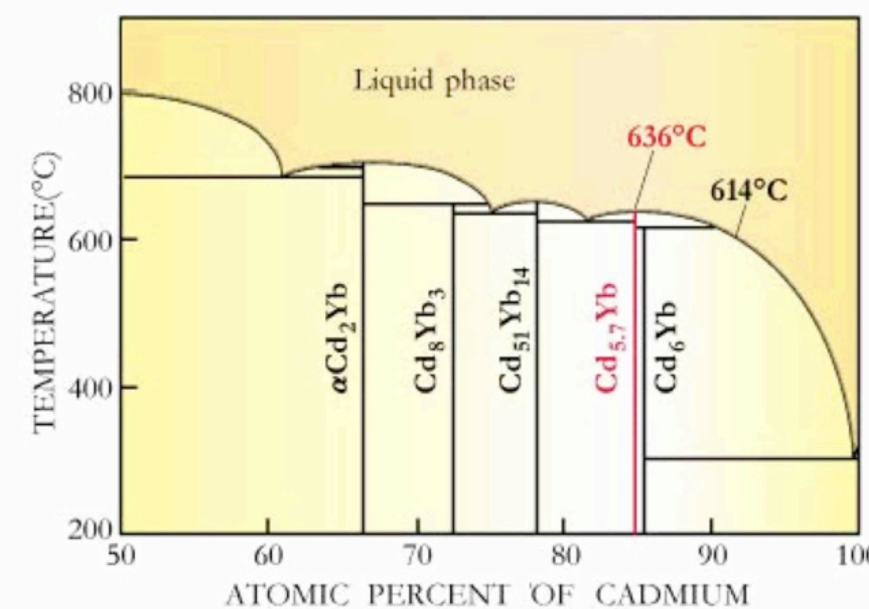
Incommensurate magnetic structures



Phase diagrams
simple or complex

occur also in solids:
magnetism
structure
incommensurate phases





Binary phase diagram of cadmium-ytterbium alloys. The looping curved line marks the boundary between the liquid phase above and the solid phases below. Shown in red is the quasicrystalline $Cd_{5.7}Yb$, whose stoichiometry is almost identical to its closest neighbor on the phase diagram, the cubic Cd_6Yb.

Aperiodic Crystal: diffraction pattern with delta peaks

$$\mathbf{k} = \sum_{i=1}^{n} h_i \mathbf{a}_i^*$$

h_i integers

Rank n > Dimension D

Examples: Incommensurate modulated phases
Aperiodic composites
Quasicrystals

Aperiodic Crystal: diffraction pattern with delta peaks

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h_i integers

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Examples: Incommensurate modulated phases
Aperiodic composites
Quasicrystals

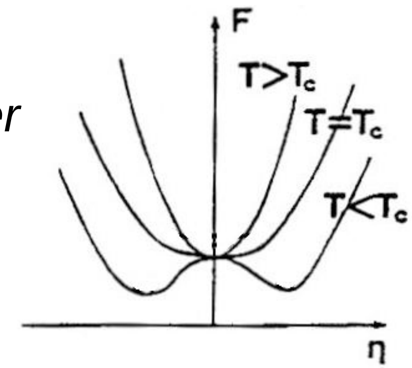
Phase transitions:
From periodic crystal to incommensurate modulated phase,
between incommensurate phases,
between various phases of aperiodic composites,
in quasicrystals and between quasicrystals and approximants

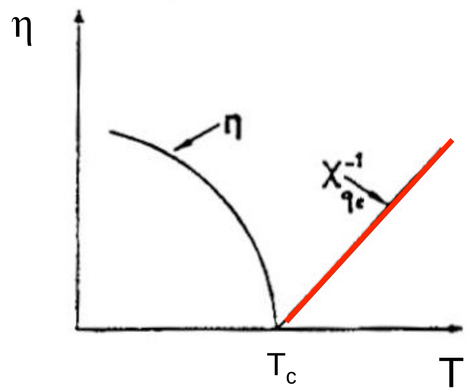
Group-subgroup Phase Transitions

Order parameter η describes deviation of order in HT phase

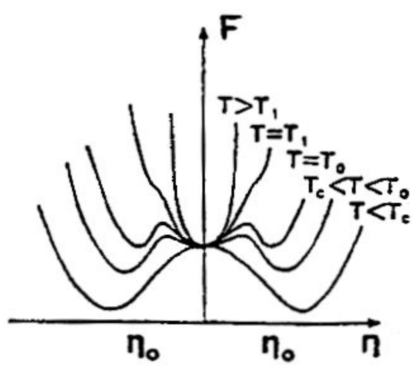
Minimization of the Free Energy F (T, η)

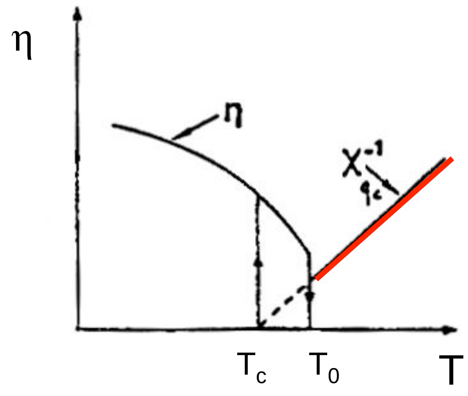
Second order





First order





Landau theory

Order parameter η describes change in structure / symmetry

Landau free energy

$$F = \frac{\alpha(T)}{2}\eta^2 + \frac{1}{4}\eta^4 + \ldots$$

Free energy is invariant under high-symmetry group G_0 ; order parameter belongs to irreducible representation of this group; order parameter is invariant under low-symmetry group G.

Landau theory

Order parameter η describes change in structure / symmetry

Landau free energy

$$F = \frac{\alpha(T)}{2}\eta^2 + \frac{1}{4}\eta^4 \quad + \ldots$$

Free energy is invariant under high-symmetry group G_0 ; order parameter belongs to irreducible representation of this group; order parameter is invariant under low-symmetry group G.

In general, higher-dimensional order parameter if dimension of the irreducible
representation is higher than 1.

$$F = \sum_{ij} \alpha(T)_{ij}\eta_i\eta_j + \sum_{ijk} \beta_{ijk}\eta_i\eta_j\eta_k + \sum_{ijkm} \gamma_{ijkm}\eta_i\eta_j\eta_k\eta_m + \ldots\ldots$$

Transition from periodic to aperiodic crystal:
characterised by irrep of the 3D space group
labelled by star of k vectors and irrep of the little group of k

$$D(R|\mathbf{t}) \;=\; \exp(i\mathbf{k}.\mathbf{t})D_\mu(R)$$

Example: from a crystal with space group Pcma towards a modulated phase with wave vector

$$\mathbf{k} = \alpha\mathbf{a}^*$$

Point group of the little group: 2mm

D_μ	E	2_x	m_y	m_z
D_1	1	1	1	1
D_2	1	1	−1	−1
D_3	1	−1	1	−1
D_4	1	−1	−1	1

$$D(m_y|0) \;=\; -1, \quad D(m_z|\mathbf{a}/2) \;=\; -\exp(i\pi\alpha)$$

Phase transitions in commensurate and incommensurate crystals

Modulated crystals

Incommensurate composites

Quasicrystals and tilings

Incommensurate magnetic structures

Acta Cryst. (1964). **17**, 614

An anomaly in the crystal structure of Na_2CO_3. By ELLY BROUNS and J. W. VISSER, *Technische Physische Dienst T.N.O.-T.H.*, and P. M. DE WOLFF, *Technische Hogeschool, Delft, The Netherlands*

(*Received 7 November* 1963)

A Guinier camera as described by Lenné (1961) was used for the high-temperature work. In this camera the powder pattern is continuously recorded on a moving film while the temperature of the sample is raised. Three phases were discernible, in accordance with the differential thermal analysis results of Reisman (1959), whose data for the transition temperatures are used below:

(*a*) The *C*-centered monoclinic γ phase below 361 °C (with extra lines)
(*b*) The *C*-centered monoclinic β phase between 361 °C and 489 °C)
(*c*) The primitive hexagonal α phase above 489 °C, stable up to the melting point.

P.M. de Wolff

High temperature:
Unmodulated crystal.
Positions: $\boldsymbol{n} + \boldsymbol{r_j}$

Incommensurate modulated phases

Positions 1D system: $\boldsymbol{n} + \boldsymbol{r_j} + \boldsymbol{f_j}\,(\boldsymbol{q}.\boldsymbol{n}\,)$

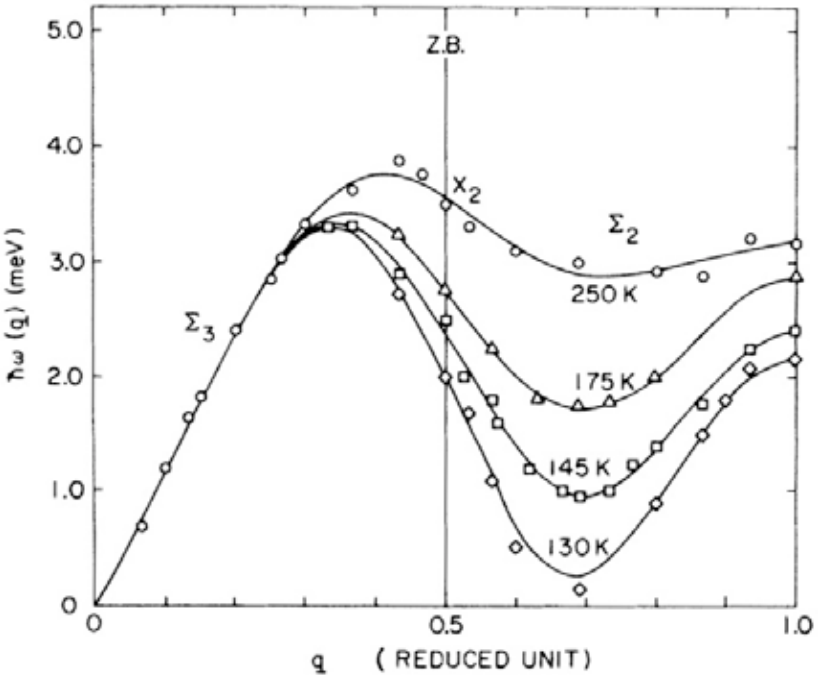
Transition from unmodulated to incommensurate modulated.

Modulation functions f may be smooth or discontinuous:
the type changes at the discommensuration transition: effects on the dynamics

Usually the wave vector of the modulation changes with temperature,
but the superspace group symmetry remains the same. Even for commensurate values. Then the 3D space group is determined by the SSG.

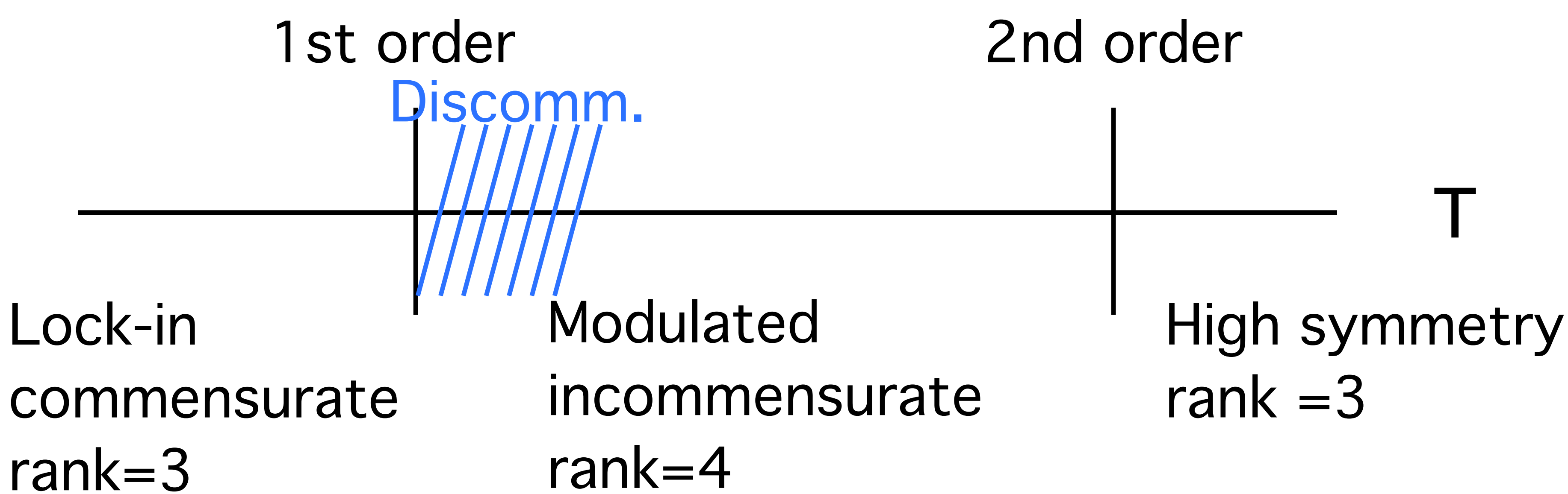
Exceptions: - when the modulation changes character;
- when more wave vectors are involved ; e.g. 1q -> 2q

Then a phase transition occurs



5.0
4.0
3.0
2.0
1.0
0
ħω (q) (meV)
Z.B.
X_2
Σ_2
Σ_3
250 K
175 K
145 K
130 K
0
0.5
1.0
q (REDUCED UNIT)

K_2SeO_4



1st order
Discomm.
2nd order
T
Lock-in
commensurate
rank=3
Modulated
incommensurate
rank=4
High symmetry
rank =3

Embedding into superspace with dimension equal to the rank

$$\mathbf{k}_s = (\mathbf{k}, \mathbf{k}_I)$$

$$\rho(\mathbf{r}) = \sum_{\mathbf{k}} \exp(i\mathbf{k}, \mathbf{r})$$

$$\downarrow$$

$$\rho_s(\mathbf{r}, \mathbf{r}_I) = \sum_{\mathbf{k}_s} \rho(\pi \mathbf{k}_s) \exp(i\mathbf{k}_s . \mathbf{r}_s)$$

Embedding into superspace with dimension equal to the rank

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$$\downarrow$$

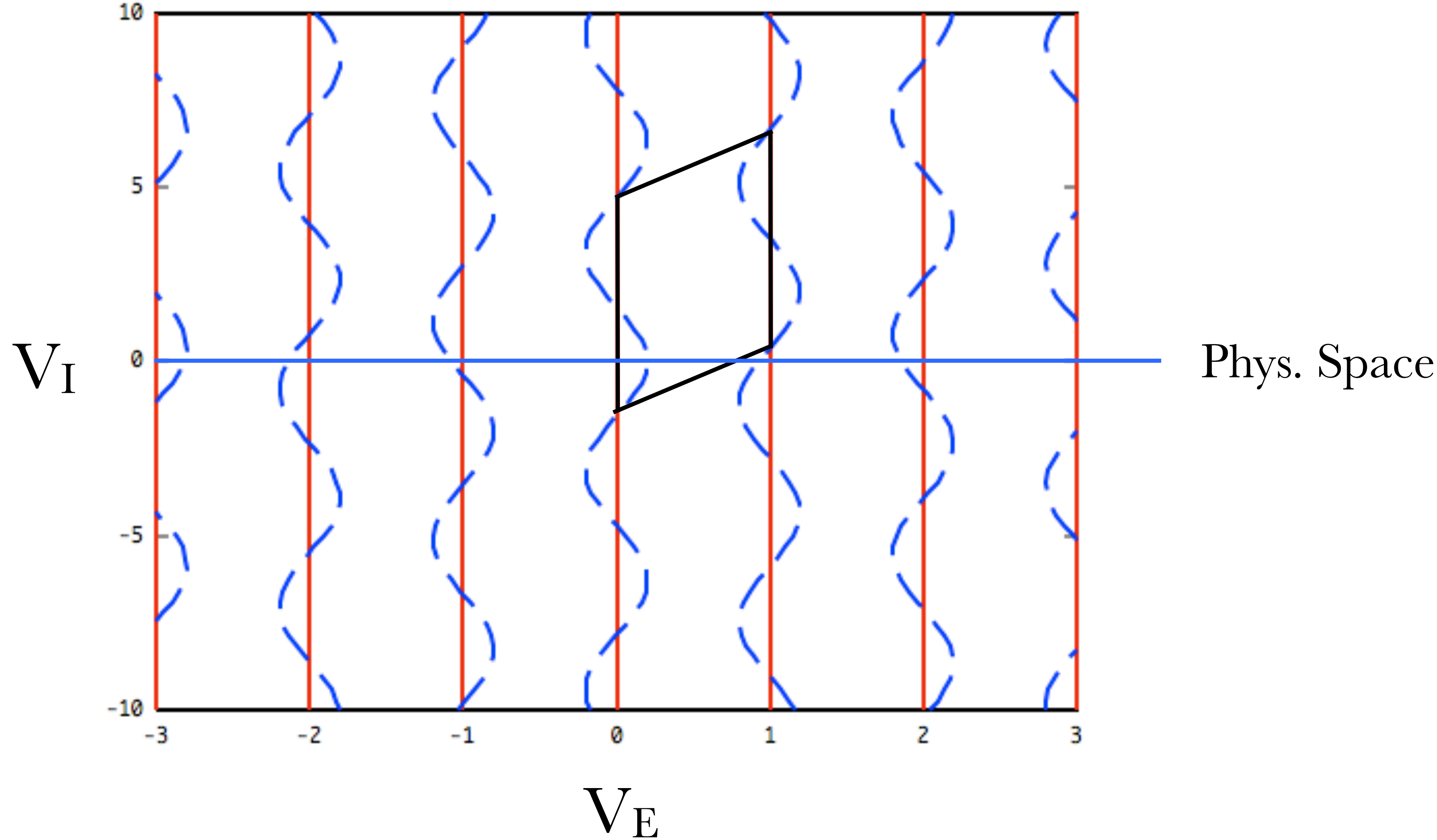
$$\rho_s(\mathbf{r}, \mathbf{r}_I) = \sum_{\mathbf{k}_s} \rho(\pi \mathbf{k}_s) \exp(i\mathbf{k}_s . \mathbf{r}_s)$$

High symmetry: without modulation

$$G = G_0 \times E^d$$

Low symmetry: with modulation

H subgroup of *G* : *n* -dimensional space group: superspace group

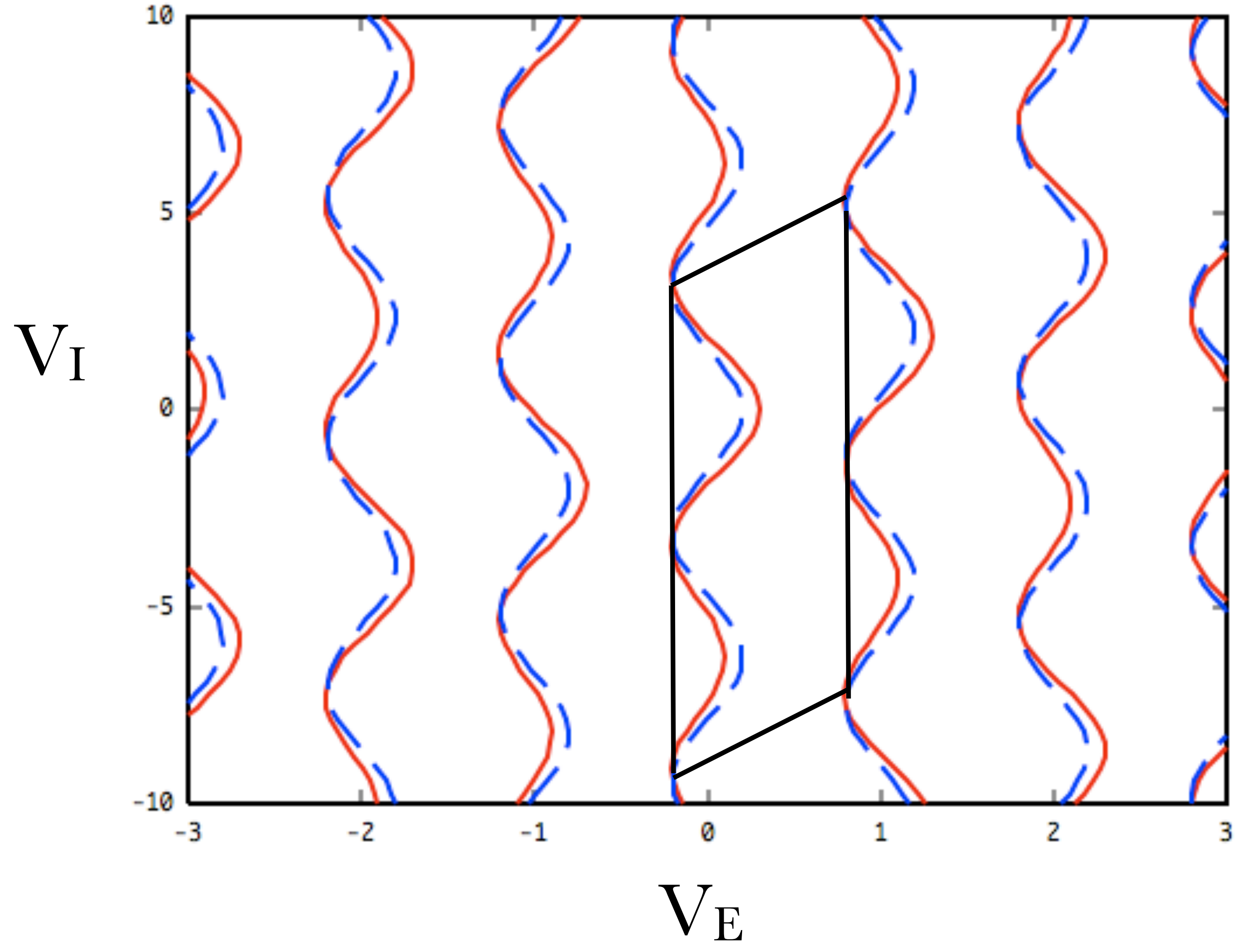


Red Blue

Transition from 1D periodic to 1D aperiodic = 2D periodic

Symmetry from $G_0 \times E^1$ -> G

Rank is 2 Diffraction $h_1\,\mathbf{a}^* + h_2\,\mathbf{q}$

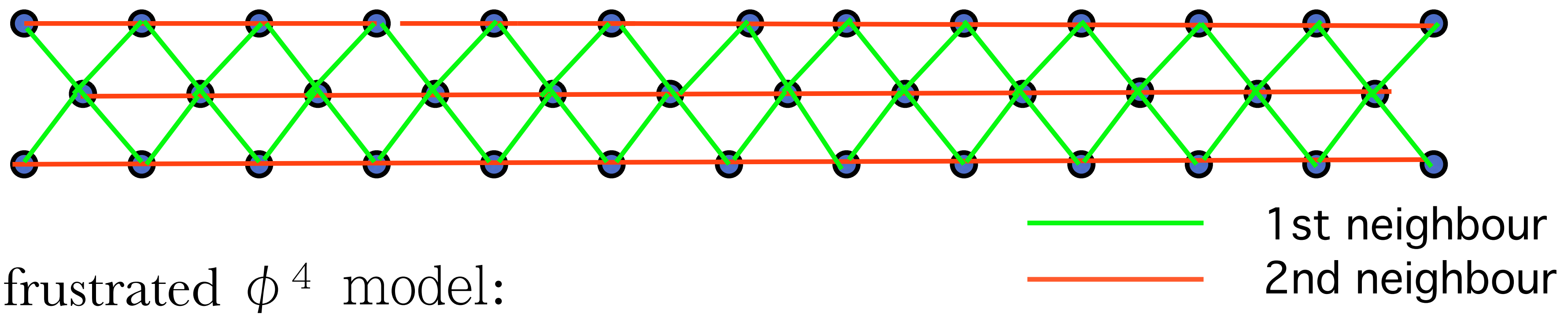


Transition from 2D periodic to 2D periodic

Rank remains 2 Diffraction $h_1\,\mathbf{a}^* + h_2\,\mathbf{q}/2$

Semi-microscopic models explain essentials of the transition

$$F = \sum_n \left(V_1(u_n) + \sum_m V_2(n-m, u_n, u_m) \right)$$



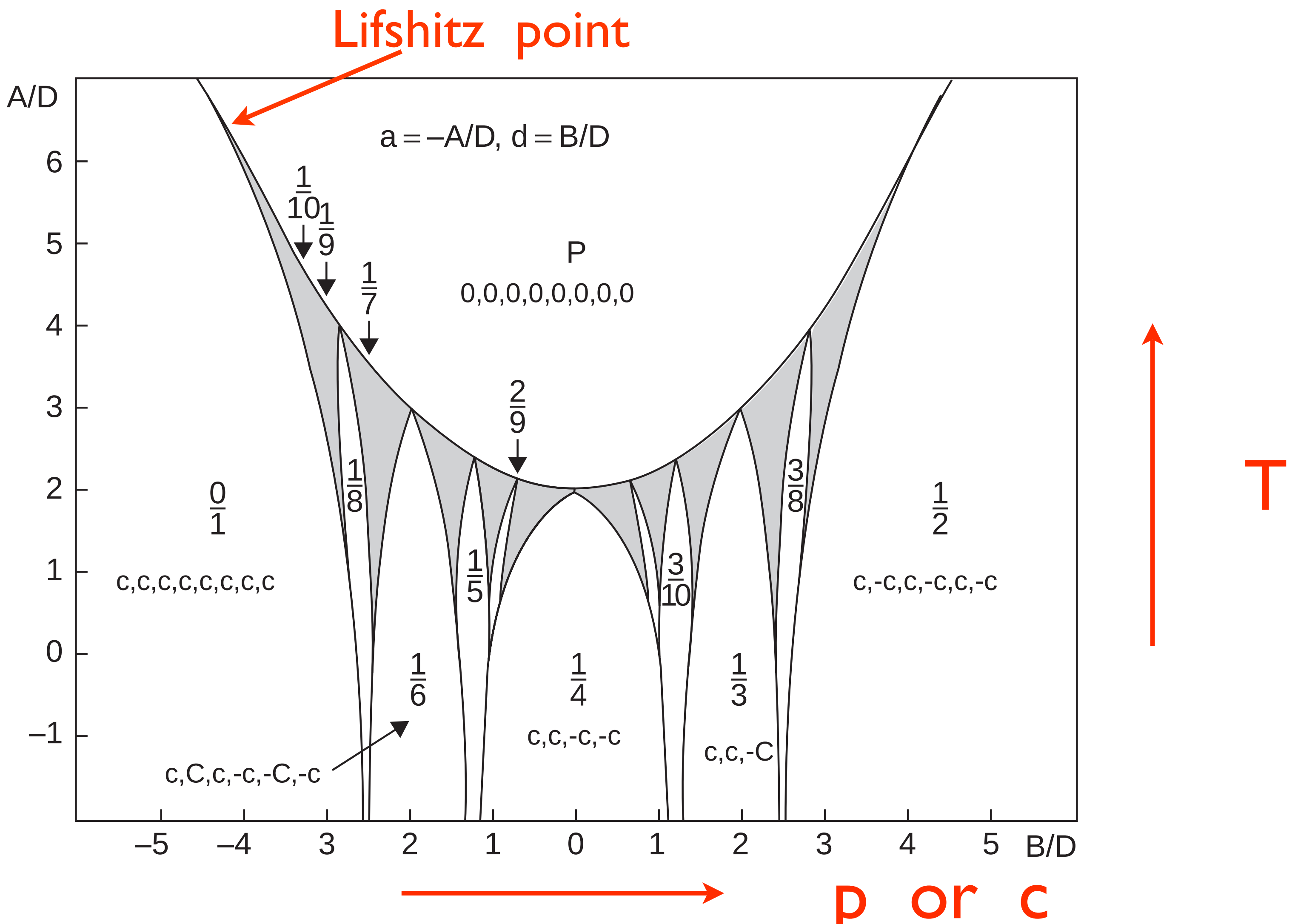
Discrete frustrated ϕ^4 model:

$$V = \sum_n \left(\frac{1}{2} A u_n^2 + u_n^4 + B u_n u_{n-c} + C u_n u_{n-a} + C u_n u_{n-b} + D u_n u_{n-2c}. \right)$$

Phases: para-phase $u_n = 0$
commensurate superstructure
incommensurate modulated phase

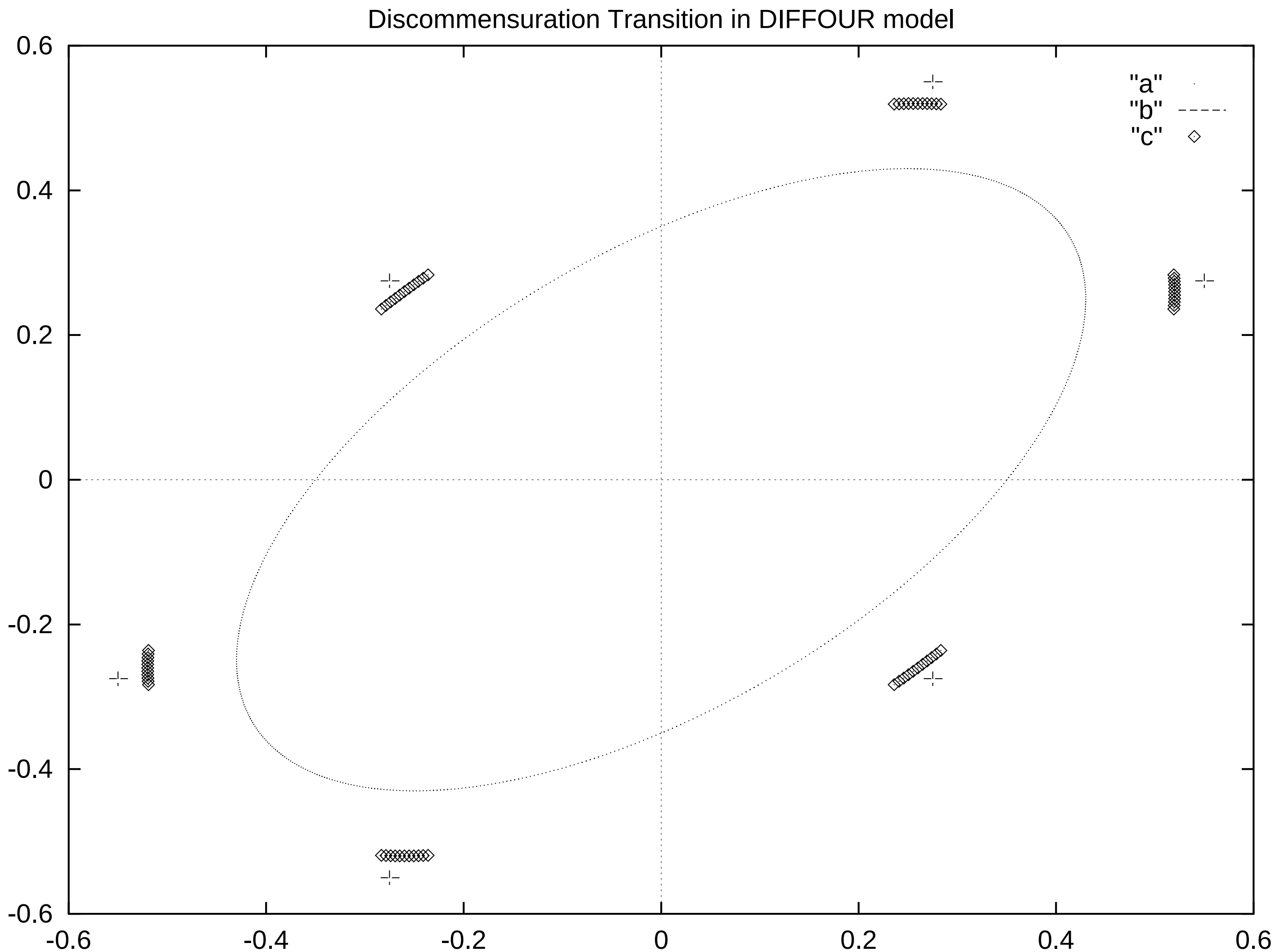
Studied with J.A. Tjon, A. Rubtsov and V. Savkin

Phase Diagram of DIFFOUR model
(discrete frustrated ϕ^4 model)



Typical phase diagram: high T : space group symmetric
below critical T: incommensurate phase
plane wave limit (continuous modulation)
discommensuration limit (discontinuous)
below lock-in T: commensurate

A/D in the model corresponds to T in mean field phase diagram



x_n versus x_{n-1}

a low-T commensurate, 6-fold

b incommensurate, smooth

c incommensurate, discommensurations

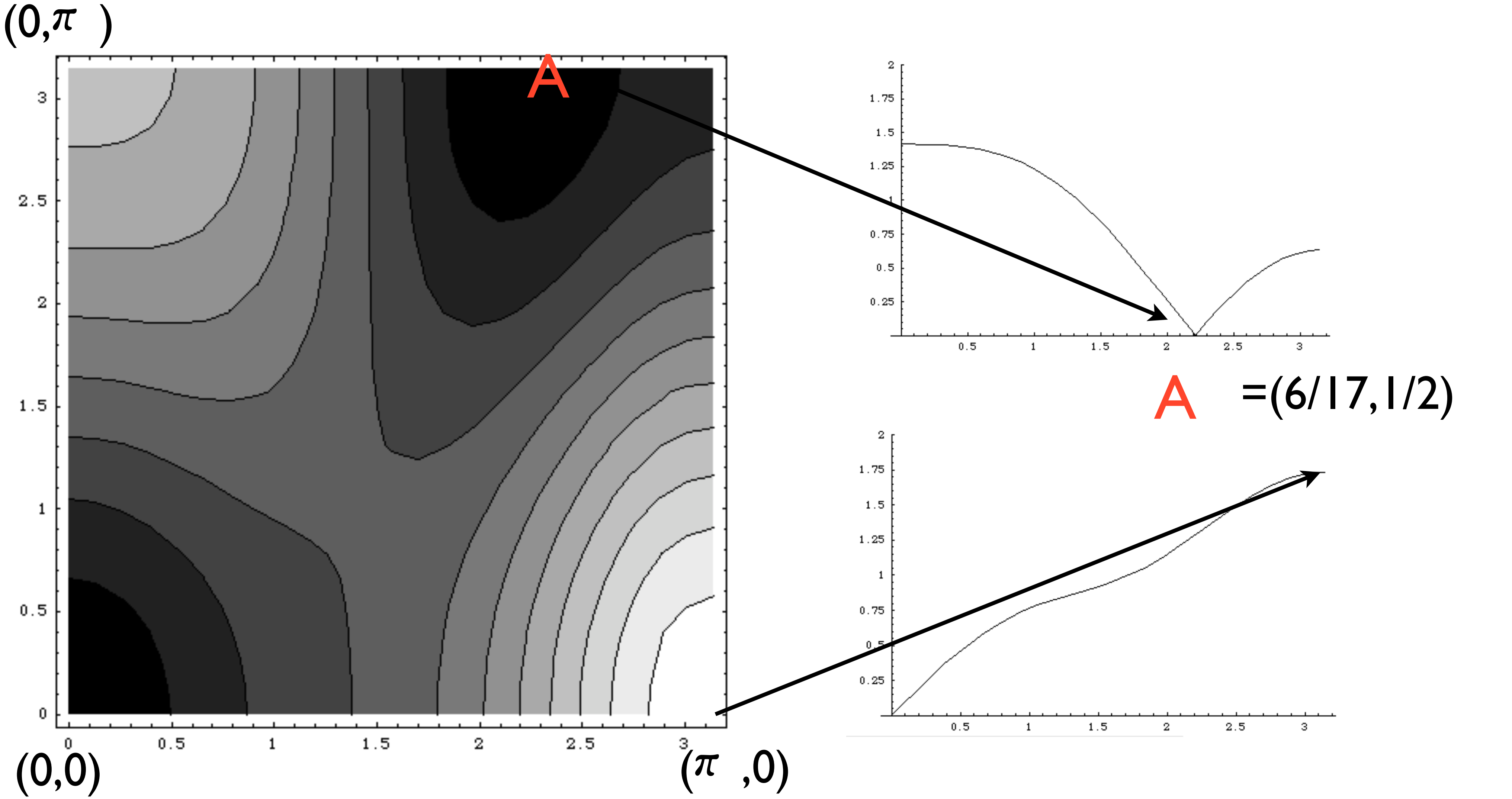
Phase transition: rank 2 (periodic) to rank 3 (aperiodic)

Example of a transition from a 2D periodic
to a 2D aperiodic (3D periodic) system:

soft mode at the zone boundary at (α, 1/2)

$$
\begin{aligned}
V &= \sum_n \left(\frac{a}{2}(u_n - u_{n-a})^2 + \frac{b}{2}(u_n - u_{n-2a})^2 + \frac{c}{2}(u_n - u_{n-3a})^2 \right. \\
&\quad \left. + \frac{d}{2}(u_n - u_{n-b})^2 + \frac{e}{2}(u_n - u_{n-a-b})^2 + \frac{g}{2}(u_n - u_{n-a+b})^2 \right)
\end{aligned}
$$

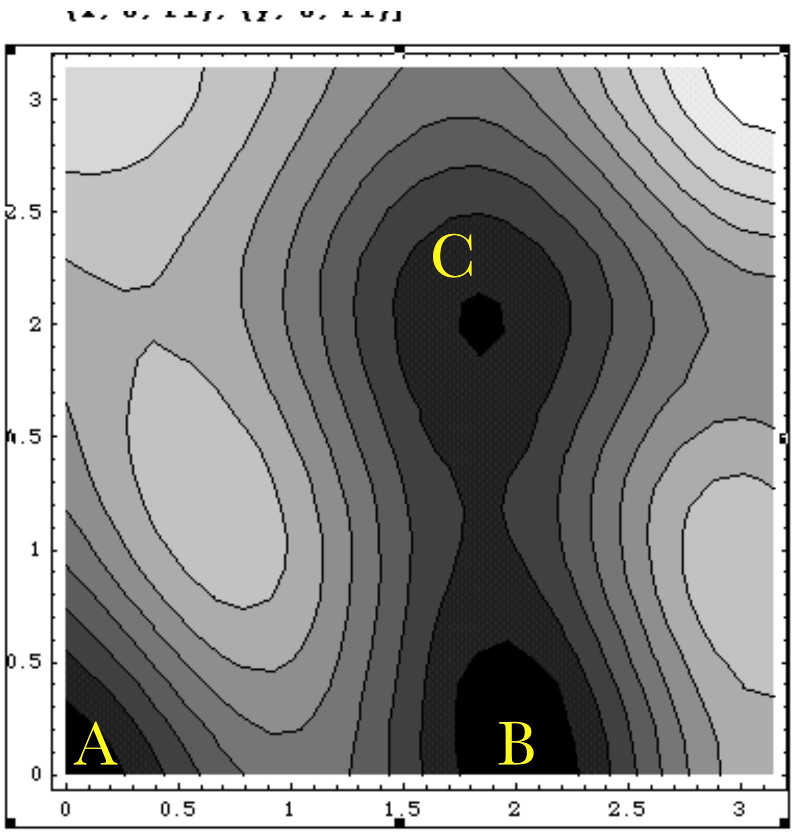
a = 0.1352, b = -0.3047, c = 0.2148, d = -0.15, e = 0.575, cg= 0.575



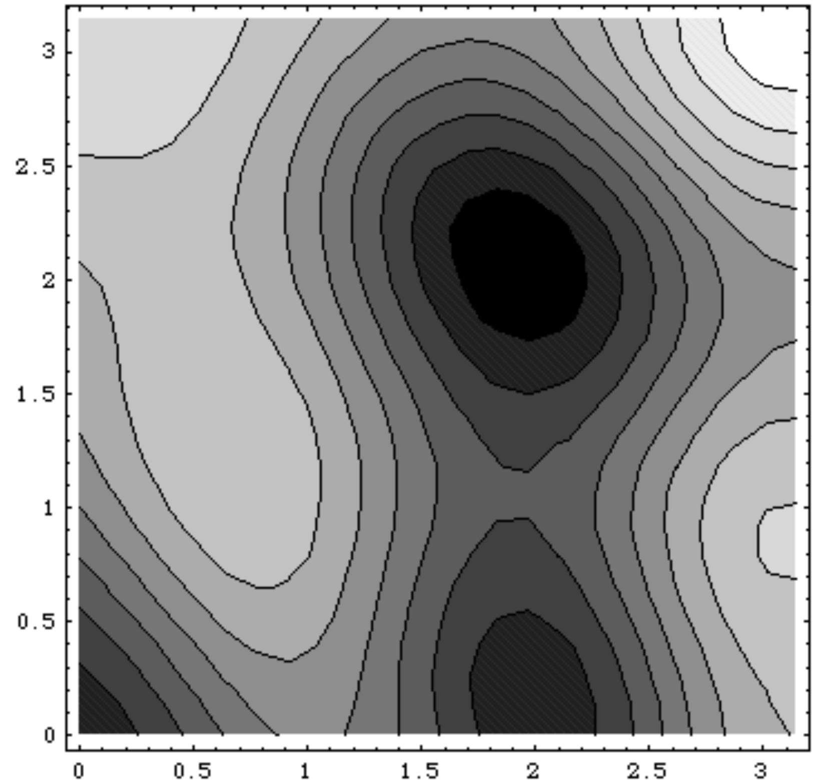
(0,π)
A
(0,0)
(π ,0)
A =(6/17,1/2)

Phase transition 1q-2q

Biphenyl and $BaMnF_4$



$T_2 < T < T_1$



$T < T_2$

Free energy on the Brillouin Zone

Cf. K. Parlinski (19920

$T > T_1$: Unmodulated : A

T_1 : Phase transition to 1q state -> rank 4 :B

T_2 : Phase transition to 2q state -> rank 5 :C

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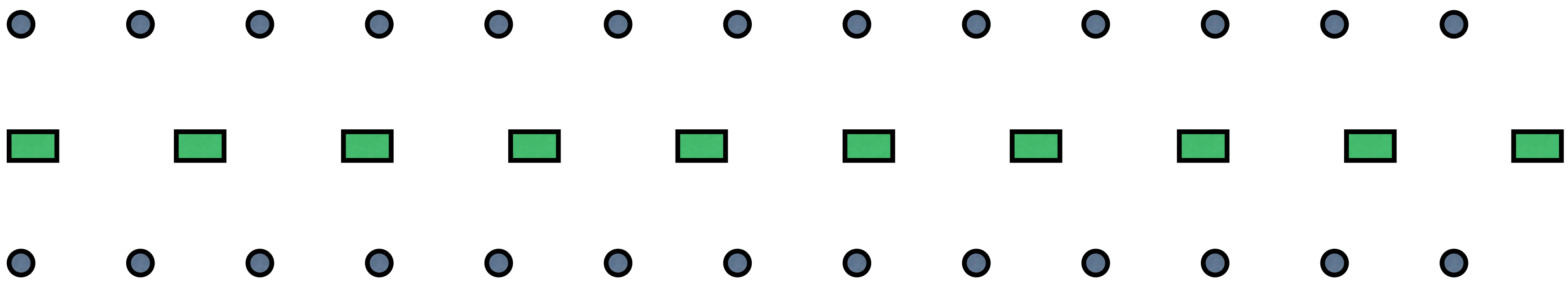
Composites

$$\begin{aligned} x_n^{(i)} &= x_0^{(i)} + na_i + f_i(x_0^{(i)} + na_i), \quad (i = 1, 2) \\ y_m^{(i)} &= (2m + i - 1)b/2, \end{aligned}$$

$$k = h_1/a_1 + h_2/a_2, \ \ \ell = h_3/b$$



Embedding of the composite

$$\left(x_0^{(i)} + na_i - Z_i t + f_i(x_0^{(i)} + na_i + \Delta t), (2m + i - 1)b/2, t\right), \ (i = 1, 2)$$

$$\Delta = Z_2 - Z_1$$

Diffraction peaks

$$\mathbf{k} \;=\; (h_1/a_1 + h_2/a_2,\; h_3/b)$$

$$\begin{array}{ll} h_1 = h_2 = 0 & \text{common reflections} \\ h_2 = 0 & \text{reflections system 1} \\ h_1 = 0 & \text{reflections system 2} \\ h_1 \neq 0,\; h_2 \neq 0 & \text{sum reflections} \end{array}$$

If sum reflections are present: each subsystem is modulated by the other one.

Aperiodic Composites by Self-hosting:
Host and guest are made from the same pure element.
Nelmes, McMahon Phys. Rev. Lett. **83**, 4081 (1999)

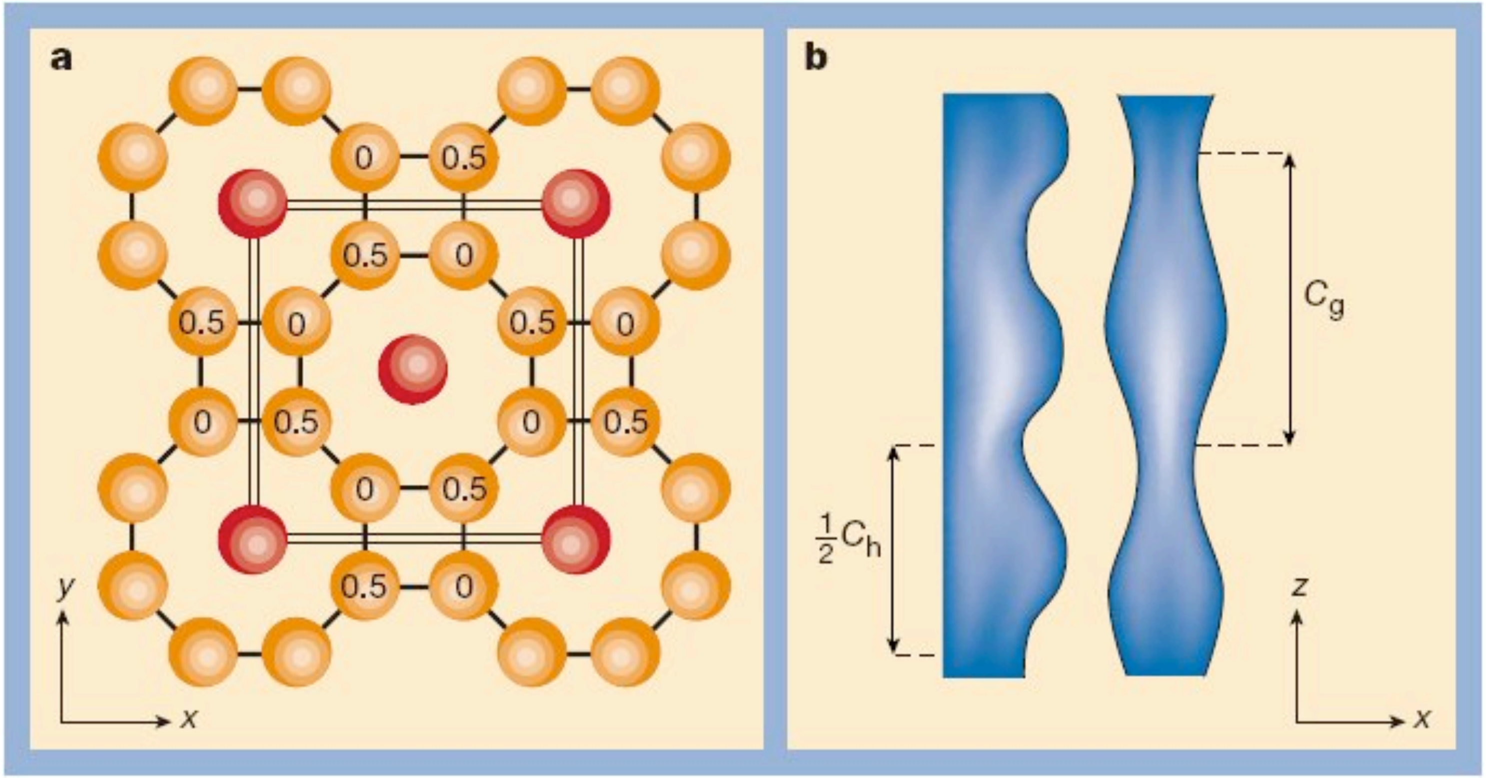
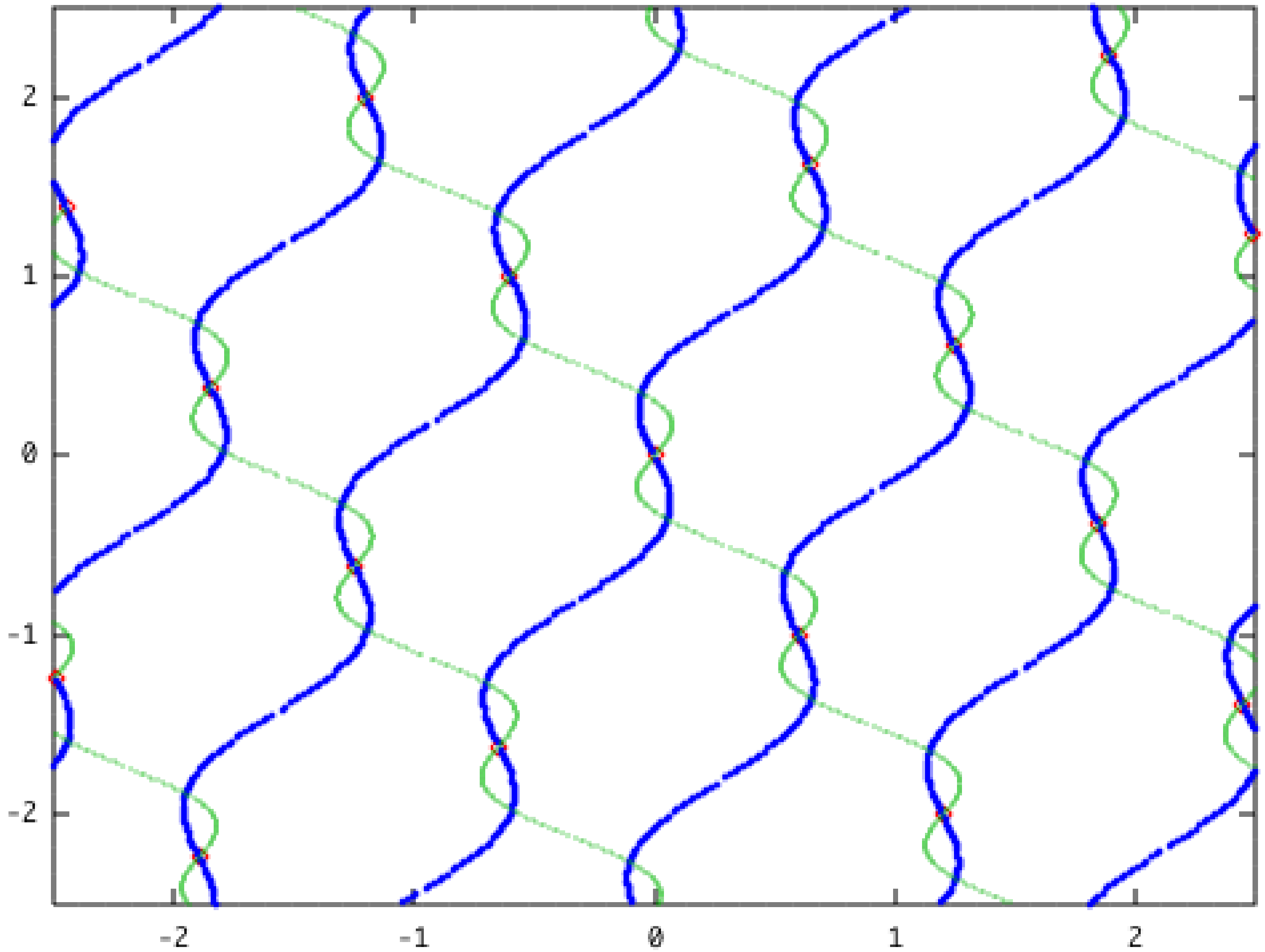


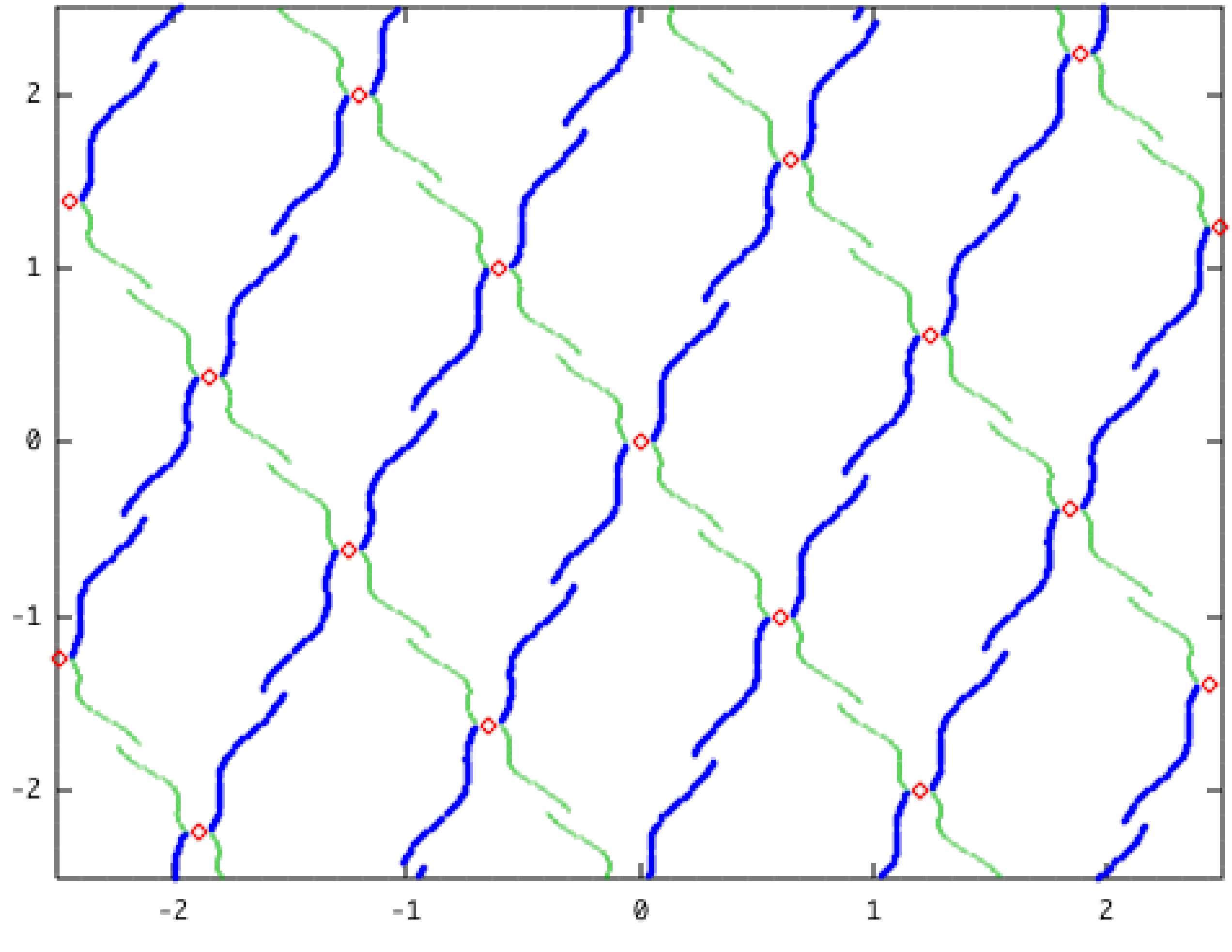
Figure 1 **The high-pressure structure of barium IV discovered by Nelmes *et al.*[2].** a, **Structure projected onto the *x–y* plane, showing the atoms of the host structure (yellow) with heights in units of c_h and the guest chains (red).** b, **Electron density map in the *x–z* plane of the atomic chain (right) with repeat distance c_g and the side of a host cylinder (left). The ratio c_g/c_h is not a rational number, making the structure incommensurate — that is, there is no distance at which it repeats exactly.**

Discommensuration transition: symmetry the same



Embedding of composite with continuous modulation.

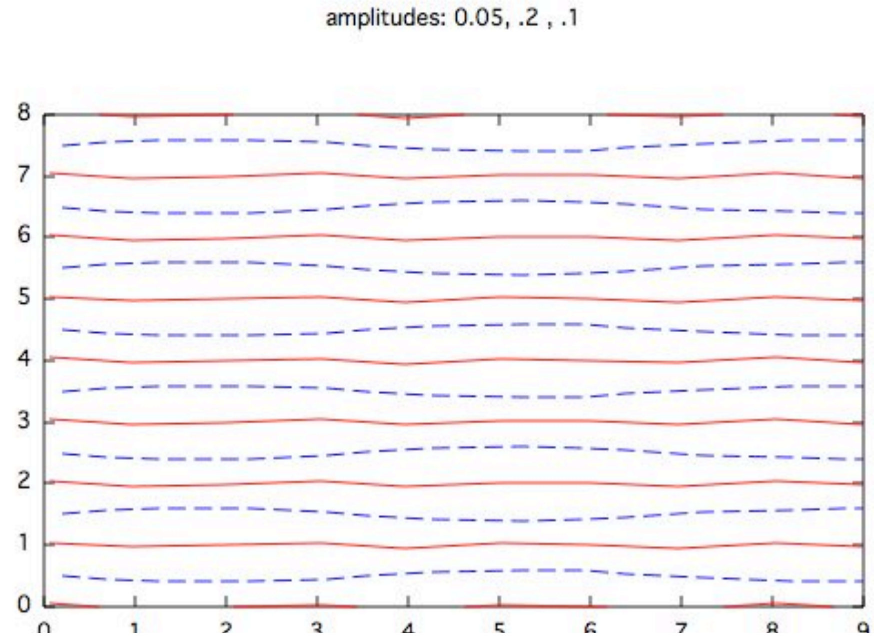
Four types of reflections: common to the subsystems, belonging to one of the subsystems, combinations of reflections of both .



Embedding of composite with discontinuous modulation.

Example of a symmetry preserving phase transition with weak anomaly in the spec. heat, and consequences for dynamics.

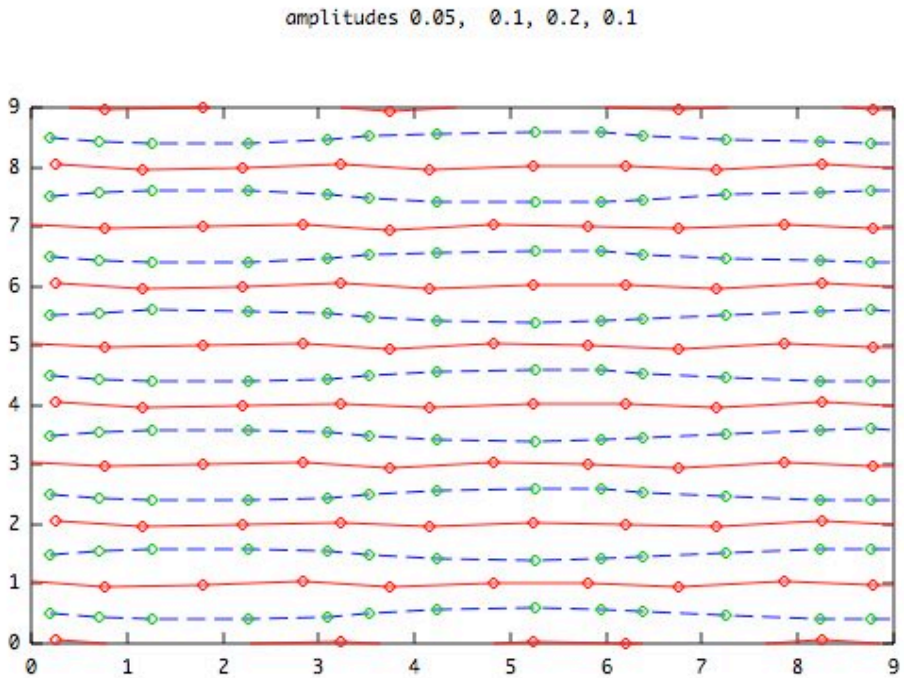
2D Example



2D composite
of rank 4

$$\mathbf{H} = h\mathbf{a}^* + k\mathbf{c}^* + m_1\mathbf{b}^* + m_2(\mathbf{c}^*/2 + \delta\mathbf{a}^*)$$
$$\mathbf{b}^* = \gamma\mathbf{a}^*$$

$$cmm(0\gamma,\ 1\delta)$$



$$= h\mathbf{a}^* + k\mathbf{c}^*/2 + m_1\mathbf{b}^* + m_2\delta\mathbf{a}^*$$
$$\mathbf{b}^* = \gamma\mathbf{a}^*$$

$$pmm(0\gamma,\ 0\delta)$$

Phase transition between phases of the same rank

Example: rank = 3

$$h_1\mathbf{a}^* \;+\; h_2\mathbf{c}^* \;+\; h_3\gamma\mathbf{c}^*$$

$$\mathbf{k} = (\mathbf{a}^* + \mathbf{c}^*)/2$$

$$h_1'(\mathbf{a}^* + \mathbf{c}^*)/2 \;+\; h_2'(\mathbf{a}^* - \mathbf{c}^*)/2 \;+\; h_3\gamma\mathbf{c}^*$$

In superspace doubling of the unit cell.
Changes in the diffraction affect main
reflections of one system only.

Change of the rank in the transition

Model example

$$F = \sum_n \left(\frac{\alpha}{2} (u_n^{(1)})^2 + \frac{1}{4} (u_n^{(1)})^4 + \beta u_n^{(1)} u_{n-1}^{(1)} + \delta u_n^{(1)} u_{n-2}^{(1)} \right)$$
$$+ \sum_n \gamma (x_n^{(2)} - x_{n-1}^{(2)} - a_2)^2 + \lambda \sum_{n,m} V(x_n^{(1)} - x_m^{(2)})$$
$$+ \zeta \sum_{i,m} (y_m^{(i)} - (2m + i - 1) b/2)^2,$$

$$u_n^{(1)} = x_n^{(1)} - n a_1$$

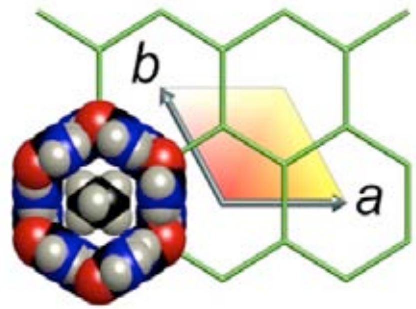
$\mathbf{a}_1^* = (1/a_1, 0)$, $\mathbf{a}_2^* = (1/a_2, 0)$, and $\mathbf{a}_3^* = (0, 1/b)$

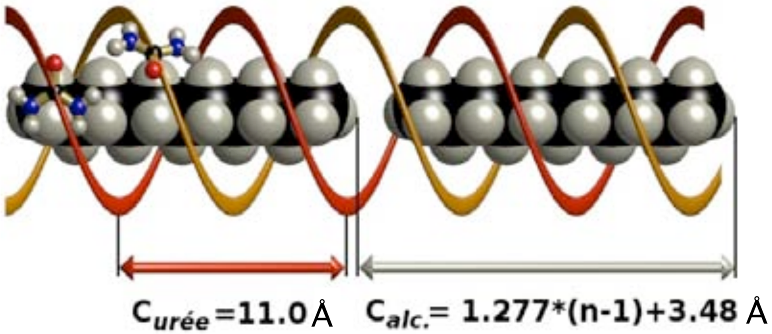
In superspace additional dimension.
Changes in the diffraction affect sum peaks.
Example: urea-nonadecane (Toudic)

Single Crystal

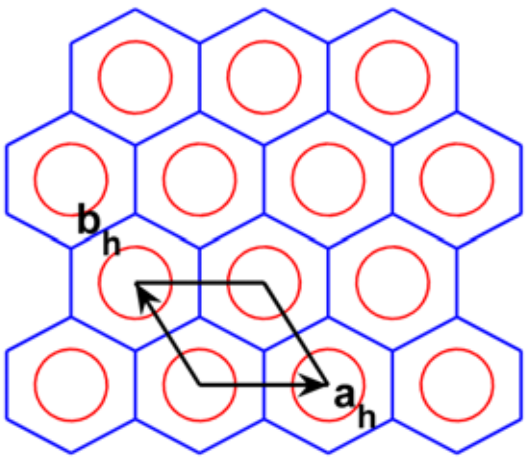
nonadecane – urea

$C_{19}D_{40}$ – $CO(ND_2)_2$



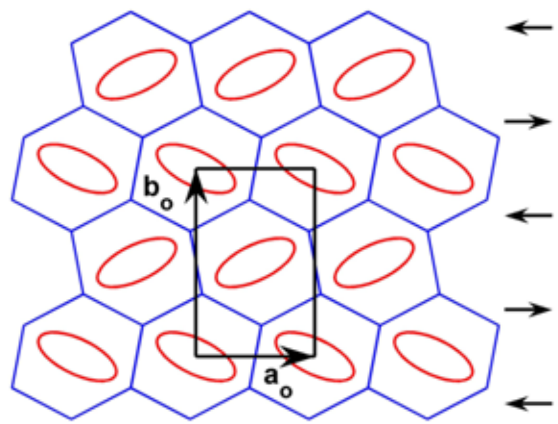


Study of the phase transition at 3 dimensions



High Symmetry Phase :
hexagonal
$P6_122$

Orientational Disorder
of the alkanes



Low Symmetry Phase :
orthorhombique
$P2_12_12_1$

Anti-ferro shearing of urea
Anti-ferro ordering of the alkanes

Diffraction Image of a Composite Aperiodic Crystal (Rank 4)

Single Crystal

nonadecane - urea

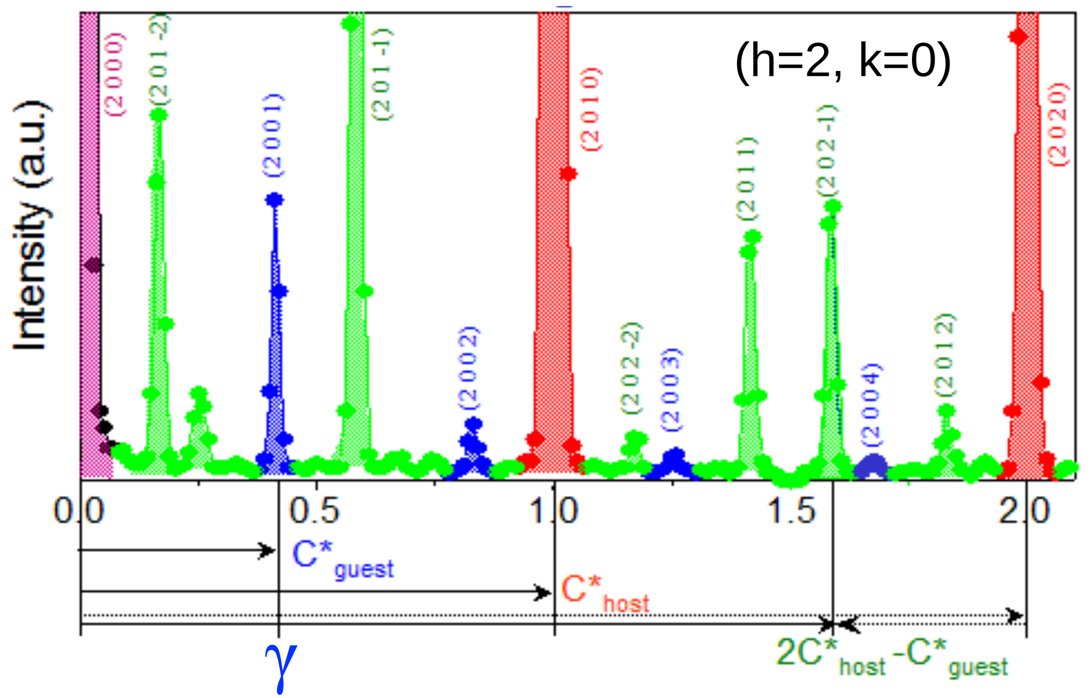
$C_{19}D_{40}$ - $CO(ND_2)_2$

$C_{urea} = 11.02$ Å

$C_{nonadecane} = 26.46$ Å

$\gamma \cong 0.42$

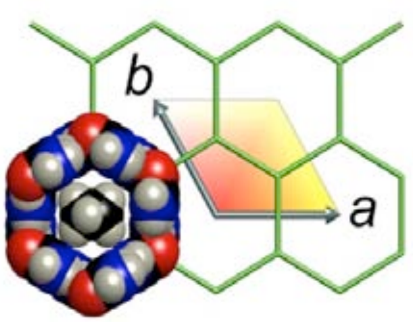
$$Q_{hklm} = h\,\mathbf{a}^* + k\,\mathbf{b}^* + l\,\mathbf{c}_1^* + m\,\mathbf{c}_2^*$$

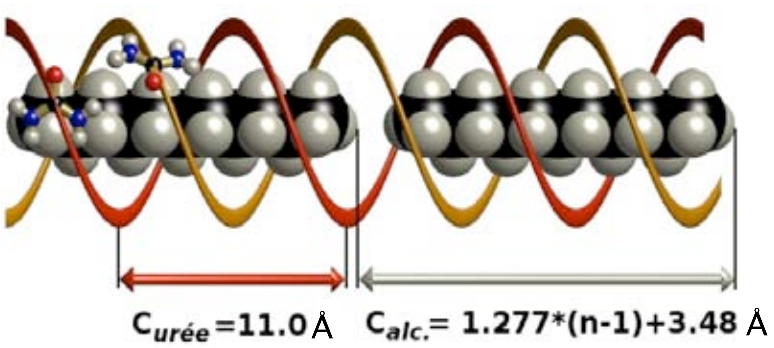


G43

LLB (Saclay)

$k_i = 2.662$ Å^{-1}





R. Lefort et al. Phys. Rev. Lett. **77**, 19 (1996); T. Weber (1996)

Hidden Degrees of Freedom in Aperiodic Materials

SCIENCE VOL 319 4 JANUARY 2008

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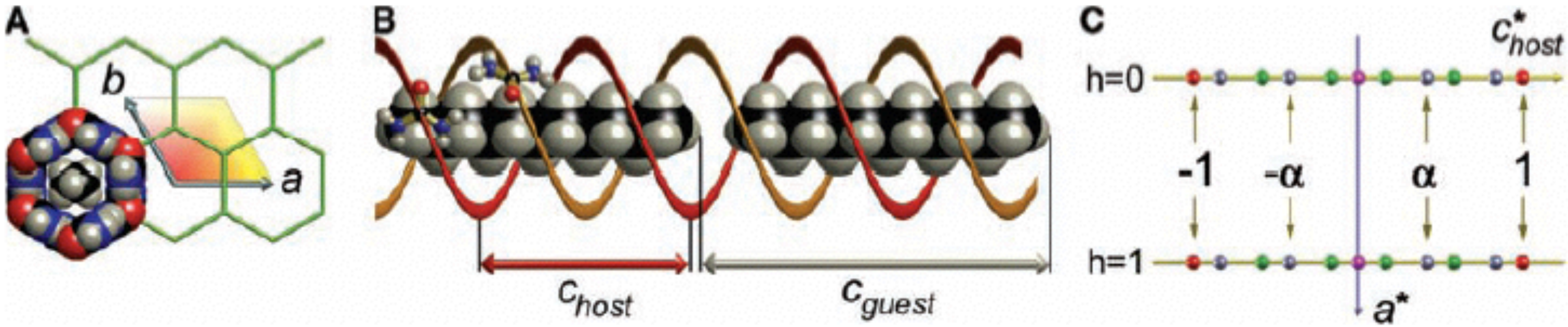
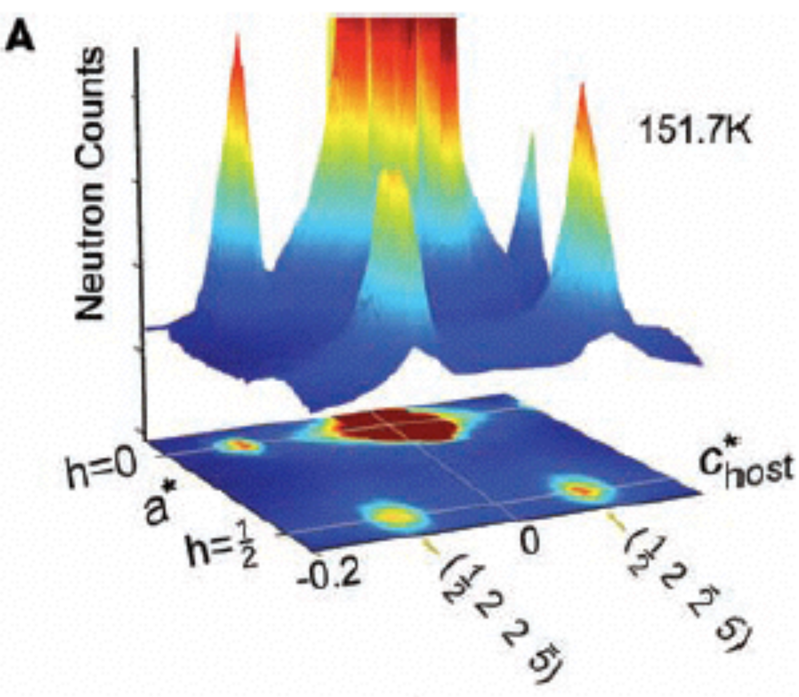
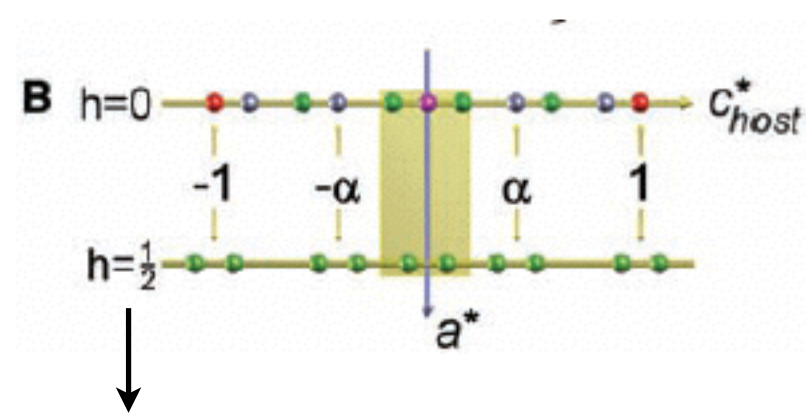
Claude Ecolivet,[1,2] Eric Collet,[1,2] Philippe Bourges,[3] Garry J. McIntyre,[4]
Mark D. Hollingsworth,[5] Tomasz Breczewski[6]







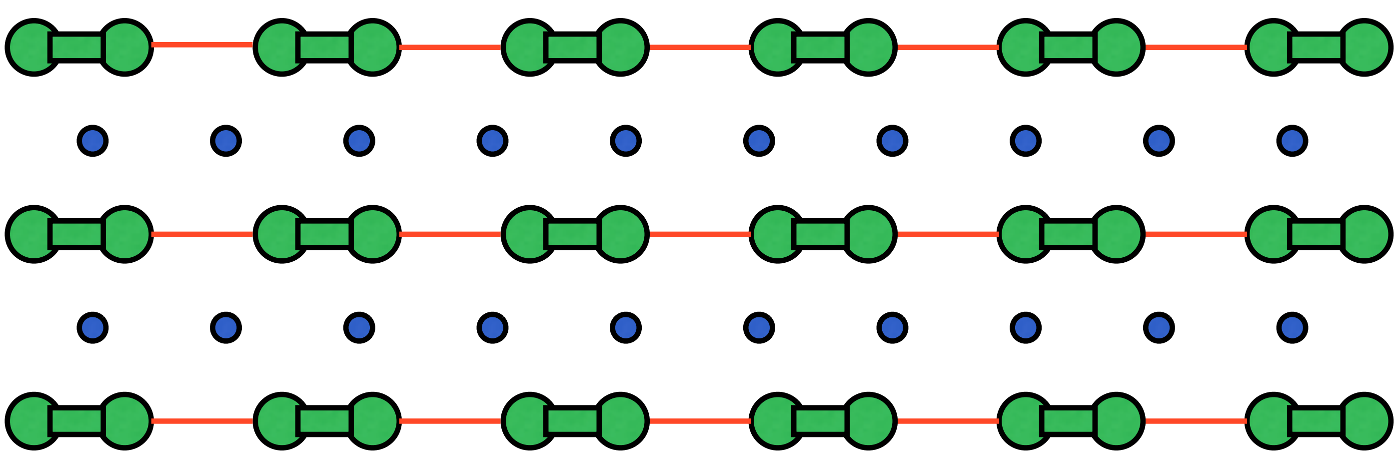
New diffraction peaks

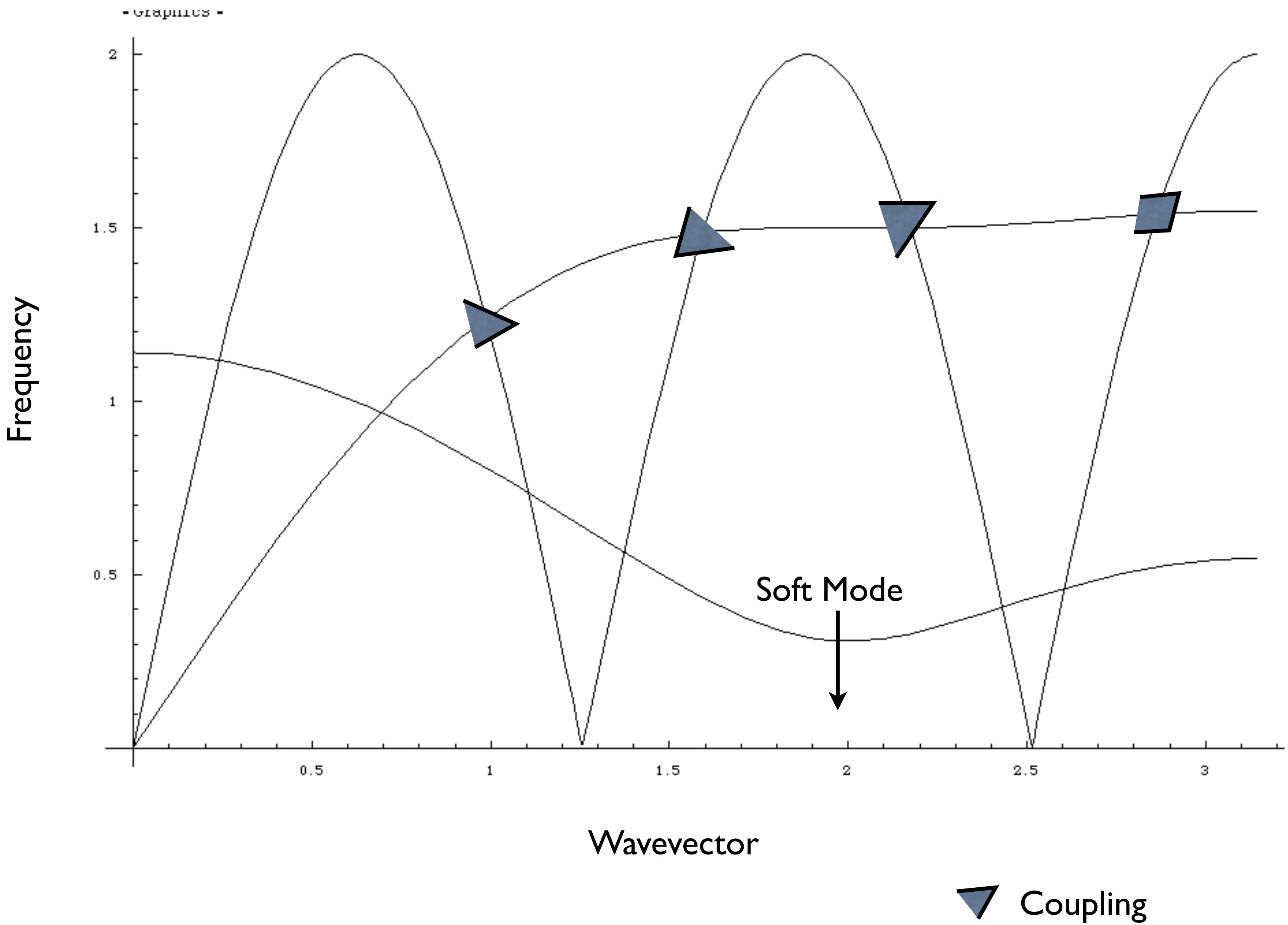
Simple model: soft optic mode

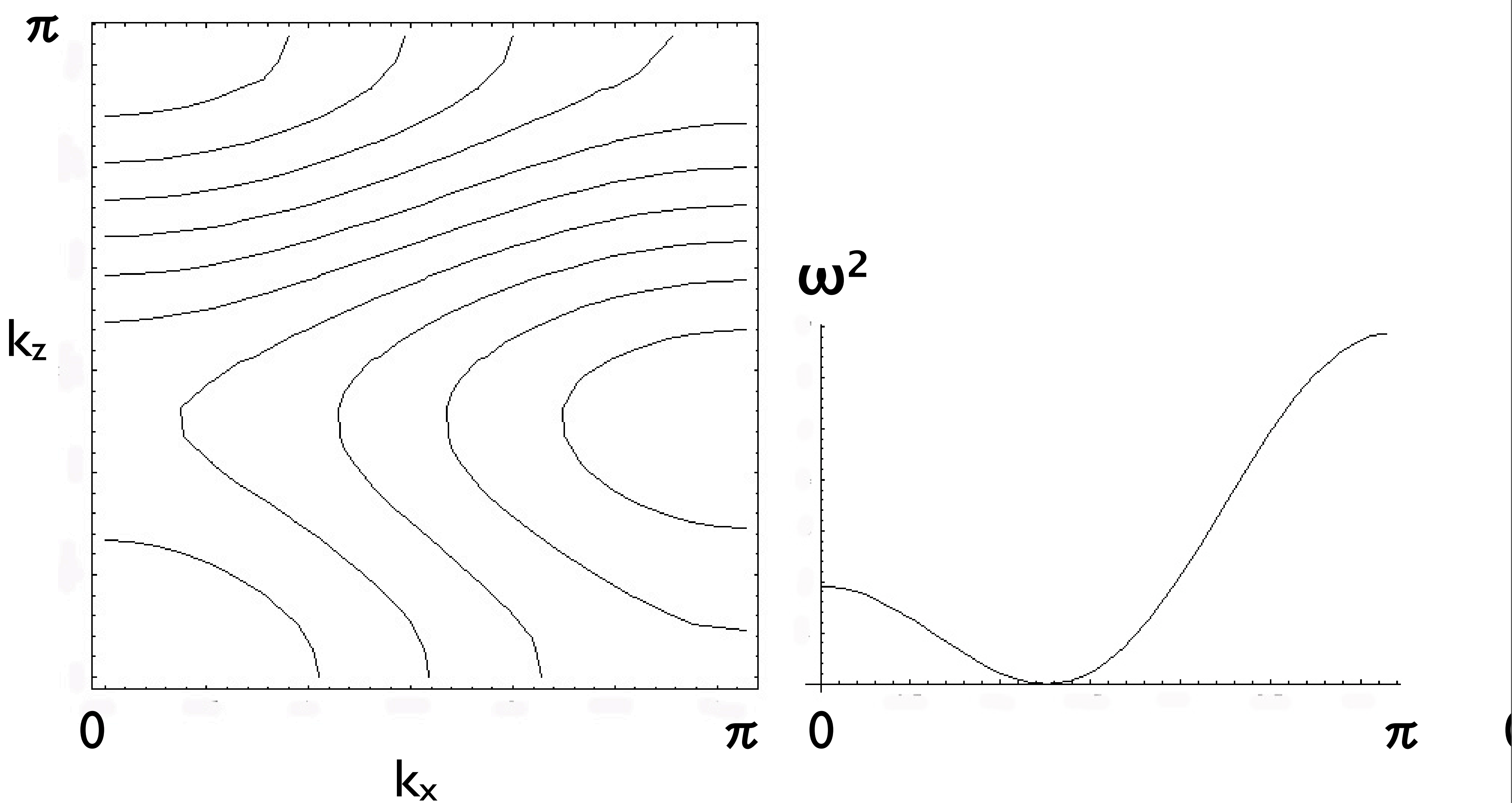
$$F = \sum_n \left(Au_n^2/2 + u_n^4/4 + Bu_nu_{n-c} + Cu_nu_{n-2c} + Du_nu_{n-a} \right)$$

$$\omega^2 = A + 2B\cos(z) + 2C\cos(2z) + 2D\cos(x)$$

Parameters with A, B, C and D are temperature dependent



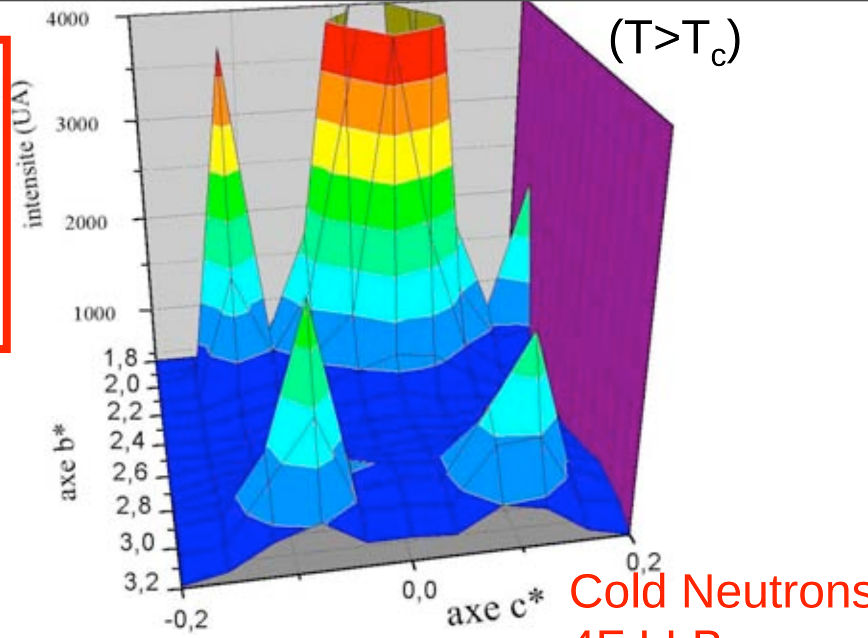

- Graphics -
2
1.5
1
0.5
0.5
1
1.5
2
2.5
3
Frequency
Wavevector
Soft Mode
Coupling



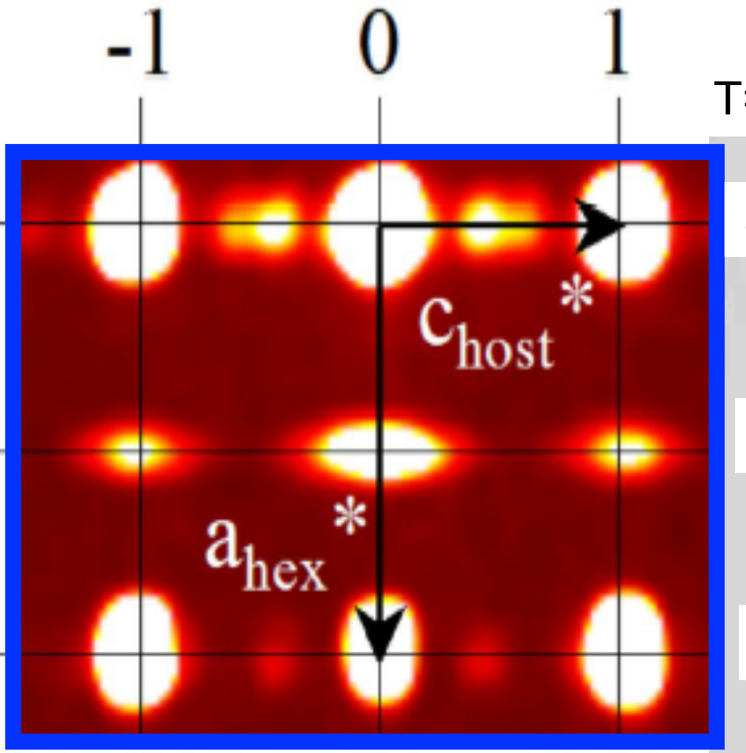
π
k_z
0
π
k_x
ω^2
0
π

Phase transition in a crystallographic superspace

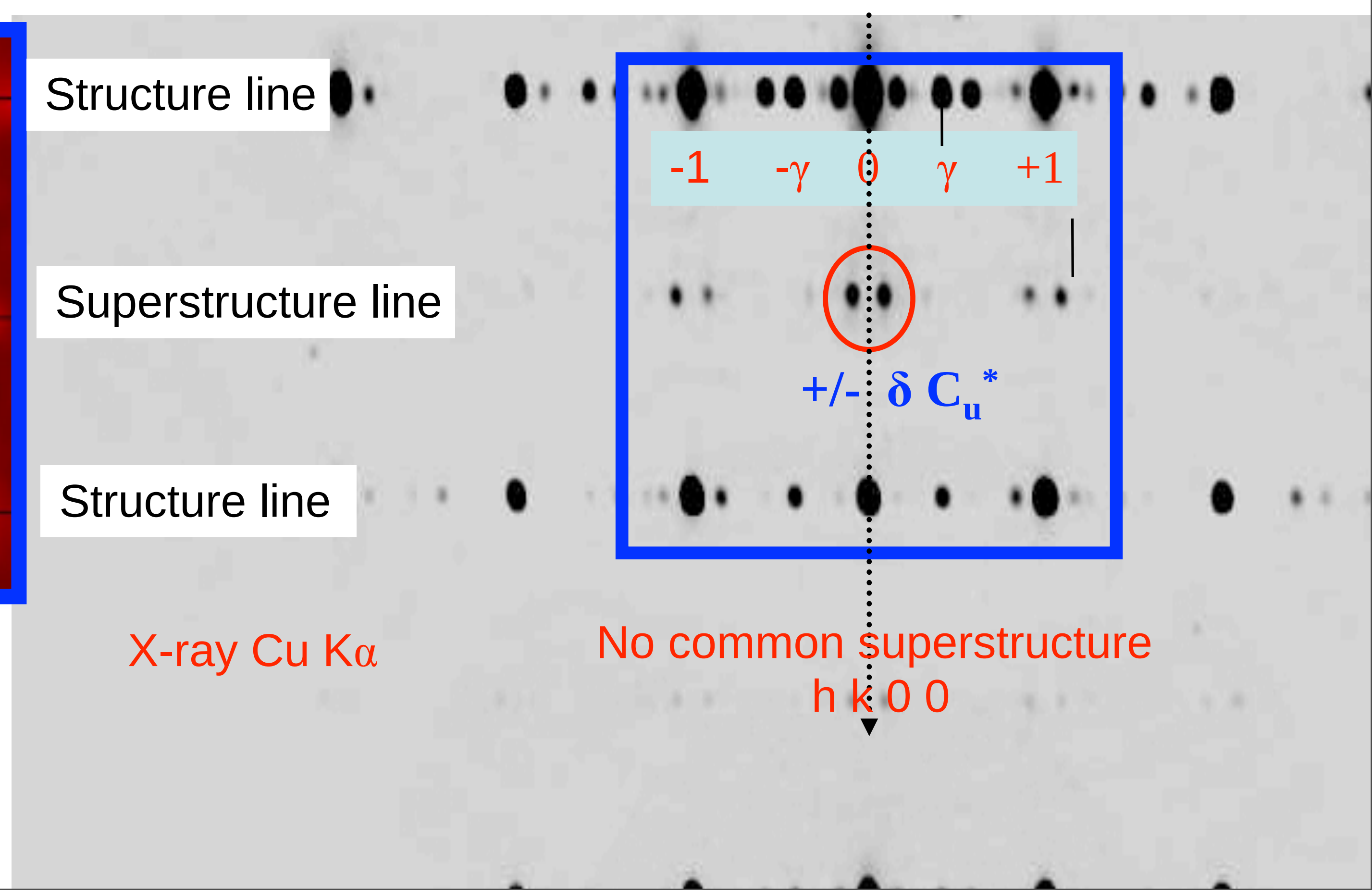
(B. Toudic et al., *Science* **319**, 69, 2008)



Nonadecane-urea: $\gamma \cong 0.42$

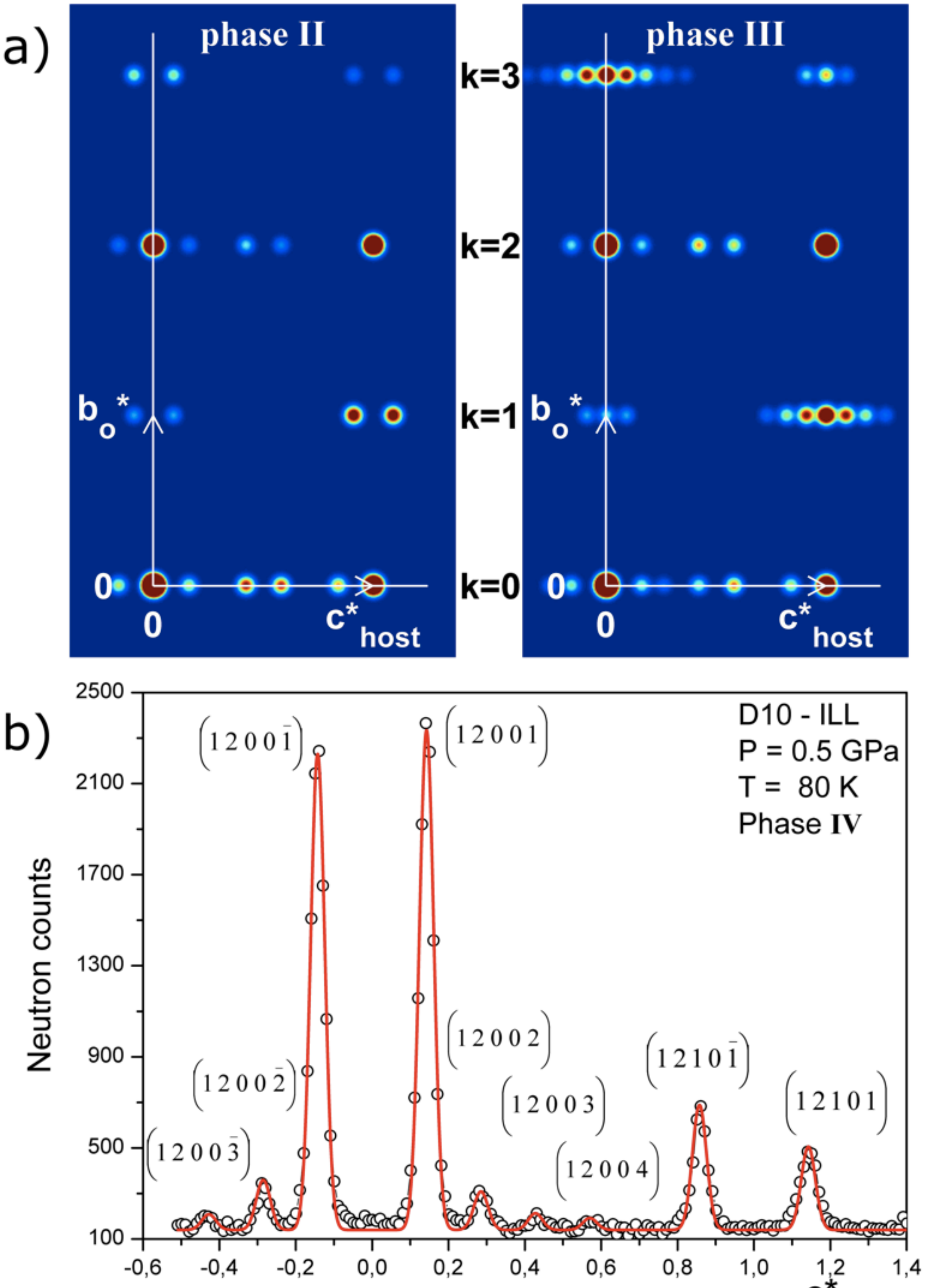


X-ray Mo



X-ray Cu Kα

No common superstructure
h k 0 0



II Orthorhombic
a^*, $2b^*$, c^*, γc^*, $b^*+\delta c^*$

III a^*, b^*, c^* ,γc^*, $b^*+\delta c^*$

(ambient pressure)

IV Scan along c^*:
sattelites at $120m_1m_2$
and $121m_1m_2$, no main
reflections 12000 or 12100

(high pressure)

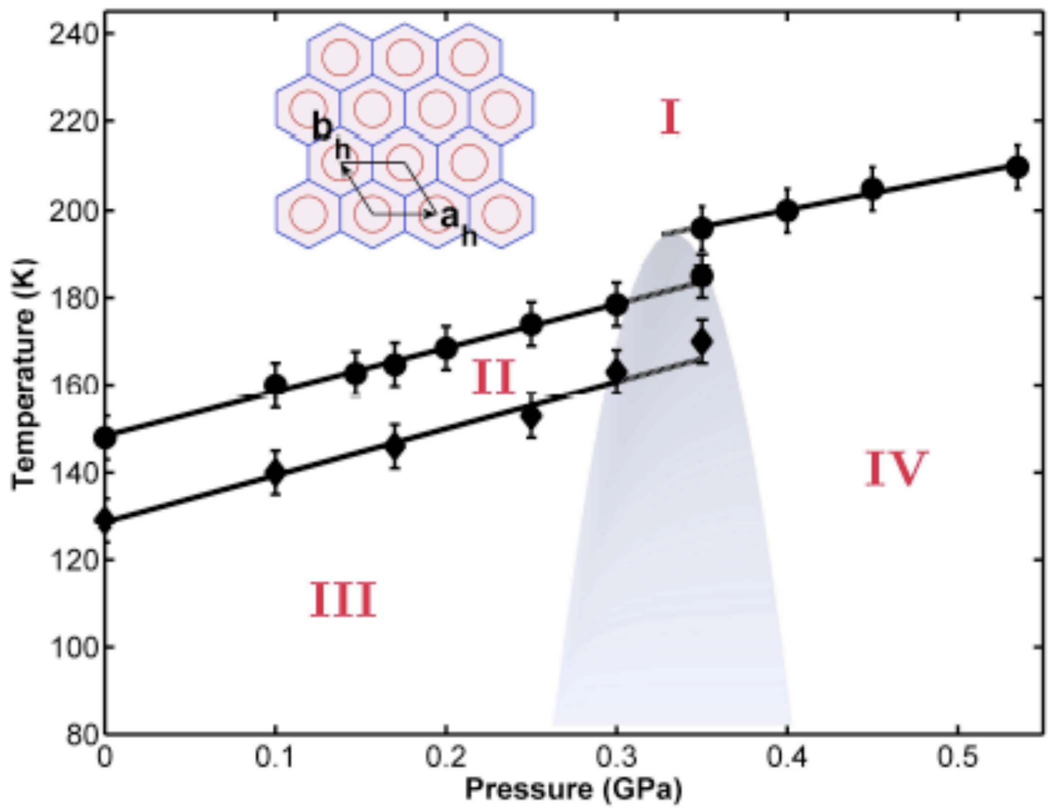


FIG. 1: Phase diagram (P,T) of the fully deuterated non-adecane urea, as determined by neutron diffraction. All the phases (I, II, III, IV) require a description within a crystallographic superspace. The dashed region indicates the metastable region, between the low-pressure phases (phases II and III) and the ordered high-pressure phase (phase IV). The insert in the high symmetry phase (phase I) illustrates the hexagonal symmetry. Color corresponds to the fourth variable defined along the internal dimension of the crystallographic superspace.

p-T phase diagram

nona-decane urea

Bertrand Toudic *et al.*
(submitted)

I hexagonal, rank = 4
II orthorhombic rank = 4
III orthorhombic rank = 5
IV orthorhombic rank = 5

III-IV first-order
phases with the same
SSG?

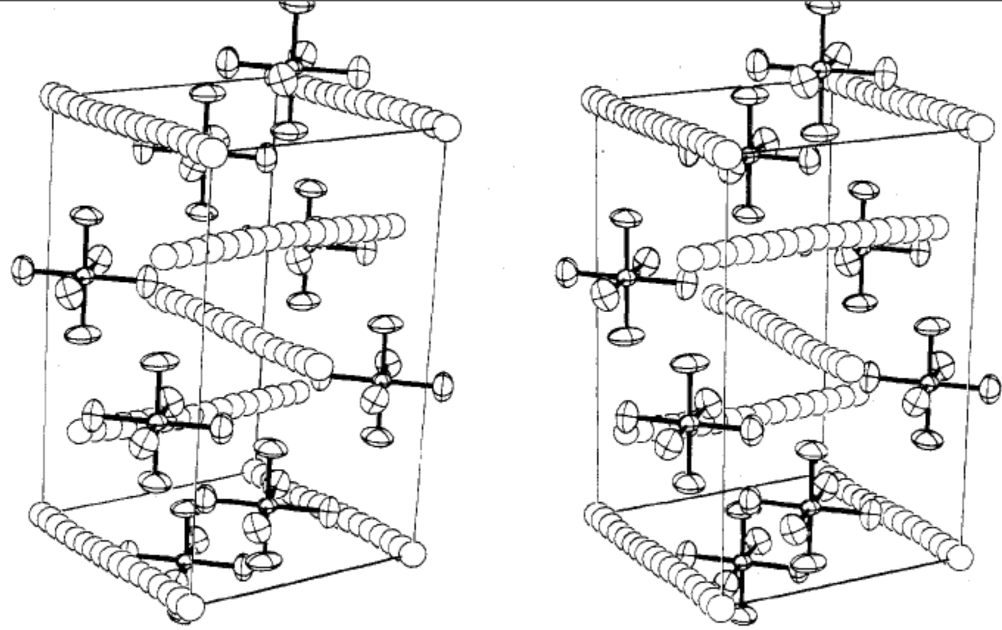


Figure 3. A stereoscopic view of the unit cell of Hg_3AsF_6 showing the disordered model for the Hg chains. Each Hg position is only partially occupied. The thermal ellipsoids are scaled to 50% probability. It should be noted that the mercury chains are not required crystallographically to be linear, such that a slight buckling of the chains is observed, with a maximum deviation from the chain axis of 0.07 (1) Å.

$Hg_{3-\delta}AsF_6$

Pouget, Shirane et al. Phys.Rev.1978)

Phase transition at 120K

Subsystem 1: AsF_6 ; Subsystems 2,3: Hg chains

$k=h_1(0,1,1)+h_2(1,0,1)+h_3(1,1,0)+h_4(\delta,\delta,0)+h_5(\delta,-\delta,0)$

$$Z^1=\begin{pmatrix}1&0&0&0\\0&1&0&0\\0&0&1&0\end{pmatrix},\quad Z^2=\begin{pmatrix}\bar{2}&2&1&1\\1&0&0&0\\0&\bar{1}&1&0\end{pmatrix},\quad Z^3=\begin{pmatrix}2&\bar{2}&1&1\\0&1&0&0\\\bar{1}&0&1&0\end{pmatrix}$$

Superspace group : basic structure Fddd(0δ0)00s

rank 5: Fddd(δ0-δ,0δ0)00n ??

(JJ, Acta Cryst. 1980))

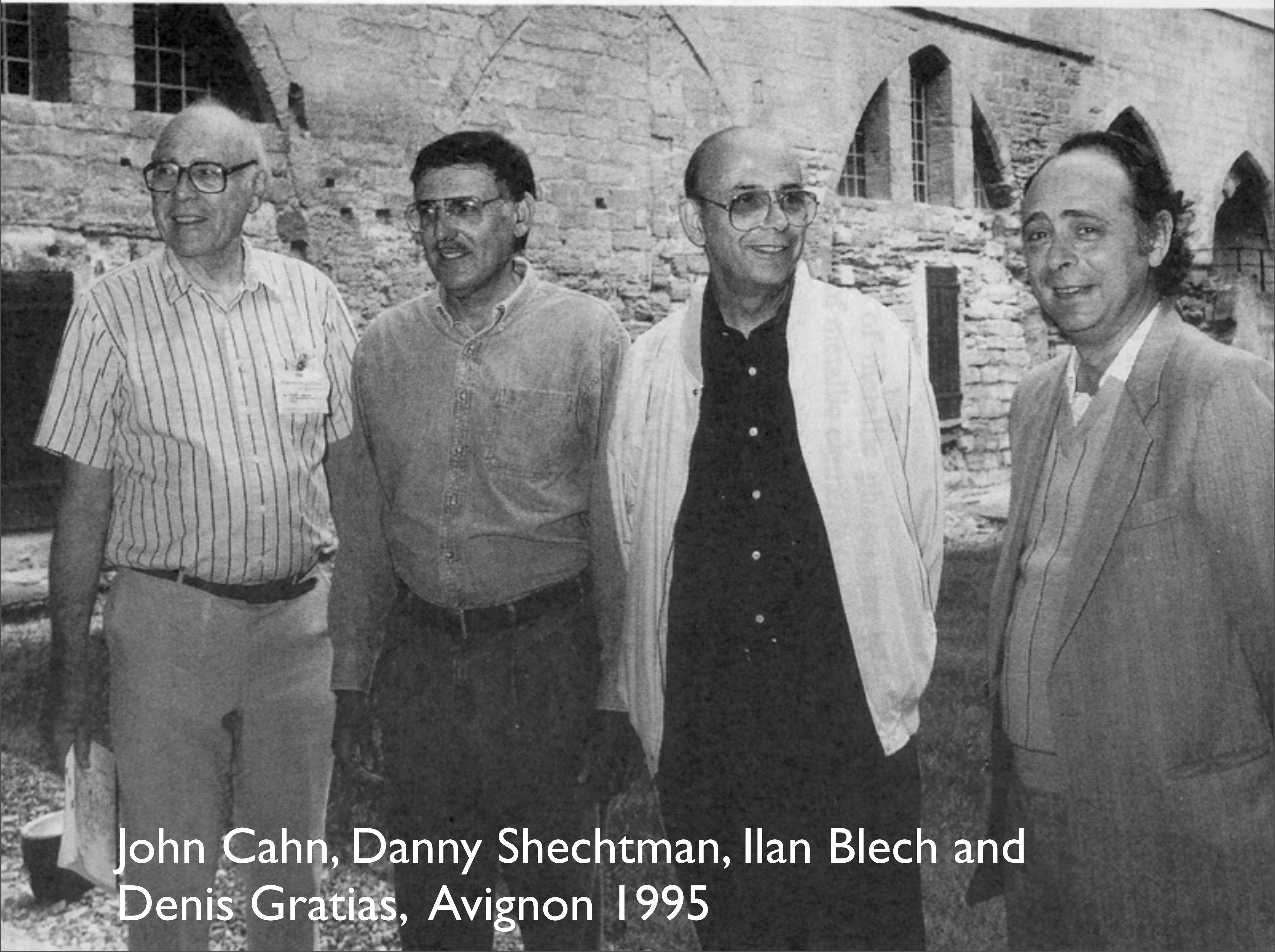
Phase transitions in commensurate and incommensurate crystals

Modulated crystals

Incommensurate composites

Quasicrystals and tilings

Incommensurate magnetic structures



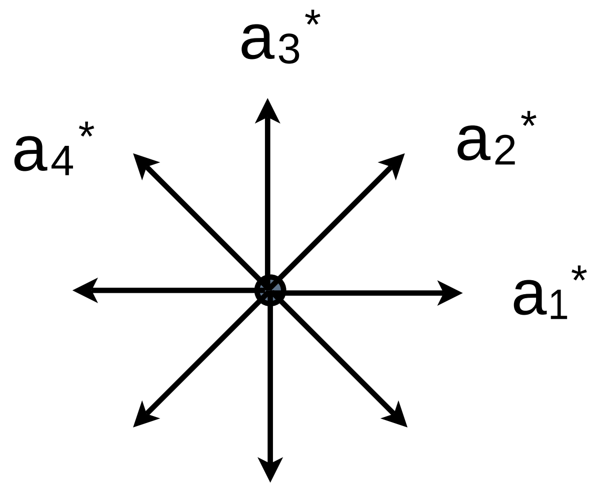
John Cahn, Danny Shechtman, Ilan Blech and
Denis Gratias, Avignon 1995

Quasicrystals

Aperiodic
Local structure with clusters
Possibly, but not necessarily, non-crystallographic symmetry

As model: tiling.

Example: Ammann-Beenker tiling:

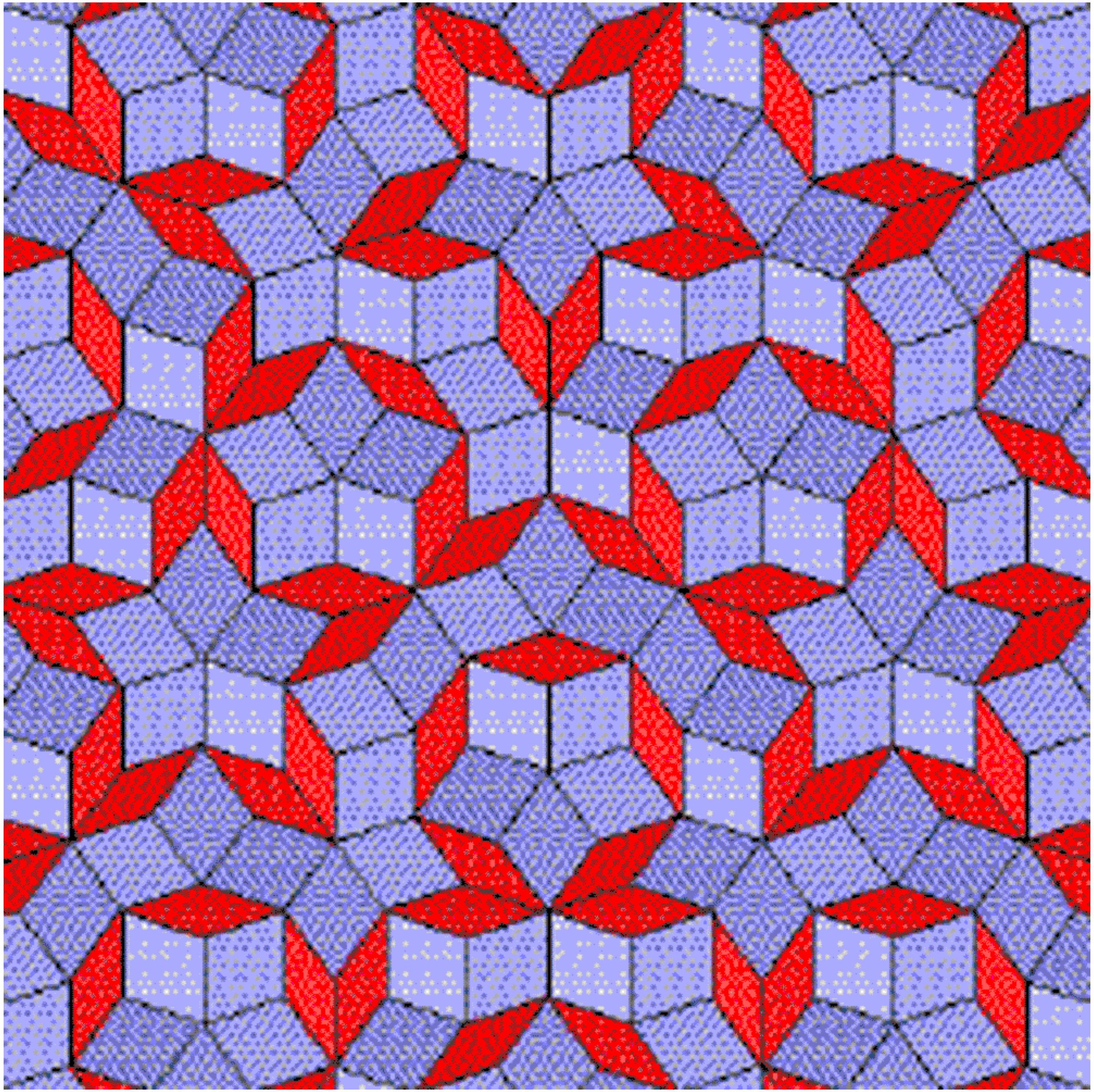


Diffraction $h_1\mathbf{a}_1^* + h_2\mathbf{a}_2^* + h_3\mathbf{a}_3^* + h_4\mathbf{a}_4^*$

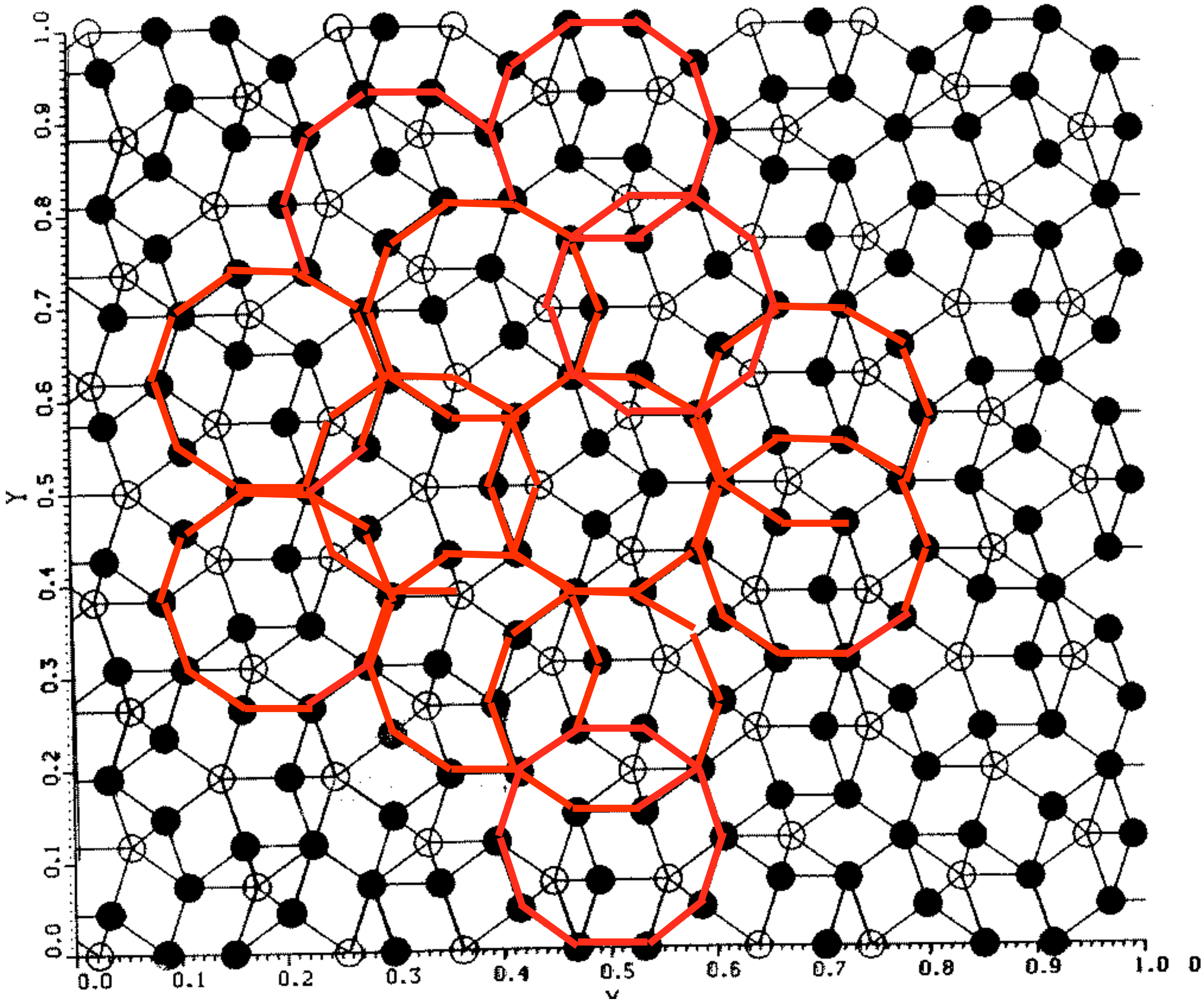
Basis Embedding in 4D $(\mathbf{a}_1^*, \mathbf{a}_1^*)$, $(\mathbf{a}_2^*, \mathbf{a}_4^*)$, $(\mathbf{a}_3^*, -\mathbf{a}_3^*)$ $(\mathbf{a}_4^*, \mathbf{a}_2^*)$

Σ^* : $(1,0,1,0)$, $(a,a,-a,a)$, $(0,1,0,-1)$, $(-a,a,a,a)$ with $a = \sqrt{\frac{1}{2}}$.

4D lattice: $\Sigma =$ dual of Σ^*.



Penrose tiling, dimension = 2, rank = 4, five-fold symmetry



Y
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0 0

Quasicrystals in *n*D superspaces

(*n*-3)D atomic surfaces in *n*D unit cell

Phase transitions:
- Phason strain, lower rank
- Commensurate modulation, same symmetry
- Commensurate modulation, lower symmetry
- Incommensurate modulation, higher rank

Quasicrystals
1. Phason strain

Embedding gives n-dimensional lattice periodic structure, with lattice characterised by the metric tensor g

Tensor elements: scalar products of pairs of basis vectors.

$$g_{ij} = a_i \,.\, a_j$$

$$g = \begin{pmatrix} A & B & B & B & B & B \\ B & A & B & -B & -B & B \\ B & B & A & B & -B & -B \\ B & -B & B & A & B & -B \\ B & -B & -B & B & A & B \\ B & B & -B & -B & B & A \end{pmatrix}$$

$$A = (2+\Phi)(1+c^2)a^2$$

$$B = \Phi(1-c^2)a^2$$

$$\Phi = (\sqrt{5}+1)/2$$

Example: 6D lattice corresponding to icosahedral standard tiling.

Approximant: periodic structure, locally similar to the quasicrystal. The embedding of the former is obtained from the latter by a ‘phason strain’.
In the transition the point group changes from 532 to 23.

Group 532						Group 23				
	E	5	5^2	3	2		E	3	3^2	2
Γ_1	1	1	1	1	1	D_1	1	1	1	1
Γ_2	3	$-\tau$	$1+\tau$	1	-1	D_2	1	ω	ω^2	1
Γ_3	3	$1+\tau$	$-\tau$	1	-1	D_3	1	ω^2	ω	1
Γ_4	4	-1	-1	1	0	D_4	3	0	0	-1
Γ_5	5	0	0	-1	1					

Order parameter is the 6D strain (phason strain).
This transforms with an irrep of 532 (icosahedral).
The lowest energy structure has symmetry 23 (tetrahedral).

1. Through phason strain: transition to lower symmetry

Change of the metric tensor: $$g' = \begin{pmatrix} A' & B' & C' & C' & C' & C' \\ B' & A' & C' & -C' & -C' & C' \\ C' & C' & A' & C' & -C' & -B' \\ C' & -C' & C' & A' & B' & -C' \\ C' & -C' & -C' & B' & A' & C' \\ C' & C' & -B' & -C' & C' & A' \end{pmatrix}$$

Incommensurate rank 6
or
commensurate rank 3:
approximant

$$\begin{aligned} A' &= (2+\Phi+c^2(1+L^2/N^2))a^2 \\ B' &= (\Phi+c^2(1-L^2/N^2))a^2 \\ C' &= (\Phi-c^2L/N)a^2 \end{aligned}$$

2. Through phason modulation: transition to higher rank

Symmetry change:

$$\mathrm{P}532(5^2 32)\times E^6 \longrightarrow \mathrm{P}532(5^2 32, 532, 5^2 32)(\alpha 00000)$$

Order parameter $\eta(\alpha \mathbf{a}_1^*)$

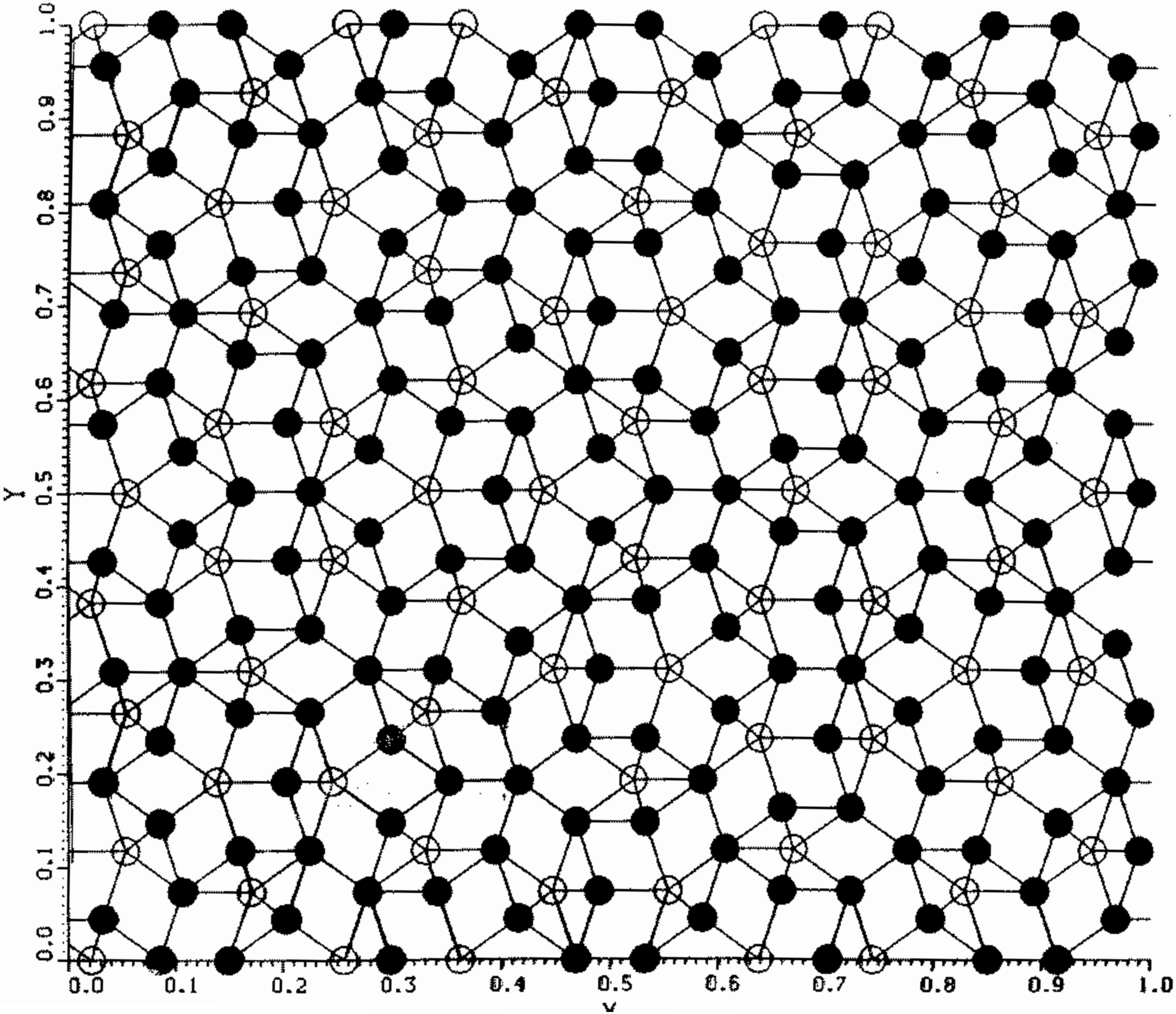
Commensurate modulation, same rank
same symmetry

$$V \;=\; \sum_{ij} V_2(|r_i, r_j|) \;+\; \lambda \sum_{ijk} V_3(|r_i - r_j, |r_j - r_k|, |r_k - r_i|, \phi_{ijk})$$

V_2 2-particle interaction, depending on interparticle distance.

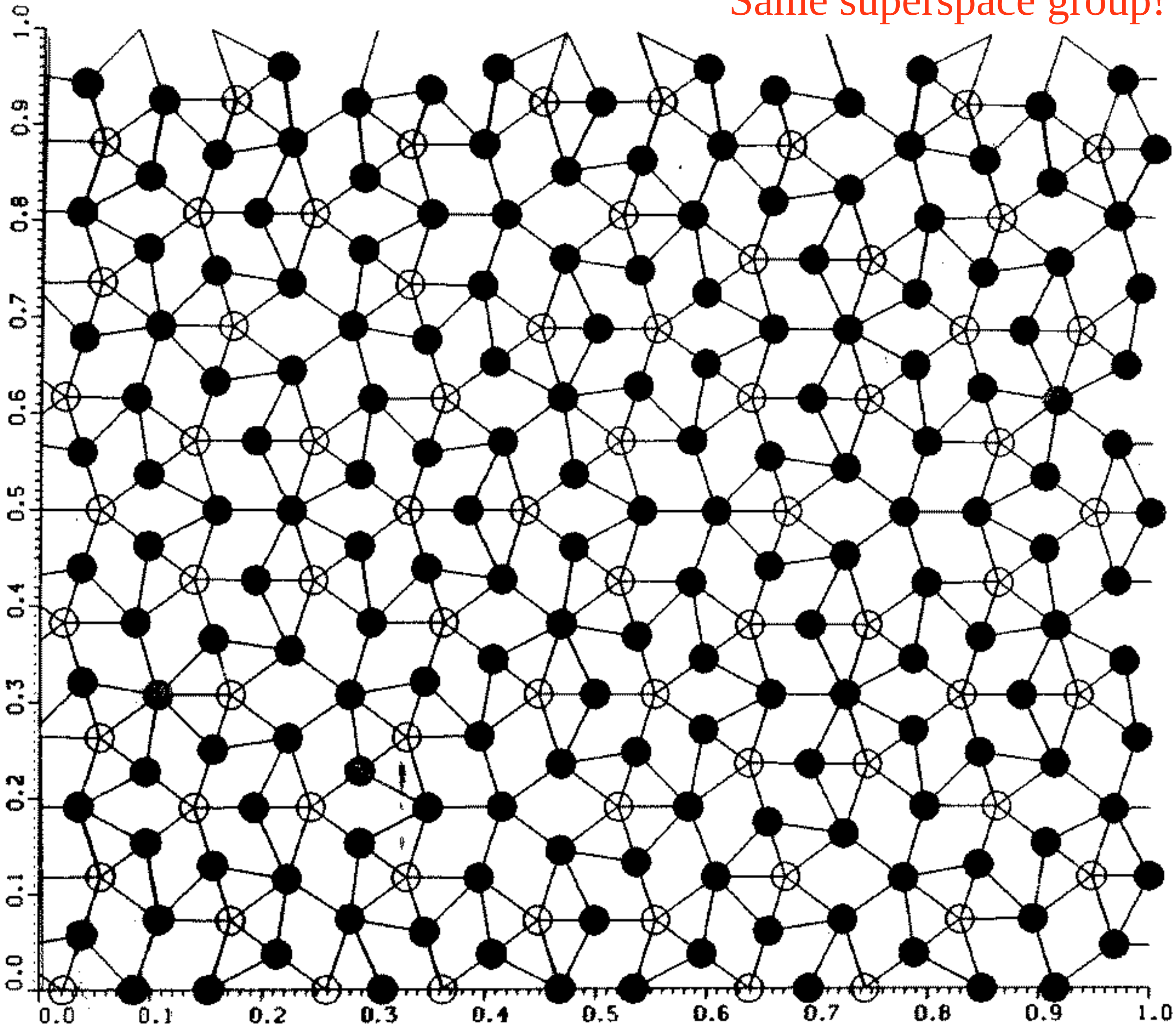
V_3 anisotropic interaction

λ interaction parameter

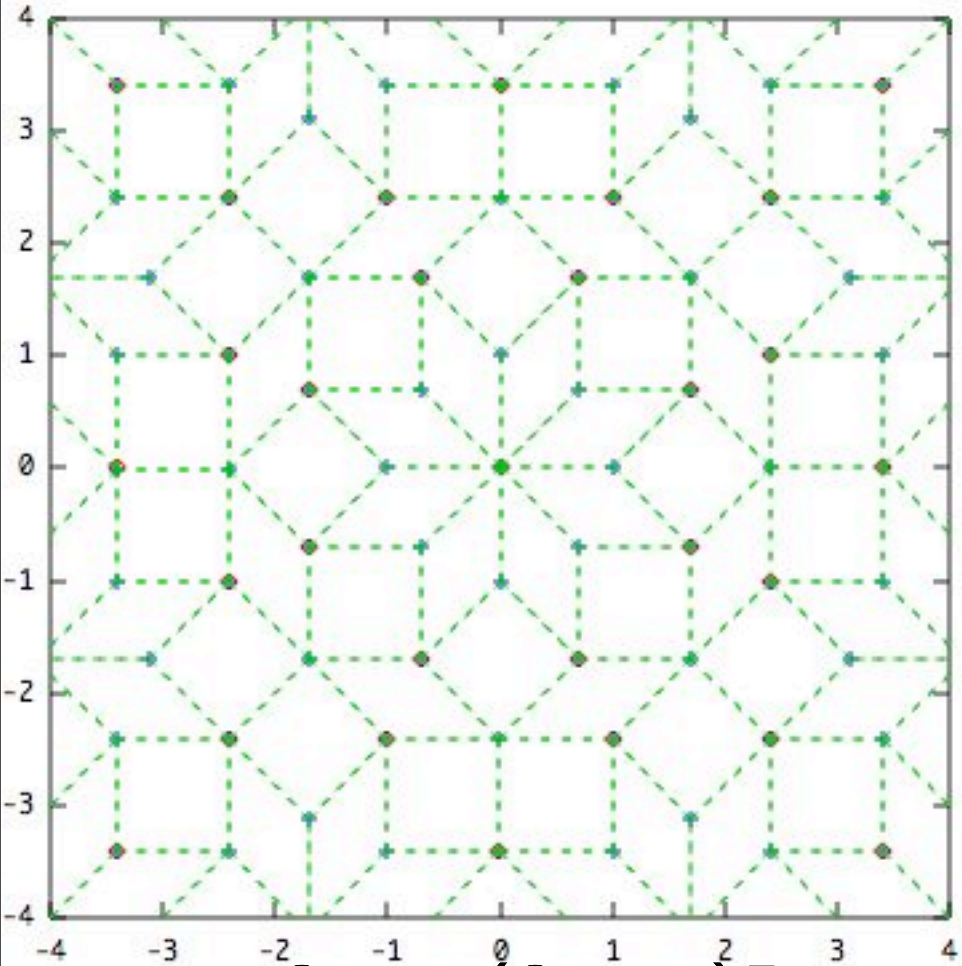


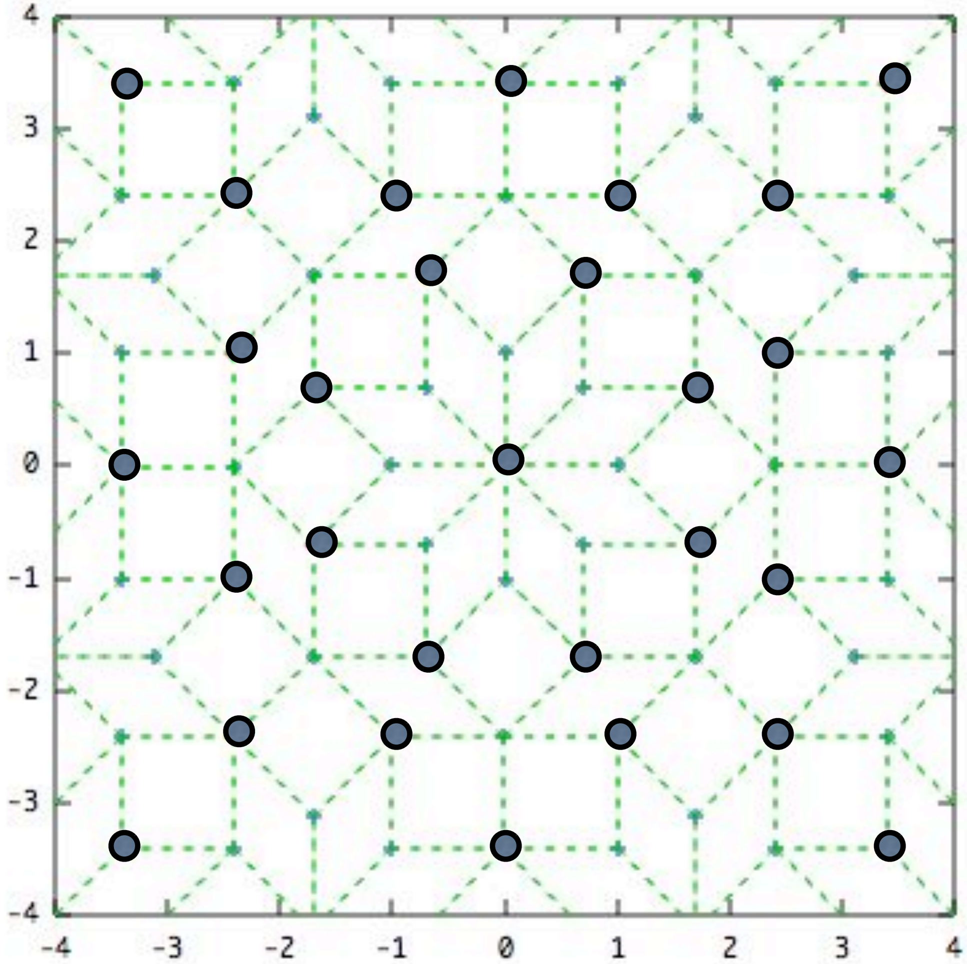
Y
X
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0

Same superspace group!



Centering transition





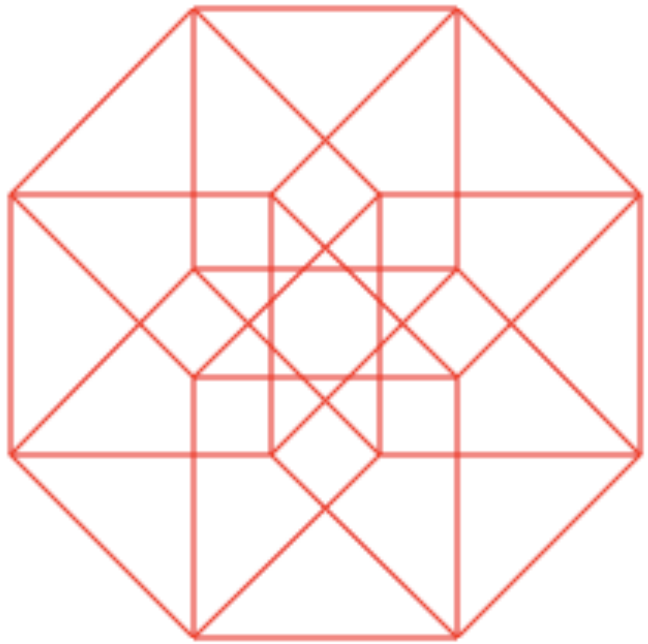
8mm(8mm)P → 8mm(8mm)I≈ 8mm(8mm)P

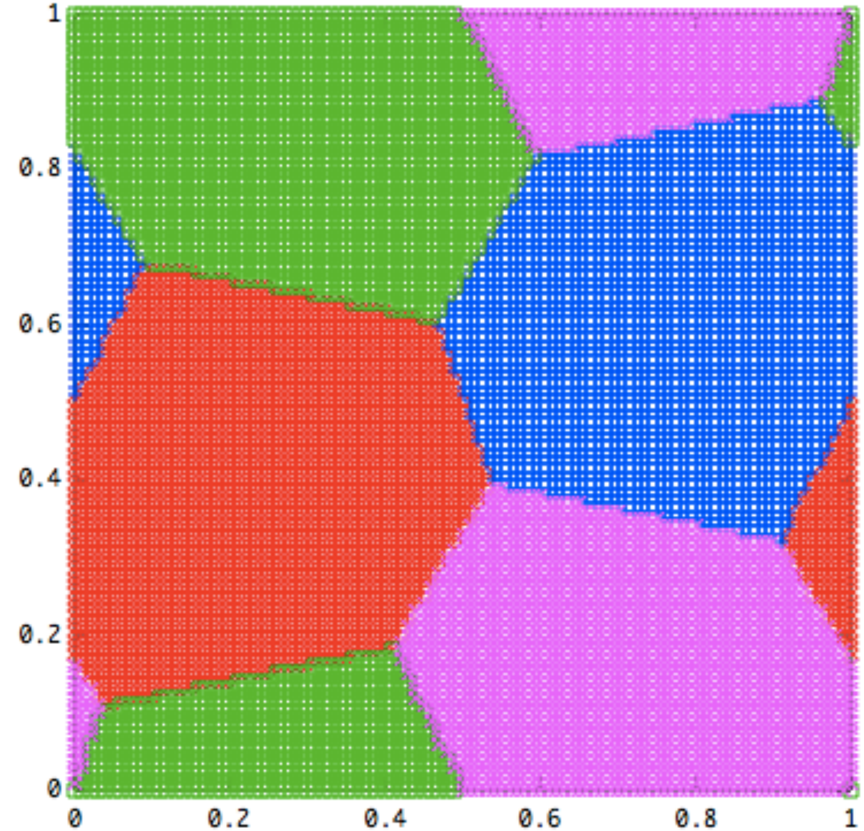
H=(h,k,l,m)/2

h+k+l+m=even

Symmetry change in superspace

1.





Projection Voronoi cell=
fundamental region of the 4D
octagonal lattice
on perp space P8mm(8mm)

Fundamental regions of the
2D space group pgg

what are aperiodic tilings
with non-symmorphic symmetry
(space group not a semidirect
product)?

Superspace group

Extension $Z^n \to G \to K$, with K an nD point group.

Infinite G-orbit of point x

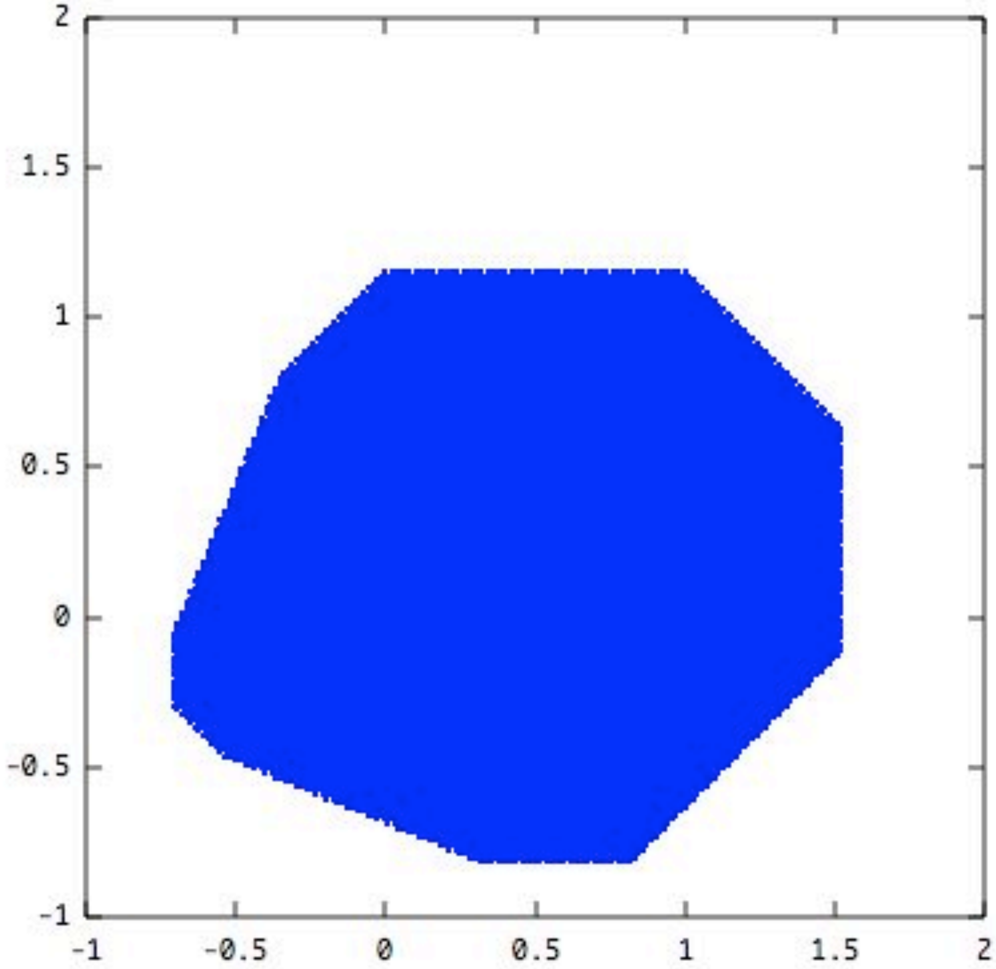
Fundamental region: set of points closer to x than to any other point of the G-orbit of x

Atomic surface: copy of the projection of the f.r. onto internal space V_I placed in x

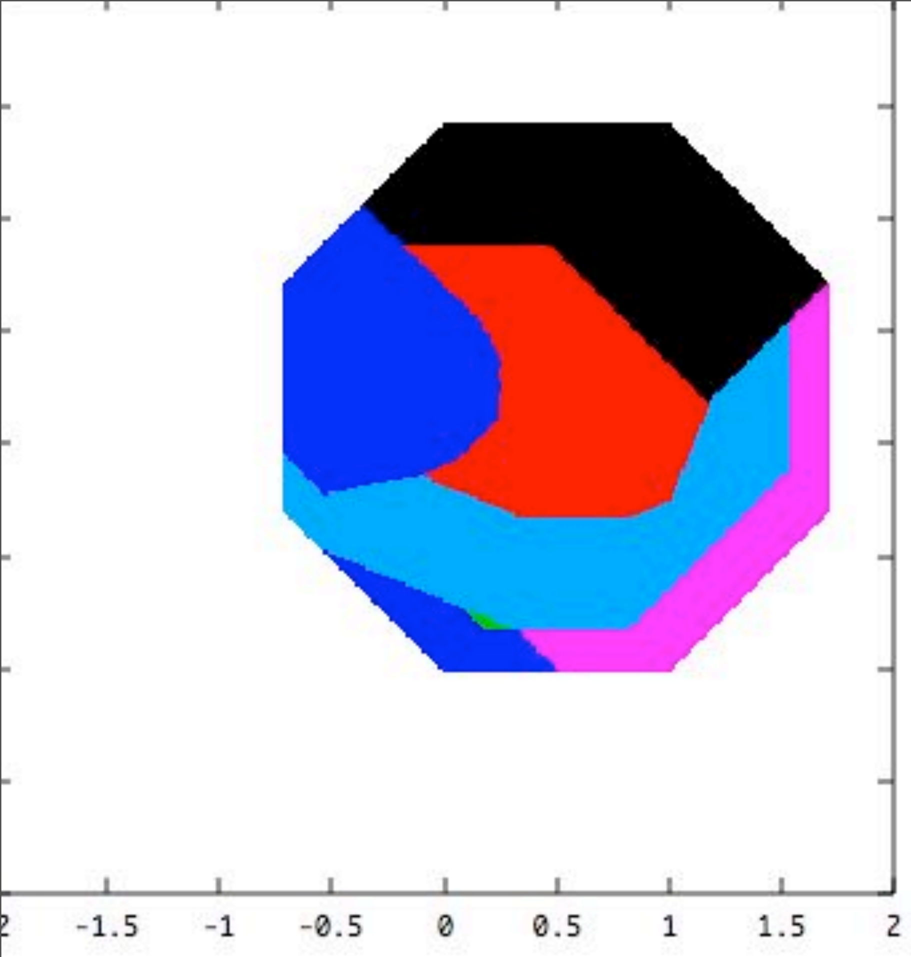
Sum of the projections of f.r. in all points of the G-orbit inside the Delone cell of the lattice gives the atomic surface corresponding to this Delone cell.

Symmetry change in superspace

2.



Projection fundamental region of space group P8um(8mm) on internal space V_I.
This may be used as atomic surface to produce a decorated tiling with P8um(8mm) symmetry.
In contrast to the usual projection of the Delone cell, this atomic surface does not have the point group symmetry of the lattice: 8mm

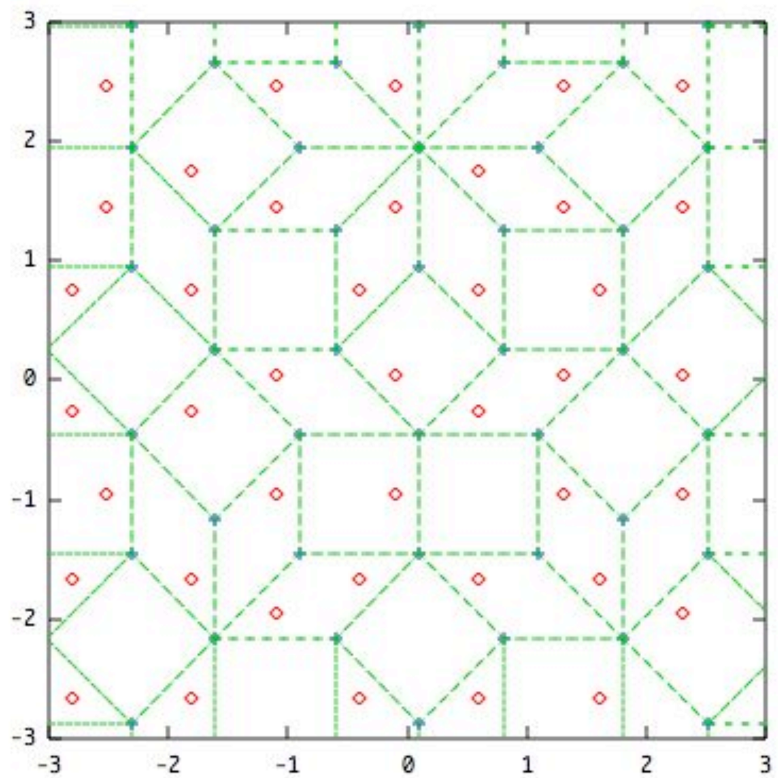


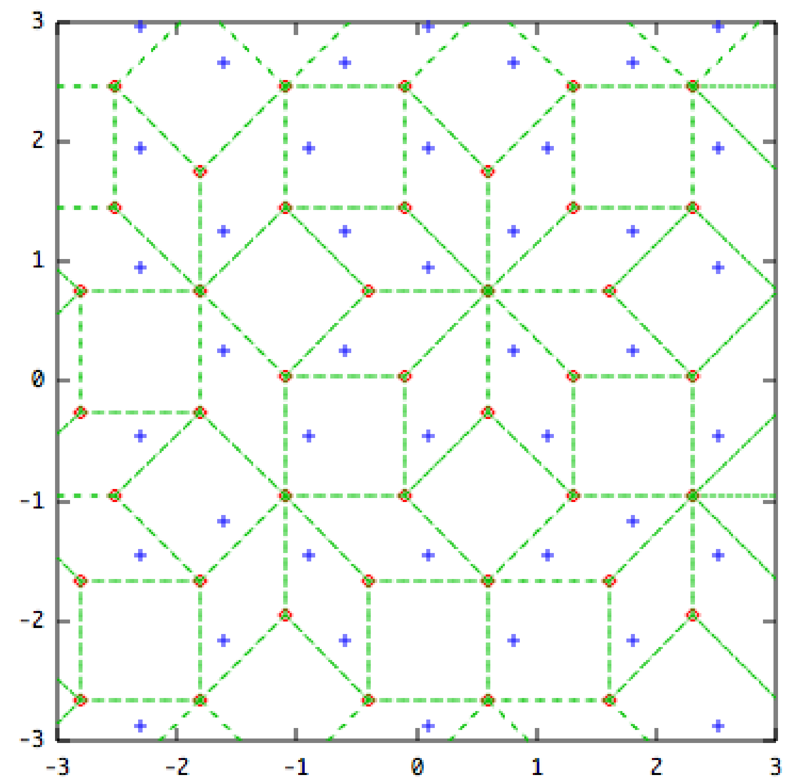
P8um(8mm)

Projection of the 8 fundamental 4D regions on V_I fill the projection of the Delone cell of the lattice

Result:

Double tiling with nonsymmorphic superspace group





p8um(8mm)

1/4,1/4,3/4,3/4

p8um(8mm)

3/4,3/4,1/4,1/4

Generators octagonal lattice in 4D

$$\begin{array}{rl} (a,0,c,0), & (a\sqrt{1/2}, a\sqrt{1/2}, -c\sqrt{1/2}, c\sqrt{1/2}, \\ (0,a,0,-c), & (-a\sqrt{1/2}, a\sqrt{1/2}, c\sqrt{1/2}, c\sqrt{1/2} \end{array}$$

Metric tensor

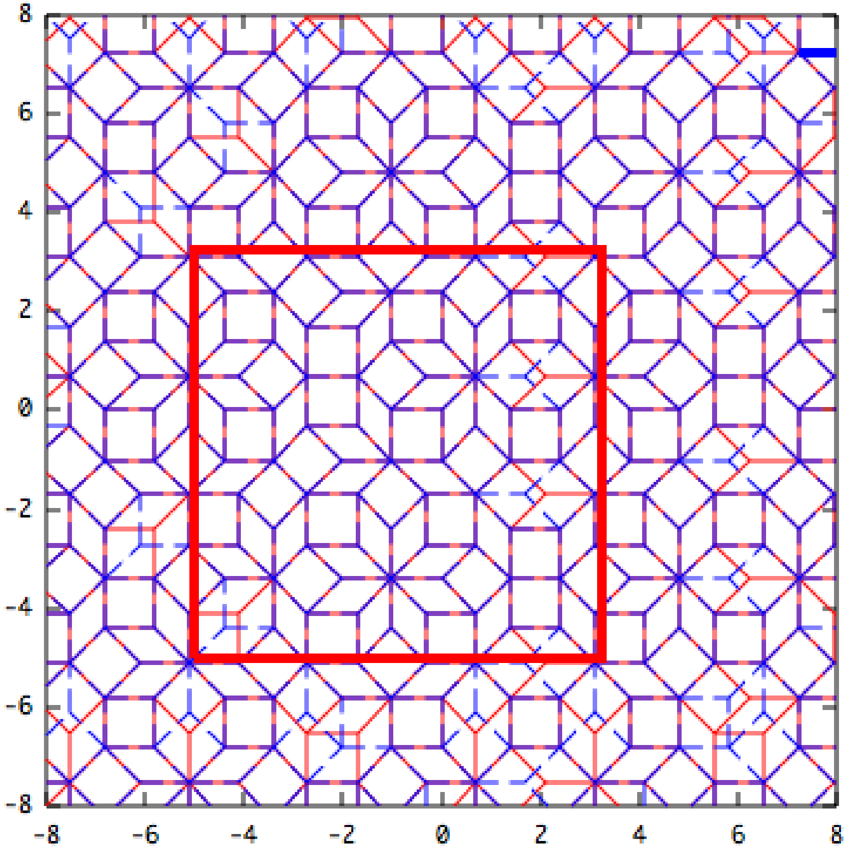
$$\begin{pmatrix} a^2+c^2 & (a^2-c^2)\sqrt{1/2} & 0 & (-a^2+c^2)\sqrt{1/2} \\ (a^2-c^2)\sqrt{1/2} & a^2+c^2 & (a^2-c^2)\sqrt{1/2} & 0 \\ 0 & (a^2-c^2)\sqrt{1/2} & a^2+c^2 & (a^2-c^2)\sqrt{1/2} \\ (-a^2+c^2)\sqrt{1/2} & 0 & (a^2-c^2)\sqrt{1/2} & a^2+c^2 \end{pmatrix}$$

Generators of the nonsymmorphic superspace group p8um(8mm)

$$\left\{ \begin{pmatrix} 0 & 0 & 0 & -1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix} \middle| \begin{pmatrix} 0 \\ 0 \\ \frac{1}{2} \\ 0 \end{pmatrix} \right\}$$

$$\left\{ \begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix} \middle| \begin{pmatrix} 0 \\ 0 \\ \frac{1}{2} \\ 0 \end{pmatrix} \right\}$$

Elements symmetry group



Transition
from qp p8mm tiling
to approximant 2/3

Blue thin lines: qp tiling
Red thin lines: approximant
Red thick line: unit cell

Transition via phason flips

Example of transition quasicrystal -> approximant

Deformed 6D lattice with basis vectors

$$a'_{is} = a_{is} + d_i.$$

$$\begin{array}{lll} d_1 = (0, \eta, 0)_I & d_2 = (0, -\eta, 0)_I & d_3 = (-\eta, 0, 0)_I \\ d_4 = (0, 0, \eta)_I & d_5 = (0, 0, -\eta)_I & d_6 = (-\eta, 0, 0)_I \end{array}$$

$$\eta = L/N - \tau$$

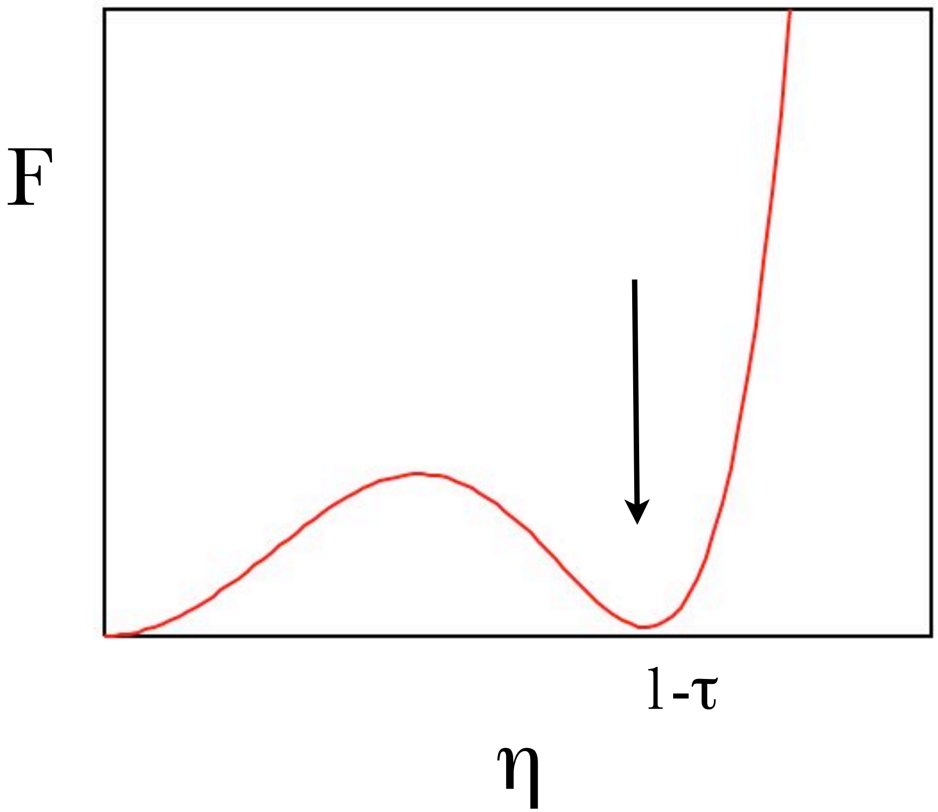
So, there is a lattice deformation of phason type which produces from the icosahedral lattice a periodic system in V_E with tetrahedral point group symmetry

The transition from the icosahedral to the tetrahedral phase can be considered as a soft phason, as appears also in, e.g., TTF-TCNQ [4]. Cf. Ishii [5].

Free Energy: $F = A\,\eta^2/2 + B\,\eta^4/4 + C\,\eta^6/6$

$$\eta = \eta(\alpha\, a_1^*)$$

Free Energy: to get the minimum at $1\text{-}\tau$ 'lock-in' terms are needed.



First order phase transition

Energy: E_c compared with E_{qc}

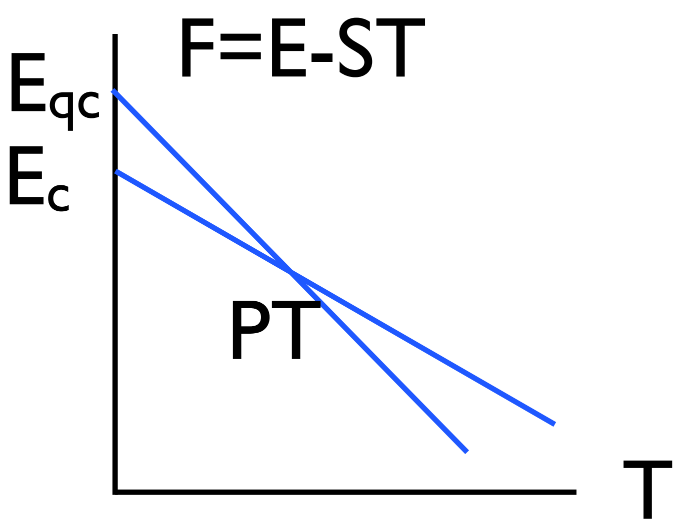
There are tiling models with decoration and interatomic interaction, with a stable quasicrystal configuration.

The energy might be a polynomial in the n-dimensional order parameter, with lock-in terms:

$$\begin{aligned} E_c^{\mathrm{anh}} &= \sum_{\mathbf{k}_i \in \mathrm{tetrahedron}} a\Delta(\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3) \\ E_{qc}^{\mathrm{anh}} &= \sum_{\mathbf{k}_i \in \mathrm{icosahedron}} b\Delta(\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3) \end{aligned}$$

Entropy: S_c compared with S_{qc}

More microstates may be reached by phason fluctuations in quasicrystal (projection dense on V_I) than for crystal approximant: $S_{qc} > S_c$



Ground state: depends on interatomic interactions. It must be determined by realistic (not phenomenological) calculations: cf. Widom & Mihalkovic.
Calculations in the RTM are not sufficient proof.

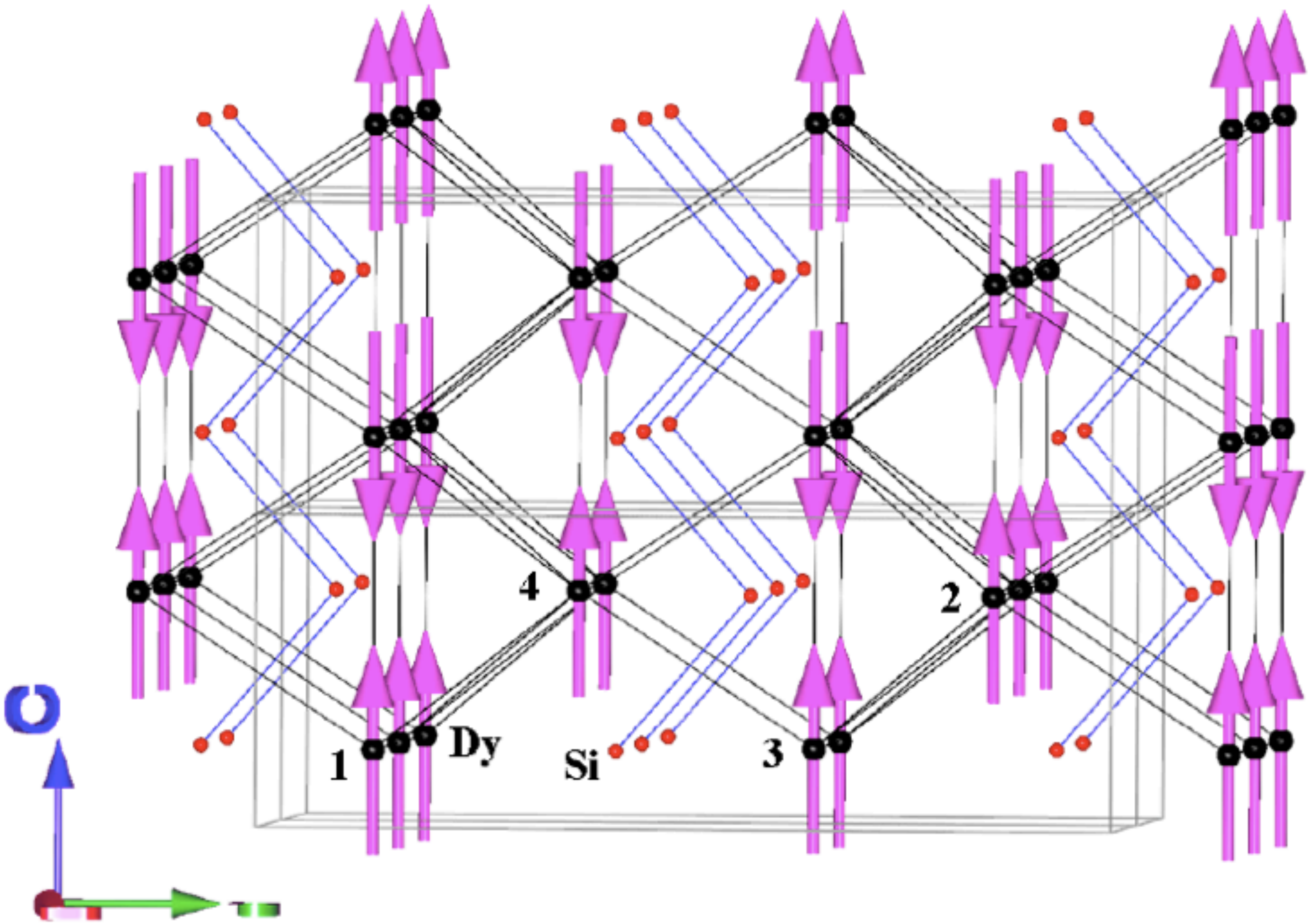
Phase transitions in commensurate and incommensurate crystals

Modulated crystals

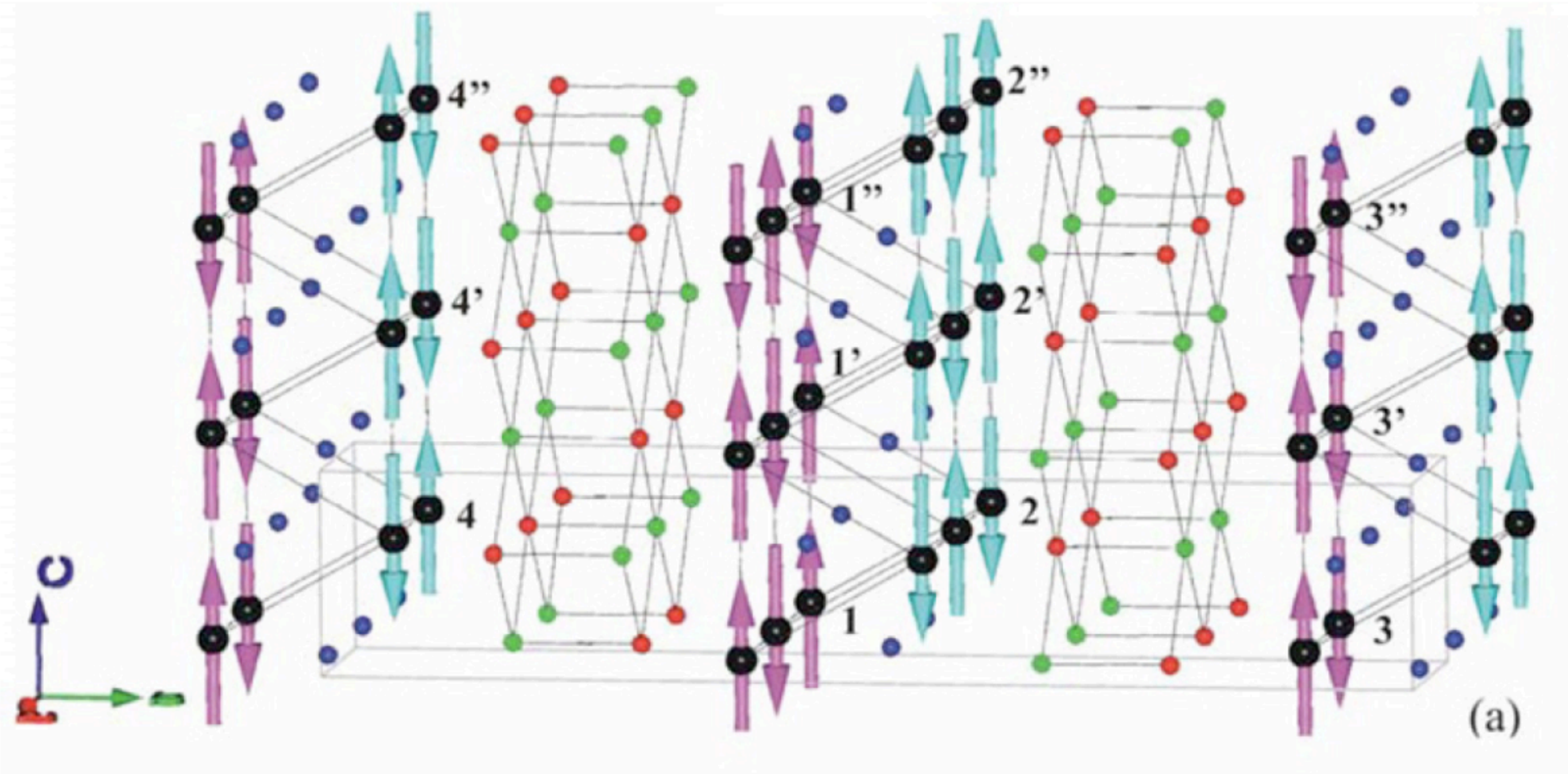
Incommensurate composites

Quasicrystals and tilings

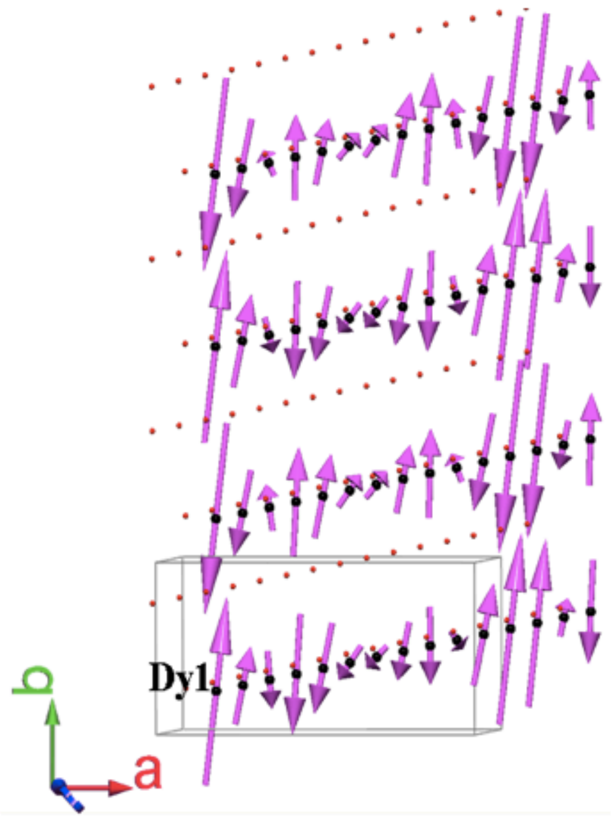
Incommensurate magnetic structures

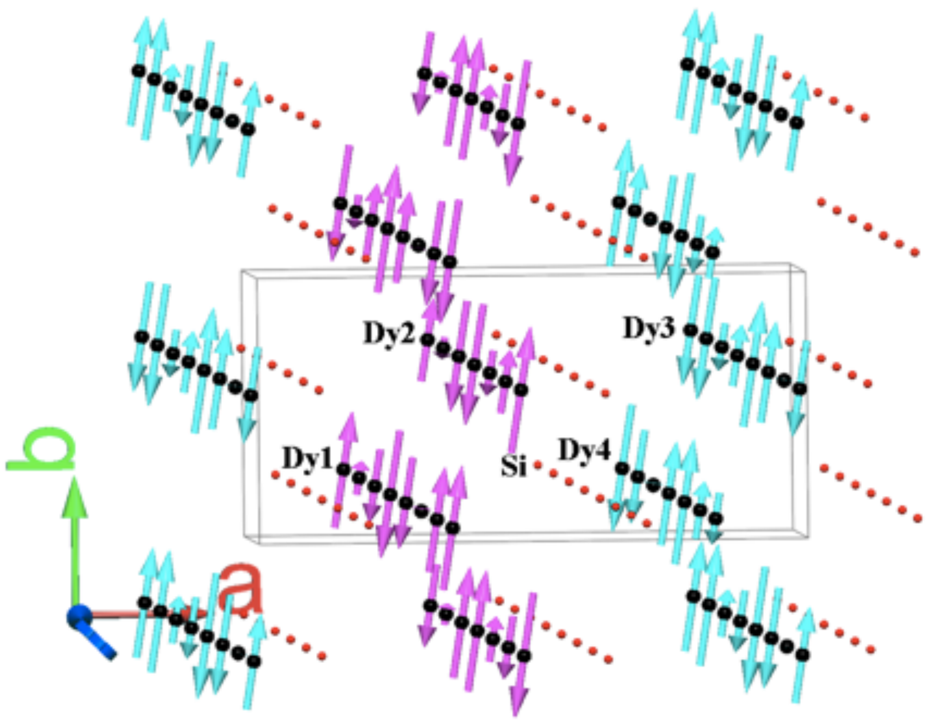


Commensurate magnetic structure DySi
(P. Schobinger-Pappamantellos)



Incommensurate magnetic structure $TbGe_3$





11. The modulated magnetic structure of the FeB-type DySi compound at 16 K assuming a coherent superposition of the refined $\boldsymbol{q}_2$ = (0, 1/2, 1/6) and $\boldsymbol{q}_3 = (0, q_y, q_z)$ Fourier coefficients for the Dy1 atom for a large number of cells (4*b* x 15*c*). The horizontal axis is *a*, while *c* runs out of the plane. The moment amplitude changes in length and direction in the plane of the wave vector mainly along the c direction

12. The sine wave modulated magnetic structure of the FeB-type DySi compound at 25 K described exclusively by $\boldsymbol{q}_3 = (0, q_y, q_z)$ for the four Dy atoms in the cell for (2*b* x 7*c*) cells. The different colours of the moments pertain to two different orbits. The amplitude of the sine wave changes in length in the plane of the wave vector mainly along the *c*. The horizontal axis is *a*, while *c* runs out of the plane.

Magnetic symmetry

$$\mathbf{S}(\mathbf{n}+\mathbf{r}_j) = \hat{\mathbf{S}}_j(\mathbf{q}) \cos\left(2\pi\mathbf{q}\cdot(\mathbf{n}+\mathbf{r}_j)+\phi_j\right)$$

$$\mathbf{S}(\mathbf{n}+\mathbf{r}_j,\, t) = \left(\hat{\mathbf{S}}(\mathbf{q}) \cos\left(2\pi(\mathbf{q}\cdot(\mathbf{n}+\mathbf{r}_j)-t)+\phi_j\right),\, t\right)$$

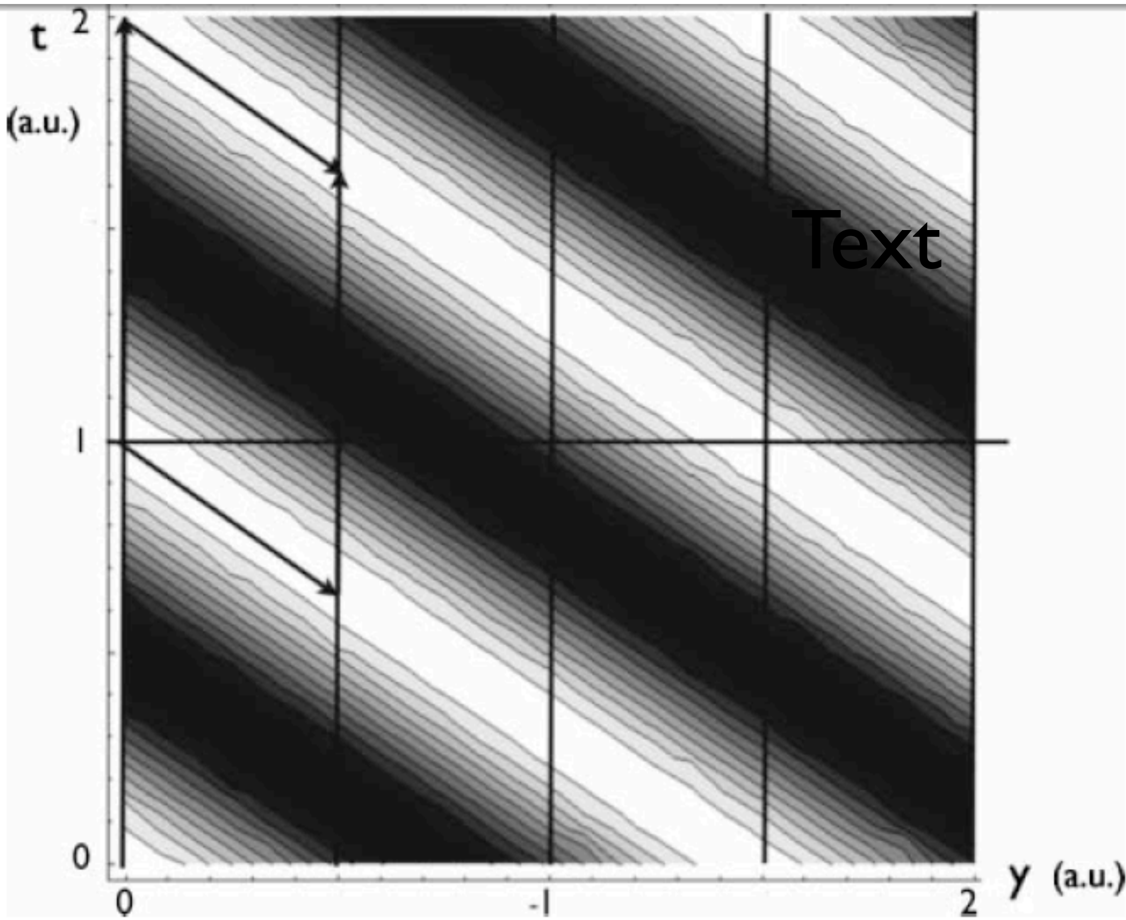


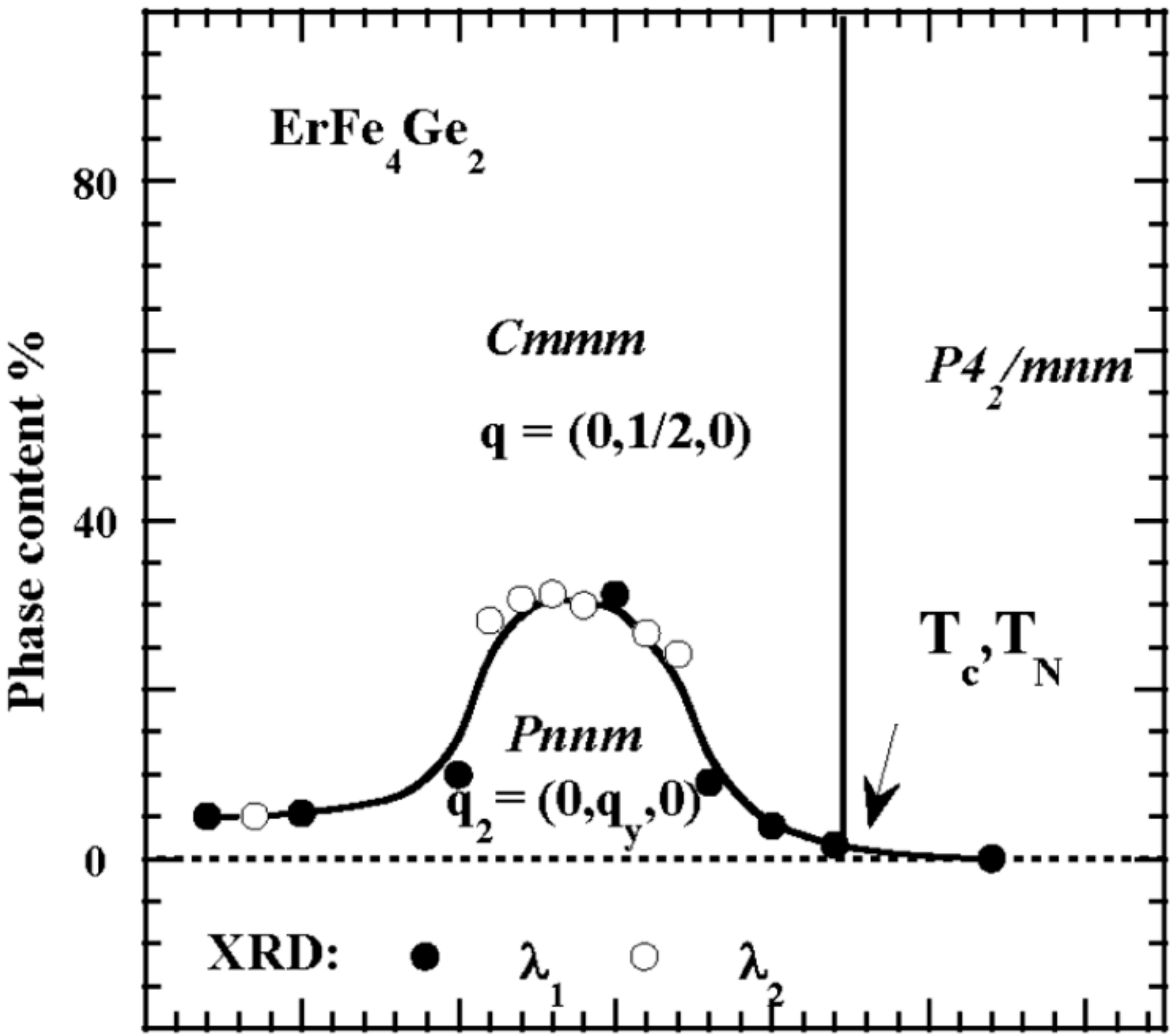
Fig. 2. Two-dimensional y–t section of the four-dimensional embedding of $ErFe_4Ge_2$. Contourplot of the value of the spin at the position

More general $\Phi_{\alpha j}$
for nonlinear polarisation

Magnetic scattering unpolarised neutrons:

$$\sigma(\mathbf{k}) \;=\; |\mathbf{P}(\mathbf{k})|^2 \;-\; \left|\mathbf{P}(\mathbf{k}).\hat{\mathbf{k}}\right|^2$$

$$\mathbf{P}(\mathbf{k}) \;=\; r_0\gamma \sum_{\mathbf{n}j} f_j(\mathbf{k})\; \mathbf{S}_{\mathbf{n}j} \exp(i\mathbf{k}.(\mathbf{n}+\mathbf{r}_j))$$



Below Tc mixture of phases ;
transition from commensurate to incommensurate structure

Magnetic superspace group

The superspace group element

$$\{(R_E, R_I) \mid (\mathbf{v}_E, \mathbf{v}_I)\}$$

transforms the embedding of

$$\mathbf{S}(\mathbf{n}+\mathbf{r}_j) = \sum_{\mathbf{q}} \mathbf{S}_j(\mathbf{q}) \exp[i(\mathbf{q}.(\mathbf{n}+\mathbf{r}_j)]$$

i.e. the 4D spin distribution

$$\mathbf{S}(\mathbf{n}+\mathbf{r}_j, t) = \sum_{\mathbf{q}} \mathbf{S}_j(\mathbf{q}) \exp[i(\mathbf{q}.(\mathbf{n}+\mathbf{r}_j) + i\mathbf{q}_I t]$$

Magnetic superspace group

The superspace group element

$$\{(R_E, R_I) \mid (\mathbf{v}_E, \mathbf{v}_I)\}$$

transforms the embedding of

$$\mathbf{S}(\mathbf{n}+\mathbf{r}_j) = \sum_{\mathbf{q}} \mathbf{S}_j(\mathbf{q}) \exp[i(\mathbf{q}.(\mathbf{n}+\mathbf{r}_j))]$$

i.e. the 4D spin distribution

$$\mathbf{S}(\mathbf{n}+\mathbf{r}_j, t) = \sum_{\mathbf{q}} \mathbf{S}_j(\mathbf{q}) \exp[i(\mathbf{q}.(\mathbf{n}+\mathbf{r}_j) + i\mathbf{q}_I t]$$

to

$$\mathrm{Det}(R_E) \times R_E \mathbf{S}(R_E^{-1}(\mathbf{n}+\mathbf{r}_j) - R^{-1}\mathbf{v}_E),\ R_I^{-1}t - R_I^{-1}\mathbf{v}_I)$$

and the time reversal T to

$$\mathrm{T}\mathbf{S}(\mathbf{n}+\mathbf{r}_j, t) = -\mathbf{S}(\mathbf{n}+\mathbf{r}_j, t)$$

Magnetic superspace group consists of all elements {R|t} and {R|t}T leaving S(r,t) invariant

Space group

Add time reversal T:

Magnetic space group

Add time shifts:

Magnetic space-time group

is actually a

(3+1)D superspace group

Generalize internal dimension:

(3+d)D superspace group

Add time reversal T:

Magnetic superspace group

Conclusions

There is a rich variety of phase transitions involving quasiperiodic structures.

A unified approach to these transitions is by using Landau theory, where the symmetry groups are superspace groups or direct products of a (super)space group en the Euclidean group E^m in m dimensions.

Phase transitions may occur between phases of the same rank, or between phases of different rank. Examples have been found in experiments.

For each n-dimensional superspace group G a (decorated) G-invariant tiling may be constructed, with the projections of the fundamental regions as atomic surfaces.

Open questions

Why is the phason always overdamped?

Is the discommensuration (or lock-in) transition
a real phase transition?

Is the quasicrystal state possibly the ground state (T=0)?

How do the phason fluctuations contribute to
the thermodynamical properties? I.e. how to
count these states?