Phase Transitions in Aperiodic Crystals and Tilings

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

School ‘Aperiodic Crystals’
Carqueiranne 2010
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.
Aperiodic Crystal: diffraction pattern with delta peaks

\[ k = \sum_{i=1}^{n} h_i a_i^* \quad h_i \text{ integers} \]

Rank n > Dimension D

Examples: Incommensurate modulated phases
Aperiodic composites
Quasicrystals
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

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 $\eta$ describes deviation of order in HT phase

Minimization of the Free Energy $F(T, \eta)$

Second order

First order
Landau theory

Order parameter $\eta$ 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 $\eta$ 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 $G$.

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

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

\[
D(R|t) = \exp(i\mathbf{k} \cdot \mathbf{t}) D_\mu(R)
\]

Example: from a crystal with space group \( \text{Pcma} \) towards a modulated phase with wave vector

\[
\mathbf{k} = \alpha \mathbf{a}^* 
\]

Point group of the little group: 2mm

<table>
<thead>
<tr>
<th>( D_\mu )</th>
<th>E</th>
<th>2x</th>
<th>( m_y )</th>
<th>( m_z )</th>
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<td>( D_1 )</td>
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<td>1</td>
<td>1</td>
<td>1</td>
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<tr>
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<td>1</td>
<td>1</td>
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<td>-1</td>
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<tr>
<td>( D_3 )</td>
<td>1</td>
<td>-1</td>
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<td>-1</td>
</tr>
<tr>
<td>( D_4 )</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
</tbody>
</table>

\[
D(m_y|0) = -1, \quad D(m_z|\mathbf{a}/2) = -\exp(i\pi\alpha)
\]
Phase transitions in commensurate and incommensurate crystals

Modulated crystals

Incommensurate composites

Quasicrystals and tilings

Incommensurate magnetic structures

(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 $\gamma$ phase below 361 °C (with extra lines)
(b) The $C$-centered monoclinic $\beta$ phase between 361 °C and 489 °C
(c) The primitive hexagonal $\alpha$ phase above 489 °C, stable up to the melting point.
Incommensurate modulated phases

Positions 1D system: \( n + r_j + f_j(q.n) \)

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. \( 1q \to 2q \)

Then a phase transition occurs
$\text{K}_2\text{SeO}_4$

1st order
Lock-in commensurate rank=3

Discomm.
Modulated incommensurate rank=4

2nd order
High symmetry rank =3

$\hbar^{\nu}(q)$ (meV)

$q$ (REDUCED UNIT)

$\Sigma_3$
$\Sigma_2$
$\Sigma_1$

ZB.
Embedding into superspace with dimension equal to the rank

\[ k_s = (k, k_I) \]

\[ \rho(r) = \sum_k \exp(ik \cdot r) \]

\[ \rho_s(r, r_I) = \sum_{k_s} \rho(\pi k_s) \exp(ik_s \cdot r_s) \]
Embedding into superspace with dimension equal to the rank

$$k_s = (k, k_I)$$

$$\rho(r) = \sum_k \exp(i k, r)$$

$$\rho_s(r, r_I) = \sum_{k_s} \rho(\pi k_s) \exp(i k_s.r_s)$$

High symmetry: without modulation

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

Low symmetry: with modulation

$H$ subgroup of $G$ : $n$ -dimensional space group: superspace group
Transition from 1D periodic to 1D aperiodic = 2D periodic
Symmetry from $G_0 \times E^1 \rightarrow G$
Rank is 2
Diffraction $h_1 a^* + h_2 q$
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 $\phi^4$ 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 $\phi^4$ 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.
Discommensuration Transition in DIFFOUR model

- a low-T commensurate, 6-fold
- b incommensurate, smooth
- c incommensurate, discommensurations

$x_n$ versus $x_{n-1}$
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 \((\alpha, 1/2)\)

\[
V = \sum_n \left( \frac{a}{2} (u_n - u_{n-a})^2 + \frac{b}{2} (u_n - u_{n-2a})^2 + \frac{c}{2} (u_n - u_{n-3a})^2 \\
+ \frac{d}{2} (u_n - u_{n-b})^2 + \frac{e}{2} (u_n - u_{n-a-b})^2 + \frac{g}{2} (u_n - u_{n-a+b})^2 \right)
\]

\(a = 0.1352, \ b = -0.3047, \ c = 0.2148, \ d = -0.15, \ e = 0.575, \ cg = 0.575\)
$A = (6/17, 1/2)$
Phase transition 1q-2q

\[ T_2 < T < T_1 \]

Free energy on the Brillouin Zone

Cf. K. Parlinski (1992)

\[ T > T_1 : \text{Unmodulated : A} \]

\[ T_1 : \text{Phase transition to 1q state} \rightarrow \text{rank 4 : B} \]

\[ T_2 : \text{Phase transition to 2q state} \rightarrow \text{rank 5 : C} \]
Phase transitions in commensurate and incommensurate crystals

Modulated crystals

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Composites

\[ x_n^{(i)} = x_0^{(i)} + na_i + f_i(x_0^{(i)} + na_i), \quad (i = 1, 2) \]
\[ y_m^{(i)} = (2m + i - 1)b/2, \]

\[ k = h_1/a_1 + h_2/a_2, \quad \ell = h_3/b \]

Embedding of the composite

\[ (x_0^{(i)} + na_i - Z_it + f_i(x_0^{(i)} + na_i + \Delta t), (2m + i - 1)b/2, t), \quad (i = 1, 2) \]
\[ \Delta = Z_2 - Z_1 \]
Diffraction peaks

\[ \mathbf{k} = \left( \frac{h_1}{a_1} + \frac{h_2}{a_2}, \frac{h_3}{b} \right) \]

- \(h_1 = h_2 = 0\) common reflections
- \(h_2 = 0\) reflections system 1
- \(h_1 = 0\) reflections system 2
- \(h_1 \neq 0, h_2 \neq 0\) sum reflections

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

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

\[ H = ha^* + kc^* + m_1 b^* + m_2 (c^*/2 + \delta a^*) \]
\[ b^* = \gamma a^* \]

\[ cmm(0\gamma, 1\delta) \]

\[ = ha^* + kc^*/2 + m_1 b^* + m_2 \delta a^* \]
\[ b^* = \gamma a^* \]

\[ pmm(0\gamma, 0\delta) \]
Phase transition between phases of the same rank

Example: rank = 3

\[ h_1 a^* + h_2 c^* + h_3 \gamma c^* \]
\[ k = (a^* + c^*)/2 \]
\[ h'_1 (a^* + c^*)/2 + h'_2 (a^* - c^*)/2 + h_3 \gamma c^* \]

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

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

\[ u_n^{(1)} = x_n^{(1)} - na_1 \]

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

In superspace additional dimension.
Changes in the diffraction affect sum peaks.
Example: urea-nonadecane (Toudic)
High Symmetry Phase: hexagonal \( \text{P6}_1\text{2}2 \)

Orientational Disorder of the alkanes

Low Symmetry Phase: orthorhombique \( \text{P}2_1\text{2}1\text{2}_1 \)

Anti-ferro shearing of urea

Anti-ferro ordering of the alkanes

Study of the phase transition at 3 dimensions

Single Crystal nonadecane – urea 
\( \text{C}_{19}\text{D}_{40} – \text{CO} (\text{ND}_2)_2 \)

\[ c_{\text{uree}} = 11.0 \text{Å} \quad c_{\text{alc.}} = 1.277(n-1)+3.48 \text{Å} \]
Single Crystal

nonadecane – urea

\( C_{19}D_{40} – CO(ND_2)_2 \)

\( C_{\text{urea}} = 11.02 \, \text{Å} \)

\( C_{\text{nonadecane}} = 26.46 \, \text{Å} \)

\( \gamma \approx 0.42 \)

G43

LLB (Saclay)

\( k_i = 2.662 \, \text{Å}^{-1} \)

Hidden Degrees of Freedom in Aperiodic Materials

Bertrand Toudic,1,2* Pilar García,1,2 Christophe Odin,1,2 Philippe Rabiller,1,2
Claude Ecolivet,1,2 Eric Collet,1,2 Philippe Bourges,3 Garry J. McIntyre,4
Mark D. Hollingsworth,5 Tomasz Breczewski6

New diffraction peaks
Simple model: soft optic mode

\[ F = \sum_n \left( A u_n^2/2 + u_n^4/4 + B u_n u_{n-c} + C u_n u_{n-2c} + D u_n u_{n-a} \right) \]

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

Parameters with A, B, C and D are temperature dependent
Phase transition in a crystallographic superspace

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

Nonadecane-urea: $\gamma \approx 0.42$

X-ray Mo

X-ray Cu Kα

Cold Neutrons 4F LLB

Structure line

Superstructure line

No common superstructure

h k 0 0

(T>T_c)
II Orthorhombic  
$a^*, 2b^*, c^*, \gamma c^*, b^*+\delta c^*$

III $a^*, b^*, c^*, \gamma c^*, b^*+\delta c^*$  
(ambient pressure)

IV Scan along $c^*$:  
satellites at 120$m_1$m_2 and 121$m_1$m_2, no main reflections 12000 or 12100  
(high pressure)
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?

FIG. 1: Phase diagram (P,T) of the fully deuterated nona-decane 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.
Phase transition at 120K

Subsystem 1: AsF$_6$; Subsystems 2,3: Hg chains

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

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

Superspace group: basic structure Fddd(0\(\delta\)0)00s

rank 5: Fddd(\(\delta\)0-\(\delta\),0\(\delta\)0)00n ??

(JJ, Acta Cryst. 1980)
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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:

\[
\text{Diffraction } h_1 a_1^* + h_2 a_2^* + h_3 a_3^* + h_4 a_4^* \\
\text{Basis Embedding in 4D } (a_1^*, a_1^*), (a_2^*, a_4^*), (a_3^*, -a_3^*) (a_4^*, a_2^*) \\
\Sigma^* : (1, 0, 1, 0), (a, a, -a, a), (0, 1, 0, -1), (-a, a, a, a) \text{ with } a = \sqrt{1/2}. \\
4D lattice: \Sigma = \text{dual of } \Sigma^*.
\]
Penrose tiling, dimension = 2, rank = 4, five-fold symmetry
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.

$$g_{ij} = a_i \cdot a_j$$

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

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

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

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

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.

<table>
<thead>
<tr>
<th>Group 532</th>
<th>Group 23</th>
</tr>
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<tbody>
<tr>
<td>E 5 5² 3 2</td>
<td>E 3 3² 2</td>
</tr>
<tr>
<td>Γ₁  1 1 1 1</td>
<td>D₁  1 1 1 1</td>
</tr>
<tr>
<td>Γ₂  3 −τ 1+τ 1 −1</td>
<td>D₂  1 ω ω² 1</td>
</tr>
<tr>
<td>Γ₃  3 1+τ −τ 1 −1</td>
<td>D₃  1 ω² ω 1</td>
</tr>
<tr>
<td>Γ₄  4 −1 −1 1 0</td>
<td>D₄  3 0 0 −1</td>
</tr>
<tr>
<td>Γ₅  5 0 0 −1 1</td>
<td></td>
</tr>
</tbody>
</table>

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

2. Through phason modulation: transition to higher rank

Symmetry change:

\[
P532(5^232) \times E^6 \rightarrow P532(5^232,532,5^232)(\alpha00000)
\]

Order parameter \( \eta(\alpha a_1^*) \)
Commensurate modulation, same rank
same symmetry

\[ V = \sum_{i,j} V_2(|r_i, r_j|) + \lambda \sum_{i,j,k} V_3(|r_i - r_j, |r_j - r_k|, |r_k - r_i|, \phi_{ijk}) \]

\( V_2 \) 2-particle interaction, depending on interparticle distance.

\( V_3 \) anisotropic interaction

\( \lambda \) interaction parameter
Same superspace group!
Centering transition

8mm(8mm)P → 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 \( Z^n \rightarrow G \rightarrow K \), with \( K \) an \( n \)D 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.
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 nonsymmetric superspace group

\[
\begin{align*}
p8\text{um}(8\text{mm}) & \quad 1/4,1/4,3/4,3/4 \\
p8\text{um}(8\text{mm}) & \quad 3/4,3/4,1/4,1/4
\end{align*}
\]
Generators octagonal lattice in 4D

\[(a, 0, c, 0), \quad (a\sqrt{1/2}, a\sqrt{1/2}, -c\sqrt{1/2}, c\sqrt{1/2}), \]
\[(0, a, 0, -c), \quad (-a\sqrt{1/2}, a\sqrt{1/2}, c\sqrt{1/2}, c\sqrt{1/2})\]

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 p\text{8um}(8\text{mm})

\[
\left\{ \begin{pmatrix}
 0 & 0 & 0 & -1 \\
 1 & 0 & 0 & 0 \\
 0 & 1 & 0 & 0 \\
 0 & 0 & 1 & 0 \\
\end{pmatrix}, \begin{pmatrix}
 0 \\
 0 \\
 0 \\
 0 \\
\end{pmatrix} \right\}
\]

\[
\left\{ \begin{pmatrix}
 -1 & 0 & 0 & 0 \\
 0 & 0 & 0 & 1 \\
 0 & 0 & 1 & 0 \\
 0 & 1 & 0 & 0 \\
\end{pmatrix}, \begin{pmatrix}
 0 \\
 0 \\
 \frac{1}{2} \\
 0 \\
\end{pmatrix} \right\}
\]

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
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-\(\tau\) ‘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:

$$E_{c}^{anh} = \sum_{k_i \in \text{tetrahedron}} a \Delta (k_1 + k_2 + k_3),$$
$$E_{qc}^{anh} = \sum_{k_i \in \text{icosahedron}} b \Delta (k_1 + k_2 + k_3)$$

Entropy: $S_c$ compared with $S_{qc}$
More microstates may be reached by phason fluctuations in quasicrystal (projection dense on $V_1$) 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.
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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 $q_2 = (0, 1/2, 1/6)$ and $q_3=(0, q_y, q_z)$ Fourier coefficients for the Dy1 atom for a large number of cells (4b x 15c). 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 $q_3=(0, q_y, q_z)$ for the four Dy atoms in the cell for (2b x 7c) 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

\[
S(n + r_j) = \hat{S}_j(q) \cos \left( 2\pi q \cdot (n + r_j) + \phi_j \right)
\]

\[
S(n + r_j, t) = (\hat{S}(q) \cos \left( 2\pi (q \cdot (n + r_j) - t) + \phi_j \right), t)
\]

More general $\Phi_{\alpha j}$ for nonlinear polarisation
Magnetic scattering unpolarised neutrons:

$$\sigma(k) = |P(k)|^2 - |P(k)\cdot\hat{k}|^2$$

$$P(k) = r_0\gamma \sum_{n_j} f_j(k) S_{nj} \exp(ik.(n + r_j))$$
Below $T_c$ mixture of phases; transition from commensurate to incommensurate structure.
Magnetic superspace group

The superspace group element

\[ \{(R_E, R_I) \mid (v_E, v_I)\} \]

transforms the embedding of

\[ S(n + r_j) = \sum_q S_j(q) \exp[i(q \cdot (n + r_j))] \]

i.e. the 4D spin distribution

\[ S(n + r_j, t) = \sum_q S_j(q) \exp[i(q \cdot (n + r_j) + iq_I t)] \]
Magnetic superspace group

The superspace group element

\[ \left\{ (R_E, R_I) \mid (v_E, v_I) \right\} \]

transforms the embedding of

\[ S(n + r_j) = \sum_q S_j(q) \exp[i(q \cdot (n + r_j))] \]

i.e. the 4D spin distribution

\[ S(n + r_j, t) = \sum_q S_j(q) \exp[i(q \cdot (n + r_j) + iq_I t)] \]

to

\[ \text{Det}(R_E) \times R_E S(R_E^{-1}(n + r_j) - R^{-1}v_E), R_I^{-1}t - R_I^{-1}v_I) \]

and the time reversal T to

\[ T S(n + r_j, t) = - S(n + r_j, t) \]

Magnetic superspace group consists of all elements \{Rlt\} and \{Rlt\}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?