Introduction to Modulated Structures

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Denver X-Ray Conference - Workshop
Goal of this workshop

What is a modulation?
What is a modulated structure?
How can we recognize a modulated structure?
What are the issues?
How we deal with modulated structure?
In which material can we observe modulation?
Why are they important?
What is a crystal?

It is a macroscopic object where the atoms or molecules are perfectly ordered in a pattern which repeats in the three directions of the space.

the nineteenth century is characterized by the development of the mathematical aspect of crystal structures

7 crystal systems

230 Space groups...

True until.....
Until ... 

Some systems have additional diffraction spots – 
*satellites reflections* 

*These structures are known as aperiodic structures*
Until ...

The problem

**Satellites** are “regularly” spaced but most of the time they cannot be indexed with three reciprocal vectors

The consequences

One or more additional *modulation vectors* have to be added to index all diffraction spots. Diffraction pattern has not a 3d lattice character anymore \(\Leftrightarrow\) the basic property of crystal 3d translation symmetry is violated *BUT* in a specific regular way.

New definition

….a crystal is an object with a *finite* number of basic periodicities.
History

- A crystal structure with a displacively modulated structure was first considered by Dehlinger (1927).
- The next truly incommensurate crystalline phases were alloys of transition elements and rare earth metals with so-called magnetic helix/spiral structures (1959-1961).

<table>
<thead>
<tr>
<th></th>
<th>(I)</th>
<th>(T')</th>
<th>(IIA)</th>
<th>(T)</th>
<th>(IIB)</th>
<th>(T_C)</th>
<th>III</th>
<th>(\mu_0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tb</td>
<td>(\theta = 236)</td>
<td>227.7 ((a,c))</td>
<td>spiral (\mu \perp c)</td>
<td></td>
<td>220 ((a))</td>
<td></td>
<td>ferro (\mu \perp c)</td>
<td>transition at 24°K ((a))</td>
</tr>
<tr>
<td>Dy</td>
<td>(\theta = 154)</td>
<td>174 ((a))</td>
<td>spiral (\mu \perp c)</td>
<td>(\angle 43^\circ \rightarrow 35^\circ)</td>
<td>140 ((b))</td>
<td>spiral (\mu \perp c) plus second harmonic</td>
<td>(\angle 35^\circ \rightarrow 26^\circ)</td>
<td>83.5 ((a)) ferro (\mu \perp c)</td>
</tr>
<tr>
<td></td>
<td>(\theta_{II} = 121)</td>
<td>179 ((b,c))</td>
<td>(\angle 43^\circ \rightarrow 35^\circ)</td>
<td>140 ((b))</td>
<td></td>
<td></td>
<td>? small (\mu \parallel c)?</td>
<td>87 ((b))</td>
</tr>
<tr>
<td>Ho</td>
<td>(\theta = 85)</td>
<td>131.6 ((a))</td>
<td>spiral (\mu \perp c)</td>
<td>35 ((b))</td>
<td>nonsinusoidal arrangement (\mu \perp c)</td>
<td>(\angle 50^\circ \rightarrow 36^\circ)</td>
<td>19.4 ((a)) ferro (\mu \perp c)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(\theta_{II} = 88)</td>
<td>125 ((b))</td>
<td>(\angle 50^\circ \rightarrow 36^\circ)</td>
<td></td>
<td></td>
<td>(\angle \sim 36^\circ) spacing 10 layers</td>
<td>small (\mu \parallel c) ferro</td>
<td>40 ((b,c))</td>
</tr>
<tr>
<td>Er</td>
<td>(\theta = 42)</td>
<td>84 ((a,c)) \sin (\mu \parallel c)</td>
<td>53.5 ((c)) \sin (\mu \parallel c)</td>
<td>harmonics</td>
<td></td>
<td></td>
<td></td>
<td>19.9 ((a)) ferro (\mu \parallel c)</td>
</tr>
<tr>
<td></td>
<td>(\theta_{II} = 61.7)</td>
<td>80 ((b))</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>20 ((b)) spiral (\mu \perp c), (\angle = 41^\circ)</td>
</tr>
<tr>
<td>Tm</td>
<td>(\theta = 20)</td>
<td>53 ((b))</td>
<td></td>
<td>sinusoid (\mu \parallel c)</td>
<td></td>
<td></td>
<td></td>
<td>20 ((c))</td>
</tr>
<tr>
<td></td>
<td>(\theta_{II} = 32.5)</td>
<td>50 ((c))</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
</tbody>
</table>

\* See references 3-7.
\* See references 8-11.
\* See references 5, 12, 13.
\* See references 13-16.
\* See references 5, 17-19.
History

SHORT COMMUNICATIONS

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

**An anomaly in the crystal structure of Na₂CO₃.** 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)

We then succeeded in obtaining a small single crystal by slow cooling of the molten salt. This was mounted in a Weissenberg camera with what proved later to be the b axis parallel to the axis of rotation. Photographs were taken of the levels $h=0$, 1, and 2. The results fully corroborated the unit cell derived from the powder pattern. The zero layer was completely normal. In the other photographs, however, extra spots were easily detectable as weak but perfectly sharp satellites of the ‘main’ spots. In reciprocal space, the extra spots form linear rows of $3-5$ equidistant points, with the main spot as a centre. Writing these rows as $h = h_k + kbf + lcf + m pf$, $m = 0, \pm 1, \pm 2$ where $h$, $k$, $l$, are the indices of the main spot ($m=0$), the observed facts can be described as follows.

1. $p^*$ is a vector independent of $h$, $b$, and $c$.
2. The intensity of the satellites, being zero for $k=0$, increases with increasing $k$ and seems to be roughly proportional to the main spot intensity, for a given $k$.

The outer satellites ($m = \pm 2$) are generally much weaker than the inner ones. In a few cases those for $m = 3$ are visible. The intensity sequence is often irregular.

All these facts were completely and quantitatively in accordance with the extra lines in the powder pattern, meaning that the extra lines and the satellite spots represent the same phenomenon. The powder diffraction angles provided the more accurate means for measuring

\[ \text{Retigram of the layer } h3l \text{ of Na}_2\text{CO}_3, \text{ taken with Cu K}\alpha \text{ radiation.} \]

Composite crystals approach was introduced by Makovicky & Hide, *Material Science Forum*, 100&101, 1-100.

Structural analysis of modulated crystals is based on theoretical works of P.M. de Wolff, A.Janner and T.Janssen.

The number of studied modulated crystals grew with improving of experimental facilities – imaging plate, CCD.
Moreover the real importance of modulations in crystals has been demonstrated by studies of organic conductors and superconductors (e.g. \((\text{BEDT-TTF})_2\text{I}_3\)) and high temperature Bi superconductor.

As superconductor

Thermoelectrics

Battery Materials, Fuel materials

Materials under extreme conditions

**Interest**

- “Real” Materials with long range order structures possess interesting physical properties. Their properties are usually governed or linked to their “atypical” structure (**modulated waves**).
History \textit{(superspace group)}

Development of the Mathematical tools \& Super space group


The Superspace Groups for Incommensurate Crystal Structures with a One-Dimensional Modulation

BY P. M. de Wolff

Vakgroep Fysische Kristallografie, Laboratory for Technical Physics, Technische Hogeschool, 2628 CJ Delft, The Netherlands

AND T. Janssen AND A. Janner

Institute for Theoretical Physics, University of Nijmegen, 6525 ED Nijmegen, The Netherlands

(Received 20 July 1980; accepted 26 January 1981)

\textbf{Sander Van Smaalen for the Composite Structure (1990-1991)}
Dan Shechtman discovered quasiperiodic crystals in April 1982, as a visiting scholar at the National Bureau of Standards in Maryland, USA. This new form of matter - also known as quasicrystals or Shechtmanite - possesses some unique and remarkable crystallographic and physical properties, embodying a novel kind of crystalline order. His findings demonstrated a clear diffraction pattern with a fivefold symmetry. The pattern was recorded from an aluminum-manganese (Al-Mn) alloy which he had rapidly cooled after melting.
Report of the number of publications associated with the “aperiodic” order
Aperiodic Structures

The term “aperiodic crystal” covers modulated, composite crystals and quasicrystals.

“The classical modulated structures”

Intergrowth compounds or composite structures

Quasicrystals N>1

occupancy position Spin

Non-crystallographic rotation symmetry
Existence of a Modulation

The reason of the satellite reflections - Periodic Deviation

The origin of the modulation may be:
- An atomic displacement
- A modification of occupation
- A magnetic moment

The loss of information coming from the satellite reflections leads to the refinement of an average structure
Existence of a Modulation

We have to use and to explain the intensities of the satellite reflections in order to solve the real structure.

Modulated Structure

- $a' = 3a$
- $a' = 2.403\ldots a$

**Commensurability**

- The modulation $w(q)$ is commensurate with the periodicity of the unit cell.

**Incommensurability**

- The modulation $w(q)$ is not commensurate with the periodicity of the unit cell.

**How we do that?**

- Treatment as supercell.
- Treatment using superspace group (SSG) with an additional dimension $(2+1)$ vectors ($a^*$, $b^*$ and $q$).
Superspace approach – Metric considerations

Additional diffraction spots:

\[ Q = h a_1^* + k a_2^* + l a_3^* + m q = H + m q \]

Modulation vector \( q \) can be expressed as a linear combination of

\[ a_1^*, a_2^*, a_3^* \Rightarrow q = q_1 a_1^* + q_2 a_2^* + q_3 a_3^* \]

\( q_1, q_2, q_3 \) ..... all rational \( \rightarrow \) commensurate structure

\( q_1, q_2, q_3 \) ..... at least one irrational \( \rightarrow \) incommensurate structure

It is rather difficult to prove irrationality only from measured values. The higher the denominators the smaller difference between commensurate and incommensurate approach. But there are clearly distinguished cases \( 1/2, 1/3 \) where commensurability plays an important role.
Modulated and composite crystals can be described in a (3+d) dimensional superspace. The theory has developed by P.M. DeWolff, A. Janner and T. Janssen (Aminoff prize 1998). This theory allows to generalize concept of symmetry and also to modify all method used for structure determination and refinement of aperiodic crystals.

The basic idea is that a real diffraction pattern can be realized by a projection from the (3+d) dimensional superspace.
$a_3^* = A_3^*$
1. The important assumption is that all satellites are clearly separated. This is true for the commensurate case or for the incommensurate case when the intensities diminish for large satellite index.

2. The additional vector \( \mathbf{e} \) is perpendicular to the real space and plays **only** an ancillary role.

All diffraction spots form a lattice in the four-dimensional superspace → there is a periodic generalized (electron) density in the four-dimensional superspace.

Reciprocal base :

\[
\mathbf{A}^*_i = \mathbf{a}^*_i \quad i = 1,2,3 \quad \mathbf{A}^*_4 = \mathbf{e} + \mathbf{q}
\]

Direct base :

\[
\mathbf{A}_i \cdot \mathbf{A}^*_j = \delta_{ij} \quad i, j = 1,2,3,4
\]

\[
\mathbf{A}_i = \mathbf{a}_i - (\mathbf{a}_i \cdot \mathbf{q}) \mathbf{e} \quad i = 1,2,3 \quad \mathbf{A}_4 = \mathbf{e}
\]
Then the generalized density fulfill the periodic condition:

\[ \tilde{\rho}(\mathbf{R}) = \tilde{\rho}((\mathbf{R} + n_1 \mathbf{A}_1 + n_2 \mathbf{A}_2 + n_3 \mathbf{A}_3 + n_4 \mathbf{A}_4)) \]

and therefore it can be expressed as a 4-dimensional Fourier series:

\[ \tilde{\rho}(\mathbf{R}) = \sum_{\mathbf{H}} F_{\mathbf{H}} \exp(-2\pi \mathbf{R} \cdot \mathbf{H}) \]

where:

\[ \mathbf{R} = (x_1, x_2, x_3, x_4) \quad \mathbf{r} = (x_1, x_2, x_3) \]
\[ \mathbf{H} = (h_1, h_2, h_3, h_4) \quad \mathbf{h} = (h_1, h_2, h_3) \]

From the definition of the direct and reciprocal base it follows:

\[ \tilde{\rho}(\mathbf{R}) = \sum_{\mathbf{H}} F_{\mathbf{H}} \exp[-2\pi \{\mathbf{r} - (\mathbf{r} \cdot \mathbf{q}) \mathbf{e} + x_4 \mathbf{e}\} \{\mathbf{h} + m \mathbf{q} + m \mathbf{e}\}] \]
\[ \tilde{\rho}(\mathbf{R}) = \sum_{\mathbf{H}} F_{\mathbf{H}} \exp[-2\pi\{(\mathbf{h} + m\mathbf{q})\mathbf{r} + m(x_4 - \mathbf{r} \cdot \mathbf{q})\}] \]

But the real diffraction pattern is a projection of the 4d pattern into \( R_3 \) which means that the term \( x_4 - \mathbf{r} \cdot \mathbf{q} \) has to be constant.

Conclusion: A real 3d density can be found as a section through the generalized density.
1. The important assumption is that all satellites are clearly separated. This is true for the commensurate case or for the incommensurate case when the intensities diminish for large satellite index.

2. The additional vector $t$ is perpendicular to the real space and plays only an ancillary role.

The definition of the modulation functions is such that they are periodic in $t$ (0-1).

$$A_4 = t$$

Where are the atoms?

A real 3d density can be found as a section through the generalized density.

$$p(x_4) = A_0 + \sum_n A_{s,n} \sin(2\pi n x_4) + \sum_n A_{c,n} \cos(2\pi n x_4)$$

Atomic rope
Super Space group Approach

Loss of periodicity in three dimensions

\[ \mathbb{R}^3 \]

Recovery of periodicity in \( 3 + d \) dimensions: “Embedding”

Structure Determination

\[ \mathbb{R}^{3+d} \]

Interpretation in three dimensions

\[ \mathbb{R}^3 \]

Can we do everything we want?
Super Space group - Symmetry

The symmetry is described by a (3+d)-dimensional space group. A 4D superspace group must be 3+1 reducible = the internal and external dimensions cannot mix together.

General form of a symmetry operation:

\[
\begin{pmatrix}
R_E & 0 \\
R_M & R_I
\end{pmatrix}
\begin{pmatrix}
\tau_E \\
\tau_I
\end{pmatrix}
\]

Example of superspace group operations:

\[ x_1, -x_2, 1/2+x_3, -x_4 \]
\[ -x_1, -x_2, x_3, 1/2+x_4 \]
Super Space group - Symmetry

How can the symmetry be determined?

The first three rows are the components of the basic space group. The sign of $R_i$ depends on the action of the symmetry operation on the $q$-vector:

2-fold: $-x_1, x_2, -x_3, -x_4$

mirror: $x_1, -x_2, x_3, x_4$
The translational part is determined from the extinction conditions in complete analogy to the 3D case:

in general:

\[ h_R = h, \ h \cdot \tau = \text{integer} \]

c-glide:

\[ x_1, -x_2, 1/2+x_3: \ h0l, \ l=2n \]

"superspace c-glide" with shift along \( x_4 \):

\[ x_1, -x_2, 1/2+x_3, 1/2+x_4: \ h0lm, \ l+m=2n \]
Symmetry in the superspace

Basic property of 3+d dimensional crystal - generalized translation symmetry:

\[ \rho(r) = \rho(r + \sum_{i=1}^{3+d} n_i A_i) \]

\[ \rho(\hat{S}r) = \rho(r) \]  \[ \hat{S}r \cdot \hat{S}r = r \cdot r \]  \[ \hat{S} = (R|t) \]

↓ basic property  ↓ unitary operator  ↓ matrix representation

Trivial symmetry operator - translation symmetry:

\[ R = E, \quad t = \sum_{i=1}^{3+d} n_i A_i \]
The rotational part of a general symmetry element

\[ \mathbf{R} = \begin{bmatrix} \Gamma_R & 0 \\ \Gamma_M & \Gamma_I \end{bmatrix} \]

1. The right upper part of the matrix is a column of three zeros. It is a consequence of the fact that the additional ancillary vector \( \mathbf{e} \) cannot be transformed into the real space.

2. From the condition that symmetry operator has to conserve scalar product it follows

\[ \det \Gamma_R = \pm 1 \quad \det \Gamma_I = \pm 1 \]

3. \( \mathbf{q} \Gamma_R - \Gamma_I \mathbf{q} = \Gamma_M \)

These conditions show that any superspace group is a four-dimensional space group but on the other hand not every four-dimensional space group is a superspace group. The superspace groups are 3+1 reducible. This allows to derive possible rotations and translation is same way as for 3d case.
1. Inversion centre

\[
\begin{bmatrix}
\alpha & \beta & \gamma
\end{bmatrix} \cdot \begin{bmatrix}
-1 & 0 & 0 \\
0 & -1 & 0 \\
0 & 0 & -1
\end{bmatrix} \pm 1 \cdot \begin{bmatrix}
\alpha & \beta & \gamma
\end{bmatrix} = \begin{bmatrix}
-\alpha \pm \alpha & -\beta \pm \beta & -\gamma \pm \gamma
\end{bmatrix}
\]

\[\Gamma_I = \begin{cases} 
-1 & \alpha \neq \beta \neq \gamma \neq 0 \\
1 & \alpha = \beta = \gamma = 0
\end{cases}\]

There is no modulation for the second case and therefore the inversion centre has to have \(\Gamma_I = 1\)
2. Two-fold axis along z direction

\[
\begin{bmatrix}
\alpha & \beta & \gamma
\end{bmatrix} \cdot \begin{bmatrix}
-1 & 0 & 0 \\
0 & -1 & 0 \\
0 & 0 & 1
\end{bmatrix} \pm 1 \cdot \begin{bmatrix}
\alpha & \beta & \gamma
\end{bmatrix} = \\
\begin{bmatrix}
-\alpha \pm \alpha & -\beta \pm \beta & \gamma \pm \gamma
\end{bmatrix}
\]

\[\Gamma_I = -1 \quad \alpha \neq 0, \beta \neq 0, \gamma = 0 \quad \text{monoclinic planar case}\]
\[\Gamma_I = 1 \quad \alpha = \beta = 0, \gamma \neq 0 \quad \text{monoclinic axial case}\]
3. Mirror with normal parallel to z direction

\[
\begin{bmatrix}
\alpha & \beta & \gamma
\end{bmatrix} \cdot \begin{bmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & -1
\end{bmatrix} \pm 1 \cdot \begin{bmatrix}
\alpha & \beta & \gamma
\end{bmatrix} = \\
\begin{bmatrix}
\alpha \pm \alpha & \beta \pm \beta & -\gamma \pm \gamma
\end{bmatrix}
\]

\[\Gamma_I = -1 \; \; \alpha = \beta = 0, \gamma \neq 0 \] monoclinic axial case
\[\Gamma_I = 1 \; \; \alpha \neq 0, \beta \neq 0, \gamma = 0 \] monoclinic planar case
<table>
<thead>
<tr>
<th>Translation part</th>
<th>Symbol</th>
<th>Reflection condition for $(hk0m)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(0,0,0,0)$</td>
<td>$\begin{pmatrix} m \ 1 \end{pmatrix}$</td>
<td>$-$</td>
</tr>
<tr>
<td>$(0,0,0,1/2)$</td>
<td>$\begin{pmatrix} m \ s \end{pmatrix}$</td>
<td>$m = 2n$</td>
</tr>
<tr>
<td>$(1/2,0,0,0)$</td>
<td>$\begin{pmatrix} a \ 1 \end{pmatrix}$</td>
<td>$h = 2n$</td>
</tr>
<tr>
<td>$(1/2,0,0,1/2)$</td>
<td>$\begin{pmatrix} a \ s \end{pmatrix}$</td>
<td>$h + m = 2n$</td>
</tr>
<tr>
<td>$(0,1/2,0,0)$</td>
<td>$\begin{pmatrix} b \ 1 \end{pmatrix}$</td>
<td>$l = 2n$</td>
</tr>
<tr>
<td>$(0,1/2,0,1/2)$</td>
<td>$\begin{pmatrix} b \ s \end{pmatrix}$</td>
<td>$l + m = 2n$</td>
</tr>
<tr>
<td>$(1/2,1/2,0,0)$</td>
<td>$\begin{pmatrix} m \ 1 \end{pmatrix}$</td>
<td>$h + k = 2n$</td>
</tr>
<tr>
<td>$(1/2,1/2,0,1/2)$</td>
<td>$\begin{pmatrix} m \ s \end{pmatrix}$</td>
<td>$h + k + m = 2n$</td>
</tr>
</tbody>
</table>
Super Space group

Symbol of the basic space group

Herman-Mauguin symbol

Definition of the intrinsic shifts in the fourth dimension
s=1/2; t=1/3
q=1/4; h=1/6

Generators:
-x₁, x₂, -x₃, (1/2)-x₄
x₁, -x₂, x₃, 1/2+x₄

Centering:
1/2 1/2 0 0
Super-space group symbols

There are three different notation

\[ B_{s1 \bar{1}}^{Pmna} \] or \[ B : Pmna: s1 \bar{1} \] or \[ Pmna(01/2\gamma)s00 \]

The rational part of the modulation vector represents an additional centring. It is much more convenient to use the centred cell instead of the explicit use of the rational part of the modulation vector.

\[ \mathbf{q} = (01/2\gamma) \rightarrow \mathbf{q}' = (00\gamma) \]
Super Space group & Refinement Procedure

3D

- Metric, symmetry, Bravais class
- Extinction rules
- Possible space group

Ex: R-3m

Direct Method or Patterson method to find the atomic positions

(3+n)D

- Metric, symmetry, Bravais class
- Extinction rules
- Possible superspace group

756 for \( n=1 \), 3355 for \( n=2 \) et 11764 for \( n=3 \)

Ex: \( R-3m(00\gamma)0s \)

Physical space

Direct Method, Patterson method, Super flip,…

to find the atomic positions for the average structure from the main reflections

Refinement of the modulation using the satellites reflections
Positional modulation - longitudinal

Modulation vector : \((\alpha, \beta, 0)\)

Modulation wave : \(u_x = U_x \cos(2\pi q \cdot r)\)

\[
u = U \cos(2\pi q \cdot r)\]

\[
F = f \exp\left(2\pi i Q \cdot r\right)J_m(2\pi U \cdot H)
\]
Positional modulation longitudinal
1st harmonic 0.1 Å
Fourier map
Positional modulation longitudinal
1st harmonic 0.1Å
Diffraction pattern
Positional modulation longitudinal
1st harmonic 0.5Å
Fourier map
Positional modulation longitudinal
1st harmonic 0.5Å
Diffraction pattern
Positional modulation - transversal

Modulation vector: \((\alpha, \beta, 0)\)

Modulation wave: 
\[ u_z = A_z \cos(2\pi q \cdot r) \]

\[ u = U \cos(2\pi q \cdot r) \]

\[ F = f \exp(2\pi i Q \cdot r)J_m(2\pi U \cdot H) \]
Positional modulation transversal – 1st harmonic 0.5Å
Fourier map
Positional modulation transversal – 1$^{\text{st}}$ harmonic 0.5Å
Diffraction pattern $l=0$
Positional modulation transversal – 1\textsuperscript{st} harmonic 0.5Å
Diffraction pattern /\!\!=\!\!\!\!=1
Composite structure
Composite structure – without modulation
Fourier map
Composite structure – without modulation
Diffraction pattern
Composite structure – with modulation
Fourier map
Composite structure – with modulation
Diffraction pattern
The periodic modulation function can be expressed as a Fourier expansion:

$$p(x_4) = A_0 + \sum_{n} A_{s,n} \sin(2\pi nx_4) + \sum_{n} A_{c,n} \cos(2\pi nx_4)$$

The necessary number of used terms depends on the complexity of the modulation function.

The modulation can generally affect all structural parameters – occupancies, positions and atomic displacement parameters (ADP),…. The set of harmonic functions used in the expansion fulfils the orthogonality condition, which prevents correlation in the refinement process.

In many cases the modulation functions are not smooth and the number of harmonic waves necessary for the description would be large. In such cases special functions or set of functions are used to reduce the number of parameters in the refinement.
Modulated Functions
(Special Functions)

Crenel function

\[ p(x_4) = 1 \quad x_4 \in (x_4^0 - \Delta/2, x_4^0 + \Delta/2) \]

\[ p(x_4) = 0 \quad x_4 \notin (x_4^0 - \Delta/2, x_4^0 + \Delta/2) \]

Examples
Perovskite $A_xBX_3$. Composite Structure

“Random” spin chain
Oxygen Vacancy controversy

$\gamma = \frac{x}{2}$
R-3m(00$\gamma$)0s

Synthesis and structure determination of two new composite compounds in the hexagonal perovskite-like sulfide family: \( \text{Eu}_{8/7}\text{TiS}_3 \) and \( \text{Sr}_{8/7}\text{TiS}_3 \).

A new structural type in the hexagonal perovskite family. Structure determination of the commensurately modulated misfit compound \( \text{Sr}_{9/8}\text{TiS}_3 \).

UNCLASSIFIED
Define a sub-network

Choice

Perovskite $A_xBX_3$

$W_1 = \begin{pmatrix}
1 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 \\
0 & 0 & 1 & 0 \\
0 & 0 & 0 & 1
\end{pmatrix}
$

$W_2 = \begin{pmatrix}
1 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 \\
0 & 0 & 0 & 1 \\
0 & 0 & 1 & 0
\end{pmatrix}
$

**Perovskite** \( A_x B X_3 \)

R3m(00\(\gamma\))

Ukei et al. Model

Discontinuity Phenomenon

Crenel function with a centro-
Superspace Group

UNCLASSIFIED
Perovskite $A_xBX_3$

$\text{Sr}_{1.2872}\text{NiO}_3$

$X_3 = 1/2, X_1 = 0.154$

$\text{R}3m(00\gamma)0s$
Perovskite $A_xNiX_3$
Perovskite $A_xCoX_3$

Co behavior in the TP site

$Sr_{14/11}CoO_3$

Classical treatment

Anharmonic treatment

### Perovskite $A_xBX_3$ - Where is the family?

Common features

From (3+1)D to 3D in a commensurate approach

<table>
<thead>
<tr>
<th>$\gamma = m/n$</th>
<th>$t = 0 \mod 1/n$</th>
<th>$t = 1/2n \mod 1/n$</th>
<th>$t = 1/4 \mod 1/n$</th>
<th>Other sections in $t$</th>
</tr>
</thead>
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<td>$m = 3k$, $n$ pair</td>
<td>$R3c$</td>
<td>$R3c$</td>
<td>$R3c$</td>
<td>$R3c$</td>
</tr>
<tr>
<td>$m = 3k$, $n$ impair</td>
<td>$R3 \bar{3}$</td>
<td>$R32$</td>
<td>$R3$</td>
<td>$R3$</td>
</tr>
<tr>
<td>$m = 3k \pm 1$, $n$ pair</td>
<td>$P3c$</td>
<td>$P3c$</td>
<td>$P3c$</td>
<td>$P3c$</td>
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<tr>
<td>$m = 3k \pm 1$, $n$ impair</td>
<td>$P3$</td>
<td>$P32$</td>
<td>$P3$</td>
<td>$P3$</td>
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</tbody>
</table>

- Same Superspace group
- Same atomic position
- Valid for commensurate and incommensurate case
Family tree...Farey tree
Family tree...Farey tree
According to Hume-Rothery’s suppositions, which are verified in the Zn-Pd system, the crystal structures of various noble metal alloys are invariant with respect to specific valence electron concentrations (\(\text{vec}\)) called “electron compounds”.

In the Zn-Pd system we focused our research on the \(\gamma\)-brass phase because we considered that similarities with quasicrystalline phases might be explained by structural rules as well as electronic rules.

\(\gamma\)-Brass Structures: \(\text{Zn}_{1-x}\text{Pd}_x\)

\[0.14 \leq x \leq 0.24\]

\[1.52 \leq \text{vec} \leq 1.72\]

\((\tau = 1.618)\)
\( \gamma \)-Brass Structures

Image From a Brucker CCD

“106.86 Å”

Satellite reflection

Main reflection

Image From IPDS

Zn_{1-x}Pd_{x} (x=0.14 to 0.24): A Missing Link Between Intergrowth Compounds And Quasicrystal Approximants O. GOURDON, Z. IZAOLA, L. ELCORO, V. PETRICEK and G. J. MILLER (2006) *Phil. Mag.* 86(3-5) 419-426.
**γ-Brass Structures**

Orthorhombic average unit cell

\[ a_s = 12.929 \ (3) \ \text{Å} \]
\[ b_s = 9.112 \ (4) \ \text{Å} \]
\[ c_s = 2.5631 \ (7) \ \text{Å} \]

\( q = \gamma c^* \)

with a unique 1D modulated wave

Family of intergrowth compounds with 2 composites such as defined:

The problem is reduced to refine 4 atomic sites

\[
\begin{pmatrix}
1 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 \\
0 & 0 & 1 & 0 \\
0 & 0 & 0 & 1
\end{pmatrix}
\]  
\[
\begin{pmatrix}
1 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 \\
0 & 0 & 1 & 0 \\
0 & 0 & 0 & 1
\end{pmatrix}
\]  

<table>
<thead>
<tr>
<th>First subsystem</th>
<th>Second subsystem</th>
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<tbody>
<tr>
<td>Zn1 at (0, 0, 0)</td>
<td>Zn2 at (1/4, 1/8, ¾)</td>
</tr>
<tr>
<td>Pd4/Zn4 at (1/4, 0, ¼)</td>
<td>Zn3/Pd3 at (~0.6, 1/6, ¾)</td>
</tr>
</tbody>
</table>
**γ-Brass Structures**

**What are the modulations?**

![Diagram](image)

- (a) [Graphical representation of γ-Brass Structures showing modulations with labels 13 and 8.]
- (b) [Graphical representation of γ-Brass Structures showing modulations with labels 18 and 11.]

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\( \gamma \)-Brass Structures

(a)

(b)

(c)

UNCLASSIFIED
Why modulations are important?

• For decades we have limited our knowledge of the atomic structure of materials to the *average* structure. However the “real materials” possess atomic arrangements which are usually more complicated than that and *deviate* from this standard description.

**Interest**

• Materials with disordered structures and long range order structures possess interesting physical properties and usually the properties are governed or linked to their atypical structure (*local structure/defect or modulated waves*).
Vacancy ordering in Battery Materials

Solvothermal synthesis of LiMn$_2$O$_{4-\delta}$

**Questions**

- High conductivity?
- Possible O vacancies?

**Answer**

- Clear Deviation from the Fd-3m cubic symmetry
- Addition of a modulation

Rietveld refinement of the powder neutron diffraction pattern using an orthorhombic Fddd(α00) superspace approach

Improved electrode kinetics in lithium manganospinel nanoparticles synthesized by hydrothermal methods: identifying and eliminating oxygen vacancies, Hao, Xiaoguang, Olivier Gourdon, Liddle, Brendan and Bartlett, Bart (2012) *Chemical Science*. 

UNCLASSIFIED
Vacancy ordering in Battery Materials

Solvothermal synthesis of LiMn$_2$O$_4$/annealed

- Annealing the sample modified the structure to an “average” Fd-3m cubic structure.
- Addition of extra oxygens
- The peak shape/Lorentzian part indicated a possible defect ordering into the material (confirmed by microscopy measurements).

Improved electrode kinetics in lithium manganospinel nanoparticles synthesized by hydrothermal methods: identifying and eliminating oxygen vacancies, Hao, Xiaoguang, Olivier Gourdon, Liddle, Brendan and Bartlett, Bart (2012)
Vacancy ordering in Battery Materials

Fddd(α00) with superspace approach $\alpha=1/3 \ a^*$

Organization of the O vacancies
Conduction associated with the diffusion thru the vacancies

Improved electrode kinetics in lithium-ion battery nanoparticles synthesized by hydrothermal methods: identifying and eliminating oxygen vacancies. Hao, Xiaoguang, Olivier Gourdon, Liddle, Brendan and Bartlett, Bart (2012) Chemical Science.
Example $\text{K}_{1/3}\text{Ba}_{2/3}\text{AgTe}_2$

How an incorrect structure analysis leads to a non-understanding of the physical properties.

*Grand interest for thermoelectricity*

*Semiconductor with small gap*

- Monoclinic Structure $\text{P}_2_1/m$
- Square Te-net
- Semi-Conductor (gap $\sim$eV)

---

[Graph and diagram showing electronic band structure and DOS (Density of States) for the material.]

**Metal**

**Square [Te] net**
Example $K_{1/3}Ba_{2/3}AgTe_2$

"Classical modulated" structures

$P2_1(\alpha 0 \gamma)$

$q = 0.3248(6) a^* - 0.071(8) c^*$

A unique distortion in $K_{1/3}Ba_{2/3}AgTe_2$. X-ray diffraction determination and electronic band structure analysis of its incommensurately modulated structure.

Example $K_{1/3}Ba_{2/3}AgTe_2$
Example $K_{1/3}Ba_{2/3}AgTe_2$

CDW and existence of nesting vectors in the Fermi surfaces.
Example $K_{1/3}Ba_{2/3}AgTe_2$

Polymerization

2:1:2:1

V pattern

2:2:1:1

W pattern

$3(a+b)$
Example $K_{1/3}Ba_{2/3}AgTe_2$
Aperiodicity is everywhere…

- **Thermoelectric materials**
- **Superconductor Materials**
- **Magnetic Materials**
- **Drugs (ephedrine)**
Aperiodicity is everywhere….

**Protein crystals can be incommensurately modulated**

Jeffrey J. Lovelace, Cameron R. Murphy, Lee Daniels, Kartik Narayan, Clarence E. Schutt, Uno Lindberg, Christer Svensson and Gloria E. O. Borgstahl

*Eppey Institute for Research in Cancer and Allied Diseases, 987696 Nebraska Medical Center, Omaha, NE 68198-7696, USA, **Rigaku Americas, The Woodlands, Texas 77381-5209, USA, †Department of Chemistry, Princeton University, NJ 08544, USA, ‡Department of Zoological Cell Biology, Stockholm University, S-10691 Stockholm, Sweden, and *MAX-lab, Lund University, PO Box 118, SE-221 00 Lund, Sweden. Correspondence e-mail: gborgstahl@unmc.edu

(a) Periodic

(b) Aperiodic, Modulated – commensurate (q = 0.25a*)

(c) Aperiodic, Modulated - incommensurate (q=0.29a*)

**profilin:actin complex**
Aperiodicity is everywhere….

Modulated structure of nepheline

The incommensurately modulated structure of a natural nepheline of composition $K_{0.13}Na_{0.13}Ca_{0.16}Al_{0.10}Si_{0.14}O_{25}$ has been determined in supercell. The compound crystallizes in the trigonal centered superspace group $X3(0y)0$ with $y = 0.204(8)$, $X = (0, 0, 0, 0, 0, 1/3, 2/3, 0, 0, 0)$, $a = 17.2998$ (8) and $c = 8.5622$ (10) Å. The structure is characterized by a framework of corner-connected $(AlSb)O_4$ tetrahedra. The additional cations are incorporated in two different types of channels of the framework. All atoms in the structure are displacively modulated with amplitudes below 0.1 Å. The modulation can be well described taking into account harmonics of first order only. Atomic positions in the smaller channels of the framework are fully occupied by $Na^+$. Cationic positions in the larger channel are occupationally modulated, yet the variation of electron density as a function of the internal coordinate is very small and indicates that the incorporation of different types of cations ($K^+$, $Na^+$, $Cu^{2+}$) and vacancies is realised in a highly disordered way. Average $T$–$O$ distances indicate a nearly complete $AlSi$ ordering in the tetrahedral framework. A large part of the $O$ atoms are approximated by split-atom positions, which are additionally affected by occupational modulation resulting in a high degree of disorder in the modulated structure. Occupational probabilities for the split-atom positions are complementary. Occupational modulations of the cations in the larger channels and the $O$ atoms of the tetrahedral framework are coupled and correlations between occupational and displacive modulations exist.
Aperiodicity is everywhere.

<table>
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<th>2</th>
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Lanthanides

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<td>Es</td>
<td>Fm</td>
<td>Md</td>
<td>No</td>
<td>Lr</td>
</tr>
</tbody>
</table>

Actinides
In 1999 two papers reported incommensurate composite character of pure metals under high pressure:


**FIG. 4.** Structure of Ba phase IVa. The host *I* structure (dark symbols) with guest chains (light symbols) is shown in a c-axis projection. The *I*-structure atoms are labeled with their z coordinates. The insets show (i) the C and (ii) the M guest structures.
Theory of aperiodic crystals and computer program – Jana2000 – has been later applied to solve and refine several analogical structures.
Aperiodicity is everywhere....
Extra-small peaks are not always a secondary phase.

Missing a modulation information can lead to a misunderstanding of the physical properties of your materials.

The modulation can be present even in very simple compounds as oxides – PbO, U₄O₉, Nb₂Zrₓ₋₂Oₓ₊₁.
Modulated Approach to treat magnetic ordering

Existence of a Modulation

Example of an hypothetical 2D crystal

Modulation on the atomic position of the white atoms

Direct Space

The origin of the modulation
A magnetic moment

Reciprocal Space

Main Reflections

Satellite reflections

\[ M_{v,m}(k \cdot r_v) = \sum [M_{v,m_s} \sin(2\pi m k \cdot r_v) + M_{v,m_c} \cos(2\pi m k \cdot r_v)] \]

Magnetic space and superspace groups, representation analysis: \( m \)
The concept of the superspace can be generalized for magnetic structures

\[ M_{v,m}(k \cdot r_v) = \sum_m [M_{v,ms} \sin(2\pi m k \cdot r_v) + M_{v,mc} \cos(2\pi m k \cdot r_v)] \]

magnetic modulated structures using harmonic ordering.

---

**Modulated Approach to treat magnetic ordering**

**Mn₅Si₃ family: Magnetic Structure**


Refinement using the magnetic super space group $\text{Ccmm1}^\prime(0\beta0)00ss$ with $q=(0,b,0)=b^*$.  

1/3 of the magnetic atoms are magnetically ordered.
Mn$_5$Si$_3$ family: Magnetic Structure

Relation from group to subgroup
a = 6.8943(3) Å, b = 11.9131(5) Å, c = 4.80742(5) Å and b = 90.268(3)$^\circ$

Refinement using the magnetic super space group C2$_1$/m1’(0β0)0ss with $q = (0,b,0) = b^*$. 2/3 of the magnetic atoms are magnetically ordered.
Mn$_5$Si$_3$ family: Magnetic Structure


Process of Inverse MCE

Entropy Change between the two magnetic configurations

C$_2'/m1'(0\beta0)0ss$ with $q=(0,b,0)=b^*$.  

Ccmm$1'(0\beta0)00ss$ with $q=(0,b,0)=b^*$.  

Operated by Los Alamos National Security, LLC for the U.S. Department of Energy's NNSA
Acknowledgements

Jana2006 team

Vasek Petricek, Michal Dusek and Lukas Palatinus