Topology of Crystal Structures: Applications of Graph Theory (the vector method)

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Outline

Part 1: basic concepts
- Some graph theory
- Underlying nets and topology
- Labelled quotient graphs
- Symmetry
- Crystallographic nets
- Barycentric embeddings

Part 2: advanced topics
- Minimal nets
- Rings and generators
- Nets as projections
- Non-crystallographic nets
- Building units
- Groupoids
Topology of Crystal Structures

Basic concepts
Crystallography and crystallochemistry

$(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40}$

Atomic positions
Chemical bonds
Topology
Electron density maps

Electron density isosurface \((0.5 \times 10^{-6} \text{ e·pm}^{-3})\)
in \(\text{Ca}_{24}\text{Al}_{28}\text{O}_{64}^{4+}\cdot4\text{e}^{-}\) (maximum entropy method analysis) superposed on the atomic structure of the unit cell

K. Hayashi, P.V. Sushko, Y. Hashimoto, A.L. Shluger, H. Hosono
Nature Communications 5 (2014) 3515

Crystal structure and electron density in the apatite-type ionic conductor

\(\text{La}_{9.71}(\text{Si}_{5.81}\text{Mg}_{0.18})\text{O}_{26.37}\)

Roushown Ali, Masatomo Yashima, Yoshitaka Matsushita, Hideki Yoshioka, Fujio Izumi

periodic nets and quotient graphs

Unit cell:
- One Rhenium atom
- Three oxygen atoms
- Six Re – O bonds

A graph $G(V, E, i)$ is defined by:
- a set $V$ of vertices,
- a set $E$ of edges,
- an incidence function $i$ from $E$ to the set of couples $\{x, y\}$ of elements of $V$. 

\[ i(e_1) = \{u, v\} \]
\[ i(e_2) = \{v, w\} \]
\[ i(e_3) = \{w, u\} \]
Graphs with an orientation ($\sigma$)

- For $G = (V, E, i)$, let $G^\sigma = (V, E^\sigma, i^\sigma)$ such that:
  - $\sigma : E^\sigma \rightarrow E$ is a two-to-one, onto mapping
  - Preimages of $e = \{u, v\}$ are noted $e^+$ and $e^-$
  - $i^\sigma(e^+) = (u, v)$ and $i^\sigma(e^-) = (v, u)$

- Notations: $e^+ = uv$, $e^- = vu$
\[ \begin{align*}
V &= \{u, v, w\} \\
E &= \{e_1, e_2, e_3\}
\end{align*} \]

\[ \begin{align*}
i(e_1) &= \{u, v\} \\
i(e_2) &= \{v, w\} \\
i(e_3) &= \{w, u\}
\end{align*} \]

\[ \begin{align*}
G &:\quad u \rightarrow v \rightarrow w \\
e_1 &:\quad u \rightarrow v \\
e_2 &:\quad v \rightarrow w \\
e_3 &:\quad w \rightarrow u
\end{align*} \]

\[ \begin{align*}
G^\sigma &:\quad u \rightarrow v \rightarrow w \\
e_1 &:\quad u \rightarrow v \\
e_2 &:\quad v \rightarrow w \\
e_3 &:\quad w \rightarrow u
\end{align*} \]

\[ \begin{align*}
e_1^+ &= e_1 = uv \\
e_1^- &= vu
\end{align*} \]
Graphs and multigraphs

Multiple edges

Simple graph: graph without loops or multiple edges
Subgraphs

\[ H \subseteq G \]

Induced subgraph

\[
\begin{align*}
V(H) &\subseteq V(G) \\
E(H) &\subseteq E(G) \\
i_H &\text{ is a restriction of } i_G
\end{align*}
\]

\[
\begin{align*}
V(H) = S &\subseteq V(G) \\
E(H) &\text{ maximal in } E(G)
\end{align*}
\]
Order, size and degrees

- Order of G: $|G|$ = number of vertices of G
- Size of G: $||G||$ = number of edges of G
- Degree of a vertex $u$: $d(u)$ = number of edges incident to $u$ (loops are counted twice)
- Regular graph of degree $r$: $d(u) = r$
Walks, paths and cycles

• **Walk**: alternate sequence of vertices and edges mutually adjacent
• **Closed walk**: the last vertex is equal to the first = the last edge is adjacent to the first one
• **Path**: a walk which traverses only once each vertex
• **Cycle**: a closed path
• **Forest**: a graph without cycle
Edges only are enough to define the walk!

- a.b.j.i walk
- b.j.d.e.f.g.h.i closed walk
- a.b.c path
- b.j.i cycle
Nomenclature

- $P_n$ path of $n$ edges
- $C_n$ cycle of $n$ edges
- $B_n$ bouquet of $n$ loops
- $K_n$ complete graph of $n$ vertices
- $K_n^{\{m\}}$ complete multigraph of $n$ vertices with all edges of multiplicity $m$
- $K_{n_1, n_2, \ldots, n_r}$ complete $r$-partite graph with $r$ sets of $n_i$ vertices ($i=1,..r$)
$P_3$

$B_4$

$C_5$
Connectivity

- **Connected graph**: any two vertices can be linked by a walk
- **Point-connectivity**: \( \kappa(G) \), minimum number of points that must be withdrawn to get a disconnected graph
- **Line-connectivity**: \( \lambda(G) \), minimum number of lines that must be withdrawn to get a disconnected graph
Determine $\kappa(G)$ and $\lambda(G)$.

$\kappa(G) = 2$

$\lambda(G) = 3$
Component = maximum connected subgraph

Tree = component of a forest

\[ F = T_1 \cup T_2 \]
Spanning graphs

G

T: spanning tree of G
Morphisms of (oriented) graphs

• A morphism between two graphs $G(V, E, i)$ and $G'(V', E' i')$ is a pair of maps $f_V$ and $f_E$ between the vertex and edge sets that respect the incidence relationships:

  for $i(e) = (u, v)$ : $i' \{ f_E(e) \} = (f_V(u), f_V(v))$

  or: $f(uv) = f(u)f(v)$

• Isomorphism of graphs: 1-1 morphism
Aut(G): group of automorphisms

- Automorphism: isomorphism of a graph on itself.
- Aut(G): group of automorphisms by the usual law of composition, noted as a permutation of the edges (invariant by reversal of the signs!)

Generators for Aut(C₃)

\{ (e₁, e₂, e₃), (e₁, e₃⁻) (e₂, e₂⁻) \}
Special case of the loops

• Inversion of a loop: \((e^+, e^-)\)
• 4th order permutation of two loops:
  \((e_1^+, e_2^+, e_1^-, e_2^-)\)
Reversal of the signs: $K_2^{\{3\}}$

Forbidden permutation: $(e_1^+, e_2^+)(e_1^-, e_3^-)$

Permitted permutation: $(e_1^+, e_2^+)(e_1^-, e_2^-)$
Quotient graphs

• Let $F$ be a subgroup of $\text{Aut}(G)$ that acts freely on $G$,
• Denote $[x]$ the orbit of $x$ in $V$ or $E$ by $F$ in $G$.
• The quotient $G/F$ is the “graph of the orbits”:
  \[
  V(G/F) = \{[v] \text{ for } v \text{ in } V\}
  \]
  \[
  E(G/F) = \{[e] \text{ for } e \text{ in } E\}
  \]
  \[
  [e] = [u][v] \text{ for } e = uv
  \]
• The graph homomorphism $q : q(x) = [x]$ is called the natural projection of $G$ on $G/F$
R: generated by \((e_1, e_2, e_3)\)

( noted \(R = \langle(e_1, e_2, e_3)\rangle\) )
Find the quotient graphs $C_4/R$, $C_4/S$ and $C_4/T$

Compare degrees in $C_4$ and its quotients
Free action automorphisms

\( f \) in Aut(\( G \)) acts freely on the graph \( G \) if there is no fixed element in \( V \) or \( E \) by \( f \)

\( (U,V,W) \) and \( (A,B,C,D) \) act freely

\( (V,W), (B,D) \) and \( (A,D)(B,C) \) do not
Periodic nets

• A net is a simple, 3-connected graph, which is locally finite (WE Klee, 2004).

• \((N, T)\) is a \(p\)-periodic net if:
  – \(N\) is a net,
  – \(T < \text{Aut}(N)\), is free abelian of rank \(p\),
  – The number of (vertex and edge) orbits in \(N\) by \(T\) is finite.

Then, \(T\) acts freely on \(N\)
Crystallographic nets

• **Crystallographic net**: simple 3-connected graph whose automorphism group is isomorphic to a crystallographic space group.

• **n-Dimensional crystallographic space group**: a group $\Gamma$ with a free abelian subgroup $T$ of rank $n$ which is normal in $\Gamma$, has finite factor group $\Gamma/T$ and whose centralizer coincides with $T$ ($T$ is maximal abelian).
Example: the square net

\[ V = \mathbb{Z}^2 \]
\[ E = \{ pq \mid q-p = \pm a, \pm b \} \]
\[ a = (1,0), \ b = (0,1) \]

\[ T = \{ t_r : t_r(p) = p+r, \ r \in \mathbb{Z}^2 \} \]
Natural projection : examples

$C_3$ $\langle (U, V, W) \rangle$

Square net

$T$
ReO$_3$: vertex and edge lattices
\( \text{ReO}_3 \) : quotient graph

\[ K_{1,3}^{(2)} \]
The $\beta$-W net

$A_t \quad B_t \quad C_t$

$K_3^{(2)}$
## Simple structure types

<table>
<thead>
<tr>
<th>Structure</th>
<th>Quotient graph</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>$K_2^{{6}}$</td>
</tr>
<tr>
<td>CsCl</td>
<td>$K_2^{{8}}$</td>
</tr>
<tr>
<td>ZnS (sphalerite)</td>
<td>$K_2^{{4}}$</td>
</tr>
<tr>
<td>SiO$_2$ (quartz)</td>
<td>$K_3^{{3}}$</td>
</tr>
<tr>
<td>CaF$_2$ (fluorite)</td>
<td>$K_{1,2}^{{4}}$</td>
</tr>
</tbody>
</table>
Drawbacks of the quotient graph

• Non-isomorphic nets can have isomorphic quotient graphs
• Different 1-complexes with isomorphic nets can have non-isomorphic quotient graphs (non-crystallographic nets for different choice of the translation group)
• Different 1-complexes can have both isomorphic nets and isomorphic quotient graph (non-ambiently isotopic embeddings)
Non-isomorphic nets with isomorphic quotient graphs
Vector method: the labelled quotient graph as a voltage graph
Labelled Quotient Graphs of Periodic Nets

(N, T) : periodic net
- A net N
- A translation group T

N/T : Labelled Quotient Graph
- Two vertex-lattices
- Three edge-lattices
- Label vectors in T
The kagome net (kgm)

A unit cell in an embedding of kgm and a fundamental transversal with its boundaries.

The fundamental transversal and the labelled quotient graph obtained after closing half-edges.
β-W net: Find the labelled quotient graph

t in $Z^2$, i=(1,0), j=(0,1)
V = \{a_t, b_t, c_t\}
E = \{a_t b_t, a_t c_t, b_t c_t, a_t b_{t+j}, a_t c_{t+j}, c_t b_{t+i}\}
“Voltage” or “edge-coloured” graphs

• Graphs with an orientation :
  for \( e = uv \) define \( e^- = vu \) (and \( e^+ = e \))

• A voltage \( \alpha \) of a graph \( G \) by a group \( A \) is a mapping
  \( \alpha : E \rightarrow A \) with \( \alpha(e^-) = [\alpha(e)]^{-1} \)

• Derived graph \( G^\alpha : \)
  \( V(G^\alpha) = \{(v, a) \in V \times A\} \)
  \( E(G^\alpha) = \{(e, a) \in E \times A\} \)
  \( (e, a) = (u, a)(v, ab) \) for \( e = uv \) and \( \alpha(e) = b \)

• \( A \) acts freely on \( G^\alpha : f(x, a) = (x, fa) \) for \( x \) in \( V \) or \( E \) and \( f \) in \( A \)
Nets and topology: why 3-connectivity?
Derived graphs : examples

A = \langle C_3 \rangle

A = \mathbb{Z}^2
Cycle and cocycle spaces on \( Z \)

- **0-chains**: \( \sum \lambda_i u_i \) for \( u_i \in V \)  
  \( \lambda_i \) in \( Z \)
- **1-chains**: \( \sum \lambda_i e_i \) for \( e_i \in E \)
- **Boundary operator**: \( \partial e = v - u \) for \( e = uv \)
- **Coboundary operator**: \( \delta u = \sum e_i \) for \( e_i = uv_i \)
- **Cycle space** = \( \text{Ker}(\delta) \) (cycle-vector \( C : \delta C = 0 \))
- **Cocycle (cut) space** = \( \text{Im}(\delta) \) (cocycle-vector \( k = \delta u \))
- **dim(cycle space)** = \( \#E - \#V + 1 \) (cyclomatic number)
Cycle and cocycle vectors

\[ \delta e_1 = A - D \]

Cycle-vector: \( e_1 + e_2 - e_3 \)

Cocycle-vector: \( \delta A = -e_1 + e_2 + e_4 \)

Find a basis for: 1) the cycle-space and 2) the cocycle-space of the cartesian product \( K_2 \times K_3 \) (trigonal prism)
Cycle and cut spaces on $F_2 = \{0, 1\}$ (non-oriented graphs)

- The cycle space is generated by the cycles of $G$
- Cut vector of $G = \text{edge set separating } G \text{ in disconnected subgraphs}$
- The cut space is generated by $\delta u$ ($u \in V$)
Find $\delta(u + v + w)$

$\delta u + \delta v + \delta w$

$\delta u + \delta v$

$\delta u$
Minimal nets

- Cyclomatic number $\gamma = \text{number of independent cycles of } G = \text{number of chords of a spanning tree } T$
- Choose $A = \mathbb{Z}^\gamma$ free abelian group of order $\gamma$
- Voltage assignment:
  - for each chord $e$ of $T$, $\alpha(e)$ is a different generator of $\mathbb{Z}^\gamma$
  - for $e$ in $T$, $\alpha(e) = 0$
- Minimal net $M[G] = \text{derived net } G^\alpha$
- The translation subgroup of $M[G] \equiv \text{Cycle-space of } G$
Example 1: graphite \((K_2^{(3)})\)

1-chain space: 3-dimensional

Two independent cycles: \(a = e_1 - e_2\), \(b = e_2 - e_3\)

One independent cocycle vector: \(e_1 + e_2 + e_3\)
$\text{Sr}[\text{Si}]_2 = \text{srs} : K_4$

Edge space: 6-dimensional

Three independent cycles: $a$, $b$, $c$

Three independent cut vectors: coboundary of three vertices
Hyperquartz : $K_3^{2}$

Archetype: 4-dimensional
Tetrahedral coordination
Cubic-orthogonal family:
$(e_1-e_4), (e_2-e_5), (e_3-e_6), \sum e_i$
Lengths: $\sqrt{2}, \sqrt{2}, \sqrt{2}, \sqrt{6}$
Space group: 25/08/03/003

Edge space: 6-dimensional

Four independent cycles: $e_1-e_4, e_2-e_5, e_3-e_6, e_1+e_2+e_3$
Two independent cut vectors
Symmetry

- $\Gamma$: Space group of the crystal structure
- $T$: Normal subgroup of translations
- $\Gamma/T$: Factor group
- $\text{Aut}(G)$: Group of automorphism of the quotient graph $G$
- $\Gamma/T$ is isomorphic to a subgroup of $\text{Aut}(G)$
Symmetry of minimal nets

- **Translation subgroup** isomorphic to the cycle space of the quotient graph $G$ (dimension equal to the cyclomatic number)
- **Factor group**: isomorphic to $\text{Aut}(G)$
- Unique embedding of maximum symmetry: the archetype (barycentric embedding)
Voltages, permutations and crystal symmetry

\[ C_4 = (a, b, -a, -b) \]
\[ C_2 = (a, -a)(b, -b) \]
Reflections

\[ \sigma = (a, -a) \]
Reflections

\[ \sigma = (b, -b) \]
Reflections

\[ \sigma = (a, b)(-a, -b) \]
Reflections

\[ \sigma = (a, -b)(b, -a) \]
ReO$_3$: $\Gamma/T \cong \text{Aut}(G) \cong O_h$

- $C_4$ Rotation: $(e_1, e_3, e_2, e_4)$
- $C_3$ Rotation: $(e_1, e_3, e_5) (e_2, e_4, e_6)$
- Reflection: $(e_1, e_2)$
Geometric crystal class: minimal nets

- Generators and conjugacy classes in Aut(G) as edge permutations
- Linear operations in the cycle-space
- Matrix invariants: order, trace, determinant
Generators of $\text{Aut}(K_{2}^{(3)})$:

- $(e_1, e_2, e_3)$
- $(e_i, -e_i)(A, B)$
- $(e_1, -e_3)(e_2, -e_2)(A, B)$

Linear operations in the cycle space (point symmetry):

$$(a, b) = (e_1 - e_2, e_2 - e_3) \rightarrow (e_2 - e_3, e_3 - e_1) = (b, -a - b)$$

In matrix form:

$$\gamma\{(e_1, e_2, e_3)\} = \begin{pmatrix} 0 & -1 \\ 1 & -1 \end{pmatrix}$$

$$\gamma\{(e_1, -e_3)(e_2, -e_2)\} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

$$\gamma\{(e_i, -e_i)\} = \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}$$
Geometric crystal class

When the net is not a minimal net:

The point group of the net is the subgroup of \text{Aut}(G) which respects the subspace of the cycle-space with zero net voltage.
Check the space group of $4.8^2$

Kernel: $c = e_4 + e_6 + e_3 - e_2$

Generators:
$(e_4,e_6,e_3,-e_2)(e_1,-e_5,-e_4,e_5)(A,B,C,D)$
$(e_4,-e_6)(e_2,e_3)(e_1,-e_1)(A,C)$

Cycle basis:
$a = e_1 + e_4 + e_5 - e_3$
$b = e_1 + e_2 - e_5 + e_6$
Notice: $a \perp b \perp c$
Point symmetry

\[(a, b) \rightarrow (-e_5 + e_6 + e_1 + e_2, -e_5 - e_4 - e_1 + e_3) = (b, -a)\]

\[(a, b) \rightarrow (-e_1 - e_6 + e_5 - e_2, -e_1 + e_3 - e_5 - e_4) = (-b, -a)\]

\[
p4mm
\begin{array}{c|c|c}
\text{Generator} & 0 & -1 \\
& 1 & 0 \\
\end{array}
\begin{array}{c|c|c}
0 & -1 \\
-1 & 0 \\
\end{array}
\]

\[
\text{Translation} \quad (0 \quad 0) \quad (0 \quad 0)
\]

Walk: A → B → C → D → A

Final translation : c = 0
Find the space group of quartz

\[ a = 1000 = e_1 - e_4 \]
\[ b = 0100 = e_2 - e_5 \]
\[ c = 0010 = e_3 - e_6 \]
\[ d = 0001 = e_4 + e_5 + e_6 \]

Hyper quartz = \( N[K_3^{(2)}] \)

Quartz = \( N[K_3^{(2)}]/\langle1110\rangle \)
Isomorphism class of a net

Find the labelled quotient graph for the double cell
Automorphisms $\phi$ of the quotient graph $G$ that leave the quotient group of the cycle space by its kernel invariant can be used to extend the translation group if the generated group acts freely:

Kernel: $e_1 - e_2$

Extension: $(e_1, e_2)(e_3, e_4)$
Isomorphism class of a net

Kernel: $e_1 - e_2$

Extension: $c = (e_1, e_2)(e_3, e_4)(A, B)$

$c^2 = a$
Show that cristobalite has the diamond net.

Kernel: \( e_2 - e_1 = e_7 - e_8 \)
\( e_3 - e_4 = e_6 - e_5 \)

\[
(1,8)(2,7)(3,6)(4,5)(A,D)(B,C)
\]

\[
e_8 - e_4 + e_1 - e_5 = 001 \rightarrow e_1 - e_5 + e_8 - e_4 = 001
\]

\[
2k = e_4 - e_8 + e_5 - e_1 = 00 -1
\]

\[
\{3,6\}(\neg \{4,5\}) = 010: \text{ voltage for } \{3,6\} = 010 + k
\]
Representation and embedding

• Euclidian representation, \( p : V \cup E \rightarrow E^n \)
  for \( u \in V \), \( p(u) \) is a point of \( E^n \)
  if \( e = uv \), \( p(e) \) is the line \( p(u)p(v) \)
  We note \( p(e) \) the vector \( p(v) - p(u) \) in \( \mathbb{R}^n \)

• Embedding:
  \[
  \begin{cases}
  p \text{ is injective on } V \\
  p(e) \cap p(e') = \emptyset \text{ unless } e \sim e'
  \end{cases}
  \]
Representation with crossing in $E^2$  

Embedding in $E^2$
Minimal net: integral embedding

- $m = |E(N/T)|$
- Embedding ($p$) in the Euclidian space $E^m$ with orthonormal basis $\{e_i, i=1,...,m\}$
- For $e_i \in E(N/T)$ set $p(e_i) = e_i$

Fix an origin in the vertex set: $p(u) = O$

- For $v \in V(N)$, let $w$ be a walk from $u$ to $v$ with projection in $N/T$: $q(w) = \sum x_i e_i$
- Set $p(v) = O + \sum x_i e_i$
Euclidian representations

• Barycentric representation:
  \[
  \rho : V(N) \rightarrow E \quad \text{(Euclidian space)}
  \]
  \[
  r(u) \rho(u) = \sum_v \rho(v) \quad r(u) = \text{degree of } u
  \]

• Periodic representation:
  \[
  * : T \rightarrow T^* \quad \text{(translation group in E)}
  \]
  \[
  \rho[t(u)] = t^*[\rho(u)] \quad \text{for any } t \in T, u \in V(N)
  \]

• Determination from the labelled quotient graph:
  - the vertex method
  - the edge method
Barycentric representation: the vertex method

Neighbours of $A_{00}$: $B_{00}$, $B_{10}$ and $B_{0-1}$

Barycentric equation: $3 \rho(A_{00}) = \rho(B_{00}) + \rho(B_{10}) + \rho(B_{0-1})$

\[
\begin{align*}
3 \rho(A_{00}) & = \rho(B_{00}) + [\rho(B_{00}) + 10] + [\rho(B_{00}) - 0-1] \\
\rho(A_{00}) & = 0 \quad \Rightarrow \quad \rho(B_{00}) = -\frac{1}{3}, \frac{1}{3}
\end{align*}
\]
Vertex method and Laplacian matrix

\[ L = (L_{ij}) \]

\[
\begin{align*}
L_{ii} &= -d(V_i) \\
L_{ij} &= m \text{ if } V_iV_j \in E(G) \text{ with multiplicity } m, \text{ for } i \neq j
\end{align*}
\]

\(\alpha(V_i) = \text{Sum of voltages over ingoing edges at } V_i\)

\[
\begin{align*}
(V): & \quad \text{column vector of } V_i \\
(\alpha(V)): & \quad \text{column vector of } \alpha(V_i)
\end{align*}
\]

\[
L.(V) = (a(V_i)) \quad \det(L) = 0!
\]

Solved by eliminating the last row of \(L\) and imposing \(V_1 = 0\)
Draw a barycentric embedding of the 2-periodic net derived from the following labelled quotient graph.
Example

\[
L = \begin{pmatrix}
-4 & 2 & 2 \\
2 & -3 & 1 \\
2 & 1 & -3
\end{pmatrix}
\]

\[
(V) = \begin{pmatrix}
A \\
B \\
C
\end{pmatrix}
\]

\[
(\alpha(V)) = \begin{pmatrix}
-1 & -1 \\
1 & 0 \\
0 & 1
\end{pmatrix}
\]

Set A at the origin:

\[
\begin{pmatrix}
B \\
C
\end{pmatrix} = \begin{pmatrix}
2 & 2 \\
-3 & 1
\end{pmatrix}^{-1} \begin{pmatrix}
-1 & -1 \\
1 & 0
\end{pmatrix} = \begin{pmatrix}
-3/8 & -1/8 \\
-1/8 & -3/8
\end{pmatrix}
\]
Periodic embeddings: principles

**Edge-space = Cycle-space ⊕ Cut-space**

G: n vertices, m edges

E: m x 1 column vector (edges)
B: m x 1 column vector (cycle and cut bases)
K: m x m matrix expressing the vectors of B as combinations of edges

\[ B = K \cdot E \quad \Rightarrow \quad E = K^{-1} \cdot B \]
Barycentric embeddings

Archetype = projection of the integral embedding on the cycle-space

Embedding = Choice of the basis $B$ in $\mathbb{R}^p$:

- **Cycle vectors**: given by the net voltages over the cycles of $G$
- **Cut vectors**: zero vectors
Graphite layer : $(6^3)$

\[
K = \begin{pmatrix}
1 & -1 & 0 \\
0 & 1 & -1 \\
1 & 1 & 1
\end{pmatrix}
\]

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

\[
E = K^{-1}B = \begin{pmatrix}
2/3 & 1/3 & 1/3 \\
-1/3 & 1/3 & 1/3 \\
-1/3 & -2/3 & 1/3
\end{pmatrix} \cdot \begin{pmatrix}
1 & 0 \\
0 & 1 \\
0 & 0
\end{pmatrix} = \begin{pmatrix}
2/3 & 1/3 \\
-1/3 & 1/3 \\
-1/3 & -2/3
\end{pmatrix}
\]
Graphite layer : \((6^3)\)

\[
E = \begin{pmatrix}
\frac{2}{3} & \frac{1}{3} \\
\frac{-1}{3} & \frac{1}{3} \\
\frac{-1}{3} & \frac{-2}{3}
\end{pmatrix}
\]

\[
a.b = -1 \\
a.a = b.b = 2
\]

\[\Rightarrow \quad \angle(a, b) = 120^\circ\]
Atomic positions

p6mm

Generator

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

Translation

\((0, 0)\) \quad \((0, 0)\) \quad \((0, 0)\)

A: \(x + T\)
B: \(x + \text{e}_1 + T\)

A: \(2a/3 + b/3 + T\)
B: \(a/3 + 2b/3 + T\)

After inversion: \(A \rightarrow -x + T = B = x + 2a/3 + b/3 + T\)

\(-2x = 2a/3 + b/3 + T\)

With \(t = b\), \(x = -a/3 - 2b/3 = 2a/3 + b/3\)
Topology of Crystal Structures

Advanced topics
Nets as quotients of the minimal net

\[ N (T = \mathbb{Z}^3) \]

[diagram]

\[ N/<111> \]

\(<111> = \text{translation subgroup generated by } 111\]

\[ N/<111>: T = \langle\{100, 010\}\rangle \]
Embeddings as projections of the archetype

3-d archetype,
2-d structures: 1-d kernel

3-cycle: $3.9^2$, $9^3$
4-cycle: $4.8^2$
Nets as quotients (projections)

\( \text{Sr[Si}_2\] (I4,32) \)

\( \cong \)

\( p4mm \)

\( p3m1 \)
Nets as quotient graphs: kernel of the projection

- \((N, T)\) a periodic net,
- \(G = N/T\), its quotient graph,
- Voltage assignment \(\alpha : N \sim G^\alpha\).
- \(M[G]\) : minimal net, with translation group \(R\).
- \(w\) : closed walk of \(G\) with zero net voltage \(\alpha(w) = 0\).
- Lifting \(w\) in \(M[G]\) defines \(\rho(w)\) in \(R\)
- \(S = \{\rho(w) : \alpha(w) = 0\}\), subgroup of \(R\)
- \(N \sim M[G]/S\)
- \(S\) is generated by strong rings of \(N\)

\(S : \text{Kernel of the projection}\)
Rings and strong rings in graphs

• A **ring** is a cycle that is not the sum of two shorter cycles
• A **strong ring** is a cycle that is not the sum of (an arbitrary number of) shorter cycles
Example 1: the square net

A cycle
A strong ring
Sum of three strong rings
Example 2: the cubic net

A strong ring: $S_1$

A ring: $R$

A 6-cycle: $C = S_2 + S_3$

$R = S_1 + C$

Rings are elements of the cycle-space: what is their origin, from the point of view of the labelled quotient graph?
Rings of the derived graph

• Net voltage on a walk:
  \[ \alpha(w) = \alpha(e_1) \alpha(e_2) \ldots \alpha(e_n) \text{ for } w = e_1 e_2 \ldots e_n \]

• Cycles of \( G^\alpha \) project on closed walks of \( G \) with net voltage 0

• No cycle in the covering tree!

• Strong ring: cannot be written as a sum of smaller cycles
Trivial rings

- G quotient graph with voltage assignment $\alpha$ in the free group $F_v$
- Rings in $M[G]$ are commutators of generators of $F_v$

$[a,b] = aba^{-1}b^{-1}$
Nets as quotients: 1-periodic examples

\[ M[B_2] = \text{square net} \]

\[ S = \langle b-2a \rangle \]

\[ N = M[B_2]/S \]
Square net:
$F_2$, relator $[a,b]$

Quotient net:
$F_2$, relators $[a,b], a^2b^2$

Check it!
\[ N / \langle a - b \rangle \]
A 2-periodic case: tfa and tfa/\langle001\rangle
$C(r)$: consequence of the relation $r$, subgroup of $\langle a, b \rangle$, contains

$r$, its conjugates $x^r = xrx^{-1}$, their inverses and combinations

Cycle-space: isomorphic to the kernel $C(r)$

Strong rings = shortest basis vectors of $C(r)$
Cyclomatic number and generators

\[ a, b: \text{free generators} \]

Commutation relationship: \( ab = ba \)

Abelian group of rank 2

Commutator:
\[ r = [a, b] = aba^{-1}b^{-1} \]

\[ [a, b^2] = ab^2a^{-1}b^{-2} = (aba^{-1}b^{-1})b(aba^{-1}b^{-1})b^{-1} = [a, b]^b[a, b] \quad \text{a consequence of } [a, b] \]
Trivial rings: hcb

A faithfull representation
A single commutator $[a, b]$

A single strong ring, up to translation
Fundamental rings: hex

Relator: $abc$ (or $c = b^{-1}a^{-1}$)

Two fundamental rings and no trivial ring:

- $[a, b]$,
- $[a, c]$,
- $[b, c]$  

$3$-cycles

- $acb$

$4$-cycles

- $acb \rightarrow bac$ (or $b(acb)b^{-1}$)
- $[a, b] = (abc)(bac)^{-1}$
Strong rings in kgm

Relators: $ac^{-1}$, $bd^{-1}$, $[a, b]$

$[a, b] = aba^{-1}b^{-1} = adc^{-1}b^{-1}$  6-cycle

8-cycle

Diagram of the strong rings in kgm with relators and cycles.
Nets defined by a graph and relators, classification of nets

- $G$ a graph with cyclomatic number $\nu$
- Choose $\alpha$ : voltage assignment in $A = \mathbb{Z}^\nu$
- $S$ subgroup of $A$ defined by a set of relators
- $N = M[G]/S$
- Nets $N$ are ordered by set-inclusion of $S$ subgroups in $A$. 
Known nets derived from $K_3^2$

<table>
<thead>
<tr>
<th>Material</th>
<th>Cycle Notation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>$adb^{-}c^{-}$</td>
<td>Sum of the 3 2-cycles</td>
</tr>
<tr>
<td>NbO</td>
<td>$adb^{-}c^{-}$</td>
<td>Sum of 2 3-cycles</td>
</tr>
<tr>
<td>Moganite</td>
<td>$adc^{-}$</td>
<td>Sum of 2 2-cycles</td>
</tr>
<tr>
<td>afw</td>
<td>$bc^{-}$</td>
<td>One 3-cycle</td>
</tr>
<tr>
<td>Kagome</td>
<td>$ad^{-}, bc^{-}$</td>
<td>Edge disjoint 3-cycles</td>
</tr>
<tr>
<td>$\beta$-W</td>
<td>$adb^{-}, bc^{-}$</td>
<td>Two tangent 3-cycles</td>
</tr>
</tbody>
</table>
Lattice classification of nets derived from $K_3^{2}$
Non-crystallographic nets

- Periodic nets \((N,T)\) such that
- \(\text{Aut}(N)\) is not isomorphic to any isometry group in the Euclidian space.

(\text{Hidden symmetries = inconsistent with translations})
Bounded automorphisms: \( \text{B}(\text{N}) \)

- \( g \in \text{Aut}(\text{N}) \), such that:
  \[ \{d(x, g(x)) \mid x \in \text{V}(\text{N})\} \text{ is bounded} \]

- \( \text{B}(\text{N}) \) is normal in \( \text{Aut}(\text{N}) \).
- For crystallographic nets: \( \text{B} = \text{T} \) (and conversely)
Example

\[ \phi = (A_0, B_0) \]

\[ t (X_i) = X_{i+1} \text{ for } X = A, B \]

\[ \phi^{-1} t \phi \notin T \]
Cu carboxylates in MOF structures

\[ \sigma : \text{transposition of two Cu centers} \]
System of imprimitivity for $B(N)$

- Partition $\sigma$ of $V(N)$ into finite subsets such that:
- For any $g \in B(N)$ and $v \in \sigma(u)$,
- $g(v)$ and $g(u)$ belong to the same cell (block) of $\sigma$
Theorem

In any non-crystallographic net, the set $F(N)$ of bounded automorphisms of finite order is a normal subgroup of the automorphism group: $F(N) < Aut(N)$

Orbits by $F(N)$ provide a system of finite blocks of imprimitivity.
F(N) and orbits

F(N) infinite, one fixed point-lattice

F(N) infinite, no fixed point-lattice

F(N) finite, no fixed point-lattice
Equitable and equivoltage partitions

• A partition of the vertex set $V(G)$ of a graph $G$ with cells $C_i$ is equitable if the number of neighbours in $C_j$ of a vertex $u$ in $C_i$ is a constant $b_{ij}$, independent of $u$;

• A vertex partition of a labelled quotient graph is equivoltage if:
  – it is equitable and
  – there is a 1-1 mapping between the stars of any two vertices of the same cell, which respects the voltages.
Fundamental theorem of NC nets

Any non-crystallographic net can be represented by a labelled quotient graph with an equivoltage partition. Any periodic barycentric representation of the NC net displays vertex collisions; vertices that are equivalent under bounded automorphisms of finite order project on the same Euclidian point.
θ: Equivoltage partition

\[ \begin{align*}
N & \xrightarrow{q_T} N/T \\
N/\sigma & \xrightarrow{q'_T} (N/\sigma)/T = (N/T)/\theta \\
\end{align*} \]

\(\sigma\): system of imprimitivity derived from \(F(N)\)
A 1-periodic example
Sequence of partitions

\[ \theta_1 = \{\{A\},\{B\},\{C,D\}\} \quad \theta_2 = \{\{A\},\{B,E\}\} \]
A 2-periodic case
Creating a NC net from $K_3^{(2)}$

$\theta = \{\{A\}, \{B, C\}\}$
4/4/019 (Sowa, 2012)
Surgery Techniques

Elementary steps: vertex or edge addition and deletion

Combined operations:

Edge subdivision

Vertex identification
Vertex decoration
Vertex decoration
Decoration – contraction

- Edge subdivision
- Vertex deletion
- Contraction
- Decoration
- Vertex identification
- Edge addition
Graphs with crossings

Vertex identification $\rightarrow K_5$
Decoration – Contraction in periodic nets
Building units and underlying nets

Labelled quotient graph of building units: the voltage rank may be 0, 1, 2 or 3.
Labelled quotient graph of the underlying net: the voltage rank may be 0, 1, 2 or 3.
Octahedra chains in rutile

rtl (rutile) labelled quotient graph

sql – like interlinking of octahedra chains
Centered sql
From kgm to hca

Change of origin for A' and C lattices
From kgm to hca

decoration

contraction

decoration

contraction
Relationships between hcb and hca
NiAs

(a) Labelled quotient graph of nia

(b) Labelled quotient graph of MoS$_2$ layers

(c) = Labelled quotient graph of MgI$_2$ layers
Bi-layers

MoS$_2$

MgI$_2$ (kgd net)
From hcb to MoS$_2$
From \textbf{hcb} to \textbf{kgd}
4 parallel hcb layers glued at equivalent vertices in MoS$_2$ bi-layers
non-equivalent vertices in MgI$_2$ bi-layers
Garnet $A_3B_2(XO_4)_3$

Unconnected $BO_6$ and $XO_4$ units,

Two 3-periodic interpenetrated components for the A-O subnet.

$Na_3Sc_2(VO_4)_3$
Garnet (80 vertices – 192 edges)

Labelled quotient graph of one A-O component

Substitution of double A-O-A edges by single A-A edges with same net voltage $\rightarrow \text{lcv}$

$T = A_3O_6$ cages

Decorated srs net
Garnet: from srs to A-O subnets

Contraction (orange edges)

Labelled quotient graph of lcv

T-decorated srs

Change of origin

Contraction (orange edges)
Garnet: local structure around $A_3O_6$ cages

$srs$-like interlinking of $A_3O_6$ cages

Top and side views of 4-helicoidal chains
Tilt of $A_3O_6$ cages: $\arccos(\sqrt{3}/3) = 54.74^\circ$

B and X interlinking of the two Interpenetrated $\text{lcv}$ A-O subnets

Distortion of $A0_8$ cubic coordination:
$\theta = \pi/2 - \arccos(1/3) = 19.47^\circ$

$\Theta = 21^\circ$
Groupoids

Translation in finite objects?  (What is the symmetry of the chess board?)

Objects: \( S = [0,4] \times [0,4] \), finite area

\( T = \langle a, b \rangle \) infinite translation group in the plane

\[
G = \{(x,t,y): x, y \in S, t \in T, x = ty\}
\]

\[
(x,u,y)(y,v,z) = (x,uv,z)
\]
Groupoids of action

\[ G=(T,S) \quad T=\langle a,b \rangle = Z^2, \quad S=\{A,B,C,D\} \]

\[ g=(C,b,B), \quad h=(B,a,A) : \quad gh=(C,ba,A) \]

<table>
<thead>
<tr>
<th>Global symmetry</th>
<th>Partial symmetry</th>
<th>Local symmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>( m, t )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( m, g )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( gt )</td>
<td>( t, g )</td>
<td>( m )</td>
</tr>
</tbody>
</table>
A groupoid is formed from those symmetry operations (isometries) of a crystal structure built by isomorphic substrutures:

- **Local Symmetries**: symmetry operations of the substructure,
- **Partial Symmetries**: symmetry operations mapping one substructure onto another,
- **Global Symmetries**: symmetry operation of the entire structure.
### Structural analysis of pyroxenes

**MgSiO$_3$**  
**HT clinoenstatite**  
**Space group: C2/c (Nº 15)**

<table>
<thead>
<tr>
<th>Atom</th>
<th>Charge</th>
<th>Site</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Fractional Coordinates</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg1</td>
<td>Mg$^{2+}$</td>
<td>4 e</td>
<td>0.</td>
<td>0.</td>
<td>0.90420(10)</td>
<td>0.25</td>
</tr>
<tr>
<td>Mg2</td>
<td>Mg$^{2+}$</td>
<td>4 e</td>
<td>0.</td>
<td>0.</td>
<td>0.28560(10)</td>
<td>0.25</td>
</tr>
<tr>
<td>Si1</td>
<td>Si$^{4+}$</td>
<td>8 f</td>
<td>0.29223(6)</td>
<td>0.09198(7)</td>
<td>0.24570(10)</td>
<td></td>
</tr>
<tr>
<td>O1</td>
<td>O$^{2-}$</td>
<td>8 f</td>
<td>0.11300(10)</td>
<td>0.0828(2)</td>
<td>0.1380(3)</td>
<td></td>
</tr>
<tr>
<td>O2</td>
<td>O$^{2-}$</td>
<td>8 f</td>
<td>0.3636(2)</td>
<td>0.2577(2)</td>
<td>0.3179(3)</td>
<td></td>
</tr>
<tr>
<td>O3</td>
<td>O$^{2-}$</td>
<td>8 f</td>
<td>0.35430(10)</td>
<td>0.0065(2)</td>
<td>0.0258(3)</td>
<td></td>
</tr>
</tbody>
</table>

**Unit cell parameters:**
- $a = 9.5387$
- $b = 8.6601$
- $c = 5.2620$
- $\beta = 108.701$
Structural module in pyroxene (HT clinoenstatite, MgSiO$_3$) in the plane ($b-a,c$) (primitive cell)

Simplified structure (Mg2 deleted)
Stacking of modules in the direction $a+b$
Interlinking of chains analysis through the labelled quotient graph
HT clinoenstatite

kgd (kagome dual)
Quotient graph of the pyroxene module in pyroxenes (primitive cell)
Layer group of the module

(a, b, c) → (b, a, c)
(b-a, c, a+b) → (a-b, c, a+b)  \( (m_x|0 1/2 0) \)
(x, y, z) → (-x, y+1/2, z)

(a, b, c) → (-b, -a, -c)
(b-a, c, a+b) → (b-a, -c, -a-b)  \( 2_x \)
(x, y, z) → (x, -y, -z)

Crystal class 2/m \( (C_{2h}) \)
Layer group p2/b11  (monoclinic/rectangular)  Nº 16
Layer group

-110

001
LT clinoenstatite: quotient graph and double modular structure in the plane \((b, c)\)
LT clinoenstatite *versus* HT clinoenstatite

Automorphism without fixed point:

$$\varphi = (A, B)(C, F)(D, E)$$

Does not change voltages over cycles

$$\varphi$$ represents a translation of the periodic net mapping one module on the other

Distortion of the Crystal structure

Along the respective direction
Interlinking of chains and alternance of modules in LT clinoenstatite

Action of the automorphism $\varphi$ on the edges

Action of the automorphism $\varphi$ on the edges

$\alpha = 010; \beta = -110$
$\gamma = 010; \delta = 110$

New translation: $\delta = \frac{1}{2} \frac{1}{2} 0$

$-10$  $01$
$\text{kgd}$  

$\alpha - \delta$  $-10$  $01$  $\delta$
Protoenstatite: quotient graph and double modular structure in the plane $(b, c)$
Protoenstatite versus clinoenstatitite

$\phi = (A, B)(C, F)(D, E)$

Does not change voltages in the plane $(a, b)$ but inverses the $c$ axis.

The linear part corresponds to a reflection
Of the periodic net mapping
one module on the other
Alternance of modules in protoenstatite

Proto

LT-clino

Topology = kgd

Translation Associated to $\varphi$

$\frac{1}{2} \frac{1}{2} 0$
Protoenstatite: inversion of chain in successive modules by $n(\frac{1}{2} \frac{1}{2} 0)[0,0,1]$
Ortoenstatite: quotient graph and quadruple modular structure in the plane \((b, c)\)
Interlinking of chains and alternance of modules in ortoenstatite

\[ \varphi = (A,D,B,C)(E,L,G,J)(F,K,H,I) : \text{automorphism of the reduced quotient graph } Q, \text{ conserves voltages along directions } 100 \text{ e } 010 \]

\[ \begin{align*}
\alpha &= 010; 4\beta = -120 \\
\gamma &= 010; 4\delta = 120
\end{align*} \]

New translation:
\[ t = \frac{1}{4} \frac{1}{2} 0 \]
Sequence of modules in ortoenstatite

\( \varphi \) does not represent an automorphism of the net:

\( \varphi \) inverses the \( c \) axis, and infinite linear chains, alternatively, two modules yes, two modules no.

\( \varphi \) represents a partial symmetry operation in a groupoid.
Space groupoid of ortoenstatite

• Translation \( t = t(\frac{1}{4} \frac{1}{2} 0) \)
• Glide reflection \( \delta = \delta(\frac{1}{4} \frac{1}{2} 0)[0,0,1] \)
• Modules: \( m_k, k \in \mathbb{Z} \)

\[
m_k = t(k-\lfloor k/2 \rfloor)\delta^\lfloor k/2 \rfloor.m_0 = \varphi_k.m_0
\]
• \( \lfloor k/2 \rfloor \): largest integer inferior or equal to \( k/2 \)
• Layer group of module \( m_k \): \( \varphi_k.p2/b11.\varphi_k^{-1} \)
• Partial symmetry operations from \( m_k \) to \( m_l \): \( \varphi_l.p2/b11.\varphi_k^{-1} \)
• Only \( \varphi_{2k} \) act upon the complete structure:

\( \varphi_{2k} = (t\delta)^k \rightarrow \) glide reflection \( a \rightarrow Pbca \)
Thank you for your attention
Main references

- Harary F., *Graph Theory*, Addison-Wesley (1972)