Topological Methods in Crystal Structure Prediction

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Why topological crystal chemistry?

Crystallography
↓
atomic positions
↓
lattices
↓
geometrical properties

Crystal chemistry
↓
chemical bonds
↓
nets
↓
topological properties
Why computer methods?

CSD \( \sim 600000 \) entries
ICSD \( \sim 140000 \) entries
CrystMet \( \sim 100000 \) entries
PCD \( \sim 200000 \) entries

Huge amount!
Why not only modeling?

Quantum mechanics Simulation

Quantitative evaluation for a single substance

Crystal chemistry Topological/geometrical properties

Qualitative/semi-quantitative evaluation for a large group of substances
TOPOS program package – since 1989

http://www.topos.samsu.ru
Topological analysis in TOPOS

- Atomic net
  - AutoCN

- Structural groups
  - ADS

- Simplified nets
  - ADS

- Entanglements
  - ADS

- Tilings, tile topologies
  - ADS

- Crystal structure data
  - DBMS

- Net of voids and channels, VDP topologies
  - Dirichlet

- Topology identification
  - ADS

- Atomic packing
  - IsoTest

- Dual nets
  - ADS

- Hierarchical comparative analysis
  - IsoTest
What is overall topology for TOPOS?


h.c.p. 3D graph

Vertices & edges of the labeled quotient graph

Labeled quotient graph
What is overall topology for TOPOS?

Valence bonds
Van der Waals bonds
Hydrogen bonds
Solid Angles
Distances
Bond Valencies
How to distinguish overall topologies in TOPOS?

1. Point symbol (PS)
2. Coordination sequence (CS)
3. Extended point symbol (ES)
4. Vertex symbol (VS)

TTD Collection 73335 entries
http://www.topos.samsu.ru
How can we generate overall topology in TOPOS?

Atom roles:
origin, removed, contracted, target

Contracted atom
Target atoms

Origin: U, Cu, P
Removed: water molecules
Contracted: phosphate oxygens
Target: P

Cu[UO$_2$PO$_4$]$_2$·12H$_2$O

Underlying net: tcs
Underlying nets in inorganic compounds

$\gamma$-Sb$_2$O$_3$ (HT, HP) \quad \text{ICSD, } \approx 6500 \text{ structure types} \quad [\text{Si}_4\text{O}_4\text{N}_6]^{10-} \text{ in Ce}_4[\text{Si}_4\text{O}_4\text{N}_6]\text{O}$


Sb: $\leftrightarrow$ Si=O
O $\leftrightarrow$ N

$\alpha,\beta$-Sb$_2$O$_3 \leftrightarrow [\text{Si}_4\text{O}_4\text{N}_6]^{10-}$

3.3T8
Local vs. overall topology

Coordination figure

[Diagram showing molecular structures with labels and atoms highlighted]
Description of local topologies

Relations between local and overall topology
Relations between local and overall topology

coordination number → complex group → coordination figure → secondary building unit → underlying topology

CN=6

octahedron

trigonal prism

square pyramid

square
Relations between overall topologies

$G \leftarrow \text{Gavrog Systre (http://gavrog.org)}$
$A \text{ (supernet)} \rightarrow S_i(A) \text{ (subnets)}; \text{ breaking edges}$

$A = \text{pcu}$

$S_1 = \text{cds}$

$S_2 = 2\text{-fold ths}$

$S_3 = \text{sql plane net}$
Net Relation Graph (NRG)

$B_i$ – different nets (supernets or subnets) = vertices of the NRG

decrease of net connectivity and symmetry
NRG Properties

Path between NRG vertices

$A_i$

decrease of net connectivity and symmetry

$S(A_i)$

decrease of net connectivity and symmetry
NRG Properties

Distance \((d)\) between NRG vertices

\[ S(A_i) \]

decrease of net connectivity and symmetry

\[ d = 1 \quad d = \infty \]
Transformation pathways

Topologically fastest transformation

$A_i$ decrease of net connectivity and symmetry

$S(A_i)$

decrease of net connectivity and symmetry
Transformation pathways

Pathways through a supernet

$A_i$, decrease of net connectivity and symmetry

subnet, supernet, subgroup, supergroup

decrease of net connectivity and symmetry

$S(A_i)$
Diamond ↔ lonsdaleite (subnets)

<table>
<thead>
<tr>
<th>dia</th>
<th>↔</th>
<th>utp</th>
<th>↔</th>
<th>lon</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Fd-3m$</td>
<td>→</td>
<td>$Pnna$</td>
<td>←</td>
<td>$P6_3/mmc$</td>
</tr>
</tbody>
</table>

Sowa, H. & Koch, E. (2001)

<table>
<thead>
<tr>
<th>dia</th>
<th>↔</th>
<th>ths</th>
<th>↔</th>
<th>lon</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Fd-3m$</td>
<td>→</td>
<td>$C2/c$</td>
<td>←</td>
<td>$P6_3/mmc$</td>
</tr>
</tbody>
</table>

ths $I4_1/amd$, Blatov, V.A. (2007)

$Fd-3m \rightarrow R-3m$  
(-1/2$a$+1/2$b$, -1/2$b$+1/2$c$, $a$+$b$+$c$)  
$C2/m$  
(-1/3$a$+1/3$b$-2/3$c$, $-a$-$b$, $c$)  
$C2/c$ ($a$, $b$, $2c$)  
$P6_3/mmc \rightarrow P-31c \rightarrow C2/c$ ($-a$-$b$, $a$-$b$, $c$)
TOPOS topological collections

TOPOS Topological Types

Observed Collection (TTO)

TTO Collection 13394 entries
http://www.topos.samsu.ru
TOPOS topological collections

TOPOS Topological Types
Relations Collection (TTR)

TTR Collection 932 entries
http://www.topos.samsu.ru
TOPOS topological collections

Net topologies for a particular structure

BASMUE: clusters – pcu
standard – sqc65
TOPOS topological collections

Net topologies for a particular structure

Representatives of a given net topology

BASMUE: clusters – pcu
standard – sqc65

1137 structures of dia topology
TOPOS topological collections

- Net topologies for a particular structure
- Representatives of a given net topology
- Relations between different nets

BASMUE: clusters – pcu
standard – sqc65

1137 structures of dia topology

ths → dia (centers of edges)
gis → dia (centers of rings)
TOPOS topological collections

Net topologies for a particular structure
Representatives of a given net topology
Relations between different nets
Most abundant and rare net topologies

BASMUE: clusters – pcu standard – sqc65
1137 structures of dia topology
ths → dia (centers of edges)
gis → dia (centers of rings)

pcu and dia are most abundant

<table>
<thead>
<tr>
<th>Topological Types</th>
<th>Occur.</th>
</tr>
</thead>
<tbody>
<tr>
<td>pcu alpha-Po primitive cubic; 6/4/c1; sqc1</td>
<td>1363</td>
</tr>
<tr>
<td>dia Diamond; 4/6/c1; sqc6</td>
<td>1153</td>
</tr>
<tr>
<td>bcu body centered cubic; 8/4/c1; sqc3</td>
<td>285</td>
</tr>
<tr>
<td>cds CdSO4; 4/6/t4; sqc5</td>
<td>208</td>
</tr>
<tr>
<td>srs SrSi2; 3/10/c1</td>
<td>208</td>
</tr>
<tr>
<td>pts PtS, Cooperite; sqc183</td>
<td>178</td>
</tr>
<tr>
<td>rtl rutile 3.6-connected</td>
<td>170</td>
</tr>
<tr>
<td>hex hexagonal primitive; 8/3/h4; sqc4</td>
<td>163</td>
</tr>
</tbody>
</table>
TOPOS topological collections

Net topologies for a particular structure
Representatives of a given net topology
Relations between different nets
Most abundant and rare net topologies
Topological descriptors (indices)

BASMUE: clusters – pcu
standard – sqc65

1137 structures of dia topology

ths → dia (centers of edges)
gis → dia (centers of rings)

pcu and dia most abundant

Point symbol, extended point symbol, vertex symbol, coordination sequence
Underlying nets in 3D coordination networks

Underlying nets in three-periodic coordination polymers: topology, taxonomy and prediction from a computer-aided analysis of the Cambridge Structural Database

E. V. Alexandrov, V. A. Blatov, A. V. Kochetkov and D. M. Proserpio

Cite this: CrystEngComm, 2011, 13, 3947

www.rsc.org/crystengcomm

HIGHLIGHT

301 up to 2003

664 2004-2009

965 interp nets

434

5.43% 9.22%

4709 nets

distribution of the first 20 most frequent underlying single nets
Underlying nets in 2D coordination networks

Topology of 2-Periodic Coordination Networks: Toward Expert Systems in Crystal Design

Tatiana G. Mitina and Vladislav A. Blatov

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Underlying nets in 2D coordination networks

L = Hydroxyacetate (glycolate)

A=Co
AL₂

\( p = 7.8\% \)

\( p = 96\% \)

\( p = 84.3\% \)

\( p = 100\% \)

\( P = 0.078 \cdot 0.96 + 0.843 \cdot 1.0 = 0.918 \)
Expert system

- Initial data
- Inference machine
- Expert conclusion

Knowledge database

1st level databases (crystallographic data)
- CSD, ICSD, PCD

2nd level databases (topol & geom properties)
- TOPOS TTD, TTO

3rd level databases (topol & geom relations)
- TOPOS TTR
TOPOS collections of local topologies

- Collection of polyhedral cages (tiles)
- Collection of metal nanoclusters
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- Collection of polynuclear complex groups
TOPOS collections of local topologies

- Collection of polyhedral cages (tiles)
- Collection of metal nanoclusters
- Collection of polynuclear complex groups
- Collection of molecular ligands (TTL)
TOPOS collections of local topologies

- Collection of polyhedral cages (tiles)
- Collection of metal nanoclusters
- Collection of polynuclear complex groups

In preparation
- Collection of molecular ligands (TTL)
- Collection of molecules (TTM)

Molecular Voronoi polyhedron for $S_8$ molecule in $\alpha$-$S_8$
Local vs. overall topology

Databases of local coordination types

Database of network topological types

TOPOS

Databases of local coordination types

Database of network topological types
Conclusion

Crystal chemistry
(Diamond, CrystalMaker, PLATON, …)

Crystal chemistry
(TOPOS, Systre, 3dt, …)
Why not only modeling?

- Quantum mechanics
  - Simulation
  - Quantitative evaluation for a single substance

- Crystal chemistry
  - Topological/geometrical properties
  - Qualitative/semi-quantitative evaluation for a large group of substances

USPEX vs. TOPOS?

1. Some structure is generated. Is it new? Are there similar structures?
2. There is a set of similar structures. Do they possess similar physical properties?
Thank you for your attention!