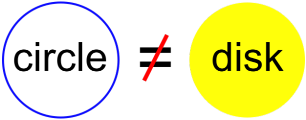
Equivalences of periodic crystals

MIF++ discussion seminar with MaThCryst
and other crystallographers across the world
Materials Innovation Factory (MIF), Liverpool

Aim to understand key definitions

It's natural that different areas have different names for the same concept. It would be great to avoid calling *different objects* by the same name, which can happen even in mathematics.

A round *circle* (a closed 1-dimensional curve with a length, area 0) differs from a round *disk* (a 2-dimensional region with a positive area).

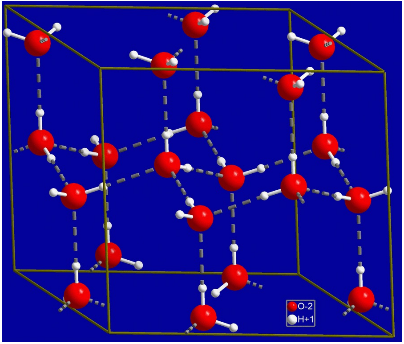


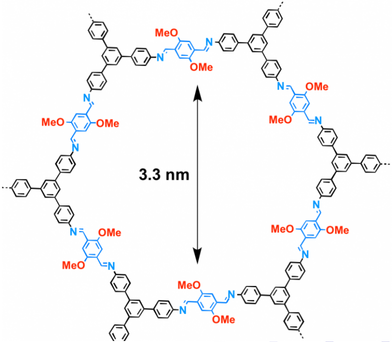
circle $\neq$ disk

How can we define a crystal (structure) mathematically?

Objects: all periodic crystals

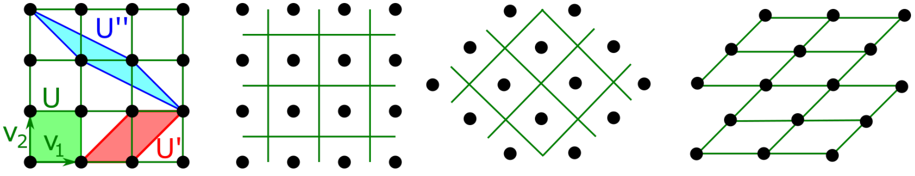
Solid crystalline materials (periodic *crystals*) can have many types, all consist of elementary blocks (*motifs*) of atoms, ions or molecules in a *unit cell* periodically repeated in three directions.





Many linear bases $\to$ one lattice

Given any linear basis $v_1, \ldots, v_n$ of $\mathbb{R}^n$, a *lattice* is $\Lambda = \{\sum_{i=1}^{n} c_i v_i \ : \ c_i \in \mathbb{Z}\}$. Any lattice Λ can be generated from infinitely many different bases.



Are the above lattices different or equivalent?

This depends on a definition of equivalence.

Any object should come with an equivalence.

Three axioms of an equivalence

A binary relation $A \sim B$ between objects is called an *equivalence* if the three axioms hold:

(1) *reflexivity*: any object $A \sim A$;

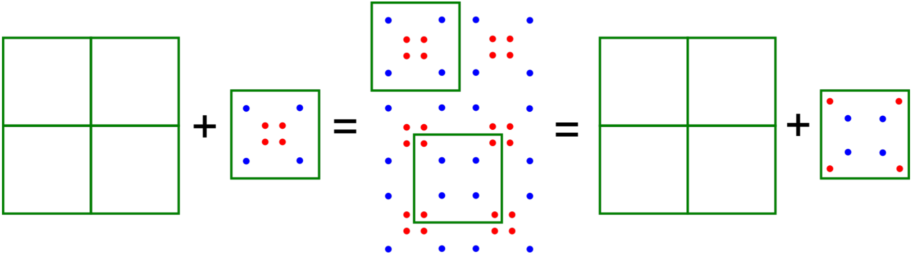
(2) *symmetry*: if $A \sim B$ then $B \sim A$;

(3) *transitivity*: if $A \sim B$ and $B \sim C$, then $A \sim C$.

The transitivity axiom guarantees that all objects split into disjoint classes $[A] = \{B \mid B \sim A\}$. If $[A], [C]$ share an object B, then $[A] = [C]$. Any justified classification needs an equivalence.

A periodic point set (crystal)

Any basis $v_1, \dots, v_n$ of $\mathbb{R}^n$ spans the *unit cell* $U = \{\sum_{i=1}^{n} c_i v_i \ : \ 0 \leq c_i < 1\}$. For any finite *motif* of points $M \subset U$, the *periodic point set* can be defined as $S = \Lambda + M = \{v + p \mid v \in \Lambda, p \in M\}$.

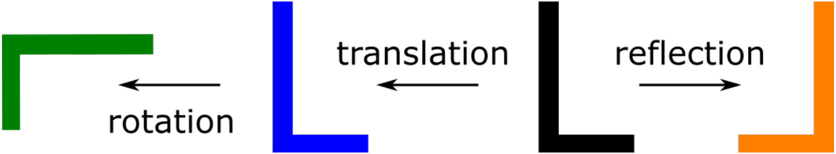


Different pairs (cell, motif) give the same set.

Equivalence by symmetry

Crystals can be called equivalent if they have the same space-group type (*isomorphic space groups*). To define it, we need an *isometry*.

An *isometry* $f : \mathbb{R}^3 \to \mathbb{R}^3$ is any map that preserves Euclidean distances: for $p, q \in \mathbb{R}^3$ $|f(p) - f(q)| = |p - q|$. Then any f decomposes into translations, rotations, mirror reflections.



The space-group type of a crystal

All isometries form the Euclidean group $\mathrm{Iso}(\mathbb{R}^3)$, an isometry can be described by 6 parameters.

The *space group* of a crystal S consists of all isometries f that keep S invariant: $f(S) = S$.

Two groups are *isomorphic* if there is a bijection $\beta : G \to H$ respecting the group operations: $\beta(g_1 \circ g_2) = \beta(g_1) \circ \beta(g_2)$. It's an equivalence.

The *space-group type* of a crystal S is the isomorphism class of its space group $G(S)$.

A group and its representations

It's tempting to write any element of a space group (a symmetry operation) in coordinates.

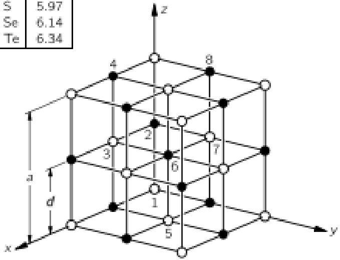
In $\mathbb{R}$, the central symmetry in 0 is $f_0(x) = -x$, the central symmetry in 1 is $f_1(x) = 2 - x$. The operations look different but generate the same group $\mathbb{Z}_2 = \{ f \mid f \circ f = \mathbf{id} \}$ up to isomorphism.

In algebra, one (isomorphism class of a) group can have many (matrix) linear representations $G \to GL(\mathbb{R}^3)$ respecting group operations.

From the 19th century to the 21st

Since an isomorphism defines an equivalence of groups, all periodic crystals in $\mathbb{R}^3$ split into 219 space-group types. Great for the 19th century!

Crystal	●	○	a (Å)
Rocksalt	Na	Cl	5.64
Sylvine	K	Cl	6.28
	Ag	Cl	5.54
	Mg	O	4.20
Galena	Pb	S	5.97
	Pb	Se	6.14
	Pb	Te	6.34



Nearest neighbor distance $d = a/2$

In 2022 we have many more periodic crystals (660K+ in the CSD), millions are simulated by Crystal Structure Prediction (with the same chemical composition).

Other equivalences of crystals

A classification in 14 Bravais classes is coarser: if crystals have the same space-group type, then they have the same Bravais class.

The classification by chemical composition gives many more classes: $NaCl$, MgO, H_2O etc. Polymorphs have the same composition and often space-group type P_1 of only translations.

What is the *strongest* equivalence of crystals? What periodic point sets should be always equivalent in any practical classification?

Back to the basic isometry

Since all crystal structures are determined in a rigid form, any *rigid motion preserves crystals*.

If crystal structures are related by rigid motion, there is little (no) sense to distinguish them.

Rigid motion is the **strongest equivalence** (not meaning unique or best) on crystals in practice.

Two mirror images are detected by a change of orientation or binary chirality. Then a *complete classification up to isometry* suffices in practice.

What is a periodic crystal?

A new, possibly unexpected answer : a periodic crystal is *not a single periodic structure* (set with fixed atomic coordinates) but an *isometry class* of all periodic point sets isometric to each other.

One periodic structure with atomic coordinates

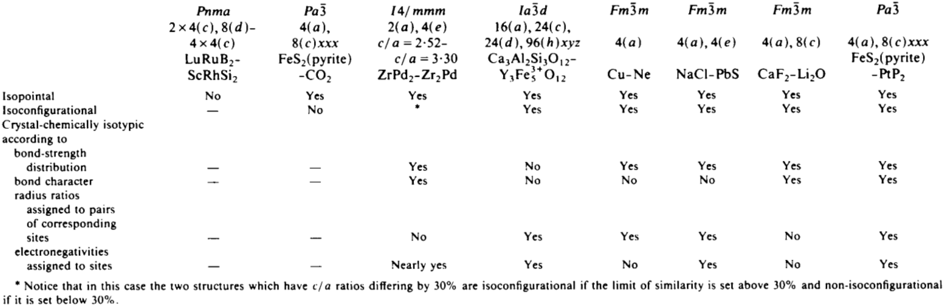
$\neq$**periodic crystal**$=$isometry class of structures

$$= \frac{\text{infinitely many periodic point sets in } \mathbb{R}^3}{\text{equivalence by isometry (or rigid motion)}},$$

quotient by the Euclidean group of isometries.

Other equivalences are coarser

Nomenclature of inorganic structure types, 1990



	Pnma $2\times4(c), 8(d)$- $4\times4(c)$ $LuRuB_2$- $ScRhSi_2$	$Pa\bar{3}$ $4(a)$, $8(c)xxx$ FeS_2(pyrite) -CO_2	$I4/mmm$ $2(a), 4(e)$ $c/a = 2{\cdot}52$- $c/a = 3{\cdot}30$ $ZrPd_2$-Zr_2Pd	$Ia\bar{3}d$ $16(a), 24(c)$, $24(d), 96(h)xyz$ $Ca_3Al_2Si_3O_{12}$- $Y_3Fe_5^{3+}O_{12}$	$Fm\bar{3}m$ $4(a)$ Cu-Ne	$Fm\bar{3}m$ $4(a), 4(e)$ NaCl-PbS	$Fm\bar{3}m$ $4(a), 8(c)$ CaF_2-Li_2O	$Pa\bar{3}$ $4(a), 8(c)xxx$ FeS_2(pyrite) -PtP_2
Isopointal	No	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Isoconfigurational	—	No	*	Yes	Yes	Yes	Yes	Yes
Crystal-chemically isotypic according to								
bond-strength distribution	—	—	Yes	No	Yes	Yes	Yes	Yes
bond character	—	—	Yes	No	No	No	Yes	Yes
radius ratios								
assigned to pairs of corresponding sites	—	—	No	Yes	Yes	Yes	No	Yes
electronegativities assigned to sites	—	—	Nearly yes	Yes	No	Yes	No	Yes

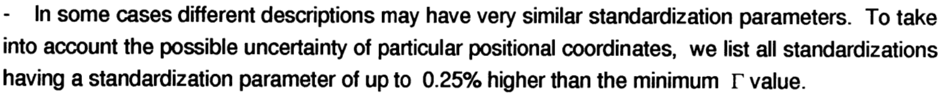
* Notice that in this case the two structures which have c/a ratios differing by 30% are isoconfigurational if the limit of similarity is set above 30% and non-isoconfigurational if it is set below 30%.

From stronger (more classes) to coarser (fewer): isostructural (isotypic) $\Rightarrow$ isoconfigurational $\Rightarrow$ isopointal. Undistinguished $FeS_2 \sim PtP_2$ in the last column: non-isometric, differ by scaling.

Past or current definitions

IUCr online dictionary: “crystals are *isostructural* if they have the *same structure* [?], but not necessarily the same cell dimensions ...”

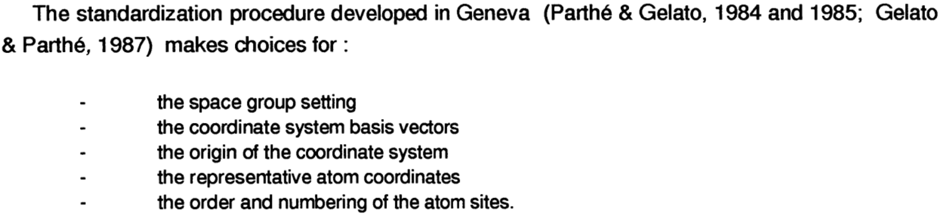
“Structures are *isopointal* if ... the complete sequence of the occupied Wyckoff positions is the same for both structures when the structural data is standardized.” [This standardization algorithm needs manually chosen thresholds].



- In some cases different descriptions may have very similar standardization parameters. To take into account the possible uncertainty of particular positional coordinates, we list all standardizations having a standardization parameter of up to 0.25% higher than the minimum Γ value.

Standardization by Parthé & Gelato

The book “TYPIX Standardized Data and Crystal Chemical Characterization of Inorganic Structure Types Volume 1” describes the STRUCTURE TIDY algorithm, which aims to recognise *isotypic structures*. If isotypic means related by isometry and scaling, it’s great!



The standardization procedure developed in Geneva (Parthé & Gelato, 1984 and 1985; Gelato & Parthé, 1987) makes choices for :

- the space group setting
- the coordinate system basis vectors
- the origin of the coordinate system
- the representative atom coordinates
- the order and numbering of the atom sites.