Symmetry and crystals

Imagine…
- having to describe an infinite crystal with an infinite number of atoms
- or even a finite crystal, with some \(10^{20}\) atoms

Sounds horrible? Well, there’s symmetry to help you out! Instead of an infinite number of atoms, you only need to describe the contents of one unit cell, the structural repeating motif…
- and life could be even easier, if there are symmetry elements present inside the unit cell!
- you only need to describe the asymmetric unit if this is the case

Lattice symmetry

- Lattice symmetry refers to the unit cell size and shape
- Without rules, there would be an infinite number of different unit cells to describe any given lattice

Unit cell choice

- By convention, a unit cell is chosen as
  - the smallest possible repeat unit
  - which has the highest symmetry
- This can result in *primitive* unit cells or *centered* unit cells
  - not all crystal systems can be centered by this definition
  - the seven crystal systems in combination with the centering operations give rise to the 14 Bravais lattices

An example of unit cell choice

- According to our definitions, the centered cell would be preferred

The 14 Bravais lattices

Why can only some lattices be centered?

- A tetragonal base centered cell can always be transformed into a tetragonal primitive cell.
Why can only some lattices be centered? (2)

- An orthorhombic base centered cell cannot be transformed into a primitive cell without losing the orthorhombic symmetry.

Symmetry elements

- When talking about symmetry operations, we must distinguish
  - point symmetry elements
  - translational symmetry

- Point symmetry elements will always leave at least one point unchanged
  - rotation axes
  - mirror planes
  - rotation-inversion axes
**Rotation axes**

- Example: A two-fold rotation axis
  - no change in handedness
  - referred to as “proper symmetry operation”
- An $n$-fold rotation axis will rotate the object by $360/n^\circ$
- Symbol: $n$ (e.g., 2, 3, 4, 6)

**Mirror planes**

- A mirror plane changes the handedness of the object it is operating on
  - cannot exist in crystals of an enantiomerically pure substance
  - referred to as “improper symmetry operation”
- Symbol: $m$
Inversion centers

- "Turning an object inside out"
- Equivalent to a "point reflection" through the inversion center
  - similar to focal point of a lens
  - changes handedness
- Symbol: \( i \)


Rotation-inversion centers

- Rotation followed by inversion
- An inversion center can be regarded as a "one-fold rotation" followed by an inversion
- Symbol: \(-n\) or \(\overline{n}\)

Watch out…

- Crystallographers work with rotation-inversion axes
- If you take a class in Group Theory or another subject involving symmetry operations, your teacher may not consider rotation-inversion axes a symmetry operation
  - they use rotation-reflection axes (symbol: $S_n$)
  - rotation-inversion and rotation-reflection axes are NOT the same!
    - an inversion center corresponds to a “$-1$ axis”, but to an $S_2$ axis!
    - however, any compound that has a $-4$ axis will also possess an $S_4$ axis

S$_4$ versus -4
Using graphical symbols