Bravais Lattice + Basis = Crystal Structure

• A crystal structure is obtained when identical copies of a basis are located at all of the points of a Bravais lattice.

• Consider the structure of Cr, a \( I \)-cubic lattice with a basis of two Cr atoms: \((0,0,0)\) and \((\frac{1}{2},\frac{1}{2},\frac{1}{2})\). It's a BCC crystal structure (\(A2\)).

• Consider the CsCl structure (\(B2\)), a \(P\)-cubic lattice with a diatomic basis containing one Cs \((\frac{1}{2},\frac{1}{2},\frac{1}{2})\) and one Cl \((0,0,0)\) ion.
  • When the basis is placed at all the vertices of \(P\)-cubic lattice, the CsCl crystal structure is formed.
  • Not BCC, since BCC structures have the same element in the corners of the unit cell as well as the center of the body. Cesium chloride has different elements at the corners of the unit cell than the one in the center of the body. In other words, you can not use the \(I\) vector to transform Cs into Cl, and vice versa.

For these two structures although they have similar geometric arrangements, neither the lattice, the basis nor the crystal structure are the same!

• Remember that the basis of a structure always has a chemical composition that is either the same as the formula unit (f.u.), or an integer multiple of the f.u.
  • Calculate \# of f.u./unit cell (u.c): Cr has 2 f.u./u.c. and CsCl has 1 f.u./u.c.
Diamond cubic and rocksalt structures both have a \textit{F-cubic lattice}, but neither have the FCC crystal structure:

- **Diamond cubic structure (A4)** has a \textit{F-cubic lattice} with two atoms (shown by white spheres) in the basis related by a displacement of \((\frac{1}{4}, \frac{1}{4}, \frac{1}{4})\).

- **The rocksalt (NaCl) structure (B1)** has a \textit{F-cubic lattice} and a two ions (shown by white spheres) NaCl basis with the ions related by a \((0,\frac{1}{2}, 0)\) displacement.

- **The HCP structure (A3)** has a \textit{P-hexagonal lattice} with two atoms (shown by white spheres) in the basis related by \((\frac{1}{3}, \frac{2}{3}, \frac{1}{2})\).
Basis Positions of Rocksalt and Fluorite Structures

• Determine the basis positions of previously discussed rocksalt structure.

• First we must know the number of lattice points within a unit cell:

\[
N = N_i + \frac{N_f}{2} + \frac{N_e}{4} + \frac{N_c}{8}
\]

• The number of lattice points tells you the number of atoms that are required to define your basis.

• If \( N = 4 \), then four basis positions (vectors) must be defined.

• Then all you need to know is what types of atoms, ions or molecules lie on each point.

• For MgO (rocksalt structure), \( N = 4 \) for Mg\(^{2+}\) and \( N = 4 \) for O\(^{2-}\).

• What is Bravais lattice and basis positions (vectors)?

• For c-ZrO\(_2\) (fluorite structure, \( CI \)), \( N = 4 \) for Zr\(^{4+}\) and \( N = 8 \) for O\(^{2-}\).

• What is Bravais lattice and basis positions (vectors)?

• You can use Crystal Maker Software for 3-D visualization.
Determine the basis positions of previously discussed sphalerite/zincblende ($B3$) structure:

- For ZnS, $N=4$ for Zn$^{2+}$ and $N=4$ for S$^{2-}$

What is Bravais lattice and basis positions (vectors)?

Determine the basis positions of chalcopyrite (CuFeS$_2$) structure ($E1_1$). (chief ore of copper)

- For CuFeS$_2$, $N=4$ for Cu$^{2+}$, $N=4$ for Fe$^{2+}$ & $N=8$ for S$^{2-}$

Each Cu and Fe atom is tetrahedrally coordinated by 4 S atoms & each S atom is tetrahedrally coordinated by 2 Cu & 2 Fe atoms.

*If distinction between Cu and Fe atom is ignored, the structure is seen to be identical to that of zincblende (unit cell consisting of two zincblende unit cells superimposed).*

*When this distinction is taken into account, the atoms at the corners of the sub-cell are no longer identical, and the larger cell becomes the true repeat (unit) cell.*

What is Bravais lattice if $a=b=5.24\text{Å}$, $c=10.3\text{Å}$ & $\alpha,\beta,\gamma=90^\circ$? What are the basis positions (vectors)?
Alternate Views of Chalcopyrite Structure

2-D Projections (down x or y-axis):

3-D Projection

(down z-axis):

$N=4$ for Cu$^{2+}$

$N=4$ for Fe$^{2+}$

$N=8$ for S$^{2-}$
• Determine the basis positions of previously discussed wurtzite structure \((B4)\).
• For \(\text{ZnO}\), \(N=2\) for \(\text{Zn}^{2+}\) and \(N=2\) for \(\text{O}^{2-}\).
• \(\text{P-hexagonal Bravais lattice (a=3.81Å and c=6.23Å)}\); what are the basis positions (vectors)?

**Extended Unit cell:**

**Unit cell:**

\(\text{puckered rings}\)
Another View of Wurtzite Structure

Stacking sequence = AaBbAaBb…….
Ordered structures based on sphalerite (zincblende):

Ordered structures based on wurtzite:

Spalerite, B3 ZnS
layered tetragonal, L10 InGaAs₂
Luzonite, H24 Cu₃AsS₄
Chalcopyrite, E11 CuFeS₂
Fematinite, H2ₐ Cu₃SbS₄
layered tetragonal, L1₁ (CrCuS₂) NaVS₂

ZnO
β-LiGaO₂
β-Li₂BeSiO₄
β-II -Li₃PO₄
β-II - Li₃ZnSiO₄
END HERE FOR MIDETERM!