Structure, Morphology Projection

Read

Ott Chapter 4, 5 (5.5, 5.7, 5.8 제외)

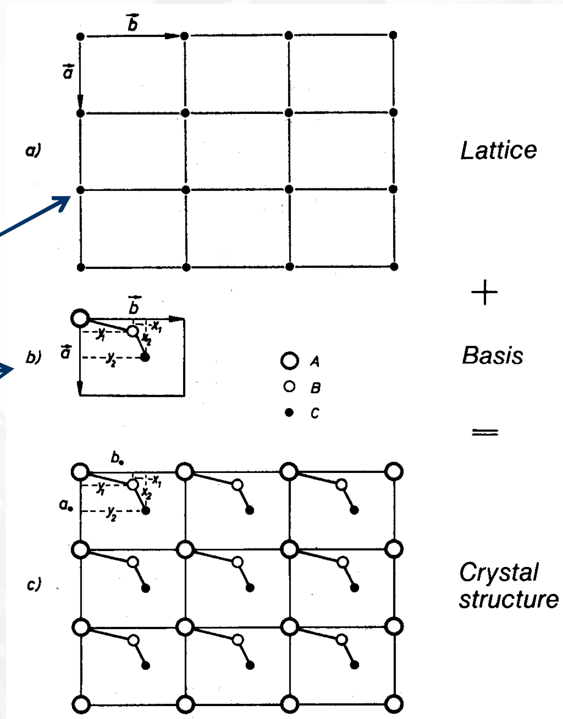
Hammond Chapter 5.1 ~ 5.6; 12.1 ~ 12.3

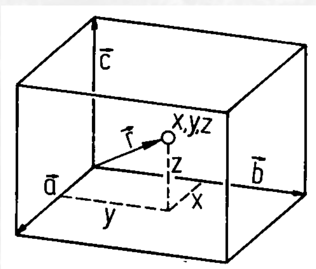
Krawitz chapter 2.5, 2.6, 2.7 (page 48-62)

Cullity 2-13 (page 70-86)

Lattice + Basis = Crystal structure

- Lattice → Crystal
  - ✓ lattice points occupied by atoms, ions, or molecules
  - ✓ lattice points - all identical, collection of objects - must be identical
- Lattice - rectangular unit cell projected on a-b plane
- Basis (motif) (arrangement of atoms in the unit cell) - molecule ABC
  - ✓ A: 0,0,0 B: $x_1, y_1\ z_1$ C:x_2, y_2, z_2





$$\vec{r} = x\vec{a} + y\vec{b} + z\vec{c}$$

$$0 \le x, y, z \le 1$$

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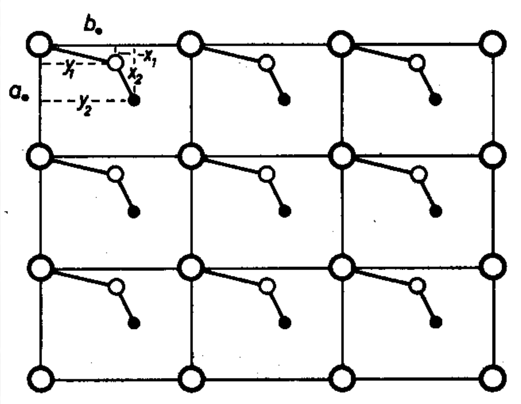
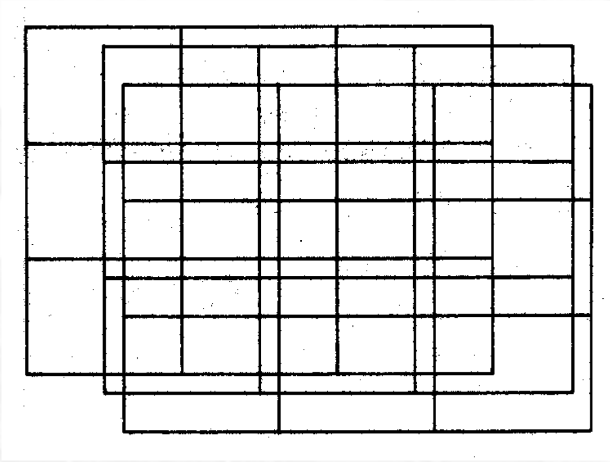
Crystal structure

- Crystals - solid chemical substance with a three- dimensional periodic array of atoms, ions, or molecules.

crystal structure





- Lattice is a pure mathematical concept.

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Lattice types - P, I, F, C, R

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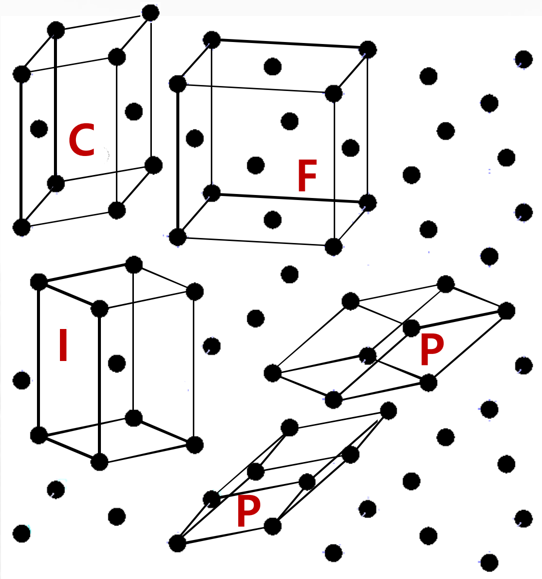


the number of lattice points in a unit cell (N)?

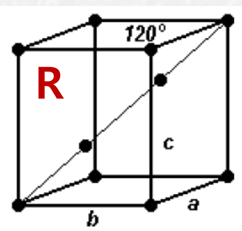
$$N = N_i + N_j/2 + N_c/8 + N_e/4$$

N_i = # of lattice points in cell interior (belong to 1 cell)

N_j = # of lattice points on cell faces (shared by 2 cells)

N_c = # of lattice points on cell corners (vertices) (shared by 8 cells)

N_e = # of lattice points on cell edges (shared by 4 cells)

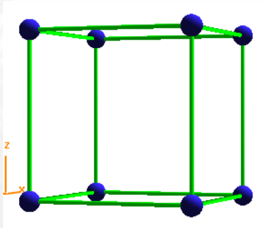


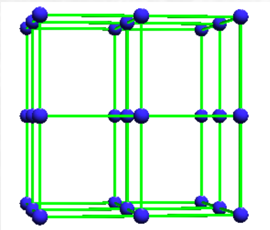
- Primitive lattice; one lattice point per unit cell
- Non-primitive lattice; more than one lattice point per unit cell

$a = b = c$

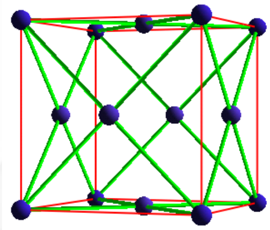
$\alpha = \beta = \gamma = 90^o$

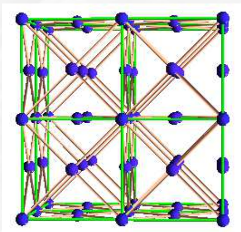
P simple cubic



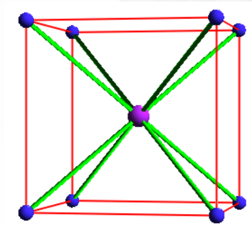


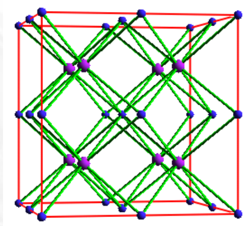
F face centered cubic



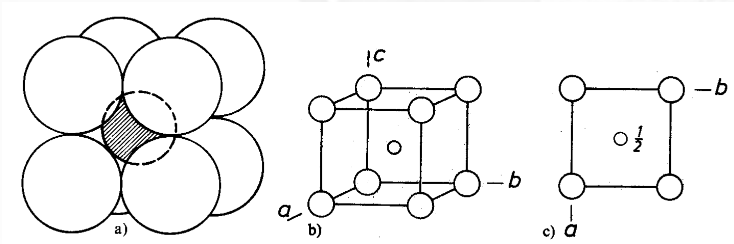


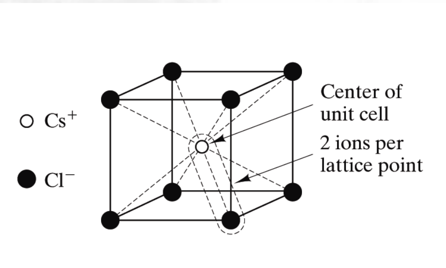
I body centered cubic

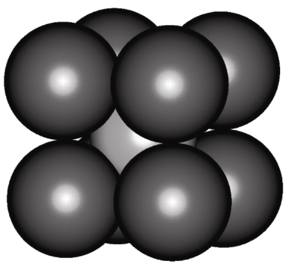




- cesium iodide (CsI)
  - ✓ $a_o = b_o = c_o = 4.57Å$,
  - ✓ $\alpha = \beta = \gamma = 90^o$
  - ✓ basis I^-: 0,0,0 Cs^+:½,½,½







Structure: CsCl type

Bravais lattice: simple cubic

Ions/unit cell: $1Cs^+ + 1Cl^-$

Z (number of formula units per unit cell) = 1

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Z; number of formula units per unit cell

- Once Z is known, density (ρ) can be calculated using structural data. (**Z** → ρ)

- ρ = m/V (g/cm^3)   m = (Z M)/N_A

  → ρ = (Z M)/(N_AV) (g/cm^3)
  - ✓ m = mass of the atoms in the unit cell
  - ✓ V = volume of the unit cell
  - ✓ M = molar mass
  - ✓ N_A = Avogadro number
  - ✓ M/N_A = the mass of one chemical formula

Thus, taking N_A as 6.023×10^{23} mol^{-1}, for CsI, where M = 259.81 g mol^{-1}

$$\varrho_{\mathrm{CsI}} = \frac{1 \cdot 259.81}{6.023 \cdot 10^{23} \cdot 4.57^3 \cdot 10^{-24}} = 4.52\ \mathrm{g\,cm^{-3}}.$$

- Z can be estimated from the measured density. (ρ → **Z**)

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Examples of crystal


Rutile (TiO$_2$)


Anatase (TiO$_2$)


Brookite (TiO$_2$)


Calcite (CaCO$_3$)


Quartz (SiO$_2$)


Corundum (Al$_2$O$_3$)


Ruby (Al$_2$O$_3$ - Cr 불순물)


Sapphire (Al$_2$O$_3$)


Magnetite (Fe$_3$O$_4$)

Morphology

- Morphology - the set of faces and edges which enclose a crystal
- Relationship between crystal structure (internal structure) and morphology (external surface)
  - ✓ Every crystal <u>face</u> lies // to a set of <u>lattice planes</u>; parallel crystal faces correspond to the same set of planes.
  - ✓ Every crystal <u>edge</u> is // to a set of <u>lattice lines</u>
- (hkl) – crystal face
- [uvw] – crystal edge

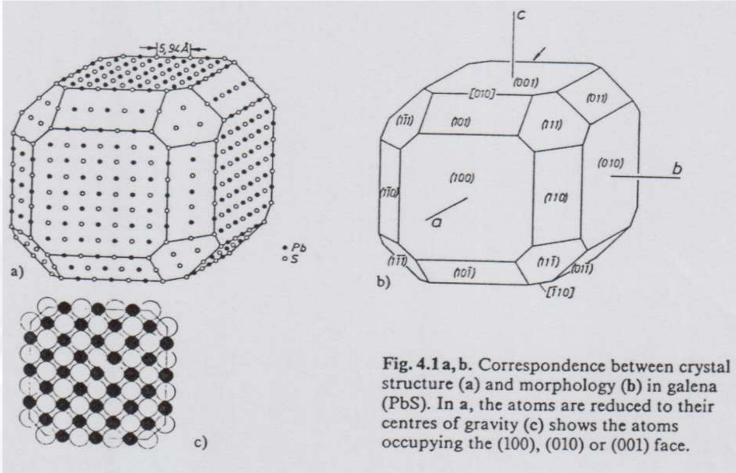

Fig. 4.1 a, b. Correspondence between crystal structure (a) and morphology (b) in galena (PbS). In a, the atoms are reduced to their centres of gravity (c) shows the atoms occupying the (100), (010) or (001) face.

PbS (galena)

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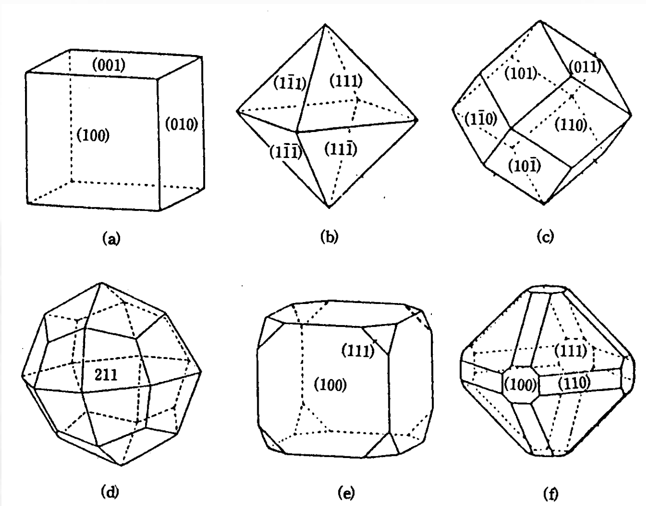
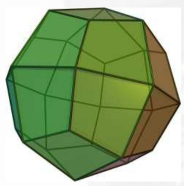
Morphology - form

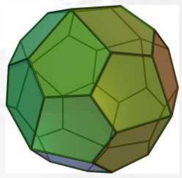
- Form (결정형): a set of "equal" faces; 한 결정에서 외형을 이루는 equivalent faces들의 집단, {hkl}로 나타냄.



결정형과 취형
(a) {100}, 정육면체 (b) {111}, 정팔면체
(c) {101}, 능면 십이면체 (d) {211}, 이십사면체
(e) {100}·{111}, 정육면체와 정팔면체의 취형
(f) {100}·{111}·{110}, 정육면체, 정팔면체, 정십이면체의 취형



Deltoidal (or trapezoidal) icositetrahedron

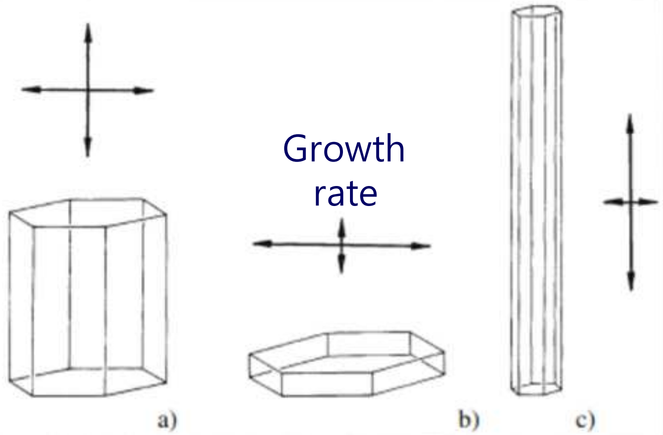


Pentagonal icositetrahedron

Morphology - habit

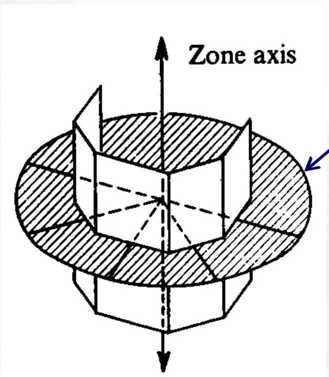
- Habit (정벽):
  - ✓ the characteristic external shape of an individual crystal or crystal group. A single crystal's habit is a description of its general shape and its crystallographic forms, plus how well developed each form is.
  - ✓ 결정 성장 속도의 차이로 인하여,다른 결정 외면의 상대적인 발달에 따라 어떤 특정한 결정형이 두드러지게 잘 나타나는 성질
  - ✓ three basic types of habit - equant, planar (tabular), prismatic (acicular)

Fig. 5.2a–c The three basic habits: (**a**) equant, (**b**) planar or tabular, (**c**) prismatic or acicular with the relative rates of growth in different directions shown by *arrows*



Morphology - zone

- **Zone**: a set of non-// planes which are all // to one axis (called zone axis)
- Tautozonal: faces belonging to the same zone
- **Zone axis**: a direction // to the lines of intersection
- normals to all the faces in a zone are coplanar → zone axis is normal to this plane.



Plane of the normals to the faces

(h_1,k_1,l_1), (h_2,k_2,l_2), (h_3,k_3,l_3) are tautozonal if and only if

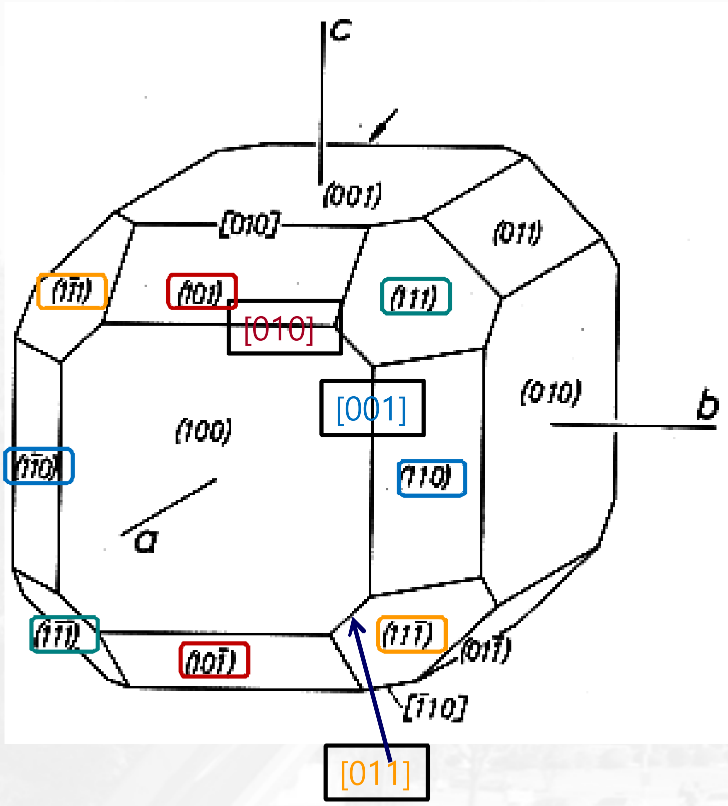
$$\begin{vmatrix} h_1 & k_1 & l_1 \\ h_2 & k_2 & l_2 \\ h_3 & k_3 & l_3 \end{vmatrix} = 0$$

$$\boxed{h_1k_2l_3 + k_1l_2h_3 + l_1h_2k_3 - h_3k_2l_1 - k_3l_2h_1 - l_3h_2k_1 = 0}$$

Does (hkl) belong to the zone [uvw]?

Check the zonal equation hu + kv + lw = 0

Zone, zone axis



(100) Belongs to the zones

[(101)/(10$\bar{1}$)] = [010]

[(110)/(1$\bar{1}$0)] = [001]

[(111)/(1$\bar{1}\bar{1}$)] = [01$\bar{1}$]

[(1$\bar{1}$1)/(11$\bar{1}$)] = [011]

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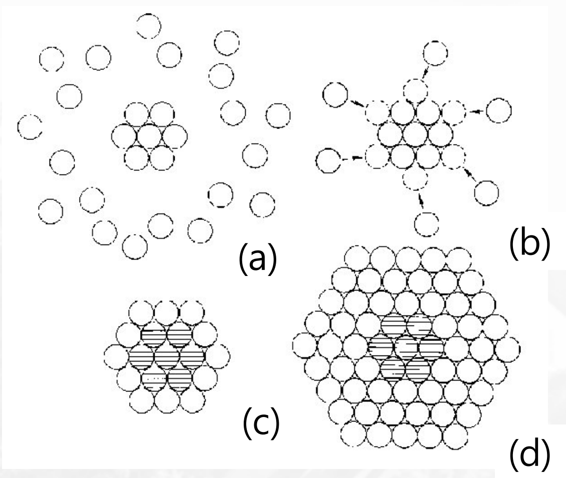
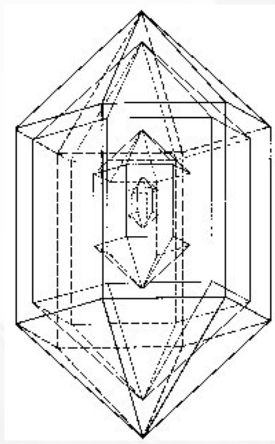
External morphology

Morphology ← formation & growth of crystals



Nucleation & Growth



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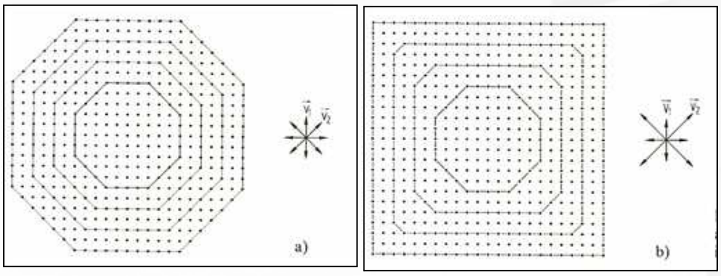
Crystal growth

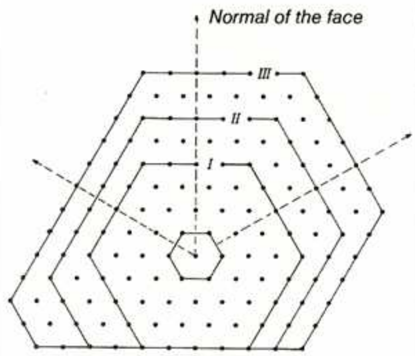
Growth rate similar
→
isotropic growth



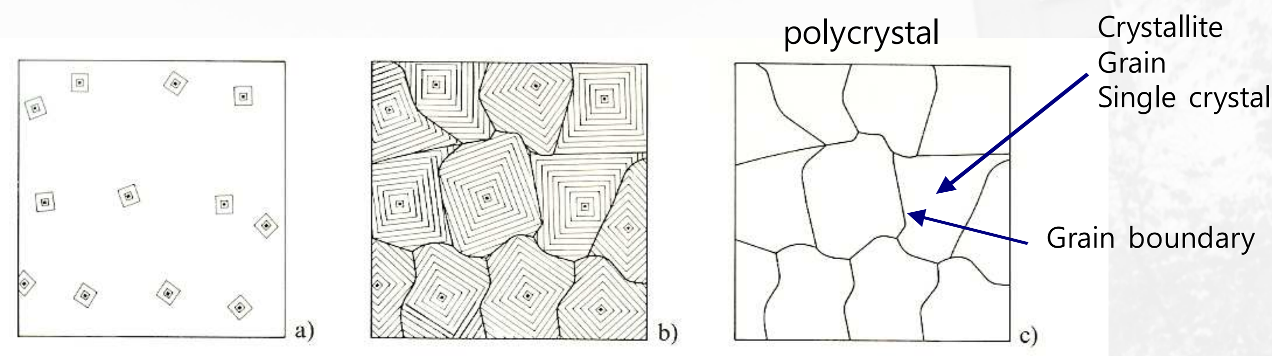
Growth rate very different
→
anisotropic growth

- Slower growing faces become more prominent than those growing more rapidly
- Faces which eventually develop generally have low Miller indices and are often densely populated with atoms

- Law of constancy of the angle
Interfacial angles remain constant



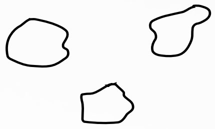
Single crystal vs Polycrystal



Development of a crystal aggregate. **a** Formation of several nuclei, which initially can grow independently. **b** Collision of growing crystallites leads to interference and irregularity in growth of the polyhedra. Eventually, the polyhedral shape of the crystallites is entirely lost. **c** The single crystal domains of the aggregate with their grain boundaries

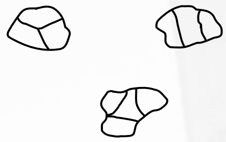
Particle Size vs. Crystallite Size

Particles can be individual crystallites.



Particle size = crystallite size

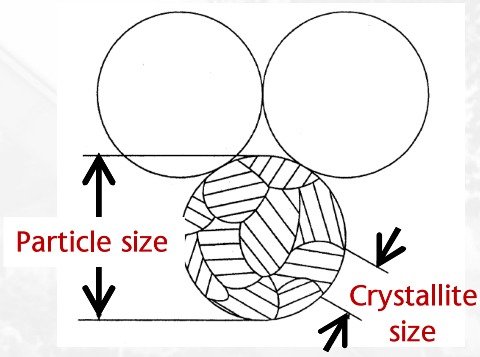
Particles may be imperfect single crystals.



Particle size > crystallite size

- Individual crystallites are perfect.
- Boundaries
  - Dislocations
  - Twin walls
  - Anti-phase walls
  - Stacking faults

From presentation of Dr. Mark Rodriguez
@ DXC 2017 "What usually causes trouble?"



Waseda et al. page 123

Stereographic Projection

1, Krawitz, Page 48 ~ 62 (must read)

2, Hammond, Chapter 12.1 ~ 12.3; 12.5.1

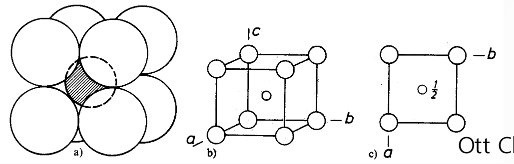
3, Ott, 5.4, 5.5, 5.6

4, Cullity 3rd edition, Page 70 ~ 86

Projections

3 dimensional objects → flat surfaces

- ➢ Parallel projection



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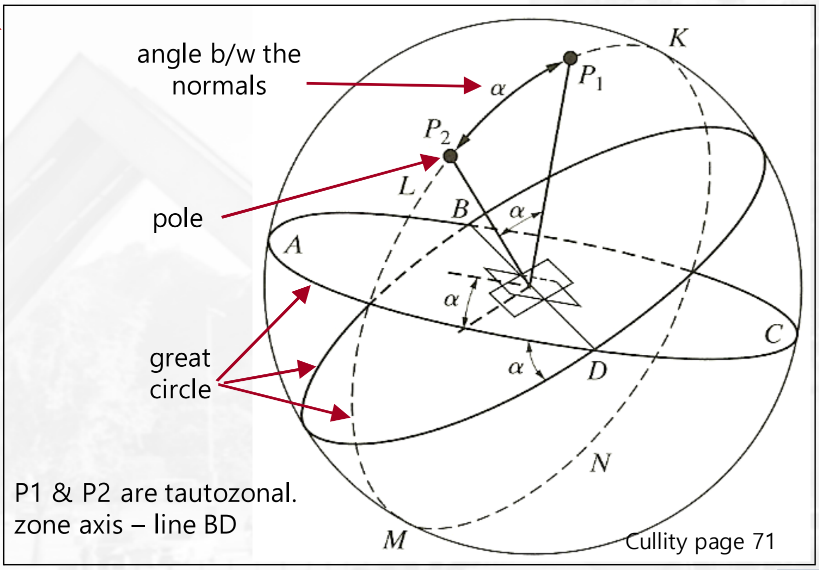
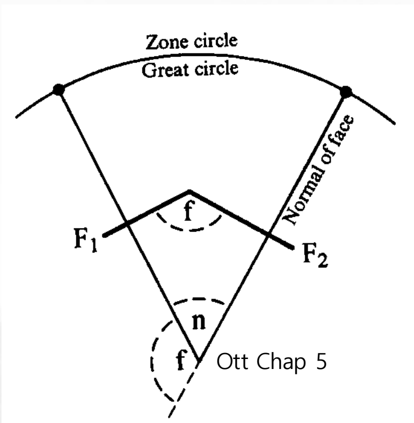
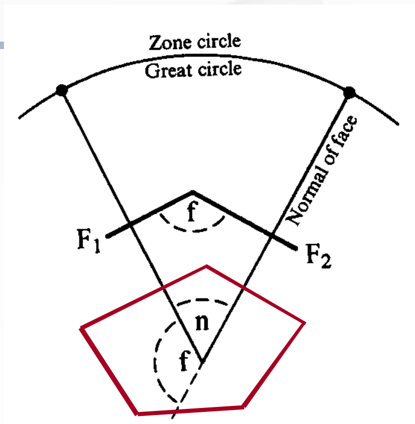
- ➢ Stereographic projection - angular relationship between lattice planes and directions
- ➢ Gnomonic projection
- ➢ Orthographic projection



Stereographic projections

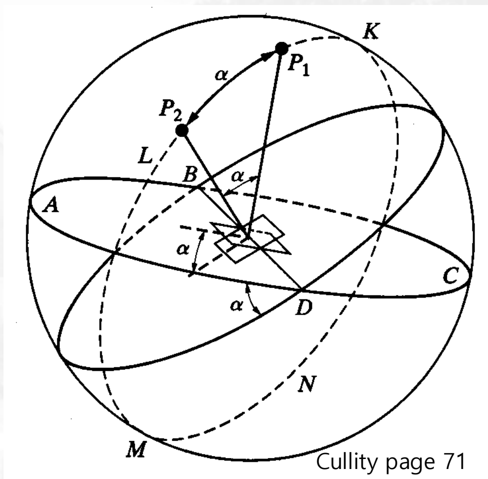




f = dihedral angle, angle b/w the faces

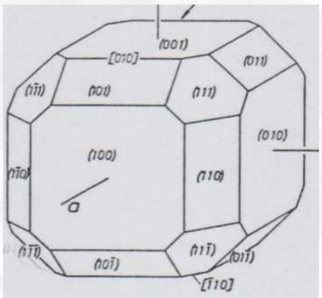
n = angle b/w poles = angle b/w normals

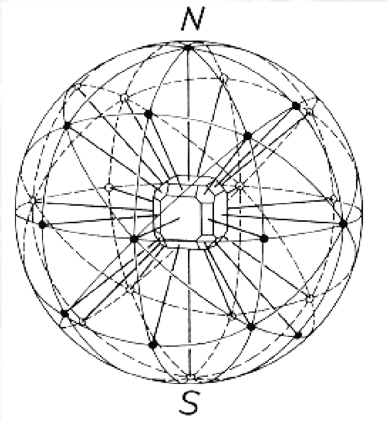
n = 180 - dihedral angle f



Stereographic projection

- place a crystal at the center of the sphere
- draw normal to each face from the center of the sphere
- cut the surface of the sphere in the indicated points → poles of the faces
- great circles- circles whose radius is that of the sphere
  - ✓ those faces whose poles lie on a single great circle → a single zone
  - ✓ zone axis ⊥ plane of the great circle
- Project a line from each poles in the northern hemisphere to the south pole (the opposite is possible)
- <u>Mark the intersection on the equator plane</u>





Stereographic projection

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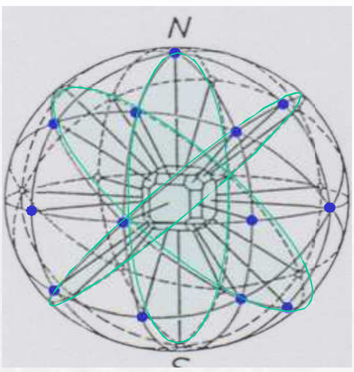
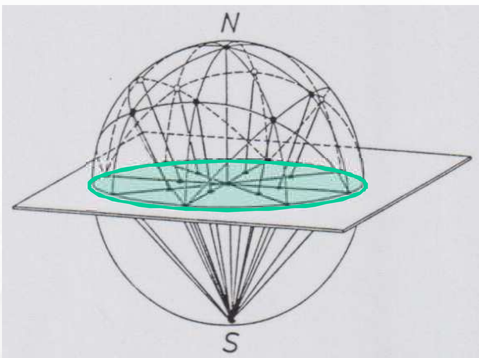
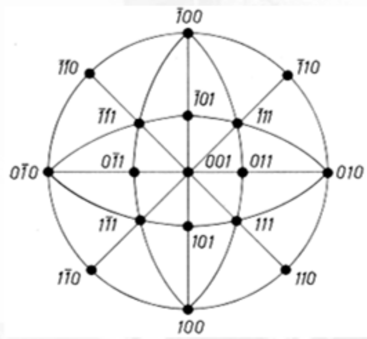
- project a line from each of the poles in the northern sphere to the south pole
- mark its intersection with the plane of the equator with a point •
- Poles in the southern hemisphere – projected to the north pole → ○

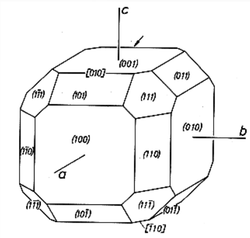


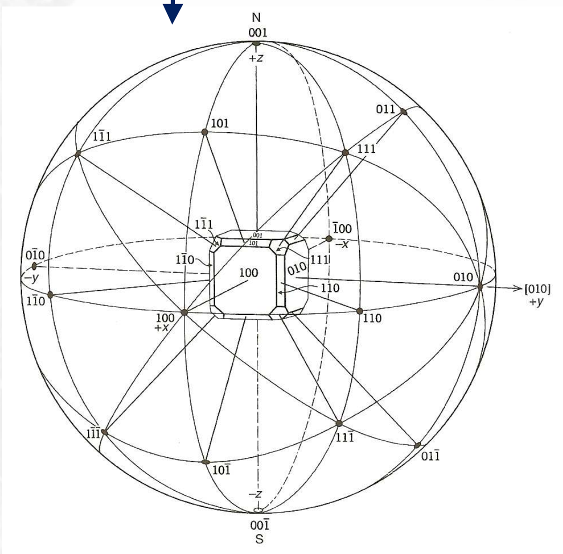


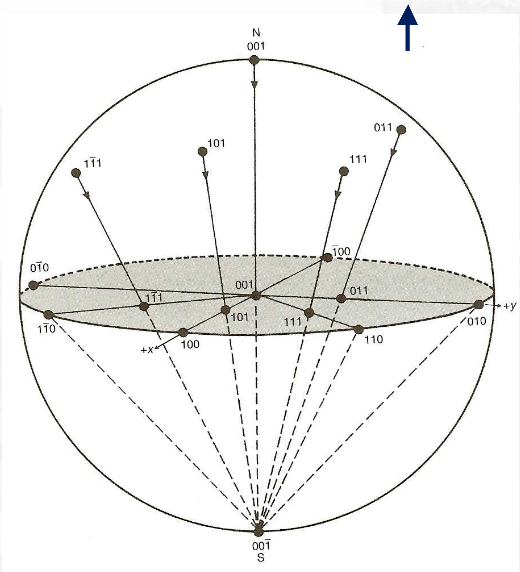


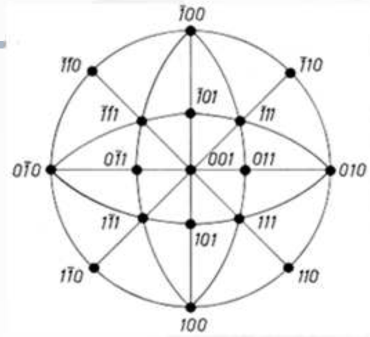
- those faces whose poles lie on a single great circle → a single zone
- zone axis ⊥ plane of the great circle

Stereographic projection









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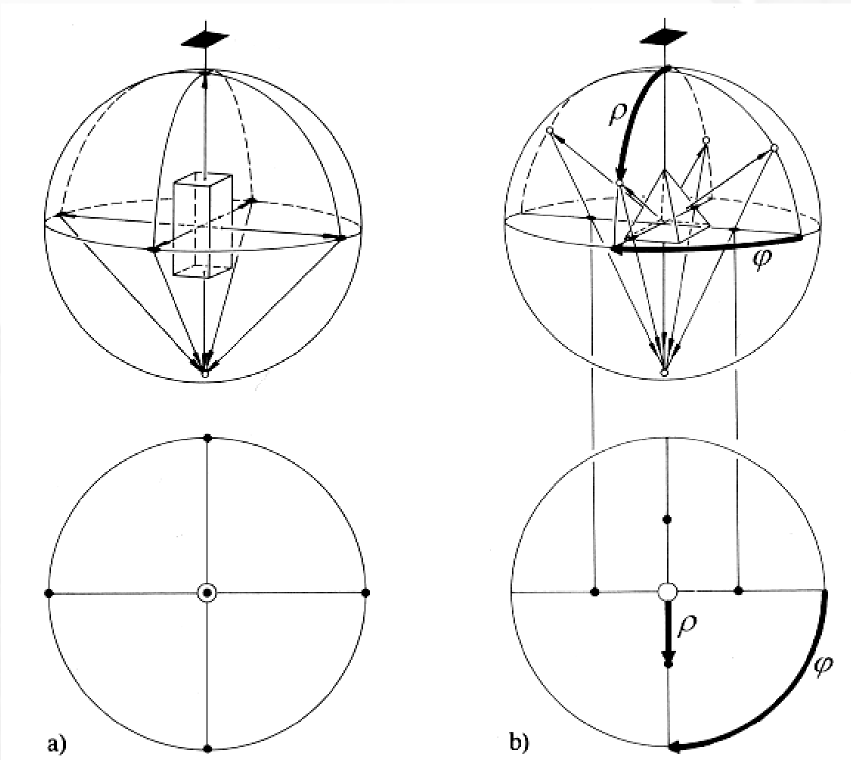
Stereographic projection



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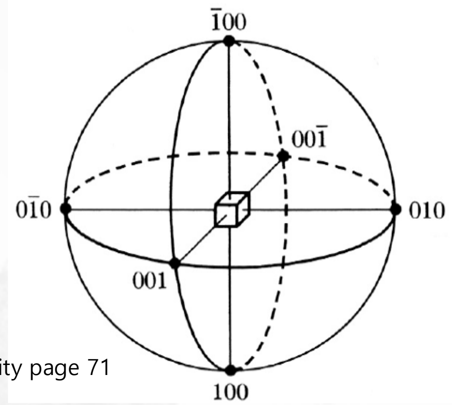
Stereographic projection



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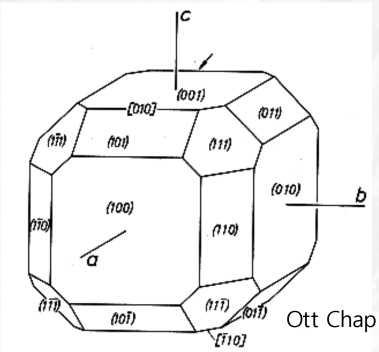
{100} poles of a cubic crystal

- Uses the inclination of the normal to the crystallographic plane
- Points are the intersection of each crystal direction with a (unit radius) sphere



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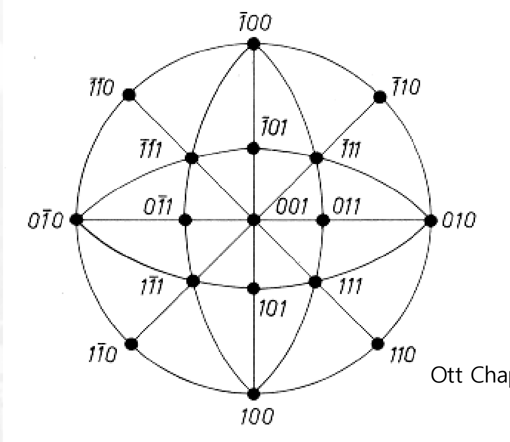

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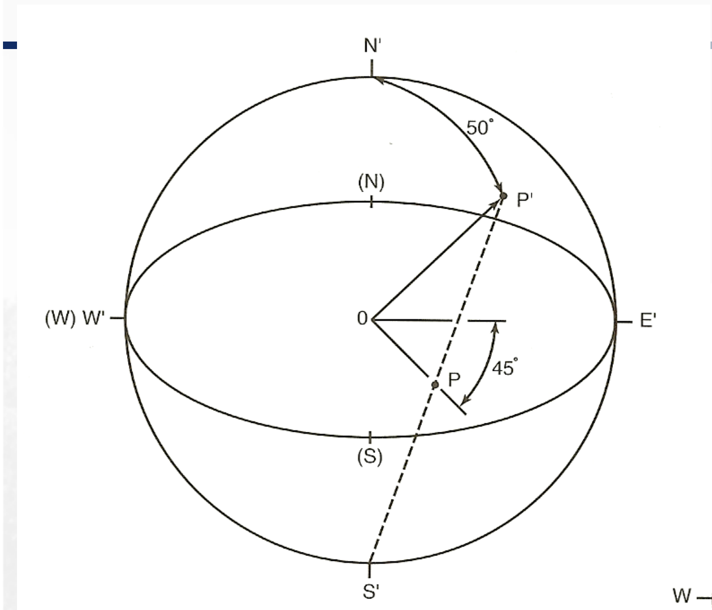
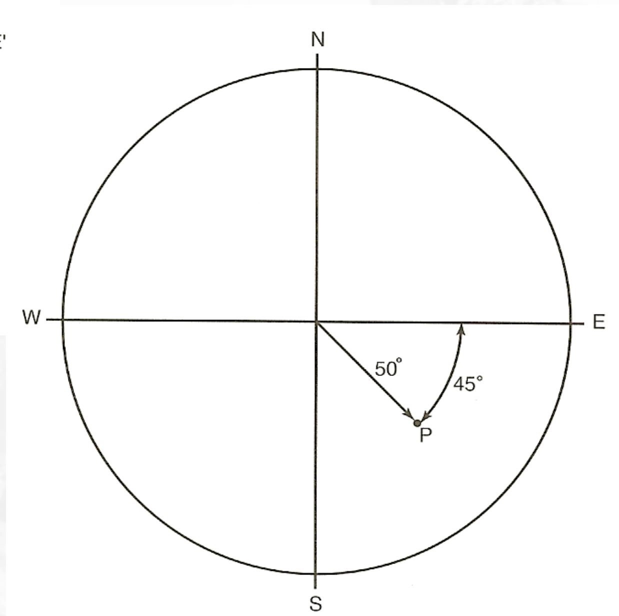
Stereographic projection





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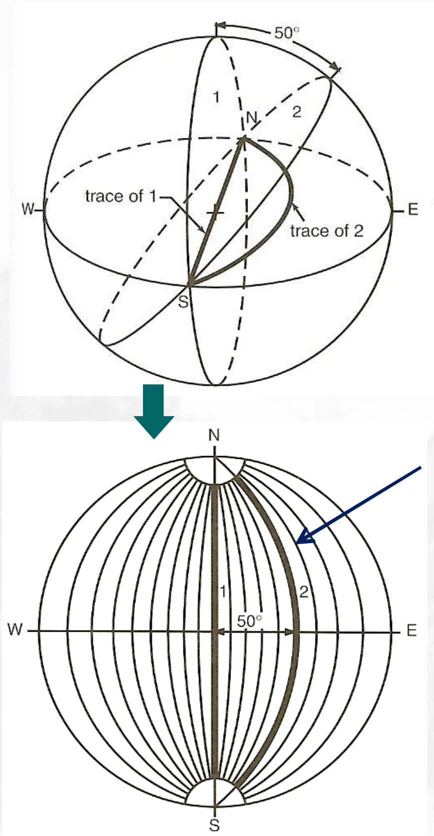
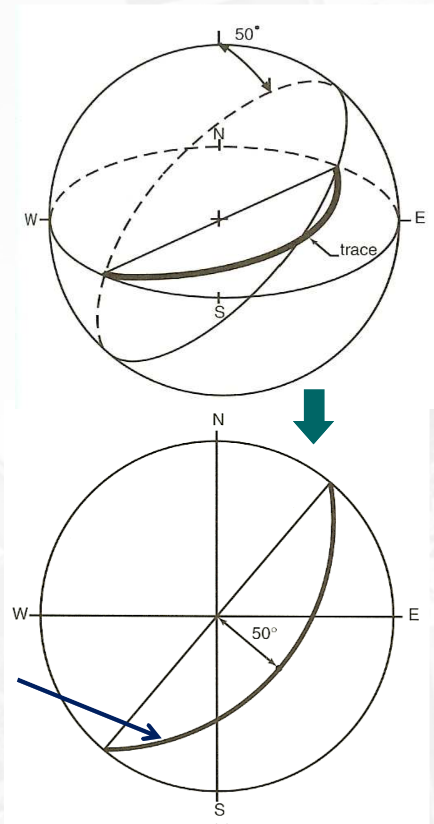
Stereographic projection – great circle



Great circles
Longitude lines



Great circles

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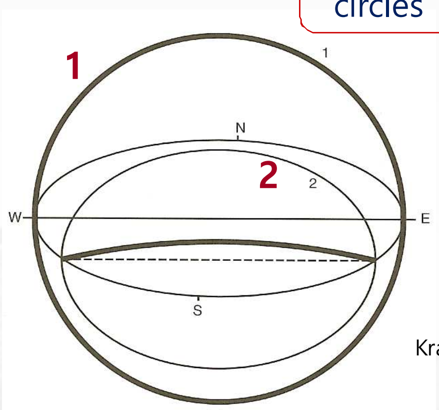
Stereographic projection – small circle

great circles + small circles → Wulff net



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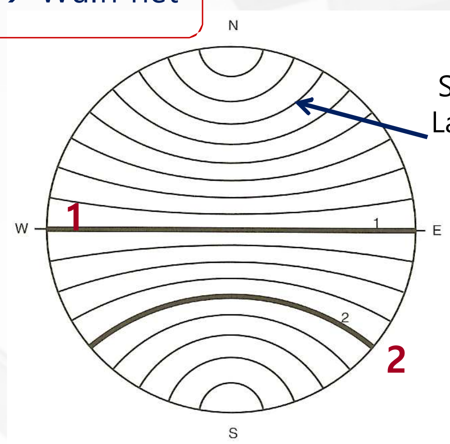
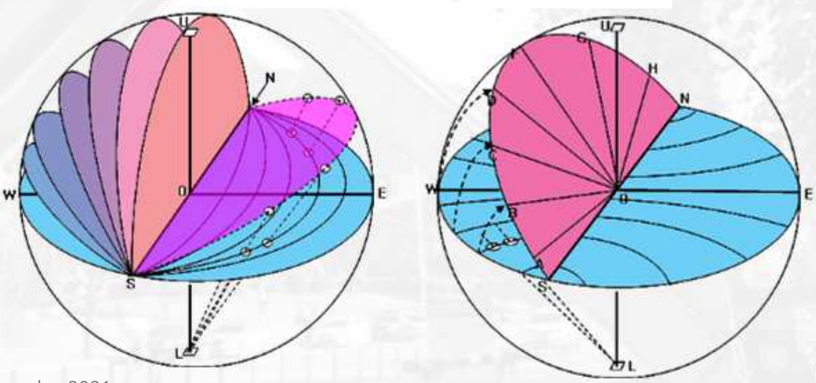


Small circles
Latitude lines

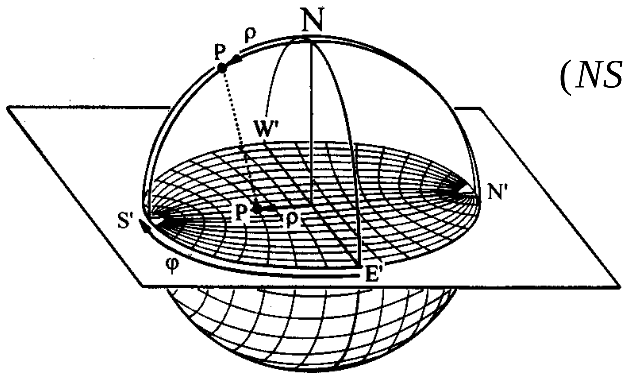
Great Circles &
Small Circles



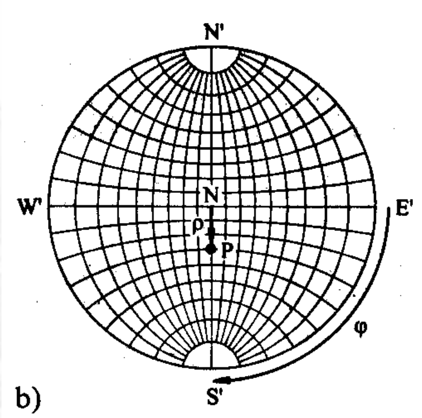
Wulff net

- a device to enable the measured crystal angles to be plotted readily as a stereographic projection.
- stereographic projection of the grid of a conventional globe oriented so that the N'-S' direction lies in the plane of projection
- equator, all meridians → great circle
- parallels except equator → small circle
- <u>azimuthal angle</u> φ (0 ~ 360°) and <u>pole distance</u> ρ
  - ✓ ρ – 0 ~ 90° for faces in northern hemisphere, –90° ~ 0 for faces in southern hemisphere

cf. 38th parallel

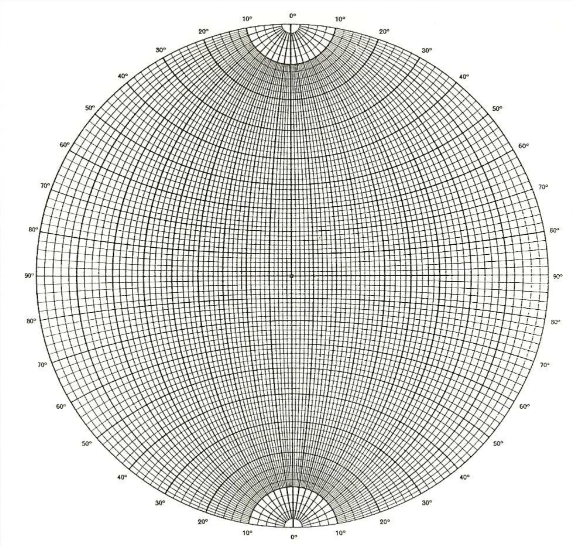


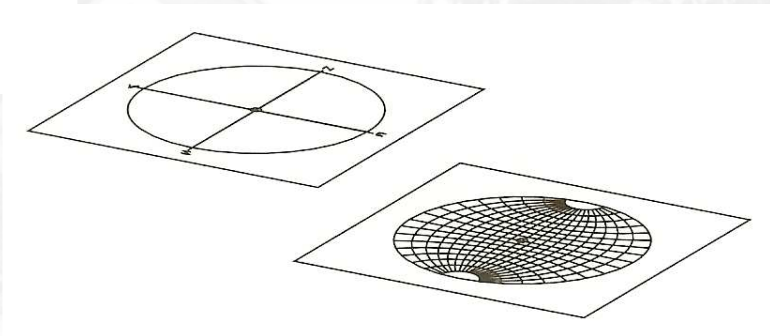
$(NS \perp N'S')$



Ott Chap 5

Wulff net





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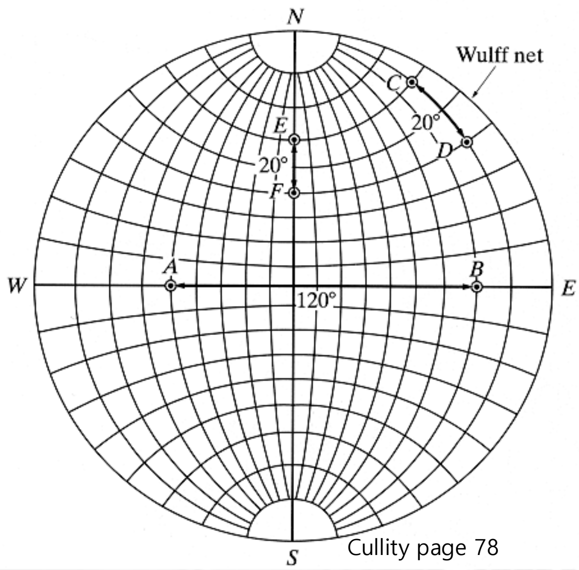
Stereographic projections

- "Only arcs of great circles are used when angles are plotted on or estimated from a stereographic projections"
- stereographic projection superimposed on Wulff net for measurement of angle between poles
- direct measurement along great circle



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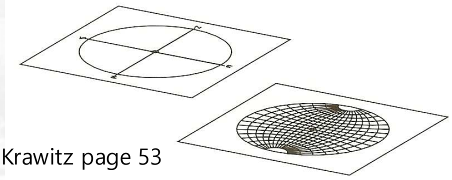
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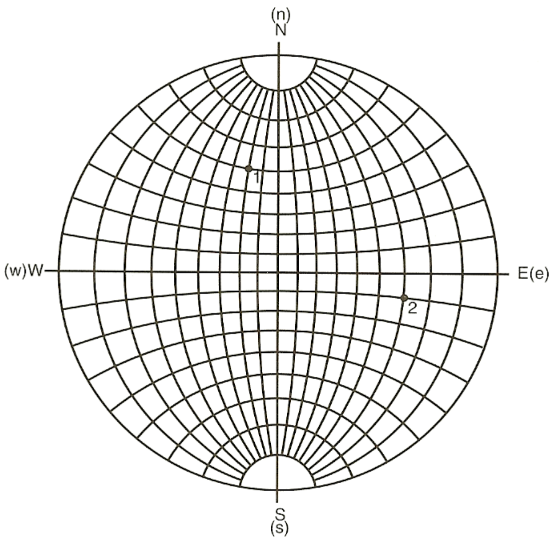
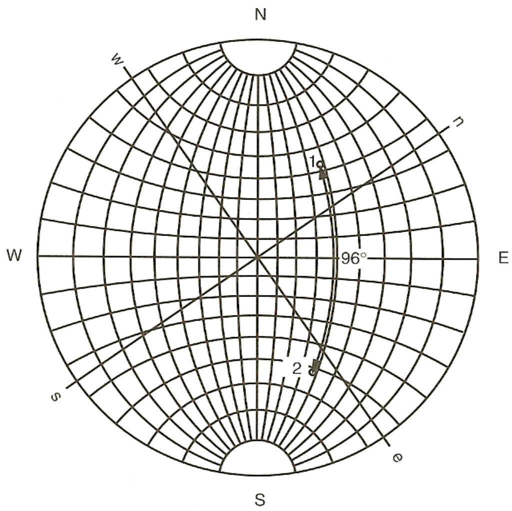
Determination of angle b/w two poles
- Rotate until two poles lie on the same great circle





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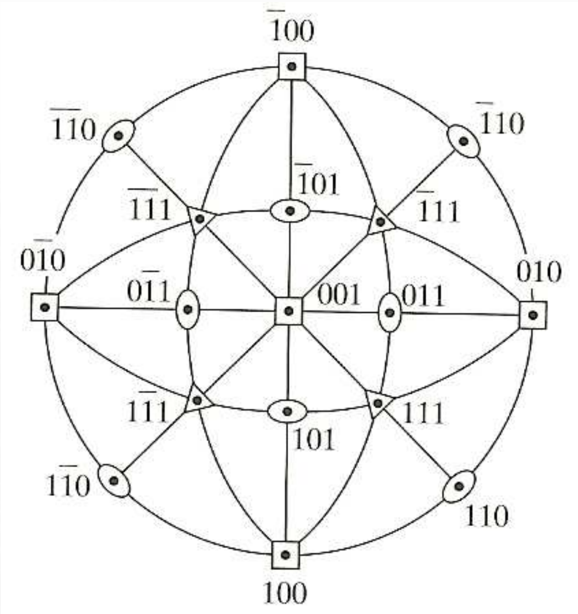
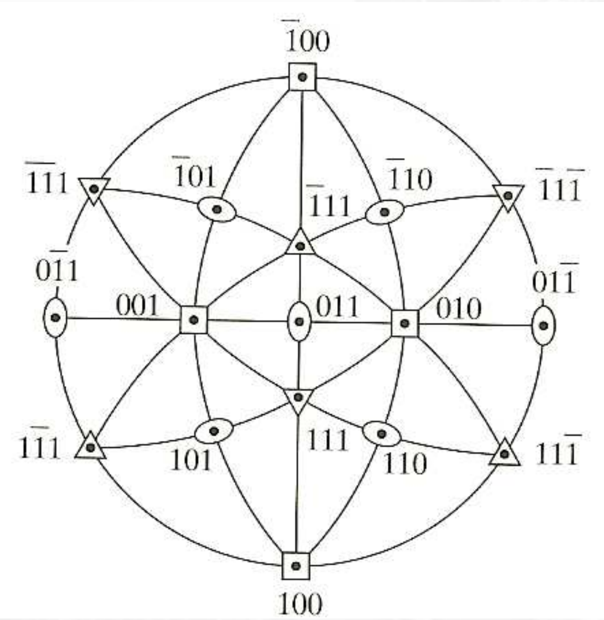
Standard projections of cubic crystals



on (001)



on (011)

Cullity page 83

todos

- Read
  - ✓ Ott Chapter 4, 5 (5.5, 5.7, 5.8 제외)
  - ✓ Hammond Chapter 5.1 ~ 5.6; 12.1 ~ 12.3; 12.5.1
  - ✓ Krawitz chapter 2.5, 2.6, 2.7 (page 48-62)
  - ✓ Cullity 2-13 (page 70-86)

Stereographic Projection

- ✓ Krawitz, Page 48 ~ 62
- ✓ Hammond, Chapter 12.1 ~ 12.3
- ✓ Ott, 5.4, 5.5, 5.6
- ✓ Cullity 3rd edition, Page 70~86

- Structure Morphology Projection HW (due in 1 week)
  - ✓ Ott chapter 4 --- 1, 2, 3, 4, 5, 6, 7
  - ✓ Ott chapter 5 --- 1, 2, 3, 4, 5, 6, 10, 11, 12
  - ✓ Krawitz --- P2.3; P2.4; P2.5; P2.12