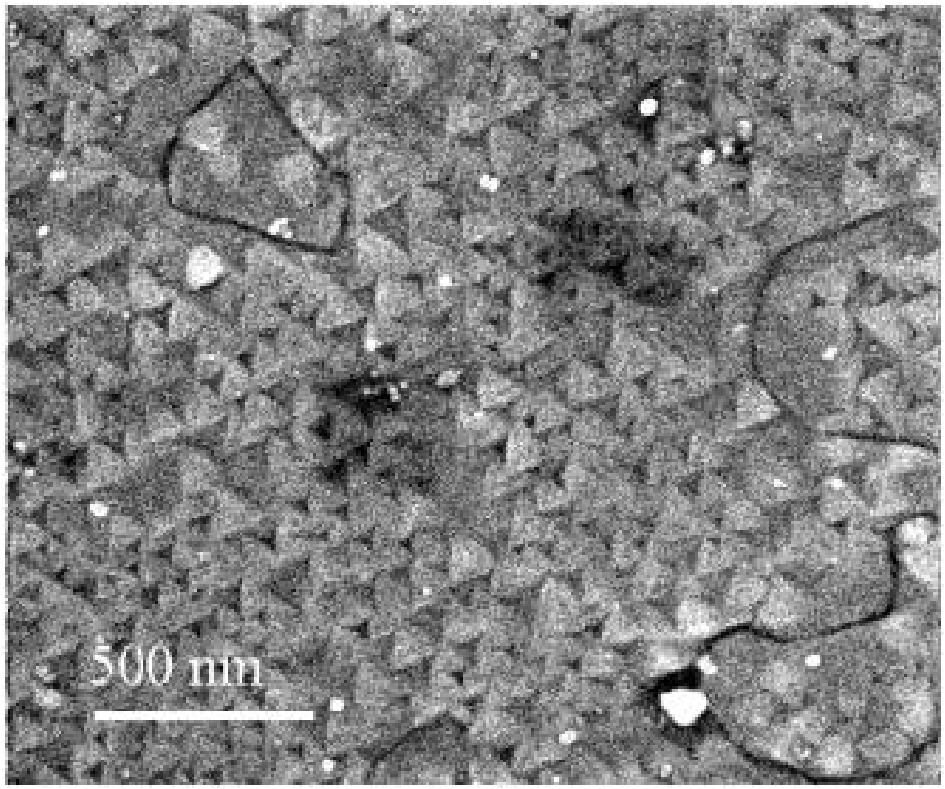
Crystallography

Reading: Warren, Chapters 2.1, 2.2, 2.6, 8

Surface symmetry: Can be a clue to underlying structure. Examples:

Snow (SnowCrystals.com)
Hexagonal, Optical micrograph

Bismuth (Bao, Kavanagh, APL **98** 66103 (2005)
Trigonal, SEM micrograph

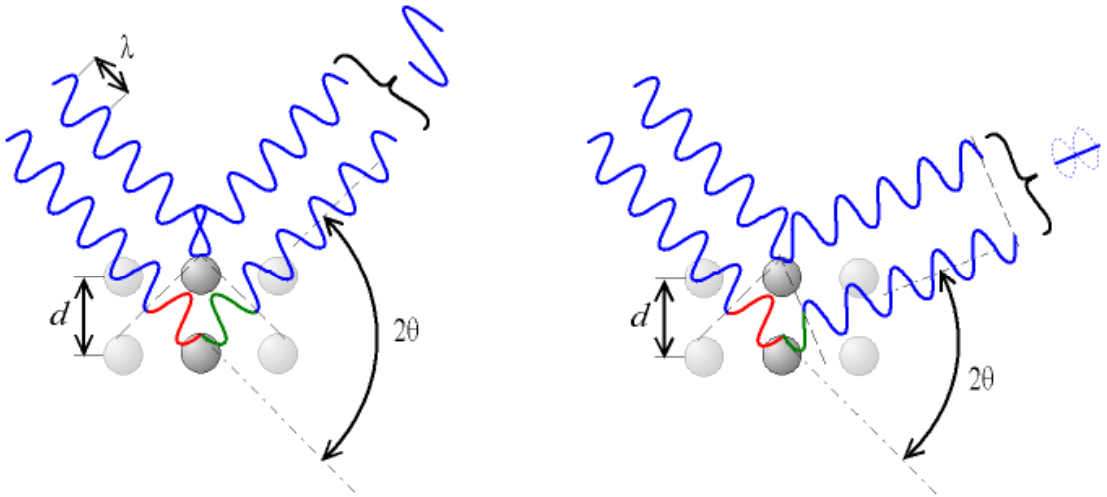


Diffraction and Crystallography

X-ray diffraction was first to uncover the secret. Bragg and von Laue working in early 1900's

Bragg's Law *Real space* $2d\sin\theta = n\lambda$

Laue Condition *reciprocal space* $\Delta \mathbf{k} = \mathbf{g}$



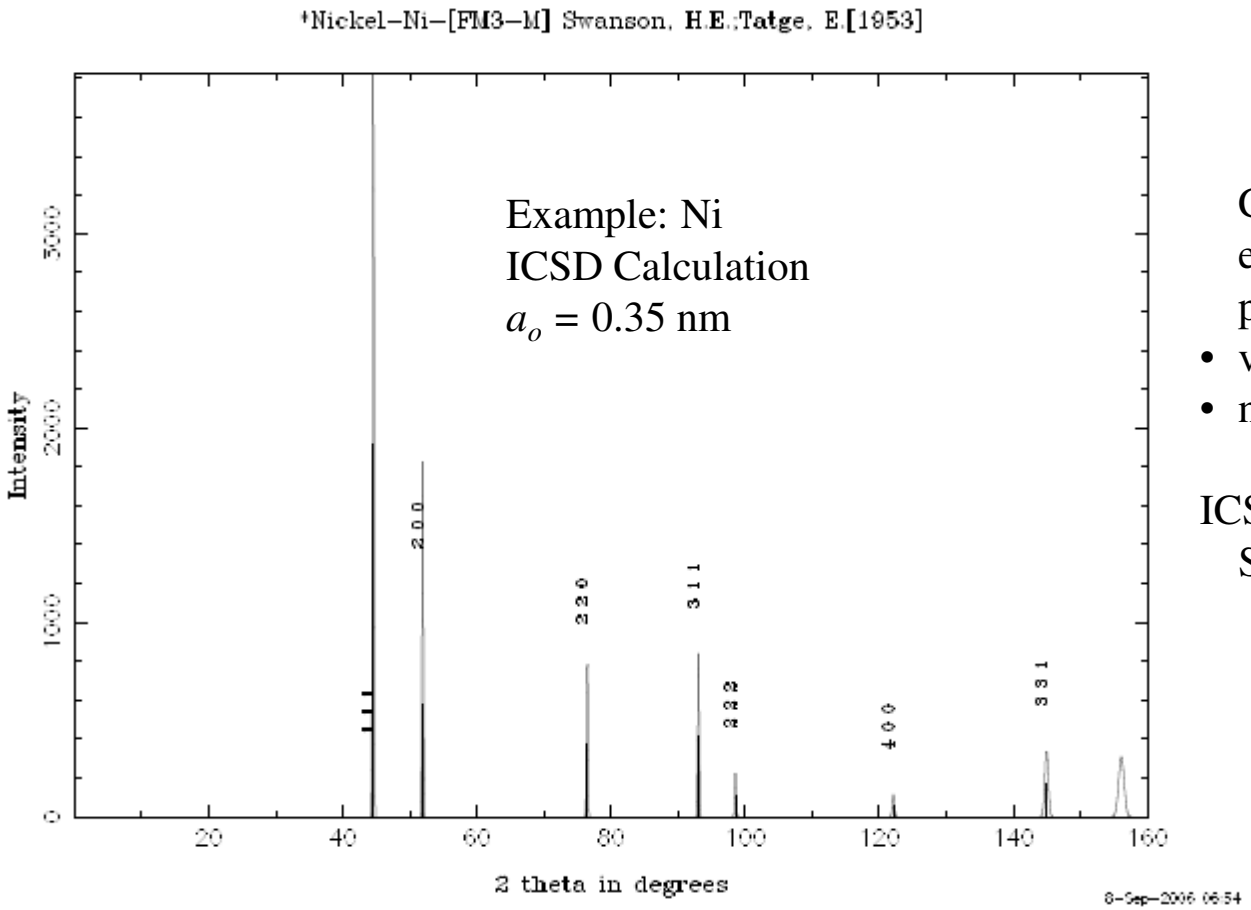
Bragg's law: according to the 2θ deviation, the phase shift causes constructive (left picture) or destructive (right picture) interferences. Auteur/author : Christophe Dang Ngoc Chan (Wikipedia)

- True for electrons, x-rays and neutron radiation (wave property)
  Path difference between two waves must be an integer number of wavelengths to constructively interfere.

Cubic crystals: planar spacing $\boxed{d_{hkl} = \frac{a_0}{\sqrt{h^2 + k^2 + l^2}}}$ where a_o = lattice parameter

h, k, l = Miller indices of the plane

$$\therefore \quad \boxed{2\theta_{hkl} = 2\arcsin\left(\frac{\lambda\sqrt{h^2 + k^2 + l^2}}{2a_0}\right)} \quad \text{from Bragg's Law}$$



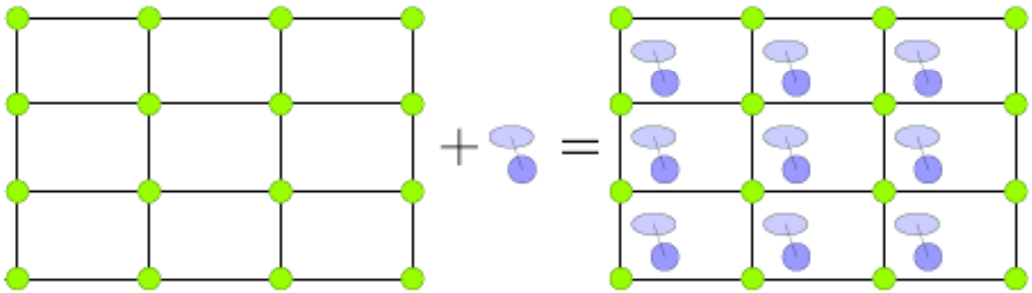
Calculation of spectra expected from polycrystalline Ni

- variation in peak intensity
- not all (*hkl*) are allowed

ICSD = Inorganic Crystal Structure Database

Crystals

- periodic, 3-dimensional, arrangement of atoms or molecules that fills space.
- consists of:
  a mathematical point lattice (Bravias lattice) 14 choices
  + a repeat unit of atoms called the Basis
  + lattice translation vectors $\vec{a}_1, \vec{a}_2, \vec{a}_3$

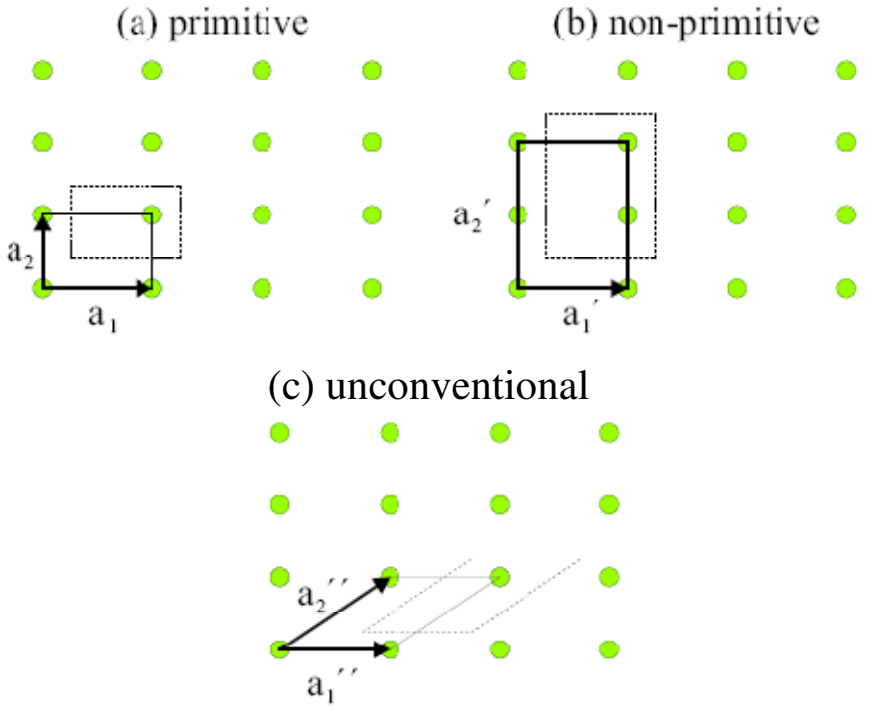


Elements of Modern X-ray Physics, Jens Als-Nielsen, Des McMorrow, Fig. 4.6

Unit cells: chosen repeat volume: $v = \vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3$

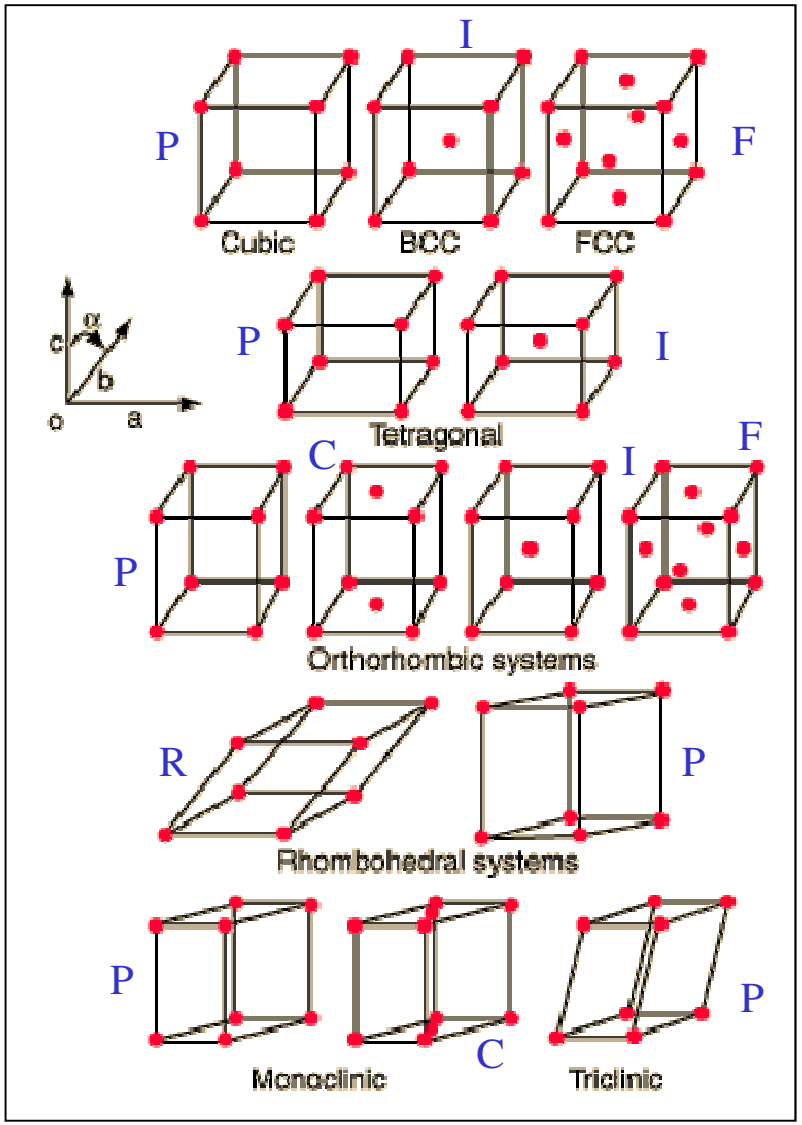
primitive unit cells P

- contain only 1 lattice point (smallest repeat unit)
- Lattice vectors do not have to originate at a point



Elements of Modern X-ray Physics,
Jens Als-Nielsen, Des McMorrow, Fig. 4.7

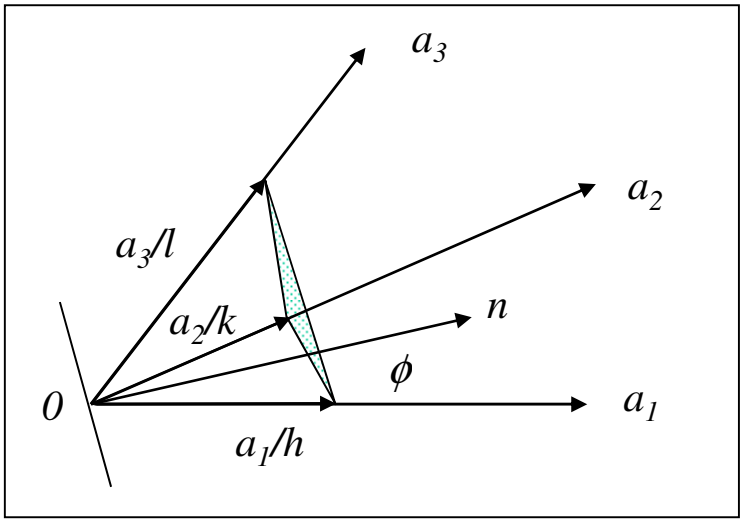
Only 14 Bravais lattices:

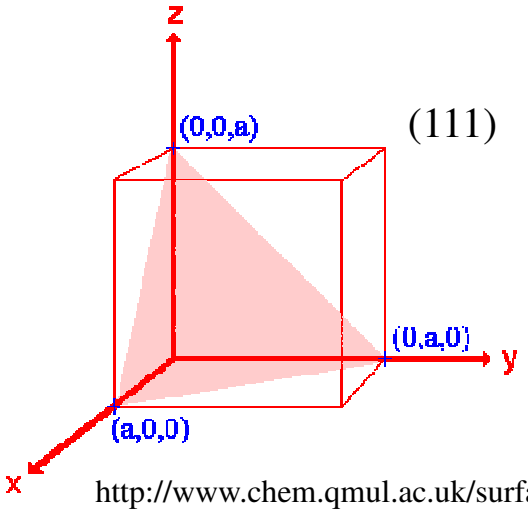


http://hyperphysics.phy-astr.gsu.edu/hbase/solids/bravais.html

Each crystal has a set of parallel planes each with equidistant spacing *d,* and (*hkl*) Miller indices

Fig. 2.2 Warren: if one plane runs through origin then the 2nd plane has intercepts: $\frac{|\vec{a}_1|}{h}, \frac{|\vec{a}_2|}{k}, \frac{|\vec{a}_3|}{l}$



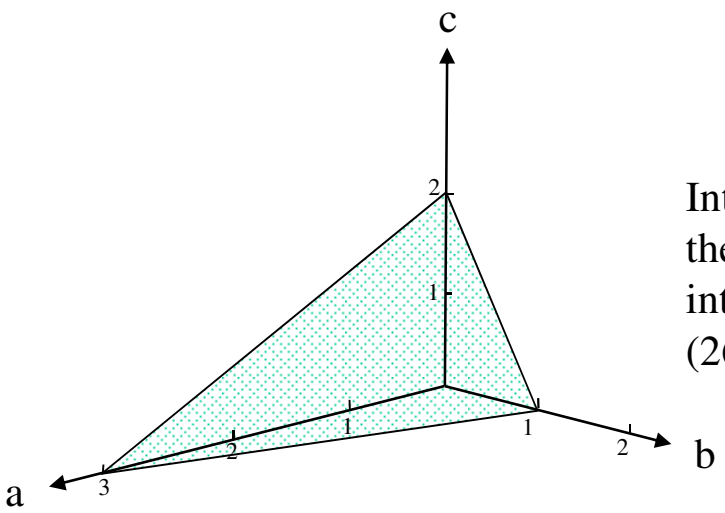


http://www.chem.qmul.ac.uk/surfaces/scc/scat1_1b.htm

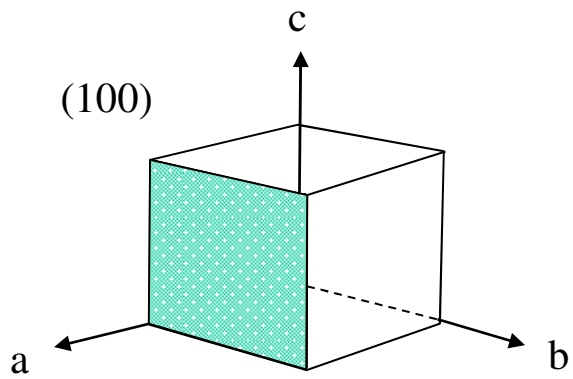
Assigning Miller indices:

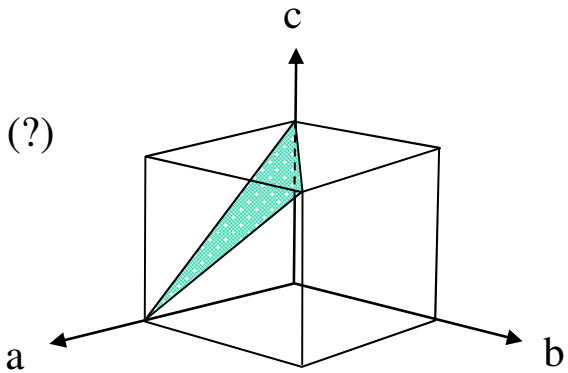
1. Find the planar intercepts with respect to the lattice vectors.
2. Take the reciprocal and reduce to the smallest 3 integers with the same ratio.

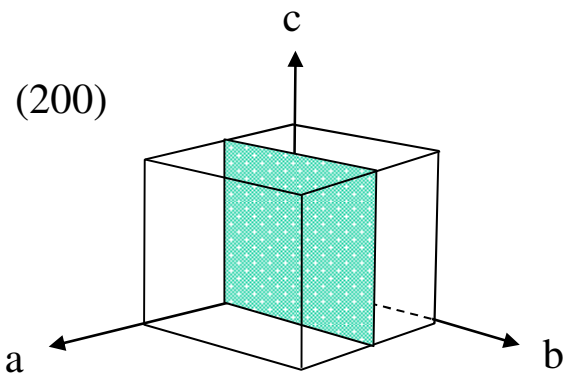
Miller directions [a, b, c] indicate a direction in the crystal with reference to axes parallel to the the lattice vectors. In the cubic system, for example, these are simply the orthogonal coordinates.

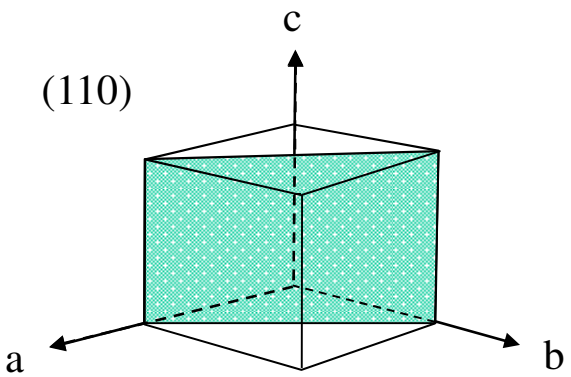


Intercepts at 3a, 1b, and 2c. The reciprocal of these numbers are 1/3, 1 and ½. The smallest 3 integers with the same ratio is 2, 6, 3 so *(hkl)* = (263).

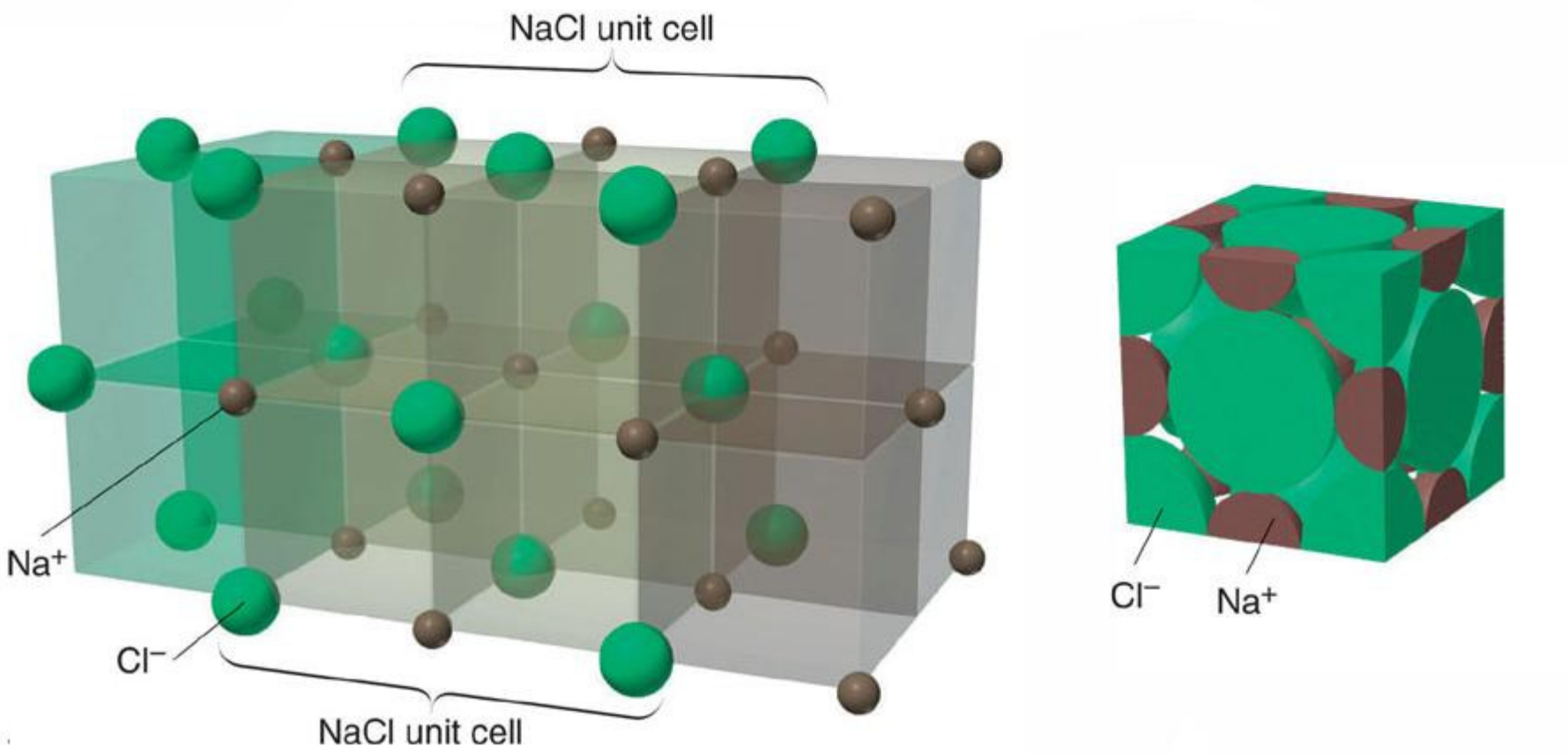








Example: What is the Bravias lattice and basis of NaCl?

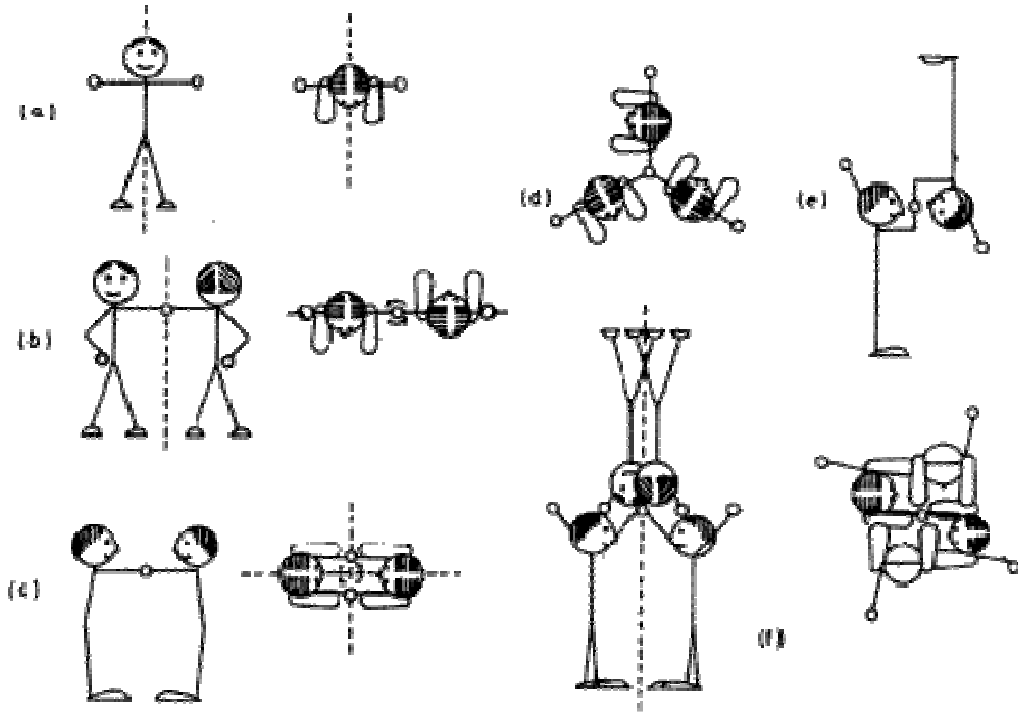


http://www.chem.ufl.edu/~itl/2045/lectures/lec_h.html

Space Groups

To describe more complicated structures we need to apply space group theory.
The basis unit is characterized by a set of symmetry operations one of 32 point groups
Point Groups are a set of Non-translational symmetry operations:

- Rotation axis, n = 1, 2, 3, 4 or 6 (object is the same after a rotation of angle about axis n)
- Inversion axis, n = $\bar{1}, \bar{2}, \bar{3}, \bar{4}, or\ \bar{6}$ (object is the same after a rotation and an inversion)
- Mirror plane, m (object is the same after a reflection through plane m)
- Centre of inversion, i



(a) m, Mirror plane
(b) 2, 2-fold rotation axis
(c) 2 and m,
(d) 3, 3-fold rotation axis
(e) i, centre of inversion
(f) $\bar{4}$, 4-fold inversion axis

http://www.iucr.org/iucr-top/comm/cteach/pamphlets/13/node1.html
After L. S. Dent Glasser, Chapter 19, The Chemistry of Cements: Academic Press, 1964.

To generate a Space Group (230 types):

Combine a basis Point Group with:

- A set of translational symmetry operations:
  - Glide plane "a, b, c, n, d" (reflection plus glide by a distance ½ vector) Fig. 8.1 Warren
  - Screw axis "a" (rotation axis plus translation of a distance ½ vector), Fig. 8.2 Warren
- and Bravais lattice translations

Example: Al or Cu
Space Group no. 225
Hermann-Mauguin Symbol: Fm3m (short form)

First letter indicates the type of Bravais lattice: P (primitive), F (face-centered), I (body-centered), A, B, C (side-centered), R (Trigonal)

Next 3 symbols refer to the highest symmetry operator of the 3 major symmetry directions of the crystal (see Table next page). Can identify crystal system since these are particular to each system:

Crystal System	Symmetry Direction			Space Group Symbol		
	Primary	Secondary	Tertiary	Primary	Secondary	
Triclinic	None					Followed by 1 or (-1)
Monoclinic	[010]					Single m, gl, 2 or 2_1
Orthorhombic	[100]	[010]	[001]	m, gl, 2 or 2_1	m, gl, 2 or 2_1	m gl, 2 or 2_1
Tetragonal	[001]	[100]/[010]	[110]	4, (-4), 4_1, 4_2 or 4_3		
Hexagonal/ Trigonal	[001]	[100]/[010]	[120]/[1 $\underline{1}$ 0]	6, (-6), 6_1, 6_2, 6_3, 6_4 or 6_5 / 3, (-3), 3_1, 3_2		
Cubic	[100]/[010] /[001]	[111]	[110]		Always 3 or -3	

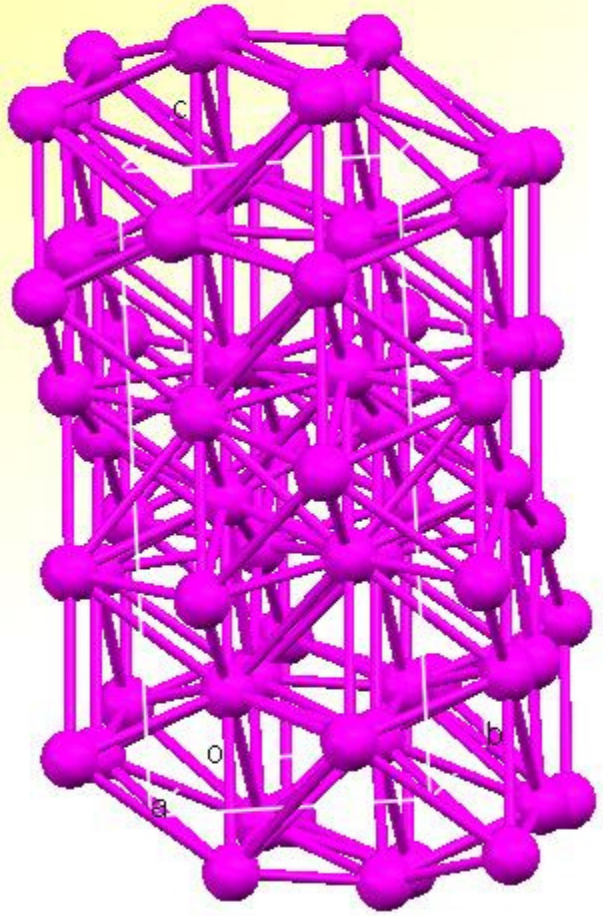
http://www.chemistry.ohio-state.edu/~woodward/ch754/sym_itc.htm

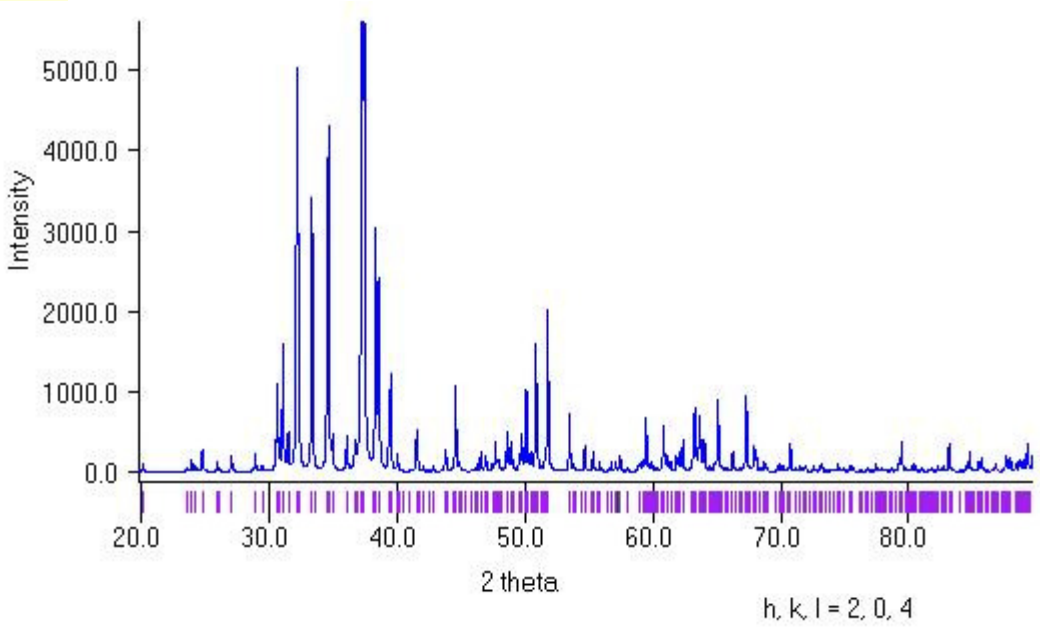
Example: Plutonium (Pu)
Determine the structure, atomic positions, and density.

Using the Inorganic Crystal Structure Database (ICSD):

- Given: Space group: long form: P121/M1 (no. 11); short form: $P2_1/m$ or P21/M
  » Primitive Monoclinic
- Given: lattice constants and angles: 6.183(1), 4.822(1), 10.963(1), 90., 101.79(1), 90.
- Given: volume unit cell: V = 319.96
- Given: atomic site symmetry 8 Wyckoff sites each with multiplicity 2: 2*e*
  International Tables for Crystallography: 2*e* has point symmetry *m* with atomic co-ordinates at (x, y, 1/4); (-x, -y, ¾)
  »8 x 2 = 16 atoms in unit cell
- Using cell volume and atomic mass of Pu you obtain density.
- Graphic output "CIF" file plots the positions in unit cell.
- Calculates the powder diffraction spectra, plots and lists *(hkl)*

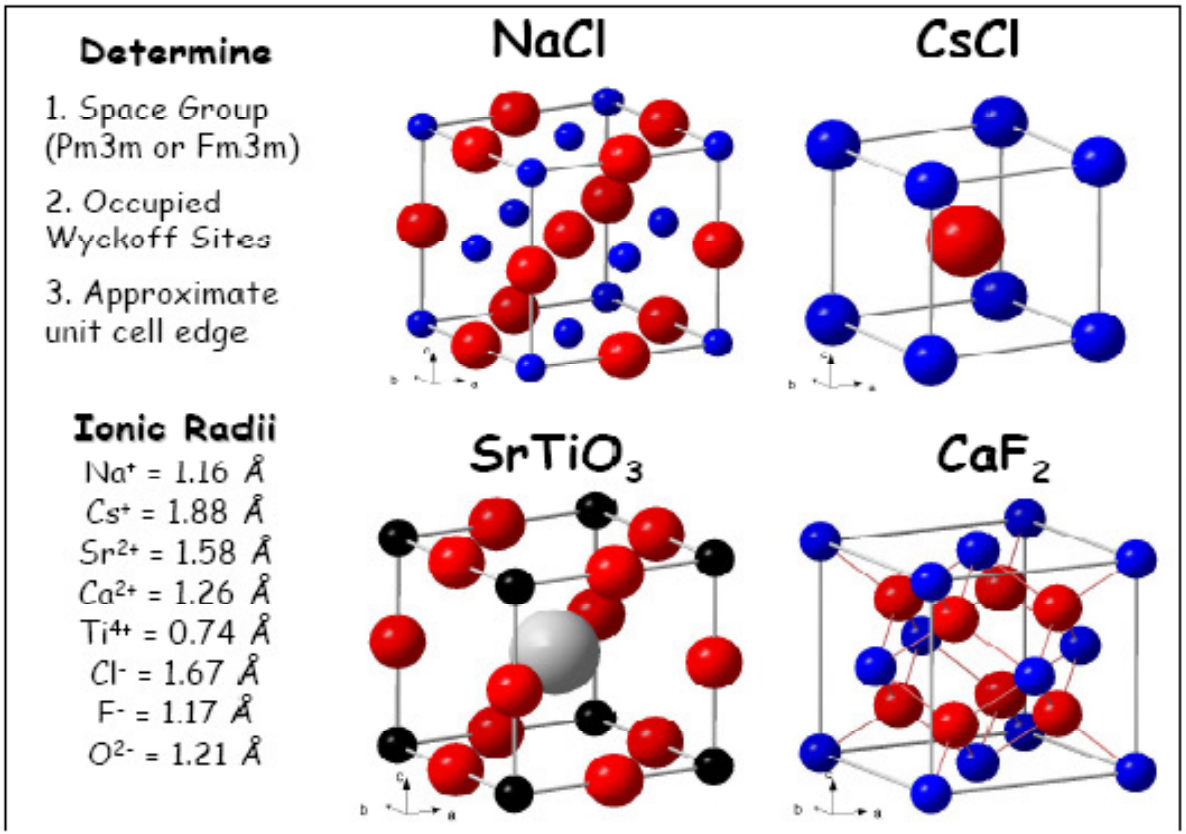
Pu


c
b
a
O


Intensity
5000.0
4000.0
3000.0
2000.0
1000.0
0.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
2 theta
h, k, l = 2, 0, 4

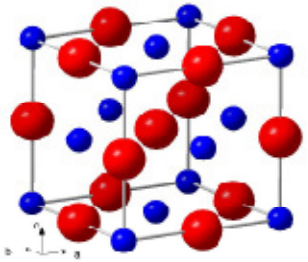
More examples:

Material	Space Group Properties				
	H-M Symbol	Number	Wyckoff Sites	Point Symmetry	Atoms in Unit Cell
Plutonium (Pu)	P21/M	11	2e	m	16
Aluminum (Al)	Fm3m	225	4a	m3m	4
$AlCrNi_2$	Fm3m	225	Al 4a Cr 4b Ni 8c	m3m m3m -43m	16
$Nd_{0.15}Sr_{0.83}Al_{0.6}Nb_{0.42}O$	Fm3m	225	Al(1) 4a Nb 4b Al(2) 4b Sr 8c Nd 8c Nb 8c O 24e	m3m m3m m3m -43m -43m -43m 4mm	60
Uranium (U) Warren 8.2	Cmcm	63	4c	mm	4



http://www.chemistry.ohio-state.edu/~woodward/ch754/lect7_inttable.pdf(2006)

NaCl

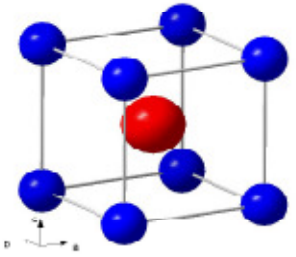


Space Group = Fm3m

a = 5.64 Å

Atom	Site	x	y	z
Na	4a	0	0	0
Cl	1b	$\frac{1}{2}$	0	0

CsCl

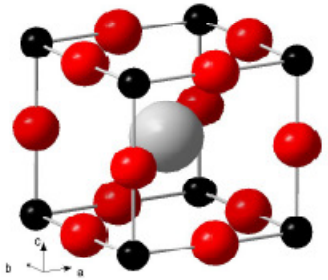


Space Group = Pm3m

a = 4.12 Å

Atom	Site	x	y	z
Cs	1a	0	0	0
Cl	1b	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$

$SrTiO_3$

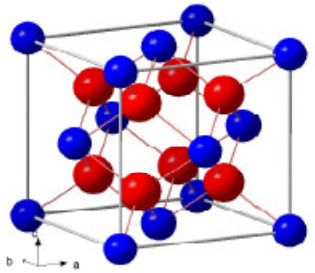


Space Group = Pm3m

a = 3.90 Å

Atom	Site	x	y	z
Ti	1a	0	0	0
Sr	1b	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$
O	3d	$\frac{1}{2}$	0	0

CaF_2



Space Group = Fm3m

a = 5.46 Å

Atom	Site	x	y	z
Ca	4a	0	0	0
F	8c	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$