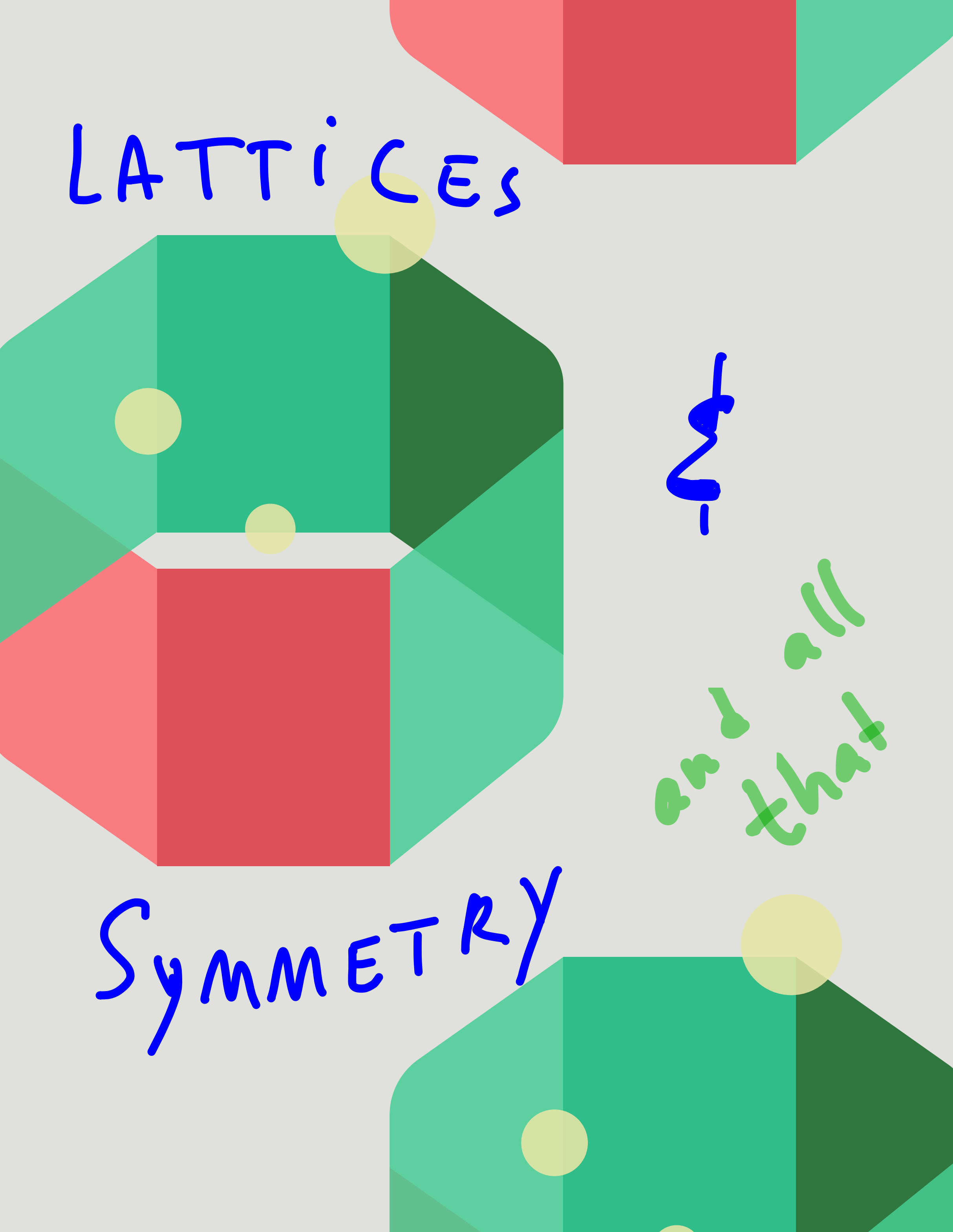


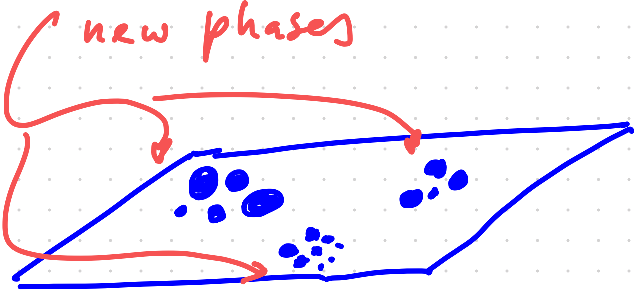
LATTICES & SYMMETRY

and all that

LATTICES & SYMMETRY

Ch. 3 MG & YK.

Crystal and broken symmetry:



In general the hamiltonian:

$$\mathcal{H} = \frac{1}{2M}\sum_{j=1}^{N} p_j^2 + \sum_{i<j} V(|r_i - r_j|)$$

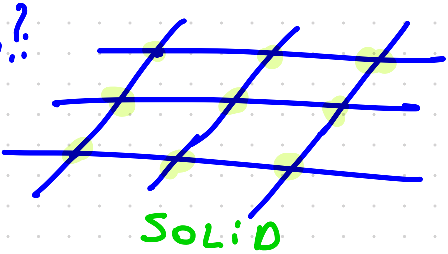
is invariant under:

translation $\bar{r}_i \to \bar{r}_i + \bar{S}$

rotation: $\bar{r}_i \to \hat{R}\,\bar{r}_i$

space inversion: $\bar{r} - \bar{R} \xrightarrow[I]{} -(r - R)$

Are those symmetries present in?



THE STATE OF XTAL is LESS SYMMETRIC!

AND SYMMETRY is SPONTANEOSLY BROKEN (see a movie of a milk droplet)

Note crystalization happens b/c particles arrange themself in to special positions to minimize energy.

For specifics of symmetry breaking, read pp 21-24 M G & KY.

Bravais lattices:

B.L. is a SIMPLEST MATHEMATICAL OBJECT with desired symmetries

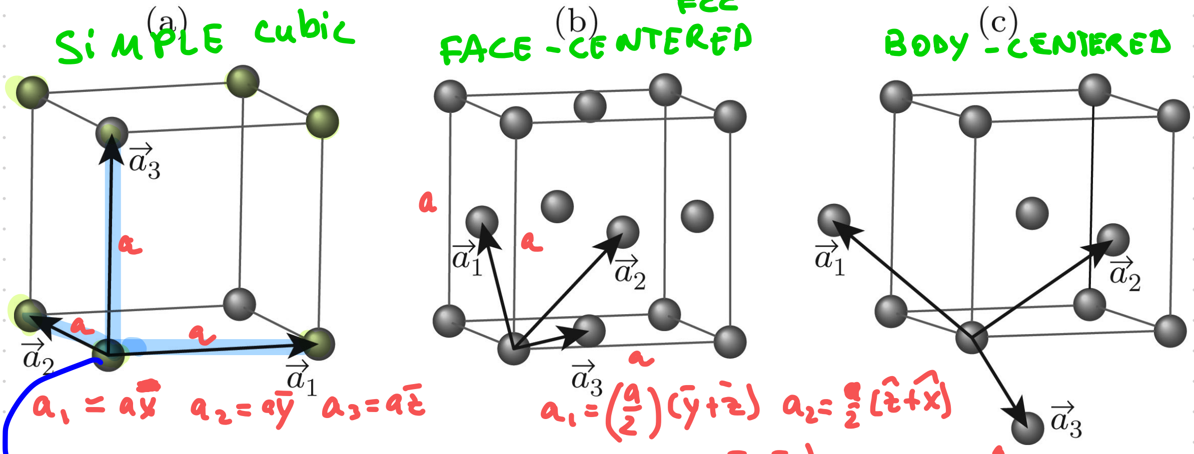
B. L. is a set o points span by:

$$\vec{R}_{\vec{n}} = n_1 \underline{\underline{\vec{a}_1}} + n_2 \underline{\underline{\vec{a}_2}} + n_3 \underline{\underline{\vec{a}_3}}$$

n = is an integer #.

$[\bar{a}_1, \bar{a}_2\ \bar{a}_3] =$ primitive LATTICE VECTORS

Primitive lattice vectors and



$a_1 = a\hat{x}$ $a_2 = a\hat{y}$ $a_3 = a\hat{z}$

those are NOT atoms!

$a_1 = \left(\frac{a}{2}\right)(\hat{y}+\hat{z})$ $a_2 = \frac{a}{2}(\hat{z}+\hat{x})$

$a_3 = \frac{a}{2}(\hat{x}+\hat{y})$

$\bar{a}_1 = \frac{a}{2}(\vec{y}+\hat{z}-\hat{x})$

$\bar{a}_2 = \frac{a}{2}(\hat{z}+\hat{x}-\hat{y})$

$\bar{a}_3 = \frac{a}{2}(\hat{x}+\hat{y}-\hat{z})$

- As you can see FCC and BCC can be obtained decorating simple cubic.

- all added points are the same as the original ones BUT new primitive vectors required

- # of nearest neighbos is called the COORDINATION NUMBER $\equiv Z$

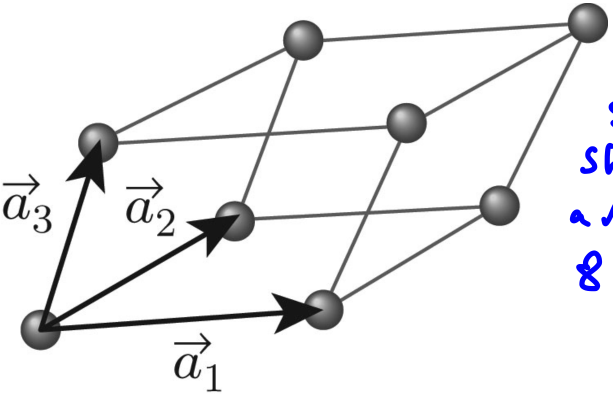
e.g. SC has $z=6$
FCC $z=12$
BCC $z=8$

in the periodic table FCC and bcc are the most common

Larger coordination = greater stability

Q: what element(s) has SC lattice?

Another way to describe B. lattice is to specify its premitive unit cell (p.u.c) with a fixed shape which when translated by primitive vectors entirely fills up crystall space without voids



Each site is shared among 8 p.u.c.

- p.u.c. is a better idea as atoms, ions etc. are not point like.

- electron w.f. spreads over xtal and the whole u.c.

- p.u.c. is not unique

Wiegner - Seitz cell =

= Special kind of p.u.c

mathematically it's defined as:

$\bar{r}$ - insid WZ p.u.c.

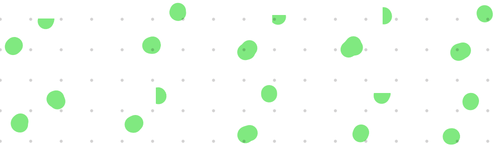
$$|r| < |\bar{r} - R_n| \Rightarrow$$

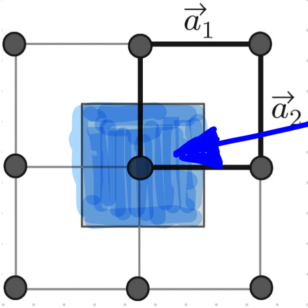
$$r^2 < \bar{r}^2 - 2\bar{r}\cdot\bar{R}_n + \bar{R}_n\cdot\bar{R}_n$$

$$\Rightarrow \left(\bar{r} - \frac{\bar{R}_n}{2}\right)\cdot R_n < 0$$

- Boundaries of WZ are planes BIsecting lattice vectors

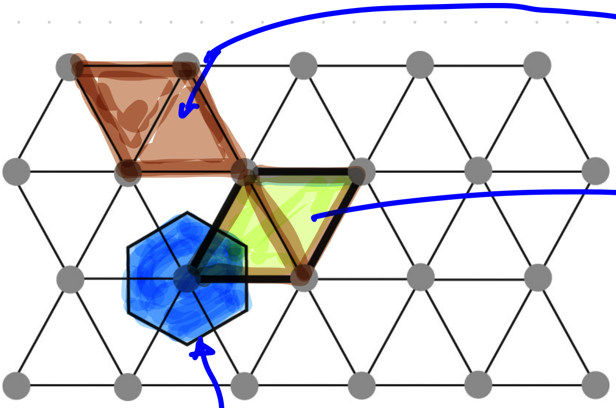
- WZ cell has full point symmetry of the B.L.
(i.g. a set of point symmetry transform. which leaves the xtal invariant)





W.Z. p.u.c. for 2D square lattice
$|\bar{a}_1| = |\bar{a}_2| = a$

The shape of W.Z. and the primitive lattic is not always the same (most often!), e.g.

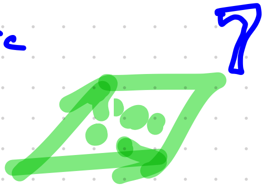


or non pritive u.c.

triangular lattic p.u.c.

W.Z. p.u.c.

In general there are more than 1 atom per u.c.



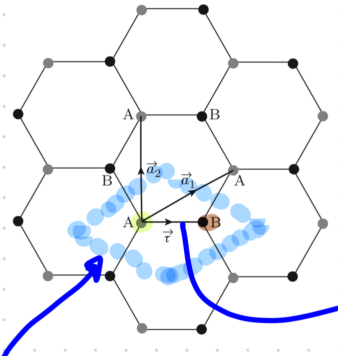
⇒ General Lattice is constructed as:

$$\vec{R}_{\vec{n},s} \equiv \vec{R}_{\vec{n}} + \underline{\vec{\tau}_s} \qquad s=1,2,\dots m$$

- we attach a set of m inequivalent points to sites of a B.L.

WE CALL THOSE = LATTICE WITH BASES

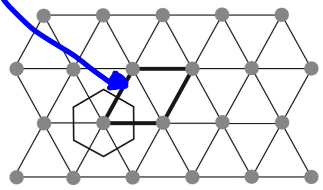
e.g. GRAPHENE :



$\bar{a}_1$ and $\bar{a}_2$ = primitive vectors

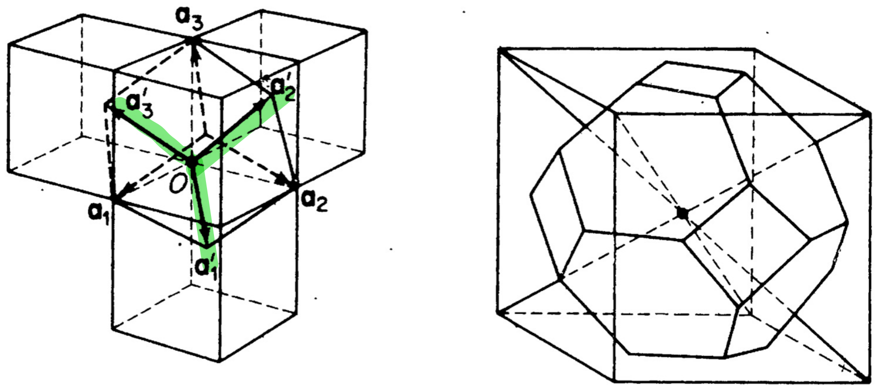
τ is <u>NOT</u> a primitive vector (A & B are inequivalent atoms)

⇓



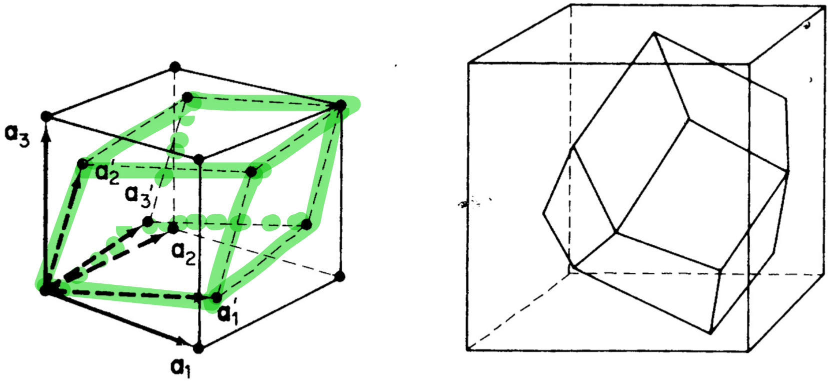
BL: → triangular lattice with 2 point Basis

What kind of lattice would you assign?



(a) (b)

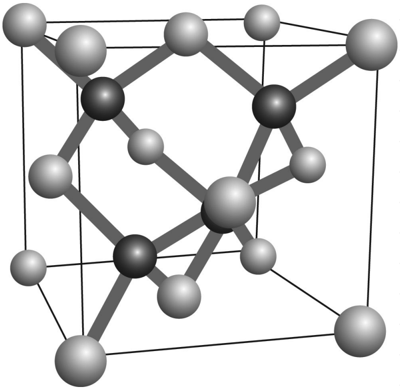
Figure 1.3 (a) Body-centered cubic lattice, showing generators of cubic and alternative (Bravais) unit cells. (b) Wigner-Seitz cell.



(a) (b)

Figure 1.4 (a) Face-centered cubic lattice, showing cubic and alternative (Bravais) unit cells. (b) Wigner-Seitz cell.

- e.g. graphene, diamond, Silicon and Germanium all 2 atom per u.c.
- b/c. those are simple elements those 2-atoms are the same.



Introduction to **VESTA** software

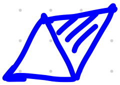
- what's this lattice (fcc)
- τ is along diagonal of the cube with 1/4 of diagonal length.

$$\bar{\tau} = \frac{a}{4}(\bar{x} + \bar{y} + \bar{z})$$

(ofthen called)

⇓

- Diamond is a 3D generalization of graphene.

- Δ lattice $z = 6$
  it can be tiled as
   with lattice sites at the vertexes.

- B sites sit at the center of each A triangle, and so is A ... ⇒ honeycomb lattice has coordination $z = 3$

- Similarly FCC lattice $z = 12$ can be tiled from regular tetrahedra with 2 different directions.

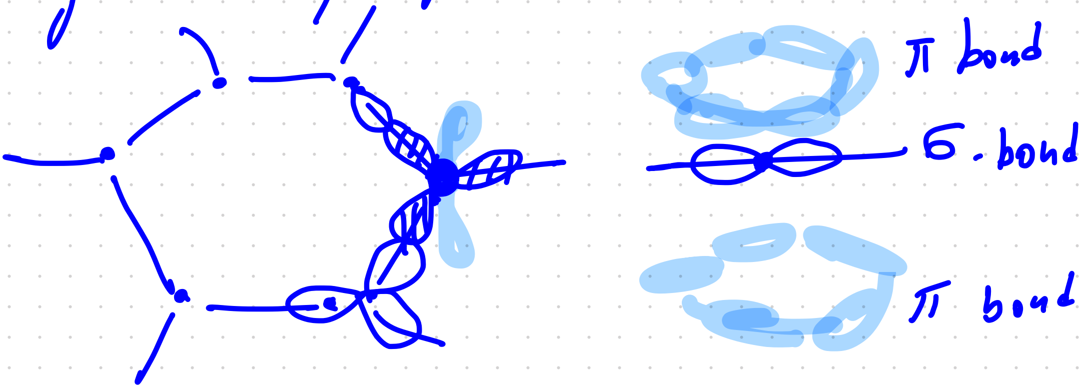
- In diamond sublattice the 2d sublatt. is in the center of 1st tetrahedron.

⇒ diamond lattice has $z = 4$.

Q: why do you think those 3D xtals have such low z?

A (hint): Consider C^{ion} = 4 valent e^- which form 4 bonds

e.g. in graphene



Na^+Cl^-: simple cubic

each u.c. Contains Na^+ and Cl^-
and B.L. is FCC

Zinc Blend: ZnS

is diamond lattice with
2 types of atom sitting
in opposite corners:
other examples: GaAs, AlAs

- they cannot form a B.L. as
each U.C. contains more than
one atom.

Conventional u.c. (c.u.c)

c.u.c. contains more than one lattice site but has a simple geometrical shape

$$V_{c.u.c} = n \, V_{p.u.c.}$$

n ← # of lattice sites in the c.u.c.

e.g. we could use Cubic c.u.c. for bcc or fcc.

SYMMETRY

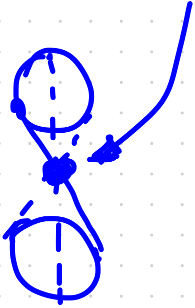
- translation symmetry is broken spontaneously

to map xtal into itself:

- **Rotation**: by $2\pi/n$
  axis are n-fold axis of rotation

- **Reflection** abou a plane
  (in 2D - line)

- **Inversion** about a special point - called an inversion center
  (in 2D an inversion = π rotation aroun an inv. center)



- Combination of all is a symmetry group

By specifying the symmetries crystals in 3D can be classified in 32 groups.
(for more see Ashcroft & Mermin)

Reciprocal Lattice

Recall F.T. is a great way to describe periodic functions:

$$\rho(\bar{R}) = \rho(\bar{R} + \bar{R}_n)$$

lets constru the lattice like this:

$$\rho(R) = \sum_{n_1 \, n_2 \, n_3} f(R - n_1\bar{a}_1 - n_2\bar{a}_2 - n_3\bar{a}_3)$$

↑ electron density of basis atoms inside one u.c.

FT: $\rho(R) = \sum_{|G|} \rho_{\bar G}\, e^{i\bar G\cdot\bar R}$

by demanding that

$$\rho(R) = \rho(R + R_n)$$

$$e^{i\bar G(\bar R + \overbrace{n_1\bar a_1 + n_2\bar a_2 + n_3\bar a_3}^{R_n})}$$

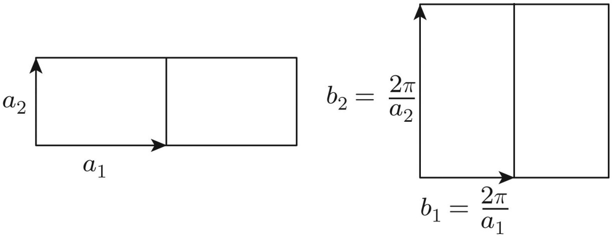
$$= e^{i\bar G\cdot\bar R} \Rightarrow e^{i\bar G\cdot R_n} = 1$$

$$\Rightarrow \bar G\cdot\bar a_j = 2\pi m_j \qquad j = 1,2,3 \quad m = 0,1,2\ldots$$

set of 3 equ.

the set of such G vectors also forms a B.L. in a momentum space ≡ reciprocal space

Example:



$$\bar{b}_1 = \frac{2\pi}{a_1}\hat{x}$$

$$b_2 = \frac{2\pi}{a}\hat{y}$$

let's check:

$$b_1 \cdot a_1 = 2\pi$$

$$b_1 \cdot a_2 = 0$$

$$b_2 \cdot a_1 = 0$$

$$b_2 \cdot a_2 = 2\pi$$

hence $G = m_1 \bar{b}_1 + m_2 \bar{b}_2$

since it satisfies:

$$\bar{G} \cdot \grave{a}_j = 2\pi m_j$$

But OFTEN R.L. is NOT THE SAME TYPE AS DIRECT LATTICE e.g. for 2D:

$$b_i = \epsilon_{ij} (\hat{z} \times \bar{a}_j)$$

where z is a unit vector along the normal direction of the lattice plane and

$$\epsilon_{ij} = -\epsilon_{ji}$$

antisymmetric Levi-Civita

$$\epsilon_{12} = -\epsilon_{21} = 1$$

$$\epsilon_{11} = \epsilon_{22} = 0$$

$$\Rightarrow \bar{a}_m \cdot \bar{b}_j = \delta_{mj} \cdot 2\pi$$

W.Z. cell of the reciprocal space is the 1st B.Z

Brillouin zone

Now in 3D:

$$\omega = \bar{a}_1 \cdot (\bar{a}_2 \times \bar{a}_3)$$

↓

a volume of p.u.c

Lets define:

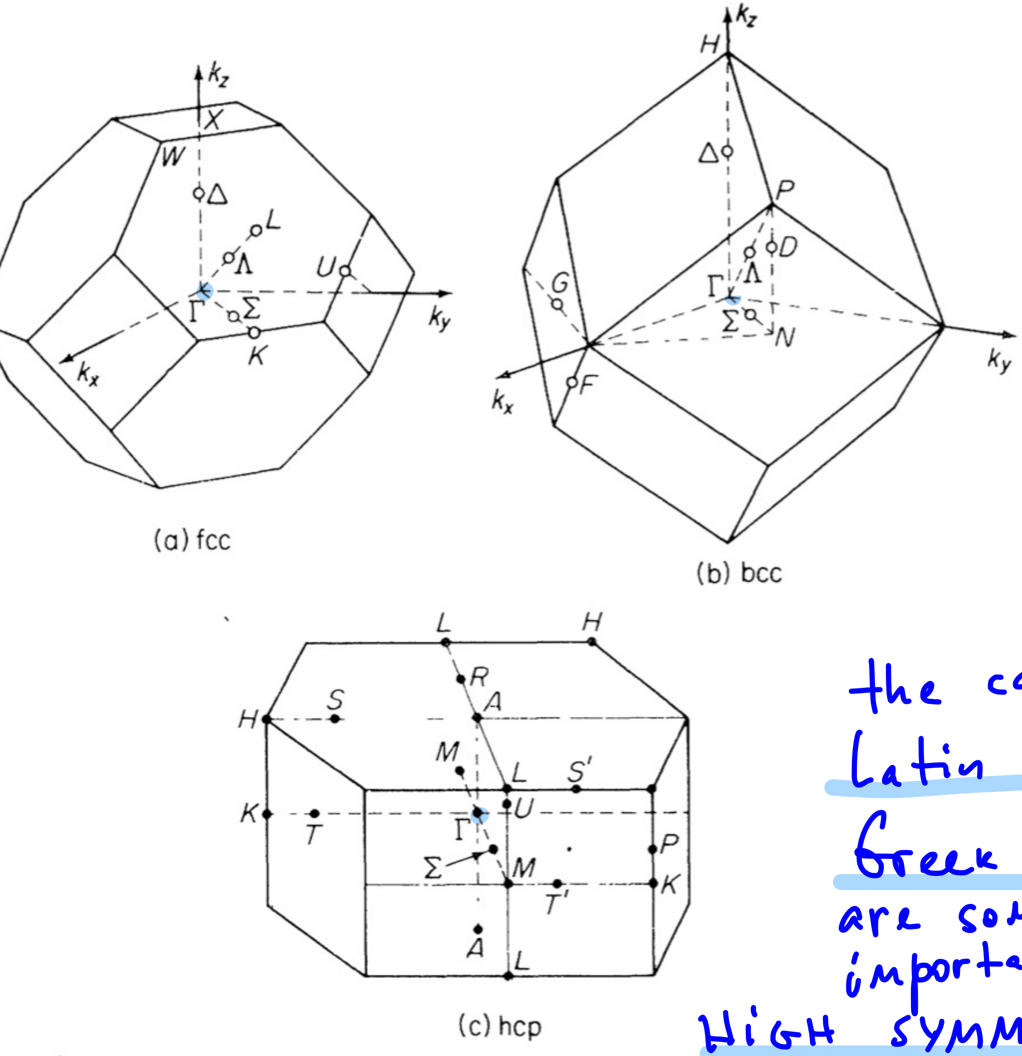
a_i:

$$\boxed{\begin{aligned} b_1 &= \frac{2\pi}{\omega} a_2 \times a_3 \\ b_2 &= \frac{2\pi}{\omega} a_3 \times a_1 \\ b_3 &= \frac{2\pi}{\omega} a_1 \times a_2 \end{aligned}}$$

$$\boxed{\bar{b}_j = \frac{1}{2} \frac{2\pi}{\omega} \epsilon_{jkl} (\bar{a}_k \times \bar{a}_l)}$$

and $\bar{a}_m \cdot \bar{b}_j = \underline{2\pi \delta_{mj}}$

1st B.Z. of common structures



(a) fcc

(b) bcc

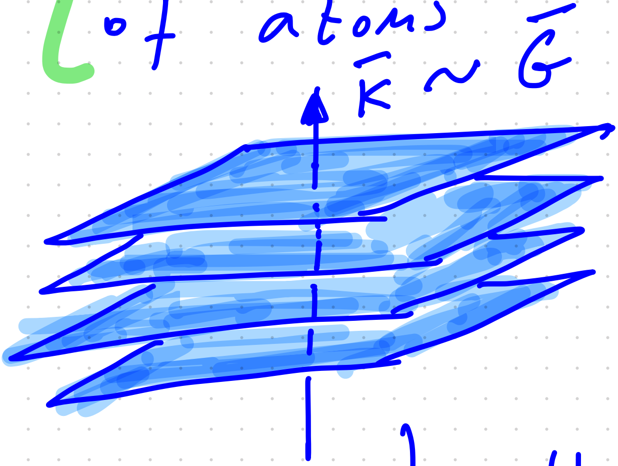
(c) hcp

Figure 1.18 Brillouin zones for the fcc, bcc, and hcp structures.

the capital Latin & Greek letters are some important HIGH SYMMETRY POINTS

Recall $\bar{b}_1 \perp$ to $\bar{a}_2$ and $\bar{a}_3$ etc.

{Now we can think of any 3D xtals a a set of 2D lattices made of plane of atoms}



So we can label this set of lattice planes by this r. l. vector

e.g. $\bar{G}_{KLM} = \overset{h}{K}\bar{b}_1 + \overset{k}{L}\bar{b}_2 + \overset{l}{M}\bar{b}_3$

from math: a plane is defined by a point and a vector ⊥ to the plane

$$\bar{G}_{KLM} \cdot \bar{r} = 0$$

(notice often we use h, k, l)

As $\bar{G}\cdot\bar{R}_j = 2\pi m_j$ for all lattice points, there exist a set of parallel planes of atoms so that

$$\bar{G}_{KLM}\cdot\bar{r} = 0, \pm 2\pi, \pm 4\pi, \ldots$$

Those planes are labeled by their MILLER'INDECES

(b.t.way I assume that $\bar{G}$ is the shortest vectr ⊥ to the plane)

We can find M.I. in the real space:

$$\underline{R}_{n_1 n_2 n_3} = n_1\bar{a}_1 + n_2\bar{a}_2 + n_3\bar{a}_3$$

So $G_{KLM}\cdot\bar{R}_{n_1 n_2 n_3} = (Kn_1 + Ln_2 + Mn_3)\cdot 2\pi = 2\pi I$

I is some integer fixed.

Lets set $h_2 = h_3 = 0$ we solve for $\bar{h}_1$

$$\left.\begin{aligned} \bar{h}_1 &= \frac{I}{K} \\ \bar{h}_2 &= \frac{I}{L} \\ \bar{h}_3 &= \frac{I}{M} \end{aligned}\right\} \Rightarrow (K, L, M) = \left(\frac{I}{\bar{h}_1}, \frac{I}{\bar{h}_2}, \frac{I}{\bar{h}_3}\right)$$

Consider examples:

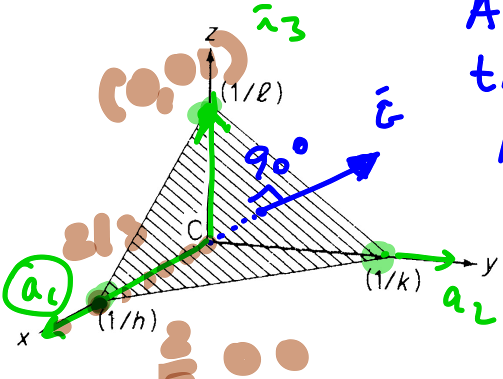


Figure 1.13 Plane specified by the Miller indices (*hkl*).

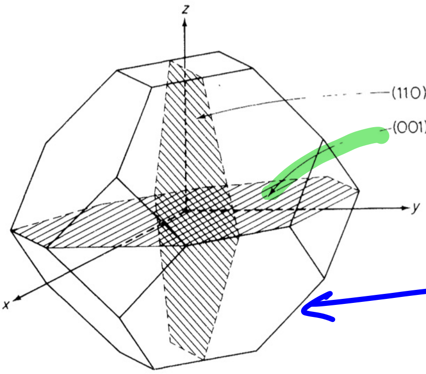
A Direction normal to a plane with Miller indices (h k l) is labeled as [h k l]

This a line passing through the point with coordinate (hkl) if the intercept is negative we say $(\bar{h} k l)$

- Alternatively, if we have 3 numbers intersecting axis the Miller. Ind. is the SMALEST integer of $\frac{1}{n_1} : \frac{1}{n_2} : \frac{1}{n_3}$

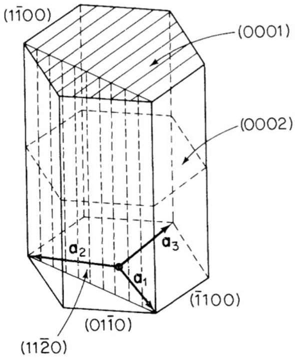
e.g. earlier, say we got $(\overset{h}{3}, \overset{k}{2}, \overset{l}{1})$

$\Rightarrow \frac{1}{3} : \frac{1}{2} : 1$ or $2:3:6 \Rightarrow$ so the M.I is (2 3 6). More examples:



W.Z. cell

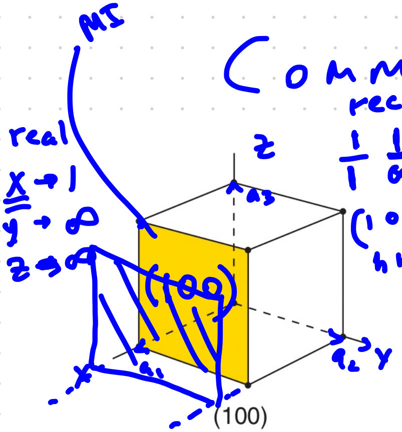
Figure 1.14 Miller indices of major symmetry planes of the bcc lattice.



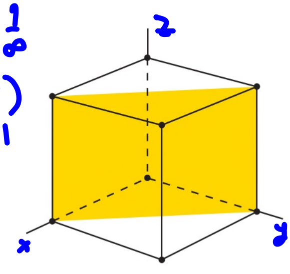
h.c.p uses 4 symbols (h k i l) where $i = -(h+k)$

hexagonal close-packed

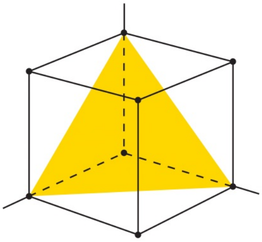
Common M.I. for planes in cubic lattice



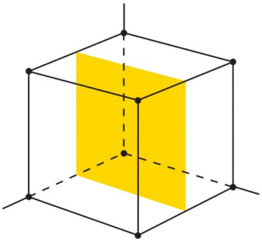
(100)



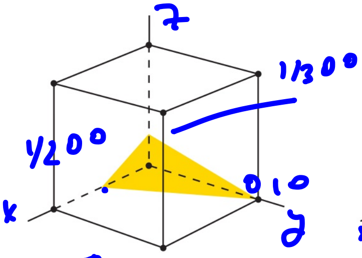
(110)

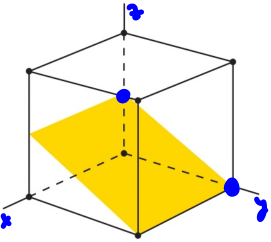


(111)



(200)





↑ ?

↑ ?

$$d^{hkl}_{spacing} = \frac{a}{\sqrt{h^2+k^2+l^2}}$$

e.g. $a = 3.61\text{Å}$ (220)

$$d_{220} = \frac{0.361}{\sqrt{2\ 2\ 0}} = 0.128\,\text{nm} = 1.28\,\text{Å}$$

Example: Let's compute some interesting numbers for NaCl.

NaCl crystalizes in a cubic structure

Molecular weight of NaCl = 56.46
22.989 + 35.453

and density at R.T. 2.167 g/cm^3

Q: what's the lattice constant of NaCl?

$$M_{NaCl\ \text{molecule}} = 58.46\ \frac{g}{\text{mole}} \cdot \frac{1}{6.02 \cdot 10^{23}\ \text{mol}}$$

$$= 9.7 \cdot 10^{-23}\ g.$$

$$\frac{\#\text{ of NaCl}}{\text{Unit volume}} = 2.167 \cdot \frac{g}{cm^3} \cdot \frac{\#\text{Molecule}}{9.7 \cdot 10^{-23}\ g}$$

$$= 2.23 \cdot 10^{22}\ \text{molecules}/cm^3$$

b/c NaCl is diatomic

$$\frac{\#\text{ of atoms}}{\text{Volume}} = \frac{2\text{ atoms}}{\text{molecule}} \cdot 2.23\cdot 10^{22}\,\frac{\text{mol}}{\text{cm}^3}$$

$$= 4.5 \cdot 10^{22}\ \text{atoms}/\text{cm}^3$$

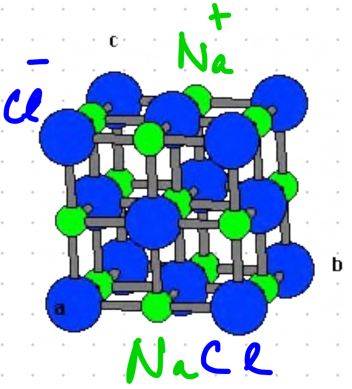
Let a to be distance measured along the edge of the cube
"n" number of atom along the edge of 1 cm × 1 cm × 1 cm cube

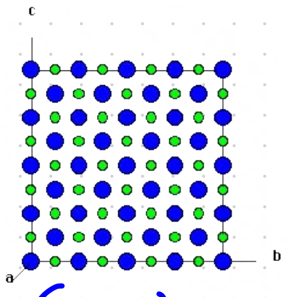
$$L_{edge} = n\cdot a \Rightarrow V = n^3 a^3$$

$n^3 = \#$ atoms in 1 cm^3 $\Rightarrow$

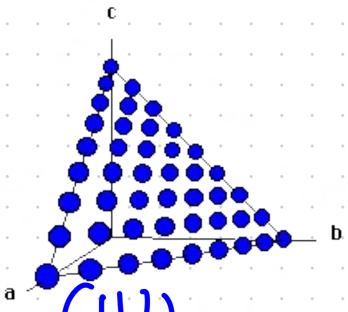
$$4.50\cdot 10^{22}\cdot a^3 = 1 \Rightarrow$$

$$a = 2.82\cdot 10^{-8} = 2.82\ \text{Å}$$



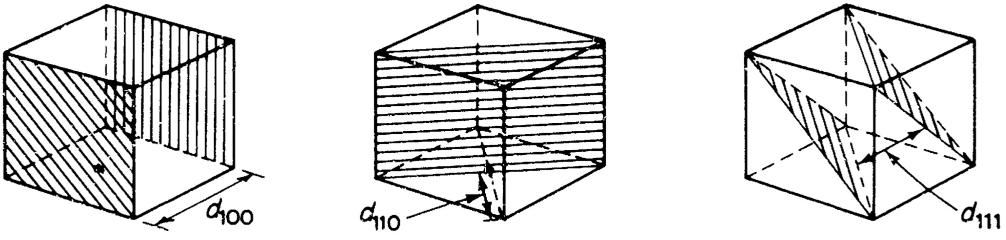


(100)



(111)

Next we can calculate spacing between xtal lattices:



(a) (b) (c)

Figure 1.16 Spacing between crystal planes in cubic lattice.

As you can see d_{00} = lattice constant = a

$$d_{110} = \frac{d_{100}}{\sqrt{2}} = 1.99 \mathring{A}$$

and

$$d_{111} = \frac{d_{100}}{\sqrt{3}} = 1.63 \mathring{A}$$

X RAY SCATTERING

from XTALs

Recall in the Born approx.

$$\frac{d\sigma}{d\Omega} \sim |F(\bar q)|^2$$

with $\bar q = \bar k - \bar k'$

at T=0K: $\rho(r) = \sum_i \rho_a(r - R_i)$

Sum of sits inside underlyig Br. lattice

and ρ_a – atomic density

$$\Rightarrow F(\bar q) = \underbrace{\int d^3\bar r\, e^{-i\bar q\cdot\bar r}}_{\text{lattice}} \overset{\text{atom}}{\underbrace{\sum_i \rho_a(\bar r - \bar R_i)}}$$

$$\Rightarrow F(q) = W(q)\cdot f(q)$$

$$\sim \sum e^{iqR_i}$$

DIFFRACTION PATTERN AS CONVOLUTION

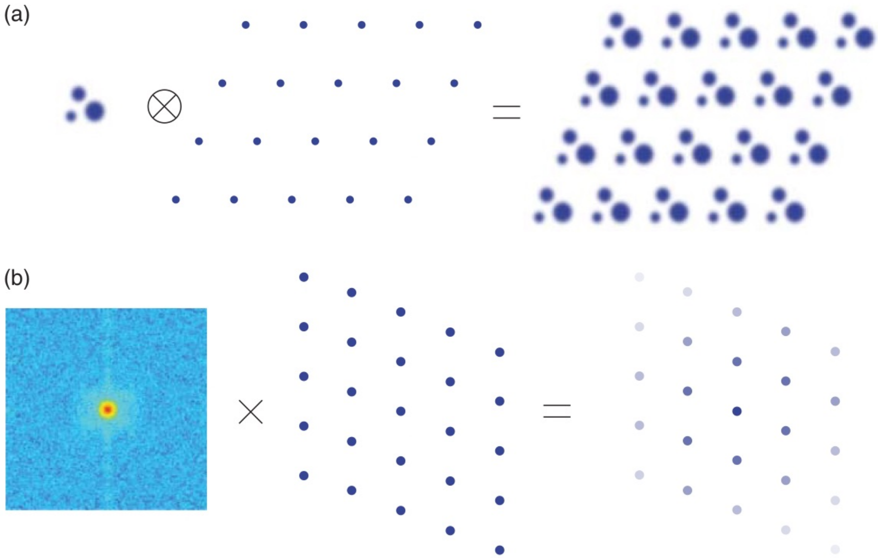


Figure 6.18 Diffraction-pattern intensities explained using the convolution theorem. (a) An infinite crystal can be thought of as the convolution of the electronic distribution within the unit cell with the Bravais lattice. (b) Using the convolution theorem, it becomes apparent that the diffraction pattern is the product of the FT of the electronic distribution in the unit cell (called the 'structure factor') and the FT of the Bravais lattice, which, like the Bravais lattice itself, is another infinite 3D comb function (see text).

Let's go back to our original discussion

$$\rho(r) = \sum_i \rho_a(r - R_i) \Rightarrow$$

$$F(q) = \underbrace{\int d^3\bar{r}\; e^{-iqr}}_{w(q)} \sum_i \underset{f(q)}{\rho_a(r - R_i)}$$

Now notice if $q = k - k'$ is not an element of G (recipr. latt.) $\Rightarrow w = 0$! if however $\bar{q} = \bar{G}$ then $e^{-iG\cdot R_i} = 1 \Rightarrow w \to \infty$

$$w(q) = \sum_{l,m,n} e^{-i\bar{q}(\bar{a}_1 l + \bar{a}_2 m + \bar{a}_3 n)} =$$

$$= N \sum_G \delta_{q,G}$$ or by using Poisson summation

$$= \sum_{K,L,M} (2\pi)^3 \delta(2\pi K - \bar{q}\cdot\bar{a}_1)\,\delta(2\pi L - \bar{q}\cdot\bar{a}_2)\,\delta(2\pi M - \bar{q}\cdot\bar{a}_3) = \frac{1}{a_1\cdot(a_2\times a_3)} \sum_G (2\pi)^3 \delta^3(q - G)$$

finally

$$\boxed{F(q) = f(q)\,\frac{(2\pi)^3}{V} \sum_G \delta^3(\bar{q} - \bar{G})}$$

How scattering pattern depends on # of scatterers?

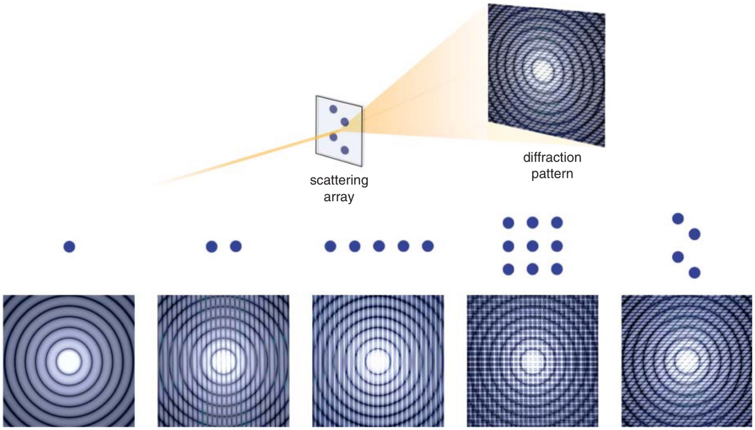
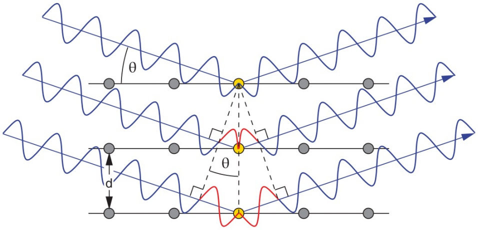


Figure 6.9 Diffraction from regular one-, and two-dimensional arrays of scatterers. The diffraction maxima become

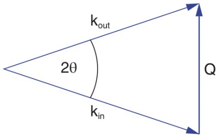
Simple view of diffraction - optics like

Scattering Techniques 2



$$\Longleftarrow \boxed{n\lambda = 2d\sin\theta}$$

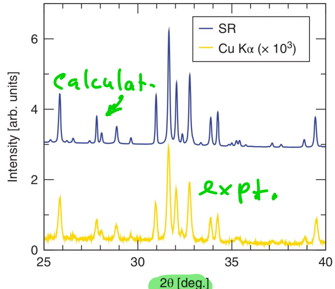
integer # of λs into the optical path difference results in interference



if we express: $\lambda = hc/E$

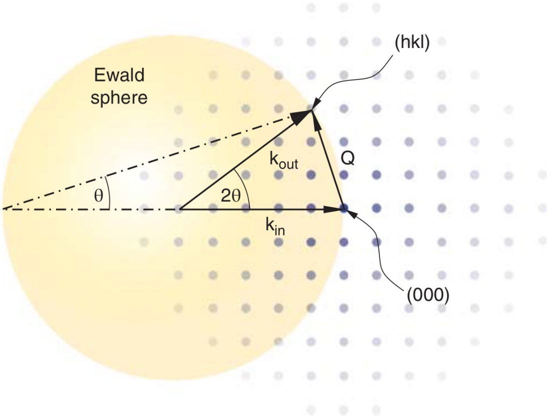
$$\Rightarrow \sin\theta_{hkl} = \frac{6.1998}{d_{hkl}\,[\text{Å}]\;E\,(\text{keV})}$$

$d_{hkl} \equiv$ Spacing between scatt. planes



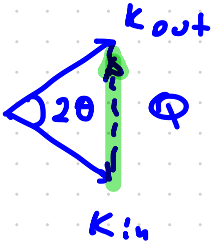
$Ca_2(PO_4)_3$ with Lab Cu Kα source

Ewalds construction in reciprocal space



- when you use random E_{in}, k_{in}, θ you see no scattered intensity. X-ray scatter off with random phases $F(q) = 0$.

- if $\Delta k = q = G$, i.e. the k_{in} ends in (000) and k_{out} ends in the site of the reciprocal lattice G → diffraction maximum.



$$Q = 2|k|\sin\theta = \frac{4\pi}{\lambda}\sin\theta \Rightarrow$$

$$m\lambda = 2d\sin\theta$$

$$\Rightarrow$$

$$|Q|_{hkl} = \frac{2\pi}{d_{hkl}}$$

which is independent on incoming energy!

But it all was about lattice symmetry what's the role of basis? (atoms?)

Periodic functions and Geometric structure factor.

A generalization of multiply periotic function:

$$\rho(r+R_n)=\rho(r)$$

where $\rho(r)=\sum_{R_n}\sum_{\alpha=0}^{s-1}\delta(r-R_n-\tau_\alpha)$

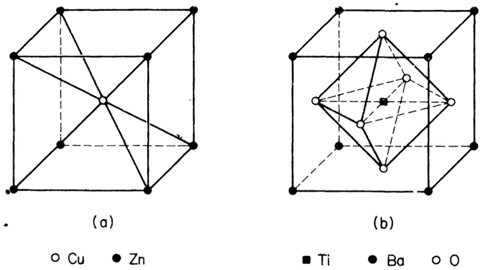
e.g. for Cu-Zn alloy we take $\tau_0=0$ to be the coordinate of Cu atom (in bcc cubic) and $\tau=\frac{1}{2}a(1,1,1)$ for Z atoms

or for $BaTiO_3$ - the most famous ferroelectric

Ti => $\tau_0=0$, Ba $\tau_1=\frac{1}{2}a(1\ 1\ 1)$

and O $\tau_2=\frac{1}{2}a(1,0,0)$

β-brass = Cu-Zn alloy


(a) (b)

$BaTiO_3$ perovskite

Based on the result

$$F(q) = \underline{w(q)} \cdot f(q)$$

we can say that BZ faces are bounded by planes whose M.I. are such that

$$w(q) \neq 0$$

e.g. Consider f.c.c cubic structure with 4 base atoms:

Atoms located at $\tau_0 = (0\ 0\ 0)$

$\tau_1 = a(1/2\ \ 1/2\ \ 0)$

$\tau_2 = a(0\ \ 1/2\ \ 1/2)$

$\tau_3\ a(\frac{1}{2}\ \ 0\ \ 1/2)$

From this $w(q)$ or often labeled as $S(q)$:

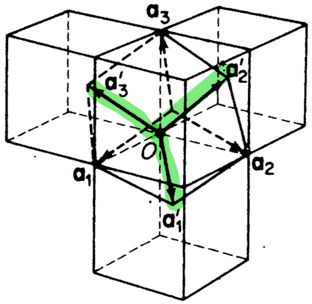
$$\frac{1}{\#\text{atoms within u.c.}} \sum_{m=0}^{3} e^{-i G \cdot \tau_m}$$ where

$$\bar{G} = \sum n_i \vec{b}_i \quad \text{and} \quad b_i \cdot a_j = 2\pi \delta_{ij}$$

for b.c.c .

$$a_1' = \frac{1}{2} a \ (1 \ 1 \ -1)$$
$$a_2' = \frac{1}{2} a \ (-1 \ 1 \ 1)$$
$$a_3' = \frac{1}{2} a \ (1 \ -1 \ 1)$$

[atomic coordinates are expressed as fraction of basis vectors]



1 atom per u.c. with a_i' :

primitive vectors:

From this set of a_i' we can generate the set of reciprocal vectors b_i :

$$b_i \cdot a_j' = 2\pi \delta_{ij} \Rightarrow b_i = \frac{2\pi \,(a_j' \times a_k')}{\underbrace{a_1' \cdot (a_2' \times a_3')}_{= 1/2\, a^3}}$$

$i, j, k = 1, 2, 3$

or $$\bar{b}_1 = \frac{2\pi\,(a_2' \times a_3')}{1/2\, a^3} = \frac{2\pi}{a} \left(1/2 \ \ 1/2 \ \ 0\right)$$

$$\bar{b}_2 = \frac{2\pi}{a} \left(0 \ \ 1/2 \ \ 1/2\right)$$

$$\bar{b}_3 = \frac{2\pi}{a} \left(\frac{1}{2} \ \ 0 \ \ \frac{1}{2}\right)$$

$$\bar{g} = \sum_i n_i \bar{b}_i \Rightarrow g \cdot \tau = \left(n_1 \bar{b}_1 + n_2 \bar{b}_2 + n_3 \bar{b}_3\right)$$
$$\left(\bar{\tau}_0 + \bar{\tau}_2 + \bar{\tau}_3 + \bar{\tau}_4\right) \Rightarrow$$

Now recall:
very generally

ATOMIC coordinates

$$\tilde{\tau}_m = x_m \bar{a}_1 + y_m \bar{a}_2 + z_m \bar{a}_3$$
$$= (x_m, y_m, z_m)$$

Reciprocal Lattice vectors:
RLV

$$G = h\bar{b}_1 + k\bar{b}_2 + l\bar{b}_3 = (h, k, l)$$

$$\Rightarrow \quad G \cdot \tilde{\tau}_m = h x_m + k y_m + l z_m$$

and hence

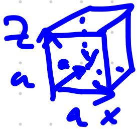
$$F(h, k, l) = \sum_{m \text{ atoms}} f_m e^{2\pi i G \cdot \tilde{\tau}_m}$$

$$= \sum_{\substack{m \\ \text{atoms}}} f_m e^{2\pi i (h x_m + k y_m + l z_m)}$$

Let's practice:

Cubic lattice - simple:

basis : $a_1 = a x \quad d_2 = a y \quad a_3 = a z$



Let's assume we have 2 basis atoms

$f_A \quad \tau_1 = (0,0,0)$

$f_B \quad \tau_2 = (x,y,z)$

Calculate

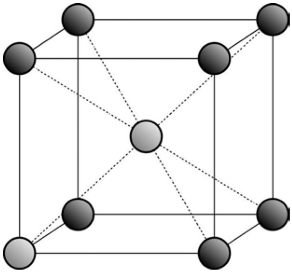
$F(hkl) =$

BCC with 2 basis atoms

$\tau_1 = (0, 0, 0)$ $\quad f_1 = f$

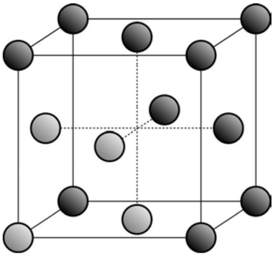
$\tau_2 = (1/2 \ 1/2 \ 1/2)$ $\quad f_2 = f$

$F(hkl) = \dots ?$



FCC with 4 atoms basis

τ_1 $(0, 0, 0)$
τ_2 $(0\ \ 1/2\ \ 1/2)$
τ_3 $(1/2\ \ 0\ \ 1/2)$
τ_4 $(1/2\ \ 1/2\ \ 0)$



$F(h\,k\,l) =$

Summary:

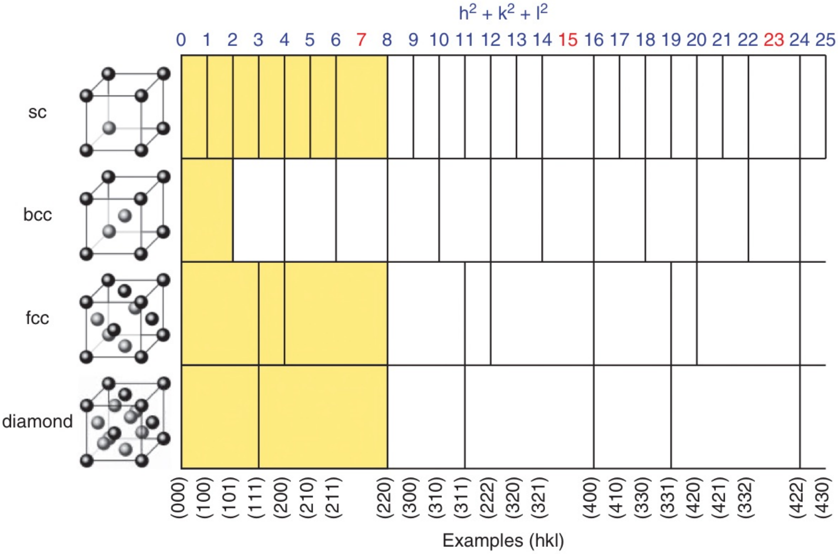
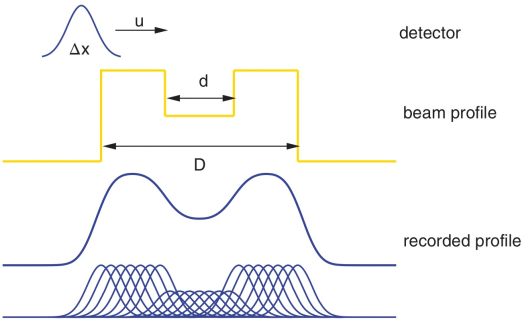


Figure 6.13 Allowed reflections as a function $h^2 + k^2 + l^2$ for the four unit cell types simple cubic (sc), body–centred cubic (bcc), face-centred cubic (fcc), and diamond. Notice that no reflections exist even in principle if $h^2 + k^2 + l^2 = 8m - 1$, where m is an integer greater or equal to unity (shown here in red font). The repeat pattern unit for each cell type is highlighted in yellow.

Convolution theorem

$c(u) = f(x) \otimes g(x) = \int f(x)\, g(u-x)\, dx$, also

$$f(x) \otimes g(x) \longleftrightarrow F(k)\, G(k)$$



f a signal resulting from the convolution of a top hat x-ray beam profile of

Allowed list of $h^2 + k^2 + l^2$ for cubic crystals

Forbidden numbers	Primitive, P	Face Centered, F	Body Centered, I	Corresponding *hkl*
	1			*100*
	2		2	*110*
	3	3		*111*
	4	4	4	*200*
	5			*210*
	6		6	*211*
7				
	8	8	8	*220*
	9			*221, 300*
	10		10	*310*
	11	11		*311*
	12	12	12	*222*
	13			*320*
	14		14	*321*
15				
	16	16	16	*400*

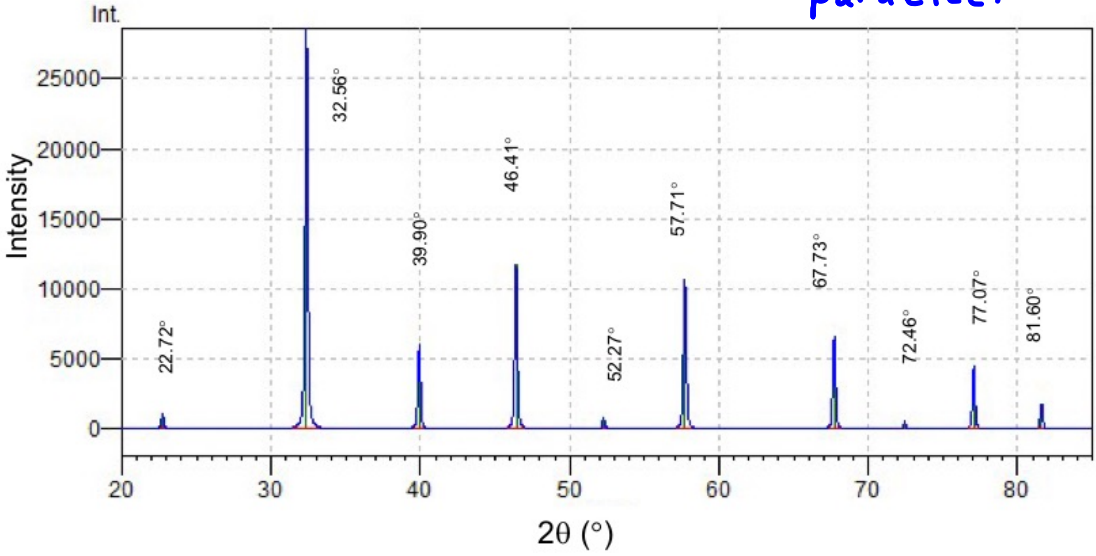
If the observed $\sin^2(\theta)$ follows in a ratio of 1, 2,3,4,5,6, 8, …, then the unit cell is likely *primitive cubic*.

-the common factor is $\lambda^2/4a^2$

Let's do real "experiment".

Indexing Example – $SrTiO_3$

perovskite
Quantum
paraelectric



Using Bragg's Law, $\lambda = 2d_{hkl}\sin\theta$

Peak #	2θ (°)	θ (°)	d (Å)
1	22.72	11.36	3.910
2	32.56	16.28	2.765
3	39.90	19.95	2.257
4	46.41	23.20	1.955
5	52.27	26.14	1.749
6	57.71	28.36	1.596
7	67.73	33.86	1.382
8	72.46	36.23	1.303
9	77.07	38.54	1.236
10	81.60	40.80	1.179

Look for a common factor, *Z*, which can be divided into each value to give an integer quotient. Let *Z* = 0.0654 in this example.

Peak #	2θ (°)	θ (°)	d (Å)	$1/d^2$	$(1/d^2)/Z$
1	22.72	11.36	3.910	0.0654	1
2	32.56	16.28	2.765	0.1308	2
3	39.90	19.95	2.257	0.1963	3
4	46.41	23.20	1.955	0.2616	4
5	52.27	26.14	1.749	0.3269	5
6	57.71	28.85	1.596	0.3926	6
7	67.73	33.86	1.382	0.5236	8
8	72.46	36.23	1.303	0.5917	9
9	77.07	38.54	1.236	0.6546	10
10	81.60	40.80	1.179	0.7194	11

$$\sin^2\theta_{hkl} = \left(\frac{n\lambda}{2d}\right)^2 (h^2 + k^2 + \ell^2)$$

Note that in this example, we obtain all integers and all the quotients are integers that indicate a primitive unit cell.

Assignment of Miller indices

Peak #	2θ (°)	θ (°)	d (Å)	$1/d^2$	$(1/d^2)/Z$	h	k	l
1	22.72	11.36	3.910	0.0654	1	1	0	0
2	32.56	16.28	2.765	0.1308	2	1	1	0
3	39.90	19.95	2.257	0.1963	3	1	1	1
4	46.41	23.20	1.955	0.2616	4	2	0	0
5	52.27	26.14	1.749	0.3269	5	2	1	0
6	57.71	28.85	1.596	0.3926	6	2	1	1
7	67.73	33.86	1.382	0.5236	8	2	2	0
8	72.46	36.23	1.303	0.5917	9^*	3 2	0 2	0 1
9	77.07	38.54	1.236	0.6546	10	3	1	0
10	81.60	40.80	1.179	0.7194	11	3	1	1

The (300) and (221) peaks fall at the same location, both give $h^2 + k^2 + l^2 = 9$.

$$\lambda = \frac{2a\sin(\theta)}{\sqrt{(h^2 + k^2 + l^2)}}$$

The lattice parameter, *a*, is 3.91 Å

Diffraction of electrons

1927 Davisson & Germer showed e^- also diffract.

Now you know that brightness of the Bragg spots is defined by the number of factors, e.g.

X-ray : electron density at the lattice sites

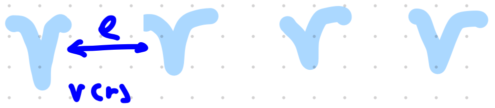
e^- beam : potential energy of e^- in the field of the lattice of atoms.

+ T of xtal and roughness of surface

and of course the geometrical structure factor $S(q)$

Electron scattering form factor

$V(r) = V(r + l)$



periodic potential v

$$V(r) = \sum_{n,\alpha} v_\alpha (r - R_n - \tau_\alpha)$$

basis atoms

lattice sites

we can measure $\sigma(\theta, \varphi)$ given by the scattering rate into the interval $dk' = k'^2 dk' \sin\theta \, d\theta \, d\varphi$ per unit of time

According to the Fermi Golden rule 2

$$R_{k\to k'} = \frac{2\pi}{\hbar} \sum_{k'} \left|\langle k'|V|k\rangle\right|^2 \delta(E_{k'}-E_k)$$

$\uparrow$ summed over the final state momenta

Now let's introduce the beam energy per e^- $E = \frac{\hbar^2 k^2}{2m}$ and assuming that $k' = k$ and $d\Omega = \sin\theta\, d\theta\, d\varphi$ we can write down:

$$\sigma(\theta,\varphi)\, dE\, d\Omega = \frac{2\pi}{\hbar} \frac{|\langle k'|V|k\rangle|^2}{v_k} \cdot \frac{1}{(2\pi)^3} \cdot k'^2\, dk' \overbrace{\sin\theta\, d\theta\, d\varphi}^{d\Omega}$$

$$\left(dE = \frac{\hbar^2 k' dk'}{2m} \right)$$

$$= \frac{2\pi}{\hbar} \frac{|\langle k'|V|k\rangle|^2}{v_k} \cdot \frac{m k'}{(8\pi^3\hbar^2)} dE\, d\Omega$$

Consider

$$\langle k'|V|k\rangle = \frac{1}{V}\int dr\, e^{-ik'r}\, V(r)\, e^{+ikr} =$$

$$= \frac{1}{V}\int dr\, e^{-i(k'-k)r} \cdot \sum_{n,\alpha} (r - R_n - \tau_\alpha)$$

$$= \sum_\alpha S_\alpha(q) \cdot W(q) \quad \text{with } q = k - k'$$

$\uparrow$ geometric structure factor

where $w(q)$ as for x-rays

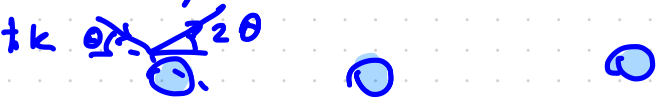
$$= \frac{1}{V_0} \int dr\, e^{-iqr}\, v(r)$$

volume of xtal

is F.T. of the atomic potential

So for electrons

e.g. if a free e^- scatters off



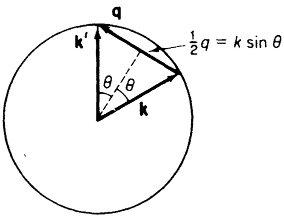


Figure 2.7 Geometry for elastic electron scattering.

$$v(r) = \begin{cases} -U & r \le R \\ 0 & r > R \end{cases}$$

$$v(q) = \frac{1}{V_0} \int dr\, e^{iqr}\, v(r) =$$

$$= -\frac{4\pi U}{V_0} \int_0^R \frac{\sin qr}{qr}\, r^2\, dr$$

$$= -\frac{4\pi U}{V_0 q^3} (\sin qR - qR \cos qR))$$

where $q = 2k \sin\theta = \frac{4\pi \sin\theta}{\lambda}$

THE END OF Lecture