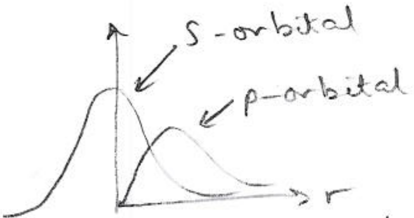
2.10 Structure factor of an atom. $n(r) = |\psi(r)|^2$

$$f_G = \int n_{Atom}(\vec{r})\, e^{i\vec{G}.\vec{r}}\, d^3\vec{r}$$



Most of the density of an atom is unchanged when it is built into a crystal, so the functions f_G can be tabulated from theory.

Atoms are spherically symmetric; so are f_G's.

To a first approximation, consider atoms to be point-like, then: [units are "electrons"].

$f_G \triangleq Z$, constant = atomic number
independent of $\vec{G}$, same everywhere.

2.11 Structure factor of multi-atom basis.

If atoms are considered to be points, the structure factor integral becomes a sum:

$$S_G = \sum_{j \in \text{Unit Cell}} f_j\, e^{i\vec{G}.\vec{r}_j}$$

The relative phases of different points in the unit cell can lead to cancellations, so some of the structure factor values = 0.

Extinctions, systematic absences, etc

Selection Rules allow us to identify different kinds of lattice.

2.12 Example : FCC selection rules.

We have two ways of seeing that the reciprocal lattice of fcc is bcc:

- direct evaluation using primitive lattice (HW)
- conventional (cartesian) unit cell + basis.

FCC has four lattice points / conventional cell:

$$0\,0\,0,\quad \tfrac{a}{2}\,\tfrac{a}{2}\,0,\quad \tfrac{a}{2}\,0\,\tfrac{a}{2},\quad 0\,\tfrac{a}{2}\,\tfrac{a}{2},\quad = \vec{r}_j$$

Reciprocal Lattice is also simple cubic:

$\vec{G} = \frac{2\pi}{a}(h, k, l)$, also Cartesian.

$$S_G = \sum_1^4 \underset{\nwarrow f=1 \text{ for simplicity.}}{1}\, e^{i\vec{G}.\vec{r}_j} = 1 + e^{\pi i(h+k)} + e^{\pi i(h+l)} + e^{\pi i(k+l)}$$

since $e^{i\pi} = -1$, this sum is real:

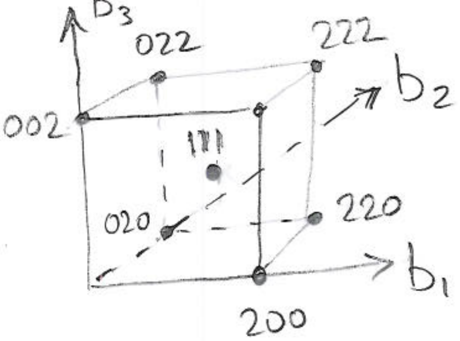
$$S_G = 1 + (-1)^{h+k} + (-1)^{h+l} + (-1)^{k+l}$$

this is symmetric in permutations of h, k, l

$S_G = 4$ hkl all even or all odd.

$ = 0$ otherwise. $\longrightarrow$ FCC selection rules

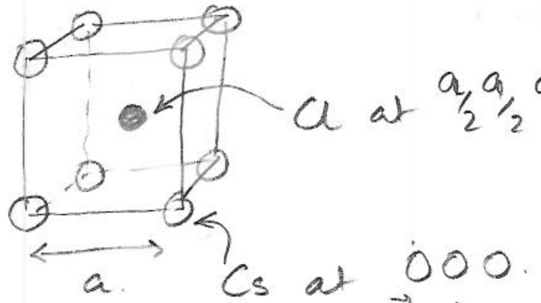
hkl	S_G	$h^2+k^2+l^2$
100	0	1
110	0	2
111	4	3
200	4	4
210	0	5
211	0	6
220	4	8
221	0	9
300	0	9
310	0	10
311	4	11
222	4	12



Selection rules map onto bcc lattice!

15.01.08
16.01.07
17.01.06

Second example: CsCl lattice
Simple cubic with chemical basis.



$$\vec{G} = \frac{2\pi}{a}(h,k,l)$$

$$S_G = \sum_{cell} f_j e^{i\vec{G}\cdot\vec{r}_j} = f_{Cs} e^{i0} + f_{Cl} e^{i\pi(h+k+l)}$$

$$= f_{Cs} + f_{Cl}(-1)^{h+k+l}$$

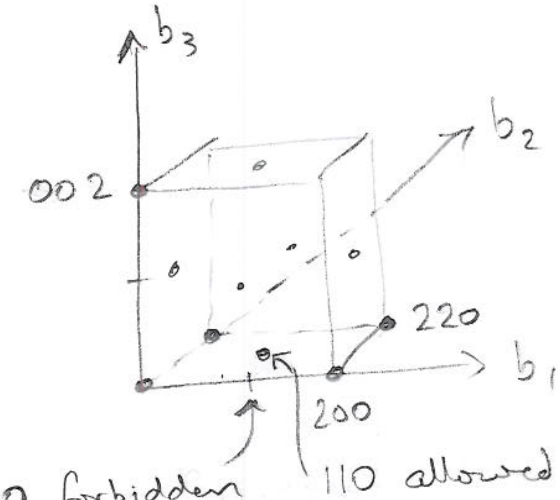
All reflections are allowed, but intensity varies:

hkl	$h^2+k^2+l^2$	S_G
100	1	$f_{Cs}-f_{Cl}$
110	2	$f_{Cs}+f_{Cl}$ ←
111	3	$f_{Cs}-f_{Cc}$
200	4	+ ←
210	5	−

Big ones at BCC positions.

Put $f_{Cs} = f_{Cl}$ to convert lattice to BCC:

100 etc vanish
110 etc remain.



BCC selection rules:
"even parity"
"all even or two odds"

FCC selection rules
"all even or all odd"

See that recip lattice of BCC is FCC!

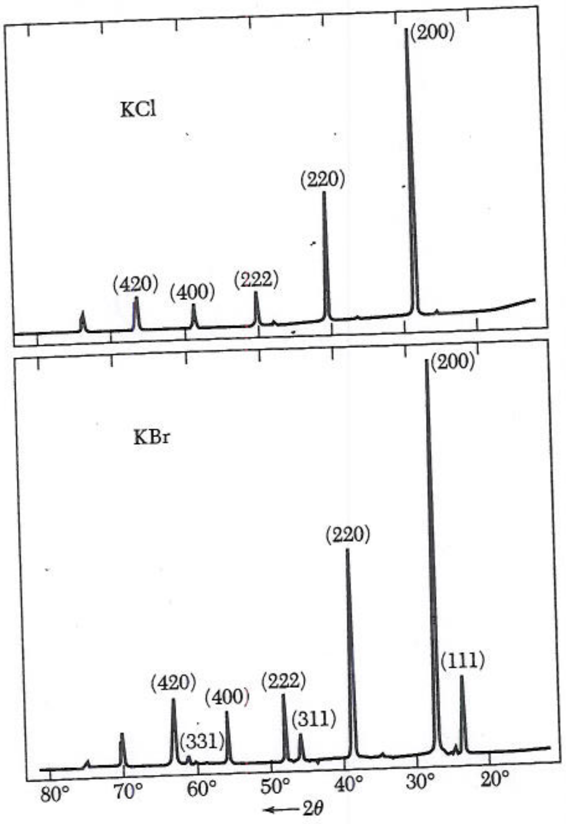


Figure 17 Comparison of x-ray reflections from KCl and KBr powders. In KCl the numbers of electrons of K^+ and Cl^- ions are equal. The scattering amplitudes $f(K^+)$ and $f(Cl^-)$ are almost exactly equal, so that the crystal looks to x-rays as if it were a monatomic simple cubic lattice of lattice constant $a/2$. Only even integers occur in the reflection indices when these are based on a cubic lattice of lattice constant a. In KBr the form factor of Br^- is quite different to that of K^+, and all reflections of the fcc lattice are present. (Courtesy of R. van Nordstrand.)

after integration over $d(\cos\alpha)$ between -1 and 1. Thus the form factor is given by

$$f_j = 4\pi \int dr\, n_j(r) r^2 \frac{\sin Gr}{Gr} \ . \tag{50}$$

If the same total electron density were concentrated at $r = 0$, only $Gr = 0$ would contribute to the integrand. In this limit $(\sin Gr)/Gr = 1$, and

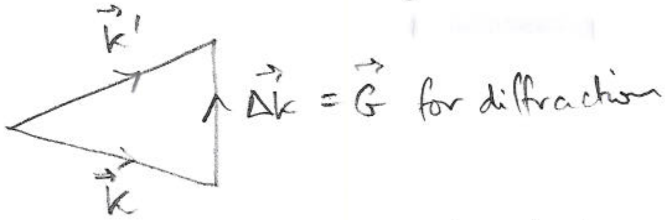
$$f_j = 4\pi \int dr\, n_j(r) r^2 = Z \ , \tag{51}$$

the number of atomic electrons. Therefore f is the ratio of the radiation amplitude scattered by the actual electron distribution in an atom to that scattered by one electron localized at a point. In the forward direction $G = 0$, and f reduces again to the value Z.

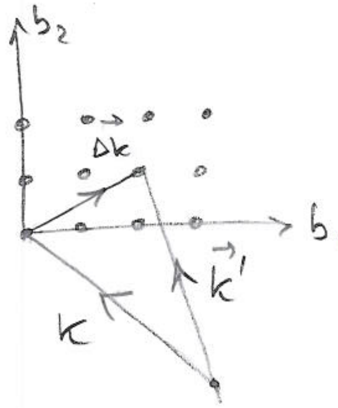
The overall electron distribution in a solid as seen in x-ray diffraction is fairly close to that of the appropriate free atoms. This statement does not mean that the outermost or valence electrons are not redistributed somewhat in forming the solid; it means only that the x-ray reflection intensities are represented well by the free atom values of the form factors and are not very sensitive to small redistributions of the electrons.

2.13 Ewald construction : Diffractometer.

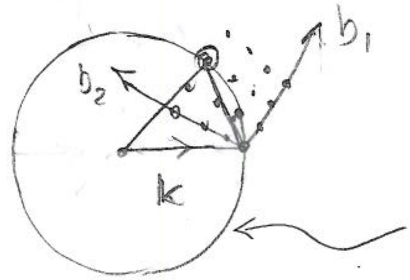
Elastic scattering can always be represented by an isosceles triangle:



i) superimpose over recip. Latt. to set up diffraction condition for single crystal : many choices.



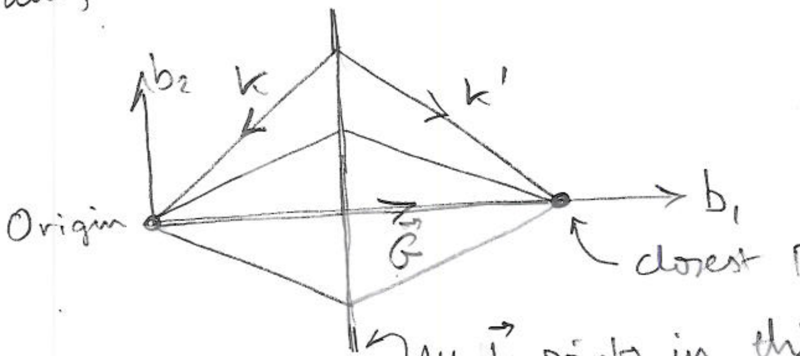
ii) fix direction of $\vec{k}$ and consider all possible $\vec{k}'$s that could arise : sphere of directions, all with length $|k|$ = radius of sphere.



Rotate crystal → rotate recip lattice until one of its points falls on Ewald sphere

2.14 Zone Boundary.

Consider region near origin of reciprocal space. How small a $\vec{k}$ vector can give any diffraction at all, whatever its direction?



closest point of recip lattice

All $\vec{k}$ points in this plane represent waves that diffract.

Minimum $|k|$ is $\frac{1}{2}|G|$

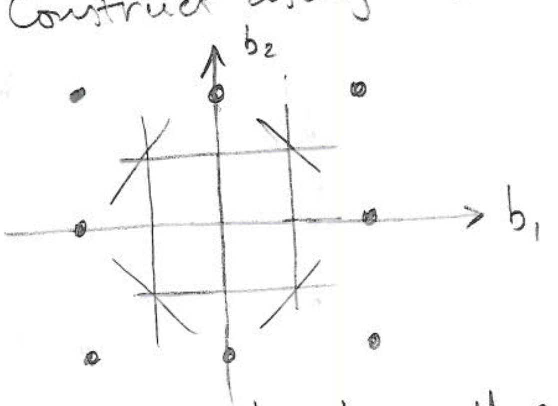
Any waves with $|k| < k_{min}$ will never experience diffraction.

2.15 Brillouin Zones.

Electrons will be represented as waves, $\vec{k}$, within the crystal, and we will study their properties.
Small-k electrons travel freely. When accelerated they <u>will</u> hit ZB.
Larger k's will be diffracted by the crystal.

The space around the origin in which these waves can run free is called the:
First Brillouin Zone.

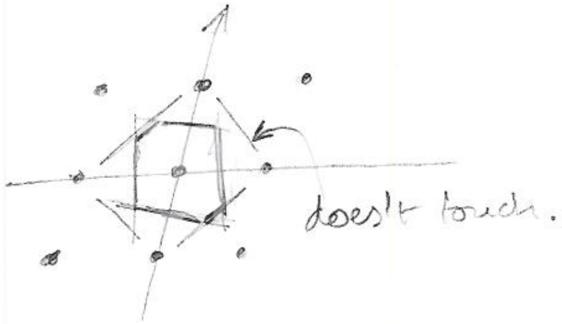
Construct using bisectors of all $\vec{G}$'s



1st BZ is a square for the square lattice.

- It is easy to show that the 1st BZ has the same volume as the primitive unit cell (recip space)
- It is also the most symmetric choice for the primitive unit cell
- Works in real-space also, called Wigner-Seitz cell.
- Keeping symmetry of the lattice, we can define higher order BZ's by assembling fragments cut off by 1 bisector → 2nd BZ.
  2 bisectors → 3rd BZ

All have the same volume = Vrecip



SECTION B

7. State the assumptions that lie behind Bragg's law, $2d \sin\theta = \lambda$ that relates the angle of incidence, θ, of an X-ray beam of wavelength λ onto planes of a crystal spaced distance d apart which gives rise to a strong diffraction peak. We will now consider the reciprocal space view of Bragg's law. **[2]**

   Draw a detailed diagram showing the positions of the atoms in a crystal of Nickel which is known to have the face-centred cubic (fcc) structure with lattice parameter, a_0. Label the axes along the edges of the conventional cubic unit cell and list the coordinates of all the atoms within the cell. Explain the how the structure is decomposed into a lattice and a basis, following the cubic convention. **[5]**

   What is the reciprocal lattice of this cubic lattice? Draw a sketch of the reciprocal lattice and label the points according to their Miller indices. Which lattice points correspond to allowed reflections and which are disallowed by the fcc structure? What is the length of the general (hkl) reciprocal lattice vector. Show, with the aid of a sketch, which lattice planes in the crystal correspond to the (111) reciprocal lattice point. **[9]**

   Draw a vector diagram showing how to construct the directions of the incident and exit X-ray beams that correspond to diffraction from the (hkl) reciprocal lattice point. Hence derive an expression for the length of the reciprocal lattice vector and the angle between these two beams, which we will call γ. In an experiment using X-rays of wavevector $k = 40.8\ nm^{-1}$, a powdered Nickel sample is found to produce it's first three diffraction peaks at angles, $\gamma = 45.4°, 52.8°$ and $78.0°$. What are the corresponding lengths of the reciprocal lattice vectors? Demonstrate that these are consistent with an fcc structure and deduce the lattice constant, a_0. **[8]**

8. Justify the use of the Lennard-Jones (LJ) potential function to model the interaction potential between two atoms of inert gas separated by a distance, R,

$$U(R) = 4\epsilon \left[\left(\frac{\sigma}{R}\right)^{12} - \left(\frac{\sigma}{R}\right)^{6} \right].$$

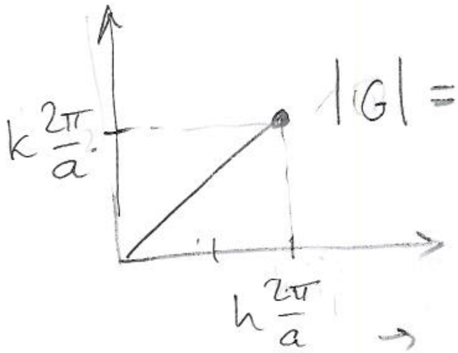
   What is the meaning assigned to the parameters σ and ϵ? **[6]**

   All the inert gases (except Helium) crystallise in the face-centred cubic (fcc) structure. Write down an expression for the cohesive energy of an inert gas solid using the LJ potential. At low temperatures, you can consider this to be purely potential energy. You may use the numerical evaluations of the lattice sums, $P_6 = 14.45392$ and $P_{12} = 12.13188$, which are defined as $P_n = \Sigma_j p_j^{-n}$, where p_j is the distance of the j'th site from the origin of the fcc lattice in units of the nearest-neighbour distance, summed over the entire lattice. **[10]**

(21a)

Worked escample: typical escam problem.
(was not very clear before). 2006 exam Q7

Length of general (hkl) recip lattice vector:

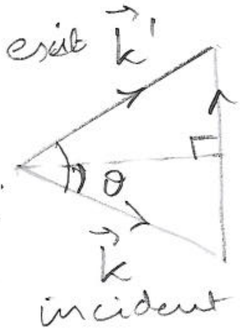


$$|G| = \frac{2\pi}{a}\left(h^2+k^2+l^2\right)^{1/2}$$

a ← lattice param.

Laue condition $\vec{\Delta k} = \vec{G}$ for diffraction

$\gamma = 2\theta.$



$\vec{\Delta k} = \vec{k}' - \vec{k}$ momentum transfer.

$|\Delta k| = 2k \sin\theta$ $\quad k = \frac{2\pi}{\lambda}$

↖ $|G|$. $\quad = 40.8\ \mathrm{nm}^{-1}$

Table of angles

$\gamma = 2\theta$	$\lvert G\rvert = 2k\sin\frac{\gamma}{2}$	÷ smallest. $\lvert G\rvert^2$	ratio	
45.4	31.5 nm^{-1}	1	3	111
52.8	36.3 nm^{-1}	1.33	4	200
78.0	51.4 nm^{-1}	2.66	8	220

The ratio $\propto h^2+k^2+l^2 \Rightarrow 111, 200, 220$

This is the pattern for FCC: all even or all odd.

Any of them would give the lattice const:

$111: \quad |G| = \frac{2\pi}{a}\sqrt{3} = 31.5\ \mathrm{nm}^{-1}$

$$a = \frac{2\pi}{31.5}\sqrt{3} = \underline{0.345\ \mathrm{nm}}$$

21.01.08.