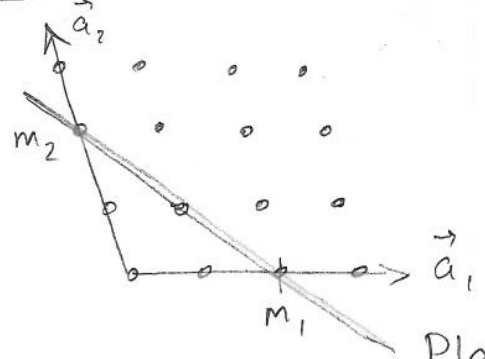


2.1 Lattice Planes

The Miller Index system is used to identify planes within a lattice. Works in 3D, but we consider 2D.



Intercepts are m_1, m_2, m_3
 Indices are $\frac{1}{m_1}, \frac{1}{m_2}, \frac{1}{m_3}$

Plane of lattice points.

The Miller indices are the integer ratios of these reciprocals. The example above:

| | | |
|----------------|-------------------------------|---------------|
| $m_1 = 2$ | $\frac{1}{m_1} = \frac{1}{2}$ | } (110) Plane |
| $m_2 = 2$ | $\frac{1}{m_2} = \frac{1}{2}$ | |
| $m_3 = \infty$ | $\frac{1}{m_3} = 0$ | |

↑ parentheses

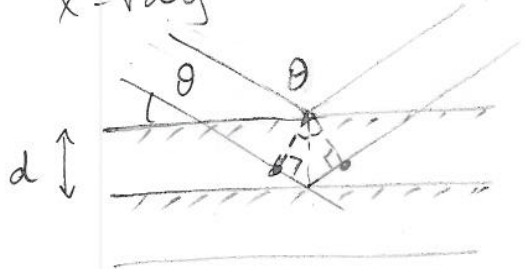
In general (hkl) are the Miller indices.

We will develop a much better way of deriving the indices using the reciprocal lattice.

10.01.2006 {hkl} set of planes [hkl] direction <hkl> set of dir.

2.2 Bragg's Law. → UCL (1915-25) Quain Professor.

In 1915 W.L. Bragg published a very simple picture of the interference effects seen in X-ray diffraction, applies also to neutrons & electrons. X-ray = e.m. wave with $\lambda \sim \text{\AA}$, similar to spacings.



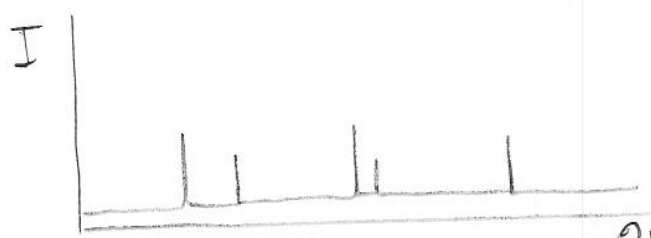
} Planes of atoms on lattice
 - assumed to be featureless mirrors for X-rays.

$$\text{Path difference} = 2d \sin \theta = (\text{integer}) \lambda$$

is the condition for constructive interference.

This simple picture can take us very far. We can figure the plane separation directly from the lattice and so determine the angles θ_{Bragg} that will diffract X-rays.

Most angles do not correspond to a plane spacing, so there are only a few sharp peaks in the powder (random sample orientation) diffraction pattern:



Bragg showed how to go from these data to structure.

$2\theta_{\text{Bragg}}$

2.3 Reciprocal Lattice.

Much more powerful way to see the origin of the diffraction effects, invented by M.V. Lave. Purely mathematical construction:

$$\vec{T} = u_1 \vec{a}_1 + u_2 \vec{a}_2 + u_3 \vec{a}_3 \quad \text{lattice}$$

$$\vec{G} = v_1 \vec{b}_1 + v_2 \vec{b}_2 + v_3 \vec{b}_3 \quad \text{reciprocal lattice}$$

the b 's are a second set of non-coplanar vectors the v 's are all possible integers.

We require $\vec{T} \cdot \vec{G} = 2\pi(\text{integer})$, so $e^{i\vec{T} \cdot \vec{G}} = 1$

[The 2π is arbitrary; crystallographers don't use it]

The solution is:

$$\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{V} \quad \vec{b}_2 = 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{V} \quad \vec{b}_3 = 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{V}$$

$V = a_1 \cdot a_2 \times a_3$ is the unit cell volume. primitive

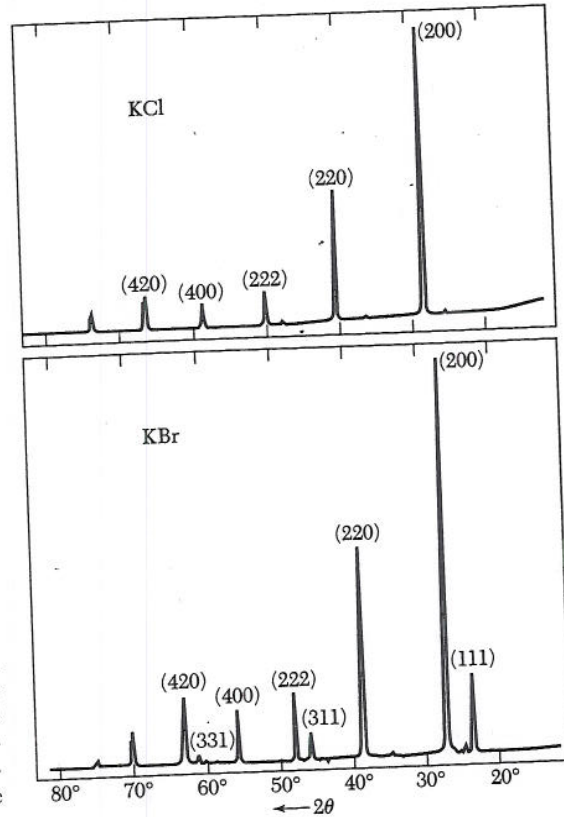


Figure 17 Comparison of x-ray reflections from KCl and KBr powders. In KCl the numbers of electrons of K^+ and Cl^- ions are equal. The scattering amplitudes $f(K^+)$ and $f(Cl^-)$ are almost exactly equal, so that the crystal looks to x-rays as if it were a monatomic simple cubic lattice of lattice 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

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

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

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

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.

Verify by substitution in definition:

$\vec{T} \cdot \vec{G}$ contains 9 terms each multiplied by 2 integers

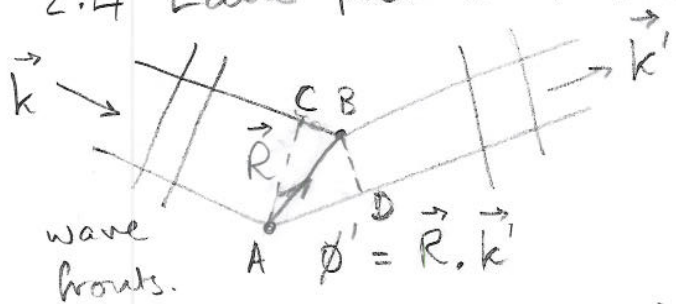
- cross terms: $\vec{b}_1 \cdot \vec{a}_2 \propto \underbrace{a_2 \times a_3 \cdot a_2}_{\text{all zero}}$

- diagonal terms: $\vec{b}_1 \cdot \vec{a}_1 = \frac{2\pi}{V} \underbrace{a_2 \times a_3 \cdot a_1}_{V} = 2\pi$

The total is 2π (big integer)

The orthogonality relation is $\vec{b}_i \cdot \vec{a}_j = 2\pi \delta_{ij}$

2.4 Laue picture of diffraction



construct b_1 as the mutual perp of $\vec{a}_2 \times \vec{a}_3$

i) Incoming e.m. wave is described by its k-vector:

$\psi(\vec{r}) = A e^{i\vec{k} \cdot \vec{r}}$ tells us the 'phase' of the complex wave at all points in space

The wave fronts are planes of constant phase, which are perpendicular to \vec{k} .

ii) Scattering by atoms. A & B is identical. Any

- Any phase shift is the same.
- New amplitude is A'
- elastic scattering. No change of wavelength

$|\vec{k}| = |\vec{k}'| = 2\pi/\lambda$

iii) Outgoing wave in direction \vec{k}' is $\psi'(\vec{r}) = A' e^{i\vec{k}' \cdot \vec{r}}$

iv) Total phase shift:

$\Delta\phi = \phi(AD) - \phi(BC) = \vec{k}' \cdot \vec{R} - \vec{k} \cdot \vec{R}$

$\psi''(\vec{r}) = A e^{i\vec{k}' \cdot \vec{r}} (1 + e^{+i\Delta\vec{k} \cdot \vec{R}} + \dots) = \Delta\vec{k} \cdot \vec{R}$ where $\Delta\vec{k} = \vec{k}' - \vec{k}$

If the sample is a crystal, it is invariant if we move from \vec{r} to $\vec{r} + \vec{T}$.

If A & B are separated by \vec{T} , the scattering will be the same. So $\vec{R} = \vec{T}$.

If phase shift is 2π (integer) we have constructive interference:

$\vec{\Delta k} \cdot \vec{T} = 2\pi$ (integer). Laue condition.

This is satisfied when $\vec{\Delta k} = \vec{G}$ any R.L. vector.

So the whole point of the argument is that the allowed \vec{k}' directions where diffraction occurs are set of discrete points, $\vec{\Delta k} = \vec{G}$

- very restrictive: all 3 components of a vector equation have to be satisfied

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2.5 Equivalence of Bragg and Laue.

i) The points of the recip lattice are the perpendiculars of the planes:

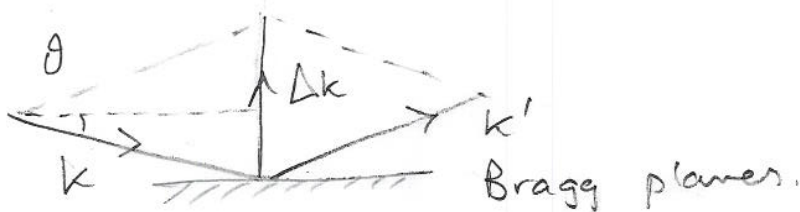
Miller indices $(hkl) = \text{integers } (v_1, v_2, v_3) \text{ in } \vec{G}$

Each vector $\vec{G} = h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3$ points along the perpendicular of the plane (hkl)

The length $|\vec{G}| = 2\pi/d$ $d = \text{Bragg spacing.}$

16.01.06

ii) Since $|\vec{k}| = |\vec{k}'|$, the vector $\vec{\Delta k}$ points in the specular direction:

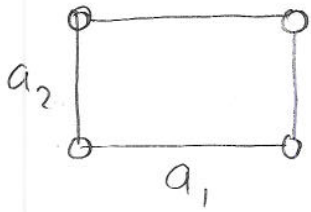


iii) $|\vec{G}| = |\vec{\Delta k}| = 2|k| \sin \theta = 2\pi/d$
(Laue) $\frac{2\pi}{\lambda}$

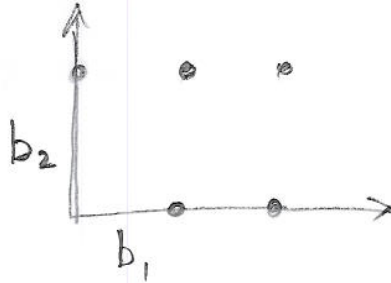
So $2d \sin \theta = \lambda$
which is Bragg's law.

(14a)

Examples of reciprocal lattice:



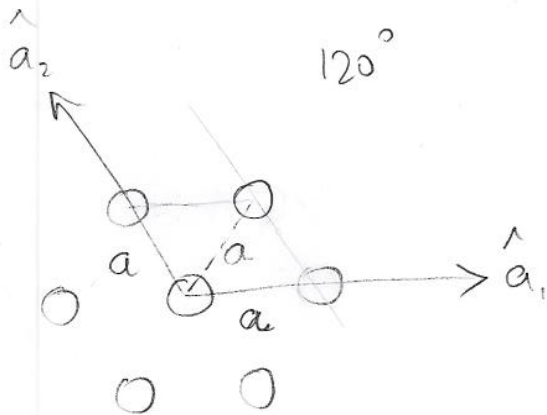
$$a_1 > a_2$$



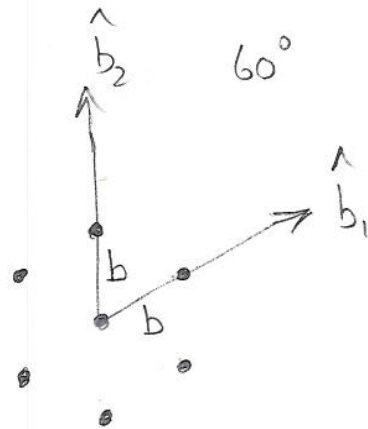
$$b_1 = 2\pi \frac{a_2 \cdot a_3}{a_1 \cdot a_2 \cdot a_3} = \frac{2\pi}{a_1}$$

$$b_2 = 2\pi \frac{a_3 \cdot a_1}{a_1 \cdot a_2 \cdot a_3} = \frac{2\pi}{a_2}$$

$$b_1 < b_2$$



$$|a_1| = |a_2| = a$$



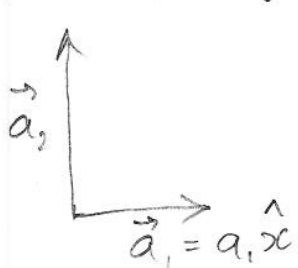
$$b_1 = 2\pi \frac{a \cdot a_3}{(a^2 \frac{\sqrt{3}}{2}) \cdot a_3} = \frac{2\pi}{a} \frac{2}{\sqrt{3}}$$

$$b_2 = \frac{2\pi}{a} \frac{2}{\sqrt{3}} = b_1 = b$$

$$b_3 = 2\pi \frac{(a^2 \frac{\sqrt{3}}{2})}{(a^2 \frac{\sqrt{3}}{2}) a_3} = \frac{2\pi}{a_3}$$

2.6 Examples of recip lattice.

i) 2D rectangular lattice, $\vec{a}_3 \perp$ page. All angles 90°



$$\vec{b}_2 = \frac{2\pi}{a_2} \hat{y}$$

so \cdot and \times products are simple products.

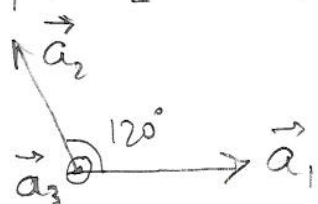
$$\vec{b}_1 = 2\pi \frac{a_2 a_3}{a_1 a_2 a_3} \hat{x} = \frac{2\pi}{a_1} \hat{x} \text{ aligned.}$$

Axis lengths are in $(nm)^{-1}$ and the long direction in real space becomes short in recip

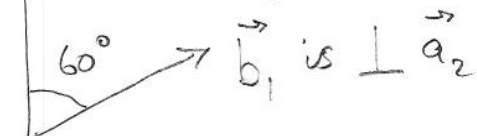
→ Special case of square lattice remains square.

ii) 2D hexagonal lattice, $\vec{a}_3 \perp$ page.

$$a_1 = a_2 \quad \vec{b}_1 = \frac{2\pi}{V} \vec{a}_2 \times \vec{a}_3 \text{ points } 30^\circ \text{ from } \vec{a}_1 \quad \cos 30 = \frac{\sqrt{3}}{2}$$



$$\vec{b}_2 = 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{V} \text{ is } \perp \vec{a}_1$$



$$V = \vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3 = \frac{\sqrt{3}}{2} a_1 a_2 a_3$$

$$\text{so } |\vec{b}_1| = 2\pi \frac{a_2 a_3}{\frac{\sqrt{3}}{2} a_1 a_2 a_3} = \frac{2}{\sqrt{3}} \frac{2\pi}{a_1} \text{ units still } nm^{-1}$$

General rule: direction of \vec{b}_1 always perpendicular to \vec{a}_2 and \vec{a}_3 ; length d $2\pi/a_1$, or $= 2\pi/d$ (100 planes)
Important in cases where the unit cell becomes distorted, as in a phase transition.

iii) 3D fcc lattice

Primitive lattice vectors complicated.

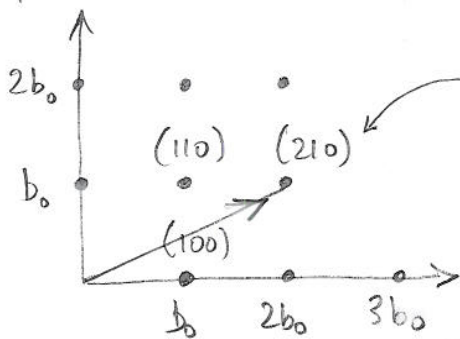
Recip lattice of fcc is bcc. See homework.

→ iv) Reciprocal of reciprocal lattice is orig lattice
Volume of recip lattice cell is $(2\pi)^3/V$.

2.7 Example of diffraction from SC lattice.

Real space lattice parameter = a_0

Reciprocal lattice, also simple cubic, spacing $2\pi/a_0 = b_0$



Miller indices (hkl)

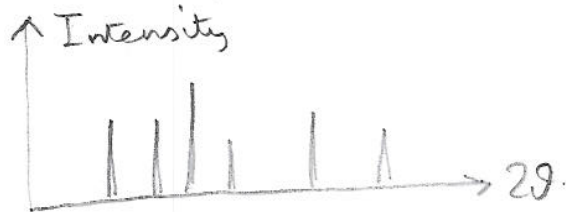
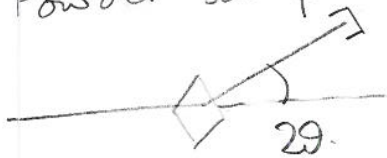
$$\vec{G} = \frac{2\pi}{a_0} (h\hat{x} + k\hat{y} + l\hat{z})$$

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

Allowed values of $|\Delta k| = \frac{2\pi}{a_0} \sqrt{h^2 + k^2 + l^2}$

$|\Delta k| = 2k \sin \theta$, Bragg angle = 2θ

Powder sample (common case) has random orientations



Analysis procedure:

i) read off 2θ values

ii) convert to list of $|\Delta k|^2 = \left(\frac{2\pi}{a_0}\right)^2 (h^2 + k^2 + l^2)$

iii) divide by smallest $|\Delta k|^2$ to factor out a_0

iv) look for simple fractions

Not all peaks will appear:

| hkl | $h^2 + k^2 + l^2$ |
|-----|-------------------|
| 100 | 1 |
| 110 | 2 |
| 111 | 3 |
| 200 | 4 |
| 210 | 5 |
| 211 | 6 |
| 220 | 8 |
| 221 | 9 (degen) |
| 300 | |

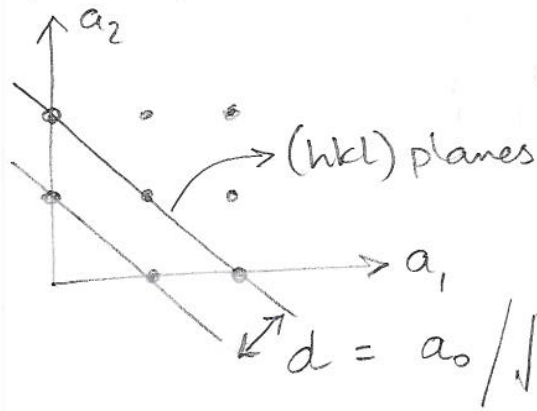
← no 7

As we will see later, pattern of peak spacings becomes rapidly more complicated:

- lower symmetry
- centred lattice
- basis.

(16)

2.8 Real-space view of same problem. (à la Bragg)



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

$$d = \frac{\lambda}{2 \sin \theta}$$

$$d = a_0 / \sqrt{h^2 + k^2 + l^2}$$

Simple formula for cubic lattice.

Analysis procedure:

- i) read off 2θ values
- ii) convert to list of $1/d^2 = 1/a_0^2 (h^2 + k^2 + l^2)$
- iii) divide by smallest $1/d^2$ as before

Method is the same; equally hard for SC case.

Problem is that "spacing formula" is non-trivial for more complicated lattices.

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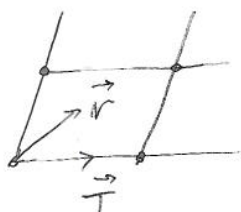
2.9 Lattice with a basis.

So far we only considered the case when $\vec{R} = \vec{T}$ when we considered diffraction.

All points related by lattice vectors \vec{T} have the same phase whenever $\Delta \vec{k} = \vec{G}$, so they interfere constructively.

For points in the basis, within the unit cell, there is a phase shift, so more complicated interference, even when $\Delta \vec{k} = \vec{G}$.

So long as we keep $\Delta \vec{k} = \vec{G}$ condition, we only have to consider one unit cell to handle the general case:



$$\Delta \vec{k} \cdot \vec{T} = 2\pi (\text{integer})$$

$$\Delta \vec{k} \cdot \vec{r} \neq 2\pi (\text{integer})$$

phase factor

(17)

$$\text{Amplitude} = \sum_{\vec{r} \in \text{unit cell}} \text{weight} \times e^{i\vec{G} \cdot \vec{r}}$$

It is electrons that scatter X-rays, so the amplitude is proportional to electron density, $n(\vec{r})$.

$$\tilde{S}_{\vec{G}} = \int_V n(\vec{r}) e^{i\vec{G} \cdot \vec{r}} d^3\vec{r}, \text{ the Structure Factor}$$

This is a precise and completely general description of the electron density of a crystal that captures its periodic property, beyond X-rays. It is the 3D Fourier transform of $n(\vec{r})$:

$$\text{Ampl}(\vec{\Delta k}) = 0 \quad \vec{\Delta k} \neq \vec{G} \quad [\text{for whole crystal}]$$

$$\text{Ampl}(\vec{\Delta k}) = S_{\vec{G}} \quad \vec{\Delta k} = \vec{G}$$

The entire function $n(\vec{r})$ is encoded in a set of discrete complex numbers, $\tilde{S}_{\vec{G}} = \text{Structure Factor}$. Set is large, infinite in general, but simpler details are contained in the first few $S_{\vec{G}}$ values.

It is the 3D analogue of the Fourier series expansion of a periodic wave in 1D.

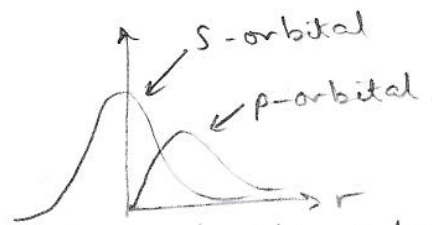


Power of the X-ray diffraction method is that the measured Bragg peak intensities are the (amplitudes)² of the structure factors, so the entire density function, $n(\vec{r})$, can be evaluated.

(18)

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

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



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"].

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

2.11 Structure factor of multi-atom basis.

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

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

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:

$$000, \frac{a}{2} \frac{a}{2} 0, \frac{a}{2} 0 \frac{a}{2}, 0 \frac{a}{2} \frac{a}{2}, = \vec{r}_j$$

Reciprocal Lattice is also simple cubic:

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

$$S_G = \sum_j e^{i\vec{G} \cdot \vec{r}_j} = 1 + e^{i\vec{G} \cdot \vec{r}_1} + e^{i\vec{G} \cdot \vec{r}_2} + e^{i\vec{G} \cdot \vec{r}_3}$$

f=1 for simplicity.

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

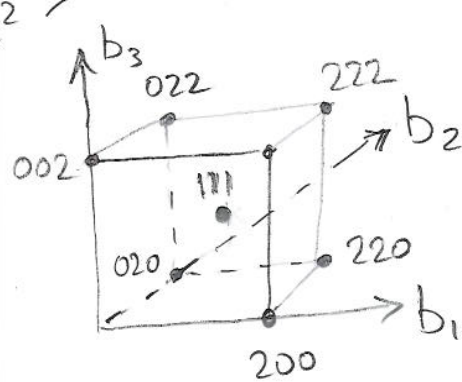
$$S_G = 1 + (-1)^{h+k} + (-1)^{h+l} + (-1)^{k+l}$$

this is symmetric in permutations of h, k, l

$$S_G = 4 \text{ hkl all even or all odd}$$

$$= 0 \text{ otherwise.}$$

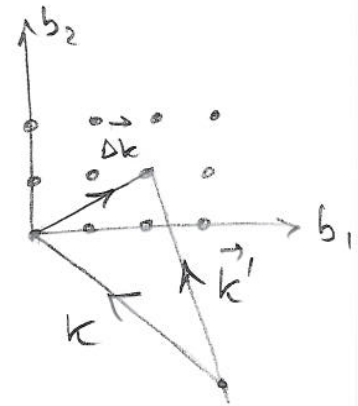
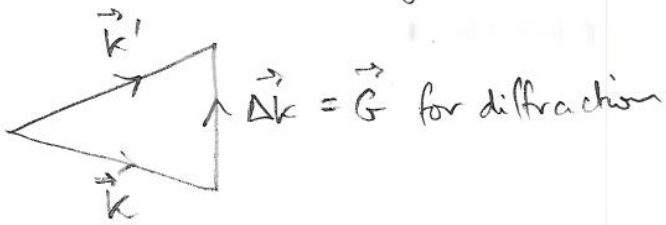
| hkl | S_G | $h^2+k^2+l^2$ | FCC selection rules |
|-----|-------|---------------|---------------------|
| 100 | 0 | 1 | |
| 110 | 0 | 2 | |
| 111 | 4 | 3 | |
| 200 | 4 | 4 | |
| 210 | 0 | 5 | |
| 211 | 0 | 6 | |
| 220 | 4 | 8 | |
| 221 | 0 | 9 | |
| 300 | 0 | 9 | |
| 310 | 0 | 10 | |
| 311 | 4 | 11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



Selection rules map onto bcc lattice!

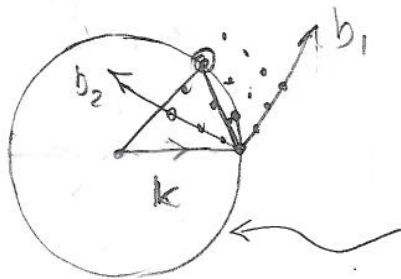
2.13 Ewald construction : Diffractometer.

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.

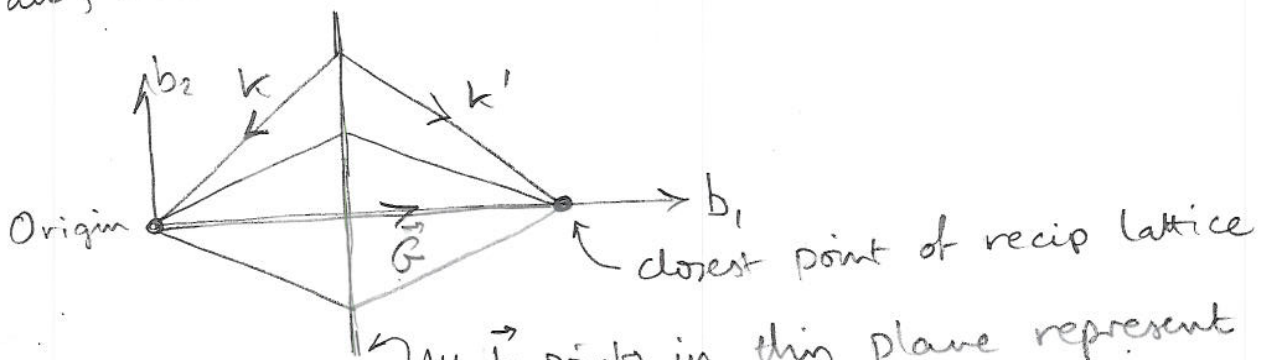
ii) fix direction of \vec{k} and consider all possible \vec{k}' 's that could arise : sphere of directions, all with length $|\vec{k}| = \text{radius of sphere}$.



Rotate crystal \rightarrow 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 ?



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

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

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

2.15 Brillouin Zones.

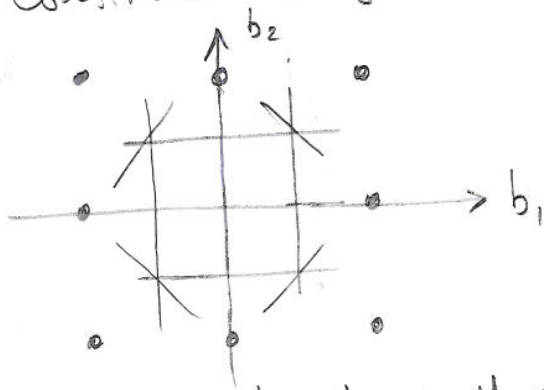
Electrons will be represented as waves, \vec{k} , within the crystal, and we will study their properties.

Small- k electrons travel freely, when accelerated they will 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.

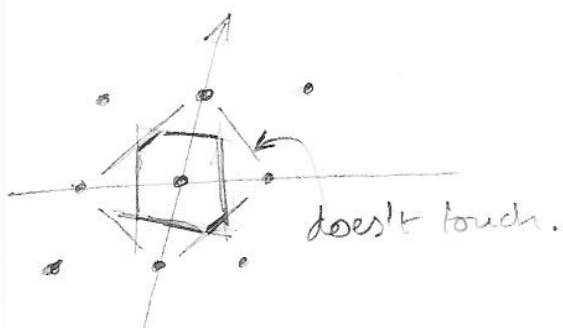
Construct using bisectors of all \vec{G} 's



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 \rightarrow 2nd BZ.
2 bisectors \rightarrow 3rd BZ

All have the same volume = V_{recip}



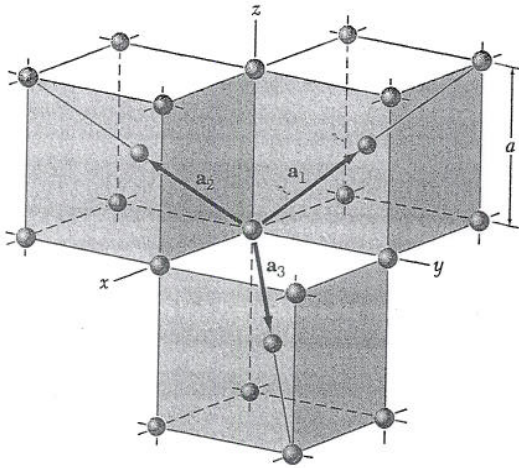


Figure 12 Primitive basis vectors of the body-centered cubic lattice.

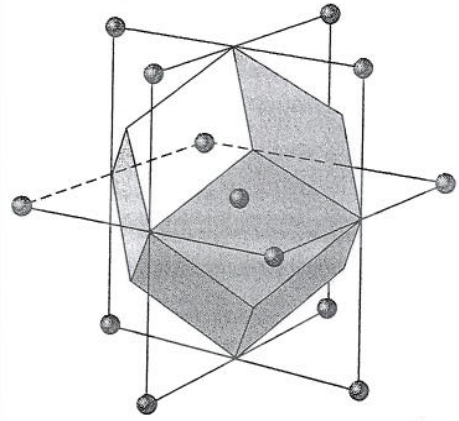


Figure 13 First Brillouin zone of the body-centered cubic lattice. The figure is a regular rhombic dodecahedron.

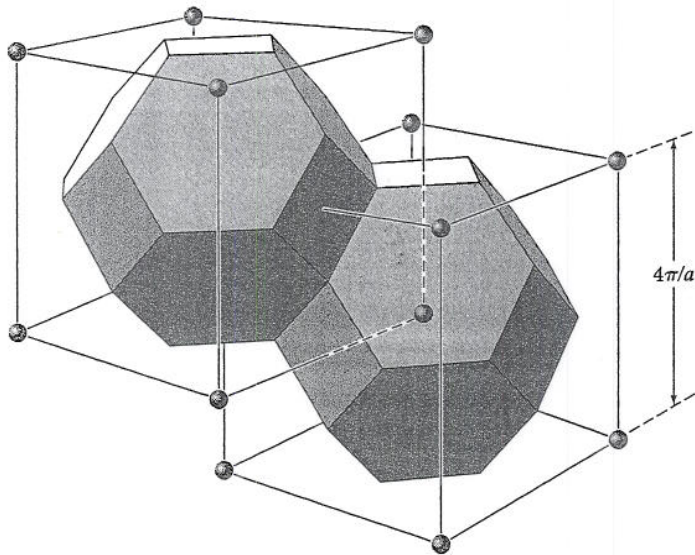


Figure 15 Brillouin zones of the face-centered cubic lattice. The cells are in reciprocal space, and the reciprocal lattice is body centered.

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 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 $k = 40.8 \text{ nm}^{-1}$, a powdered Nickel sample is found to produce its first three diffraction peaks at angles, $\gamma = 45.4^\circ, 52.8^\circ$ 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 ,

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

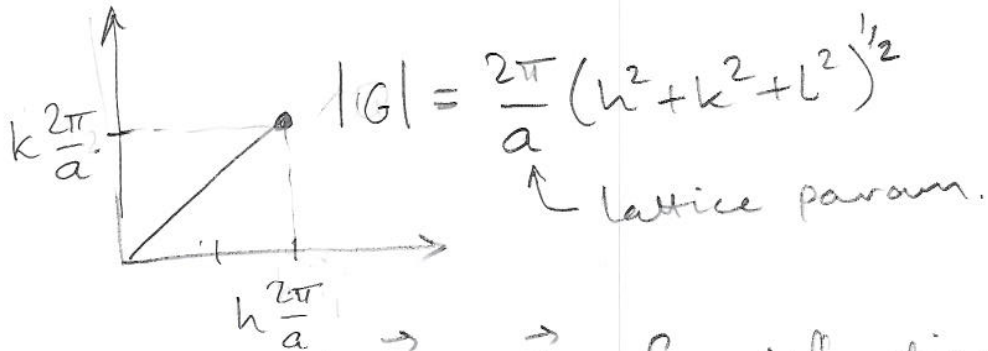
What is the meaning assigned to the parameters σ and ϵ ? [6]

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 $P_n = \sum_j p_j^{-n}$, 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]

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Worked example: typical exam problem, (was not very clear before). 2006 exam Q7

Length of general (hkl) recip lattice vector:



Laue condition $\Delta k = G$ for diffraction

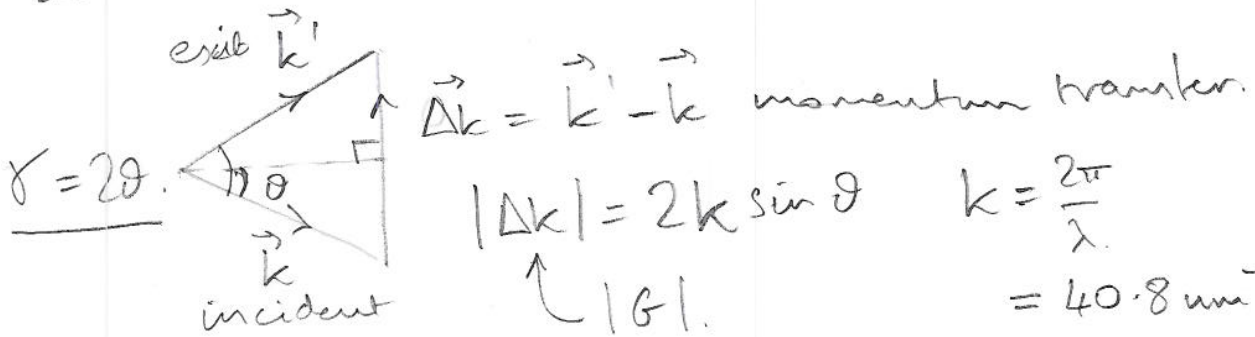


Table of angles

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

The ratio of $h^2 + k^2 + l^2 \Rightarrow 111, 200, 220$
 This is the pattern for FCC: all even or all odd.
 Any of them would give the lattice const:

111: $|G| = \frac{2\pi}{a} \sqrt{3} = 31.5 \text{ nm}^{-1}$
 $a = \frac{2\pi}{31.5} \sqrt{3} = \underline{0.345 \text{ nm}}$