E. Some examples

Example 1

- Simple cubic crystal, edge $a = 3.50\,\text{Å}$,
  X-ray of $\lambda = 3.10\,\text{Å}$ is used.

[Note: usually, we don't know the structure and lattice constant]

Find all sets of planes that satisfy the Bragg condition and the corresponding Bragg angle θ.

Recall: SC $\quad d(hkl) = \dfrac{a}{\sqrt{h^2+k^2+l^2}}$

Bragg condition $\quad \dfrac{2a}{\sqrt{h^2+k^2+l^2}} \sin\theta_n = n\lambda$

$$\Rightarrow \sin\theta_n = n\left(\frac{\lambda}{2a}\right)\sqrt{h^2+k^2+l^2} = 0.443\, n\sqrt{h^2+k^2+l^2}$$

(hkl)	θ_1 (n=1)	θ_2 (n=2)
(100) etc.+	26.3°	62.3°
(110) etc.	38.8°	
(111) etc.	50.1°	
(210) etc.	82.1°	

+ "etc." means indices can be permuted and signs can be changed.

By properly orientating the crystal, peaks corresponding to these planes can be observed.

Example 2

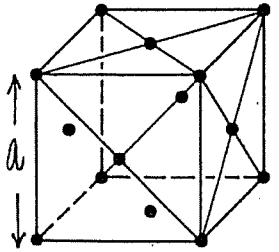
- fcc and structure factor of the basis
- Consider a fcc lattice with the same atom at every lattice point

By convention (especially in X-ray diffraction), we describe the fcc monatomic crystal using the conventional cubic unit cell. In doing so, each lattice point of the cube is decorated by a basis of 4 atoms.

i.e., we take $\vec{a}_1 = a\hat{x}$, $\vec{a}_2 = a\hat{y}$, $\vec{a}_3 = a\hat{z}$.

The 4 atoms relative to a lattice pt. are at:

$$\begin{cases} \vec{\rho}_1 = (0,0,0), \quad \vec{\rho}_2 = a\left(\frac{1}{2},\frac{1}{2},0\right) \\ \vec{\rho}_3 = a\left(\frac{1}{2},0,\frac{1}{2}\right), \quad \vec{\rho}_4 = a\left(0,\frac{1}{2},\frac{1}{2}\right) \end{cases}$$



Face-centered cubic

Real space

In this conventional description,

$$\vec{G}_\Gamma = \frac{2\pi}{a}(v_1\hat{x} + v_2\hat{y} + v_3\hat{z})$$

as $\vec{b}_1 = \frac{2\pi}{a}\hat{x}$, $\vec{b}_2 = \frac{2\pi}{a}\hat{y}$, $\vec{b}_3 = \frac{2\pi}{a}\hat{z}$

(But recall that the reciprocal lattice is actually bcc)

Recall: Intensity $I \propto |a(\Delta\vec{s})|^2 \, |\mathcal{S}(\Delta\vec{s})|^2$

We need $\Delta\vec{s} = \vec{G}$, so that it is possible to have $I \neq 0$.

Consider the structure factor of the basis:

$$\mathcal{S}(\vec{G}) = \mathcal{S}(v_1 v_2 v_3) = \sum_{j=1}^{4} f_j \, e^{-i\vec{G}\cdot\vec{r}_j}$$

since the 4 atoms are identical

$$f_1 = f_2 = f_3 = f_4 = f$$

$$\mathcal{S}(v_1 v_2 v_3) = f\left[1 + e^{-i\pi(v_1+v_2)} + e^{-i\pi(v_1+v_3)} + e^{-i\pi(v_2+v_3)}\right]$$

fcc monatomic crystal

$$= \begin{cases} 4f & \text{if } (v_1 v_2 v_3) \text{ are } \underline{\text{all even}} \\ 4f & \text{if } (v_1 v_2 v_3) \text{ are } \underline{\text{all odd}} \\ 0 & \text{otherwise} \end{cases}$$

This sounds familiar! See p. II-(23).

Now, the direct lattice is fcc. The reciprocal lattice is bcc.

However, in describing the bcc reciprocal, we used

$$\vec{G} = \frac{2\pi}{a}(v_1\hat{x} + v_2\hat{y} + v_3\hat{z}).$$

According to the discussion on p. II-(23), v_1, v_2, v_3 are either all even or all odd, for $\vec{G}$'s to map out a bcc.

∴ We will not get X-ray diffraction peaks with labels (100), (110), (210), etc.

The Bragg condition reads:

$$\sin^2\theta = \left(n\frac{\lambda}{2a}\right)^2 \underbrace{\left(h^2 + k^2 + l^2\right)}_{(\ ,\ ,\ )}$$

but hkl are either all even or all odd for fcc crystals.

Possible scatterings are:

hkl	$h^2+k^2+l^2$	hkl	$h^2+k^2+l^2$
111	3	222	12
200	4	400	16
220	8	133	19
113	11	420	20

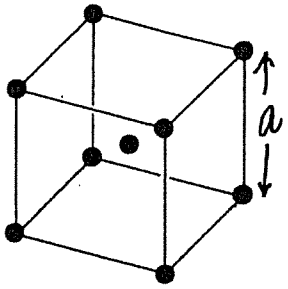
Of course, $\sin^2\theta \leq 1$. Thus, depending on $\frac{\lambda}{2a}$, some of these diffraction peaks will be observed.

Example 3

- bcc monatomic crystals

By convention, we use the cubic conventional unit cell.

$\vec{a}_1 = a\hat{x}$, $\vec{a}_2 = a\hat{y}$, $\vec{a}_3 = a\hat{z}$



A basis of 2 atoms:

$\vec{\rho}_1 = (0,0,0)$, $\vec{\rho}_2 = a(\frac{1}{2},\frac{1}{2},\frac{1}{2})$

$$\mathcal{S}(\vec{G}) = \mathcal{S}(v_1 v_2 v_3)$$
$$= f\left[1 + e^{-i\pi(v_1+v_2+v_3)}\right]$$
$$\neq 0 \ (=2f) \quad \text{if} \quad v_1+v_2+v_3 = \text{even}$$

See p.II-(23). $\vec{G} = \frac{2\pi}{a}(v_1\hat{x} + v_2\hat{y} + v_3\hat{z})$ map out a fcc lattice when $v_1+v_2+v_3$ = even, and fcc is the reciprocal lattice of bcc.

Possible scatterings are: $h+k+l$ = even

hkl	$h^2+k^2+l^2$
1 1 0	2
2 0 0	4
1 1 2	6
2 2 0	8

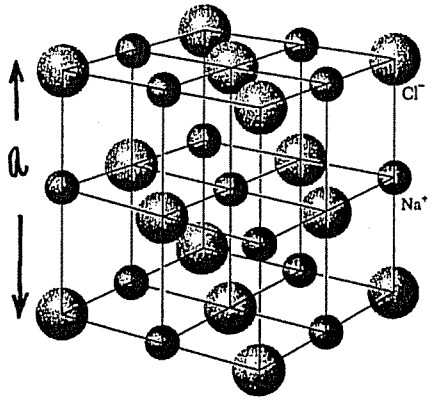
$\sin^2\theta = \left(\frac{n\lambda}{2a}\right)^2 (h^2+k^2+l^2)$

Example 4: More than one types of atom in a basis

(a) Structure factor of NaCl structure

fcc + basis of 2 ions / lattice point

- Use a non-primitive unit cell (a cube of edge a)



There are 4 lattice points in a conventional cube

$\Rightarrow$ 4 Na^+ and 4 Cl^- ions per cubic lattice pt.

Where are they?

They can be chosen to sit at:

Na^+: $(0,0,0)$; $(\frac{a}{2},\frac{a}{2},0)$; $(\frac{a}{2},0,\frac{a}{2})$; $(0,\frac{a}{2},\frac{a}{2})$

Cl^-: $(\frac{a}{2},\frac{a}{2},\frac{a}{2})$; $(0,0,\frac{a}{2})$; $(0,\frac{a}{2},0)$; $(\frac{a}{2},0,0)$

$\Rightarrow$ if we decorate each point in a SC lattice with this 8-ion basis, then we will generate the NaCl structure.

The structure factor is: $\sum_{\ell} f_\ell e^{-i\vec{G}\cdot\vec{\rho}_\ell}$ with $\vec{G} = \frac{2\pi}{a}(v_1\hat{x}+v_2\hat{y}+v_3\hat{z})$

($\sum_\ell$: over the 8 ions; $\vec{G}$: since SC is used.)

$$\mathcal{S}(\vec{G}) = \mathcal{S}(v_1 v_2 v_3)$$

$$= f_{Na}\left(1 + e^{-i\pi(v_1+v_2)} + e^{-i\pi(v_1+v_3)} + e^{-i\pi(v_2+v_3)}\right)$$

$$+ f_{Cl}\, e^{-i\pi(v_1+v_2+v_3)}\left(1 + e^{i\pi(v_1+v_2)} + e^{i\pi(v_1+v_3)} + e^{i\pi(v_2+v_3)}\right)$$

$$= \begin{cases} 4(f_{Na}+f_{Cl}) & v_1, v_2, v_3 \text{ all even} \\ 4(f_{Na}-f_{Cl}) & v_1, v_2, v_3 \text{ all odd} \\ 0 & \text{partly even/ partly odd} \end{cases}$$

- $f_{Na} \neq f_{Cl}$ as f is related to the electron charge density of an atom/ion
- The <u>intensity</u> of $(v_1 v_2 v_3)$ (all even) peaks is <u>different</u> from $(v_1 v_2 v_3)$ (all odd) peaks in X-ray diffraction experiments, as $f_{Na}+f_{Cl} \neq f_{Na}-f_{Cl}$.

<u>How about KCl?</u>

- f depends mostly on the number of electrons[+]
- Since K^+ and Cl^- ions have the <u>same number</u> of electrons, $f_{K^+} \approx f_{Cl^-}$.

Hence, <u>when v_1, v_2, v_3 are all odd</u>,

$$\mathcal{S} = 4[f_{K^+} - f_{Cl^-}] \approx 0$$

$\Rightarrow$ Allowed scattering are those with v_1, v_2, v_3 taking even integers. (see figure)

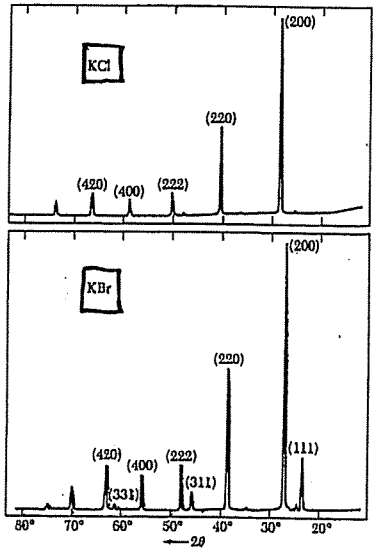
(b) <u>Diamond</u> (Ex.)

(c) <u>CsCl</u> (Ex.)

KCl vs KBr → Same structure

v_1, v_2, v_3 all even → $f_{K^+} \approx f_{Cl^-}$

v_1, v_2, v_3 all even or all odd → $f_{K^+} \neq f_{Br^-}$

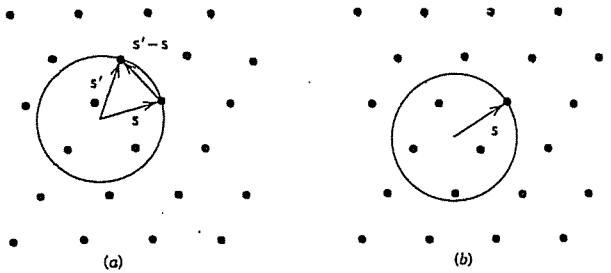


[+] f is called the atomic form factor and it is related to the Fourier transform of the electron charge density of an atom/ion.

F. A geometrical way to look at the Laue condition

- Ewald Construction

Laue condition : $\Delta\vec{s} = \vec{s}' - \vec{s} = \vec{G}$, then $a(\Delta\vec{s}) \neq 0$



An Ewald construction. The points are reciprocal lattice points, s is the propagation vector for the incident wave, and s' is the propagation vector for the scattered wave. The radius of the Ewald sphere is $2\pi/\lambda$. In (a) the Laue condition $s' = s + G$, where G is a reciprocal lattice vector, is met and an intense elastic scattering peak is produced. In (b) the condition is not met and no elastic peaks are produced.

- The incident wave gives $\vec{s}$.
- Draw the vector $\vec{s}$ so that it ends on a reciprocal lattice point.
- Since $|\vec{s}| = |\vec{s}'| = s$ for elastic scattering, a way to see how the Laue condition can be met is to draw a sphere of radius s.

- If the sphere touches other reciprocal lattice points, then it gives the direction(s) of $\vec{s}'$ that the condition $\Delta\vec{s} = \vec{G}$ is satisfied.

  ↑ a vector pointing from one point in the reciprocal lattice to another must be a $\vec{G}$

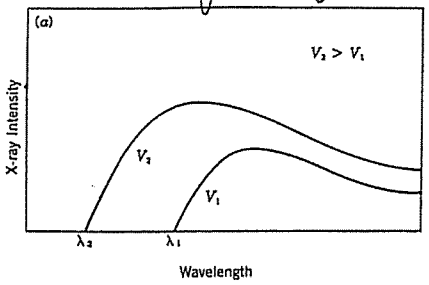
- If there is no other reciprocal lattice points on the sphere, then the Laue condition is not satisfied (for that particular value of $s = \frac{2\pi}{\lambda}$)

  ↳ i.e. for that λ, cannot find θ that satisfies the Laue condition (or Bragg condition)

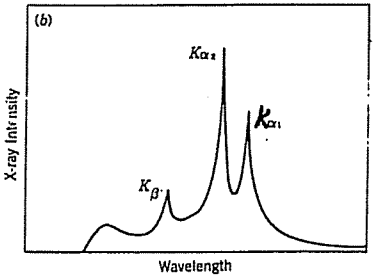
6. X-ray Crystallography†

Like other diffraction expts, measurement of separation of the X-ray diffraction maxima from a crystal gives the size of the unit cell (lattice type), and from the intensities of the diffracted beam we have information on the arrangement of atoms within the cell.

Electron hitting a target gives a continuous X-ray spectrum.



Generation of X-ray



The characteristic lines depend on the choice of target. These lines give X-rays at particular wavelengths.

(a) Bremsstrahlung spectrum for two accelerating potentials, with $V_2 > V_1$. The cutoff wavelengths are λ_1 and λ_2, respectively. The spectrum is independent of the target. (b) Bremsstrahlung and characteristic spectrum for a typical target in an x-ray tube. Different targets produce different characteristic lines.

For very complicated crystal structures (e.g. bio-material with basis of thousands of atoms), high intensity X-ray source is used – synchrotron (同步輻射).

↑ charged accelerating particles radiate.

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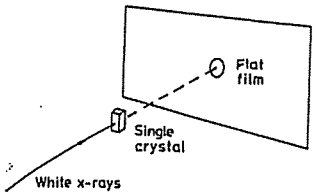
† Note: Crystallography is a big subject. Here, we give a brief introduction to the ideas behind the exptal methods, in particular related to how to satisfy the Laue condition. Details on techniques will not be discussed.

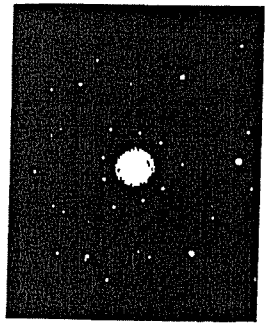
(a) Laue method:

"White" X-ray: Contains a continuous spectrum $\lambda_2 < \lambda < \lambda_1$ (scan over λ to hit the Bragg/Laue condition)

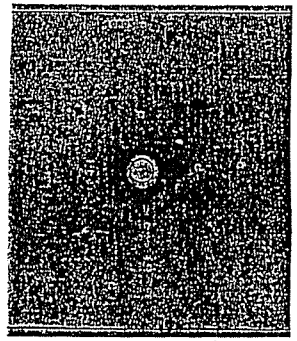
e.g. $\lambda_2 \sim 0.2$Å, $\lambda_1 \sim 3$Å



(a) Experimental geometry for a Laue photograph



(b) A Laue photograph of Si with a (1 1 1) face normal to the x-rays; note the three-fold symmetry.

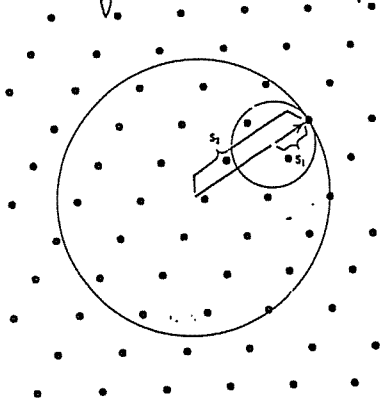


NaCl

- The diffracted beams generate a pattern of spots, which reflected the symmetry of the reciprocal lattice, and hence the direct lattice.
- Useful in deduction of symmetry and in determining the orientation of a single crystal.

Laue method: ["white" X-ray + Ewald construction]

All points in the region between the two spheres give $a(\vec{G}) \neq 0$.



Reciprocal lattice

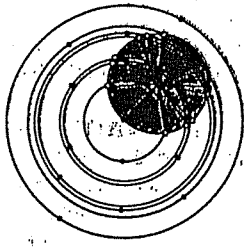
$|\vec{s}_1| = \frac{2\pi}{\lambda_1}$

$|\vec{s}_2| = \frac{2\pi}{\lambda_2}$

An Ewald construction for the Laue method. The two incident propagation vectors s_1 and s_2 are associated with the longest and shortest wavelengths, respectively, in the beam. Barring a vanishing structure factor, a scattering peak is produced for each reciprocal lattice point between the two spheres and on their surfaces.

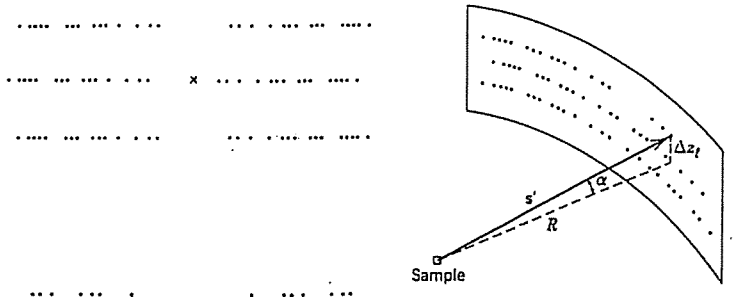
(b) Rotating Crystal method

- Monochromatic X-ray (single value of λ) onto a single crystal. The Bragg condition is unlikely to be satisfied.
- Rotate the crystal along an axis perpendicular to $\vec{s}_1$, then we can scan over θ (scan over different sets of crystal planes) and some planes will satisfy the Bragg condition.



Laue's picture showing orbits of reciprocal lattice points.

Rotating crystal method: typical pattern



(a) (b)

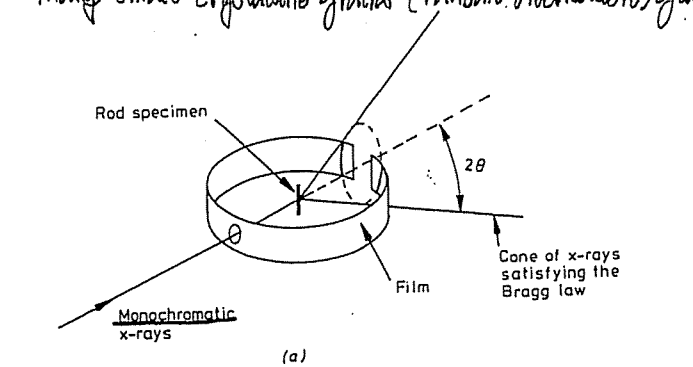
(a) Diagram of intensity peaks produced using the rotating crystal method. An orthorhombic crystal was rotated about its c axis, which was perpendicular to the incident beam. Only peaks in the forward direction are shown. X marks the place where the unscattered portion of the beam struck the film. (b) The separation Δz_1 between a row of spots and the central row is used to calculate α and the lattice constant along the axis of rotation.

- In terms of the Ewald construction, rotating the direct lattice also rotates the reciprocal lattice. Hence although we only have a sphere (monochromatic), we are rotating the reciprocal lattice around to find reciprocal lattice points that could satisfy $\Delta\vec{s} = \vec{G}_1$.

- $\vec{s}$ (or λ and the direct of $\vec{s}$) sets the Ewald sphere (which is fixed in this case)
- rotating the crystal along an axis $\Rightarrow$ rotating the reciprocal lattice along same axis

(c) Powder Method (Debye-Scherrer Method)

Sample: many small crystalline grains (random orientation) glued together



(a)

(b)

(a) Experimental geometry for a power photograph. (b) A powder photograph of molybdenum taken with Co Kα radiation. The x-rays enter the camera through the hole in the centre of the film and leave between the ends of the film. Note that the $K\alpha_1$-$K\alpha_2$ x-ray doublet (wavelengths 1.789 and 1.793 Å) is resolved for the back-scattered radiation near the entrance hole.

- All scattering peaks corresponding to reciprocal lattice vectors shorter than $\frac{4\pi}{\lambda}$ are produced. [similar to rotating crystal method]
- For a set of planes, a group of these small crystalline grains will satisfy the Bragg condition, the scattered beams form a cone of half-angle 2θ.
- On the film, we see rings.
- Measure $2\theta \Rightarrow$ structure.

e.g. Powder method observed 4 diffraction rings at the following values of scattering angle 2θ for a sample, using X-ray $\lambda = 1.5\,\text{Å}$

2θ: 42.2°, 49.2°, 72.0°, 87.3° $\Rightarrow \sin^2\theta$ known

Let's assume that we know it is a lattice in the cubic system (sc, fcc, bcc)

$$\sin^2\theta = n^2\left(\frac{\lambda}{2a}\right)^2 (h^2+k^2+l^2)$$ [Bragg condition]

(using cube of edge a to describe the structure)

$\sin^2\theta$	Ratio	
0.130	1	
0.173	1.33	(from data)
0.345	2.65	
0.476	3.66	

- Try (may be wrong) fcc: For fcc and using a cube, v_1, v_2, v_3 have to be either all even or all odd. { bcc reciprocal lattice ↓

v_1	v_2	v_3	$v_1^2+v_2^2+v_3^2$	Ratio	
1	1	1	3	1	same as observed! The sample is fcc.
2	0	0	4	1.33	
2	2	0	8	2.67	
1	1	3	11	3.67	

Cube edge a (lattice constant) can be found:

$$a = \frac{\lambda}{2}\frac{\sqrt{v_1^2+v_2^2+v_3^2}}{\sin\theta}$$

Using 1,1,1 data: $a = \frac{\lambda}{2}\frac{\sqrt{3}}{\sin(21.1^\circ)} = 3.61\,\text{Å}$ #

H. Laue Condition and the Brillouin Zone

Laue condition: $\Delta\vec{S} = \vec{G}$

Brillouin: $\vec{S}' - \vec{S} = \vec{G} \Rightarrow \vec{S} + \vec{G} = \vec{S}'$

Hence, $S^2 + 2\vec{S}\cdot\vec{G} + G^2 = S'^2 \quad (S^2 = S'^2)$

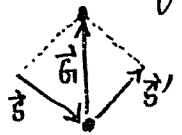
$\Rightarrow 2\vec{S}\cdot\vec{G} + G^2 = 0$

If $\vec{G}$ is a reciprocal lattice vector, $-\vec{G}$ is also a reciprocal lattice. We may well start with $\Delta\vec{S} = -\vec{G}$ and obtain

$$\boxed{2\vec{S}\cdot\vec{G} = G^2}$$ equivalent to Laue condition

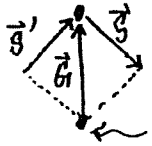
Geometrical way to see this:

(i)



pt. in reciprocal lattice

(ii) Vectors: don't change if direction and magnitude are kept fixed



$-2\vec{S}\cdot\vec{G} = G^2$

there is a reciprocal lattice point here

Re-draw:

(iii)

$2\vec{S}\cdot\vec{G}' = G'^2$

(iv) Rename $\vec{G}'$ as $\vec{G} \Rightarrow \boxed{2\vec{S}\cdot\vec{G} = G^2}$

$\therefore$ Laue condition becomes:

$$\boxed{2\vec{S}\cdot\vec{G} = G^2}$$

- useful when we put the tail of vector $\vec{S}$ at reciprocal lattice pt.

$$\Rightarrow \vec{S}\cdot\frac{\vec{G}}{2} = \frac{G^2}{4}$$

$$\Rightarrow \boxed{\vec{S}\cdot\left(\frac{\vec{G}}{2}\right) = \left(\frac{G}{2}\right)^2}$$

- equivalent to Laue/Bragg
- an equation stating which $\vec{S}$ ($|\vec{S}| \sim \frac{1}{\lambda}$, direction $\sim \theta$) will give strong intensity

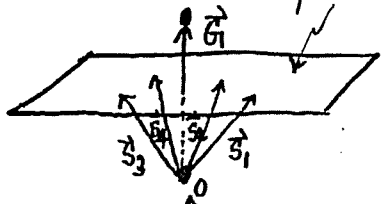
$\frac{\vec{G}}{2}$: half a reciprocal lattice vector

$(\text{magnitude})^2$ of $\frac{\vec{G}}{2}$

$$\text{LHS} = \vec{S}\cdot\frac{\vec{G}}{2} = \left(\frac{G}{2}\right)\cdot(\text{projection of } \vec{S} \text{ onto the direction of } \vec{G})$$

must be $\frac{G}{2}$ to satisfy Laue condition

$\therefore$ $\vec{S}$ must point from a reciprocal lattice point (tail) to the plane (head) bisecting $\vec{G}$

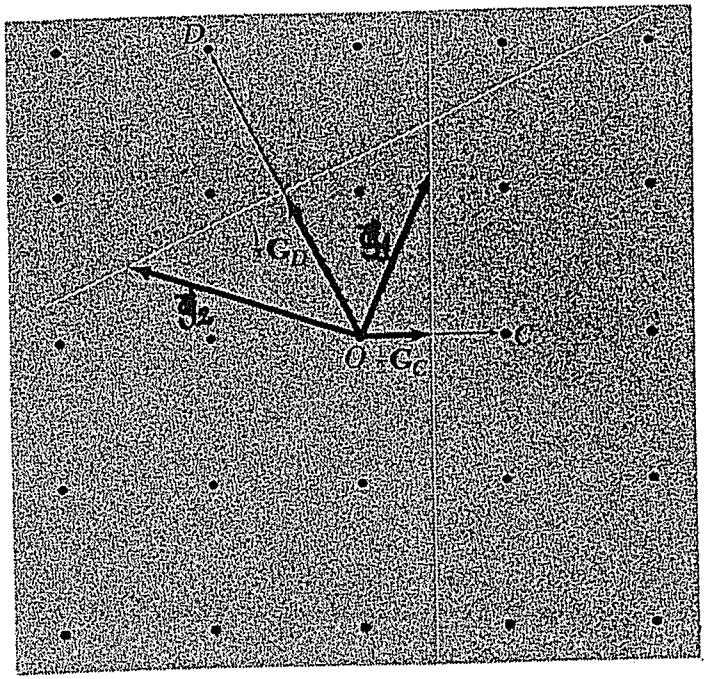


reciprocal lattice pt.

$\vec{S}_1, \vec{S}_2, \vec{S}_3, \vec{S}_4, \ldots$ that points to the plane all satisfy

$$\vec{S}\cdot\frac{\vec{G}}{2} = \left(\frac{G}{2}\right)^2$$

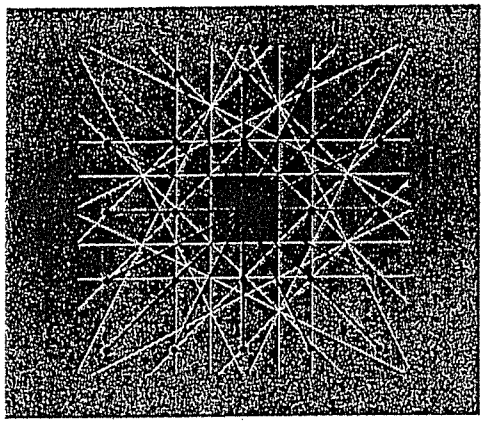
They have different magnitudes and directions (λ and θ have to match).



Reciprocal lattice points near the point O at the origin of the reciprocal lattice. The reciprocal lattice vector $\mathbf{G}_C$ connects points OC; and $\mathbf{G}_D$ connects OD. Two planes 1 and 2 are drawn which are the perpendicular bisectors of $\mathbf{G}_C$ and $\mathbf{G}_D$, respectively. Any vector from the origin to the plane 1, such as $\mathbf{k}_1$, will satisfy the diffraction condition $\mathbf{k}_1 \cdot (\frac{1}{2}\mathbf{G}_C) = (\frac{1}{2}\mathbf{G}_C)^2$. Any vector from the origin to the plane 2, such as $\mathbf{k}_2$, will satisfy the diffraction condition $\mathbf{k}_2 \cdot (\frac{1}{2}\mathbf{G}_D) = (\frac{1}{2}\mathbf{G}_D)^2$.

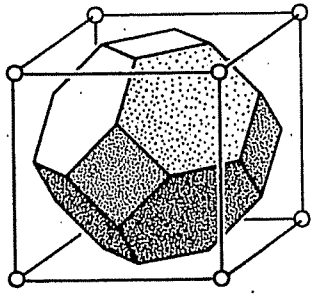
$\vec{S} \cdot \frac{\vec{G}}{2} = \left(\frac{G}{2}\right)^2$ gives planes in reciprocal space that show the $\vec{S}$ satisfying the Laue condition, These planes are of importance in the theory of wave propagation in crystals, including sound wave and electron wave.

Construction of Brillouin Zones



Square reciprocal lattice with reciprocal lattice vectors shown as fine black lines. The lines shown in white are perpendicular bisectors of the reciprocal lattice vectors. The central square is the smallest volume about the origin which is bounded entirely by white lines. The square is the Wigner-Seitz primitive cell of the reciprocal lattice. It is called the first Brillouin zone.

Area (volume) closest to origin ($\vec{G}=0$) is the 1st B.Z.



1st B.Z. of a fcc direct lattice

$\vec{S}$ from origin to the surfaces defining the 1st B.Z. are the shortest $\vec{S}$ vectors that can satisfy the Laue condition.

Summary

Students should be able to:

- argue the form of the scattered wave from a single scatterer
- write down the form of the scattered wave from a collection of scatterers
- relate intensity to scattered wave
- make use of periodicity to get at the constructive interference condition of $\Delta\vec{S} = \vec{G}$ (Laue condition)
- point out that $a(\Delta\vec{S})$ is related to the underlying lattice and the structure factor $S(\Delta\vec{S})$ is related to the basis atoms.
- point out that the atomic form factor f_j is dependent on the atom
- handle $S(\vec{G})$ for standard systems
- relate the Laue condition, Bragg condition, Ewald construction, and the Brillouin zone edges
- construct Ewald spheres and relate the search of the Bragg's condition in various exp'tal setups to the Ewald construction
- construct Brillouin Zones
- solve problems related to elastic wave scattering in solids

Appendix A : Atomic form factor (Optional)

$$S(\vec{G}) = \sum_\ell f_\ell(\vec{G})\, e^{-i\vec{G}\cdot\vec{r}_\ell}$$

$f_\ell(\vec{G})$ is the atomic form factor

The electrons in an atom are described by an electron number density $n_e(\vec{r})$.

A QM result.

$$f_\ell(\vec{G}) = \int d^3r\, e^{-i\vec{G}\cdot\vec{r}}\, n_e(\vec{r})$$

↗ Fourier transform of $n(\vec{r})$

↖ ℓ-type atom centered at $\vec{r}=0$ this causes scatterings.

A simple picture : uniformly charged sphere of radius R

N_e electrons $\quad n_e(\vec{r}) = \left(\frac{3N_e}{4\pi R^3}\right)\theta(R-r)$

then $\quad f_\ell(G) = \frac{3}{2}\frac{N_e}{(GR)^3}\left[\sin(GR) - GR\cos(GR)\right]$

$G = |\vec{G}|$

If $GR \ll 1$ (long wavelength), $f_\ell \sim N_e$

If $GR \gg 1$ $(\lambda \ll R)$, $|f_\ell|^2 \sim \frac{1}{(GR)^4}$

References:

Kittel Ch. 2

Christman Ch. 4