

The Reciprocal Lattice of a Bravais Lattice.

The set of wave vectors $\{\vec{k}\}$ that specify the periodicity of a Bravais lattice of sites $\{\vec{R}\}$.

will be useful in discussing X-ray scattering off ions and electron eigenstates in ionic potential.

Suppose we have a function $U(\vec{r})$ that is periodic on the Bravais lattice, i.e. we have

$$U(\vec{r} + \vec{R}) = U(\vec{r})$$

for all $\vec{R}$ in the Bravais lattice. You may think of the ionic potential the electron sees as a physical example. Taking the Fourier transform

$$U(\vec{r}) = \int \frac{d^3k}{(2\pi)^3} e^{i\vec{k} \cdot \vec{r}} U(\vec{k})$$

the above condition becomes

$$\begin{aligned} U(\vec{r} + \vec{R}) &= \int \frac{d^3k}{(2\pi)^3} e^{i\vec{k} \cdot (\vec{r} + \vec{R})} U(\vec{k}) \\ &= \int \frac{d^3k}{(2\pi)^3} e^{i\vec{k} \cdot \vec{r}} U(\vec{k}) = U(\vec{r}) \end{aligned}$$

If this is to be true, then the only values of $\vec{k}$ for which $U(\vec{k}) \neq 0$ must be the set of $\{\vec{k}\}$ such that $e^{i\vec{k} \cdot \vec{R}} = 1$ for all

$\vec{R}$ in the Bravais lattice. This defines the reciprocal reciprocal lattice $\{\vec{K}\}$.

Alternatively, the set of wave vectors $\{\vec{K}\}$ that yield plane waves with the periodicity of the Bravais lattice is called the reciprocal lattice.

$$e^{i\vec{K} \cdot (\vec{r} + \vec{R})} = e^{i\vec{K} \cdot \vec{r}} \quad \text{for all } \vec{R} \text{ in B.L.}$$

plane wave is invariant under translation by $\{\vec{R}\}$.

$$\Rightarrow \boxed{e^{i\vec{K} \cdot \vec{R}} = 1 \quad \text{for all } \{\vec{R}\} \text{ in B.L.}}$$

The reciprocal lattice is itself a Bravais lattice

If $\vec{a}_1, \vec{a}_2, \vec{a}_3$ are the primitive vectors of a B.L., then

$$\vec{b}_1 \equiv \frac{2\pi \vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}$$

$$\vec{b}_2 \equiv \frac{2\pi \vec{a}_3 \times \vec{a}_1}{\vec{a}_2 \cdot (\vec{a}_3 \times \vec{a}_1)}$$

$$\vec{b}_3 \equiv \frac{2\pi \vec{a}_1 \times \vec{a}_2}{\vec{a}_3 \cdot (\vec{a}_1 \times \vec{a}_2)}$$

are primitive vectors for the reciprocal lattice

proof

Note that $\vec{b}_i \cdot \vec{a}_j = 2\pi \delta_{ij}$ and that $\vec{b}_i$'s are not all in the same plane since the $\vec{a}_i$'s are not.

$\Rightarrow \{\vec{b}_i\}$ can be taken as a set of basis vectors for $\vec{k}$ -space, i.e. we can write any wave vector $\vec{k}$ as a linear combination

$$\vec{k} = k_1 \vec{b}_1 + k_2 \vec{b}_2 + k_3 \vec{b}_3 \quad (k_i \text{ not necessarily integers})$$

then for any $\vec{R}$ in the B.L.

$$\begin{aligned} \vec{k} \cdot \vec{R} &= (k_1 \vec{b}_1 + k_2 \vec{b}_2 + k_3 \vec{b}_3) \cdot (n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3) \\ &= 2\pi (n_1 k_1 + n_2 k_2 + n_3 k_3) \end{aligned}$$

If $\vec{k}$ is in the reciprocal Lattice, we must have

$$e^{i\vec{k} \cdot \vec{R}} = 1 \quad \text{for all } \vec{R}$$

$$\Rightarrow n_1 k_1 + n_2 k_2 + n_3 k_3 = \text{integer for all integers } n_1, n_2, n_3$$

$\Rightarrow k_1, k_2, k_3$ must be integer

$\Rightarrow$ reciprocal lattice vectors $\vec{K}$ must be of the form

$$\vec{K} = k_1 \vec{b}_1 + k_2 \vec{b}_2 + k_3 \vec{b}_3 \quad \text{with } k_1, k_2, k_3 \text{ integer}$$

The reciprocal of the reciprocal lattice is the original Bravais lattice - in this context the original B-L is called the "direct" lattice.

proof

If $\{\vec{G}\}$ are vectors of the reciprocal to the reciprocal lattice, then $e^{i\vec{G}\cdot\vec{K}} = 1$ for all $\vec{K}$ in R.L.

But $\{\vec{K}\}$ satisfies this ~~definition~~ condition by the definition of $\{\vec{K}\}$. So clearly $\{\vec{K}\}$ is a subset of $\{\vec{G}\}$. Now suppose there was some $\vec{G} \in \{\vec{G}\}$ but $\vec{G} \notin \{\vec{K}\}$. Then

$\vec{G} = x_1\vec{a}_1 + x_2\vec{a}_2 + x_3\vec{a}_3$ where at least one of the x_i is not an integer. But then we would have $e^{i\vec{G}\cdot\vec{K}} = \pi e^{i2\pi x_i k_i} \neq 1$, so there can't be any such $\vec{G}$. $\Rightarrow \{\vec{G}\} = \{\vec{K}\}$.

Examples

1) simple cubic $\begin{cases} \vec{a}_1 = a \hat{x} \\ \vec{a}_2 = a \hat{y} \\ \vec{a}_3 = a \hat{z} \end{cases}$

$$\Rightarrow \begin{cases} \vec{b}_1 = \frac{2\pi}{a} \hat{x} \\ \vec{b}_2 = \frac{2\pi}{a} \hat{y} \\ \vec{b}_3 = \frac{2\pi}{a} \hat{z} \end{cases}$$

so R.L. is also simple cubic
with side of length $\frac{2\pi}{a}$

2) fcc $\begin{cases} \vec{a}_1 = \frac{a}{2} (\hat{y} + \hat{z}) \\ \vec{a}_2 = \frac{a}{2} (\hat{z} + \hat{x}) \\ \vec{a}_3 = \frac{a}{2} (\hat{x} + \hat{y}) \end{cases}$

construct the $\vec{b}_i$ to get $\begin{cases} \vec{b}_1 = \frac{2\pi}{a} (\hat{y} - \hat{x} + \hat{z}) \\ \vec{b}_2 = \frac{2\pi}{a} (\hat{z} - \hat{y} + \hat{x}) \\ \vec{b}_3 = \frac{2\pi}{a} (\hat{x} - \hat{z} + \hat{y}) \end{cases}$

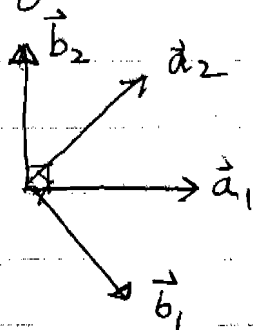
these $\vec{b}_i$ are just the primitive vectors of an bcc
lattice with side of the cubic unit cell equal
to $\frac{4\pi}{a}$

3) bcc

since the reciprocal of the reciprocal
lattice is the direct lattice, we
conclude from (2) that the reciprocal
of the bcc lattice is an fcc lattice.
If the bcc direct lattice has a unit cubic
cell of length a , then the reciprocal fcc
lattice has unit cubic cell of length $\frac{4\pi}{a}$

4) The reciprocal of the single hexagonal Bravais lattice with lattice constants a and c is also a single hexagonal lattice with lattice constants $|\vec{b}_1| = |\vec{b}_2| = \frac{4\pi}{\sqrt{3}a}$ and $|\vec{b}_3| = \frac{2\pi}{c}$

The directions of $\vec{b}_1$ and $\vec{b}_2$ are rotated with respect to $\vec{a}_1$ and $\vec{a}_2$



angle between $\vec{a}_1$ and $\vec{a}_2$
is 60°

angle between $\vec{b}_1$ and $\vec{b}_2$
is 120°

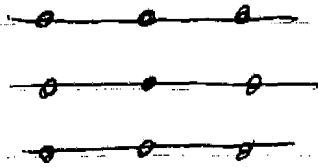
If v is the volume of the primitive cell of the direct lattice, then $(2\pi)^3/v$ is the volume of the primitive cell of the reciprocal lattice.

The Wigner-Seitz primitive cell for the reciprocal lattice is known as the First Brillouin Zone (later we will see the 2nd and higher Brillouin zones)

The 1st Brillouin zone of an fcc direct lattice is the Wigner-Seitz cell of a bcc reciprocal lattice and vice versa.

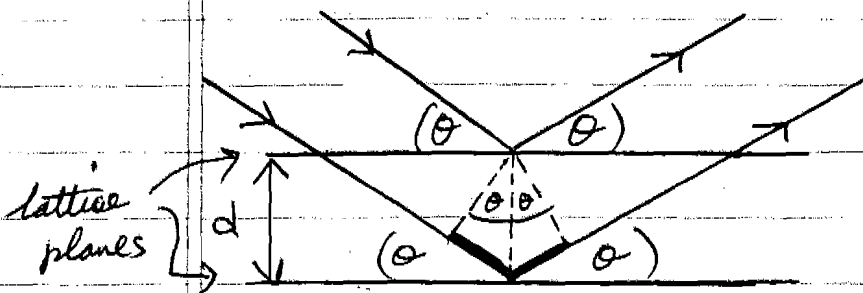
X-ray diffraction

Bragg formulation



"lattice planes" - set of parallel planes containing the points of the lattice

Imagine a set of lattice planes as if they are reflecting surfaces. An incoming light wave will get reflected by the successive planes. There will be a peak in the reflected wave amplitude when the reflections from all the planes add with constructive interference.



incoming light wave of wavelength λ gets specularly reflected ($\theta_{out} = \theta_{in}$). There

will be constructive interference between reflected waves from top plane and the one underneath it when the difference in optical path length is an integral number of wavelengths λ . If the planes have separation d , and the incident angle is θ , then the optical path length difference (heavy lines in the figure) is;

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

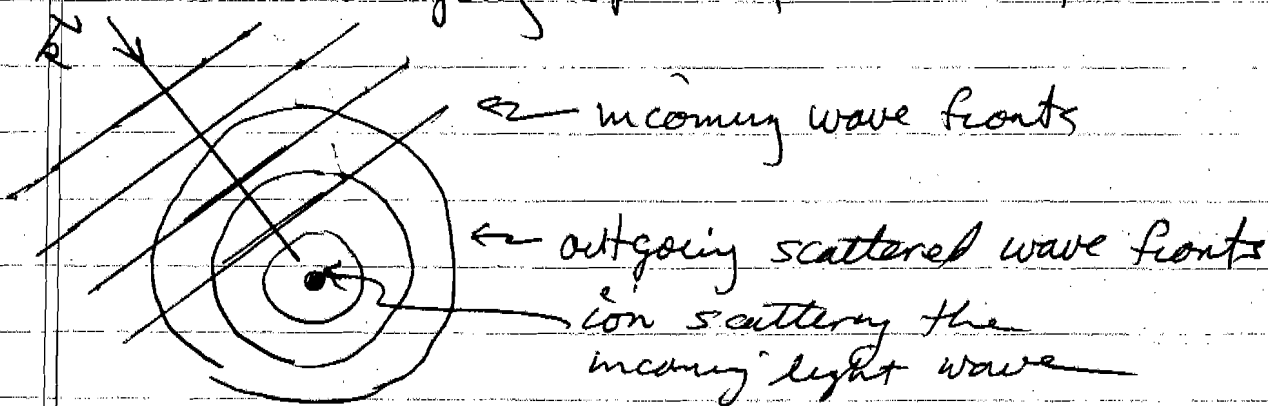
condition for Bragg scattering

In experiment we know λ , we measure the θ that produces a peak in the reflected intensity, so we thus can determine the separation between the lattice planes. In this way one can deduce the lattice constants and geometry.

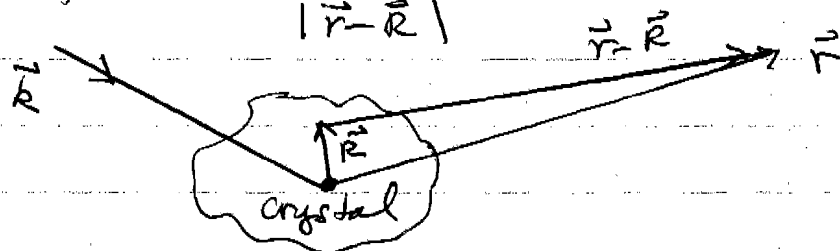
Since $n=1,2,3$, the ~~smallest~~ largest λ that can give rise to Bragg scattering is $\lambda = 2d \sim \text{\AA}$. So we cannot see Bragg scattering with visible light waves ($\lambda \sim 5000 \text{\AA}$). We need to use X-rays with $\lambda \sim \text{\AA}$.

We now want to relate the phenomenon of Bragg scattering to the reciprocal lattice $\{\mathbf{K}\}$. This gives the von Laue formulation of X-ray scattering.

Consider a plane ~~light~~ polarized light wave $e^{i\mathbf{k}\cdot\mathbf{r}}$ hitting one of the ions of the crystal structure. The interaction of the incoming wave with the ion will result in an outgoing spherical scattered wave.



If the ion is at Bravais lattice site $\vec{R}$, and the crystal is centered at the origin, then the outgoing spherical wave can be written as

$$f(\theta, \varphi) \frac{e^{i(k|\vec{r}-\vec{R}|+\delta)}}{|\vec{r}-\vec{R}|}$$


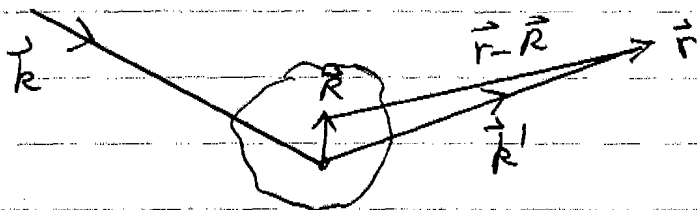
outgoing spherical wave is centered at the ion at $\vec{R}$ has same wave number $k = |\vec{k}|$ as incident plane wave $f(\theta, \varphi)$ gives scattered amplitude from ion as function of spherical direction angles θ, φ with respect to origin. The particular function form $f(\theta, \varphi)$ is determined by the details of the charge distribution within the ion and is not of interest to our argument. δ is the phase ~~shift~~ of the scattered wave as it leaves the ion at position $\vec{R}$.

When $\vec{r} = \vec{R}$, the outgoing spherical wave must have the same phase as the incoming wave, plus a possible constant (site independent) phase shift δ_0 .

$$\Rightarrow \delta = \vec{k} \cdot \vec{R} + \delta_0$$

$$f(\theta, \varphi) \frac{e^{i(k|\vec{r}-\vec{R}| + \vec{k} \cdot \vec{R})}}{|\vec{r}-\vec{R}|} e^{i\delta_0}$$

Now consider the observation point $\vec{r}$ for outside the crystal. The direction to $\vec{r}$ defines the scattered wave vector $\vec{k}'$.



since scattering off the con is elastic

$|\vec{k}'| = |\vec{k}|$ is wavelength of scattered spherical wave = wavelength incident wave

$$|\vec{r} - \vec{R}| = \sqrt{r^2 + R^2 - 2\vec{r} \cdot \vec{R}}$$

$$\approx r \left(1 - \frac{2\vec{r} \cdot \vec{R}}{r^2} + \frac{R^2}{r^2} \right)^{1/2} \quad \text{expand for small } \frac{R}{r}$$

$$\approx r \left(1 - \frac{\vec{r} \cdot \vec{R}}{r^2} \right) + O\left(\frac{R}{r}\right)^2$$

$$= r - \hat{r} \cdot \vec{R} \quad \hat{r} \text{ is direction of } \vec{r}$$

$$\Rightarrow k|\vec{r} - \vec{R}| \approx kr - k\hat{r} \cdot \vec{R} = kr - \vec{k}' \cdot \vec{R}$$

So the scattered wave from the con at $\vec{R}$ is

$$f(\theta, \varphi) e^{i\delta_0} \frac{e^{i(kr - \vec{k}' \cdot \vec{R} + \vec{k} \cdot \vec{R})}}{r}$$

$r \leftarrow \text{approx } |\vec{r} - \vec{R}| \sim r \text{ here}$

$$= f(\theta, \varphi) e^{i\delta_0} \underbrace{\frac{e^{ikr}}{r}}_{\text{outgoing spherical wave centered at origin of crystal}} \underbrace{e^{i(\vec{k} - \vec{k}') \cdot \vec{R}}}_{\text{phase shift due to position of con at } \vec{R} \text{ with respect to the origin.}}$$

outgoing spherical wave centered at origin of crystal

phase shift due to position of con at $\vec{R}$ with respect to the origin.

Above is scattered wave just from the ion at $\vec{R}$.
 Now we should add all the scattered waves
 from all the ions at BL sites $\{\vec{R}\}$.

Define the change in wave vector $\Delta\vec{k} = \vec{k} - \vec{k}'$

Then the total scattered wave is

$$\sum_{\vec{R}} f(\theta, \varphi) e^{i\delta_0} \frac{e^{i\vec{k}\cdot\vec{r}}}{r} e^{i\Delta\vec{k}\cdot\vec{R}}$$

same factor for all
 ions since each site
 of BL is identical

phase factor due to
 position of ion at $\vec{R}$
 respect to origin of
 crystal

$$= f(\theta, \varphi) e^{i\delta_0} \frac{e^{i\vec{k}\cdot\vec{r}}}{r} \left(\sum_{\vec{R}} e^{i\Delta\vec{k}\cdot\vec{R}} \right)$$

We expect that the total scattered wave will have
 a peak in intensity in those directions $\hat{k}'$ such
 that

$$\sum_{\vec{R}} e^{i\Delta\vec{k}\cdot\vec{R}} \text{ is maximized.}$$

Now if $\Delta\vec{k} = \vec{K}$ in the reciprocal lattice, then

$$e^{i\vec{K}\cdot\vec{R}} = 1 \text{ for all } \vec{R} \text{ in the B.L.}$$

~~So each term in sum takes its maximal value~~

and $\sum_{\vec{R}} e^{i\Delta\vec{k}\cdot\vec{R}} = N$ number of sites in BL
 clearly this is the max/min
 possible value of the sum

$\Rightarrow$ For an incident plane polarized plane wave with wavevector $\vec{k}$, the scattered wave will be maximum in those directions $\vec{k}'$ such that the wavevector $\vec{k} - \vec{k}'$ (with $|\vec{k}'| = |\vec{k}|$) is equal to a wavevector $\vec{K}$ in the reciprocal lattice. The change in wave vector $\Delta\vec{k} = \vec{k} - \vec{k}'$ must be in the set $\{\vec{K}\}$ of the reciprocal lattice.

Moreover, we can show that in the thermodynamic limit of $N \rightarrow \infty$ (ie a crystal with a macroscopic number of ions) the scattered amplitude vanishes unless $\Delta\vec{k} = \vec{K}$ in the reciprocal lattice.

Proof: Since the BL is invariant under translations, ie the set $\{\vec{K}\}$ is equivalent to the set $\{\vec{K} + \vec{R}_0\}$ where $\vec{R}_0$ is any particular member of the BL, then

$$\begin{aligned}
 \sum_{\vec{K}} e^{i\Delta\vec{k} \cdot \vec{K}} &= \sum_{\vec{K}} e^{i\Delta\vec{k} \cdot (\vec{K} + \vec{R}_0)} \\
 &= e^{i\Delta\vec{k} \cdot \vec{R}_0} \sum_{\vec{K}} e^{i\Delta\vec{k} \cdot \vec{K}}
 \end{aligned}$$

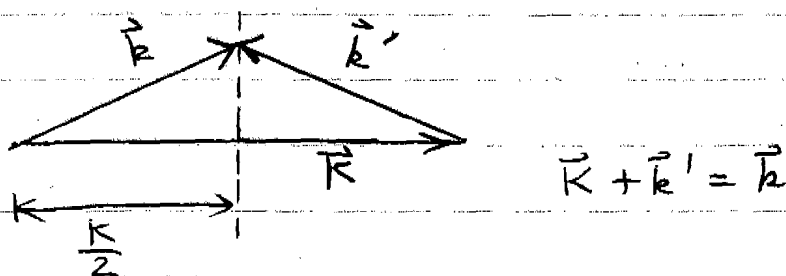
$\Rightarrow e^{i\Delta\vec{k} \cdot \vec{R}_0} = 1$ and this must be true for any $\vec{R}_0$ in the BL, ie $\Delta\vec{k} = \vec{K}$ in R.L.

OR
 $\sum_{\vec{K}} e^{i\Delta\vec{k} \cdot \vec{K}} = 0$ This must therefore be true if $\Delta\vec{k}$ is not a wave vector in the R.L.

* Hence the scattered wave will vanish in all directions $\hat{k}'$ except for those directions where $\Delta \vec{k} = \vec{k} - \vec{k}'$ is equal to a $\vec{K}$ in the R.L.

These sharp isolated peaks in the scattered intensity when $\Delta \vec{k} = \vec{K}$ are called Bragg peaks and give the familiar diffraction pattern of periodic ~~the~~ bright spots that one sees from X-ray scattering.

Since $\vec{k} - \vec{k}' = \vec{K}$, and $|\vec{k}| = |\vec{k}'| = k$, we can draw the vector difference as follows:

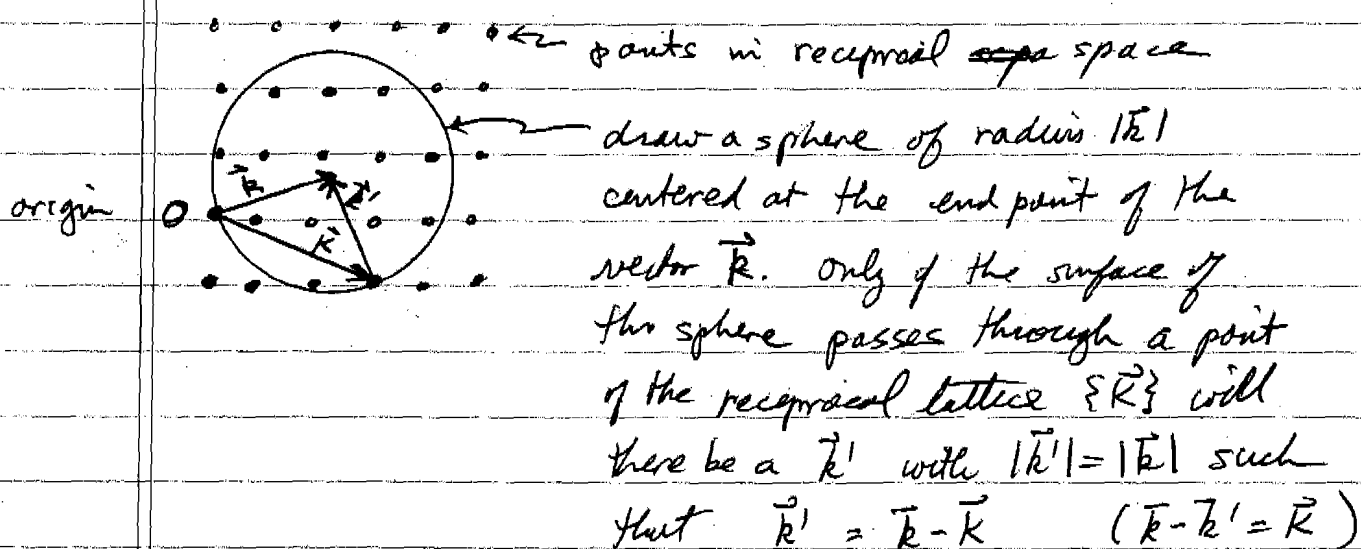


From above picture we see that there will be a Bragg peak in the diffraction pattern whenever the tip of the incident wave vector $\vec{k}$ lies on a plane in $\vec{k}$ -space that bisects a reciprocal lattice vector $\vec{K}$. Such a plane in $\vec{k}$ -space is called a Bragg plane.

Note: all $\vec{k}$ that lie on the surface of the 1st Brillouin Zone satisfy the condition for Bragg scattering since the surface of the 1st Brillouin Zone is constructed from the Bragg planes of the smallest reciprocal lattice vectors $\vec{K}$. The intersections of the Bragg planes of larger $\vec{K}$ will define the surfaces of the 2nd, 3rd, etc Brillouin Zones.

Question: For a given incident wave vector $\vec{k}$ with fixed amplitude and orientation, will there be some direction given by $\vec{k}'$ in which there will be a Bragg scattering peak?

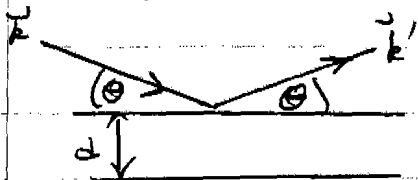
Answer: Ewald Construction say in general no!



For a general $\vec{k}$ (i.e. fixed amplitude and direction) there will in general be no $\vec{k}'$ on the surface of this sphere, hence no Bragg scattering. Therefore, in order to see Bragg peaks, one needs in general to be able to vary either the amplitude $|\vec{k}|$ or the direction $\hat{k}$.

Relation between von Laue and Bragg formulation of X-ray scattering.

Bragg formula $2d \sin \theta = n \lambda$



rewrite above as

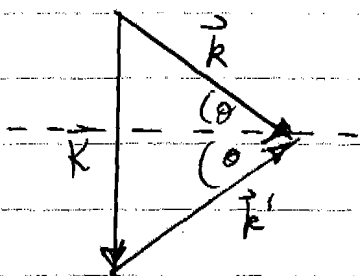
$$2d \sin \theta = n \frac{2\pi}{k}$$

$$\Rightarrow 2k \sin \theta = \frac{2\pi}{d} n$$

One can show that for any family of lattice planes there is a R.L. vector $\vec{K}$ that is normal to the planes, and that the smallest such $\vec{K}$ has a length $\frac{2\pi}{d}$ (where d is the spacing between planes) (see Ashcroft + Mermin)

Hence above is $2k \sin \theta = |\vec{K}|$

where $\vec{K} = n \vec{K}_0$ is a R.L. vector normal to the planes, and $|\vec{K}_0| = \frac{2\pi}{d}$.



we can redraw diagram above as shown now on left

We see that $k \sin \theta$ is just the projection of $\vec{k}$ (and $\vec{k}'$) onto the direction normal to the lattice planes

$\Rightarrow 2k \sin \theta = |\vec{k} - \vec{k}'| = |\vec{K}| = \frac{2\pi}{d} n \Rightarrow$ Bragg formula is same as von Laue condition