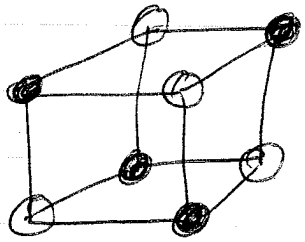
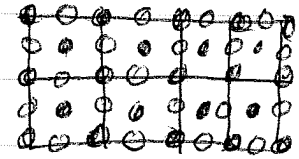
NaCl structure



Space points where atoms sit is a single cubic Bravais lattice BUT sites are not equivalent since they are alternately occupied by different atoms (Na and Cl for salt)

Need to describe this as a fcc Bravais lattice with two point basis $\vec{d}_1 = 0$, $\vec{d}_2 = \frac{a}{2}(\hat{x}+\hat{y}+\hat{z})$



- Na at sites of fcc
- Cl at center of cube

(See A+M Fig 4.24)

Cesium Chloride Structure

equal numbers of cesium and chlorine at points of a bcc lattice so that each has 8 neighbors of the other kind.

described by single cubic Bravais lattice of Cs with Cl at center of unit cube

$\vec{d}_1 = 0$ Cs

$\vec{d}_2 = \frac{a}{2}(\hat{x}+\hat{y}+\hat{z})$ Cl

Zincblend Structure equal nubers of zinc and sulfur on a deamond lattice so that each has 4 nearest neighbors of the other type.

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

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

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

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 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

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

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

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

} 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, ie we can write any wave vector $\vec{k}$ as a linear combination

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

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

$$\vec{k} \cdot \vec{R} = (k_1 \vec{b}_1 + k_2 \vec{b}_2 + k_3 \vec{b}_3)(n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3)$$

$$= 2\pi (n_1 k_1 + n_2 k_2 + n_3 k_3)$$

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

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

$\Rightarrow$ $n_1 k_1 + n_2 k_2 + n_3 k_3 =$ 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 $\{\vec{R}\}$ satisfies this ~~definition~~ condition by the definition of $\{\vec{K}\}$. So clearly $\{\vec{R}\}$ is a subset of $\{\vec{G}\}$. Now suppose there was some $\vec{G} \in \{\vec{G}\}$ but $\vec{G} \notin \{\vec{R}\}$. 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 integer. But then we would have $e^{i\vec{G}\cdot\vec{R}} = \prod e^{i2\pi x_i k_i} \neq 1$, so there can't be any such $\vec{G}$. $\therefore \Rightarrow \{\vec{G}\} = \{\vec{R}\}$.

Examples

1) single 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 single cubic with side of length $\frac{2\pi}{a}$

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

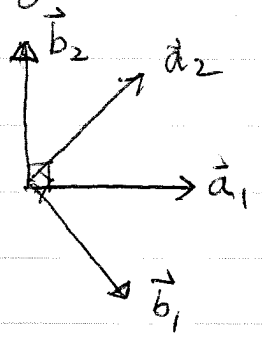
construct the $\vec{b}_i$ to get $\begin{cases} \vec{b}_1 = \frac{2\pi}{a}(\hat{y}-\hat{x}+\hat{z}) \\ \vec{b}_2 = \frac{2\pi}{a}(\hat{z}-\hat{y}+\hat{x}) \\ \vec{b}_3 = \frac{2\pi}{a}(\hat{x}-\hat{z}+\hat{y}) \end{cases}$

these $\vec{b}_i$ are just the primitive vectors of a 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 <u>simple hexagonal</u> Bravais lattice with lattice constants a and c is also a simple 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°

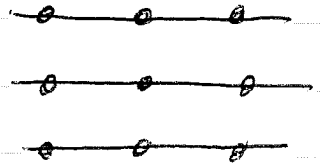
If v is the volume of the primitive cell of the direct lattice, then $(2\pi)^3/v$ is the volume of the primitive cell of the reciprocal lattice.

The Wigner-Seitz primitive cell for the reciprocal lattice is known as the <u>First Brillouin Zone</u> (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.

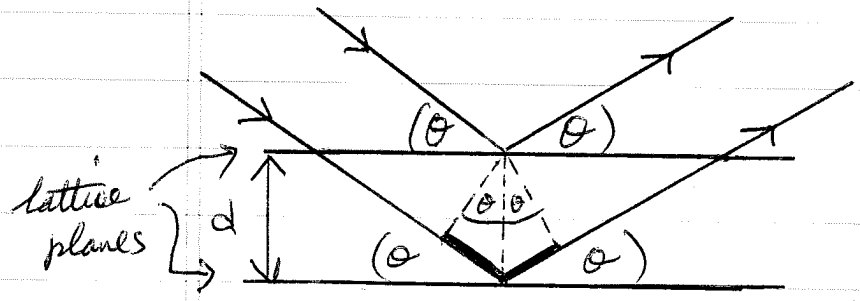
X-ray diffraction

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:

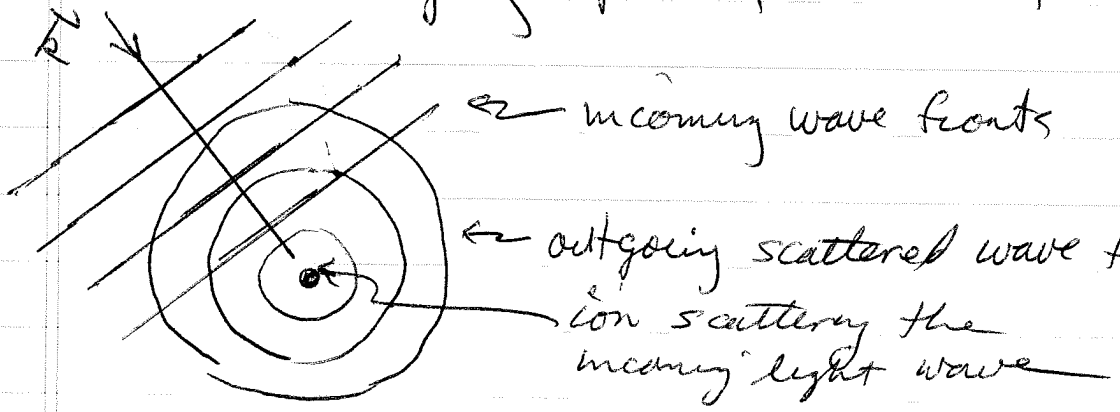
$$\boxed{2d\sin\theta = n\lambda}$$ condition for Bragg scattering

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

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

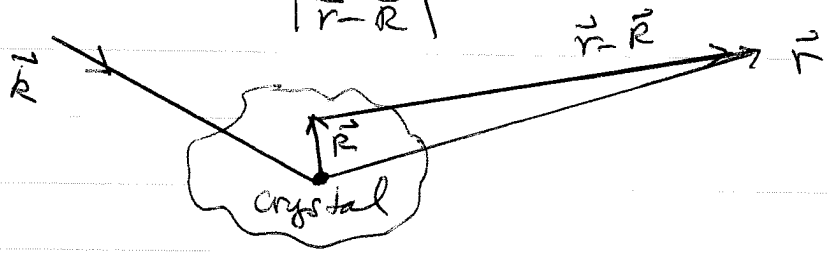
We now want to relate the phenomenon of Bragg scattering to the reciprocal lattice $\{\vec{K}\}$. This gives the <u>von Laue</u> formulation of X-ray scattering.

Consider a plane ~~light~~ polarized light wave $e^{i\vec{k}\cdot\vec{r}}$ 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

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



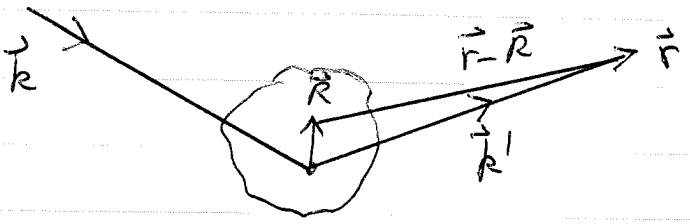
outgoing spherical wave is centered at the ion at $\vec{R}$
has same wavenumber $k = |\vec{k}|$ as incident plane wave
$f(\theta,\varphi)$ gives scattered amplitude from ion as function of spherical direction angles θ, φ with respect to origin.
The particular function form $f(\theta,\varphi)$ is determined 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.

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

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

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



since scattering off the coin is elastic
$|\vec{k}'| = |\vec{k}|$ i.e. wavelength of scattered spherical wave = wavelength incident wave

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

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

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

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

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

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

$$f(\theta,\varphi)e^{i\delta_0}\,\frac{e^{i(kr - \vec{k}'\cdot\vec{R} + \vec{k}\cdot\vec{R})}}{r} \quad \Leftarrow \text{approx } |\vec{r}-\vec{R}| \sim r \text{ here}$$

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

$\frac{e^{ikr}}{r}$: outgoing spherical wave centered at origin of crystal

$e^{i(\vec{k}-\vec{k}')\cdot\vec{R}}$: phase shift due to position of coin at $\vec{R}$ with respect to the origin.

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

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

Then the total scattered wave is

$$\sum_{\vec{R}} \underbrace{f(\theta,\varphi)\, e^{i\delta_0} \frac{e^{ikr}}{r}}_{\text{same factor for all coins since each site of BL is identical}} \underbrace{e^{i\Delta\vec{k}\cdot\vec{R}}}_{\text{phase factor due to position of coin at } \vec{R} \text{ respect to origin of crystal}}$$

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

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

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

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

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

~~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