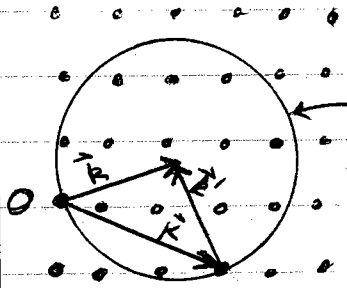
Note: all $\vec{k}$ that lie on the surface of the 1st Brillouin zone satisfy the condition for Bragg scattering since the surface of the 1st Brillouin zone is constructed from the Bragg planes of the smallest reciprocal lattice vectors $\vec{K}$. The intersections of the Bragg planes of larger $\vec{K}$ 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!



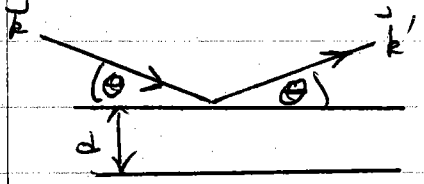
points in reciprocal ~~space~~ space

draw a sphere of radius $|\vec{k}|$ centered at the end point of the vector $\vec{k}$. Only if the surface of the sphere passes through a point of the reciprocal lattice $\{\vec{K}\}$ will there be a $\vec{k}'$ with $|\vec{k}'| = |\vec{k}|$ such that $\vec{k}' = \vec{k} - \vec{K}$ $\quad (\vec{k} - \vec{k}' = \vec{K})$

For a general $\vec{k}$ (ie 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

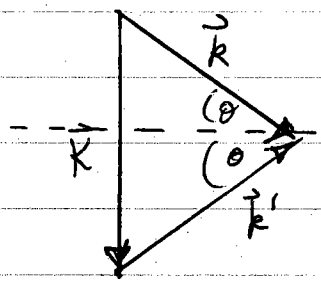
$$2d\sin\theta = n\frac{2\pi}{k}$$

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

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

electrons – a preview

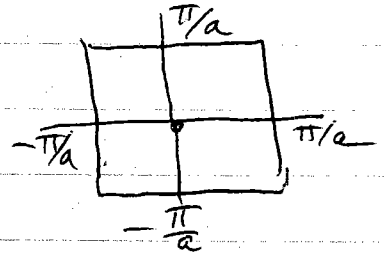
The above argument for X-rays is true for any waves. In particular it is also true for particle waves (where $\vec{p} = \hbar\vec{k}$ gives the quantum wave vector $\vec{k}$) provided one assumes the collisions of the particle with the crystal are elastic (ie the particle only exchanges momentum but not energy to the crystal). If one shot a high energy electron into the crystal, one could see electron diffraction patterns with Bragg peaks. Such electrons would scatter only if the tip of the wave vector $\vec{k}$ lay on a Bragg plane.

What about a conduction electron inside the metal? In the absence of the periodic ion potential, the electron state would be a plane wave $e^{i\vec{k}\cdot\vec{r}}$. When we turn on the ion potential, such a plane wave would scatter if $\vec{k}$ lay on a Bragg plane. But in the presence of the ion potential, $e^{i\vec{k}\cdot\vec{r}}$ is no longer an exact eigenstate. We will see that the eigenstates in the presence of the ion potential is a mixture of $e^{i\vec{k}\cdot\vec{r}}$ plus all the states $e^{i(\vec{k}+\vec{K})\cdot\vec{r}}$ into which it can be scattered by a Bragg plane. From perturbation theory in quantum mechanics, the extent to which the scattered state $e^{i(\vec{k}-\vec{K})\cdot\vec{r}}$ mixes into the free electron state $e^{i\vec{k}\cdot\vec{r}}$ is determined by

the "energy denominator" $\frac{1}{\varepsilon(\vec{k}) - \varepsilon(\vec{k}-\vec{K})}$.
Hence states $e^{i\vec{k}\cdot\vec{r}}$ where $\vec{k}$ is far from any Bragg plane (and so where $\frac{1}{\varepsilon_k - \varepsilon_{k-K}}$ is small) are very little changed from the free electron plane wave state. It is only states $e^{i\vec{k}\cdot\vec{r}}$ where $\vec{k}$ lies <u>close</u> to a Bragg plane that there will be a strong mixing in of the scattered state $e^{i(\vec{k}-\vec{K})\cdot\vec{r}}$ and the resulting eigenstate is noticeably different from the free electron state (it will look like a reflected standing wave)

this explains why metals with valence $Z=1$ are so well described by the free electron model. When $Z=1$, the Fermi surface lies away from all Bragg planes, so all electron states have little Bragg scattering and free electron states are a very good approximation

For simplicity, consider a simple cubic BL with lattice constant a and valence $Z=1$. The RL has a 1st Brillouin zone with volume $\left(\frac{2\pi}{a}\right)^3$



The Fermi wave vector k_F is given by

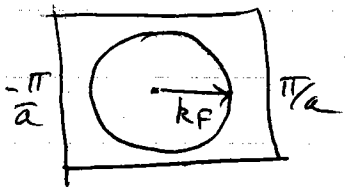
$$\frac{\frac{4}{3}\pi k_F^3}{4\pi^3} = n$$

$$k_F = (3\pi^2 n)^{1/3}$$

For $Z=1$, conduction electron density is $n = 1/a^3$

$$k_F = \frac{(3\pi^2)^{1/3}}{a} \qquad \frac{k_F}{a} = \frac{3.09}{a} < \frac{\pi}{a}$$

and so the Fermi surface lies entirely within the 1st Brillouin Zone. All electron states with the Fermi surface are therefore close to free electron-like, since they are not near any Bragg planes.



Note: volume in k-space of Fermi sphere is

$$\frac{4}{3}\pi k_F^3 = 4\pi^3 n = \frac{1}{2}\left(\frac{2\pi}{a}\right)^3 = \frac{1}{2} \text{ vol } 1^{st} \text{ B.Z.}$$

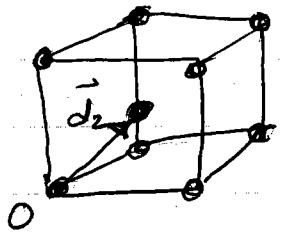
This is in general true for any B.L.

$\Rightarrow$ for $Z=1$, the Fermi surface ~~almost always lies entirely within 1st B.Z.~~ occupies a volume in k-space equal to 1/2 the volume of the 1st B.Z.

If $Z=2$ however, then conduction electron density $n = 2/a^3$ and Fermi surface will in general cut ~~over~~ across the surface of the 1st B.Z. The electron states at the BZ surface will not be free electron-like and there is now the possibility for more complicated behavior.

Example: Regard bcc as sc with a two point basis

$$\vec{d}_1 = 0, \quad \vec{d}_2 = \frac{a}{2}(\hat{x}+\hat{y}+\hat{z})$$



primitive vectors for sc are

$$a_1 = a\hat{x}, \quad a_2 = a\hat{y}, \quad a_3 = a\hat{z}$$

primitive vectors for sc RL are

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

R.L. vector $\vec{K} = \frac{2\pi}{a}(n_1\hat{x} + n_2\hat{y} + n_3\hat{z})$

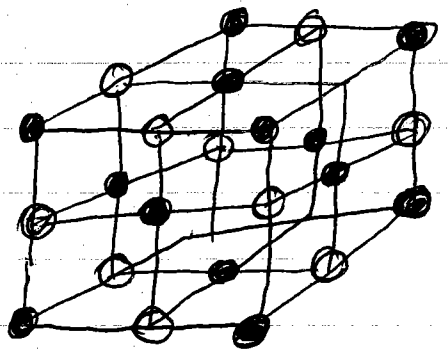
n_1, n_2, n_3 integer

Geometric form factor is

$$S_K = e^{i\vec{K}\cdot\vec{d}_1} + e^{i\vec{K}\cdot\vec{d}_2} = 1 + e^{i\pi(n_1+n_2+n_3)}$$

$$= \begin{cases} 2 & \text{if } n_1+n_2+n_3 \text{ even} \\ 0 & \text{if } n_1+n_2+n_3 \text{ odd} \end{cases}$$

— no Bragg peaks here!



for ● $S_K = 2$

for ○ $S_K = 0 \Rightarrow$ Bragg peak vanishes

Removing the sites for which $S_K = 0$ we see that we are left with an fcc RL with unit cell of length $\frac{4\pi}{a}$. But this is just what we expect for a bcc direct lattice! So all is consistent.

Suppose now we have a lattice with a basis but <u>different types</u> of ions occupy the basis sites, (for example the NaCl or zinc blend structure)

Now the angular factor $f(\theta, \varphi)$, which gave the modulation of the scattered wave on observation angle, can be different for the different type of ions. The structure factor should thus include this. We can define

$$S_K = \sum_{j=1}^{n} f_j(\vec{K}) e^{i \vec{K} \cdot \vec{d}_j}$$

↑ n point basis

scattered amplitude $\sim \frac{e^{ikr}}{r} \sum_{\vec{R}} e^{i \vec{K} \cdot \vec{R}} S(\vec{K})$

$f_j(\vec{K})$ is called the atomic form factor and depends on the momentum transfer $\vec{K} = \vec{k} - \vec{k}'$. It is determined by the internal structure of the ion at site $\vec{d}_j$ in the basis. f_j is the same for identical types of ions.

For a single model of dipole radiation

$$f_j(\vec{K}) = -\frac{1}{e} \int d^3\vec{r}\, e^{i \vec{K} \cdot \vec{r}} \rho_j(\vec{r})$$

↑ depends on $\vec{K}$

↑ charge density of ion at $\vec{d}_j$

$S_{\vec{K}}$ will not in general vanish at any $\vec{K}$. for small $\vec{K}$, above is just $i\vec{K} \cdot$ (dipole moment)