electrons - a preview

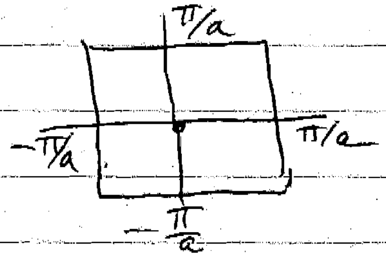
The above argument for X-rays is true for *any* waves. In particular it is also true for particle waves (where $\vec{p} = \hbar \vec{k}$ gives the quantum wave vector $\vec{k}$) provided one assumes the collisions of the particle with the crystal are *elastic* (ie the particle only ~~loses~~ exchanges 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" $\dfrac{1}{\mathcal{E}(\vec{k}) - \mathcal{E}(\vec{k}-\vec{K})}$.
Hence states $e^{i\vec{k}\cdot\vec{r}}$ where $\vec{k}$ is far from any Bragg plane (and so where $\dfrac{1}{\mathcal{E}_k - \mathcal{E}_{k-K}}$ 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 eigenstates 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

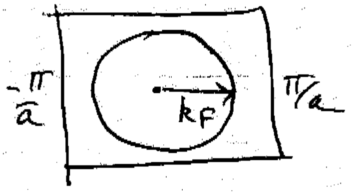
$$\frac{\frac{4}{3}\pi k_F^3}{4\pi^3} = n$$

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

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

$$k_F = \frac{(3\pi^2)^{1/3}}{a} \text{ [illegible] } = \frac{3.09}{a} < \frac{\pi}{a}$$

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.

⇒ for $Z=1$, the Fermi surface ~~almost~~ always ~~lies entirely within 1st B.Z.~~ occupies a volume in k-space equal to ½ 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 ~~[illegible]~~ 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.

X-ray scattering from BL with basis

We saw that the amplitude of the scattered X-ray will be proportional to

$$\sum_i e^{i \Delta k \cdot R_i} \qquad \text{where } \vec{\Delta k} = \vec{k} - \vec{k}'$$

This vanishes when $\vec{\Delta k} \neq \vec{K}$ in R.L.

The above calculation viewed scattering as scattering off the identical Wigner-Seitz cells that can be constructed about each BL site $\vec{R}_i$. These W-S cells are all identical so they scatter the same. But we did not need to assume anything about the ions contained in each such W-S cell. There might be a single ion at R_i or there might be several ions at positions $\vec{R}_i + \vec{d}_j$, $j = 1, \ldots, n$, in which case the crystal is a BL with a basis.

Suppose we have a BL with a basis, and all the ions are identical (ex: C ions in a diamond structure). In this case no only is the scattering off each W-S cell the same, but the scattering off each individual ion is the same.

We would then conclude that the scattered amplitude is proportional to

$$\sum_i \sum_{j=1}^{n} e^{i \vec{\Delta k} \cdot (\vec{R}_i + \vec{d}_j)} = \sum_i e^{i \vec{\Delta k} \cdot \vec{R}_i} \sum_{j=1}^{n} e^{i \vec{\Delta k} \cdot \vec{d}_j}$$

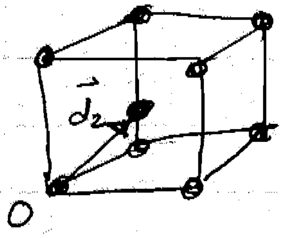
Again this vanishes unless $\vec{\Delta k} = \vec{K}$ in R.L., because of the first term. The 2nd term tells how the amplitude is modulated at different $\vec{K}$ due to the specific positions of the ions within the W-S cell.

Define
$$S_K \equiv \sum_{j=1}^{n} e^{i \vec{K} \cdot \vec{d}_j}$$

"geometric structure factor"

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

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

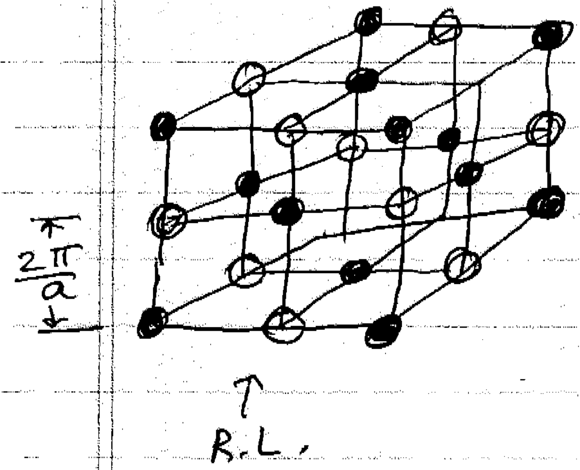
R.L. vector $\vec{K} = \frac{2\pi}{a}(n_1\hat{x} + n_2\hat{y} + n_3\hat{z})$

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

Diamond lattice - fcc with 2 point basis

⇒ RL is bcc

$$\vec{b}_1 = \frac{2\pi}{a}(\hat{y}+\hat{z}-\hat{x})$$
$$\vec{b}_2 = \frac{2\pi}{a}(\hat{z}+\hat{x}-\hat{y})$$
$$\vec{b}_3 = \frac{2\pi}{a}(\hat{x}+\hat{y}-\hat{z})$$
$$\vec{d}_1 = 0, \quad \vec{d}_2 = \frac{a}{4}(\hat{x}+\hat{y}+\hat{z})$$

$$S_K = 1 + e^{\frac{1}{2} i\pi(n_1+n_2+m_3)}$$

for $K = n_1\vec{b}_1 + n_2\vec{b}_2 + n_3\vec{b}_3$

$$= \begin{cases} 2 & n_1+n_2+n_3 = 4m, \quad m \text{ integer} \quad \text{twice even} \\ 1 \pm i & n_1+n_2+n_3 = 2m+1 \quad \text{odd} \\ 0 & n_1+n_2+n_3 = 2(2m+1) \quad \text{twice odd} \end{cases}$$

A&M fig 6.12

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

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

$\uparrow$

n point basis

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

$f_j(\vec{K})$ 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 simple model of dipole radiation

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

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

depends on $\vec{K}$

S_K will not in general vanish at any $\vec{K}$.

for small $\vec{K}$, above is just $i\vec{K}\cdot$(dipole moment)