

## X-ray scattering from BL with basis

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

$$\sum_i e^{i\vec{\Delta k} \cdot \vec{R}_i} \quad \text{where } \vec{\Delta k} = \vec{k} - \vec{k}'$$

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  $\vec{R}_i$  or there might be several ions at positions  $\vec{R}_i + \vec{d}_j$ ,  $j=1, \dots, n$ , 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 not 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.

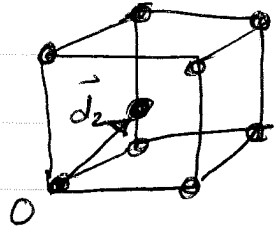
Define

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

"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

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

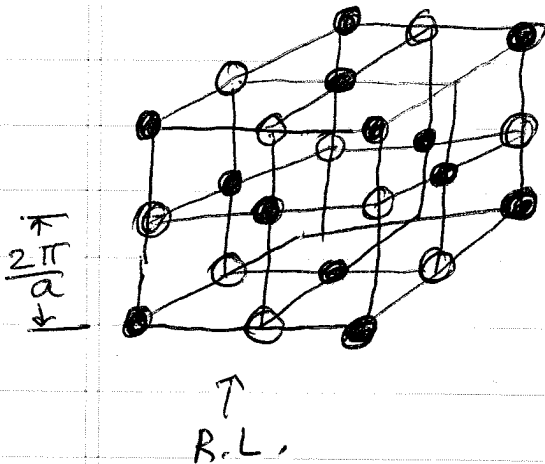
$$\text{R.L. vector } \vec{K} = \frac{2\pi}{a}(n_1\hat{x} + n_2\hat{y} + n_3\hat{z})$$

$n_1, n_2, n_3$  integers

Geometric form factor is

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

$$= \begin{cases} 2 & \text{if } n_1 + n_2 + n_3 \text{ even} \\ 0 & \text{if } n_1 + n_2 + n_3 \text{ odd} \end{cases} \quad \text{— no Bragg peaks here!}$$



$$\text{for } \bullet \quad S_K = 2$$

$$\text{for } \circ \quad S_K = 0 \Rightarrow \text{Bragg peak vanishes}$$

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

$$\vec{b}_1 = \frac{2\pi}{a} (\hat{y} + \hat{z} - \hat{x})$$

$$\vec{b}_2 = \frac{2\pi}{a} (\hat{z} + \hat{x} - \hat{y})$$

$$\vec{b}_3 = \frac{2\pi}{a} (\hat{x} + \hat{y} - \hat{z})$$

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

$$S_{\vec{k}} = 1 + e^{\frac{1}{2} i \pi (n_1 + n_2 + n_3)}$$

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

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

Atom fig 6.12

Suppose now we have a lattice with a basis but different types 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 then include this. We can define

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

↑  
n point basis

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

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

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

depends on  $\vec{K}$   
 $S_{\vec{K}}$  will not in general vanish at any  $\vec{K}$ .

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

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

## electrons - a preview

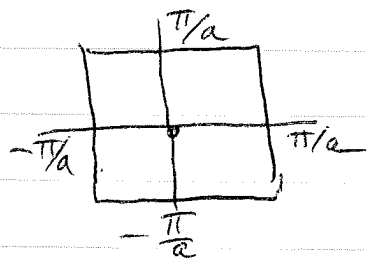
The above argument for X-rays is true for any waves. In particular it is also true for particle waves (where  $\vec{p} = \hbar\vec{k}$  gives the quantum wave vector  $\vec{k}$ ) provided one assumes the collisions of the particle with the crystal are elastic (ie the particle only ~~loses~~ <sup>exchanges</sup> 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"  $\frac{1}{E(\vec{k}) - E(\vec{k}-\vec{R})}$ .  
Hence states  $e^{i\vec{k}\cdot\vec{r}}$  where  $\vec{k}$  is far from any Bragg plane (and so where  $\frac{1}{E_{\vec{k}} - E_{\vec{k}-\vec{R}}}$  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 close to a Bragg plane that there will be a strong mixing in of the scattered state  $e^{i(\vec{k}-\vec{R})\cdot\vec{r}}$  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 1<sup>st</sup> Brillouin zone with volume  $(\frac{2\pi}{a})^3$



The Fermi wave vector  $k_F$  is given by

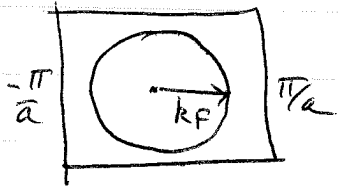
$$\frac{\frac{4}{3}\pi k_F^3}{4\pi^3} = m$$

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

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

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

and so the Fermi surface lies entirely within the 1<sup>st</sup> 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

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

This is in general true for any B.L.

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

If  $z=2$  however, then conduction electron density  $m = 2/a^3$  and Fermi surface will in general cut ~~over~~ across the surface of the 1<sup>st</sup> 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.



## Electrons in a crystal

When we discussed X-ray scattering we saw that the condition of constructive interference required that an incident wavevector  $\vec{k}$  could only scatter into wavevectors  $\vec{k}' = \vec{k} - \vec{K}$  where  $\vec{K}$  was in the R.L.

For electrons in a crystal we expect similar behavior since our argument depended only on the wave nature of the scattering.

So a free electron plane wave state  $e^{i\vec{k}\cdot\vec{r}}$  will get scattered into states  $e^{i\vec{k}'\cdot\vec{r}}$  with  $\vec{k}' = \vec{k} - \vec{K}$ . We therefore expect the eigenstates of an electron in the periodic ionic potential of the crystal will be a mixture of these scattered states

$$\begin{aligned}\psi_{\vec{k}}(\vec{r}) &= \sum_{\vec{K}} e^{i(\vec{k}-\vec{K})\cdot\vec{r}} c_{\vec{k}-\vec{K}} \\ &= e^{i\vec{k}\cdot\vec{r}} \sum_{\vec{K}} e^{-i\vec{K}\cdot\vec{r}} c_{\vec{k}-\vec{K}} \\ &= e^{i\vec{k}\cdot\vec{r}} u_{\vec{k}}(\vec{r}) \quad \text{where } u_{\vec{k}}(\vec{r}) = \sum_{\vec{K}} e^{-i\vec{K}\cdot\vec{r}} c_{\vec{k}-\vec{K}}\end{aligned}$$

$u_{\vec{k}}(\vec{r})$  is periodic on the Bravais lattice:

$$\begin{aligned}u_{\vec{k}}(\vec{r} + \vec{R}) &= \sum_{\vec{K}} e^{-i\vec{K}\cdot(\vec{r} + \vec{R})} c_{\vec{k}-\vec{K}} = \sum_{\vec{K}} e^{-i\vec{K}\cdot\vec{R}} e^{-i\vec{K}\cdot\vec{r}} c_{\vec{k}-\vec{K}} \\ &= \sum_{\vec{K}} e^{-i\vec{K}\cdot\vec{r}} c_{\vec{k}-\vec{K}} = u_{\vec{k}}(\vec{r}) \quad \text{since } e^{-i\vec{K}\cdot\vec{R}} = 1 \\ &\quad \text{for all } \vec{R} \text{ in R.L.}\end{aligned}$$

This then yields Bloch's Theorem which we prove more rigorously later.

The energy eigenstates of an electron in a potential with the periodicity of a Bravais lattice ~~can~~ can be written in the form

$$\psi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} u_{\vec{k}}(\vec{r})$$

where  $u_{\vec{k}}(\vec{r}+\vec{R}) = u_{\vec{k}}(\vec{r})$  is periodic on the B.L.

An equivalent alternative statement of Bloch's Theorem is

$$\psi_{\vec{k}}(\vec{r}+\vec{R}) = e^{i\vec{k}\cdot\vec{R}} \psi_{\vec{k}}(\vec{r})$$

If the wave vector  $\vec{k}$  lies exactly on the Bragg plane bisected by R.L. vector  $\vec{K}$ , then the two free electron plane wave states  $\vec{k}$  and  $\vec{k}' = \vec{k} - \vec{K}$  are degenerate in energy and so we expect they must mix equally in forming the new eigenstates in the presence of the periodic potential. Since we start with two states  $\vec{k}$ ,  $\vec{k}'$  we should wind up with two new states. If they mix equally, their relative coefficients should just be a phase factor  $e^{i\phi}$ . Hence we expect the two eigenstates to have the form

$$\psi_1(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} + e^{i\phi_1} e^{i\vec{k}'\cdot\vec{r}}$$

$$\psi_2(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} + e^{i\phi_2} e^{i\vec{k}'\cdot\vec{r}}$$

The new eigenstates  $\psi_1$  and  $\psi_2$  should be orthogonal

$$0 = \langle \psi_1 | \psi_2 \rangle = \int d^3r \psi_1^*(\vec{r}) \psi_2(\vec{r})$$

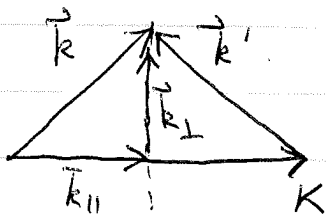
$$= \int d^3r \left[ e^{-i\vec{k}\cdot\vec{r}} + e^{-i\phi_1} e^{-i\vec{k}'\cdot\vec{r}} \right] \left[ e^{i\vec{k}\cdot\vec{r}} + e^{i\phi_2} e^{i\vec{k}'\cdot\vec{r}} \right]$$

$$= \int d^3r \left[ 1 + e^{i(\phi_2 - \phi_1)} + e^{-i\phi_1} e^{i(\vec{k} - \vec{k}')\cdot\vec{r}} + e^{i\phi_2} e^{i(\vec{k}' - \vec{k})\cdot\vec{r}} \right]$$

these two terms integrate to zero - proof later

$$= V \left[ 1 + e^{i(\phi_2 - \phi_1)} \right]$$

$$= 0 \text{ only if } \phi_2 - \phi_1 = \pi$$



$$\vec{k}' = \vec{k} - \vec{K}$$

$$\text{write } \vec{k} = \vec{k}_{\parallel} + \vec{k}_{\perp}$$

$$\text{then } \vec{k}' = -\vec{k}_{\parallel} + \vec{k}_{\perp}$$

$$\text{So } \psi_1(\vec{r}) = e^{i\phi_1/2} e^{i\vec{k}_{\perp}\cdot\vec{r}} \left\{ e^{-i\phi_1/2} e^{i\vec{k}_{\parallel}\cdot\vec{r}} + e^{i\phi_1/2} e^{-i\vec{k}_{\parallel}\cdot\vec{r}} \right\}$$

$$= e^{i\phi_1/2} e^{i\vec{k}_{\perp}\cdot\vec{r}} 2 \cos(\vec{k}_{\parallel}\cdot\vec{r} - \phi_1/2)$$

Similarly

$$\psi_2(\vec{r}) = e^{i\phi_2/2} e^{i\vec{k}_{\perp}\cdot\vec{r}} 2 \cos(\vec{k}_{\parallel}\cdot\vec{r} - \phi_2/2)$$

$$= e^{i\phi_2/2} e^{i\vec{k}_{\perp}\cdot\vec{r}} 2 \cos(\vec{k}_{\parallel}\cdot\vec{r} - \frac{\phi_1}{2} - \frac{\pi}{2})$$

$$= e^{i\phi_2/2} e^{i\vec{k}_{\perp}\cdot\vec{r}} 2 \sin(\vec{k}_{\parallel}\cdot\vec{r} - \frac{\phi_1}{2})$$

so

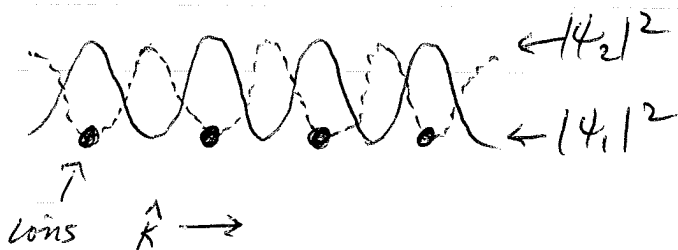
$$\left. \begin{aligned} |\psi_1(\vec{r})|^2 &\sim \cos^2(\vec{k}_{11} \cdot \vec{r} - \phi_1/2) \\ |\psi_2(\vec{r})|^2 &\sim \sin^2(\vec{k}_{11} \cdot \vec{r} - \phi_1/2) \end{aligned} \right\} \text{probability density}$$

reflection from Bragg plane gives standing waves in direction  $\parallel$  to  $\vec{k}$

Since  $\vec{k}_{11} = \frac{\vec{k}}{2}$  we have  $\vec{k}_{11} \cdot \vec{R} = \frac{\vec{k} \cdot \vec{R}}{2} = \pi n$  where  $n$  is an integer

$$\Rightarrow |\psi_1(\vec{r})|^2 \text{ and } |\psi_2(\vec{r})|^2 \text{ have the periodicity of the B.L.}$$
$$\circ \quad |\psi_1(\vec{r} + \vec{R})|^2 \approx \cos^2(\vec{k}_{11} \cdot \vec{r} + \pi n - \phi_1/2) = \cos^2(\vec{k}_{11} \cdot \vec{r} - \phi_1/2) = |\psi_1(\vec{r})|^2$$

The only difference between  $\psi_1$  and  $\psi_2$  is their relative phase shift of  $\frac{\pi}{2}$ , which shifts the location of the peaks of  $|\psi_1|^2$  and  $|\psi_2|^2$  relative to the positions of the ions. By symmetry we expect one of these, say  $\psi_1$ , will have its peaks positioned at the same sites as the ions, while the other,  $\psi_2$ , will have its peaks positioned in between the sites of the ions. For example, if  $\vec{k}$  is the smallest non-zero R.L. vector,  $|\vec{k}| = \frac{2\pi}{a}$  with  $a =$  separation between ions, we expect,



The spatial periodicity of  $\psi_1$  and  $\psi_2$  is  $\lambda = \frac{2\pi}{k_{11}} = \frac{2\pi}{(K/2)}$   
 $= \frac{2\pi}{\pi/a} = 2a$ . The spatial periodicity of  $|\psi_1|^2$  and  
 $|\psi_2|^2$  is therefore  $\frac{1}{2}\lambda = a$ . Since  $\psi_1$  and  $\psi_2$  are  $\frac{\pi}{2}$   
out of phase, then  $|\psi_1|^2$  and  $|\psi_2|^2$  are  $\pi$  out of  
phase, hence their relative peaks are separated  
by  $a/2$  as in the diagram above.

Now when one turns on the attractive ionic potential,  
the state  $\psi_1$  will have a lower energy than  
the state  $\psi_2$  since  $\psi_1$  has its peaks located  
at the ions, where the interaction is strongest,  
while  $\psi_2$  has its peaks in between the ions, where  
the interaction is weakest.

Hence we expect that the two states  $\psi_1$  and  $\psi_2$ ,  
which were degenerate in energy before turning  
on the ionic potential, now split in energy, with  
a finite energy gap between them,  $E_1 < E_2$ .

⇒ Ionic potential cause a gap to appear in  
the energy dispersion relation  $E(\vec{k})$  whenever  
 $\vec{k}$  crosses a Bragg plane. Since the  
Brillouin zones are formed by the intersections  
of Bragg planes, gaps in  $E(\vec{k})$  open as  $\vec{k}$   
crosses the boundary of any Brillouin zone.