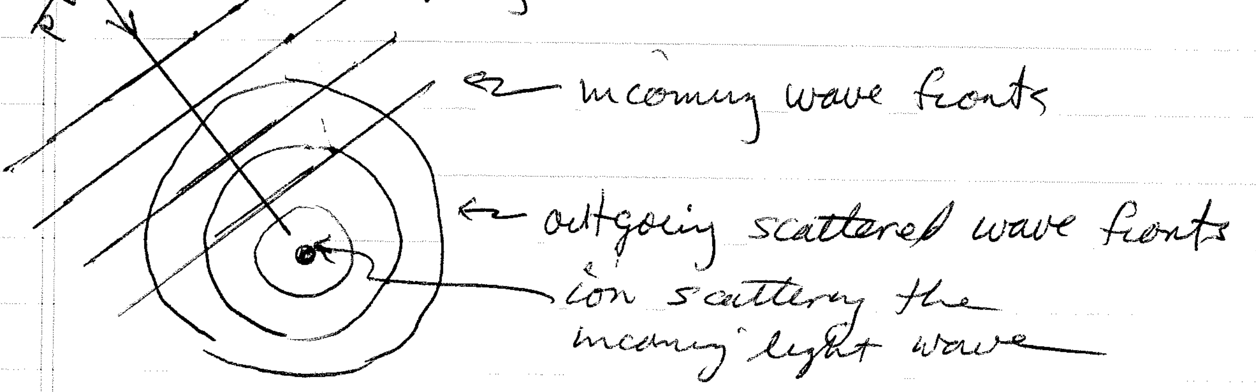
In experiment we know λ, we measure the θ that produces a peak in the reflected intensity, so we thus can determine the separation d between the lattice planes. In this way one can deduce the lattice constants and geometry.

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

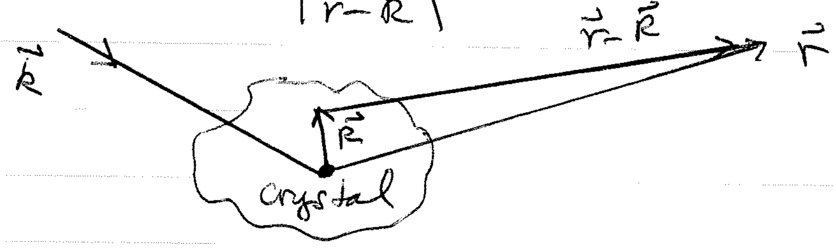
We now want to relate the phenomenon of Bragg scattering to the reciprocal lattice $\{\bar{K}\}$. This gives the von Laue formulation of X-ray scattering.

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

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



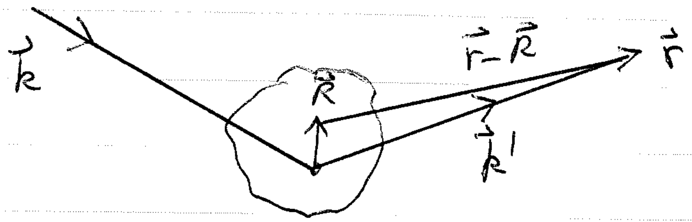
outgoing spherical wave is centered at the ion at $\vec{R}$
has same wavenumber $k = |\vec{k}|$ as incident plane wave
$f(\theta,\varphi)$ gives scattered amplitude from ion as function of spherical direction angles θ, φ with respect to origin.
The particular function form $f(\theta,\varphi)$ is determined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

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

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

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

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

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

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

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

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

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

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

Then the total scattered wave is

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

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

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

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

Now if $\Delta k = \vec{K}$ 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 $\sum_{\vec{R}} e^{i\vec{\Delta k}\cdot\vec{R}} = N$ number of sites in BL

clearly this is the maximum possible value of the sum

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

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

Proof: Since the BL is invariant under translations, ie the set $\{\vec{R}\}$ is equivalent to the set $\{\vec{R}+\vec{R}_0\}$ where R_0 is any particular member of the BL, then

$$\sum_{\vec{R}} e^{i\Delta\vec{k}\cdot\vec{R}} = \sum_{\vec{R}} e^{i\Delta\vec{k}\cdot(\vec{R}+\vec{R}_0)}$$

$$= e^{i\Delta\vec{k}\cdot\vec{R}_0} \sum_{R} e^{i\Delta\vec{k}\cdot\vec{R}}$$

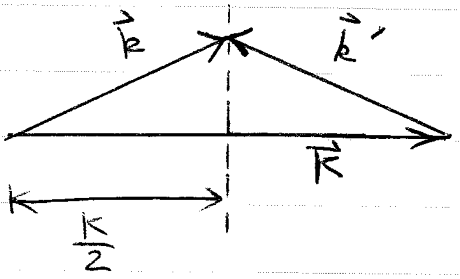
⇒ $e^{i\Delta\vec{k}\cdot\vec{R}_0} = 1$ and this must be true for any $\vec{R}_0$ in the BL, ie $\Delta\vec{k} = \vec{K}$ in R.L.

OR $\sum_{\vec{R}} e^{i\Delta\vec{k}\cdot\vec{R}} = 0$ 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 $\vec{k}'$ *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 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:



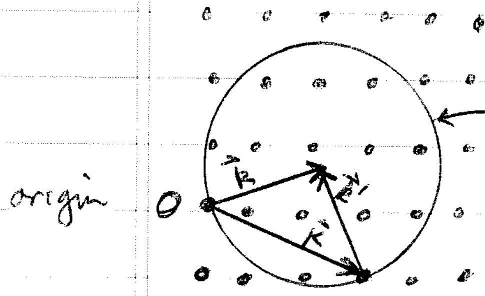
$$\vec{K} + \vec{k}' = \vec{k}$$

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 k-space is called a *Bragg plane*.

<u>Note</u>: 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.

<u>Question</u>: 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?

<u>Answer</u>: <u>Ewald Construction</u> say in general no!



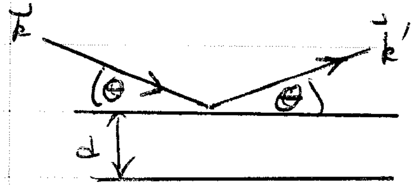
points in reciprocal ~~spa~~ space

draw a sphere of radius $|\vec{k}|$ centered at the end point of the vector $\vec{k}$. Only if the surface of this 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 formulations of X-ray scattering.

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



rewrite above as

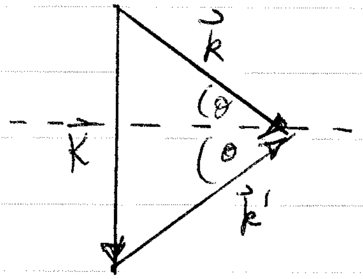
$$2d\sin\theta = n\frac{2\pi}{k}$$

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

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

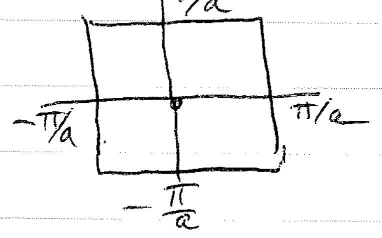
The above argument for X-rays is true for <u>any</u> waves. In particular it is also true for particle waves (where $\vec{p} = \hbar\vec{k}$ gives the quantum wave vector $\vec{k}$) provided one assumes the collisions of the particle with the crystal are <u>elastic</u> (ie the particle only ~~loses~~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

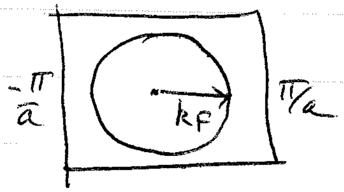
$$\frac{\frac{4}{3}\pi k_F^3}{4\pi^3} = n$$

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

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

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

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.

⇒ 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

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

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 $\vec{R}_i$ 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

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

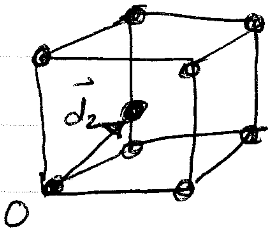
Again this vanishes unless $\vec{\Delta k} = \vec{K}$ in R.L., because of the first term. The 2nd term tells how the amplitude is modulated at different $\vec{K}$ due to the specific positions of the ions within the W-S cell.

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

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

primitive vectors for sc RL are
$\vec{b}_1 = \frac{2\pi}{a}\hat{x}$, $\vec{b}_2 = \frac{2\pi}{a}\hat{y}$, $\vec{b}_3 = \frac{2\pi}{a}\hat{z}$

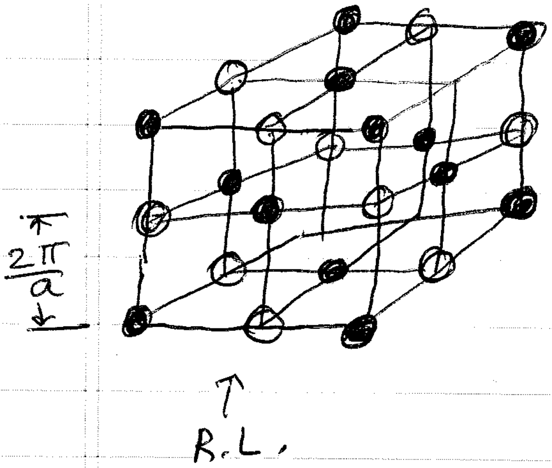
R.L. vector $\vec{K} = \frac{2\pi}{a}(n_1\hat{x} + n_2\hat{y} + n_3\hat{z})$

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

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

A+M fig 6.12

Suppose now we have a lattice with a basis but 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 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

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

$\nwarrow$ charge density of ion at $\vec d_j$

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

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