

Lecture 4 X-rays and Structure Factor

Simon: Chapter 14 (pp141-158); see also Kittel: Chapter 2 (pp30-43)

X-ray (wave) diffraction from crystals

We shall now consider the description of x-ray scattering from crystal planes.

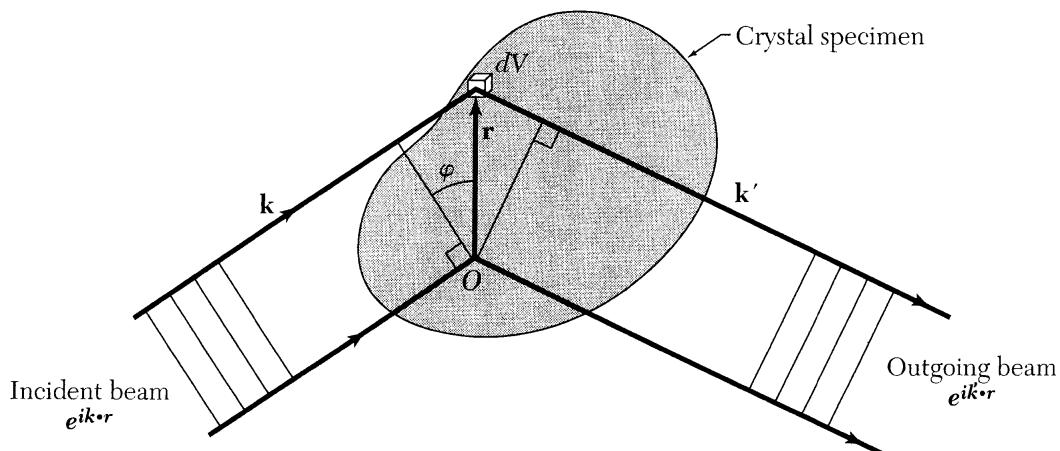


Figure 6 The difference in path length of the incident wave \mathbf{k} at the points O , \mathbf{r} is $r \sin \varphi$, and the difference in phase angle is $(2\pi r \sin \varphi)/\lambda$, which is equal to $\mathbf{k} \cdot \mathbf{r}$. For the diffracted wave the difference in phase angle is $-\mathbf{k}' \cdot \mathbf{r}$. The total difference in phase angle is $(\mathbf{k} - \mathbf{k}') \cdot \mathbf{r}$, and the wave scattered from dV at \mathbf{r} has the phase factor $\exp[i(\mathbf{k} - \mathbf{k}') \cdot \mathbf{r}]$ relative to the wave scattered from a volume element at the origin O .

Consider an incident beam on a crystal described by the expression $\exp(i\mathbf{k} \cdot \mathbf{r})$ where \mathbf{k} is the *incident* wavevector. After scattering the outgoing beam is described by the expression $\exp(i\mathbf{k}' \cdot \mathbf{r})$. These expressions are those for plane waves which model the incident and emerging x-rays.

We assume that the amplitude of the wave scattered from the crystal is proportional to the local electron concentration $n(\mathbf{r})$. (Key Physics assumption)

The amplitude of the electric and magnetic field vectors in the scattered electromagnetic wave (x-ray) is proportional to the integral (actually just a summation over the whole volume of the crystal):

$$F = \int dV n(\mathbf{r}) \exp[i(\mathbf{k} - \mathbf{k}') \cdot \mathbf{r}] = \int dV n(\mathbf{r}) \exp(-i\Delta\mathbf{k} \cdot \mathbf{r})$$

The integral is over the volume of the crystal dV and includes the expression for the electron density $n(\mathbf{r})$ and the difference in phase between the incident and scattered waves $\exp [....]$. For elastic scattering the magnitude of the vectors $\mathbf{k}' = \mathbf{k}$.

F is called the scattering amplitude and $\mathbf{k} + \Delta\mathbf{k} = \mathbf{k}'$

The quantity $\Delta\mathbf{k}$ is the change in wavevector and is called the *scattering vector*. For the particular condition of Bragg scattering any allowed value of $\Delta\mathbf{k}$ must equal a reciprocal lattice vector \mathbf{G} .

$$\Delta\mathbf{k} = \mathbf{G} \text{ is the Bragg condition}$$

Substituting for $n(\mathbf{r})$ (from Lecture 3) into the expression for F gives:

$$F = \sum_{\mathbf{G}} \int dV n_{\mathbf{G}} \exp[i(\mathbf{G} - \Delta\mathbf{k}) \cdot \mathbf{r}]$$

(Remember we can do this because $n(\mathbf{r})$ is a periodic function representing the atoms in the crystal described by Miller indices and reciprocal lattice vectors.)

When the scattering vector $\Delta\mathbf{k}$ is equal to a particular reciprocal lattice vector \mathbf{G} (the Bragg condition) the argument of the \exp function vanishes and $F = Vn_{\mathbf{G}}$

When $\Delta\mathbf{k}$ differs slightly from a reciprocal lattice vector \mathbf{G} , F becomes vanishingly small. (This behaviour gives the scattering linewidth – see Kittel chapter 2 problem 4).

As stated above, during an elastic scattering process the photon energy is conserved and the energy or frequency of the emerging photon is the same as that of the incident photon. Therefore, the *magnitudes* of \mathbf{k} and \mathbf{k}' are the same so that

$$k^2 = k'^2$$

This also applies for elastic scattering of electrons and neutrons from reciprocal lattice points (or in real space crystal planes).

From the condition vector $\Delta\mathbf{k}$ is equal to a particular reciprocal lattice vector \mathbf{G} it is straightforward to show that $\mathbf{k} + \mathbf{G} = \mathbf{k}'$ so that the diffraction condition becomes:

$$(\mathbf{k} + \mathbf{G})^2 = k^2 \quad \text{or} \quad 2\mathbf{k} \cdot \mathbf{G} + G^2$$

This is the key result of elastic scattering theory. It is more commonly written as:

$$2\mathbf{k} \cdot \mathbf{G} = G^2$$

This is an alternative statement of the Bragg scattering condition, and applies because the $\Delta\mathbf{k}$ has equivalent +ve and -ve values.

Brillouin Zones

A **Brillouin Zone** is a Wigner-Seitz primitive cell in the reciprocal lattice. The Brillouin statement of the scattering/diffraction condition is widely used in describing the properties of crystalline solids. The first Brillouin Zone is the unit cell in reciprocal space and contains all the spatial frequency information to completely reconstruct the crystal lattice.

It is used to describe the existence and properties of energy bands in solids (metals, semiconductors and insulators).

This illustrates the way in which the Brillouin zone model can describe all electronic properties of crystals and is a direct consequence of the periodic arrangement of atoms in a crystal. This will be discussed in more detail later in the course.

To develop the mathematical formulation we start with the diffraction condition:

$$2\mathbf{k} \cdot \mathbf{G} = G^2$$

This can be modified (divide by 4) to:

$$\mathbf{k} \cdot \left(\frac{1}{2}\mathbf{G}\right) = \left(\frac{1}{2}G\right)^2$$

To construct the Brillouin zone start at the origin of the reciprocal lattice (remember wavevectors and Brillouin zones only exist in *reciprocal space*). Select a reciprocal lattice vector \mathbf{G} , and draw a plane normal to the vector at its midpoint. This plane forms the boundary of the first Brillouin zone.

A x-ray will be diffracted if its wavevector \mathbf{k} has the magnitude and direction specified by the equation above.

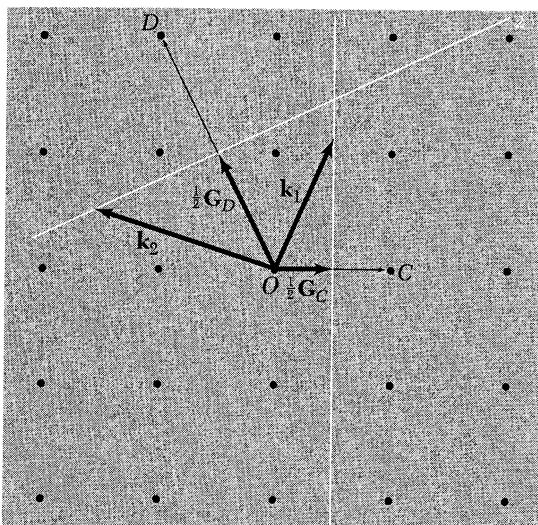


Figure 9a Reciprocal lattice points near the point O at the origin of the reciprocal lattice. The reciprocal lattice vector \mathbf{G}_C connects points OC ; and \mathbf{G}_D connects OD . Two planes 1 and 2 are drawn which are the perpendicular bisectors of \mathbf{G}_C and \mathbf{G}_D , respectively. Any vector from the origin to the plane 1, such as \mathbf{k}_1 , will satisfy the diffraction condition $\mathbf{k}_1 \cdot (\frac{1}{2}\mathbf{G}_C) = (\frac{1}{2}\mathbf{G}_C)^2$. Any vector from the origin to the plane 2, such as \mathbf{k}_2 , will satisfy the diffraction condition $\mathbf{k}_2 \cdot (\frac{1}{2}\mathbf{G}_D) = (\frac{1}{2}\mathbf{G}_D)^2$.

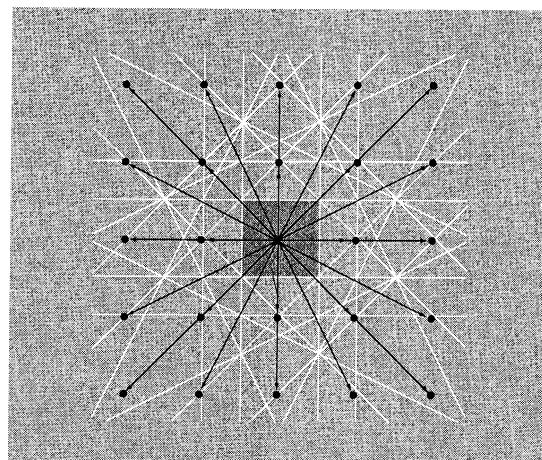


Figure 9b Square reciprocal lattice with reciprocal lattice vectors shown as fine black lines. The lines shown in white are perpendicular bisectors of the reciprocal lattice vectors. The central square is the smallest volume about the origin which is bounded entirely by white lines. The square is the Wigner-Seitz primitive cell of the reciprocal lattice. It is called the first Brillouin zone.

The set of planes that bisect the reciprocal lattice vectors define the first Brillouin zone. Any wave whose wavevector lies on the boundary of the first Brillouin zone will satisfy the diffraction condition above.

The first Brillouin zone is the small volume entirely enclosed by planes perpendicular to the midpoint of all the reciprocal lattice vectors.

We shall see later in the course that the first Brillouin zone is all that is needed to fully describe all the electronic properties of crystals. In the same way that the unit cell is analogous to the molecule in the real space crystal lattice so the first Brillouin zone can be used to describe the electronic properties.

Remember the units of the reciprocal lattice (and the first Brillouin zone) are inverse length. Consider the energy of a photon of electromagnetic radiation: $E = h\nu$. From a consideration of this we can see that energy can be expressed in units of cm^{-1} called the wavenumber (units commonly used by chemists). Reciprocal space is a natural way of describing energy and/or momentum of electrons. A constant wavevector implies a constant energy or momentum for an electron (but not a constant position). This is a more natural way of describing the properties of electron waves.

Having developed the mathematical description of the reciprocal lattice we now consider what the reciprocal lattices of real lattices (I really mean lattices in direct space) look like.

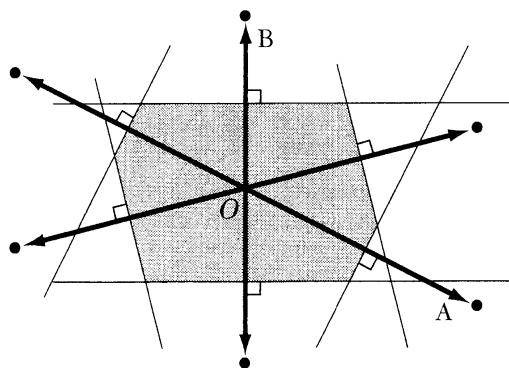


Figure 10 Construction of the first Brillouin zone for an oblique lattice in two dimensions. We first draw a number of vectors from O to nearby points in the reciprocal lattice. Next we construct lines perpendicular to these vectors at their midpoints. The smallest enclosed area is the first Brillouin zone.

Primitive cubic – reciprocal lattice

The primitive lattice vectors of a primitive cubic lattice are:

$$\mathbf{a}_1 = a\hat{x}; \quad \mathbf{a}_2 = a\hat{y}; \quad \mathbf{a}_3 = a\hat{z}$$

The vectors $\hat{x}, \hat{y}, \hat{z}$ are unit vectors of unit length and are orthogonal to each other.

The volume of the unit cell is $\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3 = a^3$.

The primitive lattice vectors of the reciprocal lattice are given by

$$\mathbf{b}_1 = (2\pi/a)\hat{x}; \quad \mathbf{b}_2 = (2\pi/a)\hat{y}; \quad \mathbf{b}_3 = (2\pi/a)\hat{z}$$

The reciprocal lattice is also a cube but now with a lattice constant of $2\pi/a$

The boundaries of the first Brillouin zone are the planes normal to the lattice vectors at the midpoint of each.

The volume of the first Brillouin zone is $(2\pi/a)^3$.

BCC Lattice – reciprocal lattice

A similar approach is used to identify the reciprocal lattice for the body centred cubic lattice.

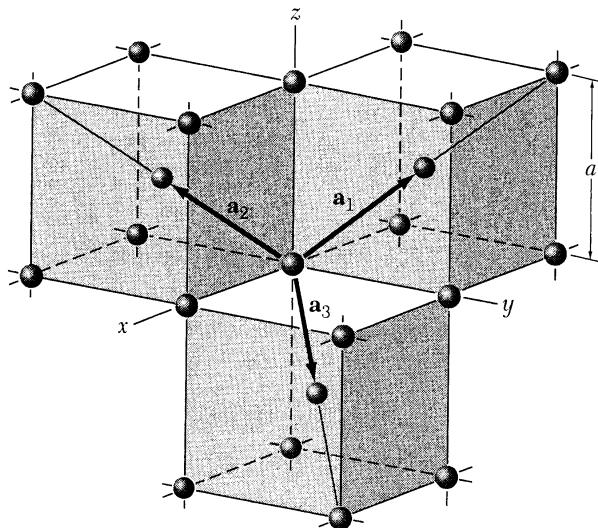


Figure 12 Primitive basis vectors of the body-centered cubic lattice.

The primitive (unit) vectors for the bcc lattice are:

$$\mathbf{a}_1 = \frac{1}{2}a(-\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}}) ; \mathbf{a}_2 = \frac{1}{2}(\hat{\mathbf{x}} - \hat{\mathbf{y}} + \hat{\mathbf{z}}) ; \mathbf{a}_3 = \frac{1}{2}a(\hat{\mathbf{x}} + \hat{\mathbf{y}} - \hat{\mathbf{z}})$$

The volume of the unit cell is $\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3 = 1/2 a^3$.

In this case the reciprocal lattice vectors are:

$$\mathbf{b}_1 = (2\pi/a)(\hat{\mathbf{y}} + \hat{\mathbf{z}}) ; \mathbf{b}_2 = (2\pi/a)(\hat{\mathbf{x}} + \hat{\mathbf{z}}) ; \mathbf{b}_3 = (2\pi/a)(\hat{\mathbf{x}} + \hat{\mathbf{y}})$$

These are the primitive lattice vectors of an fcc lattice.

An fcc lattice is the reciprocal lattice of a bcc lattice.

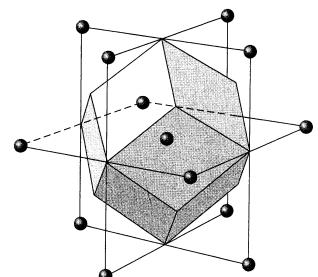


Figure 13 First Brillouin zone of the body-centered cubic lattice. The figure is a regular rhombic dodecahedron.

FCC Lattice – reciprocal lattice

The primitive unit vectors for the fcc lattice are:

$$\mathbf{a}_1 = \frac{1}{2}a(\hat{\mathbf{y}} + \hat{\mathbf{z}}) ; \mathbf{a}_2 = \frac{1}{2}a(\hat{\mathbf{x}} + \hat{\mathbf{z}}) ; \mathbf{a}_3 = \frac{1}{2}a(\hat{\mathbf{x}} + \hat{\mathbf{y}})$$

The volume of the unit cell is $1/4 a^3$

The reciprocal lattice vectors are:

$$\mathbf{b}_1 = \frac{1}{2}a(-\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}}) ; \mathbf{b}_2 = \frac{1}{2}(\hat{\mathbf{x}} - \hat{\mathbf{y}} + \hat{\mathbf{z}}) ; \mathbf{b}_3 = \frac{1}{2}a(\hat{\mathbf{x}} + \hat{\mathbf{y}} - \hat{\mathbf{z}})$$

These are equivalent to the primitive lattice vectors of a bcc lattice.

The reciprocal lattice of an fcc lattice is a bcc lattice.

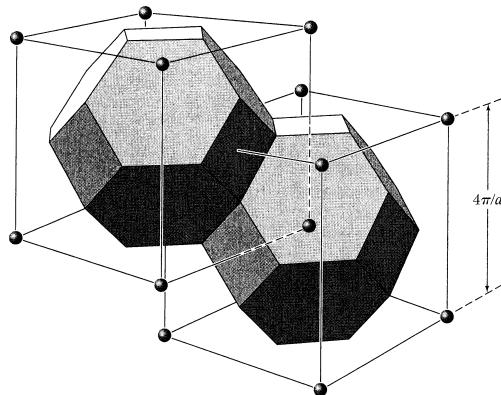


Figure 15 Brillouin zones of the face-centered cubic lattice. The cells are in reciprocal space, and the reciprocal lattice is body centered.

Fourier analysis of the lattice – form factor and the **structure factor**

The structure factor is determined by considering the scattering amplitude for a crystal of N cells. The **structure factor** describes the *intensity* of a scattered x-ray wave. Maximum scattering occurs when $\Delta\mathbf{k} = \mathbf{G}$ – the Bragg condition.

The structure factor is a mathematical description of how a crystal structure scatters incident radiation. The structure factor enables the intensity pattern produced by the scattered radiation to be correlated to the crystal structure.

The Bragg description considers parallel planes of atoms, it does not consider what interference effects may happen within a unit cell. The structure factor considers the intensity of scattered radiation within a unit cell when Bragg's Law is satisfied.

The scattering amplitude of an incident wave is then given by an integral over the unit cell with N unit cells giving the total for a crystal:

$$F_{\mathbf{G}} = N \int_{cell} dV n(\mathbf{r}) \exp(-i\mathbf{G} \cdot \mathbf{r}) = NS_{\mathbf{G}}$$

The quantity $S_{\mathbf{G}}$ is the **structure factor** and is defined as an integral over a single unit cell with the origin at $\mathbf{r} = 0$.

By considering the overall electron concentration $n(\mathbf{r})$ as a sum over all the **unique** atoms in a single cell n_j . The total electron concentration in the unit cell is then:

$$n(\mathbf{r}) = \sum_{j=1}^S n_j (\mathbf{r} - \mathbf{r}_j)$$

where there are S atoms in the unit cell.

The structure factor may now be written as integrals over s atoms in the unit cell:

$$S_{\mathbf{G}} = \sum_j \int dV n_j (\mathbf{r} - \mathbf{r}_j) \exp(-i\mathbf{G} \cdot \mathbf{r})$$

$$= \sum_j \exp(-i\mathbf{G} \cdot \mathbf{r}_j) \int dV n_j (\mathbf{p}) \exp(-i\mathbf{G} \cdot \mathbf{p})$$

where $\mathbf{p} = \mathbf{r} - \mathbf{r}_j$

The form factor is concerned about the influence of individual atoms in the crystal. (Remember that a crystal consists of a lattice and a basis. If the atoms in the basis are different the form factor will be different and the scattering power of individual atoms is different).

The *atomic form factor* is defined as:

$$f_j = \int dV n_j (\mathbf{p}) \exp(-i\mathbf{G} \cdot \mathbf{r}_j)$$

Integrated over all space (volume dV)

The structure factor describes the total scattering of an incident beam by the unique atoms of a crystal unit cell, taking into account the different scattering power of each atom through the term f_j . Because the atoms are spread out across the unit cell, there will be a difference in phase when considering the scattered amplitude from different atoms.

Combining the two expressions above gives the **structure factor of the crystal unit cell**

$$S_{\mathbf{G}} = \sum_j f_j \exp(-i\mathbf{G} \cdot \mathbf{r}_j)$$

(Remember \mathbf{r} has components a and \mathbf{G} has components b with integer pre-factors x, y, z and h, k and l

$$\mathbf{G} \cdot \mathbf{r} = 2\pi(hx_j + ky_j + lz_j)$$

Substituting for \mathbf{G} and \mathbf{r} gives:

$$S_{\mathbf{G}}(hkl) = \sum_j f_j \exp[-i2\pi(hx_j + ky_j + lz_j)]$$

$(x_j y_j z_j)$ position coordinates for \mathbf{r} and (h, k, l) coordinates of \mathbf{G}

Remember the *intensity* of the scattered radiation is $|S_{\mathbf{G}}|^2$ and that S may be complex.

Some examples: Structure Factor of bcc lattice

We can now illustrate the application of the structure factor. In mathematical terms we are applying a Fourier analysis to the crystal structure composed of lattice and basis.

The basis of the bcc lattice has atoms at: $x_1 = y_1 = z_1 = 0$ and $x_2 = y_2 = z_2 = \frac{1}{2}$. The bcc lattice unit cell has two unique atoms – one at the origin and one at the centre of the unit cell coordinates $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ (see diagram on lecture PowerPoint)

The structure factor then becomes:

$$S_G(hkl) = f[1 + \exp[-i\pi(h + k + l)]]$$

where f is the form factor for one atom. Evaluating the exponential means:

$$\begin{aligned} S &= 0 \text{ when } h + k + l = \text{odd integer} \\ S &= 2f \text{ when } h + k + l = \text{even integer} \end{aligned}$$

These are the *structure factor rules* for bcc. They indicate which sets of Miller indices are absent from the x-ray diffraction pattern.

The metal sodium has a bcc structure. The diffraction pattern does not contain lines (100) , (300) , (111) or (221) , these are systematic absences, but does have (200) , (110) and (222) for example.

The structure factor formulation indicates that the (100) reflection is not present. Why is this? This is an accident of the basis. It just happens that in sodium both atoms in the basis are the same, an accidental absence.

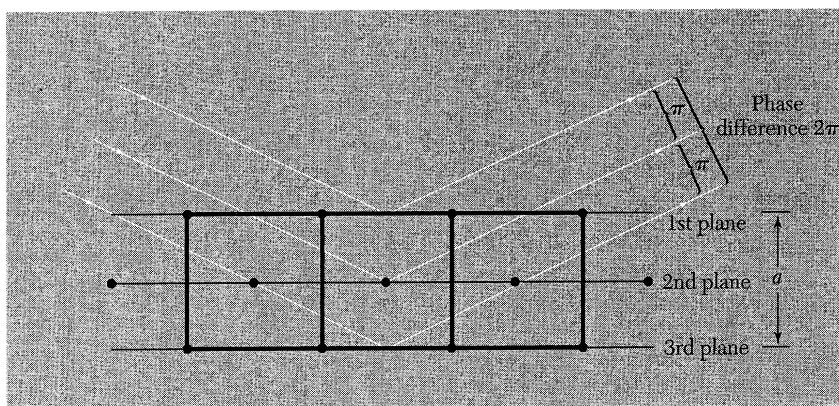


Figure 16 Explanation of the absence of a (100) reflection from a body-centered cubic lattice. The phase difference between successive planes is π , so that the reflected amplitude from two adjacent planes is $1 + e^{-i\pi} = 1 - 1 = 0$.

The (100) reflection will occur when reflections from planes differ by 2π . In the bcc lattice there is a plane of atoms in between the subsequent (100) planes – formed by the atoms at the centre of the cube. These atoms have equal scattering power to the (100) planes. The effect is to give a phase difference of only π (180°) thereby cancelling the (100) reflections.

Example: Structure factor of fcc lattice

The basis of the fcc structure has four unique atoms at the following positions:
 $000, 0\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$, $\frac{1}{2}, 0, \frac{1}{2}$ and $\frac{1}{2}, \frac{1}{2}, 0$

[Note if this is not obvious then consider a unit cell and think about the smallest number of atoms related to the cube of the unit cell such that replicating these atoms will reconstruct the full crystal structure.]

The structure factor becomes:

$$S_G(hkl) = f\{1 + \exp[-i\pi(k+l)] + \exp[-i\pi(h+l)] + \exp[-i\pi(h+k)]\}$$

If all the indices are even integers or odd integers: $S = 4f$

If only one of the integers is even, two of the exponents will be odd multiples of $-i\pi$ and will vanish. If only one of the integers is odd the same will apply. This means in the fcc lattice no reflections can occur when the indices are partly even or partly odd.

$$\begin{aligned} S &= 0 \text{ when integers mixed parity} \\ S &= 4f \text{ when integers all even or all odd} \end{aligned}$$

These are the *structure factor rules for the fcc lattice*.

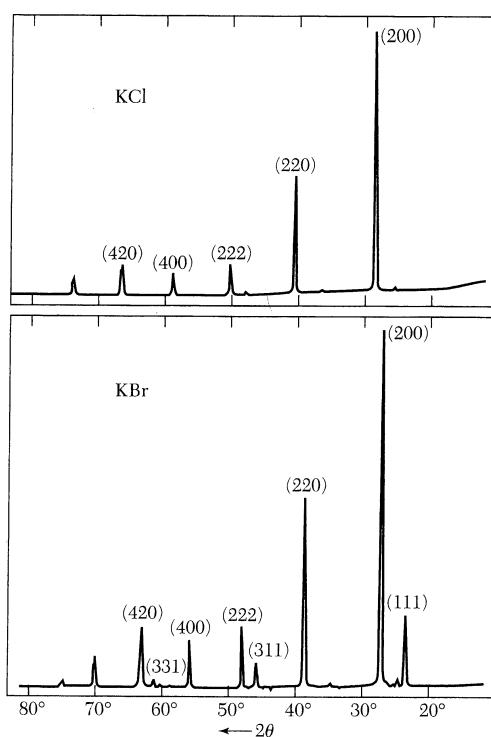


Figure 17 Comparison of x-ray reflections from KCl and KBr powders. In KCl the numbers of electrons of K^+ and Cl^- ions are equal. The scattering amplitudes $f(K^+)$ and $f(Cl^-)$ are almost exactly equal, so that the crystal looks to x-rays as if it were a monatomic simple cubic lattice of lattice constant $a/2$. Only even integers occur in the reflection indices when these are based on a cubic lattice of lattice constant a . In KBr the form factor of Br^- is quite different to that of K^+ , and all reflections of the fcc lattice are present. (Courtesy of R. van Nordstrand.)

This figure illustrates this point very well. KCl and KBr are both fcc lattices. However, in KCl the K^+ and Cl^- ions have the same number of electrons and hence scatter x-rays with identical structure factors and it behaves as if it were a primitive cubic lattice. These are accidental absences.