Wave Diffraction &
# The Reciprocal Lattice (continued)

Chapter Topics

1. Wave Diffraction by Crystals
2. Bragg Law
3. Scattered Wave Amplitude
4. Reciprocal Lattice
5. Brillouin Zones
6. Fourier Analysis of the Basis

DIFFRACTION OF WAVES BY CRYSTALLINE SOLIDS

✖ We know that a crystal is a periodic structure with unit cells that are repeated regularly.

Crystal Structure Information

can be obtained by understanding <u>the diffraction patterns of waves</u> (of appropriate wavelengths) *<u>interacting with the solid</u>*. Analysis of such diffraction patterns is a main topic of this chapter.

Diffraction
X-Rays   Neutrons   Electrons
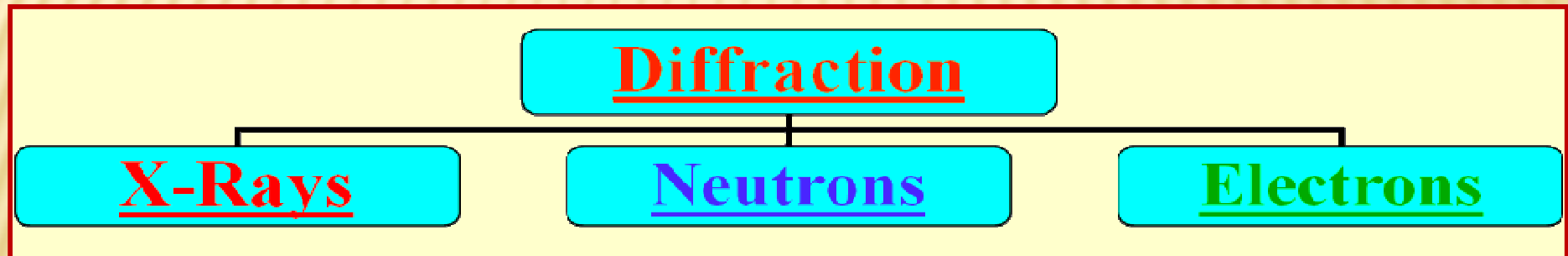
It is common to study crystal structures with

X-rays, Neutrons & Electrons.

Of course, the general principles are the same for each type of wave.

- The results of crystal diffraction depend on the crystal structure and on the wavelength.
- At optical wavelengths such as 5,000 Å, the superposition of waves scattered elastically by the individual atoms of a crystal
  results in ordinary optical refraction.
- When the wavelength of the radiation is *comparable to or smaller than the lattice constant*, diffracted beams occur in directions quite different from the direction of the incident radiation.

Wavelength vs Energy

Quantum Mechanical Result

The energy & momentum of a particle with **De Broglie Wavelength** λ are

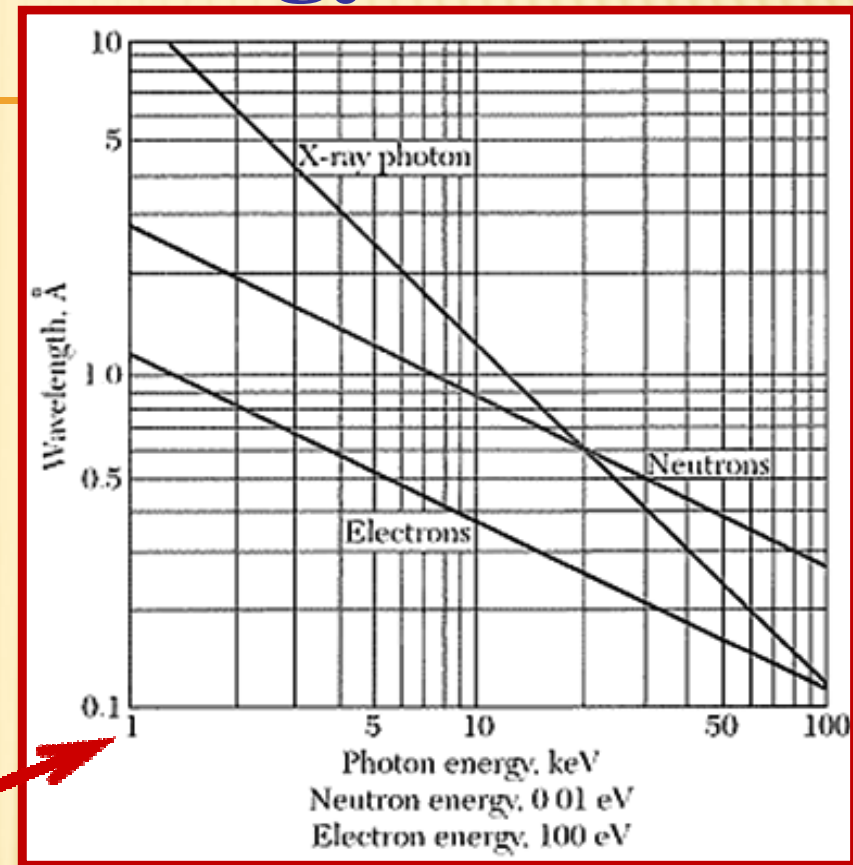$$E = (hc/\lambda) \quad \& \quad p = (h/\lambda)$$

(**h = Planck's constant**)

Diffraction from crystal planes requires λ to be of the same order of magnitude as the **distance d** between planes:

$$d \approx \text{a few Ångstroms}$$
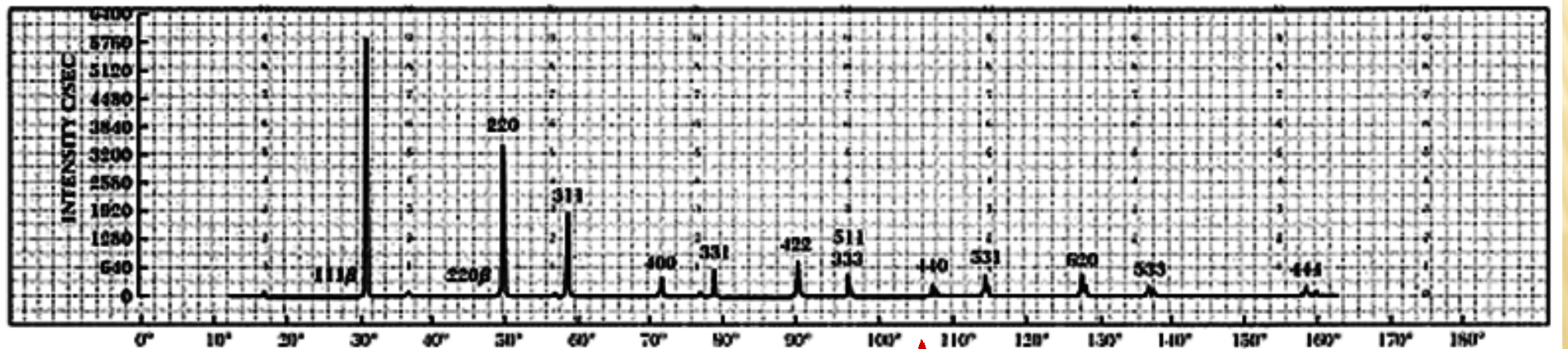
so λ must also be in that range.

X-ray photon

Neutrons

Electrons

Wavelength, Å

Photon energy, keV
Neutron energy, 0 01 eV
Electron energy, 100 eV
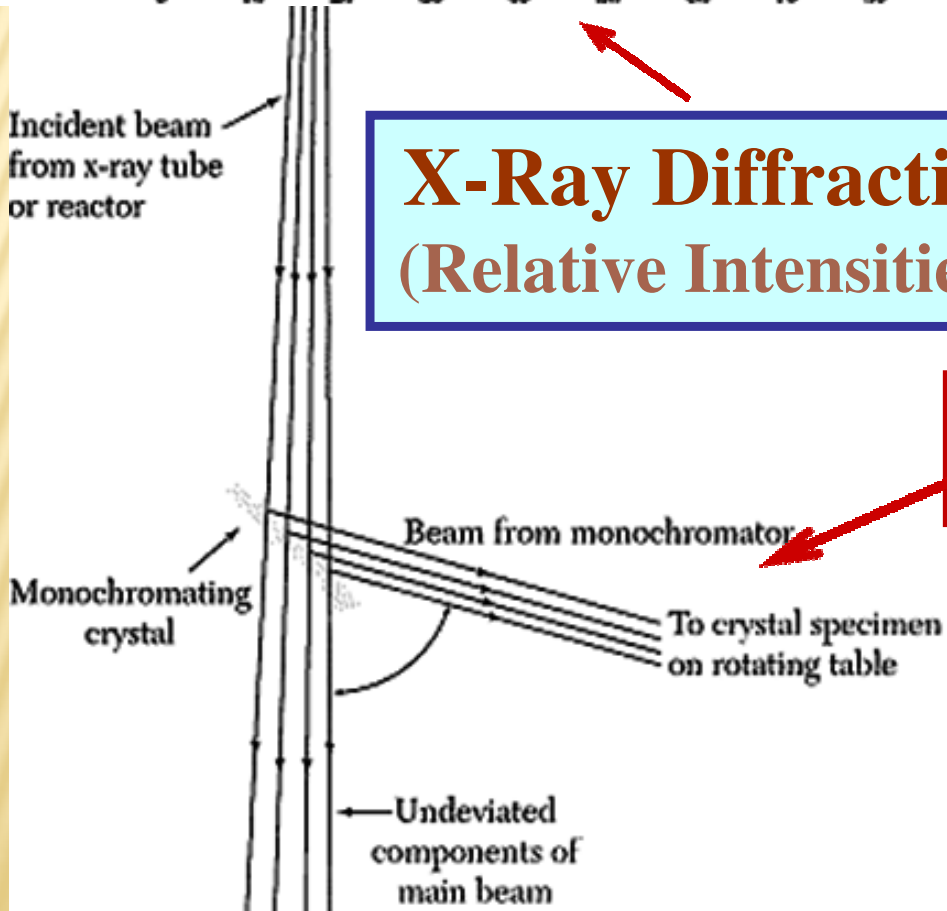
This gives
Photons: E ≈ keV
Neutrons: E ≈ 0.01 eV
Electrons: E ≈ 100 eV

Typical X-Ray Experiment & Data

X-Ray Diffraction Resultsfor Powdered Si
(Relative Intensities are Due to the 2 Atom Basis.)

Monochromator

- Crystal Structure can be found by studying the *Diffraction Pattern* of a beam of radiation incident on the crystal.
- Beam diffraction takes place *only in certain specific directions*, much as light is diffracted by a grating.
- By measuring the *directions of the diffraction* and the *corresponding intensities*, information about the *Crystal Structure* responsible for the diffraction.

X-Ray Diffraction

- W.H. & W.L. Bragg (father & son!) were the first to develop a simple explanation of the X-Ray diffracted beams from a crystal.
- The Bragg derivation is simple but it is convincing since only it reproduces the result that agrees with observations.

X-RAY DIFFRACTION & THE BRAGG EQUATION

✖ English physicists Sir W.H. Bragg & his son W.L. Bragg developed a theory in 1913 to explain why the cleavage faces of crystals _appear to reflect X-rays ONLY at certain angles of incidence_ θ.

This is an example of X-Ray Diffraction
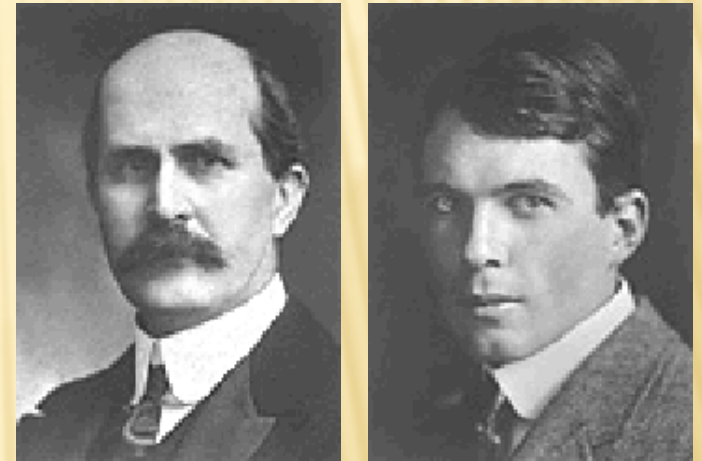
Sir William H. Bragg
(1862-1942)
Sir William L. Bragg
(1890-1971)

In 1915, the father & son were awarded the Nobel prize in physics _"For their services in the analysis of crystal structure by means of X-Rays"._

(The younger Bragg was fighting in WWI when he received the Nobel Prize!)

CRYSTAL STRUCTURE DETERMINATION

A Crystal behaves *as a 3-D Diffraction Grating* for X-Rays

* In a diffraction experiment, the spacing of lines on the grating can be found from the separation of the diffraction maxima. Also, information about the structure of the lines on the grating can be obtained by measuring the relative intensities of different orders
* Similarly, measurement of the separation of the X-Ray diffraction maxima from a crystal enables the determination of the unit cell size. Also, from the intensities of diffracted beams, information can be obtained about the arrangement of atoms within the cell.

X-Ray Crystallography

- For <u>X-Rays</u>, the wavelength λ is typically ≈ a few Ångstroms, which is comparable to the interatomic spacing (distances between atoms or ions) in crystals.

- So, for crystal structure determination, the <u>X-Rays</u> have to be of energy:
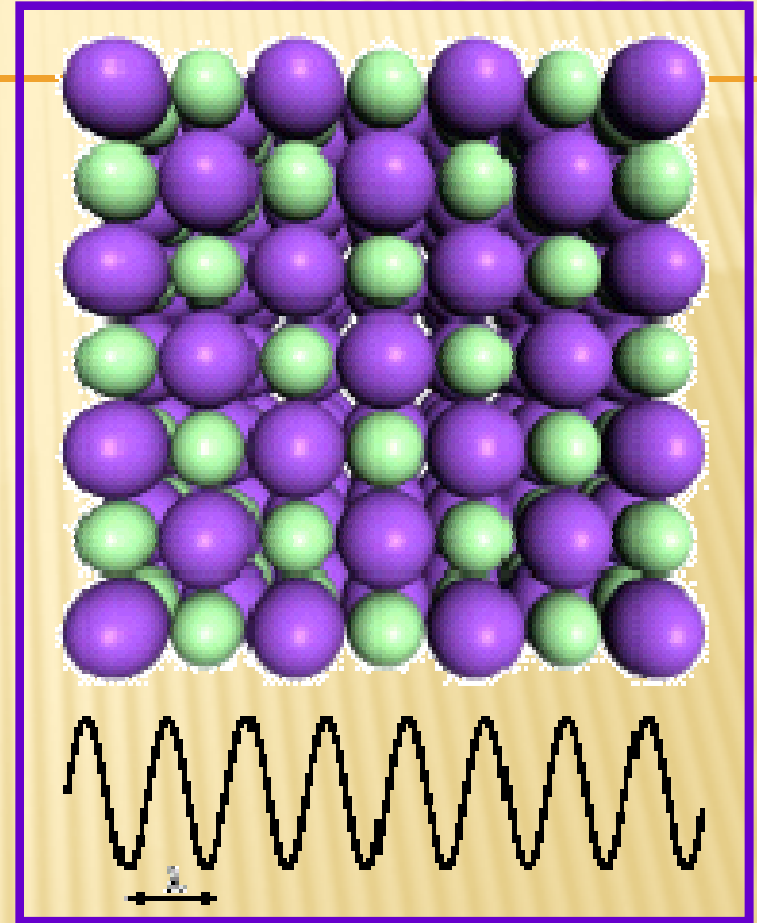
$$E_{x-ray} = \hbar\omega = h\upsilon = \frac{hc}{\lambda} = \frac{hc}{1x10^{-10}m} = 12.3x10^3\,eV$$

BRAGG LAW

✖ Consider crystals as made up of parallel planes of atoms. Incident waves are reflected specularly from parallel planes of atoms in the crystal, with each plane reflecting only a very small fraction of the radiation, like a lightly silvered mirror.

✖ In mirrorlike reflection, the angle of incidence is equal to the angle of reflection.
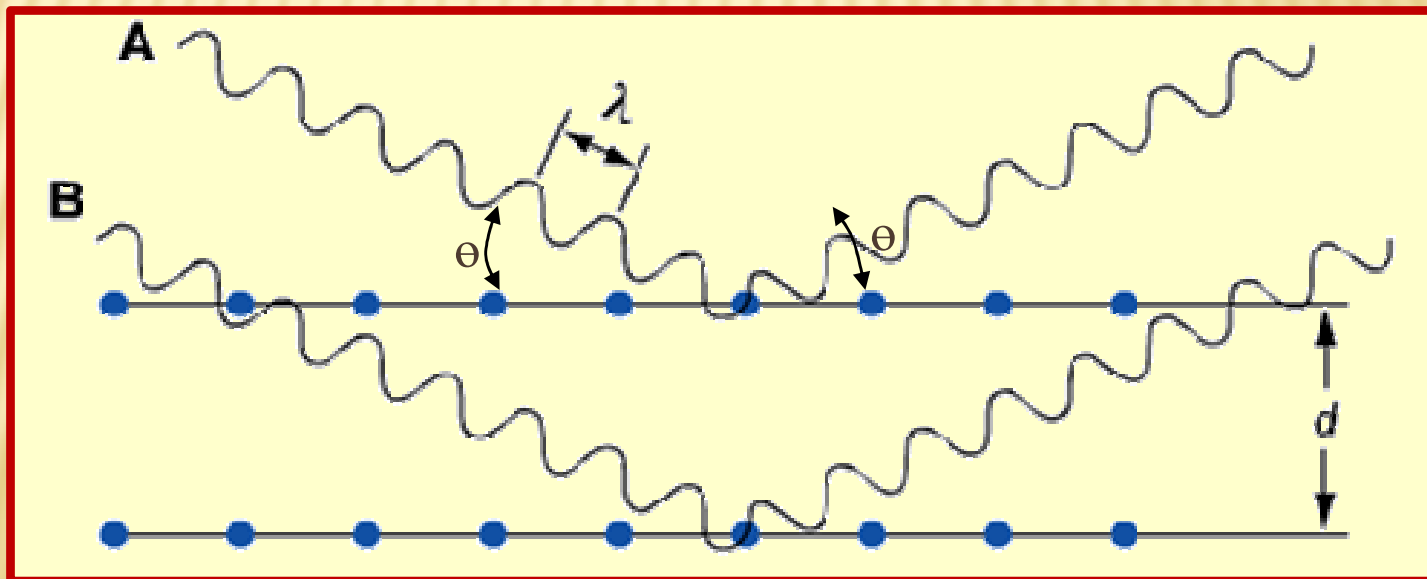
DIFFRACTION CONDITION

✖ The diffracted beams are found to have maximum intensity when the

Reflections from Planes of Atoms

Interfere Constructively.

Assume elastic scattering, in which the X-Ray energy isn't changed on reflection.

✖ So, when X-Rays strike a crystal, we want the condition for constructive interference between reflected rays from different planes. That is, *we want the condition for the reflected X-rays to be in-phase with one another* so that they that add together constructively.
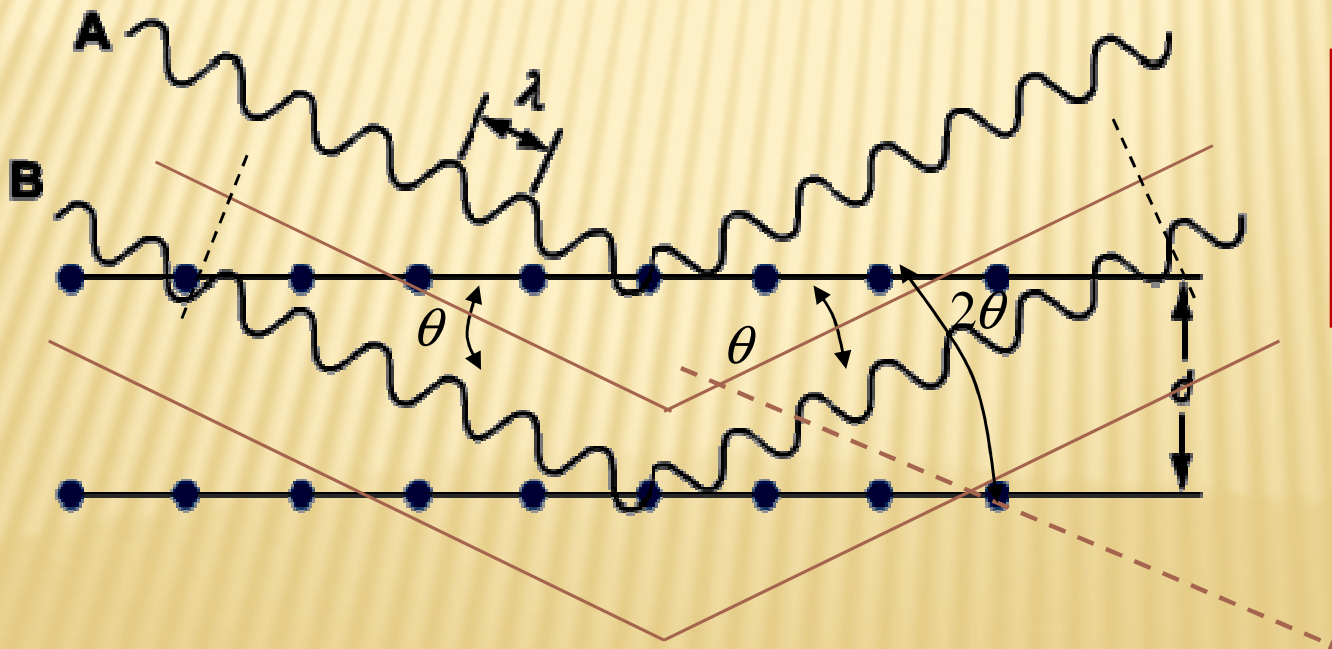
Incident Angle ≡ θ

Reflected angle ≡ θ

X-ray Wavelength ≡ λ

Total Diffracted Angle ≡ 2θ

Bragg Law

- The two X-Ray beams travel different distances. The difference in the distances traveled is related to the distance between the adjacent layers.
- *See Figure*. Connecting the two beams with perpendicular lines shows the difference in the distance traveled between top & bottom beams.
- In the figure, the length DE is the same as EF, so the total distance traveled by the bottom wave is expressed by:
- *Constructive interference* of the radiation from successive planes occurs when the path difference is an integral number of wavelengths.
- Note that line **CE = d =** distance between the 2 layers
- So:
- Giving: $\boxed{DE = d\sin\theta}$ $\boxed{EF = d\sin\theta}$ $\boxed{DE + EF = 2d\sin\theta}$

$$\boxed{n\lambda = 2d\sin\theta}$$ This is called the *Bragg Law*
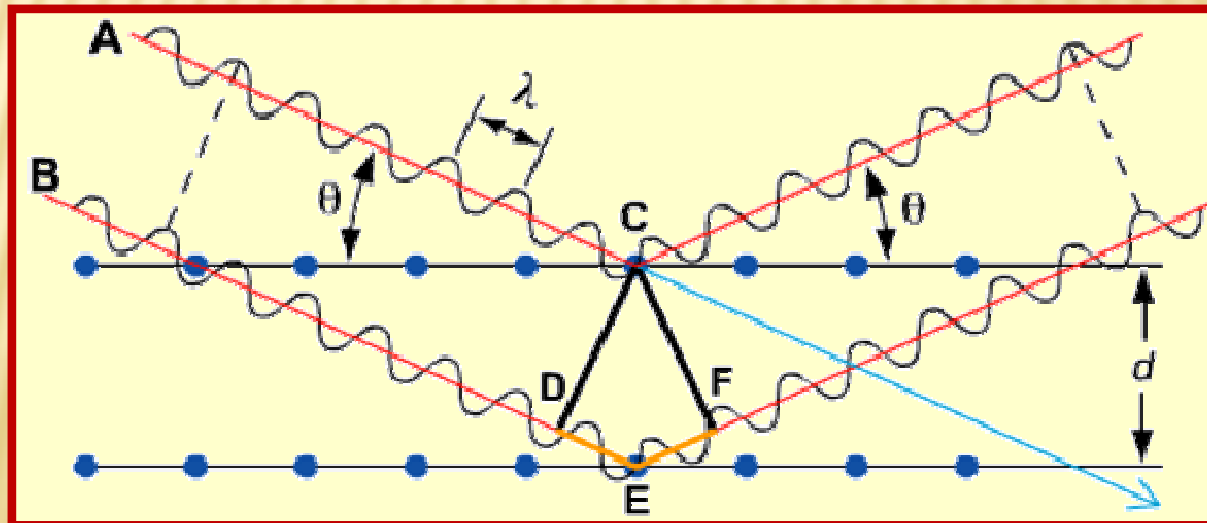
BRAGG LAW (BRAGG EQUATION)

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

d = Spacing of the Planes

n = Order of Diffraction.

- Because sin θ ≤ 1,
 *Bragg reflection can only occur for wavelengths satisfying*: $n\lambda \leq 2d$

- This is why visible light can't be used. No diffraction occurs when this condition is not satisfied.

- The diffracted beams (reflections) from any set of lattice planes can only occur at particular angles predicted by Bragg's Law.

- Now, a similar, but slightly different treatment:
- *See Figure*: Consider X-Rays incident at angle θ on one of the lattice planes. Look at the

  ## *Scattering of these X-Rays from Adjacent Lattice Points*

- There will be *Constructive Interference* of the waves scattered from the two successive lattice points A & B in the plane if the distances AC and DB are equal.
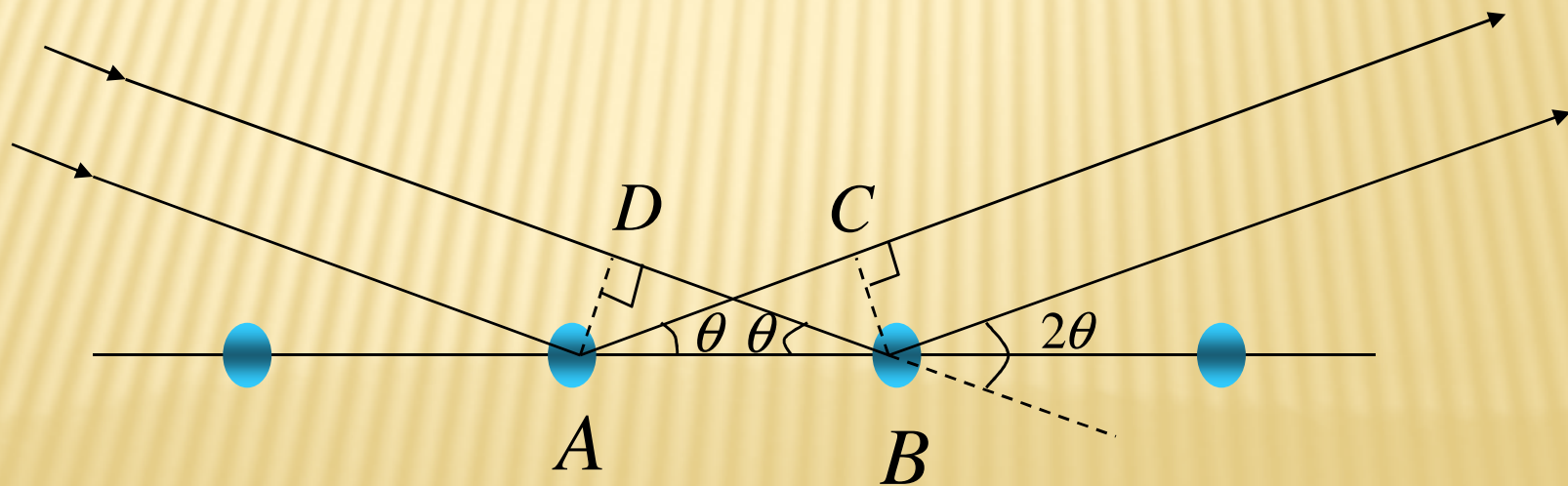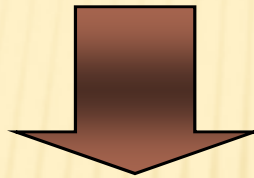
SO, LOOK AT THE CONDITIONS FOR
CONSTRUCTIVE INTERFERENCE
OF WAVES SCATTERED FROM THE SAME PLANE.

✖ If the scattered wave makes the same angle with the plane as the incident wave (see figure on the previous slide):

The diffracted wave will look as if it was reflected from the plane.

- It is common to consider

Scattering from Lattice Points Rather than Atoms

because it is the basis of atoms associated with each lattice point that is the true repeat unit of the crystal.

- The lattice point is an analogue of the line on an optical diffraction grating. The basis represents the structure of

DIFFRACTION MAXIMA

× Coherent scattering from a single plane is not sufficient to obtain a diffraction maximum. It is also necessary

That Successive Planes also Scatter in Phase.

- This will be the case *if the path difference for scattering off of two adjacent planes is an integral number of wavelengths*. That is, if

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

Additional Notes on Bragg Reflections

- Although the reflection from each plane is specular,

  Only for certain values of θ will the reflections from all planes add up in phase to give a strong reflected beam.

- Each plane reflects only 10^{-3} to 10^{-5} of the incident radiation, i.e. it is not a perfect reflector.

- **So, 10^3 to 10^5 planes contribute to the formation of the Bragg-reflected beam in a perfect crystal.**

- The composition of the basis determines the relative intensity of the various orders of diffraction.

Scattered Wave Amplitude $\Rightarrow$
Reciprocal Lattice Vectors

- Now, consider **X-Ray Scattering** from crystals & analyze the **Amplitude of the Scattered Waves**.

- The electronic number density $n(r)$ in the crystal is a periodic function in space:

$$n(r) = n(r + T)$$

with period T equal to a **Direct Lattice Translation Vector:**

$$T = n_1 a_1 + n_2 a_2 + n_3 a_3$$

- The electronic number density **n(r)** in the crystal is periodic in space: **n(r) = n(r +T)**, with **T** equal to a

  ## <u>Direct Lattice Translation Vector</u>:

  $$T = n_1 a_1 + n_2 a_2 + n_3 a_3$$

- So, **n(r)** can be expressed as a (spatial) Fourier series expansion. So, for a one-dimensional model crystal, **n(x)** can be represented as

$$n(x) = n_0 + \sum_{p>0} \left[C_p \cos(2\pi px/a) + S_p \sin(2\pi px/a) \right] = \sum_p n_p e^{i2\pi px/a}$$

where the **p's** are integers and the Fourier coefficient of the number density can be written as:

$$n_p = \frac{1}{a} \int_0^a dx\, n(x)\, e^{-i2\pi px/a}$$

- In **3 Dimensions**, *the Fourier coefficient of the number density has the form:*

$$n(\mathbf{r}) = \sum_{\mathbf{G}} n_{\mathbf{G}}\, e^{i\mathbf{G}\cdot\mathbf{r}} \rightarrow n_{\mathbf{G}} = \frac{1}{V_c}\int_0^a dV\, n(\mathbf{r})\, e^{-i\mathbf{G}\cdot\mathbf{r}}$$ **(1)**

The vectors G are called

Reciprocal Lattice Vectors

- As we said, the electronic density **n(r)** is required to be invariant (periodic) under lattice translations:

$$\mathbf{n(r) = n(r + T)} \qquad \textbf{(2)}$$

- That is, it must satisfy:

$$n(\mathbf{r}+\mathbf{T}) = \sum_{\mathbf{G}} n_{\mathbf{G}} e^{i\mathbf{G}\cdot(\mathbf{r}+\mathbf{T})} = \sum_{\mathbf{G}} n_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}} e^{i\mathbf{G}\cdot\mathbf{T}} = n(\mathbf{r}) \quad when\ e^{i\mathbf{G}\cdot\mathbf{T}} = 1$$ **(3)**

- Only ***The Set of Reciprocal Lattice Vectors*** **G** that satisfy ***both*** (**1**) & (**3**) (previous slide) lead to an electronic number density **n(r)** that is invariant under lattice translations.
- It's not too hard to show that the set of **G's** that meet this requirement are of the form

$$\mathbf{G} = v_1\mathbf{b}_1 + v_2\mathbf{b}_2 + v_3\mathbf{b}_3$$

where **υ₁, υ₂** & **υ₃** are integers & the **bᵢ**'s are vectors which are defined as:

$$\mathbf{b}_i = 2\pi \frac{\mathbf{a}_j \times \mathbf{a}_k}{\mathbf{a}_i \cdot (\mathbf{a}_j \times \mathbf{a}_k)}, \quad i = x, y, z \;\rightarrow\; \mathbf{b}_i \cdot \mathbf{a}_j = 2\pi\delta_{ij}$$

- The **aⱼ**'s are the primitive lattice vectors for the crystal structure. It also can be shown that

The Set of Reciprocal Lattice Vectors

G is a ***Bravais Lattice!***

The Diffraction Condition (Bragg's Law) in the Reciprocal Lattice

- An **X-Ray diffraction** pattern of the lattice

Can be interpreted as a map of the reciprocal lattice of the crystal.

This statement is consistent with the following theorem:

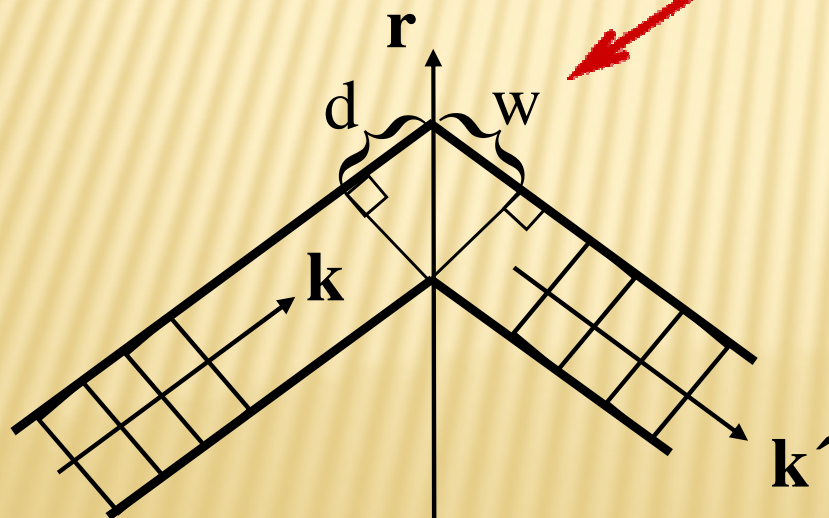*The Set of Reciprocal Lattice Vectors* **G** *determines the possible X-ray reflections.*

- An **X-Ray diffraction** pattern of the lattice

Can be interpreted as a map of the reciprocal lattice of the crystal.

In other words

The Set of Reciprocal Lattice Vectors **G** *determines the possible X-ray reflections.*

Wavevector Representation of X-ray Scattering: $\mathbf{k} \rightarrow \mathbf{k'}$

The scattered wave amplitude is:

$$F = \int dV n(\mathbf{r}) e^{i(\mathbf{k}-\mathbf{k'})\cdot\mathbf{r}}$$

$$= \int dV n(\mathbf{r}) e^{-i\Delta\mathbf{k}\cdot\mathbf{r}}$$

When **G = k** (wavevector), then **F = V n$_G$**.

- Now, look at this condition for elastic scattering (specular reflection):

$$\mathbf{G} = \Delta\mathbf{k} = \mathbf{k'} - \mathbf{k} \rightarrow 2\mathbf{k} \cdot \mathbf{G} + G^2 = 0$$

This result is called
***The Laue Condition*.**

It's not too difficult to show that
it is 100% equivalent to
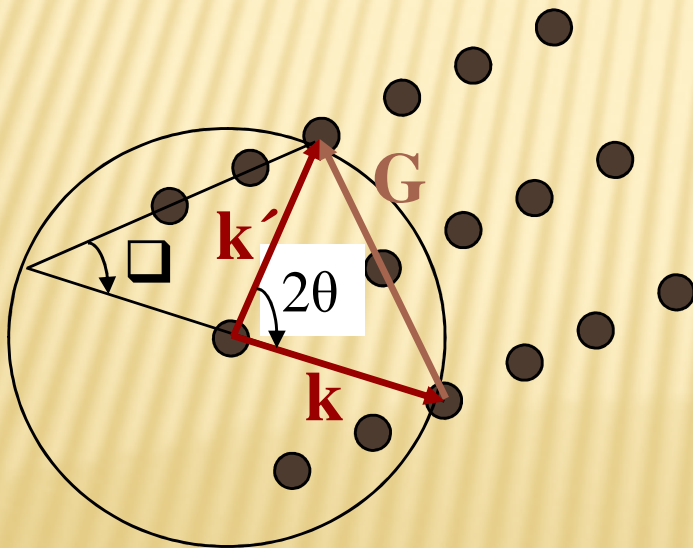***The Bragg Law!***

The Laue Condition is:.

$$\mathbf{G} = \Delta\mathbf{k} = \mathbf{k}' - \mathbf{k} \rightarrow 2\mathbf{k} \cdot \mathbf{G} + G^2 = 0$$

This is 100% equivalent to The Bragg Law!

The result that **k** = **G** can also be expressed to give the relations that are called *The Laue Relations* or the *Laue Equations*. These are obtained by taking the dot product of both **Δk** & **G** with $\mathbf{a_1}, \mathbf{a_2}$ & $\mathbf{a_3}$. *The Laue Equations are:* $\Delta\mathbf{k} \cdot \mathbf{a}_i = 2\pi v_i, \quad i = 1,2,3$

By changing **θ**, X-Ray diffraction can be used to map all **Reciprocal Lattice Vectors.**

This geometric method of finding Reciprocal Lattice Vectors is called

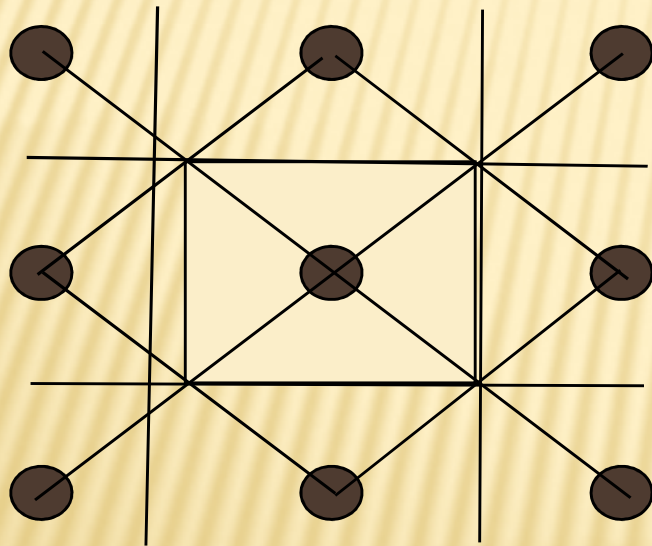## *The Ewald Construction*

Brillouin Zones & Reciprocal Lattices
for the SC, BCC & FCC Lattices
Brillouin Zones

The *First Brillouin Zone* (**BZ**) is defined as *the Wigner-Seitz primitive cell in the reciprocal lattice*. It gives a geometric interpretation, in the reciprocal lattice, of the diffraction condition.

- The Brillouin construction exhibits all wavevectors **k** that can be
### Bragg reflected
by the crystal.
- The constructions divide the reciprocal space into fragments, out of which
The First Brillouin Zone
is of the greatest importance.

Reciprocal Lattices for the SC, FCC & BCC Lattices

Direct Lattice	Reciprocal Lattice	Volume

SC

$$\begin{cases} \mathbf{a}_1 = a\mathbf{x} \\ \mathbf{a}_2 = a\mathbf{y} \\ \mathbf{a}_3 = a\mathbf{z} \end{cases} \qquad \begin{cases} \mathbf{b}_1 = (2\pi/a)\mathbf{x} \\ \mathbf{b}_2 = (2\pi/a)\mathbf{y} \\ \mathbf{b}_3 = (2\pi/a)\mathbf{z} \end{cases} \qquad (2\pi/a)^3$$

FCC

$$\begin{cases} \mathbf{a}_1 = \tfrac{1}{2}a(\mathbf{x}+\mathbf{y}) \\ \mathbf{a}_2 = \tfrac{1}{2}a(\mathbf{y}+\mathbf{z}) \\ \mathbf{a}_3 = \tfrac{1}{2}a(\mathbf{z}+\mathbf{x}) \end{cases} \qquad \begin{cases} \mathbf{b}_1 = \tfrac{2\pi}{a}(-\mathbf{x}+\mathbf{y}-\mathbf{z}) \\ \mathbf{b}_2 = \tfrac{2\pi}{a}(\mathbf{x}-\mathbf{y}+\mathbf{z}) \\ \mathbf{b}_3 = \tfrac{2\pi}{a}(\mathbf{x}+\mathbf{y}-\mathbf{z}) \end{cases} \qquad 2(2\pi/a)^3$$

BCC

$$\begin{cases} \mathbf{a}_1 = \tfrac{1}{2}a(\mathbf{x}+\mathbf{y}-\mathbf{z}) \\ \mathbf{a}_2 = \tfrac{1}{2}a(-\mathbf{x}+\mathbf{y}+\mathbf{z}) \\ \mathbf{a}_3 = \tfrac{1}{2}a(\mathbf{x}-\mathbf{y}+\mathbf{z}) \end{cases} \qquad \begin{cases} \mathbf{b}_1 = \tfrac{2\pi}{a}(\mathbf{y}+\mathbf{z}) \\ \mathbf{b}_2 = \tfrac{2\pi}{a}(\mathbf{x}+\mathbf{z}) \\ \mathbf{b}_3 = \tfrac{2\pi}{a}(\mathbf{x}+\mathbf{y}) \end{cases} \qquad 4(2\pi/a)^3$$
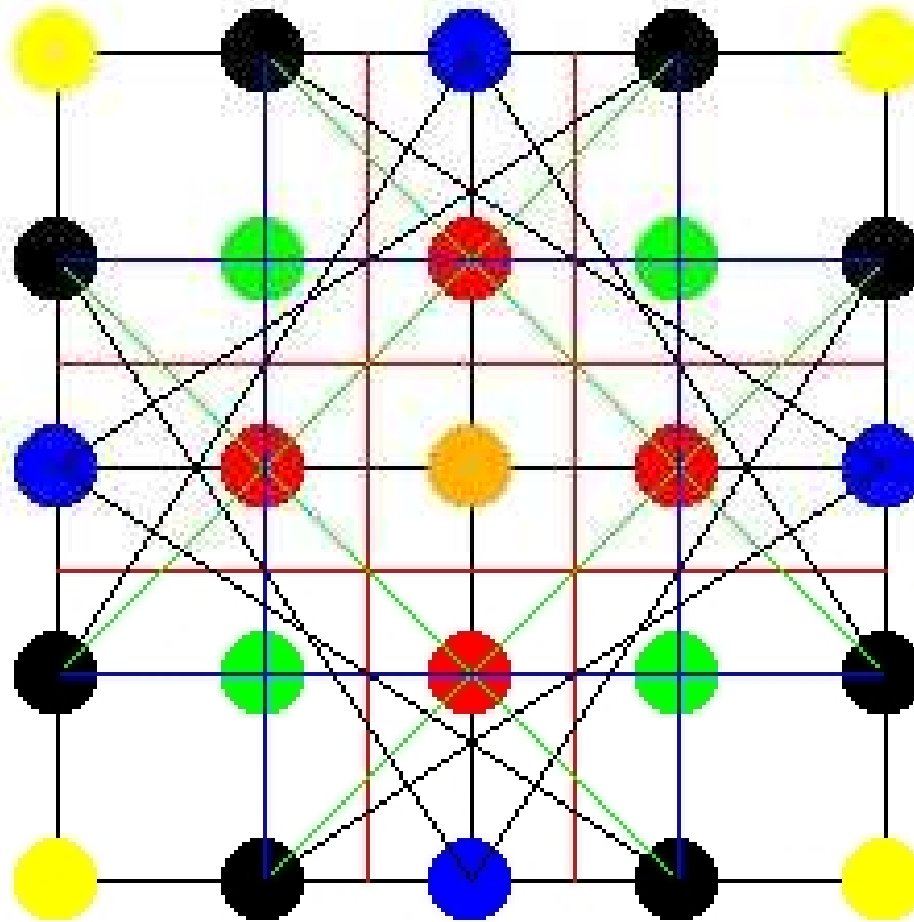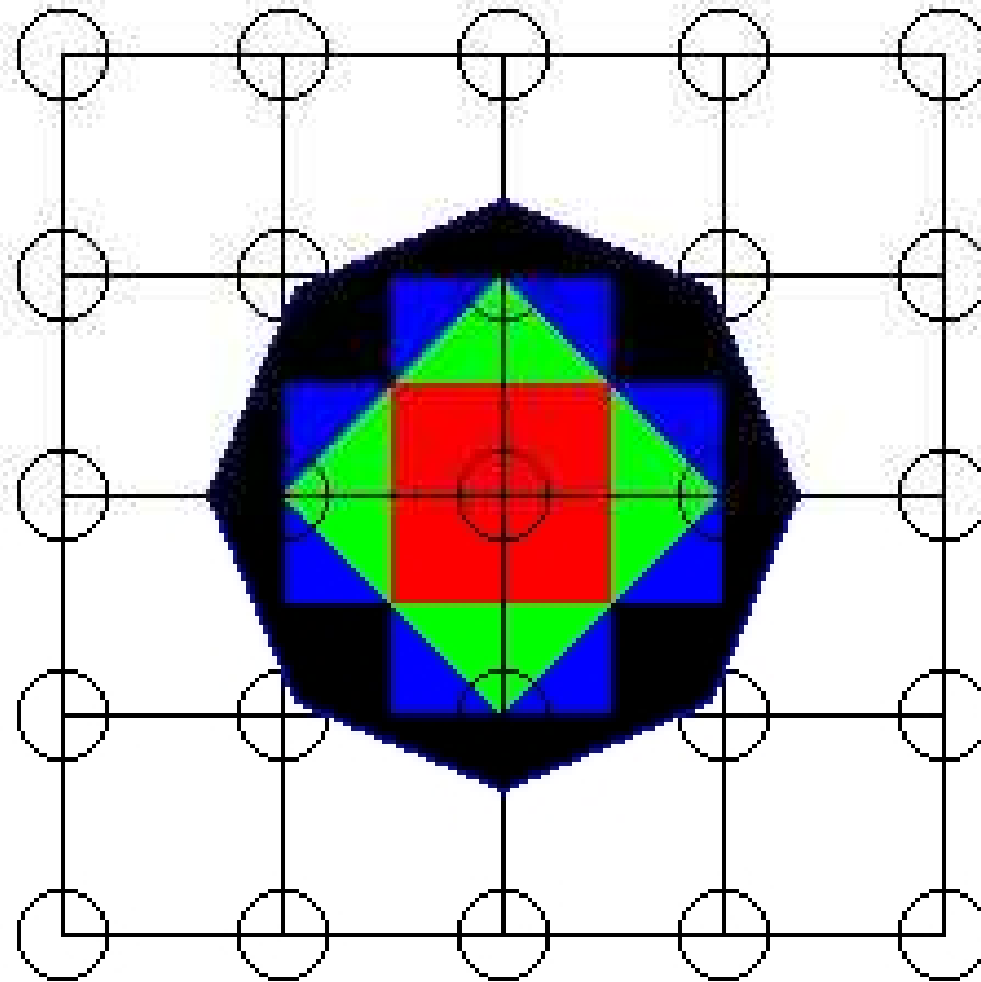
The Nearest through Fifth Nearest Neighbors
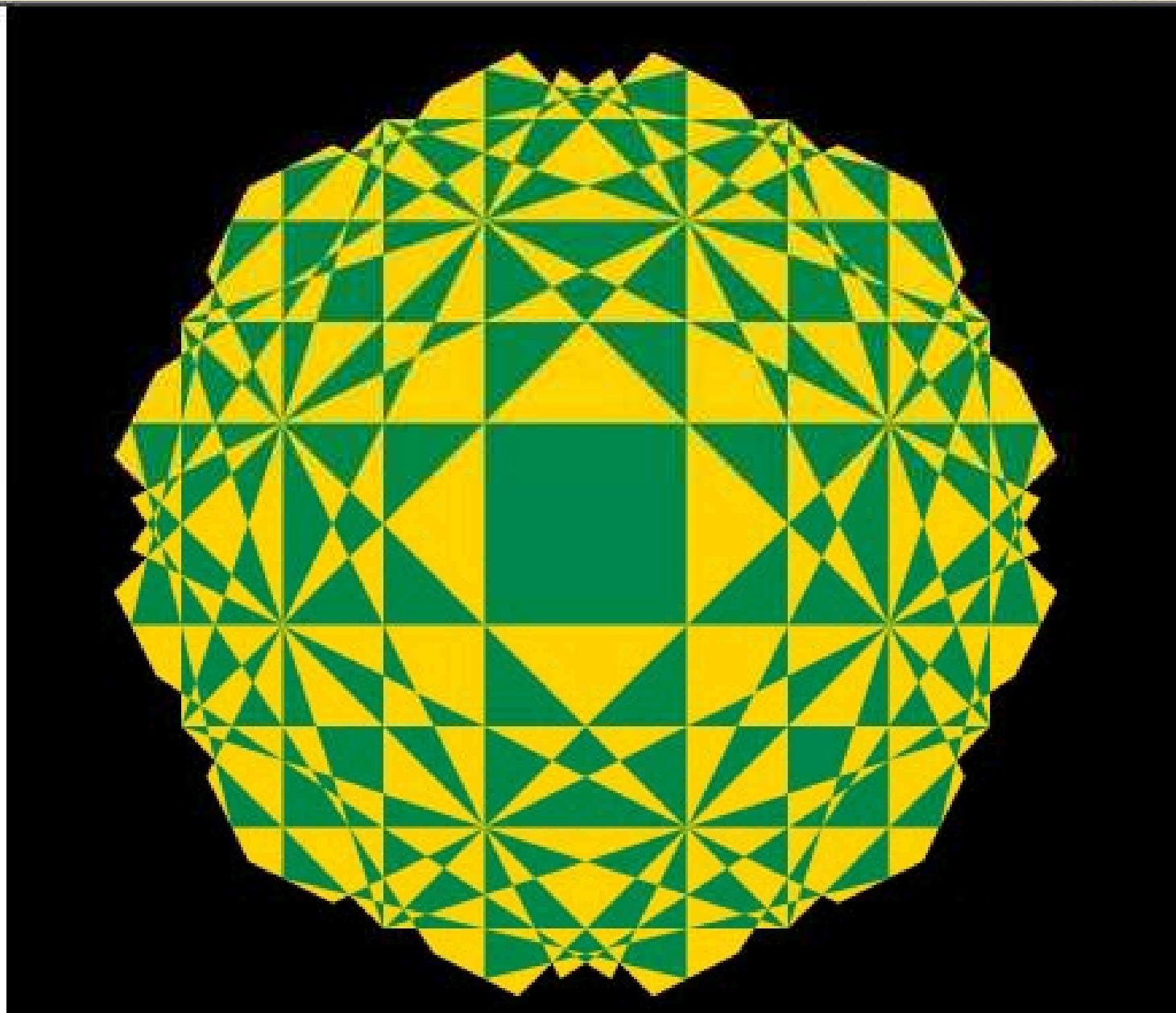for a Point in a Square Lattice
and Their Bragg Lines
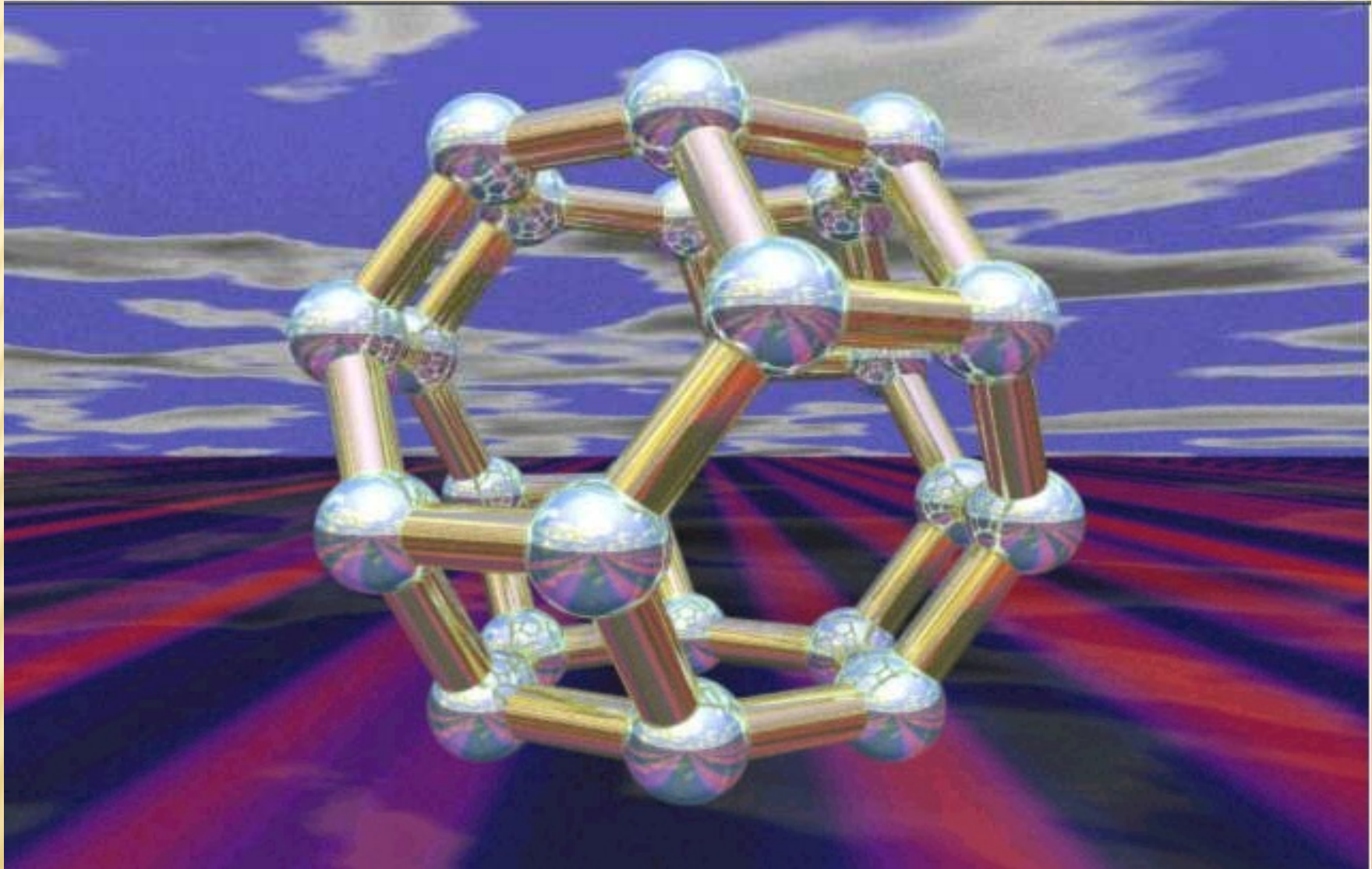
First 4 Brillouin Zones: Square Lattice

First Four Brillouin Zones for a Square Lattice
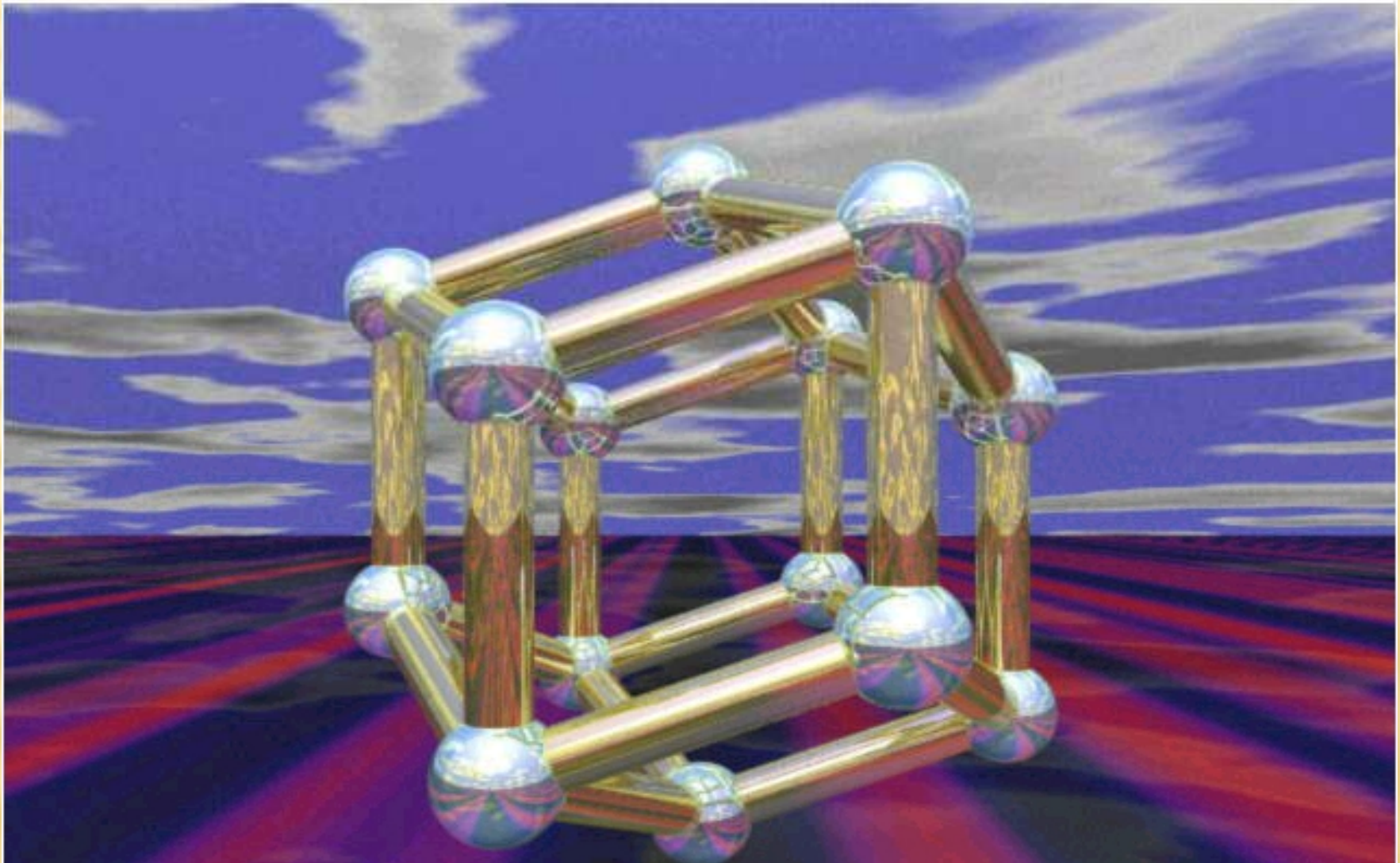
"All" Brillouin Zones: Square Lattice??

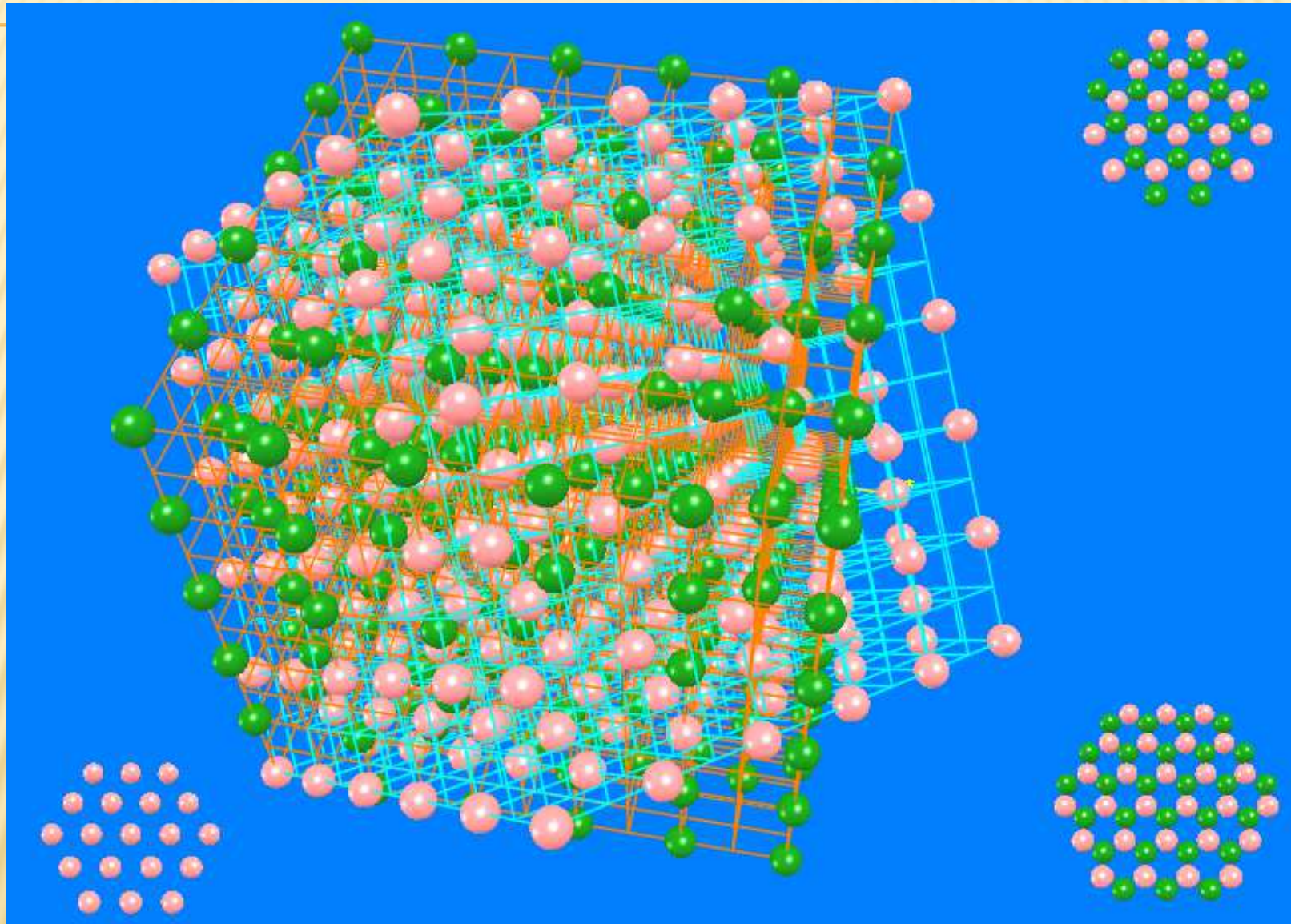# First Brillouin Zone: BCC Lattice

First Brillouin Zone: FCC Lattice

Reciprocal Lattice for Aluminium

Fourier Analysis of a Basis

Structure Factor & Atomic Form Factor.

- Earlier, we said that the scattering amplitude for a unit cell has the form:

$$F = \int_{cell} dV n(\mathbf{r}) e^{-i\mathbf{G}\cdot\mathbf{r}} = NS_G$$

The quantity S_G is called **_The Structure Factor_**. It is defined as an integral over a single unit cell. If the electron density is written as a superposition of the electron densities in the cell, taking into account the **#** of atoms in the basis, it has the form:

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

where *s* is the **#** of atoms in the unit cell.

Using this, ***The Structure Factor*** has the form:

$$S_G = \sum_{j=1}^{s} \int_{cell} dV n_j(\mathbf{r} - \mathbf{r}_j) e^{-i\mathbf{G}\cdot\mathbf{r}}$$

$$= \sum_{j=1}^{s} e^{-i\mathbf{G}\cdot\mathbf{r}_j} \int_{cell} dV n_j(\rho) e^{-i\mathbf{G}\cdot\rho} = \sum_{j=1}^{s} e^{-i\mathbf{G}\cdot\mathbf{r}_j} f_j$$

The quantity f_j is called ***The Atomic Form Factor***.
Now specifying $\mathbf{G}$ and $\mathbf{r}_j$ as

$$\mathbf{G} = v_1\mathbf{b}_1 + v_2\mathbf{b}_2 + v_3\mathbf{b}_3 \quad \text{and} \quad \mathbf{r}_j = x_j\mathbf{a}_1 + y_j\mathbf{a}_2 + z_j\mathbf{a}_3$$

gives:

$$S_G = \sum_{j=1}^{s} f_j e^{-2\pi i\left(x_j v_1 + y_j v_2 + z_j v_3\right)}$$

Note that S_G can be complex, because the scattering intensity involves the magnitude squared of S_G.

- If (& only if!) *the electron density of the atom is spherically-symmetric*, the atomic form factor f_j can be written:

$$f_j = 4\pi \int_0^\infty n_j(r) r^2 \frac{\sin(Gr)}{Gr} dr$$

This means that when the electronic density has the form

n(r) = Zg(r), then f_j **= CZ**

(**C** = constant, **Z** = atomic charge,)

That is, in this case, f_j is *the ratio of radiation amplitude scattered by the electron distribution to that scattered by a localized electron.*

Examples of Structure Factor Calculations
BCC lattice

In a **BCC lattice**, there are 2 atoms per cubic unit cell located at (**000**) & (**½½ ½**). The structure factor is then:

$$S_G = \left[1 + e^{-\pi i\left(v_1 + v_2 + v_3\right)}\right]f$$

This structure factor has its *Maximum,* $S_G = 2f$ when *the sum of the indices is even*. That is when:

$$\upsilon_1 + \upsilon_2 + \upsilon_3 = 2n \text{ (n = integer)}$$

This structure factor *Vanishes*, $S_G = 0$ when *the sum of the indices is odd*. That is when:

$$\upsilon_1 + \upsilon_2 + \upsilon_3 = 2n + 1 \text{ (n = integer)}$$

Examples of Structure Factor Calculations
FCC lattice

For a **FCC lattice**, there 4 atoms per cubic unit cell located at **(000), (0½½), (½ 0½)** & **(½½0).** The structure factor is then:

$$S_G = \left[1 + e^{-\pi i(v_1 + v_2)} + e^{-\pi i(v_1 + v_3)} + e^{-\pi i(v_2 + v_3)}\right]f$$

This structure factor has its _**Maximum,**_ **S_G = 4f** when _**all indices**_ **v_1, v_2, v_3** _**are even or odd**_, This structure factor _**Vanishes**_, **S_G = 0** when _**the indices are partially even & partially odd**_. To summarize, in a **FCC lattice**, no reflections occur when the indices are partially even and partially odd.

Observed & Calculated
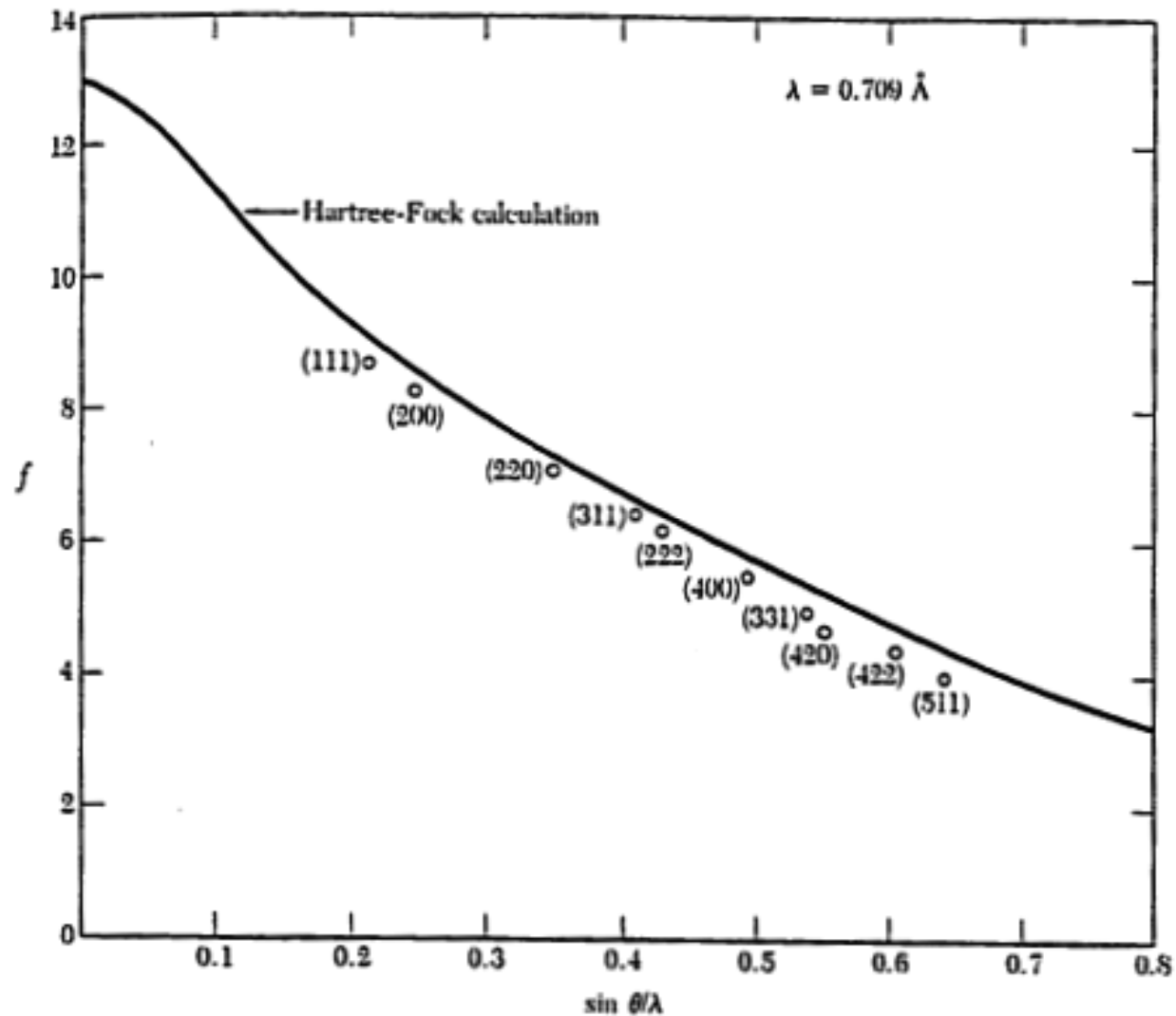## Atomic Form Factor for Aluminium

Figure 18 Absolute experimental atomic scattering factors for metallic aluminum, after Batterman, Chipman, and DeMarco. Each observed reflection is labeled. No reflections occur for indices partly even and partly odd, as predicted for an fcc crystal.

From Ch. 1:
Lattice Planes & Miller Indices

- A *Lattice Plane* is any plane containing at least three non-colinear Bravais lattice points.

- Generally, a lattice plane is described by giving a vector normal to that plane, & there happens to be reciprocal lattice vectors normal to any lattice plane.

- Choose the the shortest such reciprocal lattice vector to arrive at the *Miller indices* of the plane.

- Thus a plane with Miller indices *h, k, l,* is normal to the reciprocal lattice vector $hb_1 + kb_2 + lb_3$.

Review of Miller Indices Continued

Imagine representing a crystal structure on a grid (lattice) which is a 3D array of points (lattice points). Now, imagine dividing the grid into sets of "planes" in different orientations:
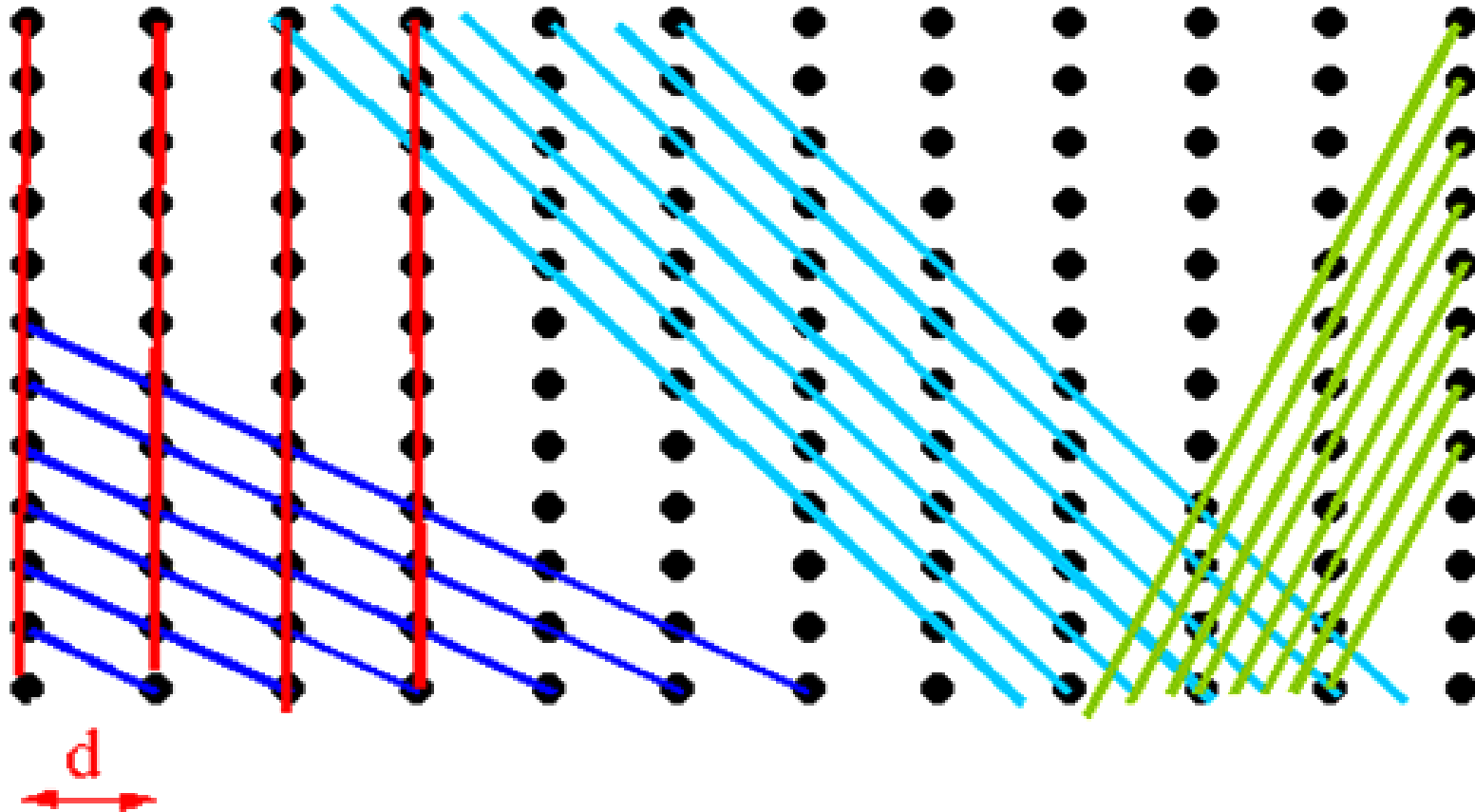
Review of Miller Indices Continued

Recall That

- All planes in a set are identical.
- The perpendicular distance between pairs of adjacent planes is the *d-spacing.*
- **Miller Indices** define the *orientation* of the plane within the unit cell.
- The **Miller Indices** define a *set of planes* parallel to one another: (002) planes are parallel to (001) planes, and so on.
- So, in analyzing crystal diffraction results, the lattice planes are labeled with their **Miller Indices (hkl)** for their identification.

LABELLING THE REFLECTION PLANES

Label reflections with the Miller indices of the planes.

* A beam corresponding to a diffraction order of n >1 could be identified by a statement such as
"The nth-order reflections from the (hkl) planes"
or a
"(nh nk nl) reflection".

p

Example

A 3rd order reflection from the (111) plane is
"a (333) reflection"

NTH ORDER DIFFRACTION OFF OF (HKL) PLANES

✖ Rewrite the <u>Bragg Law</u> in the form:

$$2\left(\frac{d}{n}\right)\sin\theta = \lambda$$

✖ This makes

the nth order diffraction off of (hkl) planes of spacing "d" <u>*look like*</u> the 1st order diffraction off planes of spacing (d/n).

✖ Planes of this reduced spacing would have Miller indices (nh nk nl).

X-RAY STRUCTURE ANALYSIS OF NACL & KCL

General Prıncıples of X-Ray Structure Analysıs
Applied to Find the Crystal Structures
of NaCl & KCl

- The Braggs measured the intensity of specular reflection from cleaved faces of NaCl & KCl crystals.
- They found 6 values of θ for which a sharp peak in intensity occurred, corresponding to 3 characteristic wavelengths (K,L and M X-Rays) in 1st & 2nd order (n = 1 & n = 2 in the Bragg Law)
- By repeating the experiment with a different crystal face they could use the Bragg Equation to find, for example, the ratio of (100) & (111) plane spacings, information that confirmed the cubic symmetry of the atomic arrangement.

DETAILS OF THE STRUCTURE

× Details of the crystal structure were then found. They also discovered some surprising differences between the diffraction patterns for NaCl and KCl.

A Major Difference

was the absence of (111) reflections in KCl compared to weak but detectable (111) reflections in NaCl.

• The explanation for this is that the K and Cl ions both have the argon electron shell structure and hence scatter x-rays almost equally. However, the Na and Cl ions have very different scattering strengths. The (111) reflection in NaCl corresponds to a one wavelength path difference between neighboring (111) planes.
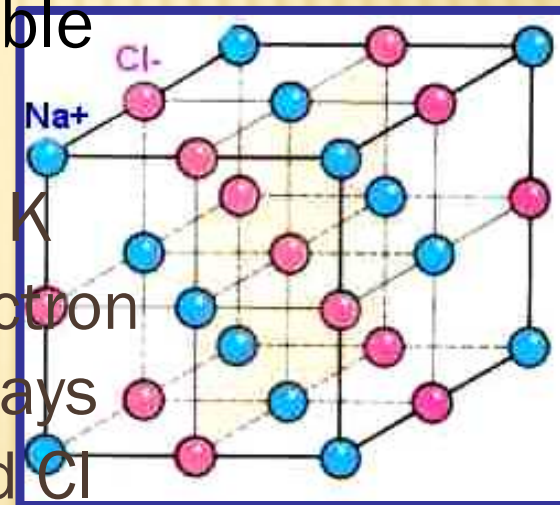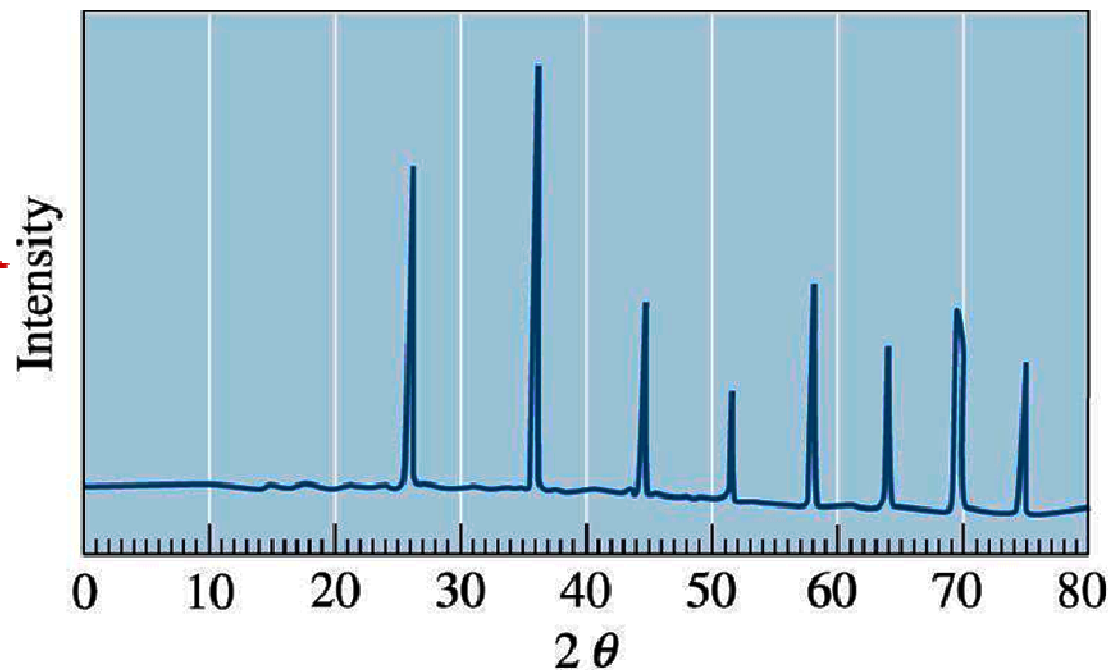
Measurement Results
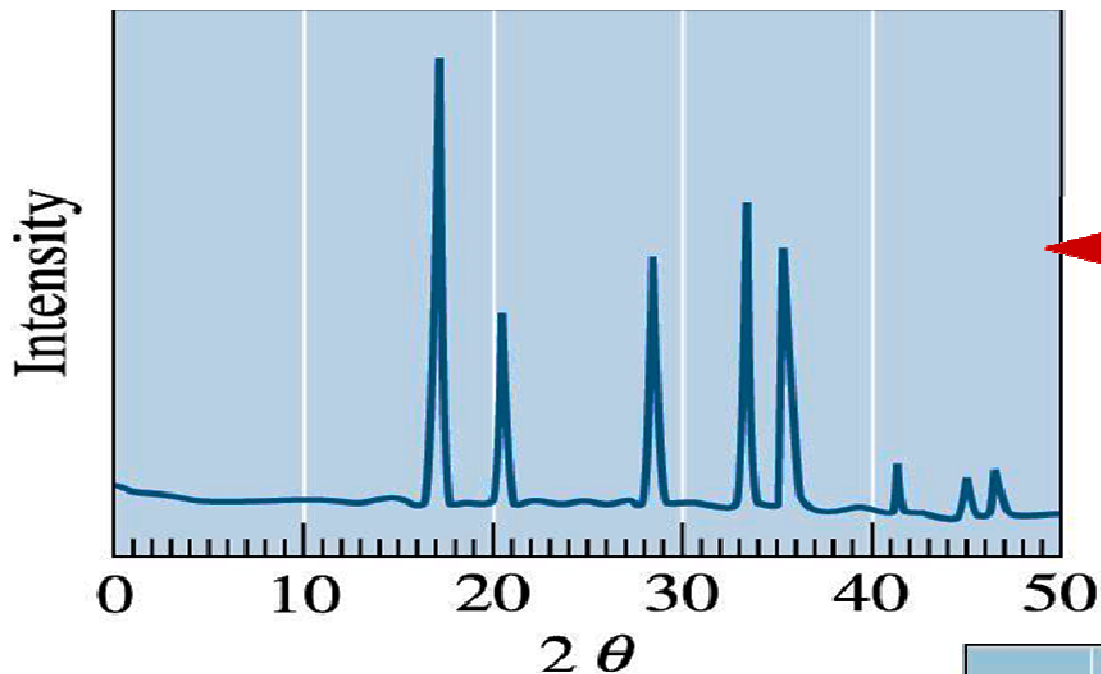
XRD Pattern for NaCl

XRD Pattern for KCl

d - Spacing Formula

d ≡ *Distance between Parallel Lattice Planes with Miller Indices* (hkl)

Its not difficult to prove the following:

Orthogonal	***Cubic***
Crystal Systems	**Crystal Systems**
(α = β = γ = 90°)	**(a = b = c)**

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$$

A cubic crystal system is a special case of an orthogonal crystal system.

BRAGG EQUATION

- Since Bragg's Law applies to all sets of crystal planes, the lattice structure can be found from the diffraction pattern, making use of *general expressions for the spacing of the planes in terms of their Miller indices (hkl), along with the Bragg Law*.
- For cubic structures:

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

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

- *Note that the smaller the spacing, the higher the angle of diffraction*, *i.e.* the spacing of peaks in the diffraction pattern is inversely proportional to the spacing of the planes in the lattice. The diffraction pattern will reflect the symmetry properties of the lattice.

SOME RESULTS FOR D⁻²
FOR SOME NON-CUBIC LATTICES

$$V = abc(1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\cos\beta\cos\gamma)^{1/2}$$

$$a^* = V^{-1}bc\sin\alpha$$

$$b^* = V^{-1}ac\sin\beta$$

$$c^* = V^{-1}ab\sin\gamma$$

$$V^* = V^{-1}$$

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \quad \text{(orthogonal)}$$

$$\frac{1}{d^2} = \frac{4}{3} \cdot \frac{h^2 + k^2 + hk}{a^2} + \frac{l^2}{c^2} \quad \text{(hexagonal)}$$

$$\frac{1}{d^2} = \frac{\begin{pmatrix} \dfrac{h^2}{a^2}\sin^2\alpha + \dfrac{k^2}{b^2}\sin^2\beta + \dfrac{l^2}{c^2}\sin^2\gamma + \\[2mm] + \dfrac{2kl}{bc}(\cos\beta\cos\gamma - \cos\alpha) + \\[2mm] + \dfrac{2hl}{ac}(\cos\alpha\cos\gamma - \cos\beta) + \dfrac{2hk}{ab}(\cos\alpha\cos\beta - \cos\gamma) \end{pmatrix}}{(1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\cos\beta\cos\gamma)} \quad \text{(triclinic)}$$

BRAGG EQUATION

- A simple example is the *difference between the series of (n00) reflections for a simple cubic and a body centred cubic lattice*. For the simple cubic lattice, all values of *n* will give Bragg peaks.
- However, for the body centered cubic lattice the (100) planes are interleaved by an equivalent set at the halfway position. At the angle where Bragg's Law would give the (100) reflection the interleaved planes will give a reflection exactly out of phase with that from the primary planes, which will

  Exactly cancel the signal.

(110)

(100)
simple cubic

- *So, in the BCC lattice, there is no signal from (n00) planes with odd values of n.* This kind of argument leads to rules for identifying the lattice symmetry from "missing" reflections, which are often quite simple.
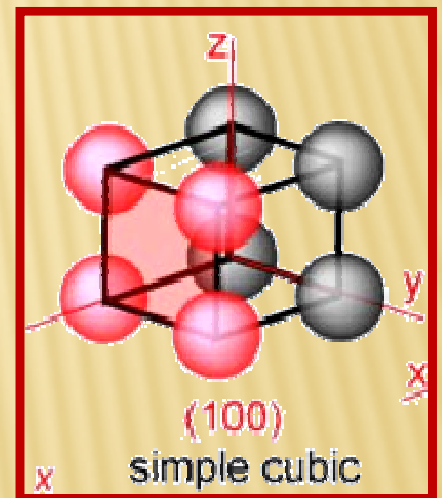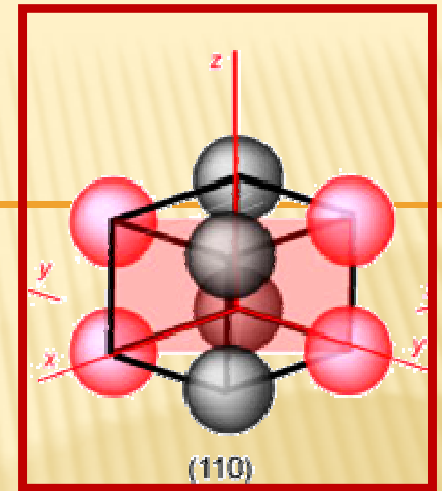
Another (Equivalent) Treatment
of The Reciprocal Lattice

- From another internet source. Slightly different notation, sorry!
- Suppose we have a **Bravias Lattice**, with **translational vector R,** & a plane wave, $e^{ik \cdot r}$. Generally, for a given **k**, the plane wave will not have the periodicity of the Bravais lattice, *R*. However,

for a given R, there will be a set of wave vectors, K, that will yield plane waves with the periodicity of the Bravais lattice.

$$e^{iK \cdot r} = e^{iK \cdot (r + R)} = e^{iK \cdot r} e^{iK \cdot R}$$

thus,

$$e^{iK \cdot R} = 1 \text{ or } K \cdot R = 2n\pi$$

The Reciprocal Lattice

- ***The Reciprocal lattice is a Bravais lattice.***

A brief proof:

$$b_i = 2\pi(a_j \times a_k)/(a_i \bullet a_j \times a_k) \text{ then } b_i \bullet a_j = 2\pi\delta_{ij}.$$

Furthermore, any vector, k, can be written as

$$k = k_1 b_1 + k_2 b_2 + k_3 b_3.$$

For any vector in the direct lattice, R,

$$k \bullet R = 2\pi(k_1 n_1 + k_2 n_2 + k_2 n_2),$$

so for $e^{ik \bullet R}$ to be unity for all R, $k \bullet R$ must be 2π times an integer n. So the coefficients k_i must also be integers.

Therefore, the set of Reciprocal Lattice Vectors, K are themselves a Bravais lattice

The Reciprocal Lattice:
Some other comments.
- The reciprocal lattice of the reciprocal lattice?
- It is just the direct lattice!

Brillouin Zone

- **Brillouin Zones** are primitive cells that arise in the theories of electronic levels

Band Theory &

Lattice Vibrations - Phonons.

- The first **Brillouin Zone** (BZ) is the **Wigner-Seitz primitive cell** of the reciprocal lattice.

Another (Equivalent) Treatment
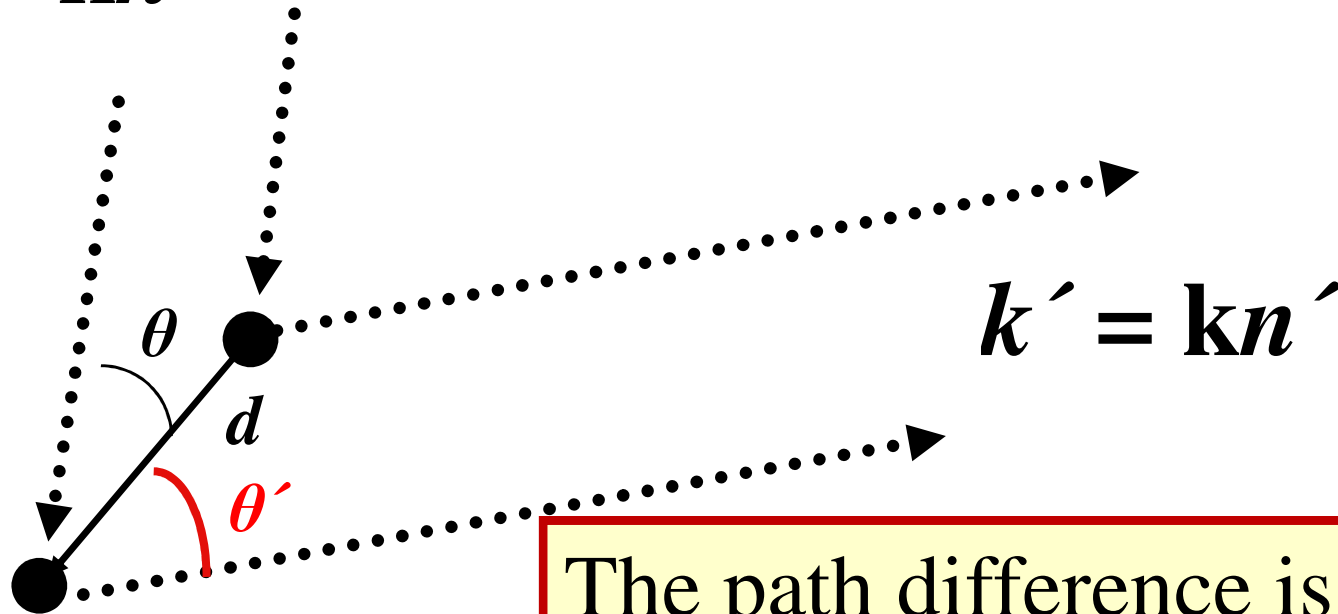## Von Laue Formulation of Crystal Diffraction

- From another internet source. Slightly different notation, sorry!
- **Doesn't assume specular reflection.**
- No sectioning by planes
- Rather, at each point on the Bravais lattice the incident ray is allowed to be scattered in all directions
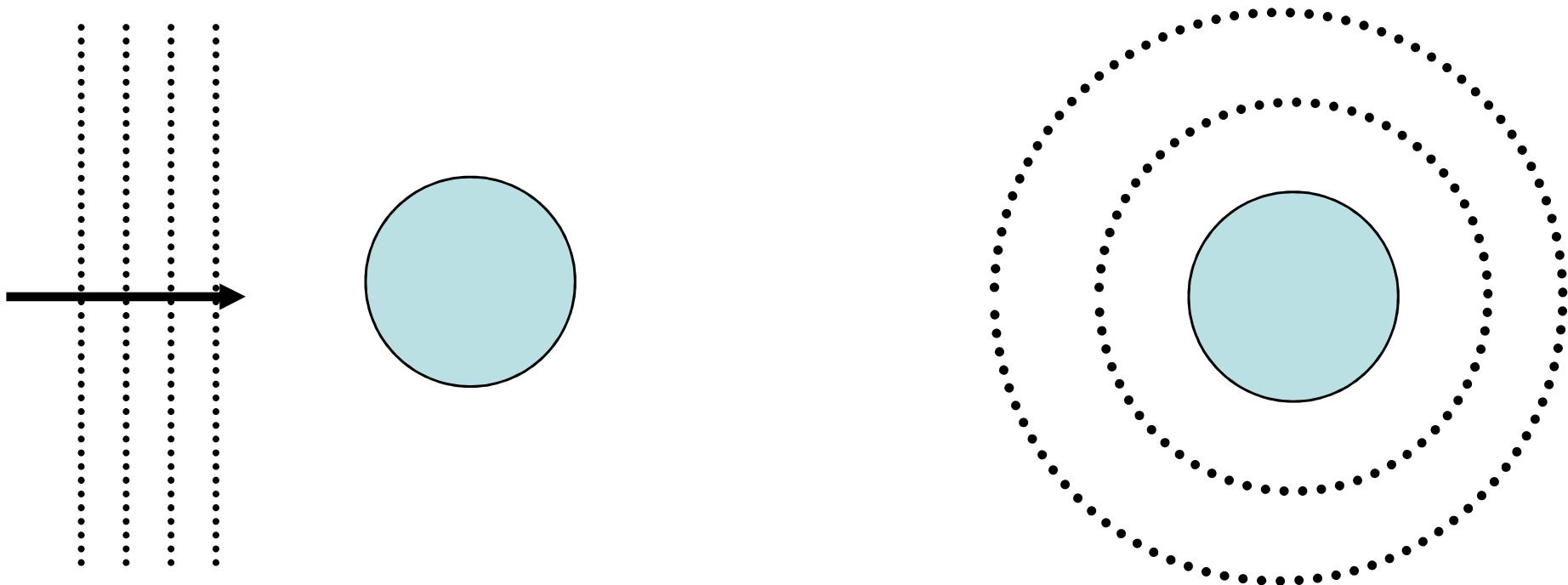
First, consider only two scatterers.

$k = kn$

$k' = kn'$

θ

d

θ'

$k = 2\pi n/\lambda$

$k' = 2\pi n'/\lambda$

The path difference is then
$$d\cos\theta + d\cos\theta' = d \cdot (n - n')$$
The condition for constructive interference is,
$$d \cdot (n - n') = m\lambda$$

- With an array of scatterers; one at each point of the Bravais lattice,
- The results on the last slide must hold for each *d* that is a Bravais lattice vector, so

$$R \bullet (k - k') = 2\pi m$$
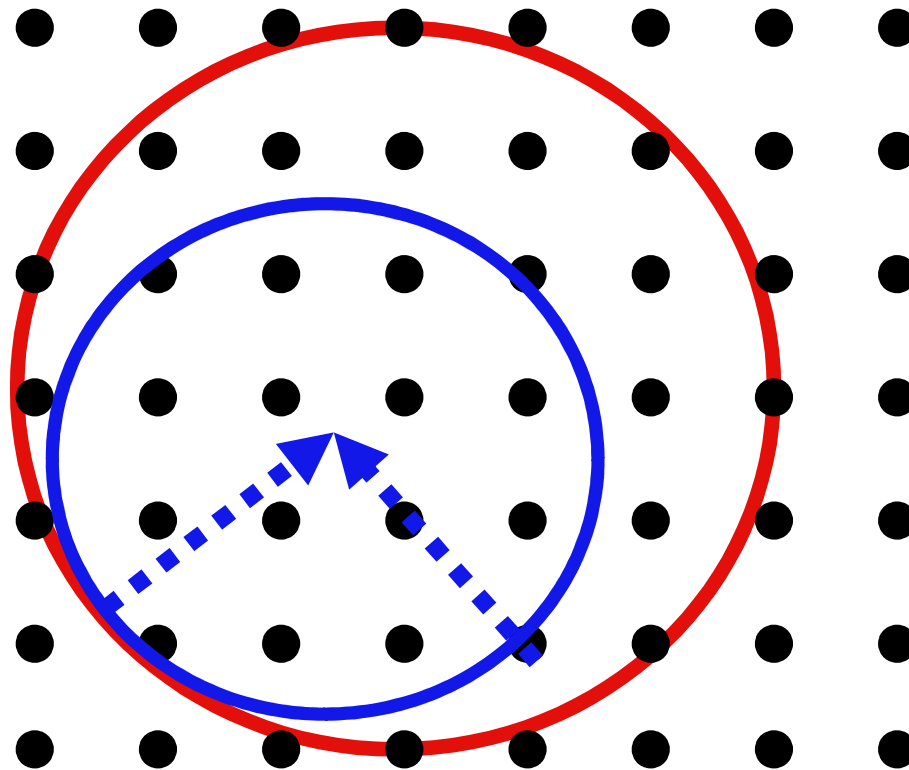$$(m = integer) \text{ or }$$
$$e^{iR \bullet (k - k')} = 1!!$$

- Compare this to the definition for the reciprocal lattice!

This is just *The Laue Condition:*
Constructive interference will occur provided that the change in wave vector,
K = k' - k, is a vector in the reciprocal lattice.

Ewald Construction

- ***The condition for constructive interference is that*** $K = k' - k$, **is a vector of the reciprocal lattice.**

Doing this for all **k & k´** generates the ***Reciprocal Lattice***