

MORE RECIPROCAL SPACE

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OVERVIEW

- Today, we will answer the following questions:
 - *How do we classify crystallographic planes using Miller indices?*
 - *What is a Brillouin Zone and how is it related to the Wigner-Seitz cell?*
 - *How do we describe scattering from a lattice with a basis?*
 - *How do we actually use X-ray diffraction to characterize crystals?*

BRAGG SCATTERING

- In the previous lecture, we discussed the Bragg condition:
 - A **monochromatic beam of X-rays** is incident on a crystalline sample
 - The beam undergoes **specular reflection at well-defined crystallographic planes**
 - Constructive interference between reflected rays gives rise to **diffraction peaks**
- The Bragg condition gives a relationship between angle of incidence/reflection, wavelength of the interrogating beam, and the distance between crystallographic planes.

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

- When this equality is satisfied, a diffraction peak will be observed.
- We developed the notion of a **reciprocal lattice** to derive the Bragg condition formally:
- Bragg scattering occurs when the **scattering vector is a reciprocal lattice vector** associated with the crystal Bravais lattice.

- We were able to re-write the Bragg condition as follows: $|\vec{\mathbf{G}}|^2 = 2\vec{\mathbf{G}} \cdot \vec{\mathbf{k}}$

BRAGG SCATTERING (CONT.)

- We hand-wavily concluded, that we can show a direct equivalence between the two Bragg conditions:

$$2d \sin \theta = n\lambda \longleftrightarrow |\vec{\mathbf{G}}|^2 = 2\vec{\mathbf{G}} \cdot \vec{\mathbf{k}}$$

- Our argument was based upon the physical interpretation of the reciprocal lattice vector, \mathbf{G}

$$\vec{\mathbf{G}} = h\vec{\mathbf{b}}_1 + k\vec{\mathbf{b}}_2 + l\vec{\mathbf{b}}_3$$

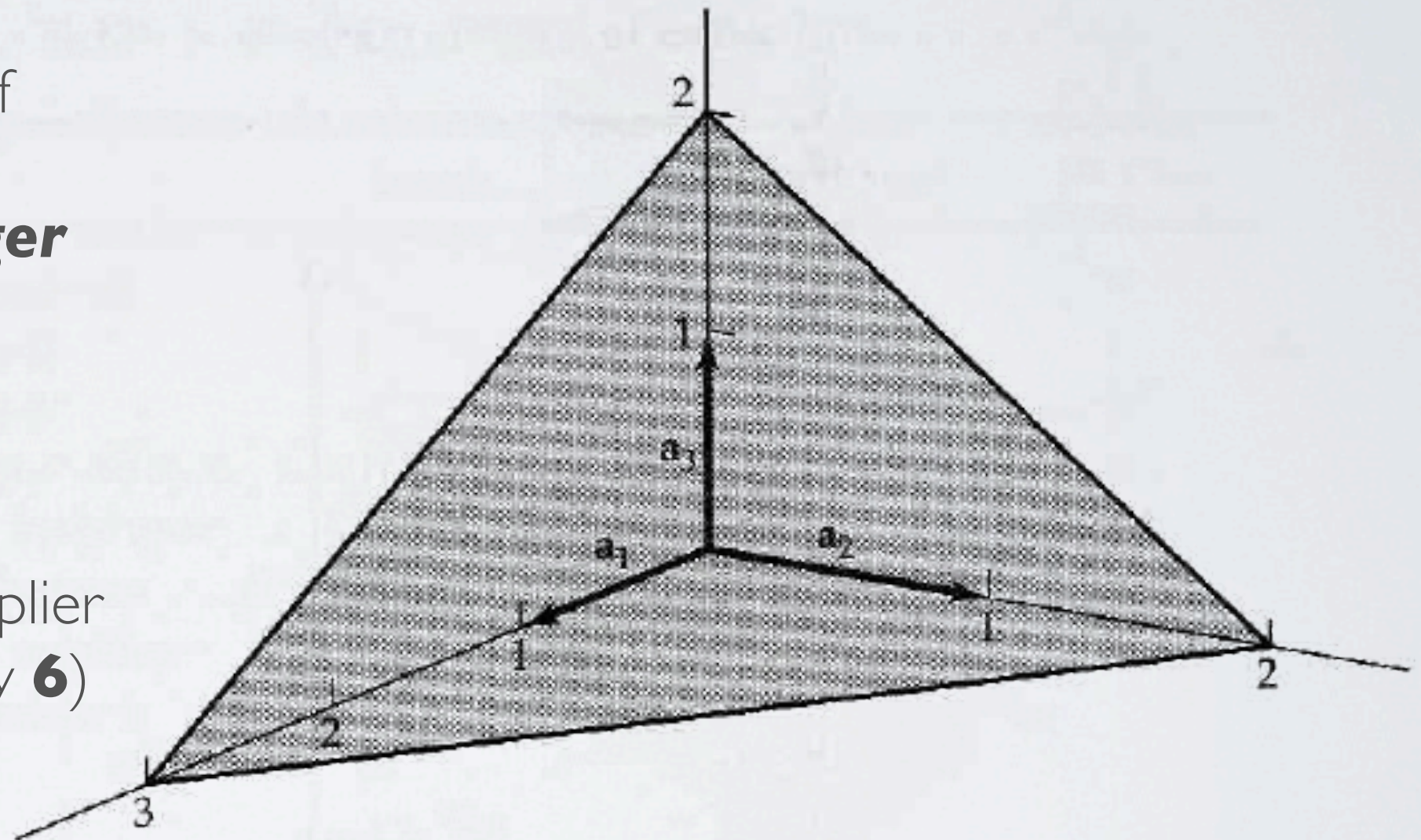
- Here, h , k , and l , are integers called **Miller indices**.
- A **single fixed set** of Miller indices describes an **infinite set of crystallographic planes**
- We claimed that the magnitude of \mathbf{G} is related to the **real space distance between these planes**

$$d(hkl) = \frac{2\pi}{|\vec{\mathbf{G}}|} \quad \text{and} \quad |\vec{\mathbf{G}}|^2 = 2\vec{\mathbf{G}} \cdot \vec{\mathbf{k}} \longrightarrow 2d(hkl) \sin(\theta) = \lambda$$

- Aside from being the glue that holds together the two ends of this derivation, Miller indices are used to label crystallographic planes, and their associated diffraction peaks.

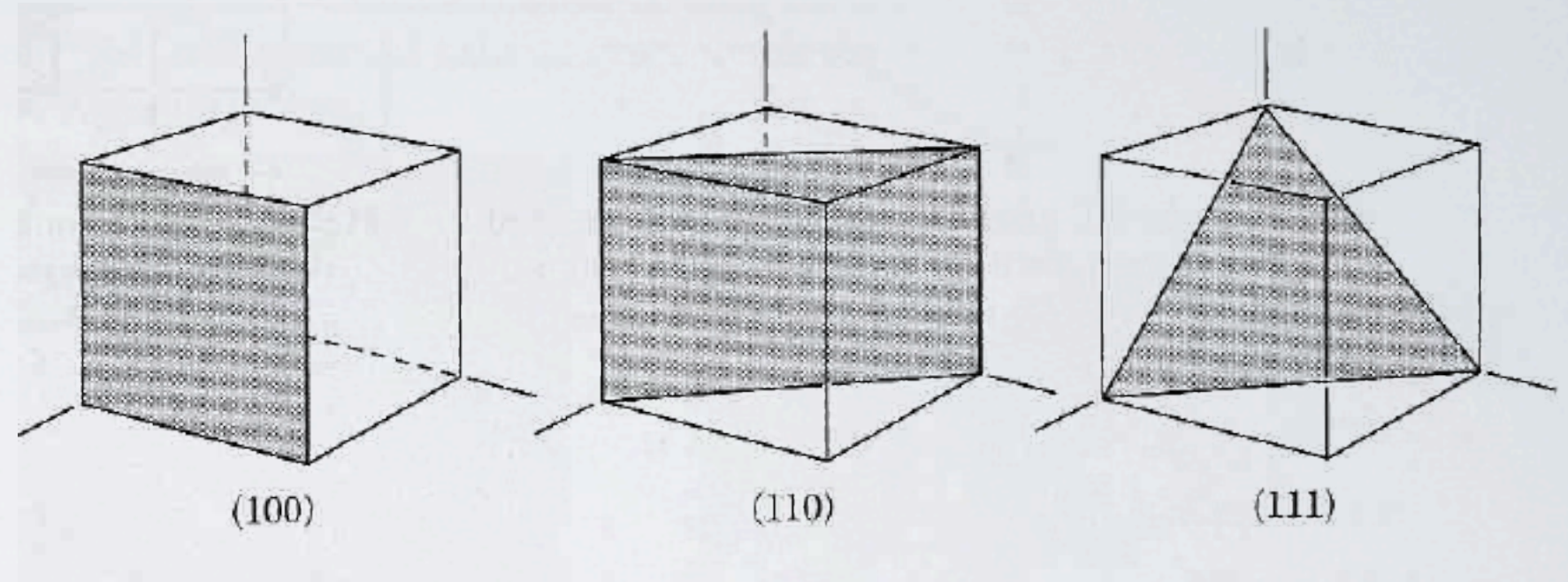
INDEXING CRYSTALLOGRAPHIC PLANES

- Other than defining a reciprocal lattice vector, these 3 integers, **h**, **k**, **l**, refer to families of crystallographic planes, that can be brought into coincidence by translation by a lattice vector.
- For a given plane, how do we construct these indices?
 - Define a unit cell with respect to a set of real lattice vectors
 - Find the intercepts of the plane at **integer multiples** of the lattice vectors
 - **3, 2, 2**
 - Take the **reciprocals** of these integers
 - **1/3, 1/2, 1/2**
 - **Clear fractions** with a common multiplier
 - **2, 3, 3** (multiplied **1/3, 1/2, 1/2** by **6**)
 - Remove **common multiples**
 - *None in this example*



INDEXING CRYSTALLOGRAPHIC PLANES

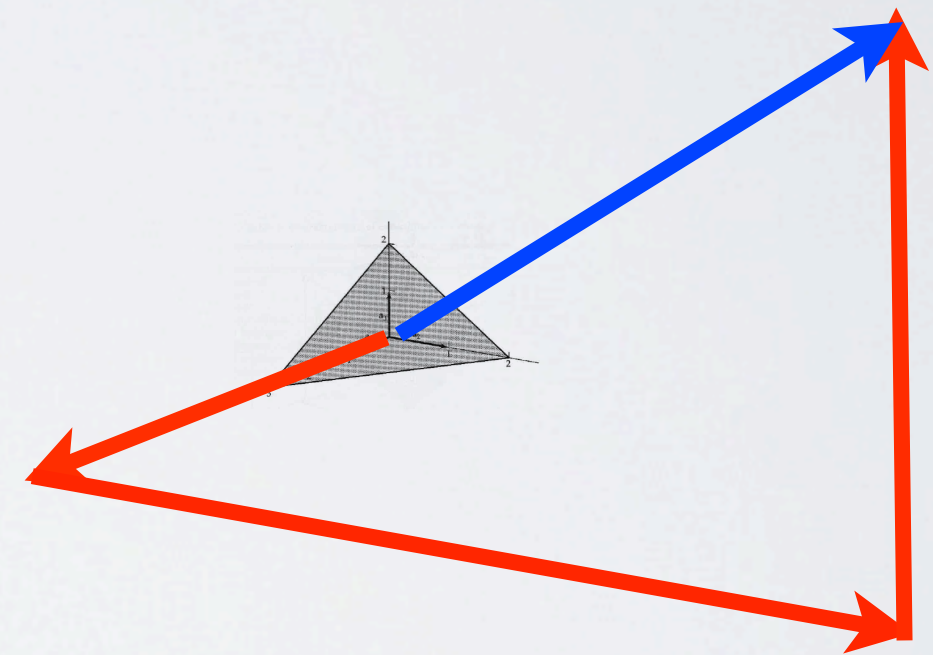
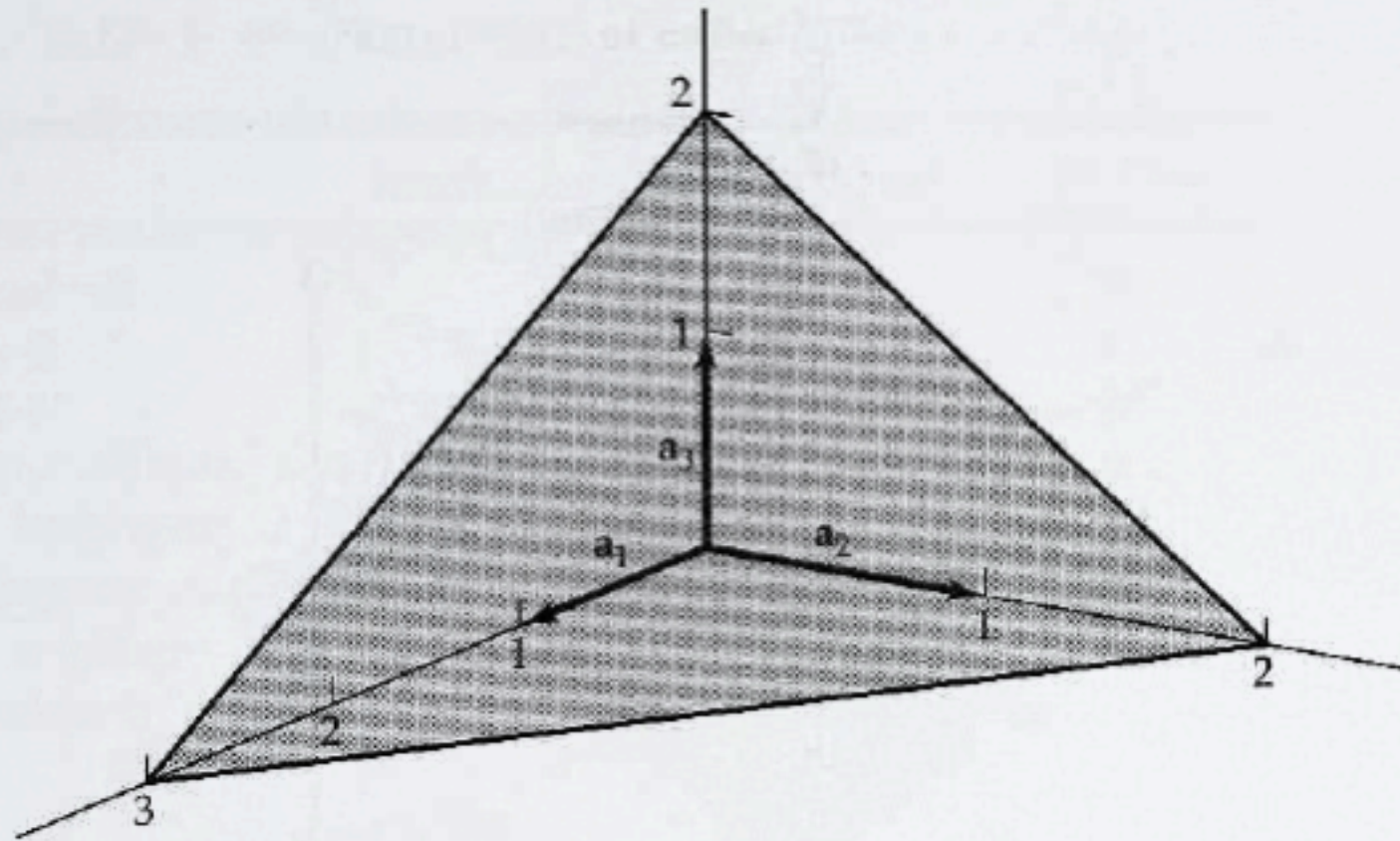
- The only 'exceptions' arise for rhombohedral and hexagonal systems, wherein a 4th index is sometimes added.
- Some of the simpler planes are illustrated to the right.



- This triplet of integer indices is referred to as Miller indices, and they don't just refer to crystal planes
- Indices are enclosed by $()$, $[\]$, $\{ \}$, or $\langle \rangle$ - **the type of brace indicates physical significance**
 - (hkl) : crystallographic **planes**, as discussed so far
 - $\{hkl\}$: **family of planes** that are mapped onto each other under lattice's group of symmetries
 - $[hkl]$: crystallographic **direction** defined by real lattice vector with components h, k, l
 - $\langle hkl \rangle$: **family of directions** mapped onto each other under lattice's group of symmetries

GEOMETRIC INTERPRETATION

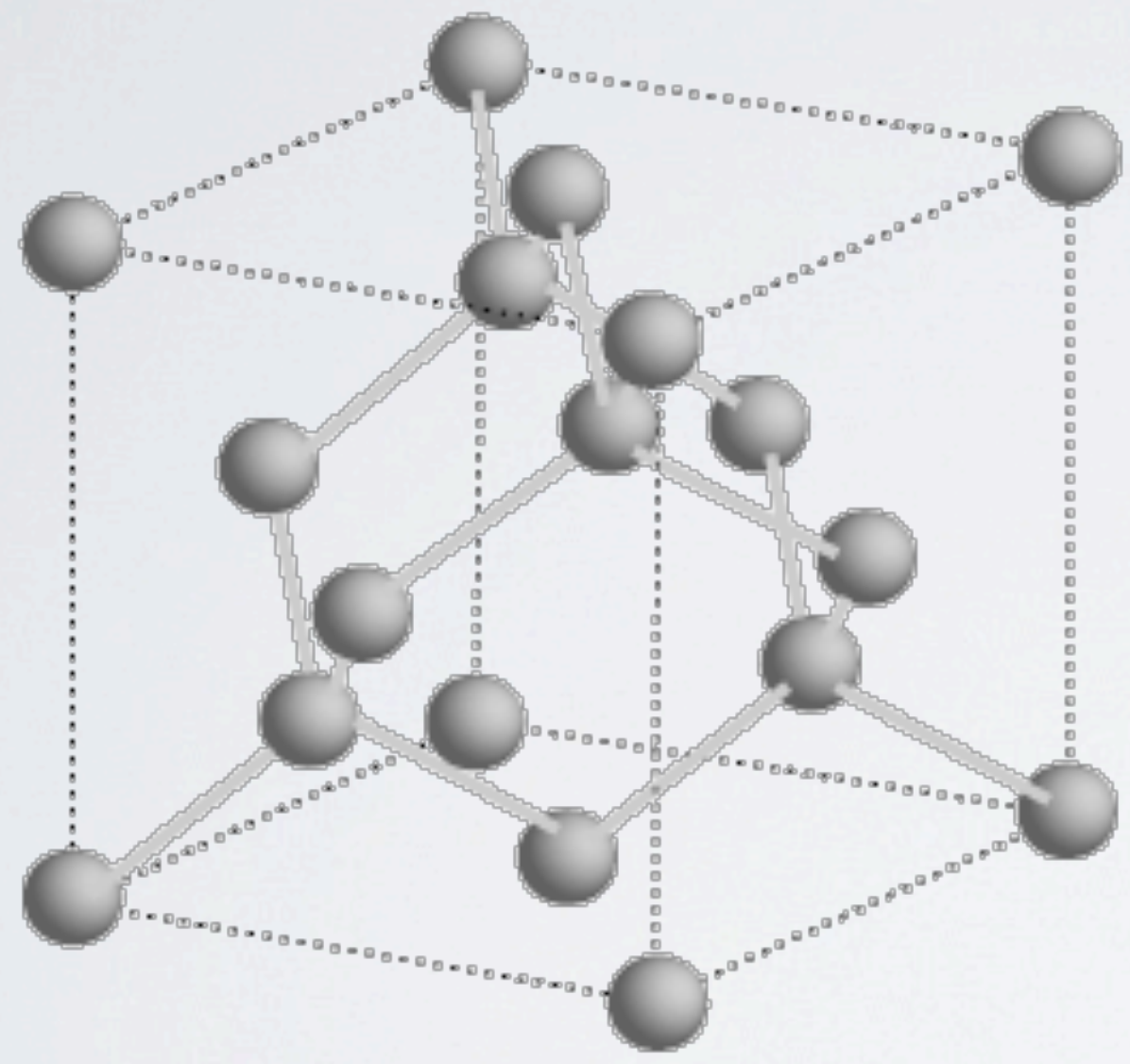
- There is one last feature of reciprocal lattice vectors & Miller indices worth noting
 - In general, one geometrically defines a plane in terms of a vector that is normal to it.
 - The reciprocal lattice vector with components h, k, l , is **normal to the set of planes (hkl)** !
 - It is actually the **shortest normal vector with integer components**.



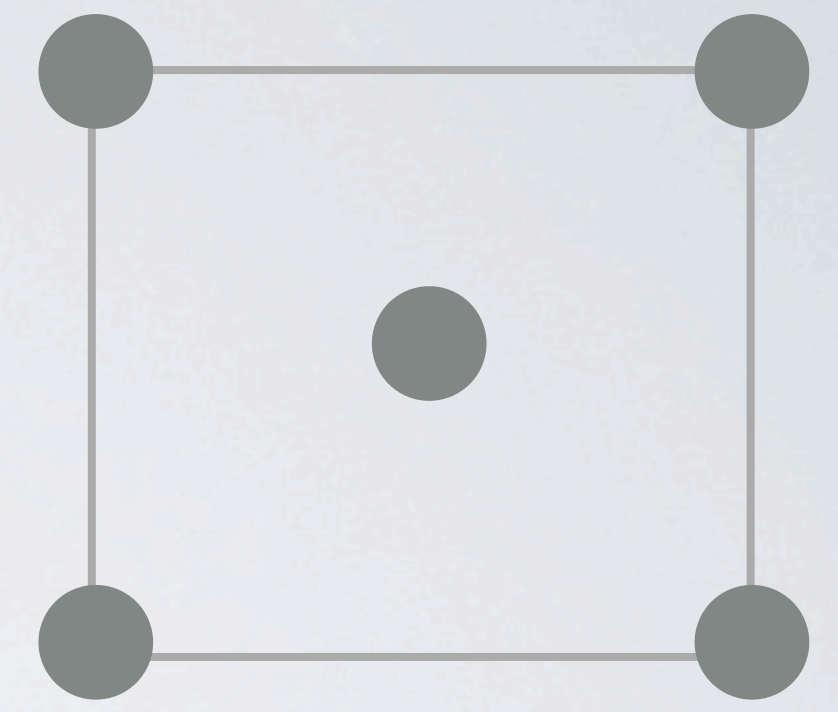
- Reciprocal lattice vector with components h, k, l is **orthogonal to plane (hkl)** , and its **magnitude scales inversely with the distance between consecutive (hkl) planes**.

EXAMPLE

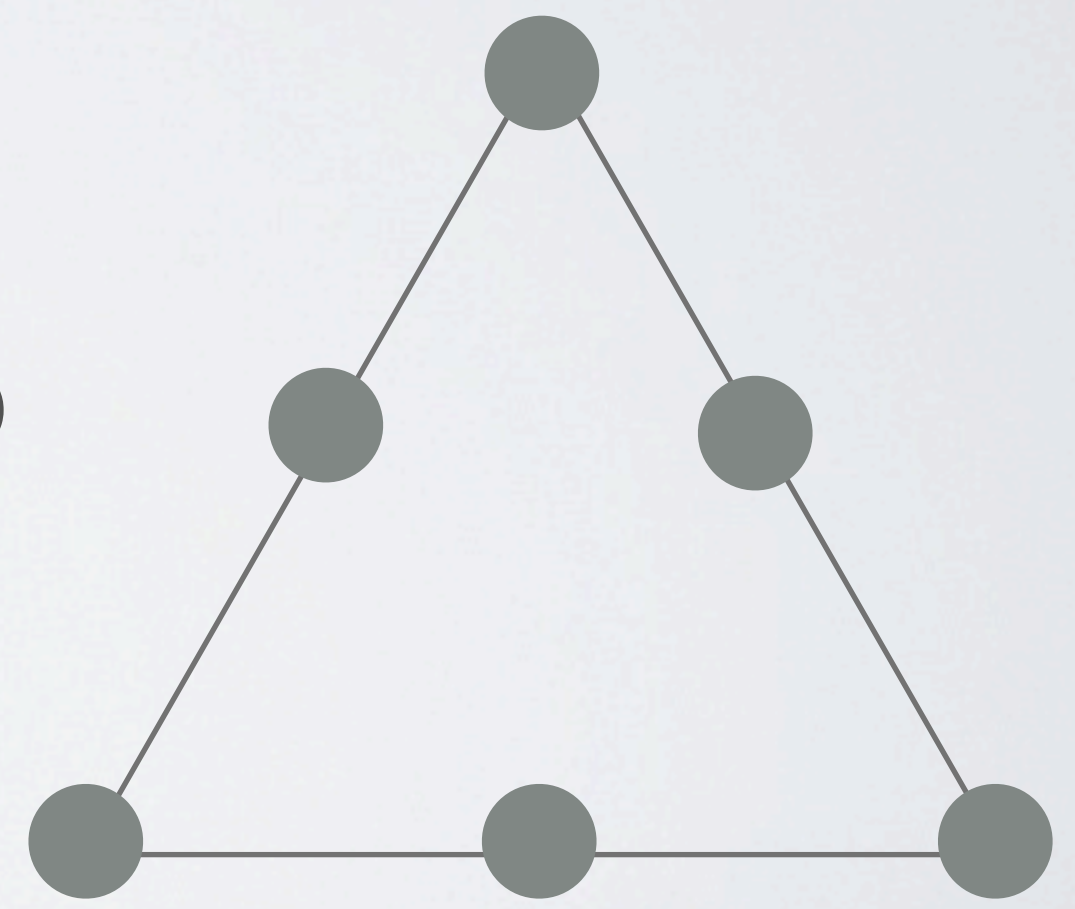
- Consider the (111) and (100) planes of Silicon.



(100)



(111)



- Which has the higher areal density of Si atoms?

EXAMPLE

- Both have 2 atoms per planar cross-section in the conventional unit cell.

- Area of (100) cross-section in unit cell = a^2

- Area of (111) cross-section in unit cell = $\frac{\sqrt{3}}{2}a^2$

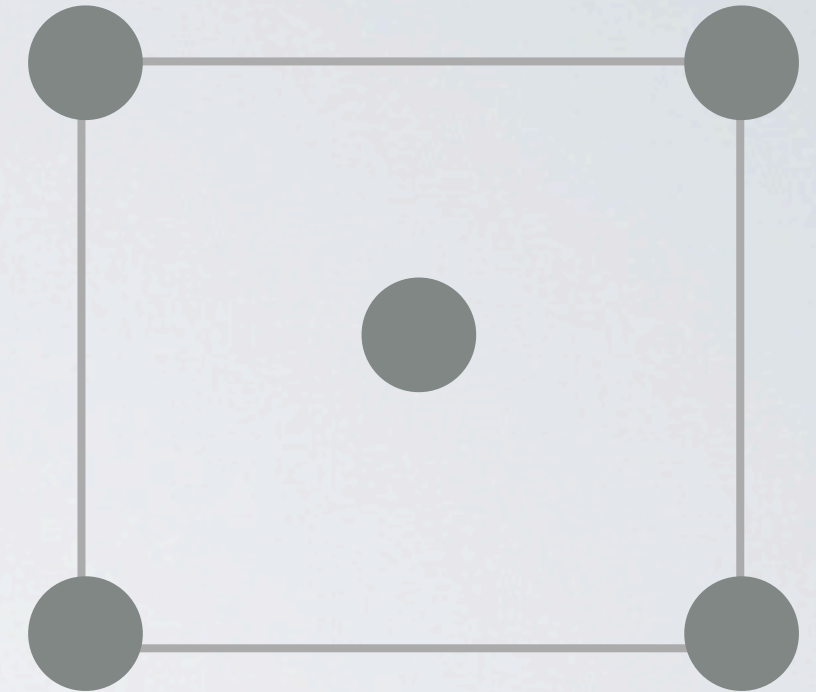
- **The (111) plane has the higher areal density**

- If you stumble upon a single crystal Si wafer, chances are it will be cleave on one of these two faces

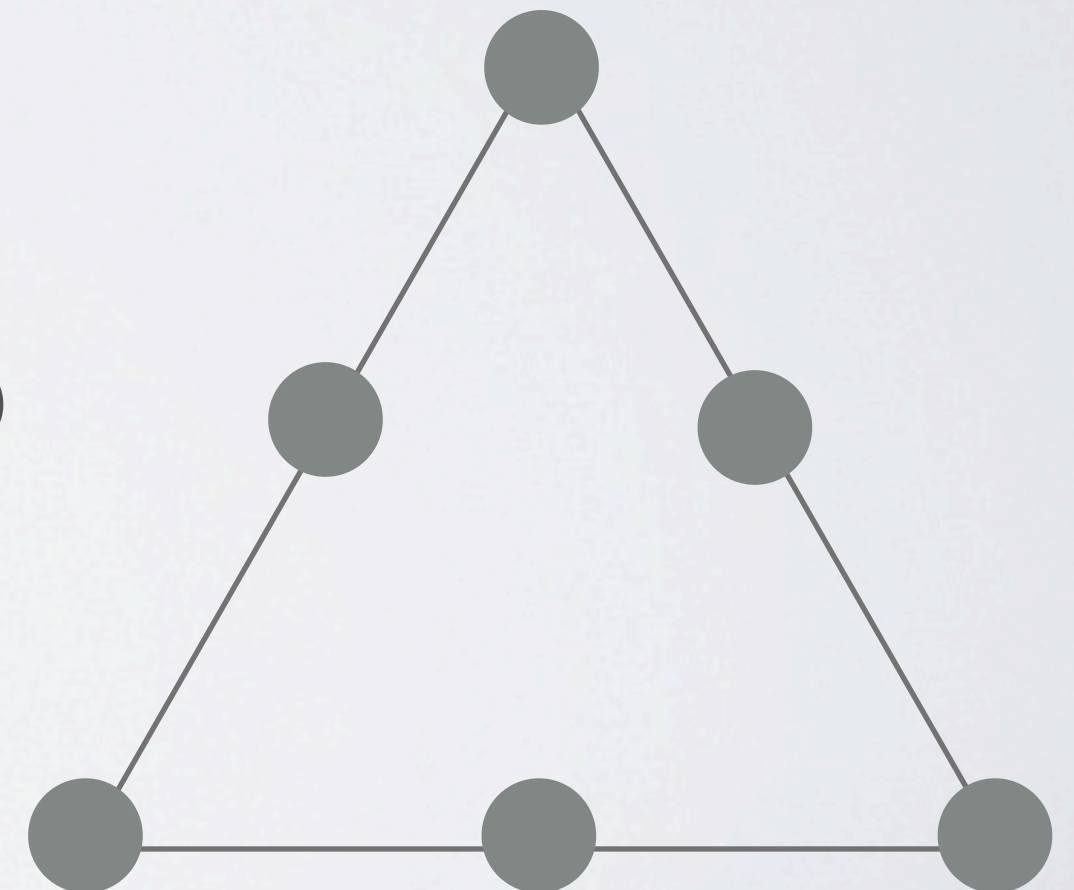
- You will see these indices in a number of contexts outside of X-ray diffraction:

- Chemical reactivity depends on surface orientation
- Grains in polycrystals
- Anisotropic elastic, optical, and electrical properties

(100)



(111)

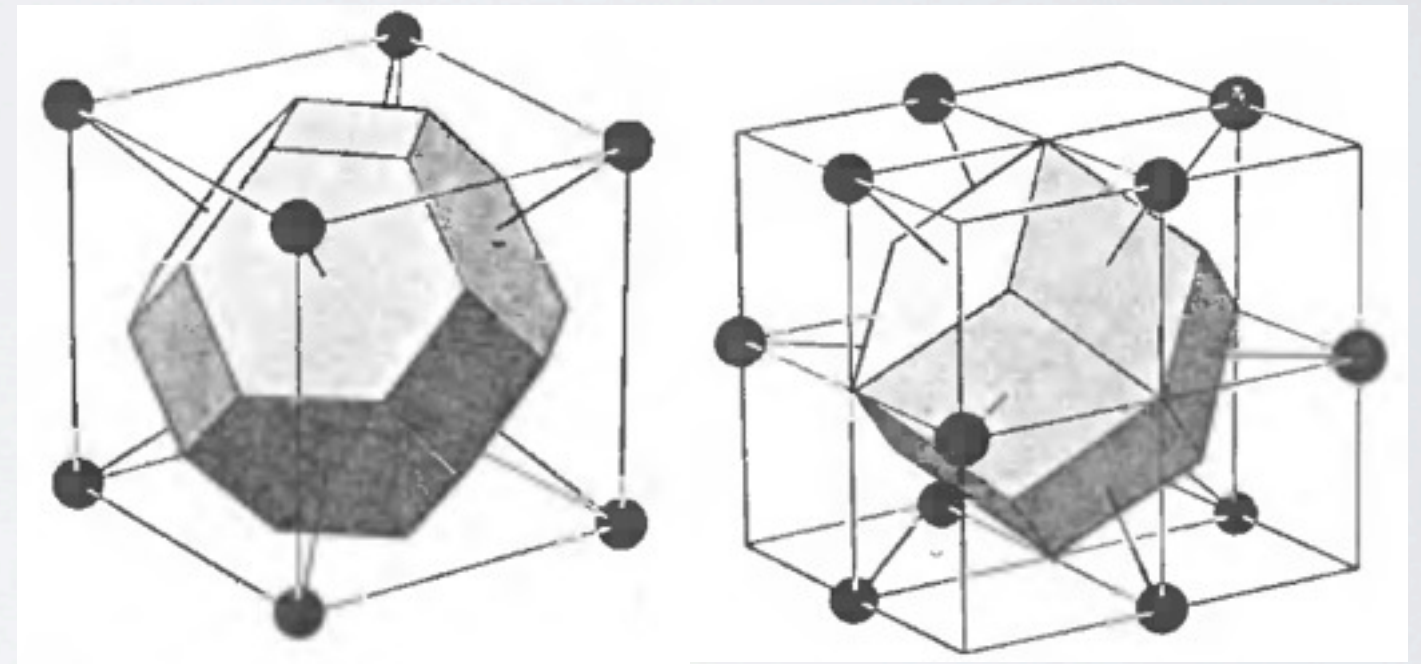


WIGNER-SEITZ REDUX

- Now that we understand the reciprocal lattice, let's revisit the Wigner-Seitz unit cell
- Wigner-Seitz cell: primitive cell such that for a fixed lattice point, the WS cell is the **volume surrounding it that is closest to that point**

- **Algorithm for construction**

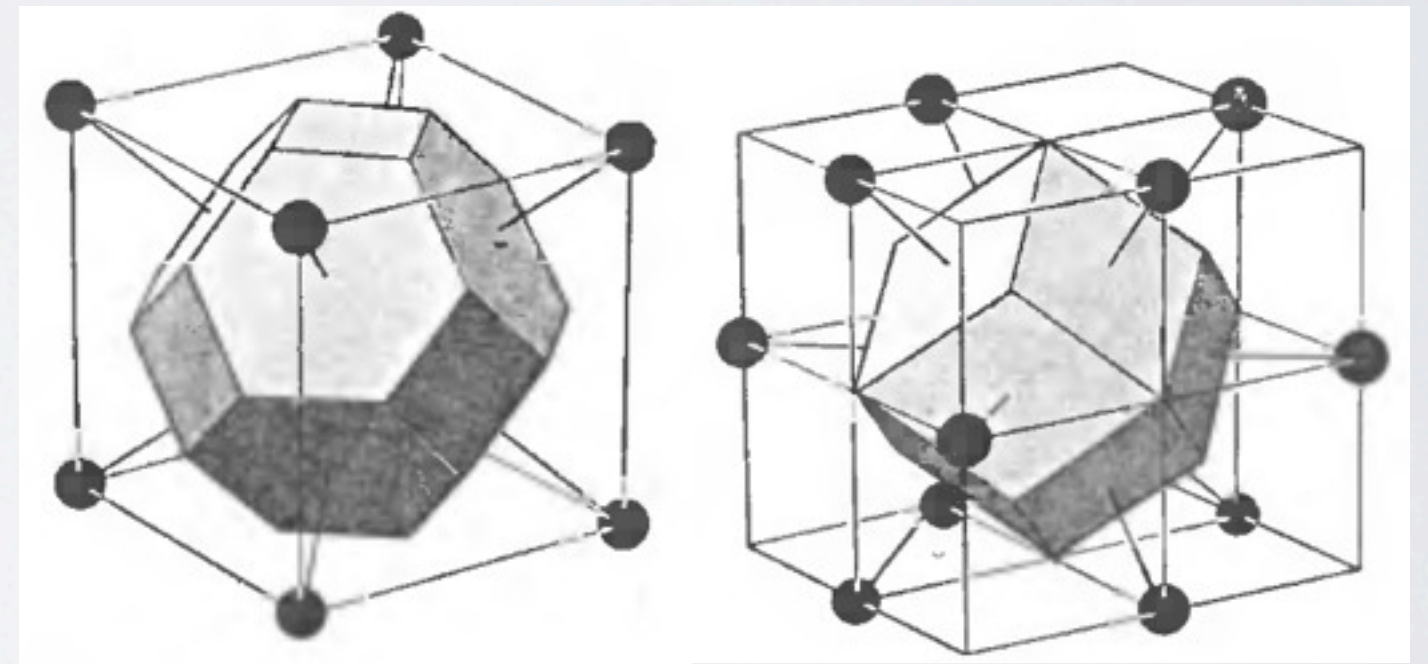
- Choose a lattice point
- Find its nearest neighbors
- Draw a line from the point to its neighbors
- Bisect this line with a plane
- Planes bound the Wigner-Seitz cell



bcc and **fcc** Wigner-Seitz cells (respectively)

BRILLOUIN ZONES

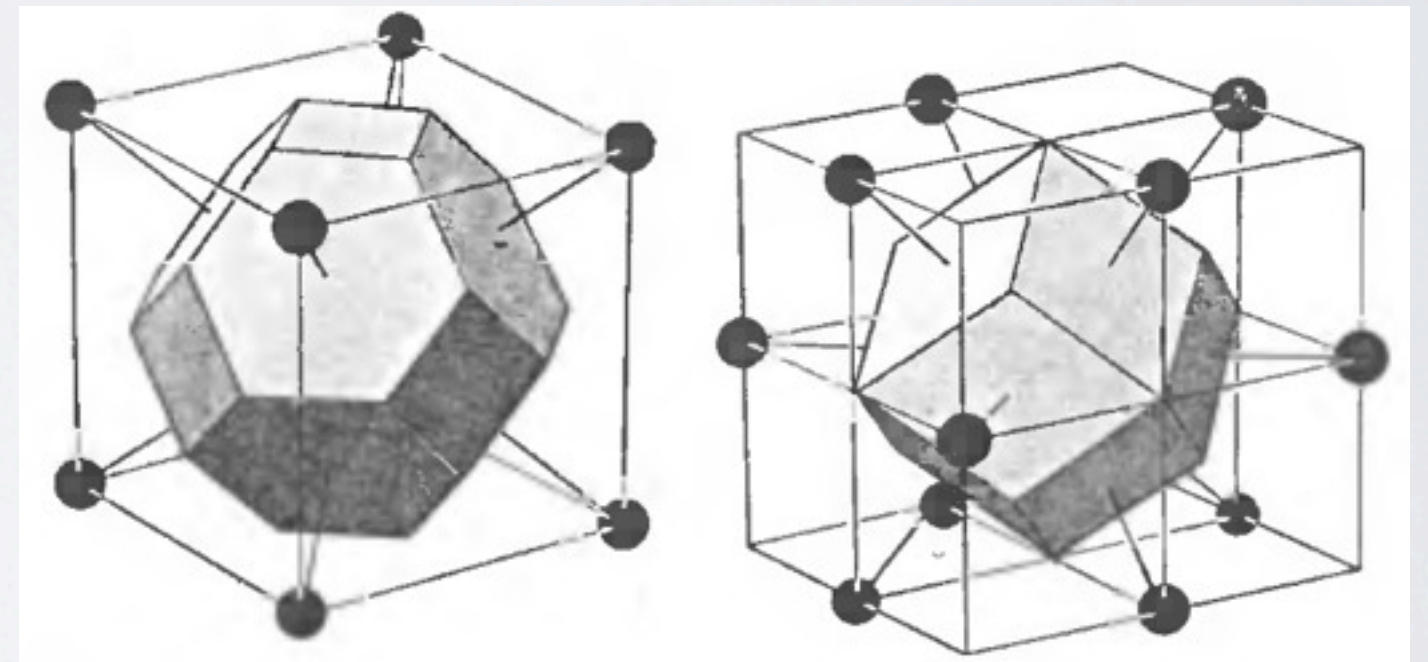
- In real space, this was just a convenient method for constructing high symmetry primitive cells
- In reciprocal space, the Wigner-Seitz construction produces what is called the **first Brillouin zone**
- **Wigner-Seitz cell** and **first Brillouin zone** refer to equivalent mathematical constructs, one is in real space, the other is in reciprocal space.
- A convenient duality exist for **bcc** and **fcc** lattices
 - Reciprocal lattice of bcc = fcc
 - Reciprocal lattice of fcc = bcc
 - **The bcc first Brillouin zone is congruent to the fcc Wigner-Seitz cell, and vice-verse!**



fcc and **bcc** first Brillouin Zones (respectively)

BRILLOUIN ZONES (CONT.)

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BRILLOUIN ZONES (CONT.)

- **So why do we care?**

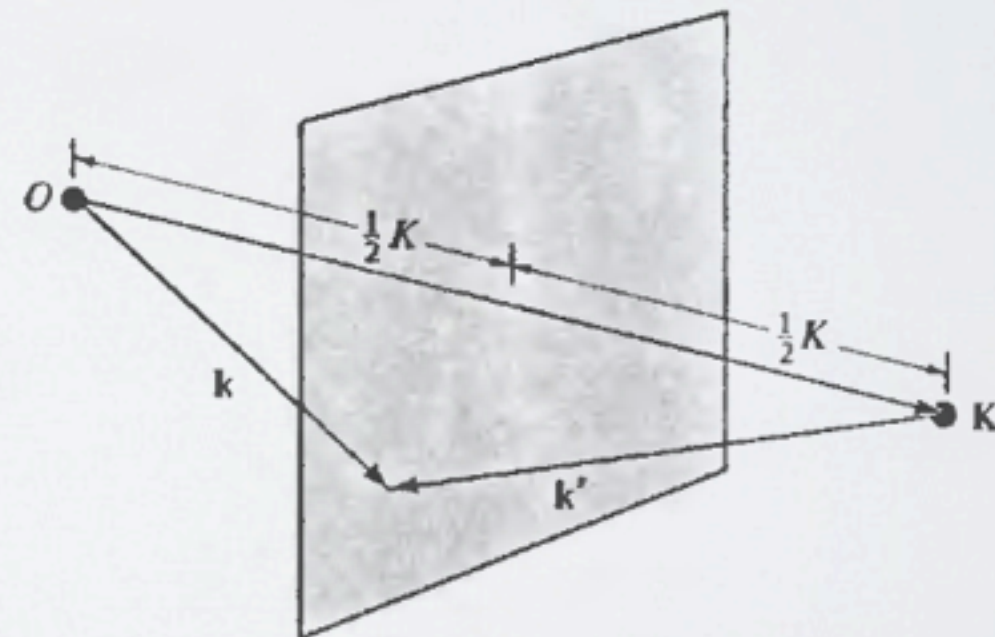
- **Bragg condition:** diffraction peak will be observed if scattering vector, $\Delta\vec{K} = \vec{k}' - \vec{k}$, is a reciprocal lattice vector

$$|\vec{G}|^2 = 2\vec{G} \cdot \vec{k} \longrightarrow \vec{k} \cdot \Delta\hat{K} = \frac{1}{2}|\Delta\vec{K}|$$

- The projection of the incident wave vector along the reciprocal lattice vector producing diffraction must be half the magnitude of the reciprocal lattice vector.

- \vec{k} vectors that satisfy this criterion define a plane in reciprocal space, that we call **Bragg plane**

- The boundaries of the first Brillouin zone (and higher) will be **Bragg planes!**



BRILLOUIN ZONES (CONT.)

- ***Here is a summary of what we know about X-ray scattering now:***

- From the real space lattice, we can construct a reciprocal lattice
 - From the reciprocal lattice, we can construct the first Brillouin zone, using Wigner-Seitz construction
 - From the Brillouin zone, we can find Bragg planes, which describe incident wave-vectors at which Bragg scattering occurs.
 - We can work this backwards just as easily!
-
- You will see that the Brillouin zone is an important concept in electronic structure as well.
 - Namely, the potential that electrons feel moving around in the lattice is also periodic.
 - Electronic dispersion will be heavily modified in the vicinity of Bragg planes
 - Basic content of the nearly free electron model.

BRAGG SCATTERING WITH A BASIS

- Before moving onto electronic structure, we will consider Bragg scattering in one more context: **with a basis assigned to the underlying Bravais lattice.**

- We previously defined the scattering amplitude for a lattice with a trivial basis:

$$F(\Delta\vec{\mathbf{K}}) = \int d\vec{\mathbf{r}} n(\vec{\mathbf{r}}) e^{-i\Delta\vec{\mathbf{K}} \cdot \vec{\mathbf{r}}}$$

- To add a basis, we need to introduce a quantity known as the **geometric structure factor.**

- For a lattice with a basis consisting of n identical atoms at $\{\vec{\mathbf{d}}_1, \dots, \vec{\mathbf{d}}_n\}$ and a scattering vector $\Delta\vec{\mathbf{K}}$

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

- This is just a phase shift that arises due to scattering from the basis atoms at each lattice point.

STRUCTURE FACTORS

- Previously, we saw that the intensity of a Bragg peak was proportional to the modulus square of the Fourier coefficient associated with the scattering vector (which was **zero unless it was in the reciprocal lattice**).

- It is now proportional to the modulus square of the geometric structure factor as well!

$$I \sim V^2 |n_{\vec{G}}|^2 \rightarrow I \sim V^2 |n_{\vec{G}}|^2 |S_{\vec{G}}|^2$$

- The net result of adding the geometric structure factor is the extinction or enhancement of certain Bragg peaks.

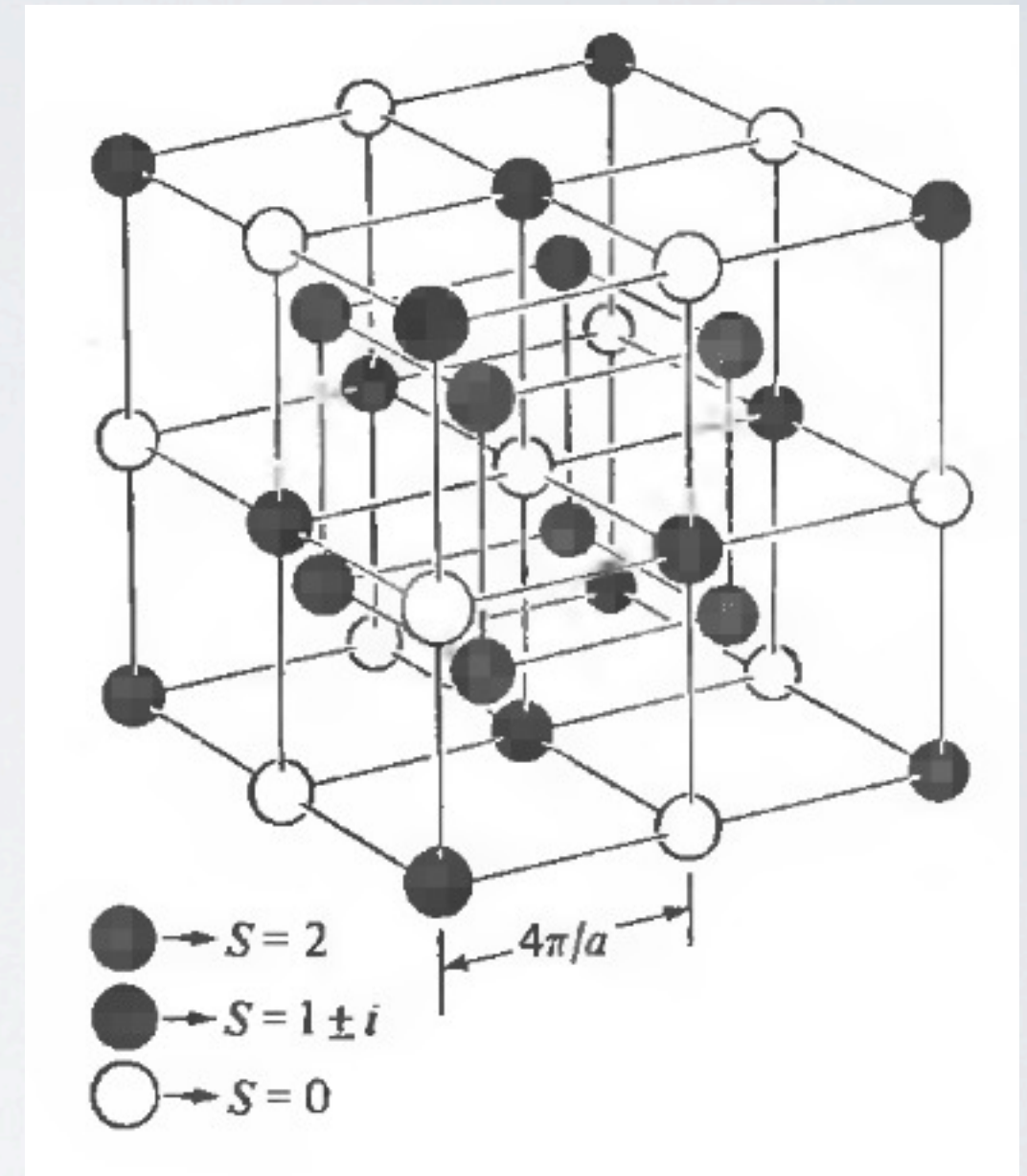
- When the Fourier coefficient of the density is non-zero, the **structure factor may still be zero!**

STRUCTURE FACTORS (CONT.)

- For the diamond crystal structure, recall that we have an **fcc** lattice with a basis of **2** atoms:
 - $(0,0,0)$ and $(1/4, 1/4, 1/4)$ - components using Cartesian basis
- The reciprocal lattice is a **bcc** with primitive vectors:
 - $(-1/2, 1/2, 1/2)$, $(1/2, -1/2, 1/2)$, and $(1/2, 1/2, -1/2)$
- On the right, the structure factor is evaluated a number of different reciprocal lattice vectors

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

- Diffraction peaks associated with white spots are **removed from the usual fcc diffraction pattern**



STRUCTURE FACTORS (CONT.)

- Not much changes when you add a polyatomic basis.
- Structure factor will now have to depend upon the charge distribution at each basis site
- Constructing structure factors for large crystals is essential to study of proteins using X ray crystallography
 - Here, the unit cell may have a basis on the order of **10,000 atoms**

CONCLUSIONS

- In summary:
 - *Miller indices are triplets of integers used to index crystal planes and directions*
 - *The Brillouin zone is just the Wigner-Seitz cell in reciprocal space*
 - *The boundaries of the Brillouin zone are Bragg planes*
 - *The introduction of a basis to the Bragg scattering problem, extinguishes certain Bragg peaks that would otherwise be there in the case of a trivial basis.*