PROBING CRYSTAL STRUCTURE

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PHY 491, October 10th, 2011

OVERVIEW

- First - we'll briefly discuss Friday's quiz.

- Today, we will answer the following questions:
  - *How do we experimentally probe crystal structure?*
  - *What is a 'reciprocal lattice'?*
  - *What does the Bragg condition for diffraction have to do with the reciprocal lattice?*

THE SCATTERING PARADIGM

- One of the most vital experimental philosophies, transcending all fields of physics, can be (crudely) summarized as follows:

  There is much knowledge to be gained from throwing known objects at unknown objects and observing what happens

- Generally, the length scale of the known probe sets the maximum length scale that can be resolved in the unknown.

- In solids, the ***interatomic spacing is on the order of Angstroms*** (10^{-10} meters).

- What can we use to resolve details on this length scale?

PHOTONS

- Wavelength of ***visible light ~100s of nm***
  - About 3 orders of magnitude larger than would be necessary to resolve crystalline structure.

- ***X-rays*** have a sufficiently short wavelength

- What are the energies associated with photons of these wavelengths?
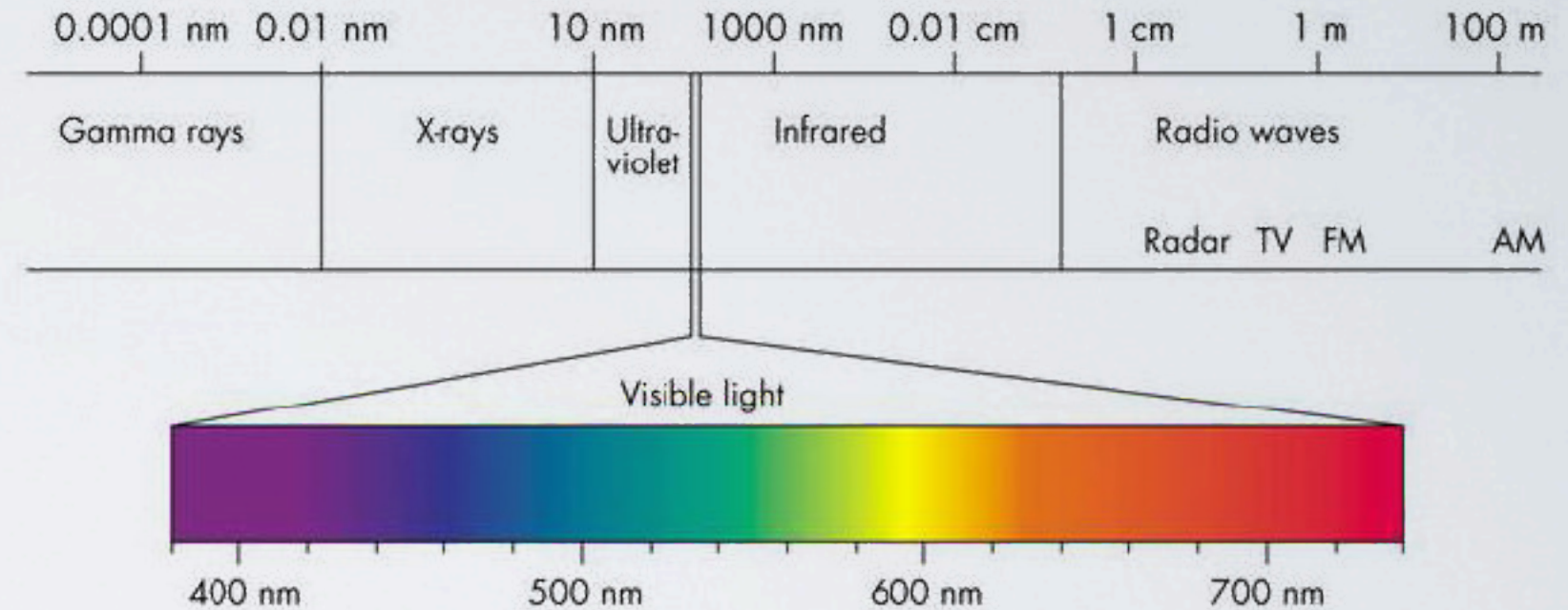
$$E = \frac{hc}{\lambda} = \frac{1240 \text{ eV nm}}{\lambda}$$

$$\lambda = 500 \text{ nm} \rightarrow E = \frac{1240 \text{ eV nm}}{500 \text{ nm}} = 2.48 \text{eV}$$

$$\lambda = 0.1 \text{ nm} \rightarrow E = \frac{1240 \text{ eV nm}}{0.1 \text{ nm}} = 12.4 \text{keV}$$

Trend worth noting: ***Energy scales inversely with wavelength***

ELECTRONS

- Massive particles have a de Broglie wavelength that scales inversely with their momentum[*]

$$\lambda = \frac{h}{p}, \quad E = \frac{p^2}{2m} \rightarrow \lambda = \frac{h}{\sqrt{2mE}}$$

- What is the energy of an electron with a de Broglie wavelength of 1 Angstrom?

$$E = \frac{h^2}{2m\lambda^2} = \frac{(hc)^2}{2mc^2\lambda^2} = \frac{(1240 \text{ eV nm})^2}{2 \times 511 \text{ keV} \times (0.1 \text{ nm})^2} = 150 \text{ eV}$$

- Note: ***Energy scales as the inverse square of wavelength***

- To double your resolution, you need to quadruple your energy...

- We can reduce the energy even further if we increase the mass of the particle...

[*] Note that we are neglecting relativistic effects. This is acceptable so long as the non-relativistic kinetic energy is much smaller than the rest mass of the electron. This isn't the case in transmission electron microscopes (TEMs)!

NEUTRONS

- Rest mass of a neutron is about 939 MeV/c^2 - **_1837 times larger than an electron!_**

- The energy of a 1 Angstrom neutron is thus reduced by a factor of 1837...

$$E_{electron,1\mathring{A}} = 150 \text{ eV} \rightarrow \quad E_{neutron,1\mathring{A}} = \frac{E_{electron,1\mathring{A}}}{1837} = 0.08 \text{ eV}$$

- Room temperature is about 0.026 eV...

$$\lambda_{\text{neutron, room temp}} = \frac{(hc)}{\sqrt{2mc^2E}} = \frac{1240 \text{ eV nm}}{\sqrt{2*939 \text{ MeV} * 0.026 \text{ eV}}} = 0.177 \text{ nm} = 1.77 \mathring{A}$$

- Relatively cold neutrons have a de Broglie wavelength short enough to resolve crystalline structure!

WHAT TO USE?

- We typically use photons, electrons, and neutrons as probes of crystal structure, as they give us both **complementary and corroborating information.**
  - X-rays interact with electronic polarizability
  - Electrons interact with electronic/nuclear charge distribution
  - Neutrons interact with nuclei directly, or with magnetic moments

- Both elastic and inelastic scattering experiments are used.
  - Elastic scattering gives us information about static structure
  - Inelastic scattering gives us information about dynamics (excitations) of the crystal

- Today, we will primarily be discussing elastic scattering techniques, in the context of X-ray scattering. The analysis is easily transferrable to other types of scattering studies, though.

- Before we start into the mathematics, let us first discuss the history and state-of-the-art for each of these techniques.

X-RAY METHODS

• Only a few years after Roentgen received the first Nobel prize for his discovery of X-rays (1901), the father-son physics duo of Bragg and Bragg pioneered X-ray crystallography techniques

• Both received the Nobel Prize in 1915. Only a year after Von Laue, who also received a Nobel Prize for work in X-ray diffraction

• Fun facts:
  • Von Laue and Franck had their Nobel prizes dissolved in aqua regia during WWII. Left on shelf at Niels Bohr Institute.
  • The younger Bragg helped Watson and Crick resolve the double helix structure of DNA
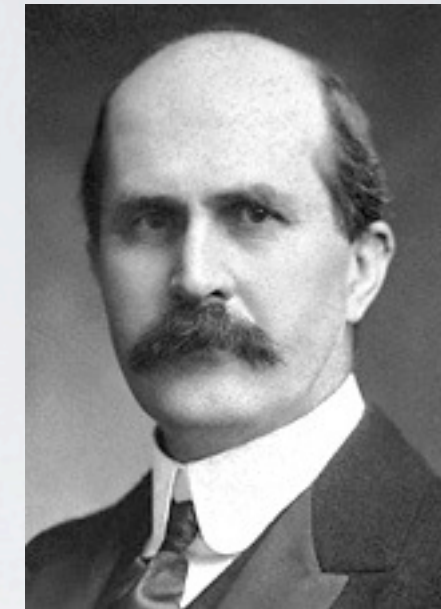
BRAGG'S LAW

- X-ray diffraction can be understood in terms of a relatively simple construction.

  - Crystal represented by planes of point-like atoms separated by a distance 'd'

  - X-ray beam characterized by wavelength (λ) and angle of incidence (θ).

- When 2 rays are scattered from different planes and experience constructive interference, a diffraction peak will be observed.

- This condition can be expressed as: $2d\sin\theta = n\lambda$

- 'n' is the index of the diffraction peak.
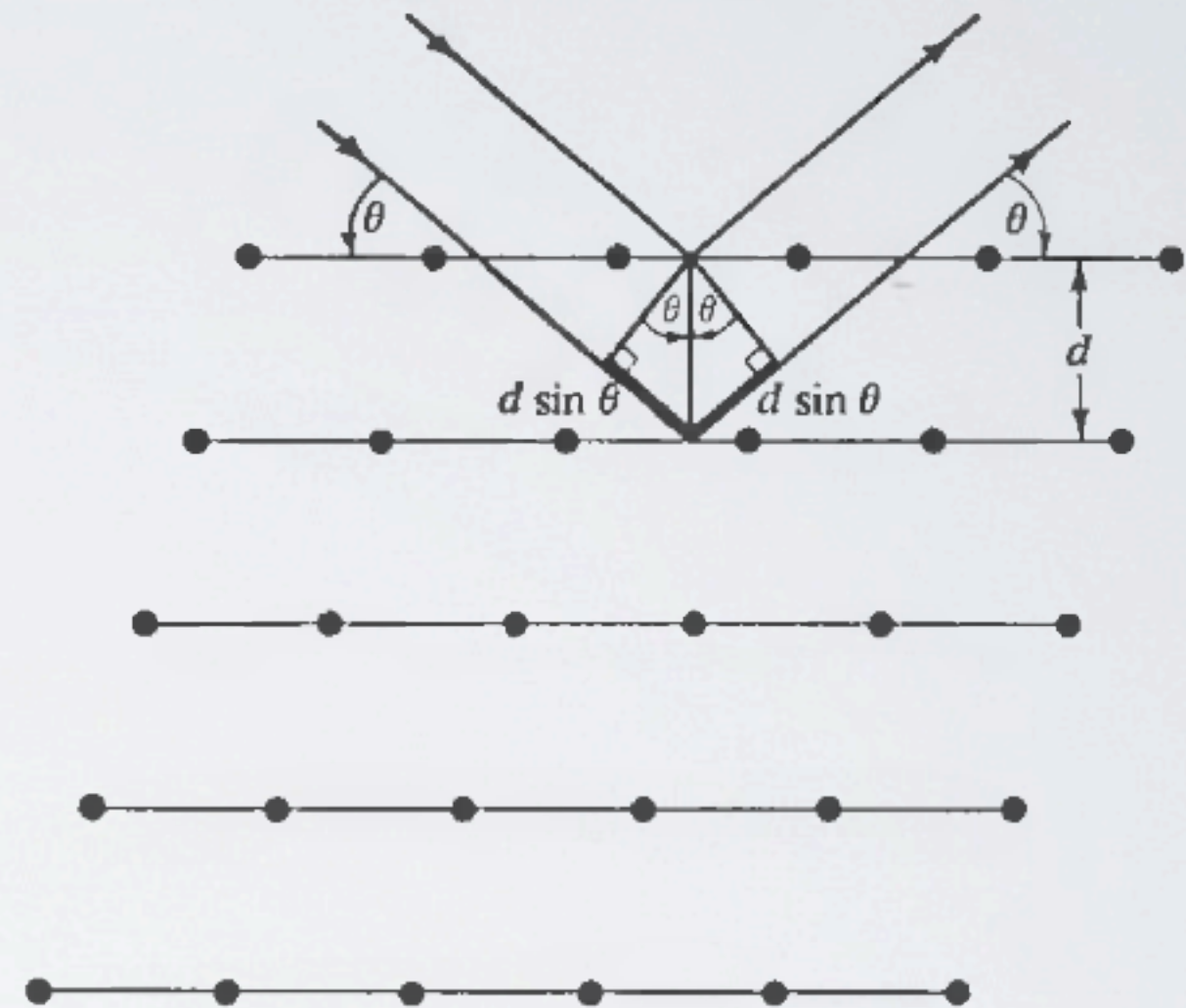
DERIVING BRAGG'S LAW

- Heuristic arguments aside, we will now construct a more rigorous approach to theoretically characterizing scattering from crystals.

- To do so, we will first develop the notion of a **reciprocal lattice**.

- Fundamentally, our probe is interacting with either a charge density, or maybe even a spin density, that has the same periodicity as the lattice:

$$n(\vec{\mathbf{r}}) = n(\vec{\mathbf{r}} + \vec{\mathbf{T}}), \quad \vec{\mathbf{T}} \in \{n_1\vec{\mathbf{a}}_1 + n_2\vec{\mathbf{a}}_2 + n_3\vec{\mathbf{a}}_3\} \quad n_i \in \mathbb{Z}$$

- The nice thing about periodic functions, like this, is that they are representable as a Fourier series:

$$n(\vec{\mathbf{r}}) = \sum_{\vec{\mathbf{G}}} n_{\vec{\mathbf{G}}} e^{i\vec{\mathbf{G}}\cdot\vec{\mathbf{r}}}$$

- Here, the sum on $\vec{\mathbf{G}}$ is over all vectors in what is known as the reciprocal lattice to our real lattice

$$n(\vec{\mathbf{r}}) = \sum_{\vec{\mathbf{G}}} n_{\vec{\mathbf{G}}} e^{i\vec{\mathbf{G}}\cdot\vec{\mathbf{r}}}$$

- We can impose strong constraints on the reciprocal lattice vectors based upon certain physical constraints
  - The quantity we are representing is a real-valued function: $n^*(\vec{\mathbf{r}}) = n(\vec{\mathbf{r}})$
  - It has the same periodicity as the lattice: $n(\vec{\mathbf{r}} + \vec{\mathbf{T}}) = n(\vec{\mathbf{r}})$

$$n^*(\vec{\mathbf{r}}) = \sum_{\vec{\mathbf{G}}} n^*_{\vec{\mathbf{G}}} e^{-i\vec{\mathbf{G}}\cdot\vec{\mathbf{r}}} = \sum_{\vec{\mathbf{G}}} n_{-\vec{\mathbf{G}}} e^{i\vec{\mathbf{G}}\cdot\vec{\mathbf{r}}} = n(\vec{\mathbf{r}}) \rightarrow n^*_{\vec{\mathbf{G}}} = n_{-\vec{\mathbf{G}}}$$

$$n(\vec{\mathbf{r}} + \vec{\mathbf{T}}) = \sum_{\vec{\mathbf{G}}} n_{\vec{\mathbf{G}}} e^{i\vec{\mathbf{G}}\cdot(\vec{\mathbf{r}}+\vec{\mathbf{T}})} = \sum_{\vec{\mathbf{G}}} n_{\vec{\mathbf{G}}} e^{i\vec{\mathbf{G}}\cdot\vec{\mathbf{r}}} = n(\vec{\mathbf{r}}) \rightarrow e^{i\vec{\mathbf{G}}\cdot\vec{\mathbf{T}}} = 1$$

More heuristically: you only need to compute Fourier coefficients for a fraction of the total lattice, and the reciprocal lattice vectors are defined with respect to the real lattice vectors

$$n(\vec{\mathbf{r}} + \vec{\mathbf{T}}) = \sum_{\vec{\mathbf{G}}} n_{\vec{\mathbf{G}}} e^{i\vec{\mathbf{G}} \cdot (\vec{\mathbf{r}} + \vec{\mathbf{T}})} = \sum_{\vec{\mathbf{G}}} n_{\vec{\mathbf{G}}} e^{i\vec{\mathbf{G}} \cdot \vec{\mathbf{r}}} = n(\vec{\mathbf{r}}) \rightarrow e^{i\vec{\mathbf{G}} \cdot \vec{\mathbf{T}}} = 1$$

- We can use the above relationship to generate the reciprocal lattice vectors from the real lattice vectors.

$$\vec{\mathbf{G}} \cdot \vec{\mathbf{T}} = 2\pi$$

- For real lattice vectors: $\{\vec{\mathbf{a}}_1, \vec{\mathbf{a}}_2, \vec{\mathbf{a}}_3\}$ we define 3 reciprocal lattice vectors: $\{\vec{\mathbf{b}}_1, \vec{\mathbf{b}}_2, \vec{\mathbf{b}}_3\}$

$$\vec{\mathbf{a}}_i \cdot \vec{\mathbf{b}}_j = 2\pi \delta_{ij}$$

- These 3 reciprocal lattice vectors span the reciprocal lattice:

$$\vec{\mathbf{G}} \in \{m_1 \vec{\mathbf{b}}_1 + m_2 \vec{\mathbf{b}}_2 + m_3 \vec{\mathbf{b}}_3\} \quad m_i \in \mathbb{Z}$$

- It is worth noting that the reciprocal lattice vectors have units of inverse length. **Why?**

- So how can we use this relation, $\vec{\mathbf{a}}_i \cdot \vec{\mathbf{b}}_j = 2\pi\delta_{ij}$, to generate reciprocal lattice vectors?

- Life is simple for cubic lattices:

$$\vec{\mathbf{a}}_1 = a\hat{\mathbf{x}}$$

$$\vec{\mathbf{a}}_2 = a\hat{\mathbf{y}} \quad\longrightarrow\quad$$

$$\vec{\mathbf{a}}_3 = a\hat{\mathbf{z}}$$

$$\vec{\mathbf{b}}_1 = \frac{2\pi}{a}\hat{\mathbf{x}}$$

$$\vec{\mathbf{b}}_2 = \frac{2\pi}{a}\hat{\mathbf{y}}$$

$$\vec{\mathbf{b}}_3 = \frac{2\pi}{a}\hat{\mathbf{z}}$$

- Things can certainly become trickier though...

$$\vec{\mathbf{a}}_1 = a\hat{\mathbf{x}}$$

$$\vec{\mathbf{a}}_2 = \frac{\sqrt{3}}{2}a\hat{\mathbf{y}} - \frac{1}{2}a\hat{\mathbf{x}}$$

$$\vec{\mathbf{a}}_3 = a\hat{\mathbf{z}}$$

Solve for the c coefficients

$$\vec{\mathbf{b}}_i = c_{i,x}\hat{\mathbf{x}} + c_{i,y}\hat{\mathbf{y}} + c_{i,z}\hat{\mathbf{z}}$$

$$\vec{\mathbf{a}}_1 = a\hat{\mathbf{x}}$$

$$\vec{\mathbf{a}}_2 = \frac{\sqrt{3}}{2}a\hat{\mathbf{y}} - \frac{1}{2}a\hat{\mathbf{x}}$$

$$\vec{\mathbf{a}}_3 = a\hat{\mathbf{z}}$$

Solve for the c coefficients

$$\vec{\mathbf{b}}_i = c_{i,x}\hat{\mathbf{x}} + c_{i,y}\hat{\mathbf{y}} + c_{i,z}\hat{\mathbf{z}}$$

- Again, use $\vec{\mathbf{a}}_i \cdot \vec{\mathbf{b}}_j = 2\pi\delta_{ij}$. This will give us 9 equations in 9 unknowns.

- $\vec{\mathbf{b}}_3 = \dfrac{2\pi}{a}\hat{\mathbf{z}}$ should be trivially evident.

- We have to solve a small system for $\vec{\mathbf{b}}_1$ and $\vec{\mathbf{b}}_2$

$$\vec{\mathbf{a}}_1 \cdot \vec{\mathbf{b}}_1 = ac_{1,x} = 2\pi, \quad \vec{\mathbf{a}}_1 \cdot \vec{\mathbf{b}}_2 = ac_{2,x} = 0$$

$$\vec{\mathbf{a}}_2 \cdot \vec{\mathbf{b}}_1 = -\frac{1}{2}ac_{1,x} + \frac{\sqrt{3}}{2}ac_{1,y} = 0, \quad \vec{\mathbf{a}}_2 \cdot \vec{\mathbf{b}}_2 = -\frac{1}{2}ac_{2,x} + \frac{\sqrt{3}}{2}ac_{2,y} = 2\pi$$

$$\vec{a}_1 = a\hat{x}$$

$$\vec{b}_1 = \frac{2\pi}{a}\left[\hat{x} + \frac{1}{\sqrt{3}}\hat{y}\right]$$

$$\vec{a}_2 = \frac{\sqrt{3}}{2}a\hat{y} - \frac{1}{2}a\hat{x} \longrightarrow \vec{b}_2 = \frac{4\pi}{\sqrt{3}a}\hat{y}$$

$$\vec{a}_3 = a\hat{z}$$

$$\vec{b}_3 = \frac{2\pi}{a}\hat{z}$$

- While this isn't all that difficult, there is a much simpler formula that can be used to generate reciprocal lattice vectors from real lattice vectors:

$$\vec{b}_i = 2\pi\frac{\vec{a}_j \times \vec{a}_k}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}, \quad \text{(i,j,k) is a cyclic permutation of (1,2,3)}$$

- Having defined the reciprocal lattice, given a function with the periodicity of the lattice, $n(\vec{\mathbf{r}})$ how do we calculate the Fourier coefficients, $n_{\vec{\mathbf{G}}}$?

- Orthogonality: $\dfrac{1}{V_{unit}} \displaystyle\int\limits_{\text{unit cell}} d\vec{\mathbf{r}}\; e^{i(\vec{\mathbf{G}}-\vec{\mathbf{G}}')\cdot\vec{\mathbf{r}}} = \delta_{\vec{\mathbf{G}}\vec{\mathbf{G}}'}$

- We simply calculate the projection of our density onto the **G'**th Fourier component:

$$\frac{1}{V_{unit}} \int\limits_{\text{unit cell}} d\vec{\mathbf{r}}\; e^{-i\vec{\mathbf{G}}'\cdot\vec{\mathbf{r}}} n(\vec{\mathbf{r}}) = \frac{1}{V_{unit}} \int\limits_{\text{unit cell}} d\vec{\mathbf{r}}\; e^{i(\vec{\mathbf{G}}-\vec{\mathbf{G}}')\cdot\vec{\mathbf{r}}} n_{\vec{\mathbf{G}}} = n_{\vec{\mathbf{G}}'}$$
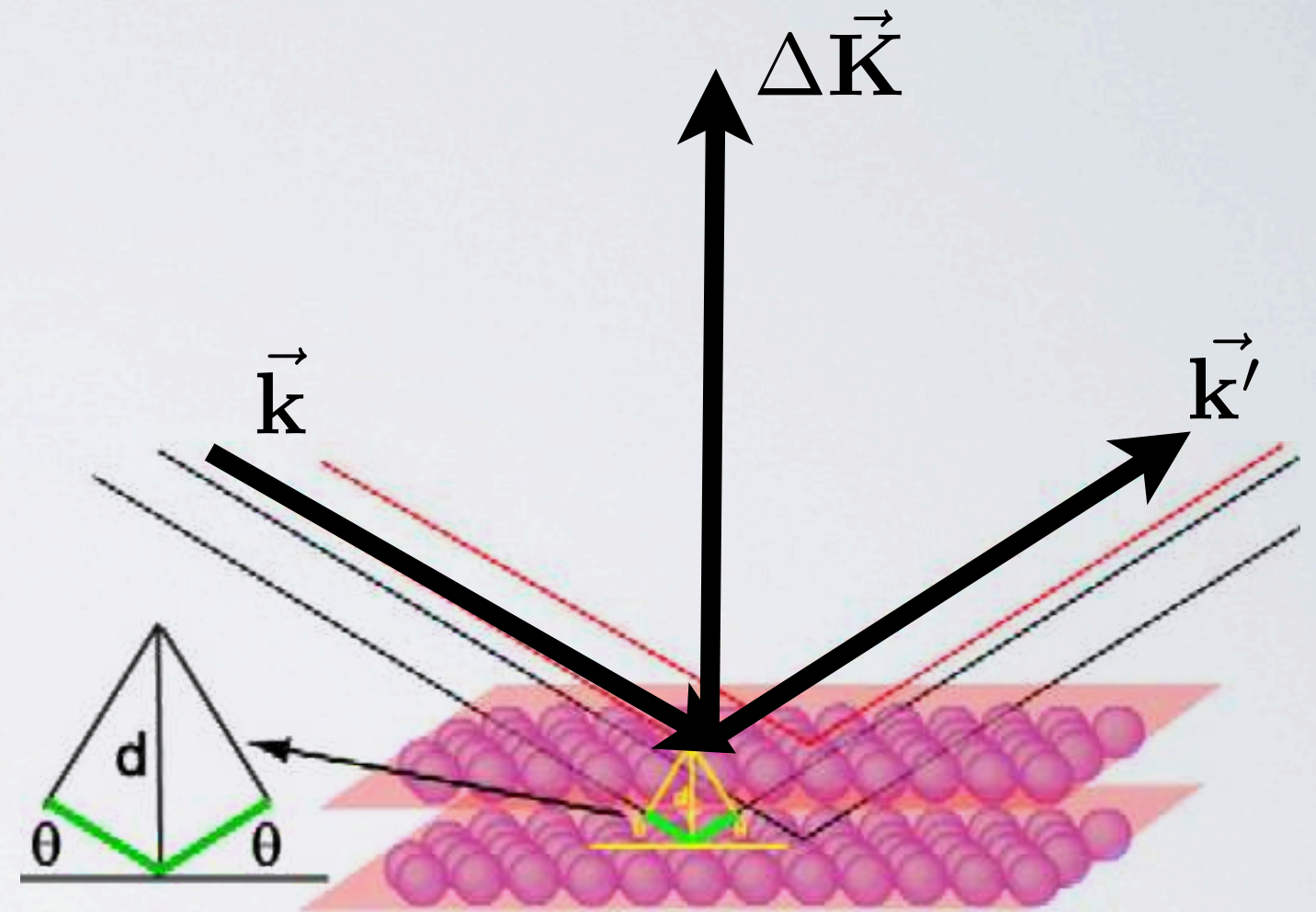
BACK TO BRAGG

• To begin formalizing things a bit more rigorously, consider the following setup:
  • A beam of x-rays is incident on our crystal with wave-vector: $\vec{\mathbf{k}}$
  • The reflected beam is characterized by a wave-vector: $\vec{\mathbf{k}'}$

• Assuming the scattering process is inelastic, then the following relationship holds: $|\vec{\mathbf{k}}| = |\vec{\mathbf{k}'}| = \dfrac{2\pi}{\lambda}$

• The difference between these vectors, $\vec{\mathbf{k}'} - \vec{\mathbf{k}} = \Delta\vec{\mathbf{K}}$ is deemed the scattering vector

- We are interested in the following quantity, the **scattering amplitude:**

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

- This is the Fourier component of the density associated with the scattering vector.

- This quantity is the coefficient, at leading order, to what is called a Born series.

$$F(\Delta\vec{K}) = \int d\vec{r} \sum_{\vec{G}} n_{\vec{G}} e^{i(\vec{G}-\Delta\vec{K})\cdot\vec{r}} = \sum_{\vec{G}} n_{\vec{G}} \int d\vec{r}\ e^{i(\vec{G}-\Delta\vec{K})\cdot\vec{r}} = V n_{\Delta\vec{K}} \delta_{\vec{G},\Delta\vec{K}}$$

At leading order, we only see scattering if the scattering vector is in the reciprocal lattice
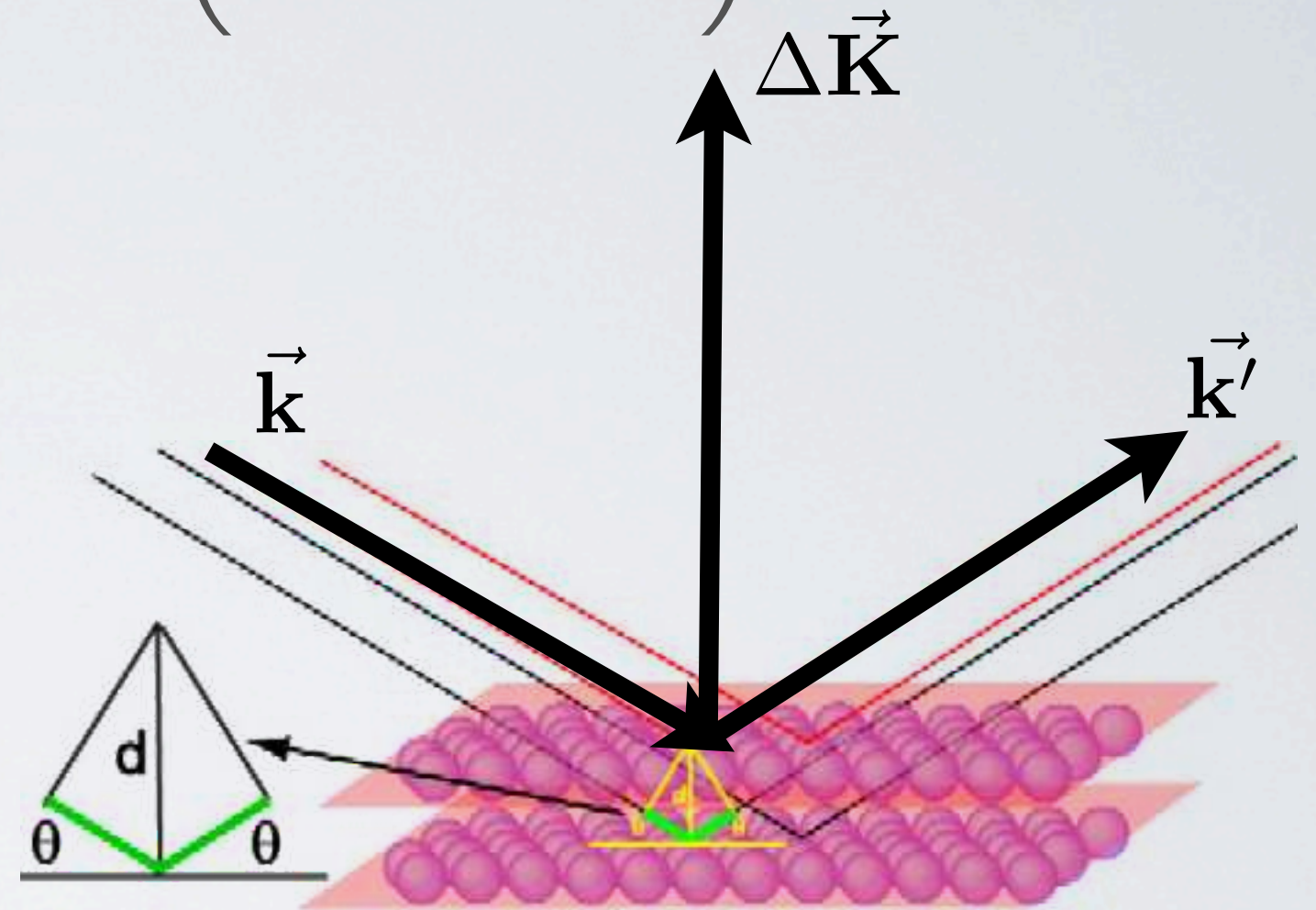
- The scattering intensity is simply the square modulus of the scattering amplitude:

$$F(\Delta \vec{\mathbf{K}}) = V n_{\vec{\mathbf{G}}} \to I \sim V^2 |\vec{\mathbf{G}}|^2$$

- This is nice, but where do we get: $2d \sin \theta = n\lambda$?

$$\vec{\mathbf{G}} - \Delta \vec{\mathbf{K}} = 0 \to \vec{\mathbf{k}}' = \vec{\mathbf{k}} + \vec{\mathbf{G}} \to |\vec{\mathbf{k}}'|^2 = |\vec{\mathbf{k}}|^2 + |\vec{\mathbf{G}}|^2 + 2\vec{\mathbf{G}} \cdot \vec{\mathbf{k}}$$

- By elasticity of the scattering process, we get: $|\vec{\mathbf{G}}|^2 + 2\vec{\mathbf{G}} \cdot \vec{\mathbf{k}} = 0$

- We can make things prettier by remember that $-\vec{\mathbf{G}}$ is also in the reciprocal lattice:

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

BACK TO BRAGG (CONT.)

- You probably still don't think that $|\vec{\mathbf{G}}|^2 = 2\vec{\mathbf{G}} \cdot \vec{\mathbf{k}}$ looks much like $2d \sin \theta = n\lambda$

- Let $\vec{\mathbf{G}} = h\vec{\mathbf{b}}_1 + k\vec{\mathbf{b}}_2 + l\vec{\mathbf{b}}_3$, the triplet [hkl] is called a Miller index, and we will learn more about them on Wednesday.

- As it turns out, this vector is perpendicular to the infinite set of parallel planes containing some set of atoms indexed by (hkl). The distance between these planes is then given as:

$$d(hkl) = \frac{2\pi}{|\vec{\mathbf{G}}|}$$

$$2\vec{\mathbf{G}} \cdot \vec{\mathbf{k}} = 2|\vec{\mathbf{G}}||\vec{\mathbf{k}}| \cos(\frac{\pi}{2} - \theta) = |\vec{\mathbf{G}}|^2 \rightarrow \frac{4\pi}{\lambda} \sin(\theta) = |\vec{\mathbf{G}}|$$

- Which can be reduced to: $2d(hkl) \sin(\theta) = \lambda$

CONCLUSIONS

- Take home messages from today's lecture:
  - *X-rays, electrons, and neutrons can all be scattered off of crystalline solids to resolve their structure.*
  - *Bragg's law very simply encapsulates the conditions necessary for the observation of a diffraction peak in an elastic scattering experiment.*
  - *We can derive the Bragg condition using the notion of a reciprocal lattice.*
  - *Given real lattice vectors, it is fairly simple to generate reciprocal lattice vectors.*
  - *Diffraction peaks will be observed for scattering vectors that are in the reciprocal lattice.*

- On Wednesday's lecture, we will answer the following questions:
  - *How do we define lattice planes in a crystal, and how are they identified from diffraction data?*
  - *What is a Brillouin zone, and how is it related to the Wigner-Seitz cell?*
  - *How is scattering from a lattice with a nontrivial basis any different from what we have discussed so far?*
  - *What is the Ewald construction, and how does it relate to what we've learned so far?*