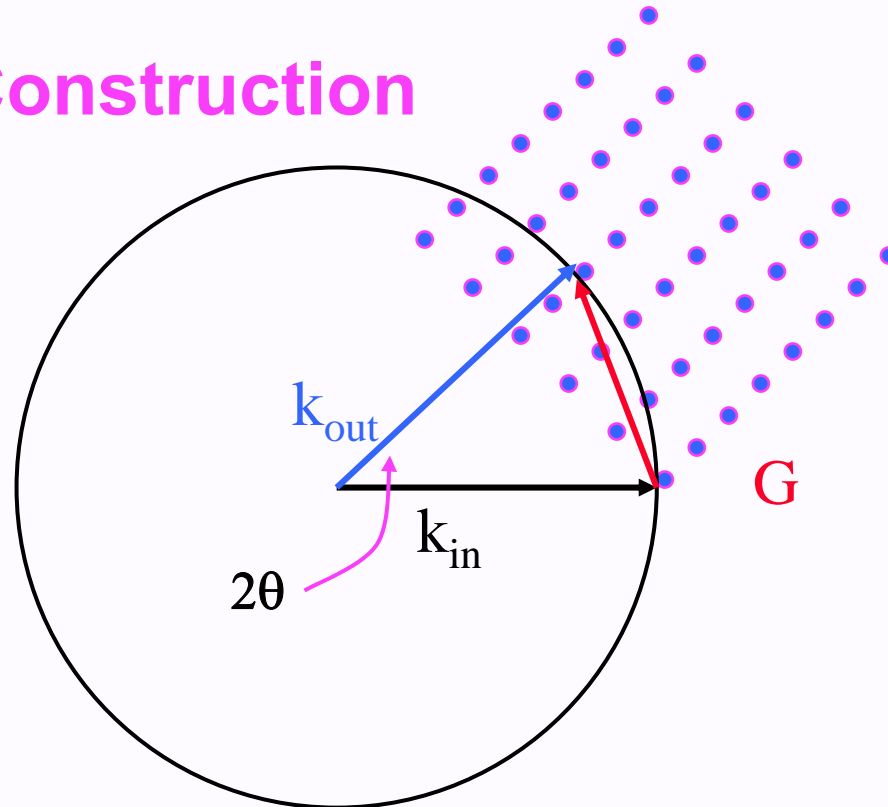


Solid State Physics 460- Lecture 5

Diffraction and the Reciprocal Lattice

Continued (Kittel Ch. 2)

Ewald Construction



Recall from previous lectures

- **Definition of a crystal – Lattice + Basis**
- **Reciprocal lattice – Lattice in Fourier space (reciprocal space)**
- **Diffraction from crystals – Bragg Condition – $2d \sin \theta = n \lambda$**
- **Diffraction and the reciprocal lattice**
- **Today:**
- **Diffraction and the reciprocal lattice continued – Ewald construction and the Brillouin Zone (BZ)**

Recall from Lecture 3 **Summary: Real and Reciprocal lattices**

- Crystal lattice of translations:

$$\mathbf{T}(n_1, n_2, \dots) = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3$$

Primitive vectors

- Reciprocal lattice:

$$\mathbf{G}(m_1, m_2, \dots) = m_1 \mathbf{b}_1 + m_2 \mathbf{b}_2 + m_3 \mathbf{b}_3 ,$$

where

$$\mathbf{b}_i \cdot \mathbf{a}_j = 2\pi \delta_{ij} , \text{ where } \delta_{ij} = 1, \delta_{ij} = 0, i \neq j$$

- Any periodic function can be written

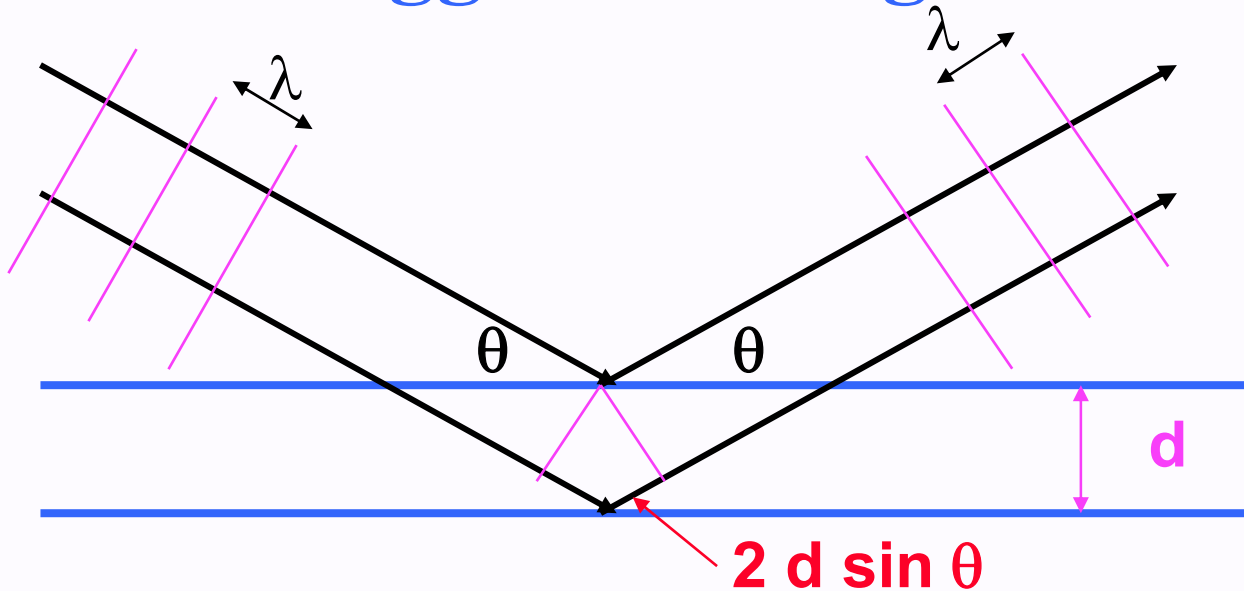
$$\mathbf{f}(\mathbf{r}) = \sum_{\mathbf{G}} \mathbf{f}_{\mathbf{G}} \exp(\mathbf{i} \mathbf{G} \cdot \mathbf{r})$$

- Information about the basis for the actual crystal is in the values of the Fourier coefficients

$$\mathbf{f}_{\mathbf{G}} = (1/V_{\text{cell}}) \int_{\text{cell}} d^3\mathbf{r} \mathbf{f}(\mathbf{r}) \exp(-\mathbf{i} \mathbf{G} \cdot \mathbf{r})$$

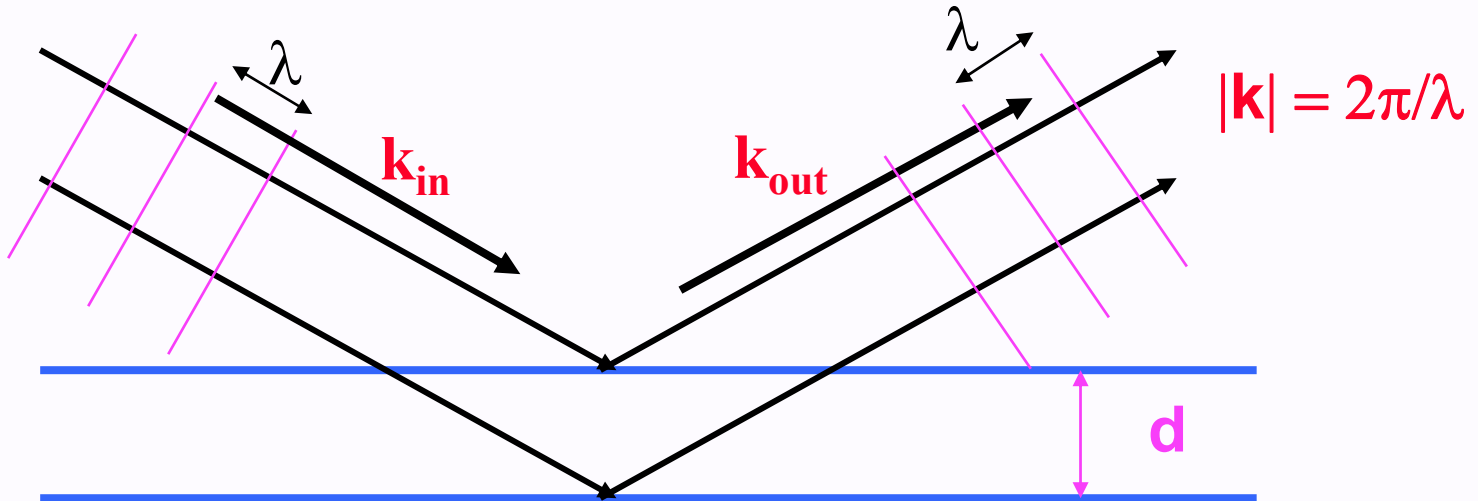
Kittel Ch. 2

Bragg Scattering Law



- Condition for constructive interference (Diffraction):
 $2d \sin \theta = n \lambda$
- **Maximum $\lambda = 2d$**
- Only waves with λ smaller than $2d$ can satisfy the Bragg scattering law for diffraction
- For a typical crystal the maximum $d \sim 0.1 - 1 \text{ nm}$, so that
 $\lambda < \sim 0.1 - 1 \text{ nm}$

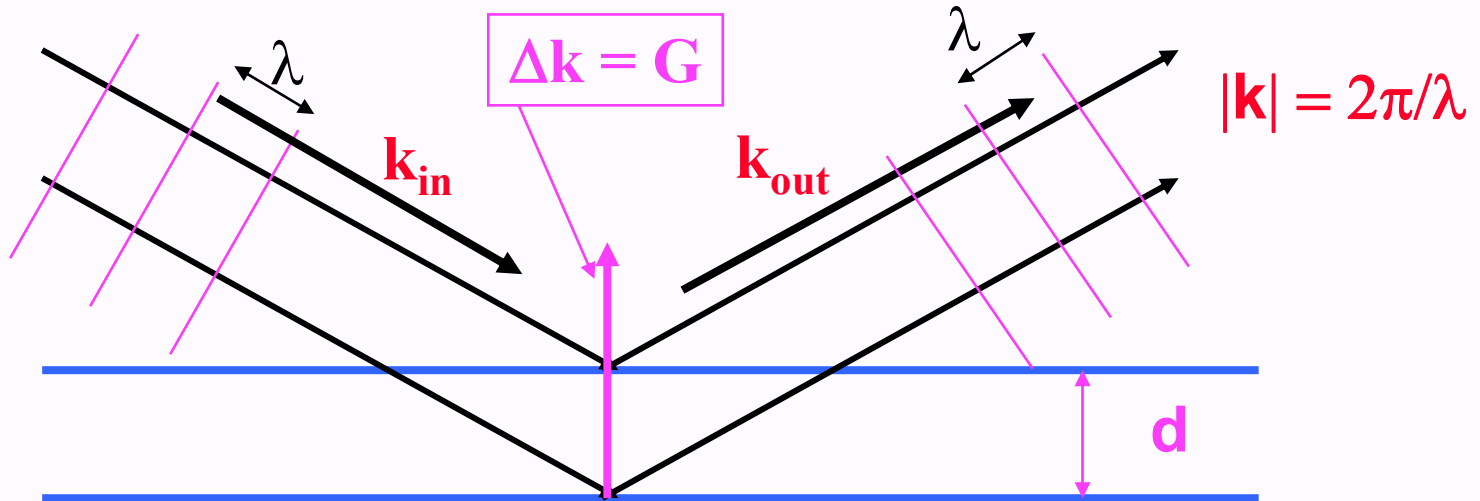
Scattering and Fourier Analysis



- Note that \mathbf{k} is a vector in reciprocal space with $|\mathbf{k}| = 2\pi/\lambda$
- The in and out waves have the form:
 $\exp(i \mathbf{k}_{in} \cdot \mathbf{r} - i \omega t)$ and $\exp(i \mathbf{k}_{out} \cdot \mathbf{r} - i \omega t)$
- If the incoming wave drives the electron density, which then radiates waves, the **amplitude** of the outgoing wave is proportional to:

$$\int_{\text{space}} d\mathbf{r} n(\mathbf{r}) \exp(i (\mathbf{k}_{in} - \mathbf{k}_{out}) \cdot \mathbf{r})$$

Scattering and Fourier Analysis



- Define $\Delta \mathbf{k} = \mathbf{k}_{in} - \mathbf{k}_{out}$
- Then we know from Fourier analysis that

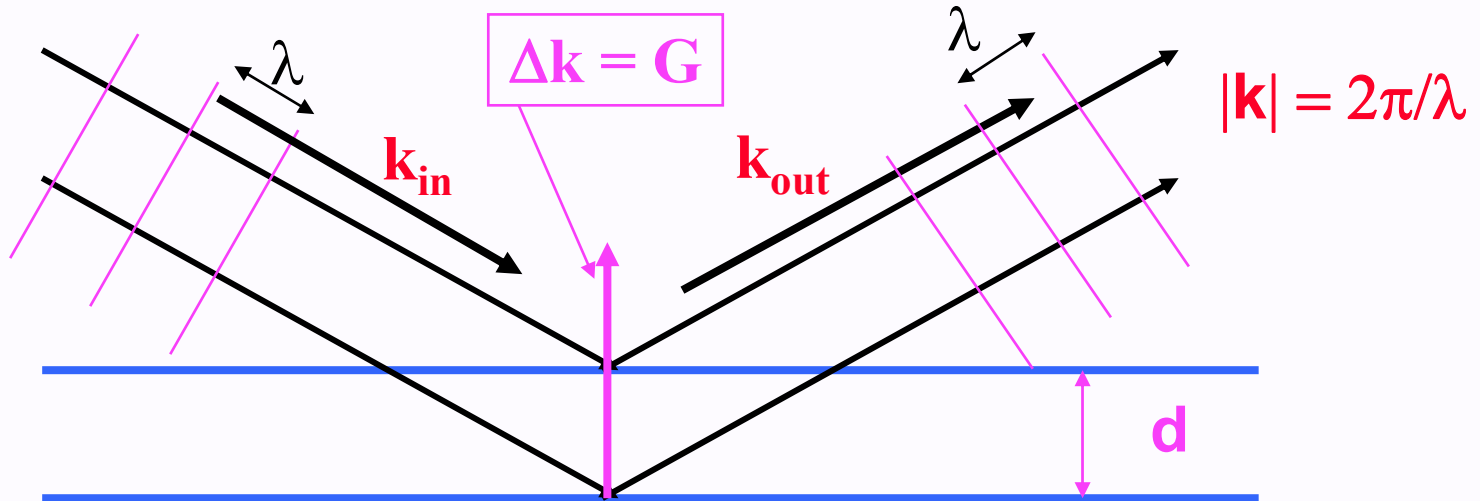
$$(1/V_{\text{cell}}) \int_{\text{cell}} d\mathbf{r} n(\mathbf{r}) \exp(-i \Delta \mathbf{k} \cdot \mathbf{r}) = \mathbf{n}_{\mathbf{G}}$$

only if $\Delta \mathbf{k} = \mathbf{G}$, where \mathbf{G} is a reciprocal lattice vector

- Otherwise the integral vanishes

Note: These statements are for a perfect crystal of size \rightarrow infinity. See prob. Kittel 2.4 for a finite crystal where the scattering is peaked at $\Delta \mathbf{k} = \mathbf{G}$ with a finite width. Physics 460 F 2006 Lect 5

Elastic Scattering



- For elastic scattering (energy the same for in and out waves)

$$|\mathbf{k}_{\text{in}}| = |\mathbf{k}_{\text{out}}|, \text{ or } k_{\text{in}}^2 = k_{\text{out}}^2 = |\mathbf{k}_{\text{in}} + \mathbf{G}|^2$$

- Then one arrives at the condition for diffraction: (using \mathbf{G} in expression above)

$$2 \mathbf{k}_{\text{in}} \cdot \mathbf{G} = G^2$$

**\mathbf{G} is any one of the
recip. lattice vectors**

- Equivalent to the Bragg condition – see next lecture

Ewald Construction

G is any one of the recip. lattice vectors

- **Condition for diffraction:**

$$\mathbf{k}_{\text{out}} = \mathbf{k}_{\text{in}} + \mathbf{G}$$

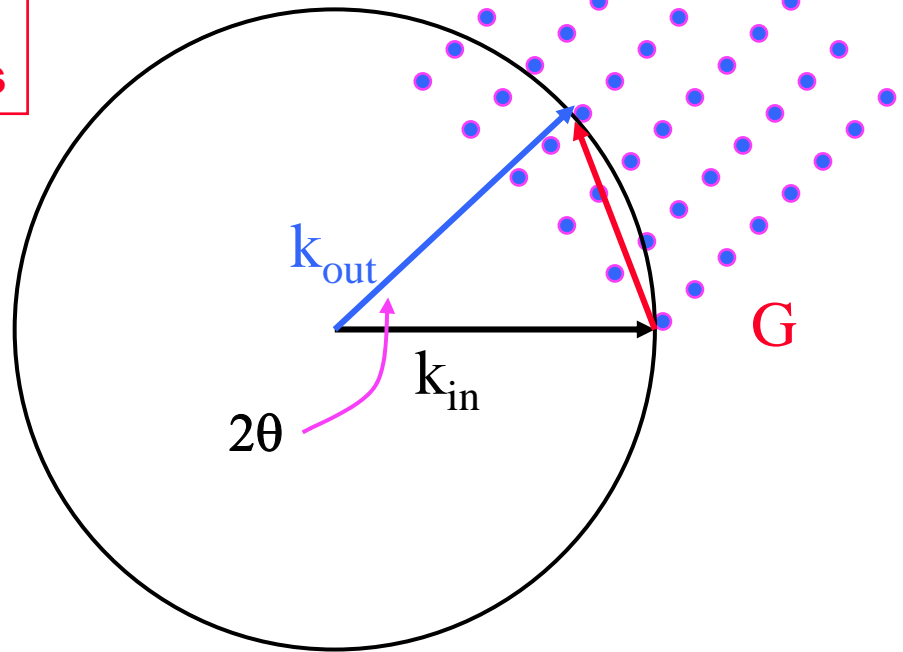
and

- $|\mathbf{G}| = 2 |\mathbf{k}_{\text{in}}| \sin \theta$

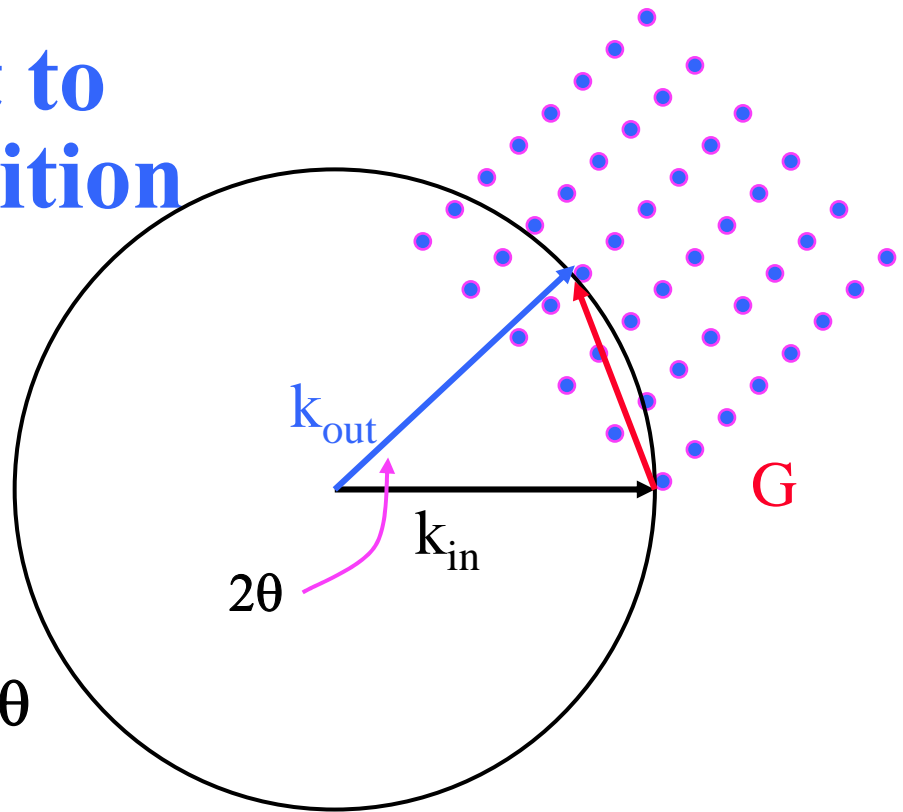
$$\Rightarrow |\mathbf{G}| = 2 |\mathbf{k}_{\text{in}}| \sin \theta$$

(note sine function, not cosine)

Why?
Discussed
in class



Equivalent to Bragg Condition



- From last slide,

$$|\mathbf{G}| = 2 |\mathbf{k}_{in}| \sin \theta$$

- But $|\mathbf{k}_{in}| = 2\pi/\lambda$, and $|\mathbf{G}| = n (2\pi/d)$, where d = spacing between planes (see homework, Kittel prob. 2-1)

- \Rightarrow Bragg condition $2d \sin \theta = n \lambda$

Geometric Construction of Diffraction Conditions

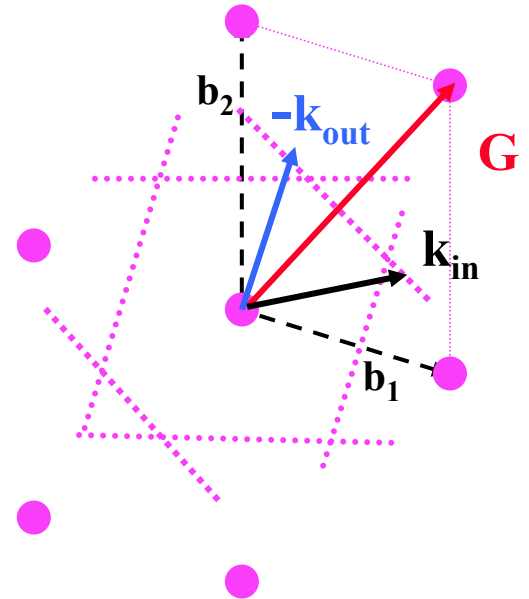
- Recall $\mathbf{k}_{in} - \mathbf{k}_{out} = \mathbf{G}$
and $|\mathbf{k}_{in}| = |\mathbf{k}_{out}|$

- Consequence of condition

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

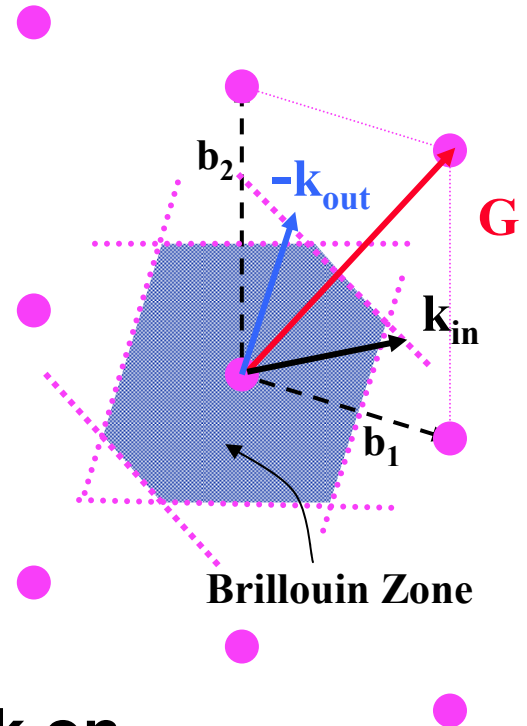
- The vector \mathbf{k}_{in} (and \mathbf{k}_{out}) lies along the perpendicular bisecting plane of a \mathbf{G} vector

- One example is shown



Diffraction and the Brillouin Zone

- **Brillouin Zone - (BZ)** - the Wigner-Seitz cell of the reciprocal lattice
- Formed by perpendicular bisectors of **G vectors**
- **Special Role of Brillouin Zone**
 - Diffraction occurs only for k on surface of Brillouin Zone
 - **No diffraction occurs for any k inside the first Brillouin Zone**
 - **Important later in course**



Comparison of diffraction from different lattices

- The Bragg condition can also be written

$$|\mathbf{G}| = 2 |k_{in}| \sin \theta$$
$$\Rightarrow \sin \theta = (\lambda / 4\pi) |\mathbf{G}|$$

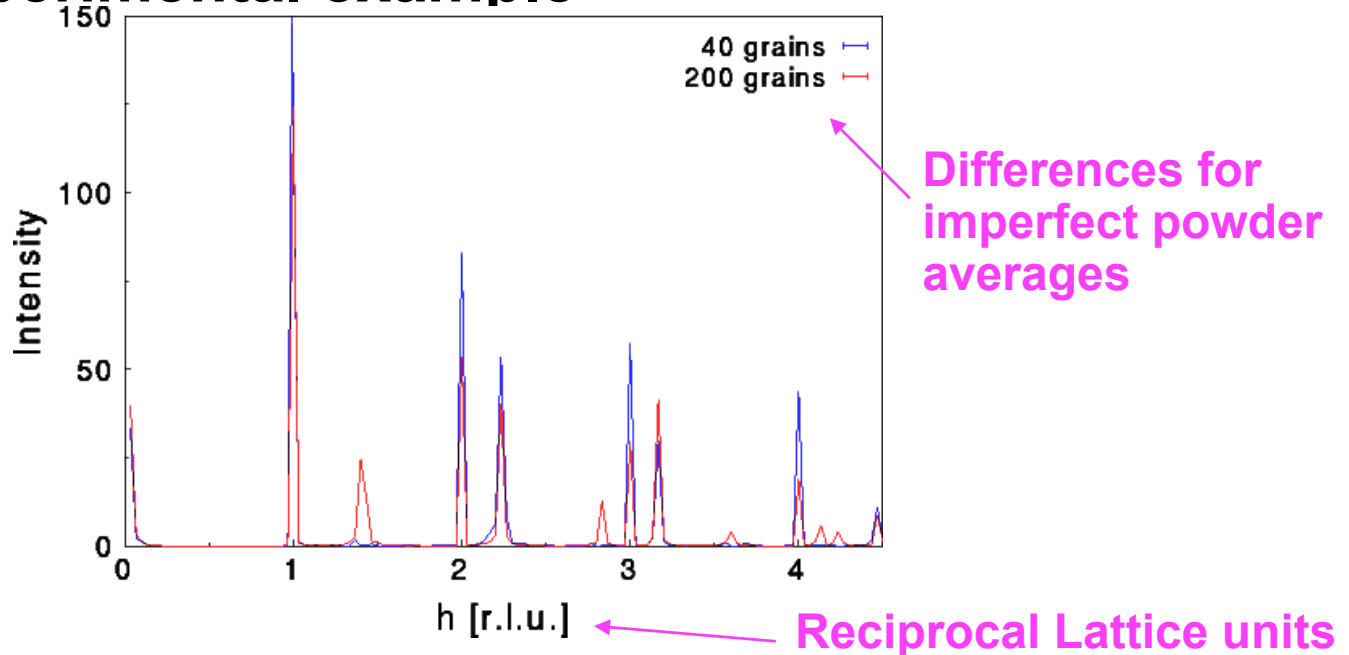
- Thus the ratios of the sines of the angles for diffraction are given by:

$$\sin \theta_1 / \sin \theta_2 = |\mathbf{G}_1| / |\mathbf{G}_2|$$

- Each type of lattice has characteristic ratios the positions of diffraction peaks as a function of $\sin \theta$
- Simple scaling with λ

Experimental Powder Pattern

- Diffraction peaks at angles satisfying the Bragg condition
- Experimental example



<http://www.uni-wuerzburg.de/mineralogie/crystal/teaching/teaching.html>

Comparison of diffraction from different lattices

- Ratios $\sin \theta_i / \sin \theta_0 = | \mathbf{G}_i | / | \mathbf{G}_0 |$, where θ_0 is the lowest angle peak (smallest \mathbf{G})
- Easiest to give ratios of squares $\mathbf{G}_i^2 / \mathbf{G}_0^2$

Simple Cubic lattice

(\mathbf{G} in units of $2\pi/a$)

\mathbf{G}_i	\mathbf{G}_i^2	ratio
1,0,0	1	1
1,1,0	2	2
1,1,1	3	3
2,0,0	4	4
2,1,0	5	5

Comparison of diffraction from different lattices - continued

FCC real space lattice

(G in units of $2\pi/a$)

G_i	G_i^2	ratio
1,1,1	3	1
2,0,0	4	4/3
2,2,0	8	8/3
3,1,1	11	11/3
2,2,2	12	4
4,0,0	16	1/3

BCC real space lattice

(G in units of $2\pi/a$)

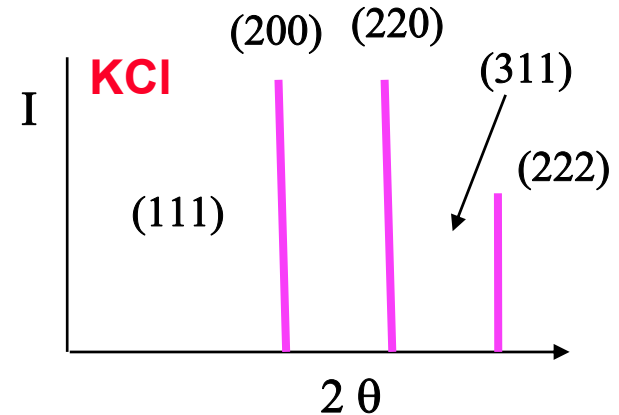
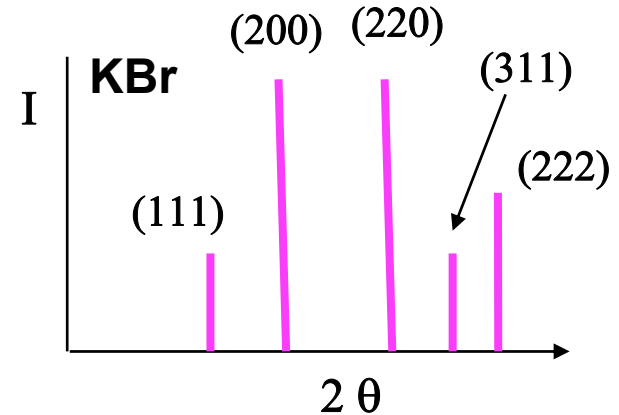
G_i	G_i^2	ratio
1,1,0	2	1
2,0,0	4	2
2,1,1	6	3
2,2,0	8	4
3,1,0	10	5
2,2,2	12	6

Same ratios as Simple cubic!

Example of KCl, KBr

- See Kittel Fig. 17
- KCl and KBr have fcc structure – expect fcc “powder patterns”
- But KCl has a special feature
 - K⁺ and Cl⁻ have the same number of electrons, they scatter x-rays almost the same ---- thus KCl has
 - a pattern like simple cubic

Why does this happen?



Comparison of diffraction from different lattices - continued

- **Lower symmetry lattices**
- **Example - Orthorhombic**
$$\mathbf{G} = (n_1 \ 2\pi/a_1, n_2 \ 2\pi/a_2, n_3 \ 2\pi/a_3)$$
 - Lengths of \mathbf{G} 's are in general not any special numbers since the a 's can be in any ratios
 - Many lines in diffraction pattern because of many different values of $|\mathbf{G}|$
- **Hexagonal** - length along c axis not related to lengths perpendicular to c axis

Fourier Analysis of the basis

- The intensity of the diffraction at each G is proportional to the square of the amplitude of the Fourier component

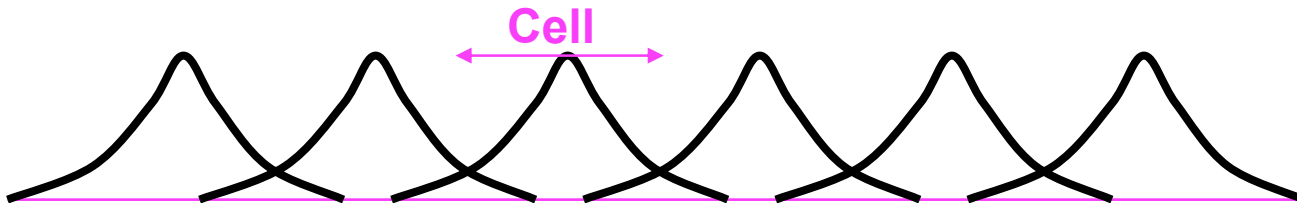
$$n_G = (1/V_{\text{cell}}) \int_{\text{cell}} dr n(r) \exp(-i G \cdot r)$$

- It is also possible to regard the crystal density $n(r)$ as a sum of atomic-like densities $n^{\text{atom}}(r - R_i)$, centered at point R_i

$$n(r) = \sum_{\text{all } i} n^{\text{atom } i}(r - R_i)$$

- Then also

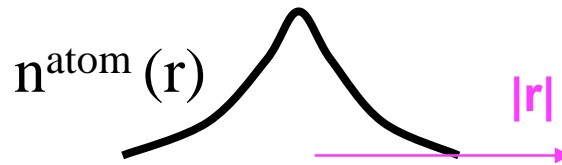
$$n_G = \sum_{i \text{ in cell}} \int_{\text{space}} dr n^{\text{atom } i}(r - R_i) \exp(-i G \cdot r)$$



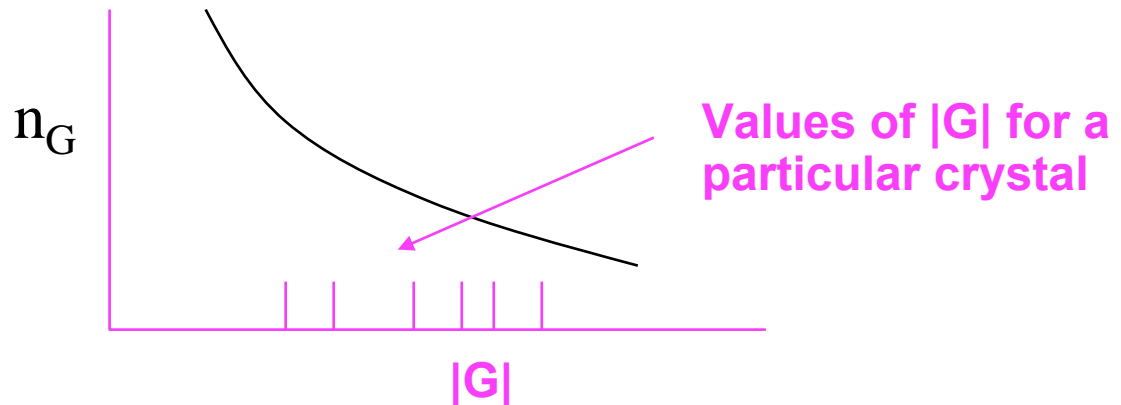
One atom per cell and Form Factor

- Then one can set $R_i = 0$ and n_G is the Fourier transform of one atom density

$$n_G = \int_{\text{space}} dr n^{\text{atom}}(r) \exp(-i \mathbf{G} \cdot \mathbf{r})$$



- Called **Form Factor**
- Example in Kittel



More than one atom per cell

- $n_{\mathbf{G}} = \sum_{i \text{ in cell}} \int_{\text{space}} d\mathbf{r} n^{\text{atom } i} (\mathbf{r} - \mathbf{R}_i) \exp(-i \mathbf{G} \cdot \mathbf{r})$

$$= \sum_{i \text{ in cell}} \exp(-i \mathbf{G} \cdot \mathbf{R}_i) \int_{\text{space}} d\mathbf{r} n^{\text{atom } i} (\mathbf{r} - \mathbf{R}_i) \exp(-i \mathbf{G} \cdot (\mathbf{r} - \mathbf{R}_i))$$

$$= \sum_{i \text{ in cell}} \exp(-i \mathbf{G} \cdot \mathbf{R}_i) \int_{\text{space}} d\mathbf{r} n^{\text{atom } i} (\mathbf{r}) \exp(-i \mathbf{G} \cdot \mathbf{r})$$

$$= \sum_{i \text{ in cell}} \exp(-i \mathbf{G} \cdot \mathbf{R}_i) n_{\mathbf{G}}^{\text{atom } i}$$

- Interpretation: **Structure Factor = Form factor** $n_{\mathbf{G}}^{\text{atom } i}$ **x phase factor** $\exp(-i \mathbf{G} \cdot \mathbf{R}_i)$ for each atom in unit cell

Structure factor

- Often the basis contains more than one atom that is same element, e.g., **diamond structure**
- Then $n_{\mathbf{G}}^{\text{atom } i} = n_{\mathbf{G}}^{\text{atom}}$ is the same for each i and

$$n_{\mathbf{G}} = \sum_{i \text{ in cell}} \exp(-i \mathbf{G} \cdot \mathbf{R}_i) n_{\mathbf{G}}^{\text{atom } i}$$

$$= n_{\mathbf{G}}^{\text{atom}} \sum_{i \text{ in cell}} \exp(-i \mathbf{G} \cdot \mathbf{R}_i)$$

- Define **“pure” structure factor**

$$S_{\mathbf{G}}^0 = (1/N_{\text{cell}}) \sum_{i \text{ in cell}} \exp(-i \mathbf{G} \cdot \mathbf{R}_i)$$

where N_{cell} = number of atoms in cell

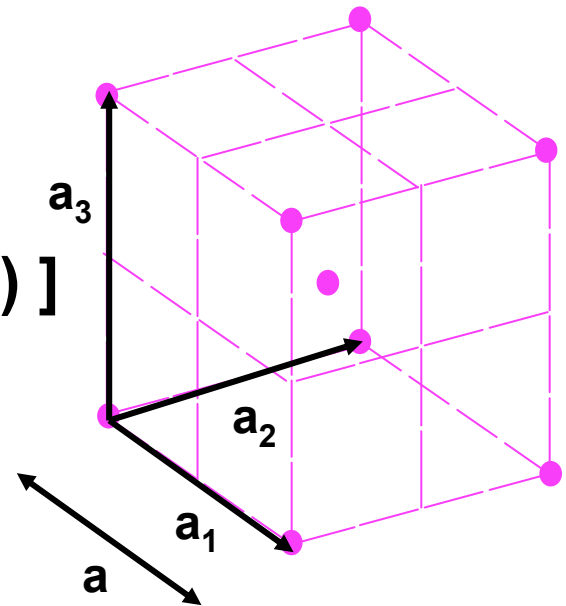
- Then $n_{\mathbf{G}} = N^0 S_{\mathbf{G}}^0 n_{\mathbf{G}}^{\text{atom}}$

NOTE - Kittel defines $n_{\mathbf{G}}$ to be the “structure factor”

Body Centered Cubic viewed as Simple Cubic with 2 points per cell

$$\begin{aligned} S_G^0 &= (1/2) \sum_{i=1,2} \exp(-i \mathbf{G} \cdot \mathbf{R}_i) \\ &= (1/2) (1 + \exp(-i \mathbf{G} \cdot \mathbf{R}_2)) \\ &= (1/2) \exp(-i \mathbf{G} \cdot \mathbf{R}_2/2) \\ &[\exp(i \mathbf{G} \cdot \mathbf{R}_2/2) + \exp(-i \mathbf{G} \cdot \mathbf{R}_2/2)] \\ &= \exp(-i \mathbf{G} \cdot \mathbf{R}_2/2) \cos (\mathbf{G} \cdot \mathbf{R}_2/2) \end{aligned}$$

Result: If $\mathbf{G} = (v_1 \ v_2 \ v_3) 2\pi/a$
 $|S_G^0| = 1$ if sum of integers
is even
 $|S_G^0| = 0$ if sum is odd



Points at $\mathbf{R}_1 = (0,0,0)$;
 $\mathbf{R}_2 = (1,1,1) a/2$

Same as we found before!
FCC reciprocal lattice

Face Centered Cubic viewed as Simple Cubic with 4 points per cell

$$S^0_{\mathbf{G}} = (1/4) \sum_{i=1,4} \exp(-i \mathbf{G} \cdot \mathbf{R}_i)$$

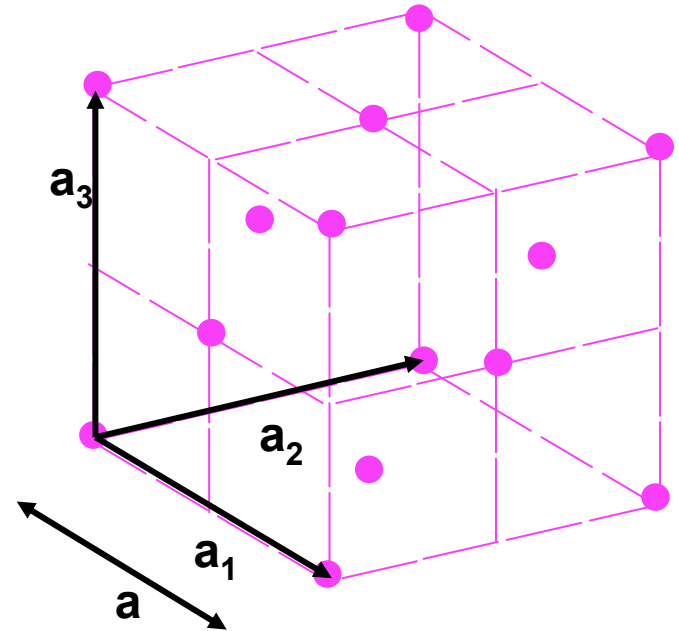
Result:

**If $\mathbf{G} = (v_1 \ v_2 \ v_3) 2\pi/a$
then**

**$S^0_{\mathbf{G}} = 1$ if all integers
are odd or all are even**

$S^0_{\mathbf{G}} = 0$ otherwise

**Same as we found before!
BCC reciprocal lattice**



Points at $(0,0,0)$; $(1,1,0) a/2$;
 $(1,0,1) a/2$; $(0,1,1) a/2$

Structure factor for diamond

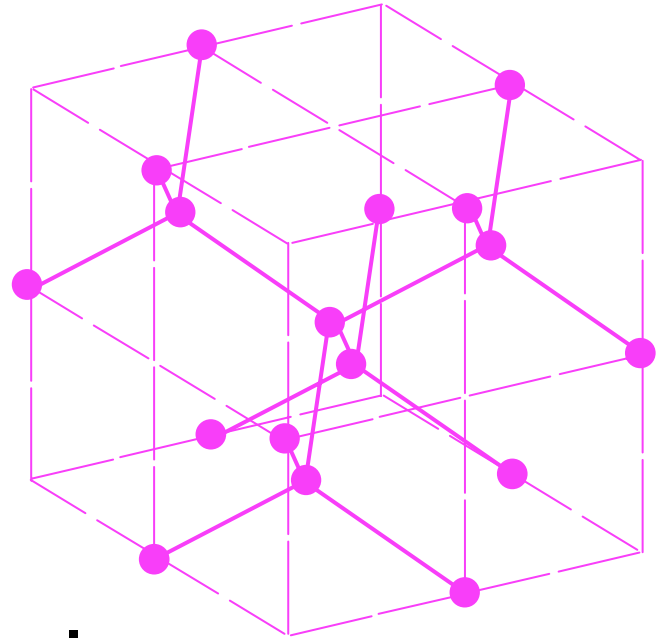
- Example: diamond structure

$$S^0_{\mathbf{G}} = (1/2) \sum_{i=1,2} \exp(-i \mathbf{G} \cdot \mathbf{R}_i)$$

- $\mathbf{R}_1 = + (1/8, 1/8, 1/8)\mathbf{a}$
 $\mathbf{R}_2 = - (1/8, 1/8, 1/8)\mathbf{a}$

- Homework problem

- Similar approach would apply to a graphite plane



Summary - Diffraction & Recip. Lattice

- Bragg Condition for diffraction
- Fourier Analysis and the Reciprocal Lattice
 $\mathbf{G}(m_1, m_2, \dots) = m_1 \mathbf{b}_1 + m_2 \mathbf{b}_2 + m_3 \mathbf{b}_3$,
where the \mathbf{b} 's are primitive vectors defined by
- $\mathbf{b}_i \cdot \mathbf{a}_j = 2\pi \delta_{ij}$, where $\delta_{ij} = 1$, $\delta_{ij} = 0$, $i \neq j$
- Examples of Reciprocal lattice: fcc, bcc, ...
- Ewald Construction
- Diffraction for \mathbf{k}_{in} , \mathbf{k}_{out} in planes - perp. bisectors of \mathbf{G} 's
- Defines Brillouin Zone - no diffraction in first BZ
- Information about the actual crystal is in the values of the Fourier coefficients $f_{\mathbf{G}}$

$$f_{\mathbf{G}} = (1/V_{\text{cell}}) \int_{\text{cell}} dr f(\mathbf{r}) \exp(-i \mathbf{G} \cdot \mathbf{r})$$

- Form factor, "Pure" Structure factor

Quasicrystals

- Not periodic in sense described before
- Example a crystal with periodicity a with a density wave that is a different period a' with a'/a not a rational number

$$n(x) = n_1 \cos(2\pi x/a) + n_2 \cos(2\pi x/a')$$

never repeats!

- Examples in higher dimensions
Orientation order without translational order

Penrose Tiles

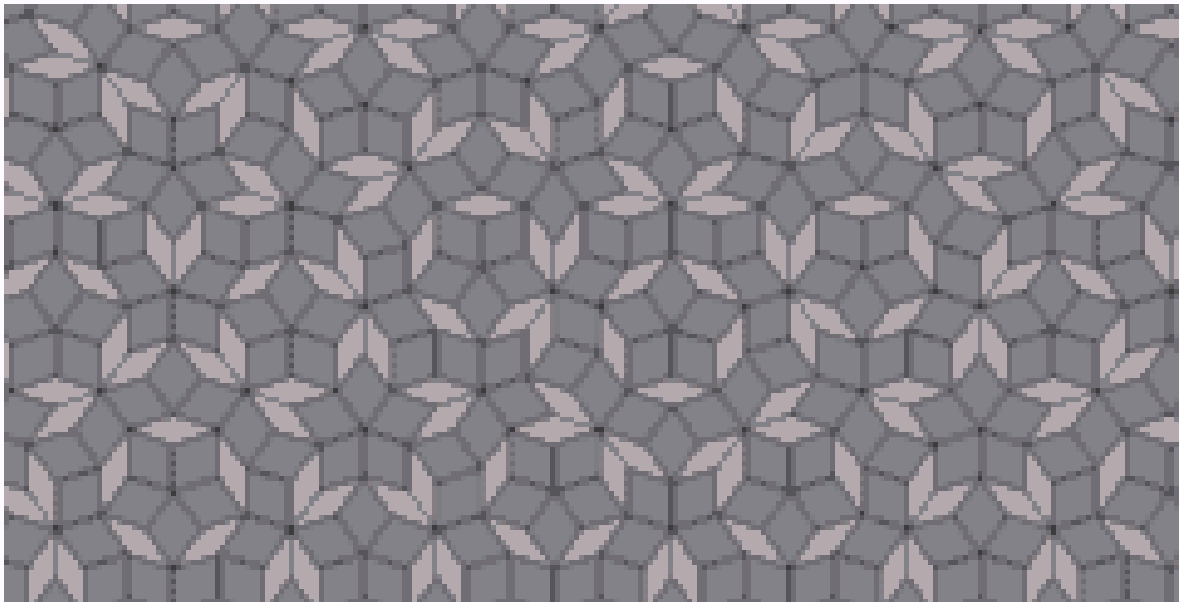
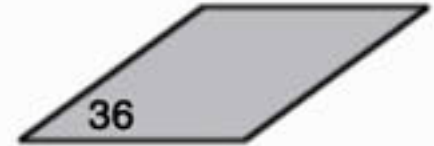
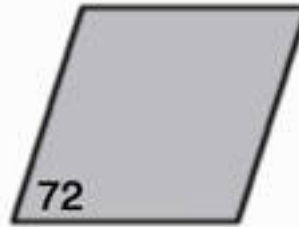
Five fold symmetry in x-ray patterns

....

Penrose Tiles

- **Many examples**
Nice WWW sites

http://www.traipse.com/penrose_tiles/index.html



See this site for a Java program for Penrose tiles

<http://www.geocities.com/SiliconValley/Pines/1684/Penrose.html>

Next Time

- **Crystal Binding (Chapter 3)**