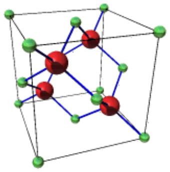
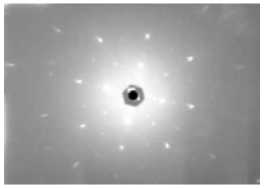


Phys 446: Solid State Physics / Optical Properties



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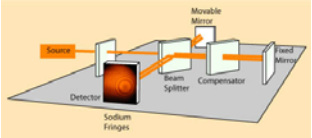


Solid State Physics

Lecture 3

(Ch. 2)

Last week:

- Crystals, Crystal Lattice, Reciprocal Lattice, Diffraction from crystals

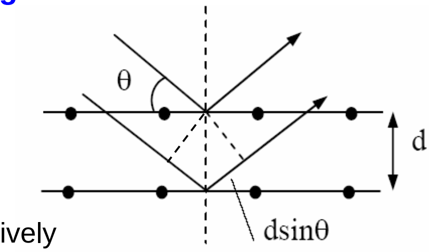
- Today:
- Scattering factors and selection rules for diffraction
- HW1 discussion

The Bragg Law

Conditions for a sharp peak in the intensity of the scattered radiation:

1) the x-rays should be specularly reflected by the atoms in one plane

2) the reflected rays from the successive planes interfere constructively



The path difference between the two x-rays: $2d\cdot\sin\theta \Rightarrow$

the Bragg formula: $2d\cdot\sin\theta = m\lambda$

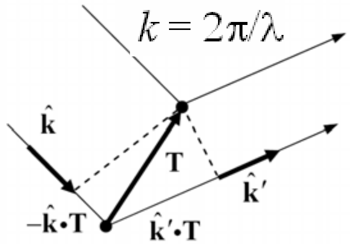
The model used to get the Bragg law are greatly oversimplified (but it works!).

- It says nothing about intensity and width of x-ray diffraction peaks
- neglects differences in scattering from different atoms
- assumes single atom in every lattice point
- neglects distribution of charge around atoms

Diffraction condition and reciprocal lattice

Von Laue approach:

- crystal is composed of identical atoms placed at the lattice sites T
- each atom can reradiate the incident radiation in all directions.
- Sharp peaks are observed only in the directions for which the x-rays scattered from all lattice points interfere constructively.



Consider two scatterers separated by a lattice vector **T**.
Incident x-rays: wavelength λ, wavevector $\mathbf{k}$; $|\mathbf{k}| = k = 2\pi/\lambda$; $(\mathbf{k}'-\mathbf{k})\cdot\mathbf{T} = 2\pi m$
Assume *elastic* scattering: scattered x-rays have same energy (same λ) ⇒ wavevector $\mathbf{k}'$ has the same magnitude $|\mathbf{k}'| = k = 2\pi/\lambda$

$\hat{\mathbf{k}} = \frac{\mathbf{k}}{|\mathbf{k}|}$ $\hat{\mathbf{k}}' = \frac{\mathbf{k}'}{|\mathbf{k}'|}$

Condition of constructive interference: $(\hat{\mathbf{k}}'-\hat{\mathbf{k}})\cdot\mathbf{T} = m\lambda$ or

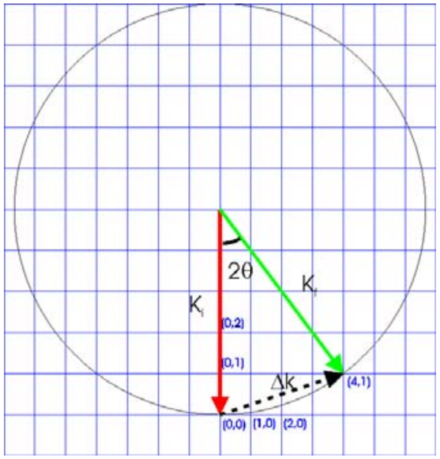
Define $\Delta\mathbf{k} = \mathbf{k}' - \mathbf{k}$ - *scattering wave vector*

Then $\Delta\mathbf{k} = \mathbf{G}$, where **G** is defined as such a vector for which $\mathbf{G}\cdot\mathbf{T} = 2\pi m$

We got $\Delta\mathbf{k} = \mathbf{k}' - \mathbf{k} = \mathbf{G} \Rightarrow |\mathbf{k}'|^2 = |\mathbf{k}|^2 + |\mathbf{G}|^2 + 2\mathbf{k}\cdot\mathbf{G} \Rightarrow G^2 + 2\mathbf{k}\cdot\mathbf{G} = 0$

$2\mathbf{k}\cdot\mathbf{G} = G^2$ – another expression for diffraction condition

Ewald Construction for Diffraction Condition and reciprocal space



Diffraction occurs for:

$\vec{k} + \vec{G} = \vec{k}'$

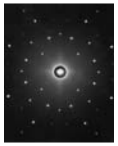
Or

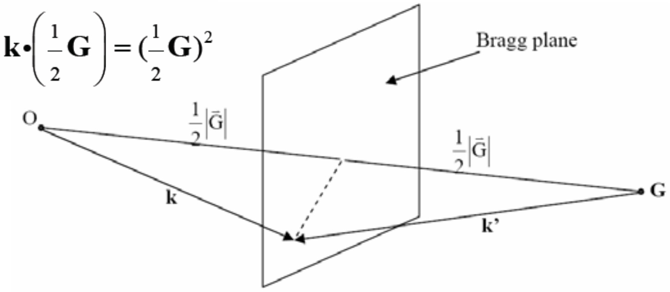
$\vec{k}' - \vec{k} = \vec{G}$

$k = 2\pi/\lambda$

Geometric interpretation of Laue condition:

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





- Diffraction is the strongest (constructive interference) at the perpendicular bisecting plane (Bragg plane) between two reciprocal lattice points.
- true for any type of waves inside a crystal, including electrons.
- Note that in the original real lattice, these perpendicular bisecting planes are the planes we use to construct Wigner-Seitz cell

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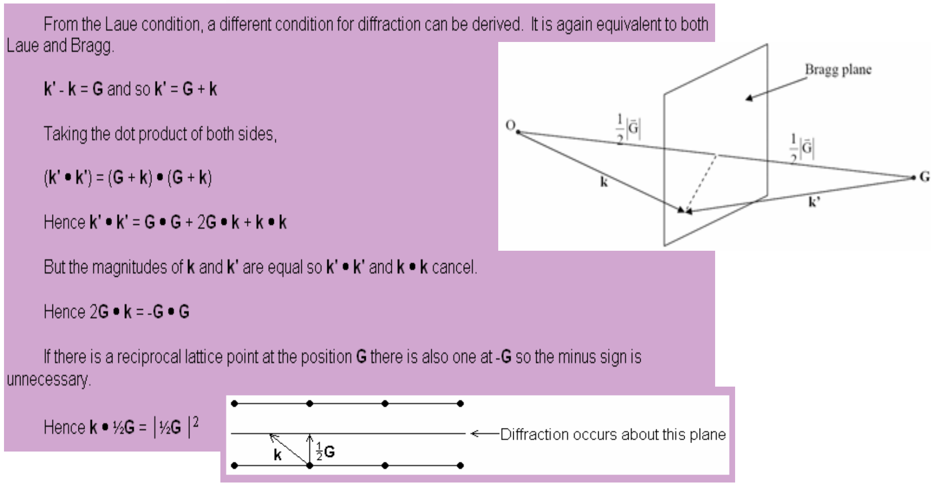
Geometric interpretation of Laue condition:

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



From the Laue condition, a different condition for diffraction can be derived. It is again equivalent to both Laue and Bragg.

k' - **k** = **G** and so **k'** = **G** + **k**

Taking the dot product of both sides,

(**k'** • **k'**) = (**G** + **k**) • (**G** + **k**)

Hence **k'** • **k'** = **G** • **G** + 2**G** • **k** + **k** • **k**

But the magnitudes of **k** and **k'** are equal so **k'** • **k'** and **k** • **k** cancel.

Hence 2**G** • **k** = -**G** • **G**

If there is a reciprocal lattice point at the position **G** there is also one at -**G** so the minus sign is unnecessary.

Hence **k** • ½**G** = |½**G** |^2

Diffraction occurs about this plane

Summary

$k = 2\pi/\lambda$

- ❖ Various statements of the Bragg condition:

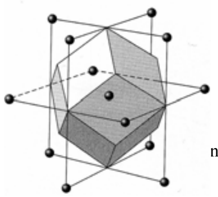
  $2d\cdot\sin\theta = m\lambda$; $\Delta\mathbf{k} = \mathbf{G}$; $2\mathbf{k}\cdot\mathbf{G} = G^2$

- ❖ Reciprocal lattice is defined by primitive vectors:

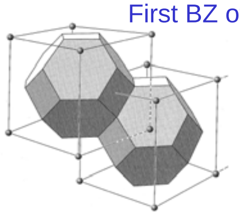
  $$\mathbf{b}_1 = \frac{2\pi}{V}\mathbf{a}_2\times\mathbf{a}_3,\quad \mathbf{b}_2 = \frac{2\pi}{V}\mathbf{a}_3\times\mathbf{a}_1,\quad \mathbf{b}_3 = \frac{2\pi}{V}\mathbf{a}_1\times\mathbf{a}_2$$

- ❖ A reciprocal lattice vector has the form $\mathbf{G} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3$
  It is normal to (hkl) planes of direct lattice
- ❖ Only waves whose wave vector drawn from the origin terminates on a surface of the Brillouin zone can be diffracted by the crystal

First BZ of bcc lattice



First BZ of fcc lattice



Solid State Physics
Lecture 3 (continued)
(Ch. 2)

Atomic and structure factors

Experimental techniques:

Neutron and electron diffraction

Diffraction process:
1) Scattering by individual atoms
2) Mutual interference between scattered rays

Scattering from atom

Consider single electron. Plane wave $u = Ae^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)}$ $k = |\mathbf{k}| = \dfrac{2\pi}{\lambda}$

Scattered field: $u' = f_e \dfrac{A}{R} e^{i(kR-\omega t)}$ f_e – *scattering length of electron*

R – radial distance

Two electrons: $u' = f_e \dfrac{A}{R} e^{ikR}\left[1 + e^{i\Delta\mathbf{k}\cdot\mathbf{r}}\right]$

or, more generally $u' = f_e \dfrac{A}{R} e^{ikR}\left[e^{i\Delta\mathbf{k}\cdot\mathbf{r}_1} + e^{i\Delta\mathbf{k}\cdot\mathbf{r}_2}\right]$

many electrons: $u' = f_e \dfrac{A}{R} e^{ikR}\sum_l e^{i\Delta\mathbf{k}\cdot\mathbf{r}_l}$ similar to single electron with $f = f_e \sum_l e^{i\Delta\mathbf{k}\cdot\mathbf{r}_l}$

---

intensity: $I \sim |f| = f_e^2 \left|\sum_l e^{i\Delta\mathbf{k}\cdot\mathbf{r}_l}\right|^2$

this is for coherent scatterers. If random then $I \sim Nf_e^2$

Scattering length of electron: $f_e = \left[\left(1+\cos^2 2\theta\right)/2\right]^{1/2} r_e$

classical electron radius $r_e = \dfrac{1}{4\pi\varepsilon_0}\dfrac{e^2}{mc^2} \approx 2.8\times10^{-15}\ \mathrm{m}$

In atom, $f_e \sum_l e^{i\Delta\mathbf{k}\cdot\mathbf{r}_l} \to f_e \int n(\mathbf{r}) e^{i\Delta\mathbf{k}\cdot\mathbf{r}_l} d^3r$

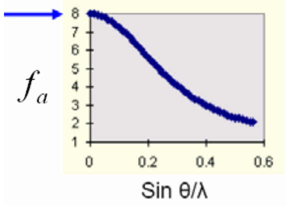
$n(\mathbf{r})$ – electron density

$f_a = \int n(\mathbf{r}) e^{i\Delta\mathbf{k}\cdot\mathbf{r}_l} d^3r$ ***- atomic scattering factor (form factor)***

Atomic scattering factor (dimensionless) is determined by electronic distribution.

If $n(\mathbf{r})$ is spherically symmetric, then

$$f_a = \int_0^{r_0} 4\pi r^2 n(r)\frac{\sin(\Delta k\cdot r)}{\Delta k\cdot r}dr$$



in forward scattering Δk = 0 so $f_a = 4\pi\int r^2 n(r)dr = Z$

Z - total number of electrons

Atomic factor for forward scattering is equal to the atomic number

(all rays are in phase, hence interfere constructively)

Scattering from crystal

crystal scattering factor: $f_{cr} = \sum_l e^{i\Delta\mathbf{k}\cdot\mathbf{r}_l} = \sum_l f_{al} e^{i\Delta\mathbf{k}\cdot\mathbf{R}_l}$

$\mathbf{R}_l$ - position of l^{th} atom, f_{al} - corresponding atomic factor

rewrite $f_{cr} = F \cdot S$

where $F = \sum_j f_{aj} e^{i\Delta\mathbf{k}\cdot\mathbf{s}_j}$ - *structure factor* of the basis, summation over the atoms in unit cell

and $S = \sum_l e^{i\Delta\mathbf{k}\cdot\mathbf{R}_l^c}$ - lattice factor, summation over all unit cells in the crystal

Where $\mathbf{R}_l = \mathbf{R}_l^c + \mathbf{s}_j$

Since $\Delta\mathbf{k} = \mathbf{G}$, the lattice factor becomes $S = \sum_l e^{i\mathbf{G}\cdot\mathbf{R}_l^c} = \sum_l e^{i2\pi m} = N$

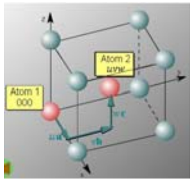
Then scattering intensity $I \sim |f_{cr}|^2$ where $f_{cr} = F \cdot N = N \sum_j f_{aj} e^{i\mathbf{G}\cdot\mathbf{s}_j}$

$\mathbf{G} = \mathbf{G}_{\text{hkl}} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3$ if $\mathbf{s}_j = u_j\mathbf{a}_1 + v_j\mathbf{a}_2 + w_j\mathbf{a}_3$

Then $F = \sum_j f_{aj} e^{i(u_j\mathbf{a}_1 + v_j\mathbf{a}_2 + w_j\mathbf{a}_3)(h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3)} = \sum_j f_{aj} e^{2\pi i(hu_j + kv_j + lw_j)}$

structure factor

Example: structure factor of bcc lattice (identical atoms)



structure factor $F = \sum_j f_{aj} e^{2\pi i(hu_j + kv_j + lw_j)}$

Two atoms per unit cell: $\mathbf{s}_1 = (0,0,0)$; $\mathbf{s}_2 = a(1/2,1/2,1/2)$

$$F = f_a\left[1 + e^{\pi i(h+k+l)}\right]$$

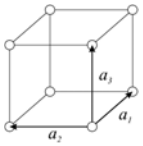
$\Rightarrow F=2f_a$ if $h+k+l$ is even, and $F=0$ if $h+k+l$ is odd

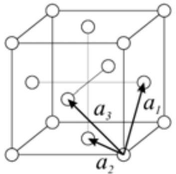
Diffraction is absent for planes with odd sum of Miller indices

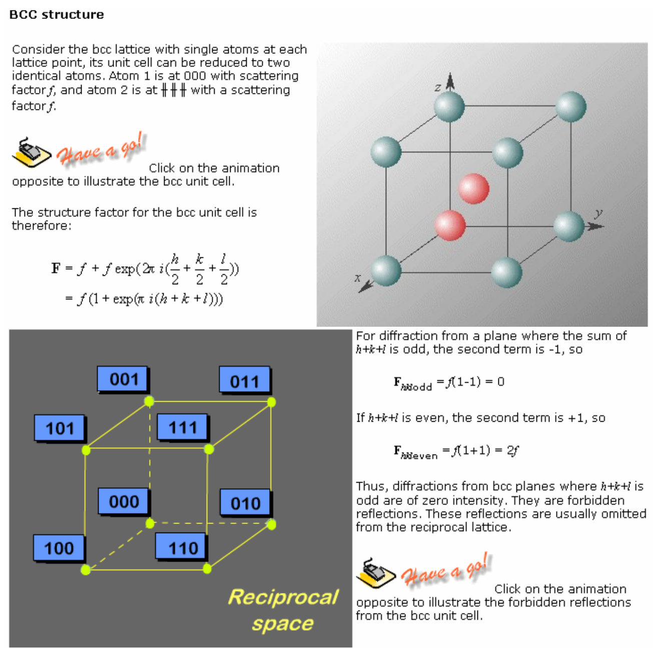
For allowed reflections in fcc lattice *h,k,and l are all even or all odd*

4 atoms in the basis.

What about simple cubic lattice ?







BCC structure

Consider the bcc lattice with single atoms at each lattice point, its unit cell can be reduced to two identical atoms. Atom 1 is at 000 with scattering factor *f*, and atom 2 is at ½½½ with a scattering factor *f*.

Click on the animation opposite to illustrate the bcc unit cell.

The structure factor for the bcc unit cell is therefore:

$$\mathbf{F} = f + f\exp(2\pi\, i(\frac{h}{2} + \frac{k}{2} + \frac{l}{2}))$$
$$= f(1 + \exp(\pi\, i(h + k + l)))$$

For diffraction from a plane where the sum of *h+k+l* is odd, the second term is -1, so

$\mathbf{F}_{hkl\text{odd}} = f(1\text{-}1) = 0$

If *h+k+l* is even, the second term is +1, so

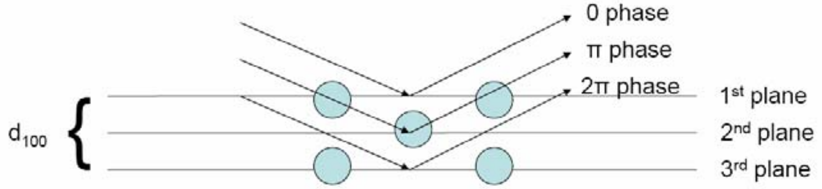
$\mathbf{F}_{hkl\text{even}} = f(1+1) = 2f$

Thus, diffractions from bcc planes where *h+k+l* is odd are of zero intensity. They are forbidden reflections. These reflections are usually omitted from the reciprocal lattice.

Click on the animation opposite to illustrate the forbidden reflections from the bcc unit cell.

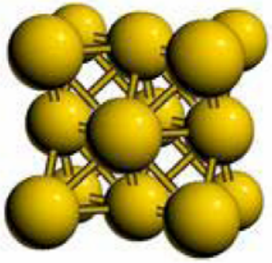
Structure factor of the BCC lattice

- What does this mean? Metallic sodium, for example, is BCC. The diffraction pattern does <u>not</u> contain lines such as (100), (300), (111), etc. – whenever the sum of integers hkl is odd. However, there are lines such as (200), (110), (222), etc.
- The physical reason is that reflections with $h+k+l$ = odd refer to planes of atoms where the rays are out of phase by π, so that each ray, from plane to plane, cancels out the next ray, and the net intensity is zero.
- An example: (100) reflection in the BCC cell:



Structure factor of the FCC lattice

- For the FCC lattice, we have the basis (identical atoms at both positions):



$x_1 = 0$ $y_1 = 0$ $z_1 = 0$
$x_2 = 0$ $y_2 = ½$ $z_2 = ½$
$x_3 = ½$ $y_3 = 0$ $z_3 = ½$
$x_4 = ½$ $y_4 = ½$ $z_4 = 0$

- So, this means that $F(h,k,l)$:

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

- Therefore, if all the indices are even integers, or all are odd $F(h,k,l)$ = 4f. If 1 is even. and 2 are odd, then F = 0. If 1 is odd, and 2 are even, then F is zero. This means that no reflections can occur for which the indices are partly even and partly odd.

Structure factor of the FCC lattice

- Nickel has an FCC structure:

All even (hkl) or All odd (hkl)

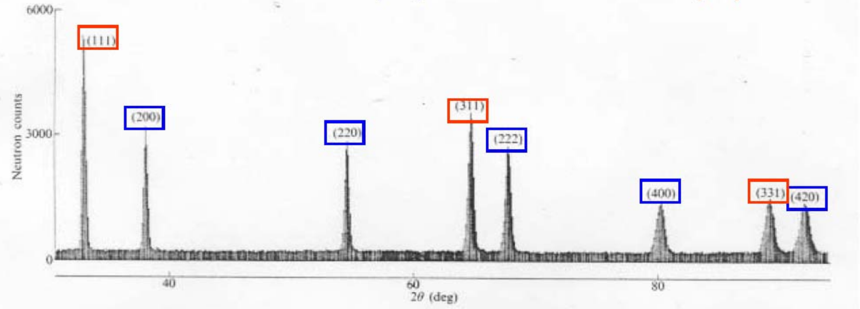
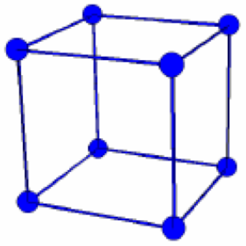


FIG. 58. A section of a powder diffraction pattern for nickel at a wavelength of 1·14 Å recorded on the PANDA diffractometer at A.E.R.E. Harwell using a germanium monochromator. Counts are made at intervals of 0·1° of 2θ. (Courtesy of R. F. Dyer.)

Note: There are <u>no</u> reflections with mixtures of odd and even indices (eg. (110))

Structure factor of the SC lattice

- The structure factor F does not have to be real, because the intensity of the x-ray goes like $F \cdot F$ However, $F \cdot F$ must be real.
- For a simple cubic lattice, the structure factor is easy to calculate:

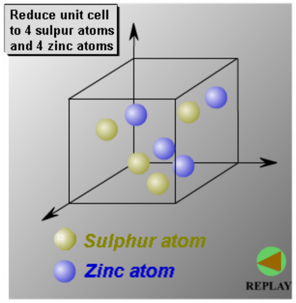


The basis is one atom, at (0, 0, 0).
(This will produce all the atoms in the unit cell by translation)

So: $F(h,k,l) = f(\exp 0)$

This means all of the reflections where $\Delta\vec{k} = \vec{G}$ are allowed (so we see all reflections of the form (hkl), eg. (100), (110), any combination of integers). We will see that this is <u>not</u> true for the BCC and FCC lattice

Structure Compound: Calculation



Structure factor calculation

Consider a general unit cell for this type of structure. It can be reduced to 4 atoms of type A at 000, 0 ╫╫, ╫ 0 ╫, ╫╫ 0 i.e. in the fcc position and 4 atoms of type B at the sites ╪╪╪ from the A sites. This can be expressed as:

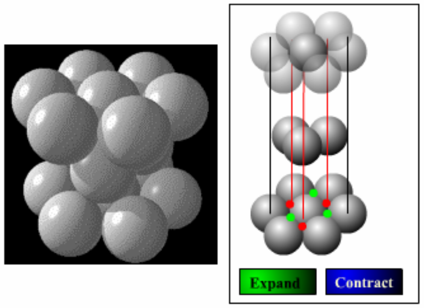
$$\mathbf{F} = (f_A + f_B e^{\frac{\pi}{2}(h+k+l)})\mathbf{F}_{fcc}$$

The structure factors for this structure are:

$\mathbf{F} = 0$ if h, k, l mixed (just like fcc)
$\mathbf{F} = 4(f_A$ ╟ $if_B)$ if h, k, l all odd
$\mathbf{F} = 4(f_A - f_B)$ if h, k, l all even and $h+k+l = 2n$ where n=odd (e.g. 200)
$\mathbf{F} = 4(f_A + f_B)$ if h, k, l all even and $h+k+l = 2n$ where n=even (e.g. 400)

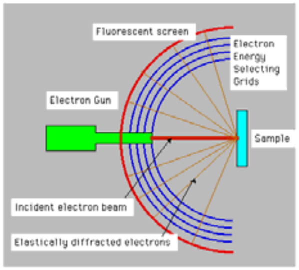
CPH

Close-packed hexagonal describes a way for atoms (considered as hard spheres) to pack together to fill space. The first layer (A) consists of an hexagonal array of atoms. The next layer (B) sits in the hollows of the first layer. The third layer duplicates layer A, giving an ABAB... structure. (See fcc.)



- forbidden reflections for the hcp structure occur when $h+2k = 3n$ and l is odd, where n is an integer (e.g. 113 is forbidden).

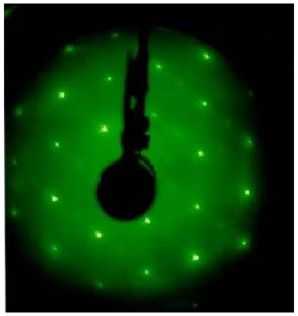
Low Energy Electron Diffraction (LEED)

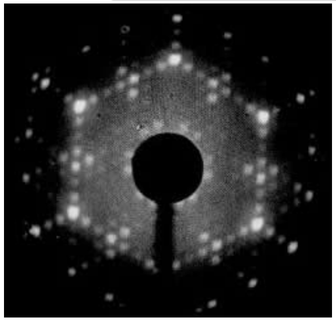


$\lambda = h/p = h/(2mE)^{1/2}$

$E = 20$ eV $\rightarrow \lambda \approx 2.7$Å;
200 eV $\rightarrow$ 0.87 Å

Small penetration depth (few tens of Å) – surface analysis

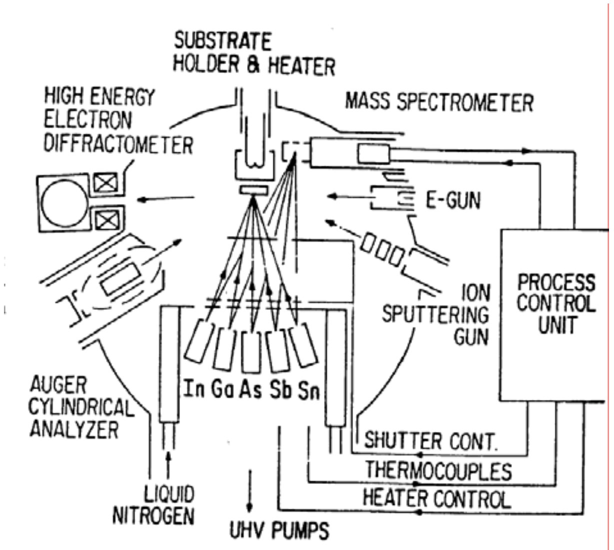




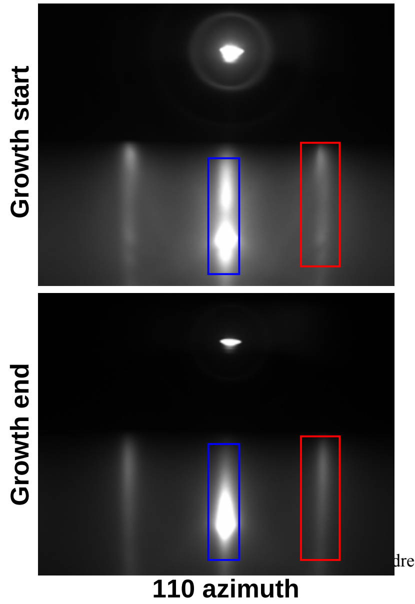
Reflection high Energy Electron Diffraction (RHEED)

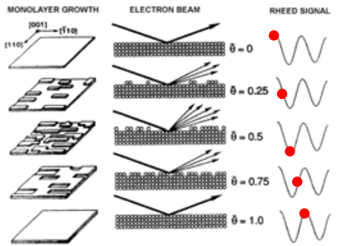
- Glancing incidence: despite the high energy of the electrons (5 – 100 keV), the component of the electron momentum perpendicular to the surface is small
- Also small penetration into the sample – surface sensitive technique
- No advantages over LEED in terms of the quality of the diffraction pattern
- However, the geometry of the experiment allows much better access to the sample during observation of the diffraction pattern. (important if want to make observations of the surface structure during growth or simultaneously with other measurements
- Possible to monitor the atomic layer-by-atomic layer growth of epitaxial films by monitoring oscillations in the intensity of the diffracted beams in the RHEED pattern.

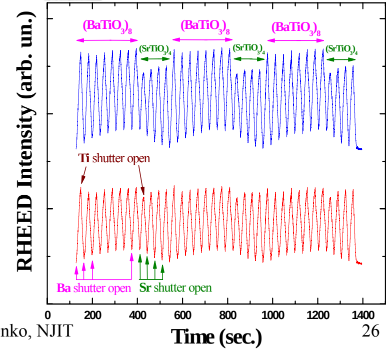
MBE and Reflection high Energy Electron Diffraction (RHEED)



Real time growth control by Reflection High Energy Electron Diffraction (RHEED)







Neutron Diffraction

- $\lambda = h/p = h/(2mE)^{1/2}$ mass much larger than electron ⇒

  $\lambda \approx 1\text{Å} \rightarrow 80$ meV Thermal energy kT at room T: 25 meV

  called "cold" or "thermal' neutrons
- Don't interact with electrons. Scattered by nuclei
- Better to resolve light atoms with small number of electrons, e.g. Hydrogen
- Distinguish between isotopes (x-rays don't)
- Good to study lattice vibrations

Disadvantages:

- Need to use nuclear reactors as sources; much weaker intensity compared to x-rays – need to use large crystals
- Harder to detect

Summary

- ❖ Diffraction amplitude is determined by a product of several factors: atomic form factor, structural factor
- ❖ Atomic scattering factor (form factor): reflects distribution of electronic cloud. $f_a = \int n(\mathbf{r}) e^{i\Delta\mathbf{k}\cdot\mathbf{r}_l} d^3 r$

  In case of spherical distribution $$f_a = \int_0^{r_0} 4\pi r^2 n(r) \frac{\sin(\Delta k \cdot r)}{\Delta k \cdot r} dr$$

  Atomic factor decreases with increasing scattering angle
- ❖ Structure factor $$F = \sum_j f_{aj} e^{2\pi i (hu_j + kv_j + lw_j)}$$

  where the summation is over all atoms in unit cell
- ❖ Neutron diffraction – "cold neutrons" - interaction with atomic nuclei, not electrons
- ❖ Electron diffraction – surface characterization technique