Structure Factor

Textbook's convention:

$$F_{\mathbf{g}} = \sum_{m \text{ atoms}} f_m \cdot \mathrm{e}^{2\pi i \mathbf{g} \cdot \mathbf{d}_m} \qquad f_m = f^{(m)}(s)$$

(Note: form factor are tabulated as functions of $s=g/2$)

Atomic coordinates:

$$\mathbf{d}_m = x_m \mathbf{a}_1 + y_m \mathbf{a}_2 + z_m \mathbf{a}_3 = (x_m, y_m, z_m)$$

(expressed as fractions of basis vectors)

RLV:

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

Notice that:

$$\mathbf{g} \cdot \mathbf{d}_m = hx_m + ky_m + lz_m$$

A general result:

$$F_{hkl} = \sum_{m \text{ atoms}} f_m \mathrm{e}^{2\pi i (hx_m + hy_m + lz_m)}$$

Example:
Simple cubic (*sc*) with two-atom basis

The basis vectors are:

$$\mathbf{a}_1 = a\hat{\mathbf{x}},\ \mathbf{a}_2 = a\hat{\mathbf{y}},\ \mathbf{a}_3 = a\hat{\mathbf{z}}$$

The "basis" sometimes refers to all the atoms in the unit cell.

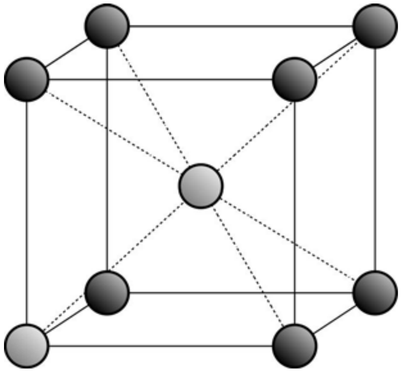
First atom:	f_A	$\mathbf{d}_1 = (0,0,0)$
Second atom:	f_B	$\mathbf{d}_2 = (x,y,z)$

$$F_{hkl} = f_A e^{i0} + f_B e^{2\pi i(hx+ky+lz)} = f_A + f_B e^{2\pi i(hx+ky+lz)}$$

This is the structure factor for *any* integers (*hkl*).

Example:
Body-centered cubic (*bcc*) structure

The *bcc* structure can be generated using a *sc* lattice with a two-atom basis.



First atom: f $\mathbf{d}_1 = (0,0,0)$

Second atom: f $\mathbf{d}_2 = (0.5,0.5,0.5)$

Structure Factors: $F_{hkl} = f \cdot \left[1 + e^{\pi i (h+k+l)}\right]$

$$e^{\pi i (h+k+l)} = \begin{cases} 1, & h+k+l = \text{even} \\ -1, & h+k+l = \text{odd} \end{cases}$$

So, $$F_{hkl} = \begin{cases} 2f, & h+k+l = \text{even} \\ 0, & h+k+l = \text{odd} \end{cases}$$

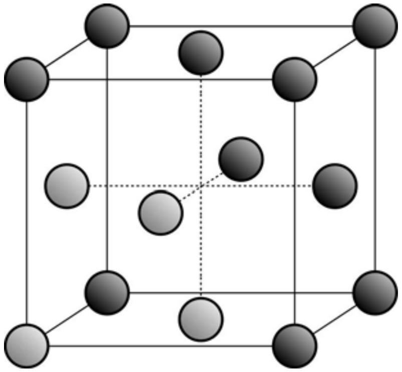
systematic absences

allowed reflections:
{110}
{200}
{202}
{222}
{400}
...

Example:
Face-Centered Cubic (fcc) Structure

The fcc structure can be generated from a sc lattice
with a four-atom basis.

First atom:	f	$\mathbf{d}_1 = (0, 0, 0)$
Second atom:	f	$\mathbf{d}_2 = (0, 0.5, 0.5)$
Third atom:	f	$\mathbf{d}_3 = (0.5, 0, 0.5)$
Fourth atom:	f	$\mathbf{d}_4 = (0.5, 0.5, 0)$



Structure Factors: $F_{hkl} = f \cdot \left[1 + \mathrm{e}^{\pi i(k+l)} + \mathrm{e}^{\pi i(h+l)} + \mathrm{e}^{\pi i(h+k)}\right]$

So, $$F_{hkl} = \begin{cases} 4f, & h,k,l \text{ all even or all odd} \\ 0, & h,k,l \text{ mixed even/odd} \end{cases}$$

allowed reflections:
{200}
{111}
{220}
{311}
{400}
...

Crystal Potential and Structure Factors

Crystal Potential: $\Phi(\mathbf{r}) = \sum_{\mathbf{g}} \Phi_{\mathbf{g}} e^{-2\pi i \mathbf{g}\cdot\mathbf{r}}$

Fourier Components: $\Phi_{\mathbf{g}} = \phi(\mathbf{g})\, X_{\mathbf{g}}$

Crystal Function: $X_{\mathbf{g}} = 1/v$ (when **g** is an RLV)

Unit-Cell Potential: $\phi(\mathbf{g}) = \sum\limits_{m \text{ atoms}} \phi_m \mathrm{e}^{2\pi i \mathbf{g}\cdot\mathbf{d}_m}$

Atomic Form Factors: $f_m = \dfrac{2\pi m e}{h^2} \phi_m$

Structure Factors: $F_{\mathbf{g}} = \sum\limits_{m \text{ atoms}} f_m e^{2\pi i \mathbf{g}\cdot\mathbf{d}_m}$

Structure Function: $U_{\mathbf{g}} = \dfrac{2me}{h^2} \Phi_{\mathbf{g}} = \dfrac{F_{\mathbf{g}}}{\pi v}$

The Fourier components of the crystal potential are normalized by the unit-cell volume.

Diamond structure

Two identical, interpenetraing *fcc* lattices offset by ¼[111]

First lattice:

$$\mathbf{d}_1 = \mathbf{0} = 0\cdot\mathbf{a}_1 + 0\cdot\mathbf{a}_2 + 0\cdot\mathbf{a}_3 = (0,0,0)$$

$$F^{(1)}_{hk\ell} = f\cdot\left[1+\mathrm{e}^{\pi i(k+\ell)}+\mathrm{e}^{\pi i(h+\ell)}+\mathrm{e}^{\pi i(h+k)}\right]$$

Second lattice:

$$\mathbf{d}_2 = a\left(\hat{\mathbf{x}}+\hat{\mathbf{y}}+\hat{\mathbf{z}}\right)/4 = \left(\mathbf{a}_1+\mathbf{a}_2+\mathbf{a}_3\right)/4 = (1/4,1/4,1/4)$$

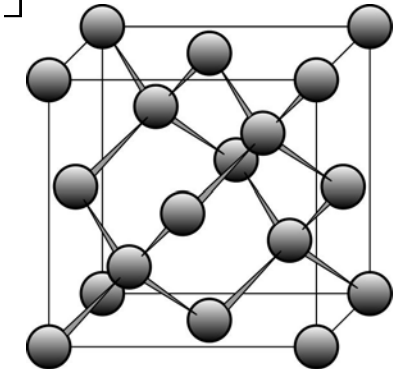
$$F^{(2)}_{hk\ell} = f\cdot\left[1+\mathrm{e}^{\pi i(k+\ell)}+\mathrm{e}^{\pi i(h+\ell)}+\mathrm{e}^{\pi i(h+k)}\right]\cdot\mathrm{e}^{\pi i(h+k+\ell)/2}$$

Structure Factors:

$$F_{hkl} = F^{(1)}_{hkl} + F^{(2)}_{hkl} = f\cdot\overbrace{\left[1+\mathrm{e}^{\pi i(k+l)}+\mathrm{e}^{\pi i(h+l)}+\mathrm{e}^{\pi i(h+k)}\right]}^{4\text{ or }0}\cdot\overbrace{\left[1+\mathrm{e}^{\pi i(h+k+l)/2}\right]}^{2,\ 1\pm i\text{ or }0}$$

for *hkl* all even/all odd:

$$F_{hk\ell} = \begin{cases} 8f, & h+k+\ell = 4N \\ 4(1\pm i)\,f, & h+k+\ell = 2N+1 \\ 0, & h+k+\ell = 4N+2 \end{cases}$$



As for *fcc*, allowed reflections have *h*,*k*,*l* all even or all odd. However, some of these reflections are *kinematically forbidden*.

Zincblende Structure

Two distinct, interpenetraing *fcc* lattices offset by ¼[111]

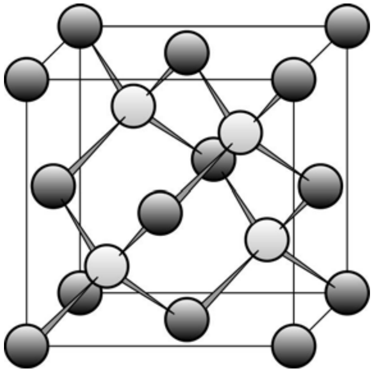
First lattice: $\mathbf{d}_1 = \mathbf{0} = 0 \cdot \mathbf{a}_1 + 0 \cdot \mathbf{a}_2 + 0 \cdot \mathbf{a}_3 = (0,0,0)$

$$F_{hk\ell}^{(1)} = f_A \cdot \left[1 + \mathrm{e}^{\pi i(k+\ell)} + \mathrm{e}^{\pi i(h+\ell)} + \mathrm{e}^{\pi i(h+k)}\right]$$

Second lattice: $\mathbf{d}_2 = 0.25a\left(\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}}\right) = 0.25\left(\mathbf{a}_1 + \mathbf{a}_2 + \mathbf{a}_3\right) = (0.25, 0.25, 0.25)$

$$F_{hk\ell}^{(2)} = f_B \cdot \left[1 + \mathrm{e}^{\pi i(k+\ell)} + \mathrm{e}^{\pi i(h+\ell)} + \mathrm{e}^{\pi i(h+k)}\right] \cdot \mathrm{e}^{\pi i(h+k+\ell)/2}$$

$$F_{hkl} = F_{hkl}^{(1)} + F_{hkl}^{(2)}$$



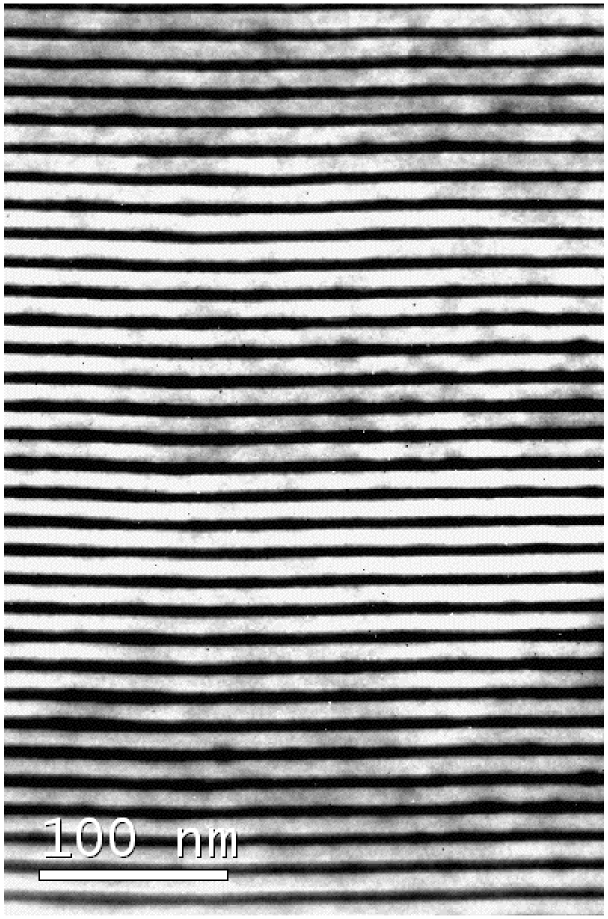
So,

$$F_{hkl} = \begin{cases} 4\left(f_A + f_B\right), & h+k+l = 4N \\ 4\left(f_A \pm i f_B\right), & h+k+l = 2N+1 \\ 4\left(f_A - f_B\right), & h+k+l = 4N+2 \end{cases}$$

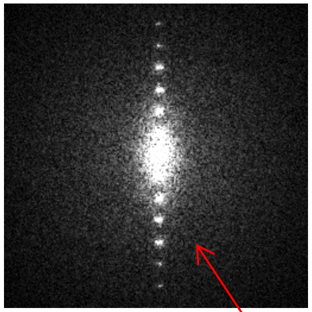
Allowed reflections have *h*,*k*,*l* all even or all odd.

Superlattices

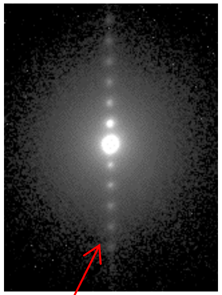
$(GaAs)_m/(InAs)_n$



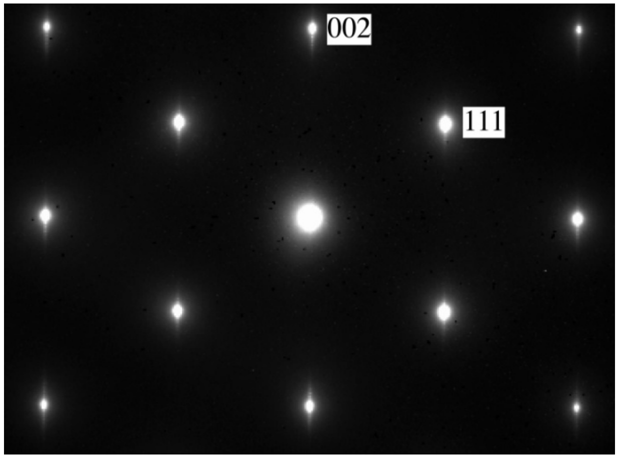
FFT

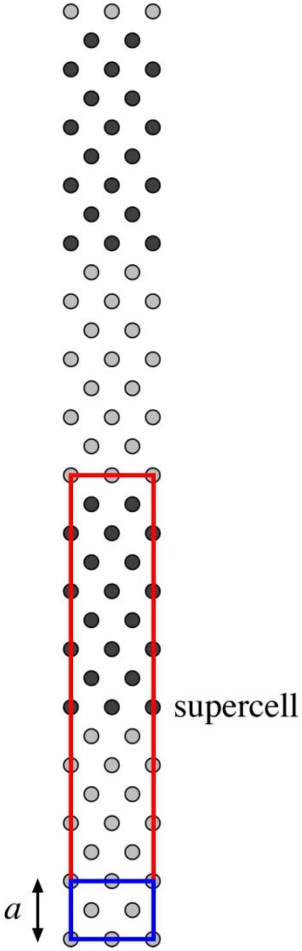


diffraction spot



SL spots have fractional Miller indices

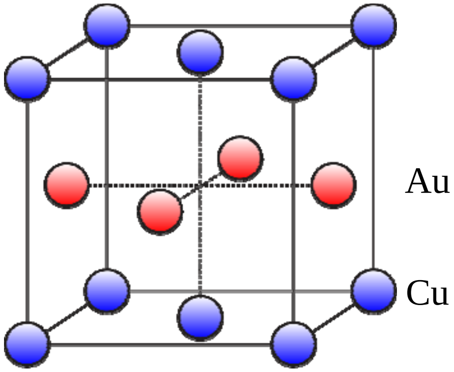




Large unit-cell built by ordering of a smaller unit cell

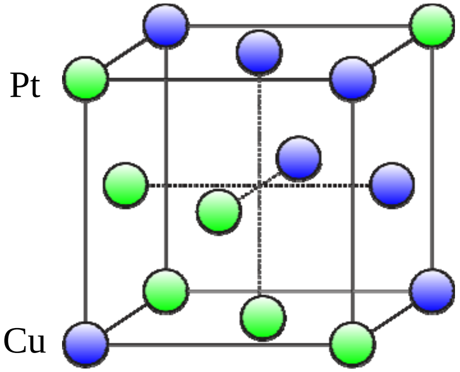
Atomic ordering in metal alloys

CuAu-I

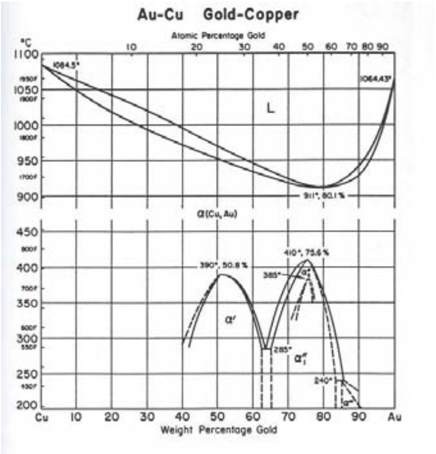


(001) superlattice

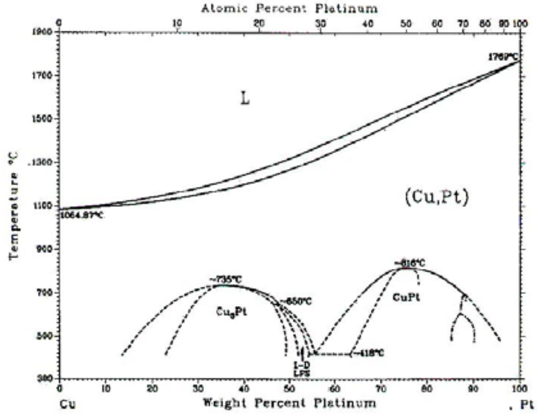
CuPt



½(111) superlattice

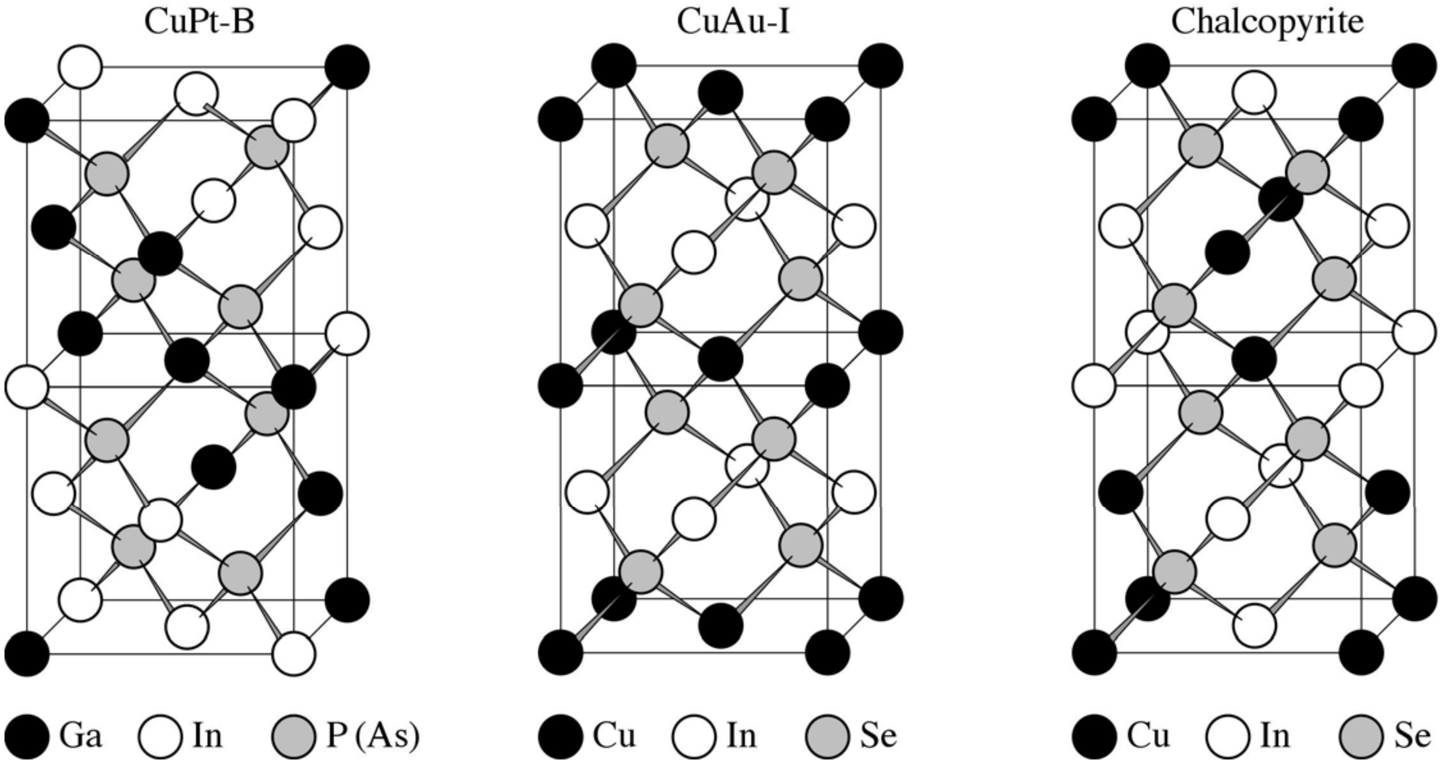


Cu - Pt



Specific atomic arrangements in normally random alloys

Atomic ordering in semiconductors

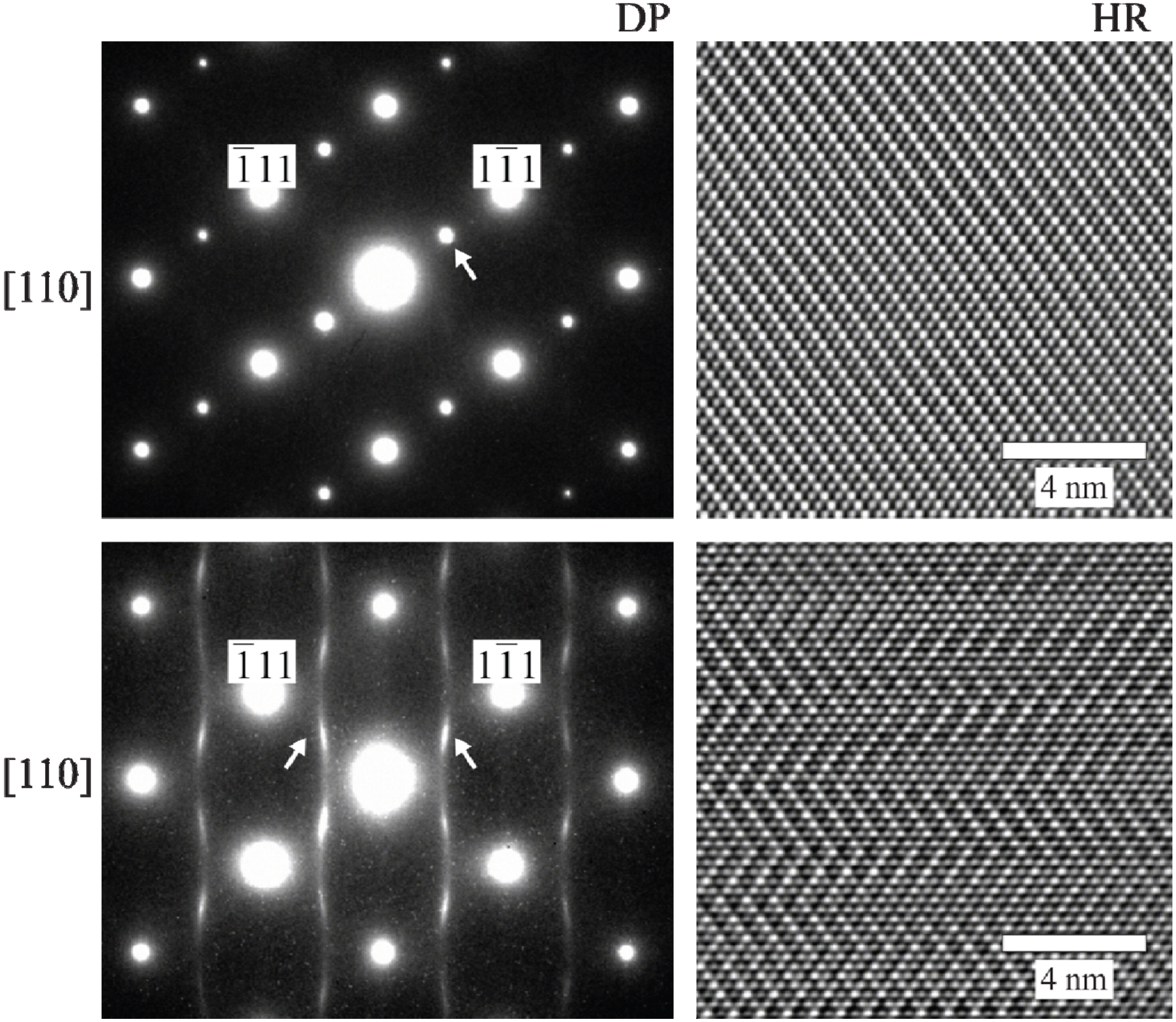


Sublattice ordering

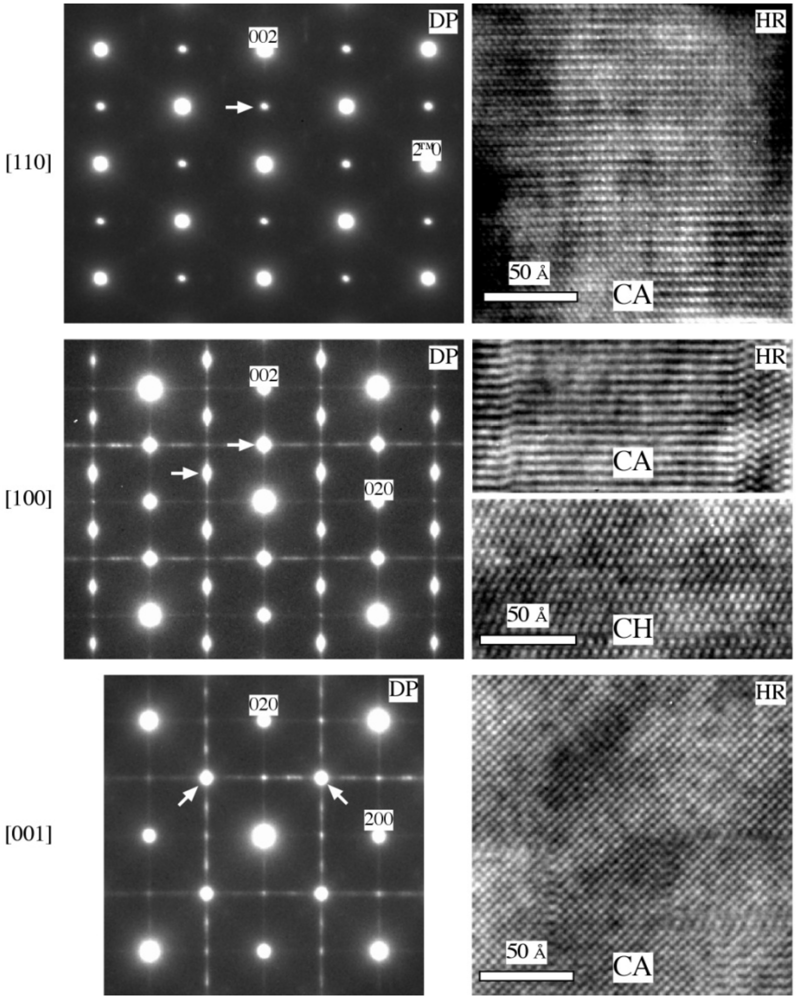
CuPt-Ordered $GaInP_2$

single-variant

double-variant



Ordering in $CuInSe_2$

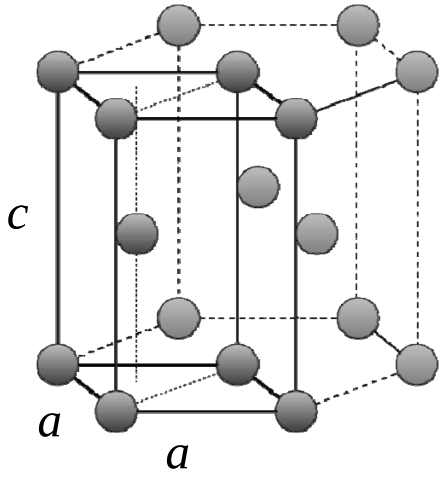


CuAu-I (CA) and
Chalcopyrite (CH)
Ordering

Example: Hexagonal close-packed structure

Basis vectors:

$$\mathbf{a}_1 = a\hat{\mathbf{x}},\ \mathbf{a}_2 = -\frac{a}{2}\hat{\mathbf{x}} + \frac{\sqrt{3}}{2}a\hat{\mathbf{y}},\ \mathbf{c} = c\hat{\mathbf{z}}$$

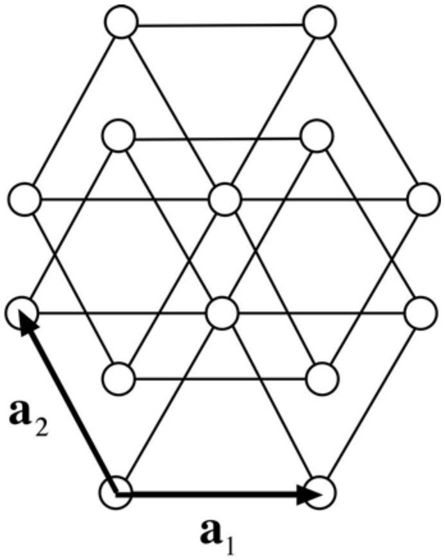


a is the nearest neighbor distance.

c/2 is the interlayer spacing.

The unit-cell volume is: $v = \frac{\sqrt{3}}{2}a^2c$

Two atoms in the unit cell:



First atom: f $\mathbf{d}_1 = (0,0,0)$

Second atom: f $\mathbf{d}_2 = \left(\frac{1}{3},\frac{2}{3},\frac{1}{2}\right)$

Structure Factors: $F_{hk\ell} = f\left[1 + \mathrm{e}^{2\pi i\left(\frac{h}{3}+\frac{2k}{3}+\frac{\ell}{2}\right)}\right]$

Notice: $F_{00\ell} = 0$ for *l*=odd

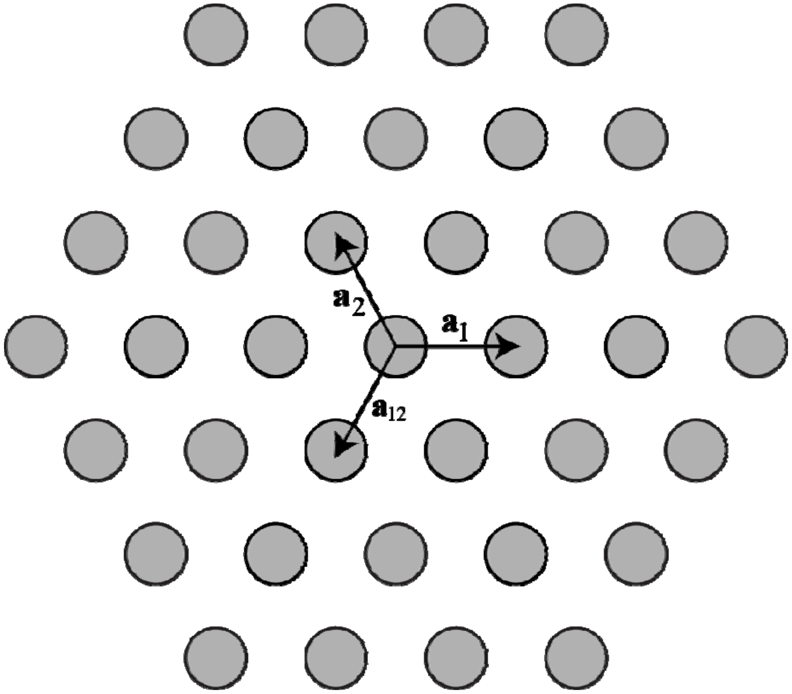
Indexing hexagonal crystals (I)

A direct-lattice vector could be written:

$$\mathbf{r}_{UVW} = U \cdot \mathbf{a}_1 + V \cdot \mathbf{a}_2 + W \cdot \mathbf{a}_3$$

There is a third, in-plane, symmetry equivalent vector:

$$\mathbf{a}_{12} = -(\mathbf{a}_1 + \mathbf{a}_2)$$



Indexing hexagonal crystals (II)

We could rewrite a vector as:

$$\begin{aligned} \mathbf{r}_{uvtw} &= u \cdot \mathbf{a}_1 + v \cdot \mathbf{a}_2 + t \cdot \mathbf{a}_{12} + w \cdot \mathbf{a}_3 = \mathbf{r}_{UVW} \\ &= u \cdot \mathbf{a}_1 + v \cdot \mathbf{a}_2 - t \cdot \left(\mathbf{a}_1 + \mathbf{a}_2 \right) + w \cdot \mathbf{a}_3 \\ \mathbf{r}_{uvtw} &= (u - t) \cdot \mathbf{a}_1 + (v - t) \cdot \mathbf{a}_2 + w \cdot \mathbf{a}_3 \end{aligned}$$

$$\begin{aligned} U &= u - t \\ V &= v - t \\ W &= w \end{aligned}$$

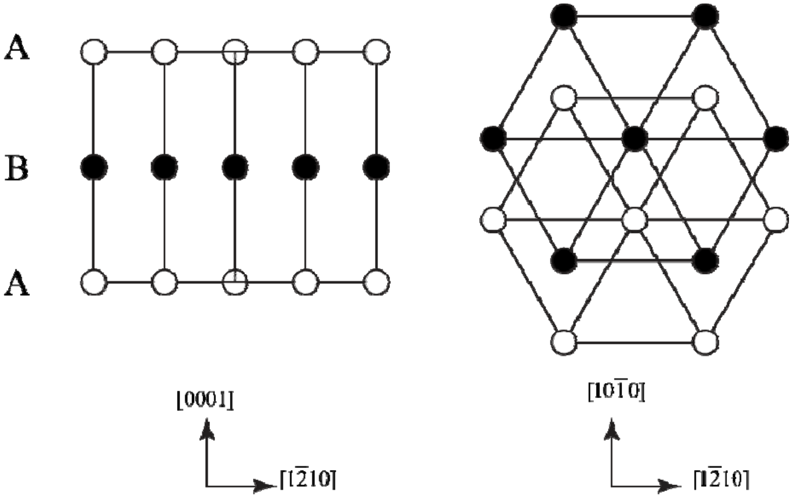
We can pick: $t = -(u + v)$ $\longrightarrow$

$$\begin{aligned} u &= (2U - V)/3 \\ v &= (2V - U)/3 \\ t &= -(U + V)/3 \\ w &= W \end{aligned}$$

$$\left. \begin{aligned} [100] &\rightarrow \frac{1}{3}[2\bar{1}\bar{1}0] \\ [010] &\rightarrow \frac{1}{3}[\bar{1}2\bar{1}0] \\ [\bar{1}\bar{1}0] &\rightarrow \frac{1}{3}[\bar{1}\bar{1}20] \end{aligned} \right\} \textit{symmetry equivalent}$$

Comparing close-packed structures: hcp and fcc

<u>hcp</u>

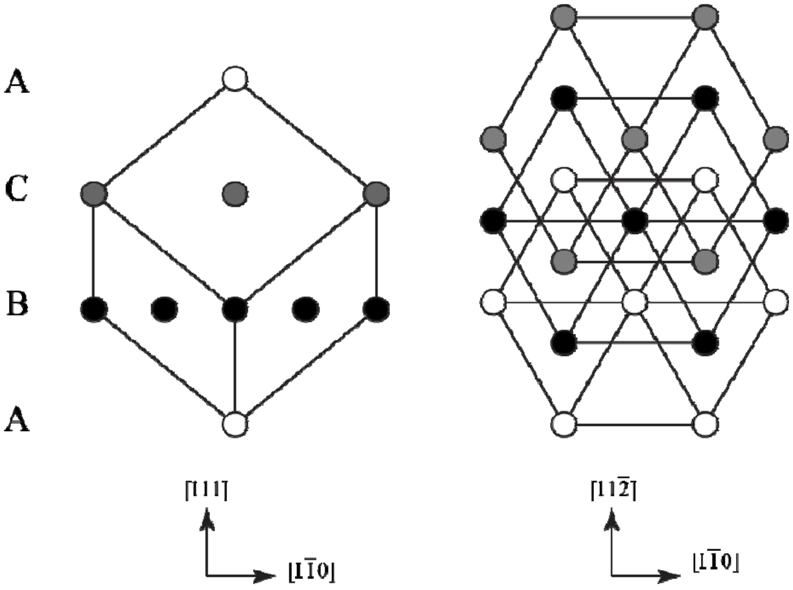


stacking sequence: AB/AB/AB/AB...

nearest-neighbor distance: $d_{\text{n-n}} = a^{(hcp)}$

interlayer spacing: $d_{002} = c/2$

<u>fcc</u>



stacking sequence: ABC/ABC/ABC...

nearest-neighbor distance: $d_{\text{n-n}} = a^{(fcc)}/\sqrt{2}$

interlayer spacing: $d_{111} = a^{(fcc)}/\sqrt{3} = \sqrt{\frac{2}{3}}d_{\text{n-n}}$

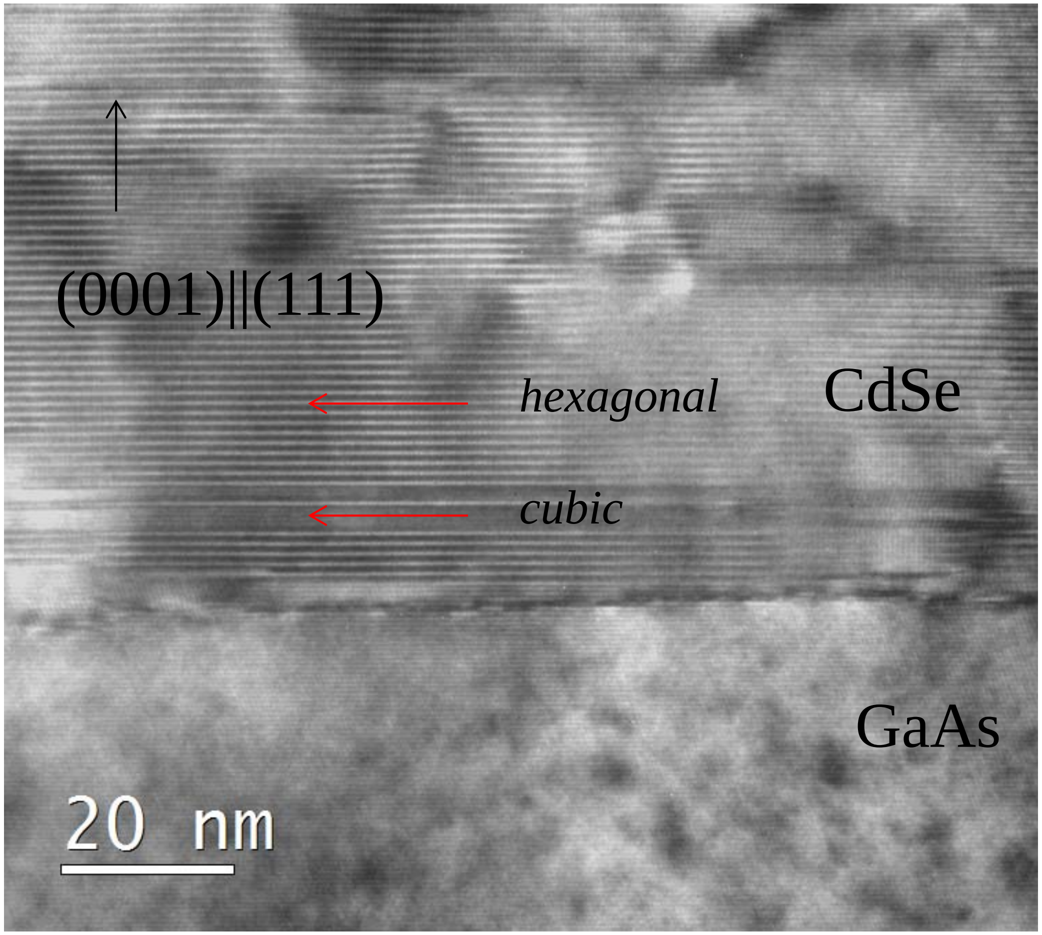
"Ideal" hexagonal close-packed

$$c^{(ideal)} = 2\sqrt{\frac{2}{3}}d_{\text{n-n}} = \sqrt{\frac{8}{3}}a^{(hcp)}$$

The two structures differ in stacking sequence.

Example: CdSe on (111) GaAs

HR



FFT