What we will see in XRD of simple cubic, BCC, FCC?

Structure Factor:
adds up all scattered X-ray from each lattice points in crystal

\[ S_k = \sum_{j=1}^{n} e^{-iK \cdot d_j} \]

\[ K = ha^* + kb^* + lc^* \]

\[ d_j = xa + yb + zc \]

\[ I_{(hkl)} \propto |S_k|^2 \]
X-ray scattered from each primitive cell interfere constructively when:

\[ e^{-iK \cdot R} = 1 \]

\[ 2d \sin \theta = n\lambda \]

For n-atom basis:

sum up the X-ray scattered from the whole basis

\[ \vec{K} = \vec{k} - \vec{k}' \]

Phase difference: \[ K \cdot (d_i - d_j) \]

The amplitude of the two rays differ: \[ e^{iK \cdot (d_i - d_j)} \]
The amplitude of the rays scattered at $d_1$, $d_2$, $d_3$, $d_4$, etc. are in the ratios:

$$e^{-iK \cdot d_j}$$

The net ray scattered by the entire cell:

$$S_k = \sum_{j=1}^{n} e^{-iK \cdot d_j}$$

$$I_{(hkl)} \propto |S_k|^2$$

For simple cubic: (0,0,0)

$$S_k = e^{-iK \cdot 0} = 1$$
For BCC: (0,0,0), (1/2, 1/2, 1/2)… Two point basis

\[ S_k = \sum_{j=1}^{2} e^{-i\mathbf{K}\cdot\mathbf{d}_j} = e^{-i\mathbf{K}\cdot0} + e^{-i\mathbf{K}\cdot\frac{1}{2}(x+y+z)} \]

\[ = 1 + e^{-i\pi(h+k+l)} \]

\[ = 1 + (-1)^{h+k+l} \]

S=2, when h+k+l even
S=0, when h+k+l odd, systematical absence
Observable diffraction peaks

\[ h^2 + k^2 + l^2 \]

Ratio

<table>
<thead>
<tr>
<th>Rules for Determining the Diffracting (hkl) Planes in Cubic Crystals</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bravais lattice</td>
</tr>
<tr>
<td>-----------------</td>
</tr>
<tr>
<td>BCC</td>
</tr>
<tr>
<td>FCC</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Cubic planes (hkl)</th>
<th>(h^2 + k^2 + l^2)</th>
<th>Sum (\Sigma(h^2 + k^2 + l^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Simple cubic</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SC: 1,2,3,4,5,6,8,9,10,11,12..</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BCC: 2,4,6,8,10,12....</td>
<td></td>
<td></td>
</tr>
<tr>
<td>FCC: 3,4,8,11,12,16,19,24....</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[ d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \]

\[ 2d \sin \theta = n\lambda \]

FCC

S=4 when \(h+k, k+l, h+l\) all even (h,k, l all even/odd)

S=0, otherwise

\[ S_k = 1 + e^{-i\pi(h+k)} + e^{-i\pi(h+l)} + e^{-i\pi(l+k)} \]
Observable diffraction peaks

\[ h^2 + k^2 + l^2 \]

Ratio

SC: 1,2,3,4,5,6,8,9,10,11,12...

BCC: 2,4,6,8,10, 12, 14.... (1,2,3,4,5,6,7....)

FCC: 3,4,8,11,12,16,19, 24....

\[ d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \]

\[ 2d \sin \theta = n\lambda \]

\[ \sin^2 \theta = \frac{a^2}{4a^2} (h^2 + k^2 + l^2) \]
What we will see in XRD of simple cubic, BCC, FCC?

\[
\frac{\sin^2 \theta_B}{\sin^2 \theta_A} = 0.5 \text{ (BCC)}; = 0.75 \text{ (FCC)}
\]

Ex: An element, BCC or FCC, shows diffraction peaks at 2\(\theta\): 40, 58, 73, 86.8, 100.4 and 114.7.

Determine: (a) Crystal structure? (b) Lattice constant? (c) What is the element?

<table>
<thead>
<tr>
<th>2theta</th>
<th>theta</th>
<th>( \sin^2 \theta )</th>
<th>( h^2 + k^2 + l^2 )</th>
<th>(hkl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>20</td>
<td>0.117</td>
<td>1</td>
<td>(110)</td>
</tr>
<tr>
<td>58</td>
<td>29</td>
<td>0.235</td>
<td>2</td>
<td>(200)</td>
</tr>
<tr>
<td>73</td>
<td>36.5</td>
<td>0.3538</td>
<td>3</td>
<td>(211)</td>
</tr>
<tr>
<td>86.8</td>
<td>43.4</td>
<td>0.4721</td>
<td>4</td>
<td>(220)</td>
</tr>
<tr>
<td>100.4</td>
<td>50.2</td>
<td>0.5903</td>
<td>5</td>
<td>(310)</td>
</tr>
<tr>
<td>114.7</td>
<td>57.35</td>
<td>0.7090</td>
<td>6</td>
<td>(222)</td>
</tr>
</tbody>
</table>

\[ a = 3.18 \text{ Å}, \text{ BCC, } \rightarrow \text{ W} \]
Polyatomic Structures

\[ S_k = \sum_{j=1}^{n} f_j e^{-iK \cdot d_j} \]

\[ K = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* \]
\[ d_j = x\mathbf{a} + y\mathbf{b} + z\mathbf{c} \]

\[ f_j: \text{atomic scattering factor} \]
\[ \propto \text{No. of electrons} \]

Simple Cubic Lattice

Caesium Chloride (CsCl) is **primitive cubic**

Cs (0,0,0)

Cl (1/2,1/2,1/2)

\[ S_k = f_{Cs} + f_{Cl} e^{-i\pi(h+k+l)} \]

What about CsI?
### FCC Lattices

#### Sodium Chloride (NaCl)

**Na:** (0,0,0)(0,1/2,1/2)(1/2,0,1/2)(1/2,1/2,0) 

Add (1/2,1/2,1/2)

**Cl:** (1/2,1/2,1/2) (1/2,0,0)(0,1/2,0)(0,0,1/2)

### Table of Interplanar Reflections

<table>
<thead>
<tr>
<th>(hkl)</th>
<th>CsCl</th>
<th>CsI</th>
</tr>
</thead>
<tbody>
<tr>
<td>(100)</td>
<td>√</td>
<td></td>
</tr>
<tr>
<td>(110)</td>
<td>√</td>
<td>√</td>
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<tr>
<td>(111)</td>
<td>√</td>
<td></td>
</tr>
<tr>
<td>(200)</td>
<td>√</td>
<td>√</td>
</tr>
<tr>
<td>(210)</td>
<td>√</td>
<td></td>
</tr>
<tr>
<td>(211)</td>
<td>√</td>
<td>√</td>
</tr>
<tr>
<td>(220)</td>
<td>√</td>
<td>√</td>
</tr>
<tr>
<td>(221)</td>
<td>√</td>
<td></td>
</tr>
<tr>
<td>(300)</td>
<td>√</td>
<td></td>
</tr>
<tr>
<td>(310)</td>
<td>√</td>
<td>√</td>
</tr>
<tr>
<td>(311)</td>
<td>√</td>
<td></td>
</tr>
</tbody>
</table>
$S_k = [f_{Na} + f_{Cl} e^{-i\pi(h+k+l)}][1 + e^{-i\pi(h+k)} + e^{-i\pi(h+l)} + e^{-i\pi(l+k)}]$ 

S=4 (f_{Na} + f_{Cl}) when h, k, l, all even;
S=4(f_{Na} - f_{Cl}) when h, k, l all odd
S=0, otherwise

<table>
<thead>
<tr>
<th>(hkl)</th>
<th>NaCl</th>
<th>KCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>(100)</td>
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</tr>
<tr>
<td>(311)</td>
<td>√</td>
<td></td>
</tr>
</tbody>
</table>
Diamond Lattice

A-Cell

Perovskite CaTiO$_3$

CaO$_{12}$ cuboctahedra

TiO$_6$ octahedra

B-Cell

Chem 253, UC, Berkeley

Unit Cell
Diamond Lattice

\[ S_{Si}(hkl) = S_{fcc}(hkl)[1 + \exp(i\pi/2)(h+k+l)]. \]

\( S_{Si}(hkl) \) will be zero if the sum \( (h+k+l) \) is equal to 2 times an odd integer, such as (200), (222). \[ h+k+l = 2(2n+1) \]

\( S_{Si}(hkl) \) will be non-zero if

1. \((h,k,l)\) contains only even numbers and
2. the sum \( (h+k+l) \) is equal to 4 times an integer. \[ h+k+l = 4n \]

\( S_{hkl} \) will be non-zero if \( h,k,l \) all odd: \[ 4(f_{Si} \pm if_{Si}) \]

FCC:
\[ S=4 \text{ when } h+k, k+l, h+l \text{ all even (h,k,l all even/odd)} \]
\[ S=0, \text{ otherwise} \]

Silicon Diffraction pattern
\[ h^2 + k^2 + l^2 = \text{constant} \]

Sample APCVD 79 A
Y = 0
PolySiC/SiO2/Si(111)
AS-DEPOSITED
NOT ANNEALED

APCVD 79 A
Y = 0
PolySiC/SiO2/Si
0.70 km APCVD
AS-DEPOSITED
Bond charges in covalent solid

(1/8,1/8,1/8), (3/8,3/8,1/8),(1/8,3/8,3/8) and (3/8,1/8,3/8).

Bond charges form a "crystal" with a fcc lattice with 4 "atoms" per unit cell.

origin : (1/8,1/8,1/8).

Bond charge position: (0,0,0), (1/4,1/4,0),(0,1/4,1/4) and (1/4,0,1/4).

$S_{\text{bond-charge}}(hkl) = S_{\text{fcc}}(hkl)[1+\exp(i\pi/2)(h+k)+\exp(i\pi/2)(k+l)+\exp(i\pi/2)(h+l)].$

For h=k=l=2:

$S_{\text{bond-charge}}(222)=S_{\text{fcc}}(222)[1+3\exp(i\pi/2)4]=4S_{\text{fcc}}(222) \text{ non-zero!}$

$$S_k = \sum_{j=1}^{n} f_j e^{-iK \cdot d_j} = \sum_{j=1}^{n} f_j e^{-2\pi(ihx+jky+lz)}$$
Nanocrystal X-ray Diffraction

Finite Size Effect

Figure 7
TEM micrographs of PbSe (a) at high resolution, revealing lattice imaging of the NCs; (b) at low resolution, showing an ensemble of NCs.
Bragg angle: $\theta_B$
in phase, constructive

For $\theta_1 > \theta_B$
Phase lag between two planes: 

$$\lambda + \delta \lambda$$

At j+1 th plane:
Phase lag: 

$$\sum \delta \lambda = j \cdot \delta \lambda = \frac{\lambda}{2}$$

2j planes: net diffraction at $\theta_1 : 0$

---

Bragg angle: $\theta_B$
in phase, constructive

For $\theta_2 < \theta_B$
Phase lag between two planes: 

$$\lambda - \delta \lambda$$

At j+1 th plane:
Phase lag: 

$$\sum \delta \lambda = j \cdot \delta \lambda = \frac{\lambda}{2}$$

2j planes: net diffraction at $\theta_2 : 0$
How particle size influence the peak width of the diffraction beam.

Full width half maximum (FWHM)
The width of the diffraction peak is governed by \# of crystal planes \(2j\), i.e. crystal thickness/size.

**Scherrer Formula:**

\[
t = \frac{0.9 \lambda}{B \cos \theta_B}
\]

\[B^2 = B_M^2 - B_S^2\]

- \(B_M\): Measured peak width at half peak intensity (in radians)
- \(B_S\): Corresponding width for standard bulk materials (large grain size >200 nm)

*Readily applied for crystal size of 5-50 nm.*

- Suppose \(\lambda=1.5\ \text{Å}, \ d=1.0\ \text{Å}, \ \text{and} \ \theta=49^\circ\). Then for a crystal 1 mm in diameter, the breadth \(B\), due to the small crystal effect alone, would be about \(2\times10^{-7}\ \text{radian} \ (10^{-5}\ \text{degree})\), or too small to be observable. Such a crystal would contain some \(10^7\) parallel lattice planes of the spacing assumed above.

- However, if the crystal were only 500 Å thick, it would contain only 500 planes, and the diffraction curve would be relatively broad, namely about \(4\times10^{-3}\ \text{radian} \ (0.2\degree)\), which is easily measurable.