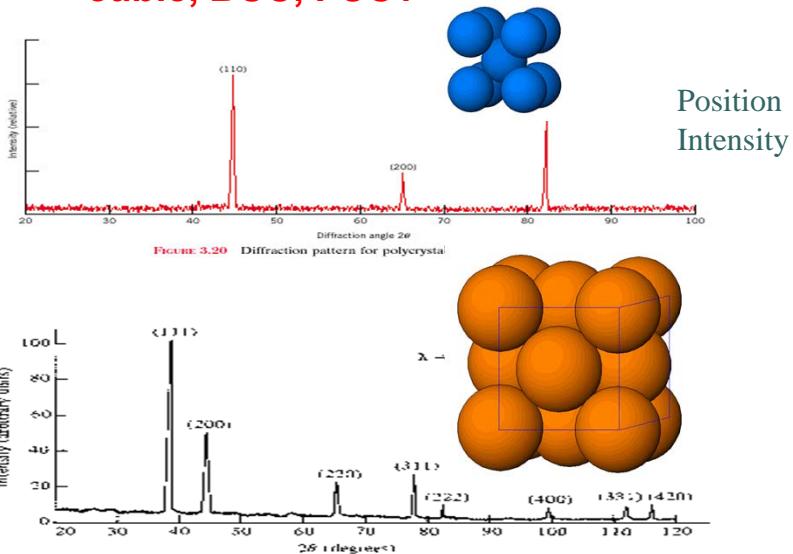


What we will see in XRD of simple cubic, BCC, FCC?



Structure Factor:

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

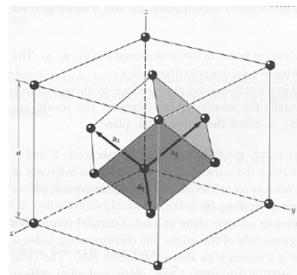
$$S_k = \sum_{j=1}^n e^{-iK \cdot d_j}$$

$$K = ha^* + kb^* + lc^*$$

$$\vec{d}_j = x \vec{a} + y \vec{b} + z \vec{c}$$

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

X-ray scattered from each **primitive** cell interfere constructively when:

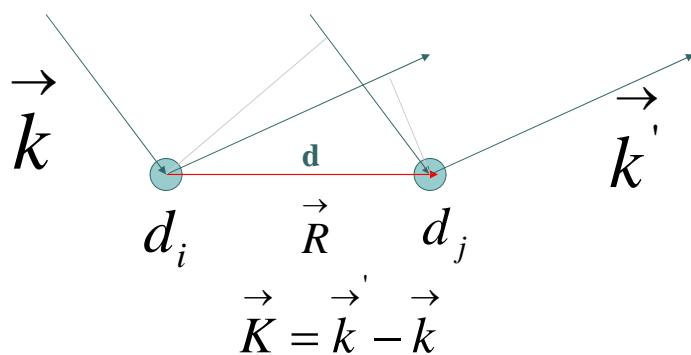


$$e^{-i\mathbf{k} \cdot \mathbf{R}} = 1$$

$$2d \sin \theta = n\lambda$$

For n-atom basis:

sum up the X-ray scattered from the whole basis



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 $\mathbf{d}_1, \mathbf{d}_2, \mathbf{d}_3, \dots$ are in
the ratios :

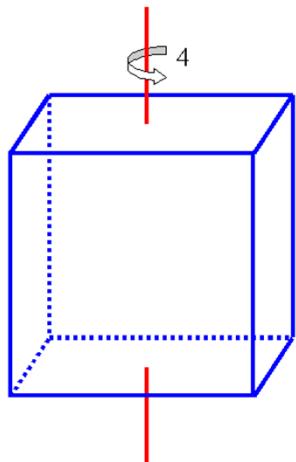
$$e^{-iK \cdot d_j}$$

The net ray scattered by the entire cell:

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

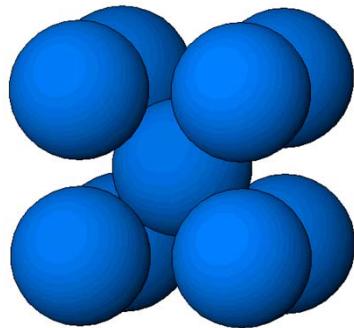
$$I_{(hkl)} \propto |S_k|^2$$

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



$$\begin{aligned} S_k &= \sum_{j=1}^2 e^{-i\mathbf{k} \cdot \mathbf{d}_j} = e^{-i\mathbf{k} \cdot \mathbf{0}} + e^{-i\mathbf{k} \cdot \frac{1}{2}(\vec{x} + \vec{y} + \vec{z})} \\ &= 1 + e^{-i\pi(h+k+l)} \\ &= 1 + (-1)^{h+k+l} \end{aligned}$$

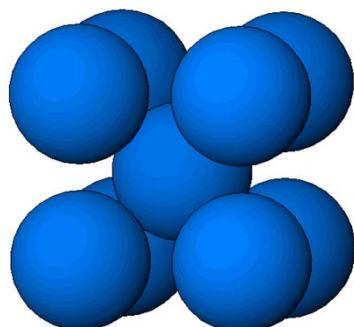
S=2, when h+k+l even

S=0, when h+k+l odd, systematical absence

For BCC: (0,0,0), (1/2, 1/2, 1/2).... Two point basis

S=2, when h+k+l even

S=0, when h+k+l odd, systematical absence



(100): destructive

(200): constructive

Rules for Determining the Diffracting $\{hkl\}$ Planes in Cubic Crystals			
Bravais lattice	Reflections present	Reflections absent	
BCC	$(h + k + l) = \text{even}$	$(h + k + l) = \text{odd}$	
FCC	(h, k, l) all odd or all even	(h, k, l) not all odd or all even	
Observable diffraction peaks			
$h^2 + k^2 + l^2$ Ratio			
Miller Indices of the Diffracting Planes for BCC and FCC Lattices			
Cubic planes $\{hkl\}$	Simple cubic	Cubic diffracting planes $\{hkl\}$	
	Sum $\Sigma(h^2 + k^2 + l^2)$	FCC	BCC
{100}	$1^2 + 0^2 + 0^2$	1	...
{110}	$1^2 + 1^2 + 0^2$	2	110
{111}	$1^2 + 1^2 + 1^2$	3	111
{200}	$2^2 + 0^2 + 0^2$	4	200
{210}	$2^2 + 1^2 + 0^2$	5	
{211}	$2^2 + 1^2 + 1^2$	6	211
{220}	$2^2 + 2^2 + 0^2$	8	220
{221}	$2^2 + 2^2 + 1^2$	9	
{310}	$3^2 + 1^2 + 0^2$	10	310

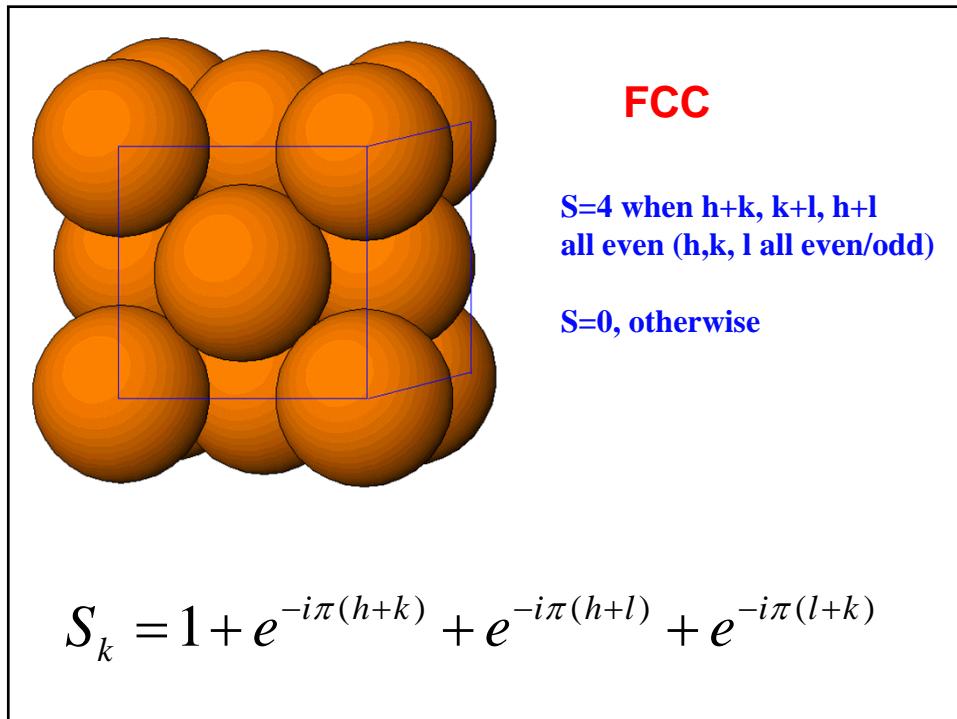
SC: 1,2,3,4,5,6,8,9,10,11,12...

BCC: 2,4,6,8,10, 12....

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

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

$$2d \sin \theta = n\lambda$$



Rules for Determining the Diffracting $\{hkl\}$ Planes in Cubic Crystals		
Bravais lattice	Reflections present	Reflections absent
BCC	$(h + k + l) = \text{even}$	$(h + k + l) = \text{odd}$
FCC	(h, k, l) all odd or all even	(h, k, l) not all odd or all even

Miller Indices of the Diffracting Planes for BCC and FCC Lattices			
Cubic planes $\{hkl\}$	Simple cubic	Cubic diffracting planes $\{hkl\}$	
	Sum $h^2 + k^2 + l^2$	FCC	BCC
{100}	$1^2 + 0^2 + 0^2$	1	...
{110}	$1^2 + 1^2 + 0^2$	2	110
{111}	$1^2 + 1^2 + 1^2$	3	111
{200}	$2^2 + 0^2 + 0^2$	4	200
{210}	$2^2 + 1^2 + 0^2$	5	200
{211}	$2^2 + 1^2 + 1^2$	6	211
{220}	$2^2 + 2^2 + 0^2$	8	220
{221}	$2^2 + 2^2 + 1^2$	9	...
{310}	$3^2 + 1^2 + 0^2$	10	310

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...

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

$$2d \sin \theta = n\lambda$$

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Observable diffraction peaks

$$h^2 + k^2 + l^2$$

Ratio

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

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

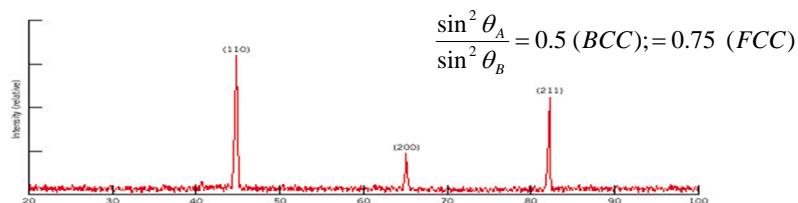
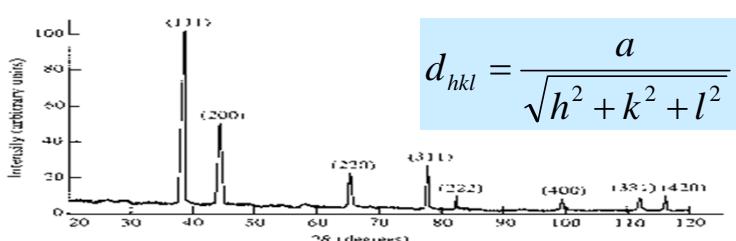
BCC: 2,4,6,8,10, 12, 14....
(1,2,3,4,5,6,7...)

$$2d \sin \theta = n\lambda$$

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

$$\sin^2 \theta = \frac{\lambda^2}{4a^2} (h^2 + k^2 + l^2)$$

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

FIGURE 3.20 Diffraction pattern for polycrystalline α -iron.

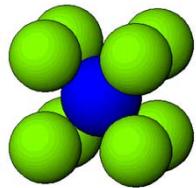
Ex: An element, BCC or FCC, shows diffraction peaks at 2θ : 40, 58, 73, 86.8, 100.4 and 114.7.

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

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

$$a = 3.18 \text{ \AA}, \text{BCC, } \rightarrow \text{W}$$

Polyatomic Structures



$$S_k = \sum_{j=1}^n f_j(k) \bar{e}^{iK \cdot \vec{d}_j} \quad K = ha^* + kb^* + lc^*$$

$$\vec{d}_j = x \vec{a} + y \vec{b} + z \vec{c}$$

f_j : atomic scattering factor
 \propto No. of electrons

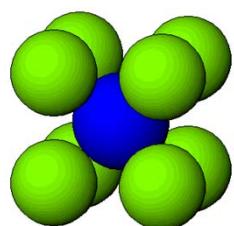
$$S_k = \sum_{j=1}^n f_j e^{-iK \cdot d_j} = \sum_{j=1}^n f_j e^{-2\pi i(hx+ky+lz)}$$

Simple Cubic Lattice

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

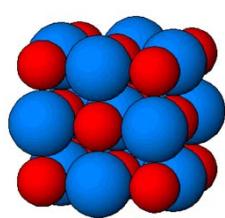
Cs (0,0,0)
 Cl (1/2,1/2,1/2)

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



What about CsI?

(hkl)	CsCl	CsI
(100)	✓	
(110)	✓	✓
(111)	✓	
(200)	✓	✓
(210)	✓	
(211)	✓	✓
(220)	✓	✓
(221)	✓	
(300)	✓	
(310)	✓	✓
(311)	✓	



FCC Lattices

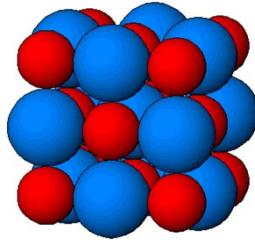
Sodium Chloride
(NaCl)

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)



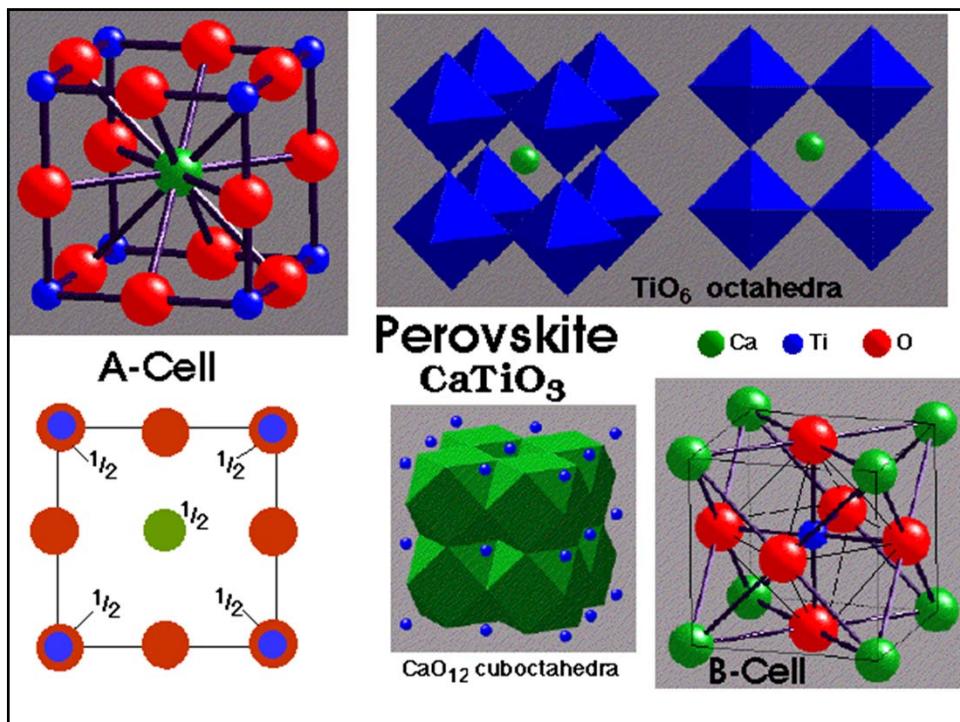
$$S_k = [f_{Na} + f_{Cl} e^{-i\pi(h+k+l)}][1 + e^{-i\pi(h+k)} + e^{-i\pi(h+l)} + e^{-i\pi(l+k)}]$$

S=4 ($f_{Na} + f_{Cl}$) when h, k, l , all even;

S=4($f_{Na}-f_{Cl}$) when h, k, l all odd

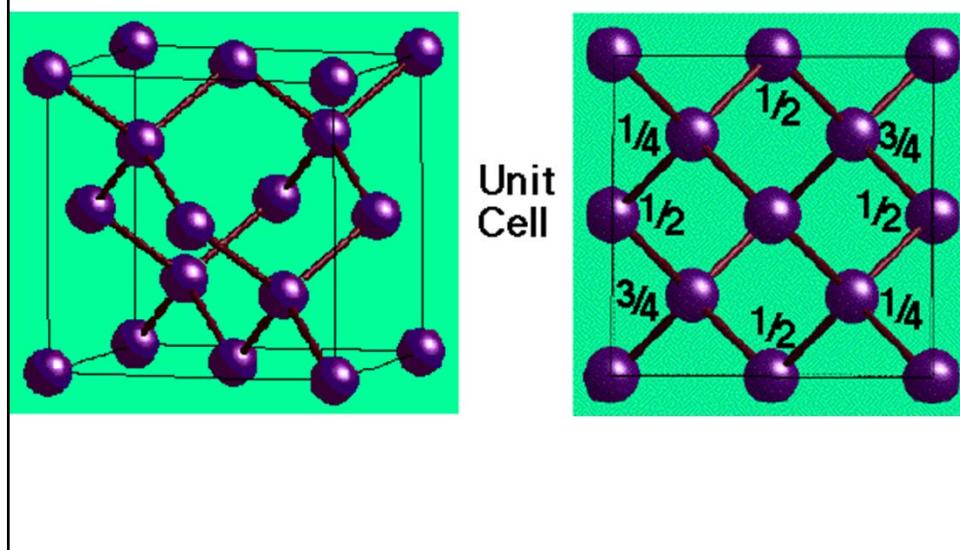
S=0, otherwise

(hkl)	NaCl	KCl
(100)		
(110)		
(111)	✓	
(200)	✓	✓
(210)		
(211)		
(220)	✓	✓
(221)		
(300)		
(310)		
(311)	✓	



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Diamond Lattice



$$S_{fcc} = 1 + e^{-i\pi(h+k)} + e^{-i\pi(h+l)} + e^{-i\pi(l+k)}$$

Diamond Lattice

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

FCC:
S=4 when $h+k, k+l, h+l$
 all even (h, k, l all
 even/odd)
S=0, otherwise

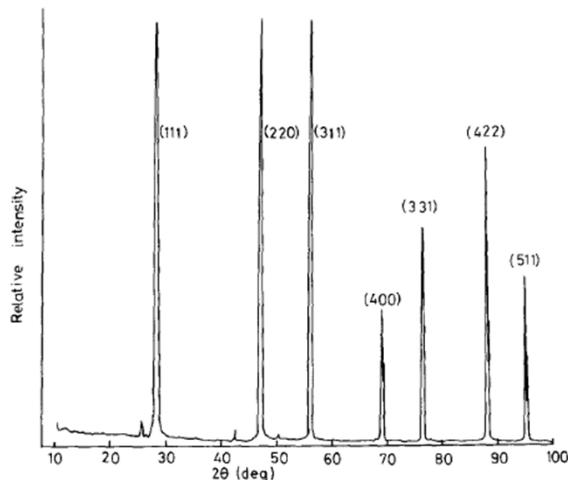
$S_{Si}(hkl)$ will be zero

if the sum $(h+k+l)$ is equal to 2 times an odd integer, such
 as (200), (222). [$h+k+l=2(2n+1)$]

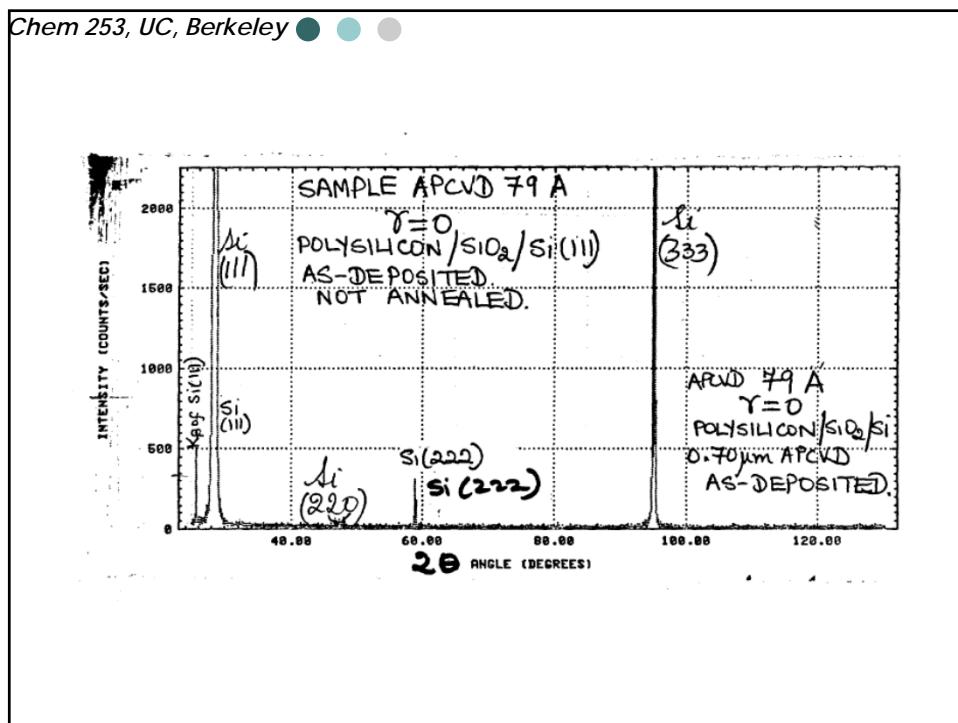
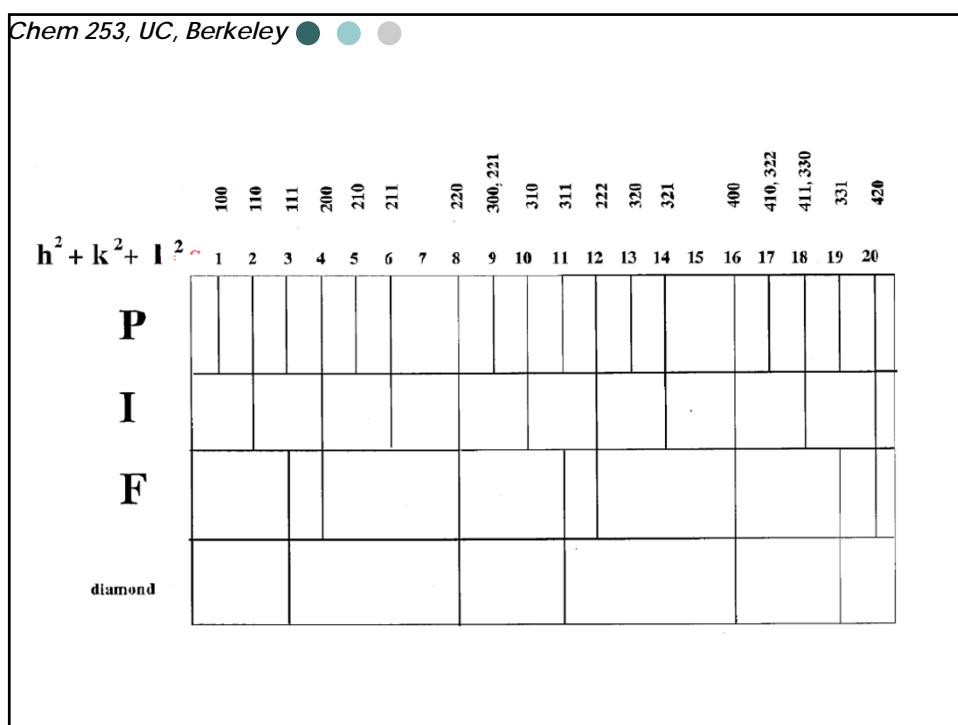
$S_{Si}(hkl)$ will be non-zero if

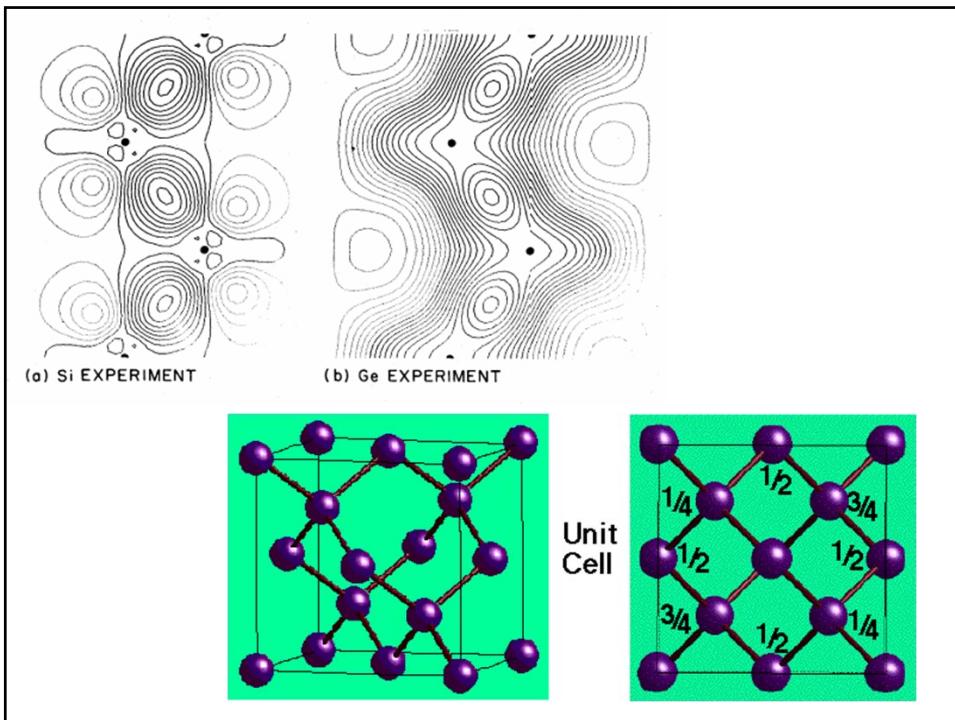
- (1) (h, k, l) contains only even numbers and
- (2) the sum $(h+k+l)$ is equal to 4 times an integer.
[$h+k+l=4n$]

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



Silicon Diffraction pattern





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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 $(1/4,0,1/4)$.

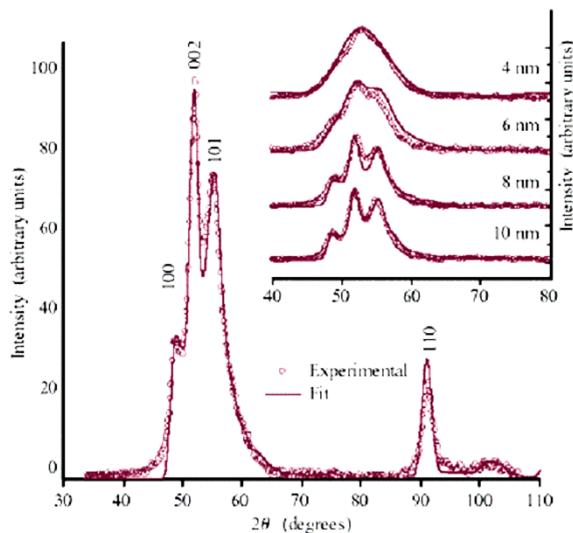
$$S_{\text{bond-charge}}(hkl) = S_{\text{fcc}}(hkl)[1 + \exp(i\pi/2)(h+k) + \exp(i\pi/2)(k+l) + \exp(i\pi/2)(h+l)].$$

For $h=k=l=2$:

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

$$S_k = \sum_{j=1}^n f_j e^{-iK \cdot d_j} = \sum_{j=1}^n f_j e^{-2\pi i(hx+ky+lz)}$$

Nanocrystal X-ray Diffraction



Finite Size Effect

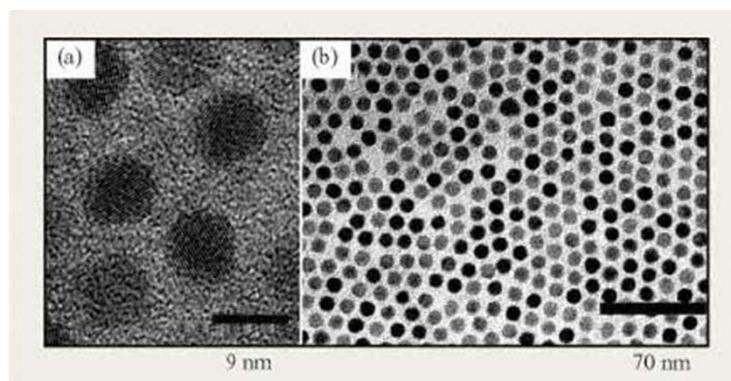
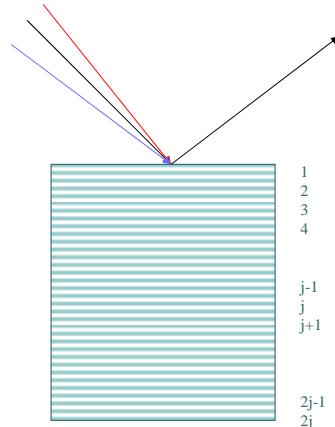


Figure 7

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: θ_B
in phase, constructive

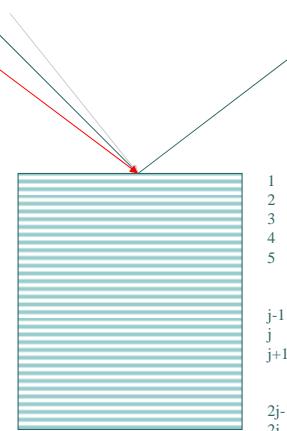
For $\theta_1 > \theta_B$

Phase lag between two planes:
 $\lambda + \delta\lambda$

At $j+1$ th plane:

$$\text{Phase lag: } \sum \delta\lambda = j \cdot \delta\lambda = \frac{\lambda}{2}$$

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



Bragg angle: θ_B

in phase, constructive

For $\theta_2 < \theta_B$

Phase lag between two planes:

$$\lambda - \delta\lambda$$

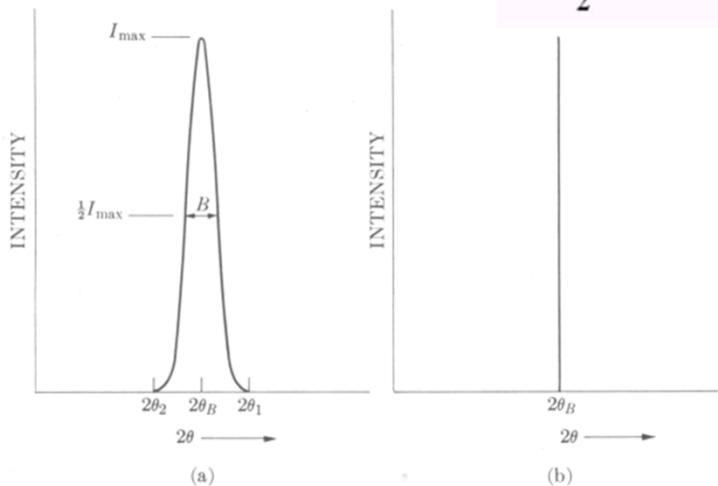
At $j+1$ th plane:

$$\text{Phase lag: } \sum \delta\lambda = j \cdot \delta\lambda = \frac{\lambda}{2}$$

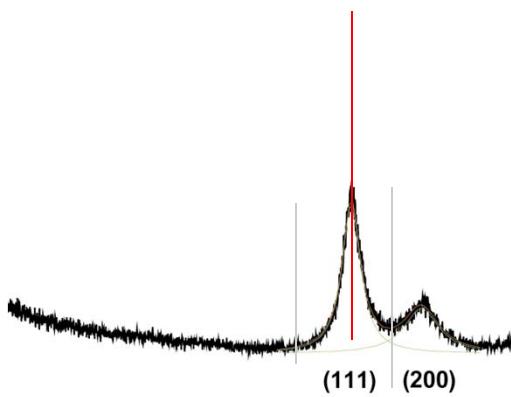
$2j$ planes: net diffraction at $\theta_2 : 0$

How particle size influence the peak width of the diffraction beam.

$$B = \frac{1}{2}(2\theta_1 - 2\theta_2) = \theta_1 - \theta_2$$



Full width half maximum (FWHM)



The width of the diffraction peak is governed by # of crystal planes $2j$. i.e. crystal thickness/size

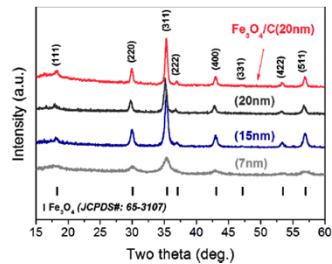
Scherrer Formula:

$$t = \frac{0.9\lambda}{B \cos \theta_B} \quad B^2 = B_M^2 - B_S^2$$

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 $\lambda=1.5 \text{ \AA}$, $d=1.0 \text{ \AA}$, 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 **$2 \times 10^{-7} \text{ radian}$ (10^{-5} 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 **$4 \times 10^{-3} \text{ radian}$ (0.2°)**, which is easily measurable.