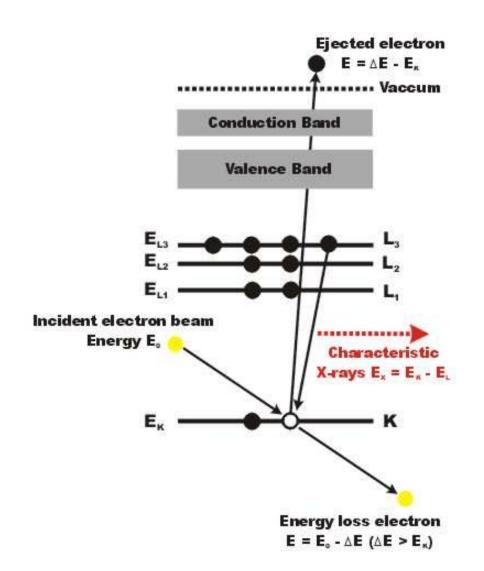


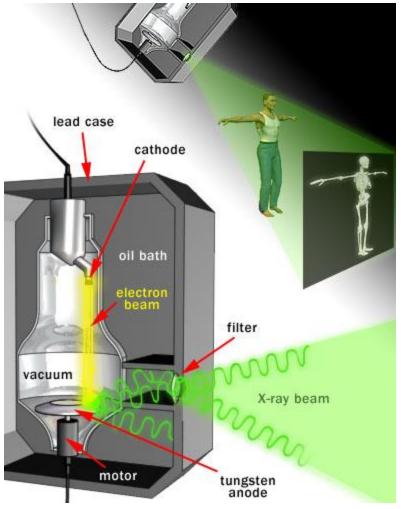
Electromagnetic Spectrum

						Violet	Indigo	Blue	Green	Yellow	Orange	Red											
											,		1								Audio		ê
									¥.						UHF	VHF	HF	MF	5				ž
	Gamma-Rays				X-Rays			Ultraviolet	Visible Light	Near Infrared	Far Infrared			Microwave					Radio				
				1Å				UVIS EUV - 55.8-118rm UVIS FUV - 110-190rm	1 µm			1 mm	1 cm		1 m			100 km					5
10-5 nm	10-4 nm	10-3 nm	10-2 nm	10-1 nm	l nm	10 nm	10 nm	100 nm	10 ³ nm	10 mm	100 µm	1000 ит	10 mm	10 cm	100 cm	10 m	100 m	1000 m	10 km	100 km	1 Mm	10 Mm	100 Mm

4

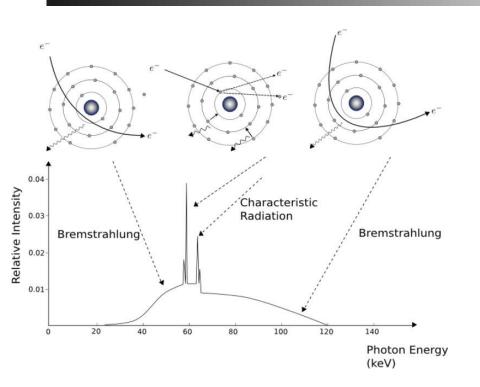
Generation of X-rays

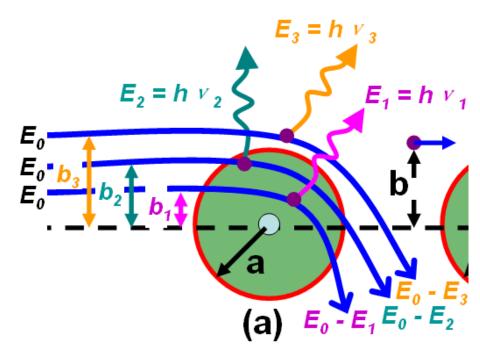






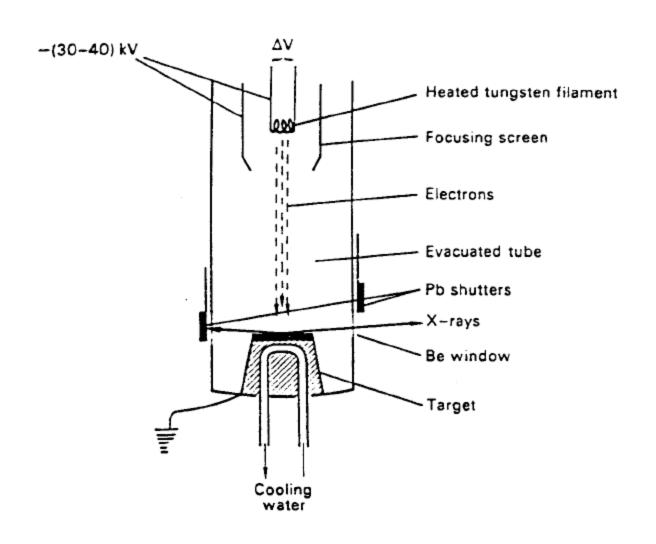
Characteristics X-ray





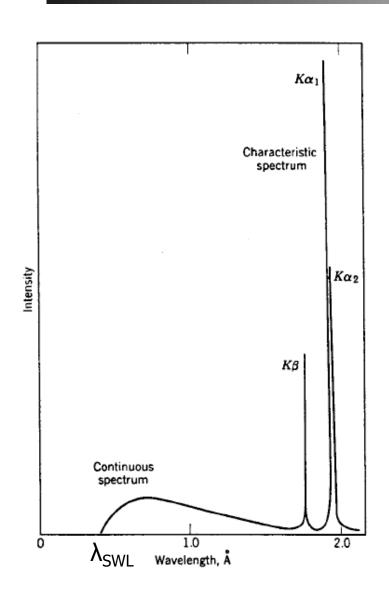
4

Commercial X-ray Tube





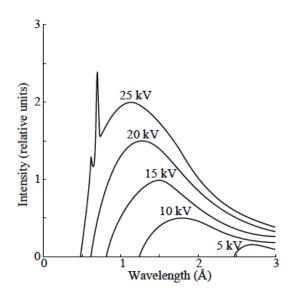
X-ray Spectrum from an Iron target



- Short Wavelength Limit $\lambda_{SWL}(nm) = \frac{12400}{V}$
- \triangleright Continuous spectrum $I_{CS} = AiZV^m$
- Characteristic X-ray Moseley's Law

$$\sqrt{v} = C(Z - \sigma)$$

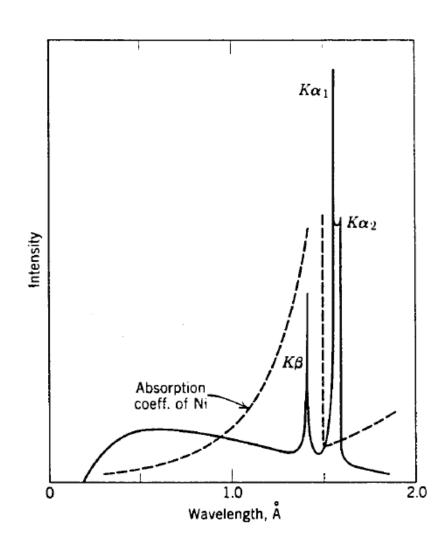
$$I_K = Bi(V - V_k)^n$$





Use of Filter

Ni filter for Cu Target





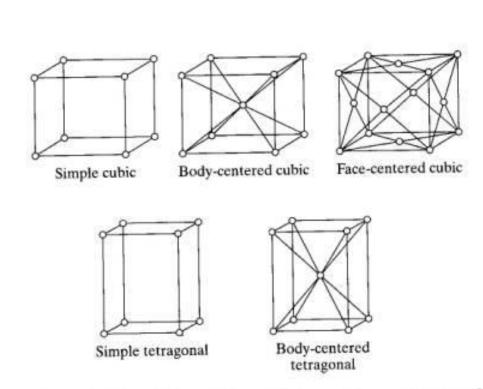
Crystal Systems and Bravais Lattices

Face-centered

orthorhombic

Body-centered

orthorhombic

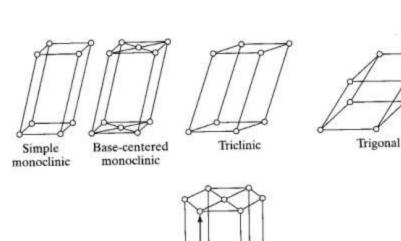


Base-centered

orthorhombic

Simple

orthorhombic



Hexagonal



Structure of Common Materials

Metals

Copper: FCC

• α-Iron: BCC

Zinc: HCP

Silver: FCC

Aluminium: FCC

Ceramics

SiC: Diamond Cubic

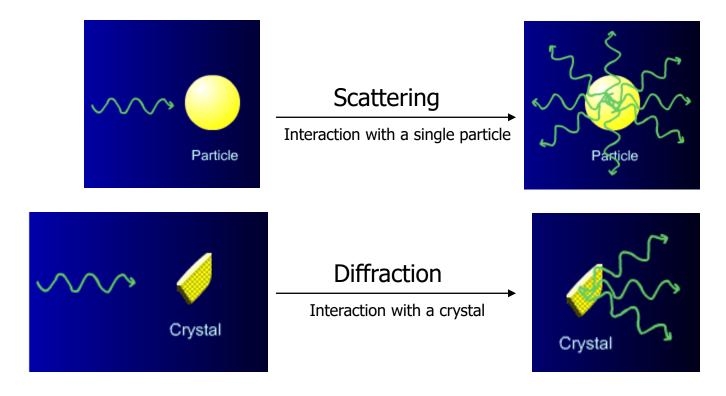
Al₂O₃: Hexagonal

MgO: NaCl type



Diffraction

 A diffracted beam may be defined as a beam composed of a large number of scattered rays mutually reinforcing each other

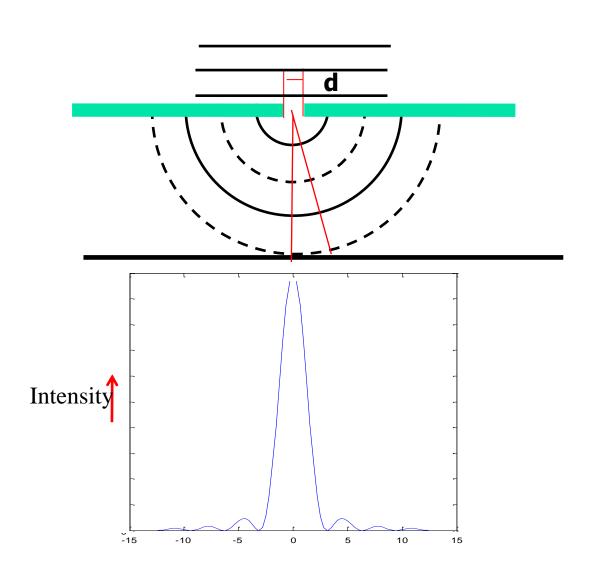


Scattering Modes

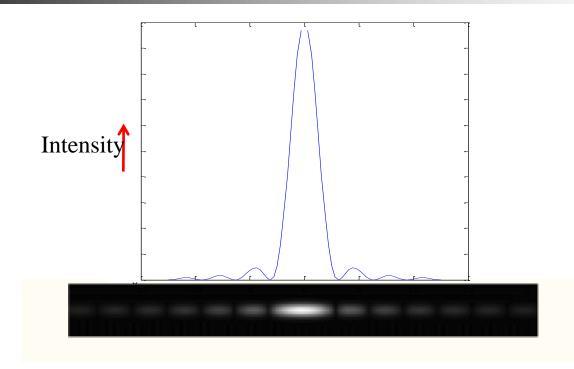
- Random arrangement of atoms in space gives rise to scattering in all directions: weak effect and intensities add
- By atoms arranged periodically in space
 - In a few specific directions satisfying Bragg's law: strong intensities of the scattered beam: Diffraction
 - No scattering along directions not satisfying Bragg's law



Diffraction of light through an aperture







Minima

Maxima

$$\frac{\sin\theta}{\lambda} = \frac{n}{a}$$

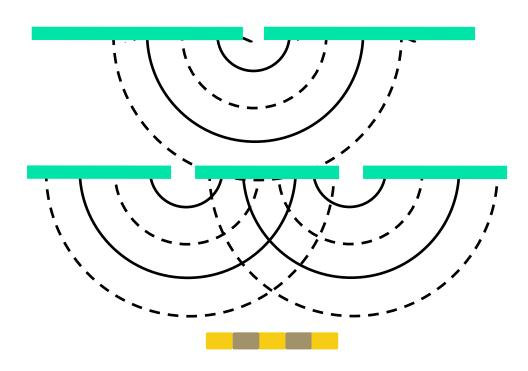
$$n = 0, 1,...$$

$$\frac{\sin \theta}{\lambda} = \frac{2n+1}{2a}$$

$$n = 1, 2,...$$



Young's Double slit experiment



$$d \sin\theta = m\lambda, m = 1,2,3....$$

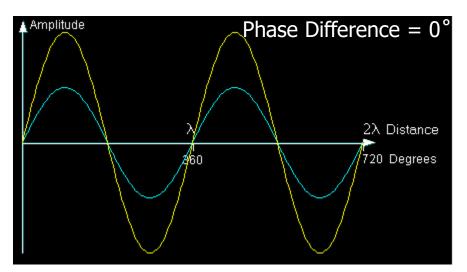
Constructive Interference

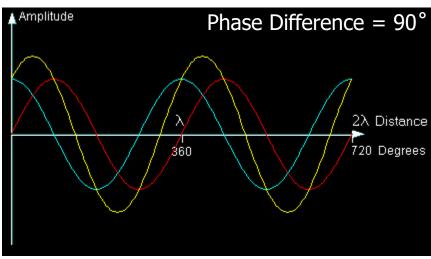
$$d \sin\theta = (m+1/2)\lambda, m = 1,2,3....$$

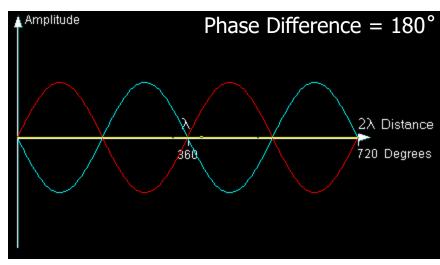
Destructive Interference



Interference









Bragg's Law

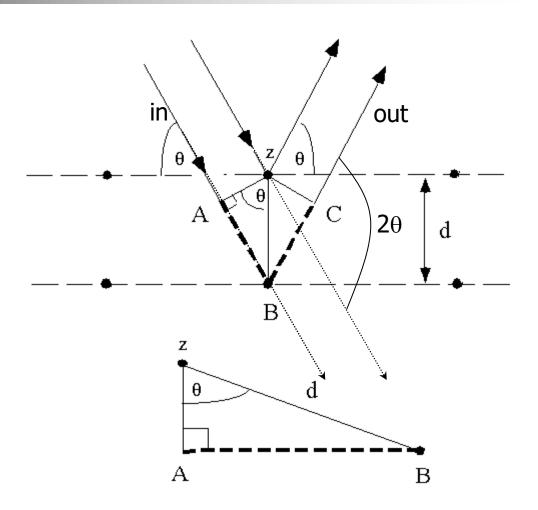
 $n\lambda = 2d.\sin\theta$

n: Order of reflection

d: Plane spacing

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

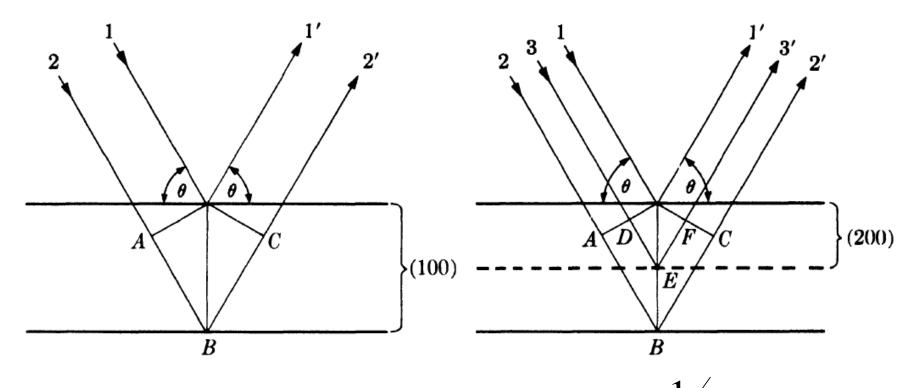
θ: Bragg Angle



Path difference must be integral multiples of the wavelength $\theta_{in} = \theta_{out}$



Braggs Law



$$d = \frac{n\lambda}{2\sin\theta}$$

$$\sin \theta = \frac{1}{2} \frac{d}{\lambda}$$



Geometry of Bragg's law

- > The incident beam, the normal to the reflection plane, and the diffracted beam are always co-planar.
- > The angle between the diffracted beam and the transmitted beam is always 2θ (usually measured).
- Sin θ cannot be more than unity; this requires $n\lambda < 2d$, for n=1, $\lambda < 2d$

λ should be less than twice the d spacing we want to study



Order of reflection

- ► Rewrite Bragg's law λ =2 sin θ d/n
- A reflection of any order as a first order reflection from planes, real or fictitious, spaced at a distance 1/n of the previous spacing
- \rightarrow Set d' = d/n

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

An nth order reflection from (hkl) planes of spacing d may be considered as a first order reflection from the (nh nk nl) plane of spacing d' = d/n

*The term reflection is only notional due to symmetry between incoming and outgoing beam w.r.t. plane normal, otherwise we are only talking of diffraction.



Reciprocal lattice vectors

➤ Used to describe Fourier analysis of electron concentration of the diffracted pattern.

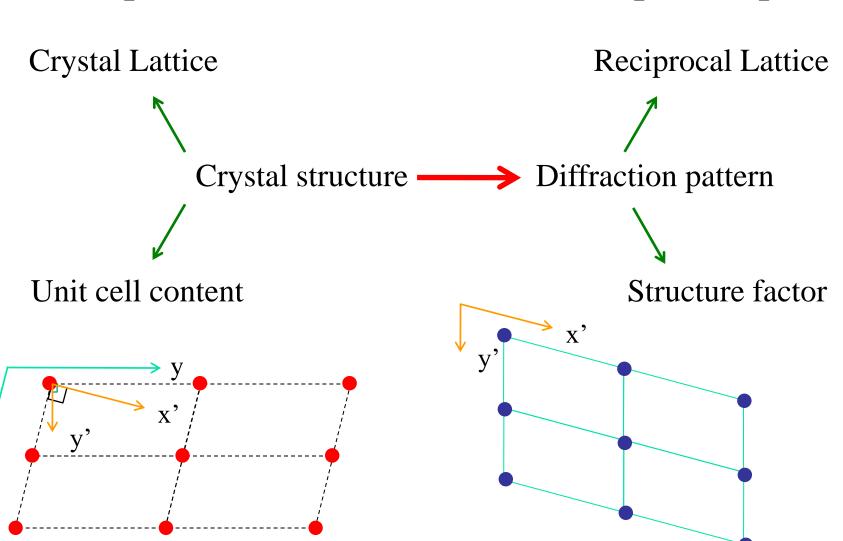
Every crystal has associated with it a crystal lattice and a reciprocal lattice.

A diffraction pattern of a crystal is the map of reciprocal lattice of the crystal.



Real space

Reciprocal space





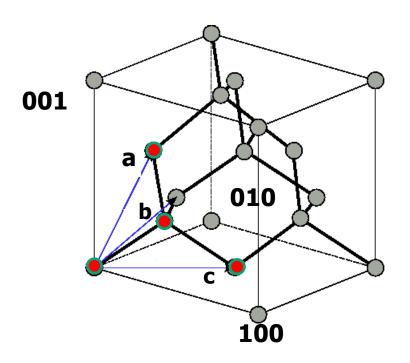
Reciprocal space

$$a^* = \frac{b \times c}{a \bullet (b \times c)}$$

$$b^* = \frac{c \times a}{a \bullet (b \times c)}$$

$$c^* = \frac{a \times b}{a \bullet (b \times c)}$$

Reciprocal lattice of FCC is BCC and vice versa





Structure Factor

$$F_{hkl} = \sum_{1}^{N} f_n e^{2\pi i (hu_n + kv_n + lw_n)}$$
 Intensity of the diffracted beam α |F|²

- h,k,/: indices of the diffraction plane under consideration
- $-u_{\nu}v_{\nu}w$: co-ordinates of the atoms in the lattice
- N: number of atoms
- $-f_n$: scattering factor of a particular type of atom

Bravais Lattice	Reflections possibly present	Reflections necessarily absent
Simple	All	None
Body Centered	(h+k+l): Even	(h+k+l): Odd
Face Centered	h, k, and l unmixed i.e. all odd or all even	h, k, and l: mixed

Examples of Structure Factor Calculations BCC lattice

In a **BCC lattice**, there are 2 atoms per cubic unit cell located at (000) & $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$. The structure factor is then:

$$S_G = \left[1 + e^{-\pi i \left(v_1 + v_2 + v_3\right)}\right] f$$

This structure factor has its <u>Maximum</u>, $S_G = 2f$ when <u>the sum of the indices is even</u>. That is when:

$$v_1 + v_2 + v_3 = 2n$$
 (n = integer)

This structure factor <u>Vanishes</u>, $S_G = 0$ when <u>the</u> <u>sum of the indices is odd</u>. That is when:

$$v_1 + v_2 + v_3 = 2n + 1$$
 (n = integer)

Group: Find the structure factor for FCC.

Four atom basis:
$$r = (0,0,0)$$
, $r = (\frac{1}{2},\frac{1}{2},0)$, $r = (\frac{1}{2},0,\frac{1}{2})$ & $r = (0,\frac{1}{2},\frac{1}{2})$

$$S_{hkl} \ \mathbf{f} \left\{ \mathbf{l} + \exp \left[-\pi \mathbf{i} \left(\mathbf{h} + \mathbf{k} \right) \right] + \exp \left[-\pi \mathbf{i} \left(\mathbf{k} + \mathbf{l} \right) \right] + \exp \left[-\pi \mathbf{i} \left(\mathbf{h} + \mathbf{l} \right) \right] \right\}$$

So:

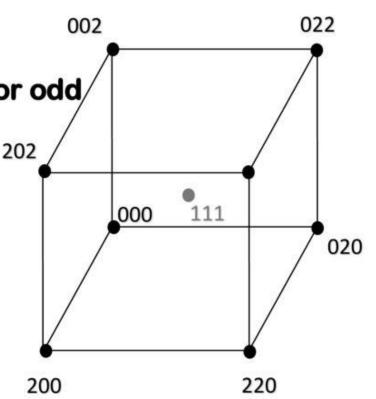
 S_{hkl} =4f if h,k,l all even or odd

 S_{hkl} =0 if h,k,l are mixed even or odd

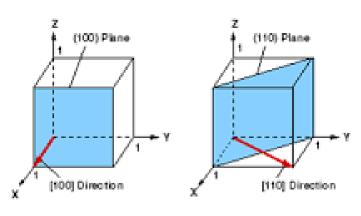
Allowed low order reflections are: 111, 200, 220, 311, 222, 400, 331, 310

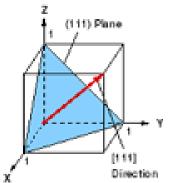
Forbidden reflections:

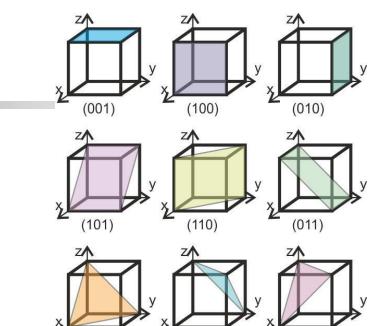
100, 110, 210, 211

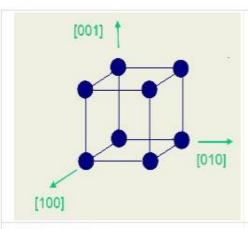


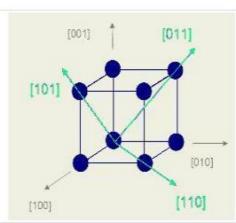


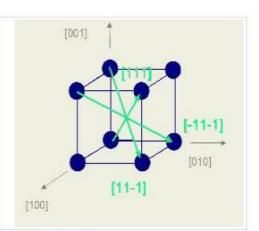










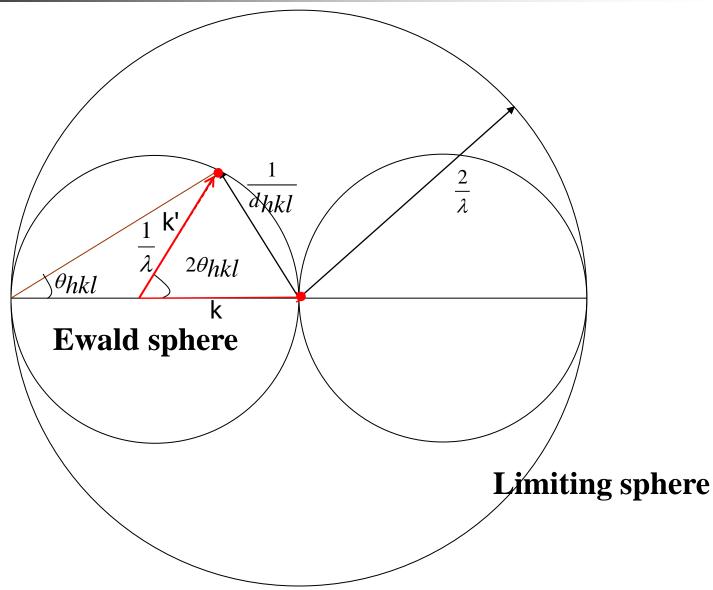


type: <100> Equivalent directions: [100],[010],[001]

type: <110>
Equivalent directions: [110], [011], [101], [-1-10], [-1-1], [-10-1], [-110], [0-11], [1-10], [01-1], [10-1]

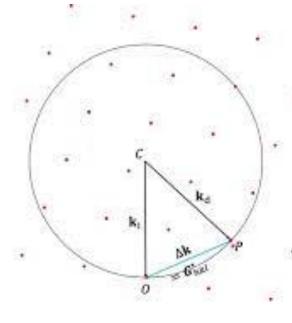
type: <111> Equivalent directions: [111], [-111], [1-11], [11-1]







Ewald sphere



Elastic Scattering

$$|\mathbf{k_d}| = |\mathbf{k_l}| = \frac{1}{\lambda}$$

Bragg's law in reciprocal space

$$\Delta \mathbf{k} \equiv \mathbf{k}_{d} - \mathbf{k}_{i}$$

$$= G_{hkl}^{*}$$

$$= ha_{1}^{*} + ka_{2}^{*} + la_{3}^{*}$$

rotation axis rotation axis of of crystal and reciprocal lattice axis of film $+ la_3^*$ sphere of reflection $\frac{1}{\lambda} = \frac{1}{100} = \frac$

Derive Bragg's Law starting from Diffraction Conditions.

Diffraction Conditions

$$2k \cdot G = G^2$$

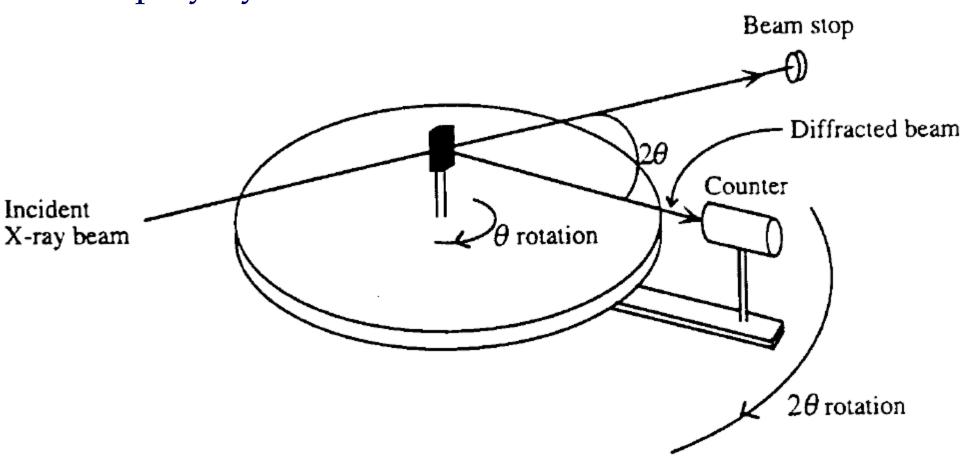
Bragg's Law

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



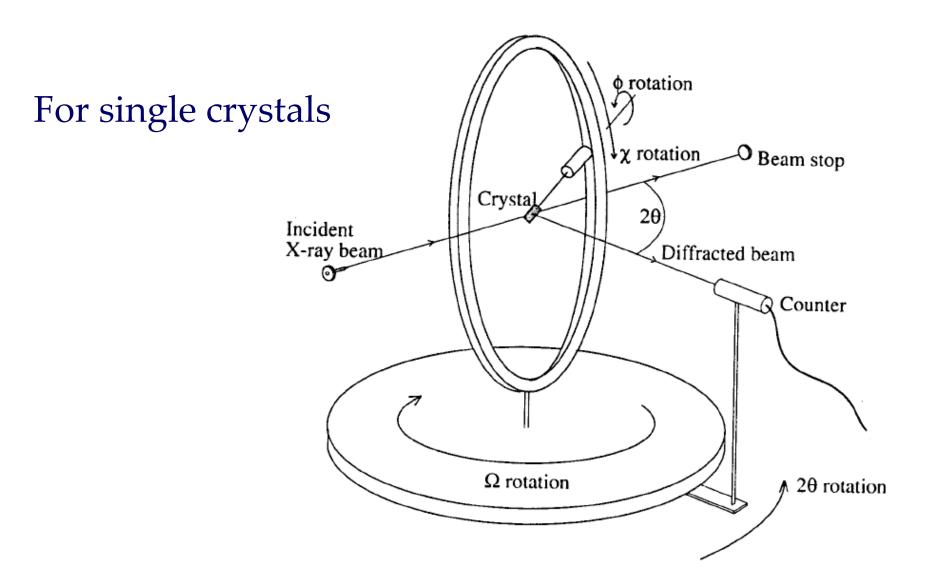
Two Circle Diffractometer

For polycrystalline Materials



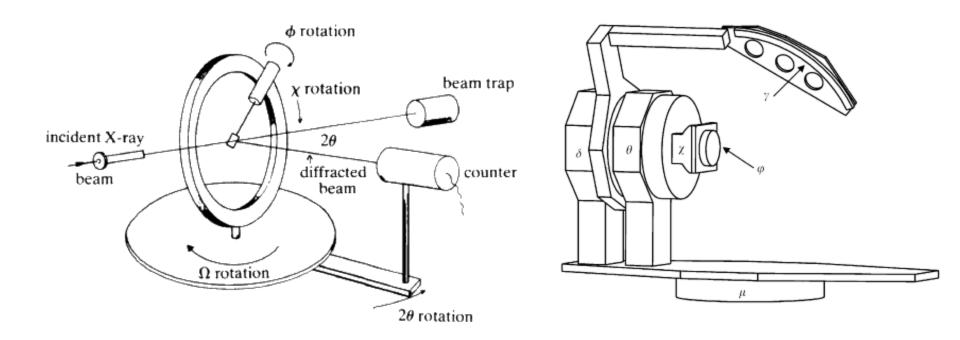


Four Circle Diffractometer





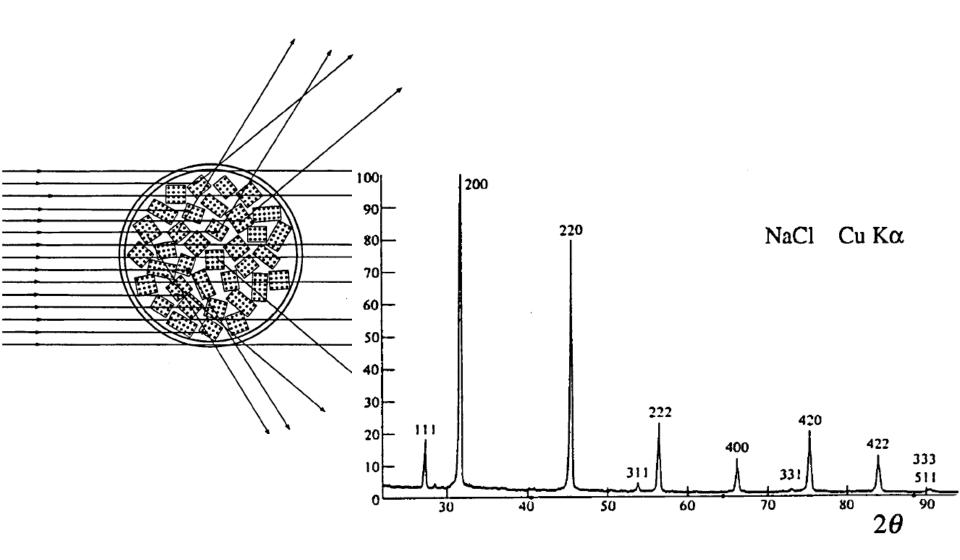
- \geq 2 Circle diffratometer \Rightarrow 20 and ω
- \triangleright 3 and 4 circle diffractometer \rightarrow 20, ω , φ , χ
- \triangleright 6 circle diffractometer \rightarrow θ , φ , χ and δ , γ , μ



www.serc.carleton.edu/

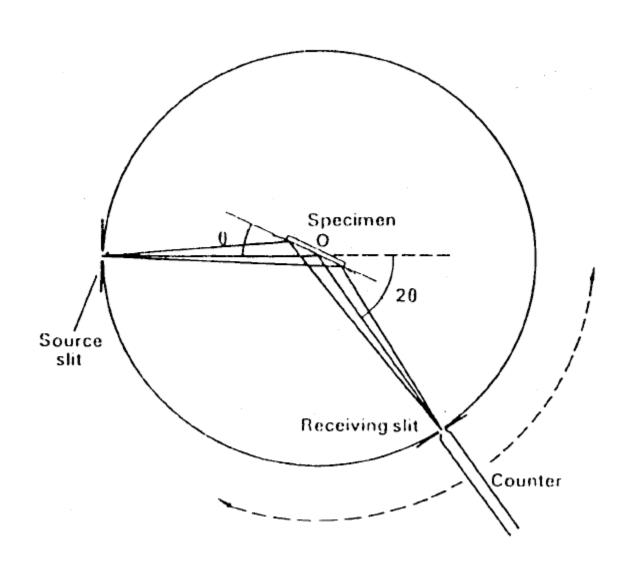


NaCl crystals in a tube facing X-ray beam



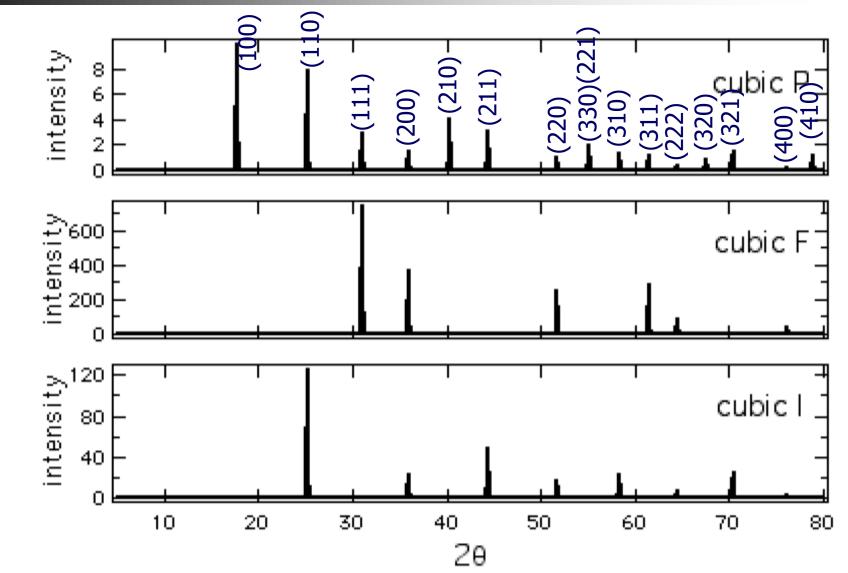


Powder Diffractometer





Calculated Patterns for a Cubic Crystal





Structure Factor

$$F_{hkl} = \sum_{1}^{N} f_n e^{2\pi i (hu_n + kv_n + lw_n)}$$
 Intensity of the diffracted beam α |F|²

- h,k,/: indices of the diffraction plane under consideration
- $-u_{\nu}v_{\nu}w$: co-ordinates of the atoms in the lattice
- N: number of atoms
- $-f_n$: scattering factor of a particular type of atom

Bravais Lattice	Reflections possibly present	Reflections necessarily absent
Simple	All	None
Body Centered	(h+k+l): Even	(h+k+l): Odd
Face Centered	h, k, and l unmixed i.e. all odd or all even	h, k, and l: mixed



Systematic Absences

Permitted Reflections

Simple Cubic	(100), (110), (111), (200), (210), (211), (220), (300), (221)
BCC	(110), (200), (211), (220), (310), (222)
FCC	(111), (200), (220), (311)

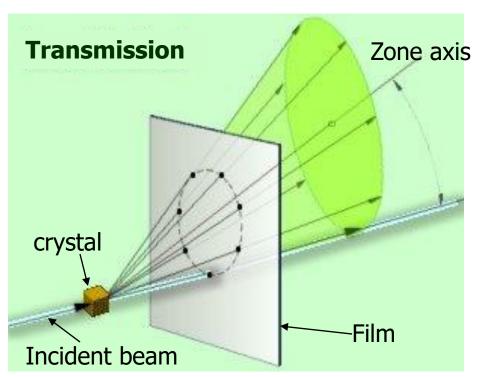


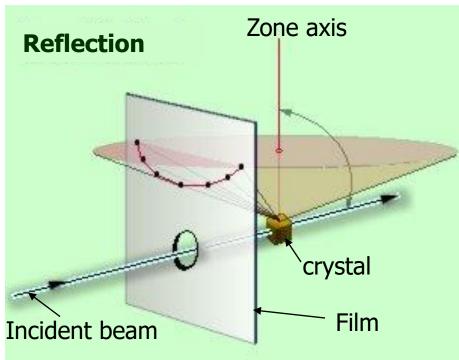
Diffraction Methods

Method	Wavelength	Angle	Specimen
Laue	Variable	Fixed	Single Crystal
Rotating Crystal	Fixed	Variable (in part)	Single Crystal
Powder	Fixed	Variable	Powder



Laue Method

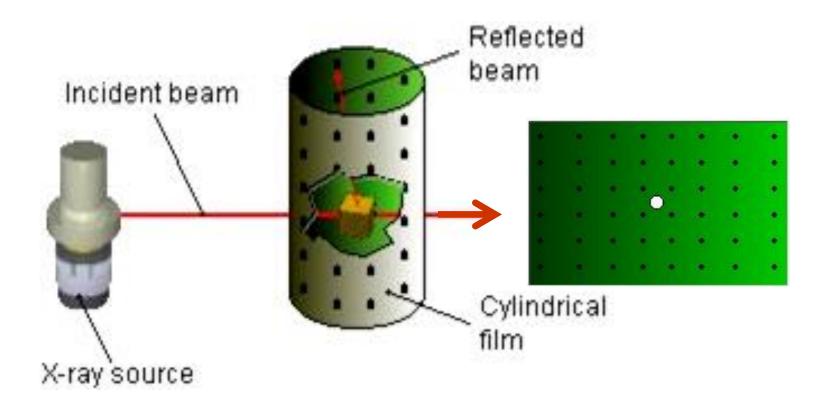




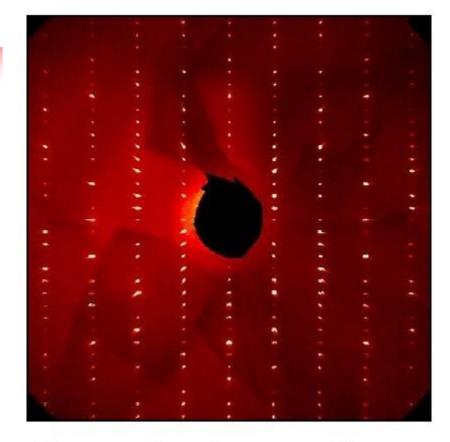
- Uses Single crystal
- Uses White Radiation
- Used for determining crystal orientation and quality



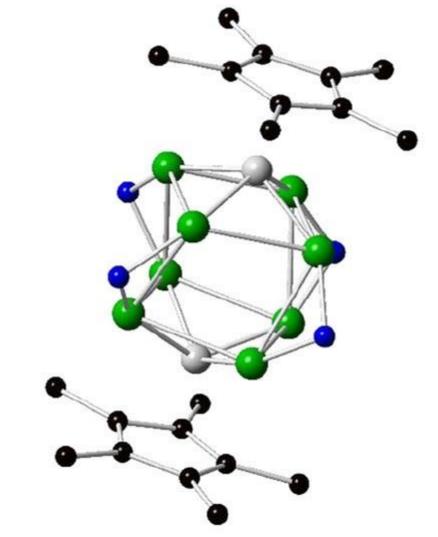
Rotating Crystal Method



Determination of unknown crystal structures



Precession image of a diffraction pattern

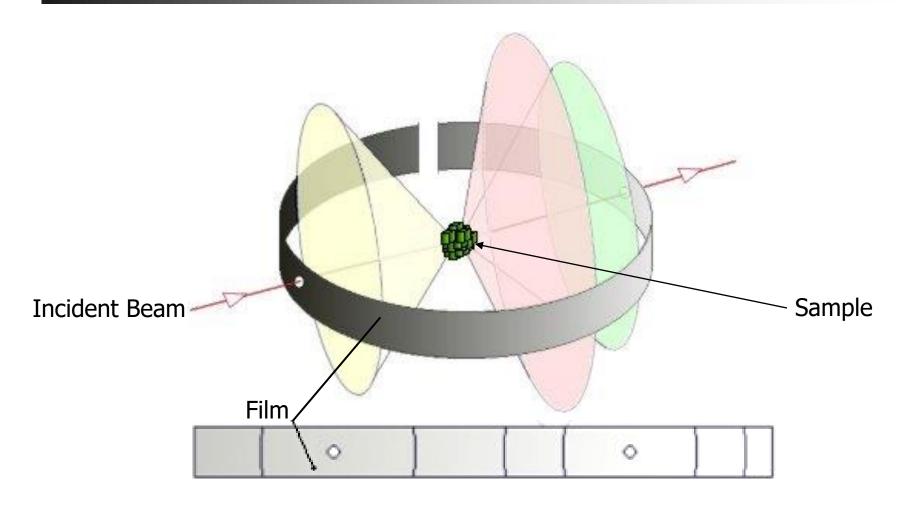


Solved crystal structure:

 C (black), Al (blue), Ti (grey) and F (green)



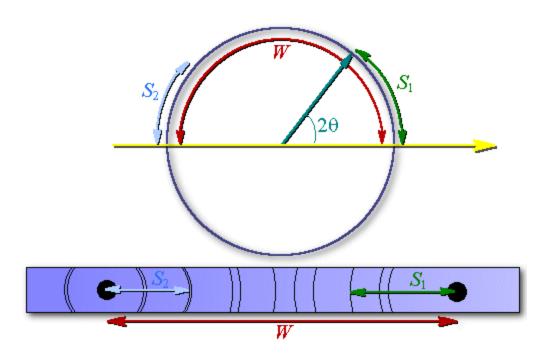
Powder Method



 Useful for determining lattice parameters with high precision and for identification of phases



Indexing a powder pattern



$$\theta = \frac{\pi S_1}{2W}$$
 (for front reflections) or

$$\theta = \frac{\pi}{2} \left(1 - \frac{S_2}{W} \right) \text{ (for back reflections)}$$

Bragg's Law $n\lambda = 2d \sin\theta$

For cubic crystals

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

which gives rise to

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

which is a constant



	Simple Cubic						
S ₁ (mm)	θ(°)	sin²θ	h ² +k ² +l ²	$\sin^2\theta/h^2+k^2+l^2$			
38	19.0	0.11	1	0.11			
45	22.5	0.15	2	0.75			
66	33.0	0.30	3	0.10			
78	39.0	0.40	4	0.10	Not Cimple		
83	41.5	0.45	5	0.09	Not Simple Cubic		
97	49.5	0.58	6	0.097			
113	56.5	0.70	8	0.0925			
118	59.0	0.73	9	0.081			
139	69.5	0.88	10	0.088			
168	84.9	0.99	11	0.09			
		•		Not Constant			



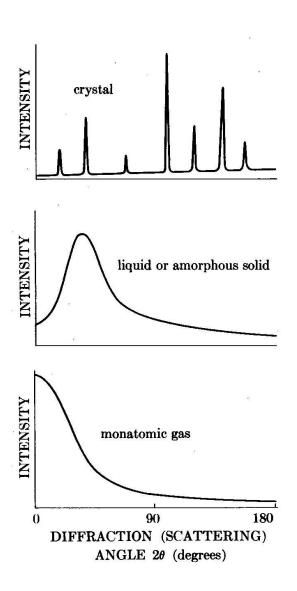
			BCC		
S ₁ (mm)	θ(°)	$\sin^2\theta$	h ² +k ² +l ²	$\sin^2\theta/h^2+k^2+l^2$	
38	19.0	0.11	2	0.055	
45	22.5	0.15	4	0.038	
66	33.0	0.30	6	0.050	
78	39.0	0.40	8	0.050	Not BCC
83	41.5	0.45	10	0.045	Not bee
97	49.5	0.58	12	0.048	
113	56.5	0.70	14	0.050	
118	59.0	0.73	16	0.046	
139	69.5	0.88	18	0.049	
168	84.9	0.99	20	0.050	
				Not Constant	



	FCC; wavelength=1.54056Å						
S ₁ (mm)	θ(°)	sin ² θ	h ² +k ² +l ²	$\sin^2\theta/h^2+k^2+l^2$	Lattice Parameter, a (Å)		
38	19.0	0.11	3	0.037	4.023		
45	22.5	0.15	4	0.038	3.978		
66	33.0	0.30	8	0.038	3.978		
78	39.0	0.40	11	0.036	4.039		
83	41.5	0.45	12	0.038	3.978		
97	49.5	0.58	16	0.036	4.046		
113	56.5	0.70	19	0.037	4.023		
118	59.0	0.73	20	0.037	4.023		
139	69.5	0.88	24	0.037	4.023		
168	84.9	0.99	27	0.037	4.023		
				Constant; so i	t is FCC		



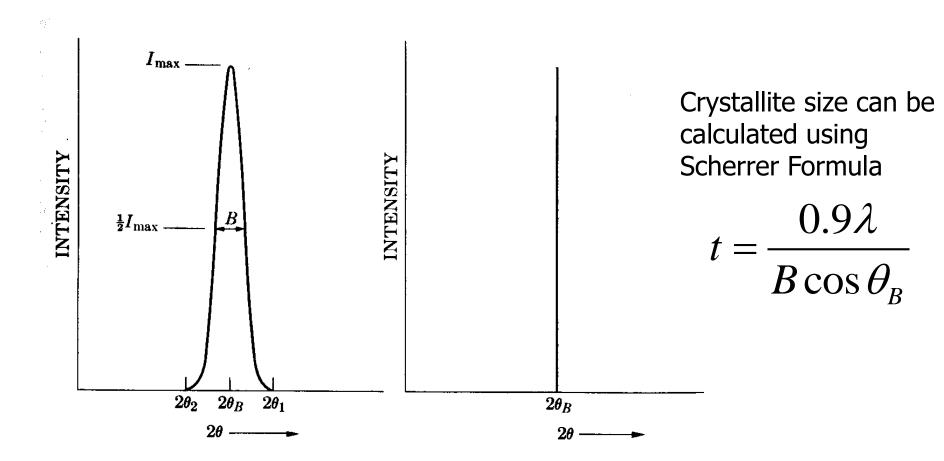
Diffraction from a variety of materials



(From "Elements of X-ray Diffraction", B.D. Cullity, Addison Wesley)



Reality



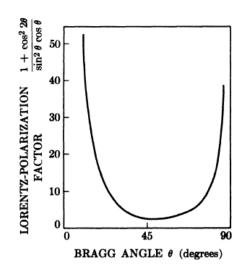
Instrumental broadening must be subtracted

(From "Elements of X-ray Diffraction", B.D. Cullity, Addison Wesley)



Intensity of diffracted beam

- polarization factor
- structure factor (F²)
- multiplicity factor
- Lorentz factor
- absorption factor
- temperature factor



For most materials the peaks and their intensity are documented

- > JCPDS
- > ICDD

4

Name and formula

Reference code: 00-001-1260

PDF index name: Nickel Empirical formula: Ni Chemical formula: Ni

Crystallographic parameters

Crystal system: Cubic Space group: Fm-3m

Space group number: 225

a (Å): 3.5175 b (Å): 3.5175

c (Å): 3.5175

Alpha (°): 90.0000 Beta (°): 90.0000

Gamma (°): 90.0000

Measured density (g/cm³): 8.90 Volume of cell (10⁶ pm³): 43.52

Z: 4.00

RIR: -

Status, subfiles and quality

Status: Marked as deleted by ICDD

Subfiles: Inorganic Quality: Blank (B)

References

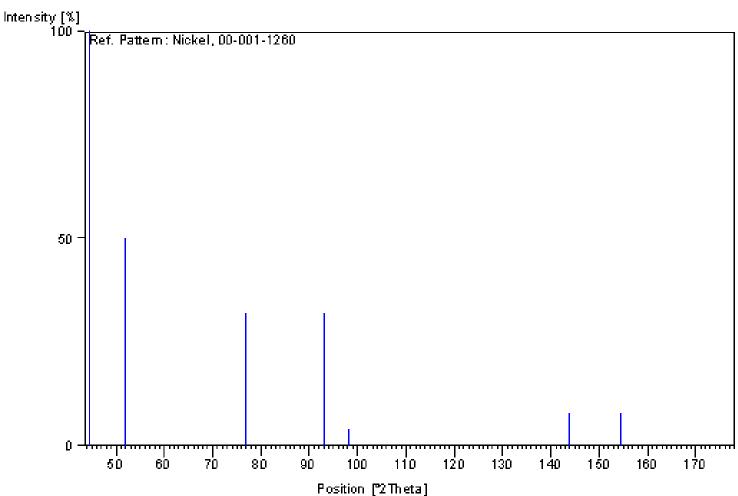
Primary reference: Hanawalt et al., *Anal. Chem.*, 10, 475, (1938)

Optical data: Data on Chem. for Cer. Use, Natl. Res. Council Bull. 107

Unit cell: The Structure of Crystals, 1st Ed.



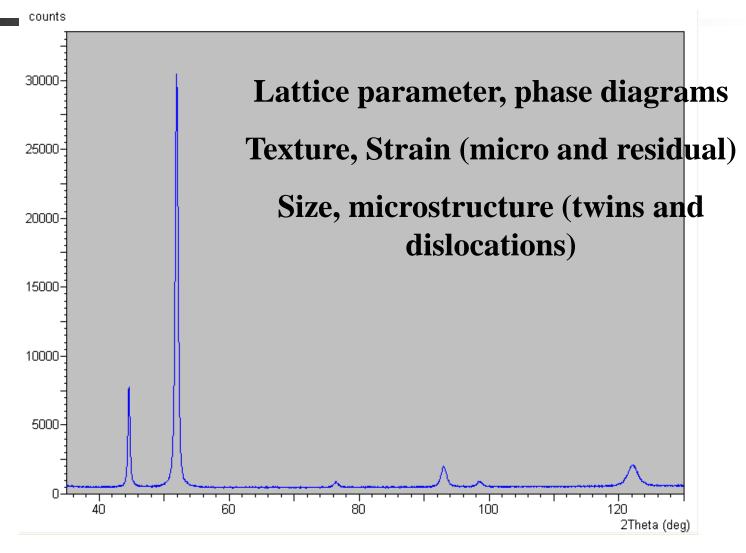
Stick pattern from JCPDS



http://ww1.iucr.org/cww-top/crystal.index.html



Actual Pattern



Bulk electrodeposited nanocrystalline nickel



Powder X-ray diffraction

is essentially a misnomer and should be replaced by

Polycrystalline X-ray diffraction

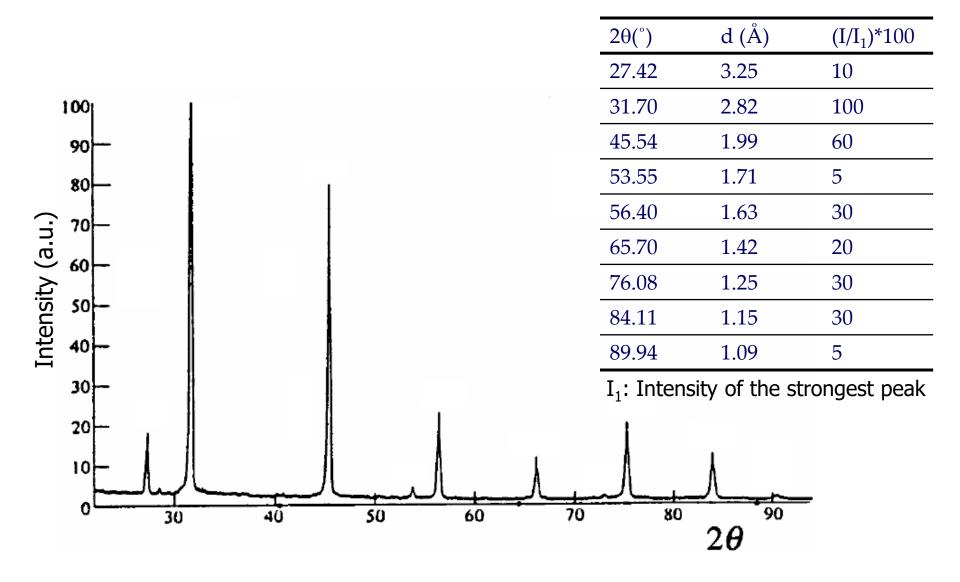


Information in a Diffraction Pattern

- Phase Identification
- Crystal Size
- Crystal Quality
- Texture (to some extent)
- Crystal Structure



Analysis of Single Phase



-

Procedure

- Note first three strongest peaks at d_1 , d_2 , and d_3
- In the present case: d_1 : 2.82; d_2 : 1.99 and d_3 : 1.63 Å
- Search JCPDS manual to find the d group belonging to the strongest line: between 2.84-2.80 Å
- There are 17 substances with approximately similar d₂ but only 4 have d₁: 2.82 Å
- Out of these, only NaCl has d₃: 1.63 Å
- It is NaCl......Hurrah

Specimen and Intensities	Substance	File Number
$2.82_9 1.99_9 2.26_x 1.61_9 1.51_9 1.49_9 3.57_8 2.66_8$	(ErSe) ₂ Q	19-443
$2.82_{x} 1.99_{6} 1.63_{2} 3.26_{1} 1.26_{1} 1.15_{1} 1.41_{1} 0.89_{1}$	NaCl	5-628
$2.82_4 1.99_4 1.54_x 1.20_4 1.19_4 2.44_3 5.62_2 4.89_2$	$(NH_4)_2WO_2Cl_4$	22-65
$2.82_{x} 1.99_{8} 1.26_{3} 1.63_{2} 1.15_{2} 0.94_{1} 0.89_{1} 1.41_{1}$	(BePd)2C	18-225

Caution: It could be much more tricky if the sample is oriented or textured or your goniometer is not calibrated



Presence of Multiple phases

- More Complex
- Several permutations combinations possible
- e.g. d_1 ; d_2 ; and d_3 , the first three strongest lines show several alternatives
- Then take any of the two lines together and match
- It turns out that 1st and 3rd strongest lies belong to Cu and then all other peaks for Cu can be separated out
- Now separate the remaining lines and normalize the intensities
- Look for first three lines and it turns out that the phase is Cu₂O
- If more phases, more pain to solve





d (Å)		I/I_1
3.01		5
2.47		72
2.13		28
2.09	*	100
1.80	*	52
1.50		20
1.29		9
1.28	*	18
1.22		4
1.08	*	20
1.04	*	3
0.98		5
0.91		4
0.83	*	8
0.81	*	10

Pattern for Cu				
d (Å)	I/I ₁			
2.088	100			
1.808	46			
1.278	20			
1.09	17			
1.0436	5			
0.9038	3			
0.8293	9			
0.8083	8			

Remaining Lines					
d (Å)	$\mathrm{I/I}_1$				
(A)	Observed	Normalized			
3.01	5	7			
2.47	72	100			
2.13	28	39			
1.50	20	28			
1.29	9	13			
1.22	4	6			
0.98	5	7			

Pattern of Cu ₂ O				
d (Å)	I/I ₁			
3.020	9			
2.465	100			
2.135	37			
1.743	1			
1.510	27			
1.287	17			
1.233	4			
1.0674	2			
0.9795	4			



Calculate Crystallite (grain) Size

STEP1: Open the XRD graph of the material, which is obtained from the instrument.

STEP2: Now zoom on the area for which you want to calculate the crystallite size and note down the angle at which peak is shown and peak Full Width at Half Maximum (FWHM).

STEP3: Now enter the measured Peak Position (i.e. 31.8) and peak FWHM (i.e. 0.5) in desire columns of the calculator. You should get the calculated results of the crystallite size in the "Calculated Result" field.

FWHM is used in XRD for calculating crystallite size

Scherrer equation

JI Langford and AJC Wilson, J. Appl. Cryst. 11 (1978) p102.

$$D = \frac{K\lambda}{\beta \cos \theta}$$

 $D \leq 200 nm$

D is the crystallite size (nm), average crystallite size

K Scherrer constant, 0.68 to 2.08, 0.94 for spherical crystallites with cubic symmetry

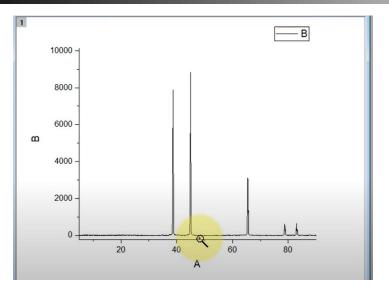
 λ is the X-ray wavelength, CuK_{α} =1.5406 Å

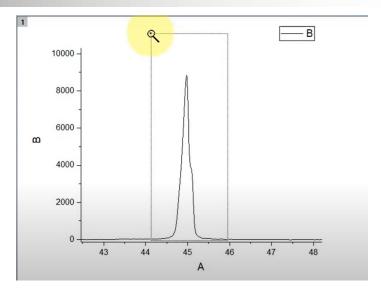
β is the line broadening at FWHM in radians

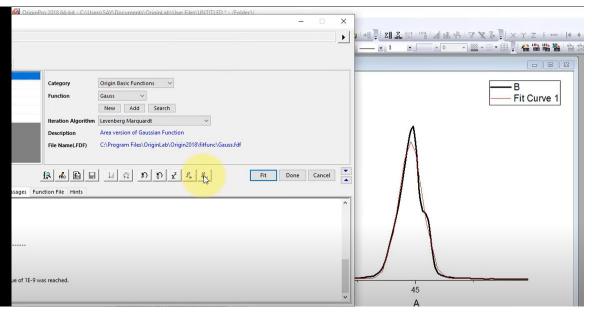
 θ is the Bragg's angle in degrees, half of 2θ



Calculate Crystallite (grain) Size









Calculate Crystallite (grain) Size

Not	tes -					
Inp	ut Data	•				
Pai	rameters	-				
		Value	Standard Error	t-Value	Prob> t	Dependency
	y0	38.25916	3.82119	10.01236	0	0.00632
	хс	44.9 <mark>5887</mark>	0.0015	29954.14192	0	(
	w	0.20196	0.00301	67.2081	0	0.33474
В	Α	1998.93924	25.81222	77.4416	0	0.3375
	sigma	0.10098	0.0015			
	FWHM	0.23779	0.00354			
	Height	7897.13997	101.68865			

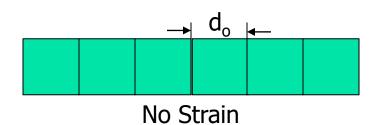
$$D = \frac{K\lambda}{\beta \cos \theta} \qquad \beta = 0.23779 \qquad 2\theta = 44.95887^{\circ}$$

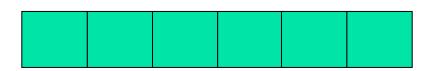
$$D = \frac{(0.94)(1.5406 \text{ Å})}{radian(0.23779)\cos(44.95887/2)}$$

$$D = \frac{1.448164 \text{ Å}}{(0.004150218)(0.924016)} = 37.76 \text{ nm}$$



Lattice Strain





Uniform Strain $\Delta\theta \alpha \Delta d \alpha$ strain



Broadeing
$$b = \Delta 2\theta = -2\frac{\Delta d}{d} \tan \theta$$

