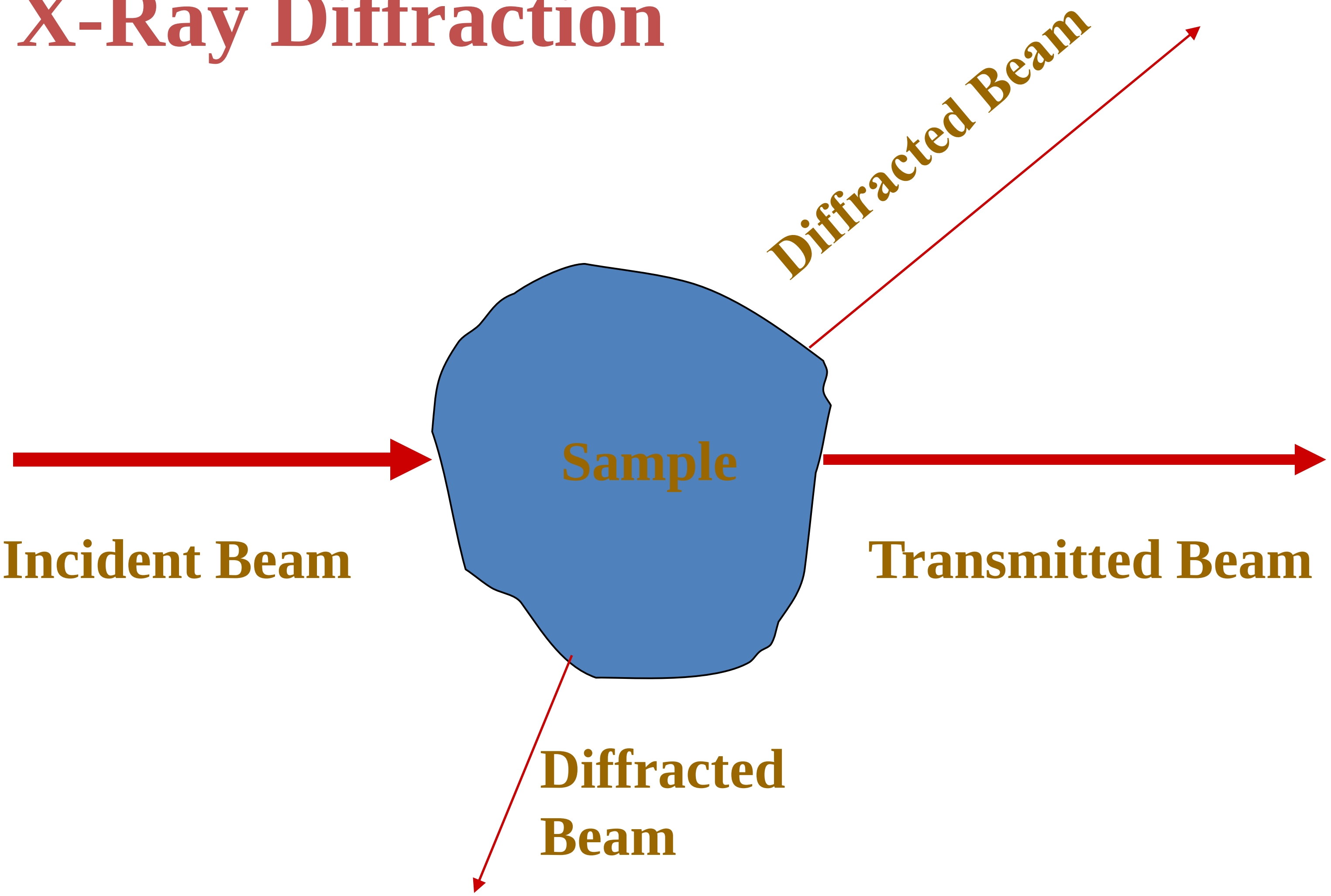
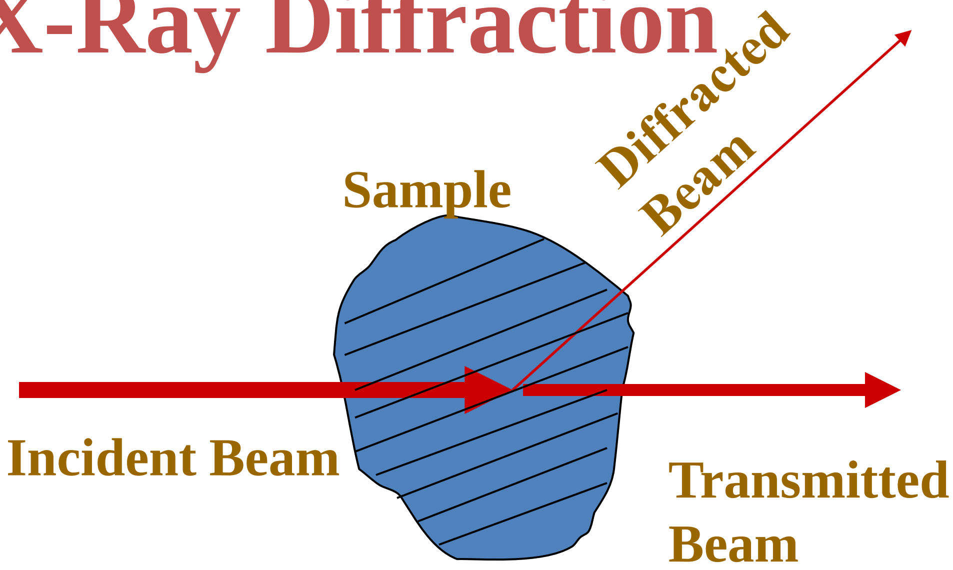
How do we determine the crystal structure?

X-Ray Diffraction



X-Ray Diffraction



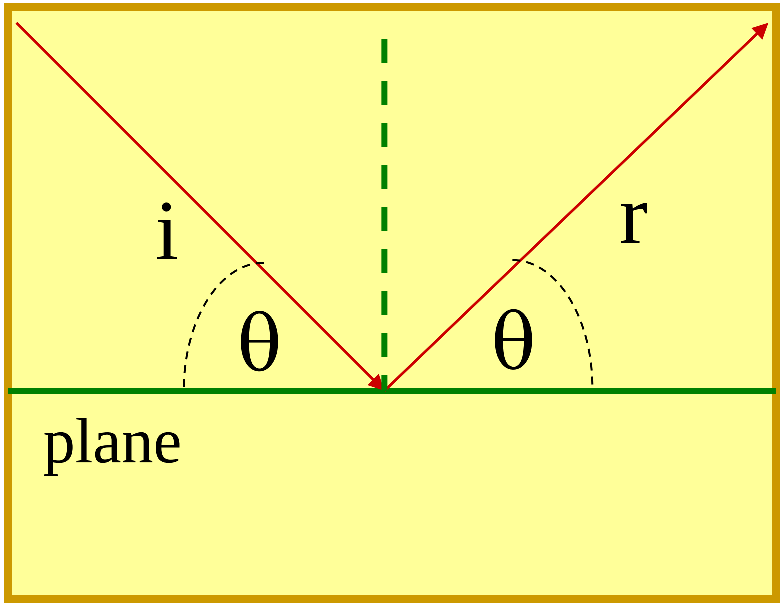
≡ Bragg Reflection

Braggs Law (Part 1): For every diffracted beam there exists a set of crystal lattice planes such that the diffracted beam appears to be specularly reflected from this set of planes.

X-Ray Diffraction

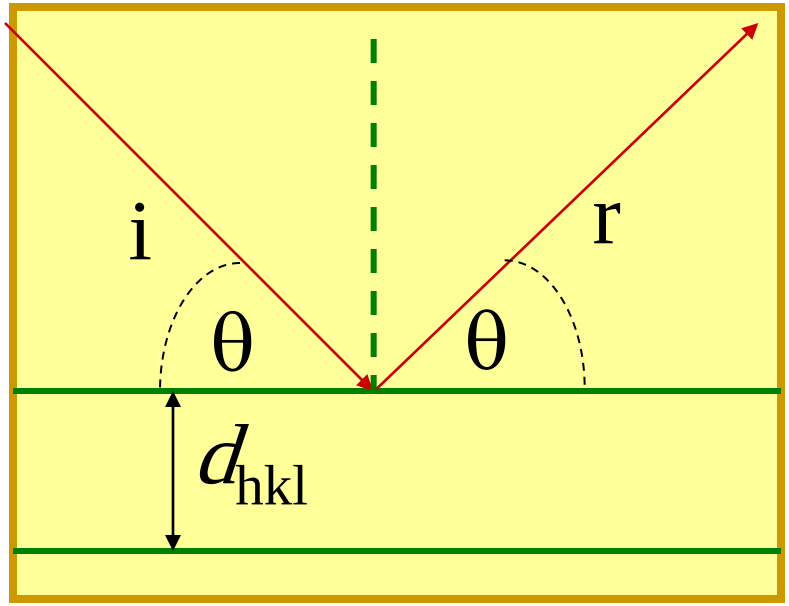
Braggs Law (Part 1): the diffracted beam appears to be **specularly** reflected from a set of crystal lattice planes.

Specular reflection:
Angle of incidence
=Angle of reflection
(both measured from the plane and not from the normal)



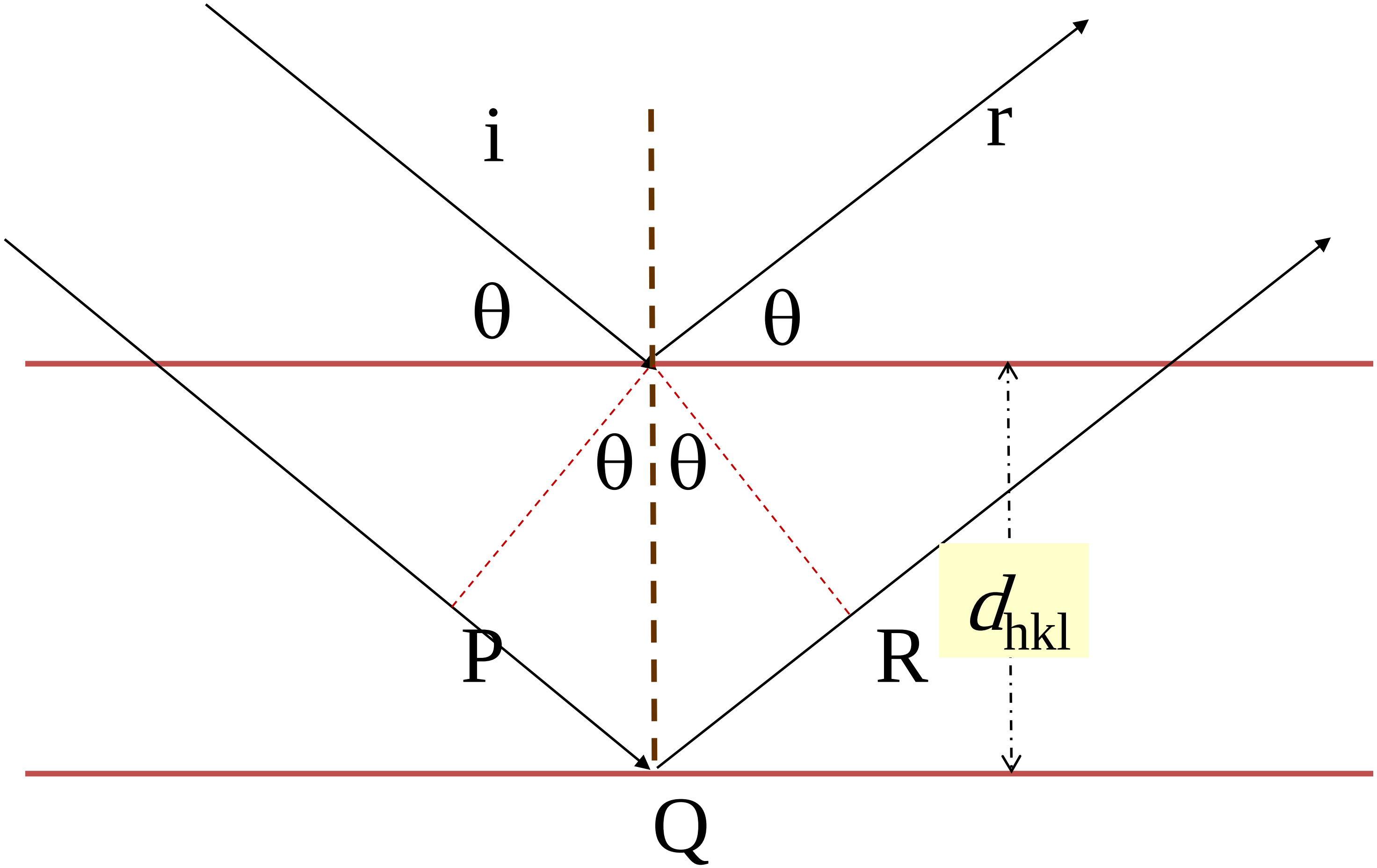
The incident beam, the reflected beam and the plane normal lie in one plane

X-Ray Diffraction

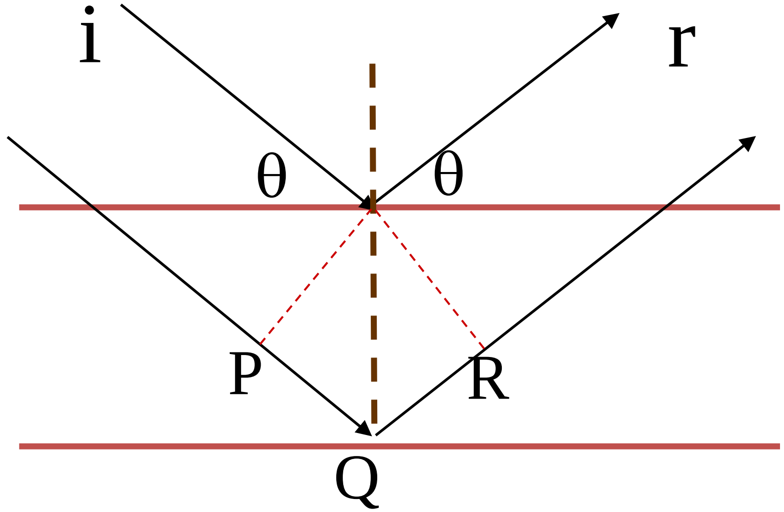


Bragg's law (Part 2):

$$n\lambda = 2d_{hkl}\sin\theta$$



Path Difference =PQ+QR= $2d_{hkl}\sin\theta$



Path Difference =PQ+QR= $2d_{hkl}\sin\theta$

Constructive inteference

$$n\lambda = 2d_{hkl}\sin\theta$$

Bragg's law

Two equivalent ways of stating Bragg's Law

$$n\lambda = 2d_{hkl}\sin\theta$$

1st Form

$$\Rightarrow \lambda = 2\frac{d_{hkl}}{n}\sin\theta$$

$$d_{nh,nk,nl} = \frac{a}{\sqrt{(nh)^2+(nk)^2+(nl)^2}} = \frac{d_{hkl}}{n}$$

$$\Rightarrow \lambda = 2d_{nhnknl}\sin\theta$$

2nd Form

Two equivalent ways of stating Bragg's Law

$$n\lambda = 2d_{hkl}\sin\theta \qquad \Rightarrow \lambda = 2d_{nhnknl}\sin\theta$$

*n*th order reflection from (*hkl*) plane $\equiv$ 1st order reflection from (*nh nk nl*) plane

e.g. a 2nd order reflection from (111) plane can be described as 1st order reflection from (222) plane

X-rays
Characteristic Radiation, K_α

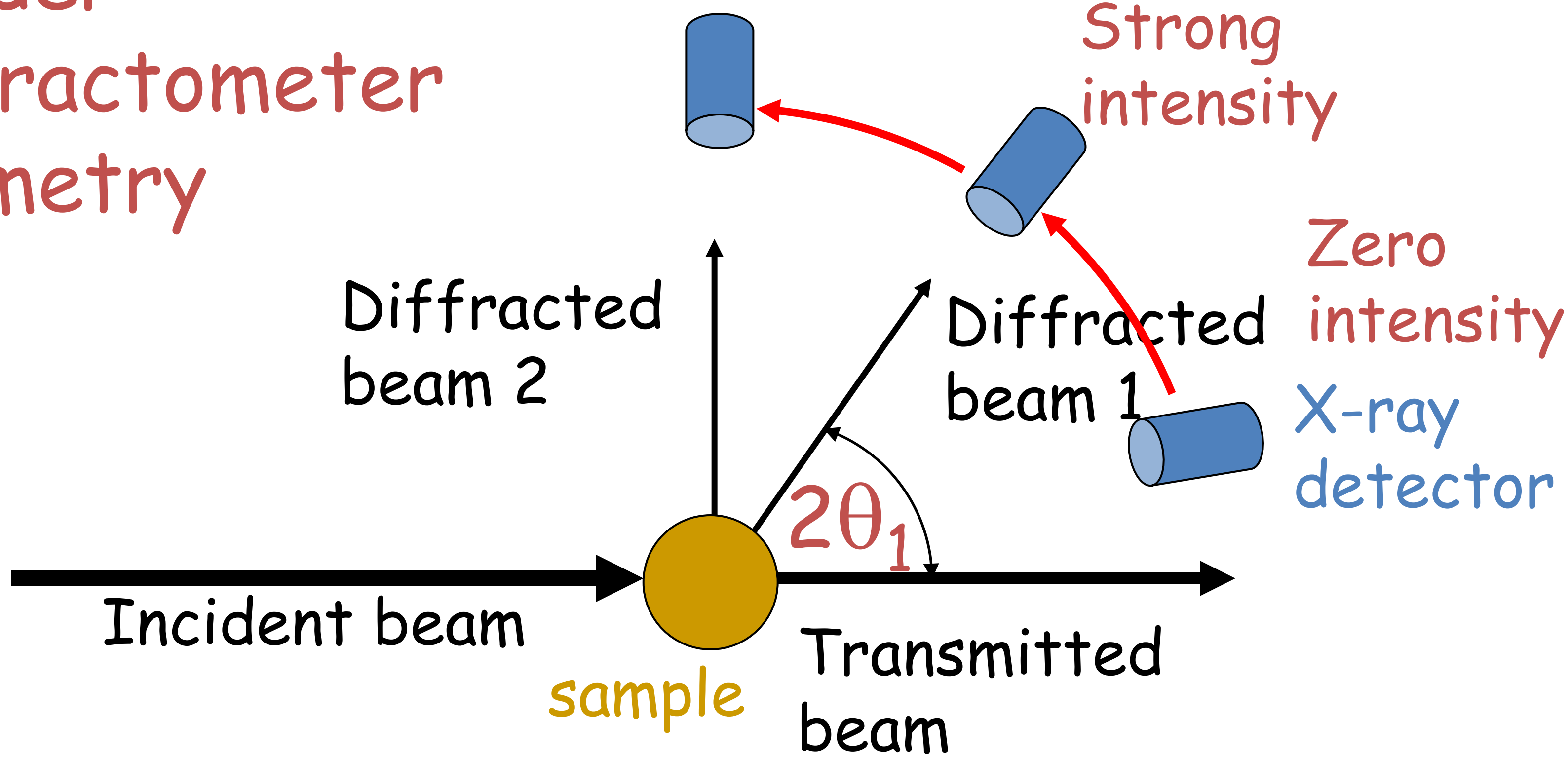
Target	*Wavelength, Å*
Mo	0.71
Cu	1.54
Co	1.79
Fe	1.94
Cr	2.29

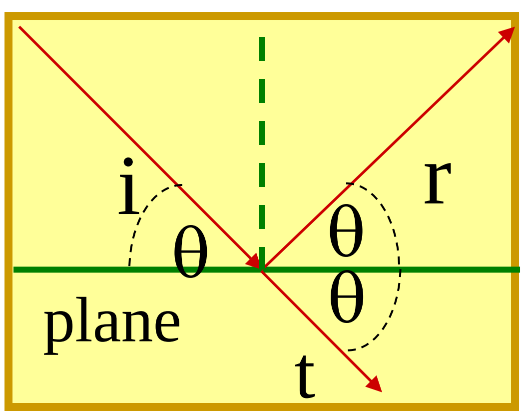
Powder Method

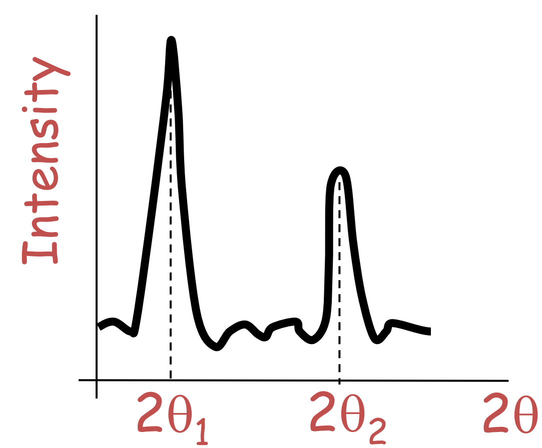
λ is fixed (K_α radiation)

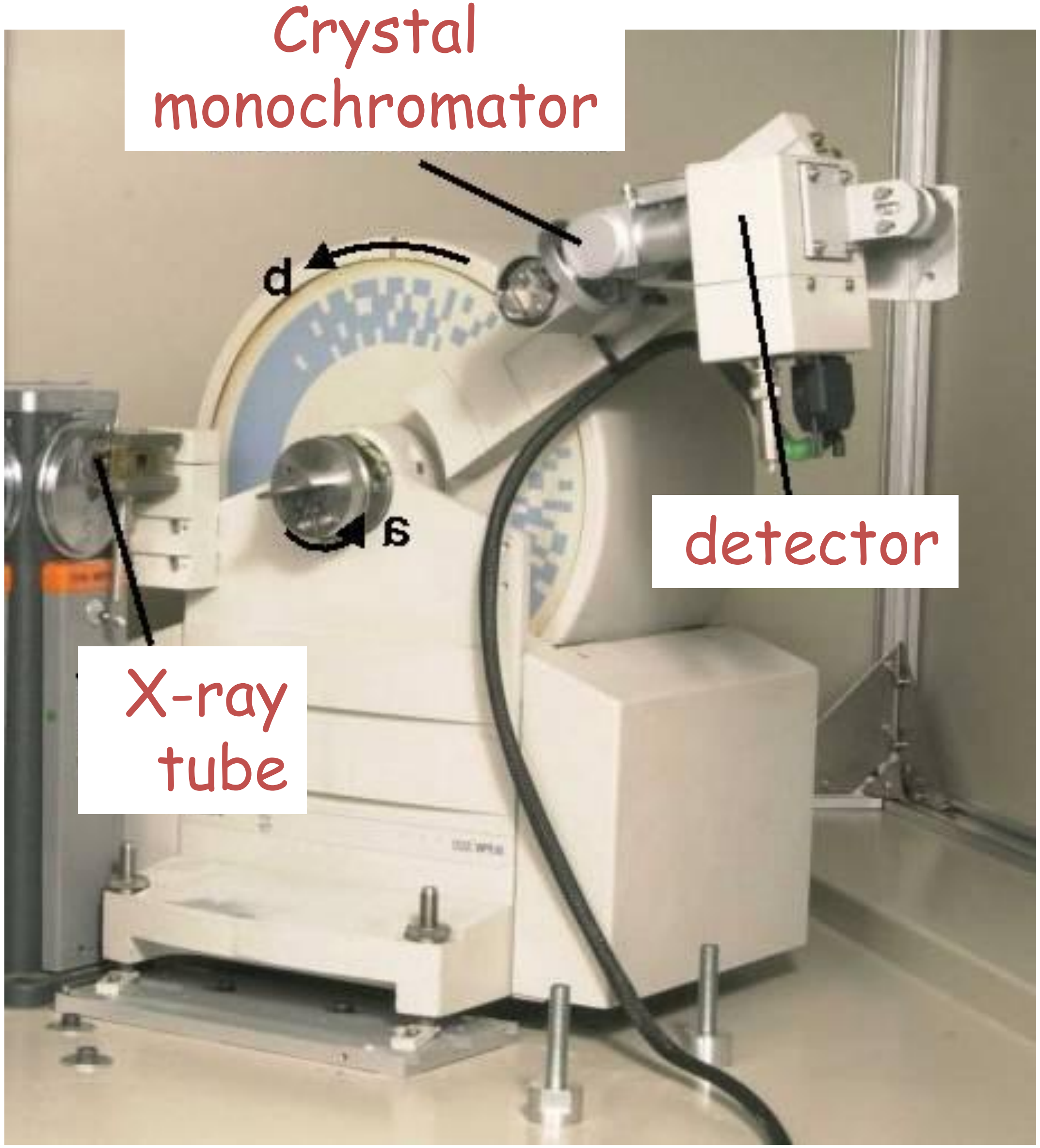
θ is variable – specimen consists of millions of powder particles – each being a crystallite and these are randomly oriented in space – amounting to the rotation of a crystal about all possible axes

Powder diffractometer geometry





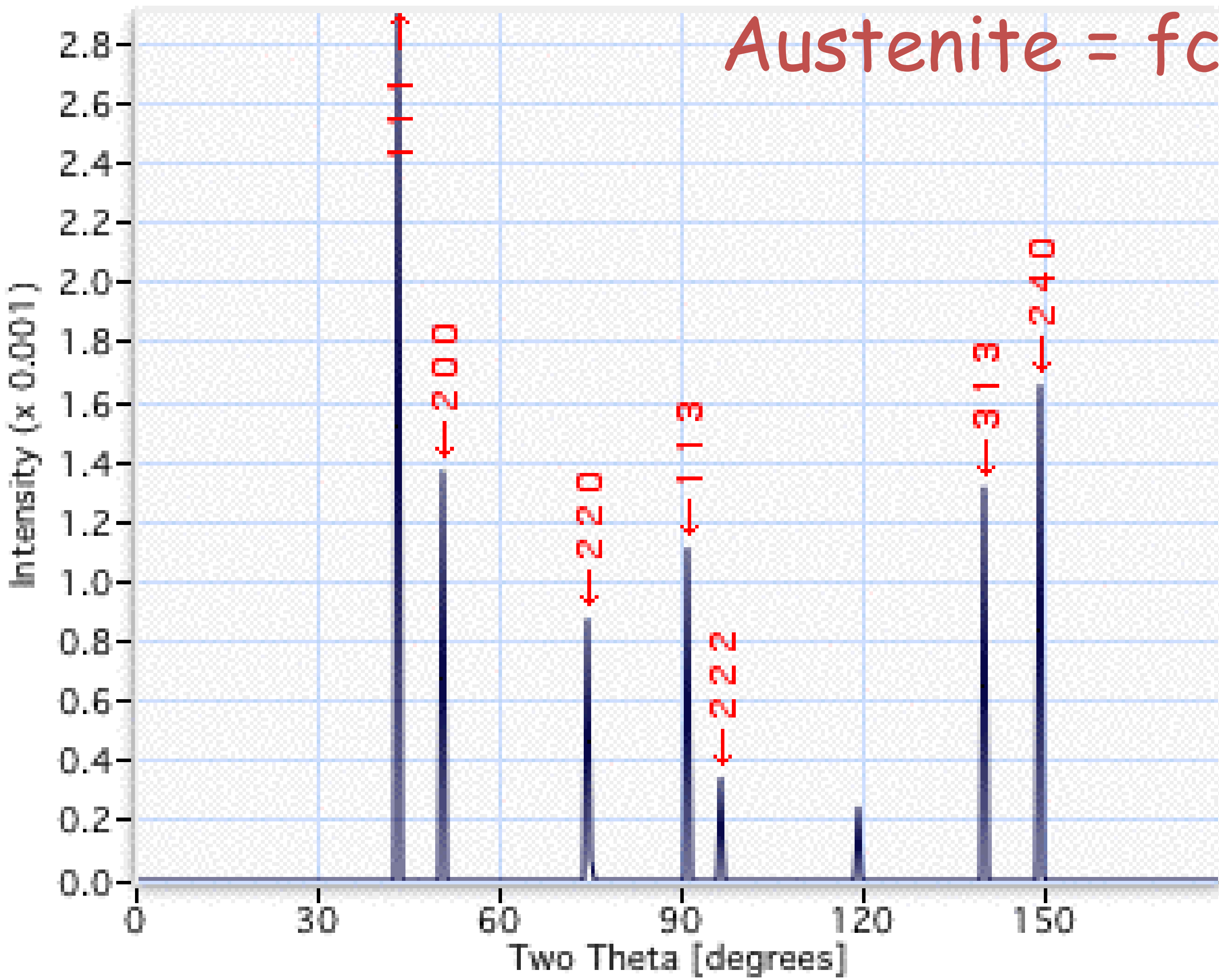


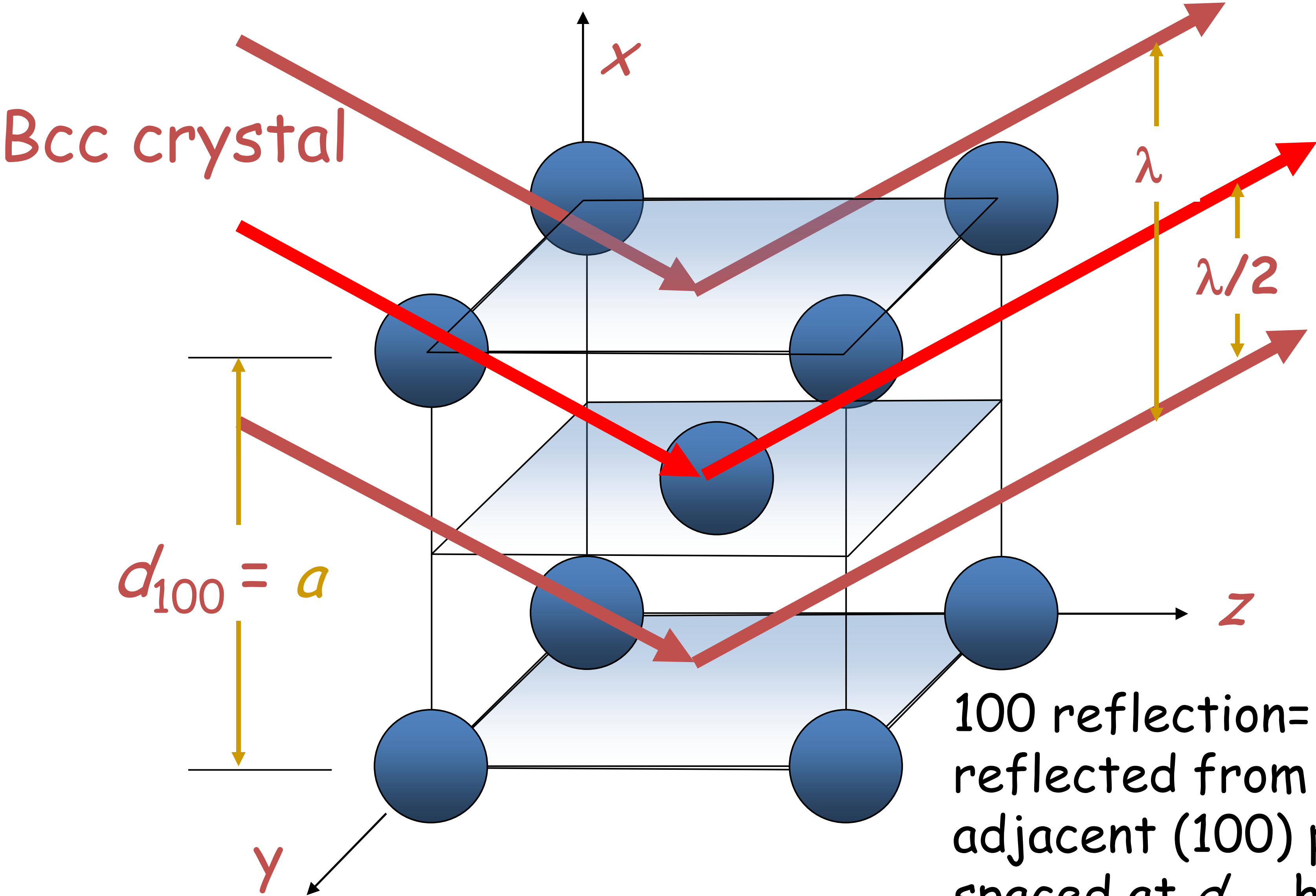


X-ray powder diffractometer

The diffraction pattern of austenite

Austenite = fcc Fe





100 reflection= rays reflected from adjacent (100) planes spaced at d_{100} have a path difference λ

No 100 reflection for bcc

No bcc reflection for $h+k+l$=odd

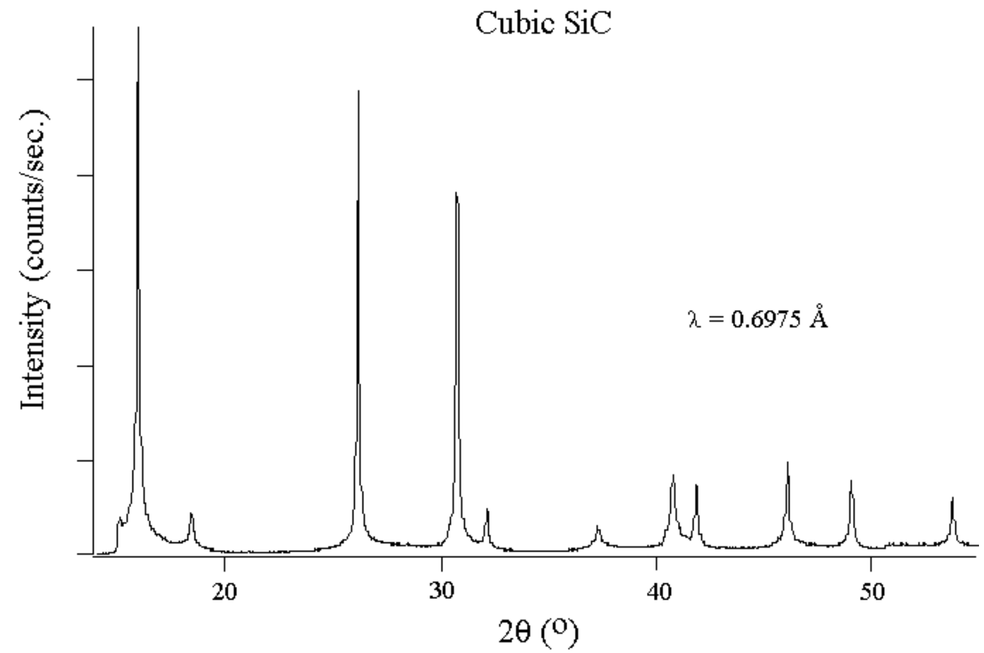
Extinction Rules: Table 3.3

Bravais Lattice	**Allowed Reflections**
SC	All
BCC	(h + k + l) even
FCC	h, k and l unmixed
DC	h, k and l are all odd *Or* *if* all are even *then* *(h + k + l) divisible by 4*

Diffraction analysis of cubic crystals

Bragg's Law:

$$\lambda = 2d_{hkl}\sin\theta \qquad (1)$$



Cubic crystals

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

(2) in (1) => $\sin^2\theta = \frac{\lambda^2}{4a^2}(h^2+k^2+l^2)$

constant

$$\sin^2\theta \propto (h^2+k^2+l^2)$$

$h^2 + k^2 + l^2$	SC	FCC	BCC	DC
1	100			
2	110		110	
3	111	111		111
4	200	200	200	
5	210			
6	211		211	
7				
8	220	220	220	220
9	300, 221			
10	310		310	
11	311	311		311
12	222	222	222	
13	320			
14	321		321	
15				
16	400	400	400	400
17	410, 322			
18	411, 330		411, 330	
19	331	331		331

Crystal Structure	Allowed ratios of Sin^2 (theta)
SC	1: 2: 3: 4: 5: 6: 8: 9…
BCC	1: 2: 3: 4: 5: 6: 7: 8…
FCC	3: 4: 8: 11: 12…
DC	3: 8: 11:16…

Ananlysis of a cubic diffraction pattern

θ	$\sin^2\theta$	$p \sin^2\theta$	$h^2+k^2+l^2$	$p \sin^2\theta$	$h^2+k^2+l^2$	$p \sin^2\theta$	$h^2+k^2+l^2$
		p=9.43		**p=18.87**		**p=27.3**	
19.0	0.11	1.0	1	2	2	2.8	3
22.5	0.15	1.4	2	2.8	4	4.0	4
33.0	0.30	2.8	3	5.6	6	8.1	8
39.0	0.40	3.8	4	7.4	8	10.8	11
41.5	0.45	4.1	5	8.3	10	12.0	12
49.5	0.58	5.4	6	10.9	12	15.8	16
56.5	0.70	6.6	8	13.1	14	19.0	19
59.0	0.73	6.9	9	13.6	16	20.1	20
69.5	0.88	8.3	10	16.6	18	23.9	24
84.0	0.99	9.3	11	18.7	20	27.0	27
			sc		bcc		fcc

This is an fcc crystal

Ananlysis of a cubic diffraction pattern contd.

θ	$h^2+k^2+l^2$	hkl	a
19.0	3	111	4.05
22.5	4	200	4.02
33.0	8	220	4.02
39.0	11	311	4.04
41.5	12	222	4.02
49.5	16	400	4.04
56.5	19	331	4.03
59.0	20	420	4.04
69.5	24	422	4.01
84.0	27	511	4.03

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

↑ Indexing of diffraction patterns

The diffraction pattern is from an fcc crystal of lattice parameter 4.03 Å

d-SPACING FORMULAS

Cubic $$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$$

Tetragonal $$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$$

Orthorhombic $$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

Hexagonal $$\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2 + hk + k^2}{a^2}\right) + \frac{l^2}{c^2}$$

Monoclinic $$\frac{1}{d^2} = \frac{1}{\sin^2\beta}\left(\frac{h^2}{a^2} + \frac{k^2 \sin^2\beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl\cos\beta}{ac}\right)$$

Triclinic $$\frac{1}{d^2} = \frac{1}{V^2}[h^2b^2c^2\sin^2\alpha + k^2a^2c^2\sin^2\beta$$

$$+ l^2a^2b^2\sin^2\gamma + 2hkabc^2(\cos\alpha\cos\beta - \cos\gamma)$$

$$+ 2kla^2bc(\cos\beta\cos\gamma - \cos\alpha)$$

$$+ 2hlab^2c(\cos\alpha\cos\gamma - \cos\beta)]$$