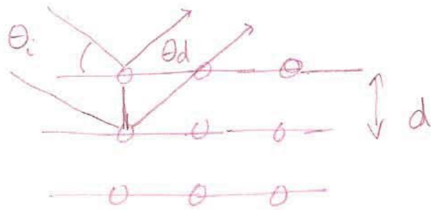
X-ray Powder Diffraction

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



set $\theta_i = \theta_d$
(experimental geometry)

$\Delta path = 2d \sin\theta$

when $\Delta path = n\lambda \rightarrow$ constructive interference

for practical calculations, set $n = 1$.

$d \equiv$ interplanar distance of $(h\,k\,l)$ planes

Miller indices $\rightarrow$ give easy way of calculating d.

<u>cubic</u>: $d_{hkl} = \dfrac{a}{\sqrt{h^2+k^2+l^2}}$, homework: prove for 2-D.

in general, <u>orthogonal</u> crystal systems:

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

tetragonal $a=b$, cubic $a=b=c$ $\rightarrow$ get back above

<u>hexagonal</u>

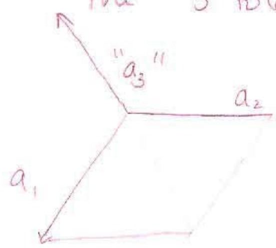
$$\frac{1}{d_{hkl}^2} = \frac{4}{3}\left(\frac{h^2 + hk + k^2}{a^2}\right) + \frac{l^2}{c^2}$$

An aside on indices in the hexagonal system.

recall: specific plane $(h\,k\,l)$
family of planes $\{h\,k\,l\}$

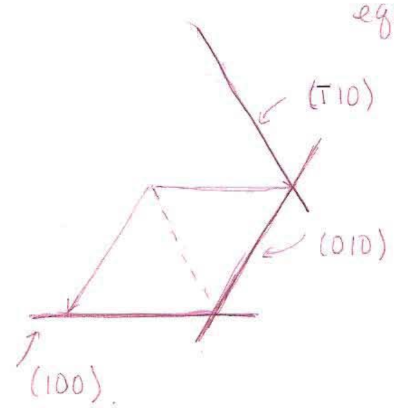
cubic: $\{100\}$ (100), (010), (001), $(\bar{1}00)$, $(0\bar{1}0)$, $(00\bar{1})$

hexagonal: would like a notation that captures the 3-fold symmetry



a_1 a_2 & "a_3" directions are equivalent
$[100]$ $[010]$ $[\bar{1}\bar{1}0]$

equivalence not immediately obvious.



← have student give indices

introduce modified notation
Miller - Bravais indices.

planes $h\,k\,l \rightarrow h\,k\,\underset{\text{redundant}}{i}\,l$ $\quad i = -(h+k)$

$(100) \rightarrow (10\bar{1}0)$ permute $(01\bar{1}0)$, $(\bar{1}100)$

$(010) \rightarrow (01\bar{1}0)$ ✓

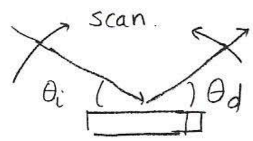
$(\bar{1}10) \rightarrow (\bar{1}100)$ ✓

analogous modification for directions, but more complex and less commonly used

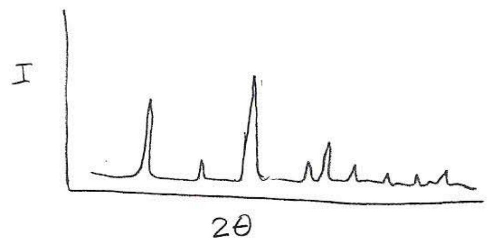
Analysis of powder diffraction data

$n\lambda = 2d\sin\theta$ take $n=1$, λ = fixed

Cu K_α: 1.54 Å



maintain $\theta_i = \theta_d$



detect intensity whenever we meet the Bragg condition.

many d's $\Rightarrow$ many θ's.

each peak corresponds to some specific d_{hkl}

$$d_{hkl} = \frac{\lambda}{2\sin\theta}$$ from the measurement

want a, $$d_{hkl}^{cubic} = \frac{a}{(h^2+k^2+l^2)^{1/2}}$$ $\Rightarrow$ need to know $h\,k\,l$. (??)

solve by noting: $\theta\uparrow \Rightarrow \sin\theta\uparrow \Rightarrow d\downarrow$

$\Rightarrow$ at low 2θ, d is large. When is d large for given a & λ? When $h^2+k^2+l^2$ is small

smallest possible value is 1

$h\ k\ l$	$h^2+k^2+l^2$
(1 0 0)	1
(1 1 0)	2
(1 1 1)	3
(2 0 0)	4
(2 0 1)	5
(2 1 1)	6
(2 2 0)	8

$\therefore$ this is the order in which peaks appear for a cubic compound.

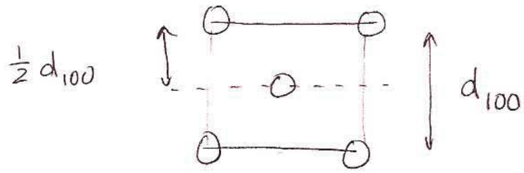
Also, as $a\uparrow$, $\Rightarrow d\uparrow$

$\Rightarrow \sin\theta\downarrow \Rightarrow 2\theta\downarrow$

$\Rightarrow$ peaks shift to smaller angles & get closer together.

But, if the lattice type is not primitive, there will be absences

e.g. FCC



Δpath $= \frac{\lambda}{2}$

$\Rightarrow$ destructive

rules FCC: h, k, l must be all odd or all even for non-zero intensity

BCC: $h+k+l$ must be even.

SC	BCC	FCC
100	—	—
110	110	—
111	—	111
200	200	200
201	—	—
211	211	—
220	220	220.