X-ray Diffraction and Crystal Structures

November 12, 2013

PHYS 4580, PHYS 6/7280

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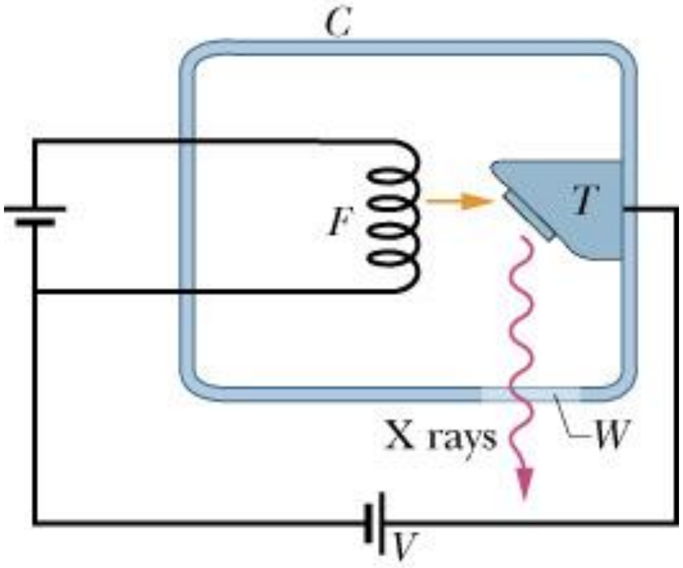
X-Ray Generation

X-rays are electromagnetic radiation with wavelength ~1 Å = 10^{-10} m (visible light ~5.5×10^{-7} m)

X-ray generation: electrons are emitted from the cathode and accelerated toward the anode. Here, Bremsstralung radiation occurs as a result of the "braking" process – X-ray photons are emitted.



X-ray wavelengths too short to be resolved by a standard optical grating

$$\theta = \sin^{-1}\frac{m\lambda}{d} = \sin^{-1}\frac{(1)(0.1\text{ nm})}{3000\text{ nm}} = 0.0019^\circ$$

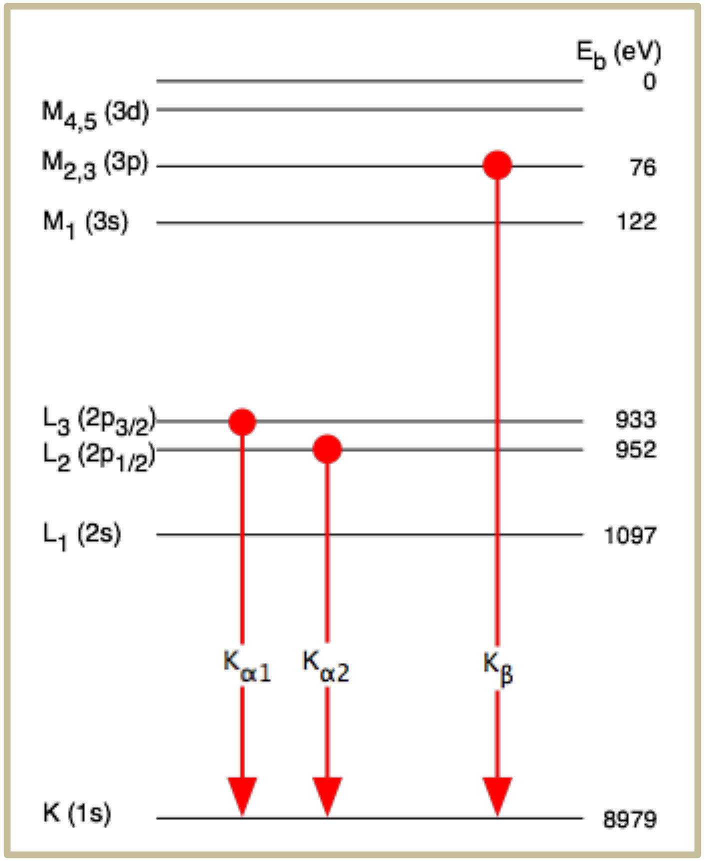
X-Ray Generation

The most common metal used is copper, which can be kept cool easily, due to its high thermal conductivity, and which produces strong K_α and K_β lines. The K_β line is sometimes suppressed with a thin (~10 µm) nickel foil.

- **K-alpha (K_α)** emission lines result when an electron transitions to the innermost "K" shell (principal quantum number 1) from a 2p orbital of the second or "L" shell (with principal quantum number 2).
- The K_α line is actually a doublet, with slightly different energies depending on spin-orbit interaction energy between the electron spin and the orbital momentum of the 2p orbital.

$$\lambda(K_\alpha) = 0.154 \text{ nm}$$

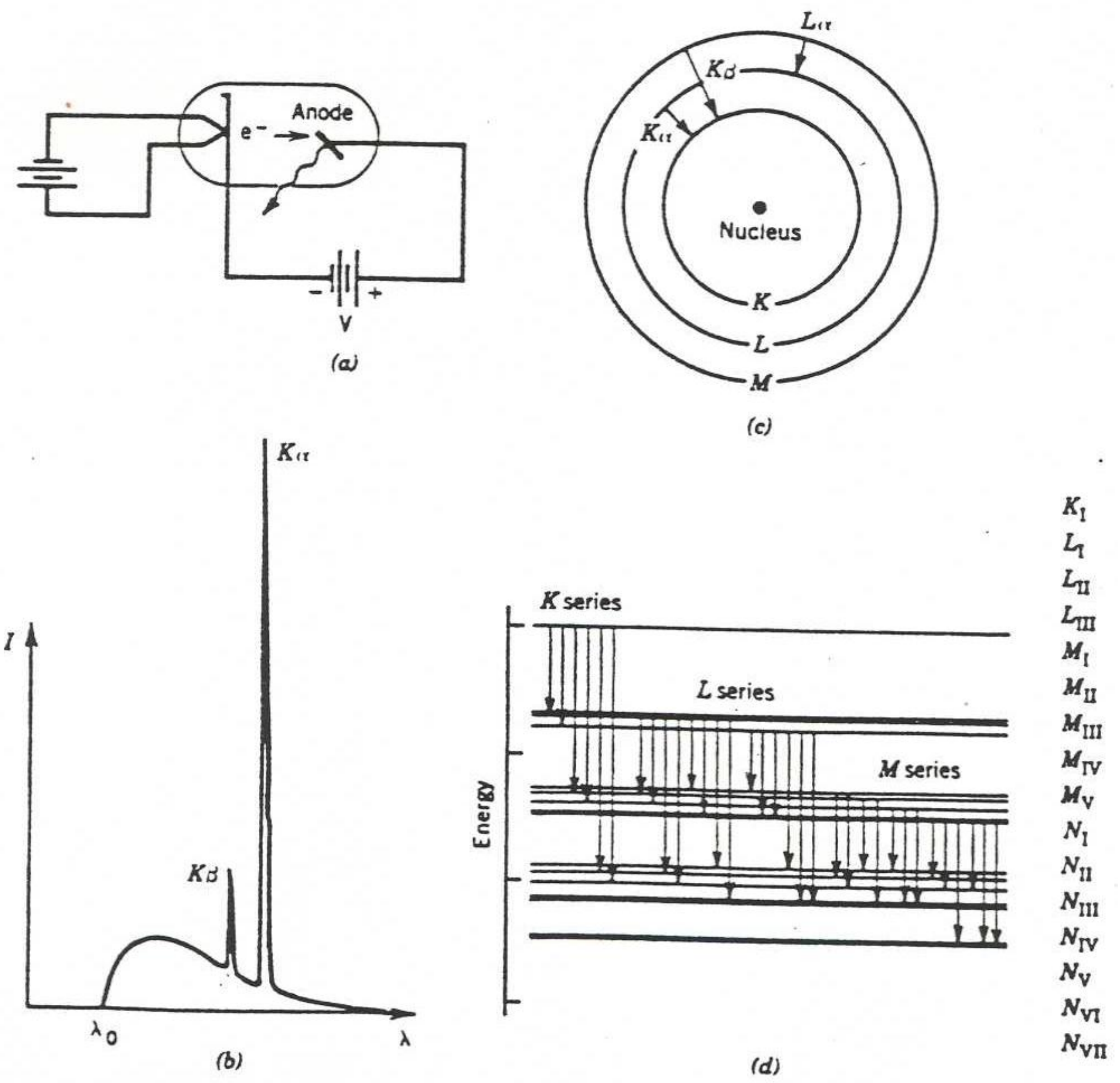
$$\lambda(K_\beta) = 0.139 \text{ nm}$$



Atomic levels involved in copper K_α and K_β emission.

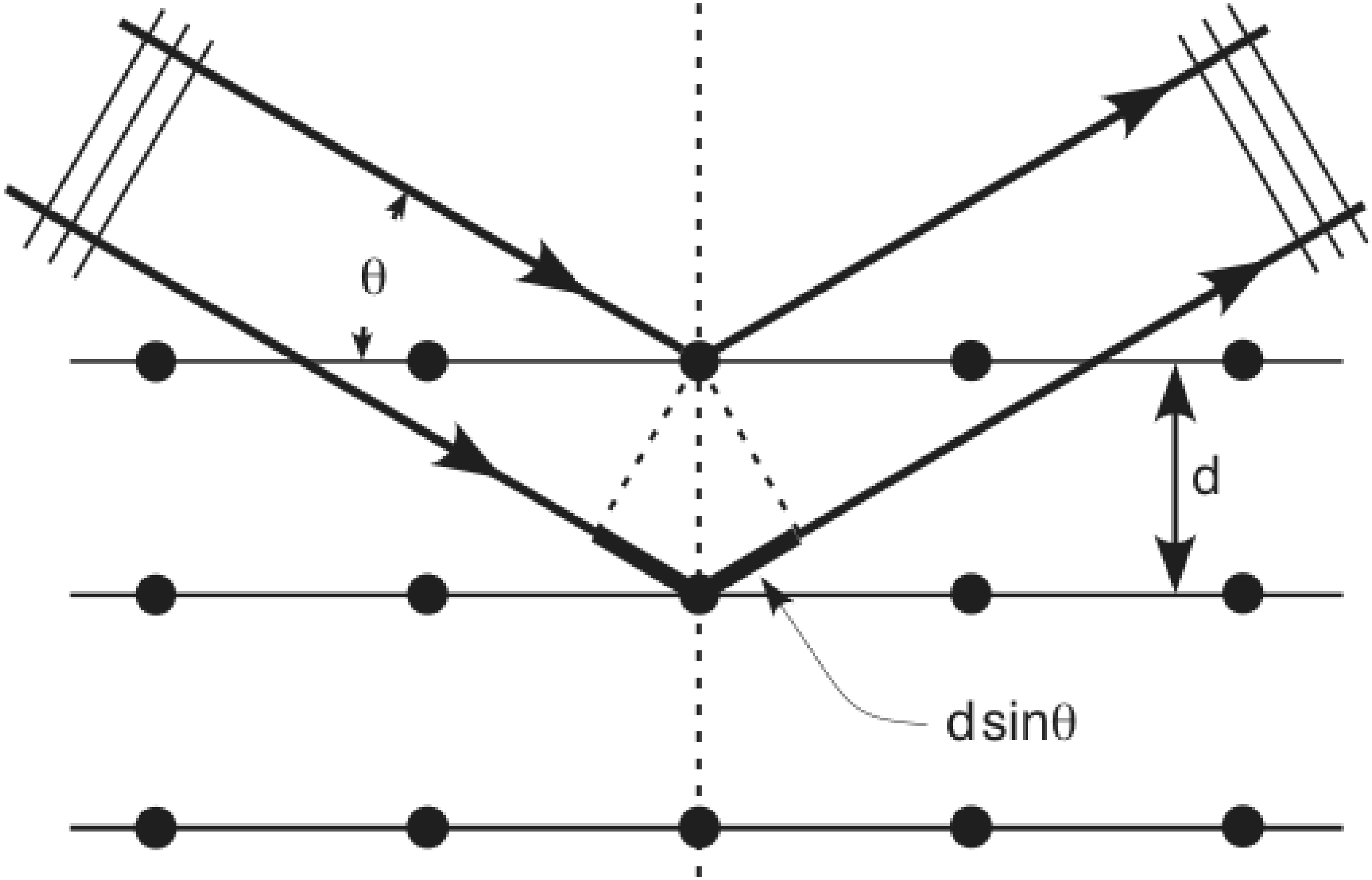
from http://en.wikipedia.org/wiki/K-alpha

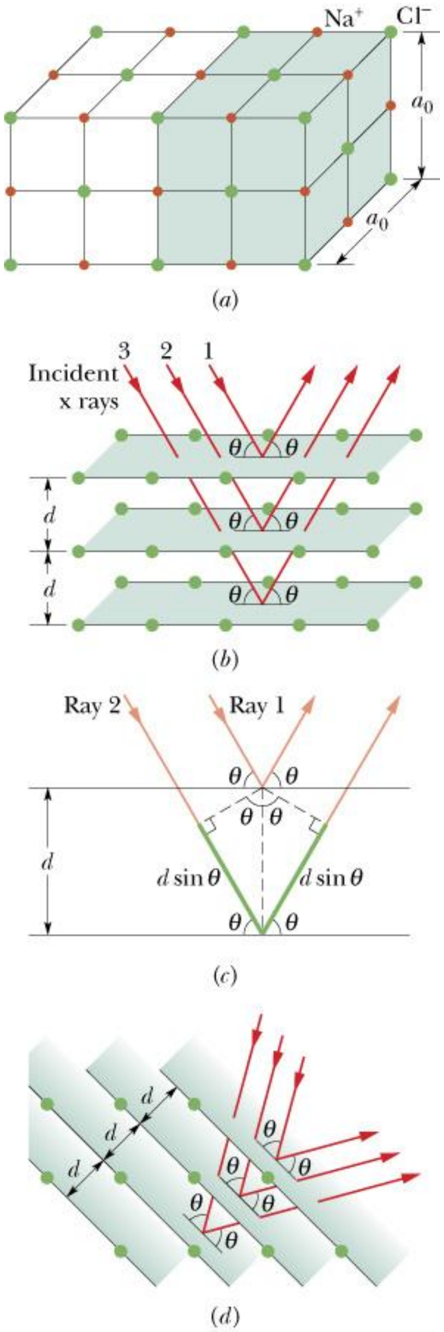
K_α and K_β X-ray lines



from Preston and Dietz, p. 191.

X-Ray diffraction





X-Ray Diffraction -- Bragg's Law

Diffraction of x-rays by crystal: spacing *d* of adjacent crystal planes on the order of 0.1 nm

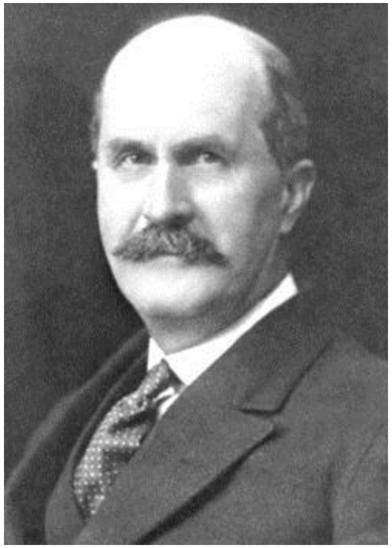
→ three-dimensional diffraction grating with diffraction maxima along angles where reflections from different planes interfere constructively

$$\boxed{2d \sin\theta = m\lambda \text{ for } m = 0, 1, 2, \ldots}$$

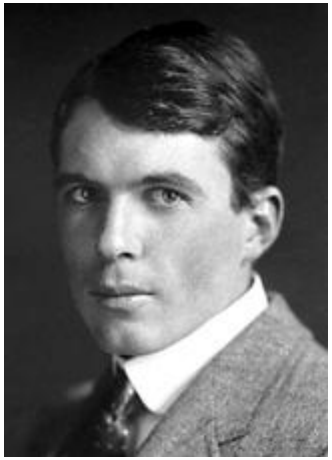
Bragg's Law

Note that your measured XRD spectra will most likely reveal only 1st order diffracted lines (i.e., those for which m = 1).

The Braggs (Bragg's Law)



Sir William Henry Bragg
1862-1942



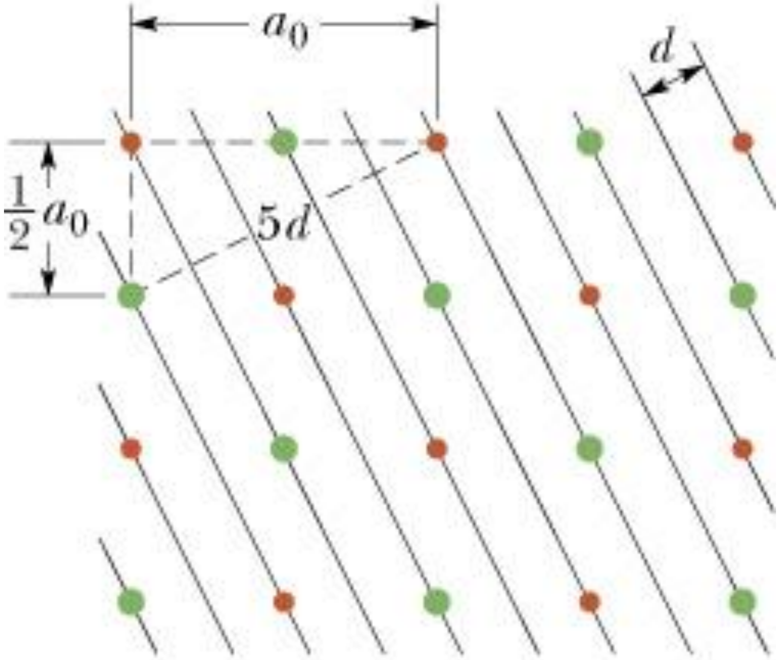
William Lawrence Bragg
1890-1971

Bragg occupied the Cavendish chair of physics at the University of Leeds from 1909. He continued his work on X-rays with much success. He invented the X-ray spectrometer and with his son, William Lawrence Bragg, then a research student at Cambridge, founded the new science of X-ray analysis of crystal structure.

In 1915 father and son were jointly awarded the Nobel Prize in Physics for their studies, using the X-ray spectrometer, of X-ray spectra, X-ray diffraction, and of crystal structure.

http://en.wikipedia.org/wiki/William_Henry_Bragg

X-Ray Diffraction, cont'd



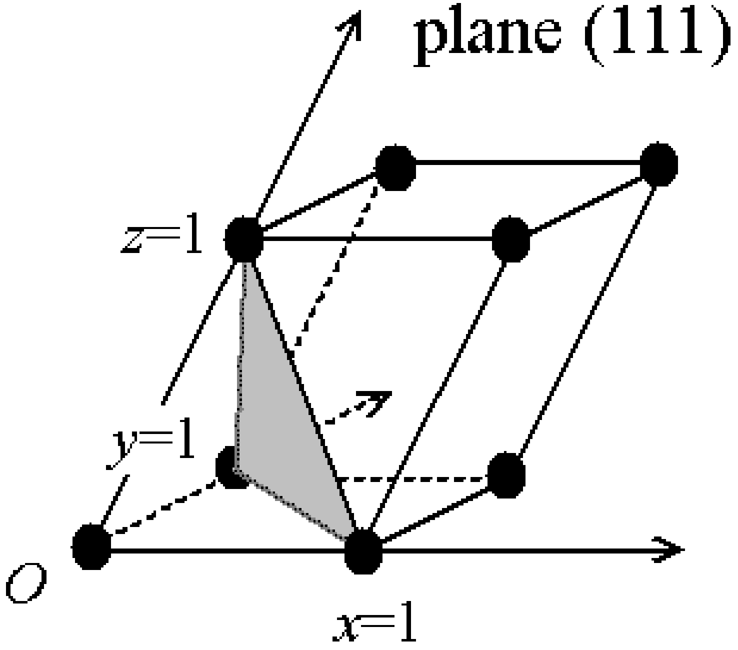
Interplanar spacing *d* is related to the unit cell dimension a_0

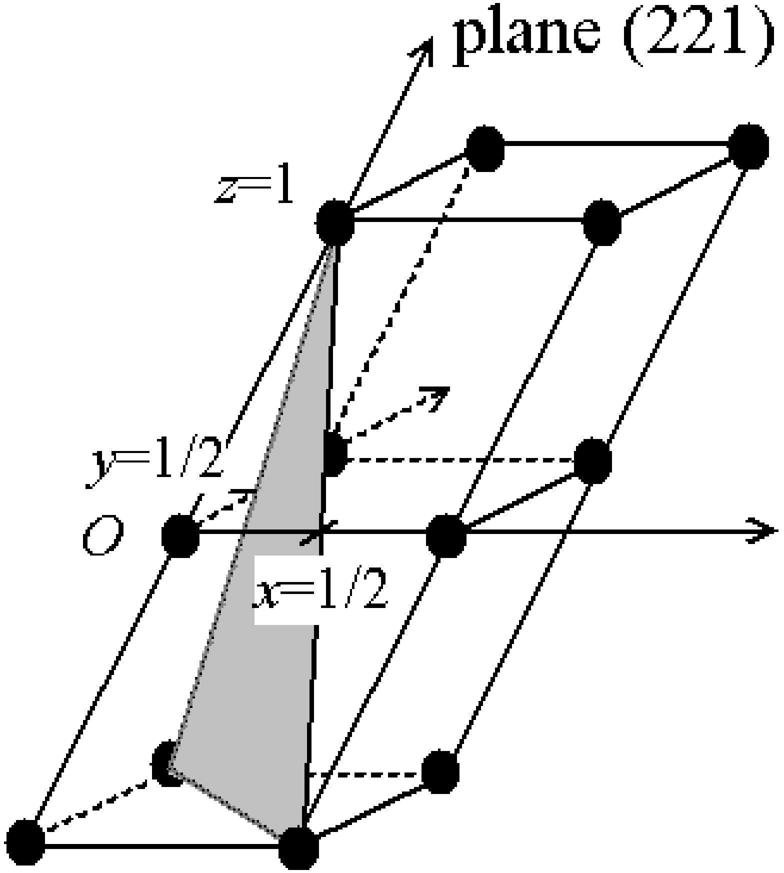
$$5d = \sqrt{\tfrac{5}{4}a_0^2} \quad \text{or} \quad d = \frac{a_0}{20} = 0.2236a_0$$

Not only can crystals be used to separate different x-ray wavelengths, but x-rays in turn can be used to study crystals, for example determine the type of crystal ordering and $a_{0.}$

Crystal structure, lattice planes, and Miller indices

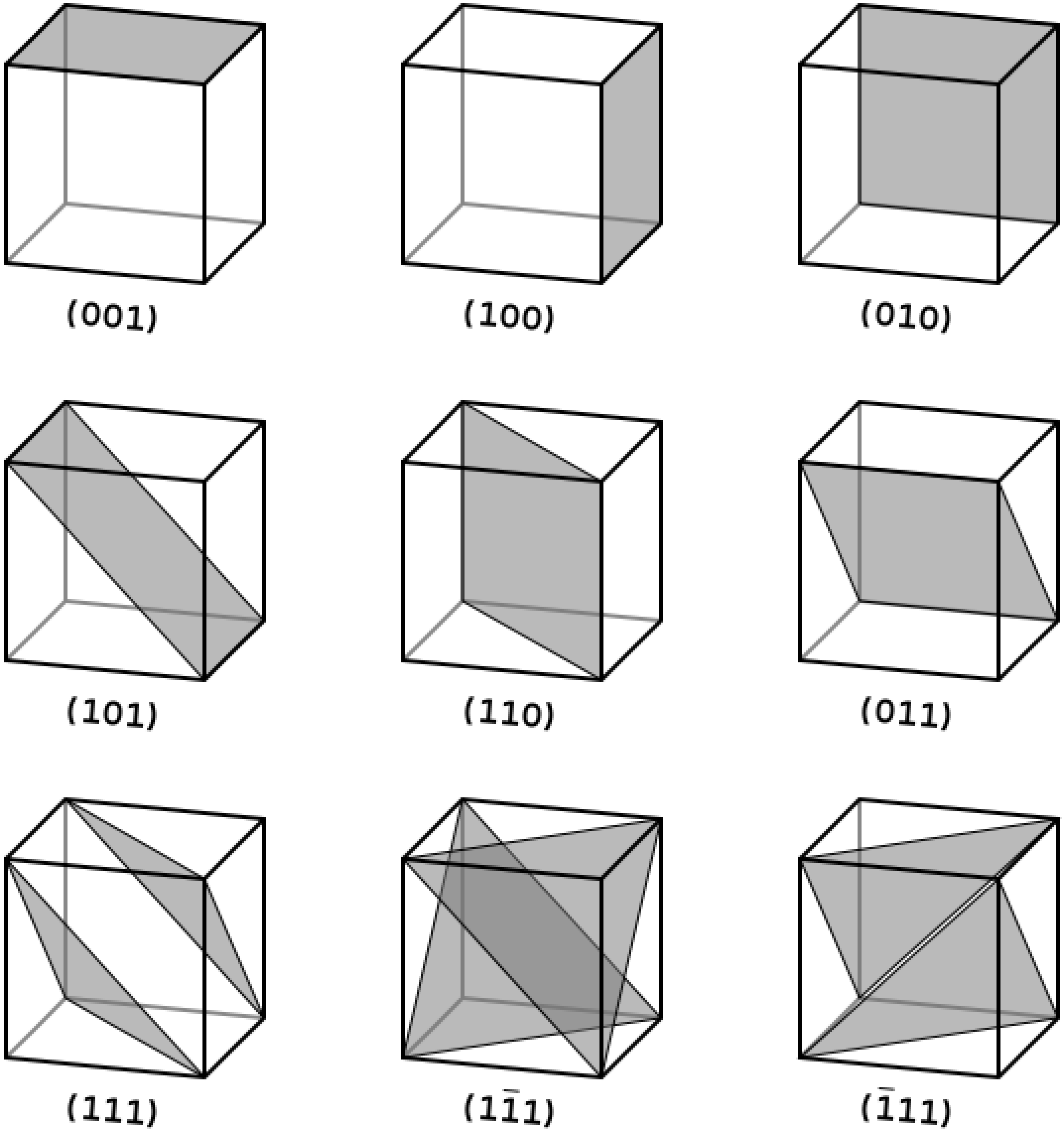
Planes with different Miller indices in cubic crystals. The *inverse* of these fractional intercepts yields the Miller indices *h, k, l*.





from http://en.wikipedia.org/wiki/Miller_index

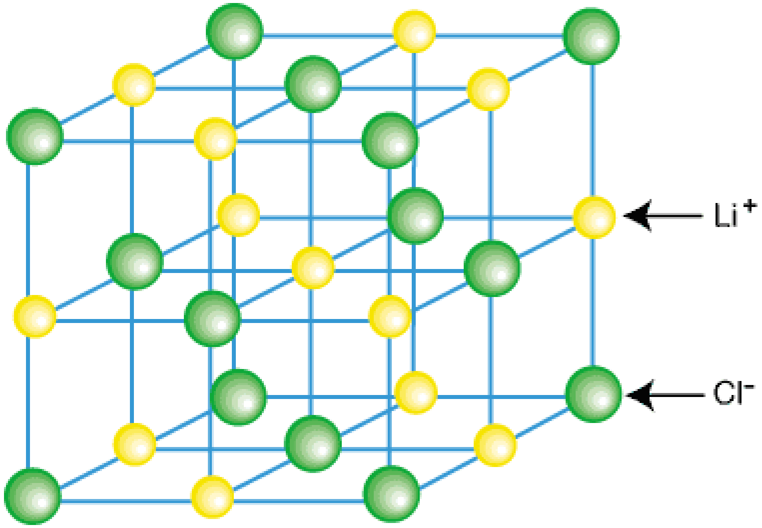
Crystal structure and Miller indices



Planes with different Miller indices in cubic crystals.

from http://en.wikipedia.org/wiki/Miller_index

Crystal structure and Miller indices



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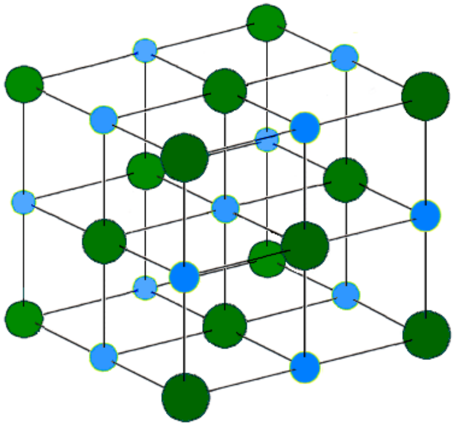
Indexing lattice planes

http://www.msm.cam.ac.uk/doitpoms/tlplib/miller_indices/lattice_index.php

Rock salt (cubic) crystal structure



$$d_{hkl} = \frac{a_0}{\sqrt{h^2 + k^2 + l^2}}$$

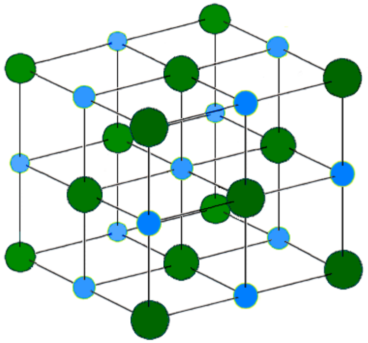
Structure factor for NaCl:

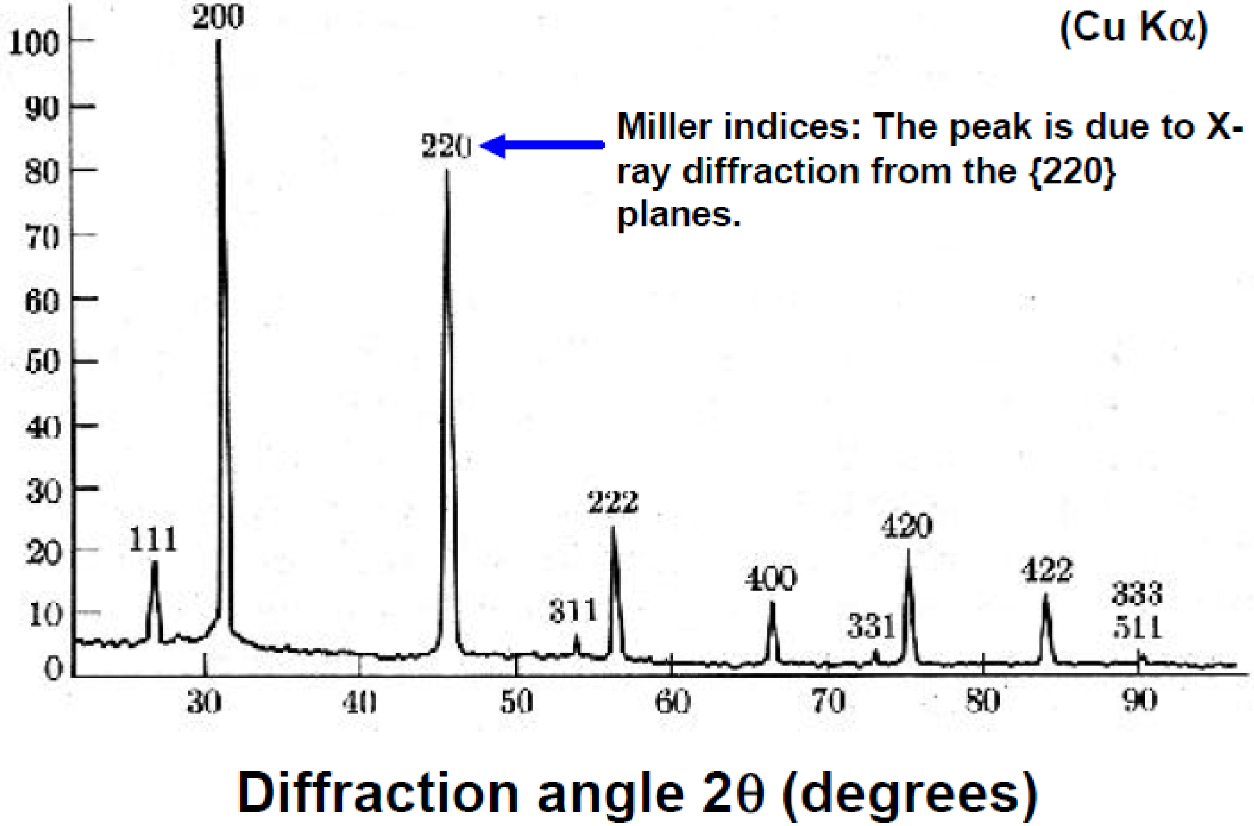
$$F = \left[f_{Na} + f_{Cl} e^{i\pi(h+k+l)} \right] \left[1 + e^{i\pi(h+k)} + e^{i\pi(h+l)} + e^{i\pi(k+l)} \right]$$

$$\boxed{\begin{array}{ll} F = 4\left(f_{Na} + f_{Cl} \right) & \text{if } h,k,l \text{ are even} \\ F = 4\left(f_{Na} - f_{Cl} \right) & \text{if } h,k,l \text{ are odd} \\ F = 0 & \text{if } h,k,l \text{ are mixed} \end{array}}$$

X-Ray diffraction: a practical approach, by C. Suryanarayana, M. Grant Norton

X-Ray diffraction (XRD) pattern (diffractogram) from NaCl





Miller indices: The peak is due to X-ray diffraction from the {220} planes.

$$d_{hkl} = \frac{a_0}{\sqrt{h^2 + k^2 + l^2}}$$

http://web.pdx.edu/~pmoeck/phy381/Topic5a-XRD.pdf

The value of d, the distance between adjacent planes in the set (hkl), may be found from the following equations.

Cubic:

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

Tetragonal:

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

Hexagonal:

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

Rhombohedral:

$$\frac{1}{d^2} = \frac{(h^2 + k^2 + l^2)\sin^2\alpha + 2(hk + kl + hl)(\cos^2\alpha - \cos\alpha)}{a^2(1 - 3\cos^2\alpha + 2\cos^3\alpha)}$$

Orthorhombic:

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

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:

$$\frac{1}{d^2} = \frac{1}{V^2}(S_{11}h^2 + S_{22}k^2 + S_{33}l^2 + 2S_{12}hk + 2S_{23}kl + 2S_{13}hl)$$

In the equation for triclinic crystals,

V = volume of unit cell

$S_{11} = b^2c^2\sin^2\alpha$,

$S_{22} = a^2c^2\sin^2\beta$,

$S_{33} = a^2b^2\sin^2\gamma$,

$S_{12} = abc^2(\cos\alpha\cos\beta - \cos\gamma)$,

$S_{23} = a^2bc(\cos\beta\cos\gamma - \cos\alpha)$,

$S_{13} = ab^2c(\cos\gamma\cos\alpha - \cos\beta)$.

d spacings for tetragonal, hexagonal, orthorhombic crystals

Bragg's Law (1):

$$d = \frac{\lambda}{2\sin\theta_c} \qquad (1)$$

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

(2) Plane spacing for cubic crystals

Combined (1) and (2):

$$\left(\frac{n\lambda}{2a}\right)^2 = \frac{\sin^2\theta}{h^2+k^2+l^2} \quad \text{or} \quad \sin^2\theta = \frac{\lambda^2}{4a^2}(h^2+k^2+l^2) \qquad (3)$$

For a particular incident x-ray wavelength and cubic crystal of unit cell size a, this equation predicts all possible Bragg angles at which diffraction can occur from planes (hkl).

Diffraction planes are determined solely by the shape and size (lattice parameters) of the unit cell.

Plane spacings for:

Tetragonal:

$$\frac{1}{d^2} = \frac{h^2+k^2}{a^2} + \frac{l^2}{c^2} \qquad (4)$$

Hexagonal:

$$\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2+hk+k^2}{a^2}\right) + \frac{l^2}{c^2} \qquad (5)$$

Orthorhombic:

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \qquad (6)$$

If crystal is tetragonal with a=a≠c then (1) and (4) become:

$$\sin^2\theta = \frac{\lambda^2}{4a^2}\left(h^2+k^2\right) + \frac{\lambda^2}{4c^2}\left(l^2\right) \qquad (7)$$

If crystal is hexagonal with a=a≠c then (1) and (5) become:

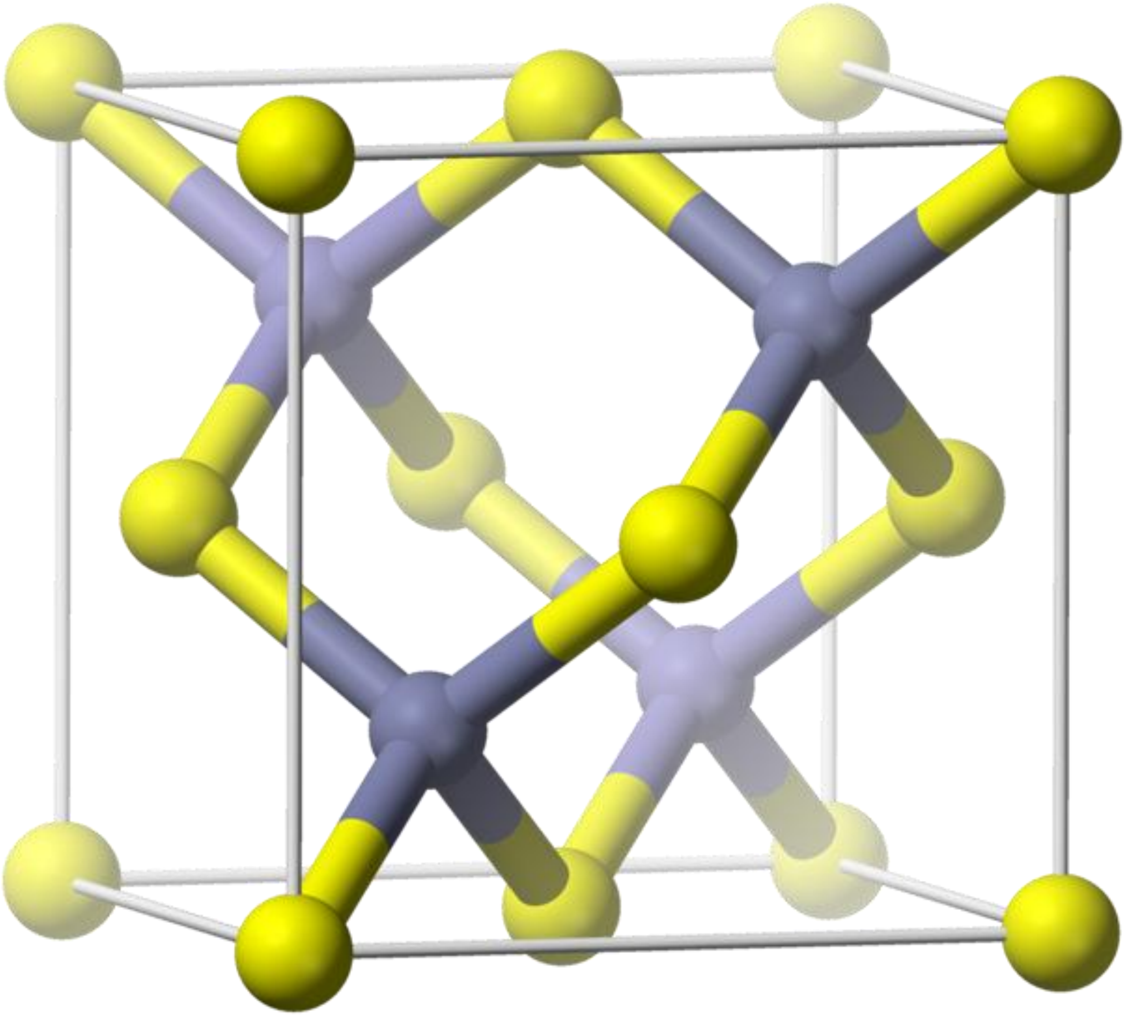
$$\sin^2\theta = \frac{\lambda^2}{3a^2}\left(h^2+k^2+hk\right) + \frac{\lambda^2}{4c^2}\left(l^2\right) \qquad (8)$$

If crystal is orthorhombic with a≠b≠c then (1) and (6):

$$\sin^2\theta = \frac{\lambda^2}{4a^2}(h^2) + \frac{\lambda^2}{4b^2}(k^2) + \frac{\lambda^2}{4c^2}(l^2) \qquad (9)$$

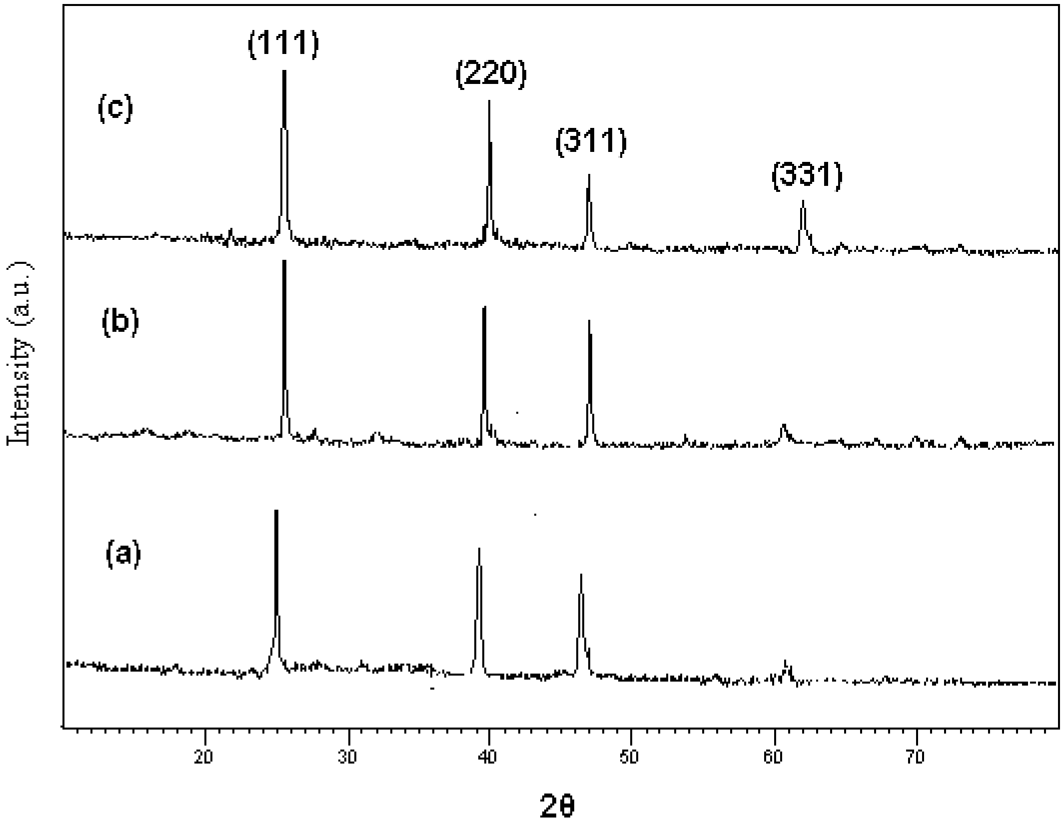
CdTe crystal structure (zincblende)

a_0 = 0.648 nm



http://en.wikipedia.org/wiki/File:Sphalerite-unit-cell-depth-fade-3D-balls.png

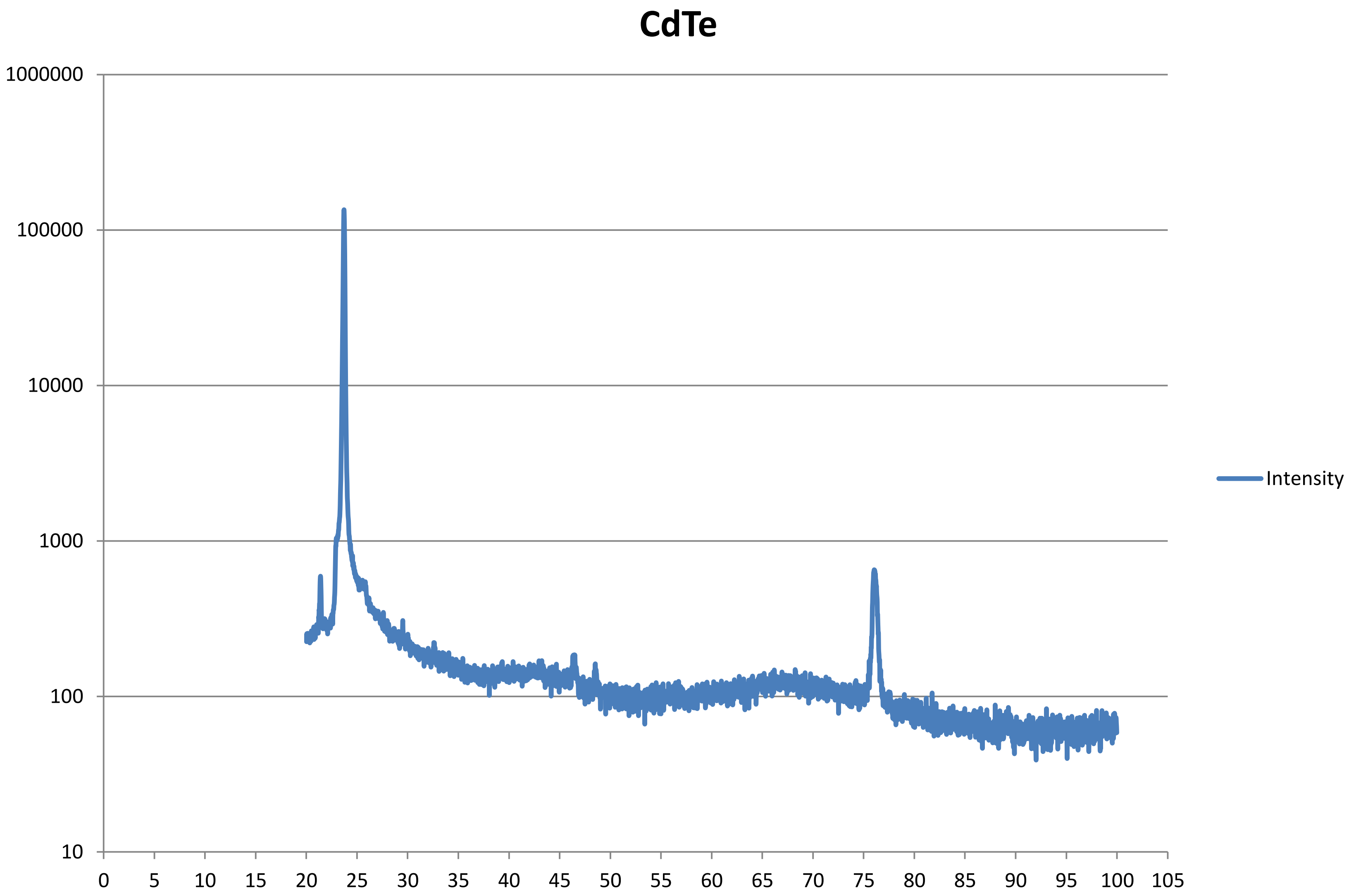
CdTe XRD pattern



X-ray diffactograms of thin films at annealing temperatures of a) 350 C, b) 400 C and c) 450 C.

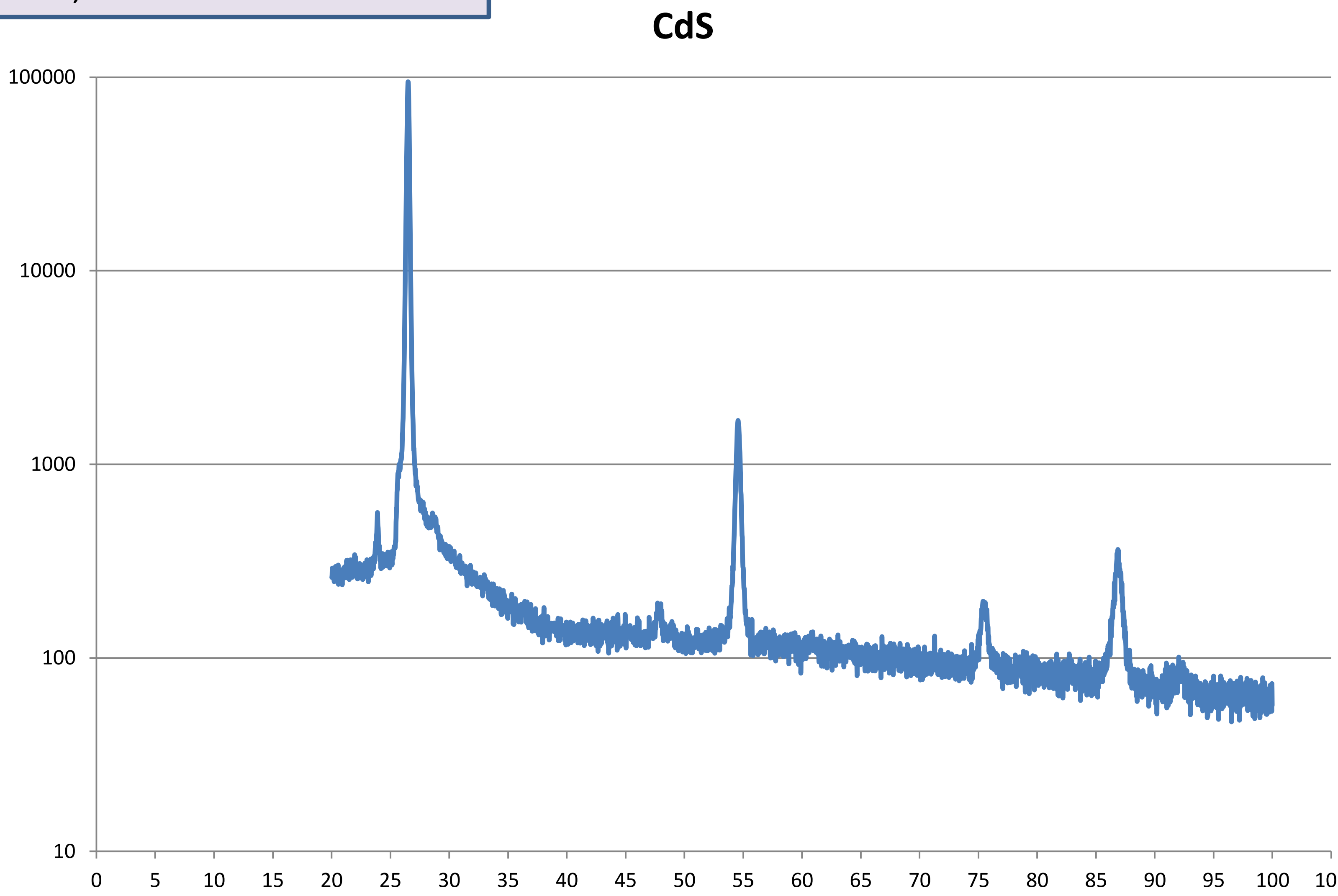
http://www.chalcogen.infim.ro/159_Deivanayaki.pdf

CdTe XRD pattern (intensity vs. 2θ)



CdS XRD pattern (intensity vs. 2θ)

a_0 = 0.5832 nm for zincblende
a = 0.4160; c = 0.6756 for wurtzite



Scherrer Equation (relationship to Shape Factor)

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

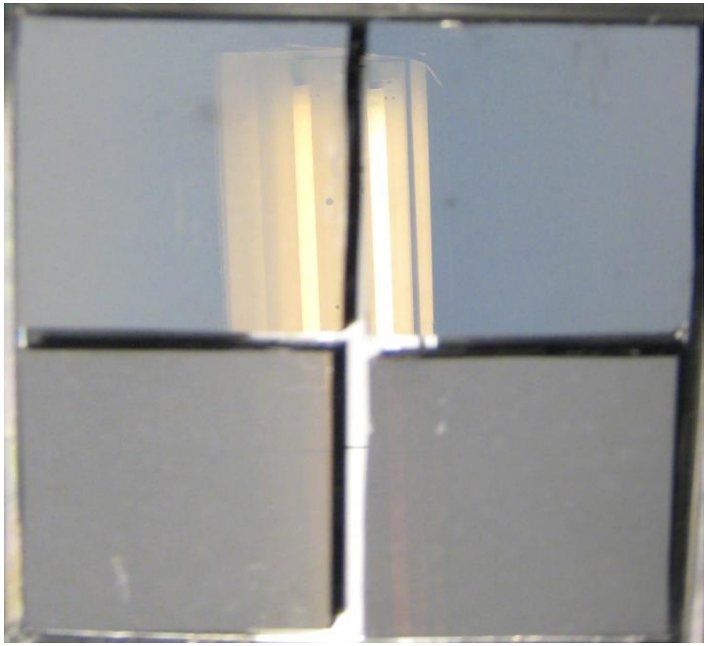
K is the shape factor, λ represents the x-ray wavelength used for the measurement, β is the line width (FWHM) in radians, θ is the Bragg angle (note, this is not the 2θ angle, just θ), and τ is the mean size of the crystalline domains. The formula yields a lower bound on the possible particle size.

The shape factor enables one to determine the average size of crystal grains within a polycrystalline thin film. Assuming a Gaussian function to fit the peak, the shape factor is 0.9, so that

$$\tau = \frac{0.9\lambda}{\beta \cos\theta}$$

http://en.wikipedia.org/wiki/Scherrer_Equation, http://www.eng.uc.edu/~gbeaucag/Classes/XRD/Chapter3html/Chapter3.html

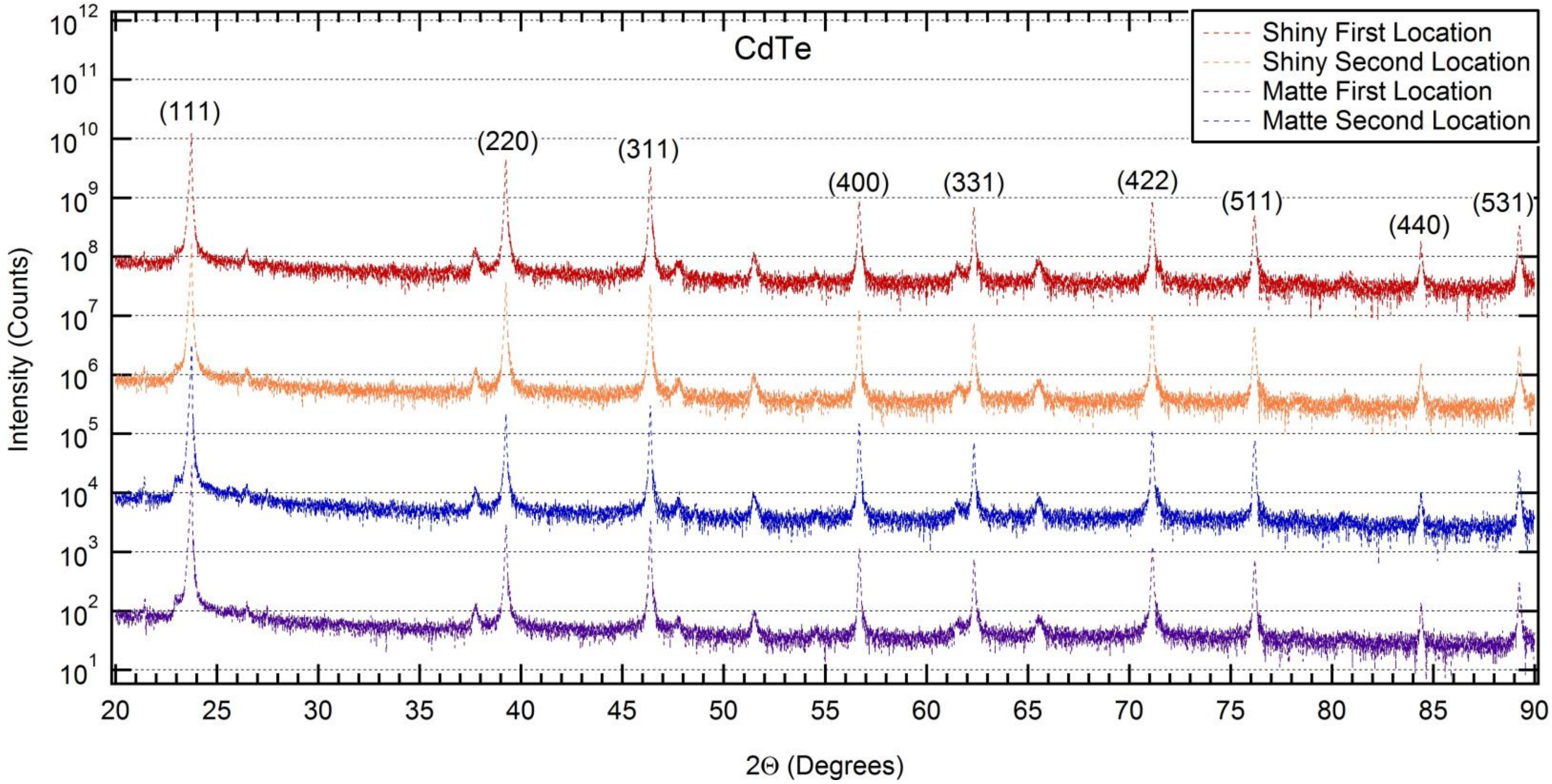
A CdTe XRD Study



Motivation

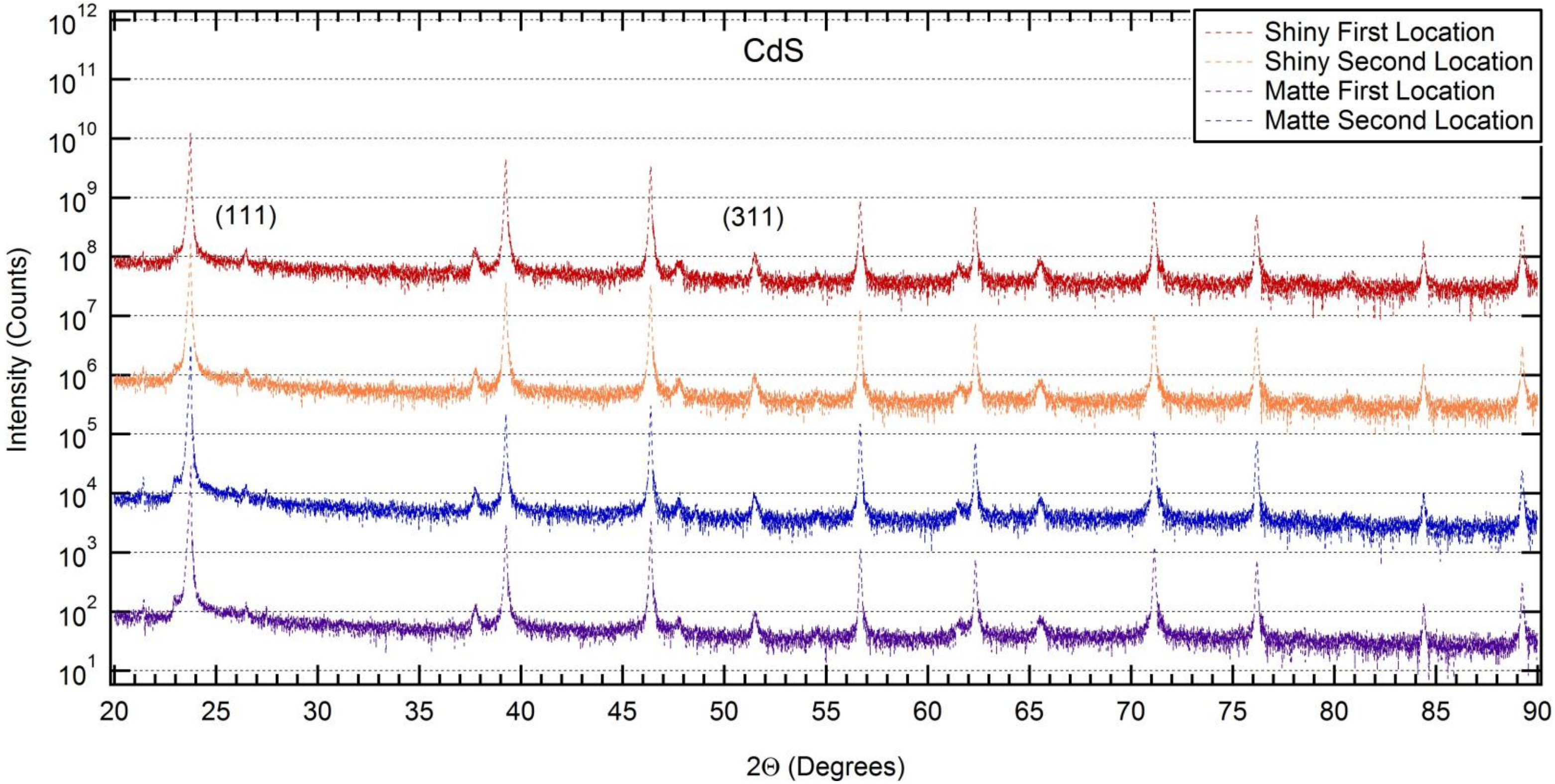
Determine why some samples appear shiny, and some appear matte.

Raw Data



Peaks were considered if they were known CdTe peaks. Peaks from other layers (ex. CdS) were not included.

Raw Data



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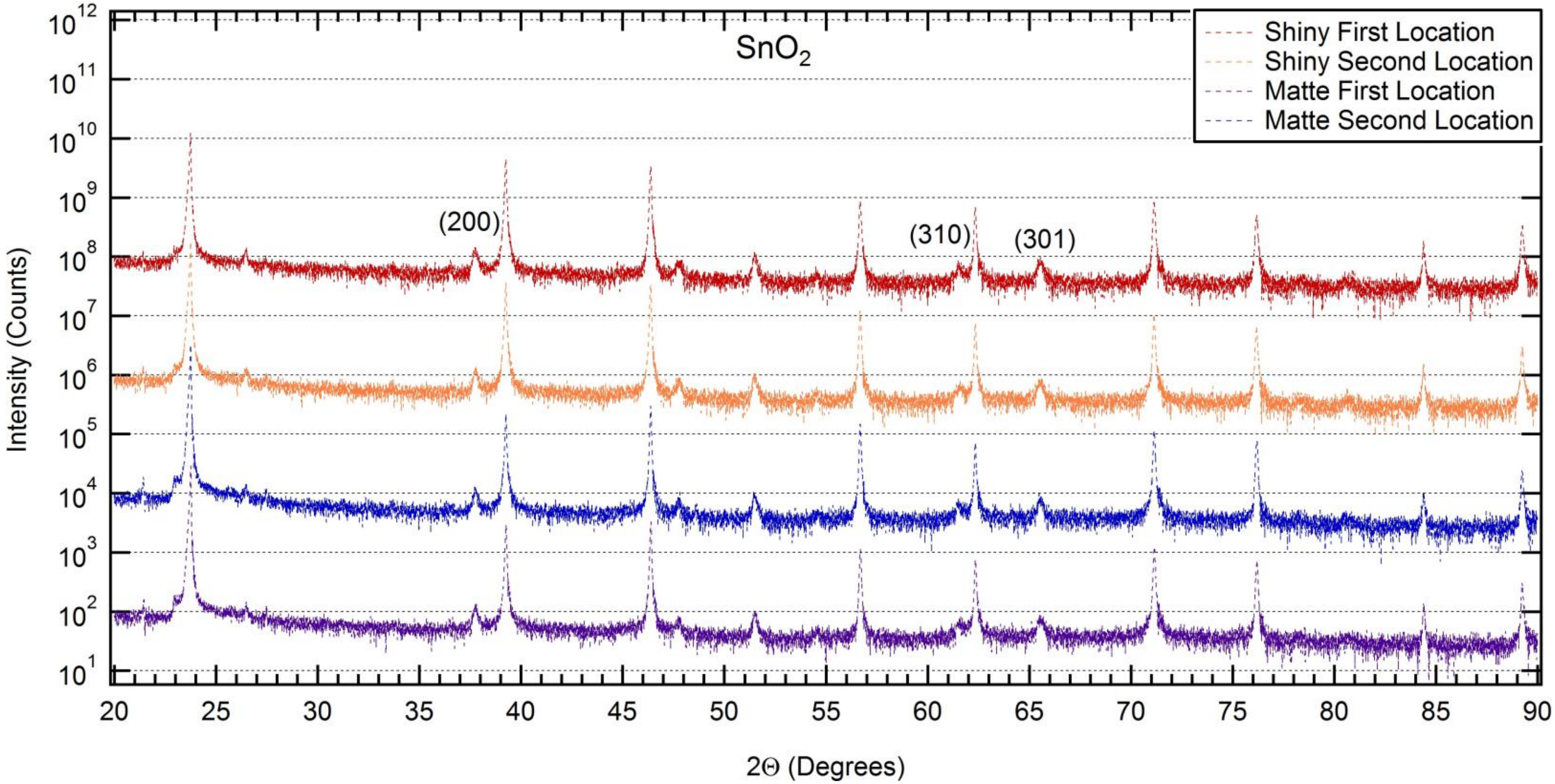

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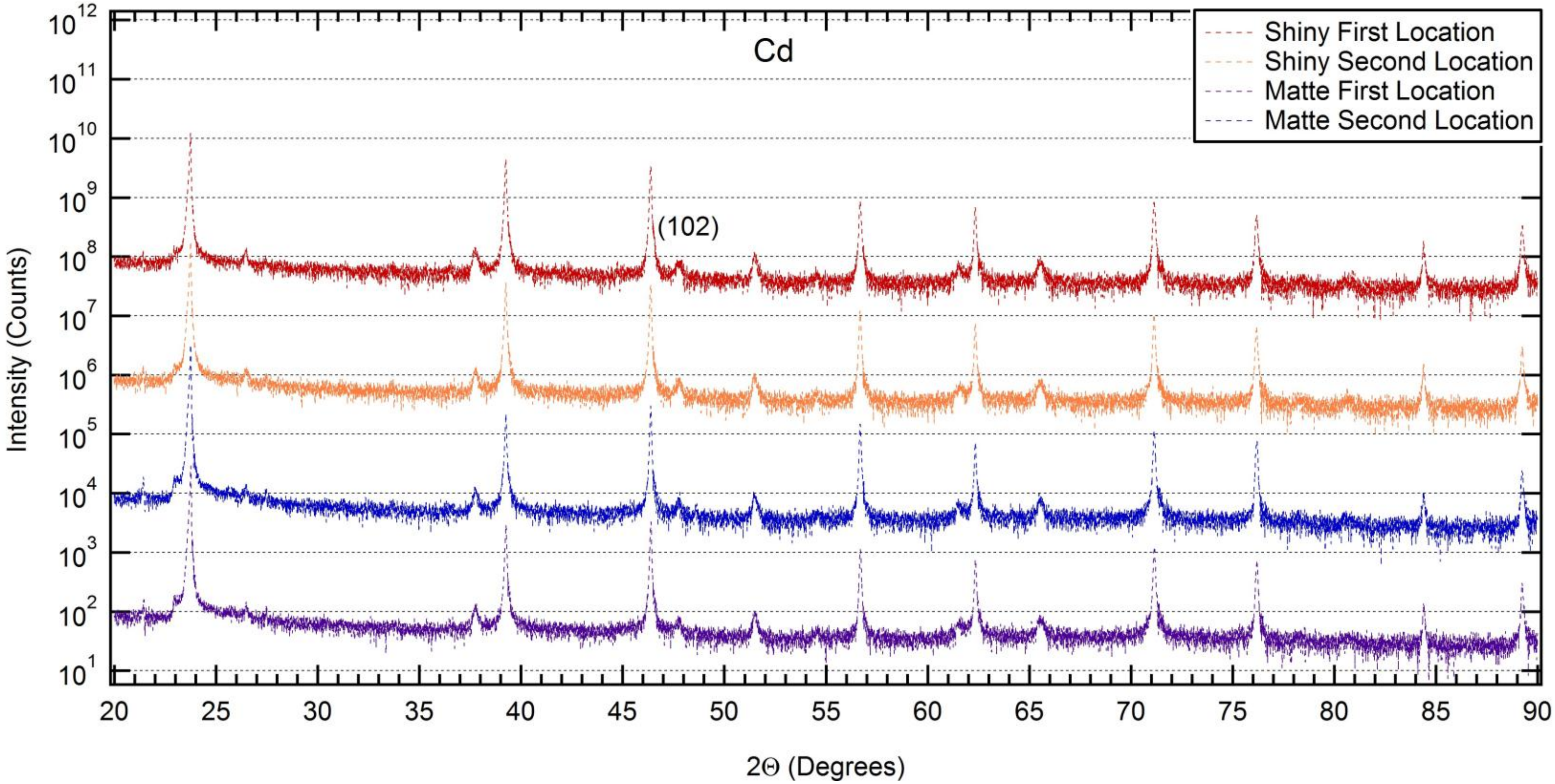
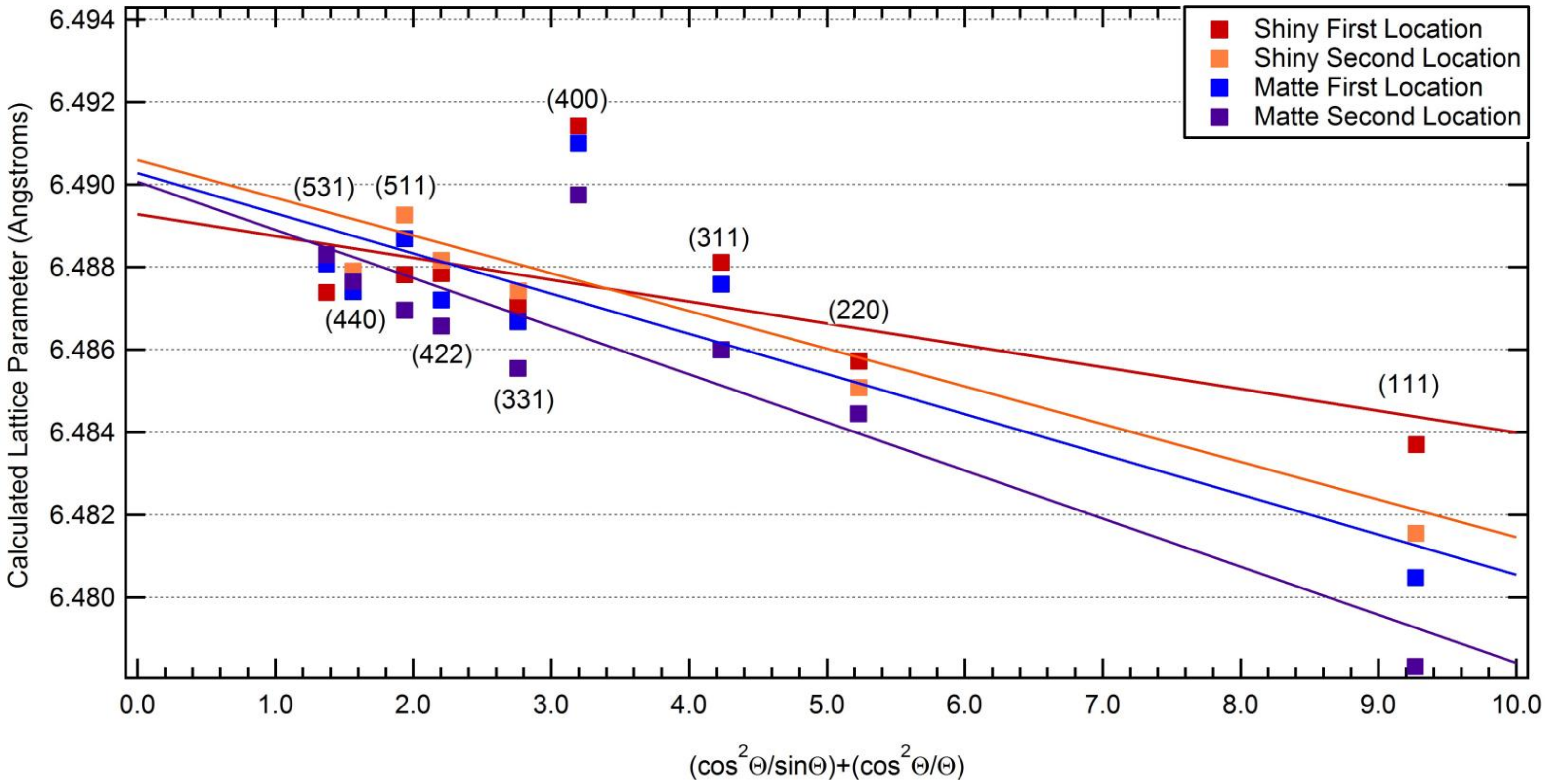


Peaks were considered if they were known CdTe peaks. Peaks from other layers (ex. CdS) were not included.

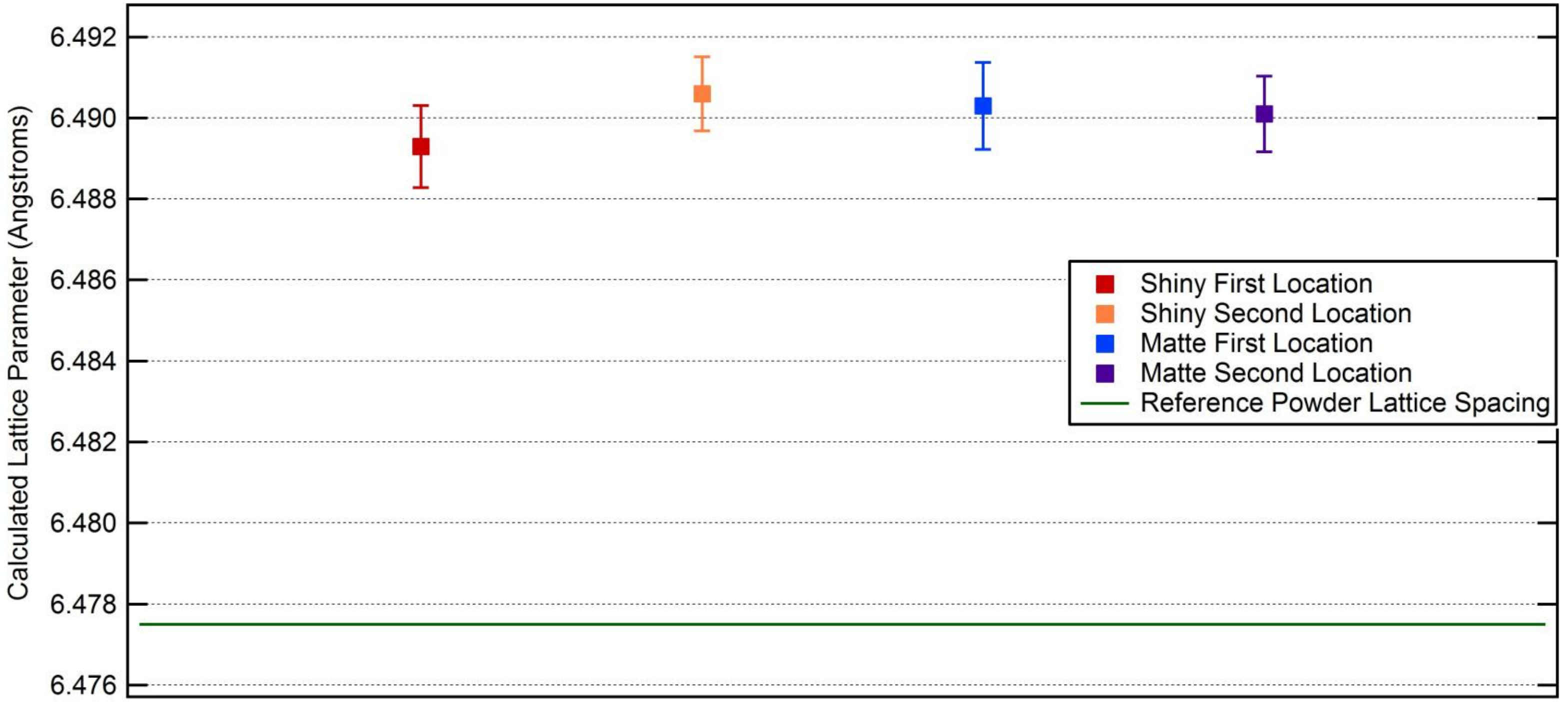
Calculated Lattice Parameter



Data points calculated using: $a = \frac{\lambda}{2}\frac{\sqrt{h^2+k^2+l^2}}{sin\theta}$

H. R. Moutinho, et. al., *Proc. 26th IEEE Photovoltaic Specialist Conf.*, 431-434 (1997)

Lattice Parameter



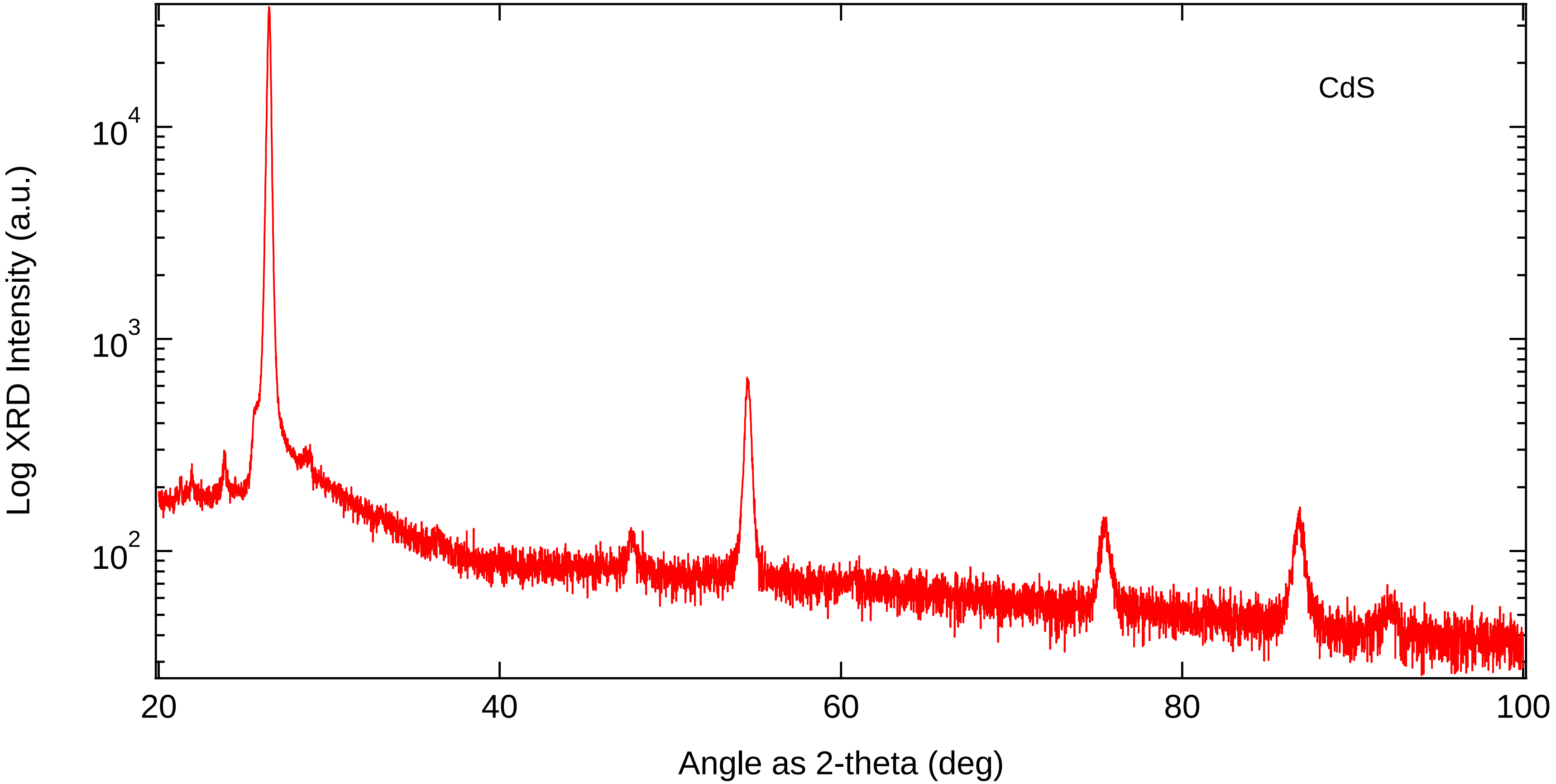
Orientation factor calculated using: $p = \frac{I}{\Sigma I} \times \frac{\Sigma I'}{I'}$ Grain size calculated using: $\tau = \frac{K\lambda}{\beta cos\theta}$

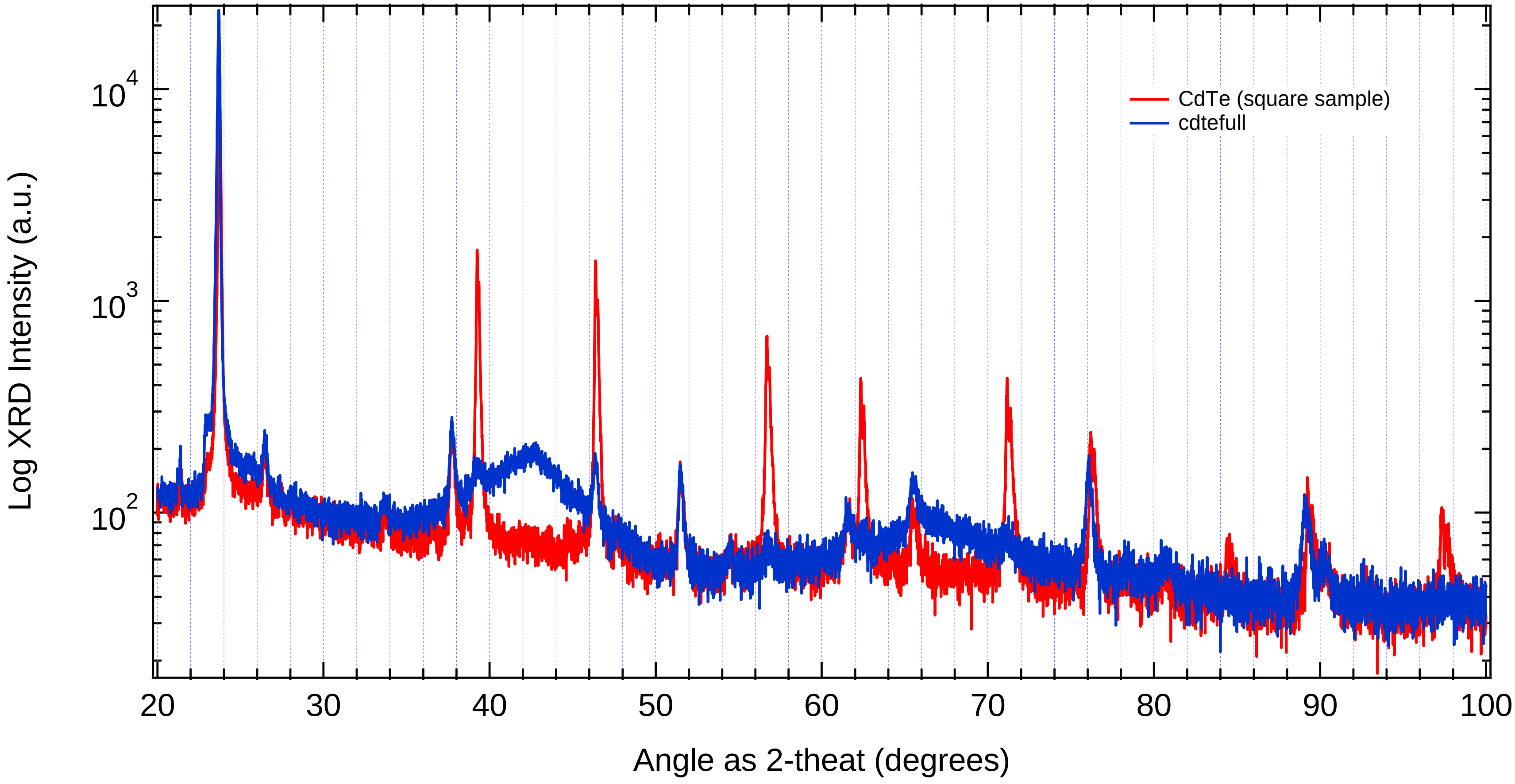
	Shiny First Location	Shiny Second Location	Matte First Location	Matte Second Location
Orientation Factor *p* for (111) Orientation	1.32	1.60	2.00	1.90
Average Grain size τ (nanometers)	264.86	302.70	302.70	325.99
Lattice Parameter *a* (angstroms)	6.4893 ± 0.0010	6.4906 ± 0.0009	6.4903 ± 0.0011	6.4901 ± 0.0009

S. Speakman, *Estimating Crystal Size using XRD.,*
http://prism.mit.edu/xray

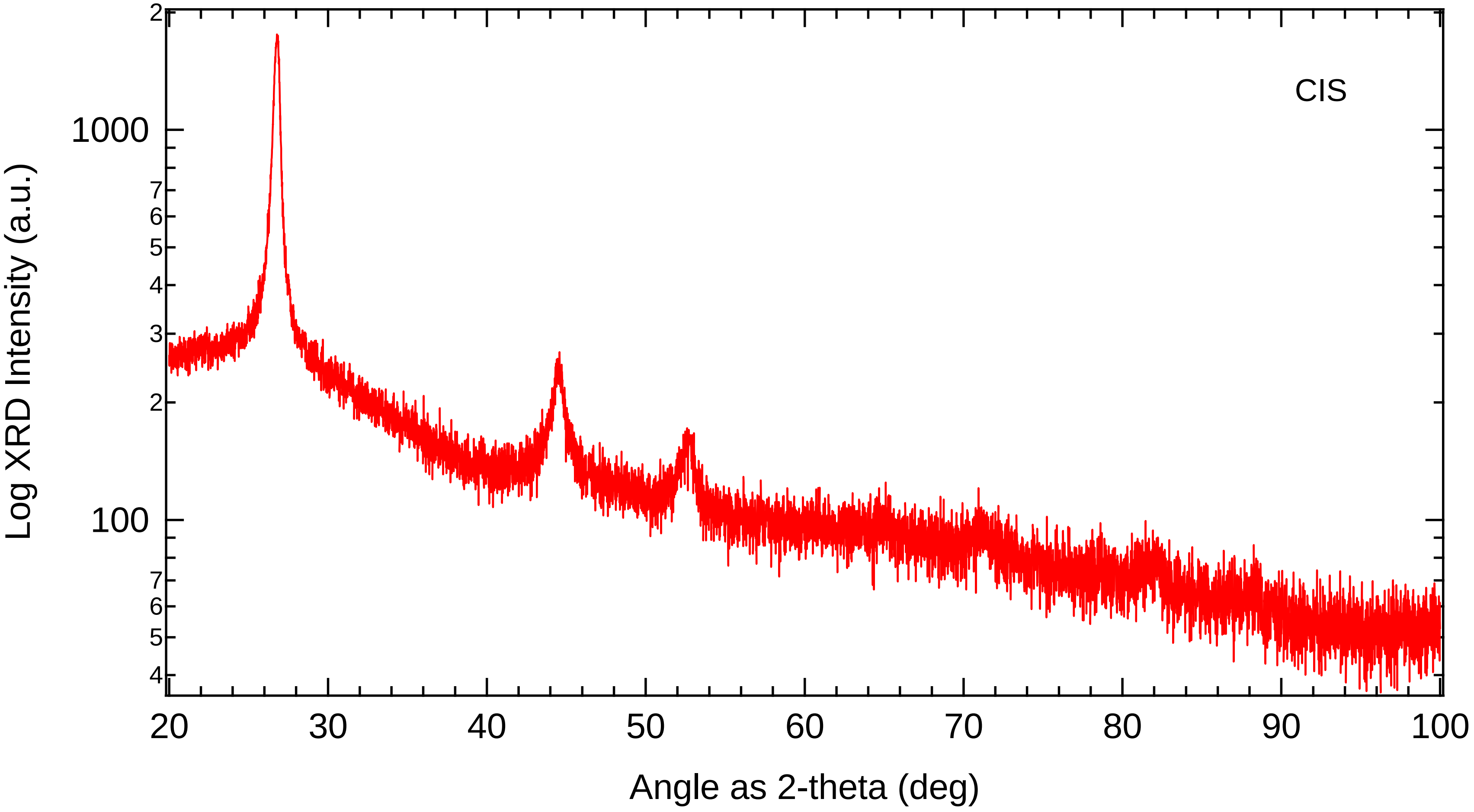
G. B. Harris, *Phil. Mag.*, **43**, 113-123 (1951)

UT Sample Data (Lab #7, 2013)


CdS
Log XRD Intensity (a.u.)
10^4
10^3
10^2
20
40
60
80
100
Angle as 2-theta (deg)



CdTe (square sample)
cdtefull
Log XRD Intensity (a.u.)
10^4
10^3
10^2
20
30
40
50
60
70
80
90
100
Angle as 2-theat (degrees)


CIS
Log XRD Intensity (a.u.)
2
1000
7
6
5
4
3
2
100
7
6
5
4
20
30
40
50
60
70
80
90
100
Angle as 2-theta (deg)