X-ray Diffraction and Crystal Structures

November 13, 2012

Molecular and Condensed Matter Lab (PHYS 4580)
PV Materials and Device Physics Lab (Physics 6/7280)
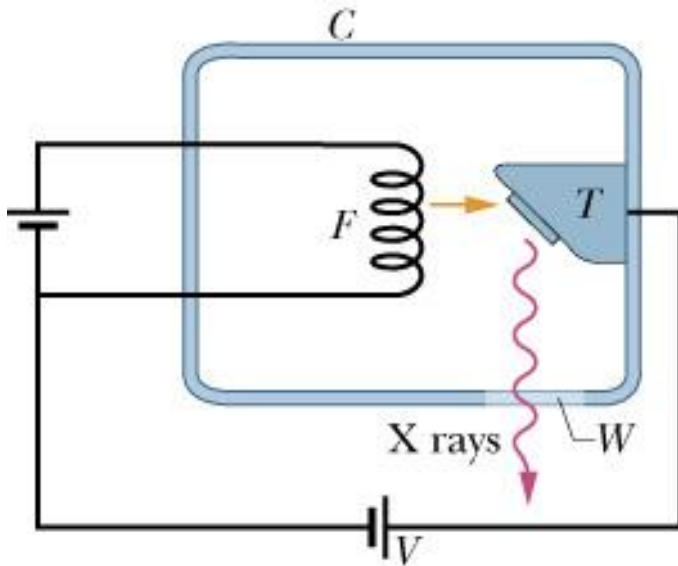
The University of Toledo
Instructors: R. Ellingson, M. Heben

X-Ray Generation

X-rays are electromagnetic radiation with wavelength ~1 Å = 10^{-10} m
(visible light ~5.5x10^{-7} m)

X-ray generation

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

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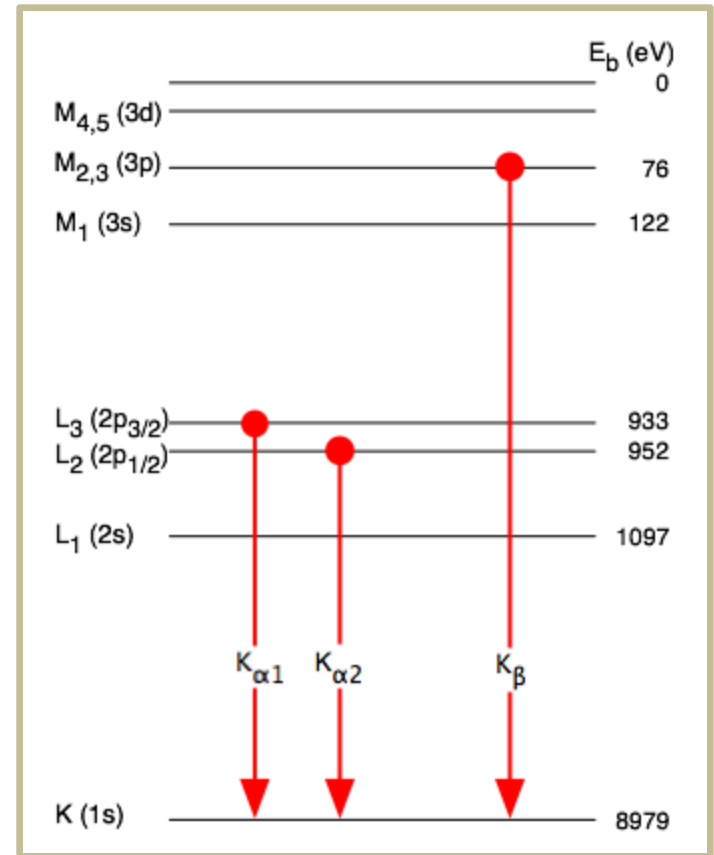
X-Ray Generation

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.
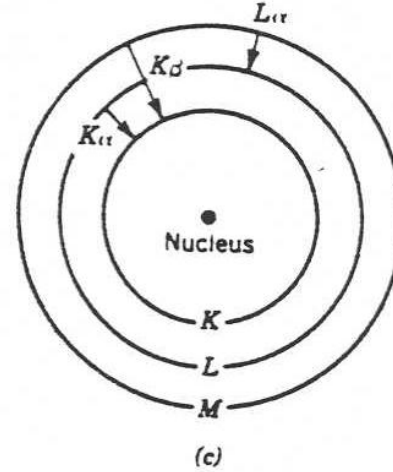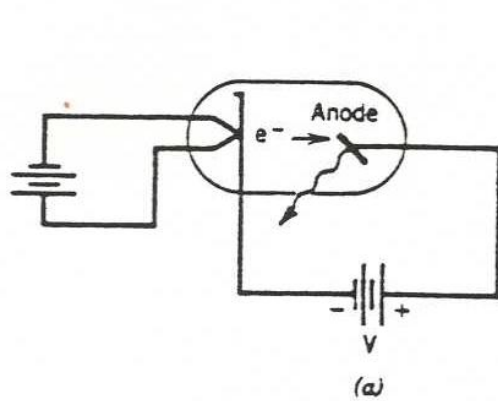
$$\lambda(K_\alpha) = 0.154 \text{ nm}$$
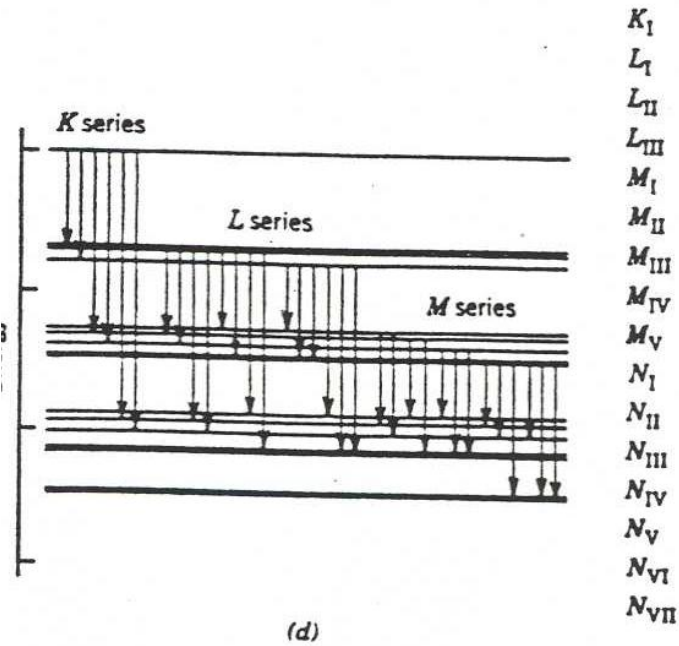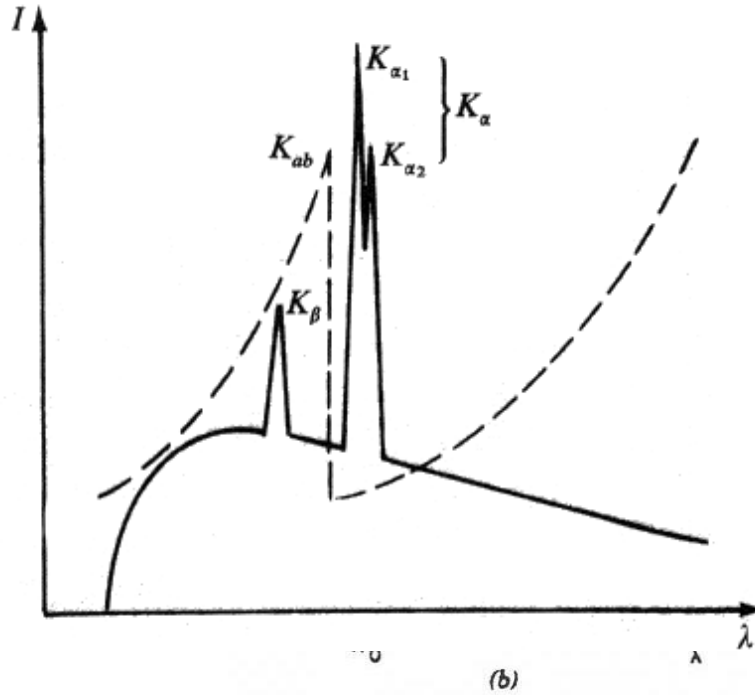
$$\lambda(K_\beta) = 0.139 \text{ nm}$$

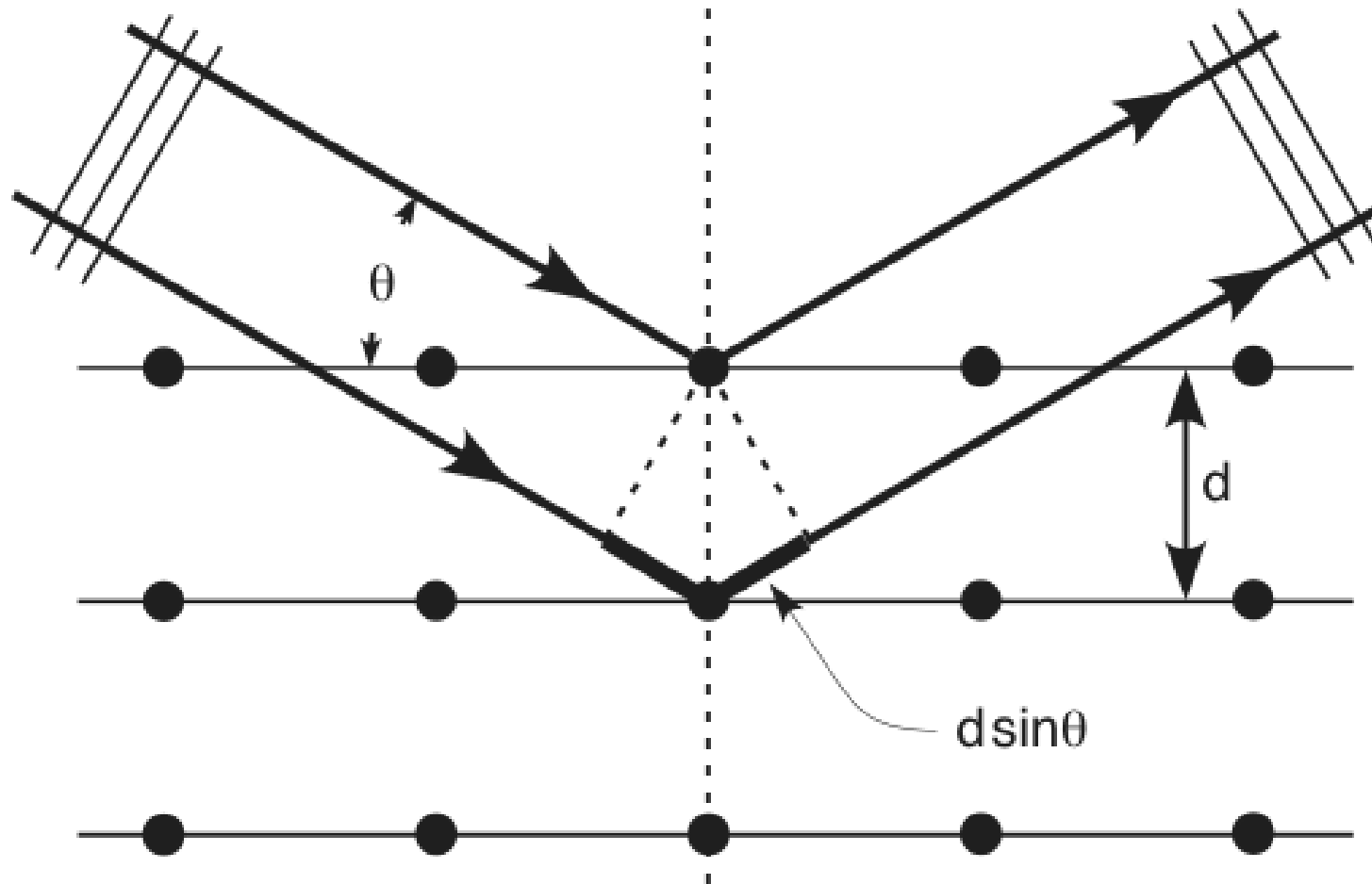Atomic levels involved in copper K_α and K_β emission.

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

K$_\alpha$ and K$_\beta$ X-ray lines

K$_1$	1.540 Å
K$_2$	1.544 Å
K$_\beta$	1.392 Å

from Preston and Dietz, p. 191.

X-Ray diffraction

X-Ray Diffraction -- Bragg's Law
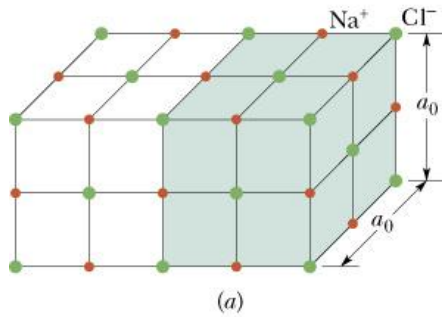
Diffraction of x-rays by crystal: spacing d of adjacent crystal planes on the order of 0.1 nm

$\rightarrow$ three-dimensional diffraction grating with diffraction maxima along angles where reflections from different planes interfere constructively
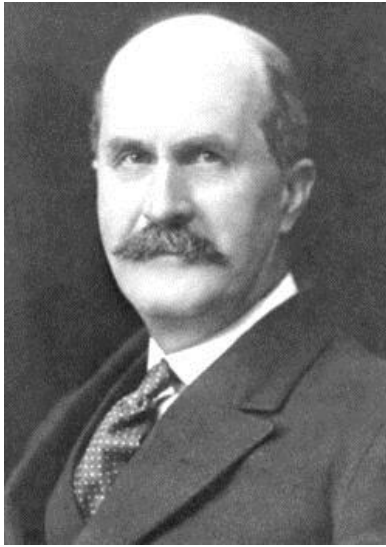
$$2d \sin \theta = m\lambda \text{ for } m = 0, 1, 2, \dots$$

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).
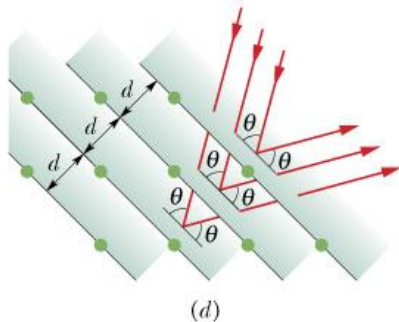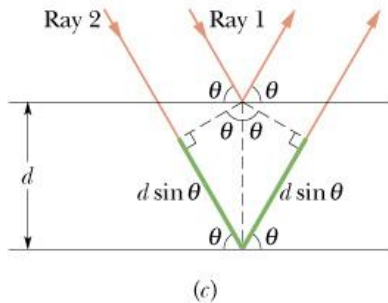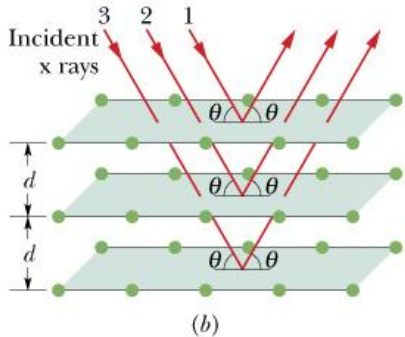
The Braggs (Bragg's Law)


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.

X-Ray Diffraction, cont'd
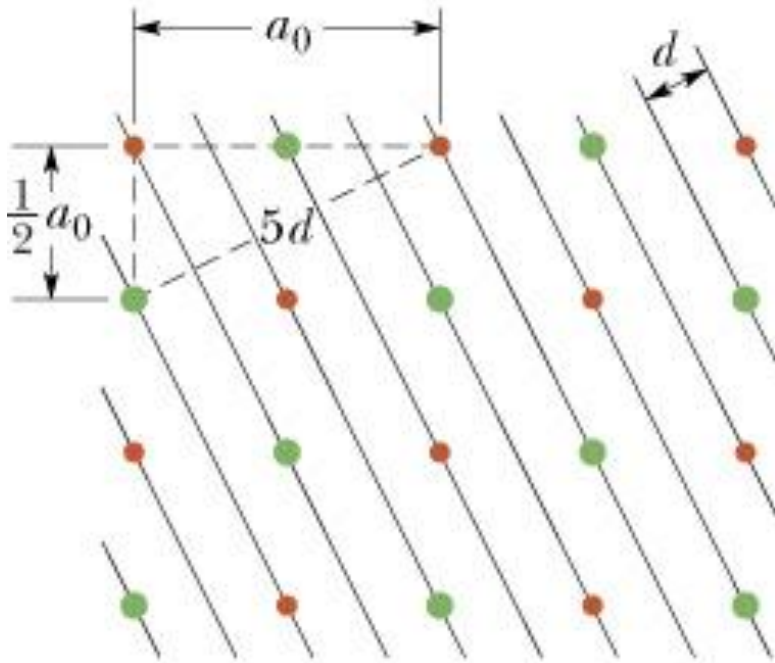
Interplanar spacing d is related to the unit cell dimension a_0

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

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.
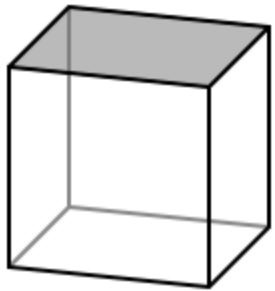
Crystal structure, lattice planes, and Miller indices
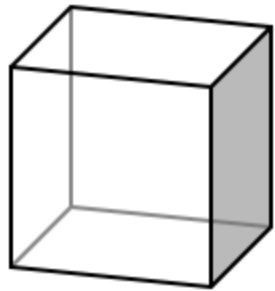
Planes with different Miller indices. The *inverse* of these fractional intercepts yields the Miller indices *h, k, l*.
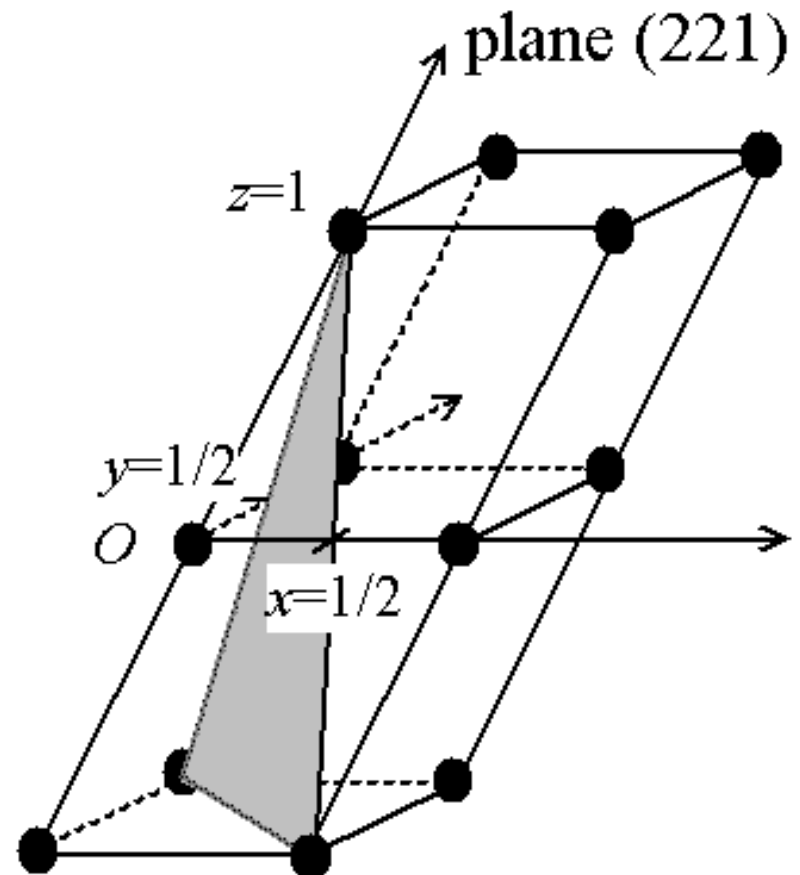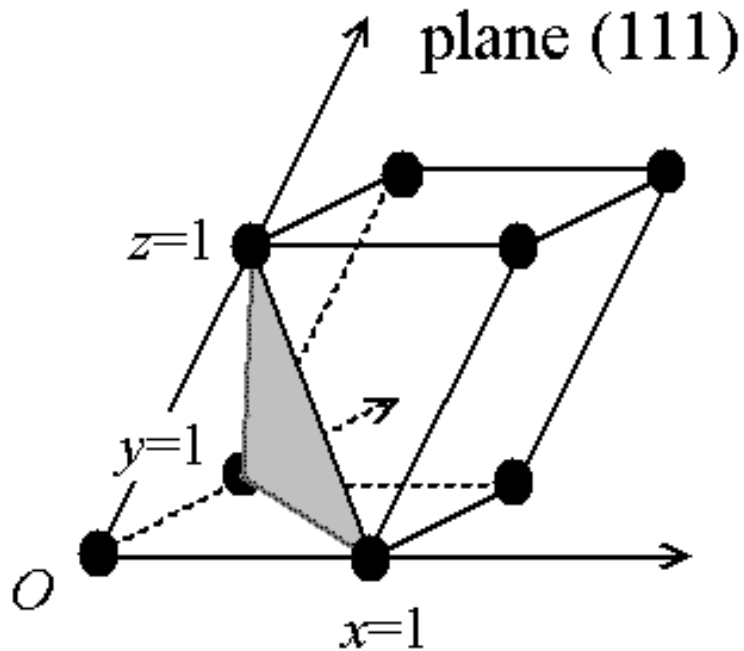
Crystal structure and Miller indices
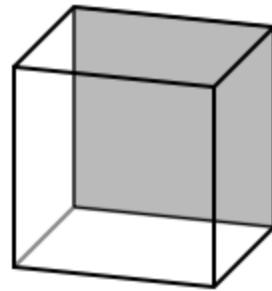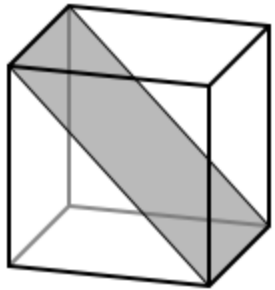

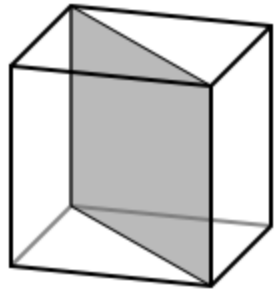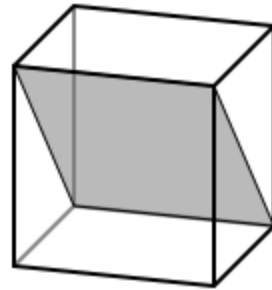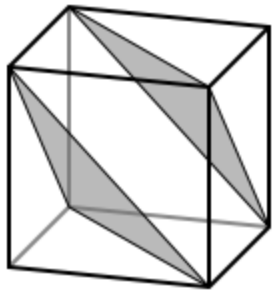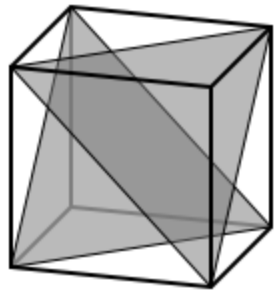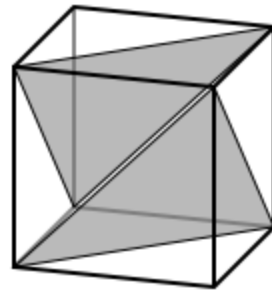Planes with different Miller indices in cubic crystals.

Crystal structure and Miller indices

Li⁺

Cl⁻

UNIVERSITY OF CAMBRIDGE
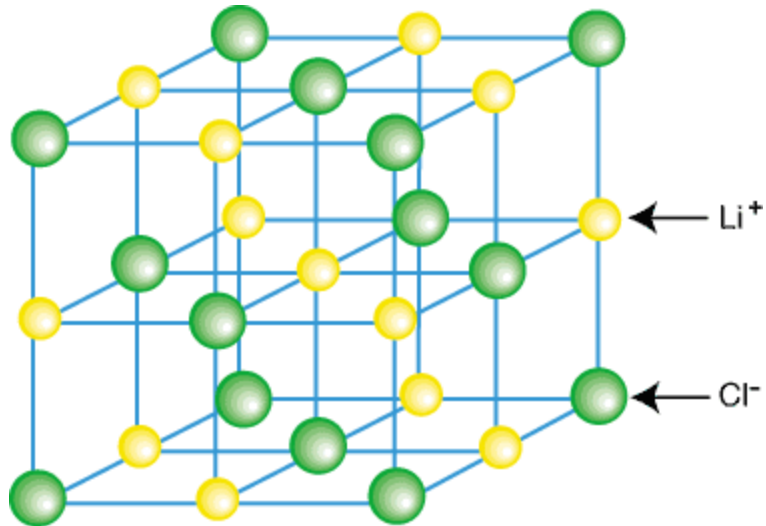
Indexing lattice planes

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

Rock salt (cubic) crystal structure
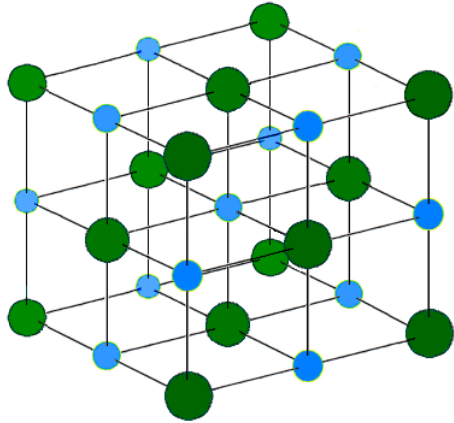
$$d_{hkl} = \frac{a_0}{\sqrt{h^2 + k^2 + l^2}}$$

Structure factor for NaCl:

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

$$F = 4\left(f_{Na} + f_{Cl} \right) \quad \text{if } h, k, l \text{ are even}$$
$$F = 4\left(f_{Na} - f_{Cl} \right) \quad \text{if } h, k, l \text{ are odd}$$
$$F = 0 \quad\qquad\qquad \text{if } h, k, l \text{ are mixed}$$

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

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

(Cu Kα)

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

Diffraction angle 2θ (degrees)
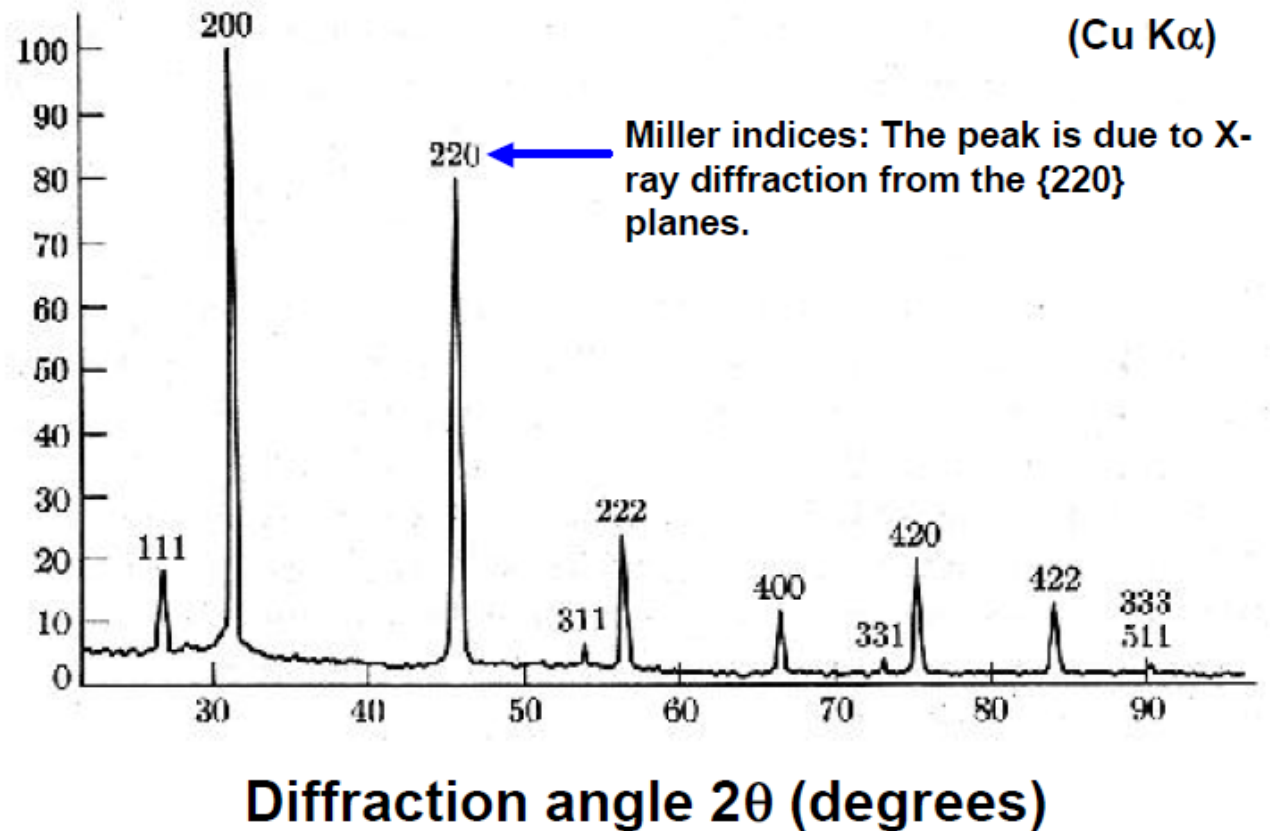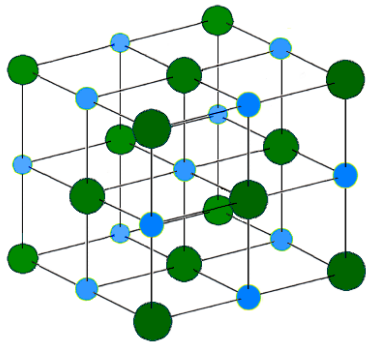
$$d_{hkl} = \frac{a_0}{\sqrt{h^2 + k^2 + l^2}}$$

LiF diffractogram (Cu K$_\alpha$)
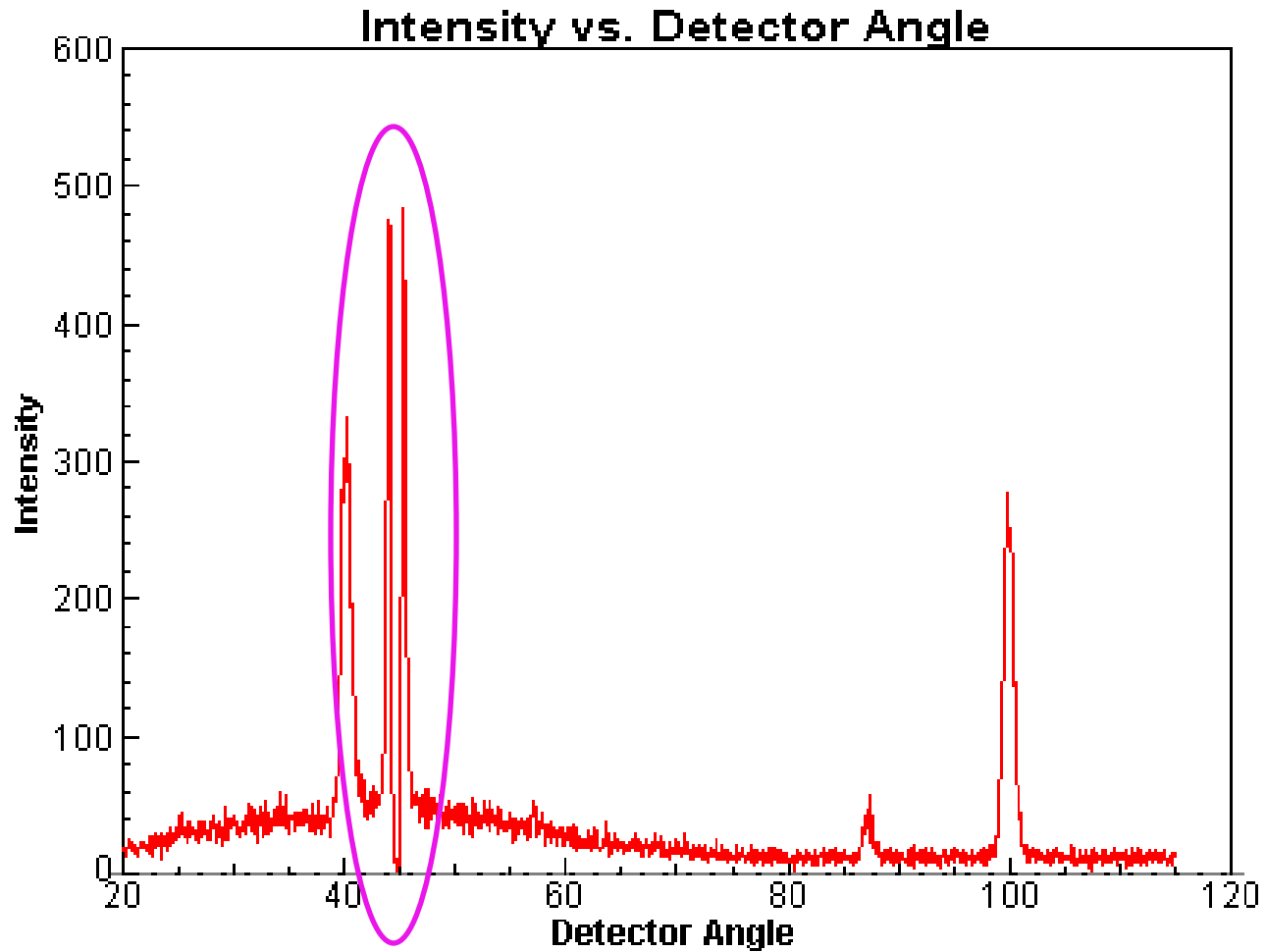
CdTe crystal structure (zincblende)

$a_0 = 0.648$ nm

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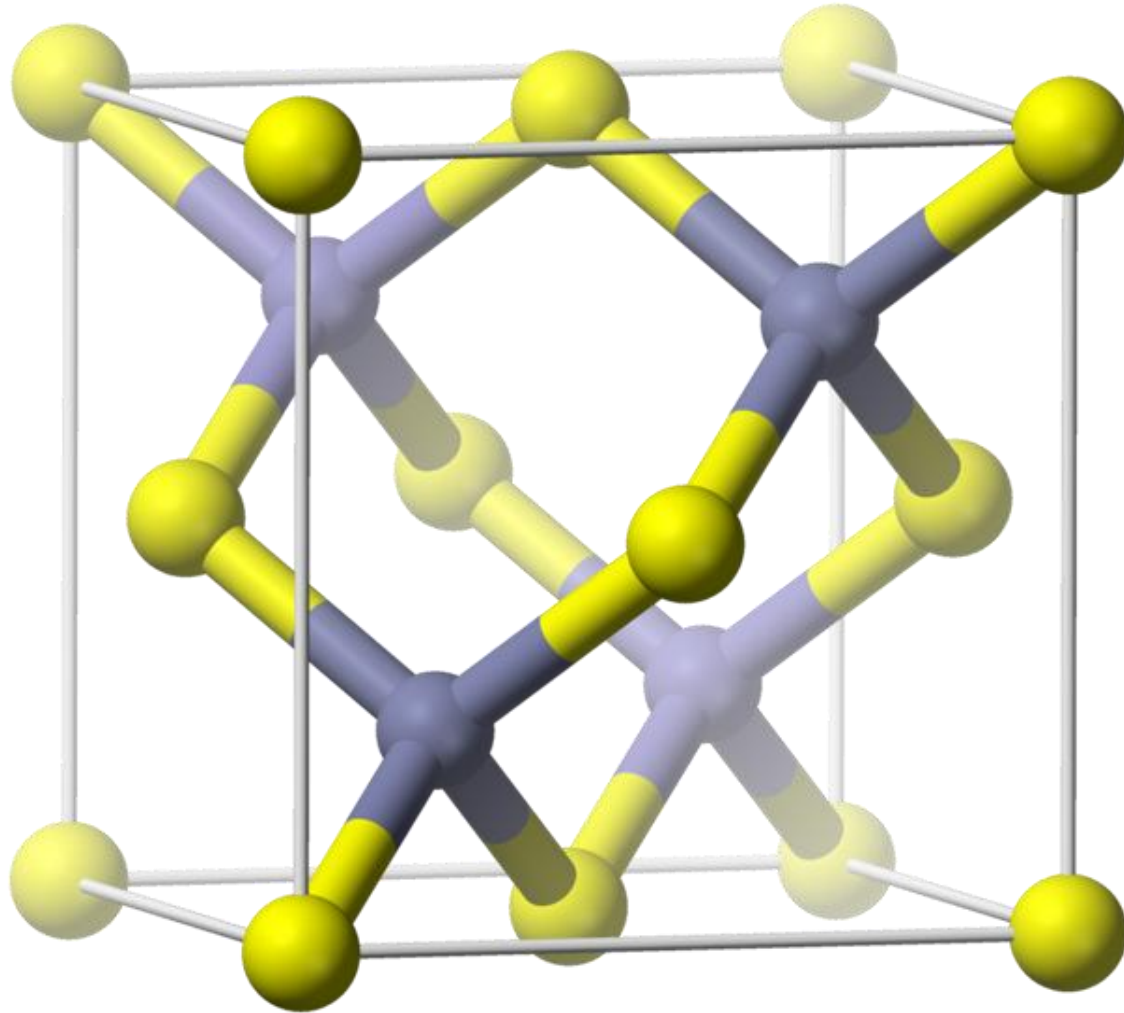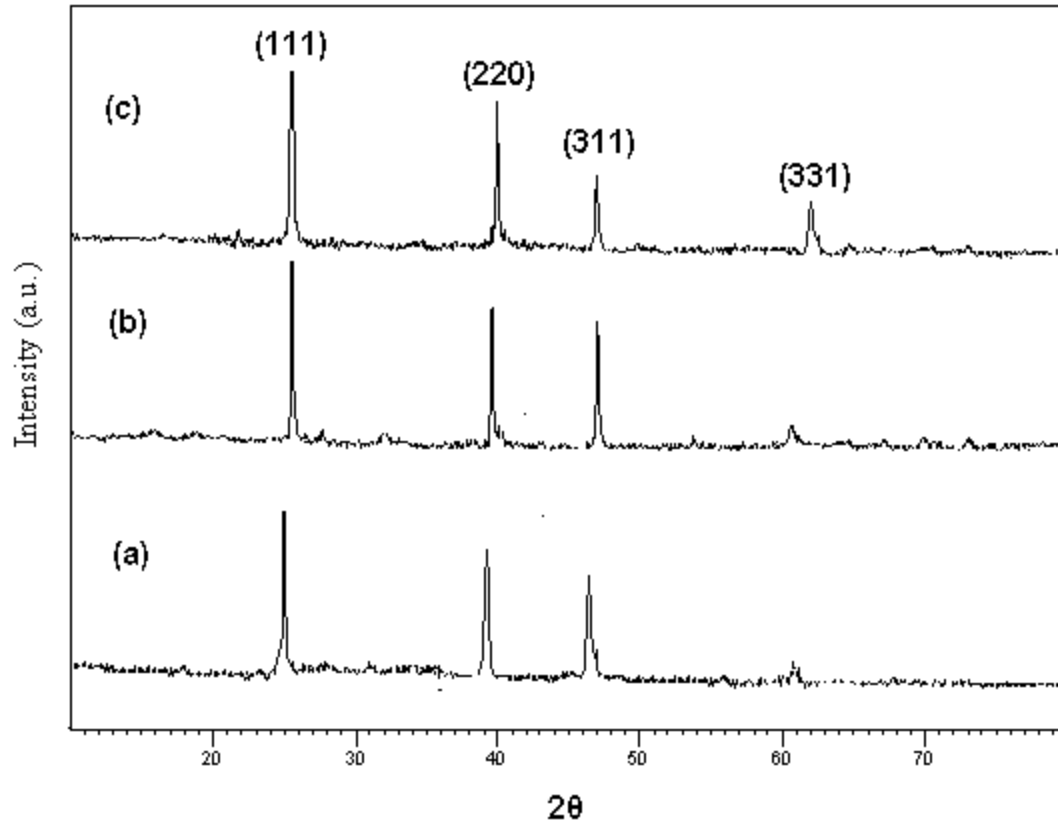
CdTe XRD pattern

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

CdTe XRD pattern (intensity vs. 2θ)

CdTe
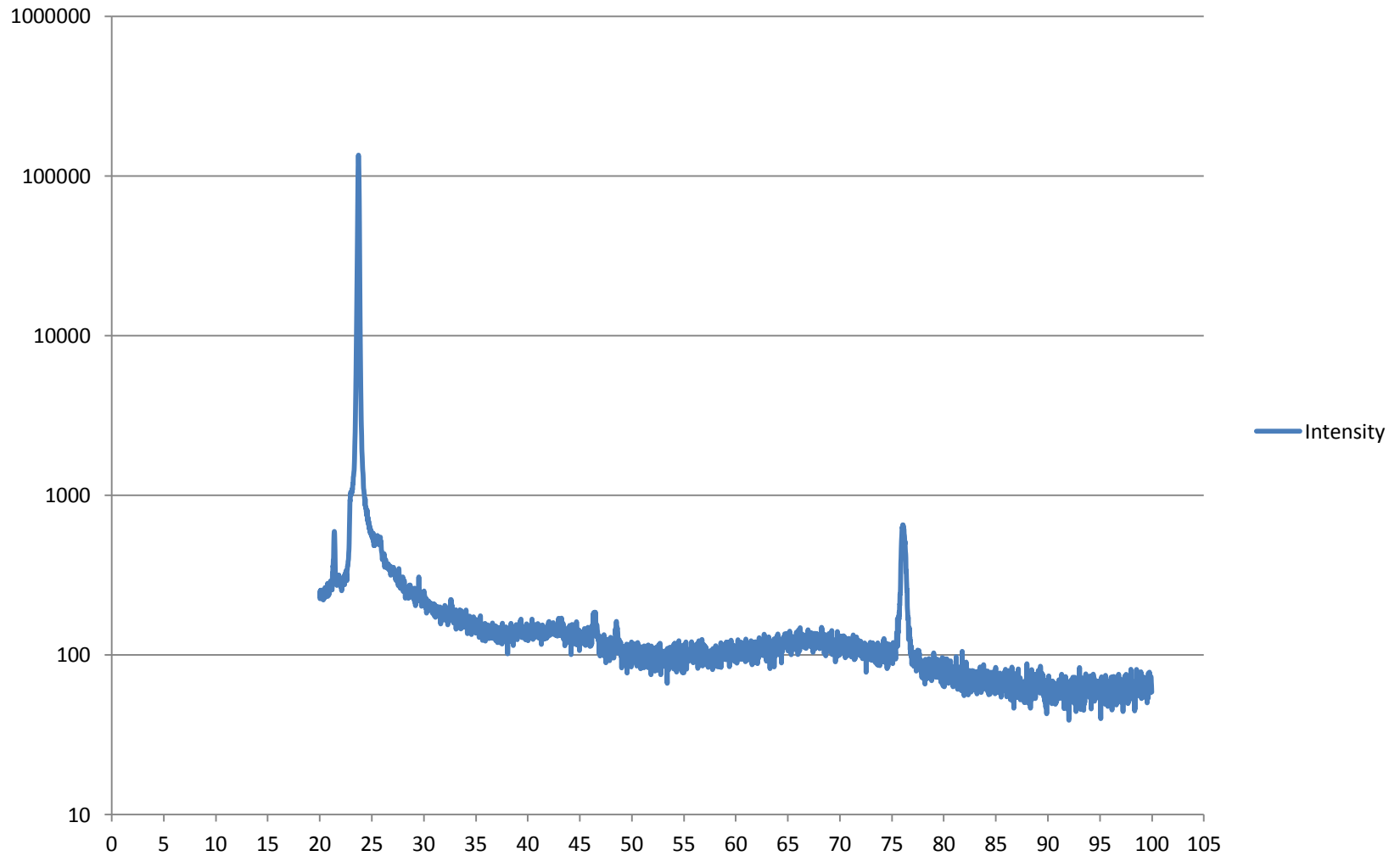
CdS XRD pattern (intensity vs. 2θ)

$a_0 = 0.5832$ nm for zincblende
a=4.160; c=6.756 for wurtzite

CdS
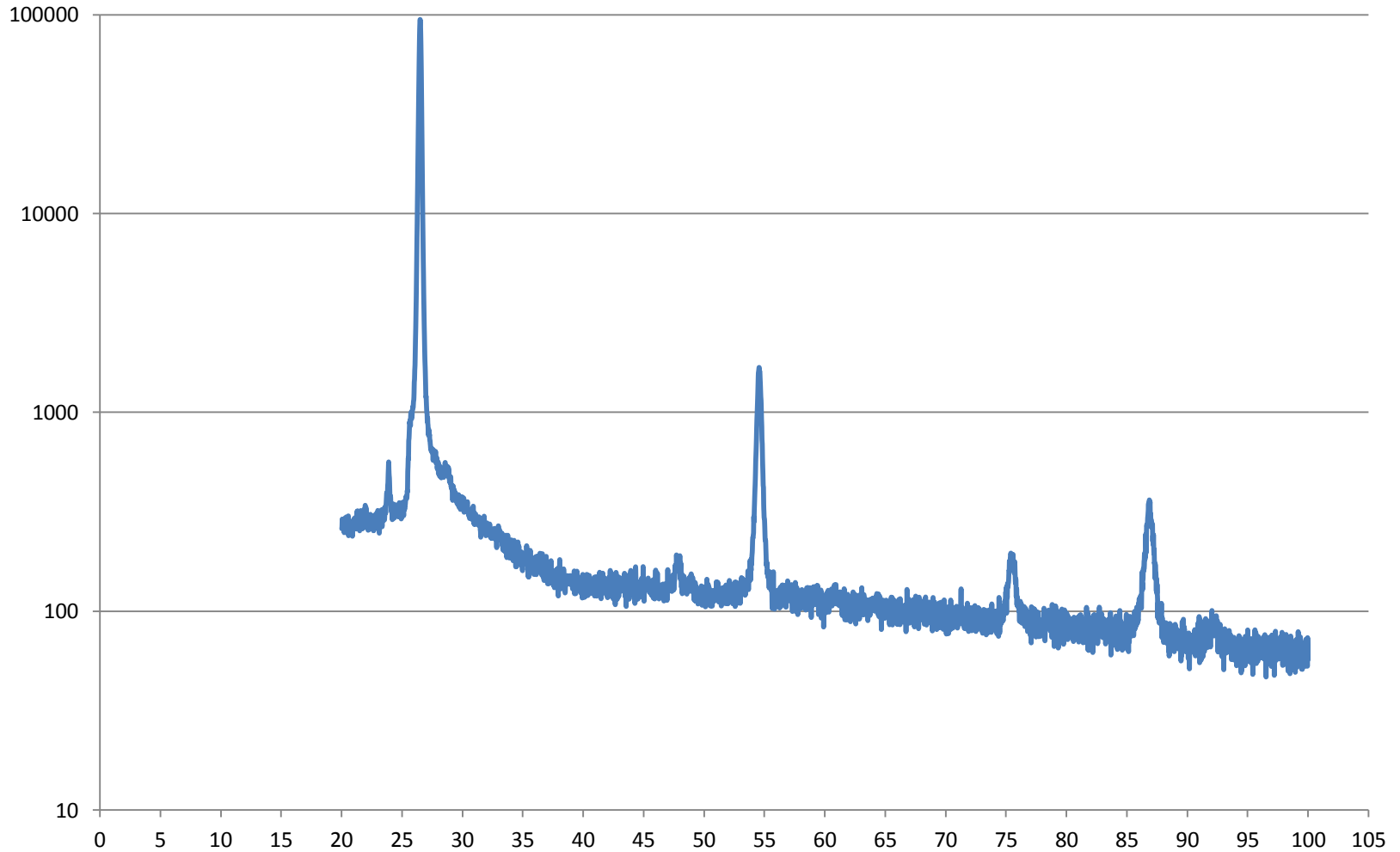
Scherrer Equation (relationship to Shape Factor)

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

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

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

Effects of Grain Orientation in Diffraction Patterns
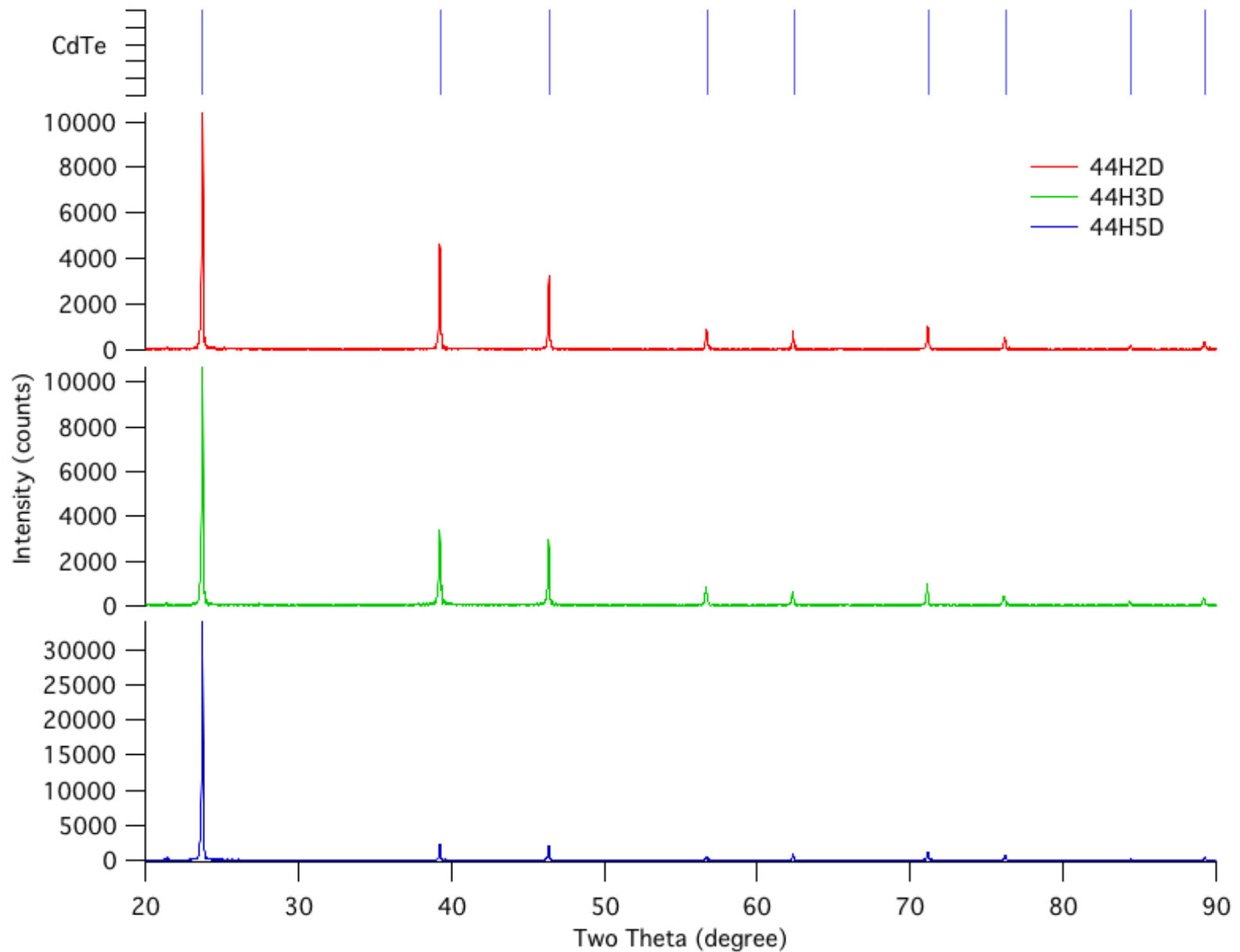
Determining Preferred Orientation

Orientation Factor P:

$$P = (I/\Sigma I)*(\Sigma I')/I'$$

- I is the intensity of the peak (orientation) of interest.
- ΣI is the summation of all peaks related to the phase of interest.
- I' is the intensity of the peak of interest in the reference powder spectra.
- $\Sigma I'$ is the sum of all reference powder peaks.

- For CdTE The calculation was performed on the (111) peak since that peak is the highest peak, meaning it is the dominant orientation (G. B. Harris, *Phil. Mag.*, **43**, 113-123 (1951)).

Orientation Factor for CdTe (111)

Legend:
- 31H5D
- 31H3D
- 31H2D
- 39H5D
- 39H3D
- 39H2D
- 44H5D
- 44H3D
- 44H2D

31---: TEC 15
39---: ALZON
44---: TEC 10

Y-axis: Orientation Factor p (111), ranging 1.4 to 2.8
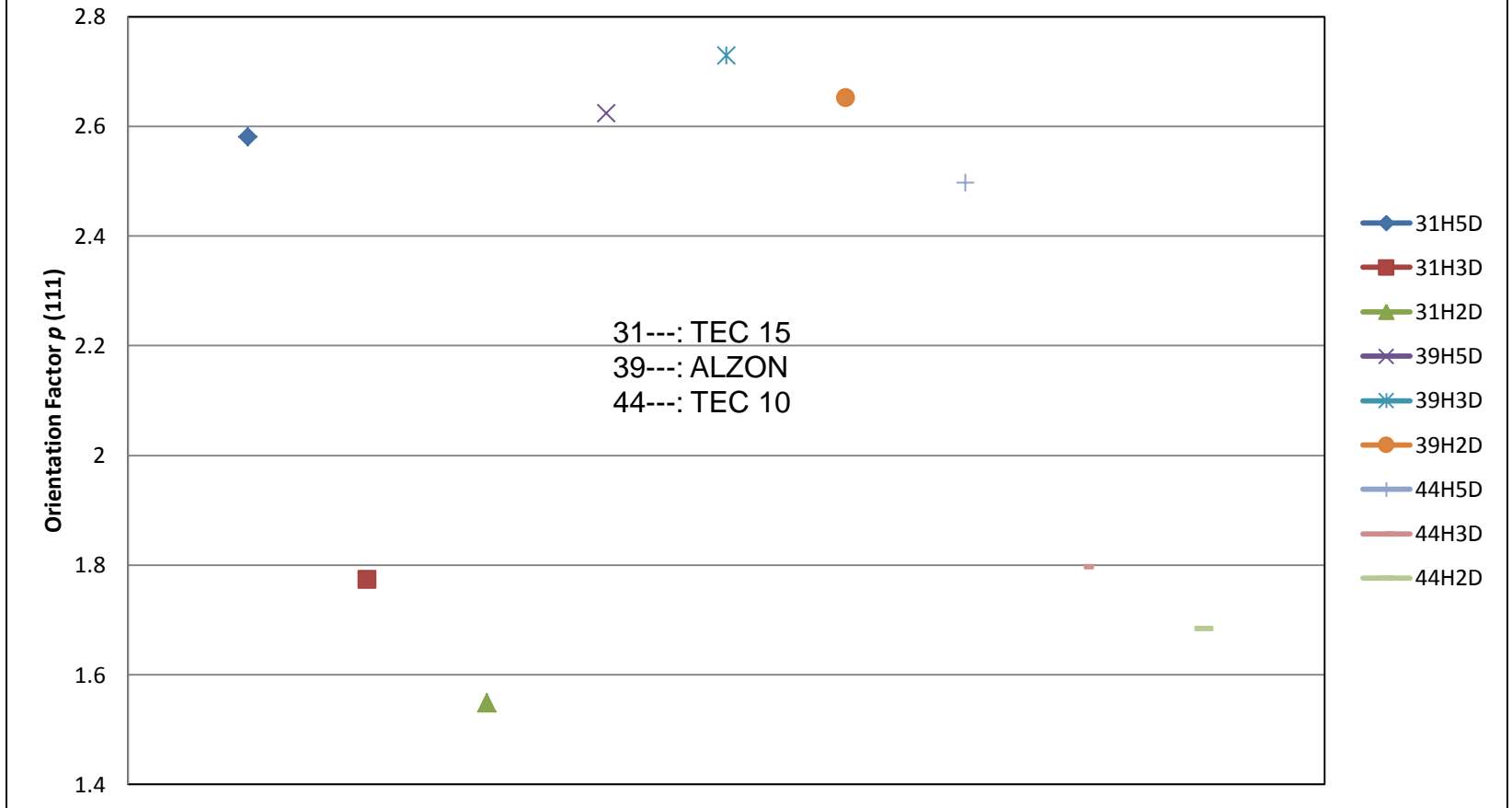
Orientation factor calculated using: $p = \dfrac{I}{\Sigma I} \times \dfrac{\Sigma I'}{I'}$

Elements of XRD Lab #9

This component will be written up individually (a carefully-prepared report (<u>10 points</u>), due Nov. 27, 2012). The goals include the following (organized into a sensible, coherent report):

1. Measure XRD patterns for thin films of CdS, CdTe, and "activated" ($CdCl_2$-treated) CdTe.

2. Plot the data as Intensity vs. 2θ for each of these samples.

3. Include a table in your report including the h,k,l values and their predicted 2θ peak positions (in degrees) for CdTe assuming the use of Cu K_α X-rays (as opposed to K_β).

4. Identify (assign) all peaks in the CdTe spectra; describe/indicate which peaks you know with certainty and which have an uncertain origin (include your basis for each assignment). All peaks in your experimental CdTe XRD spectra should be assigned (and labeled) according the Miller indices. If you observe any peaks arising from Cu K_β X-rays, point this out.

5. There are two possible crystal structures for CdS (zincblende (cubic) and hexagonal (wurtzite). Based on the XRD spectrum for CdS, deduce whether the crystal structure of our CdS is zincblende or hexagonal (note that calculation of peaks for the hexagonal structure is more complicated and not required here).

6. Analyze the degree of orientation in the films you have received. Compare contrast the results.

7. Include a discussion in your text of various key aspects you note about XRD and our thin film samples -- such as the relationship between the lattice plane spacing (d_{hkl}) and the scattering angle (2θ), how the CdTe changes with $CdCl_2$ treatment, the position of the dominant (111) peak in the CdTe samples as compared to reference spectra data, and how one can deduce the structure of our CdS based in part on the XRD measurement.