X-Ray Diffraction

Summer Open House

Thursday, Aug. 5, 2004

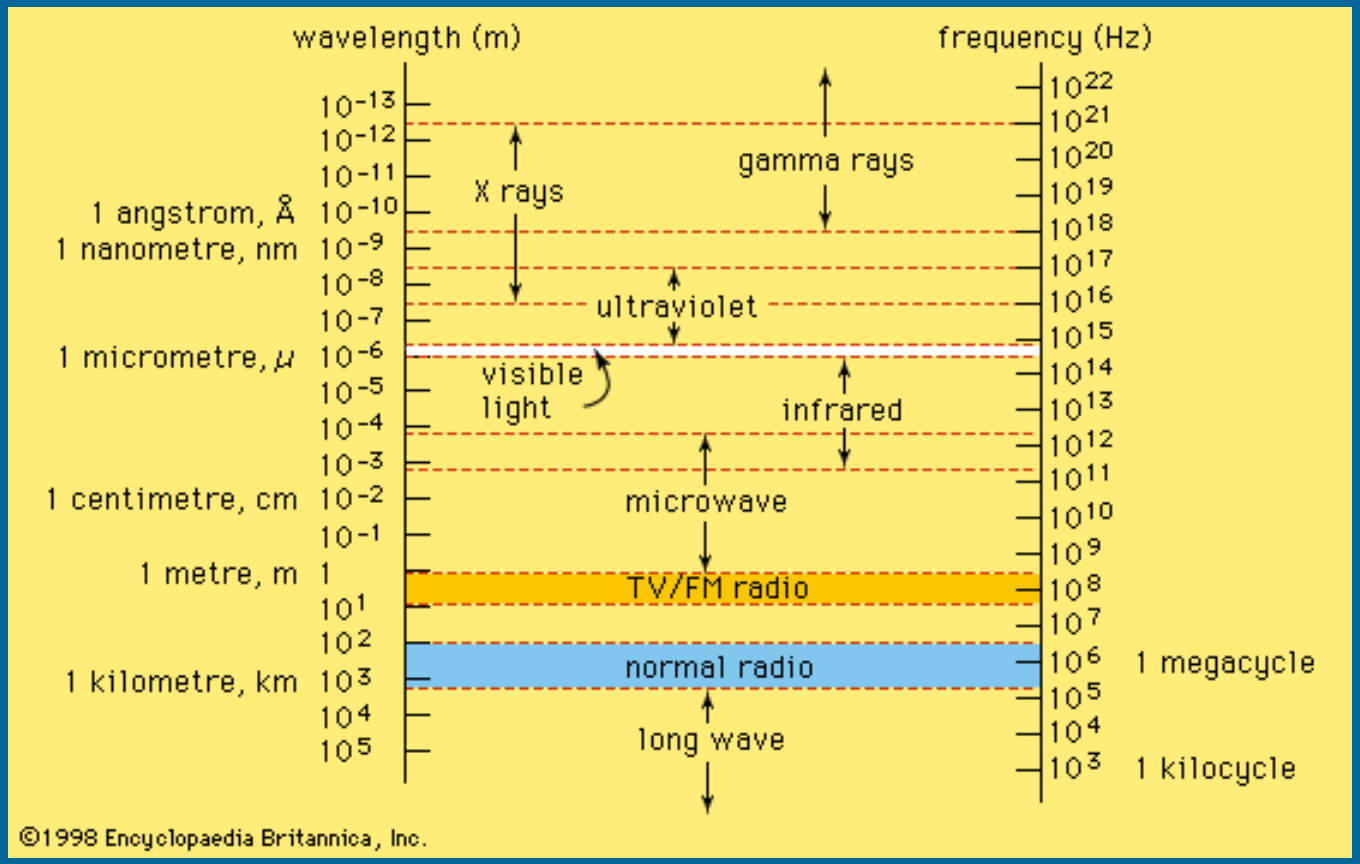
10:00 AM

250 MRL Building

Nichole Wonderling

HISTORY

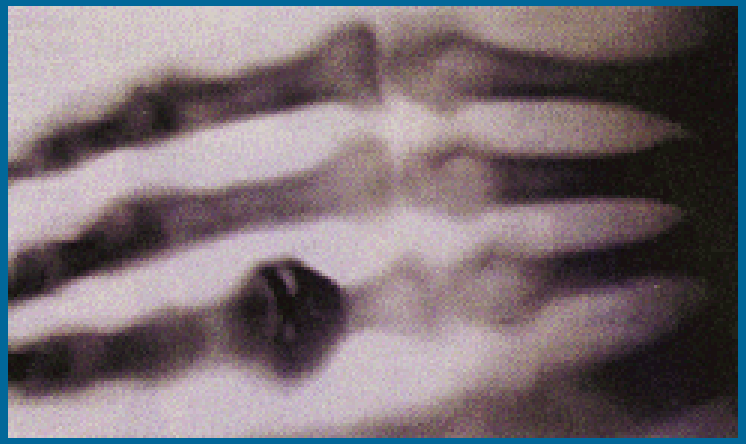
Wavelength Range of X-rays



Encyclopedia Britannica, Inc.

The Discovery of X-Rays

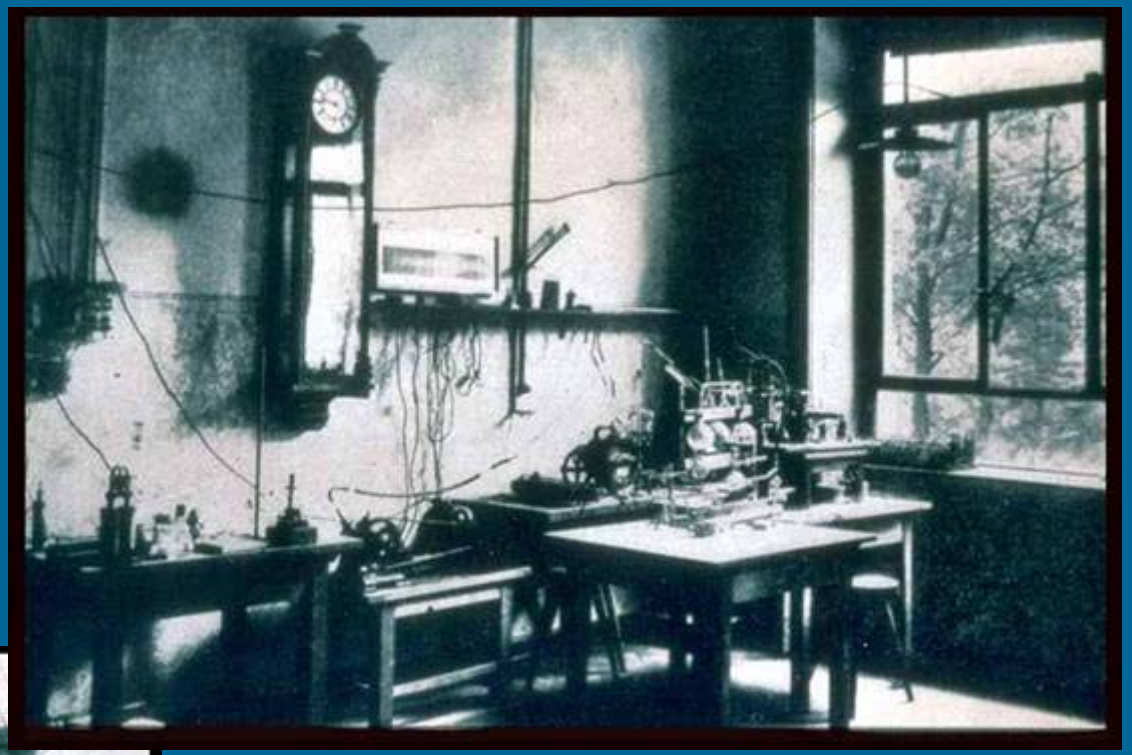
- On 8 Nov, 1895, **Wilhelm Conrad Röntgen** (accidentally) discovered an image cast from his cathode ray generator, projected far beyond the possible range of the cathode rays (now known as an electron beam). Further investigation showed that the rays were generated at the point of contact of the cathode ray beam on the interior of the vacuum tube, that they were not deflected by magnetic fields, and they penetrated many kinds of matter.



- A week after his discovery, Rontgen took an X-ray photograph of his wife's hand which clearly revealed her wedding ring and her bones. The photograph electrified the general public and aroused great scientific interest in the new form of radiation. Röntgen named the new form of radiation X-radiation (X standing for "Unknown").

http://inventors.about.com/library/inventors/blxray.htm

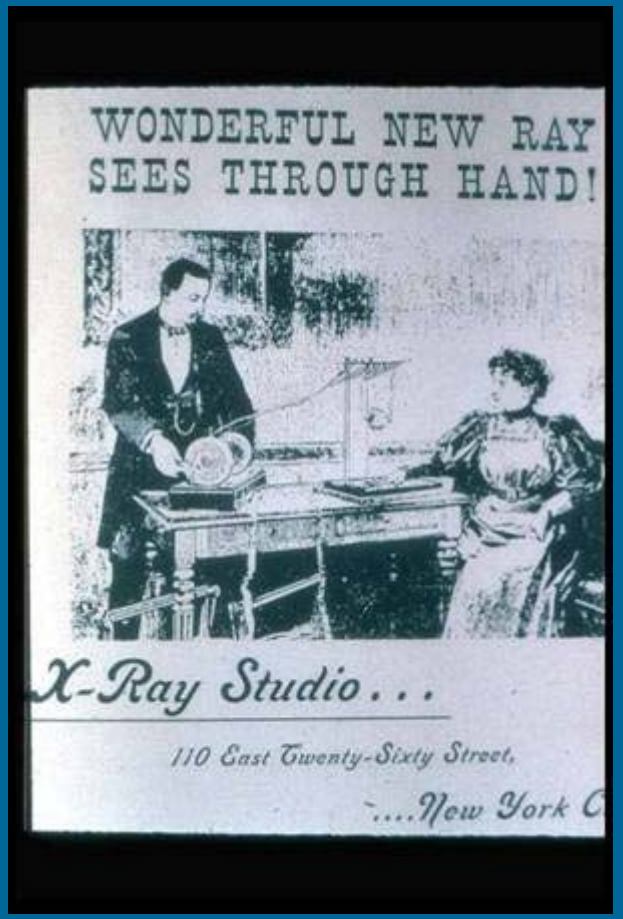
Laboratory room in which Roentgen first noted and investigated X-rays



Physical Institute of the University of Wurzburg, taken in 1896. The Roentgens lived in apartments on the upper story, with laboratories and classrooms in the basement and first floor.

http://www.xray.hmc.psu.edu/rci/ss1/ss1_2.html

It was the Rage……..



Get your
bone portrait!

Laue - 1912

Showed that if a beam of X rays passed through a crystal, diffraction would take place and a pattern would be formed on a photographic plate placed at a right angle to the direction of the rays.

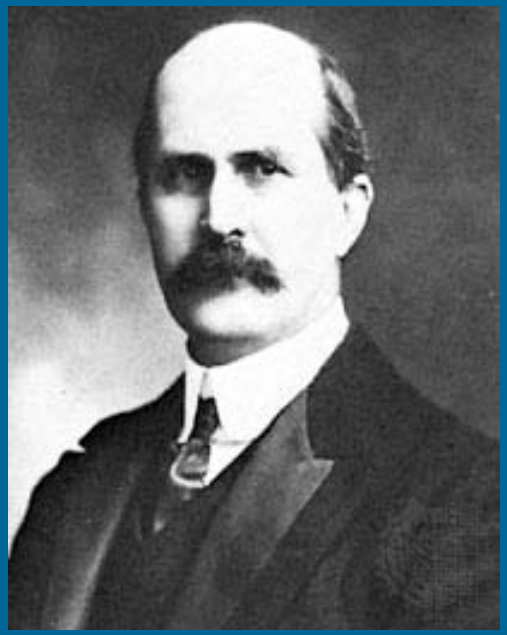
Max von Laue

Today, known as the Laue pattern

A few months later – Two Braggs

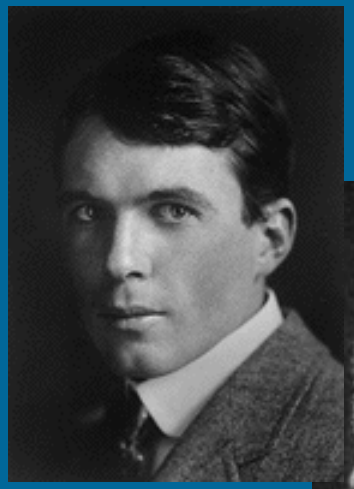
Father

Sir William Henry Bragg

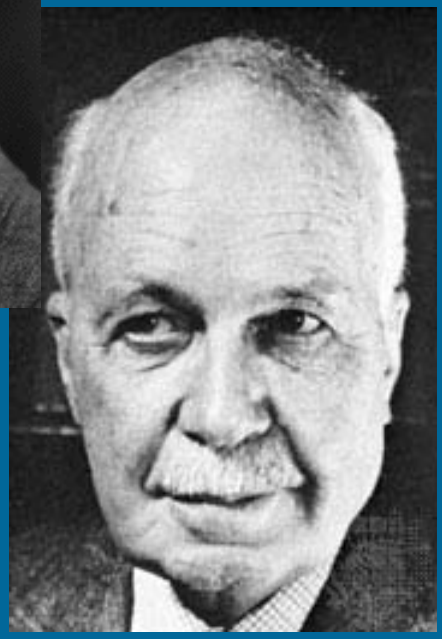


Son

Sir William Lawrence Bragg



….as a boy



as a man….

http://www.britannica.com/nobel/micro/83_18.html

THEORY

Young Bragg

- Believing that Laue's explanation was incorrect in detail, he carried out a series of experiments, the result of which he published the Bragg equation –

He was 15 years old when he did this!

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

Bragg's Law - defined

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

Assume n=1 for the first order reflection (hkl=111)

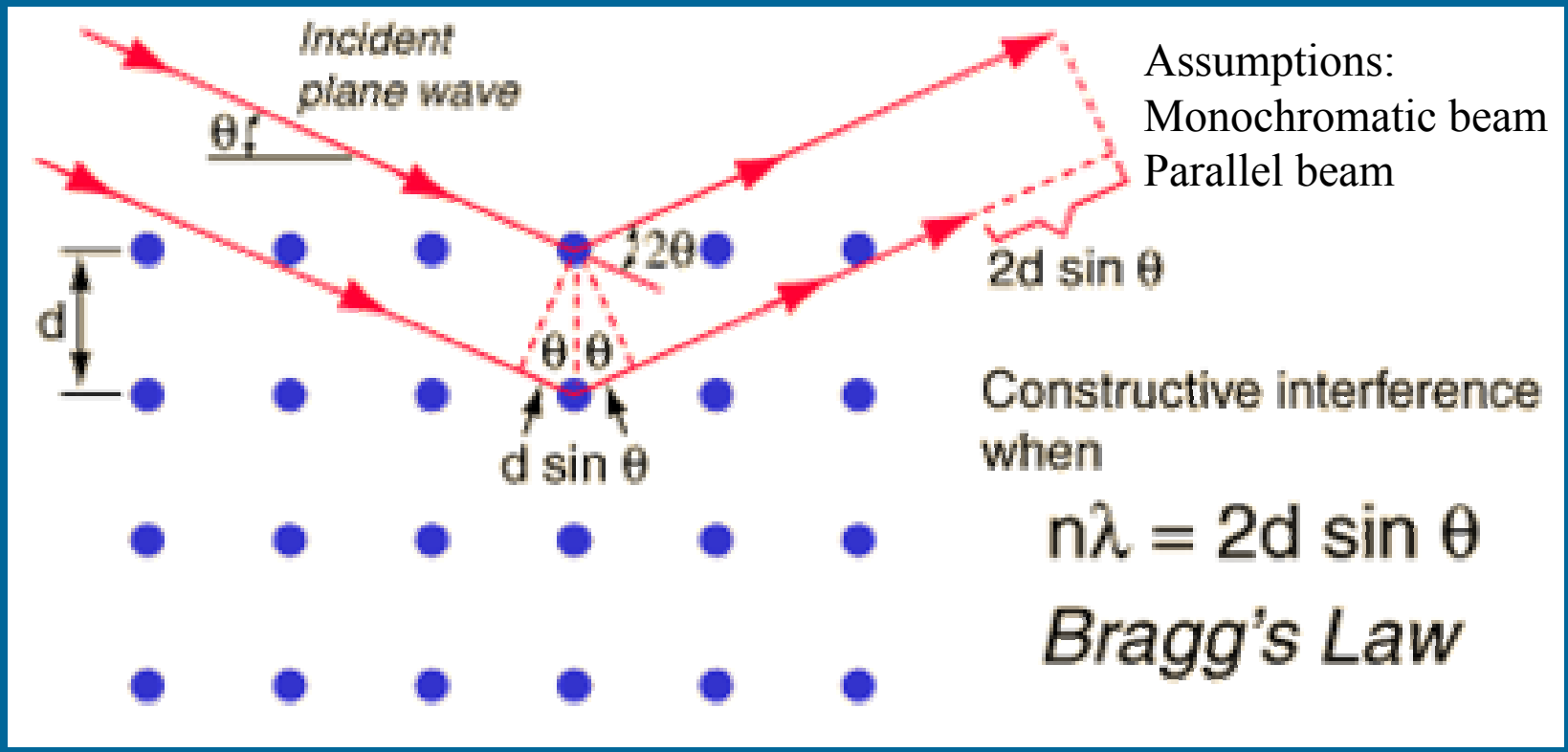
Tells us at what angles X rays will be diffracted by a crystal when the X-ray wavelength and distance between the crystal atoms are known

λ = Wavelength
1.54 A for Cu
(known value)

θ = X-ray incidence angle
(known value)

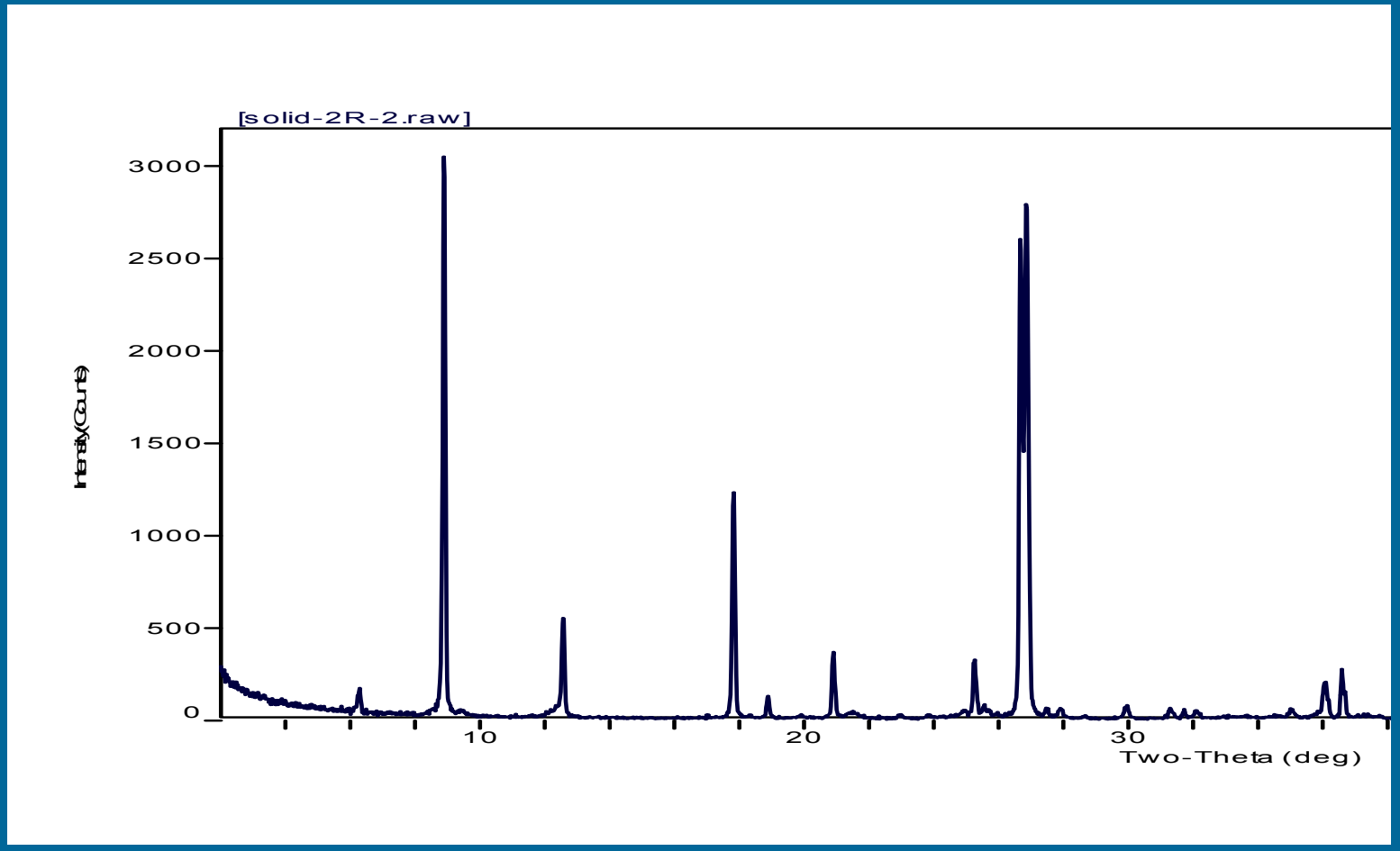
d = Lattice inter-planar spacing of the crystal

Bragg's Law



http://hyperphysics.phy-astr.gsu.edu/hbase/quantum/bragg.html

Eventually…… Bragg-Brentano Diffractometer and The Diffraction Pattern



Development of Modern Spectrometers

Invention of the X-ray Tube

- William D. Coolidge's name is inseparably linked with the X-ray tube-popularly called the 'Coolidge tube.'

Invention Impact

This invention completely revolutionized the generation of X-rays and remains to this day the model upon which all X-ray tubes are patterned.

- **William D. Coolidge**
Born Oct 23 1873 - Died Feb 4 1975

Vacuum Tube (X-Ray) - Patented 1913

http://inventors.about.com/gi/dynamic/offsite.htm?site=http://www.invent.org/hall%5Fof%5Ffame/1%5F1%5F6%5Fdetail.asp%3FvInventorID=33

The Coolidge Tube

- Ductile Tungsten
  - General Electric

•High Melting point – 3410 C
•Low evaporation at high temp.
•Tensile strength greater than steel

• Metal powder was pressed, sintered and forged to thin rods.

•Early filaments still sublimed too quickly; later added N2 and Ar to decrease tungsten evaporation

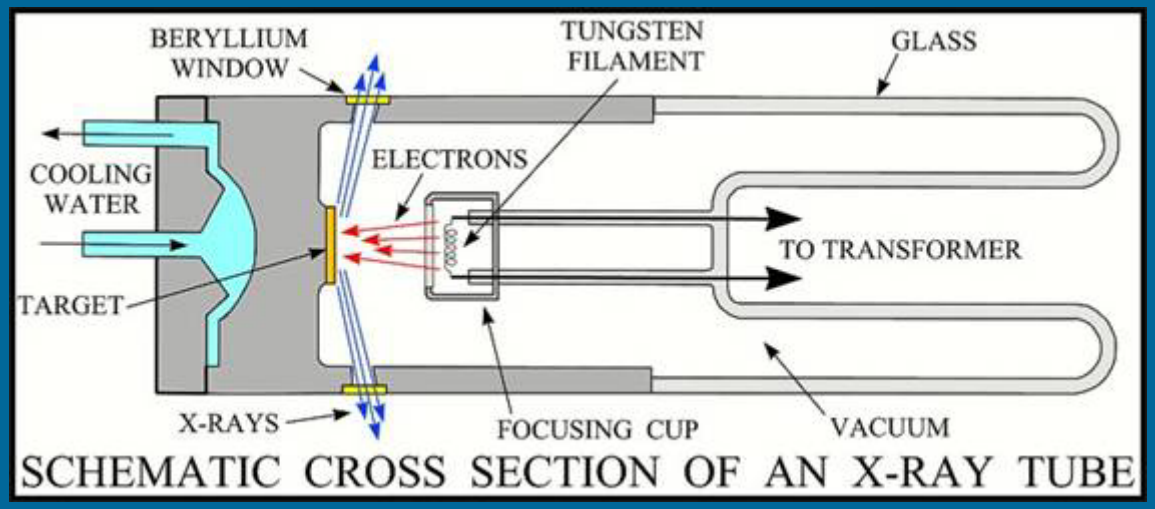
•But, these gases carried heat away from the filament – reducing brightness – winding into a fine coil reduced this heat loss.

http://inventors.about.com/gi/dynamic/offsite.htm?site=http://invsee.asu.edu/Modules/lightbulb/meathist4.htm

Modern X-Ray Tube

Cross Section

- In an X-ray tube, the high voltage maintained across the electrodes draws electrons toward a metal target (the anode). X-rays are produced at the point of impact, and radiate in all directions.



SCHEMATIC CROSS SECTION OF AN X-RAY TUBE

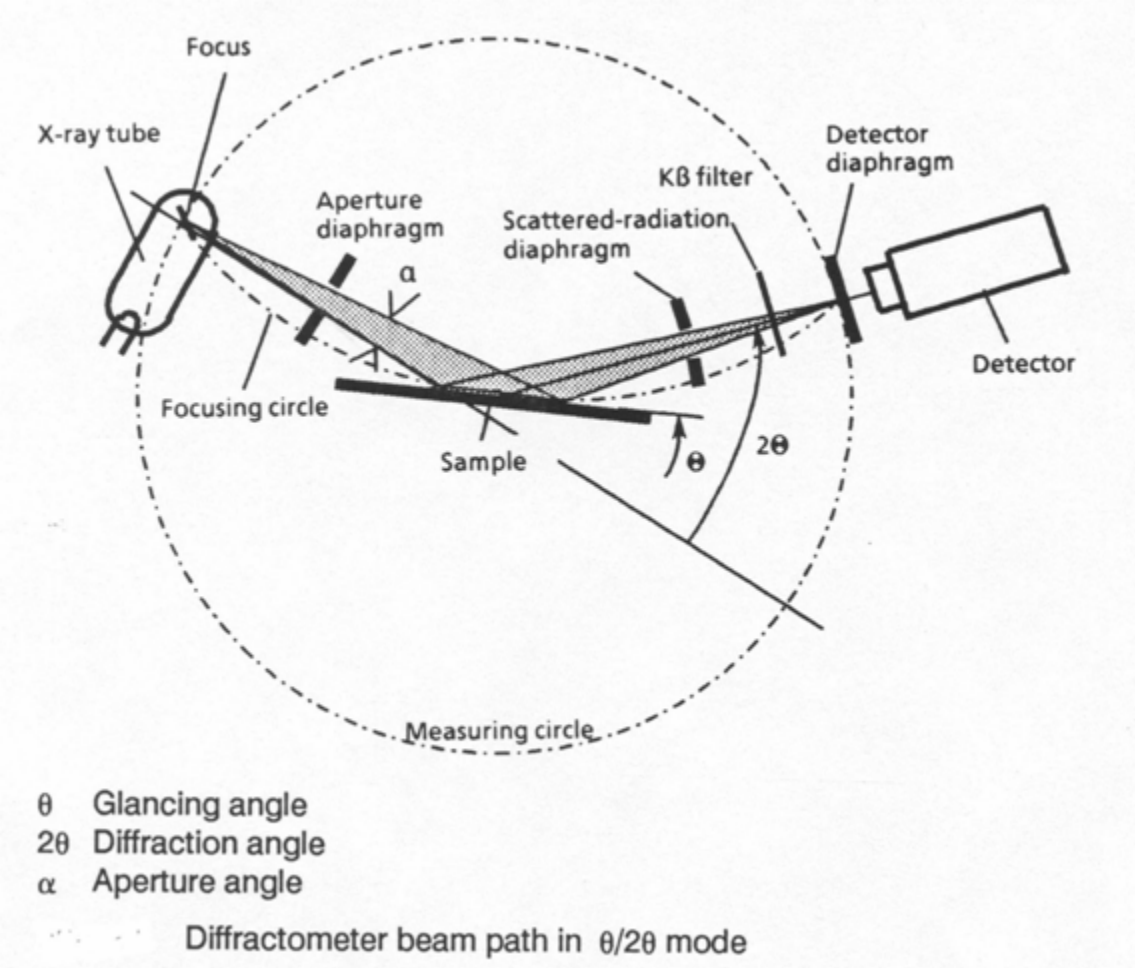
http://pubs.usgs.gov/of/of01-041/htmldocs/xrpd.htm

X-ray Tubes

ATPS - Copper, normal focus, glass, x-ray tube used in Scintag diffractometers

Ceramic x-ray tubes used in Philips diffractometers

Schematic of Bragg-Brentano Diffractometer



From the Siemens (now Bruker AXS) manual for the D5000

Strengths / Limitations

Strengths of X-ray Diffraction

- Non-destructive – small amount of sample
- Relatively rapid
- Identification of compounds / phases – not just elements
- Quantification of concentration of phases – (sometimes)
- Classically for powders, but solids possible too
- Gives information regarding crystallinity, size/strain, crystallite size, and orientation

Limitations of X-ray Diffraction

- Bulk technique – generally – unless a camera is uses
- Not a “stand-alone” technique – often need chemical data
- Complicated spectra – multiphase materials – identification / quantification can be difficult

MCL Instruments / Capabilities

Powder Diffraction

Scintag

……Scintag 1

Both horizontal θ/2θ geometry
-tube is stationary
- detector and sample move

Both used for basic powder Diffraction.

Scintag 2……

Both located in 158 MRL building

Scintag (cont'd)

Located in 158 MRL

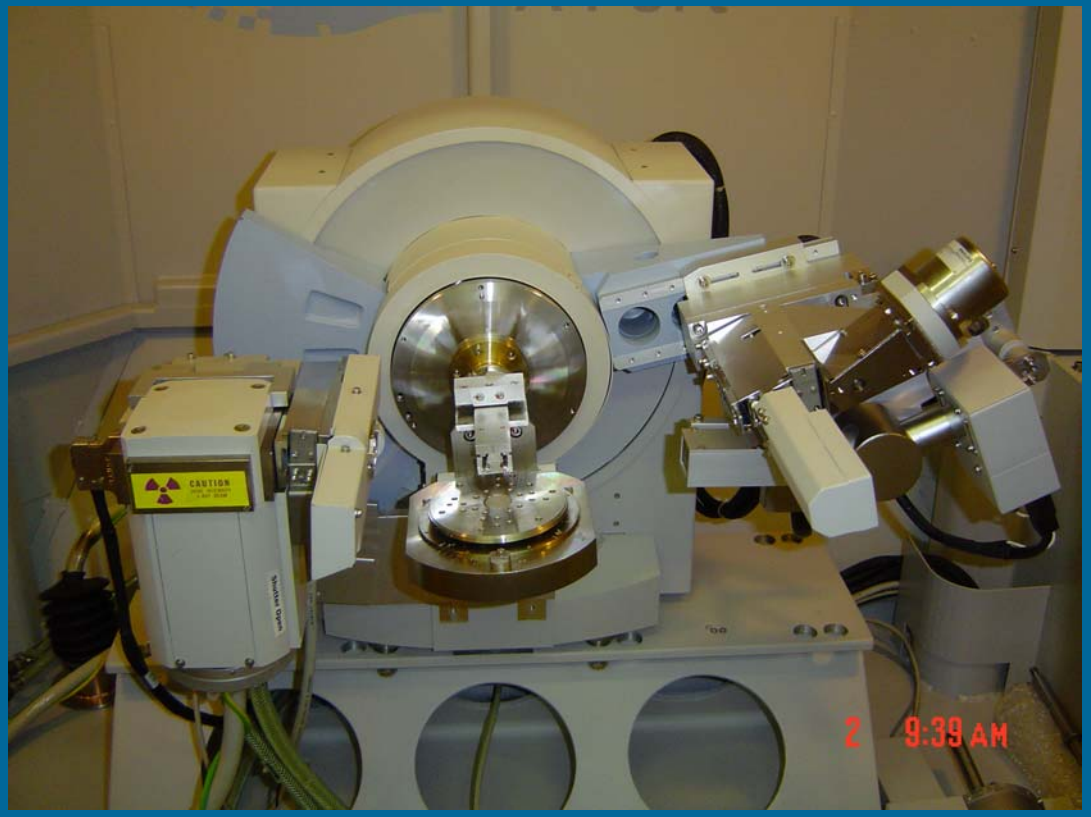
……..Scintag 3

Vertical θ/θ geometry
- sample is stationary
- tube and detector move

Hot (up to 1500C), Cold, and sample rotation stages available

Grazing angle geometry possible

Philips X'Pert MPD



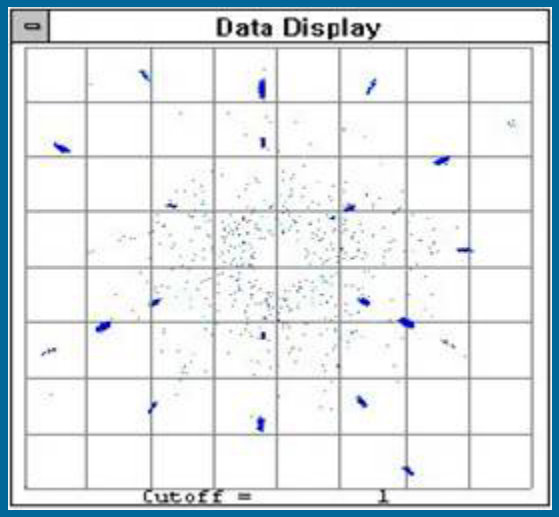
Standard θ/2θ Bragg-Brentano diffractometer
Grazing angle geometry possible.

Located in room 164 MRI building

Single Crystal Diffractometers

Laue

Multiwire Laboratories

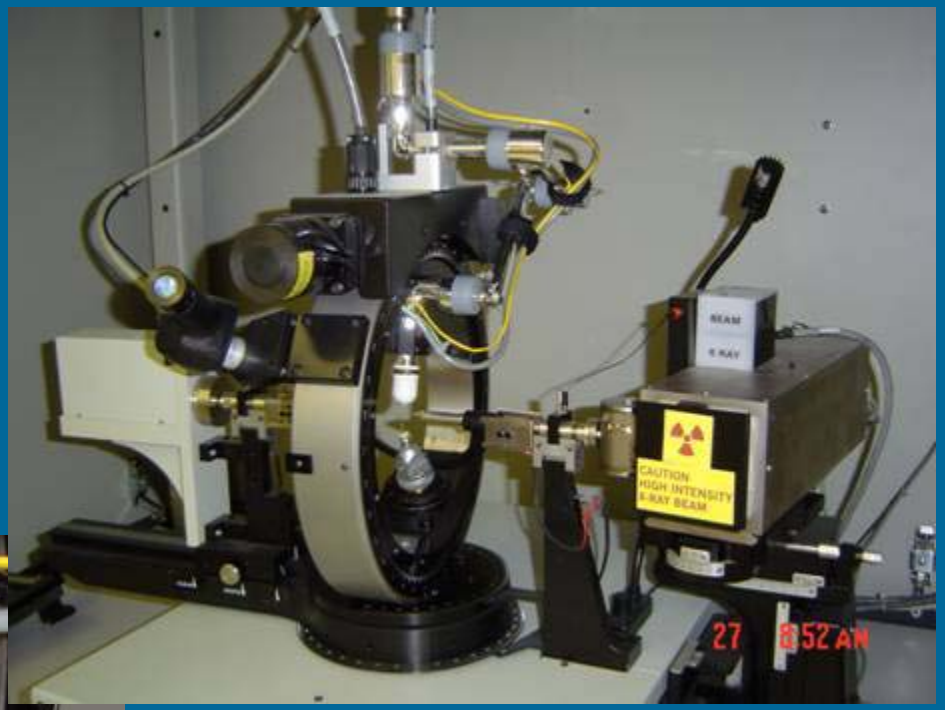


Located in 156 MRL

Consists of a position sensitive x-ray proportional counter connected to a computer system - orients and characterizes single crystals quickly in real-time.

Laue patterns can be easily stored, displayed, and printed - completely avoiding the use of film.

Bruker 4-Circle



Structure determination of Single crystals – maximum Dimension 0.3 mm.

Located in 156 MRL

Philips 4-Circle

Low Resolution Optics –
For Stress / Texture measurements in poly-crystalline aggregates.

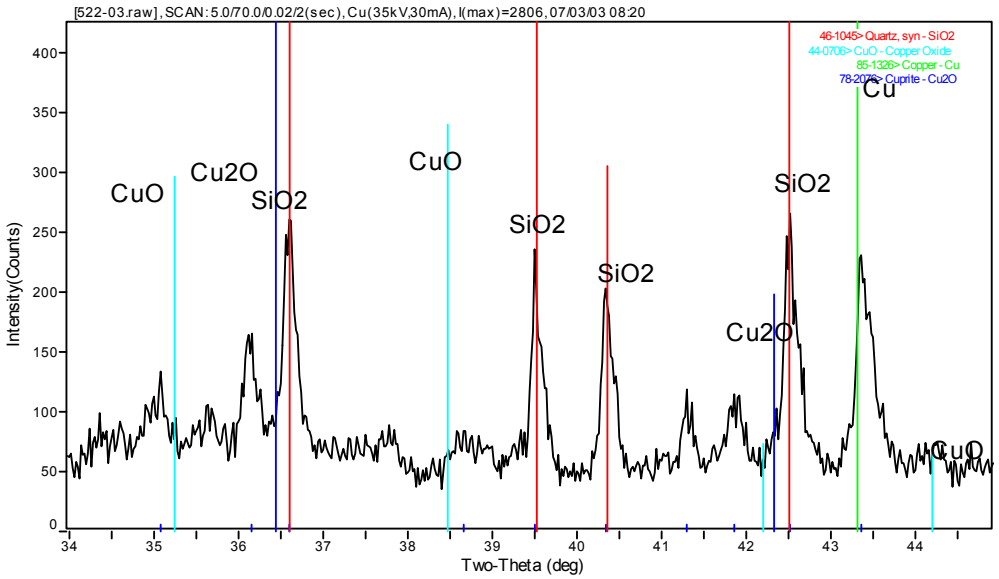
High Resolution Optics –
uses an asymmetrical Bartels monochromator for collecting rocking curve data, crystal quality, and reciprocal space mapping.

Located in room 164 MRI building

Applications at PSU

Oxidation States of Copper

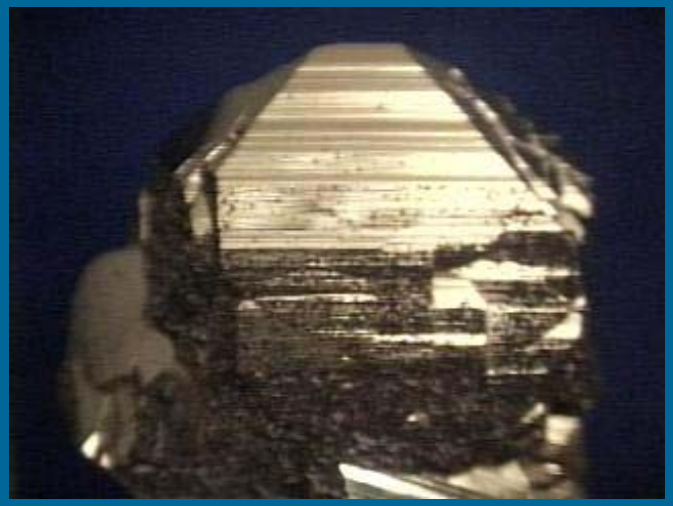
As a fungicide on roofing materials

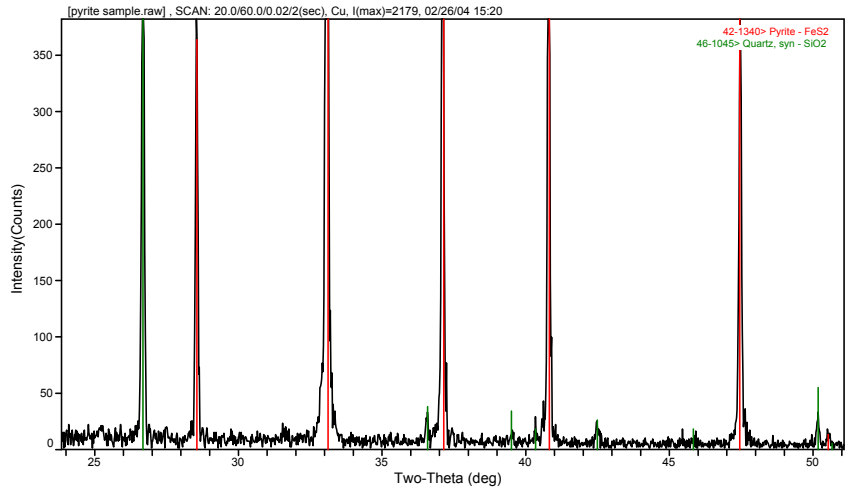


- The major phase is quartz, SiO2, (red) also a significant amount of Cu, (green). Perhaps, some Cu2O, (blue) but Cu2O directly overlaps the SiO2 lines. There is no CuO detected.
- Other unidentified phases also present.

Pyrite

- Example of the mineral pyrite, FeS_2, that was found at a local road construction site.





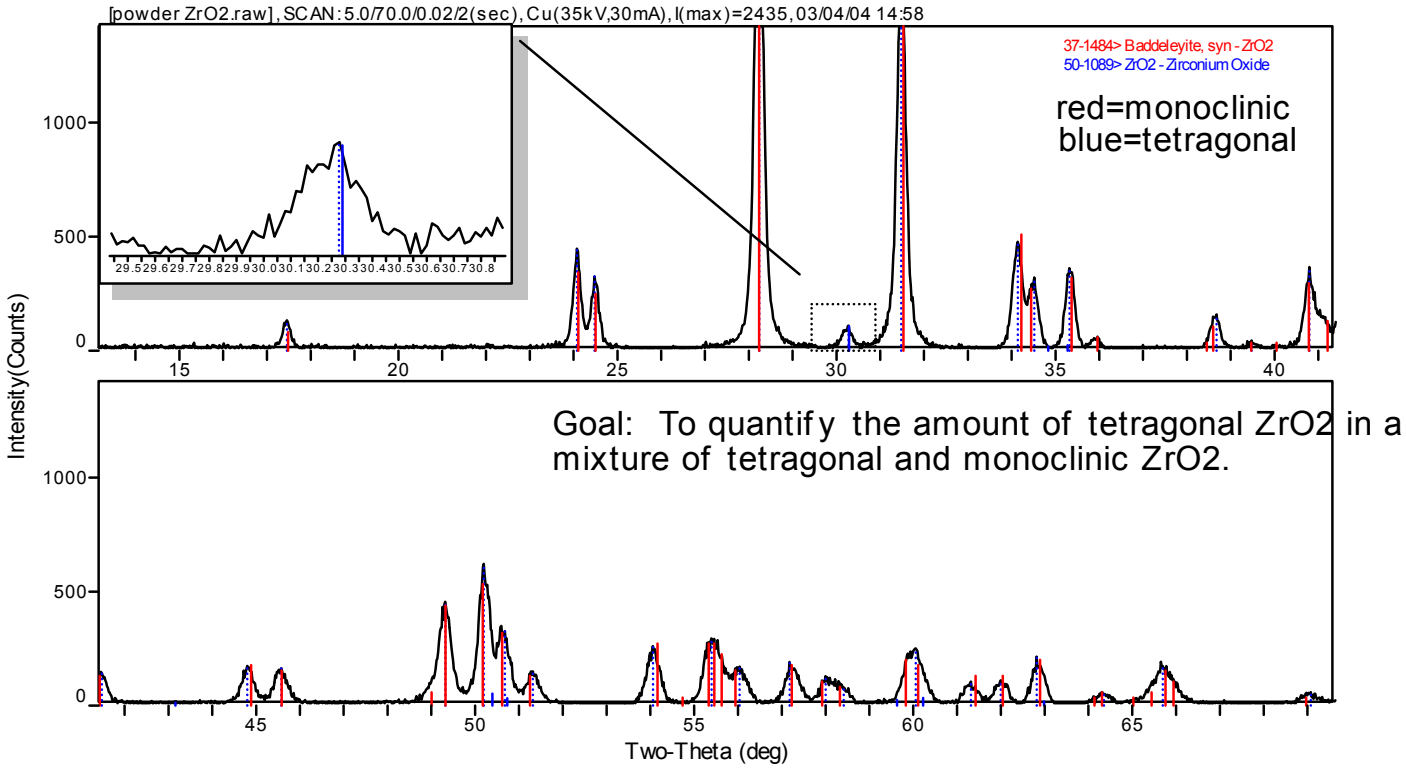
(Eq. 1) $FeS_2 + 7/2O_2 + H_2O = Fe^{2+} + 2SO_4^{2-} + 2H^+$

(Eq. 2) $Fe^{2+} + 1/4O_2 + 3/2H_2O = FeOOHppt + 2H^+$

(Eq. 3) $FeS_2 + 15/4O_2 + 7/2H_2O = Fe(OH)_3ppt + 2SO_4^{2-} + 4H^+$

Rietveld Refinement

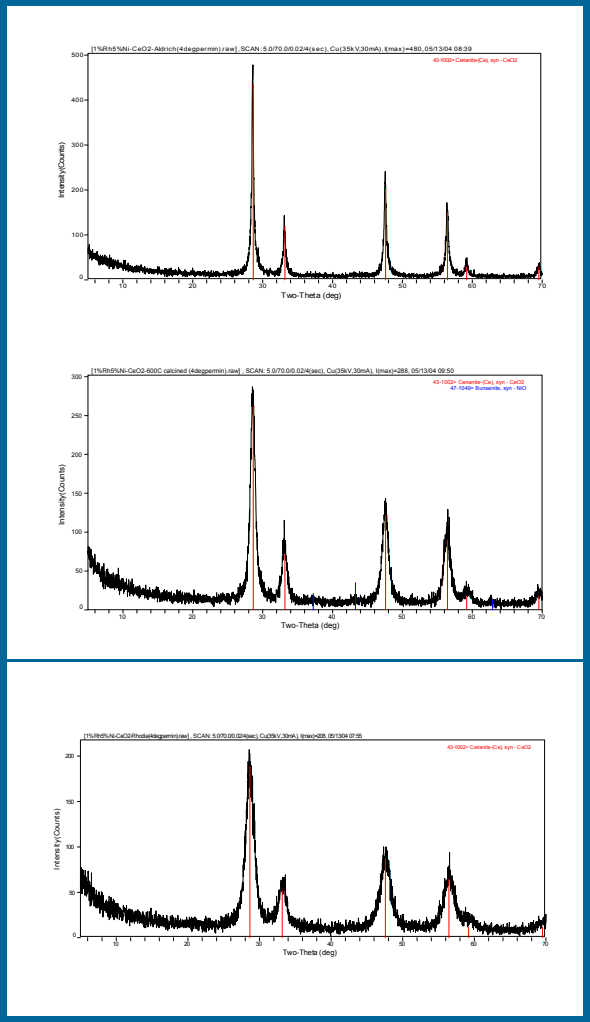
- Quantify monoclinic and tetragonal zirconia – only the 100% tetragonal peak visible / clear from overlap



Crystallite Size Measurement

Rh-Ni CeO2 powders

Decreasing crystallite size



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

τ = particle size

K = shape factor

(typically 0.85-0.9)

λ = wavelength (Angstroms)

β = corrected FWHM (radians)

θ = ½ 2θ (peak position)

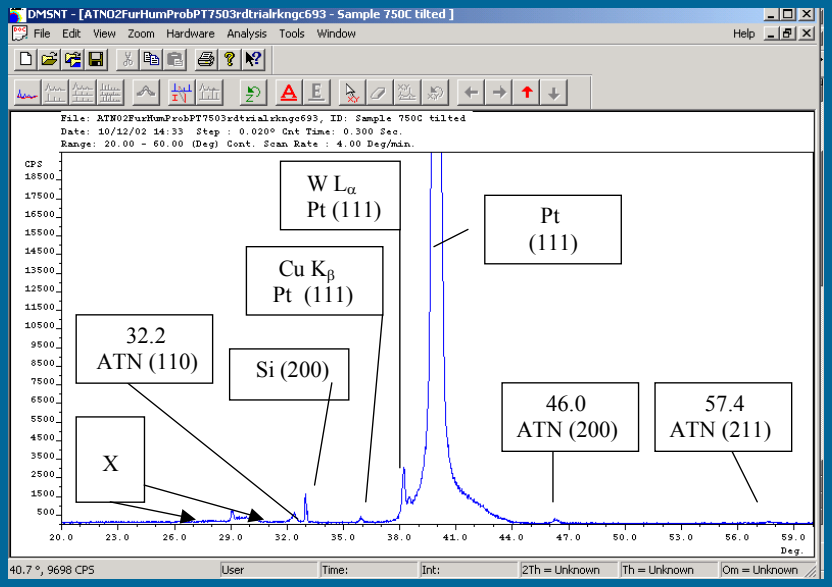
Good for particle sizes < 500A and no strain.

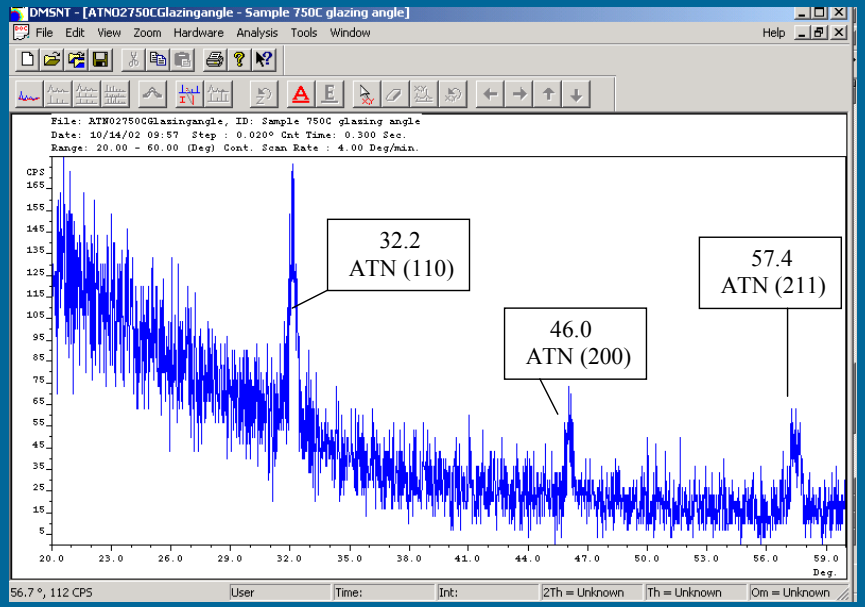
If strain, other Methods:

Warren / Averbach

Williamson-Hall plot

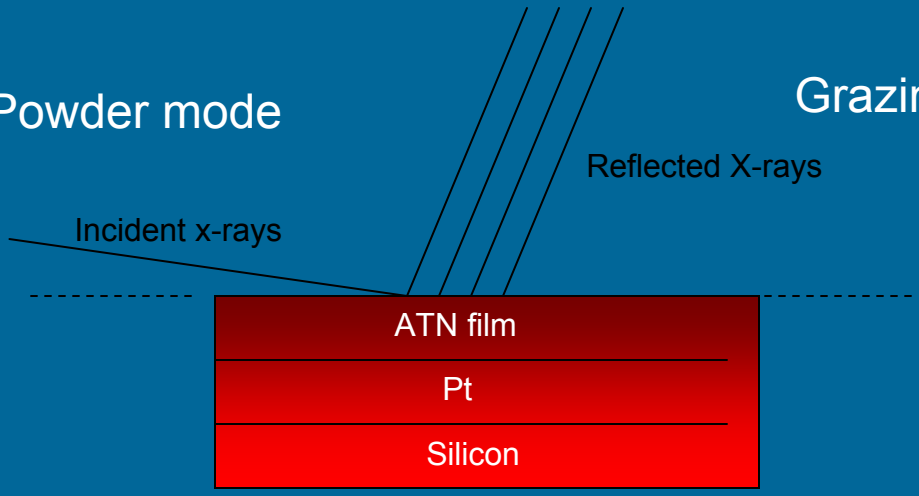
Grazing Angle Geometry

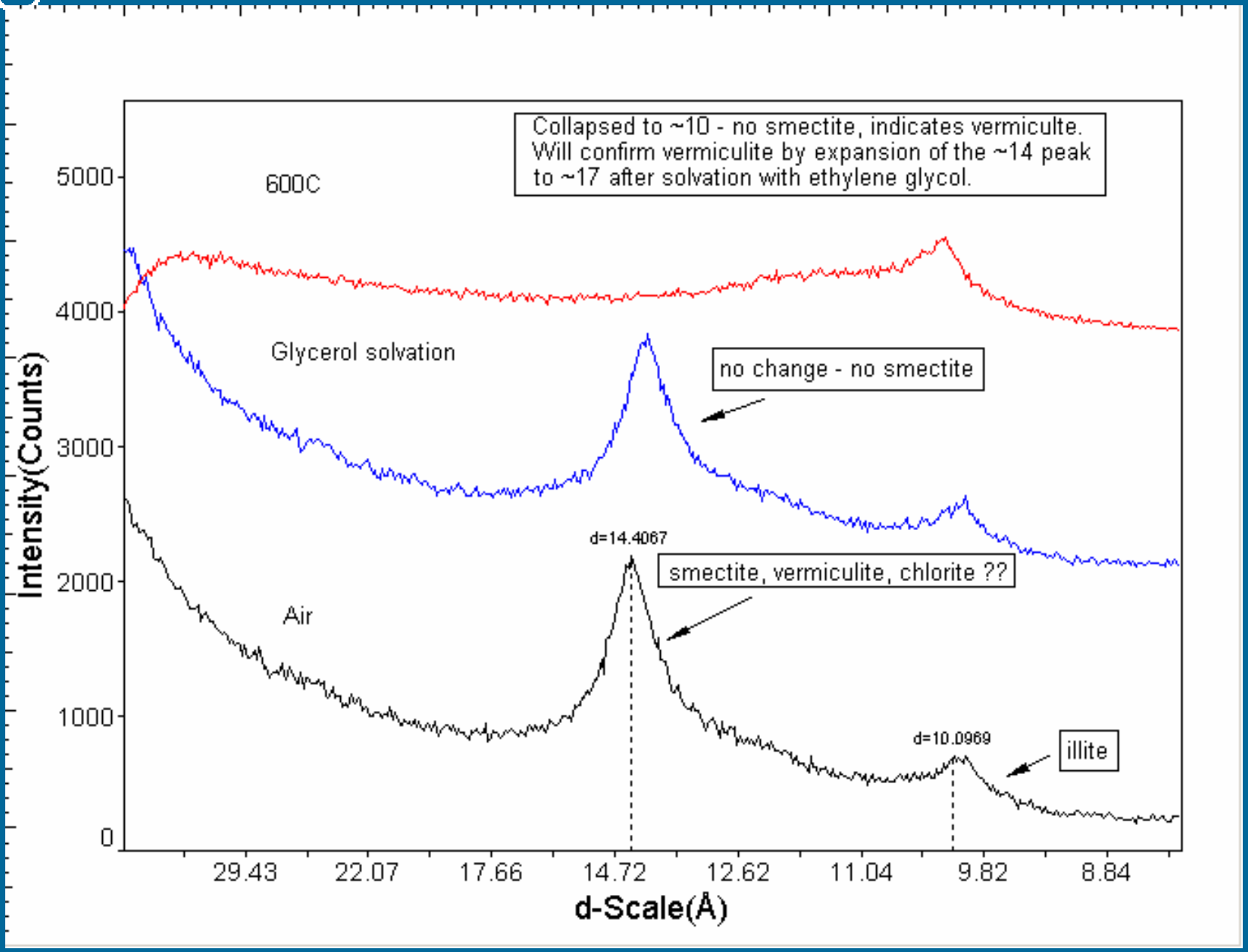




Normal Powder mode

Grazing angle mode



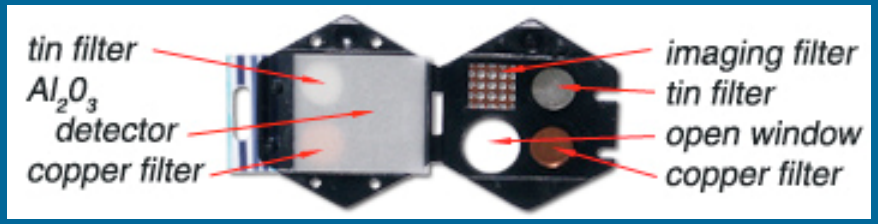

Collapsed to ~10 - no smectite, indicates vermiculte.
Will confirm vermiculite by expansion of the ~14 peak
to ~17 after solvation with ethylene glycol.
600C
Glycerol solvation
no change - no smectite
Air
d=14.4067
smectite, vermiculite, chlorite ??
d=10.0969
illite
Intensity(Counts)
5000
4000
3000
2000
1000
0
29.43
22.07
17.66
14.72
12.62
11.04
9.82
8.84
d-Scale(Å)

How to Get Started

Dosimetry

- Worn on the wrist closest to the x-ray source (varies by instrument)
- Wrist dosimeters are issued once each quarter.

Inside a Dosimeter



Measures radiation exposure due to x, gamma and beta radiation with optically stimulated luminescence (OSL) technology.

Thin strip of specially formulated aluminum oxide (Al_2O_3) crystalline material. During analysis, the Al_2O_3 strip is stimulated with selected frequencies of laser light causing it to luminesce in proportion to the amount of radiation exposure.

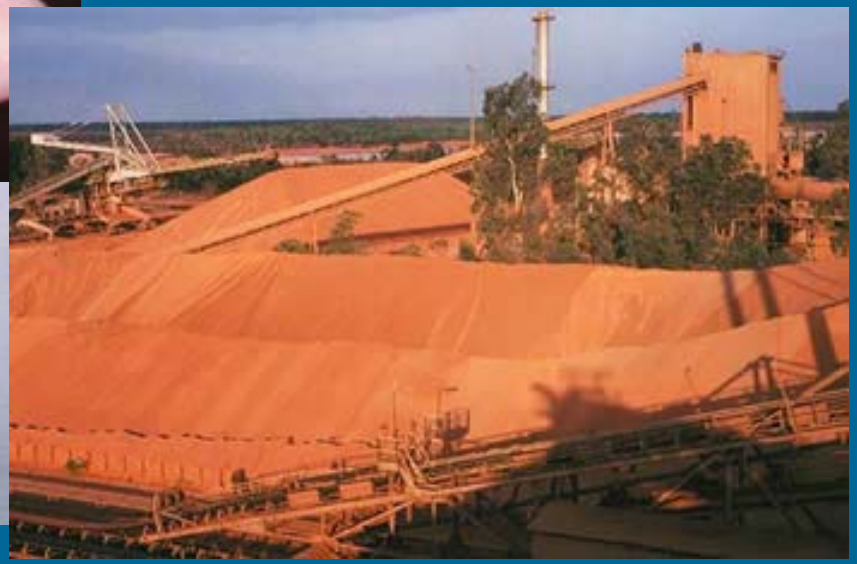
The luminescence measured during analysis is applied to a dose algorithm that relies on the response ratios between different filter positions within the dosimeter to discriminate between beta and photon (x and gamma) radiation fields to determine exposure results.

Sample Preparation

The "Perfect" Powder Sample

- A "representative" sample – is it possible?

Bauxite



http://volcano.und.nodak.edu/vwdocs/minerals/bauxite.html

The "Perfect" Powder Sample

- A "representative" sample

- Total randomness of the crystallite orientations
- Sufficient number of crystallites
- Sufficient intensity – limit of detection ~5%

Particle Size

< 325 mesh or < 400 mesh (38-44 micron) – qualitative

10 micron or less for quantitative – very difficult !

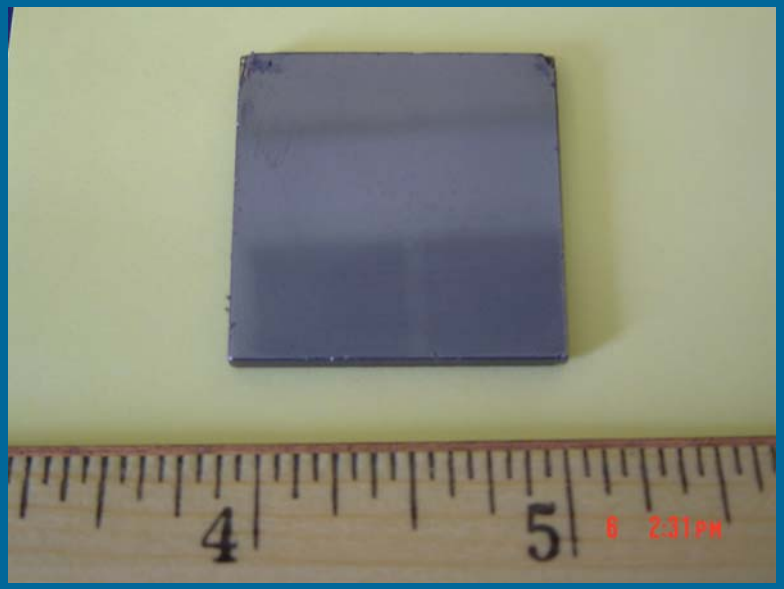
"Real World" Samples

Some things can't practically be powders:

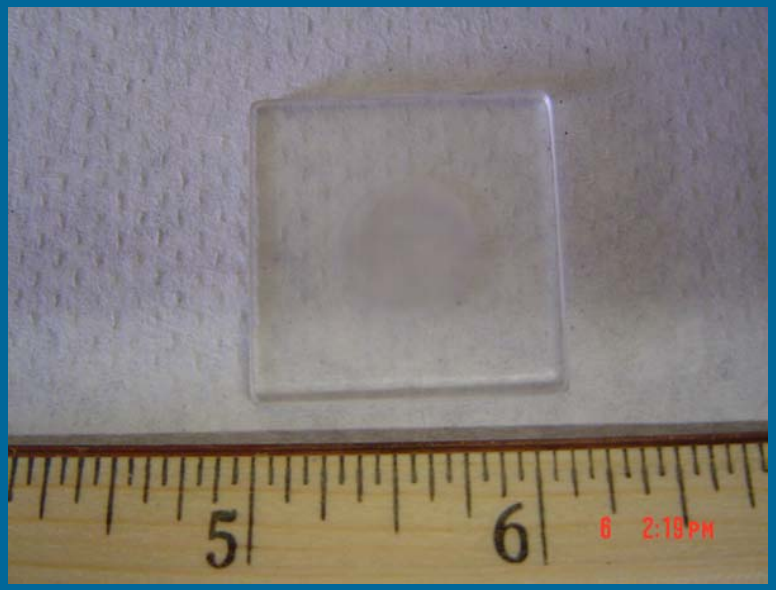
films
pellets
crystals
mineral specimens

There are techniques available to deal with many of these – ask!

Zero Background Holders (ZBH)



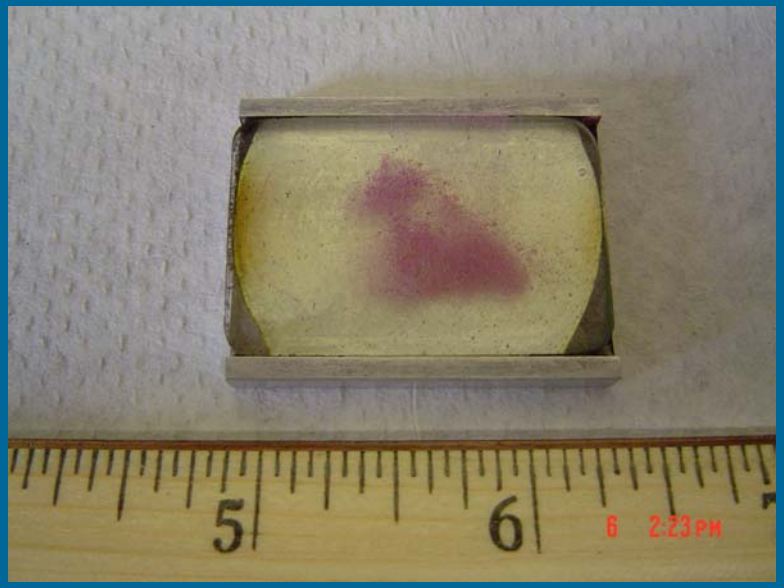
Flat Silicon ZBH
Cut parallel to Si (510)
Si (511) – *also available, but has peak at 96°θ*



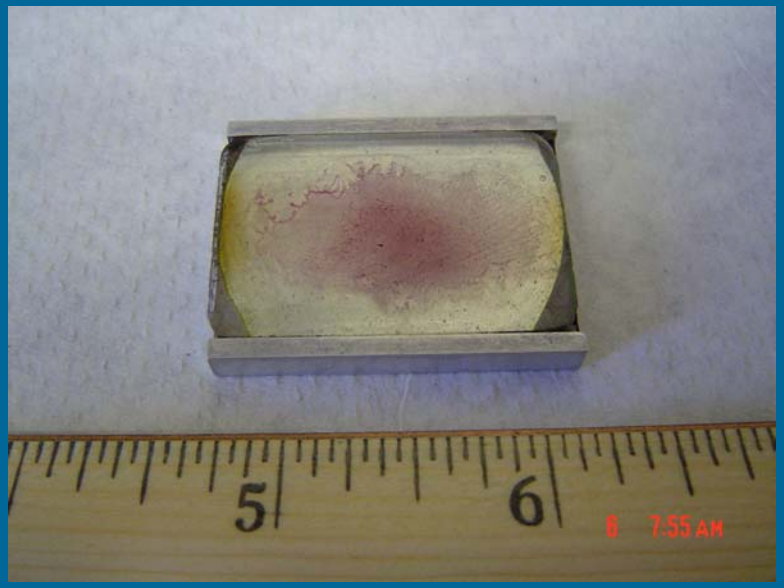
Quartz ZBH with cavity
Cut 6 º from (0001)

See www.gemdugout.com for additional information

Flat Quartz ZBH

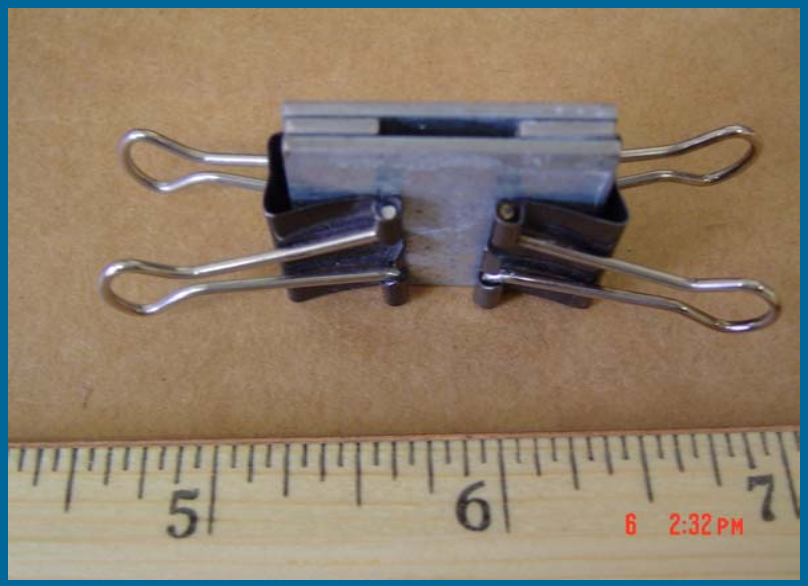


Vaseline Mount



Smear Mount

Side Drift Mount



Assembled

Disassembled

Designed to reduce preferred orientation – clay samples

Pellet Mount – plastic box

Shimmed Pellet Mount