Diffraction: Powder Method

Diffraction Methods

◆ Diffraction can occur whenever Bragg's law $\lambda = 2d\sin\theta$ is satisfied.

◆ With monochromatic x-rays and arbitrary setting of a single crystal in a beam generally will not produce any diffracted beams.

◆ Ways of satisfying Bragg's law:
   - Continuously vary λ
   - Continuously vary θ
     during the experiment.

◆ Two main diffraction methods:

Method	λ	θ
Laue	variable	fixed
Powder	fixed	variable

Principal Diffraction Methods

◆ Laue method: single crystal sample, fixed θ, variable λ

    used for orienting single crystals

◆ Powder method: polycrystalline sample, variable θ, fixed λ

    used in the determination of crystalline structure of materials in powder form

◆ Single crystal diffractometer method: single crystal sample, thin film sample, rotating θ, ω, φ and ϕ, fixed λ

    used for determining complex crystal structures from single crystal and thin film materials

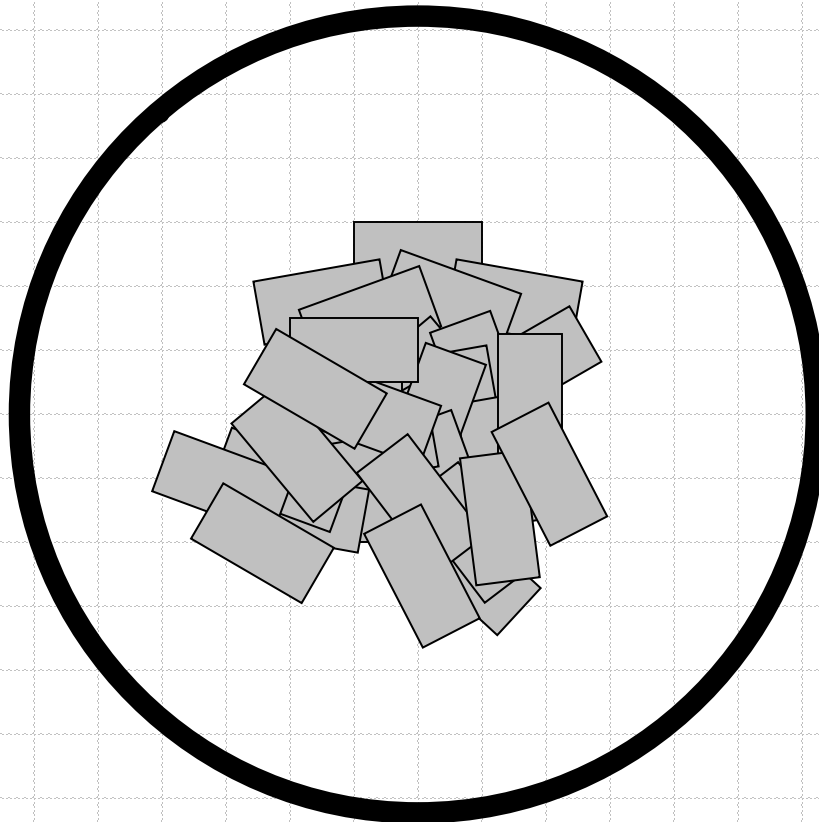# Powder Diffraction

◆ Understanding powder diffraction patterns

Pattern component	Crystal structure	Specimen property	Instrumental parameter
Peak Position	**Unit cell parameters:** a,b,c,α,β,γ	*Absorption* *Strain - Stress*	**Radiation (wavelength)** *Instrument* *Sample alignment* Beam axial divergence
Peak Intensity	**Atomic parameters:** x,y,z,B,…	*Preferred orientation* Absorption *Porosity*	Geometry/configuration **Radiation (LP)**
Peak shape	*Crystallinity* Disorder Defects	*Grain size* *Strain - Stress*	**Radiation (spectral purity)** **Geometry** **Beam conditioning**

Bold – key parameters
Italic – significant influence

Powder Diffraction

◈ Multiple single crystallites are irradiated simultaneously by a monochromatic beam
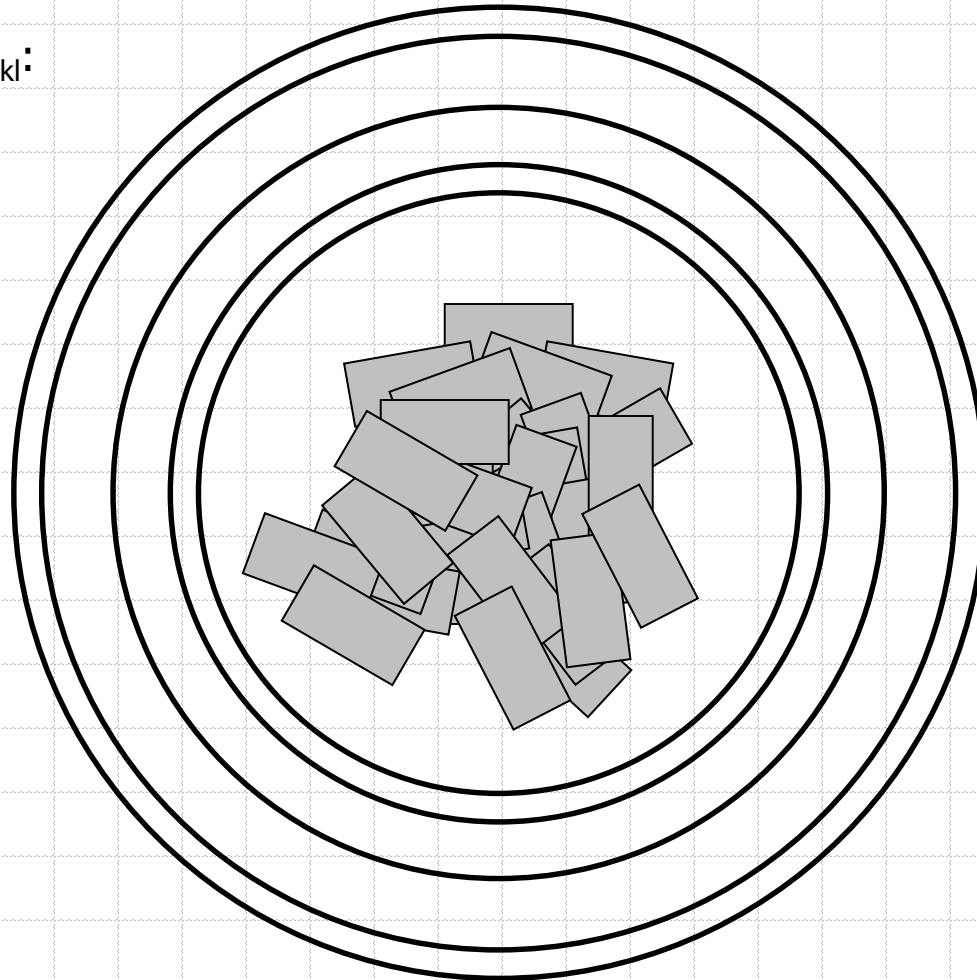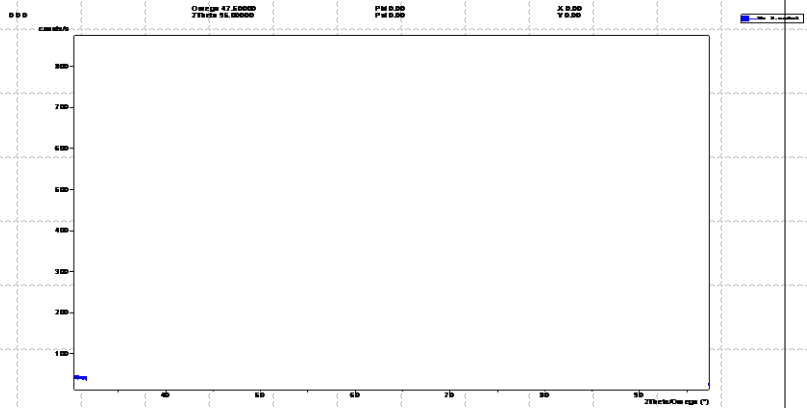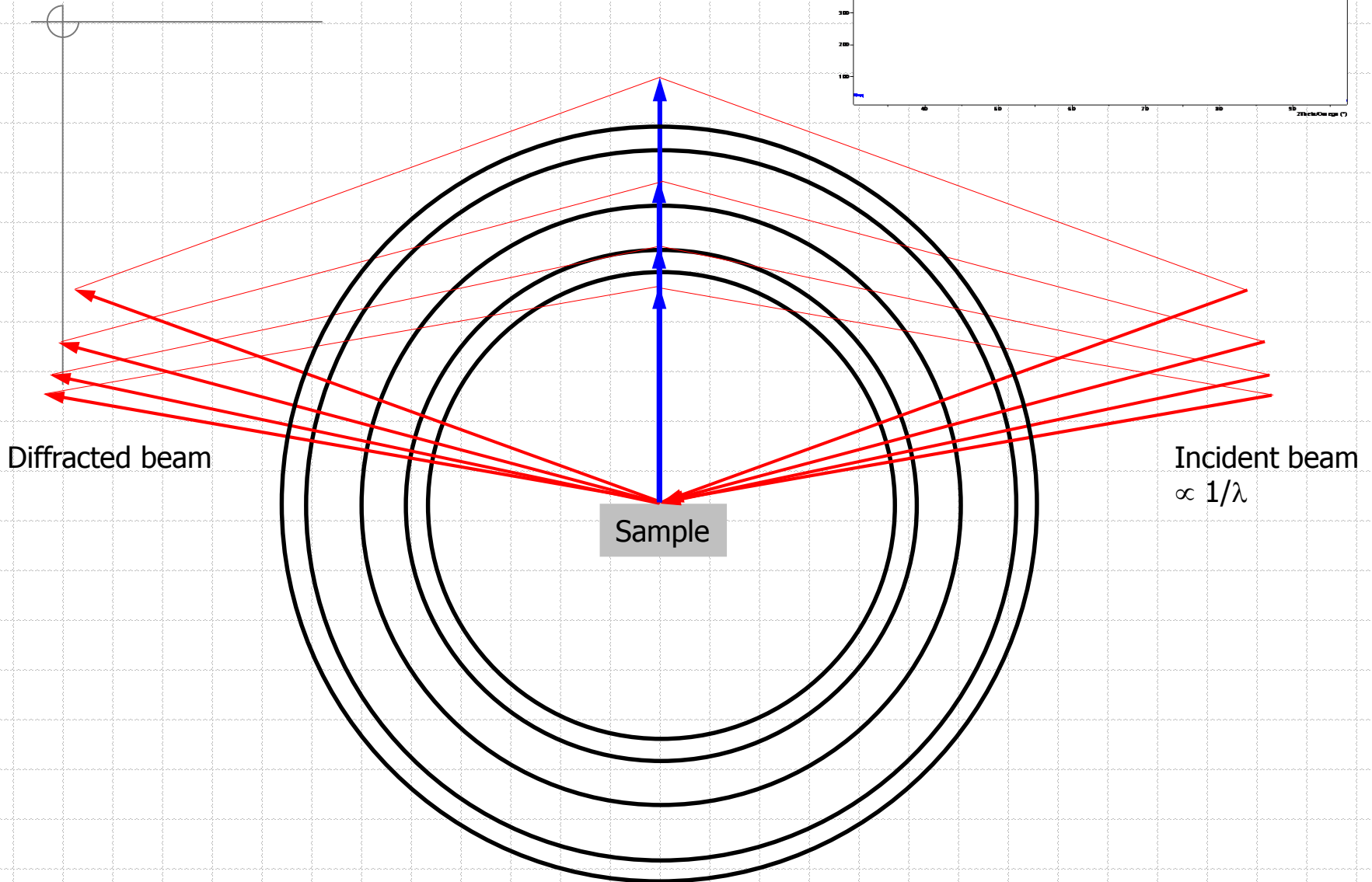
For a single d_{hkl}:

Powder Diffraction

♦ Multiple single crystallites are irradiated simultaneously by a monochromatic beam

For many d_{hkl}:

Powder Diffraction

Diffracted beam

Sample

Incident beam
$\propto 1/\lambda$

X-ray Diffraction from Polycrystalline Materials

◆ According to Euclid: "the angles in the same segment of a circle are equal to one another" and "the angle at the center of a circle is double that of the angle at the circumference on the same base, that is, on the same arc".

◆ For any two points S and D on the circumference of a circle, the angle α is constant irrespective of the position of point P.
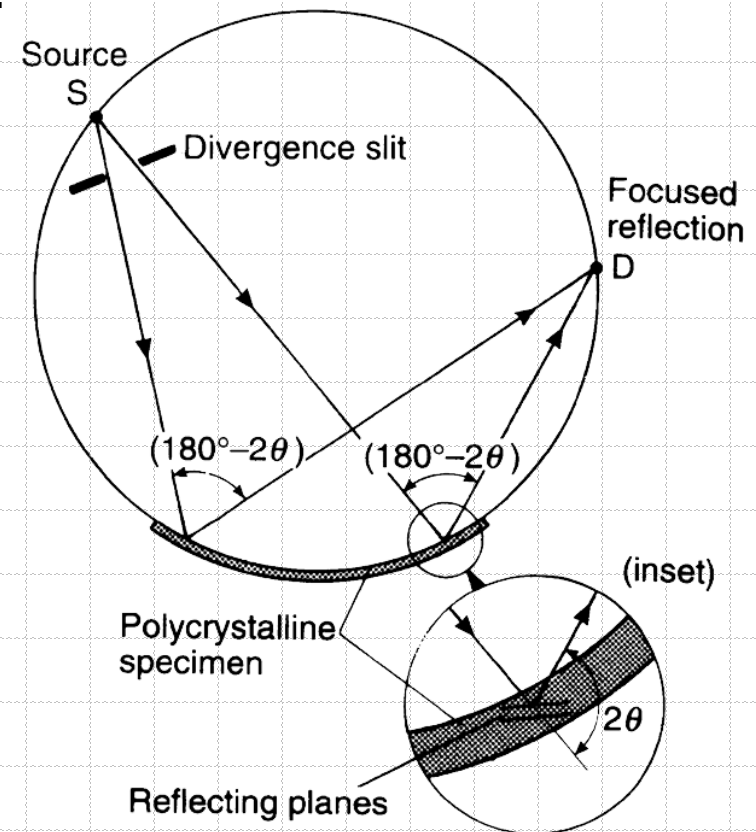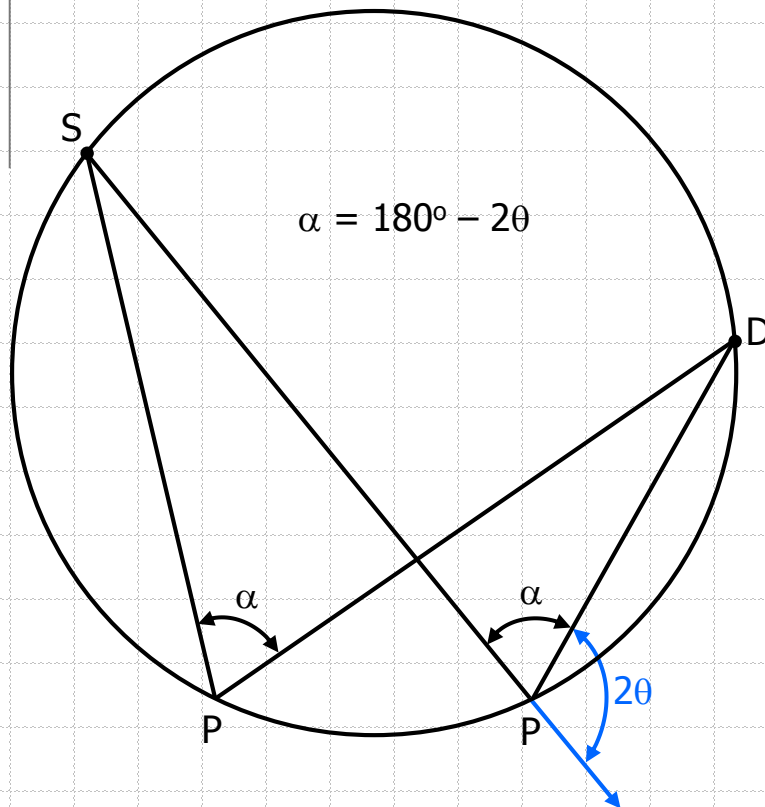
X-ray Powder Diffractometer

◆ Powder diffractometers working in the Bragg-Brentano ($\theta/2\theta$) geometry utilize a parafocusing geometry to increase intensity and angular resolution
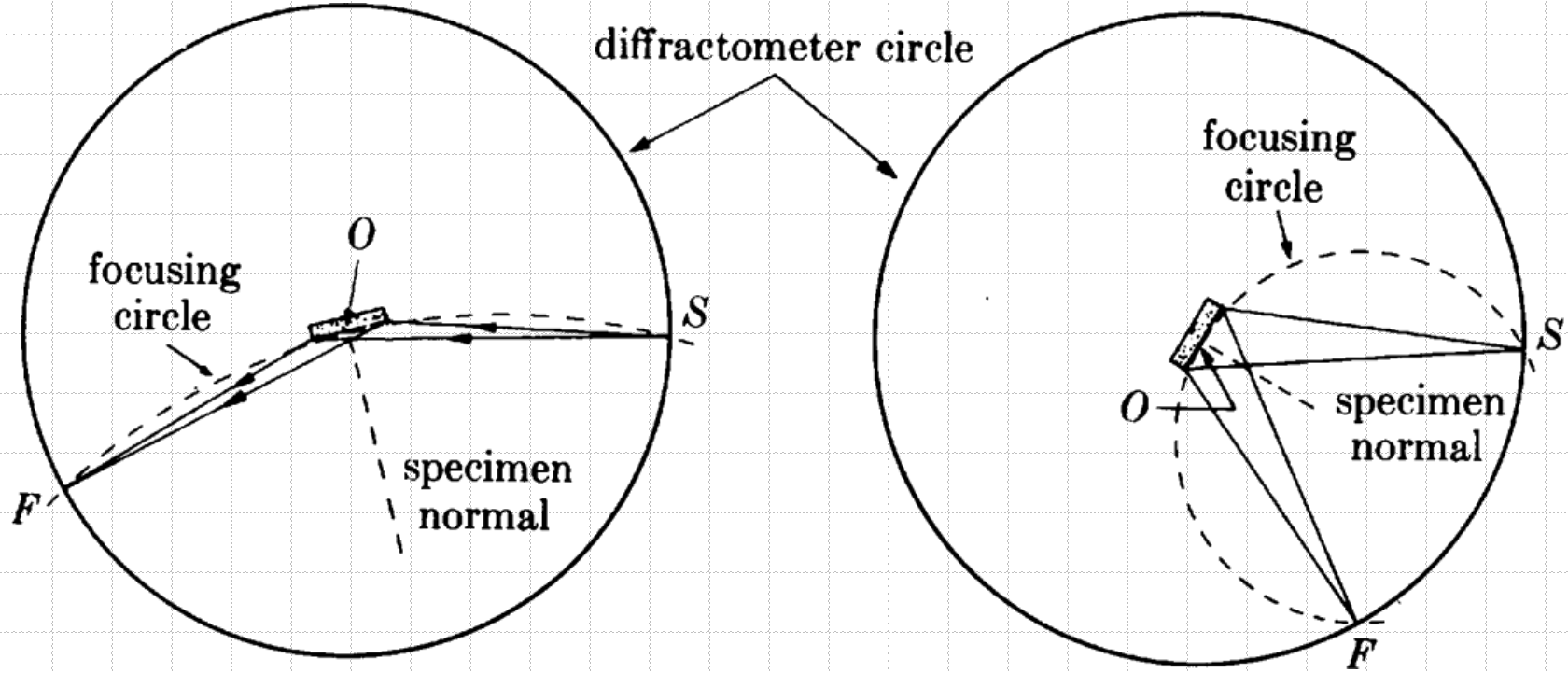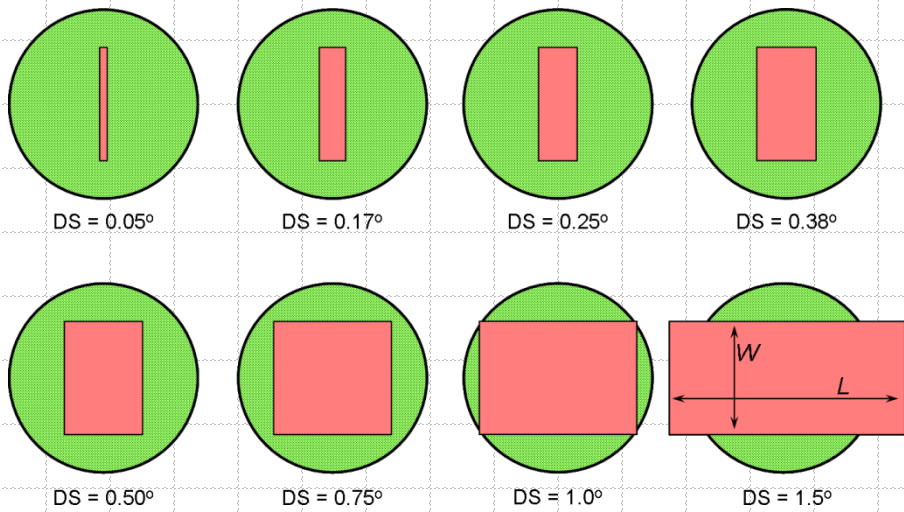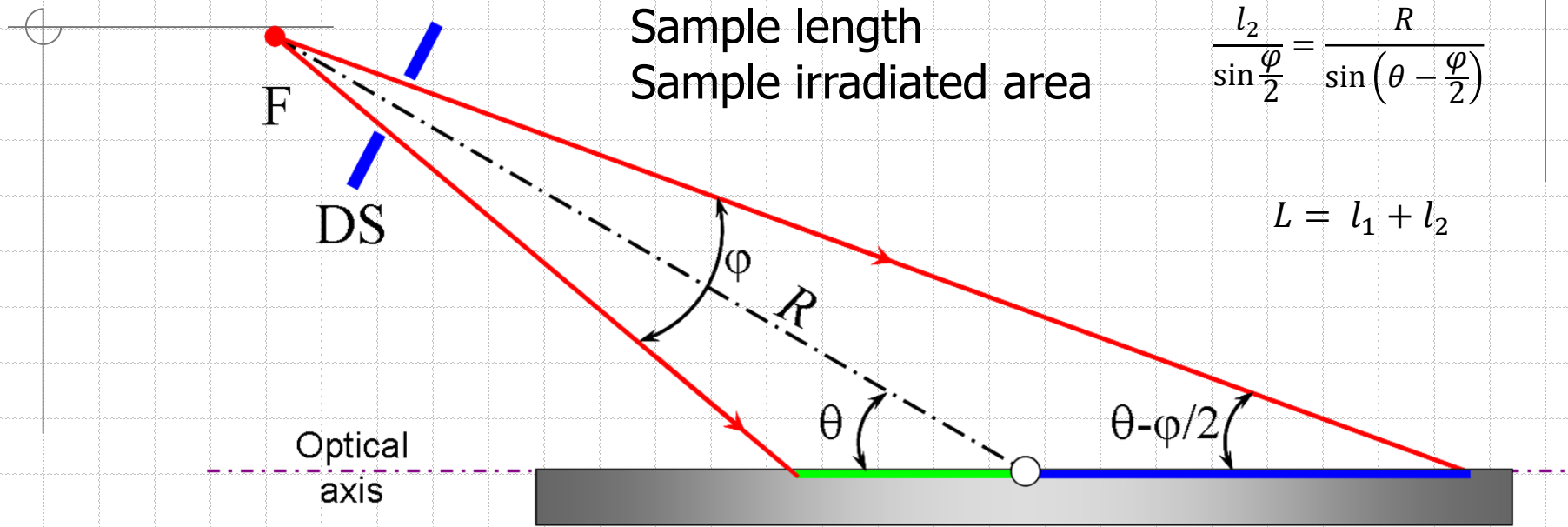

Bragg-Brentano geometry

Powder Diffraction

$$\frac{l_1}{\sin\frac{\varphi}{2}} = \frac{R}{\sin\left(\theta + \frac{\varphi}{2}\right)}$$
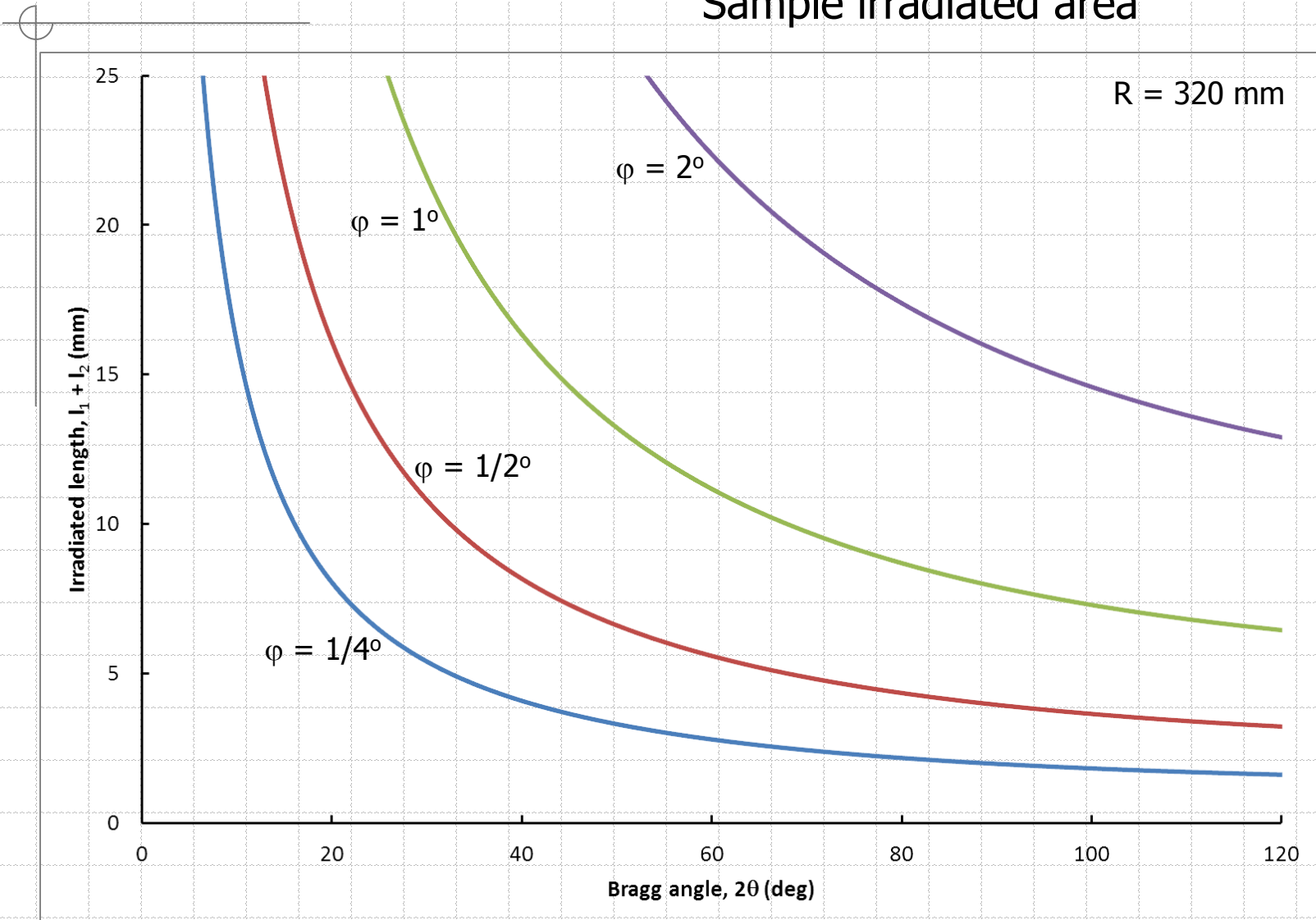
$$\frac{l_2}{\sin\frac{\varphi}{2}} = \frac{R}{\sin\left(\theta - \frac{\varphi}{2}\right)}$$

Sample length
Sample irradiated area

$$L = l_1 + l_2$$

F

DS

φ

R

θ

$\theta-\varphi/2$

Optical axis

l_1

l_2

L

DS = 0.05°

DS = 0.17°

DS = 0.25°

DS = 0.38°

DS = 0.50°

DS = 0.75°

DS = 1.0°

DS = 1.5°

W

L

Powder Diffraction

Sample length
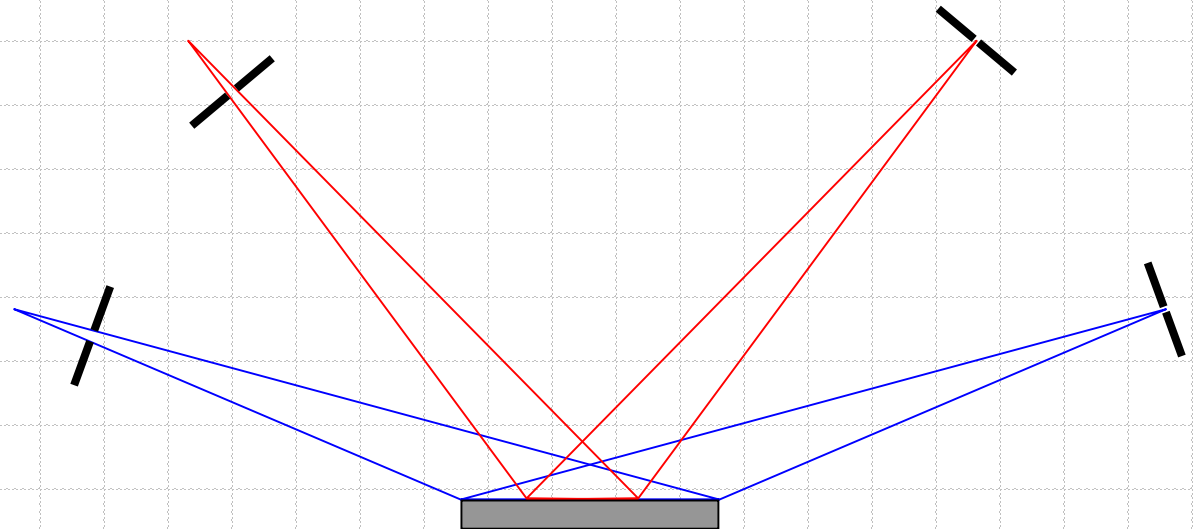Sample irradiated area

Powder Diffraction

◆ Fixed Slits

Divergence Slit:
• Match the diffraction geometry and sample size
• At any angle beam does not exceed sample size

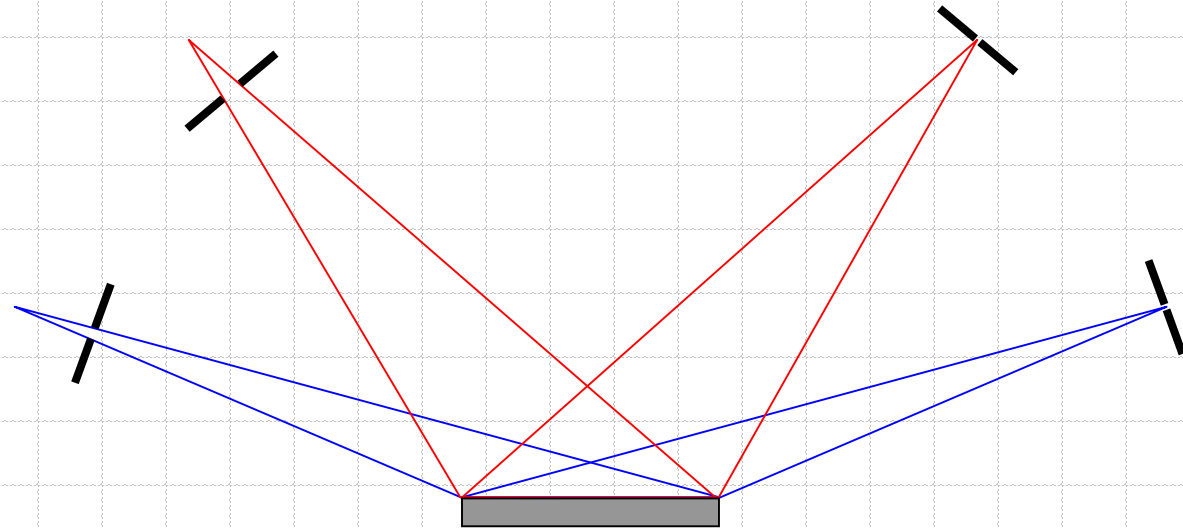$$\alpha \approx \frac{L\sin\theta}{R} \text{ (rad)}$$

Receiving Slit:
• As small as possible to improve the resolution
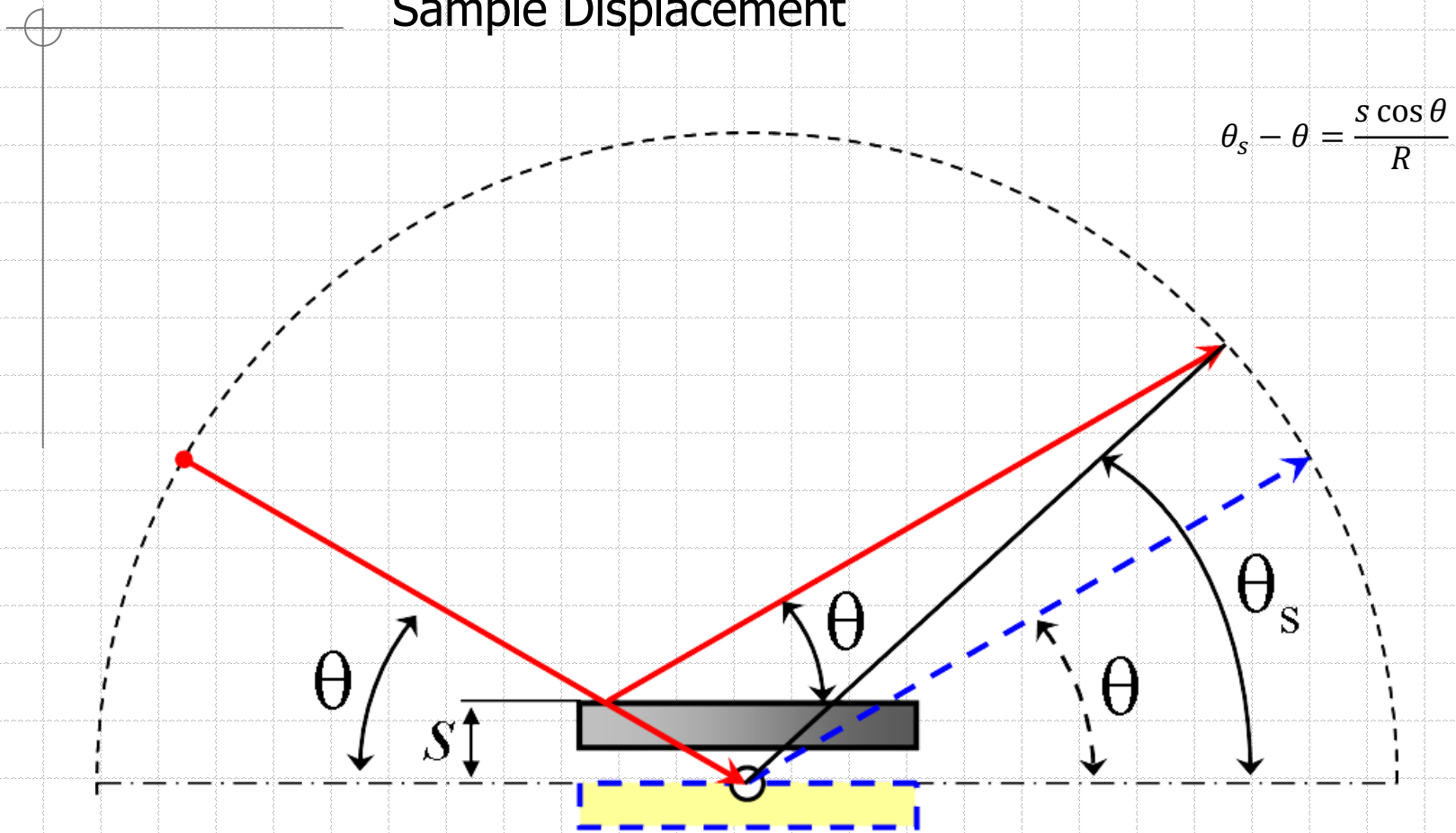• Very small slit size reduces diffracted beam intensity

Powder Diffraction

◈ Variable Slits

- Vary aperture continuously during the scan
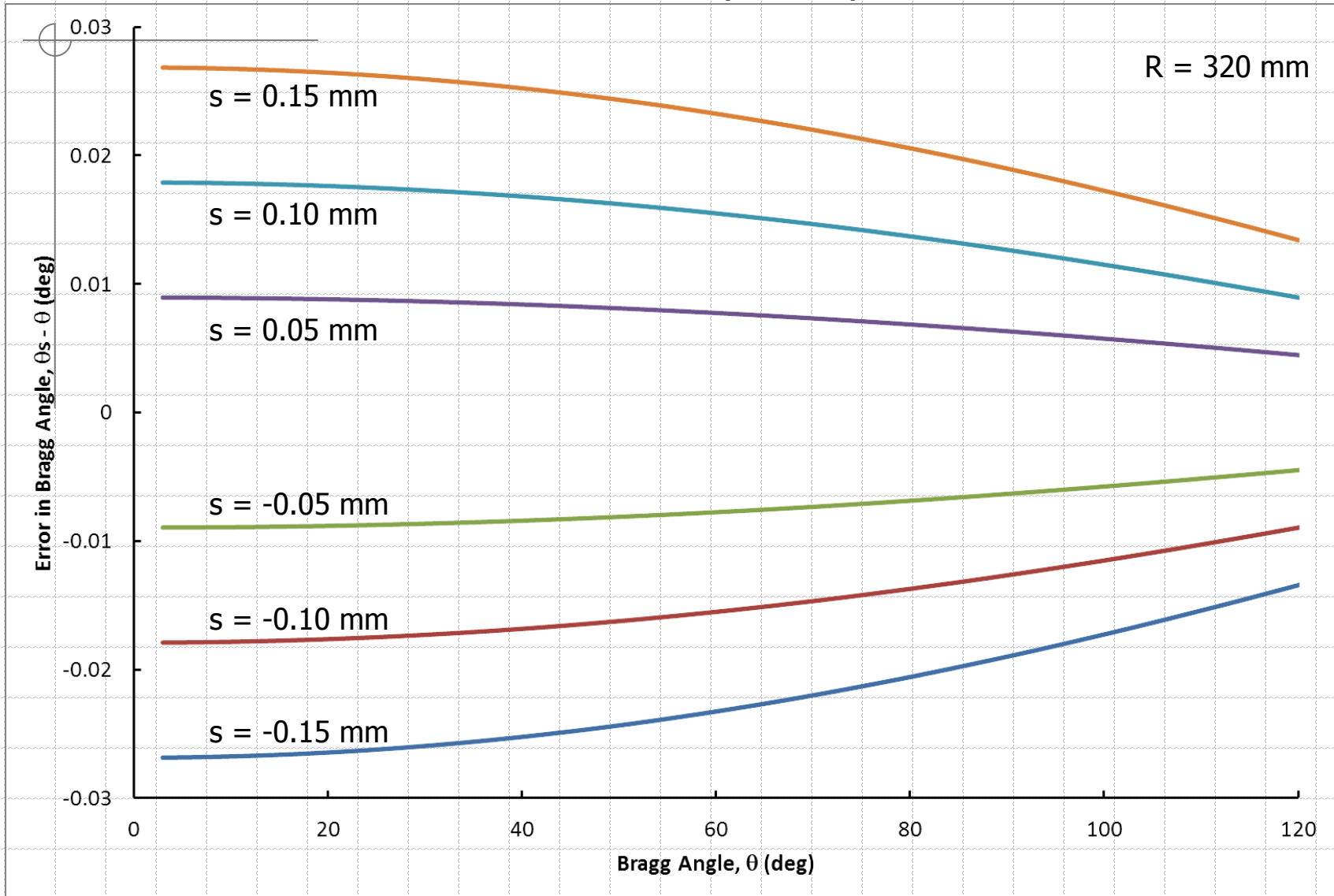- Length of the sample is kept constant

Powder Diffraction

Sample Displacement

$$\theta_s - \theta = \frac{s \cos \theta}{R}$$
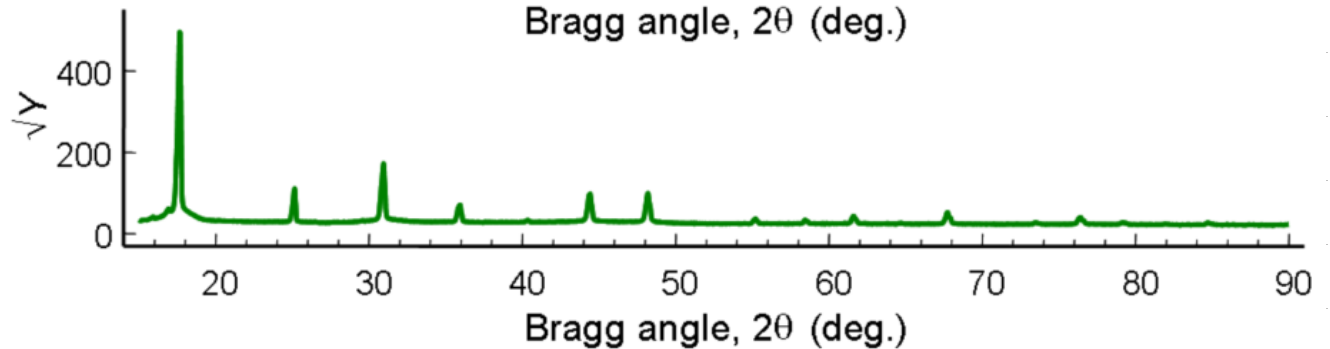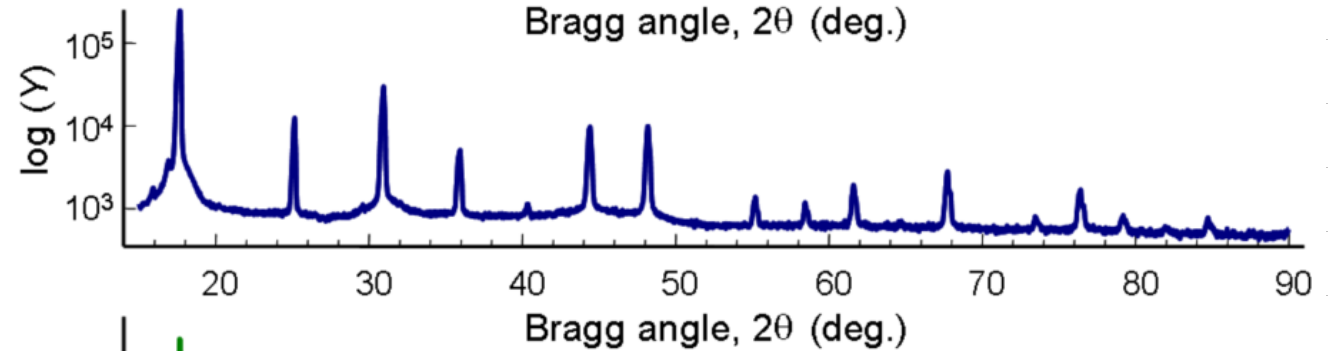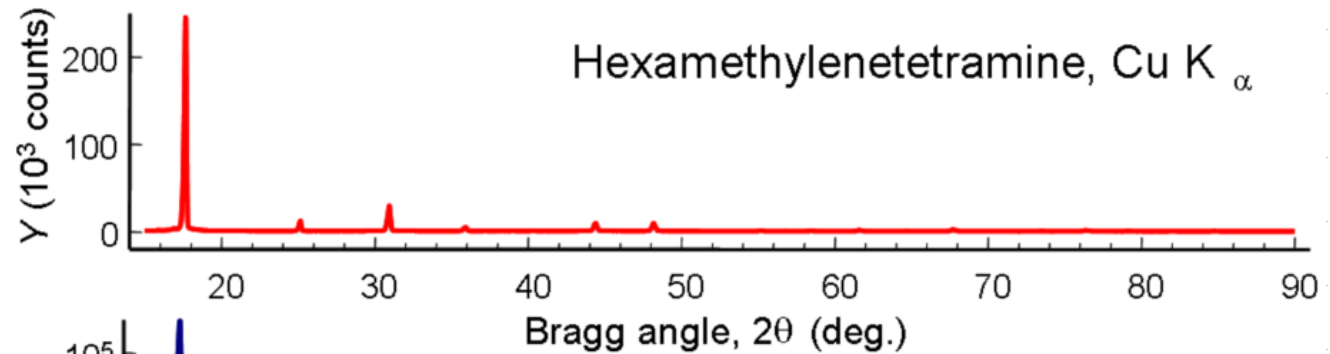
Powder Diffraction

Sample Displacement

Powder Diffraction

◆ Intensity scale:
   - Linear
   - Logarithmic
   - Square Root

Hexamethylenetetramine, Cu K$_\alpha$

Powder Diffraction

◆ Horizontal scale:
- 2θ
- $1/d$
- $1/d^2$
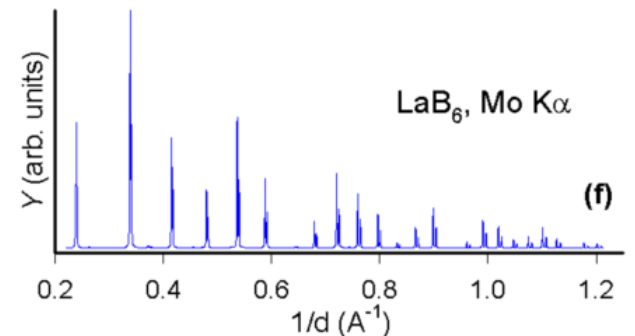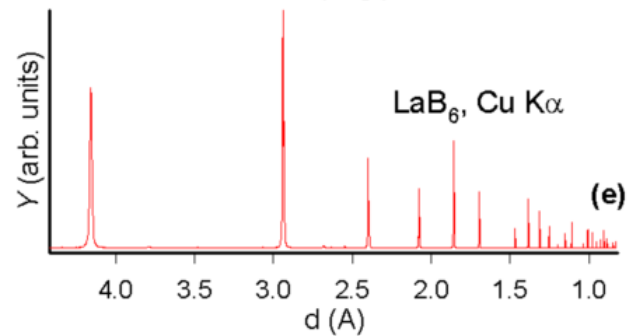
Powder Diffraction

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

$$d = \frac{\lambda(K\alpha_1)}{2\sin\theta_1} = \frac{\lambda(K\alpha_2)}{2\sin\theta_2}$$

◆ Peak shape
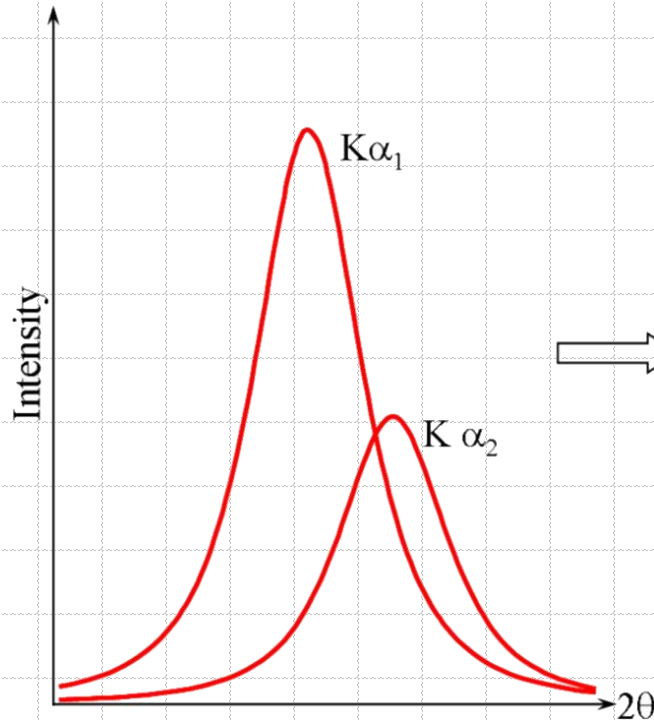
$$\lambda K\alpha_{ave} = \frac{2\lambda(K\alpha_1) + \lambda(K\alpha_2)}{3}$$

X-ray Powder Diffractometer

◆ Powder Diffraction of MgB_2 sample.
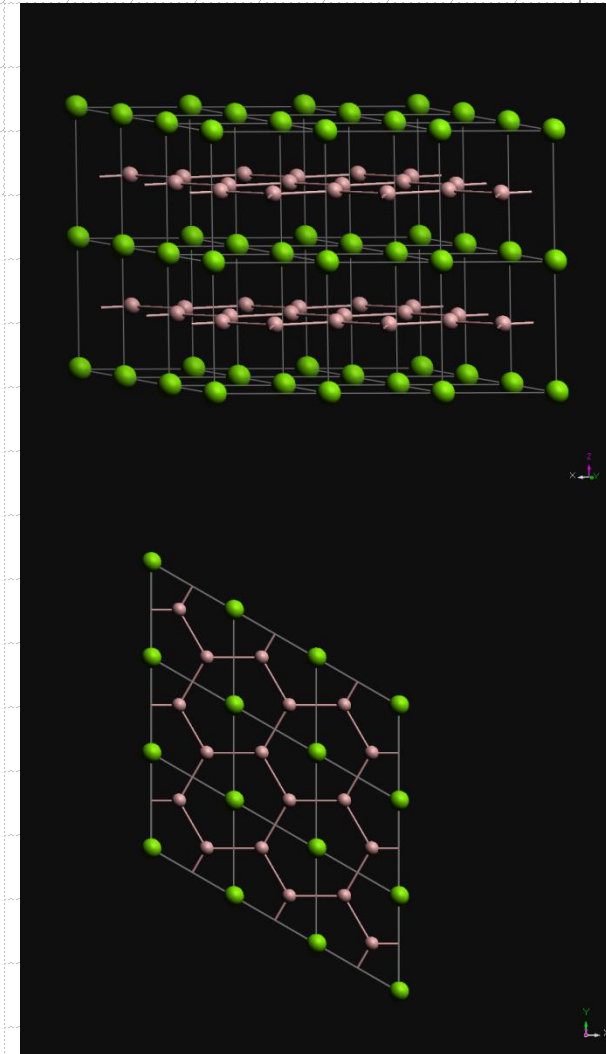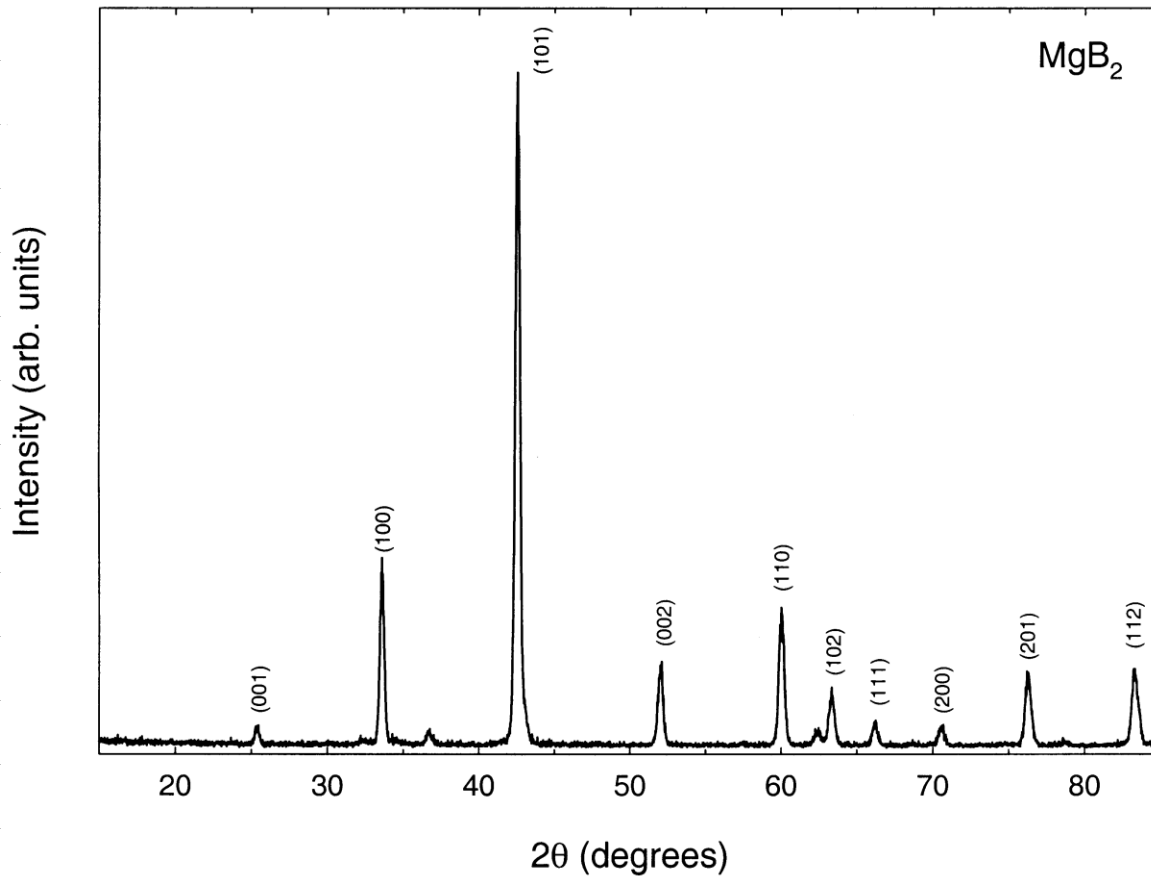
Basic Principles of Crystal Structure Analysis

◆ The angular positions of diffracted peaks gives information on the properties (size and type) of the unit cell
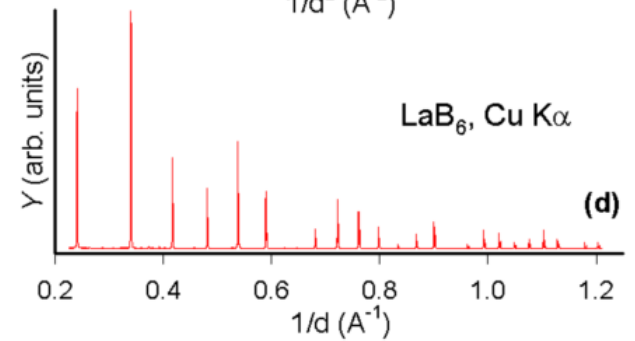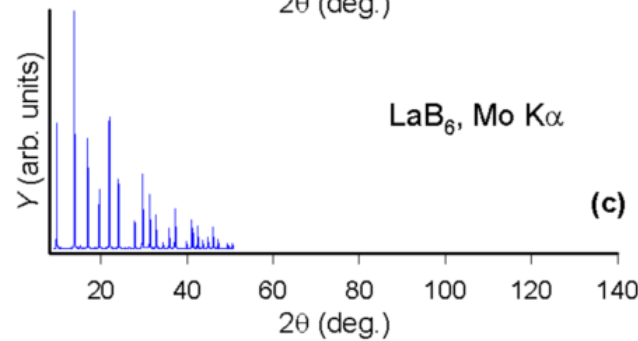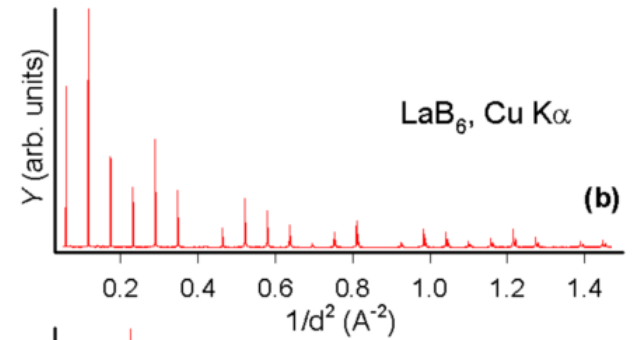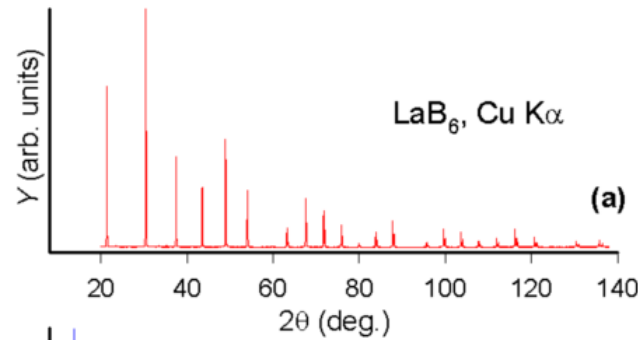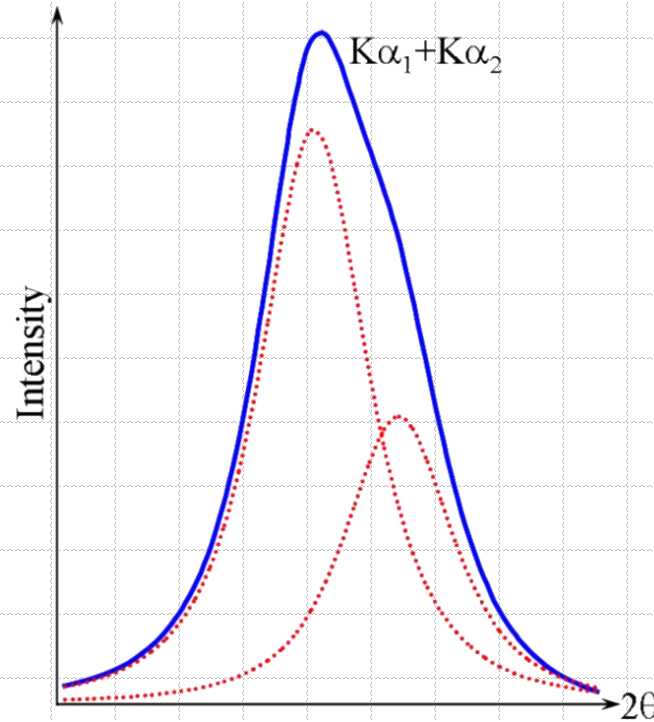
◆ The intensities of diffracted peaks gives information on the positions and types of atoms within the unit cell

◆ General procedure:

- "index the pattern" $\rightarrow$ assign hkl values to each peak
- determine the number of atoms per unit cell (chemical composition, density, and size/shape of unit cell
- determine the positions of atoms in the unit cell from the measured intensities

Indexing the pattern – an assumption is made as to which of the 7 crystal systems the unknown structure belongs and then, on the basis of the assumption, the correct Miller indices are assigned to each reflection.

Indexing of Cubic Patterns

◆ For cubic unit cell:

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

so Bragg's law becomes:

$$\lambda^2 = 4d^2 \sin^2 \theta = \frac{4a_o^2}{\left(h^2 + k^2 + l^2\right)} \sin^2 \theta$$

so:

$$\frac{\sin^2 \theta}{\left(h^2 + k^2 + l^2\right)} = \frac{\sin^2 \theta}{s} = \frac{\lambda^2}{4a_0^2}$$

constant for a given crystal

always equal to an integer

because of restrictions on h,k,l different cubic crystal structures will have characteristic sequences of diffracted peak positions

Indexing of Cubic Patterns

◆ Characteristic line sequences in the cubic system:

- Simple cubic: 1, 2, 3, 4, 5, 6, 8, 9, 10, 11, …

- Body-centered cubic: 2, 4, 6, 8, 10, 12, 14, 16, …

- Face-centered cubic: 3, 4, 8, 11, 12, 16, 19, 20, …

- Diamond cubic: 3, 8, 11, 16, 19, …

Indexing of Cubic Patterns

DISTANCE ON FILM OR CHART

$2\theta = 0°$

$\theta = 180°$

CUBIC

simple

body-centered

face-centered

diamond

$\frac{s}{}$

$\frac{hkl}{}$

1	100
2	110
3	111
4	200
5	210
6	211
8	220
9	300, 221
10	310
11	311
12	222
13	320
14	321
16	400
17	410, 322
18	411, 330
19	331
20	420
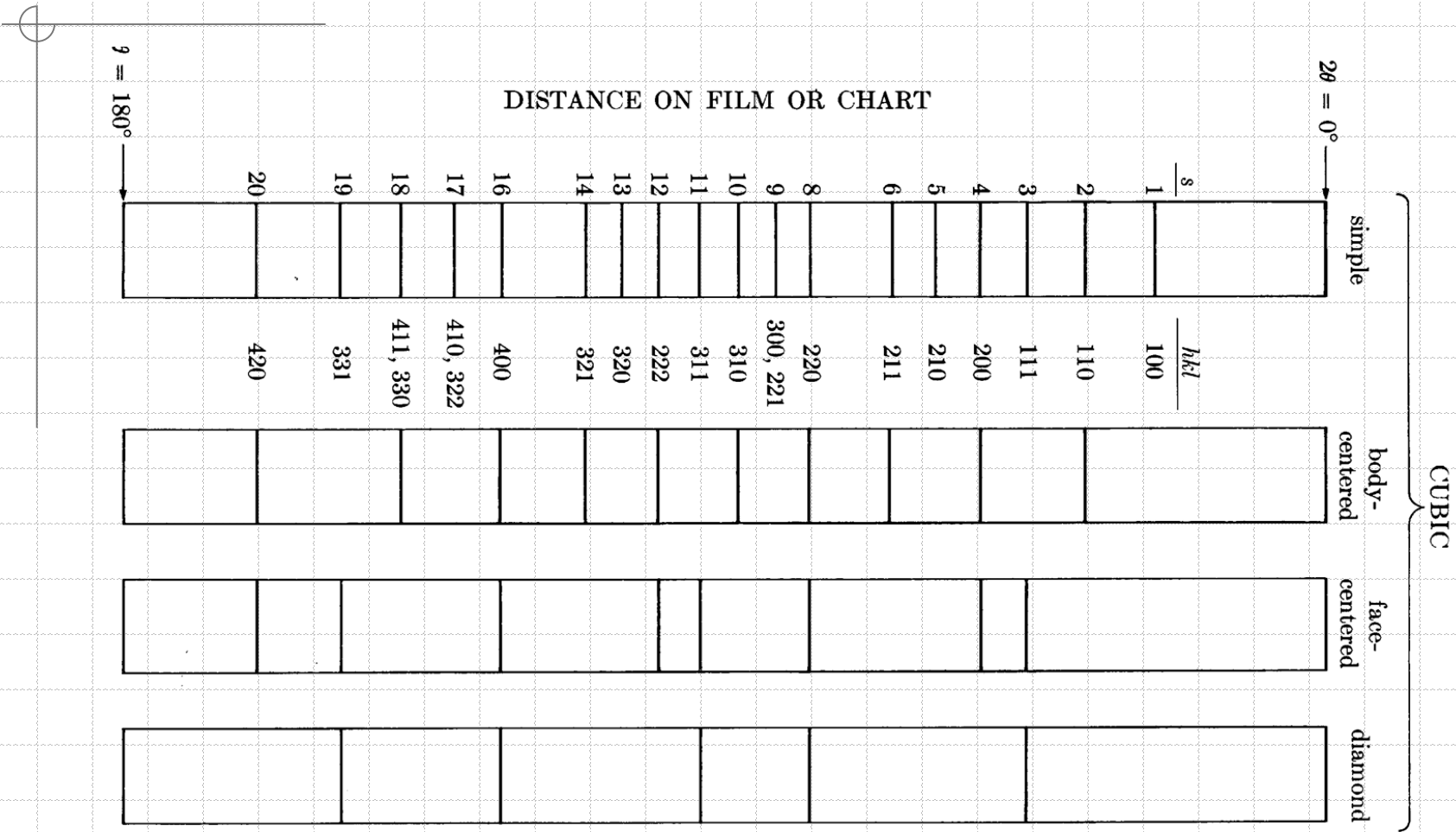
Indexing of Cubic Patterns

◆ Steps in indexing a cubic pattern:

measure sample & list angles →

calculate $(\sin^2\theta)/s$ for three Bravais lattices

|				FCC				SC		BCC
1	2	3	4	5	6	7	8	9	10	
Line	$\sin^2\theta$	$s = (h^2 + k^2 + l^2)$	$\dfrac{\sin^2\theta}{s} = \dfrac{\lambda^2}{4a^2}$	$a(\text{Å})$	hkl	s	$\dfrac{\sin^2\theta}{s}$	s	$\dfrac{\sin^2\theta}{s}$	
1	0.140	3	0.0467	3.57	111	1	0.140	2	0.0700	
2	0.185	4	0.0463	3.59	200	2	0.093	4	0.0463	
3	0.369	8	0.0461	3.59	220	3	0.123	6	0.0615	
4	0.503	11	0.0457	3.61	311	4	0.123	8	0.0629	
5	0.548	12	0.0457	3.61	222	5	0.110	10	0.0548	
6	0.726	16	0.0454	3.62	400	6	0.121	12	0.0605	
7	0.861	19	0.0453	3.62	331	8	0.108	14	0.0615	
8	0.905	20	0.0453	3.62	420	9	0.101	16	0.0566	

If the observed lines are from a particular lattice type, the $(\sin^2\theta)/s$ values should be constant.

Indexing of non Cubic Patterns

◆ Deviations from cubic
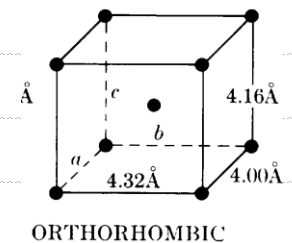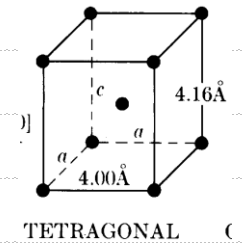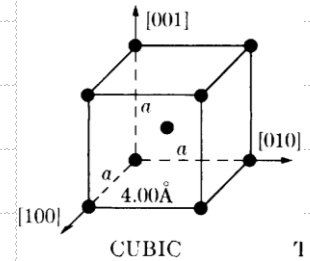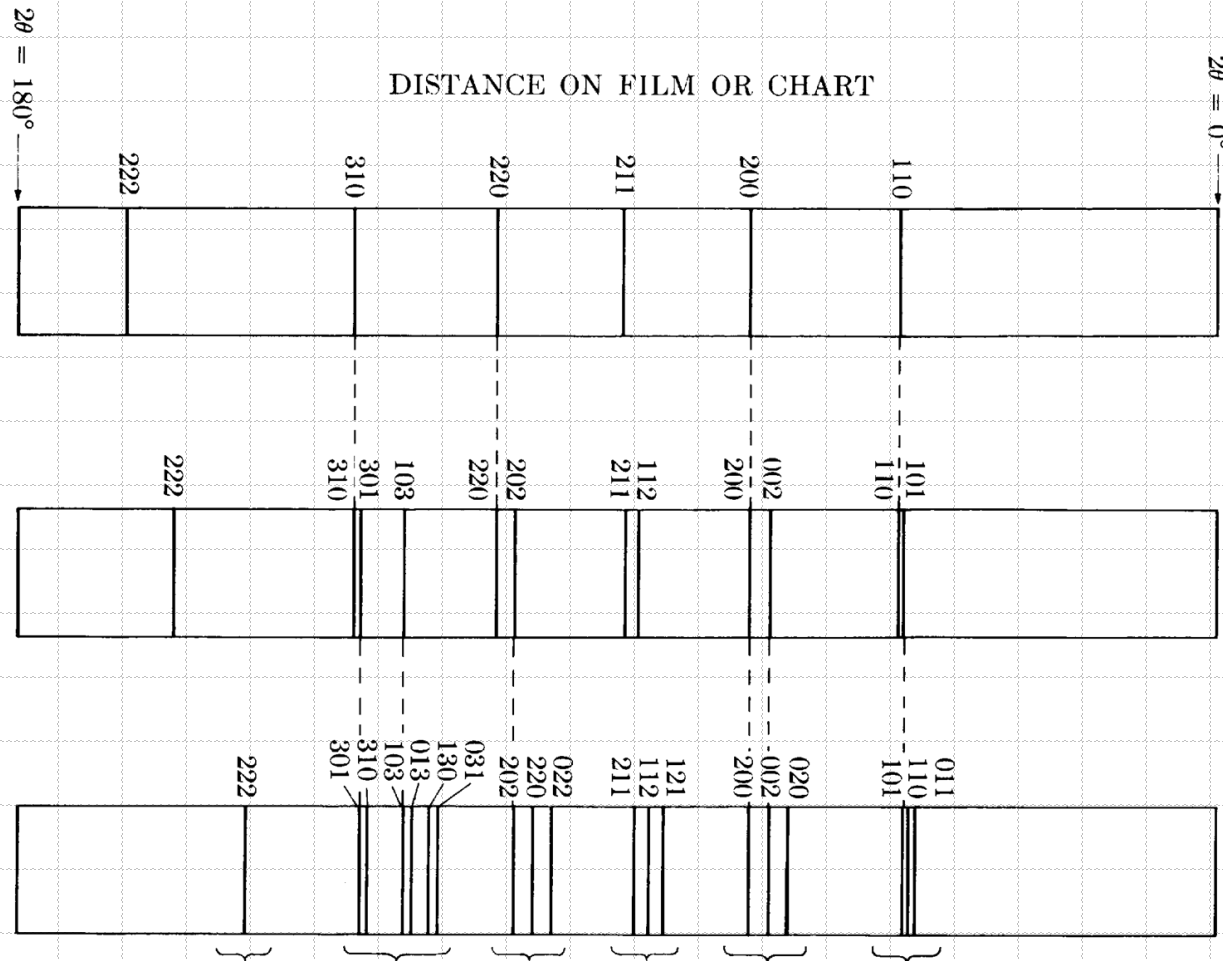
Indexing of non Cubic Patterns

◆ Non-cubic structures -- much more complex!

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

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

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

Indexing of non Cubic Patterns

◆ Tetragonal System:

- The $\sin^2\theta$ must obey relation:

$$\sin^2\theta = A(h^2 + k^2) + Cl^2$$

where: $A = \dfrac{\lambda^2}{4a^2}$ and $C = \dfrac{\lambda^2}{4c^2}$ are constants for any pattern

A can be found from $hk0$ indices:

$$\sin^2\theta = A(h^2 + k^2)$$

$(h^2 + k^2)$ are 1, 2, 4, 5, 8, …

then C can be found from other lines:

$$\sin^2\theta - A(h^2 + k^2) = Cl^2$$

Indexing of non Cubic Patterns

◆ Hexagonal System:

$$\sin^2 \theta = A\left(h^2 + hk + k^2\right) + Cl^2$$

where: $A = \dfrac{\lambda^2}{3a^2}$ and $C = \dfrac{\lambda^2}{4c^2}$

◆ Orthorhombic System:

$$\sin^2 \theta = Ah^2 + Bk^2 + Cl^2$$

where: $A = \dfrac{\lambda^2}{2a^2}$, $B = \dfrac{\lambda^2}{2b^2}$, $C = \dfrac{\lambda^2}{2c^2}$

The "trick" is to find values of the coefficients *A*, *B* and *C* that account for all the observed $\sin^2\theta$'s when h, k and l assume various integral values

Number of Atoms in the Unit Cell

◆ After establishing shape and size we find the number of atoms in that unit cell.

unit cell
volume

density

Avogadro's
number

$$n = \frac{V_C \rho N_o}{M}$$

molecular weight

- Note that the "X-ray density" is almost always larger than the measured bulk density
- We need to know the unit cell volume
- We need to index the powder pattern in order to obtain the unit cell parameters

Number of Atoms in the Unit Cell

$$\sum A = \frac{\rho V'}{1.66042}$$

V' – volume of the unit cell in Å^3

$\sum A$ – sum of the atomic weights of the atoms in the unit cell

ρ – density g/cm^3

For simple elements: $\sum A = n_1 A$ where n_1 is number of atoms per unit cell
A is atomic weight of an element

For compounds: $\sum A = n_2 M$ where n_2 is number of molecules per unit cell
M is molecular weight

Determination of Atomic Positions

◆ Relative intensities determine atomic positions.

◆ The procedure is trial and error. There is no known general method of directly calculating atom positions from observed intensities.

Intensity is given by:

$$I = K\left|F^2\right|$$

where:

$$F = \sum_{i}^{N} f_n e^{2\pi i\left(hu_n + kv_n + lw_n\right)}$$

Phase problem

Example CdTe

◆ We did chemical analysis which revealed:
  - 49.8 atomic percent as Cd
  - 50.2 atomic percent as Te

◆ Make powder diffraction and list $\sin^2\theta$

◆ Pattern can be indexed as cubic and calculated lattice parameter is: a=6.46 Å

◆ The density is determined as 5.82 g/cm^3 then

$$\sum A = \frac{(5.82)(6.46)^3}{1.66042} = 945$$

◆ Molecular weight of CdTe is 240.02, number of molecules per unit cell is 945/240.02 = 3.94, or 4.

Line	Intensity	$\sin^2\theta$	hkl
1	s	0.0462	111
2	vs	0.1198	220
3	vs	0.1615	311
4	vw	0.1790	222
5	m	0.234	400
6	m	0.275	331
7	s	0.346	422
8	m	0.391	511, 333
9	w	0.461	440
10	m	0.504	531
11	m	0.575	620
12	w	0.616	533
13	w	0.688	444
14	m	0.729	711, 551
15	vs	0.799	642
16	s	0.840	731, 553

Example CdTe

◆ Powder pattern is consistent with FCC

◆ Two structures that would be consistent with 4 molecules per unit cell are NaCl and ZnS

NaCl -- Cd at 000 & Te at ½½½
+ fcc translations

$$|F|^2 = 16(f_{Cd} + f_{Te})^2$$
if ($h+k+l$) is even

$$|F|^2 = 16(f_{Cd} - f_{Te})^2$$
if ($h+k+l$) is odd

ZnS -- Cd at 000 & Te at ¼¼¼
+ fcc translations

$$|F|^2 = 16(f_{Cd}^2 + f_{Te}^2)$$
if ($h+k+l$) is odd

$$|F|^2 = 16(f_{Cd} - f_{Te})^2$$
if ($h+k+l$) is odd multiple of 2

$$|F|^2 = 16(f_{Cd} + f_{Te})^2$$
if ($h+k+l$) is even multiple of 2

Example CdTe

1	2	3	4	5
			Calculated intensity	
Line	*hkl*	Observed intensity	NaCl structure	ZnS structure
1	111	s	0.05	12.4
	200	nil	13.2	0.03
2	220	vs	10.0 ⟷	10.0
3	311	vs	0.02	6.2
4	222	vw	3.5	0.007
5	400	m	1.7	1.7
6	331	m	0.01	2.5
	420	nil	4.6	0.01
7	422	s	. . . .	3.4
8	511, 333	m	. . . .	1.8
9	440	w	. . . .	1.1
10	531	m	. . . .	2.0
	600, 442	nil	. . . .	0.005
11	620	m	. . . .	1.8
12	533	w	. . . .	0.9
	622	nil	. . . .	0.004
13	444	w	. . . .	0.6
14	711, 551	m	. . . .	1.8
	640	nil	. . . .	0.005
15	642	vs	. . . .	4.0
16	731, 553	s	. . . .	3.3

(N.B. Calculated intensities have been adjusted so that the 220 line has an intensity of 10.0 for both structures.)

The Powder Diffraction File

◆ Experience has shown that the ensemble of d-spacings ("d" s) and intensities ("I" s) is sufficiently distinctive in order to identify phases

◆ Phase determination can be performed by a comparison of a set of experimental d's and I's with a database of d-I files

◆ d - spacings are independent of wavelength

◆ Intensities are relative (most intense = 100 or 1000 or 1)

Powder Diffraction File (PDF) Database

J. D. Hanawalt (1902 – 1987)
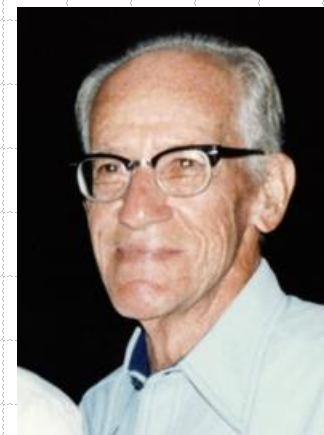
$2.43 - 2.37 \ (\pm .01)$

i	2.42x	2.39$_6$	2.33$_3$	2.98$_2$	1.59$_2$	1.27$_2$	1.26$_2$	6.94$_1$	$(Sc_5Ga_3)16H$
	2.41x	2.39x	2.49x	4.43$_8$	2.86$_8$	1.65$_8$	1.65$_8$	2.85$_6$	$HgTaS_2$
i	2.36x	2.39$_5$	2.68$_4$	1.41$_4$	1.04$_4$	0.97$_4$	2.48$_3$	1.83$_3$	$(Nb_2C)O$
*	2.44$_8$	2.38$_8$	2.61x	2.84$_7$	2.58$_7$	2.46$_7$	3.08$_6$	2.42$_6$	$(Ag_2S)24M$
i	2.43$_8$	2.38$_8$	2.31x	1.70$_8$	1.36$_8$	2.16$_7$	3.40$_6$	2.65$_6$	$(Cd_{0.49}Au_{0.51})O$
i	2.42$_7$	2.38x	2.74$_8$	1.33$_6$	1.58$_5$	1.39$_5$	0.87$_5$	0.79$_5$	$(Cd_3Sc)8H$
i	2.41$_9$	2.38x	2.66x	2.69$_7$	2.47$_7$	2.26$_7$	3.06$_7$	2.72$_7$	ZrP
i	2.44x	2.37x	2.51$_7$	1.39x	1.28x	1.18x	2.29$_7$	2.14$_7$	$(Au_{3.6}Ho)H$
i	2.43x	2.37x	2.68x	2.34x	4.53$_7$	2.46$_7$	5.18$_6$	3.62$_6$	$(Ga_9Rh_2)M$
i	2.43$_6$	2.37x	2.46$_8$	2.06$_6$	1.96$_6$	3.45$_4$	2.27$_4$	2.08$_4$	$(CuZrSi)12O$
i	2.41$_8$	2.37x	2.25x	2.34$_8$	2.23$_8$	2.00$_5$	1.90$_5$	1.79$_5$	$(NbFeSi)O$
i	2.39x	2.37$_9$	2.54$_6$	2.84$_5$	2.67$_5$	2.31$_5$	1.76$_5$	2.47$_4$	$(Zr_2S)O$
i	2.39$_8$	2.37x	2.49$_8$	1.41$_8$	1.33$_8$	1.32$_8$	1.30$_8$	2.69$_5$	$(Nb_2C)12O$
i	2.39x	2.37$_7$	2.03$_7$	2.70$_4$	2.22$_4$	1.95$_4$	1.37$_3$	0.78$_3$	$(PrZn_{11})48U$
i	2.44$_8$	2.36$_6$	2.91x	1.83$_6$	1.79$_6$	1.46$_6$	1.92$_4$	1.40$_4$	$(Te)4P$
i	2.43$_9$	2.36$_9$	2.20x	0.92x	0.81x	0.78x	1.44$_9$	1.33$_9$	$(AuGa)4H$
o	2.42x	2.36$_6$	1.88$_6$	1.77$_6$	1.53$_6$	1.31$_6$	1.27$_6$	1.23$_6$	Ir_2U_3
i	2.41$_9$	2.36$_8$	2.21x	1.96$_8$	1.45$_8$	1.34$_8$	1.24$_8$	0.79$_8$	$(AuCdIn)4H$
i	2.41$_8$	2.36x	2.20x	1.44$_8$	3.40$_5$	1.95$_5$	1.33$_5$	4.34$_4$	$(Au_3Mg)108H$
i	2.41$_8$	2.36x	1.39x	1.08x	1.71$_8$	1.18$_8$	1.04$_8$	1.36$_6$	$(MoU_2)6U$
i	2.38x	2.36$_8$	2.29$_6$	1.25$_6$	1.23$_6$	3.29$_4$	2.94$_4$	2.71$_4$	$(Ge_3Sc_5)16H$
i	2.44$_5$	2.35x	2.71$_8$	1.49$_4$	1.51$_2$	1.36$_2$	1.17$_2$	1.01$_2$	$(Al_3Zr_4)7H$
i	2.41$_8$	2.35x	2.20x	2.19$_8$	2.39$_6$	3.64$_3$	2.49$_3$	1.95$_3$	$(BiPd_3)16O$
i	2.38x	2.35x	2.73x	2.32x	2.31x	2.23x	2.13x	1.73x	$(Nb_8P_5)52O$
o	2.44x	2.34x	2.05x	1.95$_9$	1.29$_9$	3.43$_5$	2.38$_5$	1.51$_5$	$FeSiZr$

Powder Diffraction File (PDF) Database

◆ 1919 -- Hull pointed out that powder diffraction could be used for routine chemical analyses

- powder pattern is characteristic of the substance
- the patterns of a combination of phases will superimpose
- only a small amount is needed

◆ 1938 -- Hanawalt, Rinn and Frevel at Dow Chemical compiled diffraction data on about 1000 compounds as 3"x5" file cards and devised a simple means of classifying the data

◆ 1942 -- the American Society for Testing Materials (ASTM) published the first edition of diffraction data cards (1300 entries)

Card image for $Ce_2(SO_4)_3$ from PDF Set 1 as issued in 1941

Source: ICDD

Powder Diffraction File (PDF)

◆ 1962, the d-I's, formulas, and PDF numbers were first keyboarded for a computer-readable database.

◆ 1969 -- the Joint Committee on Powder Diffraction Standards (JCPDS) was formed as a non-profit corporation to oversee the database

◆ By 1971 the Powder Diffraction File (PDF) contained 21 sets of data with about 21,500 entries

◆ 1978 – name change to the International Centre for Diffraction Data (ICDD)

◆ PDF-4+ Release 2016
   ▪ 384,613 entries

PDF-4+ Entries, Entries with Structures

Powder Diffraction File (PDF)

Computer Searching of the PDF

◆ Computerization has dramatically improved the efficiency of searching the PDF database

◆ Cards are no longer printed – data are on CD-ROM

◆ Numerous third-party vendors have software for searching the PDF database

◆ Computerized "cards" can contain much more crystallographic information
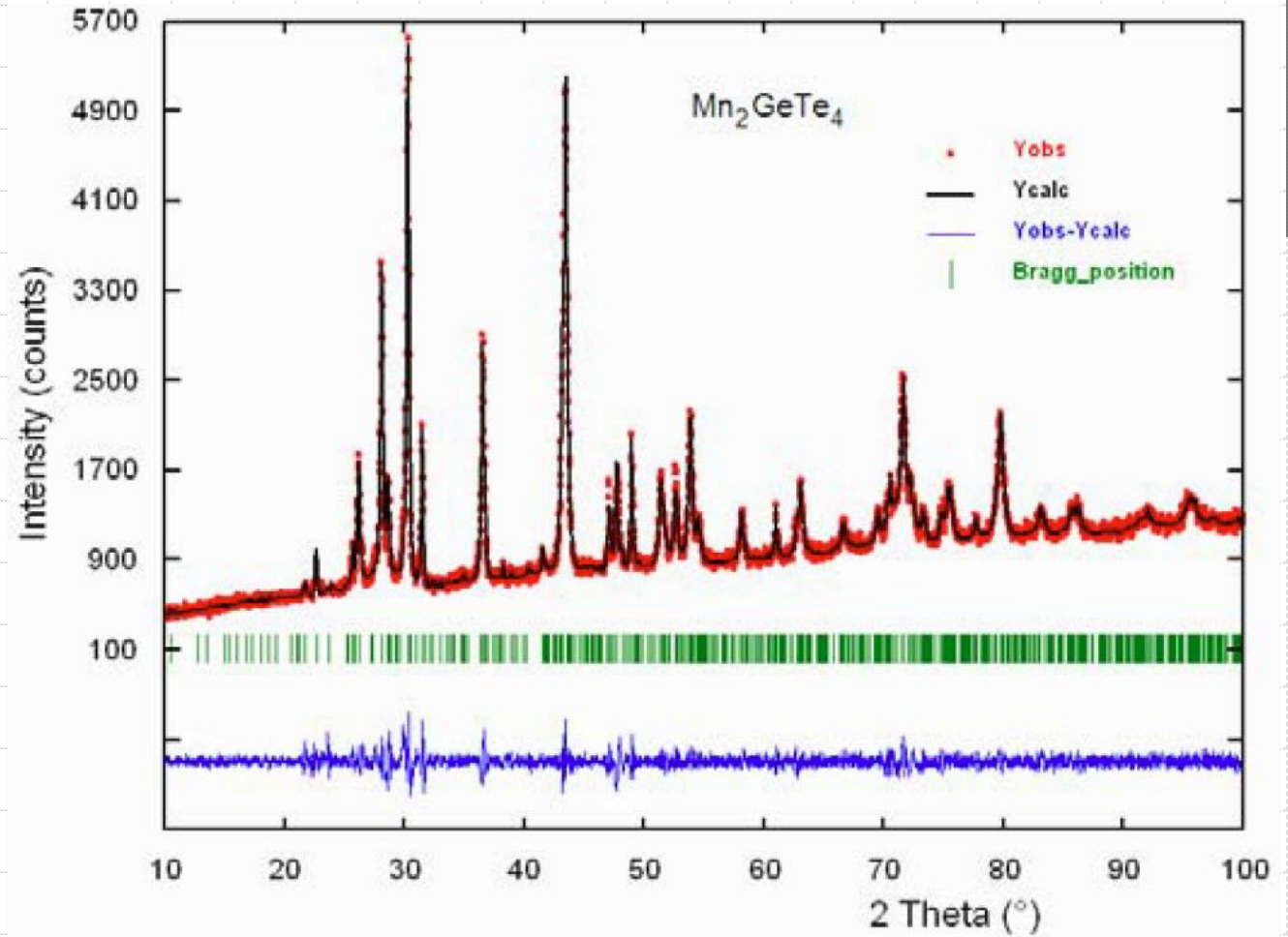
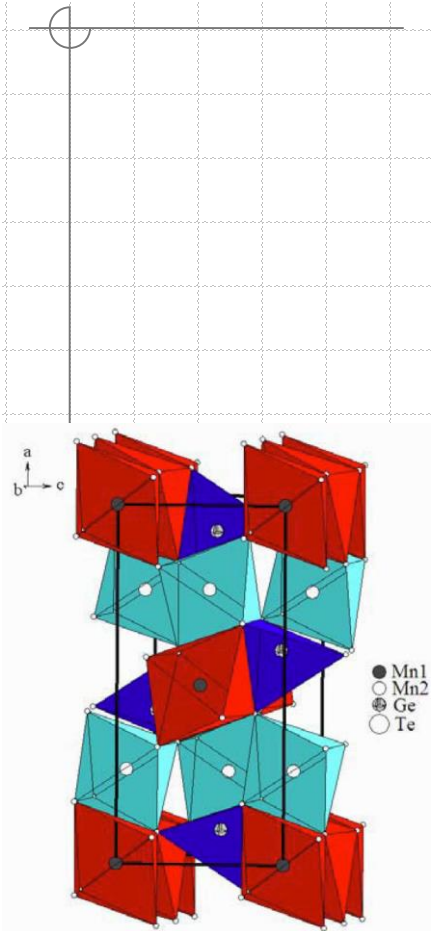◆ Evolution of the database is continuing…

Experimental Issues and Problems

◆ Searching of the PDF requires high-quality data
- **accurate** line positions are a must!
- calibration of camera and diffractometer with known d - spacing standards
- careful measurement of line intensities
- elimination of artifacts (e.g. preferred orientation)
- solid solutions and strains shift peak positions

◆ "garbage in, garbage out" -- poor quality data will usually give a poor match
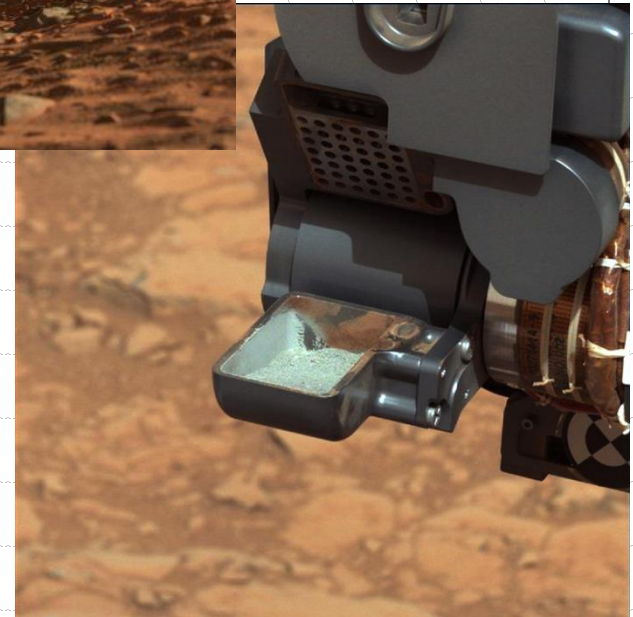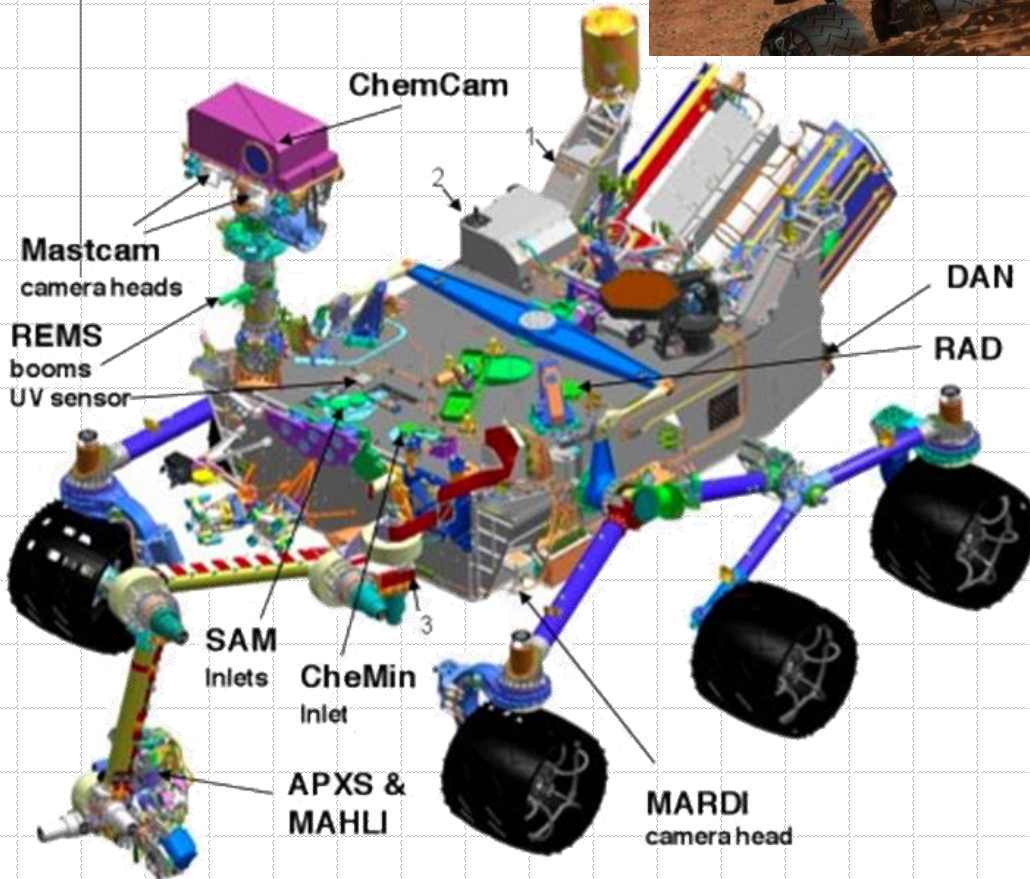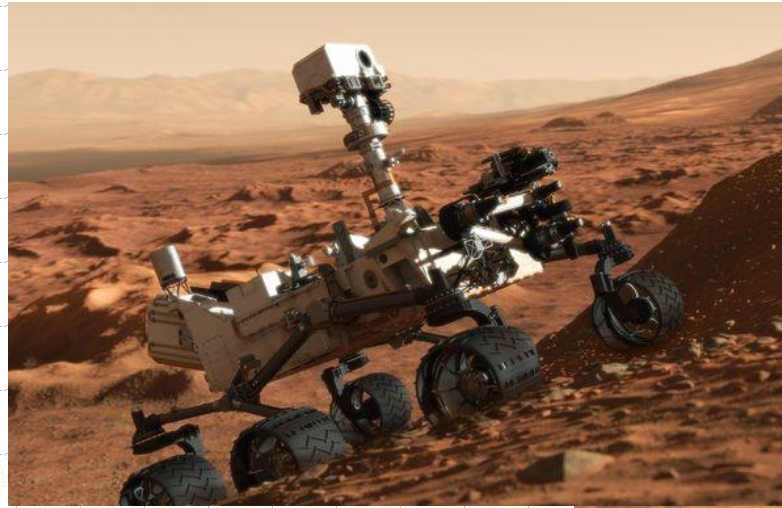
◆ mixtures of two or more phases

◆ errors in the database

Whole Pattern Fitting

◆ Traditional quantitative phase analysis focuses on the intensities of one or a small number of peaks

◆ Greater accuracy can be obtained by fitting the whole diffraction pattern to what would be expected for a mixture of components

◆ This approach gives an analysis that is an average over all of the peaks, so it is less susceptible to errors that arise from preferred orientation or poor particle statistics

◆ The Rietveld method fits the whole of the diffraction pattern to calculated intensities for the various phases that are present. Gives crystal structure information as well as composition.

Rietveld Refinement

Gerzon E. Delgado et al., Avances en Química, 4, 7- 11 (2009)

XRD on Mars

ChemCam

Mastcam
camera heads

REMS
booms
UV sensor

DAN

RAD

SAM
Inlets

CheMin
Inlet

APXS &
MAHLI

MARDI
camera head

This image from NASA's Curiosity rover shows the first sample of powdered rock extracted by the rover's drill. The image was taken after the sample was transferred from the drill to the rover's scoop. In planned subsequent steps, the sample will be sieved, and portions of it delivered to the Chemistry and Mineralogy instrument and the Sample Analysis at Mars instrument.
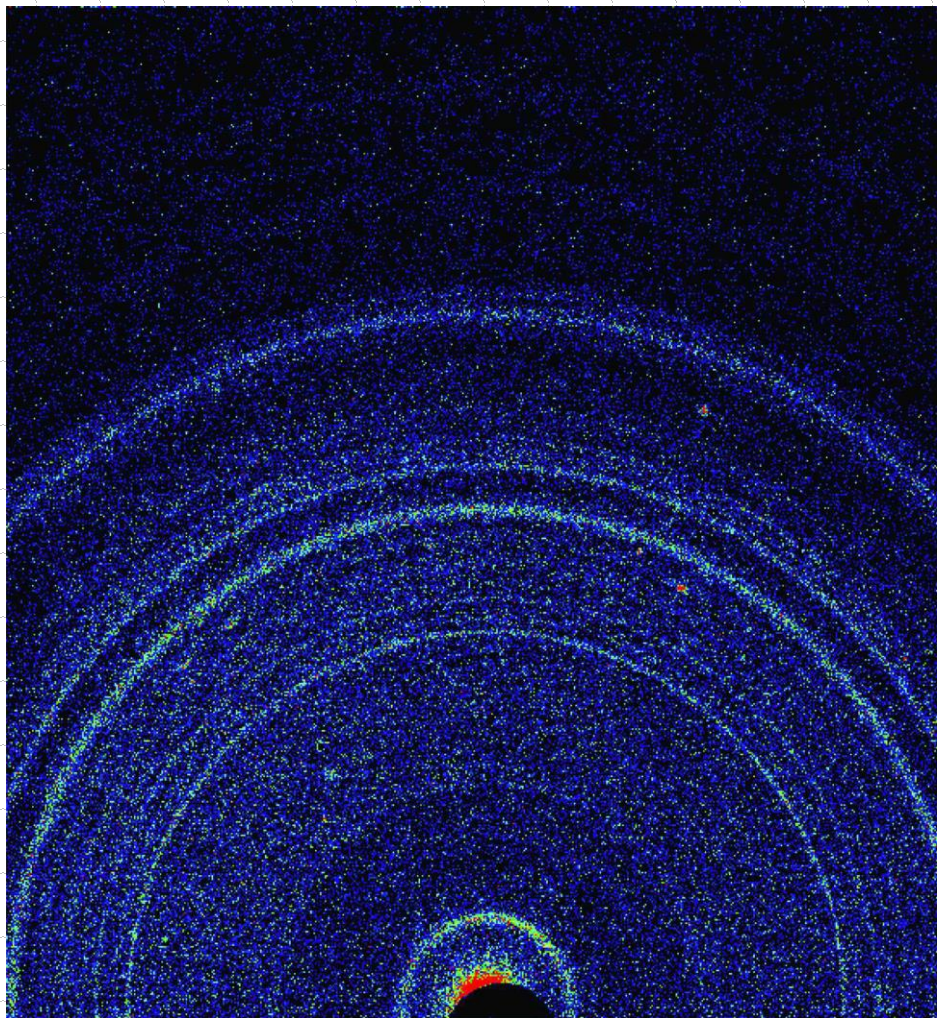
XRD on Mars
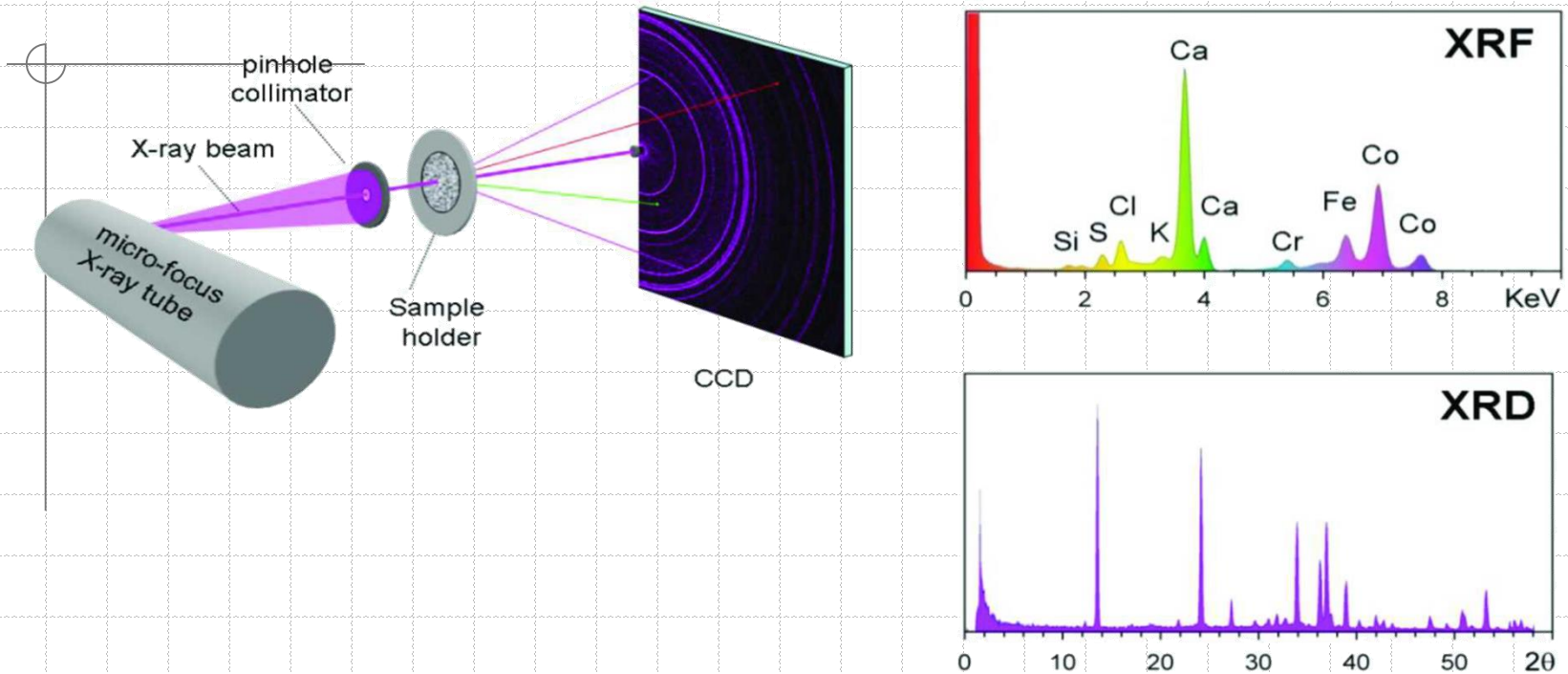
Schematic diagram of the CheMin instrument and resulting XRF and XRD data.
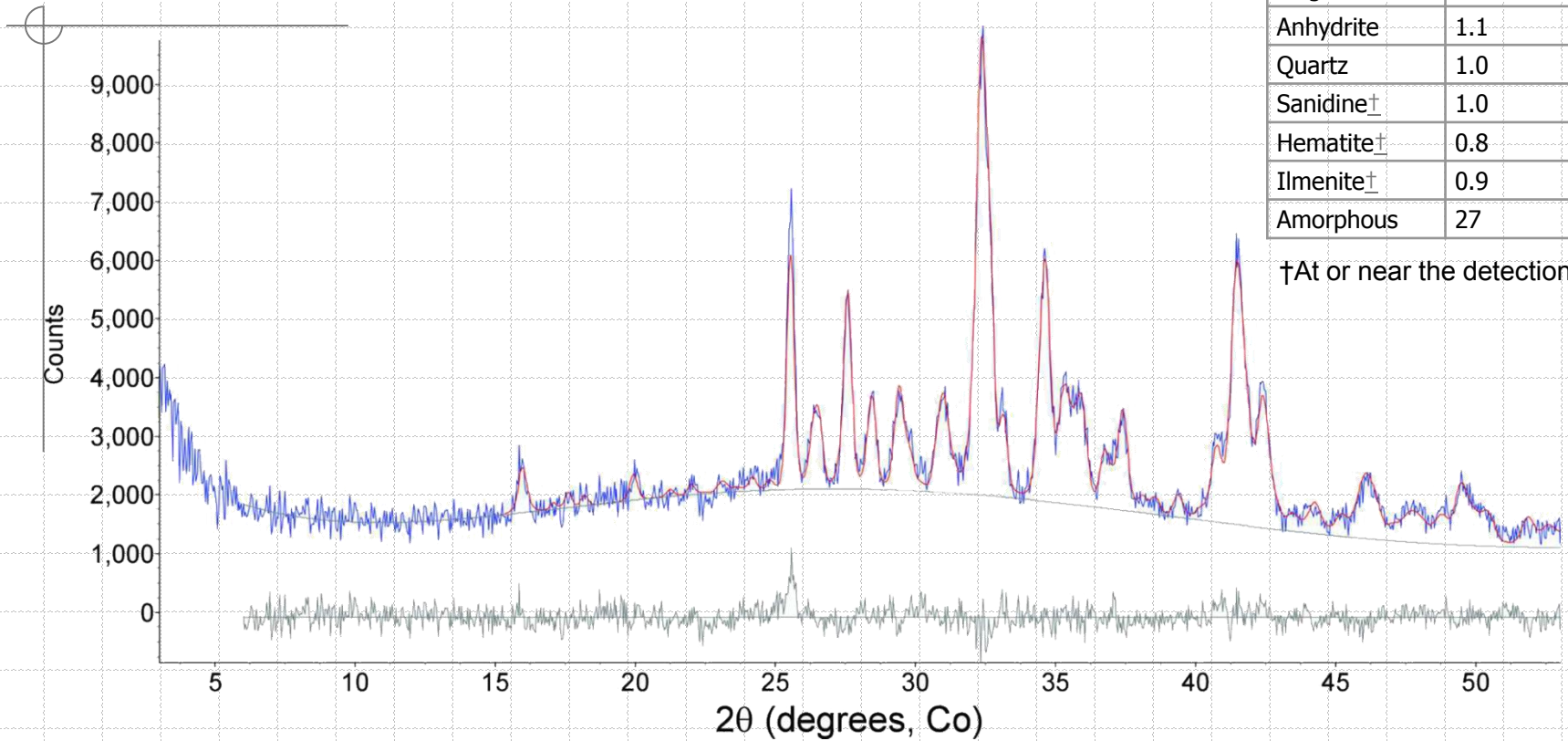
XRD on Mars
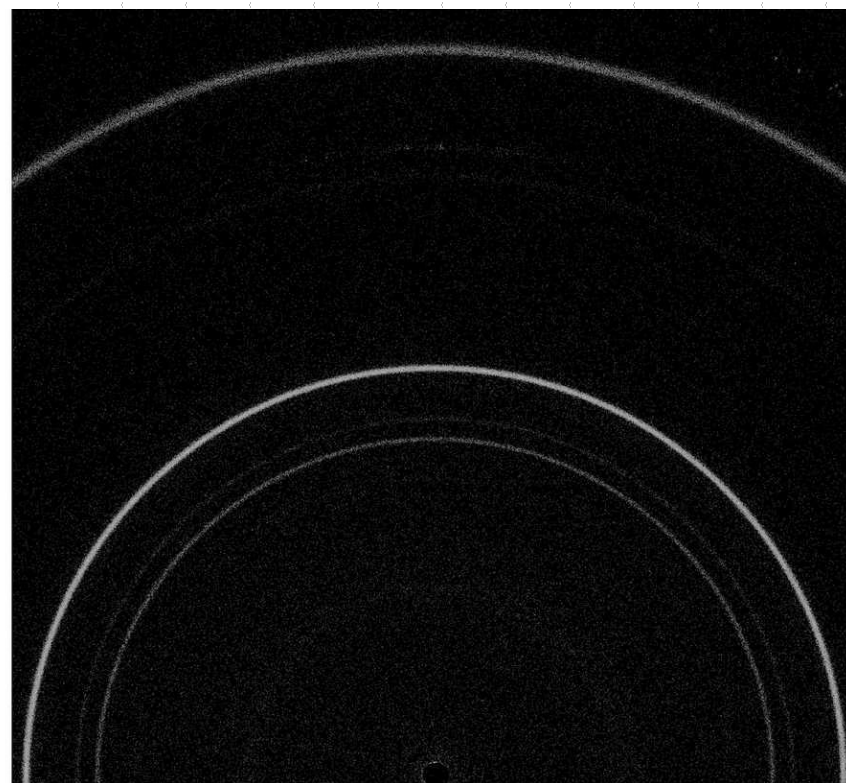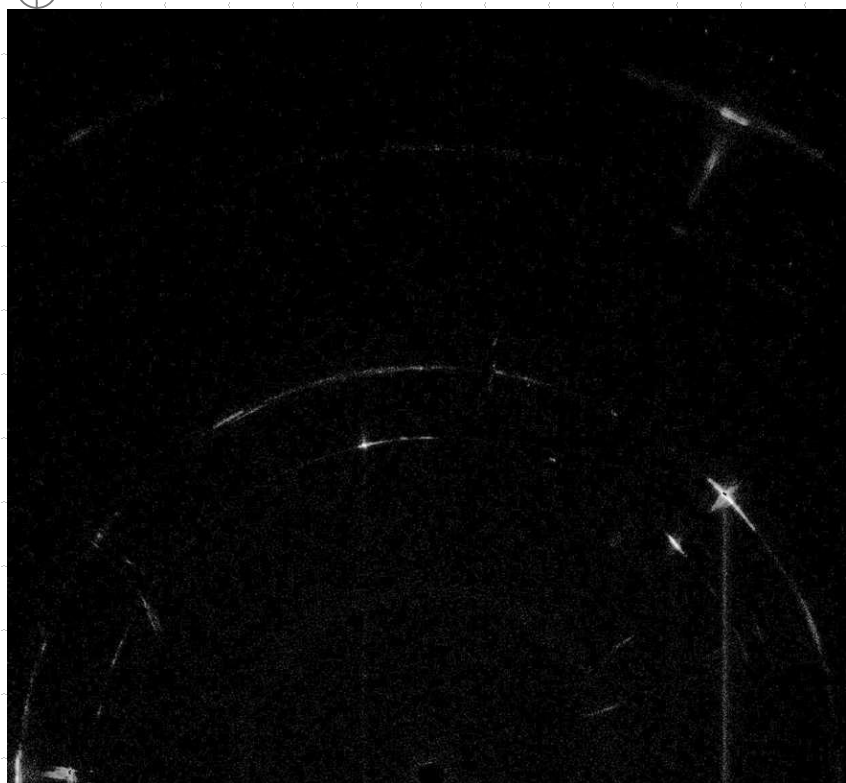
XRD patterns of crushed and sieved (150 µm) NaCl measured on the CheMin III instrument, (left) without and (right) with sonic vibration.

XRD on Mars

A two-dimensional XRD pattern for the Rocknest aeolian bedform (dune).

XRD on Mars

Mineral	Weight (%)
Plagioclase	30
Forsterite-Fe	16
Augite	11
Pigeonite	10
Magnetite	1.5
Anhydrite	1.1
Quartz	1.0
Sanidine†	1.0
Hematite†	0.8
Ilmenite†	0.9
Amorphous	27

†At or near the detection limit.

Observed (blue, integrated from the two-dimensional image in Fig.6) and calculated (red) plots from Rietveld refinement using data for Rocknest (~26.4 h integration, phases listed in Table1).