Chapter 2

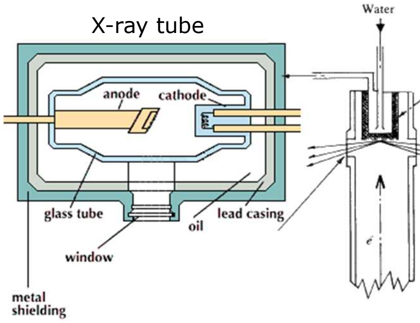
Physical Methods for Characterizing Solids

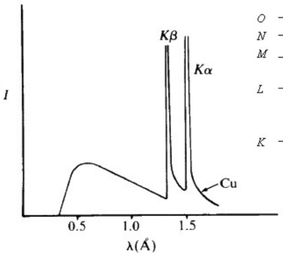
X-ray diffraction

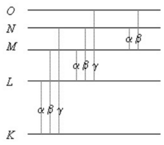
X-rays were discovered by Wilhelm Rontgen, a German physicist in 1895.

To generate x-rays, three things are needed.
- a source of electrons
- a means of accelerating the electrons at high speeds
- a target material to receive the impact of the electrons and interact with them.

X-ray tube







Frequency (wavelength) depends on the anode metal, often Cu, Mo, Co.

Lines occur because bombarding electrons knock out e^- from K shell (n = 1), which are filled by electrons in higher shells. Electrons falling from L shell (n = 2) give rise to K_a lines, whereas e^- from M shell (n = 3) give the K_b lines. ($K_{\alpha1}$ and $K_{\alpha2}$ doublets, etc.)

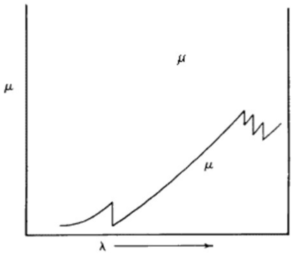
Typical cathode element is W.

Potential difference is 20-50 kV.

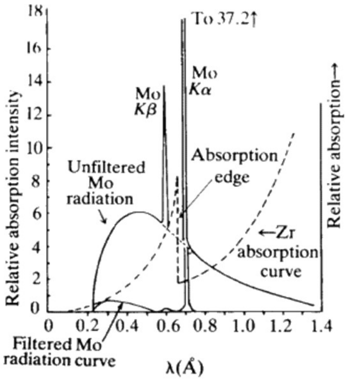
Anode must be water cooled.

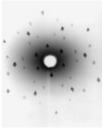
Monochromatic radiation (single wavelength or a narrow range of wavelengths) is required for X-ray diffraction.

- Typically, the K_α line is selected and the K_β line is filtered out by using a thin metal foil of the adjacent (Z-1) element. (nickel filters K_β line of copper)
- A monochromatic beam of X-rays can also be selected by reflecting from a plane of a single crystal.

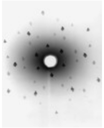


The observed intensity I is given by: $I = I_o e^{-\mu t}$ where μ is a linear absorption coefficient and t is the path length through which the X-rays are moving.





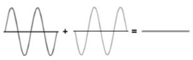
Diffraction of X-rays



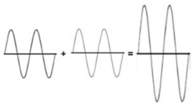
Max von Laue used a crystal of copper sulfate as the diffraction grating (Nobel Prize 1914).

Crystalline solids consist of regular arrays of atoms, ion, or molecules with interatomic spacing on the order of 100 pm or 1 Å.

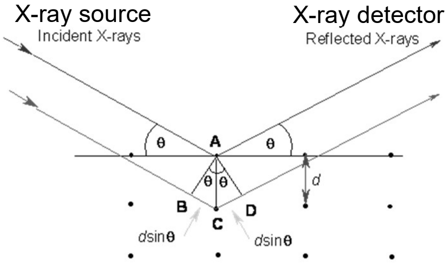
- The wavelength of the incident light has to be on the same order as the spacing of the atoms.
- W.H. and W.L. Bragg determined crystal structures of NaCl, KCl, ZnS, CaF_2, $CaCO_3$, C (diamond).
- Reflection of X-rays only occurs when the conditions for constructive interference are fulfilled.



Destructive Interference



Constructive Interference



Difference in path length = BC + CD

BC = CD = $d_{hkl}\sin\theta_{hkl}$

Difference in path length = $2d_{hkl}\sin\theta_{hkl}$

Must be an integral number of wavelengths, $n\lambda = 2d_{hkl}\sin\theta_{hkl}$

(n = 1, 2, 3, …)

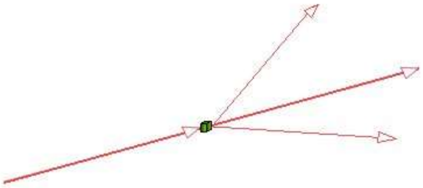
$\lambda = 2d_{hkl}\sin\theta$

Bragg Equation

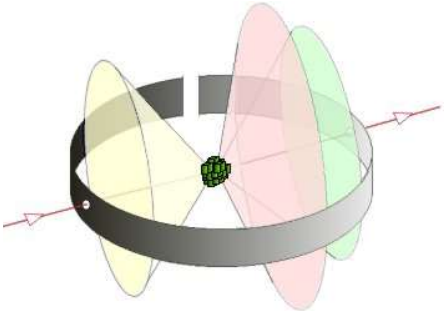
Powder Diffraction

A powder may be composed of many small and finely ground crystals, known as crystallites.

- These crystallites are (assumed to be) randomly oriented to one another.
- If the powder is placed in the path of a monochromatic X-ray beam, diffraction will occur from the planes in those crystallites that are oriented at the correct angle to fulfill the Bragg condition.
- The diffracted beams make an angle of 2θ with the incident beam.

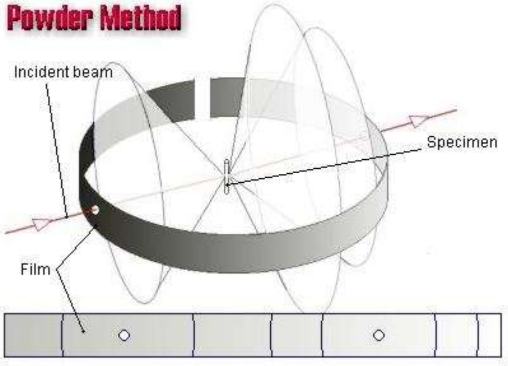


Single Crystal



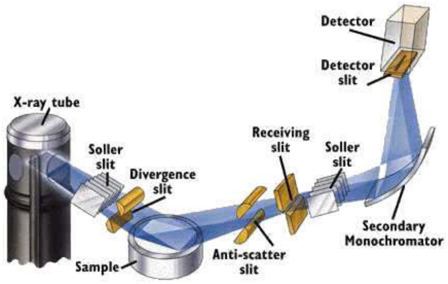
Polycrystalline Powder

In the Debye-Scherrer photographic method, a film was wrapped around the inside of a X-ray camera.



The powder, sealed in a glass capillary tube, diffracts the X-rays (Bragg's law) to produce cones of diffracted beams. These cones intersect a strip of photographic film located in the cylindrical camera to produce a characteristic set of arcs on the film. The film can be removed and examined. Using the radius of the camera and the distance along the film from the center, the Bragg angle 2θ and therefore the *d*-spacing for each reflection can be calculated.

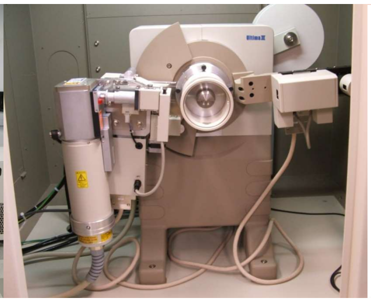
Modern X-ray Diffractometer

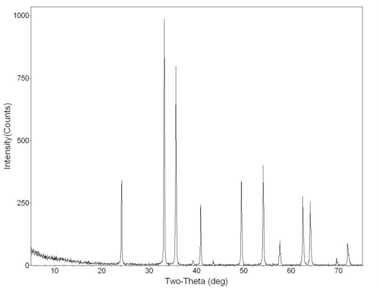


-use a scintillation or CCD detector to record the angles and intensities of the diffracted beams.

-the resolution obtained by a diffractometer is better than photographic film, since the sample helps refocus the X-ray beam.

-intensity is more readily measured and digitally stored.





Indexing the peaks

Which planes are responsible for each reflection?

-need to index the reflections (assign the correct *hkl*)

-difficulty may range from simple to extremely difficult

The planes giving rise to the smallest Bragg angle will have the largest d-spacing.

-consider a primitive cubic system, with the 100 planes having the largest separation (the 010 and 001 planes also reflect at this position)

Bragg's Law

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

For a cubic system

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

$$d_{hkl} = \frac{a}{\sqrt{(h^2+k^2+l^2)}} \Longrightarrow \lambda = \frac{2a\sin(\theta)}{\sqrt{(h^2+k^2+l^2)}} \Longrightarrow \sin^2(\theta) = \frac{\lambda^2}{4a^2}(h^2+k^2+l^2)$$

For a primitive cubic class, all integral values of the indices *h*, *k,* and *l* are possible*.*

hkl	$h^2 + k^2 + l^2$
100	1
110	2
111	3
200	4
210	5
211	6
220	8
300, 221	9

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

Note that the value 7 is missing in the sequence, since there is no possible integral value that $h^2 + k^2 + l^2 = 7$

If the intensity of diffraction of the pattern is plotted against $\sin^2(\theta)$, one would obtain equally spaced lines with the 7th, 15th, 23rd, etc. missing.

-it is easy to identify a primitive cubic system and (by inspection) assign indices to each of the reflections.

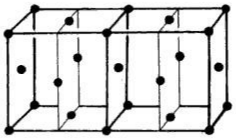
-the cubic unit cell dimension a can be obtained from *any* of the indexed reflections.

-since the experimental error is relatively constant, the reflection with the largest Bragg angle is chosen to minimize error in the lattice parameter calculation (or perform least squares on all reflections).

Absences due to lattice centering

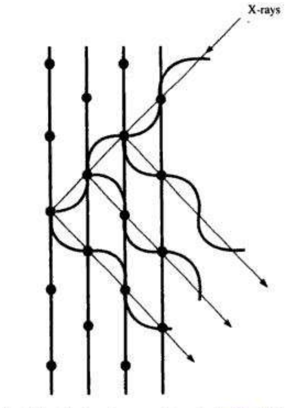
The pattern of observed lines for the two other cubic crystalline systems, body-centered and face-centered is different from primitive.

- The differences arise because the centering leads to destructive interference for some reflections and the missing reflections are known as systematic absences.



200 planes of two face centered unit cells.

If a is the cell dimension, the planes have a spacing $a/2$.



The *100* reflection from an F-centred cubic lattice.

The reflection from the 200 plane is exactly out of phase with the 100 reflection and destructive interference occurs and no 100 reflection is observed.

-furthermore, in order for a reflection to be observed for *fcc*, the *hkl* indices must be all odd or all even.

A similar analysis of the *bcc* system would find that the sum of the reflections must be even ($h+k+l = 2n$)

-these absences apply to all crystal systems, not just cubic.

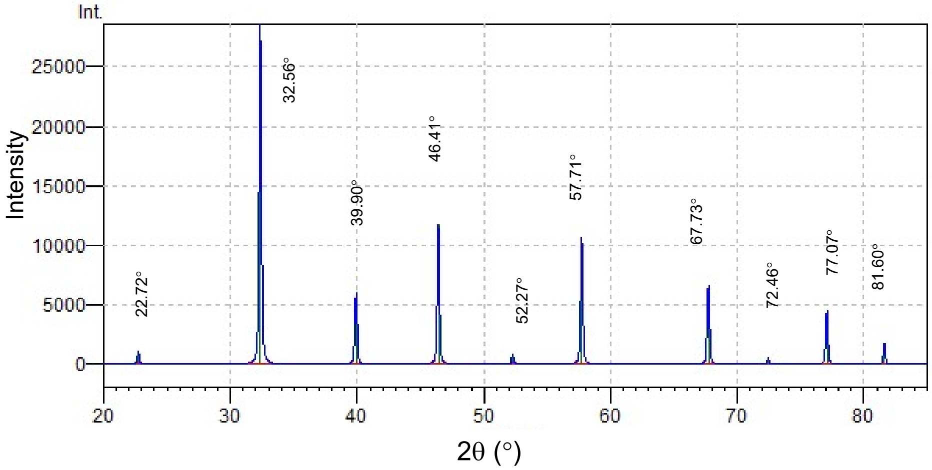
Allowed list of $h^2 + k^2 + l^2$ for cubic crystals

Forbidden numbers	Primitive, P	Face Centered, F	Body Centered, I	Corresponding *hkl*
	1			*100*
	2		2	*110*
	3	3		*111*
	4	4	4	*200*
	5			*210*
	6		6	*211*
7				
	8	8	8	*220*
	9			*221, 300*
	10		10	*310*
	11	11		*311*
	12	12	12	*222*
	13			*320*
	14		14	*321*
15				
	16	16	16	*400*

If the observed $\sin^2(\theta)$ follows in a ratio of 1, 2,3,4,5,6, 8, …, then the unit cell is likely *primitive cubic*.

-the common factor is $\lambda^2/4a^2$

Indexing Example – $SrTiO_3$



Powder X-ray diffractometer equipped with a copper X-ray source.
-copper sources emit X-rays with a wavelength, λ = 1.5406 Å.

Using Bragg’s Law, $\lambda = 2d_{hkl}\sin\theta$

Peak #	2θ (°)	θ (°)	d (Å)
1	22.72	11.36	3.910
2	32.56	16.28	2.765
3	39.90	19.95	2.257
4	46.41	23.20	1.955
5	52.27	26.14	1.749
6	57.71	28.36	1.596
7	67.73	33.86	1.382
8	72.46	36.23	1.303
9	77.07	38.54	1.236
10	81.60	40.80	1.179

Look for a common factor, *Z*, which can be divided into each value to give an integer quotient. Let *Z* = 0.0654 in this example.

Peak #	2θ (°)	θ (°)	d (Å)	$1/d^2$	$(1/d^2)/Z$
1	22.72	11.36	3.910	0.0654	1
2	32.56	16.28	2.765	0.1308	2
3	39.90	19.95	2.257	0.1963	3
4	46.41	23.20	1.955	0.2616	4
5	52.27	26.14	1.749	0.3269	5
6	57.71	28.85	1.596	0.3926	6
7	67.73	33.86	1.382	0.5236	8
8	72.46	36.23	1.303	0.5917	9
9	77.07	38.54	1.236	0.6546	10
10	81.60	40.80	1.179	0.7194	11

Note that in this example, we obtain all integers and all the quotients are integers that indicate a primitive unit cell.

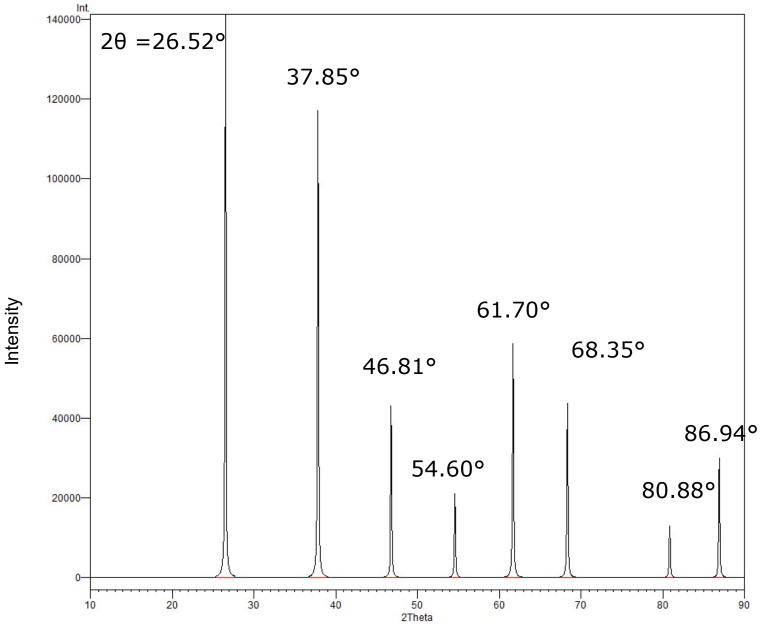
Assignment of Miller indices

Peak #	2θ (°)	θ (°)	d (Å)	$1/d^2$	$(1/d^2)/Z$	h	k	l
1	22.72	11.36	3.910	0.0654	1	1	0	0
2	32.56	16.28	2.765	0.1308	2	1	1	0
3	39.90	19.95	2.257	0.1963	3	1	1	1
4	46.41	23.20	1.955	0.2616	4	2	0	0
5	52.27	26.14	1.749	0.3269	5	2	1	0
6	57.71	28.85	1.596	0.3926	6	2	1	1
7	67.73	33.86	1.382	0.5236	8	2	2	0
8	72.46	36.23	1.303	0.5917	9*	3 2	0 2	0 1
9	77.07	38.54	1.236	0.6546	10	3	1	0
10	81.60	40.80	1.179	0.7194	11	3	1	1

The (300) and (221) peaks fall at the same location, both give $h^2 + k^2 + l^2 = 9$.

$$\lambda = \frac{2a\sin(\theta)}{\sqrt{(h^2+k^2+l^2)}}$$

The lattice parameter, a, is 3.91 Å

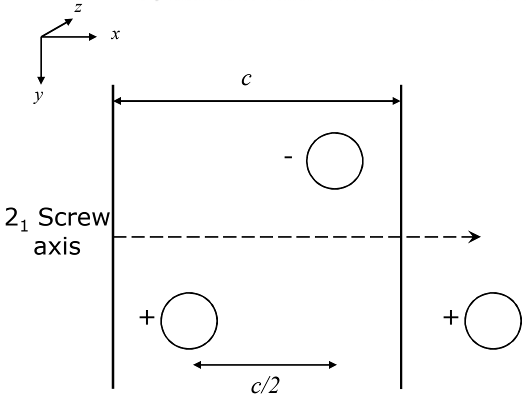


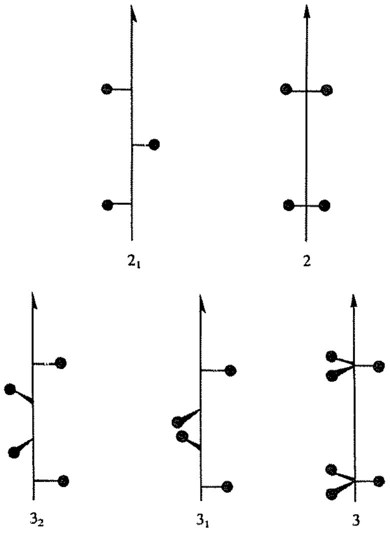
Diffractometer equipped with a copper X-ray source.
-copper sources emit X-rays with a wavelength, λ = 1.5406 Å.

Systematic absences

Symmetry element		Affected reflection	Condition for reflection to be present
Primitive lattice	P	*hkl*	none
Body-centered lattice	I	*hkl*	*h* + *k* + *l* = even
Face-centered lattice	A	*hkl*	*k* + *l* = even
	B	*hkl*	*h* + *l* = even
	C	*hkl*	*h* + *k* = even
Face-centered lattice	F	*hkl*	*h k l* all odd or even
twofold screw, 2_1 along	*a*	*h00*	*h = even*
fourfold screw, 4_2 along	*a*	*h00*	*h = even*
sixfold screw, 6_3 along	*c*	*00l*	*l* divisible by 3
threefold screw, 3_1, 3_2 along	*c*	*00l*	*l* divisible by 3
sixfold screw, 6_2, 6_4 along	*a*	*h00*	*h* divisible by 4
fourfold screw, 4_1, 4_3 along	*a*	*h00*	*h* divisible by 4
sixfold screw, 6_1, 6_5 along	*c*	*00l*	*l* divisible by 6
Glide plane perpendicular to	*b*		
Translation *a*/2 (*a* glide)		*h0l*	*h* = even
Translation *c*/2 (*c* glide)		*h0l*	*l* = even
b/2 + *c*/2 (*n* glide)		*h0l*	*h* + *l* = even
b/4 + *c*/4 (*d* glide)		*h0l*	h + l divisible by 4

Systematic absences due to screw axes and glide planes

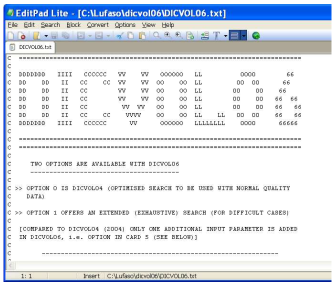




-Translational symmetry elements lead to a set of systematic absences in the *hkl* reflections.

-The effect of a glide plane is to introduce a plane of atoms halfway along the unit cell in the direction of the glide.

Pattern Indexing using Computer Software Programs



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C  ============================================================================
C
C  DDDDDDD   IIII   CCCCCC   VV    VV   OOOOOO   LL          OOOO        66
C  DD    DD   II   CC    CC  VV    VV  OO    OO  LL         OO  OO      66
C  DD    DD   II   CC        VV    VV  OO    OO  LL        OO    OO    66
C  DD    DD   II   CC        VV    VV  OO    OO  LL        OO    OO   66  66
C  DD    DD   II   CC          VV  VV  OO    OO  LL        OO    OO   66   66
C  DD    DD   II   CC    CC     VVVV   OO    OO  LL    LL   OO  OO    66   66
C  DDDDDDD   IIII   CCCCCC       VV     OOOOOO   LLLLLLLL    OOOO      66666
C
C  ============================================================================
C  ============================================================================
C
C     TWO OPTIONS ARE AVAILABLE WITH DICVOL06
C     ---------------------------------------
C
C >> OPTION 0 IS DICVOL04 (OPTIMISED SEARCH TO BE USED WITH NORMAL QUALITY
C    DATA)
C
C >> OPTION 1 OFFERS AN EXTENDED (EXHAUSTIVE) SEARCH (FOR DIFFICULT CASES)
C
C  [COMPARED TO DICVOL04 (2004) ONLY ONE ADDITIONAL INPUT PARAMETER IS ADDED
C  IN DICVOL06, i.e. OPTION IN CARD 5 (SEE BELOW)]
C
C        --------------------------------------------------------------
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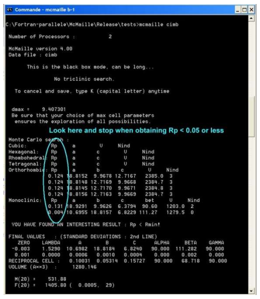
DICVOL06



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C:\Fortran-parallele\McMaille\Release\tests>mcmaille cimb

 Number of Processors :          2

 McMaille version 4.00
 Data file : cimb

      This is the black box mode, can be long...

               No triclinic search.

   To cancel and save, type K (capital letter) anytime


  dmax :    9.407301
  Be sure that your choice of max cell parameters
   ensures the exploration of all possibilities.

 Monte Carlo search :
 Cubic:         Rp      a        U     Nind
 Hexagonal:     Rp      a       c       U     Nind
 Rhombohedral:  Rp      a       c       U     Nind
 Tetragonal:    Rp      a       c       U     Nind
 Orthorhombic:  Rp      a       b       c       U     Nind
               0.124 18.8152  9.9678 12.7167   2385.0  3
               0.124 18.8148 12.7169  9.9668   2384.7  3
               0.124 18.8145 12.7170  9.9671   2384.8  3
               0.124 18.8156 12.7163  9.9669   2384.7  3
 Monoclinic:    Rp      a       b       c      bet     U     Nind
               0.131 18.9291  9.9626  6.3794  90.60   1203.0  2
               0.004 10.6955 18.8157  6.8229 111.27   1279.5  0

  YOU HAVE FOUND AN INTERESTING RESULT : Rp < Rmin!

 FINAL VALUES   : (STANDARD DEVIATIONS : 2nd LINE)
    ZERO    LAMBDA      A        B        C      ALPHA     BETA    GAMMA
  -0.003    1.5290  10.6982  18.8184   6.8240   90.000  111.282   90.000
   0.001    0.0000   0.0006   0.0010   0.0004    0.000    0.002    0.000
 RECIPROCAL CELL :   0.10031  0.05314  0.15727   90.000   68.718   90.000
 VOLUME (A**3)  :     1280.146

   M(20) =    531.88
   F(20) =   1405.80 (  0.0005,  29)
```

Look here and stop when obtaining Rp < 0.05 or less

ITO13 CRYSFIRE McMaille

… and several others.

FullProf

-Treor-90

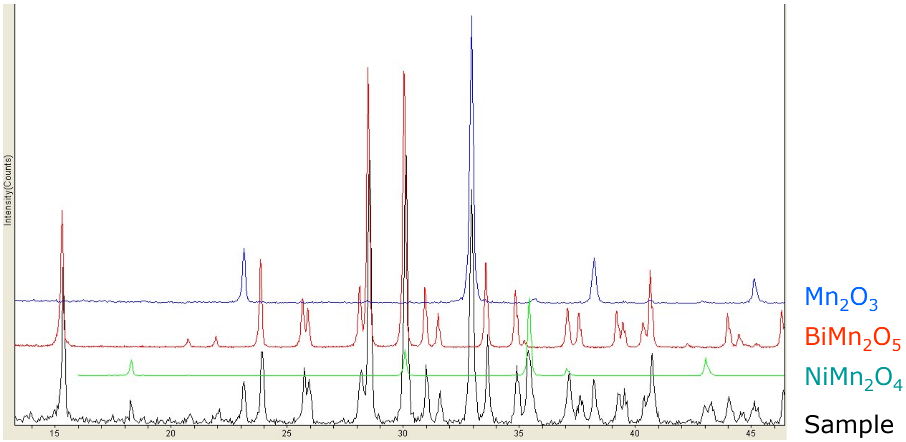
Once the pattern is indexed, the lattice parameters can also be determined from a least squares analysis.

Crystal system	**Unit Cell Volume**
Cubic	$V = a^3$
Tetragonal	$V = a^2c$
Hexagonal	$V = a^2c\sin(60°)$
Trigonal	$V = a^2c\sin(60°)$
Orthorhombic	$V = abc$
Monoclinic	$V = abc\sin(\beta)$
Triclinic	$V = abc\,(1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma) + 2(\cos(\alpha)\cos(\beta)\cos(\gamma))^{½}$

- The volume of the unit cell can be calculated from the lattice parameters.
- If the density of the crystals are known, then the mass of the contents of the unit cell can be calculated.
- From a knowledge of formula weight, the number of formula units, *Z*, can be calculated.
- The density can be measured using a mixture of liquids such that the crystals neither float nor sink. The density of the liquid can then be measured using a density bottle or equivalent technique.

$$Density = \frac{m}{v}$$

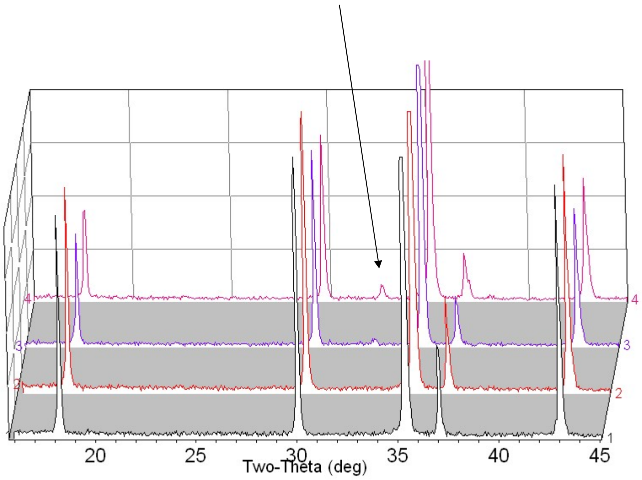
Identification of Unknowns and Phase Purity



A database from the Joint Committee for Powder Diffraction Standards has ~412,083 entries in the Powder Diffraction File (PDF-4). A computerized search-match program may be used to compare the d-spacings and intensity of the recorded peaks to the database.

-powder diffraction typically has a limit of a few percent for detection of phases.

Following Reactions using X-ray Diffraction



Incomplete Reaction

1st heat

2nd heat

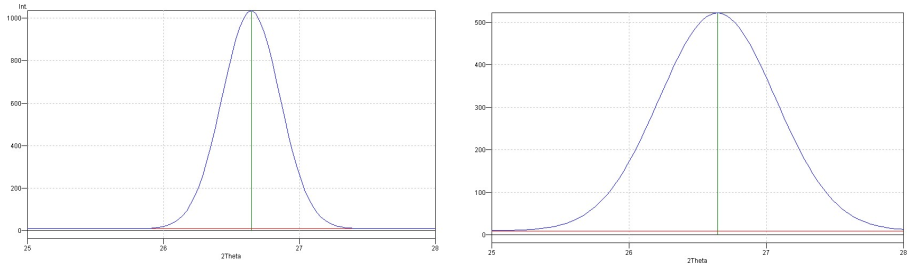
3rd heat

4th heat

Crystallite Size

A decrease in the crystallite size causes an increase in the width of the diffraction.

- On either side of the Bragg angle, the diffracted beam will destructively interfere and result in a sharp peak.
- The destructive interference is a result of the summation of all the diffracted beams.
- Close to the Bragg angle it takes diffraction from a large number of planes to produce complete destructive interference.
- In very small crystallites, there are not enough planes to produce complete destructive interference, so a broadened peak is observed.



Debye-Scherrer

$$T = \frac{C\lambda}{B\cos\theta} = \frac{C\lambda}{(B_M^2 - B_S^2)^{1/2}\cos\theta}$$

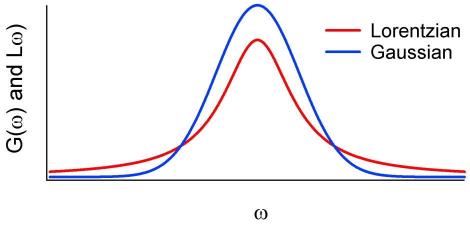
where *C* is the shape factor (~0.8-1.39), T is the mean size of the crystallite thickness, λ is the wavelength of the X-rays, θ is the Bragg angle, and *B* is the full-width at half-maximum (FWHM) of the peak (radians) corrected for instrumental broadening.

  - B_m and B_s are the FWHMs of the sample and a standard, respectively.
  - The standard is typically a highly crystalline sample with a diffraction peak in a similar position to the sample.

- The method is especially useful for plate-like crystals with specific shear planes. The peak width can give the thickness of the crystallites perpendicular to those planes.
- Solid state reaction mixtures typically become more crystalline on heating. The X-ray diffraction peaks will become narrower (smaller FWHM).
- Estimate size of nanoparticles using these techniques

Rietveld Method

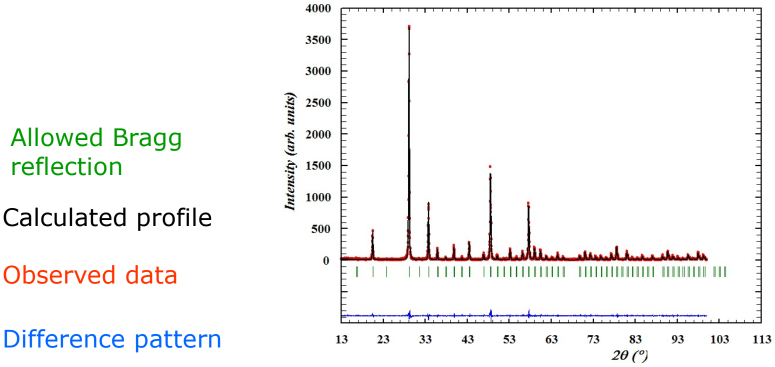
- Few peaks occur in the powder pattern in high symmetry crystal systems. The peaks are typically well-resolved and it is possible to measure their *positions* and *intensities* with accuracy, then index the reflections and solve the structure.
- Larger and less symmetrical structures have far more peak overlap and it is difficult to accurately extract the peak intensities.
- Rietveld analysis is a technique that has been developed for solving/refining crystal structures from powder diffraction data.
- Involves an interpretation of the peak positions and intensities.
  - The large amount of peak overlap requires analyzing the overall line profiles, where each allowed reflection (peak) is given convolution of a gaussian/lorentzian line shape. The peaks are allowed to overlap to form an overall line profile.



Rietveld Method – Powder Diffraction

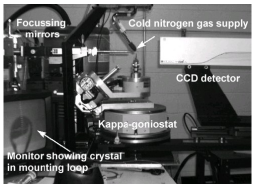
Rietveld method can be used to refined (‘solve’) a crystal structure.

- It a trial structure is known, from an isostructural compound or hypothetical model, the crystal structure may be refined.
- The method takes a trial structure, calculates a powder diffraction profile and compares it to the measured profile. The trial structure is modified by changing various refinable parameters, including atomic positions, thermal parameters, site occupancies, peak shape parameters, etc., until a best-fit match is obtained with the measured pattern.



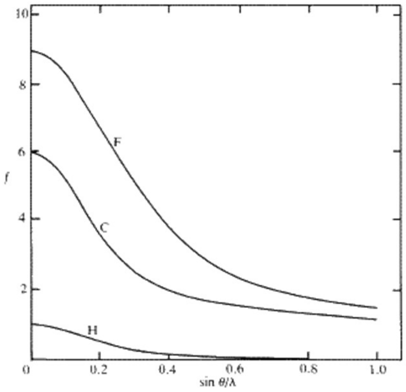
Single Crystal X-ray Diffraction

- Accurate and rapid measurement of the position and intensity of the *hkl* reflections is possible using single crystal X-ray diffraction.
- The methods available to detect X-ray do not record all the information about the diffracted X-ray, only the intensity. The detectors are not sensitive to the *phase* of the X-rays.
- Intensity is proportional to the square of the amplitude of the wave, thus the phase information is lost. The phase information is related to the atomic positions in a crystal structure, but...
- If the Bragg angles of the reflections are measured and indexed, the size of the unit cell, information on translation symmetry elements, and symmetry information is obtained.
- The intensities (and position) of the reflections are different and these can be quantified using a detector, CCD plate or scintillation counter, and recorded electronically.



X-rays interact with the electrons in the crystal, therefore a crystal with more electrons with more strongly scatter X-rays.

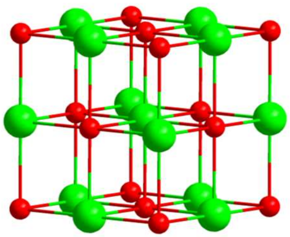
- The effectiveness of scattering X-rays is called the scattering factor (or form factor) with the symbol f_0.
- The scattering factor depends on the number of electrons around the atom, the Bragg angle *θ,* and the wavelength (λ) of the X-rays.
- The scattering power decreases as the Bragg angle increases.

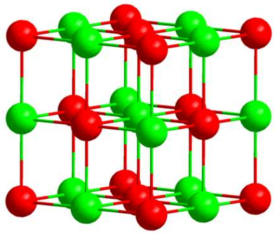


Destructive Interference

Intuitively, you might expect a plane of atoms with larger *Z* to give a more intense reflection, because the heavier an atom is, it is better at scattering X-rays.

- However, there are interactions with reflected X-rays from other planes that may produce destructive interference.


NaCl

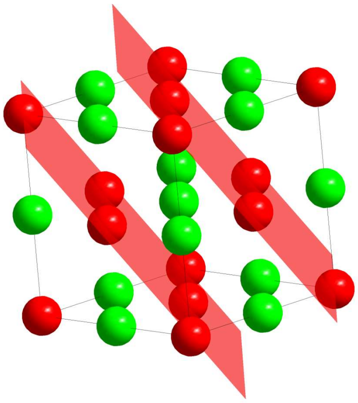

KCl

The structures may be thought of as two interlocking *ccp* arrays of Na^+ and Cl^- ions.

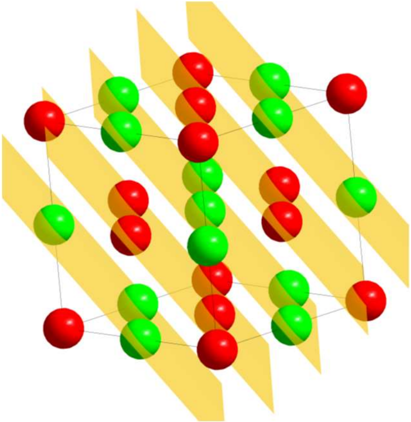
Close packed layers of Cl^- lie parallel to the body diagonal. Halfway between the *111* layers, there are close packed layers of Na^+.

- A reflection from a Cl^- close packed layer is exactly out of phase with the Na^+ layer.

- Since a Cl^- has 18 electrons it scatters X-rays more that a Na^+ with 10 electrons, the reflections will partially cancel and the intensity of the *111* reflection will be weak.
- The 222 layers contain the close-packed layers of Na^+ and Cl^-, which will be a strong reflection since the X-rays will reinforce each other.



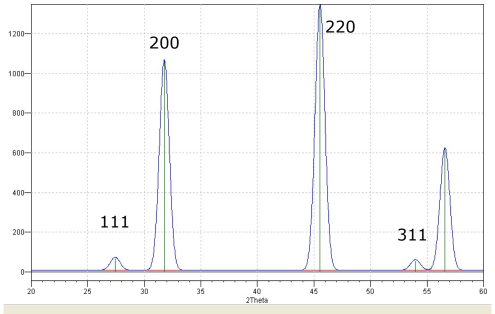
111



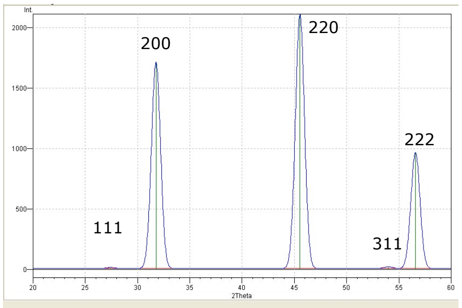
222

In KCl, the reflection from the 111 layers containing K^+ ions is exactly out of phase with the reflection from the Cl^- close packed layers.

- K^+ and Cl^- are isoelectronic and the scattering factors are nearly identical, so the net effect is that the two reflections cancel and the 111 reflection appears to be absent.
  - This means the first reflection is the 200, which is easy to mistake for the 100 reflection from a primitive cubic cell with a unit cell length half that of the actual fcc cell.



NaCl



KCl

The resultant of the waves scattered by all the atoms in the unit cell, in the direction of the *hkl* reflection, is called the structure factor (F_{hkl}). The structure factor depends on both the position of each atom and its scattering factor.

For *j* atoms in a unit cell,

$$F_{hkl} = \sum_j f_j e^{2\pi i(hx_j + ky_j + lz_j)}$$

where f_j is the scattering factor of the jth atom and x_j, y_j, and z_j are its fractional coordinates.

This series can be expressed in terms of sines and cosines (periodic nature of a wave) and is called a Fourier series.

In a crystal with a center of symmetry and *n* unique atoms in the unit cell (the unique set of atoms is known as the asymmetric unit), the above equation simplifies to:

$$F_{hkl} = 2\sum_j f_j \cos 2\pi(hx_n + ky_n + lz_n)$$

The electron density distribution within a crystal can be expressed using a three-dimensional Fourier series.

$$\rho(x, y, z) = \frac{1}{V}\sum_h \sum_k \sum_l F_{hkl} e^{-2\pi i(hx_n + ky_n + lz_n)}$$

where $\rho(x,y,z)$ is the electron density as a position *x,y,z* in the unit cell and V is the volume of the unit cell.

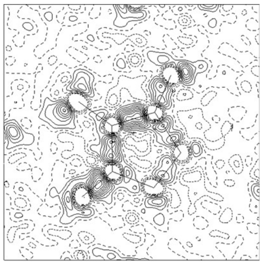
The electron density is a Fourier transform of the structure factors (and vice versa). If the structure factors are known, then it is possible to calculate the electron density distribution in the unit (atomic positions).

The intensity of an *hkl* reflection (I_{hkl}) is proportional to the square of the structure factor:

$$I_{hkl} \propto F_{hkl}^{\ 2}$$

The magnitude of the structure factor (modulus)

$$\left|F_{hkl}\right| \propto \sqrt{I_{hkl}}$$



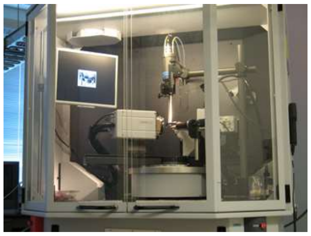
Collected data need to undergo some routine corrections, known as data reduction.

- The **Lorentz correction (L)** relates to the geometry of the collection mode.
- The **polarization correction (p)** allows the fact that a non-polarized X-ray beam may become partially polarized on reflection from the crystal.
- An **absorption correction** is applied, particularly for inorganic structures, because large Z atoms absorb some X-rays rather than scatter.
- A correction for anomalous dispersion can be made when the wavelength of the incident X-ray is close to its absorption edge.

The corrections are applied to the scattering factor (f_0) of the atom.

The structure factor (an intensity of a reflection) is dependent on both the position of each atom and its scattering factor. Knowing the atomic positions, one can calculate the structure factors, but with X-ray diffraction we want to do the reverse – we measure the structure factors and from them want to calculate the atomic positions.

-The **phase problem** occurs, since when we take the square root of the intensity, we obtain the modulus of the structure factor, thus only know its magnitude and not the sign. The phase information is lost and we need that to calculate the electron density distribution and atomic positions.



Solving Single Crystal Structures

Modern single crystal diffractometers measure the Bragg angle θ and the intensity I for each *hkl* reflection. Many diffractometers use a flat-plate detector (CCD) that collects many reflections at the same time. A full data set ($>10^3$) reflections can be collected in a matter of hours.

Information we know about the crystal structure:

- The size and shape of the unit cell from rotation photographs or automatic scanning routines on the single crystal diffractometer.
- After indexing the reflections, examine the systematic absences of the Bravais lattice and the translational symmetry elements of the structure to full determine or narrow to a choice of two or three space groups.
- Intensities of indexed reflections are measured and stored in a data file.
- Correction factors are applied to the raw intensity data.
- The square roots of the corrected data are taken to give a set of observed structure factors *(F_{obs} or F_o).*
- In order to calculate the electron density distribution in the unit cell, we need both the magnitude of the structure factors *and* the phase.

Crystal structures are solved by creating a set of trial phases for the structure factors using one of two main methods.

Patterson method: relies on the presence of at least one (not many) heavy atoms in the unit cell and is useful for solving inorganic structures.

Direct methods: is used for crystals containing atoms with similar scattering properties. A mathematical probability for the phase values and electron density map of the unit cell is created to provide a starting point in the structure solution and refining process.

After the atoms in a structure have been located, a set of structure factors, F_{calc} and F_c, are determined for comparison with the F_{obs} magnitudes.

- The positions of the atoms are refined using least-squares methods.
- Atoms also vibrate about the equilibrium position and this thermal motion depends on temperature, mass of the atom, strengths of the bonds surrounding the atom, etc.
    - The higher the temperature, the larger the amplitude of vibration and the electron density is spread out over a larger volume, causing the scattering power of the atom to fall off more quickly.
    - The isotropic displacement parameter, B, is a refinable parameter.
    - A non-spherical displacement can be refined with an anisotropic displacement parameter, which has six (or fewer) parameters.

The quality of the structure refinement and solution is given by the residual index, or R factor, which relates the observed and calculated structure factors.

$$R = \frac{\sum \left| \left(|F_o| - |F_c| \right) \right|}{\sum |F_o|}$$

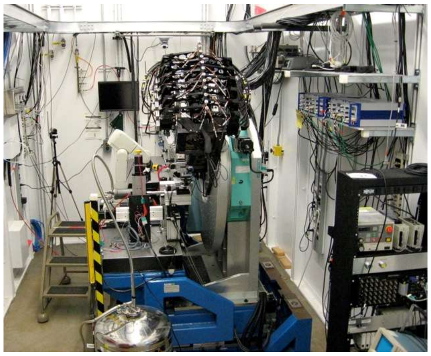
In general, a lower R value indicates a better structure determination.

-but a low R value can be an incorrect structure

-with good quality crystals, one might expect to see R below 0.05.

Low standard deviations on the atomic positions and bond lengths calculated from the atomic positions is a better guide.

High Energy X-ray diffraction



Synchrotrons produce X-rays that are monochromatic and of very high energy (short wavelengths)

In addition to conventional diffraction techniques, it enables atomic pair distribution analysis (PDF) analyzes both the sharp and diffuse scattering, enabling one to find bond distances and coordination numbers in materials that are not fully crystalline.

Neutron Diffraction

Most published crystal structures have been solved using X-ray diffraction, but neutron diffraction is an attractive alternative for certain reasons.

•The de Broglie relationship states any beam of moving particles will display wave properties according to the formula:

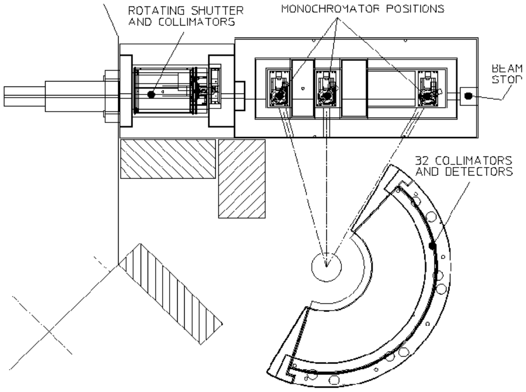
Courtesy of NIST National Center for Neutron Research

$$\lambda = \frac{h}{\rho}$$

where λ is the wavelength, ρ is the momentum of the particles (mv), and h is Planck's constant.

•Neutrons are generated in atomic fission from uranium. The neutrons have high velocity and can be slowed using heavy water (D_2O) so that they have a wavelength of about 1 Å (100 pm).

•A monochromatic beam of neutrons is created using a single crystal monochromator at a fixed angle.



- A high flux of neutrons is needed – sources are rare but include fission reactors at the National Institute for Standards and Technology (NIST) Center for Neutron Research in Gaithersburg, MD; the High Flux Isotope Reactor in Oak Ridge, TN; and the Institute Laue-Langevin (ILL) in Grenoble, France.

- The high-flux reactor at the ILL produced 1.5×10^{15} neutrons per second per cm^2, with a thermal power of 58.3 MW.

Spallation neutron sources

Neutrons may also be produced by bombarding metal targets with high energy protons.

- Spallation neutron sources differ from conventional sources (fixed λ) in that the entire moderated beam with multiple wavelengths is used at fixed angle and the diffraction pattern is recorded as the function of *time of flight* of the neutrons.
- $v = d/t$, so the wavelength of neutrons is proportional to t: $\lambda = \frac{ht}{dm}$

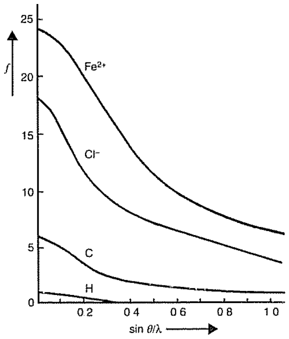
LANSCE - LANL

SNS - ORNL

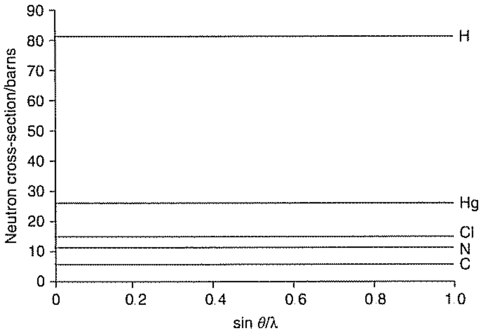
Advantages of neutron diffraction

Electrons scatter X-rays, whereas neutrons are scattered by the nucleus.

- With X-rays, the scattering factor increases linearly with the number of electrons around the nucleus. Heavy atoms scatter more effectively.
  - Since the scattering of X-rays from different parts of the electron cloud are not always in phase, the scattering factor decreases with sinθ/λ.
- Neutron scattering factors are randomly affected by resonance scattering, which occurs when a neutron is absorbed by the nucleus and later released. This feature must be accounted for.
- Nuclear scattering factors do not decrease with sinθ/λ.
  - Nuclei are similar in size and scattering factors are similar for nearly all the elements.
  - Low *Z* (light) atoms scatter as effectively as high *Z* (heavy) atoms. This enables one to accurately locate atoms such as oxygen in the presence of heavy metal atoms.
  - Crystals do not absorb neutrons, so they are useful for studying compounds that contain heavy atoms that strongly absorb X-rays.



X-ray scattering factors



Neutron scattering factors

- Similar atoms are difficult to distinguish using X-ray diffraction (O^{2-} and F^-; Zr^{4+} and Nb^{5+}), however a neutron structure determination may be able to distinguish between the two.

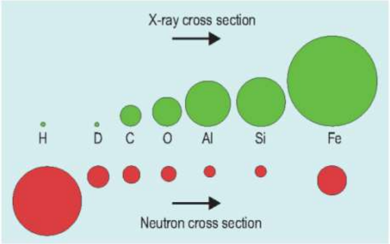


Fig. 2. Neutron and x-ray scattering cross-sections compared. Note that neutrons penetrate through Al much better than x rays do, yet are strongly scattered by hydrogen.

Neutron Diffraction – Magnetic Properties

Nuclei scatter neutrons, but there is an additional scattering of neutrons from paramagnetic atoms.

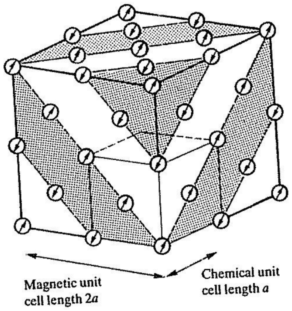
•a neutron has spin and thus has a magnetic moment which can interact with the magnetic moment of an atom.

•the atomic magnetic moment is due to the alignment of the electron spins, so this falls off with increasing Bragg angle (like X-rays).

•Ferromagnetic, ferrimagnetic, and antiferromagnetic (AF) substances have spins arranged in an ordered fashion.

•Magnetic scattering of polarized neutron beams gives rise to magnetic Bragg peaks.

•The structure of NiO is the same by either X-ray or neutrons, but below 120K additional reflections appear from magnetic order.
•These reflections double the unit cell in all three directions.
•Ni layers have their magnetic moments aligned in opposing directions (AF).



Microscopy

Optical microscopes are inexpensive and have ease of sample preparation.

-but limited to the use of visible light (400-700 nm).

-can’t resolve images which are smaller than half the wavelength.

-Near-field scanning optical microscopy improves on the technique.

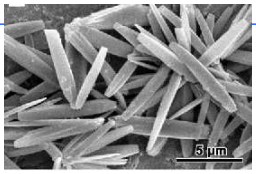
Scanning electron microscopy relies upon a finely focused beam that is rastered across the sample.

-the electrons reflected by the surface (and emitted secondary electrons) are detected to give a map of the surface topography.

-useful for nondestructive testing and to obtain information about the particle size, crystal morphology, magnetic domains, and surface defects.

-A range of magnification can be achieved, with the best of ~2 nm.

-Electrically insulating sample may need to be coated with gold or graphite to stop charge building up on the surface.

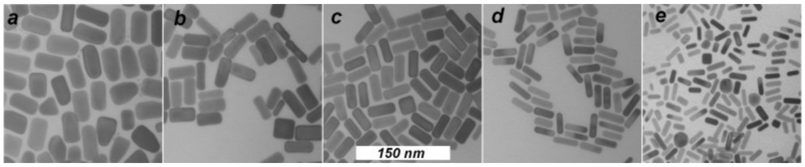


Transmission electron microscopy – requires a thin (~200 nm) sample that is subjected to a high energy, high intensity beam of electrons.

- Electrons that pass through the sample are detected forming a two-dimensional projection of the sample.
- Electrons may be elastically or inelastically scattered and the instrument may be operated in the direct (bright field) or diffracted beam (dark field).
- High resolution microscopy uses a very high potential field (10^6 V), which results in very short wavelengths.
- TEM/HREM images bulk structure and can detect crystal defects, phase boundaries, shear planes, etc.
- A resolution of ~0.5 nm can be achieved.

Scanning transmission electron microscopy

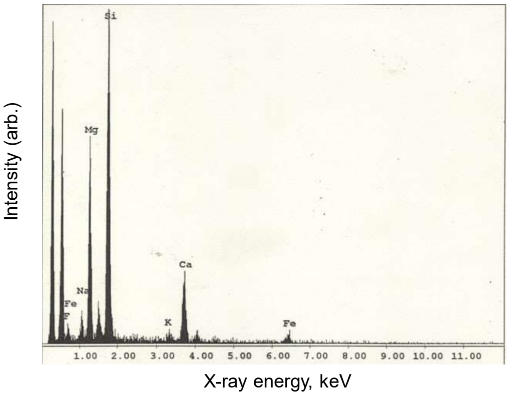
- combines scanning ability of SEM with high resolution of TEM.
- A small probe (10-15 nm) scans across the surface.

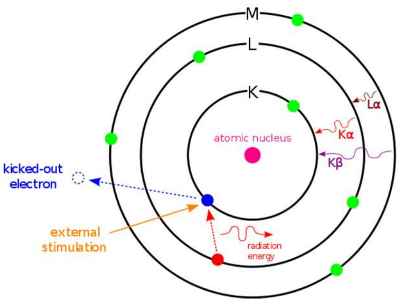


Energy Dispersive X-ray Analysis (EDAX or EDX)

Similar to the creation of X-rays in an X-ray tube, elements present in the sample emit characteristic X-rays.

- the X-rays are separated by a Si-Li detector and amplified, corrected for absorption, and other effect.
- Technique works best for elements Na and heavier and quantitative results may be obtained.

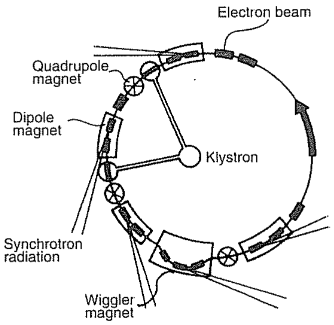


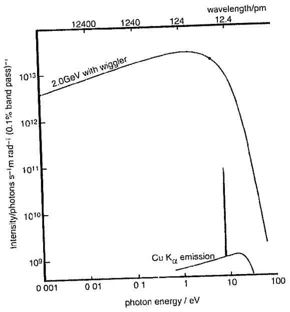


X-ray Absorption Spectroscopy

In high energy accelerators, electrons are injected into an electron storage ring (~30 m diam.).

- electrons are accelerated around this circular path by a series of magnets. When electrons are accelerated to high kinetic energies (MeV) close to the speed of light, synchrotron radiation is emitted.
- Synchrotron radiation is of uniform intensity across a broad band of wavelengths and is higher in intensity (10^4-10^6). The shortest X-rays are emitted as almost fully collimated, polarized beams.

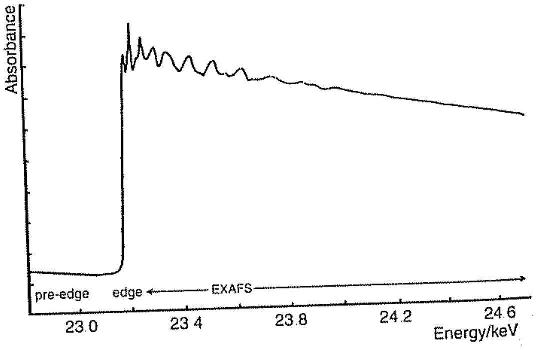




Synchrotron radiation profile at 2 GeV compared with Cu K_α emission

Extended X-ray Absorption Fine Structure (EXAFS)

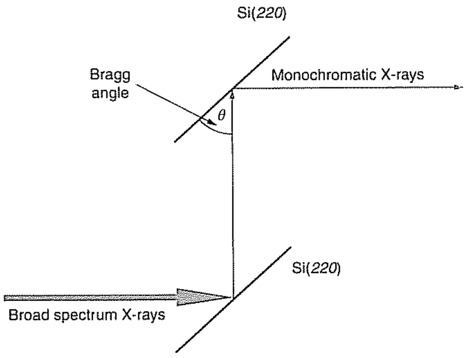
- X-ray is absorbed by a bound electron in a core shell (typ. K shell), then is ejected as a photoelectron.
- The absorption coefficient of the sample, as a function of the X-ray frequency, shows a sharp rise (absorption edge) at the K shell threshold energy.



The Rh absorption edge and EXAFS

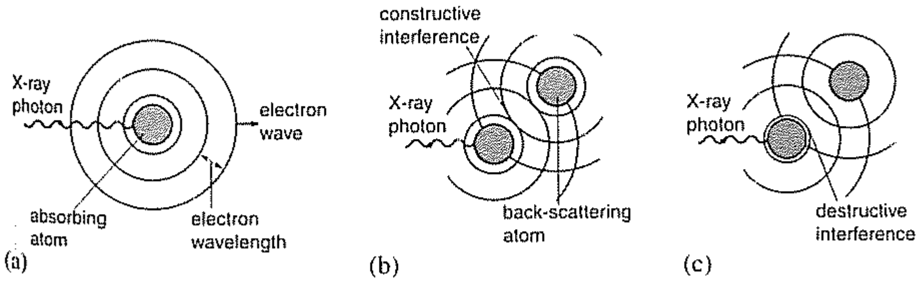
Extended X-ray Absorption Fine Structure (EXAFS)

- Each element has a characteristic K shell threshold energy, making it possible to study one type of atom in the presence of many by tuning the X-ray energy to an absorption edge.
- The appropriate frequency of X-rays is selected using the Bragg reflection from a single crystal, often a Si(220), sometimes a double crystal monochromator is used.
- If the Bragg angle is changed, a different frequency (wavelength) of X-rays is selected, thus a wise range of absorption edges may be studied.



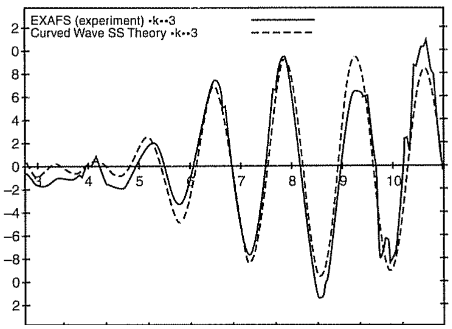
Extended X-ray Absorption Fine Structure (EXAFS)

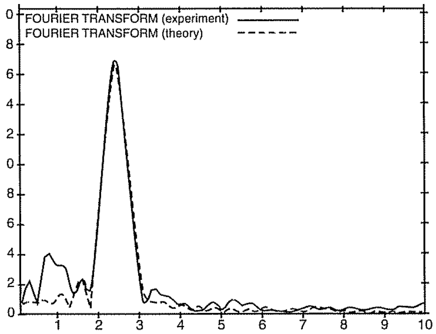
- Waves of the ejected photoelectron can be visualized as spherical waves emanating from the nucleus of the absorbing atom, which encounters neighboring atoms and produces a phase shift.
- Constructive or destructive interference is observed, which produces a net interference pattern at the nucleus of the original atom.
- Absorption by the original atom is modified, observed as sinusoidal oscillations or fine structure superimposed on the absorption edge.
- The extent to which the outgoing wave is reflected by a neighboring atom, and the intensity of the reflected wave, is partly dependent on the scattering factor of the atom.

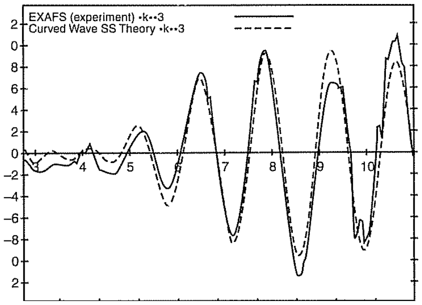


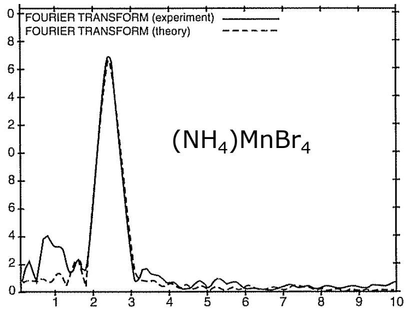
Extended X-ray Absorption Fine Structure (EXAFS)

- The interference pattern making up the EXAFS depends on the number, type of neighboring atoms, and their distance from the absorbing atom.
- The EXAFS function is obtained by subtracting the absorption due to the free atom.
- A Fourier transform of the EXAFS data gives the radial distribution function.
- Shells of neighboring atoms, known as coordination shells are obtained.
- The radial distribution function is fitted to a series of trial structural models, params. include number and types of atoms, distance, etc.
- Distance information is obtained, but no angular information.

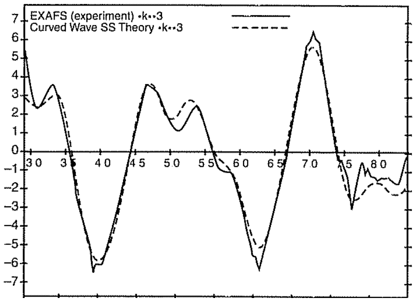


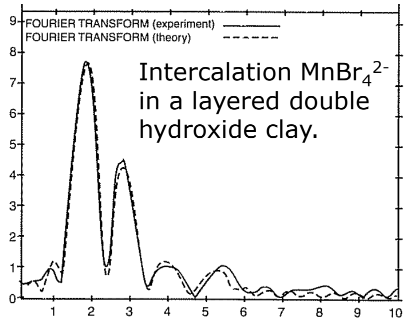






$(NH_4)MnBr_4$





Intercalation $MnBr_4^{2-}$ in a layered double hydroxide clay.

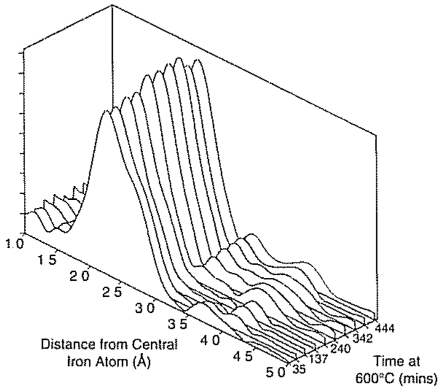
Extracted EXAFS data

Radial distribution function

X-rays are penetrating and examine the structure of the bulk of the solid

-EXAFS provides information on the interatomic distances

-has the advantage that it can be used on amorphous solids, glasses and liquids (non-crystalline materials)

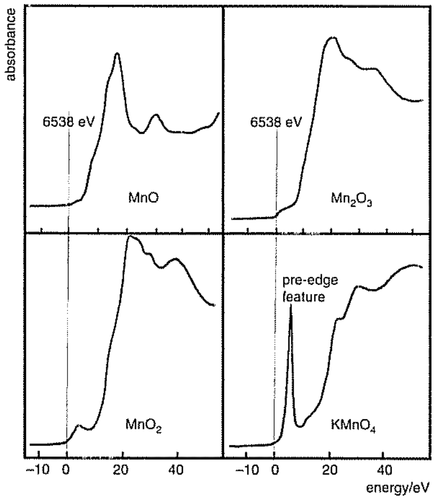


Follow phase changes over time with heating with EXAFS.

β-ferrosilicon forming from the α-ferrosilicon.

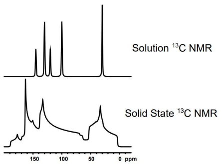
X-ray Absorption Near-Edge Structure (XANES)

Precise position of absorption edge varies with chemical state of the absorbing atom, which combined with structure in the pre-edge region can give information on the oxidation state and chemical environment.



Solid State Nuclear Magnetic Resonance Spectroscopy (MAS NMR)

Solid state NMR differs from solution NMR in the fact that dipolar interactions and anisotropic effects are averaged out by molecular motion in solution, but not in a solid.

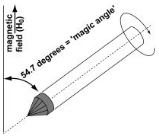


NMR spectra of solids are broadened out by three main effects:

1. Magnetic dipolar interactions can be removed by the application of a high power decoupling field at the resonance frequency.

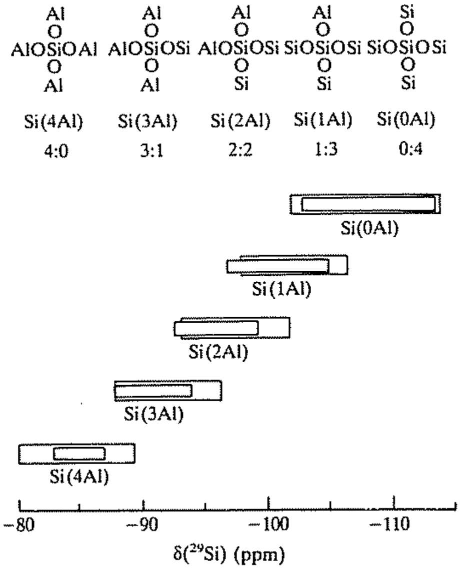
2. Isotopes in low abundance have a long spin-lattice relaxation time which give rise to poor signal to noise ratios. Sensitivity may be improved using cross polarization, in which a complex pulse sequence is used to transfer polarization from an abundant nucleus to the dilute spin, enhancing the signal.

3. The chemical shift of a particular atom varies with the orientation of the molecule to the field. In a solid, this gives rise to a range of values, an effect known as the chemical shielding anisotropy, which broadens the band. The line broadening is due to anisotropic interactions, which have a $3\cos^2\theta-1$ term. The term becomes zero when θ = 54.7°, the "magic angle". Improves resolution of the chemical shift of the spectra.



MAS NMR is useful for most spin I = ½ isotopes.

- Important in elucidating the structures of zeolites, which are silicates with Al occupying many of the Si sites.
- Al/Si have similar scattering factors, so they are difficult to distinguish from X-ray diffraction.
- ^{29}Si (I=½) gives sharp lines and has high natural abundance (4.7%).
- Five different peaks (environments) are observed in zeolites.
- ^{27}Al (I=5/2) has 100% natural abundance, but has second-order quadrupolar effects.



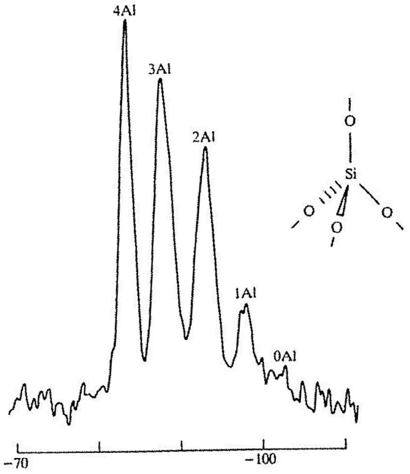
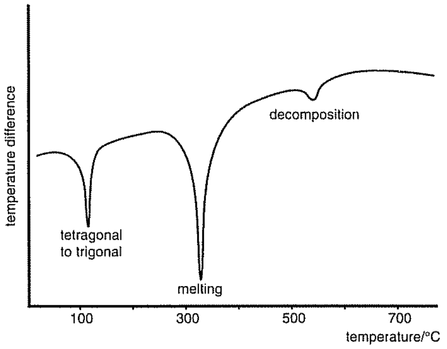


FIGURE 2.28 ^{29}Si MAS NMR spectrum at 79.6 MHz of analcite, illustrating five absorptions characteristic of the five possible permutations of Si and Al atoms attached at the corners of the SiO_4 tetrahedron as indicated.

Differential Thermal Analysis (DTA)

A phase change produces either an absorption of an evolution of heat.

- The sample is placed in one crucible, another solid that doesn't undergo a phase change in the other crucible.
- Both are heated at a controlled uniform rate in a furnace, and the difference in temperature is recorded against time.
- Any reaction in the sample will be represented as a peak in the ΔT.
- Exothermic reactions shown an increase in T, endothermic a decrease – the peaks appear in opposite directions.

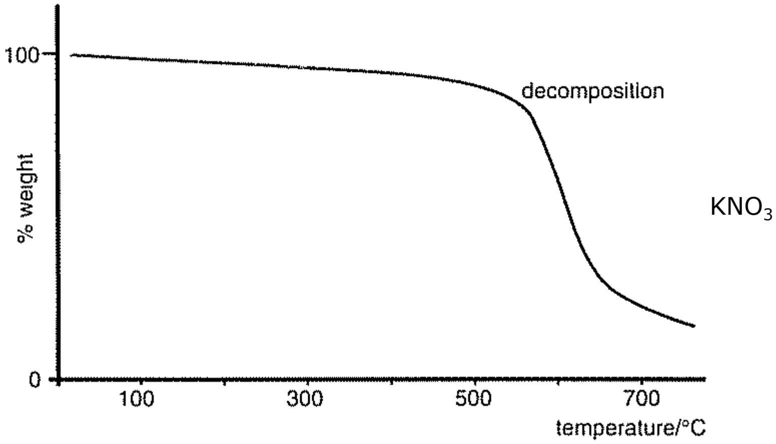


KNO_3

Thermogravimetric Analysis (TGA)

Sample weight is monitored as a function of time as the temperature is increased at a controlled rate.

- Monitor loss of water of crystallization, volatiles, and decomposition.



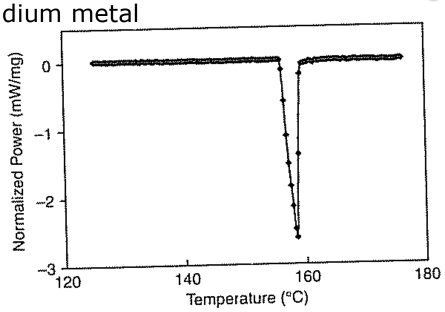
Example:

Potassium nitrate decomposes to form nitrogen dioxide, potassium oxide, and oxygen.

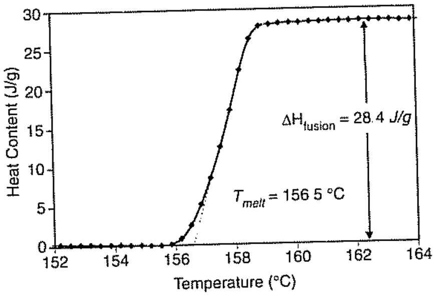
If 0.5000 g KNO_3 is placed in a TGA, calculate the expected weight percent remaining after decomposition.

Differential Scanning Calorimetry (DSC)

Indium metal



- Measures amount of heat released by the sample as the temperature is increased or decreased at a controlled uniform rate.

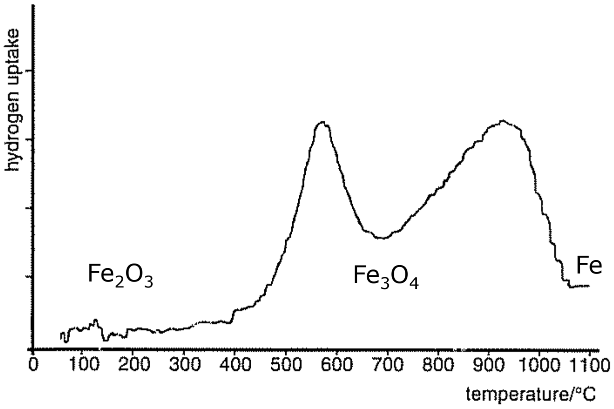


- Can measure heats of reaction for phase changes.

-heat of fusion for metallic In is shown to the left.

Temperature Programmed Reduction (TPR)

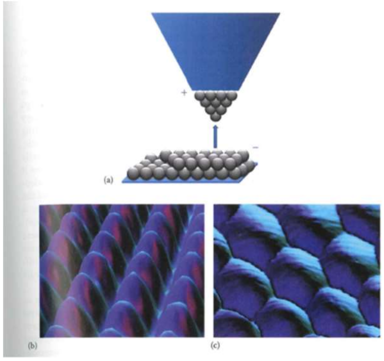
- measures reaction of hydrogen with a sample at various temperatures.
- can give information of presence of different oxidation states, etc.
- Typically measured with 10% H_2 in N_2. H_2 has a high electrical conductivity, so a decrease in H_2 is marked by a decrease in conductivity.
- Area under the peak gives amount of hydrogen used.
- Oxidation, sulfidation, and desorption may also be measured.

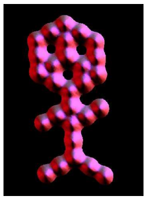


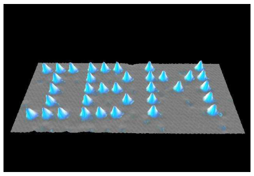
Scanning Tunneling Microscopy (STM)

A sharp metal tip is brought sufficiently close (<1 nm) to a surface that that electron wave functions overlap, finite probability the electron can be found on the other side of the barrier (quantum mechanical tunneling)

- Electrons tunnel between the tip and sample, and vice-versa.
- A potential is applied and a tunneling current is measured (pA, nA).
- The magnitude is sensitive (exponentially) to the gap.
- The metal tip is scanned across the sample, either in constant current or constant height feedback mode, imaging the atoms.
- The created map features both the topography and the electronic structure.



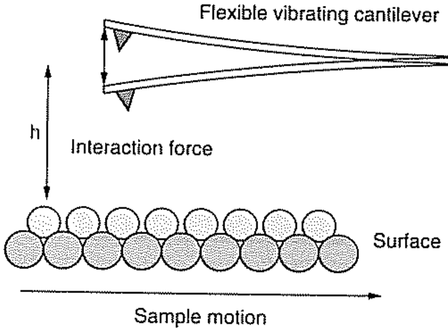




Atomic Force Microscopy (AFM)

AFM detects very small (nN) forces between a sharp tip and a surface, producing a surface maps.

- Can be used on nonconductive surfaces
- Contact mode, the deflection of tip measured, a feedback loop maintained constant force
  - Can obtain lateral information e.g. friction, hydrophobicity, but delicate surfaces may be damaged.
- Noncontact dynamic mode (tapping or AC mode), a feedback loop maintains a constant oscillation frequency and/or amplitude, this is measured by cantilever deflection to generate a surface map



Other Characterization Techniques

- Mössbauer Spectroscopy
- Electron Spectroscopies
  - XPS, UVPS, AES, EELS
- Low energy electron diffraction (LEED)
- Vibrational Spectroscopy
  - Infrared (IR) and Raman spectroscopy
- Ultraviolet-Visible Spectroscopy
- Capacitance Measurements
- Resistivity Measurements
- Magnetic Measurements
- Heat Capacity Measurements