Laboratory Manual 1.0.6

Background

What is X-ray Diffraction?

X-rays scatter off of electrons, in a process of absorption and re-admission. Diffraction is the accumulative result of the x-ray scattering of a group of electrons that are spaced in an orderly array. For an incident X-ray photon of monochromatic wavelength $\boldsymbol{\lambda}$, coherent waves are produced from the sample at an angle of θ (2-θ with respect to the incident x-ray beam) if the electron groups interact with the x-ray beam and are spaced at a repeat distance ***d***. The interaction is described by Bragg's law : $n\lambda=2d\sin\theta$. The intensity of the scattered x-ray is proportional to the number of electrons that the x-ray is scattered from.

Why use X-rays?

Normally one would use a microscope to view small objects. For a microscope, light is scattered by an object and collected using lenses, which in turn magnifies the image of the object. The limit of the microscope is intrinsic to the nature of the electromagnetic radiation that is used to probe the object. If we use white light we cannot look at objects smaller than the wavelength of light, which is about 10^{-6} m. Since the atom has dimensions of about 10^{-10} m we cannot image an atom with a photon of white light. X-rays, on the other hand, have a wavelength of about 10^{-10} m and are suitable for imaging objects at the atomic scale.

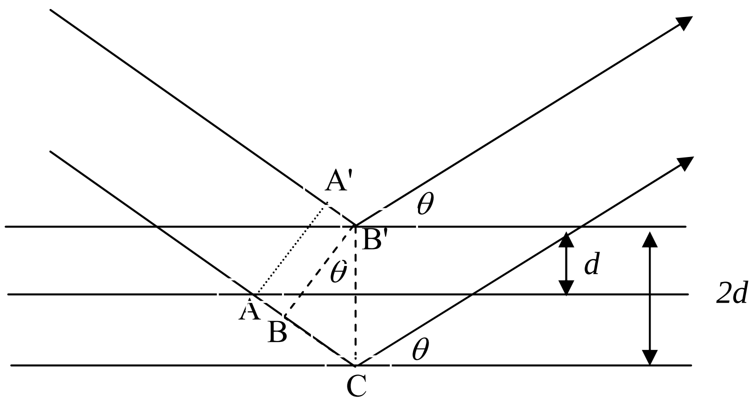
What are X-rays

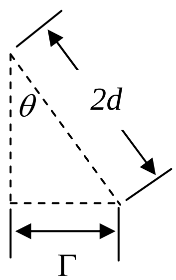
X-rays are electromagnetic radiation of wavelength about 1 Å (10^{-10}m) which is about the same size as an atom. They occur in that portion of the electromagnetic spectrum between gamma rays and the ultraviolet. The discovery of X-rays in 1895 enabled scientists to probe crystalline structure at the atomic level. X-ray diffraction has been employed in two main areas: for the fingerprint characterization of crystalline materials and the determination of their structure. Each crystalline solid has its unique characteristic X-ray powder pattern, which may be used as a "fingerprint" for its identification. Once the material has been identified, X-ray crystallography may be used to determine its structure, i.e. how the atoms pack together in the crystalline state and what the inter-atomic distance and angle are etc. X-ray diffraction is one of the most important characterization tools used in solid-state chemistry and materials science.

We can determine the size and the shape of the unit cell for any compound most easily using the diffraction of x-rays.

Diffraction of X-rays

Given that two parallel rays will strike a grating at an angle theta where the grating separation is given as *d* then :





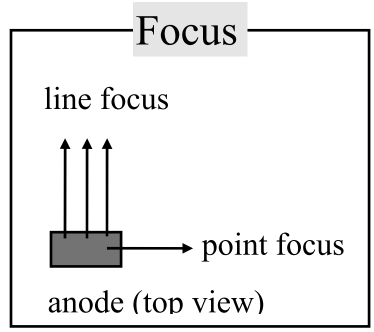
$$\sin\theta = \frac{\Gamma}{2d}$$
$$2d\sin\theta = \Gamma$$
$$\Gamma = AC - A'B'$$
$$given\ A'B' = AB\ then\ \Gamma = AC - AB = BC$$
$$\Gamma = BC = \lambda\ (path\ difference)$$
$$2d\sin\theta = \lambda$$

An interference maximum will be observed when Γ is an integral multiply (n) of λ.

This leads to the **Bragg equation**:

$$\mathbf{n\lambda = 2d\sin\theta}$$

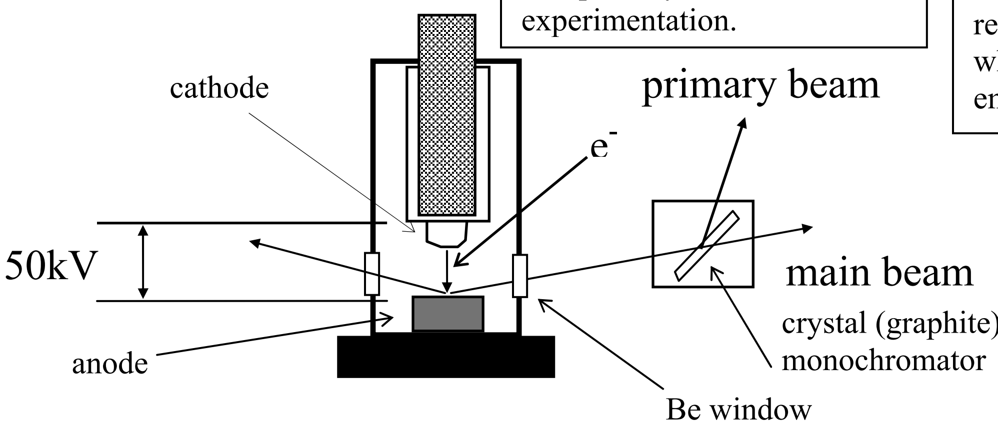
X-ray Sources



Single crystal work requires a point focus, while powder work employs the line focus

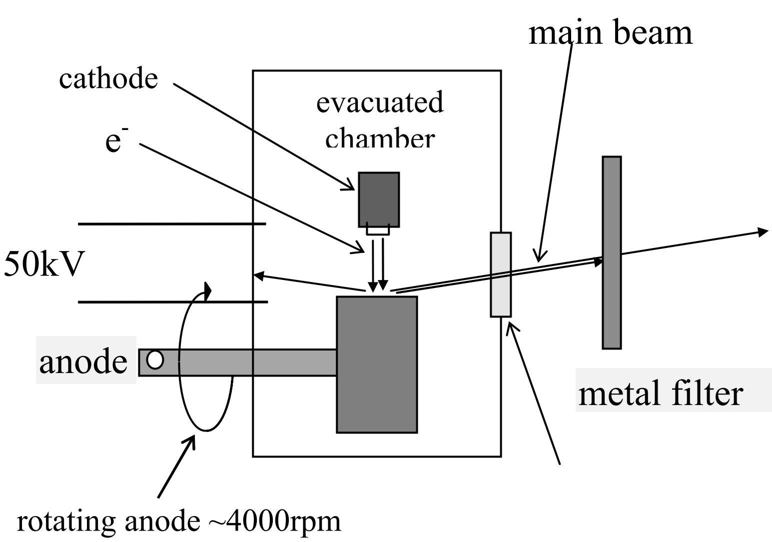
sealed tube

The primary beam is used for experimentation.



Normal operation 40kV and 40ma the power = 1600 watts

rotating anode

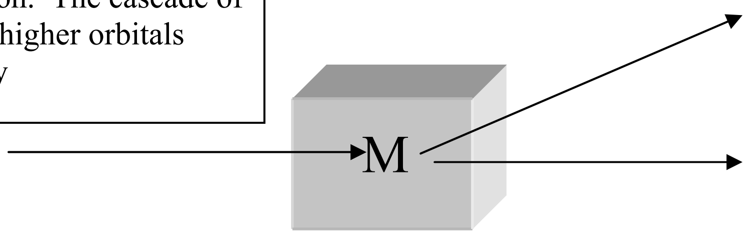


Normal operation 50kV x 180ma the power = 9000 watts

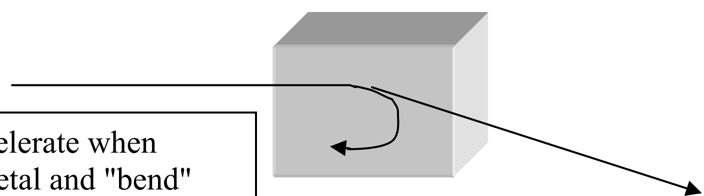
The x-rays that are generated are of two types

1) **Characteristic (ejection of electrons from the atom in the anode**
2) **White Radiation (synchrotron effect)**

Electron strikes the target and ejects an electron. The cascade of electrons from higher orbitals generates X-ray



Characteristic X-rays
K_{alpha} K_{beta}



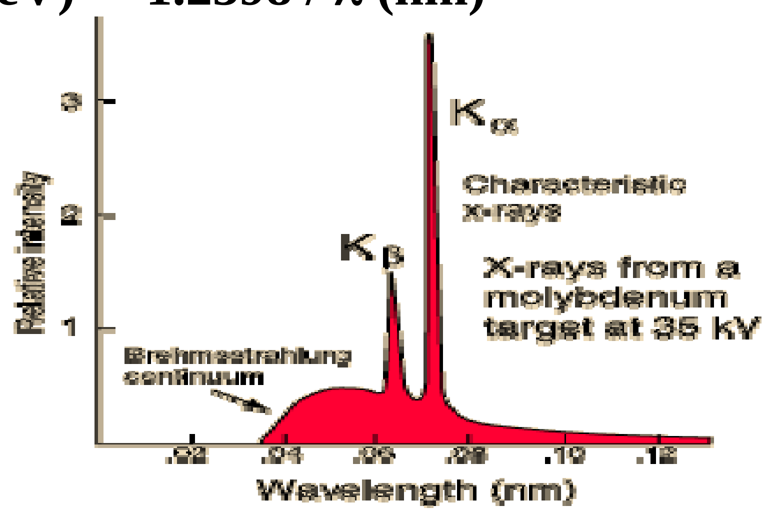
White Radiation "Bremsstrahlung" or breaking radiation

Electron reaccelerate when entering the metal and "bend" their trajectory path. Loss of momentum results in generation of X-rays.

The energy of the X-ray is determined from the observed wavelength and is given by the formula :

$$\textbf{Energy (KeV)} = \mathbf{1.2398 / \lambda\ (nm)}$$

Profile of X-rays generated by electron ejection and momentum loss. K alpha and K beta are the characteristic X-rays from the lowest electron shells and are superimposed on the white radiation.



Energy for K alpha (for Mo) = 17.28 KeV

Powder and Single Crystal Diffraction normally employ the K_{α} characteristic radiation, due to its intensity and monochromatic wavelengths.

Laboratory 1.
Radiation Safety for X-ray Diffractometers

To begin the X-ray Crystallography Laboratory you must complete the on-line X-ray Devices training offered by Texas A & M University, Environmental Health and Safety Office.

Start any web browser and go to

http://vpfninet.tamu.edu/twa/do/events/list

Find : X-ray Devices: On-line Radiation Safety Training

Complete the general training.

now go to : http://www.chem.tamu.edu/xray/safety.htm

and complete the site specific training course.

Bring the TAMU radiation safety certificate AND a signed x-ray safety check list and certification form to your first lab session.

The following appendix is available for your information and not necessary reading.

Bibliography

"Procedures Manual for Use of Radioisotopes and Radiation Producing Devices", Office of Radiological Safety, Texas A & M University

"A Guide to the Safe Use of X-ray Diffraction and Spectrometry Equipment", Martin, E., Science Reviews Ltd., Ash Drive, Leeds, LS 17 8RA U.K.

"A Case History of Severe Radiation Burns from 50 kVC X-rays", Steidley, K., Stabile, R. & Santillippo, L. *Health Physics* (1981). 40 399-405.

"Analytical X-ray Hazards: A Continuing Problem" Lubenau, J., Davis, J., McDonald, D. & Gerusky, T. *Health Physics* (1969). 16, 739-746.

"Occupational Hazards in X-ray Analytical Work" Lindel, B. *Health Physics* (1968). 15, 481-486.

"Incidence, Detection and Monitoring of Radiation from X-ray Analytical Instrumentation" Jenkins, R. & Haas, D. *X-ray Spectrom* (1975). 4, 33-39.

"Protection Against Radiation Injury" Cook, J. & Oosterkamp, W. *International Tables for Crystallography* (1962). 333 -338.

Laboratory 3. Indexing Powder Patterns

Learning Experiences

- o - How to manually index a simple powder pattern.
- o - Mathematics involved in pattern indexing

In this lab you will manually index the powder pattern for Silicon. An example of how to index powder patterns is presented. The mathematics are introduced and the step by step procedure is presented. You will need a calculator and a pencil.

For the peak positions of Silicon use the values that you determined in Laboratory 2. or ask your Laboratory assistant for the values.

Example How to Index the powder pattern for NaCl

Analytical Method : Equations

Given Bragg's Law

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

$$\sin\theta = \frac{n\lambda}{2d}$$

$$\sin^2\theta = \frac{\lambda^2}{4d^2}$$

d^* can be determined as :

$$d^* = 1/\mathrm{d} = (h^2a^* + k^2b^* + l^2c^* + 2hka^*b^*\cos\gamma^* + 2hla^*c^*\cos\beta^* + 2klb^*c^*\cos\alpha^*)^{1/2}$$

See "Crystal Structure Determination" by Werner Massa pp 23-25.

For a cubic system $a^* = b^* = c^* = 1/a$ and $\alpha^* = \beta^* = \gamma^* = 90$ $\cos\gamma^* = 0.000$ then

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

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

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

Let $X = \lambda^2/4a^2$ and $M = h^2+k^2+l^2$

Now create a table for M values given *h*,*k* and *l* are integers

Table 1. $M_n = h^2+k^2+l^2$

n	*h*	*k*	*l*	M_n
1	1	0	0	1
2	1	1	0	2
3	1	1	1	3
4	2	0	0	4
5	2	1	0	5
6	2	1	1	6
7	2	2	0	8
8	2	2	1	9
9	3	0	0	9
10	3	1	0	10
11	3	1	1	11
12	2	2	2	12
13	3	2	0	13
14	3	2	1	14
15	4	0	0	16
16	3	2	2	17
17	4	1	0	17
18	3	3	0	18
19	4	1	1	18
20	3	3	1	19
21	4	2	0	20
22	4	2	1	21
23	3	3	2	22
24	4	2	2	24
25	4	3	0	25
26	5	0	0	25
27	4	3	1	26
28	5	1	0	26
29	3	3	3	27
30	5	1	1	27

Note for cubic systems :

1 0 0 = 0 1 0 = 0 0 1   2 0 0 = 0 2 0 = 0 0 2
1 1 0 = 1 0 1 = 0 1 1   2 2 0 = 2 0 2 = 0 2 2
etc …

some *h,k,l* values share $h^2+k^2+l^2$ sums e.g. *2,2,1* and *3,0,0* sum to $h^2+k^2+l^2 = 9$

h, k and l must be integers.

Not all $h^2+k^2+l^2$ sums have integer *h, k, l* values (i.e. some $h^2+k^2+l^2$ values are not possible)

From the X-ray powder pattern we find the peak positions at $2\theta = 38.52$, 44.76, 65.14, 78.26, 82.47, 99.11, 112.03 and 116.6°

Table 2

2θ	θ	$\sin^2\theta/M_1$	$\sin^2\theta/M_2$	$\sin^2\theta/M_3$	$\sin^2\theta/M_4$	$\sin^2\theta/M_5$	$\sin^2\theta/M_6$	$\sin^2\theta/M_7$	$\sin^2\theta/M_8$	$\sin^2\theta/M_9$	$\sin^2\theta/M_{10}$	$\sin^2\theta/M_{11}$
38.52	19.26	0.108805	0.054402	**0.036268**	0.027201	0.021761	0.018134	0.013601	0.012089	0.01088	0.01088	0.009891
44.76	22.38	0.144969	0.072484	0.048323	**0.036242**	0.028994	0.024161	0.018121	0.016108	0.014497	0.014497	0.013179
65.14	32.57	0.289799	0.144899	0.0966	0.07245	0.05796	0.0483	**0.036225**	0.0322	0.02898	0.02898	0.026345
78.26	39.13	0.398265	0.199132	0.132755	0.099566	0.079653	0.066377	0.049783	0.044252	0.039826	0.039826	**0.036206**
82.47	41.235	0.434477	0.217239	0.144826	0.108619	0.086895	0.072413	0.05431	0.048275	0.043448	0.043448	0.039498
99.11	49.555	0.579165	0.289583	0.193055	0.144791	0.115833	0.096528	0.072396	0.064352	0.057917	0.057917	0.052651
112.03	56.015	0.687546	0.343773	0.229182	0.171887	0.137509	0.114591	0.085943	0.076394	0.068755	0.068755	0.062504
116.6	58.3	0.72388	0.36194	0.241293	0.18097	0.144776	0.120647	0.090485	0.080431	0.072388	0.072388	0.065807
137.47	68.735	0.868462	0.434231	0.289487	0.217115	0.173692	0.144744	0.108558	0.096496	0.086846	0.086846	0.078951

Largest common $\sin^2\theta/M$ value(s) (X) are (see bold values above)

$0.036268 = 0.036242 = 0.036225 = 0.036206 = 0.0362 \pm 0.001 = X$

inserting = 0.0362 into the equation affords :

$0.0362 = \lambda^2/4a^2$ **$a = (1.54056\ \text{Å})^2 / 4\,(0.0362)^2 = 4.049\ \text{Å}$**

From Table 2 we see that 0.0362 is the result for $\sin^2\theta/M_3$: M_3 is the result for *h* =1, *k* =1 and *l* =1. Completing the table for the first 4 peaks we now can assign these peaks with *h,k,l* values

Table 3. $M = h^2 + k^2 + l^2$

h	*k*	*l*	*M*
1	1	1	3
2	0	0	4
2	2	0	8
3	1	1	11

Or we can solve Bragg's equation for each observed peak. For example for 2θ = 38.52 : $\sin^2\theta/0.0362 = 3.005652$ or 3.00. From table 1 we see that M=3 is equivalent to *h*=1, *k*=1 and *l* =1. Therefore the peak at 38.52 is assigned as the (1,1,1) reflection. Table 4 summarizes the results for all peaks and assigns their *h,k,l* values.

Table 4

2θ	$\sin^2\theta/0.0362$	M	*h,k,l*
38.52	3.005652	3	1,1,1
44.76	4.004662	4	2,0,0
65.14	8.005491	8	2,2,0
78.26	11.00178	11	3,1,1
82.47	12.00214	12	2,2,2
99.11	15.99904	16	4,0,0
112.03	18.99298	19	3,3,1
116.6	19.99667	20	4,2,0
137.47	23.99066	24	4,2,2

Laboratory Particle: Index the following.

First Task. Fill in Table 1

e.g. for n=1 h=1,k=0,l=0 will afford $M_1 = 1$

Table 1. Table of indices

n	*h*	*k*	*l*	M_n
1	1	0	0	1
2	1	1	0	2
3	1	1	1	3
4				4
5				5
6				6
7				8
8				9
9				9
10				10
11				11
12				12
13				13
14				14
15				16
16				17
17				17
18				18
19				19

Note for cubic systems :

1 0 0 = 0 1 0 = 0 0 1   2 0 0 = 0 2 0 = 0 0 2
1 1 0 = 1 0 1 = 0 1 1   2 2 0 = 2 0 2 = 0 2 2
etc …

some *h,k,l* values share $h^2+k^2+l^2$ sums e.g. *2,2,1* and *3,0,0* sum to $h^2+k^2+l^2 = 9$

h, k and l must be integers.

Not all $h^2+k^2+l^2$ sums have integer *h, k, l* values (i.e. some $h^2+k^2+l^2$ values are not possible)

Table 2. List of $\sin^2\theta$ / M_n *(n=1,..)* use only observed M_n

From your peak list from Laboratory 2 fill in this table. For example a peak at 26° 2θ will afford θ = 13°
$\sin^2(13) = 0.0506$ $\sin^2(13)/M_1 = 0.0506/1 = 0.0506$ $\sin^2(13)/M_2 = 0.0506/2 = 0.0253$
Complete this table for your peaks. (or you may generate a spread sheet in EXCEL to do the same thing)

#	2θ	Θ	$\sin^2\theta/M_1$	$\sin^2\theta/M_2$	$\sin^2\theta/M_3$	$\sin^2\theta/M_4$	$\sin^2\theta/M_5$	$\sin^2\theta/M_6$	$\sin^2\theta/M_8$	$\sin^2\theta/M_9$	$\sin^2\theta/M_{10}$	$\sin^2\theta/M_{11}$	$\sin^2\theta/M_{12}$	$\sin^2\theta/M_{14}$	$\sin^2\theta/M_{15}$	$\sin^2\theta/M_{16}$
1																
2																
3																
4																
5																
6																
7																
8																
9																
10																

Continue for M_{17} to M_{30}

$\sin^2\theta/M_{17}$	$\sin^2\theta/M_{18}$	$\sin^2\theta/M_{19}$	$\sin^2\theta/M_{20}$	$\sin^2\theta/M_{21}$	$\sin^2\theta/M_{22}$	$\sin^2\theta/M_{23}$	$\sin^2\theta/M_{24}$	$\sin^2\theta/M_{25}$	$\sin^2\theta/M_{26}$	$\sin^2\theta/M_{27}$	$\sin^2\theta/M_{28}$	$\sin^2\theta/M_{29}$	$\sin^2\theta/M_{30}$

Largest common $\sin^2\theta$ value from Table 2 (value of **X**) = __________

Remember **X** = $\lambda^2/4a^2$

Calculate unit cell a given λ = 1.54056Å __________

Now complete Table 3 from the given information assign the *h,k,l* value for each peak.

Table 3 List of *h, k, l* values

Peak #	$\sin^2\theta$	$\sin^2\theta$/A	$h^2+k^2+l^2=M$	*hkl*
1				
2				
3				
4				
5				
6				
7				
8				
9				
10				