X Ray Generation

Source:
http://xrayweb.chem.ou.edu/notes/xray.html

X-Ray photons are electromagnetic radiation with wavelengths in the range 0.1 - 100 Å. X Rays used in diffraction experiments have typical wavelengths of 0.5 - 1.8 Å. X Rays can be produced by conventional generators, by synchrotrons, and by plasma sources. Electromagnetic radiation from nuclear reactions, called γ radiation, can also occur at the same energies as X rays, but γ radiation is differentiated from X ray radiation simply by the source of the radiation.

X rays are sometimes called Röntgen rays after their discoverer, Wilhelm Conrad Röntgen.[1] For this discovery, he received the first Nobel Prize in physics in 1901.

A great deal of information about the properties of X rays and X-ray generation is available at the X-Ray Data Book. Electromagnetic radiation is made up of waves of energy that contain electric and magnetic fields vibrating transversely and sinusoidally to each other and to the direction of propogation of the waves. Conventional generators are by far the most widely used sources of X rays in a laboratory setting.

Conventional Generators

X Rays are produced in labs by directing an energetic beam of particles or radiation, at a target material. X Rays for crystallographic studies are typically generated by bombarding a metal target with an energetic beam of electrons. The electrons are produced by heating a metal filament, emitting photo electrons. The electrons coming from the filament are then accelerated towards the target by a large applied electrical potential between the filament and the target. When the beam of electrons hits the target (or anode) a variety of events occur. This rapid deceleration of electrons causes the emission of X-ray radiation, photoelectrons, Auger electrons, and a large amount of heat. Actually two types of X rays are emitted in this process. X Rays are emitted in a continuous band of white radiation as well as a series of discrete lines that are characteristic of the target material.

White Radiation

Some of the collisions between the photo-electrons and the target result in the emission of a continuous spectrum of X rays called white radiaion or *Bremsstrahlung*. White radiation is believed due to the collision of the accelerated electrons with the atomic electrons of the target atoms. If all of the kinetic energy carried by an electron is converted into radiation, the energy of the X-ray photon would be given by

$$E_{max} = h\nu_{max} = eV$$

where h = Plank's constant, ν_{max} = the largest frequency, e = charge of an electron, V = applied voltage. This maximum energy or minimum wavelength is called the Duane-Hunt limit.

$$h\nu_{max} = hc/\lambda_{min} = eV$$
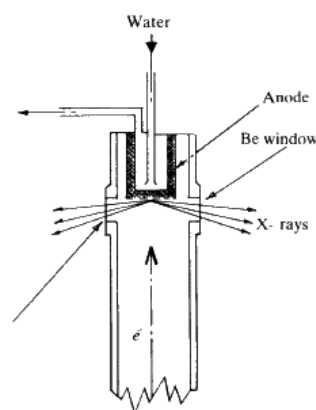
$$\lambda_{min} = hc / eV = 12398. / V \text{ (volts)}$$
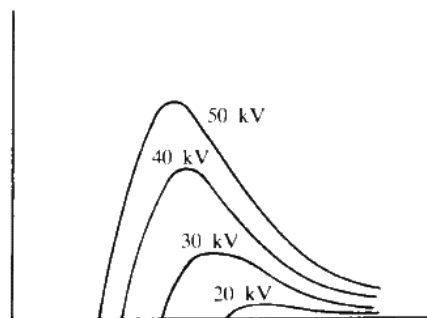

Figure 1. X-ray Tube Schematic.[2]

Figure 2. White Radiation from an X-Ray Generator.[2] The intensity of the beam is plotted as a function of the wavelength of the radiation.

The majority of collisions that produce white radiation do not completely dissipate the kinetic energy of the electron in a single collision. Typically, these colliding electrons hit electrons in the target material with a glancing blow dissipating some energy as emitted X-ray photons. Then these photoelectrons hit other electrons in the target material emitting lower energy X-ray photons or hit valence electrons producing heat.

Thus the white radiation spectrum does have a minimum wavelength or maximum energy related to the kinetic energy of the incident radiation beam, and continues to longer wavelengths or lower energies until all of the kinetic energy is absorbed. The highest intensity of emitted white radiation spectrum is obtained at a wavelength that is about 1.5 times the minimum wavelength. The white radiation intensity curve may be fit to an expression of the form:

$I_w = A \, i \, Z \, V^n$, n ~ 2

where i is the applied current, Z is the atomic number of the target, V is the applied voltage and A is a proportionality constant. The only type of diffraction experiment that uses white radiation is the Laue experiment.

Characteristic Radiation

When the energy of the electron beam is above a certain threshold value, called the *excitation potential*, an additional set of discrete peaks is observed superimposed on the white radiation curve. The energies of these peaks are characteristic of the type of target material.

These peaks are generated by a two-stage process. First an electron from the filament collides with and removes a core electron from an atom of the target. Then an electron in a higher energy state "drops down" to fill the lower energy, vacant hole in the atom's structure, emitting an X-ray photon. These emitted X-ray photons have energies that are equal to the difference between the upper and lower energy levels of the electron that filled the core hole. The excitation potential for a material is the minimum energy needed to remove the core electron.
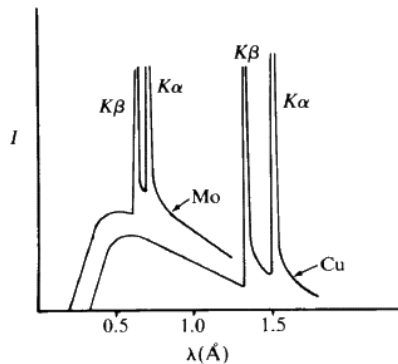

Figure 3. Characteristic radiation from an X-ray generator.[2]

The characteristic lines in an atom's emission spectra are called *K, L, M, ...* and correspond to the n = 1, 2, 3, ... quantum levels of the electron energy states, respectively. When the two atomic energy levels differ by only one quantum level then the transitions are described as α lines (n = 2 to n = 1, or n = 3 to n = 2). When the two levels are separated by one or more quantum levels, the transitions are known as β lines (n = 3 to n = 1 or n = 4 to n = 2).

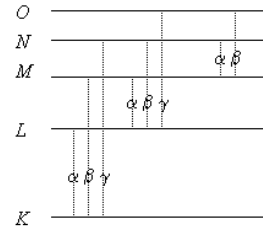Figure 4. Electronic energy levels of an atom of the anode.[2]

Because all *K* lines (n = 1) arise from a loss of electrons in the n = 1 state, the *K*α and *K*β lines always appear at the same time. The n = 2 and higher energy levels (L, M, N, O) are actually split into multiple energy levels causing the α and β transitions to split into a variety of closely spaced lines at high resolution. Thus, the observed Cu *K*α line can be resolved at high scattering angle (high resolution) into *K*α$_1$ and *K*α$_2$ lines with separate wavelengths. The *K*α$_1$ line is about twice as intense as the *K*α$_2$ line. At low resolution (lower scattering angle) the *K*α wavelength is considered as a weighted average of the *K*α$_1$ and *K*α$_2$ lines with λ(*K*α$_{ave}$) = [2*(λ(*K*α$_1$)) + λ(*K*α$_2$)]/3. The *K*α line is about 5 - 10 times as intense as the *K*β line.

The intensity of the *K*α line can be approximately calculated by

$I_k = B \, i \, (V - V_k)^{1.5}$

where i = applied current, V_k = excitation potential of the target material, V = applied voltage. It can be shown that the ratio I_k / I_w is a maximum if the accelerating voltage is chosen to be about 4 times the excitation potential of the anode.

The wavelengths of characteristic X-ray lines were found to be inversely related to the atomic number of the atoms of the target material. Moseley found that

$\sqrt{f} = K_1 [Z - \sigma]$

where f is the frequency of the radiation, K_1 is a proportionality constant, Z is the atomic number of the target atom type, and σ is the shielding constant that typically has a value of just less than 1. Today this formula is more typically recast as

$1/\lambda = K_2 [Z - \sigma]^2$

where λ is the wavelength of the radiation, K_2 is a proportionality constant, Z is the atomic number of the target atoms, and σ is the shielding constant.

The notation for describing the characteristic X-ray lines shown above was first presented by Siegbahn. In 1991, the

International Union of Pure and Applied Chemists (IUPAC) recommended that X-ray lines be referred to by writing the initial and final levels separated by a hyphen, e.g. Cu K- L_3, rather than using the Siegbahn notation, e.g. Cu $K\alpha_1$, which is based on the relative intensities of the lines.[3] A table of the correspondence between IUPAC and Siegbahn notations is given in the "International Tables for Crystallography," Vol. C.[4] The Siegbahn notation remains common in the chemical and crystallographic literature.

The shape of the incident beam depends on the focal projection of the filament onto and the anode material. X-Ray beams that are parallel with wide projection of the filament have a focal shape of a *line*. X-Ray beams that are parallel with the narrow projection of the filament have an approximate focal shape of a square, which is usually labeled as a *spot*. These two focal projections are necessarily about 90 ° apart in the plane normal to the filament-anode axis. The X-ray beams emitted from the anode travel in a variety of angular directions from the anode surface. As the angle from the anode surface is increased, the intensity of the beam increases, but the spot also becomes less focused. Thus take-off angles are typically selected in the 3 - 6 ° range.
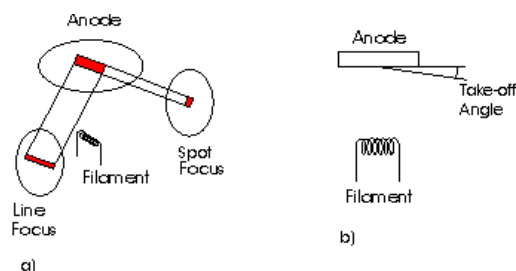
Two cartoons of an X-ray tube. Drawing a) shows the line and spot focus patterns of a typical sealed tube. Drawing b) shows the take-off angle of a tube.

The generation of X rays is very inefficient. In addition to white radiation and characteristic lines, laboratory sources also produce Auger electrons and photo-electrons. However, the vast majority of the power used in generating X rays results in the collision of accelerated electrons with valence electrons of the target material producing heat. A small fraction of the energy applied to the tube actually produces the characteristic radiation used in diffraction experiments.

Sealed-tube X-ray generators use a stationary anode. These tubes are limited in the power that can be applied to the tube by the amount of heat that can be dissipated through water cooling. One way to increase the heat dissipating ability of the system, and thus increase the X-ray beam intensity, is to move or rotate the anode surface so that the beam of electrons continually hits a new region of the anode. These rotating-anode generators typically yield about 5 times the flux of X-rays as is routinely produced by sealed-tube generators with normal-focus X-ray tubes.

Because macromolecular crystallographers need the most intense beam available, they typically use rotating-anode X-ray generators. Rotating-anode generators require a considerable amount of maintenance to replace filaments, and repair or replace the anode bearings as well as vacuum and water seals. To keep from burning the filament, it must remain in a high vacuum. The anode with its constant flow of cooling water must be continuously rotating at speeds of 6000 rpm or more. Special ferro-fluidic seals are used to maintain the vacuum along the rotating shaft of the anode. Sealed-tube sources with their minimal maintenance requirements are generally quite adequate for most small molecule needs.

Another type of sealed-tube source that produces beam fluxes comparable to rotating-anode systems is a micro-focus generator. Because heat dissipates rather quickly in a metal block, manufacturers have found that when the focal size is reduced to 10-300 μm then the power can be increased to make the beam flux much higher than for normal- or even fine-focus sealed tube sources. One of the great advantages of a micro-focus radiation source is that the electrical power needs are in the range of 30-80 Watts not the 2-3 kWatts that are required of a typical sealed tube generator, or the 3-12 kWatts required by a rotating anode generator.

Other Sources

There are other sources of X-ray photons that have special applications in the laboratory. Synchrotrons produce the highest flux sources available. Unfortunately, because synchrotrons are very expensive to build and maintain, there are few such sources available throughout the world.

Certain radioactive materials decay to produce photons with energies in the X-ray region (e.g., [55]Fe). The flux of photons of this radioactive material is so low that it is not used as a source of X-rays for diffraction experiments. However, small samples of [55]Fe are often used to test the functioning of X-ray detectors.

A new method of generating X rays that is not yet commercially available uses an electron-impact beam impinging on a stream of liquid gallium.[5] These authors have already reported achieving beam fluxes greater that modern rotating anodes, with the theoretical capability of increasing this flux by another 3 orders of magnitude.

As a side note, X rays may also be produced by very different means, for example, when doing such simple tasks as unrolling adhesive tape from a tape dispenser. Tribologists found that low energy X rays were emitted even when unrolling the tape at rather slow rates of a few centimeters per second.[6]

Choice of Radiation

Most X-ray tubes used for diffraction studies have targets (anodes) made of copper or molybdenum metal. The characteristic wavelengths and excitation potentials for these materials are shown below. Copper radiation is preferred when the crystals are small or when the unit cells are large. Copper radiation (or softer) is required when the absolute configuration of a compound is needed and the compound only contains atoms with atomic numbers & 10. A copper source is preferred for most types of powder diffraction.

Molybdenum radiation is preferred for larger crystals of strongly absorbing materials and for very high resolution, $\sin(\theta) / \lambda < 0.6$ Å, data. The scintillation point detectors, often used in small molecule diffraction, have somewhat higher quantum efficiencies for molybdenum radiation than for copper radiation. Because the diffraction spots are closer together for molybdenum radiation than for copper radiation, molybdenum is the preferred radiation source when using area detectors to study small molecules. The solid angle coverage of most area detectors is such that with molybdenum radiation, it is usually possible to collect an entire data set with the detector sitting at a single position. However, because a brighter incident beam of X-rays is produced from a copper tube than from a molybdenum tube at the same power level, very small crystals of even strongly absorbing materials will often yield better diffracted intensities from copper radiation than from molybdenum radiation.

Occasionally, other types of target materials, e.g. Cr, Fe, W, or Ag, are chosen for specialized diffraction experiments. Sources with Cr or Fe targets are often chosen when protein crystals are very small or when anomalous differences need to be enhanced. When samples are very strongly absorbing or when extremely high resolution data are needed then X-ray tubes with sources such as W or Ag are usually selected.

Table 1. Selected X-Ray Wavelengths and Excitation Potentials.

	Cr	Fe	Cu	Mo
Z	24	26	29	42
$K\alpha_1$, Å	2.28962	1.93597	1.54051	0.70932
$K\alpha_2$, Å	2.29351	1.93991	1.54433	0.71354
$K\alpha_{ave}$, Å	2.29092	1.93728	1.54178	0.71073
$K\beta$, Å	2.08480	1.75653	1.39217	0.63225
β filter	Ti	Cr	Ni	Nb
Resolution, Å	1.15	0.95	0.75	0.35
Excit. Pot. (kV)	5.99	7.11	8.98	20.0

Monochromatization and Collimation of X Rays

Nearly all of the data collection experiments require that the energy of the X-ray radiation be limited to as narrow a band of energies (and hence wavelengths) as possible. Using a narrow wavelength band of X rays significantly reduces the fluorescent radiation given off by the sample and makes absorption corrections much simpler to perform. It has been noted that when the applied voltage for K excitation occurs, both the $K\alpha$ and $K\beta$ lines as well as the white radiation curve are observed. Usually the $K\alpha$ band is selected for diffraction experiments because of its greater intensity.

Also, typical data collection methods require that the incident beam be a parallel beam of photons. To assure that the beam is as parallel as possible (lacking divergence), the incident beam path is collimated to produce an incident beam that is about 0.5 mm in diameter.

Filters

When the energy of a photon beam is just above the *excitation potential* or *absorption edge* of a material, that material strongly absorbs the given photon beam. If another substance can be found that has an absorption edge between the $K\alpha$ and $K\beta$ lines of the incident photon beam, this other substance can be used to significantly reduce the intensity of the $K\beta$ line relative to the $K\alpha$ line. The absorption edges of elements with $Z_{Filter} = Z_{Target} - 1$ (or - 2) meet this requirement. The thickness of the filtering material is usually chosen to reduce the intensity of the $K\beta$ line by a factor of 100 while reducing the intensity of the $K\alpha$ line by a factor of 10 or less.

The absorption of X rays follows Beer's Law:

$$I / I^o = \exp(-\mu \times t)$$

where I = transmitted intensity, I^o = incident intensity, t = thickness of material, μ = linear absorption coefficient of the material. The linear absorption coefficient depends on the substance, its density, and the wavelength of radiation. Since μ depends on the density of the absorbing material, it is usually tabulated as the mass absorption coefficient $\mu_m = \mu / \varrho$.

Monochromators

An alternative way to produce an X-ray beam with a narrow wavelength distribution is to diffract the incident beam from a single crystal of known lattice dimensions. X-Ray photons of different wavelengths are diffracted from a given set of planes in a crystal at different scattering angles according to Bragg's Law. Therefore a narrow band of wavelengths can be chosen by selecting a particular scattering angle for the monochromator crystal. Crystal monochromators need to have the following properties.

1. The crystal must be mechanically strong and stable in the X-ray beam.
2. The crystal must have a strong diffracted intensity at a reasonably low scattering angle for the wavelength of the radiation being considered.

3. The mosaicity of the crystal, which determines the divergence of the diffracted beam and the resolution of the crystal, should be small.

A variety of geometries are possible for crystal monochromators. Most monochromators are cut with one face parallel to a major set of crystal planes. These monochromators are then oriented to diffract $K\alpha$ lines from this major set of planes. Some monochromators are cut at an angle to the major set of planes in order to produce a diffracted beam with a smaller divergence. By properly curving the monochromator crystal, the diffracted beam may be focused onto a very small area. This curving may be achieved either by bending or grinding or both bending and grinding. Curved monochromators are usually reserved for special applications such synchrotons.

Graphite crystals cut on the (0002) face are the most common crystals used as monochromators in X-ray diffraction laboratories. Other special purpose monochromator materials include germanium and lithium fluoride. In all commercially available single-crystal instruments, the monochromator is placed in the incident beam path. Powder diffraction instruments with a point detector typically place a monochromator in the diffracted beam path to remove any fluorescent radiation from the sample. Crystal monochromators systematically alter the polarization of the incident beam, requiring different geometric corrections be applied to the intensity data.

Collimators

Collimators are objects inserted in the incident- or diffracted-beam path to shape the X-ray beam. Metal tubes are typically used in single-crystal experiments. The inside radius of the collimators is typically chosen to be somewhat larger than the size of the sample so that the sample may be bathed in the incident beam at all times. Incident-beam collimators are usually manufactured with two narrow regions. The region closest to the X-ray source carries out the collimation functions. The second narrow region has a slightly larger diameter than the first and is used to remove the "parasitic" radiation that takes a bent path due to interaction with the edge of the first narrow region of the collimator. Diffracted beam collimators only function to remove any stray radiation from hitting the detector.
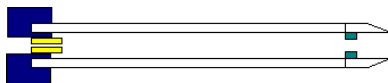
The left end of the collimator shown is mounted on the X-ray tube (or incident beam monochormator). The small yellow-colored region at the left is the part of the collimator where the size of the beam is determined. The green region at the right is chosen to have an opening slightly larger than the region drawn in yellow. This green region removes the "parasitic" radiation.

Recently, manufacturers have been selling metal collimators with a single or multiple glass capillaries. These glass capillaries redirect much of the X-ray beam that would otherwise be blocked by the collimator. Such capillary inserts in a collimator have been shown to increase the intensity of the incident beam by a factor of between two and four.

When a very intense and very small point source is needed, such as in protein crystallography, X-ray mirrors may be used to shape the incident beam. Mirrors are sometimes made from materials that act as beta filters for the radiation in use. Mirrors are primarily used with very bright X-ray sources such as rotating-anode generators or synchrotrons.

Powder diffraction experiments usually require a line-shaped incident beam that is produced from a pair of parallel knife edges. A set of Soller slits are used in the beam path after the knife edges to remove parasitic radiation that scatters from the edges of the blades. Soller slits are a set of parallel thin foil sheets that absorb nearly all of the X rays not traveling parallel to the metal sheets.

X-ray mirrors are sometimes used in the incident beam to shape the beam as is done by a collimator. Even with Cu radiation, the spots in protein diffraction patterns are often very close together. The mirrors act to focus the incident beam into an very small cross section producing very sharp spots in the diffraction pattern. Mirrors are often constructed to absorb more of the $K\beta$ radiation than the $K\alpha$ radiation making the beam approximately monochromatic. Monochromators significantly reduce the intensity of the incident beam; omitting the monochromator maximizes the incident beam flux. Macromolecular structures are crystalline to only low resolution. The $K\beta$ and $K\alpha$ peaks are generally not separated at these low scattering angles.

References

1. Wilhelm Conrad Röntgen, "Über eine neue Art von Strahlen" (On a New Kind of Rays) presented to the Würzburg Physical and Medical Society, 1895. Translated by Arthur Stanton, *Nature*, **1896**, *53*, 274-276.
2. Michael Liang, **1997**, "An Introduction to the Scope, Potential and Applications of X-ray Analysis" in International Union of Crystallographers Teaching Pamphlets available at: http://www.iucr.org/education/pamphlets.
3. R. Jenkins, R. Manne, J. Robin, & C. Senemaud, *Pure and Appl. Chem.*, **1991**, *63*, 735-746.
4. "International Tables for Crystallography, Vol. C," **1995** Kluwer: Boston, p 167.
5. M. Otendal, T. Tuohimaa, U. Vogt, and H. M. Hertz, A 9 keV electron-impact liquid-gallium-jet x-ray source., *Rev. of Sci. Inst.*, **2008**, *79*, 016102-3. doi: 10.1063/1.2833838
6. C. G. Camara, J. V. Escobar, J. R. Hird, and S. J. Putterman, Correlation between nanosecond X-ray flashes and stick-slip friction in peeling tape. *Nature*, **2008**, *455*, 1089-1092. doi: 10.1038/nature07378

X-ray Diffraction: Indexing Cubic Diffractograms

When atoms are chemically bound to one another they have well-defined equilibrium separations that are determined by the condition that the total energy is minimized. Therefore, in a solid composed of many identical atoms, the minimum energy is obtained only when every atom is in an identical environment. This leads to a three-dimensional periodic arrangement that is known as the crystalline state. The same is true for solids that are composed of more than one type of element. In this case, certain "building blocks" comprising a few atoms are the periodically repeated units. Periodicity gives rise to a number of typical properties of solids. Periodicity also simplifies the theoretical understanding and the formal theory of solids enormously.

A two-dimensional lattice is spanned by two vectors a and b. Every point on the lattice can be reached by a lattice vector of the form

$$\mathbf{R} = n_1\mathbf{a} + n_2\mathbf{b} \tag{1}$$

where n_1 and n_2 are integers. Depending on the ratio of the lengths of the vectors a and b, and on the angle γ between them, lattices of various geometries can be constructed. The most general lattice, with no additional symmetry, is obtained when $a \neq b$ and $\gamma \neq 90°$ (Fig. 2.1).
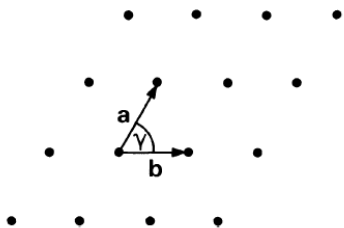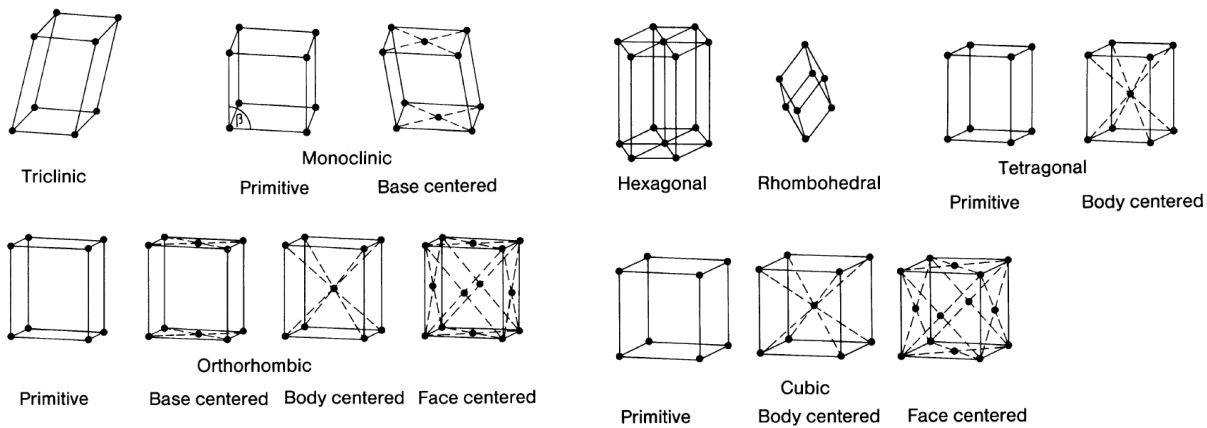

We state without proof[1] that if eq. 1 is extended in three dimensions ($\mathbf{R} = n_1\mathbf{a} + n_2\mathbf{b} + n_3\mathbf{c}$) we have the following types of crystal systems. Draw these structures to visualise them.

Basis vectors/crystal axes	Angles	Crystal system
$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$	triclinic
$a \neq b \neq c$	$\alpha = \gamma = 90° \; \beta \neq 90°$	monoclinic
$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$	orthorhombic
$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	tetragonal
$a = b \neq c$	$\alpha = \beta = 90° \; \gamma = 120°$	hexagonal
$a = b = c$	$\alpha = \beta = \gamma \neq 90°$	rhombohedral
$a = b = c$	$\alpha = \beta = \gamma = 90°$	cubic

Such lattices are known as Bravais lattices.

Triclinic

Monoclinic
Primitive   Base centered

Hexagonal   Rhombohedral

Tetragonal
Primitive   Body centered

Orthorhombic
Primitive   Base centered   Body centered   Face centered

Cubic
Primitive   Body centered   Face centered

14 unique Bravais lattices are possible in three dimensions

Consider a set of points **R** constituting a Bravais lattice, and a plane wave defined by:

$$e^{i\mathbf{K}\cdot\mathbf{r}} = \cos(\mathbf{K}\cdot\mathbf{r}) + i\sin(\mathbf{K}\cdot\mathbf{r})$$

If this plane wave has the same periodicity as the Bravais lattice, then it satisfies the equation:

$$e^{i\mathbf{K}\cdot(\mathbf{r}+\mathbf{R})} = e^{i\mathbf{K}\cdot\mathbf{r}}$$
$$\therefore e^{i\mathbf{K}\cdot\mathbf{r}} e^{i\mathbf{K}\cdot\mathbf{R}} = e^{i\mathbf{K}\cdot\mathbf{r}}$$
$$\Rightarrow e^{i\mathbf{K}\cdot\mathbf{R}} = 1 \tag{2}$$

Mathematically, we can describe the reciprocal lattice as the set of all vectors **K** that satisfy the above identity for all lattice point position vectors **R**. This reciprocal lattice is itself a Bravais lattice, and the reciprocal of the reciprocal lattice is the original lattice.

For an infinite three dimensional lattice, defined by its primitive vectors
$(\mathbf{a} \rightarrow \mathbf{a}_1; \mathbf{b} \rightarrow \mathbf{b}_1; \mathbf{c} \rightarrow \mathbf{c}_1;$ with $\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3)$, its reciprocal lattice can be determined by generating its three reciprocal primitive vectors, through the formulae

$$b_1 = 2\pi \frac{a_2 \times a_3}{a_1 \cdot (a_2 \times a_3)}$$

$$b_2 = 2\pi \frac{a_3 \times a_1}{a_1 \cdot (a_2 \times a_3)}$$

$$b_3 = 2\pi \frac{a_1 \times a_2}{a_1 \cdot (a_2 \times a_3)}$$

What are the reciprocal lattice vectors of the simple cubic structure?

Typical interatomic distances in a solid are on the order of an angstrom (10^{-8} cm). An electromagnetic probe of the microscopic structure of a solid must therefore have a wavelength at least this short, corresponding to an energy of order

$$\hbar\omega = \frac{hc}{\lambda} = \frac{hc}{10^{-8}\ \text{cm}} \approx 12.3 \times 10^3\ \text{eV}. \tag{6.1}$$

Energies like this, on the order of several thousands of electron volts (kilovolts or keV), are characteristic X-ray energies.

A lattice acts like a diffraction grating for X-rays and the condition for constructive interference is the the well known Bragg's law ($2d\sin\theta = n\lambda$) as shown below

Figure 6.1
A Bragg reflection from a particular family of lattice planes, separated by a distance d. Incident and reflected rays are shown for the two neighboring planes. The path difference is $2d \sin \theta$.
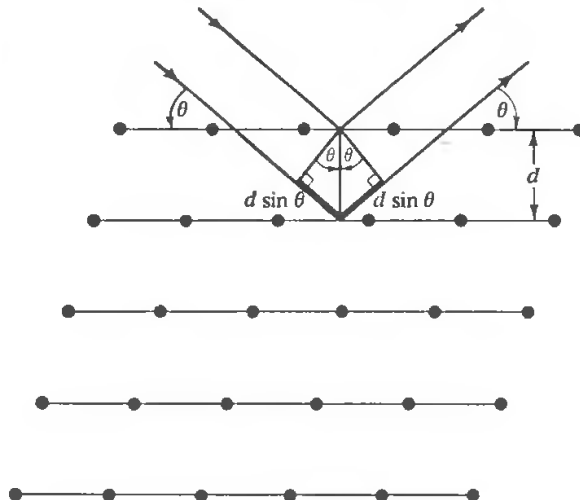
To find the condition for constructive interference, consider first just two scatterers, separated by a displacement vector **d** (Figure 6.4). Let an X ray be incident from very far away, along a direction $\hat{n}$, with wavelength λ, and wave vector $\mathbf{k} = 2\pi\hat{n}/\lambda$. A scattered ray will be observed in a direction $\hat{n}'$ with wavelength[6] λ and wave vector $\mathbf{k}' = 2\pi\hat{n}'/\lambda$, provided that the path difference between the rays scattered by each of the two ions is an integral number of wavelengths. From Figure 6.4 it can be seen that this path difference is just

$$d \cos \theta + d \cos \theta' = \mathbf{d} \cdot (\hat{n} - \hat{n}'). \tag{6.3}$$

The condition for constructive interference is thus

$$\mathbf{d} \cdot (\hat{n} - \hat{n}') = m\lambda, \tag{6.4}$$

for integral m. Multiplying both sides of (6.4) by $2\pi/\lambda$ yields a condition on the incident and scattered wave vectors:

$$\mathbf{d} \cdot (\mathbf{k} - \mathbf{k}') = 2\pi m, \tag{6.5}$$

for integral m.

Next, we consider not just two scatterers, but an array of scatterers, at the sites of a Bravais lattice. Since the lattice sites are displaced from one another by the Bravais lattice vectors $\mathbf{R}$, the condition that all scattered rays interfere constructively is that condition (6.5) hold simultaneously for all values of $\mathbf{d}$ that are Bravais lattice vectors:

$$\mathbf{R} \cdot (\mathbf{k} - \mathbf{k'}) = 2\pi m, \quad \begin{array}{l} \text{for integral } m \text{ and} \\ \text{all Bravais lattice} \\ \text{vectors } \mathbf{R}. \end{array} \tag{6.6}$$

This can be written in the equivalent form

$$e^{i(\mathbf{k'}-\mathbf{k}) \cdot \mathbf{R}} = 1, \quad \text{for all Bravais lattice vectors } \mathbf{R}. \tag{6.7}$$

This implies that constructive interference will occur if the difference between scattered and incident X-ray wave vectors is a reciprocal lattice vector.

$$\mathbf{K} = \mathbf{k'} - \mathbf{k}$$

This condition can illustrated as shown below
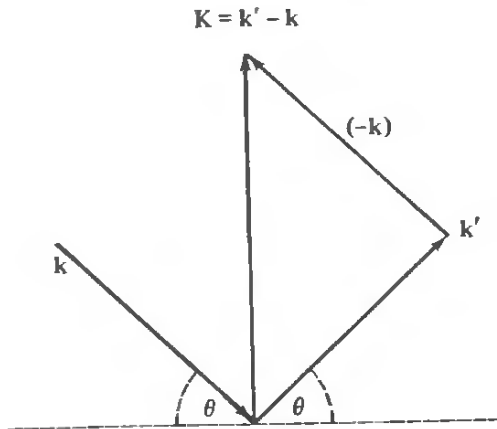
$$\text{with } K = 2k \sin\theta = 2\frac{2\pi}{\lambda}\sin\theta = \frac{2\pi}{\lambda}\frac{n\lambda}{d} = \frac{2\pi}{d}n$$

This result implies for any set of lattice planes separated by a distance d, there exists a set of reciprocal lattice vectors of length $n2\pi/d$. It is natural to choose the shortest reciprocal lattice vectors to represent the orientation of different lattice planes.

The Miller indices of a lattice plane are the coordinates of the shortest reciprocal lattice vector normal to that plane, with respect to a specified set of primitive reciprocal lattice vectors. Thus a plane with Miller indices h, k, l, is normal to the reciprocal lattice vector $h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3$.

As so defined, the Miller indices are integers, since any reciprocal lattice vector is a linear combination of three primitive vectors with integral coefficients. Since the normal to the plane is specified by the shortest perpendicular reciprocal lattice vector, the integers h, k, l can have no common factor. Note also that the Miller indices depend on the particular choice of primitive vectors.

In simple cubic Bravais lattices the reciprocal lattice is also simple cubic and the Miller indices are the coordinates of a vector normal to the plane in the obvious cubic coordinate system.

The Miller indices of a plane have a geometrical interpretation in the direct lattice, which is sometimes offered as an alternative way of defining them. Because a lattice

plane with Miller indices h, k, l is perpendicular to the reciprocal lattice vector $\mathbf{K} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3$, it will be contained in the continuous plane $\mathbf{K} \cdot \mathbf{r} = A$, for suitable choice of the constant A. This plane intersects the axes determined by the direct lattice primitive vectors $\mathbf{a}_i$ at the points $x_1\mathbf{a}_1$, $x_2\mathbf{a}_2$, and $x_3\mathbf{a}_3$ (Figure 5.4), where the x_i are determined by the condition that $x_i\mathbf{a}_i$ indeed satisfy the equation of the plane: $\mathbf{K} \cdot (x_i\mathbf{a}_i) = A$. Since $\mathbf{K} \cdot \mathbf{a}_1 = 2\pi h$, $\mathbf{K} \cdot \mathbf{a}_2 = 2\pi k$, and $\mathbf{K} \cdot \mathbf{a}_3 = 2\pi l$, it follows that

$$x_1 = \frac{A}{2\pi h}, \quad x_2 = \frac{A}{2\pi k}, \quad x_3 = \frac{A}{2\pi l}. \tag{5.13}$$

Thus the intercepts with the crystal axes of a lattice plane are inversely proportional to the Miller indices of the plane.
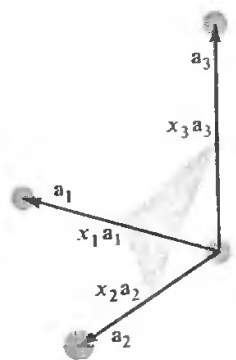
Figure 5.4
An illustration of the crystallographic definition of the Miller indices of a lattice plane. The shaded plane can be a portion of the continuous plane in which the points of the lattice plane lie, or any plane parallel to the lattice plane. The Miller indices are inversely proportional to the x_i.

Crystallographers put the cart before the horse, *defining* the Miller indices to be a set of integers with no common factors, inversely proportional to the intercepts of the crystal plane along the crystal axes:

$$h{:}k{:}l = \frac{1}{x_1} : \frac{1}{x_2} : \frac{1}{x_3}. \tag{5.14}$$

For cubic crystals with lattice spacing a, show that $\dfrac{1}{d^2} = \dfrac{1}{a^2}\left(h^2 + k^2 + l^2\right)$

Examples of Miller indices are shown below:

(001)   (100)   (010)

(101)   (110)   (011)

Source: http://www.diracdelta.co.uk/science/source/m/i/miller%20indices/source.html
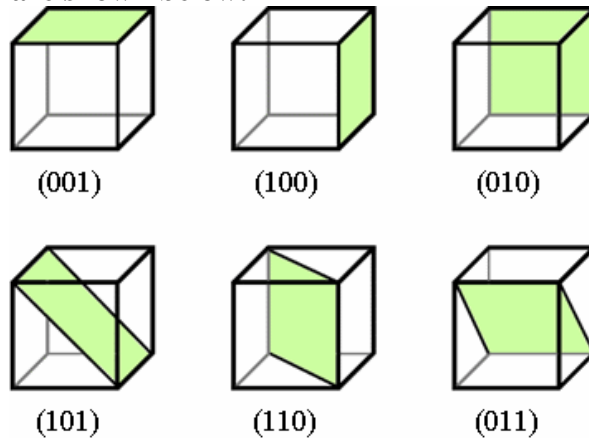
Braggs law can therefore be written as $\lambda = 2d_{hkl}\sin\theta$

The typical X-diffraction measurement geometry is shown below. This is known as Bragg-Brentano geometry
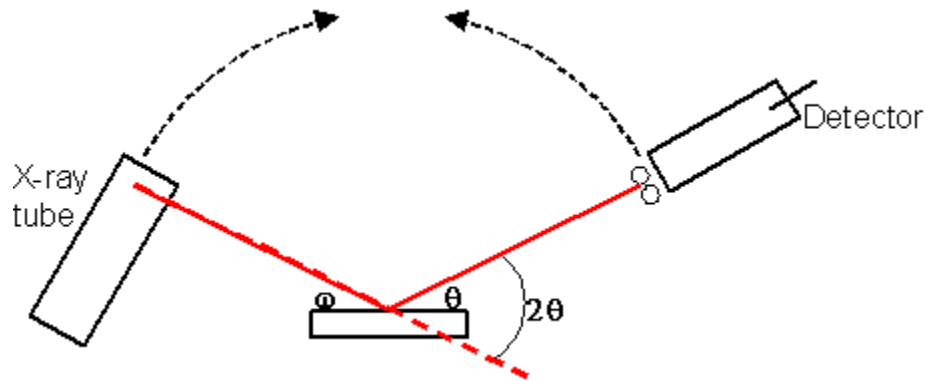
The incident angle, ω, is defined between the X-ray source and the sample. The diffracted angle, 2θ, is defined between the incident beam and the detector angle. The incident angle ωis always ½ of the detector angle 2θ .

A single crystal specimen in a Bragg-Brentano diffractometer would produce only one family of peaks in the diffraction pattern.

At 20.6 °2θ, Bragg's law fulfilled for the (100) planes, producing a diffraction peak.

The (110) planes would diffract at 29.3 °2θ; however, they are not properly aligned to produce a diffraction peak (the perpendicular to those planes does not bisect the incident and diffracted beams). Only background is observed.

The (200) planes are parallel to the (100) planes. Therefore, they also diffract for this crystal. Since d_{200} is ½ d_{100}, they appear at 42 °2θ.

A polycrystalline sample should contain thousands of crystallites. Therefore, all possible diffraction peaks should be observed.
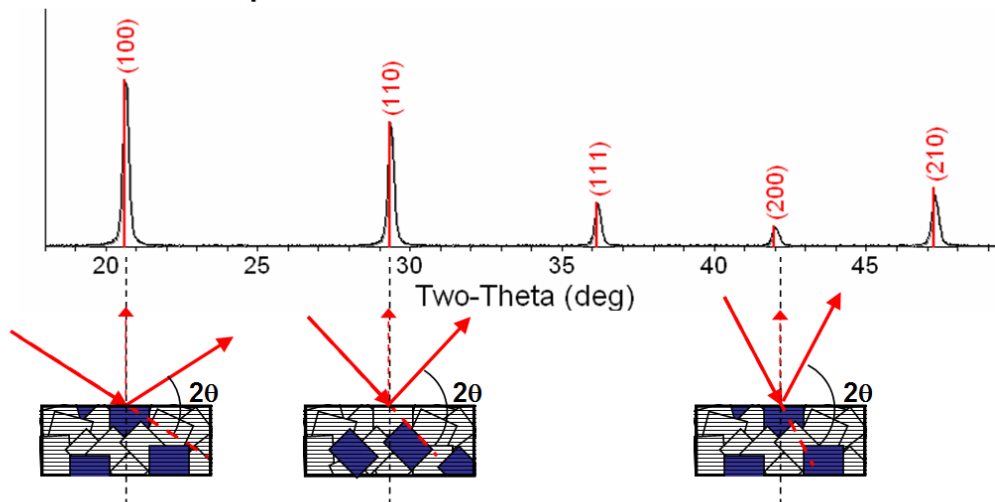
- For every set of planes, there will be a small percentage of crystallites that are properly oriented to diffract (the plane perpendicular bisects the incident and diffracted beams).
- Basic assumptions of powder diffraction are that for every set of planes there is an equal number of crystallites that will diffract and that there is a statistically relevant number of crystallites, not just one or two.

Braggs law can be rewritten as

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

Combining this relationship with the plane spacing equation gives us a new relationship:

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2} = \frac{4\sin^2\theta}{\lambda^2},$$

which can be rearranged to:

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

The term in parentheses $\left(\dfrac{\lambda^2}{4a^2}\right)$ is constant for any one pattern (because the X-ray wavelength λ and the lattice parameters a do not change). Thus $\sin^2\theta$ is proportional to $h^2 + k^2 + l^2$. This proportionality shows that planes with higher Miller indices will diffract at higher values of θ.

Since $\left(\dfrac{\lambda^2}{4a^2}\right)$ is constant for any pattern, we can write the following relationship for any two different planes:

$$\frac{\sin^2 \theta_1}{\sin^2 \theta_2} = \frac{\left(\dfrac{\lambda^2}{4a^2}\right)\left(h_1^2 + k_1^2 + l_1^2\right)}{\left(\dfrac{\lambda^2}{4a^2}\right)\left(h_2^2 + k_2^2 + l_2^2\right)} \quad \text{or} \quad \frac{\sin^2 \theta_1}{\sin^2 \theta_2} = \frac{\left(h_1^2 + k_1^2 + l_1^2\right)}{\left(h_2^2 + k_2^2 + l_2^2\right)}.$$

The ratio of $\sin^2 \theta$ values scales with the ratio of $h^2 + k^2 + l^2$ values.

In cubic systems, the first XRD peak in the XRD pattern will be due to diffraction from planes with the lowest Miller indices, which interestingly enough are the close packed planes (*i.e.:* simple cubic, (100), $h^2 + k^2 + l^2 = 1$; body-centered cubic, (110) $h^2 + k^2 + l^2 = 2$; and face-centered cubic, (111) $h^2 + k^2 + l^2 = 3$).

Since h, k, and l are always integers, we can obtain $h^2 + k^2 + l^2$ values by dividing the $\sin^2 \theta$ values for the different XRD peaks with the minimum one in the pattern (*i.e.*, the $\sin^2 \theta$ value from the first XRD peak) and multiplying that ratio by the proper integer (either 1, 2 or 3). This should yield a list of integers that represent the various $h^2 + k^2 + l^2$ values. You can identify the correct Bravais lattice by recognizing the sequence of allowed reflections for cubic lattices (*i.e.*, the sequence of allowed peaks written in terms of the quadratic form of the Miller indices).

Primitive $h^2 + k^2 + l^2 = 1,2,3,4,5,6,8,9,10,11,12,13,14,16\ldots$
Body-centered $h^2 + k^2 + l^2 = 2,4,6,8,10,12,14,16\ldots$
Face-centered $h^2 + k^2 + l^2 = 3,4,8,11,12,16,19,20,24,27,32\ldots$

Why do different Bravais lattices have different set of Miller indices? As we go from a simple cubic (primitive cubic) to a body centered cubic to face centered cubic, the number of atoms per unit cell increases. This implies additional or intervening lattice planes. Certain reflections present in the simple cubic structure destructively interfere with reflections from the additional lattice planes. Therefore certain sets of planes and their corresponding Miller indices are absent in the diffractogram pattern. You will read about this quantitatively in the Condensed Matter Physics course.

Source:
http://bama.ua.edu/~mweaver/courses/MTE481/Laboratory1-2006.pdf
http://prism.mit.edu/xray/BasicsofXRD.ppt
Solid State Physics, by Ibach and Luth
Solid State Physics, by Ashcroft and Mermin

The lattice parameters can be calculated from:

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

which can be re-written as:

$$a^2 = \frac{\lambda^2}{4\sin^2\theta}\left(h^2 + k^2 + l^2\right) \text{ OR } a = \frac{\lambda}{2\sin\theta}\sqrt{h^2 + k^2 + l^2}$$

Your task is to index the given power diffraction pattern and determine the lattice parameters
Steps:
  (1) Identify the peaks.
  (2) Determine $\sin^2\theta$.
  (3) Calculate the ratio $\sin^2\theta / \sin^2\theta_{min}$ and multiply by the appropriate integers.
  (4) Select the result from (3) that yields $h^2 + k^2 + l^2$ as an integer.
  (5) Compare results with the sequences of $h^2 + k^2 + l^2$ values to identify the Bravais lattice.
  (6) Calculate lattice parameters.

You will be given a diffractogram corresponding to a cubic lattice. The indexing of other lattice types is non-trivial. Interested students may refer to
http://bama.ua.edu/~mweaver/courses/MTE481/Laboratory1-2006.pdf

Here is an example of an indexed pattern:

When you index a diffraction pattern, you assign the correct Miller indices to each peak (reflection) in the diffraction pattern. An XRD pattern is properly indexed when ALL of the peaks in the diffraction pattern are labeled and no peaks expected for the particular structure are missing.
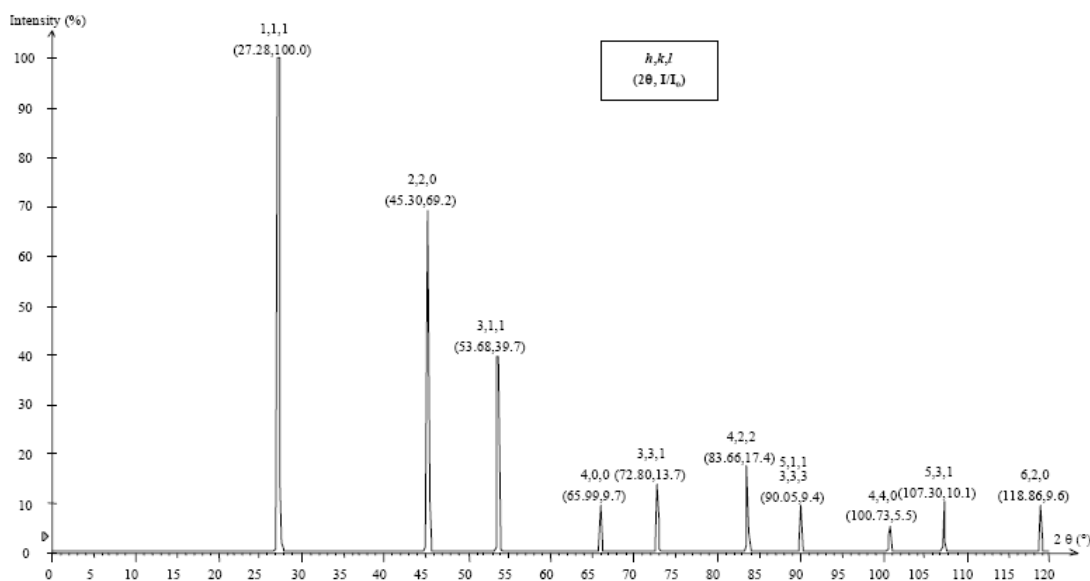
This is an example of a properly indexed diffraction pattern. All peaks are accounted for. One now needs only to assign the correct Bravais lattice and to calculate lattice parameters.

Pattern to be indexed -1

Consider the following XRD pattern for Aluminum, which was collected using CuKα radiation.
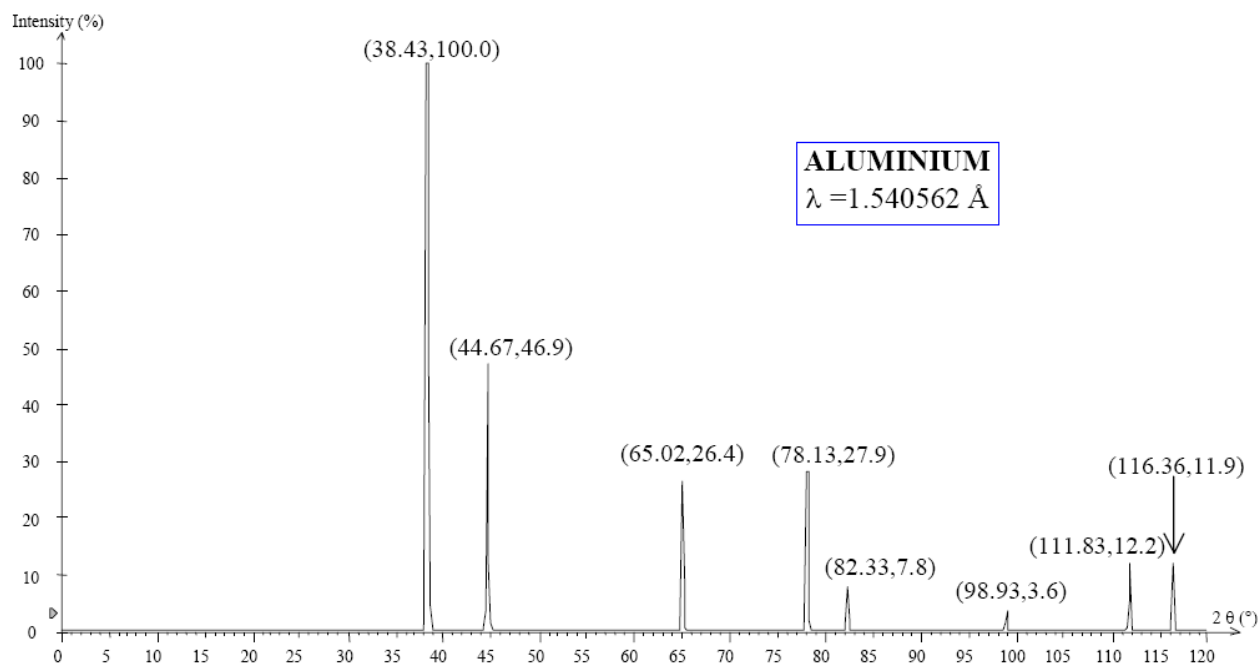
Peak No.	2θ
1	38.43
2	44.67
3	65.02
4	78.13
5	82.33
6	98.93
7	111.83
8	116.36

Laboratory Module 1
Indexing X-Ray Diffraction Patterns

LEARNING OBJECTIVES

Upon completion of this module you will be able to index an X-ray diffraction pattern, identify the Bravais lattice, and calculate the lattice parameters for crystalline materials.

BACKGROUND

We need to know about crystal structures because structure, to a large extent, determines properties. X-ray diffraction (XRD) is one of a number of experimental tools that are used to identify the structures of crystalline solids.

The XRD patterns, the product of an XRD experiment, are somewhat like fingerprints in that they are unique to the material that is being examined. The information in an XRD pattern is a direct result of two things:

(1) The size and shape of the unit cells determine the relative positions of the diffraction peaks;
(2) Atomic positions within the unit cell determine the relative intensities of the diffraction peaks (remember the structure factor?).

Taking these things into account, we can calculate the size and shape of a unit cell from the positions of the XRD peaks and we can determine the positions of the atoms in the unit cell from the intensities of the diffraction peaks.

Full identification of crystal structures is a multi-step process that consists of:
(1) Calculation of the size and shape of the unit cell from the XRD peak positions;
(2) Computation of the number of atoms/unit cell from the size and shape of the cell, chemical composition, and measured density;
(3) Determination of atom positions from the relative intensities of the XRD peaks

We will only concern ourselves with step (1), calculation of the size and shape of the unit cell from XRD peak positions. We loosely refer to this as "indexing." The laboratory module is broken down into two sections. The first addresses how to index patterns from cubic materials. The second addresses how to index patterns from non-cubic materials.

PART 1
## PROCEDURE FOR INDEXING CUBIC XRD PATTERNS

When you index a diffraction pattern, you assign the correct Miller indices to each peak (reflection) in the diffraction pattern. An XRD pattern is properly indexed when ALL of the peaks in the diffraction pattern are labeled and no peaks expected for the particular structure are missing.
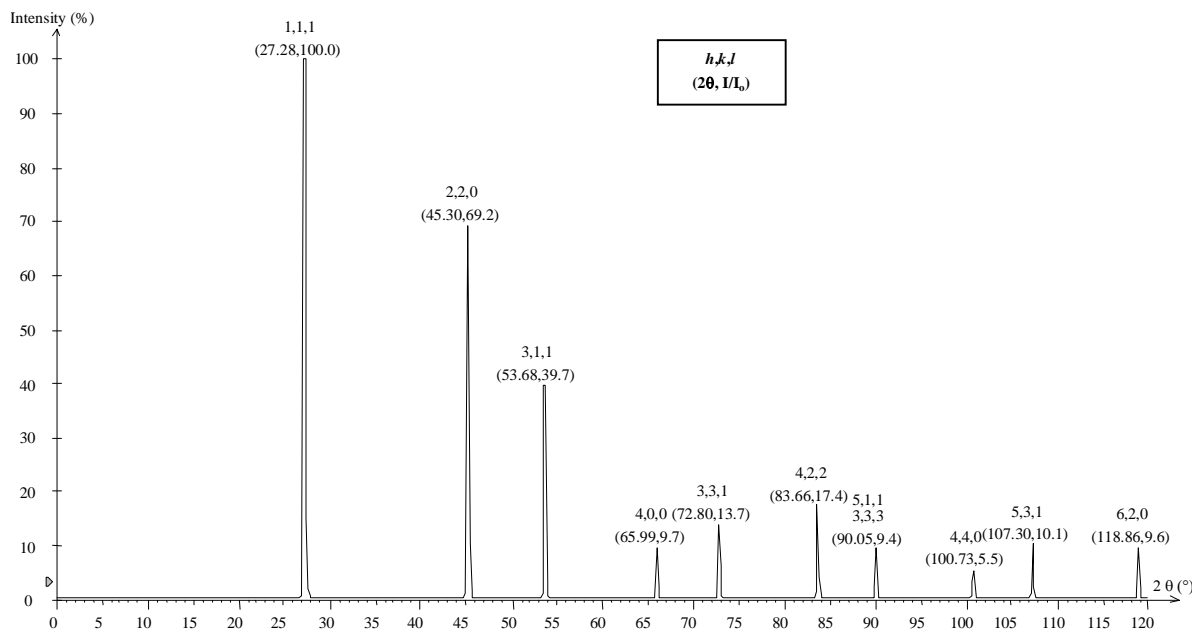
This is an example of a properly indexed diffraction pattern. All peaks are accounted for. One now needs only to assign the correct Bravais lattice and to calculate lattice parameters.

How to we correctly index a pattern? The correct procedures follow.

PROCEDURE FOR INDEXING AN XRD PATTERN

The procedures are standard. They work for any crystal structure regardless of whether the material is a metal, a ceramic, a semiconductor, a zeolite, etc… There are two methods of analysis. You will do both. One I will refer to as the mathematical method. The second is known as the analytical method. The details are covered below.

Mathematical Method

Interplanar spacings in cubic crystals can be written in terms of lattice parameters using the plane spacing equation:

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

You should recall Bragg's law ($\lambda = 2d \sin\theta$), which can be re-written either as:

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

Combining this relationship with the plane spacing equation gives us a new relationship:

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2} = \frac{4\sin^2\theta}{\lambda^2},$$

which can be rearranged to:

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

The term in parentheses $\left(\dfrac{\lambda^2}{4a^2}\right)$ is constant for any one pattern (because the X-ray wavelength λ and the lattice parameters a do not change). Thus $\sin^2\theta$ is proportional to $h^2 + k^2 + l^2$. This proportionality shows that planes with higher Miller indices will diffract at higher values of θ.

Since $\left(\dfrac{\lambda^2}{4a^2}\right)$ is constant for any pattern, we can write the following relationship for any two different planes:

$$\frac{\sin^2\theta_1}{\sin^2\theta_2} = \frac{\left(\frac{\lambda^2}{4a^2}\right)\left(h_1^2 + k_1^2 + l_1^2\right)}{\left(\frac{\lambda^2}{4a^2}\right)\left(h_2^2 + k_2^2 + l_2^2\right)} \ \text{ or } \ \frac{\sin^2\theta_1}{\sin^2\theta_2} = \frac{\left(h_1^2 + k_1^2 + l_1^2\right)}{\left(h_2^2 + k_2^2 + l_2^2\right)}.$$

The ratio of $\sin^2\theta$ values scales with the ratio of $h^2 + k^2 + l^2$ values.

In cubic systems, the first XRD peak in the XRD pattern will be due to diffraction from planes with the lowest Miller indices, which interestingly enough are the close packed planes (*i.e.*: simple cubic, (100), $h^2 + k^2 + l^2 = 1$; body-centered cubic, (110) $h^2 + k^2 + l^2 = 2$; and face-centered cubic, (111) $h^2 + k^2 + l^2 = 3$).

Since h, k, and l are always integers, we can obtain $h^2 + k^2 + l^2$ values by dividing the $\sin^2 \theta$ values for the different XRD peaks with the minimum one in the pattern (*i.e.*, the $\sin^2 \theta$ value from the first XRD peak) and multiplying that ratio by the proper integer (either 1, 2 or 3). This should yield a list of integers that represent the various $h^2 + k^2 + l^2$ values. You can identify the correct Bravais lattice by recognizing the sequence of allowed reflections for cubic lattices (*i.e.*, the sequence of allowed peaks written in terms of the quadratic form of the Miller indices).

Primitive $h^2 + k^2 + l^2 = 1,2,3,4,5,6,8,9,10,11,12,13,14,16\ldots$
Body-centered $h^2 + k^2 + l^2 = 2,4,6,8,10,12,14,16\ldots$
Face-centered $h^2 + k^2 + l^2 = 3,4,8,11,12,16,19,20,24,27,32\ldots$
Diamond cubic $h^2 + k^2 + l^2 = 3,8,11,16,19,24,27,32\ldots$

The lattice parameters can be calculated from:

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

which can be re-written as:

$$a^2 = \frac{\lambda^2}{4\sin^2 \theta} \left(h^2 + k^2 + l^2 \right) \text{ OR } a = \frac{\lambda}{2\sin \theta} \sqrt{h^2 + k^2 + l^2}$$

Worked Example

Consider the following XRD pattern for Aluminum, which was collected using CuKα radiation.
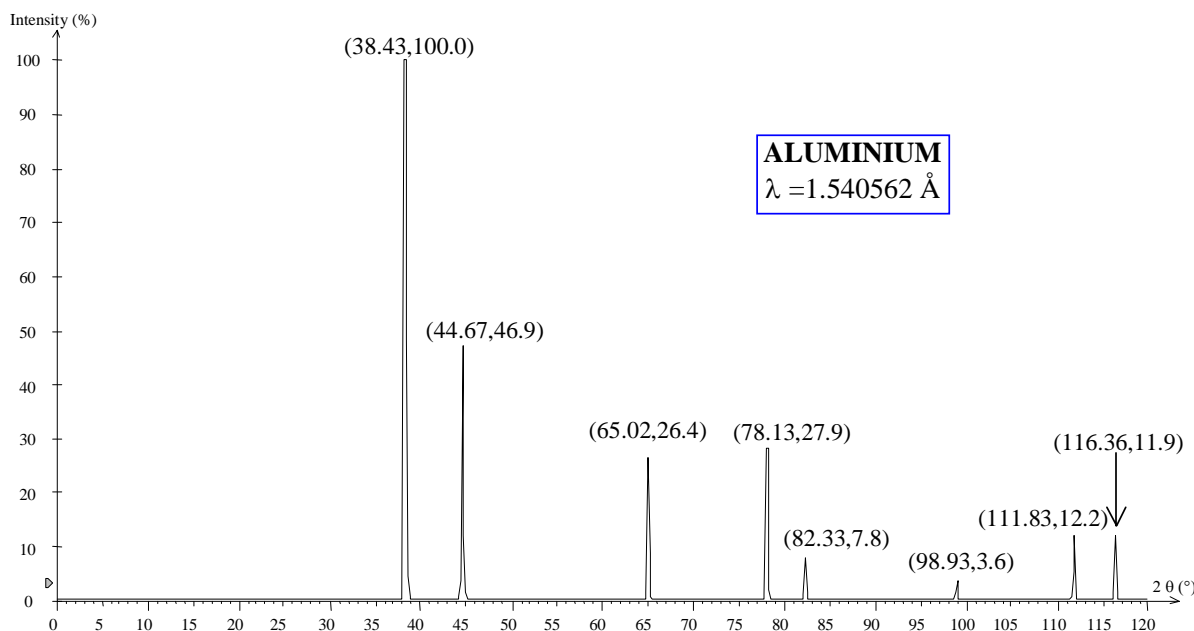
Index this pattern and determine the lattice parameters.

Steps:
   (1) Identify the peaks.
   (2) Determine $\sin^2 \theta$.
   (3) Calculate the ratio $\sin^2 \theta / \sin^2 \theta_{min}$ and multiply by the appropriate integers.
   (4) Select the result from (3) that yields $h^2 + k^2 + l^2$ as an integer.
   (5) Compare results with the sequences of $h^2 + k^2 + l^2$ values to identify the Bravais lattice.
   (6) Calculate lattice parameters.

Here we go!

   (1) Identify the peaks and their proper 2θ values. Eight peaks for this pattern. Note: most patterns will contain α_1 and α_2 peaks at higher angles. It is common to neglect α_2 peaks.

Peak No.	2θ	$\sin^2\theta$	$1 \times \dfrac{\sin^2 \theta}{\sin^2 \theta_{min}}$	$2 \times \dfrac{\sin^2 \theta}{\sin^2 \theta_{min}}$	$3 \times \dfrac{\sin^2 \theta}{\sin^2 \theta_{min}}$	$h^2+k^2+l^2$	hkl	a (Å)
1	38.43							
2	44.67							
3	65.02							
4	78.13							
5	82.33							
6	98.93							
7	111.83							
8	116.36							

   (2) Determine $\sin^2 \theta$.

Peak No.	2θ	$\sin^2\theta$	$1 \times \dfrac{\sin^2 \theta}{\sin^2 \theta_{min}}$	$2 \times \dfrac{\sin^2 \theta}{\sin^2 \theta_{min}}$	$3 \times \dfrac{\sin^2 \theta}{\sin^2 \theta_{min}}$	$h^2+k^2+l^2$	hkl	a (Å)
1	38.43	0.1083						
2	44.67	0.1444						
3	65.02	0.2888						
4	78.13	0.3972						
5	82.33	0.4333						
6	98.93	0.5776						
7	111.83	0.6859						

| | 8 | 116.36 | 0.7220 | | | | | |

(3) Calculate the ratio $\sin^2\theta / \sin^2\theta_{min}$ and multiply by the appropriate integers.

Peak No.	2θ	$\sin^2\theta$	$1\times\dfrac{\sin^2\theta}{\sin^2\theta_{min}}$	$2\times\dfrac{\sin^2\theta}{\sin^2\theta_{min}}$	$3\times\dfrac{\sin^2\theta}{\sin^2\theta_{min}}$	$h^2+k^2+l^2$	hkl	a (Å)
1	38.43	0.1083	1.000	2.000	3.000			
2	44.67	0.1444	1.333	2.667	4.000			
3	65.02	0.2888	2.667	5.333	8.000			
4	78.13	0.3972	3.667	7.333	11.000			
5	82.33	0.4333	4.000	8.000	12.000			
6	98.93	0.5776	5.333	10.665	15.998			
7	111.83	0.6859	6.333	12.665	18.998			
8	116.36	0.7220	6.666	13.331	19.997			

(4) Select the result from (3) that most closely yields $h^2+k^2+l^2$ as a series of integers.

Peak No.	2θ	$\sin^2\theta$	$1\times\dfrac{\sin^2\theta}{\sin^2\theta_{min}}$	$2\times\dfrac{\sin^2\theta}{\sin^2\theta_{min}}$	$3\times\dfrac{\sin^2\theta}{\sin^2\theta_{min}}$	$h^2+k^2+l^2$	hkl	a (Å)
1	38.43	0.1083	1.000	2.000	3.000			
2	44.67	0.1444	1.333	2.667	4.000			
3	65.02	0.2888	2.667	5.333	8.000			
4	78.13	0.3972	3.667	7.333	11.000			
5	82.33	0.4333	4.000	8.000	12.000			
6	98.93	0.5776	5.333	10.665	15.998			
7	111.83	0.6859	6.333	12.665	18.998			
8	116.36	0.7220	6.666	13.331	19.997			

(5) Compare results with the sequences of $h^2+k^2+l^2$ values to identify the miller indices for the appropriate peaks and the Bravais lattice.

Peak No.	2θ	$\sin^2\theta$	$1\times\dfrac{\sin^2\theta}{\sin^2\theta_{min}}$	$2\times\dfrac{\sin^2\theta}{\sin^2\theta_{min}}$	$3\times\dfrac{\sin^2\theta}{\sin^2\theta_{min}}$	$h^2+k^2+l^2$	hkl	a (Å)
1	38.43	0.1083	1.000	2.000	3.000	3	111	4.0538
2	44.67	0.1444	1.333	2.667	4.000	4	200	4.0539
3	65.02	0.2888	2.667	5.333	8.000	8	220	4.0538
4	78.13	0.3972	3.667	7.333	11.000	11	311	4.0538
5	82.33	0.4333	4.000	8.000	12.000	12	222	4.0538
6	98.93	0.5776	5.333	10.665	15.998	16	400	4.0541
7	111.83	0.6859	6.333	12.665	18.998	19	331	4.0540
8	116.36	0.7220	6.666	13.331	19.997	20	420	4.0541

Bravais lattice is Face-Centered Cubic

(6) Calculate lattice parameters.

Peak No.	2θ	$\sin^2\theta$	$1\times\dfrac{\sin^2\theta}{\sin^2\theta_{min}}$	$2\times\dfrac{\sin^2\theta}{\sin^2\theta_{min}}$	$3\times\dfrac{\sin^2\theta}{\sin^2\theta_{min}}$	$h^2+k^2+l^2$	hkl	a (Å)
1	38.43	0.1083	1.000	2.000	3.000	3	111	4.0538
2	44.67	0.1444	1.333	2.667	4.000	4	200	4.0539
3	65.02	0.2888	2.667	5.333	8.000	8	220	4.0538
4	78.13	0.3972	3.667	7.333	11.000	11	311	4.0538
5	82.33	0.4333	4.000	8.000	12.000	12	222	4.0538
6	98.93	0.5776	5.333	10.665	15.998	16	400	4.0541
7	111.83	0.6859	6.333	12.665	18.998	19	331	4.0540
8	116.36	0.7220	6.666	13.331	19.997	20	420	4.0541

Average lattice parameter is 4.0539 Å

Analytical Method

This is an alternative approach that will yield the same results as the mathematical method. It will give you a nice comparison.

Recall:

$$\sin^2\theta = \left(\frac{\lambda^2}{4a^2}\right)\left(h^2 + k^2 + l^2\right) \text{ and } \left(\frac{\lambda^2}{4a^2}\right) = \text{constant for all patterns}$$

If we let $K = \left(\dfrac{\lambda^2}{4a^2}\right)$, we can re-write these equations as:

$$\sin^2\theta = K\left(h^2 + k^2 + l^2\right)$$

For any cubic system, the possible values of $h^2 + k^2 + l^2$ correspond to the sequence:

$$h^2 + k^2 + l^2 = 1,2,3,4,5,6,8,9,10,11\ldots$$

If we determine $\sin^2\theta$ for each peak and we divide the values by the integers 2,3,4,5,6,8,9,10,11…, we can obtain a common quotient, which is the value of K corresponding to $h^2 + k^2 + l^2 = 1$.

K is related to the lattice parameter as follows:

$$K = \left(\frac{\lambda^2}{4a^2}\right) \text{ OR } a = \frac{\lambda}{2\sqrt{K}}$$

If we divide the $\sin^2 \theta$ values for each reflection by K, we get the $h^2 + k^2 + l^2$ values. The sequence of $h^2 + k^2 + l^2$ values can be used to label each XRD peak and to identify the Bravais lattice.

Let's do an example for the Aluminum pattern presented above.

Steps:
    (1) Identify the peaks.
    (2) Determine $\sin^2 \theta$.
    (3) Calculate the ratio $\sin^2 \theta$ /(integers)
    (4) Identify the lowest common quotient from (3) and identify the integers to which it corresponds. Let the lowest common quotient be K.
    (5) Divide $\sin^2 \theta$ by K for each peak. This will give you a list of integers corresponding to $h^2 + k^2 + l^2$.
    (6) Select the appropriate pattern of $h^2 + k^2 + l^2$ values and identify the Bravais lattice.
    (7) Calculate lattice parameters.

Here we go again!

(1) Identify the peaks.

Peak No.	2θ	$\sin^2 \theta$	$\dfrac{\sin^2 \theta}{2}$	$\dfrac{\sin^2 \theta}{3}$	$\dfrac{\sin^2 \theta}{4}$	$\dfrac{\sin^2 \theta}{5}$	$\dfrac{\sin^2 \theta}{6}$	$\dfrac{\sin^2 \theta}{8}$
1	38.43							
2	44.67							
3	65.02							
4	78.13							
5	82.33							
6	98.93							
7	111.83							
8	116.36							

(2) Determine $\sin^2 \theta$.

Peak No.	2θ	$\sin^2 \theta$	$\dfrac{\sin^2 \theta}{2}$	$\dfrac{\sin^2 \theta}{3}$	$\dfrac{\sin^2 \theta}{4}$	$\dfrac{\sin^2 \theta}{5}$	$\dfrac{\sin^2 \theta}{6}$	$\dfrac{\sin^2 \theta}{8}$
1	38.43	0.1083						
2	44.67	0.1444						
3	65.02	0.2888						
4	78.13	0.3972						
5	82.33	0.4333						
6	98.93	0.5776						

	7	111.83	0.6859						
	8	116.36	0.7220						

(3) Calculate the ratio $\sin^2\theta$ /(integers)

Peak No.	2θ	$\sin^2\theta$	$\dfrac{\sin^2\theta}{2}$	$\dfrac{\sin^2\theta}{3}$	$\dfrac{\sin^2\theta}{4}$	$\dfrac{\sin^2\theta}{5}$	$\dfrac{\sin^2\theta}{6}$	$\dfrac{\sin^2\theta}{8}$
1	38.43	0.1083	0.0542	0.0361	0.0271	0.0217	0.0181	0.0135
2	44.67	0.1444	0.0722	0.0481	0.0361	0.0289	0.0241	0.0181
3	65.02	0.2888	0.1444	0.0963	0.0722	0.0578	0.0481	0.0361
4	78.13	0.3972	0.1986	0.1324	0.0993	0.0794	0.0662	0.0496
5	82.33	0.4333	0.2166	0.1444	0.1083	0.0867	0.0722	0.0542
6	98.93	0.5776	0.2888	0.1925	0.1444	0.1155	0.0963	0.0722
7	111.83	0.6859	0.3430	0.2286	0.1715	0.1372	0.1143	0.0857
8	116.36	0.7220	0.3610	0.2407	0.1805	0.1444	0.1203	0.0903

(4) Identify the lowest common quotient from (3) and identify the integers to which it corresponds. Let the lowest common quotient be *K*.

Peak No.	2θ	$\sin^2\theta$	$\dfrac{\sin^2\theta}{2}$	$\dfrac{\sin^2\theta}{3}$	$\dfrac{\sin^2\theta}{4}$	$\dfrac{\sin^2\theta}{5}$	$\dfrac{\sin^2\theta}{6}$	$\dfrac{\sin^2\theta}{8}$
1	38.43	0.1083	0.0542	**0.0361**	0.0271	0.0217	0.0181	0.0135
2	44.67	0.1444	0.0722	0.0481	**0.0361**	0.0289	0.0241	0.0181
3	65.02	0.2888	0.1444	0.0963	0.0722	0.0578	0.0481	**0.0361**
4	78.13	0.3972	0.1986	0.1324	0.0993	0.0794	0.0662	0.0496
5	82.33	0.4333	0.2166	0.1444	0.1083	0.0867	0.0722	0.0542
6	98.93	0.5776	0.2888	0.1925	0.1444	0.1155	0.0963	0.0722
7	111.83	0.6859	0.3430	0.2286	0.1715	0.1372	0.1143	0.0857
8	116.36	0.7220	0.3610	0.2407	0.1805	0.1444	0.1203	0.0903

$K = 0.0361$

(5) Divide $\sin^2\theta$ by *K* for each peak. This will give you a list of integers corresponding to $h^2 + k^2 + l^2$.

Peak No.	2θ	$\sin^2\theta$	$\dfrac{\sin^2\theta}{K}$	$h^2 + k^2 + l^2$	hkl
1	38.43	0.1083	3.000		
2	44.67	0.1444	4.000		
3	65.02	0.2888	8.001		
4	78.13	0.3972	11.001		
5	82.33	0.4333	12.002		
6	98.93	0.5776	16.000		
7	111.83	0.6859	19.001		

	8	116.36	0.7220	20.000		

(6) Select the appropriate pattern of $h^2 + k^2 + l^2$ values and identify the Bravais lattice.

Peak No.	2θ	$\sin^2\theta$	$\dfrac{\sin^2\theta}{K}$	$h^2 + k^2 + l^2$	hkl
1	38.43	0.1083	3.000	3	111
2	44.67	0.1444	4.000	4	200
3	65.02	0.2888	8.001	8	220
4	78.13	0.3972	11.001	11	311
5	82.33	0.4333	12.002	12	222
6	98.93	0.5776	16.000	16	400
7	111.83	0.6859	19.001	19	331
8	116.36	0.7220	20.000	20	420

Sequence suggests a Face-Centered Cubic Bravais Lattice

(7) Calculate lattice parameters.

$$a = \frac{\lambda}{2\sqrt{K}} = \frac{1.540562 \ \mathring{A}}{2\sqrt{0.0361}} = \underline{4.0541 \ \mathring{A}}$$

These methods will work for any cubic material. This means metals, ceramics, ionic crystals, minerals, intermetallics, semiconductors, etc…

PART 2
PROCEDURE FOR INDEXING NON-CUBIC XRD PATTERNS

The procedures are standard and will work for any crystal. The equations will differ slightly from each other due to differences in crystal size and shape (*i.e.*, crystal structure). As was the case for cubic crystals, there are two methods of analysis that involve calculations. You will do both. One I will refer to as the mathematical method. The second I will refer to as the analytical method. Both the mathematical and graphical methods require some knowledge of the crystal structure that you are dealing with and the resulting lattice parameter ratios (*e.g.*, *c*/*a*, *b*/*a*, etc…).

This information can be determined graphically using Hull-Davey charts. We will first introduce the concept of Hull-Davey charts prior to showing how to proper index patterns.

Hull-Davey Charts

The graphical method developed by Hull and Davey[1] are convenient for indexing diffraction patterns, in particular for systems of lower symmetry. The reason is that this method allows one to determine structure even if lattice parameters are unknown. The mathematical methods that will be illustrated in later sections of this module require such knowledge, in particular the values of the various lattice parameter ratios (c/a, b/a, c/b etc…). The steps involved in constructing and indexing patterns using Hull-Davey charts is very straightforward.

First, consider the plane spacing equations for the crystal structures of interest. Some examples are shown below:

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

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

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

Etc.

You should recall Bragg's law ($\lambda = 2d \sin\theta$), which can be re-written either as:

$$\lambda^2 = 4d^2 \sin^2\theta$$

or

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

Combining Bragg's law with the plane spacing equations yields the relationship:

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

Tetragonal
$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} = \frac{4\sin^2\theta}{\lambda^2}$$

Orthorhombic
$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} = \frac{4\sin^2\theta}{\lambda^2}$$

Etc…

which can be rearranged in terms of $\sin^2\theta$ to:

[1] A.W. Hull and W.P. Davey, *Phys. Rev.*, vol. 17, pp. 549, 1921; W.P. Davey, *Gen. Elec. Rev.*, vol. 25, pp. 564, 1922.

Hexagonal	$\sin^2\theta = \left(\dfrac{\lambda^2}{4}\right) = \left[\dfrac{4}{3}\left(\dfrac{h^2 + hk + k^2}{a^2}\right) + \dfrac{l^2}{c^2}\right]$
Tetragonal	$\sin^2\theta = \left(\dfrac{\lambda^2}{4}\right)\left(\dfrac{h^2 + k^2}{a^2} + \dfrac{l^2}{c^2}\right)$
Orthorhombic	$\sin^2\theta = \left(\dfrac{\lambda^2}{4}\right)\left(\dfrac{h^2}{a^2} + \dfrac{k^2}{b^2} + \dfrac{l^2}{c^2}\right)$

You should note that as unlike cubic systems where $\left(\dfrac{\lambda^2}{4a^2}\right)$ is constant, your results for non-cubic systems will depend upon ratios of lattice parameters (*i.e.*, *c/a*, *b/a*, etc.) and your interaxial angles (*i.e.*, α, β, γ). We will illustrate this ("sort of") below. This is due to the non-equivalence of indices in these systems (*e.g.*, tetragonal – 001 ≠ 100; orthorhombic – 001 ≠ 010 ≠ 100; etc…).

Let's concentrate on hexagonal systems for the time being. <u>I may ask you to derive relationships for tetragonal and orthorhombic systems in a homework assignment.</u> As noted previously, the mathematical method requires knowledge of the *c/a* ratio. We don't know what it is so we need to construct a Hull-Davey chart. To accomplish this goal, we must first rewrite our revised *d*-spacing equations as follows:

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

$$\Downarrow$$

$$2\log d = 2\log a - \log\left[\frac{4}{3}\left(h^2 + hk + k^2\right) + \frac{l^2}{(c/a)^2}\right]$$

Letting the term in brackets equal s, we finally end up with:

$$2\log d = 2\log a - \log\left[s\right]$$

We can now construct the Hull-Davey chart by plotting the variation of log [s] with c/a for different *hkl* values. One axis will consist of *c/a* values while the other will consist of -log [s] values with the origin set at log [1] = 0. A representative chart is presented on the next page.

Hull-Davey Plot for HCP
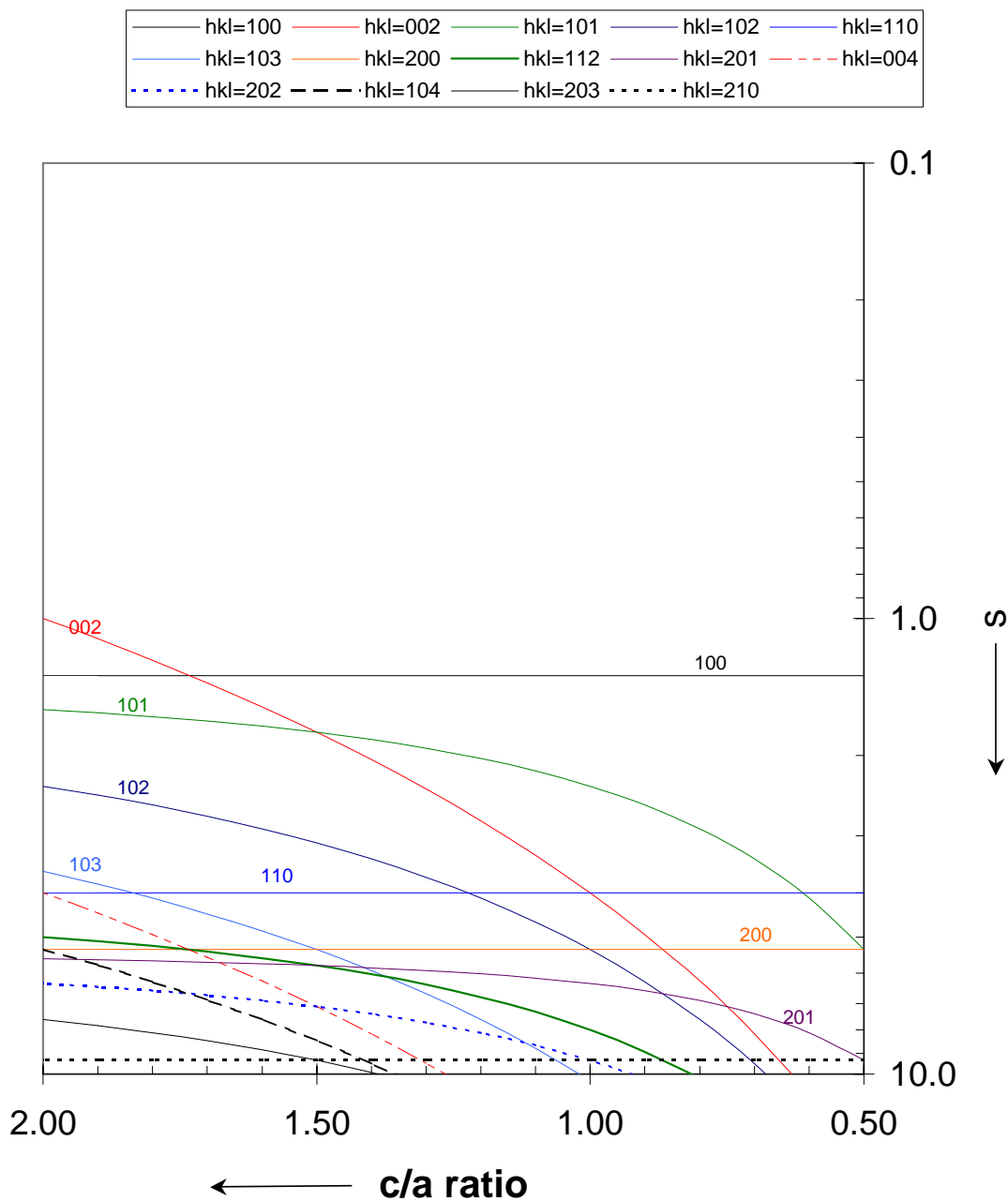
To determine the *c/a* ratio, one only needs to collect an XRD pattern, identify the peak locations in terms of the Bragg angle, calculate the *d*-spacing for each peak and to construct a single range *d*-spacing scale (2·log *d*) that is the same size as the logarithmic [*s*] scale (you can use $\sin^2\theta$ instead if you prefer). I know this is confusing so I have schematically illustrated what I mean in the next set of figures.
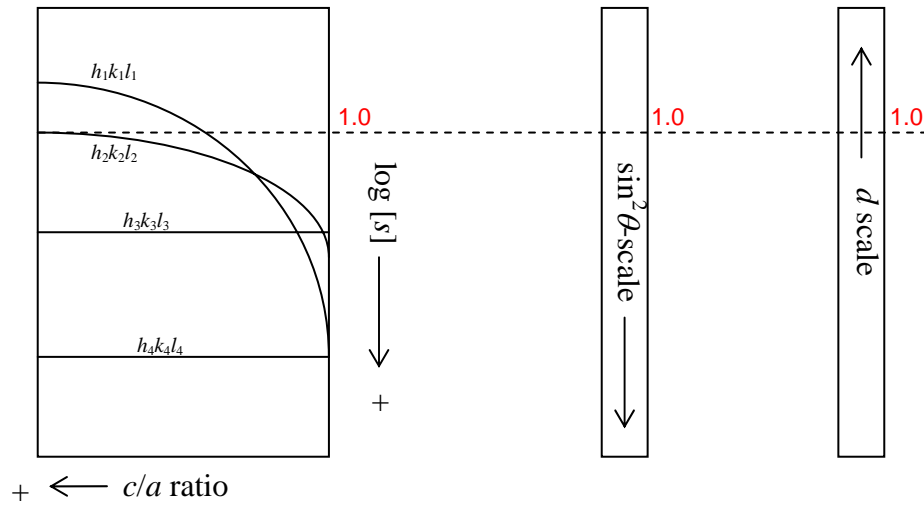
Next, you need to calculate the d-spacing or $\sin^2\theta$ values for the observed peaks and mark them on a strip laid along side the appropriate d- or $\sin^2\theta$- scale.
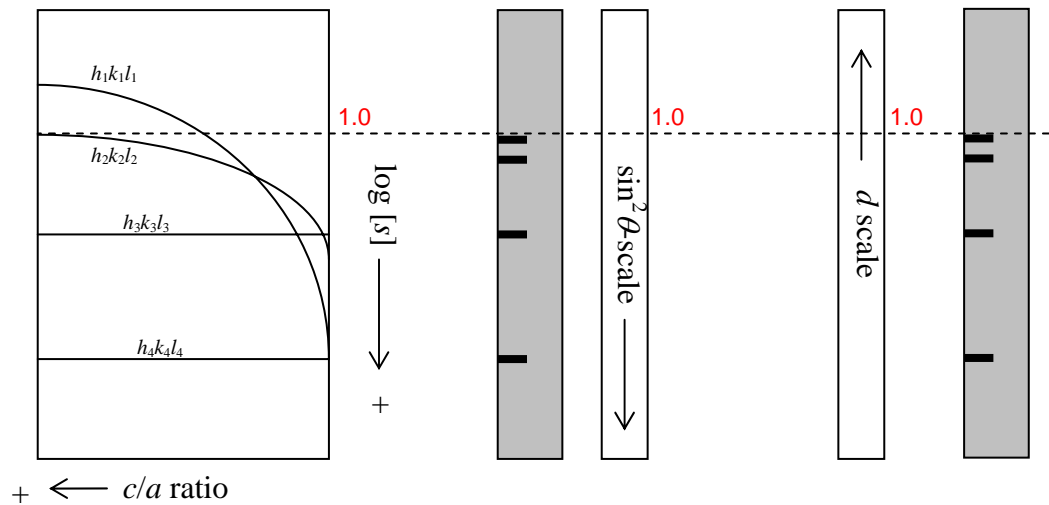
The strip should be moved horizontally and vertically across the log $[s]$ – c/a plot until a position is found where each mark on your strip coincides with a line on the chart. This is illustrated schematically on the next figure.

Please keep in mind that my illustrations for the Hull-Davey method are ***SCHEMATIC***. This method is very difficult to convey. You should consult the classical references to find out more information about this technique.

0.10   10.0

$h_1k_1l_1$

1.0   1.0

$h_2k_2l_2$

$h_3k_3l_3$

$h_4k_4l_4$

+

10.0   1.0
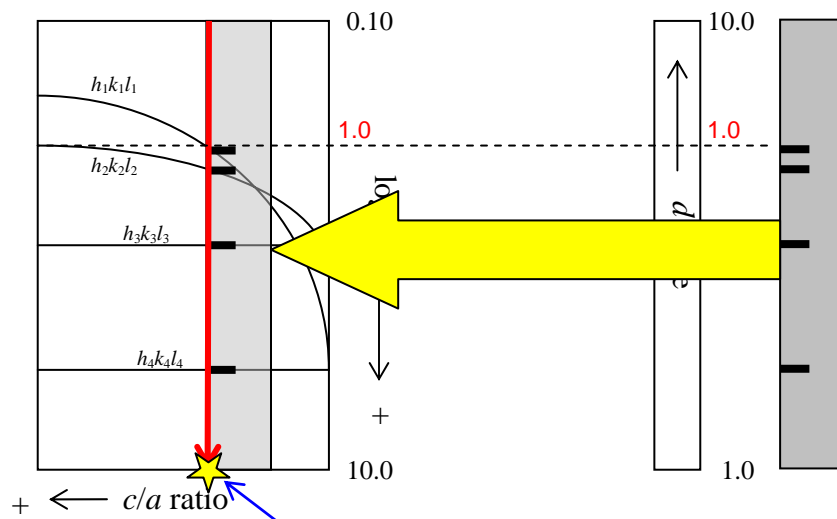
+ ← *c/a* ratio

This is our c/a ratio for the pattern!

This method really does work as I showed you in class. Once you know your *c/a* ratio, you can index the XRD pattern. As we noted above, there are two ways to do this. The first is the mathematical method.

Mathematical Method for Non-Cubic Crystals

Recall the following equation:

$$\sin^2 \theta = \left(\frac{\lambda^2}{4a^2} \right) \left[\frac{4}{3} \left(h^2 + hk + k^2 \right) + \frac{l^2}{(c/a)^2} \right]$$

Note that the lattice parameter *a* and the ratio of lattice parameters *c/a* are constant for a given diffraction pattern. Thus, $\left(\dfrac{\lambda^2}{4a^2} \right)$ is constant for any pattern. The pattern can now be indexed in by considering the terms in brackets:

$$\frac{4}{3} \left(h^2 + hk + k^2 \right)$$

$$\frac{l^2}{(c/a)^2}$$

Let's start with term 1. This term only depends on the indices *h* and *k*. Thus its value can be calculated for different values of *h* and *k*. This is done below for various *hk* values.

Term 1 calculated for various values of *hk*

		k			
		0	1	2	3
	0	0.000	1.333	5.333	12.000
h	1	1.333	4.000	9.333	17.333
	2	5.333	9.333	16.000	25.333
	3	12.000	17.333	25.333	36.000

The second term can be determined by substituting in the known c/a ratio. This is illustrated for zinc ($c/a = 1.8563$) in the table below.

Term 2 calculated for zinc ($c/a = 1.8563$)

l	l^2	$l^2/(c/a)^2$
0	0	0.000
1	1	0.290
2	4	1.161
3	9	2.612
4	16	4.643
5	25	7.255
6	36	10.447

The next step is to add the values for the two terms that are permitted by the structure factor (*i.e.*, the values corresponding to the allowed *hkl* values) and to rank them in increasing order. The structure factor calculation for hexagonal systems yields the following rules:

1. When $h + 2k = 3N$ (where N is an integer), there is no peak.
2. When l is odd, there is no peak.

Both criteria must be met!

Indices (*hkl*)	*l*	*h* + 2*k*	Peak
301	Odd	3	NO
103	Odd	$1 \neq 3N$	YES
Etc…			

Compare with values in appendix 9 in Cullity.

Several values for the bracketed quantity are calculated below minus the peaks forbidden by the structure factor.

h	k	l	sum
0	0	2	1.1608
1	0	0	1.3333
1	0	1	1.6235
1	0	2	2.4942
1	0	3	3.9452
1	1	0	4.0000
0	0	4	4.6433
1	1	2	5.1608
2	0	0	5.3333
2	0	1	5.6235
1	0	4	5.9766
2	0	2	6.4942

The values in this table have been calculated for specific (*hkl*) planes. We can assign specific *hkl* values for each of the peaks in a hexagonal unknown by noting that the sequence of peaks will be the same as indicated in the table.

Lattice parameters can be determined in two ways:

We can calculate *a* by looking for peaks where $l = 0$ (*i.e.*, *hk*0 peaks). If you substitute $l = 0$ into:

$$\sin^2 \theta = \left(\frac{\lambda^2}{4a^2} \right) \left[\frac{4}{3} \left(h^2 + hk + k^2 \right) + \frac{l^2}{(c/a)^2} \right]$$

you will get,

$$\sin^2 \theta = \left(\frac{\lambda^2}{4a^2} \right) \left[\frac{4}{3} \left(h^2 + hk + k^2 \right) \right]$$

OR

$$a = \frac{\lambda}{\sqrt{3} \sin \theta} \sqrt{h^2 + hk + k^2}$$

You can now perform this calculation for every *hk*0 peak, which will yield values for *a*. Similarly, values for c can be determined by looking for 00*l* type peaks. In these instances, $h = k = 0$. Thus,

$$\sin^2 \theta = \left(\frac{\lambda^2}{4a^2} \right) \left[\frac{4}{3} \left(h^2 + hk + k^2 \right) + \frac{l^2}{(c/a)^2} \right]$$

becomes

$$c = \frac{\lambda}{2\sin\theta} l$$

Worked Example

Consider the following XRD pattern for Titanium, which was collected using CuKα radiation.
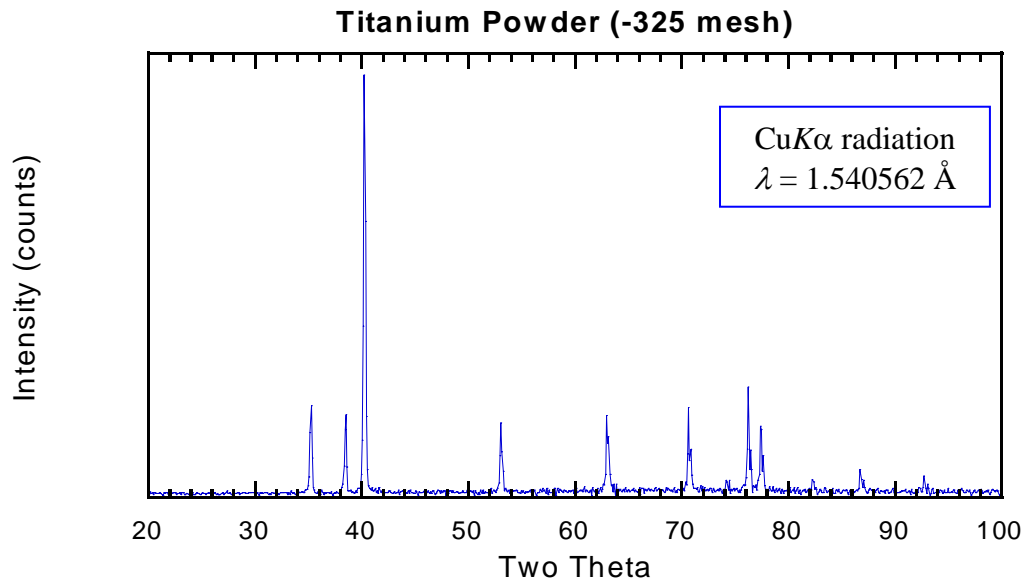
Titanium Powder (-325 mesh)

CuKα radiation
$\lambda = 1.540562$ Å

Index this pattern and determine the lattice parameters.

Steps:

(1) Identify the peaks.

(2) Determine values of $\frac{4}{3}\left(h^2 + hk + k^2\right)$ for reflections allowed by the structure factor.

(3) Determine values of $\frac{l^2}{(c/a)^2}$ for the allowed reflections and the known c/a ratio

(4) Add the solutions from parts (2) and (3) together and re-arrange them in increasing order.

(5) Use this order to assign indices to the peaks in your diffraction pattern.

(6) Look for $hk0$ type reflections and calculate a for these reflections.

(7) Look for $00l$ type reflections. Calculate c for these reflections.

Here we go!

(1) Identify the peaks.

Peak	I/Io	$\sin^2\theta$	d
35.275	21	0.0918	2.542
38.545	18	0.1089	2.334
40.320	100	0.1188	2.235
53.115	16	0.1999	1.723
63.095	11	0.2737	1.472
70.765	9	0.3353	1.330
74.250	10	0.3643	1.276
76.365	8	0.3821	1.246
77.500	14	0.3918	1.231
82.360	2	0.4335	1.170
86.940	2	0.4733	1.120
92.900	10	0.5253	1.063

(2) Determine values of $\dfrac{4}{3}\left(h^2 + hk + k^2\right)$ for reflections allowed by the structure factor.

		k			
		0	1	2	3
	0	0.000	1.333	5.333	12.000
h	1	1.333	4.000	9.333	17.333
	2	5.333	9.333	16.000	25.333
	3	12.000	17.333	25.333	36.000

(3) Determine values of $\dfrac{l^2}{(c/a)^2}$ for the allowed reflections and the known c/a ratio.

Titanium: $c/a = 1.587$

l	l^2	$l^2/(c/a)^2$
0	0	0.000
1	1	0.397
2	4	1.588
3	9	3.573
4	16	6.352
5	25	9.925
6	36	14.292

(4) Add the solutions from parts (2) and (3) together and re-arrange them in increasing order.

hkl	Pt.1+Pt.2
002	1.588
100	1.333
101	1.730
102	2.921
103	4.906
110	4.000
004	6.352
112	5.588
200	5.333
201	5.730
104	7.685
202	6.921
203	8.906
105	11.258
114	10.352
210	9.333
211	9.730
204	11.685
006	14.292
212	10.921
106	15.625
213	12.906
300	12.000
205	15.258
302	13.588

hkl	Pt.1+Pt.2
100	1.333
002	1.588
101	1.730
102	2.921
110	4.000
103	4.906
200	5.333
112	5.588
201	5.730
004	6.352
202	6.921
104	7.685
203	8.906
210	9.333
211	9.730
114	10.352
212	10.921
105	11.258
204	11.685
300	12.000
213	12.906
302	13.588
006	14.292
205	15.258
106	15.625

(5) Use this order to assign indices to the peaks in your diffraction pattern.

Peak	I/Io	$\sin^2\theta$	d (nm)	hkl	a	c	h^2+hk+k^2	l^2
35.275	21	0.091805	2.5423	100				
38.545	18	0.108941	2.3338	002				
40.320	100	0.118779	2.2351	101				
53.115	16	0.199895	1.7229	102				
63.095	11	0.273744	1.4723	110				
70.765	9	0.335278	1.3303	103				
74.250	10	0.36428	1.2763	200				
76.365	8	0.382132	1.2461	112				
77.500	14	0.39178	1.2307	201				
82.360	2	0.433526	1.1699	004				
86.940	2	0.473309	1.1197	202				
92.900	10	0.525296	1.0628	104				
				AVG				

(6) Look for *hk*0 type reflections and calculate *a* for these reflections.

Peak	I/Io	$\sin^2\theta$	d (nm)	*hkl*	*a*	*c*	h^2+hk+k^2	l^2
35.275	21	0.091805	2.5423	100	2.936		1	
38.545	18	0.108941	2.3338	002				
40.320	100	0.118779	2.2351	101				
53.115	16	0.199895	1.7229	102				
63.095	11	0.273744	1.4723	110	2.945		3	
70.765	9	0.335278	1.3303	103				
74.250	10	0.36428	1.2763	200	2.947		4	
76.365	8	0.382132	1.2461	112				
77.500	14	0.39178	1.2307	201				
82.360	2	0.433526	1.1699	004				
86.940	2	0.473309	1.1197	202				
92.900	10	0.525296	1.0628	104				
				AVG	2.943		c/a:	

(7) Look for 00*l* type reflections. Calculate *c* for these reflections.

Peak	I/Io	$\sin^2\theta$	d (nm)	*hkl*	*a*	*c*	h^2+hk+k^2	l^2
35.275	21	0.091805	2.5423	100	2.936		1	
38.545	18	0.108941	2.3338	002		4.668		4
40.320	100	0.118779	2.2351	101				
53.115	16	0.199895	1.7229	102				
63.095	11	0.273744	1.4723	110	2.945		3	
70.765	9	0.335278	1.3303	103				
74.250	10	0.36428	1.2763	200	2.947		4	
76.365	8	0.382132	1.2461	112				
77.500	14	0.39178	1.2307	201				
82.360	2	0.433526	1.1699	004		4.680		16
86.940	2	0.473309	1.1197	202				
92.900	10	0.525296	1.0628	104				
				AVG	2.943	4.674	c/a:	1.588

Pretty good correlation with ICDD value. Actual *c/a* for Titanium is <u>1.5871</u>

This method, though effective for most powder XRD data, can yield the wrong results if XRD peaks are missing from your XRD pattern. In other words, missing peaks can cause you to assign the wrong *hkl* values to a peak. Other methods should be available.

Analytical Method for Non-Cubic Crystals

To accurately apply this technique, one must first consider our altered plane spacing equation:

$$\sin^2 \theta = \left(\frac{\lambda^2}{4a^2}\right)\left[\frac{4}{3}\left(h^2 + hk + k^2\right) + \frac{l^2}{(c/a)^2}\right]$$

Since a and c/a are constants for any given pattern, we can re-arrange this equation to:

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

where $A = \frac{\lambda^2}{3a^2}$ and $C = \frac{\lambda^2}{4c^2}$. Since h, k, and l are <u>always</u> integers, the term in parentheses, $h^2 + hk + k^2$ can only have values like 0, 1, 3, 4, 7, 9, 12... and l^2 can only have values like 0, 1, 4, 9,....

We need to calculate $\sin^2 \theta$ for each peak, divide each $\sin^2 \theta$ value by the integers 3, 4, 7, 9... and look for the common quotient (*i.e.*, the $\sin^2 \theta / n$ value that is equal to one of the observed $\sin^2 \theta$ values). The $\sin^2 \theta$ values representing this common quotient refer to $hk0$ type peaks. Thus this common quotient can be tentatively assigned as A.

We can now re-arrange terms in our modified equation to obtain C. This is done as follows:

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

$$\Downarrow$$

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

We get the value of C by subtracting from each $\sin^2 \theta$ the values of $n \cdot A$ (*i.e.*, A, $3A$, $4A$, $7A$,...) where A is the common quotient that we identified above. Next, we need to look for the remainders that are in the ratio of 1, 4, 9, 16..., which will be peaks of the $00l$ type. We can determine C from these peaks. The remaining peaks are neither $hk0$-type nor $00l$ type. Instead they are hkl-type. They can be indexed from a combination of A and C values. Let's do an example.

Worked Example

Steps:
   (1) Identify the peaks and calculate $\sin^2 \theta$ for each peak.
   (2) Divide each $\sin^2 \theta$ value by the integers 3, 4, 7, 9....
   (3) Look for the common quotient.
   (4) Let the lowest common quotient represent A.
   (5) Assign $hk0$ type indices to peaks.
   (6) Calculate $\sin^2 \theta$ - nA where $n = 1, 3, 4, 7$....

(7) Look for the lowest common quotient. From this we can identify 00*l* type peaks. Recall, that 001 is not allowed for hexagonal systems. The first 00*l* type peak will be 002. We can calculate *C* from:
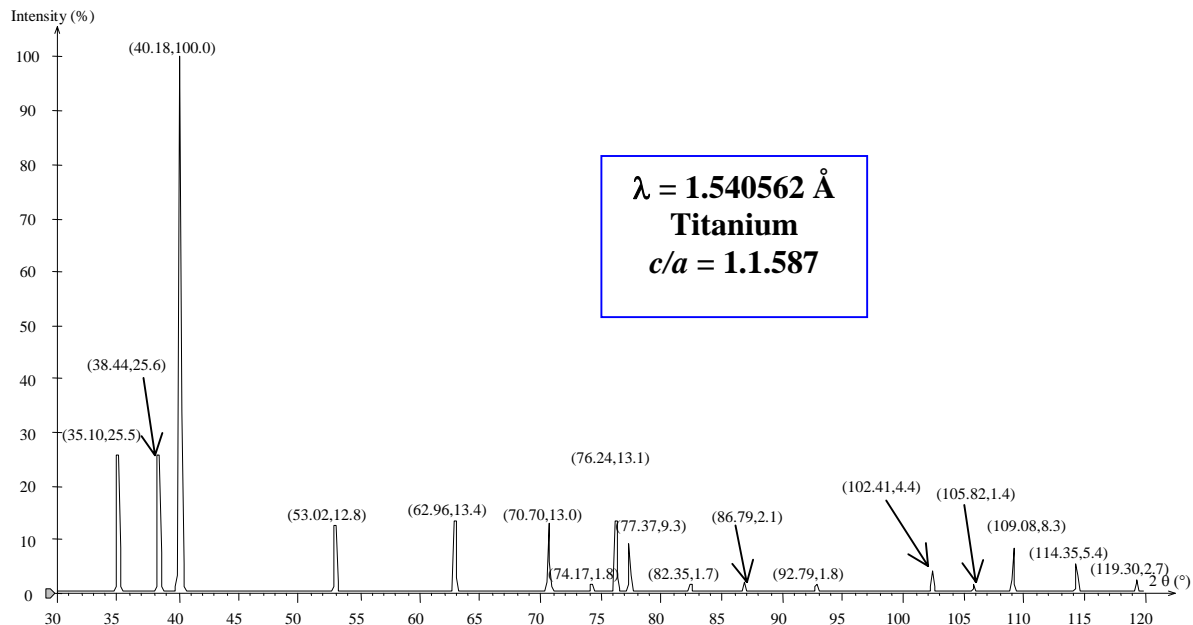
$$C \cdot l^2 = \sin^2 \theta - A \cdot (h^2 + hk + k^2)$$

(8) Look for values of $\sin^2 \theta$ that increase by factors of 4, 9… (this is because *l* = 1, 2, 3… and l^2 = 1, 4, 9…). Peaks exhibiting these characteristics are 00*l* type peaks, which can be assigned the indices 004, 009, etc…). Also note that the values of $\sin^2 \theta$ will be some integral number times the value observed in (7) which indicates the indices of the peak

(9) Peaks that are neither *hk*0 nor 00*l* can be identified using combinations of our calculated *A* and *C* values.

(10) Calculate the lattice parameters from the values of *A* and *C*.

Confused yet? You could be. I was the first time I learned these things. Let me show you an example that should make all things clear.

Here we go!

Consider the diffraction pattern for Titanium as shown below. This one is a little different than the specimen that we analyzed above.

Intensity (%)

λ = 1.540562 Å
Titanium
c/a = 1.1.587

(40.18,100.0)
(38.44,25.6)
(35.10,25.5)
(76.24,13.1)
(102.41,4.4)
(105.82,1.4)
(53.02,12.8)
(62.96,13.4)
(70.70,13.0)
(77.37,9.3)
(86.79,2.1)
(109.08,8.3)
(74.17,1.8)
(82.35,1.7)
(92.79,1.8)
(114.35,5.4)
(119.30,2.7)
2 θ (°)

Steps to success:

1. Calculate $\sin^2\theta$ for each peak
2. Divide each $\sin^2\theta$ value by integers 3, 4, 7…
    (from h^2+hk+k^2 allowed by the structure factor)
3. Look for lowest common quotient.
4. Let lowest common quotient = A.
5. Peaks with lowest common quotient are $hk0$ type peaks. Assign allowed $hk0$ indices to peaks.

Peak	I/Io	$\sin^2\theta$	$(\sin^2\theta)/3$	$(\sin^2\theta)/4$	$(\sin^2\theta)/7$	$(\sin^2\theta)/9$	$(\sin^2\theta)/12$	hkl		$(\sin^2\theta)/LCQ$
35.100	25.5	**0.0909**	0.0303	0.0227	0.0130	0.0101	0.0076	100		1.0
38.390	25.6	0.1081	0.0360	0.0270	0.0154	0.0120	0.0090		= 3 x A	1.2
40.170	100	0.1179	0.0393	0.0295	0.0168	0.0131	0.0098			1.3
53.000	12.8	0.1991	0.0664	0.0498	0.0284	0.0221	0.0166		= 4 x A	2.2
62.940	13.4	0.2725	**0.0908**	0.0681	0.0389	0.0303	0.0227	110		3.0
70.650	13	0.3343	0.1114	0.0836	0.0478	0.0371	0.0279			3.7
74.170	1.8	0.3636	0.1212	**0.0909**	0.0519	0.0404	0.0303	200		4.0
76.210	13.1	0.3808	0.1269	0.0952	0.0544	0.0423	0.0317			4.2
77.350	9.3	0.3905	0.1302	0.0976	0.0558	0.0434	0.0325			4.3
82.200	1.7	0.4321	0.1440	0.1080	0.0617	0.0480	0.0360			4.8
86.740	2.1	0.4716	0.1572	0.1179	0.0674	0.0524	0.0393		= 7 x A	5.2
92.680	1.8	0.5234	0.1745	0.1308	0.0748	0.0582	0.0436			5.8
102.350	4.4	0.6069	0.2023	0.1517	0.0867	0.0674	0.0506			6.7
105.600	1.4	0.6345	0.2115	0.1586	**0.0906**	0.0705	0.0529	210		7.0
109.050	8.3	0.6632	0.2211	0.1658	0.0947	0.0737	0.0553			7.3
114.220	5.4	0.7051	0.2350	0.1763	0.1007	0.0783	0.0588			7.8
119.280	2.7	0.7445	0.2482	0.1861	0.1064	0.0827	0.0620			8.2

$A =$ **0.0908**

Indices correspond to:
$h^2+hk+k^2 = 1, 3, 4, 7…$
or
$hk = 10, 11, 20, 21$

6. Subtract from each $\sin^2\theta$ value $3A$, $4A$, $7A$...
   (from h^2+hk+k^2 allowed by the structure factor)

7. Look for lowest common quotient (LCQ). From this you can identify $00l$-type peaks.
   The first allowed peak for hexagonal systems is 002. Determine C from the equation:
   $$C \cdot l^2 = \sin^2\theta - A\,(h^2+hk+k^2)$$
   since $h=0$ and $k=0$, then:
   $$C = LCQ/l^2 = \sin^2\theta/l^2$$

8. Look for values of $\sin^2\theta$ that increase by factors of 4, 9, 16... (because l = 1,2,3,4..., l^2=1,4,9,16...)
   The peaks exhibiting these characteristics are $00l$-type peaks (002...).

We identify the 4th peak as 102 because we observe the LCQ for $\sin^2\theta$-1A. Recall that the 1 comes from the quadratic form of Miller indices (i.e., $h^2+hk+k^2=1$).

We identify the 8th peak as 112 because we observe the LCQ for $\sin^2\theta$-3A. Recall that the 1 comes from the quadratic form of Miller indices (i.e., $h^2+hk+k^2=3$).

We identify the 11th peak as ...

etc...

λ
1.54062

Peak	I/Io	$\sin^2\theta$	$\sin^2\theta$-A	$\sin^2\theta$-3A	$\sin^2\theta$-4A	$\sin^2\theta$-4A	h	k	l	C=LCQ/l²	l²=LCQ/C
35.100	25.5	0.0909					1	0	0		
38.390	25.6	**0.1081**	0.0173				**0**	**0**	**2**	0.0270	4.0
40.170	100	0.1179	0.0271								
53.000	12.8	0.1991	**0.1083**				1	0	2	0.0271	
62.940	13.4	0.2725	0.1817	0.0001			1	1	0		
70.650	13	0.3343	0.2435	0.0618							
74.170	1.8	0.3636	0.2728	0.0911	0.0003		2	0	0		
76.210	13.1	0.3808	0.2900	**0.1083**	0.0175		1	1	2	0.0271	
77.350	9.3	0.3905	0.2997	0.1180	0.0272						
82.200	1.7	**0.4321**	0.3413	0.1597	0.0688		**0**	**0**	**4**	0.0270	16
86.740	2.1	0.4716	0.3807	0.1991	**0.1083**		2	0	2	0.0271	
92.680	1.8	0.5234	0.4326	0.2509	0.1601						
102.350	4.4	0.6069	0.5161	0.3345	0.2436						
105.600	1.4	0.6345	0.5436	0.3620	0.2711		2	1	0		
109.050	8.3	0.6632	0.5724	0.3907	0.2999	0.0274					
114.220	5.4	0.7051	0.6143	0.4326	0.3418	0.0693					
119.280	2.7	0.7445	0.6537	0.4721	0.3812	**0.1087**					

LCQ = 0.1083

This peak is 004 because sqrt(LCQ/C)=4

9. Peaks that are not $hk0$ or $00l$ can be identified using combinations of A and C values.
   This is accomplished by considering:

   $\sin^2\theta = C \cdot l^2 + A(h^2 + hk + k^2)$

   Cycle through allowed values for l and hk, and compare $\sin^2\theta$ value to labeled peaks.

10. Once A and C are known, the lattice parameters can be calculated.

$\sin^2\theta = C \cdot l^2 + A \cdot (h^2 + hk + k^2)$

A	C
0.0908	0.0270

Peak	I/Io	$\sin^2\theta$	h	k	l	$\sin^2\theta$ Calculated
35.100	25.5	0.0909	1	0	0	0.0908
38.390	25.6	0.1081	0	0	2	0.1081
40.170	100	0.1179	1	0	1	0.1179
53.000	12.8	0.1991	1	0	2	0.1989
62.940	13.4	0.2725	1	1	0	0.2725
70.650	13	0.3343	1	0	3	0.3341
74.170	1.8	0.3636	2	0	0	0.3633
76.210	13.1	0.3808	1	1	2	0.3806
77.350	9.3	0.3905	2	0	1	0.3903
82.200	1.7	0.4321	0	0	4	0.4324
86.740	2.1	0.4716	2	0	2	0.4714
92.680	1.8	0.5234	1	0	4	0.5232
102.350	4.4	0.6069	2	0	3	0.6065
105.600	1.4	0.6345	2	1	0	0.6358
109.050	8.3	0.6632	2	1	1	0.6628
114.220	5.4	0.7051	1	1	4	0.7049
119.280	2.7	0.7445	2	1	2	0.7439

10. Once A and C are known, the lattice parameters can be calculated.

a	c	c/a
2.951	4.686	1.588

HOW DO THESE VALUES COMPARE WITH THOSE FROM THE ICDD CARDS?

X-ray Characteristics

After gaining adequate background (document enclosed. Feel free to find your own resource) in the generation and properties of X-rays, the following tasks need to be performed:

1. Obtain the X-ray spectrum from a Cu X-ray tube after reading instructions provided in the document titled, 'Characteristic X-rays of Copper'.
2. Establish the Duane-Hunt displacement law and obtain the value of the Planck's constant after reading the appropriate document.
3. Establish the similarity between Bremsstrahlung radiation and back-body radiation. (Read paper by C. T. Ulrey. Study relevant portions more carefully. For eg. Section on discussion of results)
4. Determine the X-ray equivalent of Wein's displacement law.
5. Monochromatize the X-ray beam after reading the appropriate document.

Please note: The instructions concerning the hardware and software provided by the manufacturer has to be strictly followed.

Related topics

X-ray tube, bremsstrahlung, characteristic X-rays, energy levels, crystal structures, lattice constant, interference, Bragg equation.

Principle and task

By means of an x,y-recorder, X-ray spectra are recorded as a function of the anode voltage. From the short-wave length limit of the bremsspectrum, the Duane-Hunt displacement law and Planck's "quantum of action" are determined.

Equipment

X-ray unit, w. recorder output	09056.97	1
Counter tube, type A, BNC	09025.11	1
Pulse rate meter	13622.93	1
xyt recorder	11416.97	1
Screened cable, BNC, l 750 mm	07542.11	1
Connecting cord, 1000 mm, red	07363.01	2
Connecting cord, 1000 mm, blue	07363.04	2

Problems

1. The intensity of the X-rays emitted by the copper anode at various anode voltages is to be drawn as a function of the Bragg angle by an x,y-recorder.

2. The short wavelength limit (or maximum energy) of the bremsspectrum is to be determined for the spectra of 1.

3. The Duane-Hunt displacement law and Planck's "quantum of action" are to be verified by these measurements.

Set-up and procedure

The experiment is set up as shown in Fig. 1. The aperture of $d = 2$ mm is introduced into the outlet of X-rays.

By pressing the "zero key", the counter tube and crystal holder device are brought into starting position. The crystal holders are mounted with the crystal surface set horizontally. The counter tube, with horizontal slit aperture, is mounted in such a way that the mid-notch of the counter tube closes onto the back side of the holder.

Typical settings of the peripheral equipment are:

Pulse rate meter:	Couter tube voltage	500 V
	Sensitivity	10^5 imp/min
	Time constant	0.5 or 1.5 s
x,y-recorder:	x-axis (ϑ-axis)	1 V/cm, additionally variable
	y-axis (intensity)	0.1 V/cm, additionally variable

The output of the pulse rate meter is connected to the y-input of the recorder. The angle-proportional direct-current voltage (0.1 V/degree) of the X-ray unit lies on the x-input. The plotting of the spectra is performed at a slow velocity of rotation (positions "V_1" and "Auto"), crystal and counter tube must rotate in synchronization.

First, at maximum anode voltage, a general spectrum (Fig. 2) is drawn. After, that, the bremsspectra for various anode voltages are recorded up to the K_β-line. (Fig. 3)

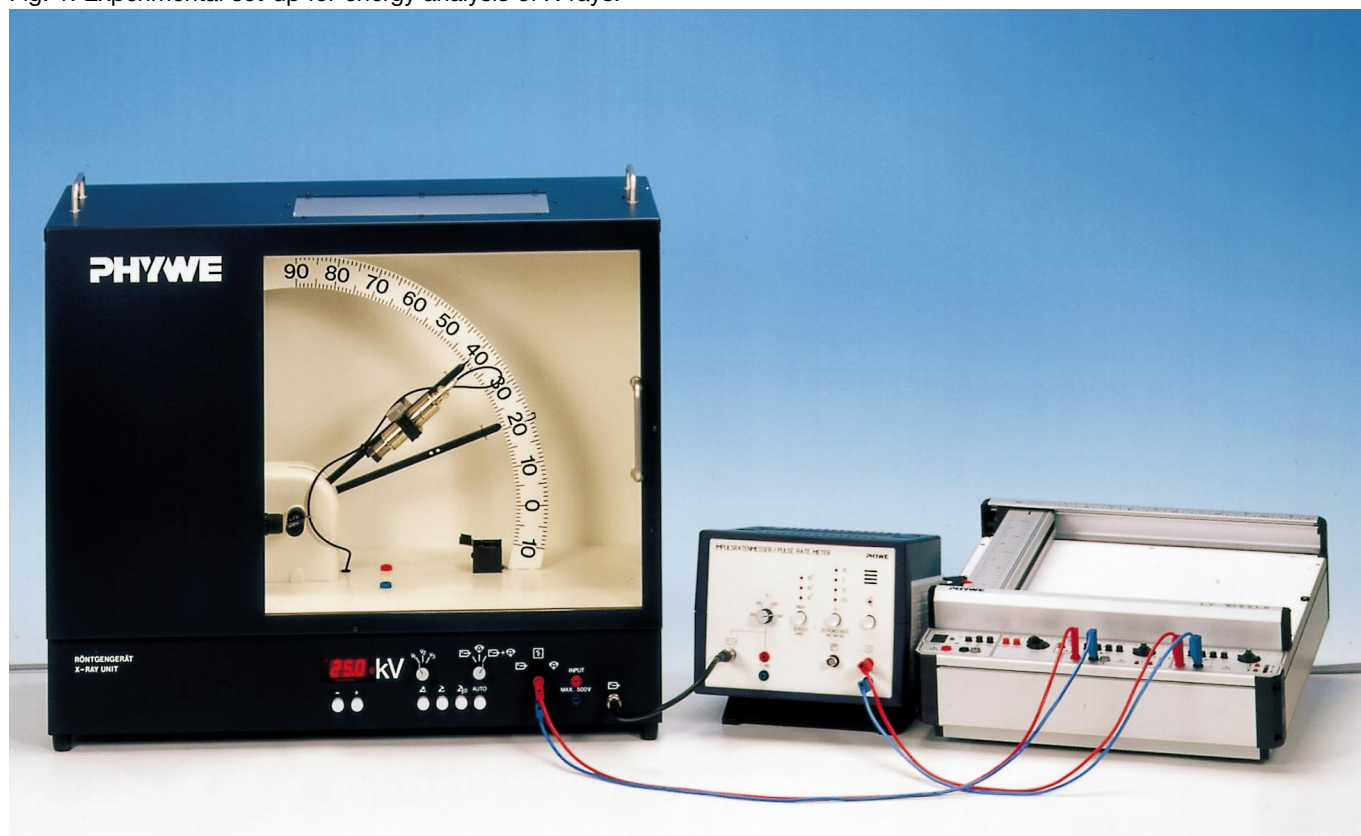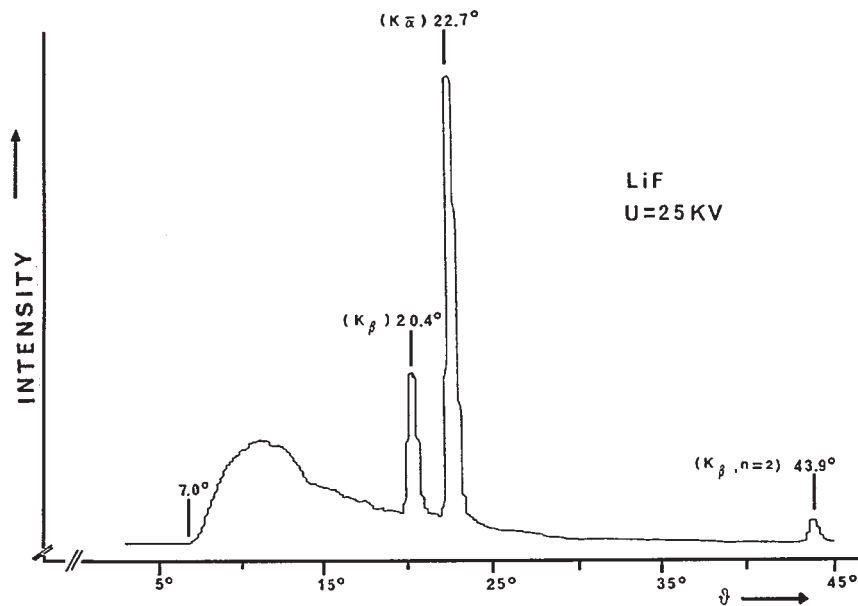Fig. 1: Experimental set-up for energy analysis of X-rays.

Fig. 2: Copper X-ray spectrum with LiF-analyzer.

In order to obtain exact angle determination of the brems-spectra, the sensitivity of the x-channel must be increased accordingly and calibrated carefully; likewise, the zero-line of the y-axis must be displaced for each new measurement.

Note:

The counter tube should never be exposed to primary radiation for any longer period of time.

Theory and evaluation

A positve voltage, lying on the anode of the x-ray tube, accel-erates the electrons emitted from the cathode with a rather low energy distribution.

In reaching the anode, the electrons have the kinetic energy:

$$E_{kin} = eU \quad (e = \text{elementary charge}) \qquad (1)$$

At arrival, a part of the electrons will be progressively slowed down, thus converting their kinetic energy into electro-mag-netic radiation with continuous energy distribution. This bremsspectrum has a short wavelength limit which has been determined in that the entire kinetic energy of some electrons is converted into radiation in just on step. In 1915, Duane and Hunt empirically found that the product of anode voltage and the shortest wavelength λ_{min} is constant, and that the follow-ing formula holds:

$$U \cdot \lambda_{min} \sim 1.25 \cdot 10^{-6} \text{ V} \cdot \text{m} \qquad (2)$$

This relationship can easily be derived from Einstein's energy equation, according to which:

$$E_{kin} = eU = hf_{max} = h \cdot \frac{c}{\lambda_{min}} \qquad (3)$$

where $h = 6.6256 \cdot 10^{-34}$ Js   Planck's constant
             $c = 2.9979 \cdot 10^8$ ms^{-1} velocity of light
             $e = 1.6021 \cdot 10^{-19}$ As   elementary charge

The shortest wavelength is calculated to be:

$$\lambda_{min} = 1.2398 \cdot 10^{-6} \frac{1}{U} \text{ V} \cdot \text{m}$$

The analysis of the polychromatic X-rays is carried out by the use of a monocrystal. If the X-rays impinge under a glancing angle ϑ, constuctive interference will only appear in reflection if the paths of the partial waves reflected on the lattice planes differ by one or more wavelengths. This situation is described by the Bragg equation.

This situation is explained by the Bragg equation:

$$2d \sin \vartheta = n \cdot \lambda \qquad (4)$$

(LiF-lattice constant $d = 201.4$ pm, n = order of diffraction)

The short wavelength limit of the bremsspectrum is deter-mined by the appertaining glancing angle ϑ. In conjunction with (4), λ_{min} can be calculated.

In Fig. 5, λ_{min} is represented as a function of the reciprocal value of the anode voltage.
The slope of the resulting line is:

$$m = \frac{\lambda_{min}}{1/U} = (1.233 \pm 0.007) \cdot 10^{-6} \text{ V} \cdot \text{m}$$

This formula is acceptably consistent with the Duane-Hunt displacement law.

By using the same measured curves, it is also possible to determine Planck's "quantum of action".

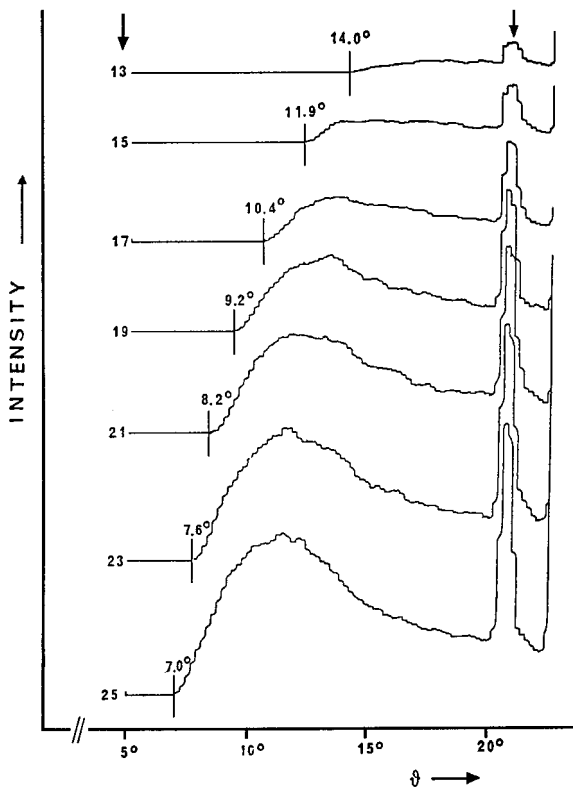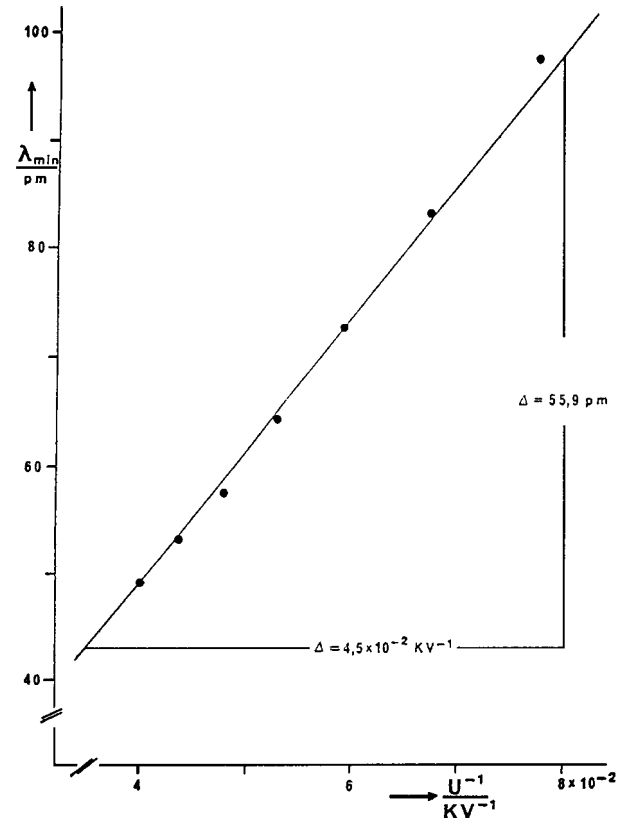Fig. 3: Bremsspectra as functions of the anode voltage.

Fig. 5: Duane-Hunt displacement law. λ_{min} as a function of reciprocal anode voltage.

From (3) and (4) follows:

$$U = \frac{h \cdot c}{2 \cdot e \cdot d \cdot \sin \vartheta} \qquad (5)$$

In Fig. 6, the anode voltage is drawn as a function of (sin ϑ^{-1}). Using the slope m of the resulting line, it is possble to attain:

$$h = m \cdot \frac{2 \cdot e \cdot d}{c} = (6.59 \pm 0.04) \cdot 10^{-34} \, Js; \frac{\Delta h}{h} = \pm 0.5\%$$

In conjunction with (5) and glancing angle values from Fig. 2, the energies of the characteristic copper X-ray lines can be calculated to be:

n = 1	E-K$_{\overline{\alpha}}$	= 7.98 KeV
	K-K$_{\beta}$	= 8.83 KeV
n = 2	E-K$_{\beta}$	= 8.88 KeV

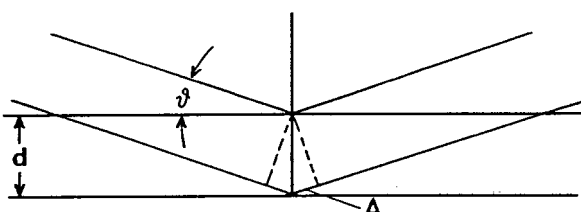These values are in good approximation with the literature values. (See also experiment 5.4.1)

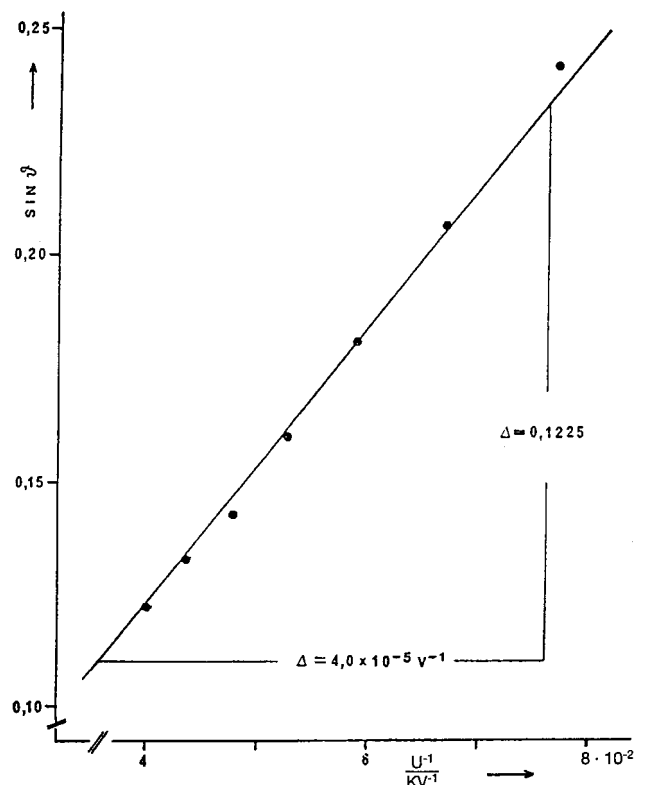Fig. 4: Bragg scattering on the lattice planes.

Fig. 6: Planck's "quantum of action". sin ϑ_{min} as a function of reciprocal anode voltage.