GLY 4200

X-Rays and X-ray Mineralogy

X-radiation is a type of electromagnetic radiation, like visible light, UV, IR, etc. The range in wavelength from approximately 10^{-6} to 10^{-1} nm. They were first discovered by Wilhelm Conrad Roentgen in 1895. In 1912, Friedrich, Knipping, and von Laue first demonstrated that X-rays were diffracted by passage through a crystal. Since diffraction is most effective when the wavelength of the radiation is about the same as the spacing in the diffraction grating (here, a crystal) the wavelength of x-rays tells us something about the spacing of atoms in a crystal.

Before examining the behavior of X-rays in crystals, we should review some properties common to all electromagnetic radiation.
The Einstein equation is one such property:

$$E = h\upsilon = hc/\lambda$$

where E = energy, h = Planck's constant, υ = frequency, c = speed of light, and λ = wavelength. X-rays and heat are generated when electrons hit a target. If all the kinetic energy of an electron is converted to X-ray quanta, we can rewrite the equation as:

$$eV = hc/\lambda$$

where e = charge on the electron, and V = voltage. Replacing constants with their numerical values and expressing voltage in kilovolts, we get:

$$\lambda_{(nm)} = 1.24/kV,$$

where kV = kilovolts. This is the minimum wavelength of radiation that may be generated by a given difference in voltage between a cathode and an anode. In practice, most electrons will be involved in several collisions on the way from the filament to the target. They lose some energy in each collision, so the actual output of an X-ray tube will be a continuous spectrum of radiation, with the

shortest wavelength (highest energy) given by the above equation. Figure 1 shows a diagram of the intensity of radiation versus wavelength for excitation potentials of 20, 30, and 40 kilovolts. This type of radiation is known as white radiation, because it is a continuous spectrum of radiation, like white light. (Fig. 136a, p141, Battay)

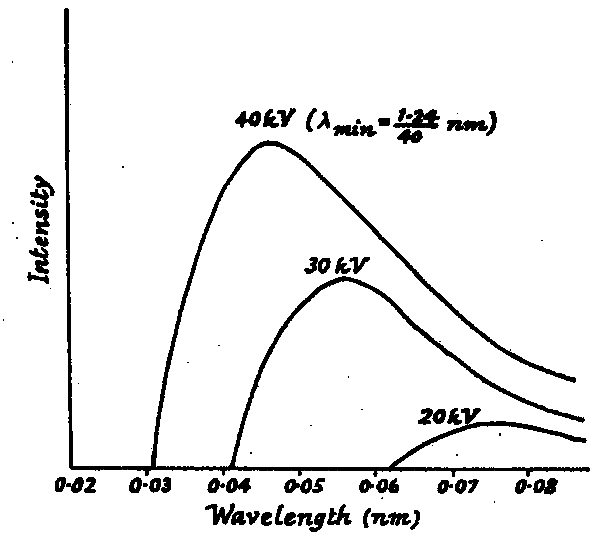

Figure 1 - Effect of excitation potential on minimum wavelength

X-rays with shorter wavelengths are more energetic, and more penetrating. They art less absorbed, and do less damage in biologic systems, and are called "hard." Hard X-rays are used for medical and dental work. Long wavelength X-rays are called "soft" radiation, are more easily absorbed in biologic systems, and are more damaging. Soft X-rays are used in crystallography. However, all X-ray can and does cause damage to tissue exposed to it. When working with X-rays, it is very important that all necessary steps be taken to insure that no one is exposed to an X-ray beam, directly or indirectly.

Figure 2 shows a schematic diagram of a typical X-ray tube. A current applied to the filament allows electrons to "boil" off. They are focused by the focusing shields, which have an applied negative potential. They are accelerated toward the target by the excitation potential, an applied voltage of 20-100 kilovolts. The entire tube is evacuated, like an incandescent light bulb. The electrons accelerate in flight, and hit the target with a great deal of energy. The

collision with target atoms produces X-rays. The X-rays are emitted through four ports, 90° apart. The ports are covered with a light metal, usually beryllium. Be is very light so it does not adsorb many x-rays. It is not too reactive, so can be exposed to air. Lithium, which is even lighter, would react quickly with air. The target is a piece of a particular metal, such as copper or molybdenum. Running through the target are channels through which water flows continually. This is necessary in order to cool the target. If the target weren't cooled, it would quickly melt and destroy the tube.
(Fig. 135, p141, Battay)

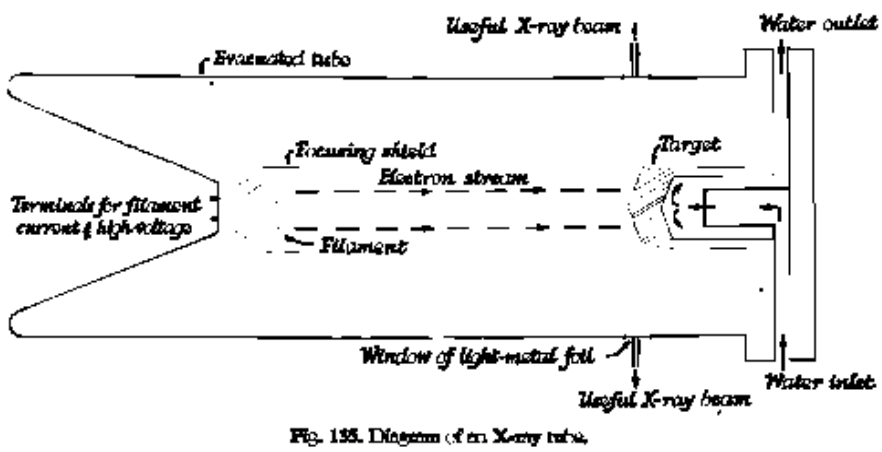

Figure 2 - X-ray tube schematic diagram

<u>Characteristic Radiation</u>

Electrons hitting atoms in the target dislodge electrons from the various electron shells of the atom. Recall from the beginning of the course that X-ray terminology uses the letters K, L, M, N, O,... to represent the n = 1, 2, 3, 4, 5, ... shells, respectively. An incoming electron may eject a 1s electron completely. It place is quickly taken by an electron falling from the L (n=2) or M (n=3) shells. Such radiation is known as K_α or K_β radiation. Similarly, radiation created by electrons falling from the M or N shells to the L shell is known as L_α or L_β radiation. See figure 3. (Fig.136b, p141, Battay)

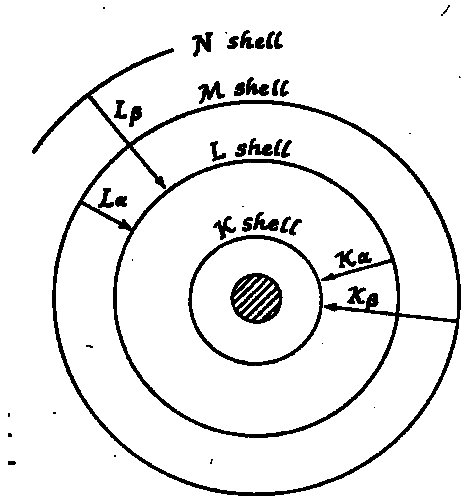

Figure 3 - Electron infall from outer to inner shells

X-rays produced in this manner have wavelengths corresponding to the energy-change involved in falling from a particular high level to a specific lower level. The energy values are different for each element. The resulting wavelengths, or <u>lines</u>, are characteristic lines of the atom producing it. Such characteristic radiation is superimposed on the white radiation which is always present. They stand out as intensity peaks in the spectrum of intensity vs. wavelength (see Figure 4). (Fig. 137a, p142, Battay)

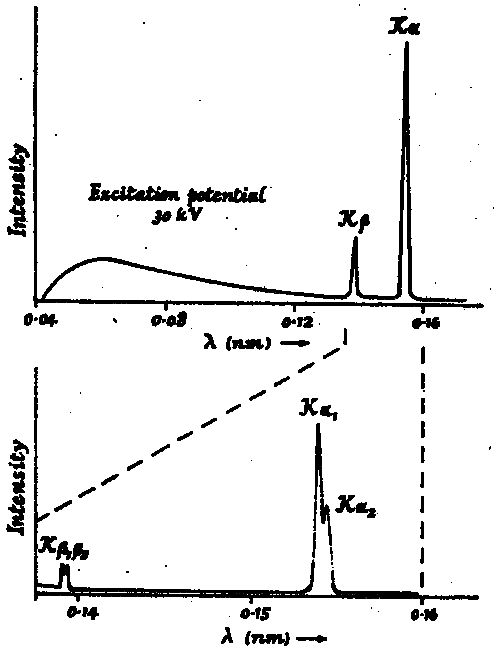

Figure 4 - X-ray spectrum of Cu

The characteristic peaks for a particular element corresponding to different infalls from out to inner shells can be shown in a diagram such as Figure 5, which is for copper. Note that there are two values of K_α radiation, corresponding to transitions from 2p to 1s shells. The 2p levels are slightly split, leading to $K_{\alpha 1}$ and $K_{\alpha 2}$ peaks. Note that $K_{\alpha 1}$ is assigned to the more energetic transition. K_β peaks correspond to transitions from 3p to 1s. (Fig. 137b, p142, Battay)

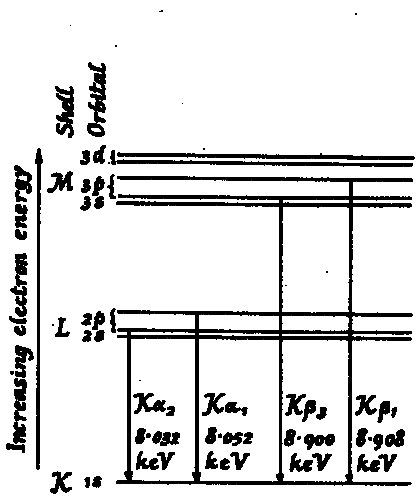

Figure 5 - Energy-level diagram for electron transitions in Cu

From Figure 4, we can see that the K_β peaks are more energetic (shorter wavelength) than the K_α peaks, but the K_α peaks are far more intense. Intensity reflects the probability of aa particular transition, and the L to K shell transition is far more probable than the M to K transition. If we could isolate the K_α radiation, we would have a source of nearly monochromatic energy. Fortunately, the way in which X-rays interact with metals provides a very convenient method for generating nearly monochromatic radiation.

X-rays of different wavelengths will be absorbed to different degrees by different metals. Absorption is controlled by the same rules that govern emission. X-rays with just enough energy to dislodge inner shell electrons, and those with higher energies (shorter wavelengths) will be absorbed strongly by interactions with a metal absorber. Those whose energy is insufficient to dislodge inner electrons will pass through the absorber will little interaction. A

thin metal foil with an absorption edge just higher in energy than the K_α peaks will filter out the K_β peaks and the short wavelength edge of the continuous radiation. The absorption edge corresponds to the minimum energy needed to dislodge an inner shell electron. The element with the next lower atomic number than the target will have an absorption edge just higher than the K_α peaks of the target. Thus, for copper, a nickel absorber is used, as shown in figure 6. The resulting X-ray beam, after filtration, has a spectrum in which the 0.154 nm peak is overwhelmingly dominating. (Fig. 138, p143, Battay)

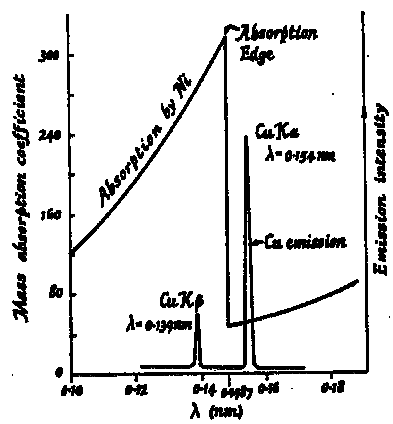

Figure 6 - Absorption edge of Ni in relation to the emission spectrum of Cu

Diffraction of X-rays by crystals

X-ray wavelengths used in crystallography are less than the distance between lattice points, but are of the same order of magnitude as lattice point spacings. In a manner very similar to the way light is diffracted from a grating of closely-spaced lines etched on a diffraction grating, X-rays are diffracted from the three-dimensional array of equivalent points in a crystal lattice. In the diffraction of light, each aperture in the grating acts as a new source of rays. An example of the visible light diffraction effect in crystals is the Play of Colors seen in feldspars, when the spacing between ex-solution lamellae is the same as the wavelength of light hitting it. Crystals consist of three-dimensional structures with characteristic periodicities, called identity periods, along each crystallographic axis. X-rays striking such 3-D arrangements cause electrons in their path to vibrate with the frequency of the incident X-radiation. The vibrating electrons absorb some of the X-ray energy and act as a source of new waves fronts by emitting energy of the same wavelength. The process is called

scattering. Generally, the scattered waves interfere destructively, but in specific directions, reinforcement occurs. The cooperative scattering from a three-dimensional grating, where spherical wave shells interfere constructively producing wave fronts that are in phase, is known as diffraction. Figure 7 shows the effect. (Fig. 7.34, p311, Klein)

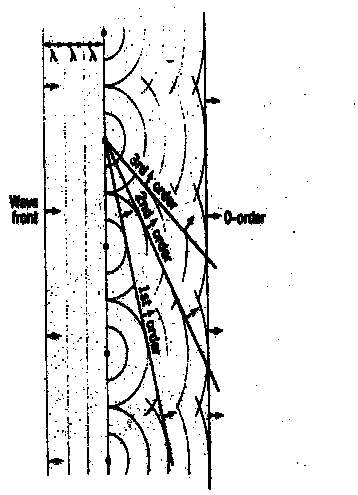

Figure 7 - Scattering of X-rays by a row of equally spaced, identical atoms

Shortly after Friedrich, Knipping, and von Laue demonstrated in 1912 that X-rays were diffracted in a crystal, William L. Bragg was able to show that X-rays behaved as though they were reflected from planes of atoms making up the crystal structure. Scattering from a medium continuous in two dimensions, such as a plane of atoms in a crystal structure, is called reflection. However, it if common for the terms diffraction and reflection to be interchanged.

If a train of X-rays strikes a set of atomic planes at angle θ, the X-rays will penetrate the layers, but will also be reflected by them. Figure 8 shows the effect. Ray *a* will be reflected by the first layer, ray *b* by the second layer, ray *c* by the third layer, etc. The reflected rays from the layers all take the same direction. Normally, they will be out of phase, and they will destroy each other. Reinforcement can only occur if the path difference between rays reflected from successive planes is an even number of wavelengths. (Fig. 139a, p143, Battay)

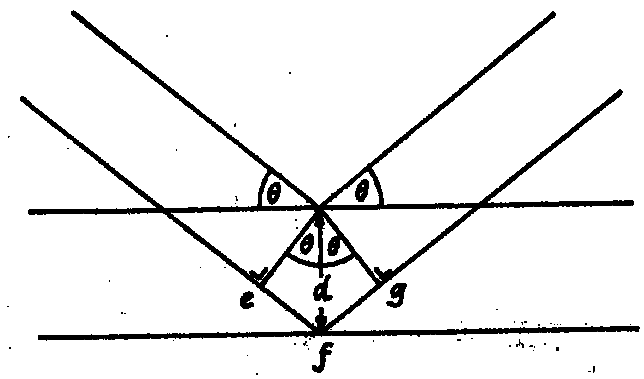

Figure 8 - Path difference = 2d sinθ

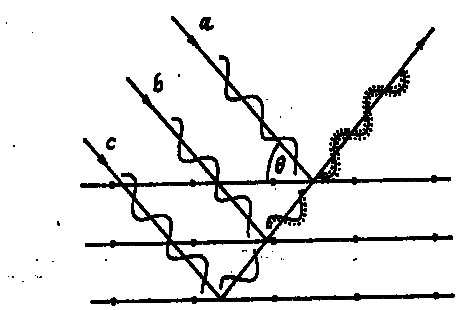

Figure 9 - Condition for reflection

Figure 9 shows the path difference between rays reflected at successive planes to be ef + fg. We can also see that

$$ef = fg = d \sin \theta$$

Therefore the condition for successful reinforcement is given by the <u>Bragg Equation</u>,

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

where n is an integer, d is the distance between successive parallel planes (the "interplanar" spacing), and θ = <u>glancing angle of incidence</u>. (Note that the

glancing angle of incidence, used in X-ray crystallography, is the complement of the angle of incidence used in optics). From the Bragg equation, it is evident that a family of planes with a particular spacing can reflect X-rays of a given wavelength at one angle of incidence only. Unlike the optical case, where reflection from a surface can occur at any angle of incidence, X-ray reflection only occurs when the Bragg equation is satisfied. (Fig. 139b, p143, Battay)

Diffraction for a specific value of $n\lambda$ gives specific value of θ, which results in a cone of diffracted X-rays, as shown in figure 10.

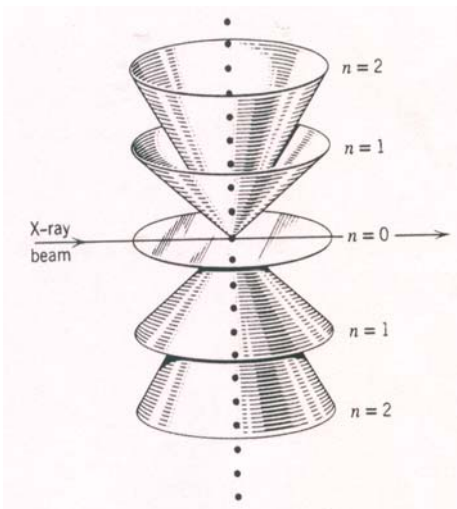

Figure 10 - Diffraction cones from a row of atoms

The scattered rays will be in phase for the same angle on the other side of the beam, so there will actually be two cones. Each value of n gives another set of cones, which collectively are nested. (Fig. 7.36, p312, Klein)

A three-dimensional lattice has three axial directions. Along each axial direction there is a characteristic periodicity of scattering points, each of which is capable of generating a series of nested cones with characteristic apical angles. Diffraction cones from three non-coplanar rows of scattering may or may not intersect each other. Only when three cones intersect in aa common line is there a diffraction beam. Max von Laue showed that the geometry of the three intersecting cones can be expressed as three independent equations, today called the von Laue equations. The three cone angles (θ_1, θ_2, and θ_3) must define a common direction, as shown by the path of the arrow in figure 11. This represents a simultaneous solution of all three von Laue equations. The Bragg Equation expresses the same thing as the simultaneous solution of the von Laue equations in a much simpler style, and the von Laue equations are thus much

less commonly used. (Fig. 7.37, p312, Klein)

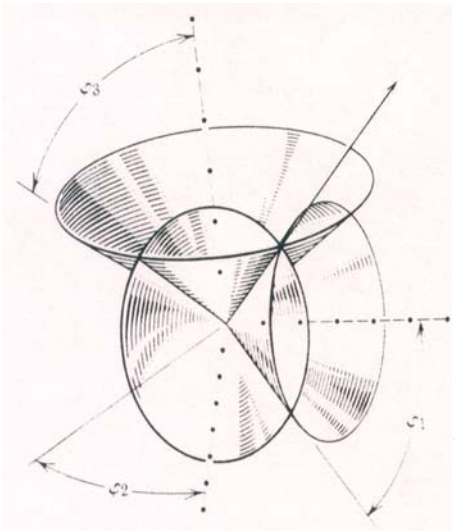

Figure 11 - Diffraction cones from three noncoplanar rows of scattering atoms, intersecting in a common line

The Bragg equation can be used to calculate the interplanar spacing, if λ is known and θ is measured. A typical experimental instrument is shown in Figure 12. An incident beam enters a camera, strikes the specimen, and is diffracted by various families of planes of atoms. The diffracted X-rays are recorded on a stripe of film that circles the specimen. A beam stop is used to keep radiation from escaping the camera and endangering those around it. (Fig. 141, p145, Battay)

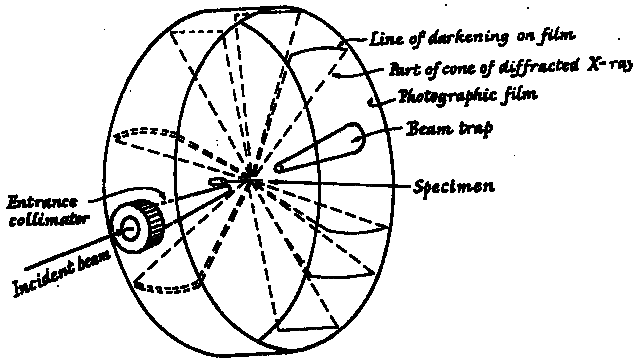

Figure 12 - Arrangement for a powder photograph

The experimental measurement is done by measuring the angle from the position of the incident beam to the line corresponding to diffraction from a single family of planes. As shown in Figure 13, the angle measured is actually 2θ. (Fig. 142b, p145, Battay)

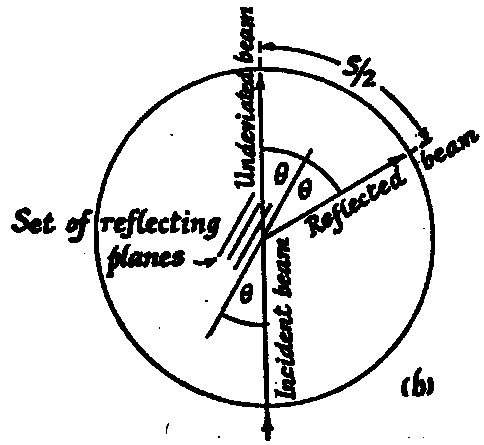

Figure 13 - Diagram showing the formation of lines from a powder

X-ray diffraction may be used with either single crystals, or with powders, which are collections of large numbers of randomly oriented single crystals. Each type of analysis is useful in different ways, so they will be discussed separately.

Single-Crystal X-ray Diffraction

In this method, a very small single crystal, typically up to about 1 mm, is irradiated with X-radiation. The diffracted beams was traditionally recorded on photographic film. Starting in the 1970's, X-ray detectors, which produce an electronic signal when a beam strikes them, were introduced. Since the electronic signal can be easily integrated with computers, detectors are often used today. The film cameras involved film in a light tight wrapping at a fixed distance from the crystal. The Laue method, named for Max von Laue, was the earliest single crystal technique. A representative diagram is shown in figure 14. A crystal of vesuvianite, with point group 4/m2/m2/m, is oriented so the A_4 axis is parallel to the X-ray beam. The resulting photograph clearly shows the A_4

symmetry. (Fig.7.39, p313, Klein)

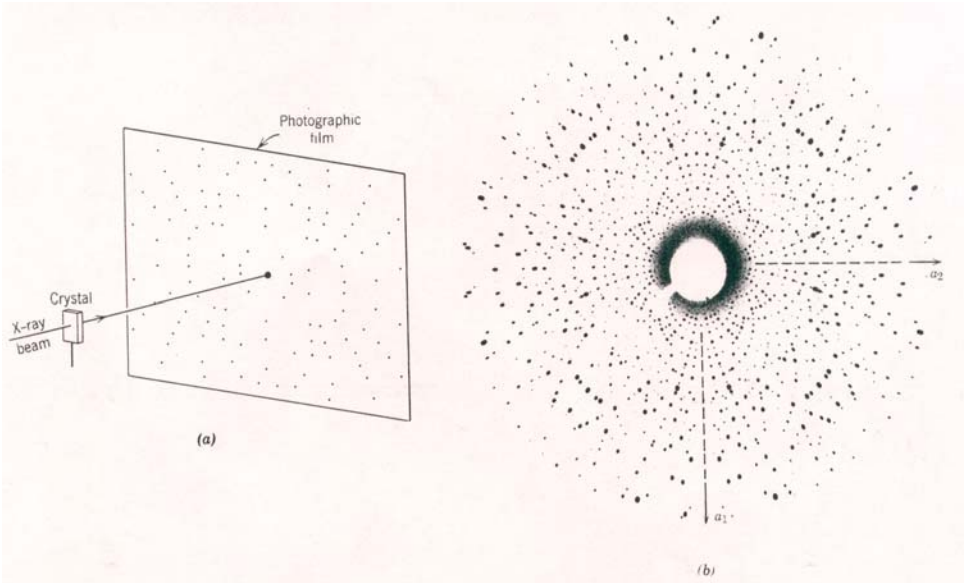

Figure 14 - a) Obtaining a Laue photograph with a stationary crystal. b) Laue photograph of vesuvianite,
taken along the four-fold axis. Axial directions a1 and a2 were inked onto the photograph after development

The Laue technique uses a flat film, and neither the crystal nor the film move. The X-radiation is unfiltered, so it is not monochromatic. The big drawback of this technique is our inability to index the points on the film. Indexing means the assignment of a particular point on the photo to a particular direction within the crystal. This greatly limits our ability to use the Laue technique, and it means we are unable to determine d-spacings and the size of the unit cell. The Laue technique is still sometimes used to orient the axes of a crystal. Such work is time-consuming, because it involves the taking of many photographs before the location of the axes are determined. A Laue photograph of an unknown mineral, also with a four-fold axis, is shown in figure 15. (from http://tetide.geo.uniroma1.it/ipercri/crix/single.htm)

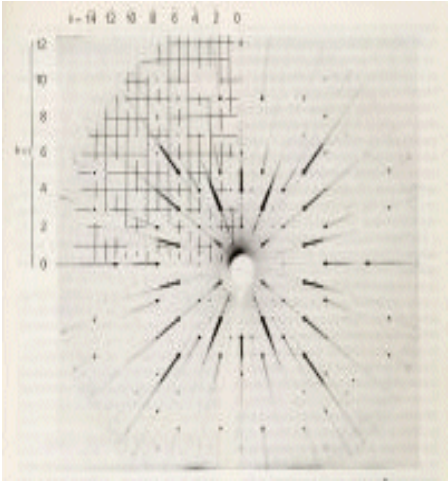

Figure 15 - Precession Camera Photograph, mineral unknown

An improvement on the Laue technique was the introduction was the rotation camera. A single crystal is rotated around a zone axis in monochromatic radiation. A cylindrical film is placed around the specimen. Three photographs, taken with suitably chosen axes which are mutually orthogonal, allows the crystallographer to measure d-spacings and determine the lattice dimensions. However, the spots sometimes overlap in this technique.

Another technique is the oscillation technique. The crystal is oscillated through an angle up to about 15° about an axis of rotation. The film is cylindrical, and the radiation is monochromatic. This eliminates the problem of overlapping spots and makes the assignment of Miller Indices to the reflections easier.

There are several "moving film" techniques. The advantage to these methods is that each lattice plane will yield a distinct diffraction. Two of the most important are the Weissenberg and the Buerger Precession methods. The Weissenberg technique, named for Austrian physicist Karl Weissenberg, involves synchronized rotation of the crystal and translation of the film. The spots are distorted, but in a systematic way. Another moving film technique is the Buerger precession camera, named for its designer M.J. Buerger. In this camera, the crystal and the film move so that a selected lattice plane remains parallel to the film at all times. The film shows and undistorted replica of the corresponding reciprocal lattice plane. Each diffraction may be indexed, and various θ_{hkl} values measured directly. A precession camera is shown in Figure 16 (Fig. 10.31a, p260, Z&S), and a precession film of wavellite in Figure 17.

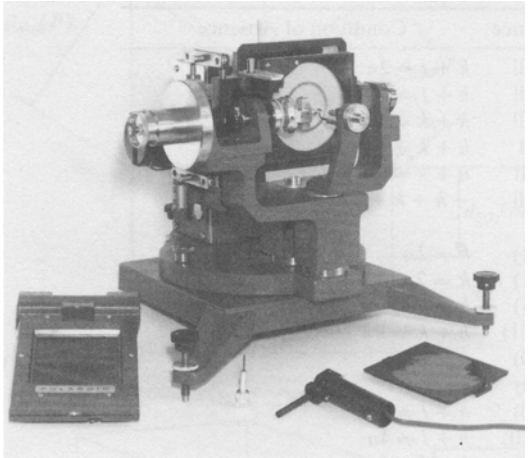

Figure 16 - Buerger precession camera

The modern equivalent of the moving film cameras is the single-crystal X-ray diffractometer. (Figure 18) A detector takes the place of film. The crystal and the detector both move. The detector finds all diffractions, and measures the

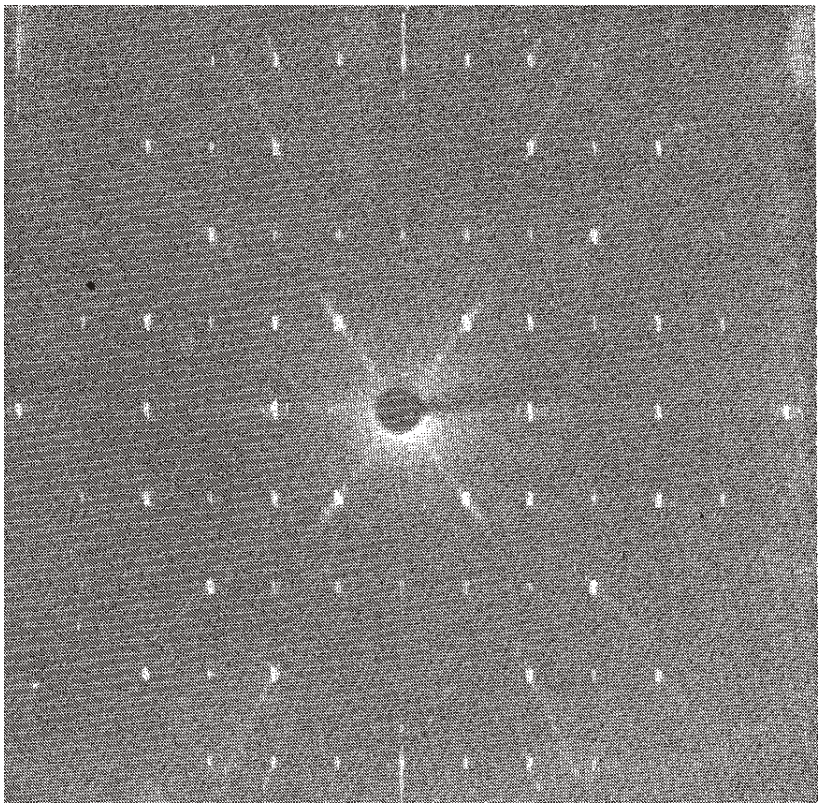

Figure 17 - Precession photograph of the (*h*01) reciprocal lattice plane of wavelite.

position and intensity of all diffractions. The machine is coupled to a dedicated computer, which controls the movement of crystal and detector, and records all data. The computer searches and finds each diffraction peak, indexes it, and measures its intensity. For an overnight run, it is routine to record more than a thousand individual diffractions. Data can be transferred to larger computers for analysis, with the product being a refined crystal structure. The human role is confined to mounting the crystal and turning the machine on.

Single crystal work is generally done with the aim of determining a crystal structure. If the mineral is indeed a new species, this is quite important. Knowledge of the crystal structure helps greatly in determining where a mineral should be classified. It suggests which minerals it has a structural relationship with, and may guide further research into possible solid solution series. Knowledge of the crystal structure can also confirm the identity of a mineral where other tests have failed to give an unambiguous result. Retroactive structure studies of minerals collected long ago sometimes results in finding that two minerals, with different names, are indeed the same mineral. This usually results in the mineral named first surviving, and the other name being withdrawn from the mineral list.

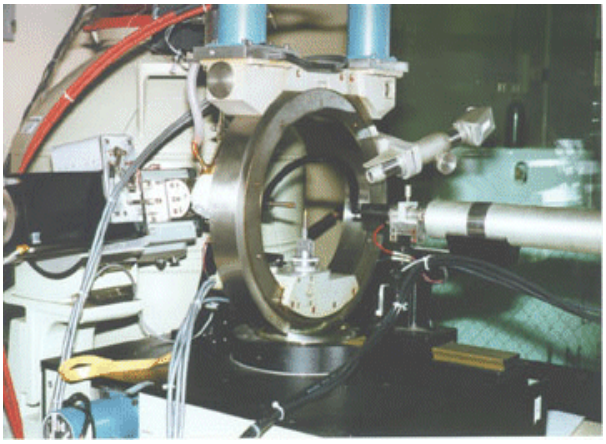

Figure 18 - Four circle diffractometer

Powder X-ray Diffraction

The objective of powder diffraction is usually the rapid identification of the mineral in question. A sample is purified, if necessary, so that only one mineral is present. It is ground to a fine powder, and then in one of several ways:

1. Placed in fine capillary tube of 0.2mm bore

2. Coated on a fine glass fiber - the fiber is dipped in a liquid such as alcohol and then rolled in the powder

3. Mixed with gum arabic and rolled between slips of glass into a fine spindle or a tiny ball, no more then 0.3 mm in diameter

4. Sprinkled on a piece of tape mounted over a hole drilled in a circular piece of metal.

Specimens prepared in one of these fashions, provided the powder if fine, will have some grains in every conceivable orientation. To insure that all grains are exposed to the X-ray beam, it is customary to rotate the sample.

The sample is mounted in the camera, and film of the appropriate size is inserted in a darkroom. The film will have been previously prepared for the camera in question, for example by punching holes to match holes in the wall of the camera where the beam enters and exits, or by notching to indicate the orientation of the film in the camera. The loaded camera is placed in the apparatus, and the rotation motor is turned on. The X-ray unit is then set for the desired exposure conditions, including excitation potential and length of exposure. After exposure, the film is developed. Depending on the film, measurements are taken which give the value of θ, and the intensity of the line on the film. The latter is measured using a device called a microdensiometer.

When all lines have been measured, the data can be compared with all known powder diffraction records to determine the identity of the mineral. Formerly, this was done by first checking indices of major lines, called the Hannawalt and Fink Indicies, to determine the likely identity of each sample. Then, a card index from the Powder Diffraction File (PDF) was examined. The PDF is published by the International Center for Diffraction Data (ICDD). The Powder Diffraction File continues to expand with new patterns being added each year. In 2007, the File contains data on more than 95% of all classified mineral species as defined by Fleischer's Glossary of Mineral Species and the International Mineralogical Association. More information is available at http://www.icdd.com/ . Today the data is available in a number of computer

readable formats, and virtually all searching is done using automated searching routines.

As with single crystals, powders can also be analyzed utilizing an automatic powder diffractometer, which uses a detector crystal instead of film. The machine is programed to rotate through a range of θ values, collecting the θ and intensity value on each line. The θ is converted to interplanar spacing values using the Bragg equation. The intensity data is recalulated, with the value of the most intense line being set to 100, and the other values adjusted accordingly. The d and I (intensity) data are then stored electronically and analyzed by comparison with the PDF file.

The powder method has several advantages.

1. It is fast, with an analysis being completed in two hours or less.

2. It requires very small sample amounts, which is especially important in cases where the material is rare.

3. Sample preparation times are usually small.

4. The cost of each analysis is low, although there is an initial investment in the X-ray equipment and associated computer.

There are other uses for the powder method as well. In solid solution series, where known data for a number of samples exists, it is often possible to quickly get a good estimate of composition of the sample by measuring a powder pattern and comparing it with known samples in the PDF.

Mixtures of minerals can also be used. In this case, the observed pattern will have lines from two or more minerals. Measurements of the intensities of the lines may be compared with patterns obtained from mixtures with known compositions, and the relative proportion of each mineral estimated.

Finally, a recent development if the *Rietveld refinement method*, which allows structural information to be extracted from powder data, rather than the much more labor intensive single-crystal methods. This becomes especially important for minerals whose habit is typically a fine powder, rather than discrete single crystals. These type of minerals include the clays, some zeolites,

manganese and iron oxides and hydroxides. The Rietveld method does require some prior knowledge of the actual crystal structure, which is used as a starting model in the refinement. For example, if the mineral is known to be a clay, the structures of a common clay mineral, such as kaolinite or montmorillionite, can be tried.

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October 31, 2011