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ADVANCED PHYSICS LABORATORY

PXR

Powder Methods of X-Ray Analysis

Revisions:

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Please send any corrections, comments, or suggestions to the professor currently supervising this experiment, the author of the most recent revision above, or the Advanced Physics Lab Coordinator.

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INTRODUCTION

The use of powder in X-ray analysis was first demonstrated about 1916 when Debye and Scherrer in Germany and Hull in the United States working independently obtained X-ray diffraction patterns from aggregates of microscopic crystals or powders (Barrett and Massalski: Chapter 7). The method has proved of great importance. X-ray analysis provides information on the structure of crystalline materials. The overall structure as well as individual atomic positions can be determined. Monochromatic X-rays, in a narrow, well collimated beam are used. If the grains or tiny crystals in the powder (or in a polycrystalline solid sample) are oriented at random some of them will be set at the right angle to give a strong reflection, i.e. constructive interference of the diffracted rays, from a particular set of planes. Since the orientation is random in three dimensions the reflected X-rays from all the grains will lie on the surface of a cone of semi-vertical angle 2θ relative to the incident beam (fig. 1), where θ satisfies Bragg's law for the wavelength of the incident X-rays:

$$n\lambda = 2d \sin \theta \quad (1)$$

The Bragg condition (1) is a simple interference maximum, sharply defined when the number of parallel planes and their estimate is large.

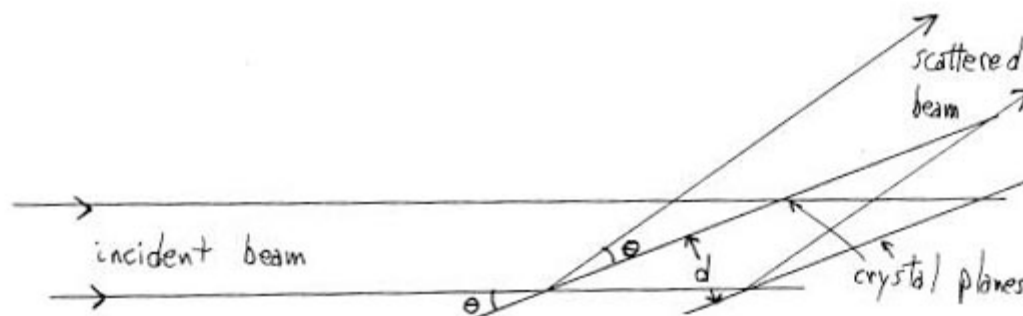


Figure 1: The cone referred to in the text (above) is generated by rotating the figure about the line of incidence of the X-rays. Note particularly that the scattering angle in this figure is 2θ , twice the Bragg angle. Crystallographers depart strongly from researchers in other branches of physics who use the symbol θ to denote the angle through which the beam has been scattered.

Thus a monochromatic beam of X-rays passing through a finely divided powder will produce upon a flat photographic film, set normal to the direction of incidence, a series of concentric rings, each uniformly intense and corresponding to one set of planes of spacing d and one order of interference. Figure 2 shows how a set of values for θ may be derived using a cylindrical camera. Substituting these in Bragg's equation, with the wavelength of the X-rays known from other information, a set of (d/n) values is obtained which may be used to determine the crystalline structure of the substance and its lattice parameters, or to identify the substance itself from the standard comparison values that are available.

Monochromatic X-rays are used in powder work because of the difficulty, if more than one wavelength is present in the beam, of determining which wavelength produced a given ring. The monochromatic X-rays are usually produced by exciting the K_α and K_β lines of a target in an evacuated X-ray tube. To remove the K_β lines one places in the external X-ray beam a filter of a material having an absorption edge of wavelength between the K_α and K_β of the target spectrum. This means that the filter is of an element one or two atomic numbers lower than the target in the X-ray tube; for example, a nickel filter is used with a copper target and a zirconium filter with a molybdenum target. (See Barrett - Chapter 3).

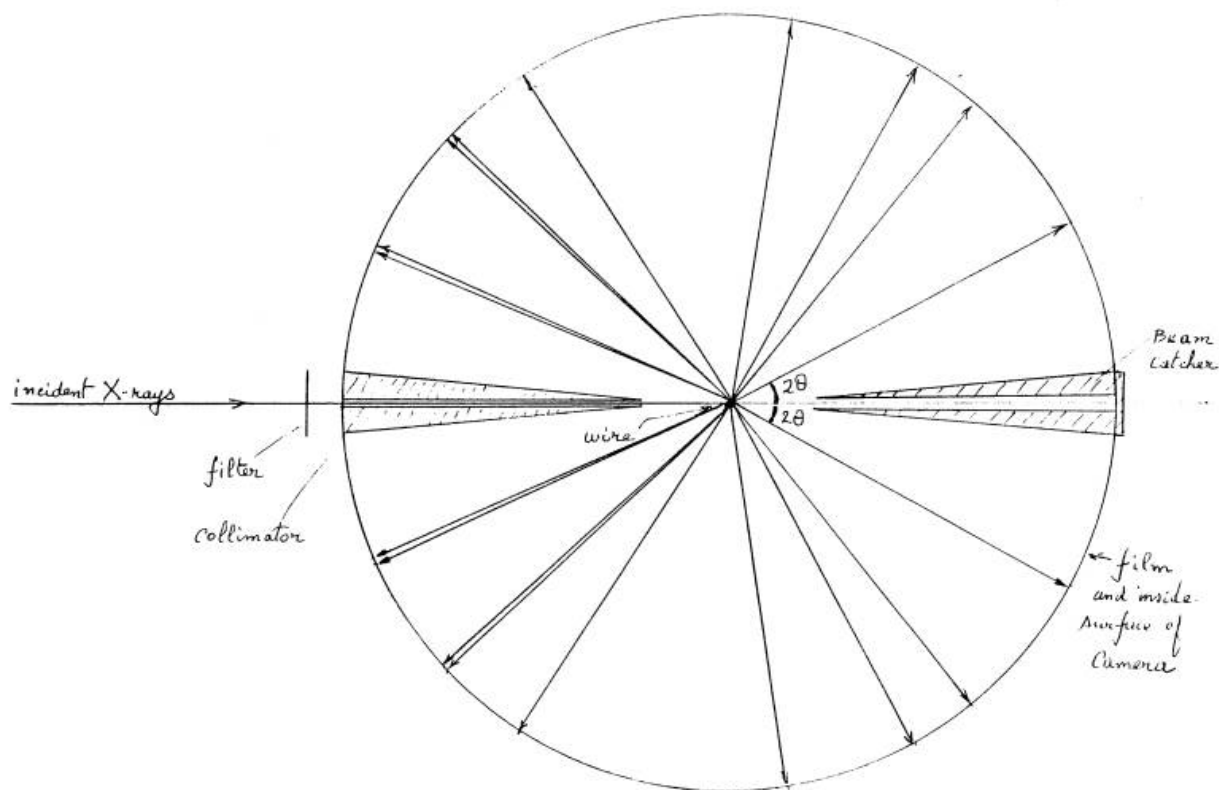


Figure 2: Camera geometry.

It is essential in the powder method that the specimen under investigation be rotated during the irradiation so as to bring as many crystal planes as possible into orientations satisfying Bragg's law. If the crystals in the powder or the grains of the polycrystalline sample are too large there will be too few of them to span the full range of different orientations and the rings will therefore appear spotty. In the cylindrical camera schematically illustrated in Figure 2 the film is made to conform tightly to its inner cylindrical surface, and the specimen must be accurately centered within the cylinder.

For the method to work, the specimen must be somewhat transparent to the X-rays. Nevertheless there is usually considerable absorption in the specimen, which gives rise to the need for systematic correction of results.

EXPERIMENTAL

Safety Reminders

- Any student doing this experiment must wear a radiation dosimeter. These may be obtained from the APL technologists in MP 250. Dosimeters are not to be taken home, but returned to Room 250.
- The X-Ray shielding must always be in place and not tampered with in any way.
- The X-Ray machine uses high voltage and requires water cooling. Do not attempt to open the X-ray machine. If any sparking is seen or heard, or there is any burning smell, all power to the apparatus should be turned off and a Professor or Technologist consulted.
- **CAUTION: Do not exceed the maximum X-Ray tube load rating:** The **maximum** loading for a copper target is 50 kVp, 20 mA and is based on X-ray tube operation with a minimum water flow rate of 2.5 quarts per minute. The rating should never be exceeded. Lowering kV does not permit increasing mA above the maximum rated limit, even though the product kV x mA does not exceed the maximum power limit. Operation within these limits should prevent burnout, severe target pitting, and deterioration of focal spot during the useful life of the tube.
- All chemicals used for developing the film must be properly handled and disposed of, following the instructions available from the APL technologists.

NOTE: This is not a complete list of every hazard you may encounter. We cannot warn against all possible creative stupidities, e.g. juggling cryostats. Experimenters must use common sense to assess and avoid risks, e.g. never open plugged-in electrical equipment, watch for sharp edges, don't lift too-heavy objects, If you are unsure whether something is safe, ask the supervising professor, the lab technologist, or the lab coordinator. When in doubt, ask! If an accident or incident happens, you must let us know. More safety information is available at <http://www.ehs.utoronto.ca/resources.htm>.

X-Ray Unit

The following instructions are taken from the operating manual of the X-ray machine:

Turning the unit on

Beginning with the unit turned completely off:

- (a) Push the overload reset switch upward to ON
- (b) Set the timer to some nominal value (e.g. one hour) to cover the duration of testing
- (c) Turn on cooling water
- (d) Turn the key-operated line switch clockwise to ON
- (e) Push the line START button
- (d) Turn the KILOVOLTS and MILLIAMPERES control knobs to their full counter-clockwise positions.

NOTE: The panel lamp can be turned on and off with the toggle switch mounted underneath the instrument table, above the upper right hand corner of the control panel.

- (f) Push the X-RAY ON button. The rectifier pilot lights will light, indicating that the filament circuit of each high voltage rectifier tube is receiving power. (Pilot light numbers correspond to rectifier tube numbers on the tank cover). After a few seconds warm up, the X-RAY light will come on, indicating that the X-ray tube high voltage circuit is receiving power. The unit is now ready to be used.

Operating

Applying Power to Tube: With a sample in position and all shields properly in place, apply power to the tube as follows:

- (a) Turn the kilovolts control knob slowly to the desired value as indicated on the kilovolts meter (40 KV).
- (b) Turn the milliamperes control knob to the desired value as indicated on the mA meter. The usual current value is 15 mA.

Measurements

Use the X-ray unit with a copper target and a nickel filter to take powder photographs of polycrystalline samples of copper and/or molybdenum and/or tungsten. Use the cylindrical (Debye-Scherrer) camera.

Centering of the wire sample in the camera is important for obtaining an X-ray photograph that will provide a nice measurement. The camera has a radial rod for the purpose of centering of the sample mount hub but it is better to back this off so that it doesn't rub against the hub and to centre the hub using pressure from your fingers. The final centering can be done by sighting through the beam entrance and exit ports but still by using finger pressure to move the hub. Mounting your specimen accurately parallel to the axis of the camera is also of great importance.

Finally you will determine the structure of an "unknown" powder sample. You may also be able to identify it on the basis of the structure and lattice constants. Grind the powder finely and carefully insert into a quartz sample tube. About 1 cm length of sample will do. Proceed as above to get a powder spectrum. Analyze the spectrum in terms of a basic cubic structure to find the compound's structure. Pay close attention to systematic absences. Once the structure has been determined as well as the lattice constant try using the card index to identify this compound.

THEORY AND INTERPRETATION

A full understanding of X-ray diffraction requires study of the concept of reciprocal lattice, and the reciprocal lattice vectors, \mathbf{G} (Barrett and Massalski: chapter 4; Kittel: chapter 2). The set of reciprocal lattice vectors determine the possible X-ray reflections, the condition being

$$2\mathbf{k} \cdot \mathbf{G} = G^2 \quad (2)$$

which is equivalent to the Bragg condition (1). For cubic crystals there is only one lattice constant: a , the length of the edge of the unit cell. The spacing, d , between adjacent atomic planes is related to the lattice constant by the formula

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad (3)$$

where h , k and l are the Miller indices (Barrett and Massalski: chapter 1; Kittel: chapter 1).

However, reflections from some of the planes (h,k,l) do not occur when the crystal has addition symmetry beyond that of the simple cubic lattice.

For face-centred cubic structures, reflections are missing if h , k and l are mixed odd and even. For body-centred cubic structures, reflections are missing if $h + k + l$ is odd (Barrett and Massalski: chapters 4, 7).

Exceptions to the above correspond to variations in scattering power between atomic planes: differences in the atomic form factor (Barrett and Massalski: chapter 4).

DATA ANALYSIS

Determine the lattice constants as accurately as possible, considering the sources of error discussed in Chapter 7 of Barrett and Massalski. Use a Nelson-Riley plot to determine a lattice parameter for a bcc crystal and/or an fcc crystal and give a realistic estimate of the experimental error for your measured lattice constants. The Nelson-Riley procedure consists of plotting the lattice constant determined for each angle $a(\theta)$ versus $a_0(1+k_2)\left(\frac{\cos^2\theta}{\theta} + \frac{\cos^2\theta}{\sin\theta}\right)$ (Barrett and Massalski: chapter7).

This formula is empirical in character and is supposed to yield an accurate value of a at $2\theta = 180^\circ$. The deviations at other angles arise from the non zero radius of the wire and are due to the opacity of the sample wire to X-rays and to the divergence of the beam. It is simple to show how a correction

proportional to $\frac{\cos^2\theta}{\theta}$ might arise from opacity. The origin of the $\frac{\cos^2\theta}{\sin\theta}$ term in the Nelson-Riley

function is relatively obscure. Some students have performed three plots: $a(\theta)$ versus each of the above, and obtained reasonable fits in all three cases. The plots yielded slightly different $a(0)$ values for the corrected lattice constant, indicating that there is a systematic error inherent in the method which plots of the Nelson-Riley type do not remove entirely.

In addition to computing a best lattice parameter, it is important to graph the Nelson-Riley plot in your lab book.

Systematic Errors

The Nelson-Riley correction is only one that needs to be carried out in this experiment. Correction for film shrinkage (if any) is relevant, and you should take care to look out for the resolution of the two K_{α} lines at slightly different energies. If your pictures are clear, it should be easy to measure the $K_{\alpha 1}$ and $K_{\alpha 2}$ lines separately at the larger Bragg angles.

REFERENCES

1. **Barrett**, C.S. and T.B. Massalski, "Structure of Metals; crystallographic methods, principles and data (McGraw-Hill 3rd edition 1966, revised 3rd edition 1980).
2. **Kittel**, C., "Introduction to Solid State Physics", (John Wiley 6th edition 1986)
3. **Ashcroft**, N.W. and N.D. Mermin (1976) *Solid State Physics*, Holt, Rinehart and Winston.
4. **Clark**, G.L., (1955) *Applied X-Rays* (McGraw-Hill).