

THE DEBYE-SCHERRER POWDER METHOD

Laboratory sessions (Mr. D. Cullen):

Object

- 1) To become acquainted with the experimental arrangement of the Debye-Scherrer Powder Method and to use this technique to accurately determine the lattice parameter of a cubic metal.

Lattice Parameter Determination and Identification for a Cubic Metal

Theory The angular positions of x-ray beams diffracted by a crystalline substance are determined solely by the size and shape of the unit cell. This relationship can be expressed by Bragg's law

$$\lambda = 2d_{hkl}\sin\theta \quad (1)$$

where the interplanar spacing d_{hkl} of the diffracting planes (hkl) is a function of the lattice parameter. For a cubic material d_{hkl} is given by

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

For a particular substance and specified wavelength all possible values of the Bragg angle θ can be expressed by combining equations (1) and (2), that is:

$$\begin{aligned} \sin^2\theta &= (\lambda^2/4a^2)(h^2+k^2+l^2) \\ \text{or} \quad \sin^2\theta &= KN \end{aligned}$$

where $K = (\lambda^2/4a^2)$ which is a constant for a particular pattern and $N = (h^2+k^2+l^2)$ is an integer.

The analysis of a powder pattern of a cubic substance is particularly simple. It reduces to the problem of finding a set of integers N such that $(\sin^2\theta)/N$ is a constant for all observed diffraction lines. Once the values of N have been determined, the lines can be assigned Miller indices and the lattice parameter can be calculated from K.

The Bravais lattice of the substance can be identified by inspection of the values of N, since each type of lattice is characterized by a particular set of values, i.e.,:

$$\begin{aligned} N_P &= 1,2,3,4,5,6... \\ N_I &= 2,4,6,8,10,12... \\ N_F &= 3,4,8,11,12,16... \\ N_{\text{Diamond}} &= 3,8,11,16... \end{aligned}$$

(Note: N never equals 7,15,23,28,31... since these numbers cannot be formed by the sum of the squares of the three integers h,k,l.)

Due to errors inherent in the Debye-Scherrer Method, the values of $(\sin^2\theta)/N$ may not be exactly constant; however, they are usually close enough to permit selection of the proper integers.

Powder patterns are invariably taken with the most intense component of the incident x-radiation, the K_α characteristic line, and a filter is usually employed to nearly eliminate the K_β line. However, if no filter is used, the occurrence of K_β reflections in the powder pattern must be considered. Let λ_α and λ_β be the wavelengths of the K_α and K_β characteristic lines, respectively; let θ_α and θ_β be the corresponding Bragg angles.

$$\begin{aligned} (\sin^2\theta_\alpha) / (\sin^2\theta_\beta) &= (\lambda_\alpha)^2 / (\lambda_\beta)^2 \\ &= 1.23 \text{ for Cu radiation} \end{aligned}$$

Thus, if the ratio of $\sin^2\theta$ for a pair of closely spaced diffraction maxima is 1.23 and if one of them (the K_β reflection) is considerably weaker than the other, then both are most probably produced by the same plane.

The Straumanis method for preparing Debye-Scherrer powder patterns will be used here. In this method, the film is loaded in the camera so that it intercepts both the transmitted and incident beams. (This requires that a hole be punched in the film to accommodate the entrance collimator.) After photographic development, the film is laid flat on an illuminated reader with the transmitted-beam (low-angle) end at the left, and the diffraction lines are numbered starting at the beam stop.

The position of each line is measured in millimeters from an arbitrary origin, and the positions of the transmitted and incident beams are determined from these measurements. The center of the transmitted beam ($2\theta = 0^\circ$) lies halfway between the measured positions of lines 1, 2, etc. The best estimate of the location $2\theta = 0^\circ$ is obtained by averaging the midpoints calculated from all pairs of lines centered on the low-angle side. Similarly, the center of the incident beam ($2\theta = 180^\circ$) is obtained from the measured positions of all pairs of lines centered on the high-angle side. Since the distance (W) between these two centers corresponds to 180° , the millimeter scale can be calibrated in degrees, and the film can be analyzed without the use of

an angular scale. Conversely, this information can be used to provide a film-shrinkage correction for the angular scale of the film reader.

Procedure

The demonstrator will outline the experimental method of Straumanis for production of Debye-Scherrer powder patterns, and will give you a powder from which you should produce a diffraction pattern and analyze the results.

A good project will also attempt to produce a diffraction pattern using an atmosphere of helium rather than air in the camera. The major difference(s) between the two patterns should be noted.

Results

1. Measure the powder pattern and tabulate.
 - a) Position of each line in mm.
 - b) $\sin^2\theta$ for each line with the effect of film shrinkage eliminated.
 - c) Estimated relative intensity of each line, that is, Very Strong (VS), Moderate (M), Weak (W), or Very Weak (VW).
 - d) Identification of any lines due to $K\beta$.
 - e) Value of N for each line.
 - f) Value of K for each line.
2. Determine the Bravais lattice of the sample.
3. Calculate the lattice parameter of the sample.

Note: Systematic errors arise in the Debye-Scherrer method which decrease with increasing θ , the lattice parameter can be determined, therefore, with greatest precision by extrapolation to $\theta = 90^\circ$. Hence, in order to obtain the most accurate value of the lattice parameter, plot the values of the lattice parameter, a , determined from each reflection against the Nelson-Riley function,

$$N-R = \left(\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta} \right)$$

and extrapolated to $N-R = 0$ to obtain a_0 . (See pp. 352-358 in Cullity Elements of X-ray Diffraction for a detailed explanation.) Your value for a_0 should include an estimate of the possible error in its value.

4. If possible, identify the material from its lattice parameter

THE DIFFRACTOMETER

Object

The purpose of this laboratory session is for you to become acquainted with the x-ray diffractometer and the JCPDS index

Phase Identification

Theory: The lattice structure and atomic arrangement within the lattice produce a unique diffraction pattern for each crystalline material. This is expressed by the position and intensity of the diffraction peaks from a specimen. The JCPDS file is an index of these patterns for a large number of crystalline materials and is therefore useful as a means of identification. It is also possible to identify more than one constituent in an unknown sample since the peaks from each substance in general do not interfere with one another. (The substances must not, of course, react chemically.)

Procedure

1. Determine the peaks, relative intensity values and calculate d values from Bragg's law.
2. The JCPDS files containing the d values of the strongest line are then identified. Considerable leeway must be given with regard to the precision of the determination of d, especially when radiation other than copper K_{α} is used (the radiation with which most of the samples of the JCPDS index have been determined). (The intensity relations may also be considerably different for other radiations.) This makes it necessary to examine files with a variation in d of perhaps 1-2%. The files are examined for coincidence of the second or third strongest line and, if a plausible agreement is found, comparison of the rest of the lines is made. **Note:** Complete agreement in the stronger lines should be possible, while very weak lines may be absent in either file or in the diffraction pattern. (In the case of a mixture, the second or third overall strongest line may belong to the other constituents. The second and third strongest line properly belonging to the first constituent in question will then be found among the weaker lines.)

After all the lines for the first constituent have been sorted out, the second and third strongest line may be looked up, if they have not been indexed as belonging to the first constituent, and the process of sorting is repeated.

Note: It is also possible to carry out approximate quantitative analysis by this method under favorable conditions. This can be done by taking the intensities of the most prominent lines as a measure of the percentage of the material in question. A linear correlation cannot be expected and calibration patterns with known amounts of constituents must be made.

Results

Using the JCPDS card index, identify the unknown or unknowns in two diffraction patterns.