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Experiment 5

X-ray Analysis of a Solid

M. Stanley Whittingham

Notes for Instructors

Purpose

To measure the spacing between crystallographic planes of a layered solid.

Method

X-ray diffraction and the Bragg equation, $n\lambda = 2d \sin \theta$. *See* Chapter 4. When crystalline materials are used in a powder diffractometer, only the crystallographic planes parallel to the sample stage are aligned for diffraction and a set of peaks equally spaced in 2θ are observed. By choosing samples with a natural orientation such as layered solids or crystals with cleavage planes parallel to a cubic unit cell the set of crystallographic planes whose spacing is being measured can be easily identified. By choosing samples with a spacing d large compared with the wavelength, many diffraction orders can be observed.

Materials

X-ray diffractometer

Samples of layered minerals:

2725-X/93/0385$06.00/1

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Molybdenite (Ward's Natural Science; layer spacing should be 12.295 Å.)

Vermiculite (type of mica used as packing material; vermiculite often expands like popcorn when heat-treated; select a sample that still looks like mica. The layer spacing is expected to be about 20 Å.)

Biotite (layer spacing should be 10.16 Å × sin 99.05°)

Muscovite (layer spacing should be 20.05 Å × sin 95.77°)

Chlorite (layer spacing should be 14.29 Å × sin 97.13°)

Cubic crystals with cleavage planes:

KCl (layer spacing should be 6.2929 Å)

KBr (layer spacing should be 6.5982 Å)

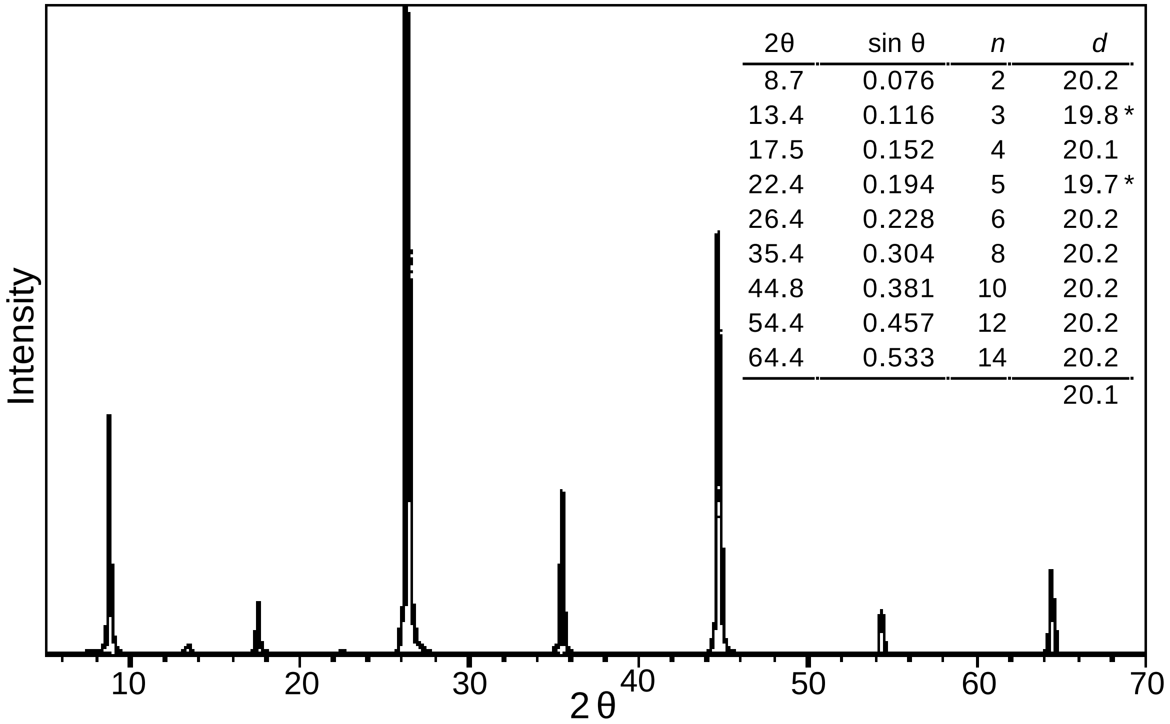
Other Information

It is possible to compare *d* spacings with literature values of unit cell parameters. When the stacking of the planes is not perpendicular ($\beta \neq 90°$), the measured distance between the planes will be $c \sin \beta$ rather than *c*; this distinction is small as long as β is close to 90°.

Some symmetries result in systematically absent reflections with the result that only the even diffraction orders are seen in this experiment; labeling orders 2, 4, 6... as 1, 2, 3... will result in an answer that is half the actual spacing.

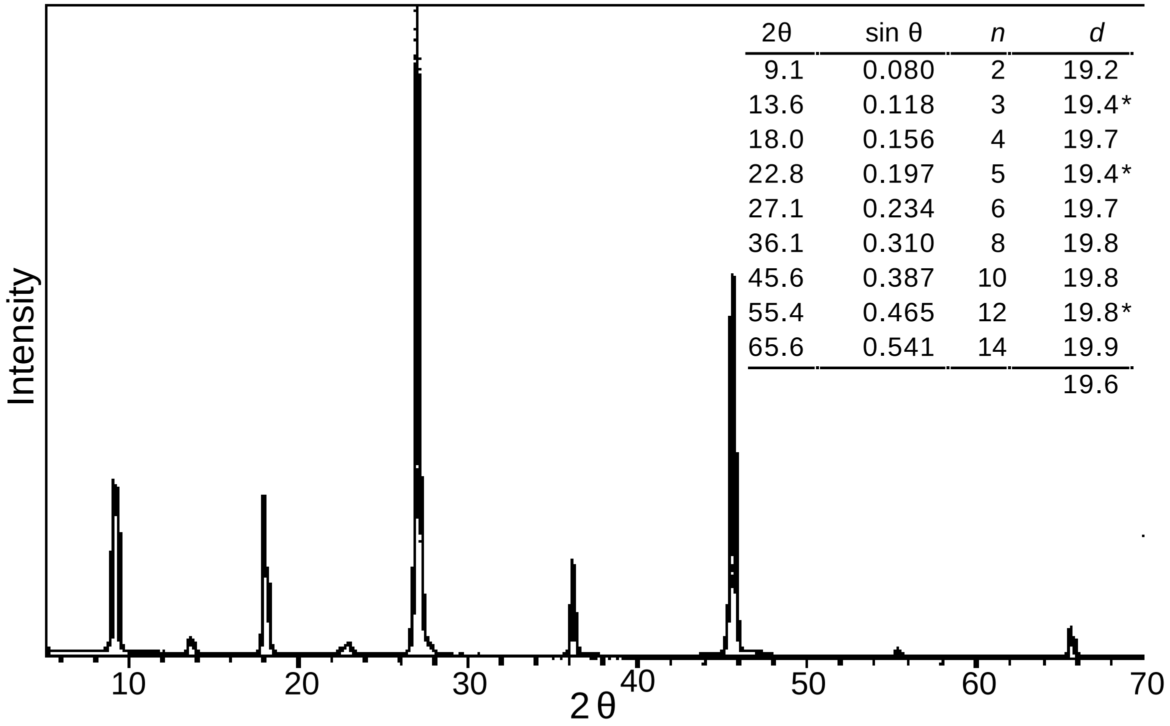
Sample Data and Calculations

Figures 1–6 show sample data and calculations. Values with * are low intensity and are expected to have a larger error.



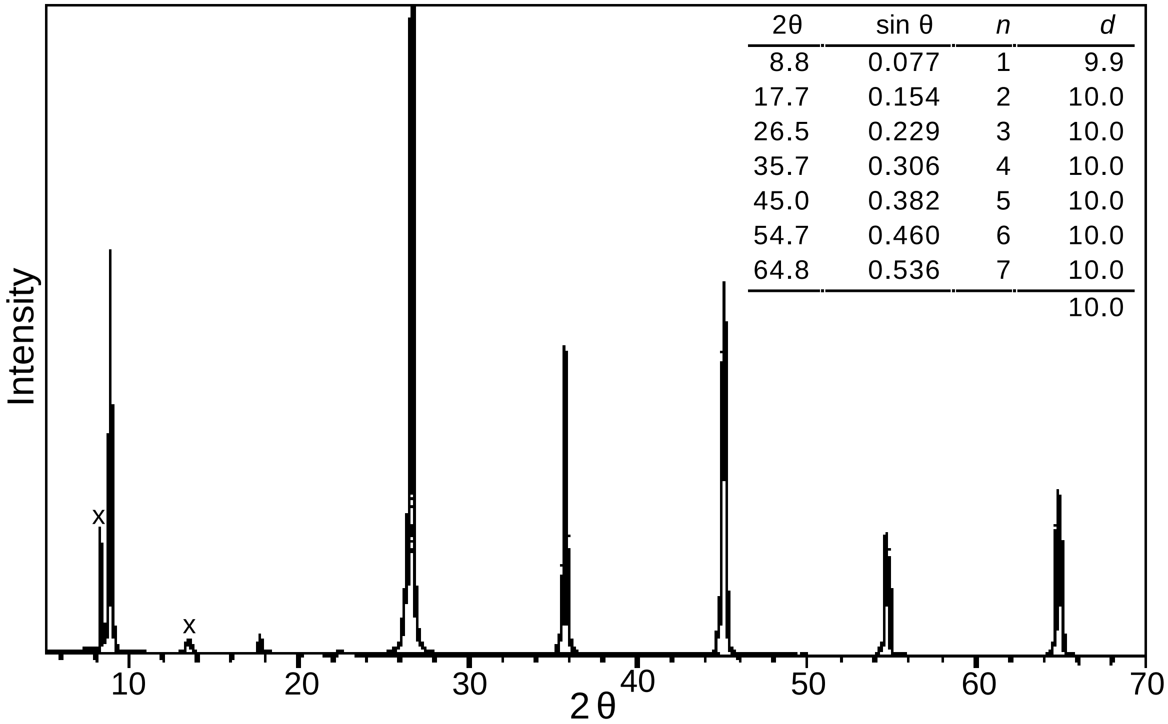
2θ	sin θ	*n*	*d*
8.7	0.076	2	20.2
13.4	0.116	3	19.8*
17.5	0.152	4	20.1
22.4	0.194	5	19.7*
26.4	0.228	6	20.2
35.4	0.304	8	20.2
44.8	0.381	10	20.2
54.4	0.457	12	20.2
64.4	0.533	14	20.2
			20.1

Figure 1. X-ray powder diffraction pattern for a sample of vermiculite packing material (Aldrich).



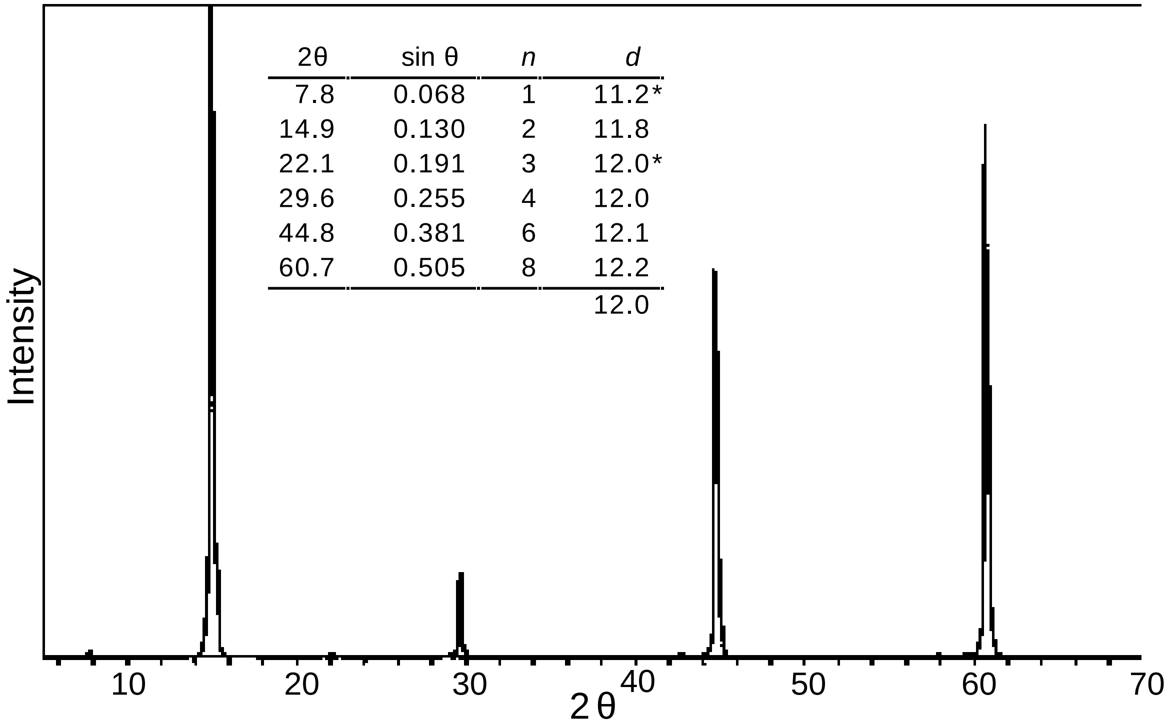
2θ	sin θ	*n*	*d*
9.1	0.080	2	19.2
13.6	0.118	3	19.4*
18.0	0.156	4	19.7
22.8	0.197	5	19.4*
27.1	0.234	6	19.7
36.1	0.310	8	19.8
45.6	0.387	10	19.8
55.4	0.465	12	19.8*
65.6	0.541	14	19.9
			19.6

Figure 2. X-ray powder diffraction pattern for a sample of muscovite from Delaware County, PA.



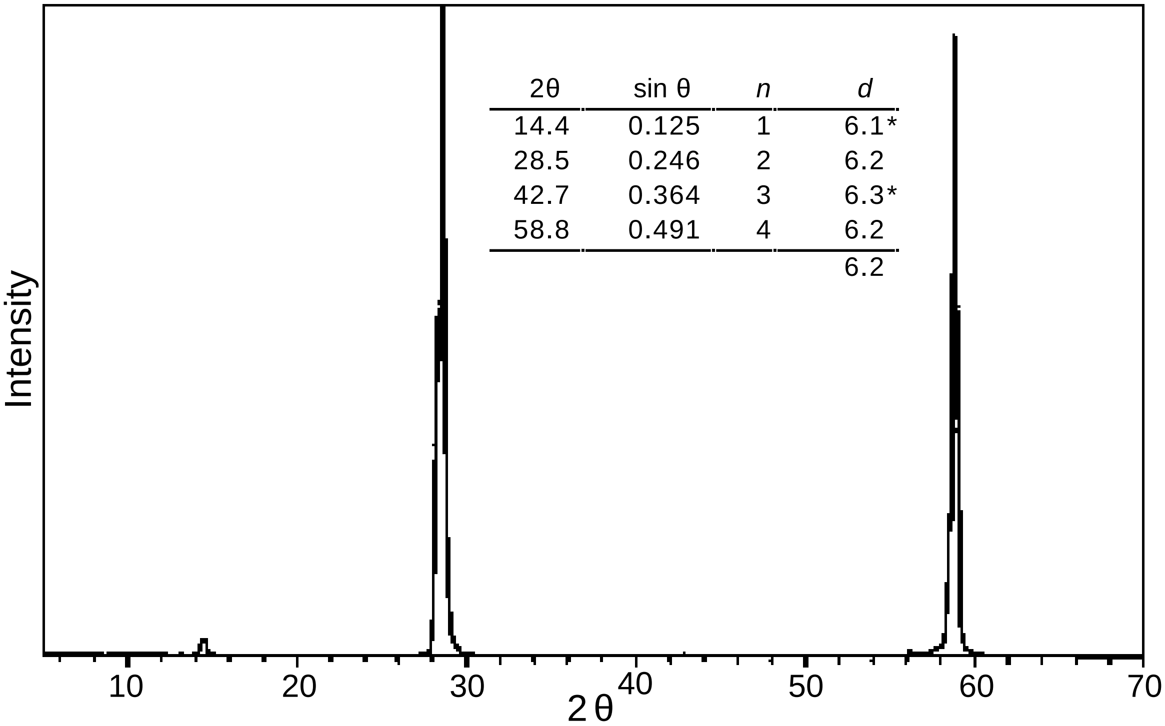
2θ	sin θ	*n*	*d*
8.8	0.077	1	9.9
17.7	0.154	2	10.0
26.5	0.229	3	10.0
35.7	0.306	4	10.0
45.0	0.382	5	10.0
54.7	0.460	6	10.0
64.8	0.536	7	10.0
			10.0

Figure 3. X-ray powder diffraction pattern for a sample of biotite from West Philadelphia, PA. Peaks marked x are from an impurity.



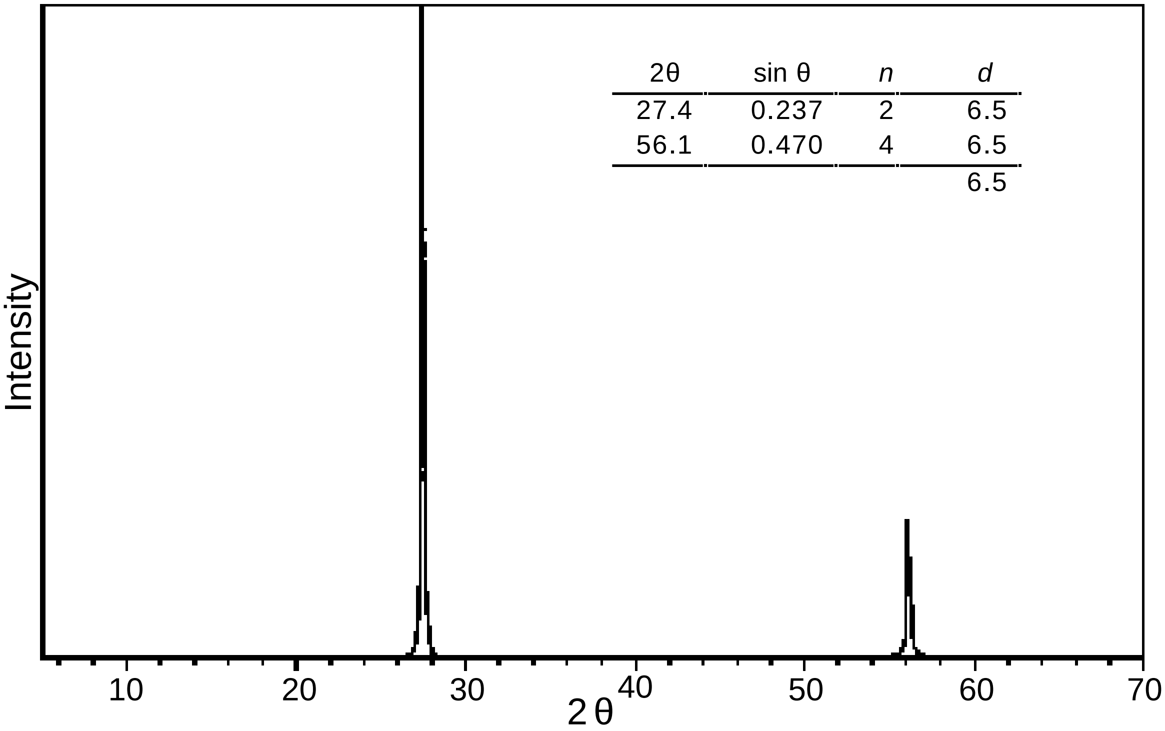
2θ	sin θ	*n*	*d*
7.8	0.068	1	11.2*
14.9	0.130	2	11.8
22.1	0.191	3	12.0*
29.6	0.255	4	12.0
44.8	0.381	6	12.1
60.7	0.505	8	12.2
			12.0

Figure 4. X-ray powder diffraction pattern for a sample of MoS_2 from Ontario.



2θ	sin θ	*n*	*d*
14.4	0.125	1	6.1*
28.5	0.246	2	6.2
42.7	0.364	3	6.3*
58.8	0.491	4	6.2
			6.2

Figure 5. X-ray powder diffraction pattern for a sample of KCl (oriented on a cleaved face).



2θ	sin θ	*n*	*d*
27.4	0.237	2	6.5
56.1	0.470	4	6.5
			6.5

Figure 6. X-ray powder diffraction pattern for a sample of KBr (oriented on a cleaved face).

X-ray Analysis of a Solid

Purpose

To measure the spacing between crystallographic planes of a layered solid.

Introduction

X-rays are electromagnetic radiation with a wavelength of about 1 Å (10^{-10} m), the approximate size of an atom. X-ray diffraction has been used in two main ways to probe crystalline structure at the atomic level. First, each crystalline solid has a unique characteristic X-ray powder pattern, which may be used as a "fingerprint" for its identification if the pattern for the known material has been recorded. Second, X-ray crystallography may be used to determine the structure, that is, how the atoms pack together in the crystalline state and the interatomic distances and angles. X-ray diffraction is one of the most important characterization tools used in materials science.

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

In Figure 1, the path difference between two waves is:

$$2x = 2d \sin \theta$$

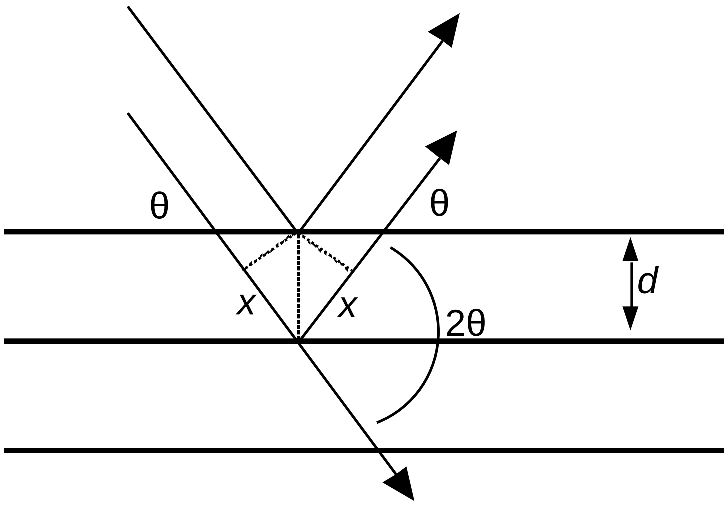


Figure 1. Reflection of X-rays from two planes of atoms in a solid.

NOTE: This experiment was written by M. Stanley Whittingham, Department of Chemsitry, State University of New York at Binghamton, NY 19302.

For constructive interference between these waves, the path difference must be an integral number of wavelengths:

$$n\lambda = 2x$$

This leads to the Bragg equation:

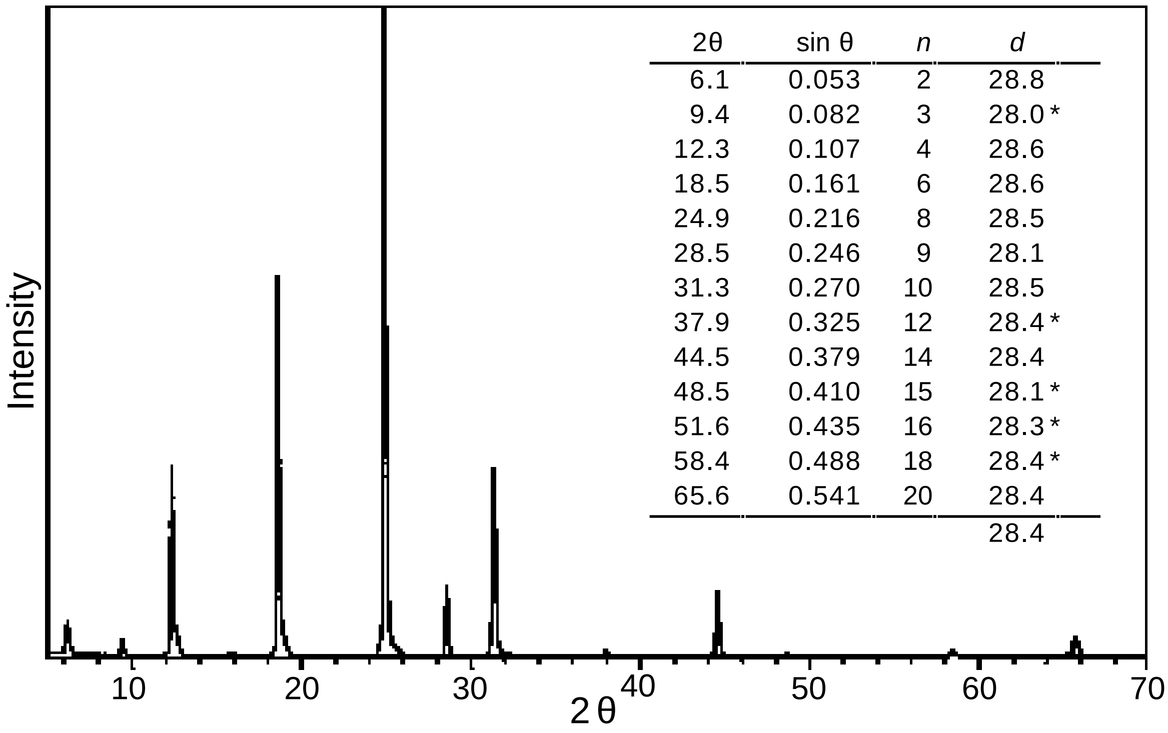
$$n\lambda = 2d \sin \theta$$

For example, when the diffraction pattern of copper metal was measured with X-ray radiation of wavelength $\lambda = 0.711$ Å, the first-order ($n = 1$) Bragg diffraction peak was found at an angle 2θ of 11.3°. To calculate the spacing between the diffracting planes in the copper metal, rearrange the Bragg equation for the unknown spacing d:

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

where $\theta = 5.64°$, $n = 1$, and $\lambda = 0.711$ Å, and therefore $d = 1 \times 0.711/(2 \times 0.4266) = 3.62$ Å.

Figure 2 shows the X-ray diffraction pattern from a layered silicate sample. Strong intensities can be seen for a number of values of n; from each of these lines we can calculate the value of d, the interplanar spacing between the atoms in the crystal.



2θ	sin θ	*n*	*d*
6.1	0.053	2	28.8
9.4	0.082	3	28.0*
12.3	0.107	4	28.6
18.5	0.161	6	28.6
24.9	0.216	8	28.5
28.5	0.246	9	28.1
31.3	0.270	10	28.5
37.9	0.325	12	28.4*
44.5	0.379	14	28.4
48.5	0.410	15	28.1*
51.6	0.435	16	28.3*
58.4	0.488	18	28.4*
65.6	0.541	20	28.4
			28.4

Figure 2. X-ray powder diffraction pattern of a sample of chlorite from Westchester, PA. The values followed by * are from weak reflections and are expected to be less precise.

The X-ray diffraction experiment requires an X-ray source, a sample and a detector to measure the intensity of the diffracted X-rays. Figure 3 is a schematic diagram of a powder X-ray diffractometer.

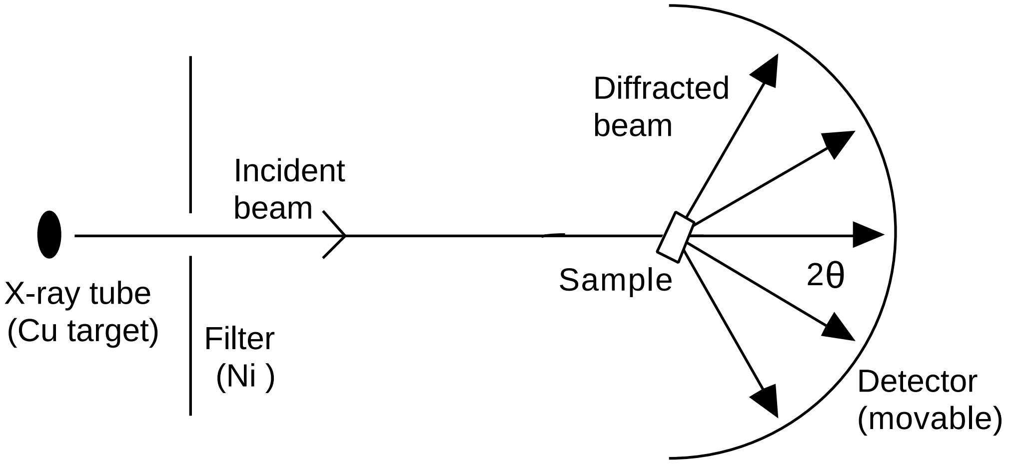


Figure 3. Schematic of an X-ray powder diffractometer.

The X-ray radiation most commonly used is that emitted by copper, whose characteristic wavelength for the so-called K_α radiation is $\lambda = 1.5418$ Å. When the incident beam strikes a powder sample, diffraction occurs in every possible orientation of 2θ. The diffracted beam may be detected by using a moveable detector, which is connected to a chart recorder. In normal use, the counter is set to scan over a range of 2θ values at a constant angular velocity. Routinely, a 2θ range of 5° to 70° is sufficient to cover the most useful part of the powder pattern. The scanning speed of the counter 2θ is usually 2° min^{-1} and therefore, about 30 minutes are needed to obtain a trace.

General Procedure

Place your sample onto double-sided tape that is then placed on a sample holder; if you are preparing a powder sample, use a spatula to spread the powder onto the double-side tape.

Slide the sample holder into the diffractometer. **WARNING: X-rays are hazardous to your health. Do not open the chamber while the red alarm light is on.**

Record the scan between 2θ = 70° and 2θ = 5°.

Determine the 2θ values for each peak from the chart recorder output. Perform the calculations indicated in Table 1 and then calculate the average repeat distance.

Table 1. Laboratory Calculations

2θ	θ	sin θ	*n*	*d* = *n*λ/(2sin θ)
			1	
			2	
			3	
			4	
			5	
			6	
			7	
			8	

NOTE: λ = 1.5418 Å for Cu K_α radiation; λ = 0.711 Å for Mo K_α radiation.