

EXPERIMENT 1 DEMONSTRATION OF X-RAY DIFFRACTION

The activities in this laboratory experiment involve observation, analysis and evaluation. The activities are designed so that students should complete the lab and calculations in class.

Objective

To observe one method of evaluating atomic crystalline structure by using x-ray diffraction. To understand the use of Bragg's Law and its relation to crystal structure.

Introduction

X-ray diffraction can be used to determine a materials crystalline structure and lattice parameter. This information can then be used to identify the material being analyzed since each metallic element in the periodic table has a unique combination of lattice structure and parameter at room temperature.

When an x-ray beam is directed at a metallic crystal the beam hits the atoms and produces two types of x-rays, white x-rays and characteristic x-rays. White x-rays include a wide range of wavelengths and are not of interest in this experiment. Characteristic x-rays are caused by the ejection of an electron from an inner shell of an atom hit by the incident x-ray. When an outer shell electron moves to fill the space created in the inner shell, energy in the form of an x-ray photon is emitted.

Bragg's law is used to determine a crystal parameters from its characteristic x-ray pattern. The x-rays that strike a crystal have a wavelength of about the same length as the space between atoms in the crystal lattice. Bragg's law can be derived by considering a cubic crystal lattice that consists of parallel planes of atoms. If each plane is assumed to act as a surface which is struck by the incident x-ray beam we see the beam reflected in some cases and not reflected in others. In the case of reflection it is seen that the beams exiting the crystal are in phase and act to reinforce each other. This occurs when the incident beam hits the parallel planes at certain angles known as Bragg Angles, θ . In the nonreflecting case, the waves leaving the crystal are out of phase and cancel each other. Non-reflectance occurs when the incident beam strikes at arbitrary angles. Each case is illustrated in Figure 1.

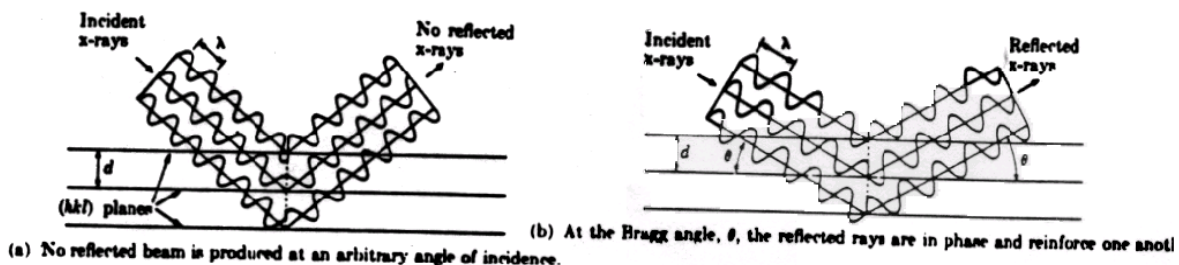


Figure 1 - The reflection of x-rays in the (hkl) planes of a crystal. (Guy & Hren)

If one examines the geometry of the reflected beam the relationship between Bragg's angle, the wavelength of the x-ray, λ , and the interplanar spacing, d , can be found.

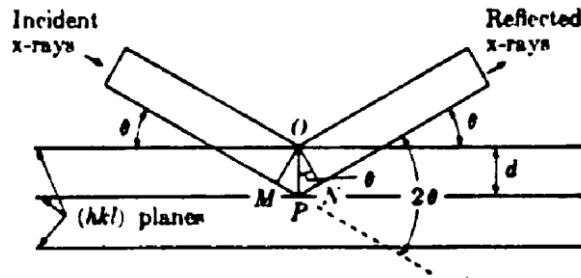


Fig. -2 - Diffraction angle. (Guy & Hren)

Figure 2 shows arbitrary planes of atoms whose indices are (hkl) and which have interplanar spacing d . If the x-rays entering the crystal are in phase at OM and those reflected are in phase at ON then the distance along MPN must equal an integral number of wavelengths, $n\lambda$. The geometry shows that $MP=PN$ and that each of these equals $d\sin\theta$. Therefore for reflected x-ray beams:

$$n\lambda = 2d\sin\theta \quad (\text{This is Bragg's Law}) \quad (1)$$

where $n=1,2,3,\dots$. For our purposes we assume $n=1$.

In the powder method of x-ray diffraction the material to be analyzed is placed in the camera that is sketched in Figure 3. The specimen sits in the center of the camera with the film located in a circle around it. When a monochromatic x-ray beam is directed at the specimen diffraction takes place and characteristic x-rays are emitted in conical sections that intersect and expose the film at different arcs. When the film is flattened out these arcs are seen as lines as shown in Figure 4. The distance between the beam exit and entrance on the x-ray film corresponds to a Bragg angle of 90° . The Bragg angle of each characteristic line on the film can then be found by using the following ratio:

$$\frac{S_i}{S_n} = \frac{\theta_i}{\theta_n} \quad (2)$$

where S_i is the distance **from the exit to the line of interest**, S_n is the distance from the exit to the entrance, 90° is the Bragg angle from exit to entrance, and θ is the Bragg angle of the line in question. Once all the Bragg angles have been found it is possible to determine the crystalline structure of the sample by considering the geometry of the crystal. For pure metals in a cubic structure:

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

where d_{hkl} is the interplanar spacing between (hkl) planes, a is the lattice parameter, and h,k,l are Miller indices of the planes. Substituting eqn. (3) into Bragg's law eqn. (1) gives:

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

Letting $Q^2 = h^2 + k^2 + l^2$, we can rewrite eqn. (4) as:

$$\lambda^2 = \frac{4a^2 \sin^2 \theta}{Q^2} \quad (5)$$

or

$$\frac{Q^2 \lambda^2}{4a^2} = \sin^2 \theta \quad (6)$$

since $\frac{\lambda^2}{4a^2}$ is a constant we can say:

$$Q^2 C = \sin^2 \theta \quad (7)$$

Eqn. (7) states that the squares of the sines of the angles that result in a diffraction peak (line on the film) occur in a certain **ratio of whole numbers**. This is due to the structure factor of the lattice. We can use these ratios to determine the crystal lattice structure. The lines shown in Figure 5 correspond to the planes which diffract x-rays for cubic lattice structures. Once the crystalline structure has been found the lattices parameter can be found by remembering that:

$$\frac{\lambda^2}{4a^2} = \text{constant} \quad (8)$$

which becomes:

$$a = \frac{\lambda}{2\sqrt{C}} \quad (9)$$

From eqn. (7) we see that the constant is equal to:

$$C = \frac{\sin^2 \theta}{Q^2} \quad (10)$$

Knowing a_0 and the lattice structure we can then find the corresponding metal on the attached table of crystal structures.

Procedure

You will do this experiment in two parts. In the first part you will be provided data and asked to determine the crystal structure and lattice parameter that will allow you to identify the material. In the second part you will be shown a strip of film from the CSUN diffraction camera. Using the film you will determine the Bragg Angles, Crystalline structure and lattice parameter.

Part 1 - During a lunar exploration an unknown metallic crystalline substance is discovered whose external morphology indicates that it is a cubic material. A diffraction pattern of this material, using radiation of wavelength 1.54\AA , provides the following data:

Diffraction peak #	Bragg Diffraction angle, θ_i	$\sin\theta_i$	$\sin^2\theta_i$	$\frac{\sin^2\theta_i}{\sin^2\theta_1}$	Q^2	C	a
#1	19.1						
#2	22.2						
#3	32.2						
#4	38.8						
#5	40.85						

1. Construct a table similar to the one shown above.
2. Using the given diffraction data calculate $\sin\theta$ and $\sin^2\theta$ for each diffraction peak.
3. Find the ratio of $\frac{\sin^2\theta_i}{\sin^2\theta_1}$ for each diffraction peak where $\sin^2\theta_1$ is the value for each successive peak.
4. Determine the crystalline structure of the material by comparing the ratios you have found to the characteristic lines in Figure 5. **Hint: you may be required to multiply all of the ratios you have calculated by a common value to do the comparison.** The ratios calculated are Q^2 .
5. Find the lattice parameter for the material. ($\lambda=1.54\text{\AA}$)
6. Assuming that you have a pure substance, which element do you have? (Use a table of lattice structures and parameters for each of the elements).
7. If the metal weighed 100 pounds would it be worth bringing back if you get to keep it yourself?

Part 2 – From the MSE 227 Lab website select a film strip (Group 1, FILM #1). You will be able to use your computer screen to see the film.

1. Measure the arc lengths S_1 through S_n and determine the Bragg angles for each diffraction peak. Make the measurements along the center of the film. Use the darker lines where double sets of lines exist (double lines indicate secondary peaks.)
2. Repeat steps 1-6 of part one above to determine the material you have been given a diffraction film of. ($\lambda=1.54\text{\AA}$)

3. Give the reason that this material cannot be a simple cubic.

	peak #	Bragg angle, θ_i	$\sin \theta_i$	$\sin^2 \theta_i$	$\sin^2 \theta_i / \sin^2 \theta_1$	$\approx Q^2$	Q^2	C	a
	mm								
S1									
S2									
S3									
S4									
S5									
S6									
S7									
S8									
Sn									

Write Up

A memo report is required for this experiment.

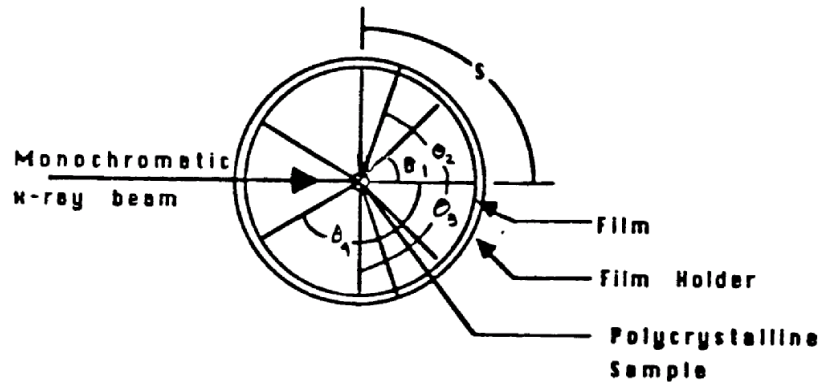


Fig. 3 - Sketch of x-ray diffraction camera.

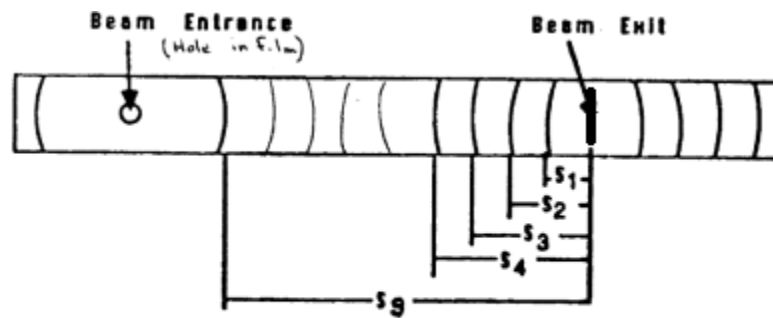


Fig. 4 - X-ray film showing diffraction lines.

$(hkl) \rightarrow$
values

(100)	(110)	(111)	(200)	(210)	(211)	(220)	(221)	(300)	(310)	(311)	(222)	(320)	(321)	(400)

SIMPLE CUBIC

--	--	--	--	--	--	--	--	--	--	--	--	--	--	--

BODY-CENTERED-CUBIC

--	--	--	--	--	--	--	--	--	--	--	--	--	--	--

FACE-CENTERED-CUBIC

$$Q^2 = h^2 + k^2 + l^2$$

1 2 3 4 5 6 8 9 10 11 12 13 14 16

Table A-6 The crystal structure of the elements* (Cont.)

Element: form (transformation temp. °C)	Temp. °C	Structure	Type	Lattice constants			Inter-atomic dist., A	Density g per cm ³	Atomic weight (1939)**	Vol per at.	
				a in A (space group; parameters)	b in A (parameters)	c in A (α or β)					
Indium (In)	R.T.	Tetrag.	A6	4.5979	(f.c. cell)		4.9467	3.251	7.290	114.82	26.1
	R.T.	Tetrag.	A6	3.2512	(b.c. cell)		4.9467	3.251	7.290	114.82	26.1
	4°K	Tetrag.	A6	4.5557			4.9342				
Iodine (I)	26	Orthorhomb.		4.79	7.25			3.54	4.953	126.91	42.6
Iridium (Ir)	26	F.c.c.	A1	3.8389				2.714	22.55	192.2	14.1
Iron, α (Fe)	20	B.c.c.	A2	2.8664				2.482	7.873	55.85	11.7
γ 911 to 1392	918	F.c.c.	A1	3.6468				2.579	7.646		
δ 1392 to m.p.	1394	B.c.c.	A2	2.9322				2.539	7.356		
Krypton (Kr)	4°K	F.c.c.	A1	5.644					3.093	83.90	46.6
Lanthanum, α (La)	20	Hex.		3.770	ABAC...‡	12.131	3.733	6.174	138.92	37.1	
β 310 to 868	500	F.c.c.	A1	5.303			3.750	6.126			
γ 868 to m.p.		B.c.c.	A2	4.26			3.69	5.98			
Lead (Pb)	25	F.c.c.	A1	4.9502			3.500	11.341	207.21	30.1	
Lithium (Li)†	20	B.c.c.	A2	3.5092			3.039	0.533	6.940	21.6	
Below ~ 72°K	78°K	C.p.h.	A3	3.111			5.093	3.11			
Deformed below ~ 110°K	78°K	F.c.c.	A1	~ 4.40			3.11				
Lutetium (Lu)†	R.T.	C.p.h.	A3	3.5050			5.5486	3.434	9.842	174.99	29.1
1400 to m.p.		?									
Magnesium (Mg)	25	C.p.h.	A3	3.2094			5.2105	3.197	1.737	24.32	23.1
Manganese, α (Mn)	25	Cubic	A12	8.9139	(I43m)			2.24	7.473	54.94	12.1
β 742 to 1095	25	Cubic	A13	6.315	(P43m)			2.37	7.24		
γ 1095 to 1133	1095	F.c.c.	A1	3.862				2.731	6.33		
δ 1133 to m.p.	1134	B.c.c.	A2	3.081				2.668	6.23		
Mercury (Hg)	-46	Rhomb.	A10	3.005			α = 70°31'	3.005	14.26	200.61	23.1
77°K after pressure	77°K	B.c.t.		3.995			2.825	14.77			
Molybdenum (Mo)	20	B.c.c.	A2	3.1468				2.725	10.22	95.95	15.1
Neodymium, α (Nd)	R.T.	Hex.		3.6582	P6 ₃ mmc	11.802	3.658	7.004	144.27	34.1	
868 to m.p.		B.c.c.	A2	4.13				3.58	6.80		
Neon (Ne)	4°K	F.c.c.	A1	4.1636				3.155	1.508	20.183	22.1
Neptunium, α (Np)	20	Orthorhomb.	Fnma	4.723	4.887	6.663	2.60-2.64	20.45	(237)	19.1	
β 280 to 577	313	Tetrag.	F42 ₁	4.897	u = 0.375	3.388	2.75	19.36			
γ 577 to m.p.	600	B.c.c.	(?)	3.52				18.12			
Nickel† (Ni)	18	F.c.c.	A1	3.5236				2.492	8.907	58.71	10.1
Niobium (Nb)	20	B.c.c.	A2	3.3007				2.858	8.578	92.91	17.1
(Columbium)											
Nitrogen, α (N ₂)	20°K	Cubic		5.661	Pa3			1.026		14.008	
β 35.6-63.1°K	50°K	Hex.		4.036	P6 ₃ /mmc	6.630		0.987			
Osmium (Os)	20	C.p.h.	A3	2.7353		4.3101	2.675	22.58	190.2	13.1	
Oxygen, α (O ₂) < 23°K	-232	?						1.46	16.000		
β 23-44°K	27°K	Rhomb.		4.210	R3m	α = 46°16'					
γ 44°K - m.p.	48°K	Cubic		6.83	Pm3m			1.30			
Palladium (Pd)	22	F.c.c.	A1	3.8907			2.751	11.995	106.4	14.1	
Phosphorus, white (P)	-35	Cubic		7.17				2.22			
Complex form	-198	?							30.975		
Black† (C ₆₀)	R.T.	Orthorhomb.		3.32	10.52	4.30	2.18	2.69		16.1	
Red	R.T.	Cubic		11.31				2.35			
Yellow, above -70	R.T.	Cubic		18.8	I43m			1.80			
Platinum (Pt)	20	F.c.c.	A1	3.9239				2.775	21.47	195.09	15.1
Plutonium, α (Pu)	21	Monoclin.		6.1835	4.8244	10.973	3.1-3.3	19.814	(242)	23.1	
β 122 to 206	190	Monoclin.		P2 ₁ /m β = 101.81° 9.284 10.463			7.859	2.97- 3.10	17.70		
γ 206 to 319	235	Orthorhomb.		3.159 5.768			10.162	3.026	17.14		
δ 319 to 451	320	F.c.c.	A1	4.637				3.279	15.92		
ε 451 to 485	477	Tetrag.		3.339		4.446		3.27	16.01		
ε 476 to m.p.	490	B.c.c.	A2	3.636				3.149	16.51		
Polonium, α (Po)	~10	Simple cubic		3.345 (1 atom/cell)				3.338	9.31	210	37.1
β	~75	Rhomb.		3.359	R3m	α = 98°13'		9.47			
Potassium (K)	78°K	B.c.c.	A2	5.247			4.544	0.809	39.100	75.1	
	5°K	B.c.c.	A2	5.225			4.525	0.909			

Table A-6 The crystal structures of the elements* (Cont.)

Element: form (transformation temp. °C)	Temp. °C	Structure	Type	Lattice constants			Inter-atomic dist., Å	Density g per cm ³	Atomic weight (1959)**	Volume per atom in Å ³
				a in Å (space group);	b in Å (parameters)	c in Å (α or β)				
Praseodymium, α† (Pr)	R.T.	Hex.		3.6702	ABAC...‡	11.828	3.633	6.779	140.92	34.15
β 798 to m.p.		B.c.c.	A2	4.13			3.58	6.64		
Protactinium (Pa)	R.T.	B.c. tetrag.		3.925		3.238	3.210	15.37	231	24.94
Radium (Ra)									226	
Radon (Rn)									222	
Rhenium (Re)	26	C.p.h.	A3	2.760		4.458	2.741	21.03	186.22	14.70
Rhodium (Rh)	20	F.c.c.	A1	3.8044			2.690	12.42	102.91	13.77
Rubidium (Rb)	-196	B.c.c.	A2	5.610			4.858	1.607	85.48	92.67
	5°K	B.c.c.	A2	5.585			4.837	1.629		
Ruthenium (Ru)	25°K	C.p.h.	A3	2.7057		4.2816	2.650	12.36	101.1	13.57
Samarium† (Sm)	20	Rhomb.		8.996	R3m	23°13'	3.588	7.536	150.35	33.01
				ABABCBCAC...‡						
917 to m.p.		?								
Scandium, α† (Sc)	R.T.	C.p.h.	A3	3.3080		5.267	3.252	2.992	44.96	23.41
Selenium† (Se)	25	Rhomb.	A8	4.3656	(Hex. axes)	4.9590	2.32	4.808	78.96	27.27
α (red metastable)	R.T.	Monoclin.	P2 ₁ /n	9.05	9.07	11.61				
						β = 90°46'				
						9.31				
β (red metastable)	R.T.	Monoclin.	P2 ₁ /c	12.85	8.07					
						β = 93°8'				
Silicon (Si)	20	Cubic	A4	5.4305	Fd3m		2.351	2.329	28.09	30.02
Silver (Ag)	25	F.c.c.	A1	4.0857			2.889	10.50	107.873	17.06
Sodium (Na)	20	B.c.c.	A2	4.2906			3.716	0.9660	22.991	39.50
(metastable)	5°K	B.c.c.	A2	4.225			3.659			
Below ~36°K	5°K	C.p.h.	A3	3.767		6.154	3.767	1.009		
Strontium† (Sr)	25	F.c.c.	A1	6.0849			4.302	2.583	87.63	56.32
~225 to 570 (?)	300	C.p.h.	A3	4.32		7.056	4.32			
~570 to m.p.	614	B.c.c.	A2	4.87			4.23			
Sulfur α, yellow† (S)	R.T.	Orthorhomb.		10.414	10.845	24.369		2.086	32.066	25.52
β, Monoclinic	R.T.	Monoclin.	P2 ₁ /c	10.92	10.98	11.04		2.063		
						β = 83°16'				
Rhombohedral	R.T.	Rhomb.	R3	6.45		α = 115°18'		2.81		
γ Monoclinic	R.T.	Monoclin.	P2 ₁ /n	8.57	13.05	8.23				
						β = 112°54'				
Tantalum (Ta)	20	B.c.c.	A2	3.3026			2.860	16.67	180.95	18.01
Technetium (Tc)	R.T.	C.p.h.	A3	2.743		4.400	2.71	11.497	(99)	14.21
Tellurium (Te)	25	Hex.	A8	4.4566	P3 ₂ 1 or P3 ₂ 1	5.9268	2.864	6.247	127.61	33.98
Terbium† (Tb)	25	C.p.h.	A3	3.5990		5.696	3.525	8.272	158.93	31.14
1310 to m.p.		?								
Thallium, α† (Tl)	18	C.p.h.	A3	3.4566		5.5248	3.457	11.87	204.39	28.58
β 230 to m.p.	262	B.c.c.	A2	3.882			3.362	11.60		
Thorium, α† (Th)	~25	F.c.c.	A3	5.0843			3.595	11.72	232	32.86
β 1400 to m.p.	1450	B.c.c.	A2	4.11			3.56	11.10		
Thulium (Tm)	20	C.p.h.	A3	3.5372		5.5619	3.537	9.325	168.94	30.10
Tin, α, gray (Sn)	20	Cubic	A4	6.4892			2.810	5.765	118.70	27.65
β, white† 13.2 to m.p.	25	Tetrag.	A5	5.8315	I4 ₁ /amd	3.1814	3.022	7.285		
Titanium, α† (Ti)	25	C.p.h.	A3	2.9506		4.6788	2.890	4.508	47.90	17.65
β ~882 to m.p.	900	B.c.c.	A2	3.2065			2.863	4.400		
Tungsten (wolfram) (W)	21	B.c.c.	A2	3.1650			2.741	19.253	183.86	15.85
Uranium, α† (U) Cmcn	25	Orthorhomb.	A20	2.8536	5.8699	4.9555	2.754	19.05	238.07	20.81
				y = 0.10245						
	4°K	Orthorhomb.	A20	2.8444	5.8689	4.9316				
				y = 0.10242						
β 662 to 774	720	Tetrag.		10.759	P4 ₁ /mmm	5.656	2.7-3.3	18.11		
γ 774 to m.p.	800	B.c.c.	A2	3.534			3.061	18.06		
Vanadium (V)	30	B.c.c.	A2	3.0282			2.622	6.09	50.95	13.88
Xenon (Xe)	4°K	F.c.c.	A1	6.131			4.535	3.784	131.30	61.04
Ytterbium† (Yb)	R.T.	F.c.c.	A1	5.481			3.876	6.97	173.04	33.02
798 to m.p.		B.c.c.	A2	4.44			3.85	6.54		
Yttrium (Y)	20	C.p.h.	A3	3.6474		5.7306	3.554	4.475	88.91	33.01
1460 to m.p.		B.c.c.	A2	4.11			3.56			
Zinc (Zn)	25	C.p.h.	A3	2.6649		4.9468	2.665	7.134	65.38	15.24
Zirconium, α† (Zr)	25	C.p.h.	A3	3.2312		5.1477	3.172	6.507	91.22	23.27
β 862 to m.p.	862	B.c.c.	A2	3.6090			3.125	6.443		

* Density is computed from x-ray data (with a few exceptions). Unit cell dimensions in angstroms (values in brackets were multiplied by 1.00202). Data are from original sources and from "International Tables for X-ray Crystallography", vol. 3, Kynoch, Birmingham, England, 1962; also from W. B. Pearson, "Handbook of Lattice Spacings of Metals and Alloys," Pergamon, New York, 1958.

† The form judged to be the stable one at ordinary temperatures and pressures. See p. 233 for high-pressure forms.

‡ The sequence of letters indicates the sequence of close-packed atomic layers.

** Atomic weights of 1959 were based on the O¹⁶ = 16 scale; to convert to the new international C¹² = 12 scale, divide these by 1.000043. However, newer values of greater precision appear frequently.