X-Ray Diffraction

Objectives: To become familiar with the basic principles of x-ray diffraction. To measure and analyze the x-ray diffraction pattern of several specimens. To determine the crystal structure and lattice constant for each specimen. To identify an unknown specimen based on the x-ray diffraction pattern.

Reference:

- B.D. Cullity and S.R. Stock, <u>Elements of X-Ray Diffraction</u>, $2^{n}d$ Ed. (Prentice Hall: New Jersey, 2001).

Also see standard introductory solid-state physics textbooks such as *Solid State Physics* by Ashcroft & Mermin or *Introduction to Solid State Physics* by Kittel.

Apparatus:

GE X-ray spectrometer and power system

Tracer Northern analyzer

Mech-Tronics amplifier

A 1 KV HV supply

PC with PHA/MCA software & manual

Important: Read the *Diffractometer Operating Procedure* <u>before</u> turning on the diffractometer. Always remember that you will be working with an x-ray source. Exercise appropriate caution at all times when the diffractometer is in operation!

Introduction: The apparatus is essentially an x-ray specrometer which may be used in one of two modes:

- To measure the x-ray spectra of a source using a crystal of a known structure

- To study crystalline and non-crystalline materials by looking at how they diffract x-rays of a known wavelength

We will be using the unit in the latter mode, so the instrument will be referred to as a diffractometer. The essential features of the diffractometer are shown on Figure 1.

A specimen is supported on a table that is free to rotate about its perpendicular axis (located at the origin in Figure 1). An X-ray source (molybdenum anode) supplies X-rays that are scattered from the sample and focussed at the slit before going to the detector. Wavelength selection is achieved by using a beam monochromator (see Figure 2) that contains a LiF crystal.

The purpose of the monochromator is to reduce the continuous background, K_β radiation and fluorescent radiation emitted from the sample. The electronics are used to amplify and filter signal pulses from the detector. The upper level discriminator (ULD) is used to eliminate high energy pulses generated by pileup, while the low level discriminator (LLD) is used to take out the lower energy pulses due to fluorescence and the escape peak. These two discriminators define an energy window where pulses are counted for a set dwell
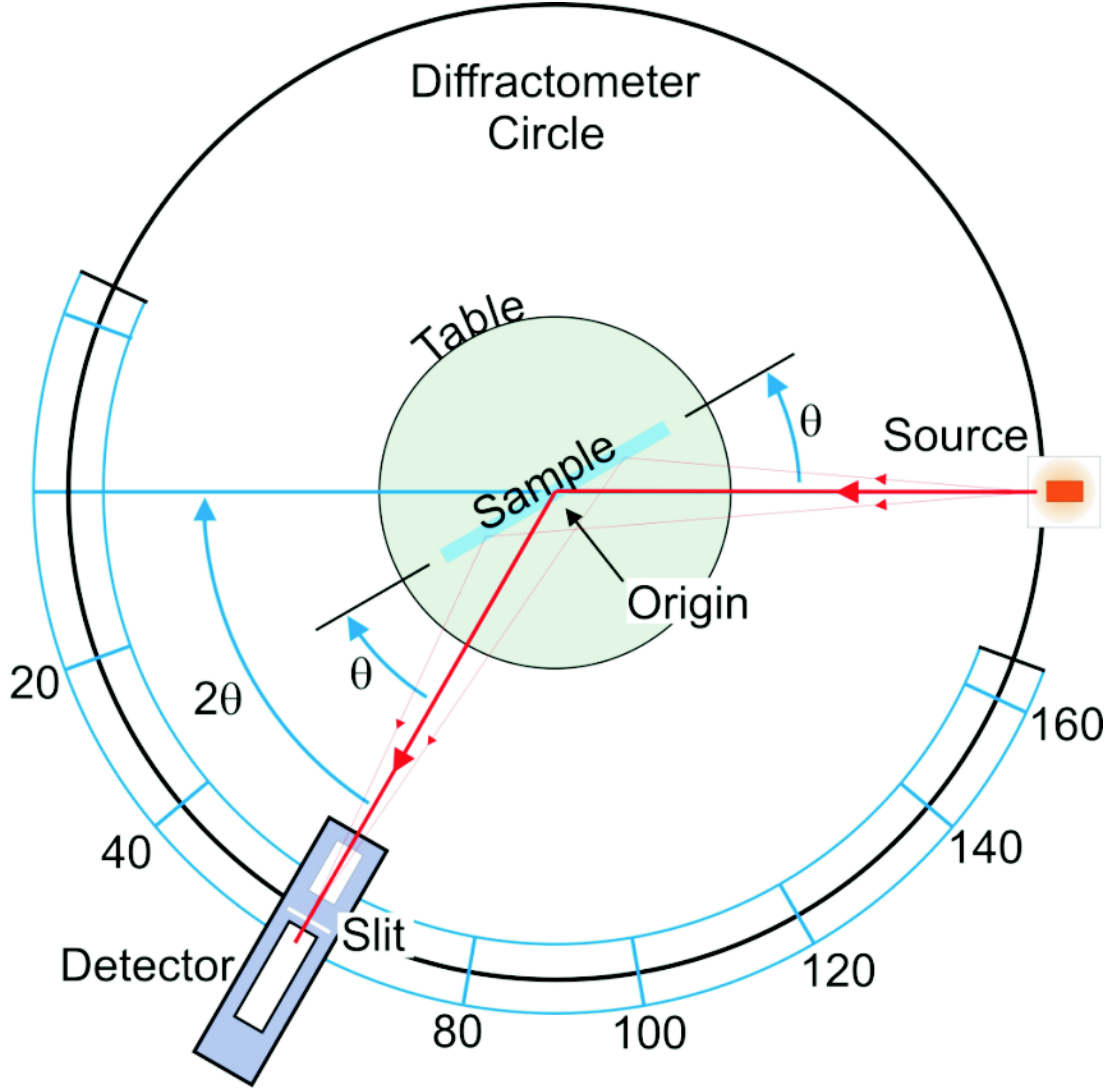
Figure 1: Table and detector rotate about origin.

time using a multichannel analyzer. As the sample is rotated, the count rate will reflect the flux of diffracted x-ray photons for that orientation.

Strong peaks are expected when the Bragg condition is satisfied:

$$n\lambda = 2d\ \sin\theta \tag{1}$$

where n is the order of diffraction (usually n =1), λ is the x-ray wavelength and d is the spacing between planes of given Miller indices h, k and l. See references for more details concerning the Miller indices and the Bragg condition. In the cubic system, the plane spacing is related to the lattice constant a and the Miller indices by the following relation:

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \tag{2}$$

Combining equations 1 and 3, we get:

$$\left(\frac{\lambda}{2a}\right)^2 = \frac{\sin^2\theta}{h^2 + k^2 + l^2} \tag{3}$$
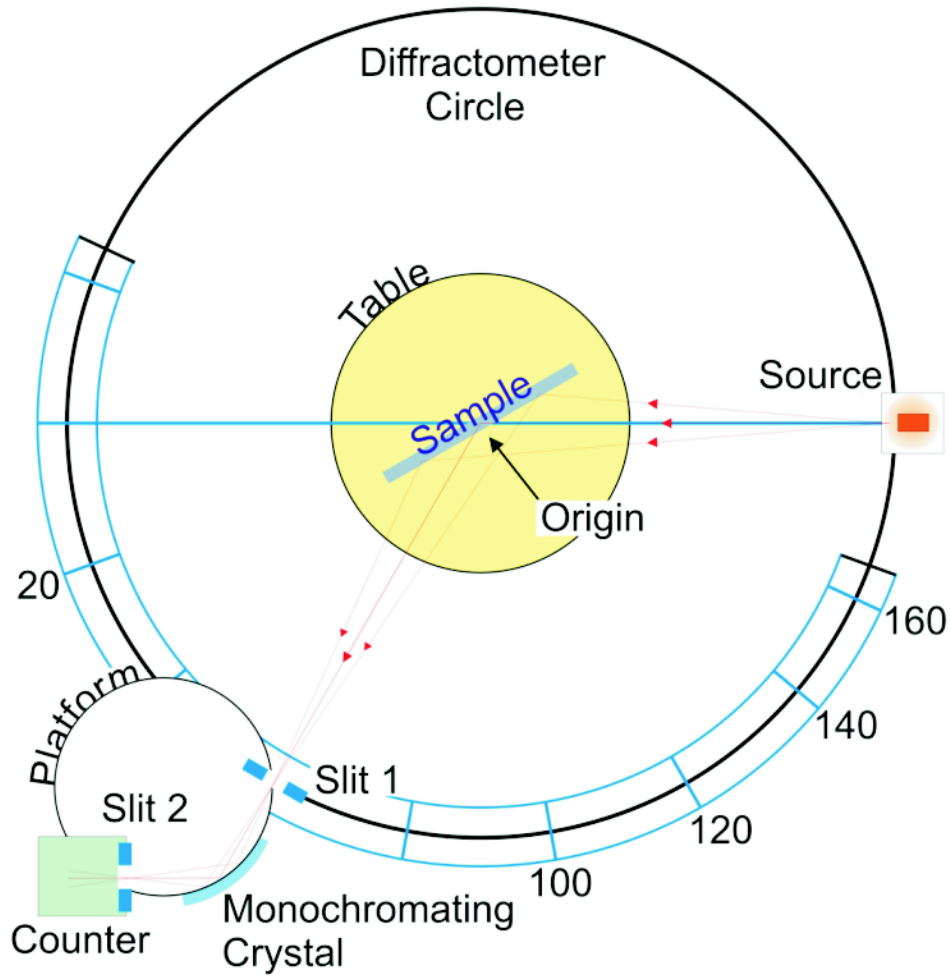
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Figure 2: The Monochromator: Slit 1, the crystal and the counter are all mounted on the platform and move together.

Thus for all sets of Miller indices there is an angle that will satisfy the Bragg condition such that the value of $\frac{\lambda}{2a}$ is a constant. The distinction between the simple cubic (SC), body-centred cubic (BCC) and face-centred cubic (FCC) crystal structures can therefore be made by comparing the allowed Miller indices with those evaluated from the x-ray spectrum. The value of the lattice constant follows directly from the x-ray wavelength, which is 0.711 Å for this experiment.

The allowed values of the Miller indices are determined from the crystal structure factor $S(h, k, l)$, defined as:

$$S(h, k, l) = \sum_m f_m \ \exp\left[-2\pi i\left(u_m h + v_m k + w_m l\right)\right] \tag{4}$$

where f_m is the atomic scattering factor, (u,v,w) are the coefficients for the basis vectors of the atoms in the unit cell of the crystal structure. It can be shown that for the FCC structure, the Miller indices must be all even or all odd or else the structure factor is zero. Only non-zero $S(h, k, l)$ values yield diffraction peaks hence only these need be considered. Similar rules apply for the SC and BCC structures, and **the student should derive these selection rules as part of the lab report**.

Experiment: Before starting the actual experiment, you should make sure you have read the *Diffractometer Operating Guide* and understand how to operate the diffractometer. You should also make sure that the PHA/MCA software is configured as a multi-channel analyzer (MCA), where each channel corresponds to a time bin of user-defined duration, as opposed to each channel corresponding to an energy bin, as is the case for a pulse-height analyzer (PHA). The number of channels and bin time are set within the *"Header: Preset"* menu. In general, 1024 channels should be used, as this allows for a diffraction pattern to be collected over the range $1° < 2\theta < 70°$ in a reasonable amount of time. The bin time is set by typing in the desired value (in microseconds) in the *"Dwell time"* box. *Please do not collect data for $2\theta < 1°$ as this allows unscattered x-rays from the x-ray source to pass directly into the detector, which will saturate your diffraction pattern and may damage the detector.*

Adjustments of the electronics for the GE diffractometer

- Set the bias voltage to +900 V.

- Set the gain to about x128. You will not be using the scaler on this amplifier so you may ignore the E and ΔE settings.

- With a copper sample in the targe chamber, turn on the x-ray source and position the diffractometer to about 1 degree. This should provide you with a moderate count rate so that the discriminators can be adjusted.

- The discriminators should be set to the widest possible window: LLD to minimum value, ULD to its maximum value.

- Collect some counts and adjust the LLD and ULD to see the effect of narrowing the pulse window. You should confirm that no pulses are counted in the window if the x-ray source is powered down, or if the diffractometer is set to an angle where the Bragg condition is not satisfied. This is typically accomplished by slightly increasing the LLD from its minimum value. The student should explain why this should be the case.

Settings for the drive motor of the diffractometer scanning arm

Transmission	Motor	Scan Rate
High	High	15 sec/deg
	Low	30 sec/deg
Low	High	150 sec/deg
	Low	300 sec/deg

- Using copper as a sample, collect a reference pattern that you can use to calibrate the diffractometer. Copper is known to have a FCC crystal structure with a lattice constant $a = 3.6148$ Å. Using this information, the student should calculate the angles θ for which the Bragg condition is satisfied using equation 3 before starting the experiment. Generate a calibration curve relating channel number to Bragg angle θ. If you do not observe peaks at the expected angles, you may need to adjust the orientation of the monochromator. The student should be careful not to confuse θ and 2θ!

- Record and analyze the diffraction patterns of the other samples present: aluminum, brass and the unknown metals, labelled $U1$ and $U2$. In each case, attempt to determine the crystal structure (FCC, BCC or SC) and evaluate the lattice constant. **Quantitatively justify** your conclusion by comparing the results of your assignment with the results obtained assuming the structures. Use of linear least squares fitting is recommended.