

Experiment 2

Bragg reflection: determining the lattice constants of monocrystals

(Modified *Properties of crystals, X-ray structural analysis*. Leybold Physics Leaflets)

Theory

The objective of this experiment is the determination of a lattice constant a_0 of LiF and NaCl monocrystals. For that purpose, the X-ray diffraction method (XRD) will be used to investigate the Bragg reflection from the monocrystals.

Analytical methods using X-rays are among the most powerful techniques for materials characterization. X-rays are produced when an atom is bombarded by electrons or photons of sufficient energy to remove an electron from its inner shell. The energy required to remove an electron from a shell is termed the binding energy of a shell. The K-shell electrons have the highest binding energy for a given atom and binding energies decrease progressively for successive shells (Figure 1). Not only is the binding energy characteristic of a given shell, it is also specific to a given atom. As a result, an electron from an outer shells falling into a vacancy in the inner shell radiates energy characteristic of the element. The resulting spectrum is called characteristic or line spectrum. A typical X-ray spectrum (Figure 2) is composed of characteristic and Bremsstrahlung radiation. The latter is primarily produced by the deceleration of electrons by atoms.

When X-rays encounter matter, a variety of processes may take place including reflection, refraction, diffraction, scattering, absorption, fluorescence, and polarization. The diffraction of X-rays by matter is a consequence of two different phenomena: (a) scattering by each individual atom and (b) interference of the scattered waves. When X-rays hit an atom, they make the electronic cloud move as does any electromagnetic wave. The movement of these charges re-radiates waves with the same frequency; this phenomenon is known as the Rayleigh scattering (or elastic scattering). The scattered waves interfere with each other either constructively or destructively (overlapping waves either add together to produce stronger peaks or subtract from each other to some degree), producing a diffraction pattern on a detector or film. The resulting wave interference pattern is the basis of diffraction analysis.

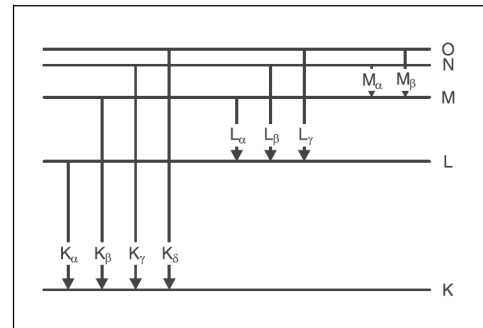


Figure 1. Simplified term diagram of an atom and definition of the K, L, and M series of the characteristic X-ray radiation.

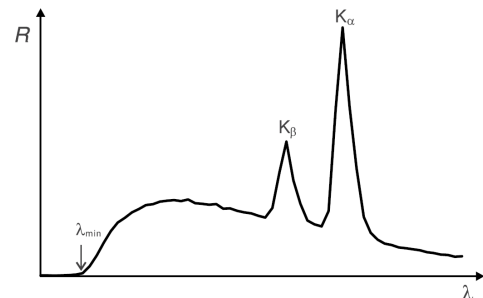


Figure 2. Emission spectrum of an X-ray tube with the characteristic K_{α} and K_{β} lines.

The law governing the diffraction of plane waves off crystal surfaces was derived by physicists Sir W.H. Bragg and his son Sir W.L. Bragg in 1913. It describes the diffraction of plane waves at a monocrystal as the selective reflection of the waves at a set of lattices planes within the crystal. The regular arrangement of atoms in a crystal can be understood as an array of lattice elements on parallel lattice planes. When we expose such a crystal to parallel x-rays, then each element in a lattice plane acts as a “scattering point”, at which a spherical wavelet forms. According to *Huygens*, these spherical wavelets are superposed to create a “reflected” wavefront. In this model, the wavelength λ remains unchanged with respect to the “incident” wave front, and the radiation directions which are perpendicular to the two wave fronts fulfill the condition “angle of incidence = angle of reflection”.

Constructive interference arises in the rays reflected at the individual lattice planes when their path differences Δ are integral multiples of the wavelength λ

$$\Delta = n \cdot \lambda \text{ with } n = 1, 2, 3, \dots \quad (1)$$

From the geometry of the system, as shown in Figure 3, for the two adjacent lattice planes with the spacing d it can be seen that the path differences Δ_1 and Δ_2 of the incident and reflected rays with the angle ϑ

$$\Delta_1 = \Delta_2 = d \cdot \sin \vartheta \quad (2)$$

and the total path difference is

$$\Delta = 2 \cdot d \cdot \sin \vartheta \quad (3)$$

Combining (1) and (3) gives us Bragg’s law of reflection.

$$n \cdot \lambda = 2 \cdot d \cdot \sin \vartheta \quad (4)$$

n – diffraction order

λ – wavelength

d – spacing of lattice planes

The angle ϑ shows the direction of the incident and reflected wave with respect to the set of lattice planes and is often referred to as the glancing angle.

In a cubic crystal with NaCl structure (Figure 4), the lattice planes run parallel to the surfaces of the crystal’s unit cells in the simplest case. Their spacing d corresponds to one half of the lattice constant:

$$d = \frac{a_0}{2} \quad (5)$$

This allows us to use the Bragg’s law of reflection for determining the lattice constant a_0 :

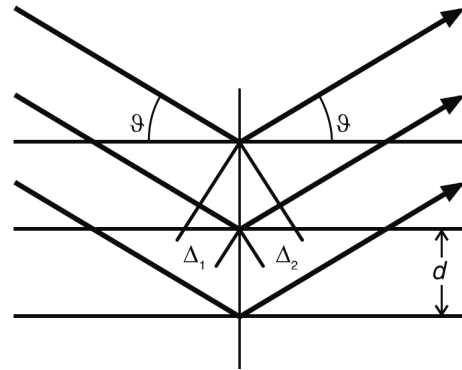


Figure 3. Diagram of the reflection of the X-rays at the lattice planes of a monocrystal. Δ_1 , Δ_2 – path differences, ϑ – glancing angle, d – spacing of lattice planes.

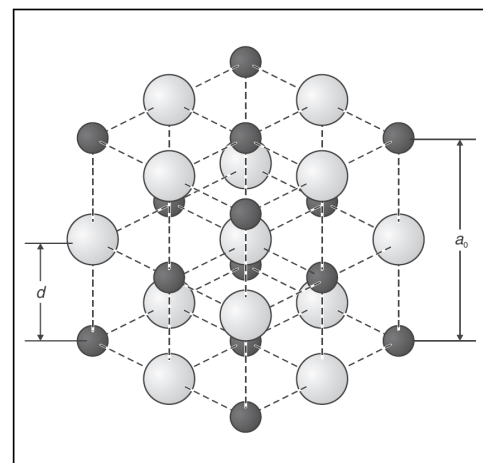


Figure 4. Structure of NaCl; d – spacing of lattice planes in $[1,0,0]$ direction; a_0 – lattice constant

$$n \cdot \lambda = a_0 \cdot \sin \vartheta \quad (6)$$

The X-ray wavelengths are comparable with inter-atomic distances (~150 pm) and thus are an excellent probe for this length scale. The study of crystalline materials has utilized X-ray diffraction techniques in characterizing new compounds and/or used as an analytical tool for determination of sample impurity, phase changes and diagrams, structure refinement, identification of known phases, and the determination and refinement of lattice parameters.

Experimental

XRD instruments (Figure 5) measure the intensity of x-rays reflected from lattice planes as a function of glancing angle ϑ (Figure 6). The counter-tube and the crystal are both pivoted with respect to the incident x-ray beam in 2ϑ coupling – the counter-tube is turned by twice the angle of the crystal (for every degree the sample rotates, the detector rotates by two degrees). The zero point of the measuring system $\vartheta = 0^\circ$ refers to the orientation of the sample in which the lattice planes are parallel to the incident X-ray beam and the axis of the counter-tube. The lattice planes are seldom precisely parallel to the surface of the crystal; the zero point of each crystal must be calibrated individually.

In this experiment, the molybdenum x-rays are used as radiation of a known wavelength. The wavelengths of the characteristic X-ray radiation of molybdenum are shown in (Table 1).

Table 1. Wavelengths of the characteristic x-ray radiation of molybdenum.

Line	λ / pm
K_α	71.08
K_β	63.09

THE GLASS WINDOWS MUST REMAIN CLOSED AT ALL TIMES

Do not open the glass door when the tube high voltage is on. High voltage indicator lamp (HV ON/OFF) is located on the front panel of the instrument. Switch the X-ray source off before opening the door.

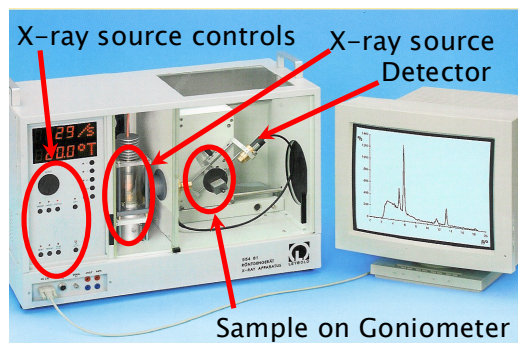


Figure 5. X-ray apparatus.

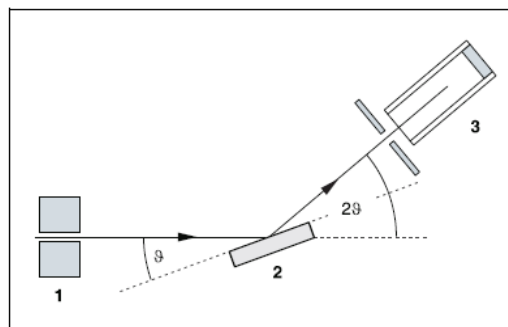


Figure 6. Schematic diagram of diffraction of X-rays at a monocrystal and 2θ coupling between counter-tube angle and scattering angle (glancing angle). 1 collimator, 2 monocrystal, 3 counter-tube

Note: NaCl and LiF crystals are hygroscopic and extremely fragile. Store the crystals in a desiccator; avoid mechanical stress on the crystals; handle the crystals by the short faces only.

The important details of the experimental setup are shown in Figure 7. Using the X-ray apparatus controls (cf. Figure 5) you can adjust the X-ray source parameters as well as change the scanning mode. The latter controls the relative motion of the target (f) and sensor(e). The instrument can be in one of the three scanning modes. The 2θ coupling mode in which both the counter-tube (e) and the sample stage (f) are pivoted with respect to the incident X-ray beam is activated by pressing the *COUPLED* key. In this mode the counter-tube is turned by twice the angle of the sample stage. The other two modes are sensor and target scanning modes in which only the counter-tube or sample stage turns, respectively. The target scanning mode is activated by pressing *TARGET* and the sensor scanning mode is activated by pressing *SENSOR*.

Bragg reflection at an NaCl monocrystal:

Installing the sample and setting the X-ray source parameters

- Loosen the knurled screw (g), place the NaCl crystal flat on the target stage (f), carefully raise the target stage with crystal all the way to the stop and gently tighten the knurled screw (prevent skewing of the crystal by applying a slight pressure).
- Shut the glass window and switch the power to the apparatus on (the power switch is located on the lower left side of the instrument).
- Press *ZERO* key to return the target and sensor to the current zero position. The target (f) and sensor (b) arm should be aligned horizontally as shown in Figure 7. If they are not: press *SENSOR* key and align the sensor arm (b) and collimator (a) horizontally using the *ADJUST* knob. Next press *TARGET* key and align the target and the sensor arm horizontally also using the *ADJUST* knob. Save these positions as the “zero position of the measuring system” by pressing *TARGET*, *COUPLED*, and β -limits simultaneously.
- Set the x-ray tube high voltage. Press the *U* button and then turn the *ADJUST* dial until 35.0 kV appears on the readout area. (Note: All settings appear on the lower readout area)
- Set the emission current. Press the *I* button and rotate the *ADJUST* dial until readout of 1.00 mA appears.

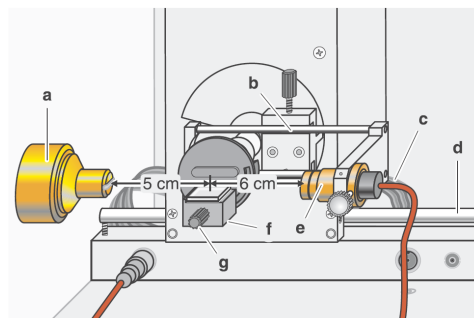


Figure 7. Experiment set up.

Determining the zero position of the measuring system

- Press the *COUPLED* key to activate the coupled scanning mode and set the target to about 7.2° using the *ADJUST* knob.

- b) Switch on the tube high voltage with *HV on/off* button.
- c) Press the *SENSOR* button to activate sensor scanning mode and dialing the *ADJUST* knob find the maximum counting rate for the first reflection maximum of the K_{α} line. In this mode the target position remains unchanged.
- d) Set the instrument to target scanning mode by pressing *TARGET* button and find the counting rate maximum by turning the *ADJUST* dial. In this mode only the target angle varies while the sensor angle remains fixed.
- e) Switch between the sensor and target scanning modes and check whether you have found the counting rate maximum.
- f) In coupled scanning mode, move the target back by 7.2° (even if it takes you into the negative range).
- g) Save the positions of the target and sensor as the “zero position of the measuring system” by pressing *TARGET*, *COUPLED*, and β *LIMITS* simultaneously.

Recording the diffraction spectrum

- a) Start the software “X-ray apparatus” by double-clicking the respective icon on the desktop. Press *F4* to clear any existing measurement data.
- b) Set the measuring time per angular step by depressing the Δt button on the instrument and rotate the *ADJUST* dial until 10s appears.
- c) Set the angular step width by pressing the $\Delta\beta$ key and use *ADJUST* knob to set the 0.1° value.
- d) Press the *COUPLED* key to activate the 2θ coupling of target and sensor and set the lower limit of the target angle to 4° and the upper limit to 26° . Set the lower limit of the angular scan by depressing the β_{limits} button on the instrument (down arrow should appear on the readout area) and rotating the *ADJUST* dial until 4° appears. Set the upper limit of the angular scan by pressing the β_{limits} button on the instrument again (up arrow should appear on the readout area) and rotating the *ADJUST* dial until 26° appears.
- e) Start measurement and data transfer to the PC by pressing the *SCAN* key.
- f) When the scan has finished (angle on the readout area should have reached 26°), save the data under an appropriate filename by pressing *F2* key. An image should also be printed out for your records. Before sending any data to the printer make sure the switch box next to the printer is set to accept data from the XRD computer. The Electrochemistry and DSC computer also uses this printer.

Bragg reflection at an LiF monocrystal:

Installing the sample and setting the X-ray source parameters

- a) Press the ZERO key to return the target and sensor to the current zero position.
- b) Make sure the tube high voltage is off. Remove the NaCl crystal and carefully mount the LiF crystal in its place. Close the sliding door.
- c) You will be using the same parameters of the X-ray tube as before, thus the tube high voltage $U = 35$ kV and emission current $I = 1.00$ mA should not be changed.

Determining the zero position of the measuring system

- a) In coupling scanning mode (press *COUPLED* to activate this mode), set the target to about 10.2° using *ADJUST* knob.
- b) Switch on the tube high voltage with *HV ON/OFF*.
- c) In sensor scanning mode (press *SENSOR* to switch to this mode) find the counting rate maximum for the first reflection maximum of the K_α line using the *ADJUST* knob.
- d) Leave the sensor unchanged in the maximum counting rate position. Activate the target mode by pressing *TARGET* and find the maximum of the counting rate.
- h) Switch between the sensor and target scanning modes and check whether you have found the counting rate maximum.
- i) In coupled scanning mode, move the target back by 10.2° (even if it takes you into the negative range).
- e) Save the positions of the target and sensor as the “zero position of the measuring system” by pressing *TARGET*, *COUPLED*, and β *LIMITS* simultaneously.

Recording the diffraction spectrum

- a) Press *F4* to clear any existing measurement data. If the “X-ray apparatus” software is not started click the respective icon on the desktop to start it.
- b) Set the measuring time per angular step by depressing the Δt button on the instrument and rotate the *ADJUST* dial until 10s appears.
- c) Set the angular step width by pressing the $\Delta\beta$ key and use *ADJUST* knob to set the 0.1° value.
- d) Press the *COUPLED* key to activate the 2θ coupling of target and sensor and set the lower limit of the target angle to 4° and the upper limit to 35° . Set the lower limit of the angular scan by depressing the β_{limits} button on the instrument (down arrow should appear on the readout area) and rotating the *ADJUST* dial until 4° appears. Set the upper limit of the angular scan by pressing the β_{limits} button on the instrument again (up arrow should appear on the readout area) and rotating the *ADJUST* dial until 35° appears.
- e) Start measurement and data transfer to the PC by pressing the *SCAN* key.
- f) When the scan has finished (angle on the readout area should have reached 34°), save the data under an appropriate filename by pressing *F2* key. An image should also be printed out for your records. Before sending any data to the printer make sure the switch box next to the printer is set to accept data from the XRD computer. The Electrochemistry and DSC computer also uses this printer.

Shut down procedure

- Use the ADJUST knob to set $U = 0.0$ kV and $I = 0.0$ mA.
- Turn off the high voltage, press the HV ON/OFF key.
- Switch the instrument OFF by pressing the power switch on the side of the instrument.
- Open the glass door and remove the sample. Loosen knurled screw, carefully lower the stage, holding the stage in place remove the sample, gently tighten the knurled screw. Close the glass window.
- Please the sample in a desiccator.

Evaluations

- In each diffraction spectrum you have collected, click the right mouse button to access the evaluation functions of the software “X-ray apparatus” and select the command “Calculate Peak Center” to evaluate the diffraction spectra.
- Using the left mouse button, mark the “full width” of each peak (click below and then above the peak of interest) and write down the center values in the table as the glancing angle ϑ . The peak center will be calculated and displayed on the lower left hand corner of the screen.
- For each glancing angle ϑ , calculate $\sin \vartheta$ and plot $n\lambda$ as a function of $\sin \vartheta$ for the NaCl and LiF monocrystals. In each case the results should lie along a straight line. In accordance with equation 6; its slope corresponds to the lattice constant. Using least-square analysis calculate the slopes and compare the results with the literature values of the lattice constants of NaCl and LiF. Comment on the relative size of the lattice constants (Hint: What would you expect based on the radii of ions involved).

Table of X-ray Diffraction Peaks

ϑ	$\sin \vartheta$	Line	n	$n\lambda$ /pm
		K_{β}	1	
		K_{α}	1	
		K_{β}	2	
		K_{α}	2	
		K_{β}	3	
		K_{α}	3	

Refer to texts, **Principles of Instrumental Analysis** by Douglas Skoog, 5th ed. Saunders, Philadelphia (1998); **A Practical Guide to Instrumental Analysis** by Erno Pungor, Chapter 11.