Debye-Scherrer photographs of polycrystalline samples with a cubic crystal structure (Item No.: P2541401)
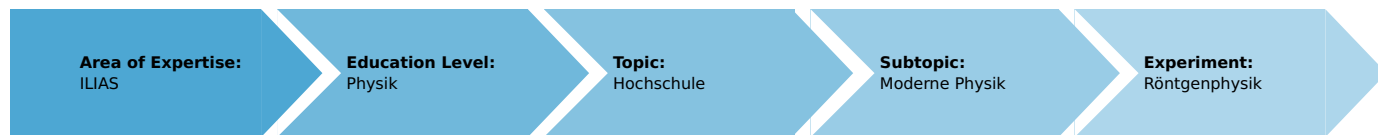
Curricular Relevance

| Area of Expertise: ILIAS | Education Level: Physik | Topic: Hochschule | Subtopic: Moderne Physik | Experiment: Röntgenphysik |

Difficulty	**Preparation Time**	**Execution Time**	**Recommended Group Size**
Difficult	1 Hour	2 Hours	2 Students

Additional Requirements:	**Experiment Variations:**

Keywords:

Characteristic X-radiation, Bravais lattices, reciprocal lattices, Miller indices, atomic form factor, structure factor, Bragg scattering

Overview

Short description

Principle

When polycrystalline samples are irradiated with X-rays a characteristic diffraction pattern results. These Debye-Scherrer reflections are photographed and then evaluated.

This experiment is included in the upgrade set "XRS 4.0 X-ray structural analysis". Instead of the X-ray films 09058-23, self-developing x-ray films (9057-20) can be used for the experiment. For more details, see appendix.

Fig. 1: P2541401

Equipment

1	XR 4.0 expert unit	09057-99
1	X-ray plug-in unit with a molybdenum X-ray tube	09057-60
1	Mortar and pestle, 70 ml, porcelain	32603-00
1	Microspoon, steel, l = 150 mm	33393-00
1	Vernier calliper	03010-00
1	X-ray fluorescent screen	09057-26
1	X-ray film holder	09057-08
1	Slide mount for the optical bench	08286-01
1	X-ray optical bench	09057-18
1	X-ray diaphragm tube, d = 1 mm	09057-01
1	Sodium chloride, 250 g	30155-25
1	Caesium chloride, 5 g	31171-02
1	X-ray film, (90 x 20) cm, 10 sheets	06696-03
1	X-ray film developer for 4.5 l	06696-20
1	X-ray film fixing salt for 4.5 l	06696-30
3	Laboratory tray, PP, (18 x 24) cm, white	47481-00

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Tasks

1. Take photographs of the Debye-Scherrer reflections of the powdered samples of sodium chloride and caesium chloride.

2. Assign the Debye-Scherrer rings to the corresponding lattice planes.

3. Calculate the lattice constants of the crystals.

4. Determine the number of atoms in the unit cell.

Questions

A. Wieso?

B. Weshalb?

C. Warum?

D. Wer nicht fragt, bleibt dumm!!!

E. BASTA

Safety instructions

When handling chemicals, you should wear suitable protective gloves, safety goggles, and suitable clothing. Please refer to the appendix for detailed safety instructions.

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Setup and Procedure

Procedure

Prior to starting the experiment, take the goniometer out of the experiment chamber.
Then, insert the diaphragm tube with a diameter of
1 mm into the beam outlet of the X-ray plug-in unit.
Position the film in darkness in the film holder (see fig. 2) and confirm that the holder is firmly closed. Fix the holder into the holder of the fluorescent screen and position it on the internal optical bench at a distance of $x \approx 35mm$ from the crystal. The precise determination of this distance is very important for the subsequent evaluation. The film plane should be parallel to the crystal surface.
The X-ray tube is used at maximum power (anode voltage U_A = 35 kV, anode current I_A = 1 mA). The exposure time of 2.5 hours can be set and activated as follows:

- Select the tube operating parameters under "X-ray parameters" and confirm them with "Enter".
- Under "Menu", select "Timer" (Fig. 3) → "Duration". Set the desired time with the aid of the arrow buttons. Confirm with "Enter".
- The window "Mode" appears. Select "On" and confirm with "Enter" (Fig. 4).
- To start the experiment, close and lock the sliding door and press the button under "Start" (Fig. 5).

Fig. 2: Position of the film in the film holder

Fig. 3

Fig. 4

Fig. 5

The irradiation starts. It will stop automatically after the preset exposure time. On the display, the remaining time can be observed based on a backwards running clock and a display bar.
Longer exposure times offer the advantage of better visibility of the outer reflection rings. However, on the downside, the central primary beam outshines the inner reflection rings.
We recommend keeping the prepared samples for future experiments (as caesium chloride is hygroscopic, samples of it should be kept in an airtight container containing silica gel).
X-ray films must be developed in a darkroom, following the instructions on the packaging. Then, the films are rinsed in a water bath before they are fixed for approximately 10 minutes. After that, the films are re-watered for 10 minutes and then dried in the air.

Sample preparation:

The thickness of the samples should be between 0.2 and 0.4 mm. If the samples are not thick enough, the edge absorption effect cannot be made visible. On the other hand, samples that are too thick absorb nearly the entire primary beam intensity. This is why the following method is recommended for preparing samples of a suitable thickness:

First, pulverise the samples with the aid of a mortar. Then, use an office punch and punch several sheets of paper of a suitable thickness (2 to 3 layers of standard printing paper) and seal the hole on one side with some transparent adhesive tape (see Fig. 6a). The result is a little "pot". Fill the sample powder into the pot with a spatula and smooth the surface. Seal the pot with another piece of transparent adhesive tape. Then, fasten the strip of paper that has been cut to size in front of the diaphragm tube (aperture diameter 1 mm) with some transparent adhesive tape (Fig. 6d).
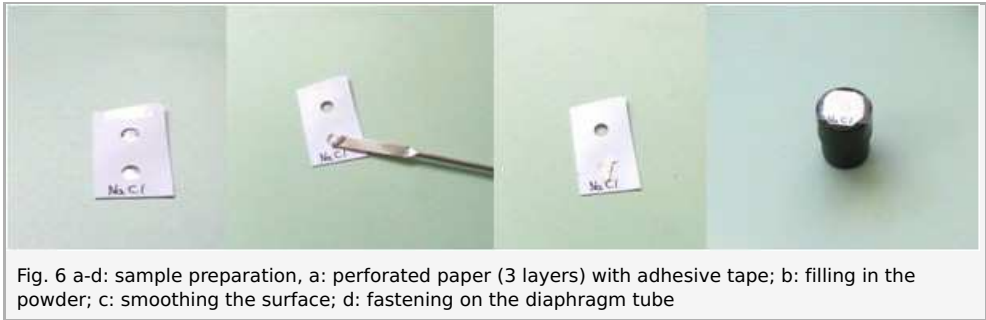

Fig. 6 a-d: sample preparation, a: perforated paper (3 layers) with adhesive tape; b: filling in the powder; c: smoothing the surface; d: fastening on the diaphragm tube

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Theory and Evaluation

Theory

On atoms, X-rays are scattered by the electrons of the atoms. As a result, the scattering power of an atom that is represented by the atomic form factor f (atomic scattering factor) is proportional to the number of electrons in those atoms and, thereby, also to the atomic number Z:

$$f \propto Z \qquad (1)$$

If the atoms in a solid are arranged in a periodic manner, X-rays can be reflected in a constructive manner on the lattice planes. If, at the same time, the Bragg condition (2) is fulfilled, they interfere in a constructive manner:

$$2d sin\vartheta = n\lambda (n = 1, 2, 3, \ldots) \qquad (2)$$
(d = interplanar spacing, ϑ = glancing angle, λ = wavelength of the X-radiation, n = 1, 2, 3, ...).

The intensity I of the scattered radiation is proportional to the square of the so-called structure factor F. The latter is obtained by the summation of the partial waves that are scattered on the individual n-atoms and of their phases.

If the n-atoms in a unit cell have the coordinates $u_n, v_n, and w_n$, the following relationship is valid for $F(h, k, l)$ with the Miller indices h, k, l of the reflecting lattice plane:

$$F(h, k, l) = \sum_n f_n \cdot exp[-2\pi i (h u_n + k v_n + l w_n)] \qquad (3)$$

A body-centred cubic (bcc) unit cell has atoms with the coordinates (000) and $\left(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right)$.
Equation (3) leads to: $F = 0$, if the sum of the Miller indices is an odd number $(h + k + l) = 2n$ +1 (with n = 0, 1, 2, 3, ...). If, however, the sum is an even number $(h + k + l) = 2n$, then $|F|^2 = 4f^2$.

The atoms in the unit cell of a face-centred cubic (fcc) crystal have the coordinates (000), $\left(\frac{1}{2}, \frac{1}{2}, 0\right), \left(\frac{1}{2}, 0, \frac{1}{2}\right), and (0, \frac{1}{2}, \frac{1}{2})$.
In this case, F = 0 if $h, k, and l$ are mixed, i.e. if there are even and odd indices. If, however, all of the indices are either even or odd, then $|F|^2 = 16f^2$.
A polycrystalline sample consists of many crystallites with different spatial orientation. When monoenergetic X-rays impinge upon such a sample, there will always be some crystallites with a position with regard to the primary beam that fulfil the Bragg condition. Therefore, all of the reflections that belong to a particular interplanar spacing are located on the mantle of a cone with an aperture angle of 4ϑ (see Fig. 7). An X-ray film that is positioned perpendicularly to the cone axis will thus record concentric circles as reflection images (Debye-Scherrer rings).
If the diameter of a reflection ring is D and x is the distance between the sample and the film, the following results for the glancing angle ϑ (see Fig. 7):

$$\vartheta = \frac{1}{2} arctan \frac{D}{2x} \qquad (4)$$

For a cubic crystal with the lattice constant a, the following is valid for the distance $d_{h,k,l}$ between the lattice planes:
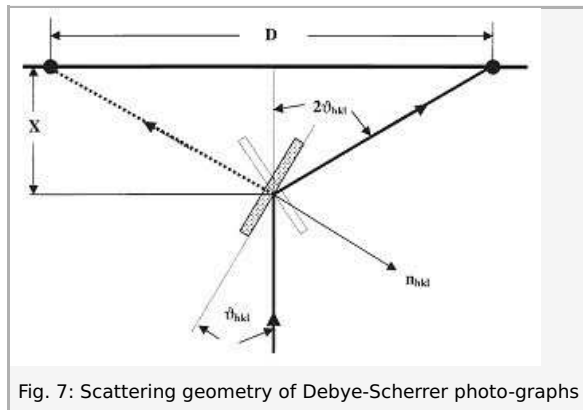
$$d_{h,k,l} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \qquad (5)$$

Using (4) and (5) and $n = 1$, we obtain from (2):

$$sin^2\vartheta = sin^2\left(\frac{1}{2} arctan \frac{d}{2x}\right) = \frac{\lambda^2}{4a^2}(h^2 + k^2 + l^2) \qquad (6)$$

With (4), the following method can be applied in order to assign the reflections to the various lattice planes:
Based on the calculated glancing angles of the reflection rings, the quotients $sin^2\vartheta_n / sin^2\vartheta_{min}$, ($\vartheta_{min}$ = glancing angle of the first, innermost reflection ring) are formed. The quotients must correspond to the fractions of integral numbers, i.e. to $N_n / N_{min} (N = h_2 + k_2 + l_2)$. Then, all of the possible combinations of the Millers indices (001, 011, 111, 002, ...) are listed for Nn and then the corresponding quotients with the triplet (001) for $N_m in$ should be attempted to be formed. If no match can be found, continue with Nmin and the triplets (011) or (111).

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Fig. 7: Scattering geometry of Debye-Scherrer photo-graphs

Task 1

Sodium chloride

Take photographs of the Debye-Scherrer reflections of the powdered sample.

Figure 8 shows the Debye-Scherrer ring pattern of NaCl. Up to 7 reflection rings can be seen in the original photograph.

Fig. 8: Debye-Scherrer pattern of a powdered sample of NaCl. Thickness of the sample: 0.4 mm. Ex-posure time: 2.5 h. Mo X-ray tube: UA = 35 kV; IA = 1 mA

Task 2

Assign the Debye-Scherrer rings to the corresponding lattice planes.

Table 1 shows the evaluation. Measure the ring diameters D with the vernier calliper and calculate the glancing angles ϑ with the aid of equation (4). The corresponding interplanar distances d are obtained from the Bragg conditions (2). The quotients of the sin^2 values (column 5) only match the N_n/N_{min} quotients (column 6) if the first ring reflection is assigned to the (111) lattice plane.

Table 1:Evaluation of the Debye-Scherrer rings of NaCl. Distance between the sample and film: x = 32 mm + 0.5 mm thickness of the film. Wavelength: λ(Kα) = 71.1 pm, (mean value of the Mo-Kα1 and Kα2

1	very weak	14.8	6.4	1.00	1.00	011	318.9	552.4
2	very strong	16.7	7.2	1.26	1.33	002	283.6	567.3
3	very strong	24.6	10.3	2.65	2.66	022	198.8	562.4
4	strong	30.7	12.6	3.83	4.00	222	163.0	564.5
5	weak	36.2	14.6	5.11	5.33	004	141.0	564.1
6	medium	42.0	16.4	6.4	6.66	024	125.9	563.1
7	weak	47.6	18.1	7.76	8.00	224	114.4	560.6

Task 3

Calculate the lattice constants of the crystals.

Determine the lattice constant α from the Miller indices of the individual lattice planes based on (5).
The following results for the mean value of the individual values of α:
α = (562.0 $\pm$ 4.7) pm; $\Delta\alpha/\alpha = \pm$ 0.8% (literature value: α (NaCl) = 563.9 pm).
Column (7) includes either only even or only odd Miller indices. The (113) reflection is only visible after a longer exposure time.
NaCl, therefore, forms an fcc-lattice.

Task 4

Determine the number of atoms in the unit cell.

The density ρ of a crystal is given by the quotient of the total mass M of the n-atoms in the unit cell and of the volume V of the cell.

$$p = \frac{n \cdot m}{V} = \frac{n \cdot m}{\alpha^3} \qquad (7)$$

With the corresponding values for NaCl, the following results:

$$p = 2.16 g \cdot cm^{-3}; m = \frac{1}{N_A}(m_{Na} + m_{Cl})$$

$$m = \frac{1}{6.022 \cdot 10^{23}}(22.9 + 35.45)g = 9.70 \cdot 10^{-23}g$$
(N_A = Avogadro constant, m_{Na}, m_{Cl} = atomic weights)

$$n = \frac{2.16 \cdot 5.62^3 \cdot 10^{-24} g \cdot cm^{-3} cm^3}{9.70 \cdot 10^{-23}g} = 3.95 \approx$$

This means that the unit cell includes 4 atoms, as is required for an fcc-lattice (see also P2541301).

Task 1

Caesium chloride

Take photographs of the Debye-Scherrer reflections of the powdered sample.

Figure 9 shows the result for CsCl. Up to seven ring reflections can be seen in the original photograph.

Fig. 9: Debye-Scherrer pattern of a powdered sample of CsCl. Thickness of the sample: 0.4 mm. Ex-posure time: 2.0 h. Mo X-ray tube: UA = 35 kV; IA = 1 mA

Task 2

Assign the Debye-Scherrer rings to the corresponding lattice planes.

Table 2 shows the corresponding evaluation. In this case, the indices of the lattice planes (column 7) are mixed and their sum is always even-numbered. CsCl, therefore, forms a bcc-lattice.

Table 2:Evaluation of the Debye-Scherrer rings of CsCl.
Distance between the sample and film: x = 30 mm + 0.5
mm thickness of the film. Wavelength: λ(Kα) = 71.1 pm,
(mean value of the Mo-Kα1 and Kα2

1	very strong	15.5	7.1	1.00	1.00	011		287.6	406.7
2	very weak	19.4	8.8	—	—	002 (Kb)		206.2	412.4
3	very strong	22.3	10.0	1.97	2.00	002		204.7	409.4
4	strong	27.9	12.3	2.97	3.00	112		166.9	408.8
5	weak	32.9	14.2	3.94	4.00	022		144.9	409.9
6	medium	37.8	15.9	4.91	5.00	013		129.8	410.5
7	weak	42.7	17.8	5.92	6.00	222		118.2	409.5

Task 3

Calculate the lattice constants of the crystals.

Based on the individual values of the lattice constant a (column 9), the following mean value results:
α = (409.6 $\pm$ 1.7) pm; $\Delta\alpha/\alpha = \pm$ 0.5% (literature value: α (CsCl) = 411.0 pm)

Task 4

Determine the number of atoms in the unit cell.

The following applies to CsCl:

$$p = 3.97 g \cdot cm^{-3}; m = \frac{1}{2 \cdot N_A}(m_{Cs} + m_{Cl})$$

$$m = \frac{1}{2 \cdot 6.022 \cdot 10^{23}}(13291 + 35.45)g = 13.97 \cdot 10^{23}g$$

(8) then leads to:

$$n = 1.95 \approx 2$$

This means that the unit cell of CsCl includes 2 atoms, as is required for a bcc-lattice.
(As the atomic weights of Cs and Cl differ distinctly, it makes sense to use the mean value of the two masses for the determination of m).

Note

Disposal

Do not dispose of heavy-metal-containing waste via household waste.

Appendix

Safety

Symbol, signal word	Hazard statements	Precautionary statements
Sodium chloride (NaCl)		
-	--	-
Caesium chloride (CsCl)		
-	--	-

Taking a Laue photograph with the aid of self-developing X-ray film

A monocrystal X-ray structure analysis can be performed live during a lecture with the aid of self-developing X-ray films (09057-20) in combination with the XR 4.0 expert unit. If a Cu X-ray tube is used, the photography only takes 12.5 minutes and, with molybdenum tubes, good results can be achieved after just 5 minutes. The development itself takes only 2 to 3 minutes.
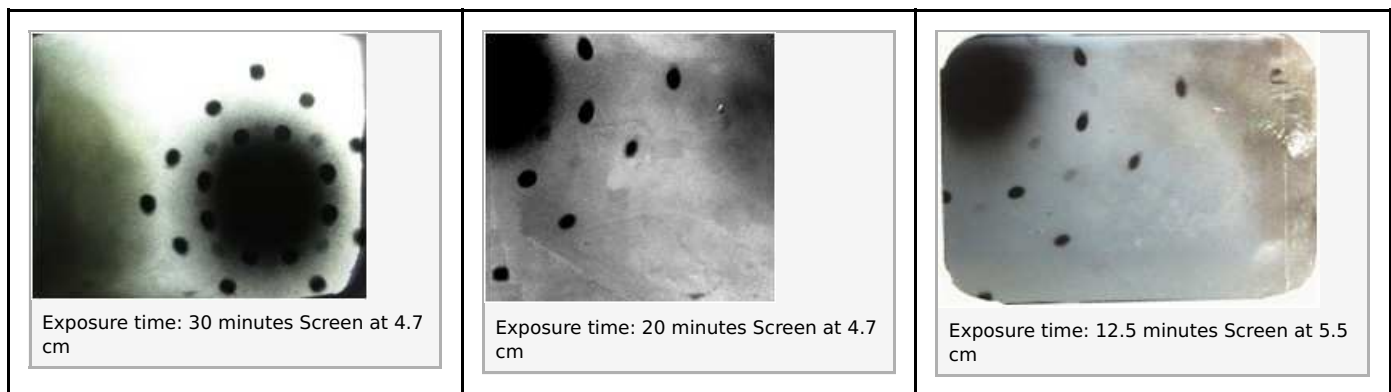

Set-up in the X-ray unit

Data

Cu X-ray plug-in unit   09057-50
Tube voltage: 35 kV
Beam current: 1 mA
Diaphragm: 1 mm (09057-01)
Exposure time: 10-30 minutes
The position of the screen is determined with the aid of the mm scale on the optical bench.

Exposure time: 30 minutes Screen at 4.7 cm

Exposure time: 20 minutes Screen at 4.7 cm

Exposure time: 12.5 minutes Screen at 5.5 cm

The X-ray film is not positioned centrally in front of the crystal. Instead, it is offset, since only a quadrant of the diagram is sufficient for the evaluation. The picture should be enlarged in order to evaluate it. We recommend scanning the photo and then enlarging it digitally.
As far as the development of the film is concerned, please refer to the instructions for use that are enclosed with the films. We recommend developing the film for 2 minutes instead of only 50 seconds. It is very important to hold the developed film under flowing water once it has been taken out of the wrap. Do not dry it with towels. Only let it air-dry.