X-ray investigation of cubic crystal structures / Debye-Scherrer powder method

Physics > Modern Physics > Production & use of X-rays

Difficulty level	Group size	Preparation time	Execution time
hard	2	45+ minutes	45+ minutes

PHYWE excellence in science

General information

Application

PHYWE excellence in science

Setup

Most applications of X rays are based on their ability to pass through matter. Since this ability is dependent on the density of the matter, imaging of the interior of objects and even peaple becomes possible. This has wide usage in fields such as medicine or security.

PHYWE excellence in science

Robert-Bosch-Breite 10
37079 Göttingen

Tel.: 0551 604 - 0
Fax: 0551 604 - 107

info@phywe.de
www.phywe.de

Other information (1/2)

PHYWE excellence in science

Prior knowledge

The prior knowledge for this experiment is found in the Theory section.

Main 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.

Other information (2/2)

PHYWE excellence in science

Learning objective

The goal of this experiment is to get to analyse the crystal structur of sodium chloride and caesium chloride.

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.

PHYWE excellence in science

Robert-Bosch-Breite 10
37079 Göttingen

Tel.: 0551 604 - 0
Fax: 0551 604 - 107

info@phywe.de
www.phywe.de

Safety Instructions

When handling chemicals, you should wear suitable protective gloves, safety goggles, and suitable clothing.

Theory (1/5)

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:

$$2d \sin(\theta) = n\lambda \qquad (2)$$

(d = interplanar spacing; θ = glancing angle; λ = wavelength; n = 1, 2, 3, ...)

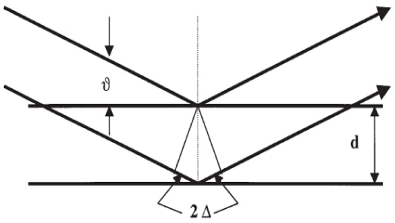


Fig. 1: Bragg scattering on a pair of lattice planes

Robert-Bosch-Breite 10
37079 Göttingen
Tel.: 0551 604 - 0
Fax: 0551 604 - 107
info@phywe.de
www.phywe.de

Theory (2/5)

PHYWE excellence in science

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, w_n, the following relationship is valid for F(h,k,l) with the Miller indices h, k, l of the reflecting lattice plane:

$$F(h,k,l) = \sum_n f_n \cdot \exp[-2\pi i(hu_n + kv_n + lw_n)] \qquad (3)$$

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 $|F|^2 = 4f^2$.

Theory (3/5)

PHYWE excellence in science

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 $\left(0, \frac{1}{2}, \frac{1}{2}\right)$,. 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 θ (see Fig. 2). An X-ray film that is positioned perpendicularly to the cone axis will thus record concentric circles as reflection images (Debye-Scherrer rings).

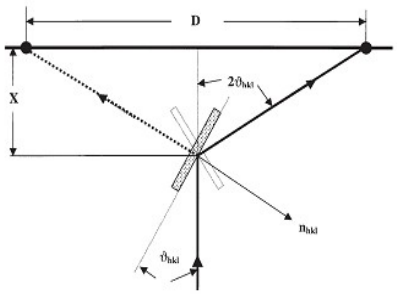


Fig. 2: Scattering geometry of Debye-Scherrer photo-graphs

PHYWE excellence in science
Robert-Bosch-Breite 10
37079 Göttingen
Tel.: 0551 604 - 0
Fax: 0551 604 - 107
info@phywe.de
www.phywe.de

Theory (4/5)

PHYWE excellence in science

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. 2):

$$\theta = \frac{1}{2}\arctan\left(\frac{\mathrm{D}}{2\mathrm{d}}\right) \qquad (4)$$

For a cubic crystal with the lattice constant a, the following is valid for the distance $\mathrm{d_{h,k,l}}$ between the lattice planes:

$$\mathrm{d_{h,k,l}} = \frac{\mathrm{a}}{\sqrt{\mathrm{h^2+k^2+l^2}}} \qquad (5)$$

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

$$\sin(\theta_{\mathrm{hkl}}) = \sqrt{\mathrm{h^2+k^2+l^2}} \cdot \frac{\lambda}{2\mathrm{a}} \qquad (6)$$

Theory (5/5)

PHYWE excellence in science

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 $\sin(\theta_{\mathrm{n}}/\sin(\theta_{\mathrm{min}})$, ($\theta_{\mathrm{min}}$ = glancing angle of the first, innermost reflection ring) are formed. The quotients must correspond to the fractions of integral numbers, i.e. to $\mathrm{N_n/N_{min}(N = h^2 + k^2 + l^2)}$. Then, all of the possible combinations of the Millers indices (001, 011, 111, 002, ...) are listed for $\mathrm{N_n}$ and then the corresponding quotients with the triplet (001) for $\mathrm{N_m}$ should be attempted to be formed. If no match can be found, continue with Nmin and the triplets (011) or (111).

PHYWE excellence in science

Robert-Bosch-Breite 10
37079 Göttingen

Tel.: 0551 604 - 0
Fax: 0551 604 - 107

info@phywe.de
www.phywe.de

Equipment

Position	Material	Item No.	Quantity
1	XR 4.0 expert unit, 35 kV	09057-99	1
2	XR4 X-ray Plug-in Cu tube	09057-51	1
3	XR 4.0 X-ray structural analysis upgrade set	09145-88	1
4	Sodium chloride 250 g	30155-25	1

PHYWE excellence in science
Robert-Bosch-Breite 10
37079 Göttingen
Tel.: 0551 604 - 0
Fax: 0551 604 - 107
info@phywe.de
www.phywe.de

PHYWE excellence in science

Setup and Procedure

Procedure (1/4)

PHYWE excellence in science

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. 3) 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 $x \approx 35\,mm$ 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:

Fig. 3: Position of the film in the film holder

PHYWE excellence in science
Robert-Bosch-Breite 10
37079 Göttingen
Tel.: 0551 604 - 0
Fax: 0551 604 - 107
info@phywe.de
www.phywe.de

Procedure (2/4)

Fig. 4

Fig. 5

- Select the tube operating parameters under “X-ray parameters” and confirm them with “Enter”.
- Under “Menu”, select “Timer” (Fig. 4) → "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. 5).
- To start the experiment, close and lock the sliding door and press the button under “Start” (Fig. 6).

Fig 6

Procedure (3/4)

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.

Robert-Bosch-Breite 10
37079 Göttingen
Tel.: 0551 604 - 0
Fax: 0551 604 - 107
info@phywe.de
www.phywe.de

Procedure (4/4)

PHYWE excellence in science

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. 7a). The result is a little “pot”. Fill the sample powder into the pot with a spatula and smooth the surface.

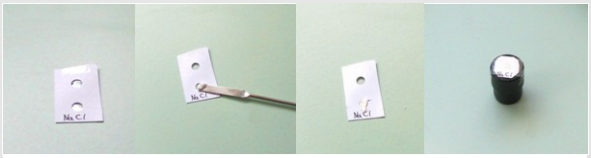


Fig. 7 a-d: sample preparation, a: perforated paper (3 layers) with adhesive tape; b: filling in the powder; c: smoothing the surface; d: fastening on the diaphragm tube

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. 7d).

PHYWE excellence in science

Evaluation

PHYWE excellence in science
Robert-Bosch-Breite 10
37079 Göttingen
Tel.: 0551 604 - 0
Fax: 0551 604 - 107
info@phywe.de
www.phywe.de

Task 1

PHYWE excellence in science

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

Figure 8 shows the Debye-Scherrer ring pattern of NaCl, Figure 9 shows the result for CsCl. Up to seven ring reflections can be seen in the original photographs.

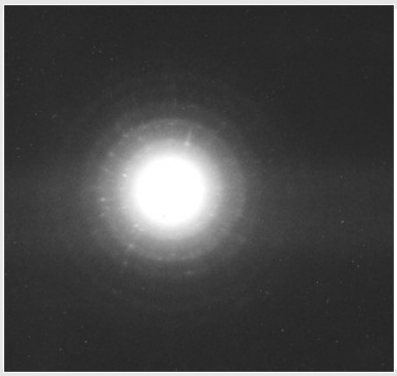


Fig. 8: Debye-Scherrer pattern of a powdered sample of NaCl. Thickness of the sample: 0.4 mm. Ex-posure time: 2.5 h.

Fig. 9: Debye-Scherrer pattern of a powdered sample of CsCl. Thickness of the sample: 0.4 mm. Ex-posure time: 2.0 h.

Task 2

PHYWE excellence in science

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

Table 1 shows the evaluation for sodium chloride. 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 2 shows the corresponding evaluation for caesium chloride. 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.

PHYWE excellence in science

Robert-Bosch-Breite 10
37079 Göttingen

Tel.: 0551 604 - 0
Fax: 0551 604 - 107

info@phywe.de
www.phywe.de

Task 2 (part 2)

PHYWE excellence in science

Reflection no.	Intensity	D [mm]	θ [°]	$\sin(\theta_n)/\sin(\theta_1)$	N_m/N_{min}	hkl	d [pm]	a [pm]
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	564.4
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

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: $\lambda(K_\alpha)$ = 71.1 pm.

Task 2 (part 3)

PHYWE excellence in science

Reflection no.	Intensity	D [mm]	θ [°]	$\sin(\theta_n)/\sin(\theta_1)$	N_m/N_{min}	hkl	d [pm]	a [pm]
1	very strong	15.6	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

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: $\lambda(K_\alpha)$ = 71.1 pm.

PHYWE excellence in science

Robert-Bosch-Breite 10
37079 Göttingen

Tel.: 0551 604 - 0
Fax: 0551 604 - 107

info@phywe.de
www.phywe.de

Task 3

PHYWE excellence in science

Calculate the lattice constants of the crystals.

Determine the lattice constant a from the Miller indices of the individual lattice planes based on (5).
The following results for the mean value of the individual values of a:

Sodium Chloride:

a = (562.0 $\pm$ 4.7) pm; $\Delta a/a = \pm$ 0.8% (literature value: a(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.

Ceasium Chloride:

a = (409.6 $\pm$ 1.7) pm; $\Delta a/a = \pm$ 0.5% (literature value: a(CsCl) = 411.0 pm).

Task 4

PHYWE excellence in science

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.

$$\rho = \frac{n \cdot m}{a^3} \qquad (7)$$

With the corresponding values for NaCl, the following results:

$$\rho = 2.16\,\mathrm{g/cm^3};\ m = \frac{1}{N_A}(m_{Na} + m_{Cl}) = 9.70 \cdot 10^{-23}\,\mathrm{g}$$

(N_A = Avogadro constant; m_{Na}, m_{Cl} atomic weights)

$$\rightarrow\ n = 3.95 \approx 4$$

This means that the unit cell includes 4 atoms, as is required for an fcc-lattice (see also P2541305).

PHYWE excellence in science
Robert-Bosch-Breite 10
37079 Göttingen
Tel.: 0551 604 - 0
Fax: 0551 604 - 107
info@phywe.de
www.phywe.de

Task 4 (part 2)

PHYWE excellence in science

Determine the number of atoms in the unit cell.

The following applies to CsCl:

$\rho = 3.97\,\mathrm{g/cm^3};\ \mathrm{m} = \frac{1}{2\mathrm{N_A}}(\mathrm{m_{Cs}} + \mathrm{m_{Cl}}) = 13.97 \cdot 10^{-23}\,\mathrm{g}$

($\mathrm{N_A}$ = Avogadro constant; $\mathrm{m_{Cs}}, \mathrm{m_{Cl}}$ atomic weights)

$\rightarrow\ \mathrm{n} = 1.95 \approx 2$

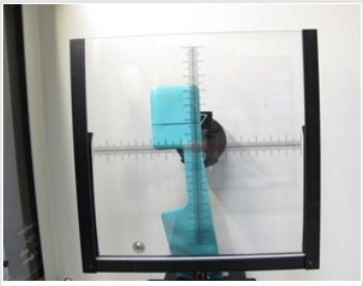
This means that the unit cell of CsCl includes 2 atoms, as is required for a bcc-lattice.
(As the atomic weights of Cs and Cl differ distinctly, it makes sense to use the mean value of the two masses for the determination of m).

PHYWE excellence in science

Appendix

PHYWE excellence in science
Robert-Bosch-Breite 10
37079 Göttingen
Tel.: 0551 604 - 0
Fax: 0551 604 - 107
info@phywe.de
www.phywe.de

Alternative Procedure (1/2)



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
Exposure time:	10-30 minutes

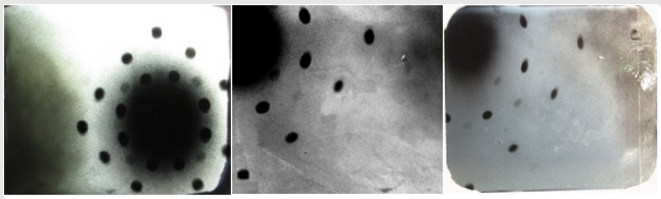
The position of the screen is determined with the aid of the mm scale on the optical bench.

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 in combination with the XR 4.0 expert unit. If a Cu X-ray tube is used, the photography only takes 12.5 minutes. The development itself takes only 2 to 3 min.

Alternative Procedure (2/2)

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.



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

PHYWE excellence in science
Robert-Bosch-Breite 10
37079 Göttingen
Tel.: 0551 604 - 0
Fax: 0551 604 - 107
info@phywe.de
www.phywe.de