Debye-Scherrer photographs of a polycrystalline sample with a hexagonal crystal structure (Item No.: P2541501)

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

A polycrystalline zirconium foil is irradiated with X-rays. The resulting Debye-Scherrer reflections are photographed and then evaluated.

This experiment is included in the upgrade set “XRS 4.0 X-ray structural analysis”.

Student's Sheet

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Fig. 1: P2541501

Note: This experiment can also be performed with a copper X-ray tube (09057-50). 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.

Equipment

Position No.	Material	Order No.	Quantity
1	XR 4.0 expert unit, X-ray unit, 35 kV	09057-99	1
2	XR 4.0 X-ray Plug-in Mo tube	09057-61	1
3	XR 4.0 X-ray Diaphragm tube w. zirconium foil	09058-03	1
4	Vernier calliper, plastic	03011-00	1
5	XR 4.0 X-ray film holder	09057-08	1
6	XR 4.0 X-ray films, 100 pieces	09058-23	1
7	XR 4.0 X-ray film developer, for 9 l solution	06696-20	1
8	XR 4.0 X-ray film fixing, for 9 l solution	06696-30	1
9	Tray (PP), 180x240mm, white	47481-00	3
10	XR 4.0 X-ray optical bench	09057-18	1
11	Slide mount for optical bench expert, h = 30 mm	08286-01	1

Tasks

1. Take photographs of the Debye-Scherrer reflections of a thin, polycrystalline zirconium foil.
2. Assign the Debye-Scherrer rings to the corresponding lattice planes.
3. Calculate the lattice constants of zirconium.
4. Determine the number of atoms in the unit cell.

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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 the Zr foil (d = 0.005 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) $\rightarrow$ “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.
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.

Theory and Evaluation

Theory

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 on the lattice planes. If, at the same time, the Bragg condition (2) is fulfilled, they interfere in a constructive manner:

$$2dsin\vartheta = n\lambda(n = 1,2,3,\ldots) \qquad (2)$$

(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 of a unit cell 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:

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

A hexagonal unit cell has atoms with the coordinates (000) and $(\frac{1}{3}, \frac{2}{3}, frac12)$. With these coordinates, equation (3) leads to the following conditions for $|F|^2$.

(n = 0, 1, 2,...)

$h+2k$	l	$\lvert F\rvert^2$
$3n$	odd	0
$3n$	even	$4f^2$
$3n \pm 1$	odd	$3f^2$
$3n \pm 1$	even	f^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. 6). 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. 6):

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

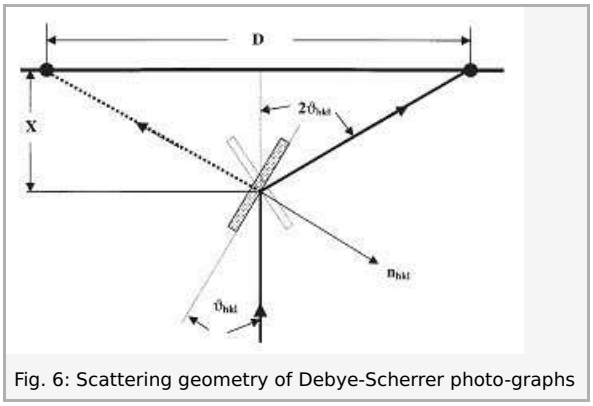

Fig. 6: Scattering geometry of Debye-Scherrer photo-graphs

The interplanar distances d_h, k, l in a hexagonal lattice with the lattice constants α and c result from the square form:

$$\frac{1}{d_h kl^2} = \frac{4}{3} \cdot \frac{h^2+hk+k^2}{\alpha^2} + \frac{l^2}{c^2} \qquad (5)$$

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

$$sin^2\vartheta = sin^2\left(\frac{1}{2}arctan\frac{D}{2x}\right) = \frac{\lambda^2}{3a^2}(h^2+hk+k^2) + \frac{\lambda^2}{4c^2}l^2 \qquad (6)$$

Task 1

Take photographs of the Debye-Scherrer reflections of a thin, polycrystalline zirconium foil.

Figure 7 shows the Debye-Scherrer ring pattern of the Zr foil. The variations in the intensities of the inner ring reflections indicate that the crystallites in the zirconium foil are not distributed fully anisotropically. The rolling process in the manufacture of the foils leads to so-called textures with a certain privileged direction of the crystallites.

Fig. 7: Debye-Scherrer pattern of a zirconium foil. Thickness of the sample: 0.05 mm. Exposure 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.

In order to evaluate the Debye-Scherrer patterns of hexagonal crystals, the following method can be applied:
With the constants $A = \lambda^2/3a^2$ and $B = \lambda^2/4c^2$, it follows from (6) that:

$$sin^2\vartheta = A(h^2+hk+k^2) + Bl^2 \qquad (7)$$

The lattice constant α can be determined by an assignment of lattice planes with $l = 0$.
To do so, divide (as shown in Table 1) the $sin^2\vartheta$ values by 1, 3, 4, 7, etc. and look for the quotients that match each other or a $sin^2\vartheta$ value, as 1, 3, 4, 7 etc. are the permissible (h^2+hk+k^2) values. This is the case with the values in bold type in Table 1. It makes sense to only check the first reflections since these always belong to lattice planes with a small index. If $sin^2\vartheta$ = 0.0160 of the first reflection is assigned to the (100) lattice plane, then reflection no. 5 must correspond to the (110) plane as $sin^2\vartheta$ = 0.04800 is threefold the $sin^2\vartheta$ value of reflection no. 1. As a result, A = 0.016 (see (7) with l = 0).

With $\lambda(Mo-K_\alpha)$ = 71.1 pm, the following results for the lattice constant: α = 323.5 pm.

Table 1: Evaluation of the Debye-Scherrer rings of zirconium: Distance between the sample and film, x = 35 mm; wavelength λ(Kα) = 71.1 pm, (mean value of the Mo-Kα1 and Kα2 lines)

Reflection no.	**Intensity**	D/mm	$\vartheta/^\circ$	$sin^2\vartheta$	$sin^2\vartheta/3$	**h k l**
1	strong	18.9	7.26	0.0160	0.00533	1 0 0
2	strong	20.9	8.0	0.0193	0.00643	
3	very strong	21.8	8.3	0.0209	0.0070	
4	weak	28.9	10.8	0.0351	0.0117	
5	strong	34.5	12.65	0.0480	0.0160	1 1 0
6	very weak	38.8	14.0	0.0585	0.0195	
7	medium	42.2	15.0	0.0671	0.0224	

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Task 3

Calculate the lattice constants of zirconium.

In order to determine the lattice constants c, tabulate $sin^2\vartheta$, $sin^2\vartheta - A$, $sin^2\vartheta - 3A$ etc. and look for Bl^2 values that are in a ratio of 1, 4, 9 etc. to each other.
In Table 2, this is indicated in an approximate manner by the values in bold type, as 0.0191/0.0049 = 3.89 is nearly 4 and 0.0425/0.0049 = 8.7 is nearly 9.
This leads to: 0.0049 = $B(1)^2$, 0.0191 = $B(2)^2$, and 0.0425 = $B(3)^2$. The resulting mean value is B = 0.0048, which in turn leads to the following relationship:
Reflection no. 2 must be assigned to the (002) lattice plane, reflection no. 3 to the (101) lattice plane, and reflection no. 6 to the (103) lattice plane.
The values that are marked with an asterisk in Table 2 must be due to lattice planes with the same l. On trying $l = 2$, we again obtain B = 0.0048.
Using this B value, the second lattice constant c = 513.1 pm. The remaining reflections can now be assigned as follows: Reflection no. 4 $\rightarrow$ (102) and reflection no. 7 $\rightarrow$ (112). For a hexagonal close-packed crystal structure, the ratio $c/a = \frac{8}{3}^{\frac{1}{2}}$ = 1.633. A comparison with the corresponding experimental values provides:
c/a = 513.1 pm/323.5 pm = 1.59.
(Literature values for zirconium: α = 323.0 pm and c = 513.3 pm)

Task 4

Determine the number of atoms in the unit cell.

Dividing the mass M of the unit cell by its volume V gives the density ρ of the crystal:

$\rho = \frac{M}{V} = n \cdot m \frac{2}{\sqrt{3}} \frac{1}{\alpha^2 c}$ (8)

(n = the number of atoms in the unit cell)

With the volume $V = (\sqrt{3/2}\alpha^2 c$ of a hexagonal unit cell, the density $\rho = 6.50 g c m^{-}3$ of zirconium and its atomic weight of m_A = 91.22 g, the following results:

$m = \frac{m}{N_A} = \frac{91.22}{6.022 \cdot 10^2 3} g = 15 \cdot 15 \cdot 10^{-23} g; V = 46.5 \cdot 10^{-24} c m^3$

(N_A = Avogadro constant)

Based on (8), the number of atoms n in the unit cell of zirconium is: $n = 1.99 \approx 2$.

Table 2

Reflection no.	$sin^2\vartheta$	$sin^2\vartheta - A$	$sin^2\vartheta - 3A$	h k l
1	0.0160			1 0 0
2	0.0193*	0.0033		0 0 2
3	0.0209	0.0049		1 0 1
4	0.0351	0.0191*		1 0 2
5	0.0480	0.0320	0	1 1 0
6	0.0585	0.0425	0.0106	1 0 3

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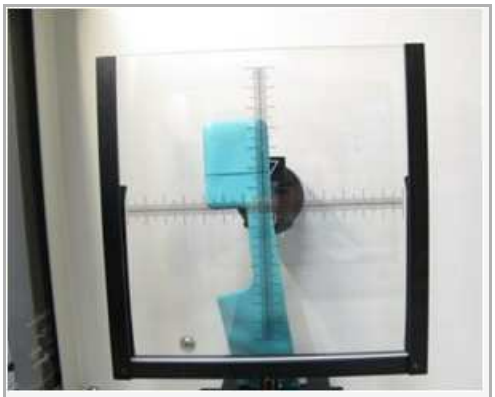
Appendix

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.

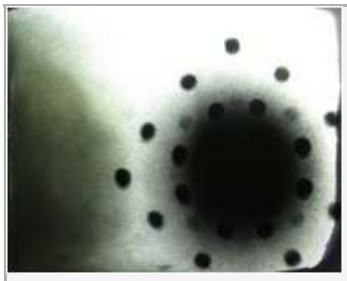


Set-up in the X-ray unit

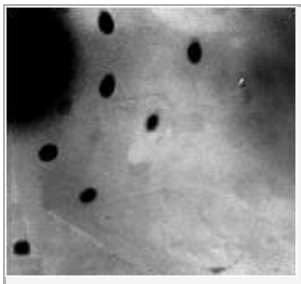
Data

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.