

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



Physics

Modern Physics

Production &amp; use of X-rays



Difficulty level

hard



Group size

2



Preparation time

45+ minutes



Execution time

45+ minutes

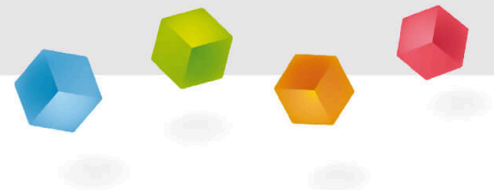
This content can also be found online at:



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# General information



## Application

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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 people becomes possible. This has wide usage in fields such as medicine or security.

## Other information (1/2)

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**Prior****knowledge****Main****principle**

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

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

## Other information (2/2)

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**Learning****objective****Tasks**

The goal of this experiment is to get to analyse the crystal structure of zirconium.

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.

## Theory (1/4)

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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  $Z$ :

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

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:

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

( $d$  = interplanar spacing;  $\theta$  = glancing angle;  $\lambda$  = wavelength;  $n = 1, 2, 3, \dots$ )

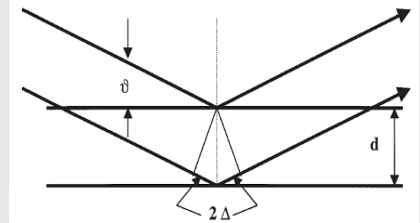


Fig. 1: Bragg scattering on a pair of lattice planes

## Theory (2/4)

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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:

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

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

$h + 2k$	$l$	$ F ^2$
$3n$	odd	0
$3n$	even	$4f^2$
$3n \pm 1$	odd	$3f^2$
$3n \pm 1$	even	$f^2$

## Theory (3/4)

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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  $\theta$  (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).

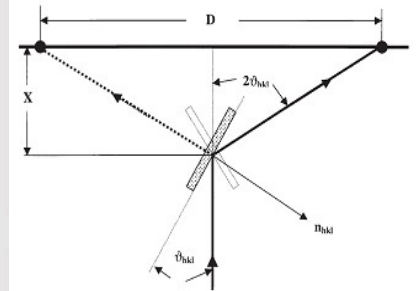


Fig. 2: Scattering geometry of Debye-Scherrer photographs

## Theory (4/4)

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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  $\theta$  (see Fig. 2):

$$\theta = \frac{1}{2} \arctan\left(\frac{D}{2x}\right) \quad (4)$$

The interplanar distances  $d_{h,k,l}$  in a hexagonal lattice with the lattice constants  $a$  and  $c$  result from the square form:

$$\frac{1}{d_{h,k,l}^2} = \frac{4}{3} \cdot \frac{h^2 + hk + k^2}{a^2} + \frac{l^2}{c^2} \quad (5)$$

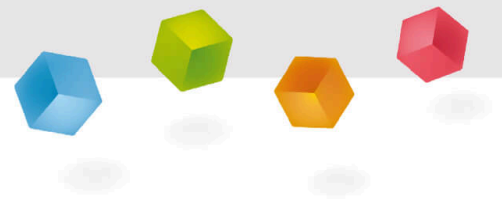
Using (4) and (5) and  $n = 1$ , we obtain from (2):

$$\sin^2(\theta_{hkl}) = \frac{\lambda^2}{3a^2} (h^2 + hk + k^2) + \frac{\lambda^2}{4c^2} l^2 \quad (6)$$

## 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

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# Setup and Procedure

## Procedure (1/3)

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Prior to starting the experiment, take the goniometer out of the experiment chamber.

Then, insert the diaphragm tube with the Zr foil ( $d = 0.005 \text{ mm}$ ) 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  $x \approx 35 \text{ mm}$  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  $U_A = 35 \text{ kV}$ , anode current  $I_A = 1 \text{ mA}$ ). The exposure time of 2.5 hours can be set and activated as follows:



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

## Procedure (2/3)

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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 (3/3)

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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.

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. Please refer to the instructions of use of the X-ray film for details concerning their use.



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# Evaluation

## Task 1

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

Figure 8 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.

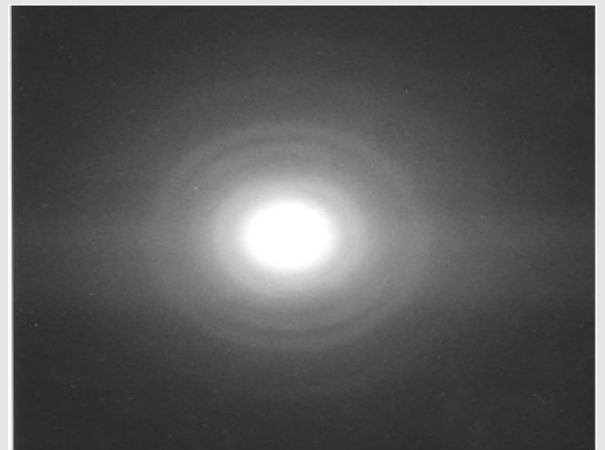


Fig. 8: Debye-Scherrer pattern of a zirconium foil. Thickness of the sample: 0.05 mm. Exposure time: 2.5 h.

## Task 2

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### 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:

$$\sin^2(\theta) = A(h^2 + hk + k^2) + Bl^2 \quad (7)$$

The lattice constant  $a$  can be determined by an assignment of lattice planes with  $l = 0$ .

## Task 2 (part 2)

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To do so, divide (as shown in Table 1) the  $\sin^2(\theta)$  values by 1, 3, 4, 7, etc. and look for the quotients that match each other or a  $\sin^2(\theta)$  value. It makes sense to only check the first reflections since these always belong to lattice planes with a small index. If  $\sin^2(\theta) = 0.0160$  of the first reflection is assigned to the (100) lattice plane, then reflection no. 5 must correspond to the (110) plane as  $\sin^2(\theta) = 0.04800$  is threefold the  $\sin^2(\theta)$  value of reflection no. 1. As a result,  $A = 0.016$  (see (7) with  $l = 0$ ).

Reflection no.	Intensity	D [mm]	$\theta$ [°]	$\sin^2(\theta)$	$\sin^2(\theta)/3$	hkl
1	strong	18.9	7.26	0.0160	0.00533	100
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	110
6	very weak	38.8	14.0	0.0585	0.0195	
7	medium	42.2	15.0	0.0671	0.0224	

**Table 1:** Evaluation of the Debye-Scherrer rings of zirconium. Distance between the sample and film:  $x = 35$  mm. Wavelength:  $\lambda(K_\alpha) = 71.1$  pm  $\rightarrow a = 323.5$  pm.

## Task 3

PHYWE

### Calculate the lattice constants of zirconium.

In order to determine the lattice constants  $c$ , tabulate  $\sin^2(\theta)$ ,  $\sin^2(\theta) - A$ ,  $\sin^2(\theta) - 3A$  etc. and look for  $B$  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  $B = 0.0048$ .

## Task 3 (part 2)

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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  $c/a = 1.633$ . A comparison with the corresponding experimental values provides:  $c/a = 513.1$  pm/ $323.5$  pm = 1.59.

(Literature values for zirconium:  $a = 323.0$  pm and  $c = 513.3$  pm)

Reflection no.	$\sin^2(\theta)$	$\sin^2(\theta) - A$	$\sin^2(\theta) - 3A$	$hkl$
1	0.0160			100
2	0.0193*	0.0033		002
3	0.0209	0.0049		101
4	0.0351	0.0191*		102
5	0.0480	0.0320	0	110
6	0.0585	0.0425	0.0106	103

## Task 4

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

Dividing the mass  $M$  of the unit cell by its volume  $V$  gives the density  $\rho$  of the crystal:

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

With the corresponding values for zirconium, the following results:

$$\rho = 6.50 \text{ g/cm}^3; m = \frac{m}{N_A} = 15.15 \cdot 10^{-23} \text{ g}$$

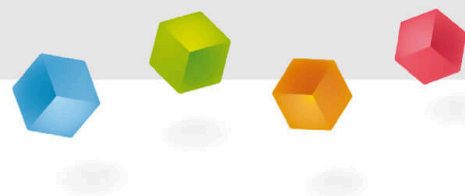
( $N_A$  = Avogadro constant;  $m$  = atomic weight)

$$\rightarrow n = 1.99 \approx 2$$

This means that the unit cell includes 2 atoms.

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## Appendix



## Alternative Procedure (1/2)

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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

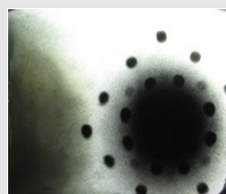
A monocrystal X-ray structure analysis can be performed live during a lecture with the aid of self-developing X-ray films in combination with the XR 4.0 expert unit. If a Cu X-ray tube is used, the photography only takes 12.5 minutes. The development itself takes only 2 to 3 min.

## Alternative Procedure (2/2)

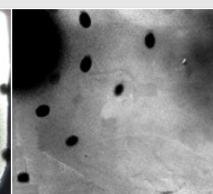
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The X-ray film is not positioned centrally in front of the crystal. Instead, it is offset, since only a quadrant of the diagram is sufficient for the evaluation. The picture should be enlarged in order to evaluate it. We recommend scanning the photo 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