

Debye-Scherrer photography: determining the lattice plane spacings of polycrystalline powder samples

Objects of the experiment

- Evaluating *Debye-Scherrer* photographs of an NaCl and an LiF sample.
- Investigating the lattice structure of NaCl and LiF crystals.
- Determining the lattice constants and the lattice plane spacings.

Principles

Debye-Scherrer photographs:

For taking a *Debye-Scherrer* photograph, a powdery crystalline sample is transilluminated with monochromatic X-rays. The interference pattern of the scattered radiation is frozen on an X-ray film. The powder sample contains minute monocrystals of about 5–50 μm diameter, so-called crystallites. A set of lattice planes in a crystallite leads to a diffraction reflection on the X-ray film if it is aligned so that the Bragg condition

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

n : diffraction order, λ : wavelength,
 d : lattice plane spacing,
 ϑ : Bragg angle relative to the primary ray

is fulfilled (see Fig. 2 and experiment P6.3.3.1). The angle between the diffraction reflection and the film, which is aligned perpendicularly to the primary ray, is 2ϑ .

In general the crystallites are randomly oriented without any privileged direction so that there are always some crystallites in the crystal powder which correspond to a rotation of the crystallite under consideration around their primary axis. In the arrangement of the film selected here, their diffraction reflections form a circle on the X-ray film with the radius

$$R = L \cdot \tan 2\vartheta \quad (II)$$

L : distance between the sample and the film

The finer the power is, the more uniformly the individual reflections of the crystallites will be lined up to form a circle.

The complete diffraction pattern is a set of concentric circles. Because of Eqs. (I) and (II), each radius R corresponds to a certain lattice plane spacing d and a certain diffraction order n or, more precisely, a certain ratio $d' = \frac{d}{n}$.

Fig. 1 Scheme of the setup for taking *Debye-Scherrer* photographs

- | | |
|--------------|--------------|
| a X-ray tube | d Sample |
| b Zrfilter | e X-ray film |
| c collimator | |

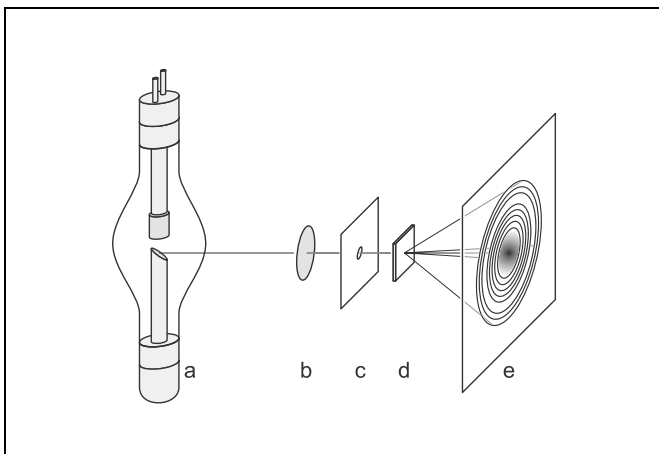
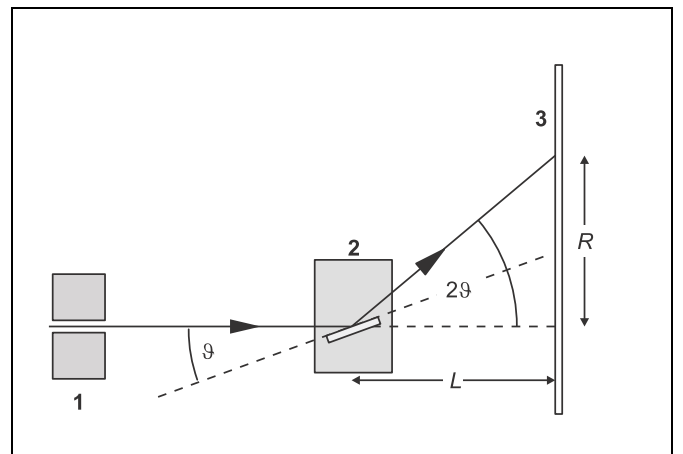


Fig. 2 Bragg reflection at an "appropriate" set of lattice planes of a particular crystallite in the powder sample

- 1: collimator,
- 2: set of lattice planes,
- 3: film



Apparatus

1 X-ray apparatus	554 811
or	
1 X-ray apparatus	554 812
1 X-ray film holder	554 838
1 filmpack 2	554 892
1 pestle, porcelain, 100 mm	667 091
1 mortar, porcelain, 63 mm Ø	667 092
1 precision vernier calliper	331 54

additionally required:

e.g. LiF, NaCl powder

Cubic crystals:

If the consideration is restricted to cubic crystals, the lattice plane spacing can be expressed in the form

$$d = \frac{a_0}{\sqrt{h^2 + k^2 + l^2}} \quad (III);$$

a_0 : lattice constant

here the integers h, k, l are the *Miller indices* of the set of lattice planes under consideration (see experiment P7.1.2.2). If (III) is inserted into Eq. (I), the quadratic form

$$\sin^2 \vartheta = \left(\frac{\lambda}{2a_0} \right)^2 \cdot \left((n \cdot h)^2 + (n \cdot k)^2 + (n \cdot l)^2 \right) \quad (IV)$$

is obtained.

Safety notes

The X-ray apparatus fulfils all regulations governing an X-ray apparatus and fully protected device for instructional use and is type approved for school use in Germany (NW 807 / 97 Rö).

The built-in protection and screening measures reduce the local dose rate outside of the X-ray apparatus to less than $1 \mu\text{Sv/h}$, a value which is on the order of magnitude of the natural background radiation.

- Before putting the X-ray apparatus into operation, inspect it for damage and make sure that the high voltage is shut off when the sliding doors are opened (see instruction sheet for X-ray apparatus).
- Keep the X-ray apparatus secure from access by unauthorized persons.

Do not allow the anode of the X-ray tube Mo to overheat.

- When switching on the X-ray apparatus, check to make sure that the ventilator in the tube chamber is turning.

It can be written in the short form

$$\sin^2 \vartheta = F \cdot Z \quad (V)$$

with

$$F = \left(\frac{\lambda}{2 \cdot a_0} \right)^2 \quad (VI)$$

and

$$Z = (n \cdot h)^2 + (n \cdot k)^2 + (n \cdot l)^2 \quad (VII).$$

Due to its components, Z is always an integer. For simple cubic crystals, every combination of integers n, h, k and l is allowed, however, the intensity of the diffraction reflections is weaker for higher diffraction orders n and greater *Miller indices* h, k, l .

Crystals with NaCl structure:

In the case of crystals with NaCl structure, the situation is more complicated because here alkali (e.g. Na) and halogenide (e.g. Cl) atoms take turns in a cubic lattice. The spatial lattice is no longer built up of simple lattice points with the distance a_0 , but it is a series of cubic unit cells with an edge length a_0 (see

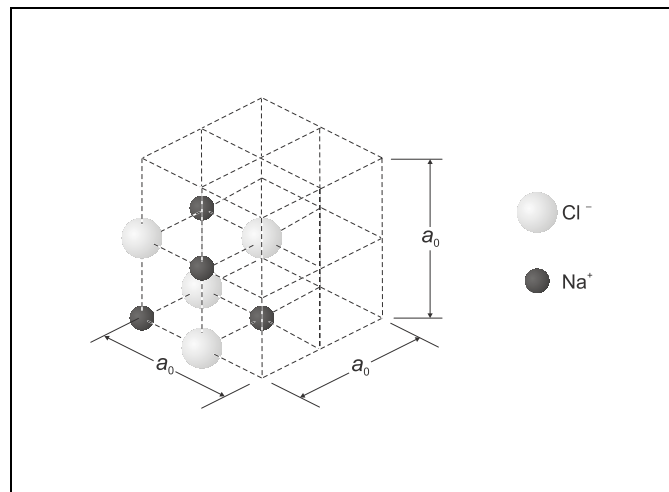


Fig. 3 Unit cell of an NaCl crystal

Fig. 3). Every unit cell contains four alkali atoms with the co-ordinates

$$r_1 = (0,0,0), r_2 = \left(\frac{a_0}{2}, \frac{a_0}{2}, 0 \right), r_3 = \left(\frac{a_0}{2}, 0, \frac{a_0}{2} \right), r_4 = \left(0, \frac{a_0}{2}, \frac{a_0}{2} \right)$$

and four halogenide atoms with the co-ordinates

$$r_5 = \left(\frac{a_0}{2}, 0, 0 \right), r_6 = \left(0, \frac{a_0}{2}, 0 \right), r_7 = \left(0, 0, \frac{a_0}{2} \right), r_8 = \left(\frac{a_0}{2}, \frac{a_0}{2}, \frac{a_0}{2} \right).$$

At each atom of the unit cell the incoming X-ray is scattered, whereby the amplitudes of the scattered partial waves depend on the atomic number of the atom. The differences of path Δ_i of the partial waves can be calculated from the co-ordinates r_i of the atoms:

$$\Delta_i = (s_1 - s_2) \cdot r_i \quad (VIII)$$

s_1 : unit vector in the direction of the primary ray

s_2 : unit vector in the direction of the diffraction reflection

The partial waves scattered at the alkali atoms A and the halogenide atoms H interfere to form a common wave that is "scattered at the unit cell". The amplitude of this wave has the form

$$A = A_A + A_H \quad (IX)$$

with

$$A_A = f_A \left(\cos\left(\frac{2\pi}{\lambda}\Delta_1\right) + \cos\left(\frac{2\pi}{\lambda}\Delta_2\right) + \cos\left(\frac{2\pi}{\lambda}\Delta_3\right) + \cos\left(\frac{2\pi}{\lambda}\Delta_4\right) \right)$$

and

$$A_H = f_H \cdot \left(\cos\left(\frac{2\pi}{\lambda}\Delta_5\right) + \cos\left(\frac{2\pi}{\lambda}\Delta_6\right) + \cos\left(\frac{2\pi}{\lambda}\Delta_7\right) + \cos\left(\frac{2\pi}{\lambda}\Delta_8\right) \right)$$

All waves that start from the unit cells interfere constructively if the *Bragg* condition (I) is fulfilled, which is equivalent to the *Laue* condition, which can be cast into the form

$$\mathbf{s}_1 - \mathbf{s}_2 = \lambda \cdot \mathbf{G} \text{ with } \mathbf{G} = (h, k, l) \cdot \frac{1}{a_0} \quad (X)$$

for cubic crystals (see experiment P7.1.2.2) By inserting Eqs. (X) and (VIII) into (IX) one obtains

$$A_A = f_A \cdot (1 + \cos((h+k) \cdot \pi) + \cos((h+l) \cdot \pi) + \cos((k+l) \cdot \pi))$$

and

$$A_H = f_H \cdot (\cos(h \cdot \pi) + \cos(k \cdot \pi) + \cos(l \cdot \pi) + \cos((h+k+l) \cdot \pi))$$

A short calculation shows that

$$A = \begin{cases} 4 \cdot f_A + 4 \cdot f_H, & \text{if } h, k \text{ and } l \text{ even} \\ 4 \cdot f_A - 4 \cdot f_H, & \text{if } h, k \text{ and } l \text{ odd} \\ 0, & \text{if } h, k \text{ and } l \text{ mixed} \end{cases} \quad (XI)$$

The amplitudes A of the waves starting from the unit cells thus only are different from zero if all indices *h, k, l* are even or if they are all odd. A combination of even indices leads to a greater amplitude A than a combination of odd indices. For other crystal structures other selection rules apply.

Evaluating a Debye-Scherrer photograph:

In this experiment, *Debye-Scherrer* photographs of crystals with NaCl structure are taken. The *Bragg* angles ϑ are obtained according to Eq. (II) from the radii *R* of the diffraction rings and the distance *L* between the sample and the film. For the evaluation, the associated values of $\sin^2\vartheta$ are decomposed into a constant factor *F* and the smallest integer *Z* (see Eq. (V)) whose *Miller* indices *h, k, l* fulfil the selection rules (XI).

From the mean value of the factors *F* obtained from the *Debye-Scherrer* photograph and the wavelength of the molybdenum K_α radiation ($\lambda = 71.1 \text{ pm}$) the lattice constant a_0 can be calculated by applying Eq. (VI). Then the lattice plane spacings *d* are derived according to Eq. (III).

Selecting the sample:

A small quantity of fine powder which is embedded between two pieces of transparent adhesive tape in a layer of approx. 0.1 to 0.5 mm thickness is an appropriate sample. This sample is centred on the pinhole diaphragm in the primary ray.

The fine graininess with a granule diameter below $10 \mu\text{m}$ is achieved by carefully grinding the salt, e.g. NaCl or LiF, in a mortar after it has been dried. As the salts are very transparent,

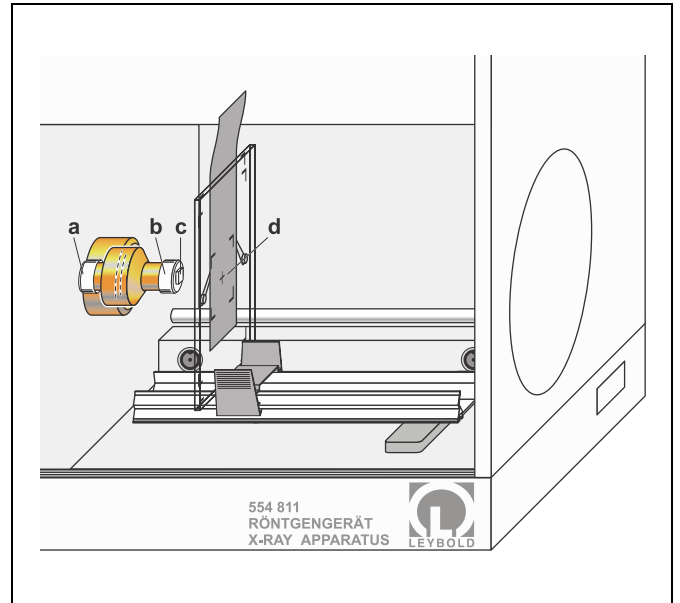


Fig. 4 Experimental setup for taking a *Debye-Scherrer* photograph of polycrystalline powder samples

the transilluminated layer has to be sufficiently thick in order that marked diffraction patterns arise.

If metallic samples with a strong attenuation are chosen, e.g. Fe or Al powder, they should be very thin. In the case of metal powders the size of the granules usually is fixed; therefore coarse-grained metal powder is not suited at all.

Setup and carrying out the experiment

The experimental setup is illustrated in Fig. 4.

- If necessary, remove the goniometer or the plate capacitor X-ray.
- Dismount the collimator, mount the Zr filter (a) (from the scope of supply of the X-ray apparatus) on the ray entrance side of the collimator and re-insert the collimator.

a) *Debye-Scherrer* photograph of NaCl:

- Carefully grind the dry NaCl salt in the mortar, and embed an approx. 0.4 mm thick layer between two pieces of transparent adhesive tape.
- Carefully attach the sample (c) to the pinhole diaphragm (b) with adhesive tape (from the scope of supply of the film holder X-ray), and put the pinhole diaphragm onto the collimator.
- Clamp the X-ray film (d) at the film holder so that it is centred on the marked area, and see to it that the entire surface of the film is planar.
- Clamp the film holder onto the experiment rail, and mount the experiment rail in the experiment chamber of the X-ray apparatus.

- Make a 13 mm long spacer from paper board and shift the film holder so that the distance between the sample and the film is 13 mm (by varying the distance between the sample and the film the area covered in the photograph is changed).
- Set the tube high voltage $U = 35$ kV, the emission current $I = 1.0$ mA and $\Delta\beta = 0.0^\circ$.
- Select the measuring time $\Delta t = 14400$ s, and start the exposure timer with the key Scan.

If the exposure time is longer, the reflections near the centre are blurred by the unscattered X-rays; however structures which are farer away from the centre become discernable.

- When the exposure time is over, take the film holder with the experiment rail out of the experiment chamber.
- Remove the X-ray film from the holder, and develop it according to the instruction sheet for the X-ray film.

b) Debye-Scherrer photograph of LiF:

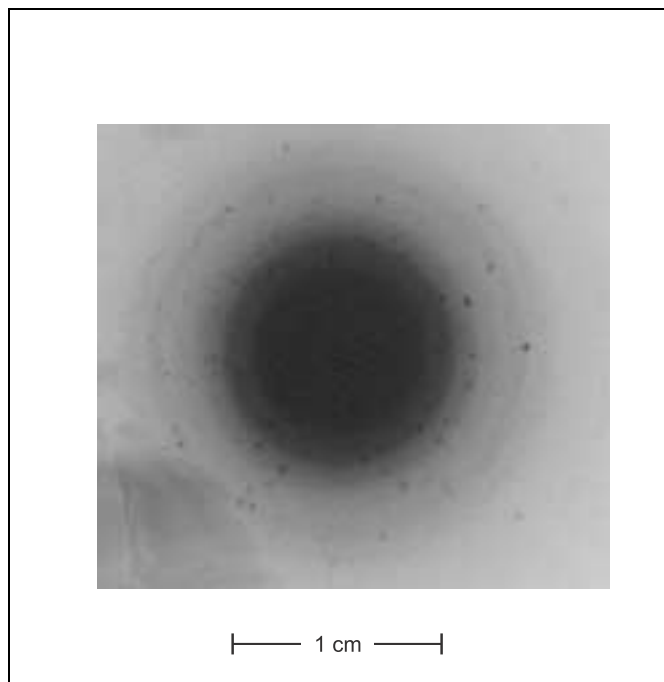
- Exchange the NaCl ample with the carefully ground LiF sample.
- Clamp a new X-ray film in the film holder, and mount the experiment rail with the film holder once more.
- Start the exposure timer with the key Scan.
- When the exposure time is over, take the X-ray film from the film holder and develop it.

Measuring example

a) Debye-Scherrer photograph of NaCl: (see Fig. 5)

b) Debye-Scherrer photograph of LiF: (see Fig. 6)

Fig. 5 Section from the Debye-Scherrer photograph of NaCl ($U = 35$ kV, $I = 1$ mA, $L = 13$ mm, $\Delta t = 4$ h, thickness = 0.4 mm)



Evaluation

- Determine the diameter D of the diffraction rings with the precision vernier calliper.
- Calculate the Bragg angle ϑ using Eq. (II) to obtain $\sin^2\vartheta$.
- "Guess" the integer factor Z , and use Eq. (V) to calculate the factor F .

a) Debye-Scherrer photograph of NaCl:

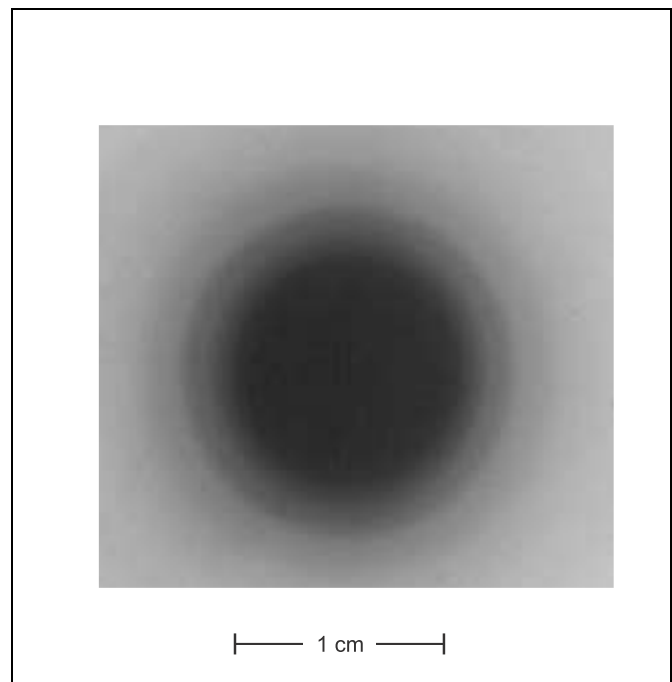
Tab. 1: Decomposition of the values of $\sin^2\vartheta$ into the factors F and Z

Nr.	$\frac{D}{\text{mm}}$	ϑ	$\sin^2\vartheta$	n	h	k	l	Z	F
1	10.0	10.5	0.033	1	2	2	0	8	0.0042
2	12.5	12.8	0.049	1	2	2	2	12	0.0041
3*	14.5	14.6	0.063	1	4	0	0	16	0.0040
4	17.0	16.6	0.082	1	4	2	0	20	0.0041
5	19.3	18.3	0.099	1	4	2	2	24	0.0041
6*	23.0	20.7	0.125	1	4	4	0	32	0.0039
7	25.0	21.9	0.139	1	6	0	0	36	0.0039
					4	4	2		
8	28.0	23.6	0.160	1	6	2	0	40	0.0040

* only weak

In Table 1, the decomposition of the experimental results for $\sin^2\vartheta$ into the factors F and Z and the associated Miller indices h, k, l and the diffraction order n are listed. The mean value of

Fig. 6 Section from the Debye-Scherrer photograph of LiF ($U = 35$ kV, $I = 1$ mA, $L = 13$ mm, $\Delta t = 4$ h, thickness = 0.4 mm)



the factors F is 0.00403. From this the lattice constant of NaCl is calculated:

$$a_0 = \frac{\lambda}{2} \cdot \frac{1}{\sqrt{F}} = 560 \text{ pm}$$

Value quoted in the literature [1]: $a_0 = 564.02 \text{ pm}$

In Table 2 the lattice plane spacings calculated from the literature value of a_0 and Eq. (III) are given.

Tab. 2: Lattice plane spacings d contributing to the Debye-Scherrer photograph of NaCl

Nr.	h	k	l	$\frac{d}{\text{mm}}$
1	2	2	0	199
2	2	2	2	163
3	4	0	0	141
4	4	2	0	126
5	4	2	2	115
6	4	4	0	100
7	6	0	0	94
	4	4	2	
8	6	2	0	89

b) Debye-Scherrer photograph of LiF:

Tab. 3: Decomposition of the values of $\sin^2\vartheta$ into the factors F and Z

Nr.	$\frac{D}{\text{mm}}$	ϑ	$\sin^2\vartheta$	n	h	k	l	Z	F
1	10	10.5	0,033	1	2	0	0	4	0.0083
2	14	14.2	0,060	1	2	2	0	8	0.0075
3	18	17.4	0,089	1	2	2	2	12	0.0074
4	22	20.1	0,118	1	4	0	0	16	0.0074
5	27	23.0	0,153	1	4	2	0	20	0.0077
6	32	25.5	0,185	1	4	2	2	24	0.0077

In Table 3, the decomposition of the experimental values for $\sin^2\vartheta$ into the factors F and Z and the associated Miller indices h, k, l and the diffraction order n are listed. The mean value of the factors F is 0.00767. From this the lattice constant of LiF is calculated:

$$a_0 = \frac{\lambda}{2} \cdot \frac{1}{\sqrt{F}} = 406 \text{ pm}$$

Value quoted in the literature [1]: $a_0 = 402.8 \text{ pm}$

In Table 4 the lattice plane spacings calculated from the literature value of a_0 and Eq. (III) are given.

Tab. 4: Lattice plane spacings d contributing to the Debye-Scherrer photograph of LiF

Nr.	h	k	l	$\frac{d}{\text{mm}}$
1	2	0	0	201
2	2	2	0	142
3	2	2	2	116
4	4	0	0	101
5	4	2	0	90
6	4	2	2	82

Results

A Debye-Scherrer photograph is a diffraction photograph of a powder sample with monochromatic X-rays.

In a plane perpendicular to the primary ray, the individual reflections of the crystallites form a system of concentric diffraction rings. These are denser and more uniform the finer the crystal powder is. Intensity maxima that occur on the rings originate from larger crystals which may be due to insufficient grinding.

From the selection rules related to the sets of lattice planes, conclusions regarding the crystal structure can be drawn.

Literature

[1] Handbook of Chemistry and Physics, 57nd Edition (1976–77), CRC Press Inc., Cleveland, Ohio, USA.