Solid-state Physics

Properties of crystals
X-ray structural analysis

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

Objects of the experiment
■ Record the Debye-Scherrer spectrum of a polycrystalline sample.
■ Calculate the lattice spacing from the result.

Principles

The Debye-Scherrer method is a way to determine the lattice constant of crystallised materials. A powdery crystalline sample is illuminated with monochromatic X-rays. The powder sample contains minute mono-crystals of about 5 - 50 μm diameter, so-called crystallites. A set of lattice planes in a crystallite leads to a reflection of the X-rays if it is aligned so that the Bragg condition:

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

n: diffraction order

λ: wave length

d: lattice plane spacing

ϑ: Bragg angle relative to the primary ray

is fulfilled (see Fig. 2 and experiment P6.3.3.1). This reflected beam is then either recorded on film (see Experiment P 7.1.2.3) or with the end-window counter tube . 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 the primary axis. The angle between the diffraction reflection and the primary ray is 2ϑ (Fig 2).

In the arrangement of this experiment, the intensity of diffrac-tion reflections will be recorded as function of the angle ϑ, where the counter tube passes through the circles of a conventional Debye-Scherrer photograph (Fig 1). The finer the power is, the more uniformly the individual reflections of the crystallites will be.

Cubic crystals:

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

$$d = \frac{a_0}{\sqrt{h^2 + k^2 + l^2}} \qquad (II)$$

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

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

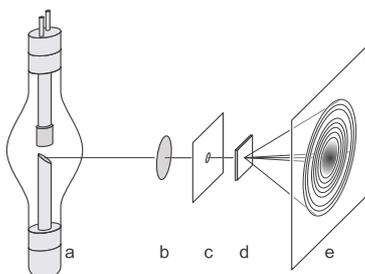is obtained (see experiment P7.1.2.3).

Fig. 1: Scheme of the classic setup for the Debye-Scherrer method. a: x-ray tube, b: Ni-filter, c: collimator, d: sample, e: screen.
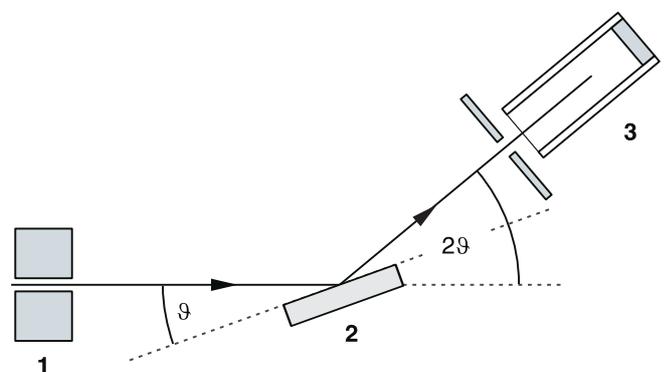

Fig. 2: Schematic diagram of diffraction of x-rays at a powder sample: 1: collimator, 2 powder sample, 3: counter tube.

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Formula (III) can be written in the short form

$$\sin^2 \vartheta = F \cdot Z \tag{V}$$

with

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

and

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

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.
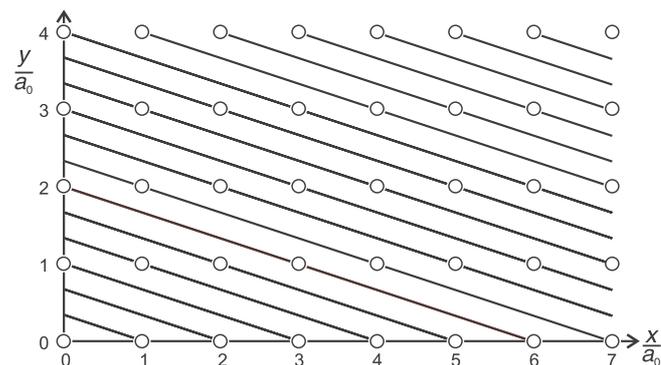

Fig 2: lattice planes with hkl = (130)

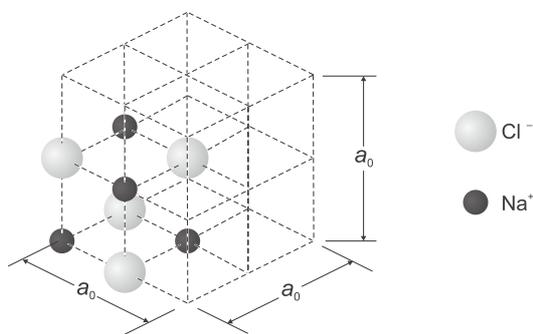**Crystals with NaCl structure:**

Fig. 3   Unit cell of an NaCl crystal

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

$$\mathbf{r}_1 = (0,0,0),\, \mathbf{r}_2 = \left(\frac{a_0}{2},\frac{a_0}{2},0\right),\, \mathbf{r}_3 = \left(\frac{a_0}{2},0,\frac{a_0}{2}\right),\, \mathbf{r}_4 = \left(0,\frac{a_0}{2},\frac{a_0}{2}\right)$$

and four halogenide atoms with the co-ordinates

$$\mathbf{r}_5 = \left(\frac{a_0}{2},0,0\right),\, \mathbf{r}_6 = \left(0,\frac{a_0}{2},0\right),\, \mathbf{r}_7 = \left(0,0,\frac{a_0}{2}\right),$$

$$\mathbf{r}_8 = \left(\frac{a_0}{2},\frac{a_0}{2},\frac{a_0}{2}\right).$$

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 $\mathbf{r}_i$ of the atoms:

$$\Delta_i = (\mathbf{s}_1 - \mathbf{s}_2) \cdot \mathbf{r}_i \tag{VIII}$$

$\mathbf{s}_1$: unit vector in the direction of the primary ray
$\mathbf{s}_2$: 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

$$A = A_A + A_H \tag{IX}$$

with

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

und

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

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

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

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

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

and

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

A short calculation shows that

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

The amplitudes A of the waves starting from the unit cells thus only are different form 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 Debye-Scherrer scans

In this experiment, Debye-Scherrer scans of crystals with NaCl structure are taken. The Bragg angles for different h, k, l indices are recorded and compared to the calculated values.

There are two different ways to record the spectra with the x-ray apparatus:

- keeping the powder sample at a fixed angle and let only the sensor rotate

- moving powder sample and sensor in a coupled motion, similar to the ordinary single crystal scans

Rotating a powder sample should not make any difference at all, but for geometrical reasons of the non-circular sample the second way is preferred. Also, rotating the sensor alone would give the angle 2ϑ, in contrast to coupled rotation, where the X-ray apparatus displays the angle ϑ.

Setup

> ### Safety notes
>
> The X-ray apparatus fulfils all regulations on the design of an X-ray apparatus and fully protected device for instructional use and is type approved for school use in Germany (BfS 05/07 V/Sch RöV).
>
> The built-in protective and shielding fixtures reduce the dose rate outside the X-ray apparatus to less than 1 µSv/h, which is of the order of magnitude of the natural background radiation.
>
> ■ Before putting the X-ray apparatus into operation, inspect it for damage
>
> ■ Protect the X-ray apparatus against access by unauthorized persons.
>
> ■ When switching the X-ray apparatus on, check whether the ventilator in the tube chamber starts rotating to avoid overheating of the X-ray tube.
>
> ■ For further details see instruction sheet of the X-ray apparatus.

Fig 4: The experiment chamber

Apparatus

1 X-ray apparatus , basic device	554 800
1 X-ray tube Cu	554 862
1 Goniometer	554 831
1 End-window counter with cable	559 01
1 Set of 2 crystal powder holders	554 842
1 NaCl, 250 g	673 5700
1 Spatula	666 960
1 Pestle, 100 mm long	667 091
1 Mortar, porcelain, 70 mm Ø	667 092

additionally suggested:

e.g. KCl or LiF powder

1 PC with Windows 98/2000/XP/Vista

- Mount the Goniometer in the experiment chamber of the X-ray apparatus. To bring the counter tube out of stray radiation, put the Goniometer to the very left position and use the full length of the sensors arm. See Fig 4

- Mount the Ni-filter on the collimator to produce monochromatic copper $K\alpha$ X-rays. The filter must be mounted on the left side on the collimator, facing the tube, not on the right hand side, where it would produce a lot of stray radiation into the experiment chamber.

- Prepare a powder sample by using the mortar and the pestle. The NaCl (or other) salt is grind in a mortar until no grains can be felt when rubbing the powder between the finger tips. Do not try to prepare to much powder at once, as it will take a lot of time. An amount of 2 times the volume of the powder holder will take approximately 5 minutes to pulverise.

Note: Coarse powder samples yield Debye-Scherrer reflections of inhomogeneous intensity distributions.

- The powder holder consists of one aluminum frame and a solid aluminum plate. Put the frame onto the plate and fill the powder into the frame, move both aluminum parts together close to the sample holder inside the X-ray apparatus and slide the frame sideways onto the sample holder, so that the powder is always supported either by the aluminum or by the plastic parts.
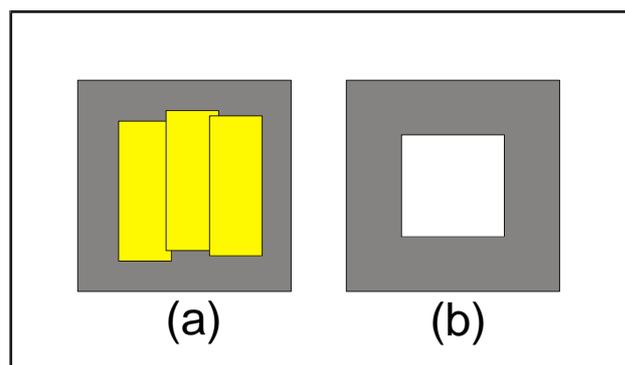

Fig. 5:   Preparation of the powder holder frame schematically:
(a) rear side with strips of scotch-tape
(b) front side with squeezed powder

Or (preferred):

- Attach strips of scotch-tape to the rear of the powder holder and fill the prepared powder into the frame (Fig. 5).

- Squeeze the powder into the frame with the spatula as dense as possible.

Note: Instead of using the crystal powder holder a self-made styrofoam block can be used, where the powder is pressed into a recess. This will lower the background radiation even more.

Carrying out the experiment

- Start the software and the x-ray apparatus (see "Recording a diffraction spectrum" in experiment P7.1.2.1)

- Set the tube high voltage to U = 35.0 kV and the emission current I = 1.0 mA.

- Set the time per angular step Δt = 10 s and the angular step width $\Delta\beta$ = 0.1°.

- Select "coupled", set appropriate start and stop angles β for the scan. Usually 10 to 40 deg is sufficient, but up to 60 ° gives additional lines.

- Switch on the high voltage and press the automatic scan button for recording the spectra.

- To check for the existence of the weak, but important <111> reflection, scan that region left of the 200 reflex (11°-18° for NaCl) with Δt = 30 s at least.
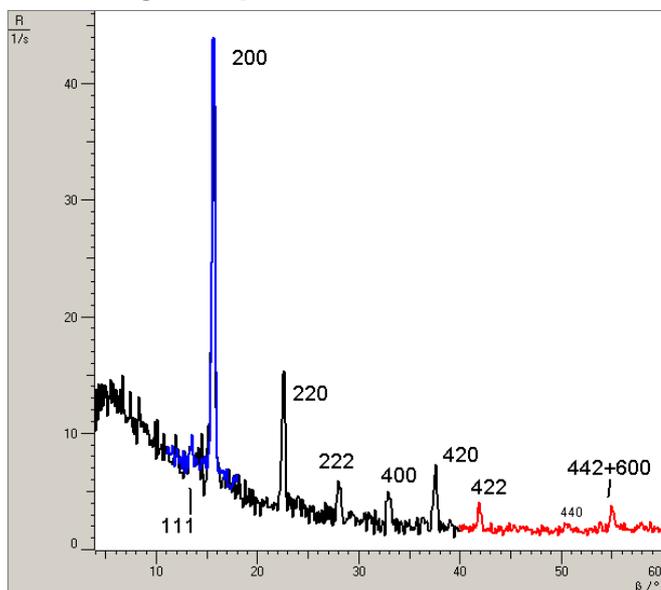
Measuring example

Fig. 6: Spectrum of a powdered NaCl sample recorded with monochromatic copper Kα x-rays. Black: 10s per point, red + blue: 30 s
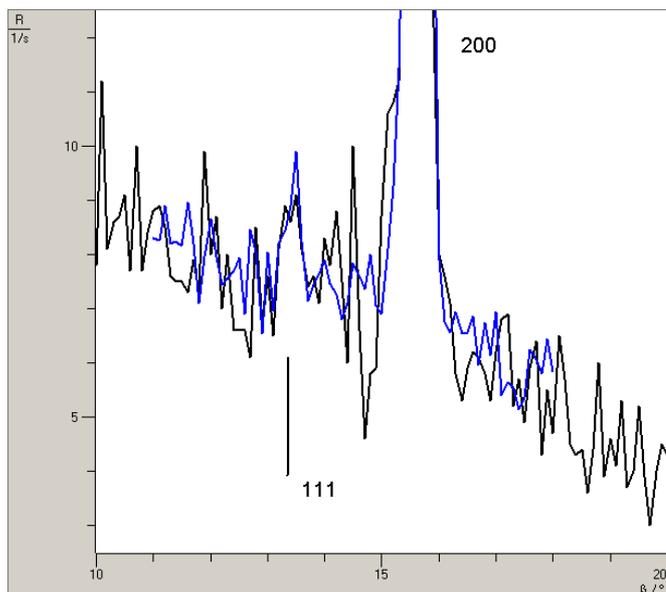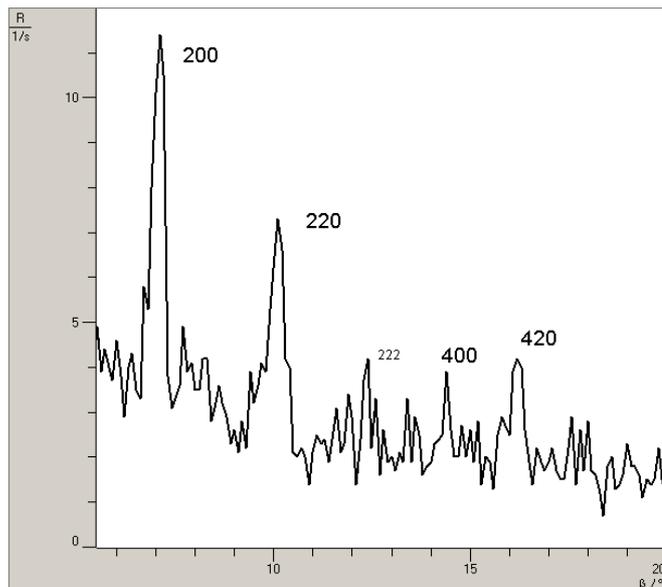

Fig. 7: Detail of the hkl = 111 reflection.

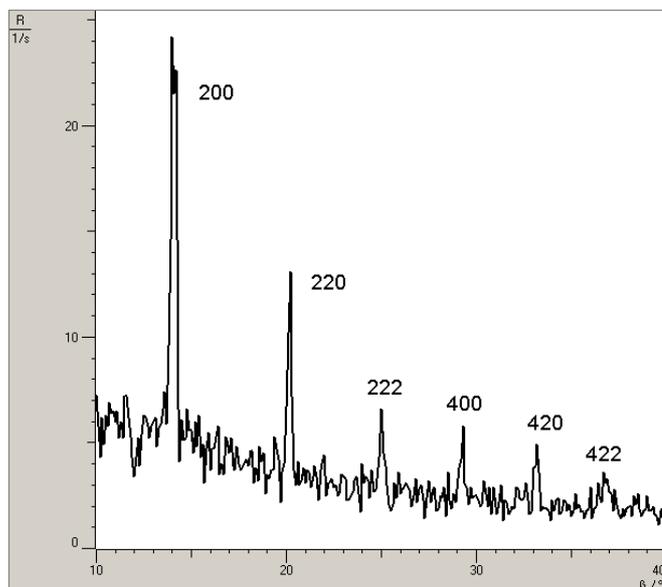Fig. 8: Spectrum of a powdered NaCl sample recorded with monochromatic molybdenum Kα x-rays. 10s per point.

Fig. 9: Spectrum of a powdered KCl sample recorded with monochromatic copper Kα x-rays. 10s per point.

Evaluation and results

The spectra show several different peaks, which correspond to the circles in a Debye-Scherrer photograph. In the measurement examples shown, these peaks are already labelled with the appropriate hkl numbers.

Several combinations of anode materials and crystal powders are shown in the measurement examples. Figure 6 and 7 show the experiment described above, copper Kα with NaCl powder, which will be evaluated in detail below.

Figure 8 shows the same powder, but using a molybdenum anode, which is also possible. The angles of reflection scale according to the wavelength, but note that the amplitude of the reflexes is much smaller than using a copper tube, as the shorter wavelength X-rays are scattered less by the given amount of powder.

Figure 9 shows the copper tube with a different powder, KCl, showing a different lattice constant. Note here, that there is

absolutely no trace of the hkl= 111 reflection. This is due to the fact that both atoms (K and Cl) show the same electronic configuration (Argon) in the crystal and therefore $f_A = f_H$. According to equation XI, the hkl all odd reflexes vanish in this case.

For a detailed analysis one can either start with the literature values for the lattice constant a0, calculate all possible hkl combinations according to equation III and match the peaks recorded to the calculated values.

The other way to do the analysis is shown in experiment P7.1.2.3, starting with an unknown lattice constant and guessing the hkl numbers so that the factor F (Equation VI) is constant.

The 111 reflection in figure 7 is of specific importance in determining the crystal structure. According to equation XI, all the reflections from a NaCl crystal are either all even number or all odd numbers. If this reflection was not present, one could also assume a simple cubic crystal with half the lattice constant.

Detailed evaluation

The literature values for different lattice constants are:

Crystal	a0/pm
LiF	402,8
NaCl	564,02
KCl	629,3
KBr	659,66

The wavelength of the Ka line is 154,2 pm for a copper anode and 71,08 pm for a molybdenum anode.

According to equation VI the combination Cu-Anode, NaCl powder yields F= 0,01869.

Choosing different combinations of hkl, it is now possible to calculate Z from equation VII and finally calculate the angle ϑ from equation V.

h	k	l	Z	ϑ
1	1	1	3	13,70
2	0	0	4	15,87
2	2	0	8	22,75
3	1	1	11	26,96
2	2	2	12	28,26
4	0	0	16	33,15
3	3	1	19	36,57
4	2	0	20	37,69
4	2	2	24	42,04
3	3	3	27	45,26
5	1	1	27	45,26
4	4	0	32	50,65
5	3	1	35	53,97
4	4	2	36	55,10
6	0	0	36	55,10
6	2	0	40	59,83
5	3	3	43	63,69
6	2	2	44	65,06

Angles marked in blue are from the all odd hkl reflection, while the black ones are from the all even ones. According to equation XI, the odd reflections are low in intensity ($f_A - f_H$), while the even reflections are of high intensity ($f_A + f_H$).

Comparing the calculated values to figure 6, the peaks can be identified and named with the correct hkl combination, verifying that the structure of the NaCl crystal is as it was assumed.