Examination of the structure of NaCl monocrystals with different orientations

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

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

This content can also be found online at:

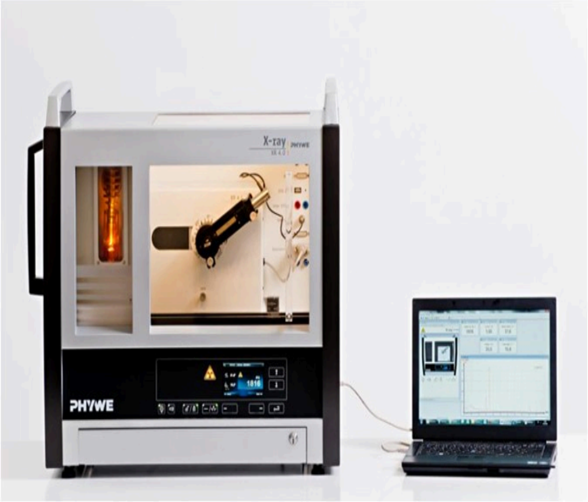
http://localhost:1337/c/5f608a137e9d5b0003e1e775

PHYWE

General information

Application

PHYWE



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.

Other information (1/2)

Prior knowledge

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

Main principle

The spectra of the X-rays that are reflected with various different orientations by NaCl monocrystals are analysed. The associated interplanar spacings are determined based on the Bragg angles of the characteristic lines.

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

Other information (2/2)

Learning objective

The goal of this experiment is to examine the structure of NaCl crystals in different orientations.

Tasks

1. Determine the intensity of the X-rays that are reflected by the NaCl monocrystals with the orientations [100], [110], and [111] as a function of the Bragg angle.
2. Assign the reflections to the corresponding lattice planes that are given by way of their respective Miller indices.
3. Determine the lattice constant and calculate the interplanar spacing.
4. Determine the mass of a cell and the number of atoms in the cell.

Theory (1/5)

If X-rays hit a parallel lattice plane family with the interplanar distance d under the glancing angle θ, the radiation will be reflected in a constructive manner provided that the so-called Bragg condition (1) is fulfilled (see Figure 1).

$$2\mathrm{d}\sin(\theta) = \mathrm{n}\lambda \qquad (1)$$

(d: interplanar spacing; n = 1, 2, 3,...)

In the context of crystal structure analyses, n is often integrated into the distance between the lattice planes.

$$2\mathrm{d}\sin(\theta) = \lambda \qquad (1\mathrm{b})$$

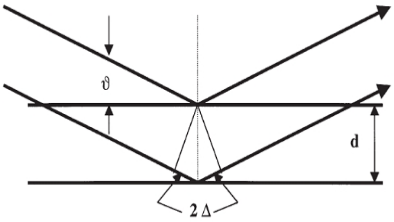


Fig. 1: Bragg scattering on a pair of lattice planes

Theory (2/5)

The reflections of the nth order are directly assigned to the diffraction on the various planes. The Miller indices are a method for naming the various planes in a crystal. They basically indicate the points of intersection of an imaginary section through the three-dimensional unit cell of the crystal. The symmetrical fundamental unit of a crystal is the unit cell. In a cubic crystal lattice, like in the case of NaCl, all of the sides of this cell are of the same length. The side length of such a cell is referred to as the lattice constant a.

Theory (3/5)

As shown in Figures 2a to 2c, NaCl monocrystals have a face-centred cubic lattice (fcc). In the primitive cell, an Na+ ion has the coordinates (0,0,0) and a Cl- ion has the coordinates $\left(\frac{1}{2},\frac{1}{2},\frac{1}{2}\right)$.

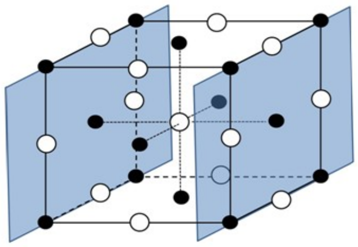


Fig. 2a: NaCl crystal with a drawn-in (100) lattice planes

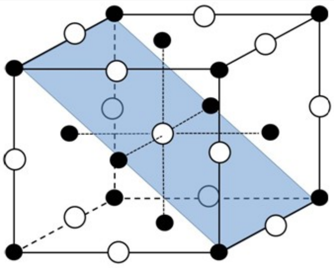


Fig. 2b: NaCl crystal with a drawn-in (110) lattice plane

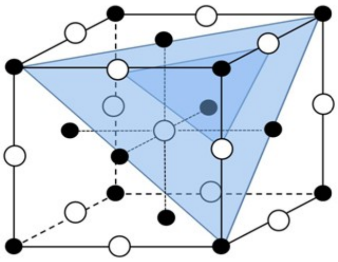


Fig. 2c: NaCl crystal with drawn-in (111) and (222) lattice planes.

Theory (4/5)

For a cubic crystal with a lattice constant a, the lattice planes that are characterised by the miller indices (h, k, l) have the following interplanar spacing d:

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

Putting (2) into (1b) results in the following connection:

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

Theory (5/5)

The relative intensity of the reflected radiation is determined by the scattering power and position of the individual atoms in the unit cell of the crystal. It is described by the so-called structure factor F(h,k,l):

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

In this equation (3), $\mathrm{f_n}$ = the atomic form factor (atomic scattering factor), and $\mathrm{u_n}, \mathrm{v_n}$ and $\mathrm{w_n}$ = the coordinates of the nth atom in the unit cell. The total backscattered beam intensity I is:

$$\mathrm{I} = \mathrm{F} \cdot \mathrm{F} = |\mathrm{F(h,k,l)}|^2 \qquad (4)$$

With the 000; 011; 101 and 110 of the basis atoms in the unit cell of an fcc crystal, it follows from (3) that F = 0 when the h, k, l triplet contains even and odd numbers, and F = 4f when all of the indices are either even or odd. In addition, in face-centred cubic crystal structures and in the case of the 100 and 110 lattice planes, the reflections of the planes with odd values for h, k and l are eliminated by systematic extinction.

Equipment

Position	Material	Item No.	Quantity
1	XR 4.0 expert unit, 35 kV	09057-99	1
2	XR 4.0 X-ray goniometer	09057-10	1
3	XR4 X-ray Plug-in Cu tube	09057-51	1
4	XR 4.0 X-ray structural analysis upgrade set	09145-88	1

Setup and Procedure

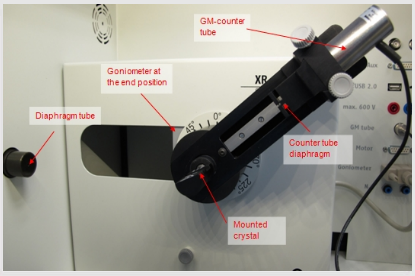
Setup

Connect the goniometer and the Geiger-Müller counter tube to their respective sockets in the experiment chamber (see the red markings in Fig. 3). The goniometer block with the analyser crystal should be located at the end position on the right-hand side. Fasten the Geiger-Müller counter tube with its holder to the back stop of the guide rails. Do not forget to install the diaphragm in front of the counter tube (see Fig. 4). Insert a diaphragm tube with a diameter of 2 mm into the beam outlet of the tube plug-in unit.

For calibration: Make sure, that the correct crystal is entered in the goniometer parameters. Then, select "Menu", "Goniometer", "Autocalibration". The device now determines the optimal positions of the crystal and the goniometer to each other and then the positions of the peaks.

← Fig. 3: Connectors in the experiment chamber

↓ Fig. 4: Set-up of the goniometer



Procedure (1/3)

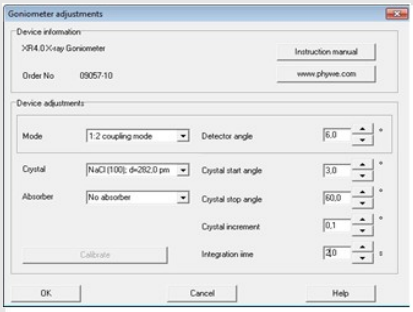
- Connect the X-ray unit via the USB cable to the USB port of your computer (the correct port of the X-ray unit is marked in Figure 5).
- Start the “measure” program. A virtual X-ray unit will be displayed on the screen.
- You can control the X-ray unit by clicking the various features on and under the virtual X-ray unit. Alternatively, you can also change the parameters at the real X-ray unit. The program will automatically adopt the settings.

Fig. 5: Connection of the computer

Procedure (2/3)

Fig. 6: Part of the user interface of the software

- If you click the X-ray tube (see the red marking in Figure 6), you can change the voltage and current of the X-ray tube. Select the parameters as shown in Fig. 7.
- If you click the X-ray tube, you can change the voltage and current of the X-ray tube. Select the following: anode voltage $U_A = 35\,\mathrm{kV}$; anode current $I_A = 1\,\mathrm{mA}$
- Mount one of the crystals in the universal crystal holder and attach it to the goniometer (Fig. 4).


Goniometer adjustments

Device information
XR4.0 X-ray Goniometer
Order No 09057-10

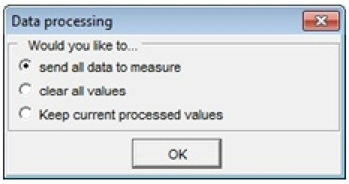
Device adjustments
Mode: 1:2 coupling mode
Detector angle: 6,0 °
Crystal: NaCl (100); d=282,0 pm
Crystal start angle: 3,0 °
Absorber: No absorber
Crystal stop angle: 60,0 °
Crystal increment: 0,1 °
Integration ime: 2,0 s

Fig. 7: Settings of the goniometer, NaCl (100) crystal

Procedure (3/3)

- Start the measurement by clicking the red circle:

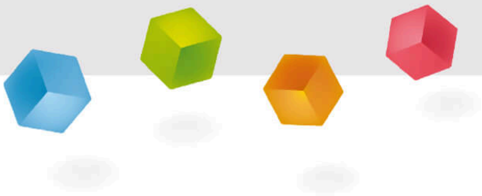
- After the measurement, the following window appears:


Data processing
Would you like to...
● send all data to measure
○ clear all values
○ Keep current processed values
OK

- Select the first item and confirm by clicking OK. The measured values will now be transferred directly to the "measure" software.

Overview of the goniometer and X-ray unit settings:

- 1:2 coupling mode
- Gate time 2 s; angle step width 0.1°
- Scanning range 3° - 60°
- Anode voltage U_A = 35 kV; anode current I_A = 1 mA



Evaluation

Task 1

Determine the intensity of the X-rays that are reflected by the NaCl monocrystals with the orientations [100], [110], and [111] as a function of the Bragg angle.

Figure 8a to 8c show the Intensity of the X-ray spectrum of copper as a function of the glancing angle θ.

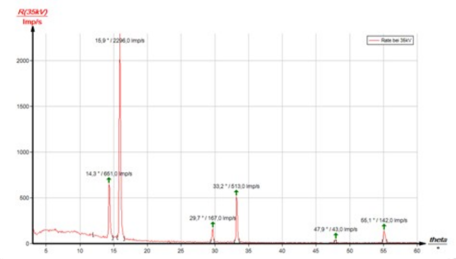


Fig. 8a: [100] crystal orientation

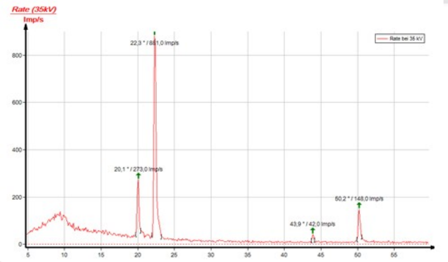


Fig. 8b: [110] crystal orientation

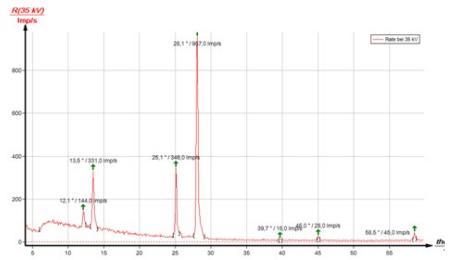


Fig. 8c: [111] crystal orientation

Task 1 (part 2)

Compared to the other spectra, the spectrum of the [111] crystal (Fig. 8c) shows a noticeable feature. While in the case of the other spectra, the intensity of the characteristic lines is always the highest for the first order (n = 1) reflections. This is the case with n = 2 in Figure 8c.

In the [111] crystal, the parallel lattice planes are occupied either only by Na+ ions or by Cl- ions. As these two ions have different scattering factors, the intensities also differ from each other. If $\mathrm{f_N a}$ and $\mathrm{f_C l}$ are the scattering factors, the following results from (3) for lattice planes with solely odd or solely even (h, k, l) indices:

$\mathrm{F = 4(f_N a + f_C l)}$ and $\mathrm{I \propto F^2 = 16(f_N a + f_C l)^2}$

Task 2

Assignment of the Miller indices

In Table 1, the glancing angles θ that were determined with the aid of Figures 8a to 8c are assigned to their respective Miller indices. Based on (3), we know that for the 100 and 110 lattice planes only even or only odd values are possible for the h, k, l triplet and that there are in fact no reflections for odd values of h, k and l at 100 and 110. These considerations resulted in the assignments shown in Table 1.

Table 1	$\theta(\mathrm{K}_\alpha)$	$\theta(\mathrm{K}_\beta)$	$(\mathrm{h,k,l})$	$\mathrm{h}^2+\mathrm{k}^2+\mathrm{l}^2$
(100) crystal				
	15.9	14.3	200	4
	33.2	29.7	400	16
	55.1	47.9	600	36
(110) crystal				
	22.3	20.1	220	8
	50.2	43.9	440	32
(111) crystal				
	13.5	12.1	111	3
	28.1	25.1	222	12
	45.0	29.7	333	27
	--	58.5	444	48

Task 3

Determine the lattice constant and calculate the interplanar spacing.

If one solves equation (2b) for a, one obtains the lattice constant a for the various reflections based on the hkl triplets that were determined in Task 1 as well as based on the glancing angle$\theta$and the wavelength of the characteristic X-radiation of copper ($\lambda_{\mathrm{K}_\alpha}$ = 154.4 pm; ($\lambda_{\mathrm{K}_\beta}$ = 139.2 pm). Table 2 shows the corresponding values. A comparison of the average value with the literature value of a = 564 pm shows good correspondence. Equation (2) can now be used to calculate the interplanar spacing for the first plane since the lattice constant a refers to a unit cell with only two planes. With this value and in accordance with equation (1), the distances between the individual lattice planes are as follows: d(200) = 282.0 pm, d(220) = 201.9 pm, and d(111) = 330.2 pm.
Literature values: d(200) = 282.0 pm, d(220) = 199.4 pm, and d(111) = 325.6 pm.

The very good agreement between the value for the distance between the (100) lattice planes that was determined experimentally and the literature value is due to the fact that ionic crystals can be split very exactly in parallel to this plane. The deviations of the other crystals are due to a slight misorientation.

Task 3 (part 2)

Table 2	θ [°]	(h, k, l)	$h^2 + k^2 + l^2$	a [pm]
(100) crystal				
K_α	15.9	200	4	567
	33.2	400	16	564
	55.1	600	36	565
K_β	14.3	200	4	564
	29.7	400	16	562
	47.9	600	36	563
			Mean value	564

Table 2	θ [°]	(h, k, l)	$h^2 + k^2 + l^2$	a [pm]
(110) crystal				
K_α	22.3	220	8	575
	50.2	440	32	568
K_β	20.1	220	8	573
	43.9	440	32	568
			Mean value	571

Task 3 (part 3)

Table 2	θ [°]	(h, k, l)	$h^2 + k^2 + l^2$	a [pm]
(100) crystal				
K_α	13.5	111	3	573
	28.1	222	12	586
	45.0	333	27	567
K_β	12.1	111	2	575
	25.1	222	12	568
	39.7	333	27	566
	58.5	444	48	566
			Mean value	572

Task 4

Determine the mass of a cell and the number of atoms in the cell.

If one calculates the volume of the unit cell of sodium chloride

$\mathrm{a} = 1.79 \cdot 10^{-28}\,\mathrm{m}^3$

the density of sodium chloride of $\rho = 2.163\mathrm{g}/\mathrm{cm}^3$ leads to the weight of a unit cell as

$\mathrm{m} = \rho \cdot \mathrm{V} = 3.87 \cdot 10^{-25}\,\mathrm{kg} = 233\,\mathrm{u}$

Since the number of Na atoms in NaCl equals the number of Cl atoms, the molar masses $\mathrm{M}_{(\mathrm{Na})}$ = 22.990g/mol and $\mathrm{M}_{(\mathrm{Cl})}$ = 35.453g/mol lead to a number of 3.99 = 4 atoms each in the Bravais lattice, which could also be expected for an fcc lattice based on the following considerations (see also Fig. 9):

Task 4 (part 2)

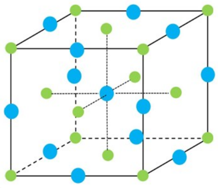


Fig. 9: The unit cell of NaCl, blue: Cl atoms; green: Na atoms

Every unit cell includes 4 (green) cations:

Each of the cations at the 8 corners counts as only $\frac{1}{8}$ to the unit cell: 8 “corner cations” $\cdot \frac{1}{8} \rightarrow$ 1 cation

The cations on the surfaces count as only $\frac{1}{2}$: 6 “surface cations” $\cdot \frac{1}{2} \rightarrow$ 3 cations

Every unit cell includes 4 (blue) anions:

Each of the anions at the 12 edges counts as only $\frac{1}{4}$ to the unit cell: 12 “edge anions” $\cdot \frac{1}{4} \rightarrow$ 3 anions

The anion in the centre belongs completely to the unit cell: 1 "center anion" $\rightarrow$ 1 anion