Diffraction measurements to determine the intensity of Debye-Scherrer reflexes using a cubic powder sample

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/5f7889e78711520003ca18ec

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

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Other information (1/2)

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Prior knowledge

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

Main principle

A polycrystalline, cubic face-centered crystallizing powder sample is irradiated with the radiation from a X-ray tube with a copper anode. A Geiger-Mueller counter tube is automatically swivelled to detect the radiation that is constructively reflected from the various lattice planes of the crystallites. The Bragg diagram is automatically recorded. The intensities of the individual reflex lines are determined and compared with those theoretically expected. In addition, the evaluation allows the Bragg reflexes to be assigned to the individual lattice planes, and both their spacing and the corresponding Bravais lattice type to be determined.

Other information (2/2)

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Learning objective

The goal of this experiment is to get to investigate Debeye-Scherrer patterns for Bragg-Brentano-geometry.

Tasks

1. Record the intensity of the Cu X-rays back scattered by a cubic powder sample as a function of the back scattering angle.
2. Calculate the lattice plane spacings from the angle positions of the individual Bragg lines.
3. Assign the Bragg reflexes to the respective lattice planes. Calculate the lattice constant of the substance and the Bravais lattice type.
4. Determine the intensity of the individual reflex lines and compare them with the theoretically expected intensities.
5. Determine the number of atoms in the unit cell.

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Theory (1/6)

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When X-rays of wavelength λ strike a mass of lattice planes of a crystal of spacing d at a glancing angle of θ, then the reflected rays will only be subject to constructive interference when Bragg's condition is fulfilled, i.e.:

$2\mathrm{d}\sin(\theta) = \mathrm{n}\lambda$ (n = 1, 2, 3, ...) (1)

The intensity $\mathrm{I_{hkl}}$ of the Bragg reflexes in the Debye-Scherrer powder method is mainly determined by the following 4 factors:

1. Polarization factor P:

A free electron that is excited by an incident, non-polarized electromagnetic wave emits directionally independent scattered radiation of the same frequency as the primary radiation. The intensity I of the scattered radiation is described by the Thomson formula, whereby 2θ is the angle between the primary radiation and the scattered radiation: $\mathrm{I} \propto \mathrm{P} = \frac{\mathrm{I}+\cos^2(2\theta)}{2}$ (2)

Theory (2/6)

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2. Lorentz factor L:

According to Bragg's conditions (equation (1)), only sharp reflex lines at a glancing angle of θ should occur. In reality, the reflex ilines exhibit a bell-shaped curve with a maximum and a definite width at half of maximum intensity. Strictly speaking, however, the line intensity is not determined by the maximum, but by the area under the curve. This fact and two further factors that take into consideration the statistical distribution of the crystals in the powder sample and the geometry of the Debye-Scherrer method, are defined by the Lorentz factor L: $\mathrm{L} = \frac{1}{\sin^2(\theta)\cos(\theta)}$ (3)

On combining both of the above factors, the so-called Lorentz polarization factor LP is obtained:

$\mathrm{LP} = \frac{1+\cos^2(\theta)}{\sin^2(\theta)\cos(\theta)}$ (4)

As ultimately only relative intensity values are to be compared, the factor 1/8 is generally done without in equation (4).

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Theory (3/6)

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3. Structure factor F:

Bragg's condition implies that all of the waves scattered at the atom are in phase and so amplify each other, whereas partial waves that are scattered in directions not fulfilling Bragg's conditions are of opposite phase and so extinguish each other. A more realistic way of looking at this must, however take the actual phase relationships of all of the partial waves scattered by the atom in a certain direction into consideration. When there are N atoms in a unit cell, then the total amplitude of the X-rays scattered by the cell is described by the structure factor F, which is calculated by summing up the atomic scattering factors f of the individual N atoms, taking their phases into account. In general, the following is valid for F:

$$\mathrm{F_{hkl}} = \sum_1^{\mathrm{N}} \mathrm{f_n} \cdot e^{2\pi i(\mathrm{hu_n + kv_n + lw_n})} \qquad (5)$$

where h, k, l = Miller indices of the reflecting lattice planes and $\mathrm{u_n}$, $\mathrm{v_n}$, $\mathrm{w_n}$ are the coordinates of the atoms in fractions of the particular edge lengths of the unit cell. As F is in general a complex number, the total scattered intensity is described by $|\mathrm{F_{hkl}}|^2$.

Theory (4/6)

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The atomic scattering factor describes the scattering power of an individual atom and is defined as the scattering amplitude of an atom divided by the scattering amplitude of a free electron. The atomic scattering factor is dependent on the wavelength and angle, and is given in Tables as $(\sin(\theta)/\lambda)$ units for each atom. Fig. 1 shows the course of the value of f as a function of $(\sin(\theta)/\lambda)$ units for Cu (Z = 29).

In the forward direction (θ = 0°), f = Z is true, as in this case all Z-electrons of the atom scatter in phase. The unit cell of the cubic, face-centered copper lattice has 4 atoms at 000, ½ ½ 0, ½ 0 ½ and 0 ½ ½. As the Cu lattice only consists of one sort of atom, the following conditions apply for the structure factor according to equation (5):

$|\mathrm{F}|^2 = 16\mathrm{f}^2$ with hkl only even or only odd; $|\mathrm{F}|^2 = 0$ with hkl mixed (6)

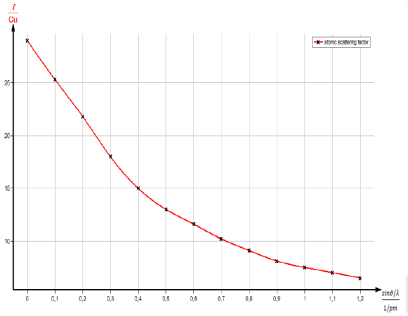

Fig. 1: Atomic scattering factor f vs. $\sin(\theta)/\lambda$

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Theory (5/6)

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4. Multiplicity factor M:

When powder samples are examined, the more equivalent lattice planes (lattice planes with the same spacing d) that belong to an index triplet (hkl), the greater the number of cases in which Bragg's conditions are fulfilled. With cubic crystals, for example, $M_{100} = 6$, because there are 6 cube faces available, namely h00, 0k0, 00l and the corresponding planes with negative indices. Table 1 shows the multiplicity factor M for the further low indexed faces of cubic crystals.

hhl	h0l/0kl/hk0	hh0	hhh	h00/0k0/00l
24	24	12	8	6

Table 1: Multiplicity factor M for the lattice planes of cubic crystals.

When one takes the above factors into consideration in the determination of the intensity I of Debye-Scherrer reflex lines, then the following is valid: $\mathrm{I} \propto |\mathrm{F}|^2 \cdot \mathrm{LP} \cdot \mathrm{M} = |\mathrm{F}|^2 \cdot \mathrm{M} \cdot \frac{1+\cos^2(\theta)}{\sin^2(\theta\cos(\theta))}$ (7)

Theory (6/6)

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The determination of the intensity I acc. to equation (7) is I principle incomplete but sufficient for an estimation, as for a complete determination of the intensity it would be necessary to take absorption and the effect of thermal vibration of the atoms resulting from the sample temperature (Debye-Waller factor) into account.

For the cubic crystal system, the spacing d of the individual lattice planes with the indices (hkl) is obtained from the quadratic form:

$\frac{1}{\mathrm{d_{hkl}}} = \frac{1}{\mathrm{a}}(\mathrm{h}^2 + \mathrm{k}^2 + \mathrm{l}^2)$ (a = lattice constant) (8)

From this and equation (1), with n = 1, the quadratic Bragg equation is obtained:

$\sin^2(\theta) = \frac{\lambda^2}{4\mathrm{a}^2}(\mathrm{h}^2 + \mathrm{k}^2 + \mathrm{l}^2)$ (9)

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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
5	Copper, powder 100 g	30119-10	1
6	Vaseline 100 g	30238-10	1

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Setup and Procedure

Setup

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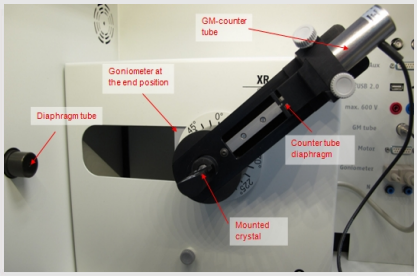
Connect the goniometer and the Geiger-Müller counter tube to their respective sockets in the experiment chamber (see the red markings in Fig. 2). The goniometer block with the analyser crystal should be located at the end position on the right-hand side. Fasten the Geiger-Müller counter tube with its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



↓ Fig. 3: Set-up of the goniometer

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Procedure (1/5)

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- 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 4).
- 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. 4: Connection of the computer

Procedure (2/5)

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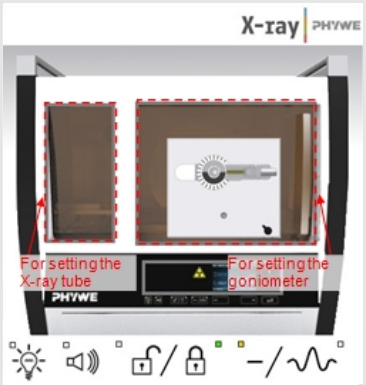

Fig. 5: Part of the user interface of the software

- Click the experiment chamber (see the red marking in Fig. 5) to change the parameters for the experiment.
- If you click the X-ray tube (see the red marking in Figure 5), you can change the voltage and current of the X-ray tube. Select the settings as shown in Figure 6.

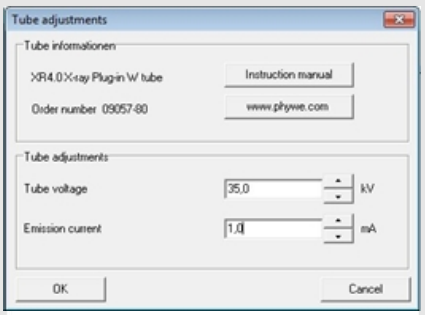

Fig 6: Voltage and current settings

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Procedure (3/5)

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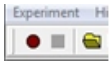
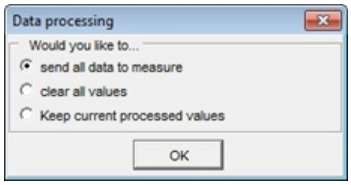
- Start the measurement by clicking the red circle: 
- After the measurement, the following window appears:



- Select the first item and confirm by clicking OK. The measured values will now be transferred directly to the “measure” software.
- At the end of this manual, you will find a brief introduction to the evaluation of the resulting spectra.

Procedure (4/5)

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Overview of the settings of the goniometer and X-ray unit:

- 1:2 coupling mode
- angle step width 0.1°
- Scanning range: 10° - 45°
- Anode voltage U_A = 35 kV UA=35kV; anode current I_A = 1 mA
- Scanning speed, when only the very intense reflex lines are to be recorded, then scanning can be relatively rapid at 10 s/°. For the identification of weaker lines, a scanning speed of at least 30 s/° is required for a better signal/noise ratio

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Procedure (5/5)

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Sample preparation:

The sample must be so finely powdered that no grains can be felt when a little of it is rubbed between finger and thumb. A relatively high sample concentration can be obtained by mixing the powder with a little vaseline. To do this, transfer a small amount of the sample onto a sheet of paper and use a spatula to knead it to a firm paste. To achieve the highest concentration of material as possible, use very little vaseline (a spatula tip of it). Fill the relatively solid sample paste into the specimen for powder samples and smooth it flush. Use the universal crystal holder to hold the specimen.

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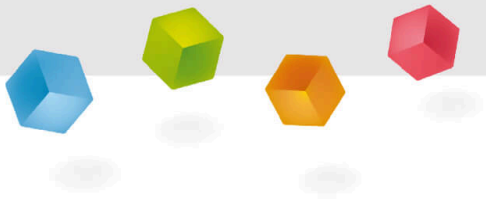

Evaluation

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Task 1

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Fig. 7 shows the Debye-Scherrer spectrum of copper (Cu, Z = 29).

As no filter is used for the monochromatization of the X-rays, when individual lines are evaluated consideration must be given to the fact that the very intense lines that result from K_α-radiation are accompanied by secondary lines that result from the weaker K_β radiation. These pairs of lines can be identified by means of equation (1). It is namely approximately true with $\lambda(\mathrm{K}_\alpha) = 154.18\,\mathrm{pm}$ and $\lambda(\mathrm{K}_\beta) = 139.22\,\mathrm{pm}$:

$$\frac{\lambda(\mathrm{K}_\alpha)}{\lambda(\mathrm{K}_\beta)} = \frac{\sin(\theta_\alpha)}{\sin(\theta_{beta})} \approx 1.1 \qquad (10)$$

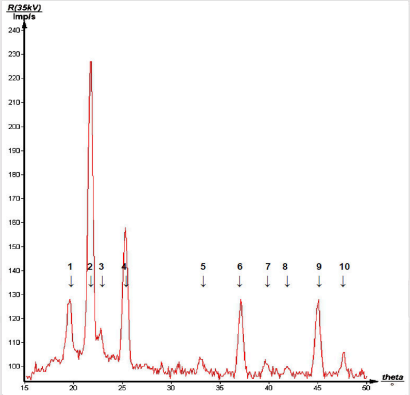

Fig. 7: Debye-Scherrer pattern of a copper powder sample.

Task 1 (part 2)

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These values correspond to the quotients of the sinq values (Fig. 7) of the pairs of lines 2-1, 4-3, 6-5, 9-7 and 10-8, showing that the lines 1, 3, 5, 7 and 8 originate from the CuK_β radiation.

The correctness of this conclusion can be shown by a control measurement using the diaphragm tube with nickel foil to reduce the intensity of the K_β radiation. The reflexes in Fig. 7 that were previously assigned to the K_β lines are no longer to be seen. As the intensity of the K_β-radiation is also somewhat weakened by the Ni foil, the detection of reflexes of weak intensity at larger glancing angles is made difficult when this is used.

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Task 2 and 3

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The glancing angles θ found in the experiment and belonging to the individual reflex lines are entered in column D of Table 2. As it has already been assumed that copper forms a face-centered lattice, only the permissible hkl triplets for this type of lattice have been taken into consideration in column B. Column G lists the lattice plane spacings d calculated using equation (1), and column H contains the values of the lattice constant a alculated using equation (9).

The mean value of a obtained is: $\mathrm{a} = (361.04 \pm 0.52)\,\mathrm{pm}; \Delta(\mathrm{a})/\mathrm{a} = \pm 0.15\%$

(Literature value: a =361.52 pm).

Task 2 and 3 (part 2)

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A	*B*	*C*	*D*	*E*	*F*	*G*	*H*
Line	$h\ k\ l$	$h^2+k^2+l^2$	ϑ/°	$\sin\vartheta$	$\sin^2\vartheta$	d/pm	a/pm
1(β)	1 1 1	3	19,54	0,334464	0,111867	208,12	360,48
2	1 1 1	3	21,73	0,370233	0,137073	208,22	360,65
3(β)	2 0 0	4	22,75	0,386711	0,149545	180,00	360,00
4	2 0 0	4	25,29	0,427000	0,182500	180,45	360,91
5(β)	2 2 0	8	33,00	0,544639	0,296632	127,81	361,50
6	2 2 0	8	37,11	0,603347	0,364203	127,77	361,39
7(β)	3 1 1	11	39,69	0,638633	0,407853	109,00	361,61
8(β)	2 2 2	12	41,85	0,667183	0,445133	105,33	361,42
9	3 1 1	11	45,08	0,708093	0,501396	108,87	361,08
10	2 2 2	12	47,65	0,739043	0,546185	104,31	361,34

Table 2: Evaluation of the K_α and K_β-Debye-Scherrer lines of Cu.

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Task 4

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The individual factors that are necessary for a determination of the intensity have been calculated and listed in Table 3. Only the K_α-lines were taken into consideration in the evaluation.

Column C shows the glancing angles determined from Fig. 7. Column D contains the values calculated for ($\sin(\theta)/\lambda$) from the CuK_α-wavelength $\lambda = 154.18\,pm$ The individual atomic scattering factors \ (\mathrm{f0_{\mathrm{Cu}}}\) were determined from Fig. 2 using these values (column E). The values for F^2 in column F were obtained using equation (6). Columns G and H contain the values for the multiplicity factor M and the Lorentz polarization factor LP. Finally, the columns I and J show the calculated values for the intensity of the reflex lines concerned (the line intensity was arbitarily set at 100 here).

The area under the reflex curve, not the peak height, is decisive for the determination of the intensities of the reflex lines from the experimental results. The following evaluation procedure is therefore recommended:

Task 4 (part 2)

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A	*B*	*C*	*D*	*E*	*F*	*G*	*H*	*I*	*J*	*K*	*L*
Line	*h k l*	$\vartheta/°$	$\frac{\sin\vartheta/\lambda}{1/pm}$	f_{Cu}	F^2	*M*	$\frac{1+\cos^2 2\vartheta}{\sin^2\vartheta\cos\vartheta}$	Intensity Calc. arbitr. units	Relative Intensity Calc.	Intensity Imp/s Experiment	Relative Intensity Experiment
2	1 1 1	21,73	$0{,}240\cdot10^{-2}$	20,4	6658	8	12,0	$6{,}39\cdot10^5$	100	230	100
4	2 0 0	25,29	0,277	19,0	5776	6	8,5	$2{,}95\cdot10^5$	46	155	67
6	2 2 0	37,11	0,391	15,6	3894	12	4,5	$2{,}10\cdot10^5$	33	125	55
9	3 1 1	45,08	0,459	14,2	3226	24	3,7	$2{,}86\cdot10^5$	45	155	67
10	2 2 2	47,65	0,479	13,8	3047	8	2,7	0,66·105	10	70	30

Table 3: Determination of the intensities of the reflex lines.

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Task 4 (part 3)

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Cut out the region around a reflex line using the zoom function for magnification. Mark the region of the line above the bottom points of the reflex line and onward with the marker (cross symbol on the function bar) to define the contained area that is to be determined. Activate the intergral function for the area contained by the reflex line. This is then displayed in Imp/s. The intensities of the individual reflex lines experimentally determined in this way are given in column K. For a better comparison with the theoretical intensity values, the line intensities standardized on the 111 reflex are given in column L. Although the comparison of the relative intensity values of the individual reflex lines in columns J and L do not show exact agreement because absorption and the Debye-Waller factors were disregarded, it is satisfactorily clear that both theory and experiment indicate that the 111 line is the most intensive line. In addition, there is the following further agreement between the theoretical and practical results:

1. The 200 and 311 reflexes are equally strong and have the greatest intensity after the 111 reflex.

2. The 220 reflex has an average intensity, whereas the 222 reflex has the lowest intensity.

Task 5

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On dividing the total mass M of a unit cell by its volume V, the density ρ is given, so that:

$$\rho = \frac{M}{V} = n \cdot m \cdot \frac{1}{a^3} \text{ with } m = \frac{m_A}{N} \rightarrow n = \frac{\rho \cdot N \cdot a^3}{m_A} \qquad (11)$$

where n = the number of atoms or molecules in the unit cell; m = atomic/molecular mass; m_A = atomic/molecular weight;= $N = 6.022 \cdot 10^{23}$ = Avogadro's number. The following are known values for Cu, $\rho = 8.92\,g/cm^3$ and $m_A = 63.546\,g$ Using these values and a = 361.04 pm in equation (11), $n = 3.98 \approx 4$is obtained, i.e. there really are 4 atoms in the unit cell.

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