5.4.23-00 Diffractometric Debye-Scherrer patterns of powder samples
with a hexagonal lattice structure

What you can learn about ...

- ➔ Crystal lattices
- ➔ Crystal systems
- ➔ Bravais-lattice
- ➔ Reciprocal lattice
- ➔ Miller indices
- ➔ Structure factor
- ➔ Atomic scattering factor
- ➔ Bragg scattering
- ➔ Characteristic X-rays
- ➔ Monochromatization of X-rays

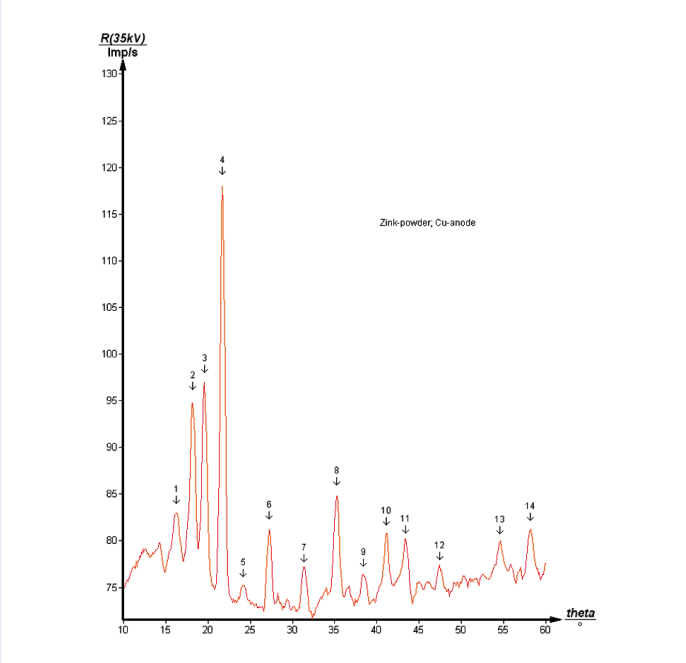
Principle:

A polycrystalline powder sample of zinc 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 Debye-Scherrer pattern is automatically recorded. The evaluation of the pattern not only allows the Bragg reflexes to be assigned to the individual lattice planes and so also the corresponding Bravais lattice type to be obtained, but in addition results in values for their spacing as well as for the lattice constants of zinc and the number of atoms in the unit cell.

What you need:

X-ray basic unit, 35 kV	09058.99	1
Goniometer for X-ray unit, 35 kV	09058.10	1
Plug-in module with Cu X-ray tube	09058.50	1
Counter tube, type B	09005.00	1
Lithium fluoride monocrystal, mounted	09056.05	1
Universal crystal holder	09058.02	1
Probe holder for powder probes	09058.09	1
Diaphragm tube with nickel foil	09056.03	1
Zinc powder, 100 g	31978.10	1
Micro spoon, special steel	33393.00	1
Vaseline, 100 g	30238.10	1
Recording equipment:		
XYt-recorder	11416.97	1
Connecting cable, l = 100 cm, red	07363.01	1
Connecting cable, l = 100 cm, blue	07363.04	1
or		
Software X-ray unit, 35 kV	14407.61	1
Data cable, 2 x SUB-D, 9 pin	14602.00	1
PC, Windows® 95 or higher		

Complete Equipment Set, Manual on CD-ROM included
Diffractometric Debye-Scherrer patterns of powder samples with a hexagonal lattice structure P2542300



Debye-Scherrer Cu-K_α and Cu-K_β lines of zink.

Tasks:

1. Record the intensity of the Cu X-rays back scattered by a zinc powder sample as a function of the scattering angle.
2. Calculate the lattice constants of the substance from the angular positions of the individual Bragg lines.
3. Assign the Bragg reflexes to the respective planes of the zinc lattice and determine the Bravais lattice type of it.
4. Determine the number of atoms in the unit cell.

Diffractometric Debye-Scherrer patterns of powder samples with a hexagonal lattice structure

LEP 5.4.23 -00

Related topics
Crystal lattices, crystal systems, Bravais-lattice, reciprocal lattice, Miller indices, structure factor, atomic scattering factor, Bragg scattering, characteristic X-rays, monochromatization of X-rays.

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Set-up and Procedure
Sample preparation
A relatively high sample concentration can be obtained by mixing the powder with a little vaseline. To do this, transfer a little of the zinc powder 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 zinc paste into the specimen for powder samples and smooth it flush. Use the universal crystal holder to hold the specimen.
X-ray unit settings:
Acceleration voltage U_a = 35 kV, anode current I_a = 1 mA. Use the 2 mm diameter double pinhole. Set the goniometer block

Fig. 1: Experimental set-up

with line marking at position 4.5. To obtain a good angle resolution, push the counter tube holder to the back stop.

Calibration of the goniometer with the LiF single-crystal:
Exact angular positions of Debye-Scherrer reflections are only to be expected when the goniometer is correctly adjusted. Should the goniometer be out of adjustment for any reason whatever, this can be overcome by stepwise carrying out of the following procedure: In the coupled 2:1 mode, set the LiF single-crystal at an angle of ϑ = 22.5°. Theoretically, the very intense 200 reflection from LiF lies at this angle. Now uncouple the rotation of the crystal and the Geiger-Müller counter tube. Search for the maximum intensity of the reflection by turning the crystal and counter tube alternately and separately through a few 0.1° angular steps. Should the maximum be found at 22.3°, for example, i.e. 0.2° below the theoretical value, then couple the crystal and counter tube together again and turn the crystal through -0.2° past the zero position. Save this corrected zero position by pressing "ENTER". The maximum intensity must now be situated exactly at the angle of 22.5°. Carry out a corresponding positive zero position correction should the maximum be found at an angle greater than 22.5°.
Further settings:
Scanning range: see the Figures showing the spectra: Stepping 0.1°; Scanning speed, when only 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 40 s/° is required for a better signal-noise ratio.

Theory and Evaluation
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.:

$$2\ d\ \sin\vartheta = n\lambda \qquad (n = \text{order of diffraction}) \qquad (1)$$

When there is only one atom a unit cell, then all reflexes that occur fulfill Bragg's conditions (see Fig. 2). When there are N atoms in a unit cell, however, 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 each individual atom of the N atoms, taking their phases into account.
The following is generally valid for F:

$$F_{hkl} = \sum_{1}^{N} f_n \cdot e^{2\pi i\,(hu_n + kv_n + hw_n)} \qquad (2)$$

where h, k, l = Miller indices of the reflecting lattice planes and u_n, v_n, 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 $|F_{hkl}|^2$.
The unit cell of a hexagonal system with the most dense packing of spheres contains two atoms with positions 0, 0, 0 and 2/3, 1/3, 1/2. According to equation (2), therefore, the structure factor F for this lattice type is given by:

$$F = f(e^{2\pi i(0)} + e^{2\pi i\,(2/3\,h + 1/3\,k + 1/2\,l)}) \qquad (3)$$

Table 1 gives the selection rules for structure factor F.

Table 1: Selection rules for the structure factor F of hexagonal crystal systems

$h+2k$	l	$\lvert F \rvert^2$
3n	odd	0
2n	even	$4\,f^2$
3n ± 1	odd	$3\,f^2$
3n ± 1	even	f^2

n = 0, 1, 2, 3, 4,....

For a hexagonal crystal system, the spacings d of the individual lattice planes with the indices (hkl) are obtained from the quadratic form:

$$\frac{1}{d_{hkl}^2} = \frac{4}{3}\left(\frac{h^2+hk+k^2}{a^2}\right) + \frac{l^2}{c^2} \quad (a, c = \text{lattice constants}) \quad (4)$$

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

$$\sin^2\vartheta = \frac{\lambda^2}{4}\left[\frac{4}{3}\frac{(h^2+hk+k^2)}{a^2} + \frac{l^2}{c^2}\right] \qquad (5)$$

Fig. 3 shows the Debye-Scherrer spectrum of a zinc powder sample.

For the evaluation of the spectrum, equation (5) is rearranged as follows:

$$\sin^2\vartheta = A(h^2+kh+k^2) + Bl^2 \text{ with } A = \frac{\lambda^2}{3a^2} \text{ and } \frac{\lambda^2}{4c^2} \quad (6)$$

The value for A is determined solely by the hk lines. With l = 0, it follows from equation (6) that:

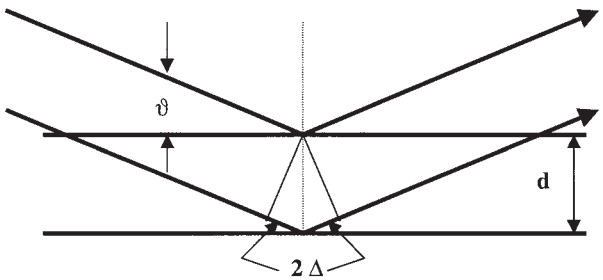
$$\sin^2\vartheta = A\,(h^2+hk+k^2) \qquad (7)$$

The permissible values for ($h^2 + hk + k^2$) are 1, 3, 4, 7, 9, 12, ... (see Table 2).

Table 2: Permissible h,k combinations

$h\ k$	1 0	1 1	2 0	2 1	3 0	2 2	3 1
h^2+hk+k^2	1	3	4	7	9	12	13

Fig. 2: Bragg-condition for constructive reflection of x-rays by lattice planes of a crystal



Divide the $\sin^2\vartheta$ values by 3, 4, 7, ... and search for quotients that are equal to each other, or to $\sin^2\vartheta$ values, as it can be assumed that these belong to the hk lines.
Only the first reflex lines need be examined here, as these always belong to the low indexed lattice planes (see Table 3).

It is clear from Table 3 that for lines 3 and 8 the bold face values are nearly in agreement.
On calculating the mean value of these, A = 0.1117 is obtained.
Using this value for A and λ (K_α) = 154.18 pm, it follows from equation (6) that for the first lattice constant: a = 266.3 pm.
On carrying out a trial that suggests itself, i.e. by assigning the value A = 0.1117 to line 3 of index 100, then the $\sin^2\vartheta$ value of line 8 must be assigned to the 110 reflex, as this is about 3 times the corresponding value of line 3.
Now subtract A, $3A$, $4A$ etc. from the $\sin^2\vartheta$ values and search for Bl^2 values that are in a ratio to each other of 1, 4, 9, 16 etc.:

We find from Table 4 that the bold face values 0.0251, {1/4(0.0973+0.0984+0.0976+0.0954) = 0.0972}, 0.2216 and 0.3857 approximately fulfill this.
B can so be determined from the relationships: 0.0251 = 1^2 B, 0.0972 = 2^2 B, 0.2216 = 3^2 B, 0.3857 = 4^2 B. A mean value of B = 0.0245 is found.
The second lattice constant for the hexagonal lattice can be obtained using this value for B and equation (6): c = 492.5 pm.
In addition, it follows that the lines 2 and 9 have the indices 002 and 004, because with (h^2 + hk+ k^2) = 0, from equation (6):
Line 2: $\sin^2\vartheta = 0.0972 = B \cdot l^2 = 0.0245 \cdot l^2 \rightarrow l = 1.99 \approx 2$
Line 9: $\sin^2\vartheta = 0.3857 = B \cdot l^2 = 0.0245 \cdot l^2 \rightarrow l = 3.96 \approx 4$
(h,k,l) can only be integer numbers)
Line 4, for example, has the indices h = 1, k = 0 and l = 1, as: $\sin^2\vartheta = 0.1368 \approx A+B = 0.1362$ or $\sin^2\vartheta - A = 0.0251 \approx B$ = 0.0245.
The indices of all other lines with the exception of lines 1, 5 and 7 can be correspondingly found, as given in Table 4.

Table 3: Evaluation of the K_α- lines for the determination of lattice constant a.

Line	ϑ/°	$\sin\vartheta$	$\sin^2\vartheta$	$\sin^2\vartheta/3$	$\sin^2\vartheta/4$	$\sin^2\vartheta/7$	$h\ k\ l$
1	16.25	0.2798	0.0783	0.0261	0.0196	0.0112	
2	18.18	0.3120	0.0973	0.0324	0.0243	0.0139	
3	19.58	0.3351	**0.1123**	0.0374	0.0281	0.0160	1 0 0
4	21.71	0.3699	0.1368	0.0456	0.0342	0.0195	
5	24.17	0.4094	0.1676	0.0559	0.0419	0.0239	
6	27.28	0.4583	0.2101	0.0700	0.0525	0.0300	
7	31.38	0.5207	0.2711	0.0904	0.0678	0.0387	
8	35.26	0.5773	0.3333	**0.1111**	0.0833	0.0476	1 1 0
9	38.39	0.6210	0.3857	0.1286	0.0964	0.0551	

Table 4: Evaluation of the reflex lines for the determination of lattice constant c and the assignment of Miller indices.

Line	$\sin^2\vartheta$	$\sin^2\vartheta$-A	$\sin^2\vartheta$-3A	$\sin^2\vartheta$-4A	$h\ k\ l$
1	0.0783				0 0 2 (K_β)
2	**0.0973**				0 0 2
3	0.1123	0.0006			1 0 0 and 1 0 1 (K_β)
4	0.1368	**0.0251**			1 0 1
5	0.1676	0.0559			1 0 2 (K_β)
6	0.2101	0.0984			1 0 2
7	0.2711	0.1594			1 1 0 (K_β)
8	0.3333	**0.2216**			1 1 0
9	**0.3857**	0.2740	0.0506		0 0 4
10	0.4327	0.3210	**0.0976**		1 1 2
11	0.4712	0.3595	0.1361	0.0244	2 0 1
12	0.5422	0.4305	0.2071	**0.0954**	2 0 2
13	0.6643	0.5526	0.3292	0.2175	2 0 3
14	0.7223	0.6106	0.3872	0.2755	1 0 5

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

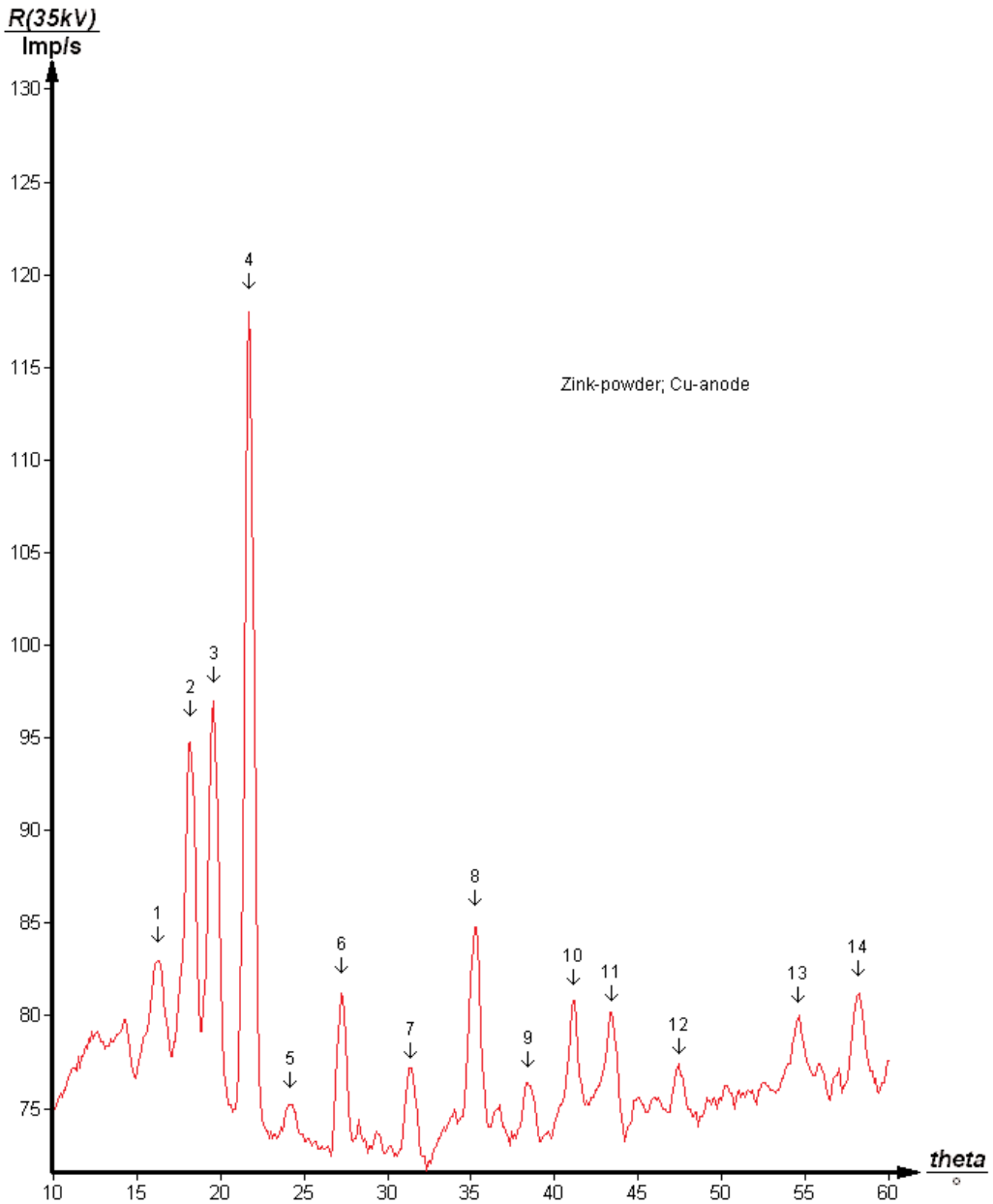
$$\frac{\lambda(K_\alpha)}{\lambda(K_\beta)} = \frac{\sin\vartheta_\alpha}{\sin\vartheta_\beta} = \frac{154.18\ \text{pm}}{134.22\ \text{pm}} \approx 1.1 \qquad (8)$$

This value corresponds with the quotients of the $\sin^2$ values (Table 4) of the pairs of lines 2-1, 4-3, 6-5 and 8-7, showing that the lines 1, 3, 5, and 7 originate from the Cu K_β radiation.

The correctness of this conclusion can be shown by a control measurement (see Fig. 4) using the diaphragm tube with nickel foil to reduce the intensity of the K_β radiation. The reflexes in Fig. 3 that were previously assigned to the K_β lines are no longer to be seen. As the intensity of the K_α- radiation is also somewhat weakened by the Ni foil, the detection of reflexes of weak intensity at larger glancing angles is made difficult when it is used.

The experiment gives values of a = 266.3 pm and c = 492.5 pm for the two lattice constants of the hexagonal zinc lattice.
(Literature values for the lattice constants: a = 266.5 pm and c = 494.7 pm)

Fig. 3: Debye-Scherrer Cu-K_α and Cu-K_β–lines of zink



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

$$\rho = \frac{M}{V} = n \cdot m \cdot \frac{1}{V} \qquad (9)$$

with $$m = \frac{m_A}{N} \rightarrow n = \frac{\rho \cdot N \cdot \left(\frac{1}{2}\sqrt{3a^2} \cdot c\right)}{m_A}$$

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 zinc, ρ = 7.14 g·cm^{-3} and m_A = 63.38 g. Using these values and a = 266.5.1 pm and c = 494.7 pm in equation (9), $n = 2.06 \approx 2$ is obtained, i.e. there are 2 atoms in the unit cell of the zinc lattice.

Fig. 4: Debye-Scherrer diagram only with Cu-K_α beam (a nickel filter was used here)