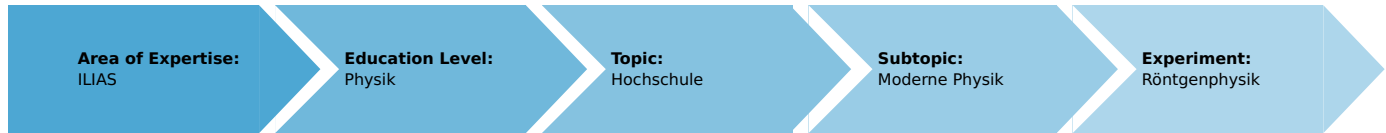


Diffraction Debye-Scherrer patterns of powder samples with a hexagonal lattice structure (Bragg-Brentano) (Item No.: P2542301)

Curricular Relevance



Difficulty



Difficult

Preparation Time



1 Hour

Execution Time



2 Hours

Recommended Group Size



2 Students

Additional Requirements:

- PC

Experiment Variations:

Keywords:

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

Overview

Short description

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.



Fig. 1: P2542301

Equipment

Position No.	Material	Order No.	Quantity
1	XR 4.0 expert unit, X-ray unit, 35 kV	09057-99	1
2	XR 4.0 X-ray goniometer	09057-10	1
3	XR 4.0 X-ray Plug-in Cu tube	09057-51	1
4	Geiger-Mueller counter tube, 15 mm (type B)	09005-00	1
5	XR 4.0 X-ray LiF crystal, mounted	09056-05	1
6	XR 4.0 X-ray Universal crystal holder for X-ray unit	09058-02	1
7	XR 4.0 X-ray Diaphragm tube w. nickel foil	09056-03	1
8	XR 4.0 X-ray Diaphragm tube d = 2 mm	09057-02	1
9	Microspoon, steel	33393-00	1
10	Vaseline 100 g	30238-10	1
11	XR 4.0 Software measure X-ray	14414-61	1
12	Data cable USB, plug type A/B, 1.8 m	14608-00	1
13	XR 4.0 X-ray sample holder for powder samples (diffractometry)	09058-09	1
14	Zinc, powder 100 g	31978-10	1

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.

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. 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. Insert a diaphragm tube with a diameter of 2 mm into the beam outlet of the tube plug-in unit.



Fig. 2: Connectors in the experiment chamber

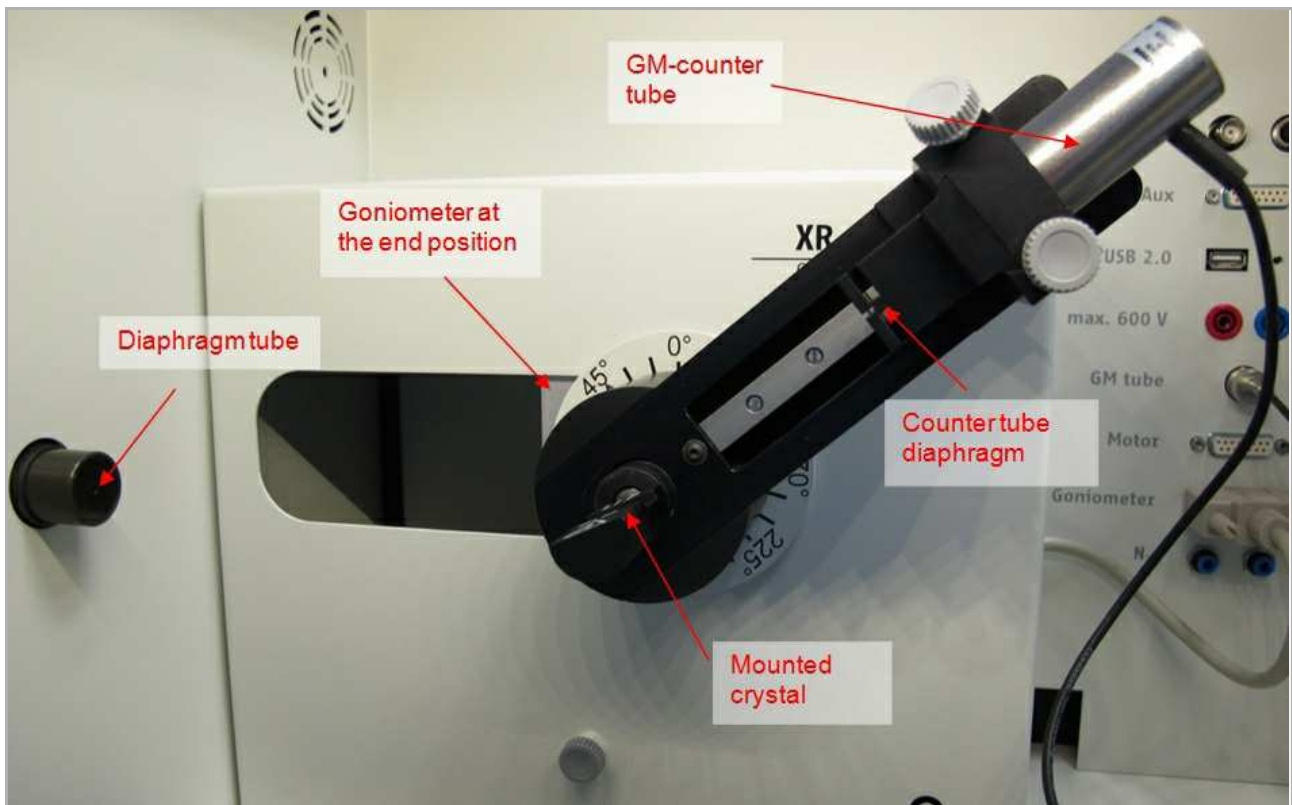


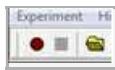
Fig. 3: Set-up of the goniometer

Note

Details concerning the operation of the X-ray unit and goniometer as well as information on how to handle the monocrystals can be found in the respective operating instructions.

Procedure

- 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.
- Click the experiment chamber (see the red marking in Figure 5) to change the parameters for the experiment. Select the parameters as shown in the text box.
- 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 parameters as shown in the text box: Anode voltage $U_A = 35$ kV; anode current $I_A = 1$ mA..
- 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.



Fig. 4: Connection of the computer



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

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

- 1:2 coupling mode
- angle step width 0.1°
- Scanning range 10° - 60° bzw. Mit Filter: 10 - 28°
- Anode voltage $U_A = 35$ kV; 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/ $^\circ$. For the identification of weaker lines, a scanning speed of at least 40 s/ $^\circ$ is required for a better signal/noise ratio

Note

Never expose the Geiger-Müller counter tube to the primary X-radiation for an extended period of time.

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.

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 fault can be corrected either manually or by means of the autocalibration function:

Automatic calibration:

The anode material of the X-ray tube is automatically identified. The crystal must be manually set under "Menu", "Goniometer", "Parameter". For calibration, 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. The display shows the corresponding calibration curves. The newly configured zero position of the goniometer system is saved even after switch-off of the X-ray unit.

Manual calibration

The crystal for analysis must be manually brought to the theoretical Bragg angle ϑ (counter tube correspondingly to 2ϑ). Now search for the intensity maximum of the line by iterative turning of the crystal and counter tube by a few $\pm 1/10^\circ$ around this angular position. Following this and in coupled mode, bring the crystal and counter tube to the particular zero position corrected by the error value and then confirm with "Menu", "Goniometer" and "Set to zero".

Theory and Evaluation

Theory

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.:

$$2d\sin\vartheta = n\lambda; (n = 1, 2, 3, \dots) \quad (1)$$

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 :

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

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 $\frac{2}{3}, \frac{1}{3}, \frac{1}{2}$. According to equation (2), therefore, the structure factor F for this lattice type is given by:

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

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	$ F ^2$
$3n$	odd	0
$2n$	even	$4f^2$
$3n \pm 1$	odd	$3f^2$
$3n \pm 1$	even	f^2

$n = 0, 1, 2, 3, 4, \dots$

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

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

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

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

Task 1

Fig. 7 shows the Debye-Scherrer spectrum of a zinc powder sample.

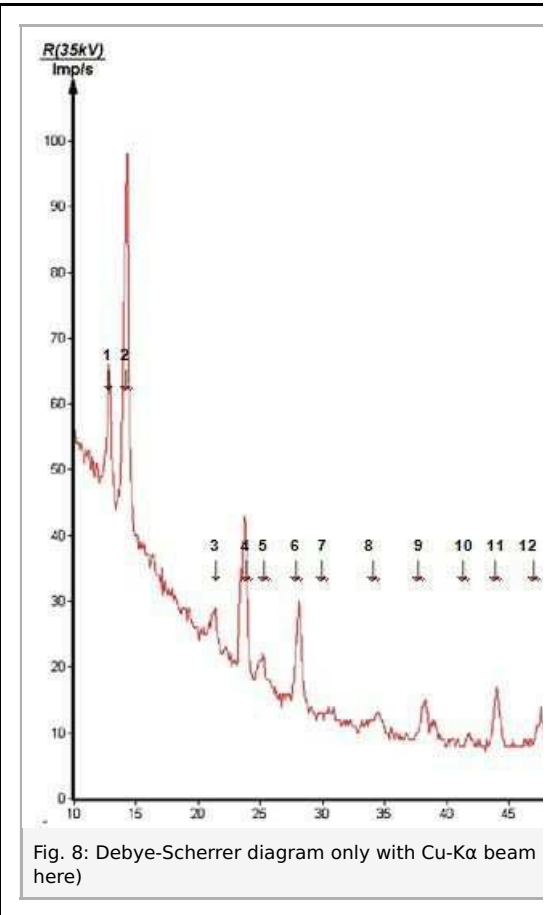
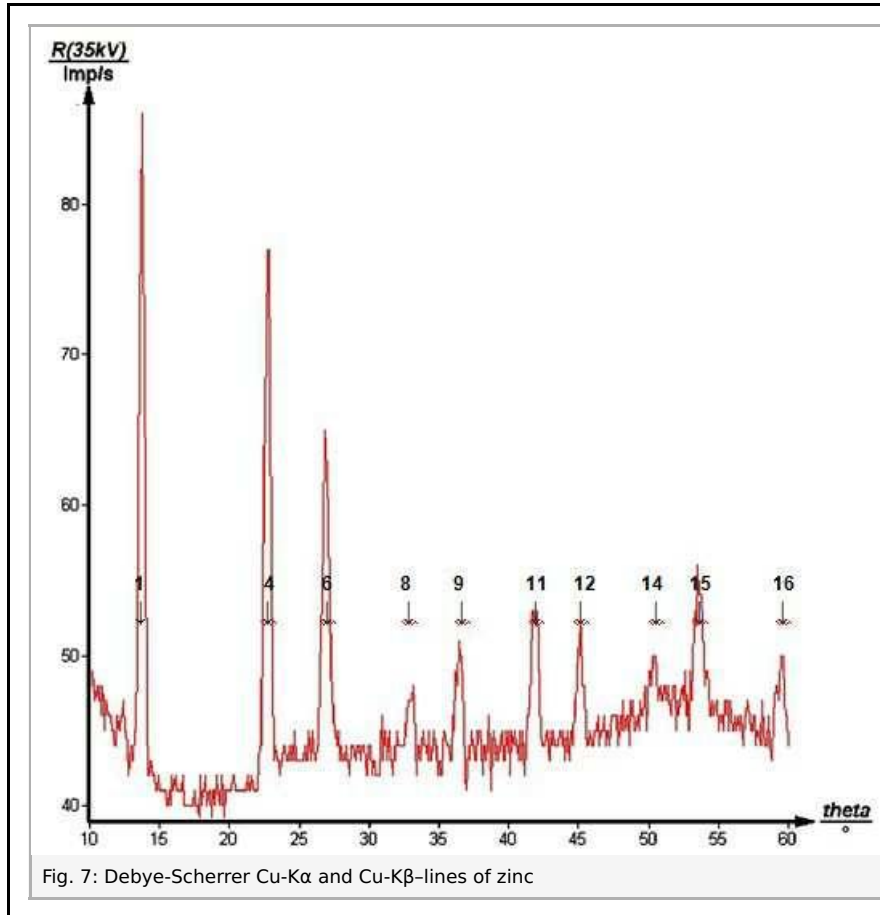
As no filter is used for the monochromatization of the X-rays, the fact that the very intense lines resulting from the K_α -radiation are accompanied by secondary lines resulting from the weaker K_β radiation must be taken into consideration when individual lines are evaluated.

Such pairs of lines can be identified by means of equation (1). It is namely approximately true with $\lambda(K_\alpha) = 154.18 \text{ pm}$ and $\lambda(K_\beta) = 139.22 \text{ pm}$ that:

$$\frac{\lambda(K_\alpha)}{\lambda(K_\beta)} = \frac{\sin^2 \vartheta_\alpha}{\sin^2 \vartheta_\beta} = \frac{154,18 \text{ pm}}{139,22 \text{ pm}} \approx 1,1 \quad (8)$$

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. 8) 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_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.



Task 2 and 3

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

$$\sin^2 \vartheta = A(h^2 + hk + k^2) + Bl^2 \quad \text{mit } A = \frac{\lambda^2}{3a^2} \quad \text{und } B = \frac{\lambda^2}{4c^2} \quad (6)$$

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

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

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

hk	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

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).

The first lattice constant α :

- 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 $\lambda(K_\alpha) = 154.18$ pm, it follows from equation (6) that for the first lattice constant: $\alpha = 266.3$ 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.:

Table 3: Evaluation of the $K\alpha$ - lines for the determination of lattice constant a.

Line	$\vartheta/^\circ$	$\sin\vartheta$	$\sin^2\vartheta$	$\sin^2\vartheta/3$	$\sin^2\vartheta/4$	$\sin^2\vartheta/7$	hkl
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	

The second lattice constant c :

We find from Table 4 that the bold face values 0.0251, $\{\frac{1}{4}(0.0973+0.0984+0.0976+0.0954) = 0.0972\}$, 0.2216 and 0.3857 approximately fulfill this.

B can so be determined from the relationships: $0.0251 = 1^2B$, $0.0972 = 2^2B$, $0.2216 = 3^2B$, $0.3857 = 4^2B$. 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 4: Evaluation of the reflex lines for the determination of lattice constant c and the assignment of Miller indices.

Line	$\sin^2\vartheta$	$\sin^2\vartheta - A$	$\sin^2\vartheta - 3A$	$\sin^2\vartheta - 4A$	hkl
1	0,0783				002 (K_β)
2	0,0973				002
3	0,1123	0,0006			100 und 101 (K_β)
4	0,1368	0,0251			101
5	0,1676	0,0559			102 (K_β)
6	0,2101	0,0984			102
7	0,2711	0,1594			110 (K_β)
8	0,3333	0,2216			110
9	0,3857	0,2740	0,0506		004
10	0,4327	0,3210	0,0976		112
11	0,4712	0,3595	0,1361	0,0244	201
12	0,5422	0,4305	0,2071	0,0954	202
13	0,6643	0,5526	0,3292	0,2175	203
14	0,7223	0,6106	0,3872	0,2755	105

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

Task 4

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

$$\rho = \frac{M}{V} = n \cdot m \cdot \frac{1}{V} \quad \text{mit } m = \frac{m_A}{N} \rightarrow n = \frac{\rho \cdot N \cdot (\frac{1}{2} \sqrt{3} \alpha^2 \cdot c)}{m_A} \quad (9)$$

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, $\rho = 7.14 \text{ g} \cdot \text{cm}^{-3}$ and $m_A = 63.38 \text{ g}$. Using these values and $\alpha = 266.5.1$ 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.