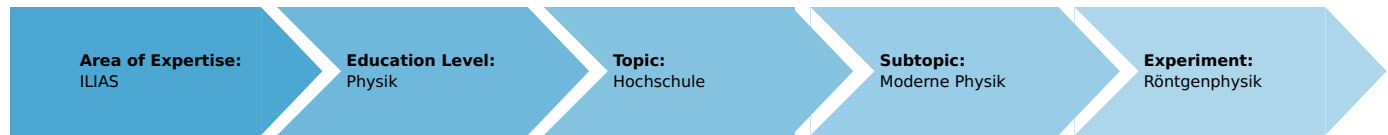


Diffractionmetric Debye-Scherrer patterns (according to Bragg-Brentano) of powder samples with diamond structure (Item No.: P2542201)

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, Bragg-Brentano Geometry

Overview

Short description

Principle

Polycrystalline germanium and silicon powder samples, which crystallize in a diamond form, are irradiated with the radiation from a X-ray tube with a copper anode. A swivelling Geiger- Mueller counter tube detects the radiation that is constructively reflected from the various lattice planes of the crystallites. The Debye-Scherrer patterns are automatically recorded. Their evaluation 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 also results in the determination of values for their spacings as well as for the lattice constants of the samples and the number of atoms in the unit cell.



Fig. 1: P2542201

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	Germanium, Powder, 99%, 10 g	31768-03	1
10	Silicium, finest powder, 50 g	31155-05	1
11	Microspoon, steel	33393-00	1
12	Vaseline 100 g	30238-10	1
13	Mortar w. pestle, 70ml, porcelain	32603-00	1
14	XR 4.0 Software measure X-ray	14414-61	1
15	Data cable USB, plug type A/B, 1.8 m	14608-00	1
16	XR 4.0 X-ray sample holder for powder samples (diffractometry)	09058-09	1

Tasks

1. Record the intensity of the Cu X-rays back scattered by a germanium and a silicon powder sample as a function of the scattering angle.
2. Assign the Bragg reflexes to the respective lattice planes.
3. Calculate the lattice plane spacings appropriate to the angular positions of the individual Bragg reflexes. Determine the lattice constants of the samples and their Bravais lattice type.
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

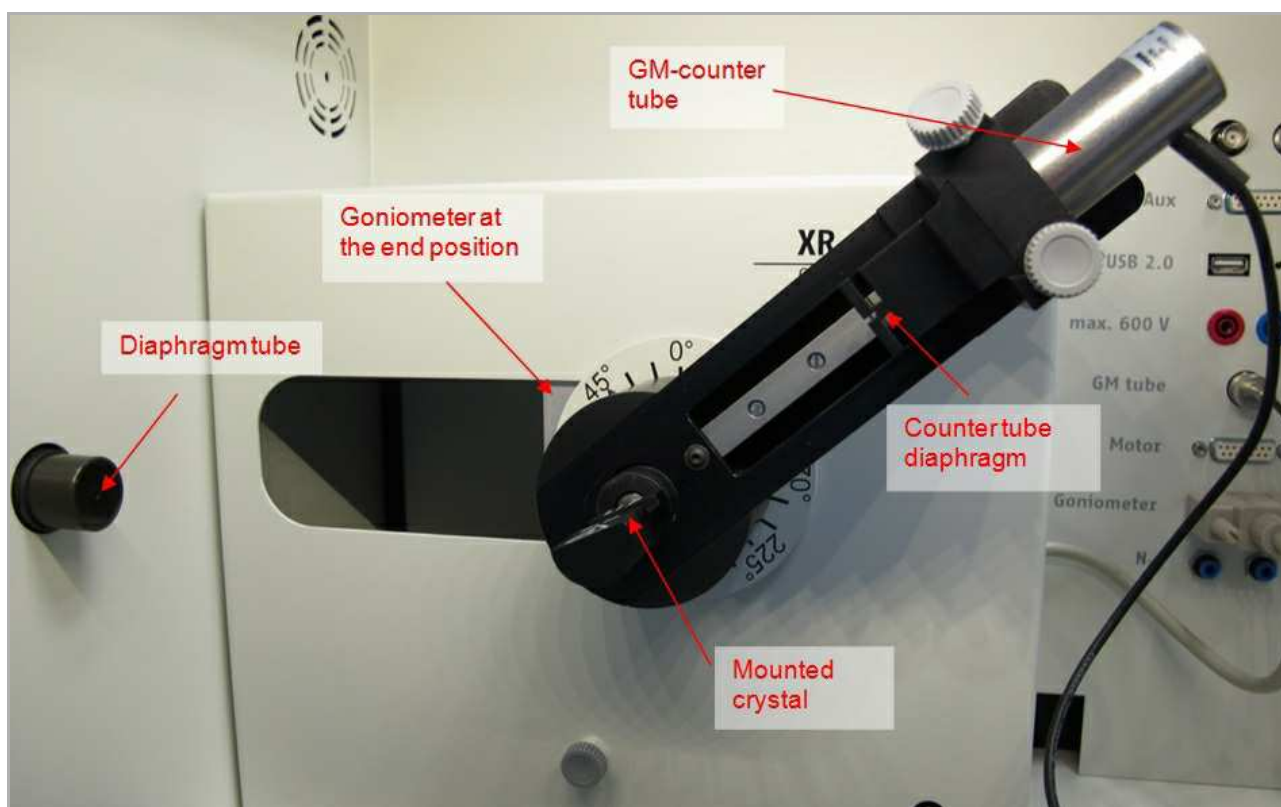


Fig. 3: Set-up of the goniometer

Note

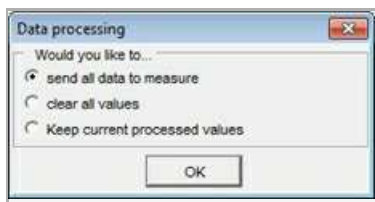
Details concerning the operation of the X-ray unit and goniometer as well as information on how to handle the monocrystals can be found in the respective

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°
- 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:

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.

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 diamond lattice form is distinguished by two fcc lattices which are pushed one within the other, whereby the origin of the second fcc lattice is displaced by $\frac{1}{4}\frac{1}{4}\frac{1}{4}$ relative to the space diagonals of the first lattice. The unit cell contains 8 atoms, the two origin atoms and 6 additional atoms which lie at the coordinates $\frac{1}{2}\frac{1}{2}0, \frac{1}{2}0\frac{1}{2}, 0\frac{1}{2}\frac{1}{2}$ and $\frac{3}{4}\frac{3}{4}\frac{3}{4}, \frac{3}{4}\frac{1}{4}\frac{3}{4}, \frac{3}{4}\frac{3}{4}\frac{1}{4}$ relative to the origin atoms. The structure factor F for the diamond lattice form can so be calculated from:

$$F = f(e^{2\pi i(0)} + e^{2\pi i(\frac{1}{4}h + \frac{1}{4}k + \frac{1}{4}l)} \cdot 1 + e^{\pi i(h+k)} + e^{\pi i(h+l)} + e^{\pi i(k+l)} \quad (3)$$

The expression in curved brackets is the same as for fcc lattices, i.e. mixed index hkl triplets are not allowed and a value of 4 is obtained for the unmixed indices.

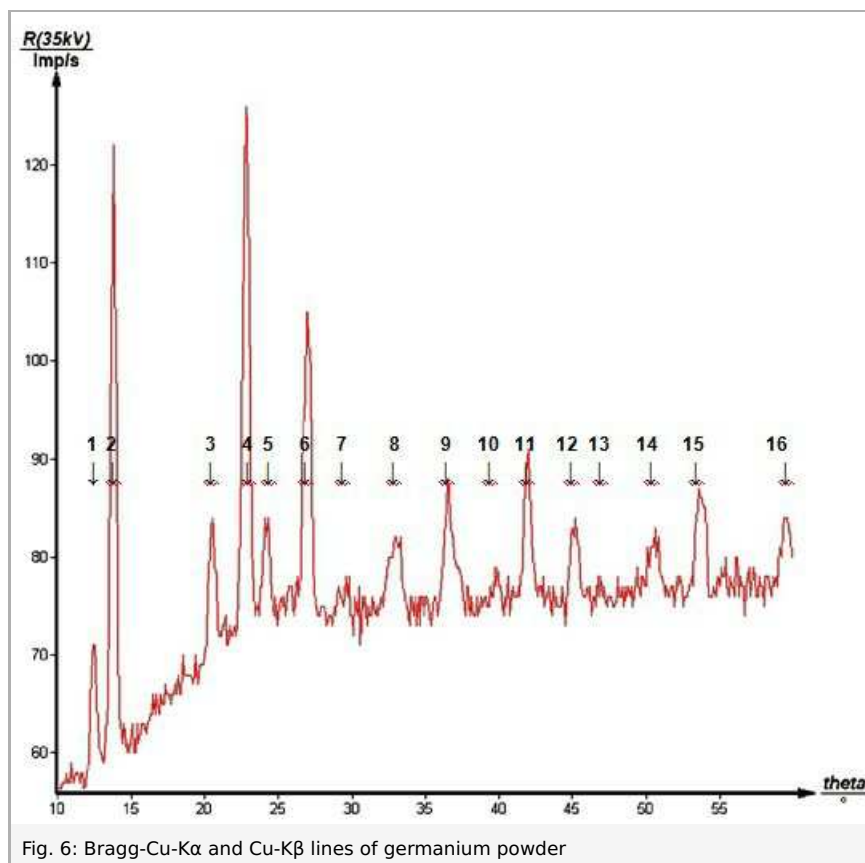
The expression in round brackets is only unequal to zero when $(h + k + l) = 4n$ with $n = 1, 2, 3, \dots$

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

$$\frac{1}{d_{hkl}^2} = \frac{1}{a^2}(h^2 + k^2 + l^2) \quad (a = \text{lattice constant}) \quad (4)$$

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

$$\sin^2 \vartheta_{hkl} = \frac{\lambda^2}{4a^2}(h^2 + k^2 + l^2) \quad (5)$$



Evaluation of Germanium

Task 1

Fig. 6 shows the Bragg spectrum of germanium.

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 the characteristic wavelengths of Cu X-rays, $\lambda(K_\alpha) = 154.18 \text{ pm}$ and $\lambda(K_\beta) = 139.22 \text{ pm}$:

$$\frac{\lambda(K_\alpha)}{\lambda(K_\beta)} = \frac{\sin\vartheta_\alpha}{\sin\vartheta_\beta} = \frac{154,18\text{pm}}{139,22\text{pm}} \approx 1,1 \quad (6)$$

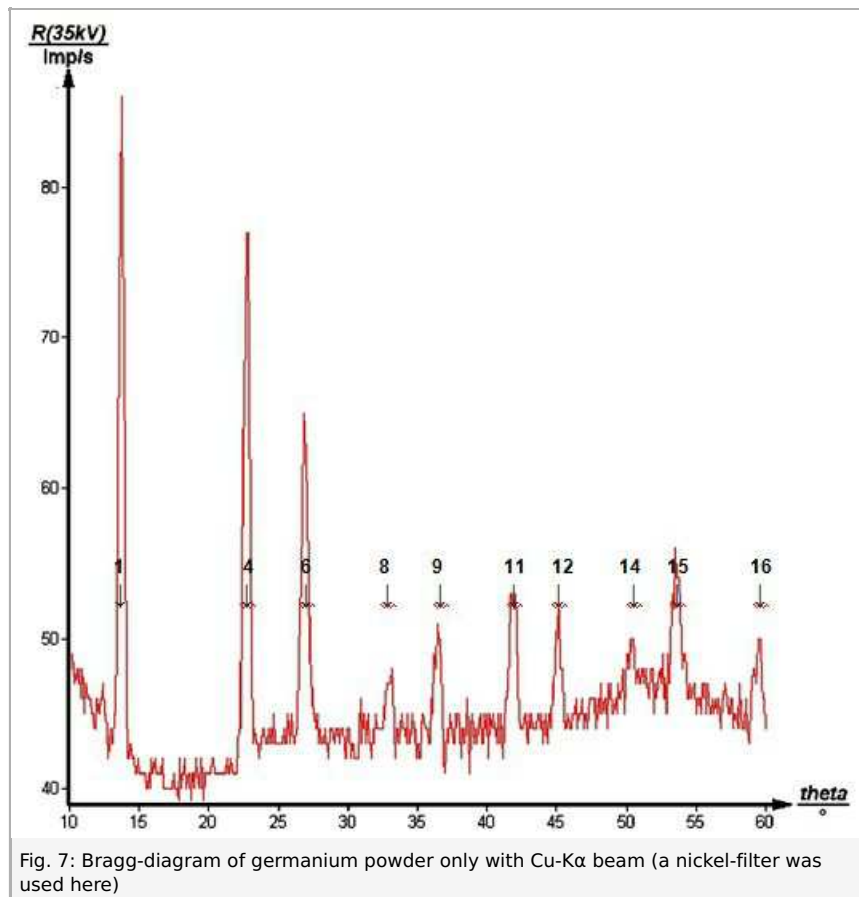


Fig. 7: Bragg-diagram of germanium powder only with Cu- K_α beam (a nickel-filter was used here)

These values correspond to the quotients of the $\sin\vartheta$ values (Fig. 6) of the pairs of lines 2-1, 4-3, 6-5, 8-7, 11/10 and 13/12, which shows that the lines 1, 3, 5, 7, 10 and 13 originate from the Cu K_β radiation.

The correctness of this conclusion can be shown by a control measurement (see Fig. 7) using the diaphragm tube with nickel foil to reduce the intensity of the K_β radiation.

The reflexes in Fig. 6 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 this is used.

Task 2

The following method for evaluating the spectrum is given as a representative example for the germanium spectrum.

First determine the $\sin\vartheta$ and $\sin^2\vartheta$ values for each individual reflex from the angle of diffraction ϑ of the individual lines. From equation (4), the ratios of the observed $\sin^2\vartheta$ values of the individual lines must be representable by the ratios of the sums of the squares of the three integer numbers (h, k, l) .

As shown in column *I* of Table 1 for the K_α - reflexes, calculate the ratios of the $\sin^2$ values of the individual lines (*n*) to the $\sin^2$ values of the first line (here line 2). The numbering in column *E* relates to the reflex lines indicated in Fig. 6. In column *A*, all of the possible h, k, l combinations of numbers are listed. Columns *B*, *C* and *D* show the individual ratios of the sums of squares of these numbers.

When an attempt is made to assign the indices 100 or 110 to the first reflex, then no agreement with the ratios of the $\sin^2\vartheta$ values is found. When, however, the index 111 is assigned to the first line, then all of the other lines can be assigned hkl index

Student's Sheet

Printed: 21.08.2017 12:22:58 | P2542201

triplets with the accuracy required.

Table 1: Evaluation of the K α - lines of germanium

A	B	C	D	E	G	H	I	J	K	L
hkl	$h^2 + k^2 + l^2$	$\frac{h^2 + k^2 + l^2}{(h^2 + k^2 + l^2)_0 11}$	$\frac{h^2 + k^2 + l^2}{(h^2 + k^2 + l^2)_1 11}$	Reflex no.	$\vartheta / ^\circ$	$\sin \vartheta$	$\sin^2 \vartheta$	$\frac{\sin^2 \vartheta(n)}{\sin^2 \vartheta(2)}$	d/pm	α/pm
100	1									
110	2	1								
111	3	1.5	1	2	13.72	0.23718	0.05625	1.00	325.02	562.95
200	4	2	1.33							
210	5	2.5	1.67							
211	6	3	2							
220	8	4	2.67	4	22.74	0.38655	0.14942	2.66	199.43	564.08
221/300	9	4.5	3							
310	10	5	3.33							
311	11	5.5	3.67	6	26.89	0.45228	0.20456	3.64	170.45	565.31
222	12	6	4							
320	13	6.5	4.33							
321	14	7	4.67							
400	16	8	5.33	8	33.08	0.54581	0.29791	5.30	141.24	564.96
410/322	17	8.5	5.67							
441/330	18	9	6							
331	19	9.5	6.33	9	36.47	0.59440	0.35331	6.28	129.69	565.32
420	20	10	6.67							
421	21	10.5	7							
332	22	11	7.33							
422	24	12	8	11	41.89	0.66770	0.44583	7.93	115.46	565.62
500/430	25	12.5	8.33							
510/431	26	13	8.67							
511/333	27	13.5	9	12	45.10	0.70834	0.50174	8.92	108.83	565.51
520/432	29	14.5	9.67							
521	30	15	10							
440	32	16	10.67	14	50.39	0.77040	0.59352	10.55	100.06	566.05
522/441	33	16.5	11							
530/433	34	17	11.33							
531	35	17.5	11.67	15	53.56	0.80448	0.64719	11.51	95.83	566.91
600/442	36	18	12							
610	37	18.5	12.33							
611/532	38	19	12.67							
620	40	20	13.33	16	59.56	0.86216	0.74332	13.21	89.41	565.51

Table 2: Evaluation of the K β lines of germanium

A	B	C	D	E	F	G	H	I	J	K
hkl	$h^2 + k^2 + l^2$	$\frac{h^2 + k^2 + l^2}{(h^2 + k^2 + l^2)_0 11}$	$\frac{h^2 + k^2 + l^2}{(h^2 + k^2 + l^2)_1 11}$	Reflex no.	$\vartheta / ^\circ$	$\sin \vartheta$	$\sin^2 \vartheta$	$\frac{\sin^2 \vartheta(n)}{\sin^2 \vartheta(3)}$	d/pm	α/pm
111	3	1.5	1	1	12.35	0.21388	0.04575	1	325.46	563.72
220	8	4	2.67	3	20.52	0.35053	0.12286	2.69	198.58	561.68
311	11	5.5	3.67	5	24.25	0.41072	0.16869	3.69	169.48	562.11
400	16	8	5.33	7	29.43	0.49136	0.24143	5.28	141.67	566.67
511/333	27	13.5	9	10	39.83	0.64051	0.41026	8.98	108.68	564.71
531	35	17.5	11.67	13	47.11	0.73266	0.53679	11.73	95.01	562.09

Task 3

Task 4

Table 2 gives the results of the evaluation of the $K\beta$ lines 1, 3, 5, 7, 10 and 13 that occur in Fig. 6. On dividing the total mass M of a unit cell by its volume V , the density ρ is given, so that:

$$\rho = \frac{M}{V} = n \cdot m \cdot \frac{1}{\alpha^3} \quad \text{mit } m = \frac{m_A}{N} \rightarrow n = \frac{\rho \cdot N \cdot \alpha^3}{m_A} \quad (7)$$

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 germanium, $\rho = 5.3234 \text{ g} \cdot \text{cm}^{-3}$ and $m_A = 72.59 \text{ g}$. Using these values and $\alpha = 564.56 \text{ pm}$ in equation (7), $n = 7.95 \approx 8$ is obtained, i.e. there are 8 atoms in the unit cell of the diamond lattice form.

Evaluation of Silicon

The Bragg spectrum of silicon, recorded without Ni filter, is shown in Fig. 8. The evaluation of this spectrum carried out according to the above procedure is shown in abbreviated form for the two Cu wavelengths in Tables 3 and 4.

It is again seen here that only uneven hkl index triples occur, or such for which $(h + k + l) = 4n$. According to this, silicon also has a diamond lattice form. Column K contains the values for the lattice constant a determined using equation (4).

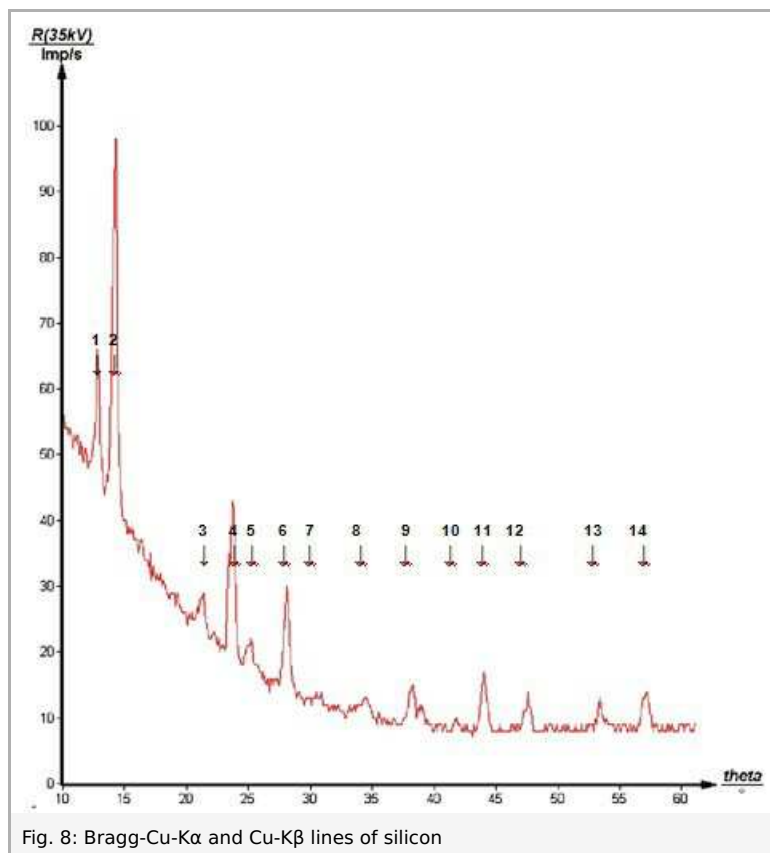


Fig. 8: Bragg-Cu- $K\alpha$ and Cu- $K\beta$ lines of silicon

The mean value from the $K\alpha$ - and $K\beta$ lines is:

$$\alpha = (543.17 \pm 1.01) \text{ pm}; \quad \Delta(\alpha)/\alpha < 0.2\%;$$

(literature value: $\alpha = 543.05 \text{ pm}$)

Together with the known values for silicon, $\rho = 2.32 \text{ g} \cdot \text{cm}^{-3}$ and $m_A = 28.086 \text{ g}$, we again obtain (equation 7): $n = 7.97 \approx 8$.

Table 3: Evaluation of the K α - lines of silicon

A	B	C	D	E	F	G	H	I	J	K
hkl	$h^2 + k^2 + l^2$	$\frac{h^2+k^2+l^2}{(h^2+k^2+l^2)_{011}}$	$\frac{h^2+k^2+l^2}{(h^2+k^2+l^2)_{111}}$	Reflex no.	$\vartheta / ^\circ$	$\sin \vartheta$	$\sin^2 \vartheta$	$\frac{\sin^2 \vartheta(n)}{\sin^2 \vartheta(2)}$	d/pm	α/pm
111	3	1.5	1	2	14.21	0.24548	0.06026	1	314.04	543.93
220	8	4	2.67	4	23.68	0.40163	0.16131	2.69	191.94	542.89
311	11	5.5	3.67	6	28.11	0.47117	0.22000	3.65	163.62	542.67
400	16	8	5.33	8	34.49	0.56626	0.32065	5.32	136.14	544.56
331	19	9.5	6.33	9	38.26	0.61923	0.38344	6.36	124.49	542.64
422	24	12	8	11	44.04	0.69516	0.48325	8.00	110.89	543.25
511/333	27	13.5	9	12	47.60	0.73846	0.54532	9.05	104.39	542.43
440	32	16	10.67	13	53.42	0.80303	0.64485	10.70	96.00	543.06
531	35	17.5	11.67	14	57.15	0.84001	0.70576	11.71	91.76	542.86

Table 4: Evaluation of the K β lines of silicon

A	B	C	D	E	F	G	H	I	J	K
hkl	$h^2 + k^2 + l^2$	$\frac{h^2+k^2+l^2}{(h^2+k^2+l^2)_{011}}$	$\frac{h^2+k^2+l^2}{(h^2+k^2+l^2)_{111}}$	Reflex no.	$\vartheta / ^\circ$	$\sin \vartheta$	$\sin^2 \vartheta$	$\frac{\sin^2 \vartheta(n)}{\sin^2 \vartheta(2)}$	d/pm	α/pm
111	3	1.5	1	1	12.83	0.22206	0.04931	1	313.48	542.96
220	8	4	2.67	3	21.34	0.36390	0.13242	2.69	191.29	541.05
311	11	5.5	3.67	5	25.11	0.42436	0.18001	3.65	164.04	544.06
400	16	8	5.33	7	30.71	0.51069	0.26081	5.29	136.30	545.20
511/333	27	13.5	9	10	41.78	0.66627	0.44392	9.00	104.48	542.89