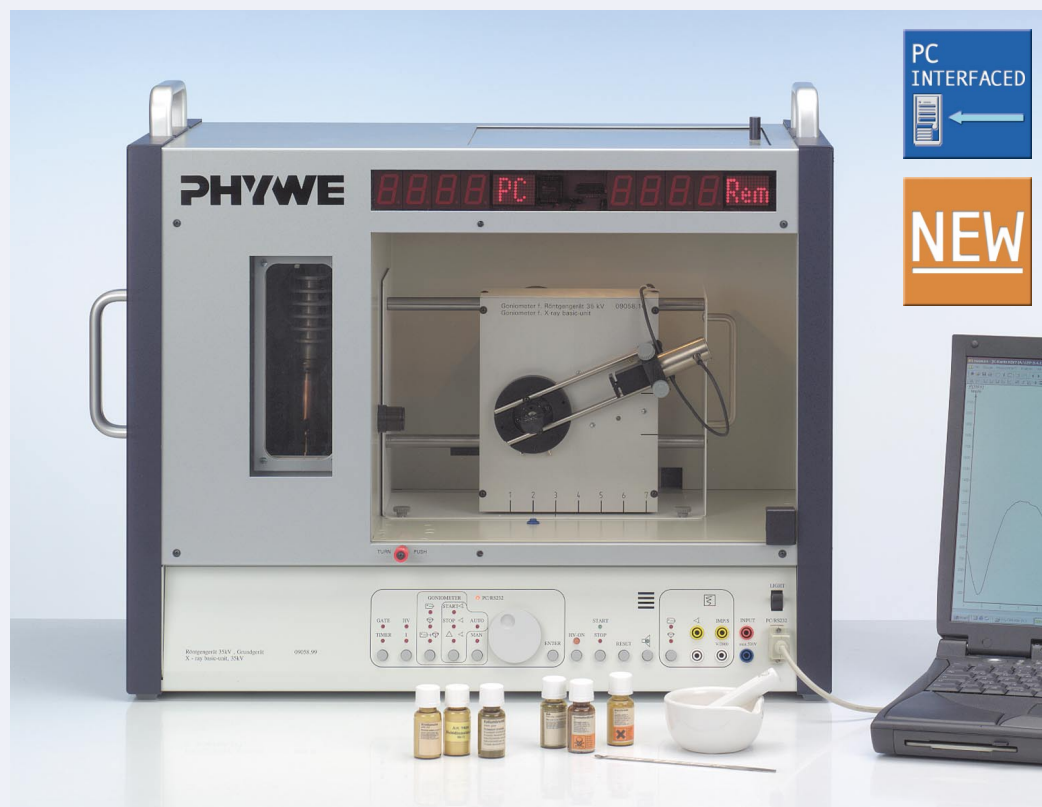


Diffractometric measurements to determine the intensity of Debye-Scherrer reflexes using a cubic lattice powder sample 5.4.26-00



What you can learn about ...

- Wavelength
- Crystal lattices
- Crystal systems
- Bravais-lattice
- Reciprocal lattice
- Miller indices
- Structure factor
- Atomic scattering factor
- Lorentz-polarization factor
- Multiplicity factor
- Debye-Waller factor
- Absorption factor
- Bragg scattering
- Characteristic X-rays
- Monochromatization of X-rays

Principle:

A polycrystalline, cubic face-centered crystallizing powder sample is irradiated with the radiation from a Roentgen tube with a copper anode. A Geiger-Mueller counter tube is automatically swivelled to detect the

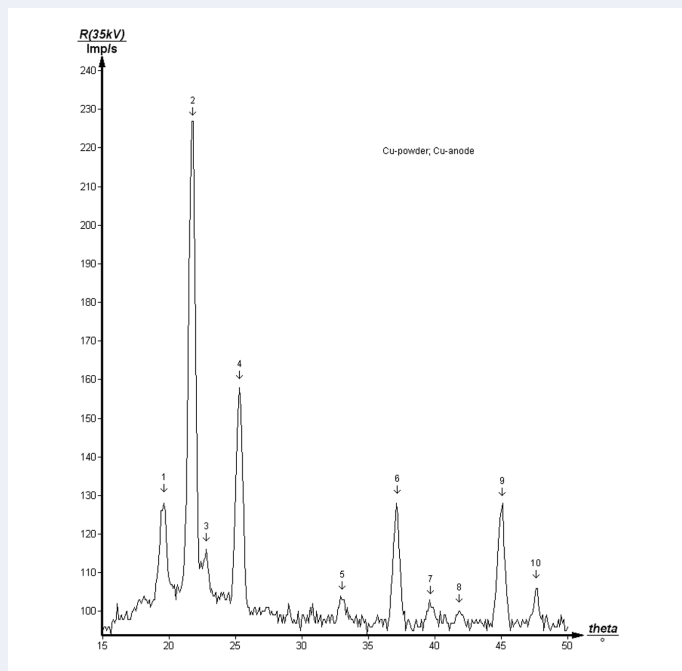
What you need:

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
Micro spoon, special steel	33393.00	1
Vaseline, 100 g	30238.10	1
Copper powder, 50 g	30119.10	1
* Software X-ray unit, 35 kV	14407.61	1
* RS232 data cable	14602.00	1
* PC, Windows® 95 or higher		
* Alternative:		
XYt-recorder	11416.97	1
Connecting cable, $l = 100$ cm, red	07363.01	1
Connecting cable, $l = 100$ cm, blue	07363.04	1

Complete Equipment Set, Manual on CD-ROM included
Diffractometric measurements to determine the intensity of Debye-Scherrer reflexes using a cubic lattice powder sample
P2542600

Tasks:

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



Debye-Scherrer pattern of a copper powder sample.

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.

Related topics

Crystal lattices, crystal systems, Bravais-lattice, reciprocal lattice, Miller indices, structure factor, atomic scattering factor, Lorentz-polarization factor, multiplicity factor, Debye-Waller factor, absorption factor, Bragg scattering, characteristic X-rays, monochromatization of X-rays.

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.

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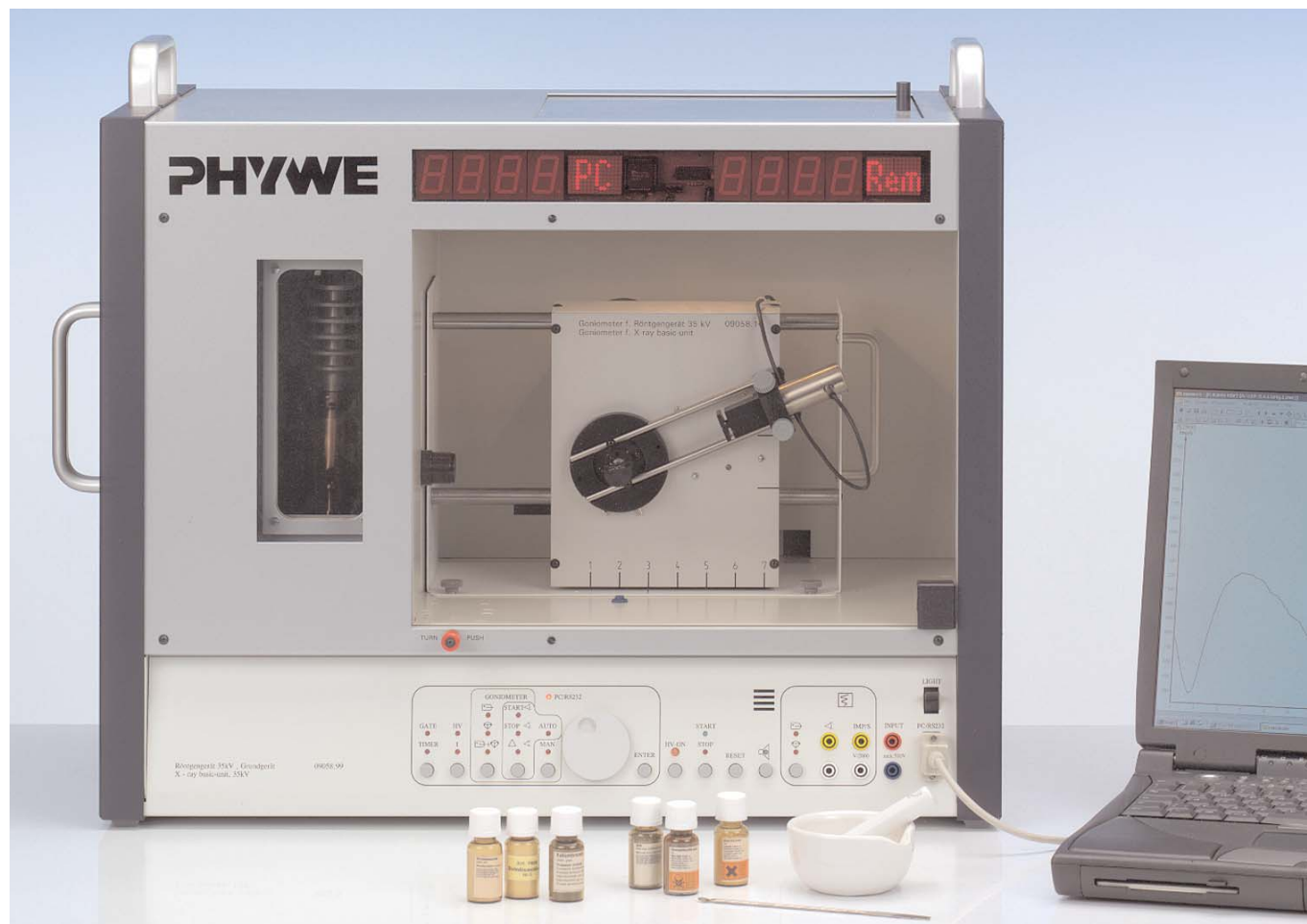
Recording equipment:

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		

Tasks

1. Record the intensity of the Cu X-rays back scattered by a cubic-crystallizing copper powder sample as a function of the 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.

Fig. 1: Experimental set-up



Set-up and Procedure**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.

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 with the line marking at position 7. 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 reflexes 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 carrying out the following procedure stepwise: In the coupled 2:1 mode, set the LiF single-crystal at an angle of $\vartheta = 22.5^\circ$. 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° . Should the capacity of the rate-meter be exceeded during the search for the maximum intensity of the LiF (200) reflex, then correspondingly reduce the anode current. When the calibration has been completed, again work with $i_a = 1$ mA.

Further settings:

Scanning range: see the Figure: Stepping 0.1° ; 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 30 s/ $^\circ$ is required for a better signal-noise ratio. For a more exact evaluation, it is additionally recommended that the position of the glancing angle be determined to two decimal places and that the zoom function be used for the region where lines are close together.

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.:

$$2 d \sin \vartheta = \lambda \quad (1)$$

The intensity 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:

$$I \propto P = \frac{1 + \cos^2 2\vartheta}{2} \quad (2)$$

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 lines 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 :

$$L = \frac{1}{4 \sin^2 \vartheta \cos \vartheta} \quad (3)$$

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

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

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

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 the sum of the atomic scattering factors f of the individual N atoms, taking their phases into account.

In general, the following is valid for F :

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

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 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 wave-

length and angle, and is given in Tables as $(\sin\vartheta/\lambda)$ units for each atom. Fig. 2 shows the course of the value of f as a function of $(\sin\vartheta/\lambda)$ units for Cu ($Z = 29$).

In the forward direction ($\vartheta = 0^\circ$), $f = Z$ 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 , $1/2\ 1/2\ 0$, $1/2\ 0\ 1/2$ and $0\ 1/2\ 1/2$. As the Cu lattice only consists of one sort of atom, the following conditions apply for the structure factor according to equation (5):

$$\begin{aligned} |F|^2 &= 16 f^2 \quad \text{with } h\ k\ l \text{ only even or only odd} \\ |F|^2 &= 0 \quad \quad \quad \text{with } h\ k\ l \text{ mixed} \end{aligned} \quad (6)$$

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 $(h\ k\ l)$, 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.

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

$h\ h\ l$	$h\ 0\ l$ $0\ k\ l$ $h\ k\ 0$	$h\ h\ 0$	$h\ h\ h$	$h\ h\ 0$ $0\ k\ 0$ $0\ 0\ l$
24	24	12	8	6

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:

$$I \propto |F|^2 \cdot LP \cdot M = |F|^2 \cdot M \cdot \frac{1 + \cos^2 2\vartheta}{\sin^2\vartheta \cos\vartheta} \quad (7)$$

The determination of the intensity I acc. to equation (7) is in 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 $(h\ k\ l)$ is obtained from the quadratic form:

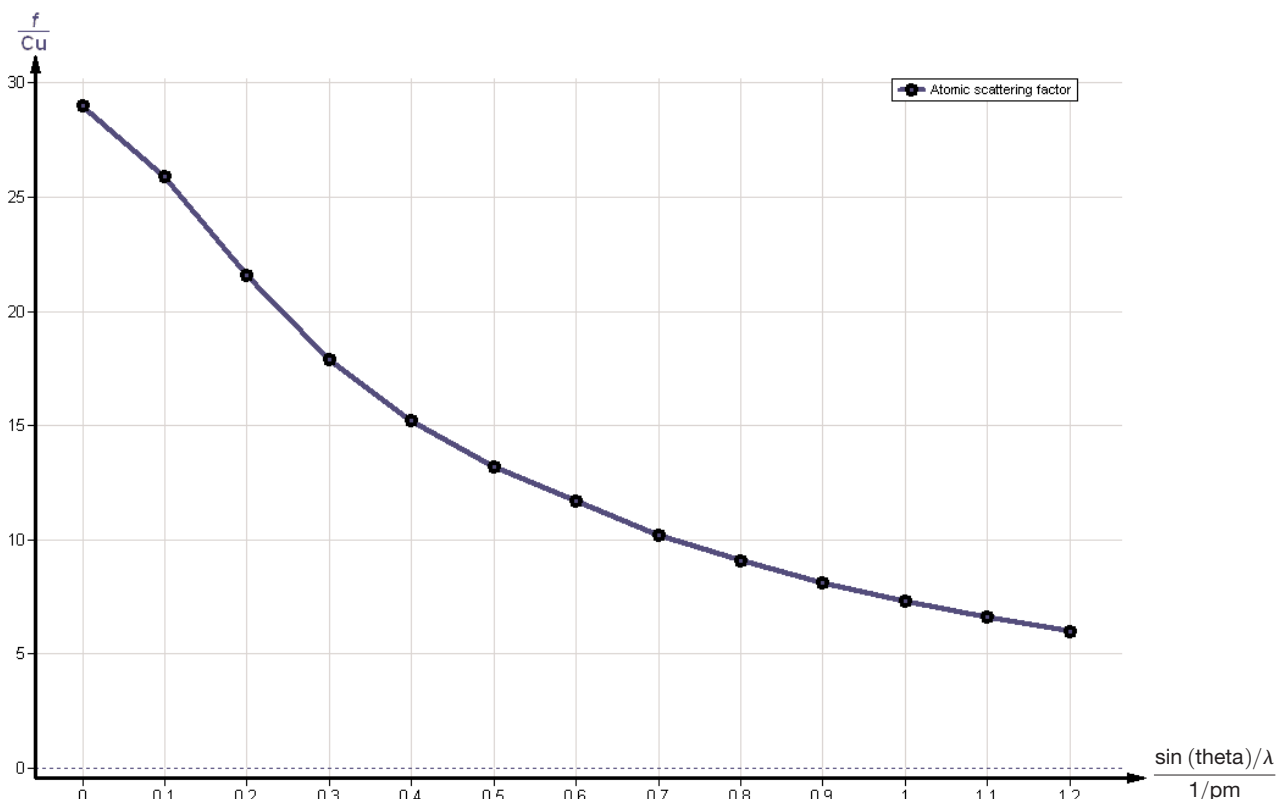
$$\frac{1}{d_{hkl}^2} = \frac{1}{a^2} (h^2 + k^2 + l^2) \quad (a = \text{lattice constant}) \quad (8)$$

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

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

Fig. 3 shows the Debye-Scherrer spectrum of copper (Cu, $Z = 29$).

Fig. 2: Atomic scattering factor f vs $\sin\vartheta/\lambda$



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 $\lambda(K_\alpha) = 154.18 \text{ pm}$ and $\lambda(K_\beta) = 139.22 \text{ pm}$ that:

$$\frac{\lambda(K_\alpha)}{\lambda(K_\beta)} = \frac{\sin\vartheta_\alpha}{\sin\vartheta_\beta} = \frac{154.18 \text{ pm}}{139.22 \text{ pm}} \approx 1.11 \quad (10)$$

Fig. 3: Debye-Scherrer pattern of a copper powder sample.

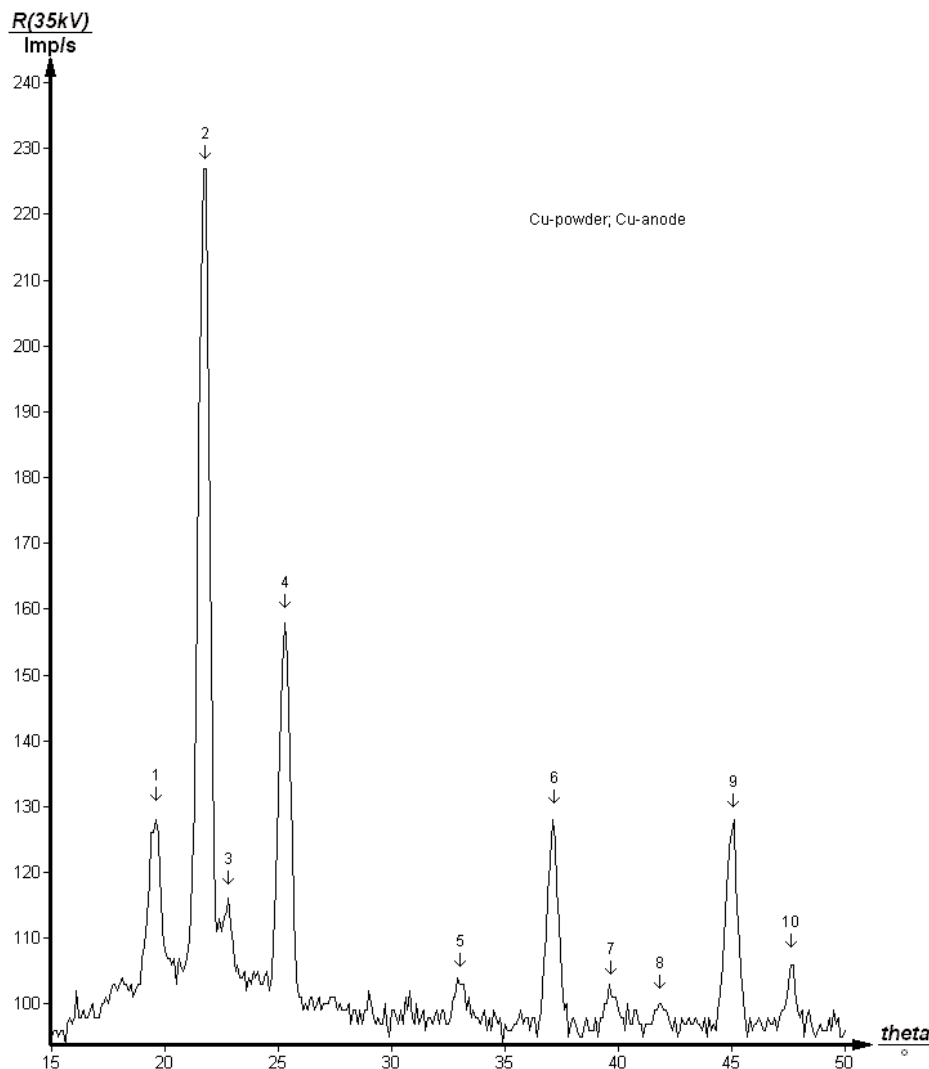


Table 2: Evaluation of the K_α - and K_β Debye-Scherrer lines of Cu.

A	B	C	D	E	F	G	H
Line	$h k l$	$h^2+k^2+l^2$	$\vartheta/^\circ$	$\sin\vartheta$	$\sin^2\vartheta$	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

This value corresponds with the quotients of the $\sin\vartheta$ values (Fig. 3) 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 Cu K_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. 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 this is used.

Table 2 shows the evaluation of the spectrum from Fig. 3.

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* calculated using equation (9).

The mean value of *a* obtained is: $a = (361.04 \pm 0.52)$ pm; $\Delta a/a = \pm 0,15$ %.

(Literature value: $a = 361.52$ pm).

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. 3. Column *D* contains the values calculated for $(\sin\vartheta/\lambda)$ from the Cu K_α - wavelength $\lambda = 154.18$ pm. The individual atomic scattering factors f_{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 arbitrarily 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:

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 integral 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.

Finally, a check is to be made as to whether the unit Cu cell actually does contain 4 atoms as assumed above.

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

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

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.

Entering the appropriate values for Cu ($\rho = 8.92$ g·cm⁻³ and $m_A = 63.546$ g) in equation (11), it follows that $n = 3.98 \approx 4$, i.e. there really are 4 atoms in the unit cell.

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

<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>	<i>E</i>	<i>F</i>	<i>G</i>	<i>H</i>	<i>I</i>	<i>J</i>	<i>K</i>	<i>L</i>
Line	<i>h k l</i>	$\vartheta/^\circ$	$\frac{\sin\vartheta/\lambda}{1/\text{pm}}$	f_{Cu}	F^2	<i>M</i>	$\frac{1 + \cos^2 2\vartheta}{\sin^2 \vartheta \cos \vartheta}$	Intensity Calc. arbitr. units	Relative Intensity Calc.	Intensity Imp/s Experiment	Relative Intensity Experiment
2	1 1 1	21.73	$0.240 \cdot 10^{-2}$	20.4	6658	8	12.0	$6.39 \cdot 10^5$	100	230	100
4	2 0 0	25.29	0.277	19.0	5776	6	8.5	$2.95 \cdot 10^5$	46	155	67
6	2 2 0	37.11	0.391	15.6	3894	12	4.5	$2.10 \cdot 10^5$	33	125	55
9	3 1 1	45.08	0.459	14.2	3226	24	3.7	$2.86 \cdot 10^5$	45	155	67
10	2 2 2	47.65	0.479	13.8	3047	8	2.7	$0.66 \cdot 10^5$	10	70	30

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