Diffractometric Debye–Scherrer patterns of powder samples   5.4.24–00
with a tetragonal lattice structure

PC INTERFACED

NEW
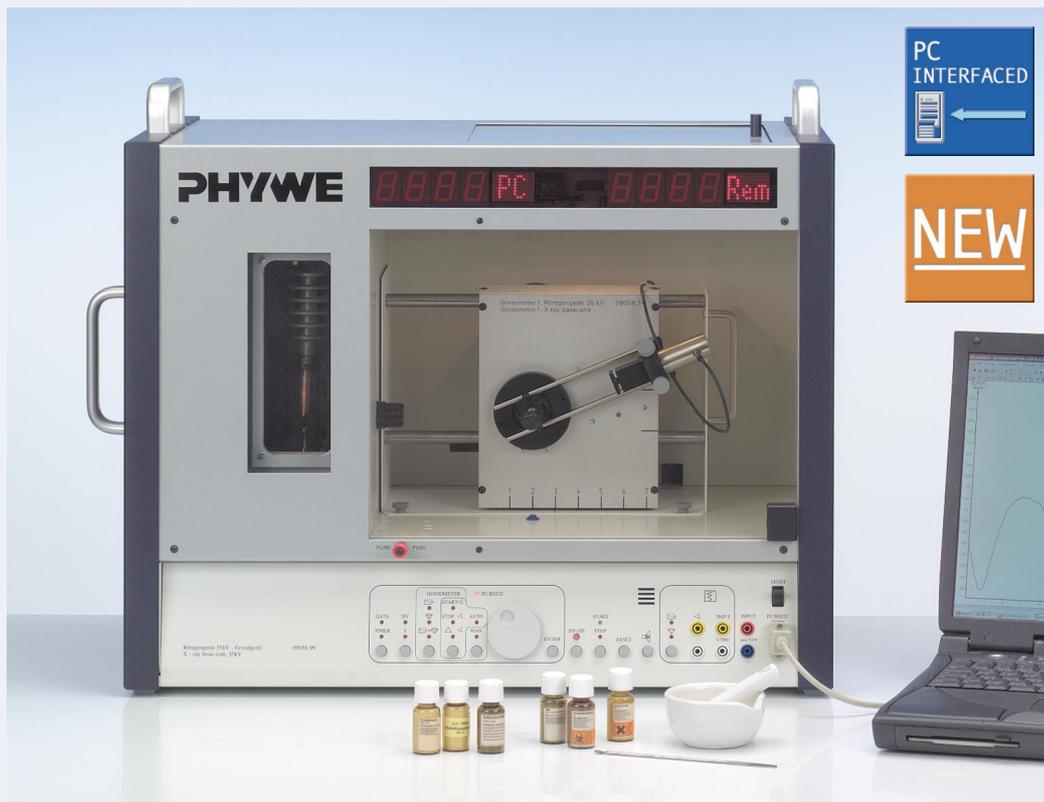
What you can learn about …

➔ **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 lead dioxide 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 individ-

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
Lead dioxide, 100 g	31122.25	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 tetragonal lattice structure   P2542400
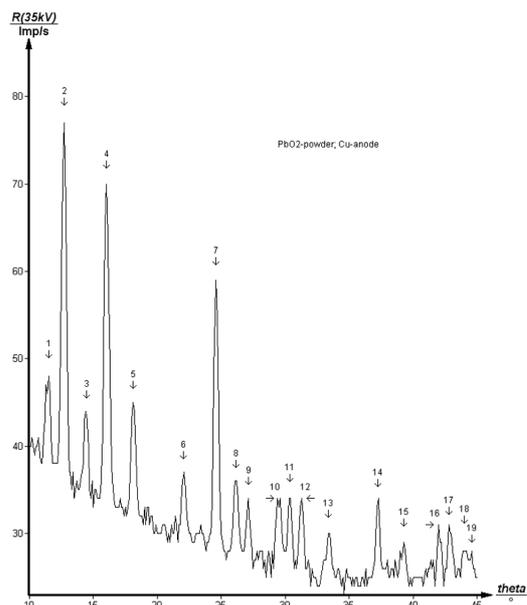
Debye-Scherrer Cu-K_α and Cu-K_β lines of lead dioxide (PbO$_2$).

ual 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 constant of lead dioxide and the number of atoms in the unit cell.

Tasks:

1. Record the intensity of the Cu-X-rays back scattered by a lead dioxide powder sample as a function of the scattering angle.

2. Calculate the lattice constant of the substance from the angular positions of the individual Bragg lines.

3. Assign the Bragg reflexes to the respective planes of the lead dioxide lattice and determine which Bravais lattice type it has.

4. Determine the number of atoms in the unit cell.

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
Transfer a little of the lead dioxide powder onto a sheet of paper, add a little vaseline and use a spatula to knead the mix-

Fig. 1: Experimental set-up
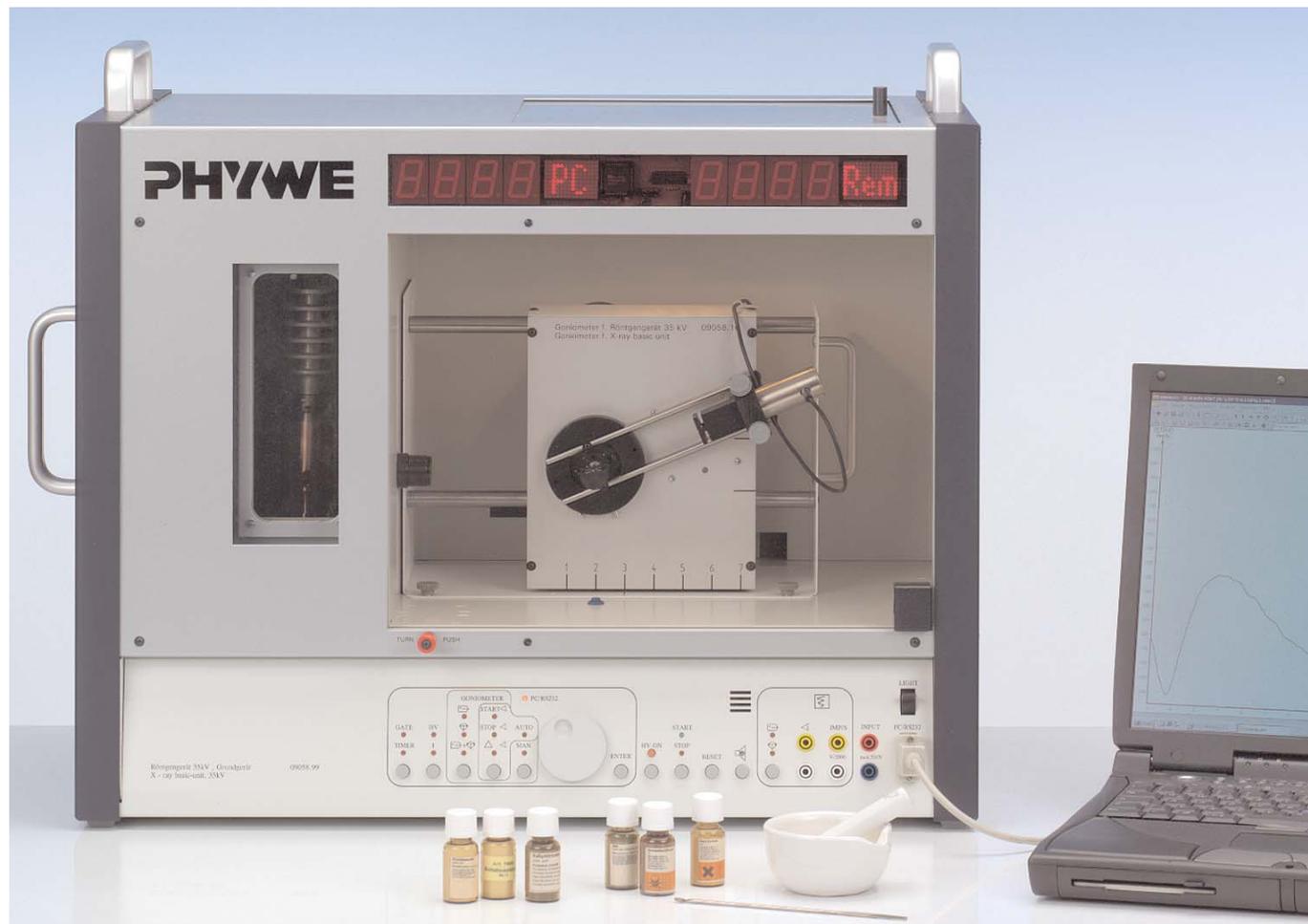
ture to a firm paste. To achieve the highest concentration of material as possible, use very little vaseline (a spatula tip of it). Fill the relatively solid paste into the specimen for powder samples and smooth it flush. Use the universal crystal holder to hold the specimen.

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 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 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 the 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 re-couple the crystal and counter tube 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. 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 tetragonal system can be simple, i.e. have only one atom at the lattice origin. Further to this, various face-centered variants, or also body-centered unit cells, can occur. Only the latter, which contains two atoms/molecules at the coordinates 0,0,0 and 1/2, 1/2, 1/2, will be considered here. According to equation (2), therefore, the structure factor F for this lattice type is given by:

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

It follows from this that, when $h + k + l = 2n + 1$, then $n = 1, 2, 3, 4..$ (i.e. the sum is odd), so $F = 0$.
If $h + k + l = 2n$ (i.e. the sum is even), however, then $F = 2f$ and $|F_{hkl}|^2 = 4f^2$.

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

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

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

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

Fig. 2 shows the Debye-Scherrer spectrum of a powder sample of lead dioxide (PbO_2).

As no filter is used for the monochromatization of the X-rays in Fig. 2, 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:

$$\frac{\lambda(K_\alpha)}{\lambda(K_\beta)} = \frac{\sin\vartheta_\alpha}{\sin\vartheta_\beta} = \frac{154.18\ \text{pm}}{134.22\ \text{pm}} \approx 1.1 \qquad (6)$$

This value corresponds with the quotients of the $\sin^2$ values (Table 3) of the pairs of lines 2-1, 4-3, 7-6, showing that lines 1, 3 and 6 originate from the Cu K_β radiation.
The correctness of this conclusion can be shown by a control measurement (see Fig. 3) using the diaphragm tube with nickel foil to reduce the intensity of the K_β radiation. The reflexes in Fig. 2 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.
For the evaluation of the spectrum in Fig. 2, equation (5) is rearranged as follows:

$$\sin^2\vartheta = A \cdot (h^2 + k^2) + Bl^2 \quad \text{with} \quad A = \frac{\lambda^2}{4a^2} \quad \text{and} \quad B = \frac{\lambda^2}{4c^2} \qquad (7)$$

The value of A is determined solely by the hk lines. With $l = 0$, it follows from equation (7) that:

$$\sin^2\vartheta = A \cdot (h^2 + k^2) \qquad (8)$$

The possible values for $(h^2 + k^2)$ are 1, 2, 4, 5, 8, 9, 10.....(see Table 1).

Table 1: Possible h, k combinations

$h\ k$	1 0	1 1	2 0	2 1	2 2	3 0	3 1
h^2+k^2	1	2	4	5	8	9	10

On dividing the $\sin^2\vartheta$ values by 2, 4, 5, 8, ... (Table 2) and searching for quotients that are equal to each other, or to a $\sin^2\vartheta$ value, it can be assumed that these belong to the hk lines.

Only the first lines need be examined here, as these always belong to the low indexed lattice planes. The analysis of the values in Table 2 reveals a difficulty. It shows, namely, that two pairs of numbers (in italics and bold face) come into question for further analysis. As the difference between the bold face values is lower, however, these should be used as a basis for further consideration.

On calculating the mean value of the bold face values of lines 2 and 5, $A = 0.024145$ is obtained.

Fig. 2: Debye-Scherrer Cu-K_α and Cu-K_β–lines of lead dioxide (PbO$_2$)
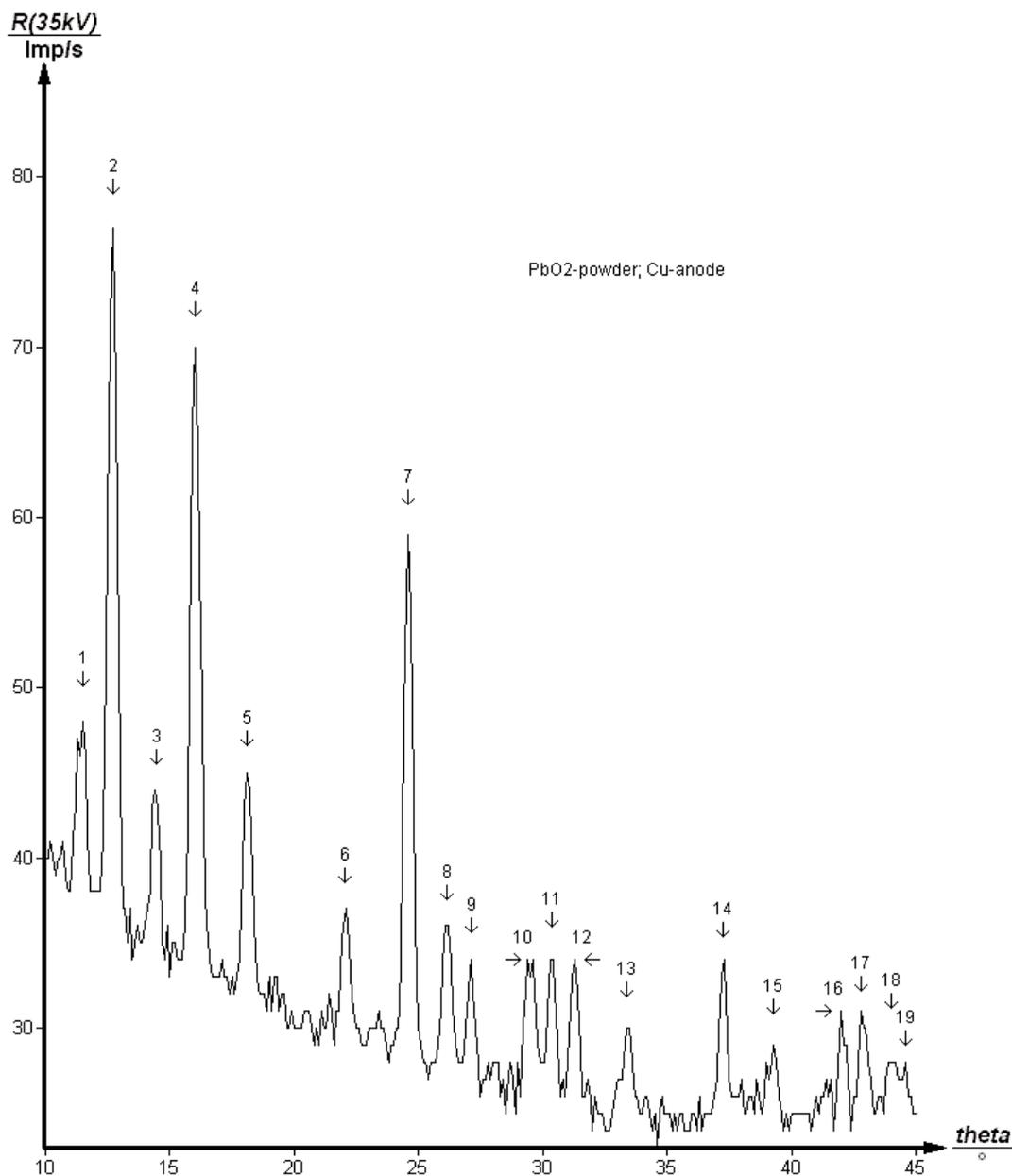
Using this value for A and λ (K_α) = 154.18 pm, it follows from equation (7) that for the first lattice constant: a = 496.1 pm. Should the assumption that has been made be correct, then line 2 must be given the index 110 and line 5 the index 200.

A, $2A$, $4A$, $5A$, $8A$ etc. is now subtracted from the $\sin^2\vartheta$ values (see Table 3) and a search made for Bl^2 values that are in a ratio to each other of 1, 4, 9, 16 etc..

A first look at Table 3 appears to show that this is fulfilled by the values in italics for the lines 2, 5, 8 and 10.

Because the following is true:

$1/2(0.19424+0.19404) / 1/2(0.04826+0.04857) \approx 4$.

This gives B = 0.048431 and, acc. to equation (6), c = 350.4 pm. With the values so determined for a and c, and using equation (9), the number of atoms in the unit cell is calculated to be $n \approx 2$.

Lines 2 and 5 would have the indices 111 and 201, i.e. odd and mixed indexed reflexes occur. This is in contradiction to the number of atoms/molecules in the unit cell. Two atoms/molecules per unit cell signifies a body-centered lattice, with which the only reflexes that should occur are those for which $h + k + l = 2n$ is valid.

The approach made above must therefore be rejected.

Fig. 3: Debye-Scherrer diagram of PbO_2 only with Cu-K_α beam (a nickel filter was used here)
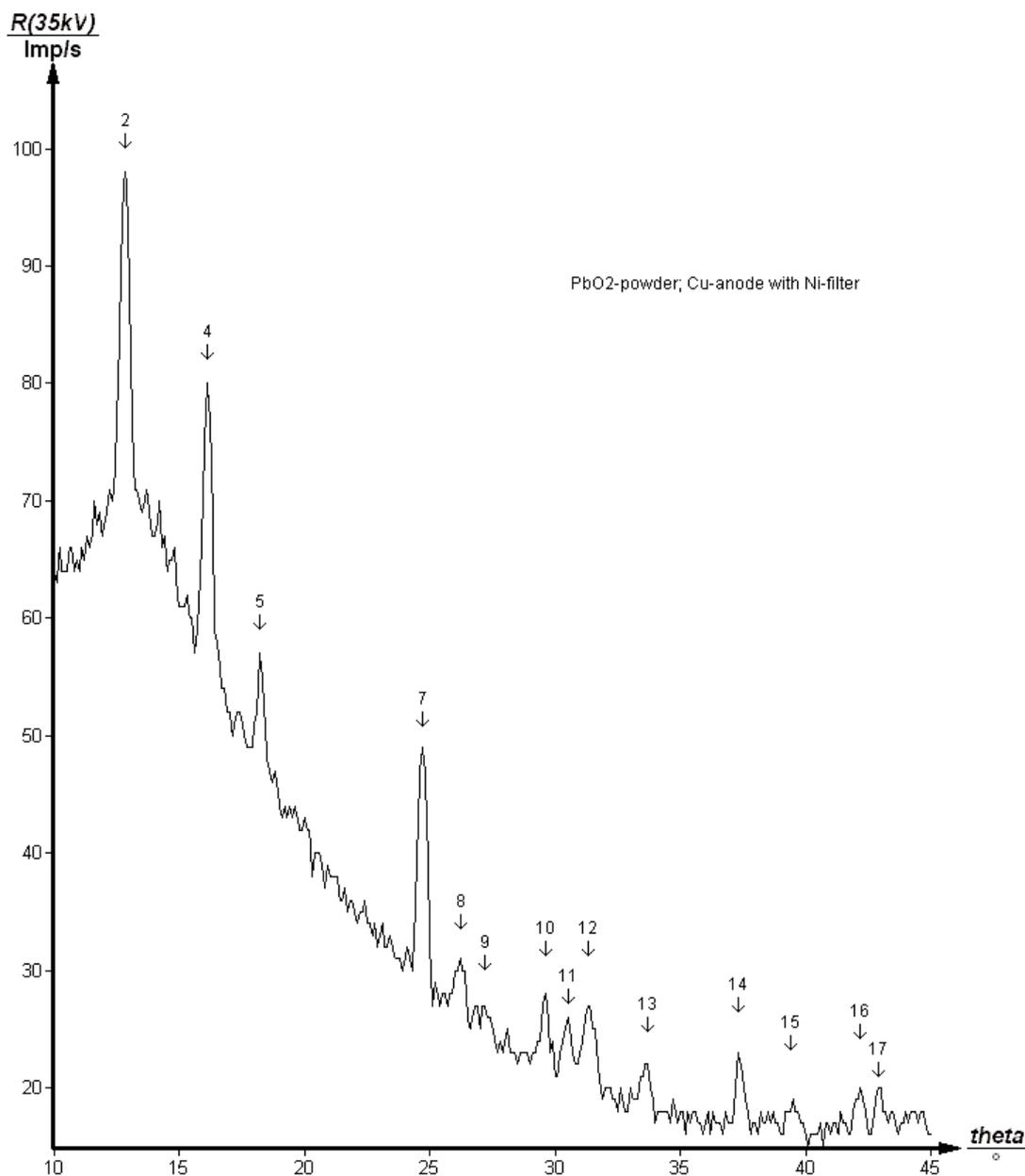
Now taking the bold type values for lines 4, 7, 11, 13 and 15, we obtain:

$\frac{1}{3}$ (0.20717+0.20725+0.20784) / $\frac{1}{2}$(0.05211+0.05243) = 3.97 ≈ 4.

This results in a mean value for
$B = \frac{1}{2}$ (0.05211 + 0.05243) = 0.05227.
With this value for B, we obtain from equation (7): $c = 337.2$ pm. Using this, we obtain the following rounded-off values for lines 4 and 7:
Line 4: $\sin^2\vartheta = 0.07625 \approx A (1^2) + B (1^2) = 0.02414 + 0.05227 = 0.0764 \rightarrow h = 1$ or $k = 1; l = 1$.

This line therefore has the index (101) or (011).
Line 7: $\sin^2\vartheta = 0.17316 \approx A (1^2 + 2^2) + B (1^2) = 0.1207 + 0.05227 = 0.1730 \rightarrow h = 1$ and $k = 2$ or $h = 2$ and $k = 1; l = 1$.
This line therefore has the index (211) or (121).
Correspondingly, we obtain the following h,k,l triplet for lines 11, 13 and 15: 112, 202/022 and 222.
The following procedure is helpful in identifying all of the remaining lines: Table 4 lists the rounded-off $\sin^2$ value for each conceivable h, k and l combination, obtained by multiplying the mean values of $A = \sin^2(100)$ and $B = \sin^2(001)$ by the sum of the squares.

Table 2: Evaluation of the K_α- lines for the determination of lattice constant a

Line	$\vartheta/°$	$\sin\vartheta$	$\sin^2\vartheta$	$\sin^2\vartheta/2$	$\sin^2\vartheta/4$	$\sin^2\vartheta/5$	$\sin^2\vartheta/8$	$h\,k\,l$
2	12.69	0.21968	*0.04826*	**0.02413**	0.01206	0.00965	0.00603	**110**
4	16.01	0.27580	0.07607	0.03803	0.01902	0.01521	0.00951	
5	18.11	0.31084	0.09662	*0.04831*	**0.02416**	0.03462	0.01208	**200**
7	24.59	0.41612	0.17316	0.08658	0.04329	0.03885	0.02165	

Table 3: Evaluation of the K_α- lines for the determination of lattice constant c and assignment of the reflexes to the lattice planes.

Line	$\sin\vartheta$	$\sin^2\vartheta$	$\sin^2\vartheta-A$	$\sin^2\vartheta-2A$	$\sin^2\vartheta-4A$	$\sin^2\vartheta-5A$	$\sin^2\vartheta-8A$	$h\,k\,l$	$\sin^2\boldsymbol{\vartheta}$	Δ
1(β)	11.44									
2	12.69	*0.04826*	0.02412					**110**	0.04829	0.00030
3(β)	14.41									
4	16.03	0.07625	**0.05211**					**101/011**	0.07641	0.00016
5	18.13	0.09683	0.07268	*0.04854*				**200/020**	0.09658	-0.00025
6(β)	22.07									
7	24.59	0.17316	0.14902	0.12487	0.07658	**0.05243**		**211/121**	0.17300	-0.00016
8	26.15	*0.19424*	0.17001	0.14595	0.09766	0.07252		**220**	0.19316	-0.00108
9	27.12	0.20780	0.17437	0.15022	0.10193	0.07778		**002**	0.20908	0.00128
10	29.49	0.24233	0.21819	*0.19404*	0.14575	0.12161	0.04917	**310/130**	0.24145	-0.00088
11	30.36	0.25546	0.23132	**0.20717**	0.15888	0.13444	0.06230	**112**	0.25737	0.00191
12	31.29	0.26975	0.24561	0.22146	0.17317	0.14093	0.07659	**301/031**	0.26958	-0.00017
13	33.45	0.30383	0.27968	0.25554	**0.20725**	0.18311	0.11003	**202/022**	0.30566	0.00183
14	37.27	0.36672	0.34256	0.31843	0.27014	0.24599	0.17356	**321/231**	0.36615	-0.00057
15	39.29	0.40100	0.37686	0.35271	0.30442	0.28027	**0.20784**	**222**	0.40224	0.00124
16	42.09	0.44493	0.42515	0.40101	0.35272	0.32858	0.24984	**312/132**	0.45053	0.00560
17	42.89	0.46321	043906	0.41492	0.36663	0.34248	0.27005	**411/141**	0.46273	-0.00048
18	44.06	0.48360	0.45946	0.43531	0.38702	0.36289	0.29044	**420/240**	0.48290	-0.00070
19	44.60	0.49302	0.46888	0.44473	0.39644	0.37230	0.29986	**310/130**	0.49457	0.00155

Table 4: Rounded-off $\sin^2$ values for PbO_2

$h\,k\,0$	h^2+k^2	$\sin\vartheta^2$	$h\,k\,0$	h^2+k^2	$\sin^2\vartheta$	$0\,0\,l$	l^2	$\sin^2\vartheta$
1 0 0	1	0.02414	3 2 0	13	0.31388	0 0 1	1	0.05227
1 1 0	2	0.04829	4 0 0	16	0.38632	0 0 2	4	0.20908
2 0 0	4	0.09658	4 1 0	17	0.41046	0 0 3	9	0.47043
2 1 0	5	0.12073	3 3 0	18	0.43461			
2 2 0	8	0.19316	3 3 1	19	0.45876			
3 0 0	9	0.21731	4 2 0	20	0.48290			
3 1 0	10	0.24145						

To obtain the $\sin^2$ value for the 231 reflex, for example, add the corresponding $\sin^2$ values for reflexes 230 and 001.

$\sin^2\vartheta$ (230)	0.31395
$\sin^2\vartheta$ (001)	0.05218
$\sin^2\vartheta$ (231)	0.36613

The $\sin^2\vartheta$ values, and so the indexes of each reflex line, can be analogously determined, as shown in Table 3. The $\sin^2\vartheta$ values in the next to last column in Table 3 are obtained by combination of the corresponding $\sin^2\vartheta$ values from Table 4. The last column of Table 3 shows the difference between the values in the next to last column and column 4 to illustrate the correctness of the indexing.

The experiment gives values for the two lattice constants of the tetragonal PbO_2 lattice of:

$a = 496.1$ pm and $c = 337.5$ pm

(Literature values for the lattice constants: $a = 495.0$ pm and $c = 336.6$ pm)

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

$$\rho = \frac{M}{V} = n \cdot m \cdot \frac{1}{V}$$

with $\qquad m = \frac{m_A}{N} \rightarrow n = \frac{\rho \cdot N \cdot (a^2 \cdot c)}{m_A}$ $\qquad$ (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 PbO_2, $\rho = 9.375$ g·cm^{-3} and $m_A = 239.19$ g. Using these values and $a = 496.1$ pm and $c = 337.5$ pm in equation (9), $n = 1.96 \approx 2$ is obtained, i.e. there are 2 atoms/molecules in the unit cell of the PbO_2 lattice. This result, and the fact that those reflexes are apparent for which $(h + k + l) = 2n$, shows that PbO_2 forms a body-centered tetragonal lattice.

With 2 atoms/molecules per unit cell, a paired face-centered lattice with unit coordinates 000, 1/21/20 or 000, 01/21/2 or 000, 1/201/2 also comes into question. For this type of lattice, however, the reflection conditions are: $(h +k) = 2n$, $(h +l) = 2n$, $(k +l) = 2n$ (see equation 2).

It follows from this that no mixed indexed $(h +k)$, $(h +l)$ or $(k +l)$ pairs should occur, which is not the case. This possible alternative lattice type can so be disregarded.