# Diffractometric Debye-Scherrer patterns of powder samples with a tetragonal lattice structure (Bragg-Brentano) (Item No.: P2542401)
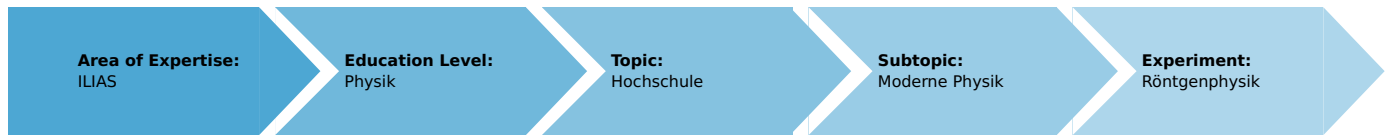
## Curricular Relevance

| Area of Expertise: ILIAS | Education Level: Physik | Topic: Hochschule | Subtopic: Moderne Physik | Experiment: Röntgenphysik |
|---|---|---|---|---|

| Difficulty | Preparation Time | Execution Time | Recommended Group Size |
|---|---|---|---|
| Difficult | 1 Hour | 2 Hours | 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 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 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 constant of lead dioxide and the number of atoms in the unit cell.

Fig. 1: P2542401

## 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 | Lead-IV oxide -lead diox.- 250 g | 31122-25 | 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 |

## 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 constants 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.

# 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.
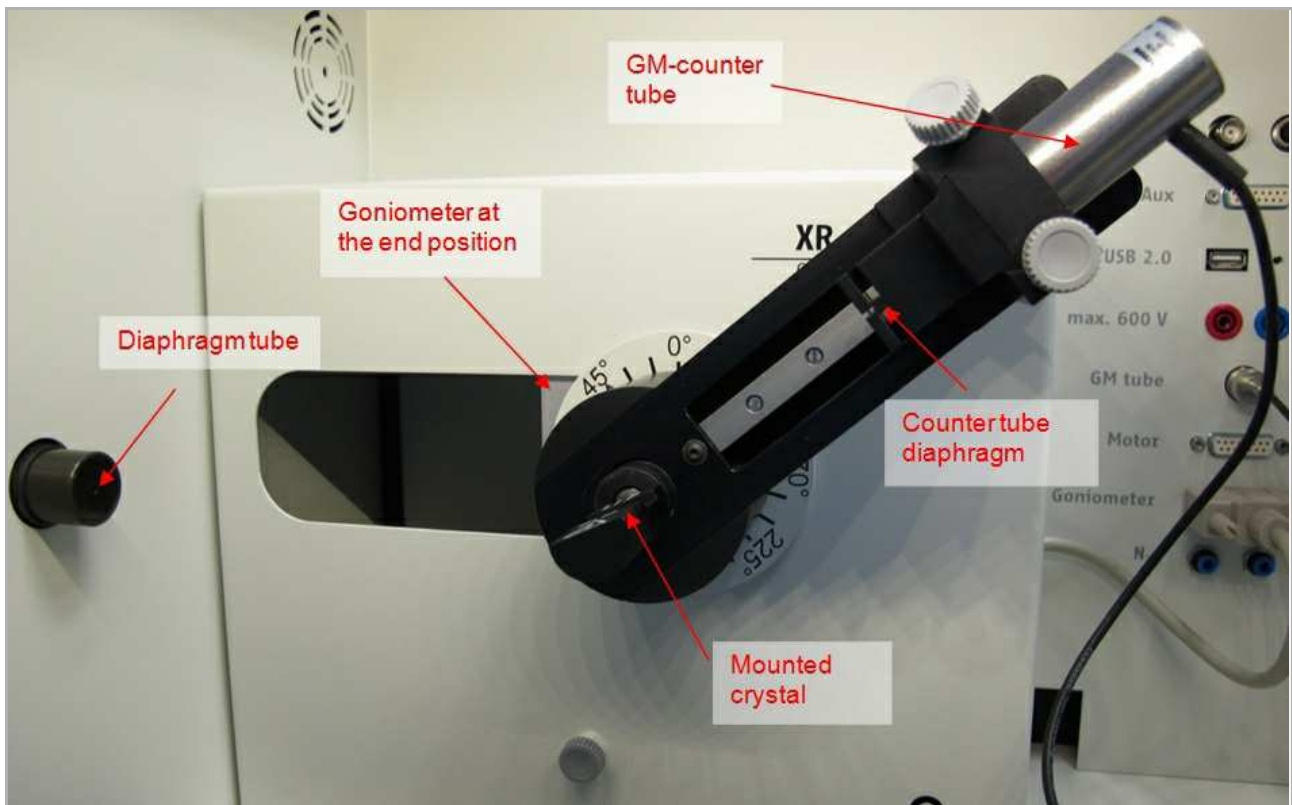


Fig. 2: Connectors in the experiment chamber



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

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- 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:
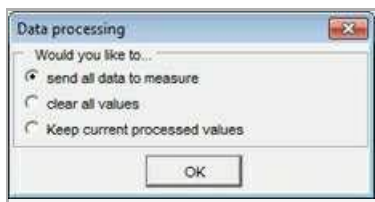
- Select the first item and confirm by clicking OK. The measured values will now be transferred directly to the "measure" software.

- 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° - 45°
- 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/°. For the identification of weaker lines, a scanning speed of at least 40 s/° 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:**

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

**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 $\vartheta$ (counter tube correspondingly to $2\vartheta$). Now search for the intensity maximum of the line by iterative turning of the crystal and counter tube by a few ±1/10° 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 $\lambda$ strike a mass of lattice planes of a crystal of spacing $d$ at a glancing angle of $\vartheta$, then the reflected rays will only be subject to constructive interference when Bragg's condition is fulfilled, i.e.:

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

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 $\left|F_{hkl}\right|^2$.
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 $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$, will be considered here. According to equation (2), therefore, the structure factor $F$ for this lattice type is given by:

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

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 |Fhkl|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:

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

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

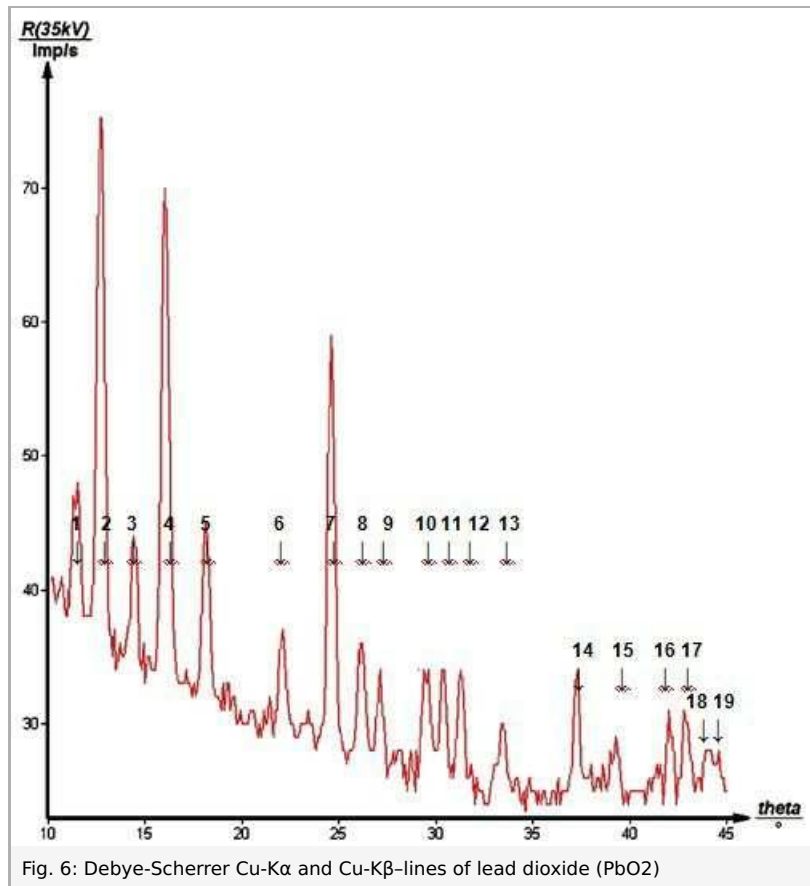$$sin^2\vartheta = \frac{\lambda^2}{4}\left[\frac{(h^2 + k^2)}{\alpha^2} + \frac{l^2}{c^2}\right] \qquad (5)$$

Fig. 6: Debye-Scherrer Cu-Kα and Cu-Kβ–lines of lead dioxide (PbO2)

## Task 1

Fig. 6 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. 6, the fact that the very intense lines resulting from $K_\alpha$-radiation are accompanied by secondary lines resulting from the weaker $K_\beta$ 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:

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

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 $K_\beta$ 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 $K_\beta$ radiation. The reflexes in Fig. 6 that were previously assigned to the $K_\beta$ lines are no longer to be seen. As the intensity of the $K_\alpha$- 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.



Fig. 7: Debye-Scherrer diagram of PbO2 only with Cu-Kα beam (a nickel filter was used here)
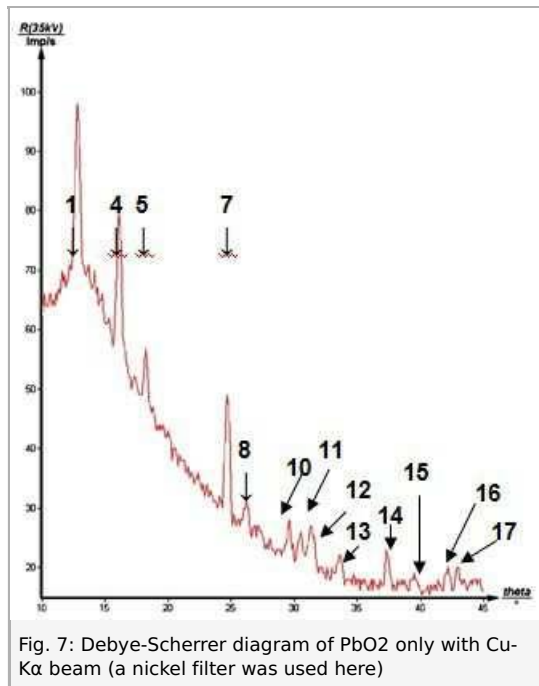
## Task 2 and 3

For the evaluation of the spectrum in Fig. 6, equation (5) is rearranged as follows:

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

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

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

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

| $hk$ | 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.

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

| Line | $\vartheta/°$ | $sin\vartheta$ | $sin^2\vartheta$ | $sin^2\vartheta/2$ | $sin^2\vartheta/4$ | $sin^2\vartheta/5$ | $sin^2\vartheta/8$ | $hkl$ |
|------|------|------|------|------|------|------|------|------|
| 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 | |

Using this value for $A$ and $\lambda(K_\alpha)$ = 154.18 pm, it follows from equation (7) that for the first lattice constant: $\alpha$ = 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. $A$, 2 $A$, $4A$, $5A$, $8A$ 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.

Table 3:Evaluation of the Kα- lines for the determination of lattice constant c and assignment of the re-flexes to the lattice planes.

| Line | $sin\vartheta$ | $sin^2\vartheta$ | $sin^2\vartheta - A$ | $sin^2\vartheta - 2A$ | $sin^2\vartheta - 4A$ | $sin^2\vartheta - 5A$ | $sin^2\vartheta - 8A$ | $hkl$ | $sin^2\vartheta$ | $\Delta$ |
|------|------|------|------|------|------|------|------|------|------|------|
| 1 ($\beta$) | 11,44 | | | | | | | | | |
| 2 | 12,69 | 0,04826 | 0,02412 | | | | | 110 | 0,04829 | 0,00030 |
| 3 ($\beta$) | 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 ($\beta$) | 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 |

Because the following is true:
$\frac{1}{2}$(0.19424+0.19404) / $\frac{1}{2}$(0.04826+0.04857) ≈ 4.
This gives $B$ = 0.048431 and, acc. to equation (6), $c$ = 350.4 pm. With the values so determined for $\alpha$ 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.
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: $sin^2\vartheta = 0.07625 \approx A\left(1^2\right) + B(1^2)$ = 0.02414 + 0.05227 = 0.0764 → $h = 1$ or $k = 1; l = 1$.
This line therefore has the index (101) or (011).
Line 7: $sin^2\vartheta = 0.17316 \approx A\left(1^2 + 2^2\right) + B\left(1^2\right)$ = 0.1207 + 0.05227 = 0.1730 → $h = 1$ 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.

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 Pb$O_2$ lattice of:

$\alpha$ = 496.1 pm and $c$ = 337.5 pm

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

Table 4: Rounded-off sin2 values for PbO2

| $hk\,0$ | $h^2+k^2$ | $sin^2\vartheta$ | $hk\,0$ | $h^2+k^2$ | $sin^2\vartheta$ | $0\,0\,l$ | $l^2$ | $sin^2\vartheta$ |
|---|---|---|---|---|---|---|---|---|
| 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 | | | | | | |

## Task 4

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

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

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 Pb$O_2$, $\rho$ = 9.375 g $\cdot cm^{-3}$ and $m_A$ = 239.19 g. Using these values and $\alpha$ = 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 Pb$O_2$ lattice. This result, and the fact that those reflexes are apparent for which $(h+k+l) = 2n$, shows that Pb$O_2$ 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.

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