5.4.25-00 Diffractometric Debye-Scherrer patterns of powder samples
with a cubic powder sample

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

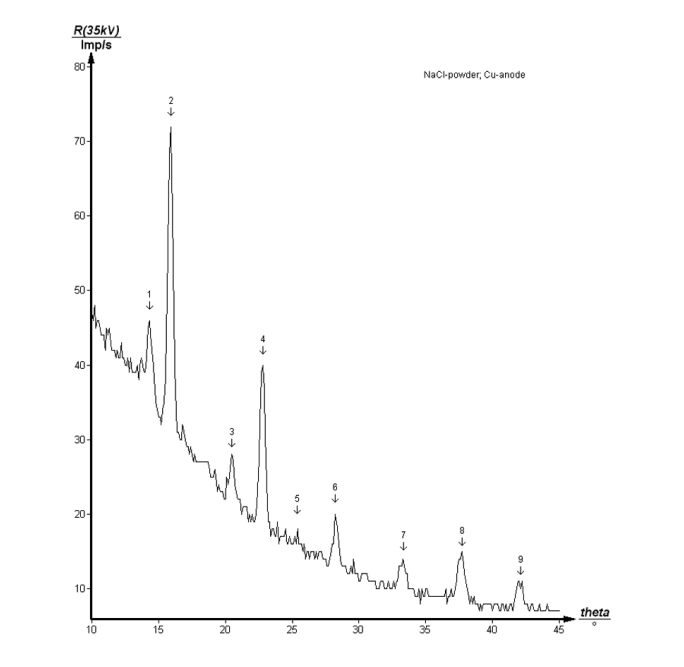
Principle:

A cubic crystalline 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. A graphical evaluation procedure is used to assign the reflexes to the individual lattice planes and to determine the corresponding Bravais lattice type as well as the lattice constant of the substance.

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
Sodium chloride, 250 g	30155.25	1
Micro spoon, special steel	33393.00	1
Vaseline, 100 g	30238.10	1
Mortar and pestle, d = 90 mm	32603.00	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 cubic powder sample P2542500



Bragg-Cu-K_α and Cu-K_β lines of NaCl.

Tasks:

1. Record the intensity of the Cu-X-rays back scattered by a cubic powder sample as a function of the back scattering angle.
2. Assign the Bragg reflexes to the respective lattice planes. Determine which Bravais lattice type it has.
3. Calculate the number of atoms in the unit cell.

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LEP 5.4.25 -00

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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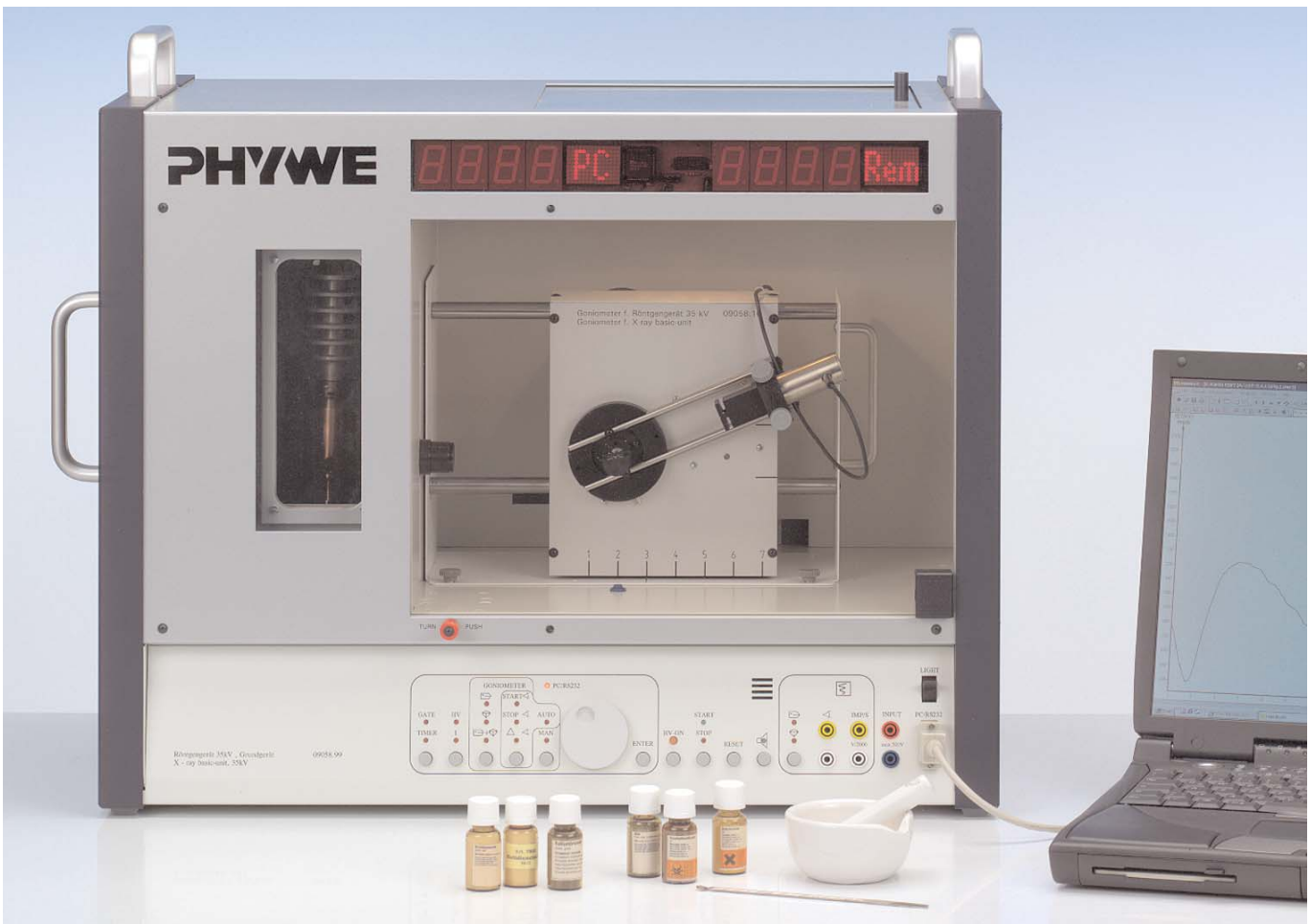
Fig.1: Experimental set-up



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 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 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/°. For the identification of weaker lines, a scanning speed of at least 30 s/° 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.:

$$2\, d \sin \vartheta = \lambda \qquad (1)$$

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 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:

$$F_{hkl} = \sum_{1}^{N} f_n \cdot e^{2\pi i\,(hu_n + kv_n + hw_n)} \qquad (2)$$

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 $|F_{hkl}|^2$.

A cubic simple unit cell contains only one atom with the coordinates 000. From equation (2), therefore, the structure factor for this lattice type is given by:

$$F = f \cdot e^{2\pi i(0)} = f \;;\; |F|^2 = f^2 \qquad (3)$$

This means that F^2 is independent of h, k and l and all Bragg reflexes can occur.

The unit cell of a cubic face-centered lattice has 4 atoms at 000, 1/2 1/2 0, 1/2 0 1/2 and 0 1/2 1/2. The unit cell of a cubic body-centered lattice has in comparison only 2 atoms at 000 and 1/2 1/2 1/2.

Should the lattice only consist of one sort of atom, then the following conditions are given for the structure factor:

fcc Lattice

$|F|^2 = 16\, f^2$ with $h\ k\ l$ only even or only odd

$|F|^2 = 0$ with $h\ k\ l$ mixed

bcc Lattice

$|F|^2 = 4\, f^2$ with $(h + k + l)$ even

$|F|^2 = 0$ with $(h + k + l)$ odd (4)

The situation is a little different when a lattice is constructed of different sorts of atoms.

Should, for example, an fcc lattice contain the atoms A and B, whereby the A atoms are at 000, 1/2 1/2 0, 1/2 0 1/2 and 0 1/2 1/2, and the B atoms at 1/2 1/2 1/2, 0 0 1/2, 0 1/2 0 and 1/2 0 0, then the following conditions are given for structure factor F:

fcc Lattice with atoms A and B:

$|F|^2 = 16\,(f_A + f_B)^2$ with $(h + k + l)$ even

$|F|^2 = 16\,(f_A - f_B)^2$ with $(h + k + l)$ odd (5)

When, in such an fcc lattice, the atomic scattering factor f is almost the same for each sort of atom ($f_A \approx f_B$), then a 111 reflex for example will only occur weakly, if at all.

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:

$$\frac{1}{d_{hkl}^2} = \frac{1}{a^2}\,(h^2 + k^2 + l^2) \quad (a = \text{lattice constant}) \qquad (6)$$

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

$$\sin^2\vartheta = \frac{\lambda^2}{4a^2}(h^2+k^2+l^2) \qquad (7)$$

The following so-called strip-matching procedure can be used to index the individual reflexes of cubic crystals. Take logarithms in equation (7):

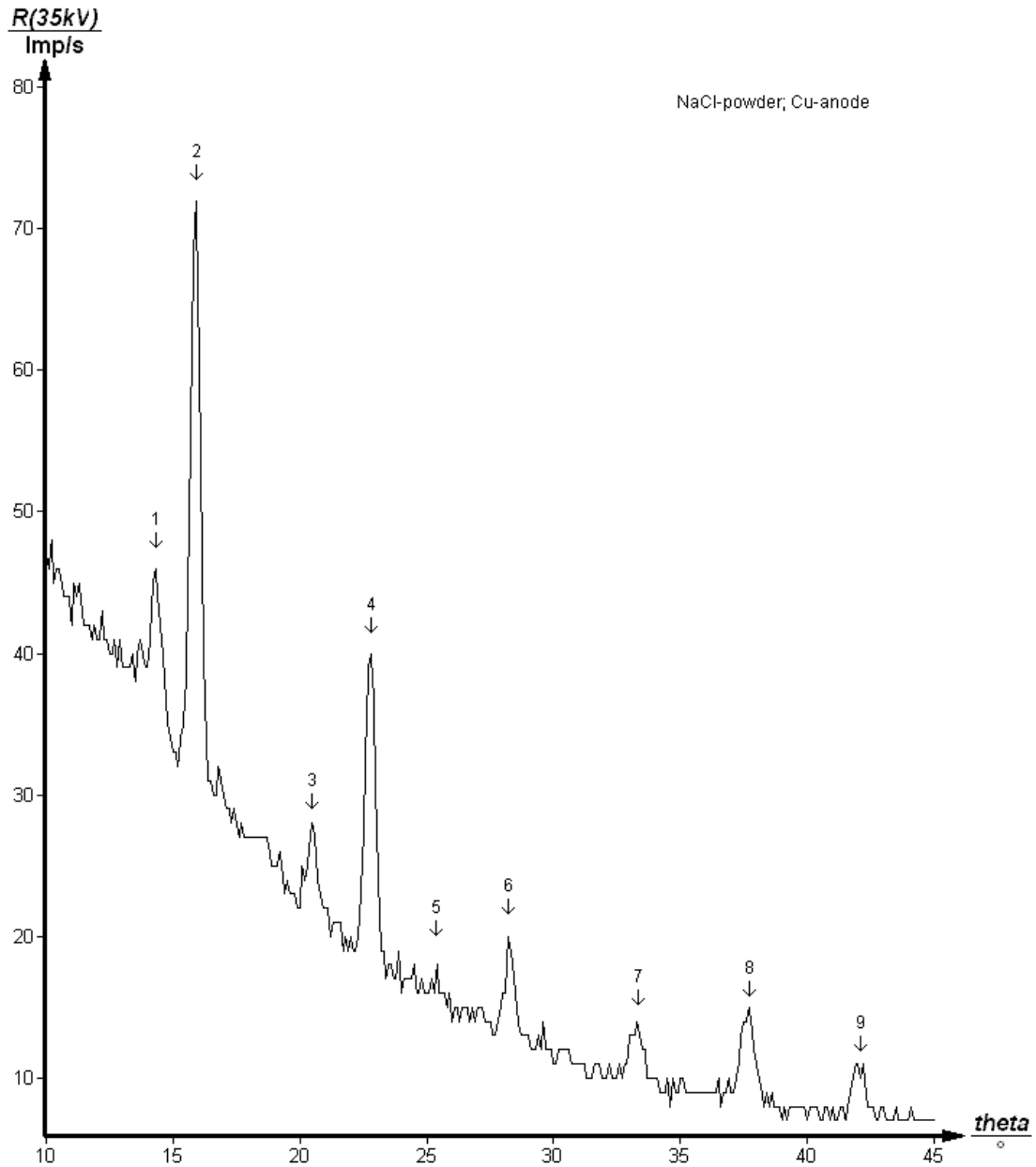
$$\lg a = \lg(\tfrac{1}{2}\lambda) + \lg(\sqrt{h^2+k^2+l^2}) - \lg(\sin\vartheta) \qquad (8)$$

Plot the experimentally determined values for lg (sinϑ) on a strip of paper. In addition, plot the 2nd term on the right hand side of equation (8) on a separate strip of paper, taking all possible index triplets into consideration.

$$\lg(\tfrac{1}{2}\lambda) + \lg(\sqrt{h^2+k^2+l^2}) \qquad (9)$$

Now move the scales against each other until a position is found at which the graduations on the two strips match up to a great extent. The distance between the zero points of the two strips now gives the value of lg(a): Taking anti-logs gives the lattice constant a of the cubic system.
Fig. 2 shows the Debye-Scherrer spectrum of sodium chloride (NaCl).
As no filter is used for the monochromatization of the X-rays, when individual lines are evaluated consideration must be

Fig. 2: Bragg-Cu-K_α and Cu-K_β-lines of NaCl



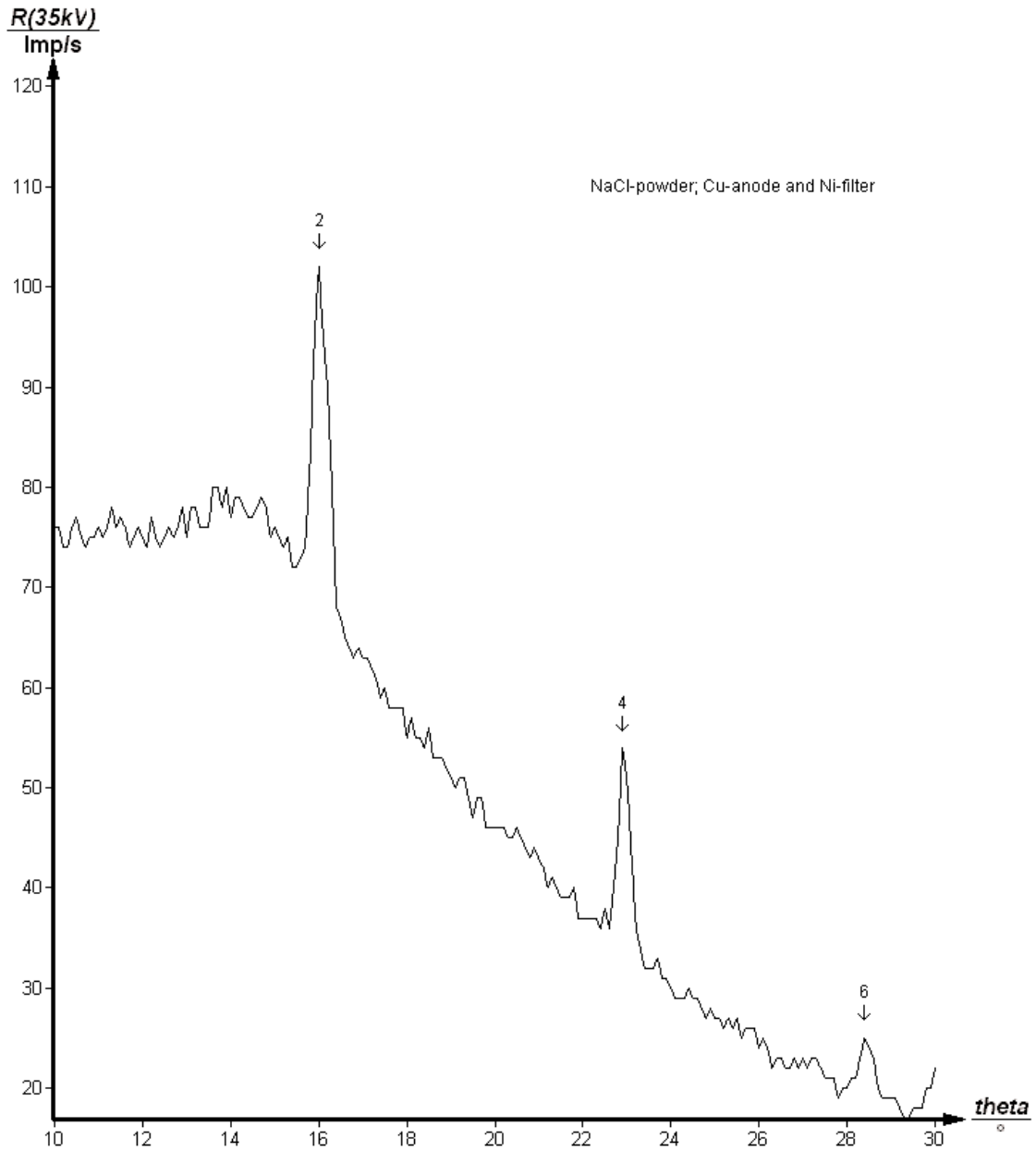
given to the fact that the very intense lines that result from K_α-radiation are accompanied by secondary lines that result from the weaker K_β radiation.
These pairs of lines can be identified by means of equation (1). It is namely approximately true with $\lambda\ (K_\alpha)$ = 154.18 pm and $\lambda\ (K_\beta)$ = 139.22 pm that:

$$\frac{\lambda(K_\alpha)}{\lambda(K_\beta)} = \frac{\sin\vartheta_\alpha}{\sin\vartheta_\beta} = \frac{154.18\ \text{pm}}{139.22\ \text{pm}} \approx 1.1 \qquad (10)$$

These values correspond with the quotients of the $\sin\vartheta$ values (Fig. 2) of the pairs of lines 2-1, 4-3 and 6-5, which shows 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 using the diaphragm tube with nickel foil to reduce the intensity of the K_β radiation (see Fig. 3). The reflexes in Fig. 2 that were previously assigned to the K_β lines have now disappeared. 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 reasons of clarity, it is assumed as a limitation in the following that NaCl does not form a simple unit cell, but rather an fcc or bcc lattice. Table 1 lists all of the possible index triplets possible in this case, i.e only non-mixed h,k,l combinations, or such for which $(h + k + l) = 2n$ is true, were considered. The wavelength $\lambda\ (K_\alpha)$ = 154.18 pm was used to calculate values from equation (9).

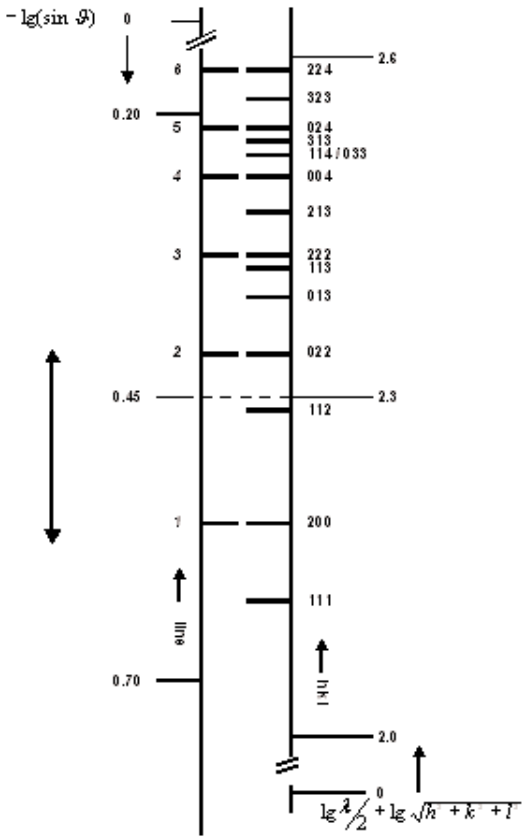
Fig. 3: Bragg-diagram of NaCl only with Cu-K_α beam (a nickel filter was used here)



For the determination of the reflex angle from Fig. 2, zooming on the corresponding angle region and accurate determination of the main part of the line to two decimal places is recommended
Table 2 lists the glancing angles of the K_α- radiation reflexes determined from Fig. 2, as well as the corresponding sin values and lg(sin) values.

To obtain satisfactory accuracy from the graphical evaluation, the two scales should preferably be prepared as shown in Fig.4, equal but expanded.
The coincidence of the two scales shows that no mixed indexed triplets occur, but only even numbered h,k,l values.

Fig. 4: Evaluation of the NaCl reflex lines using the strip-matching procedure



Lattice constant a is determined from the logarithm of the difference in the zero points of the two scales. As Fig. 4 shows, the two sclaes coincide at the values 2.30 and -0.45, i.e. the difference is 2.75. Taking the anti-log of 2.75, a = 562.3 pm is obtained for the lattice constant (literature value; a = 563.0 pm). It can be shown that the unit must be “pm“ by an example, using equation (1) to calculate the lattice plane spacing d of any of the reflexes in Fig. 2.
As only even numbered h,k,l values occur, it would seem that NaCl forms a cubic body-centered crystal lattice with 2 atoms per unit cell. This statement can be checked as follows.
On dividing the total mass M of a unit cell by its volume V, the density ρ is given, so that:

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

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 known values for NaCl (ρ = 2.164 g·cm^{-3} and m_A = 58.44 g) in equation (11), $n = 3.96 \approx 4$ is obtained, i.e. according to this, the unit NaCl cell contains not 2 but 4 atoms. This would mean that NaCl forms an fcc lattice. This contradiction to the above results can be clarified by returning to the considerations made with equation (4).
Considering the fact that the atomic scattering factor f correlates linearly with the number of electrons of an atom, among others, and that Na (Z = 11) and Cl (Z = 17) have nearly the same scattering power, it follows from equation (5) that reflexes with odd numbered h,k,l triplets can only occur very weakly, if at all.
The NaCl results of n = 4 and $(h + k + l) = 2n$ can only be brought into agreement with an fcc lattice type.

Table 2: Glancing angles of the NaCl reflexes from Fig. 2.

Line	ϑ/°	sinϑ	lg (sinϑ)
1	15.89	0.2738	-0.5626
2	22.79	0.3874	-0.4119
3	28.30	0.4741	-0.3241
4	33.25	0.5483	-0.2610
5	37.70	0.6115	-0.2136
6	42.05	0.6698	-0.1741

Table 1: Permissible h,k,l index triplets for fcc and bcc lattices.

$h\ k\ l$	$h^2+k^2+l^2$	$\lg\sqrt{h^2+k^2+l^2} + \lg\frac{1}{2}\lambda$	$h\ k\ l$	$h^2+k^2+l^2$	$\lg\sqrt{h^2+k^2+l^2} + \lg\frac{1}{2}\lambda$
1 1 1	3	2.126	2 1 3	14	2.460
2 0 0	4	2.188	0 0 4	16	2.489
1 1 2	6	2.276	1 1 4/0 3 3	18	2.515
0 2 2	8	2.339	3 1 3	19	2.526
0 1 3	10	2.387	0 2 4	20	2.538
1 1 3	11	2.408	3 2 3	22	2.558
2 2 2	12	2.427	2 2 4	24	2.577