

Diffractionmetric Debye-Scherrer patterns of powder samples with a cubic powder sample (Bragg-Brentano) (Item No.: P2542501)

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

Overview

Short description

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.



Fig. 1: P2542501

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	Sodium chloride 250 g	30155-25	1
9	Microspoon, steel	33393-00	1
10	Vaseline 100 g	30238-10	1
11	Mortar w. pestle, 70ml, porcelain	32603-00	1
12	XR 4.0 Software measure X-ray	14414-61	1
13	Data cable USB, plug type A/B, 1.8 m	14608-00	1
14	XR 4.0 X-ray sample holder for powder samples (diffractometry)	09058-09	1
15	XR 4.0 X-ray Diaphragm tube d = 2 mm	09057-02	1

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.

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

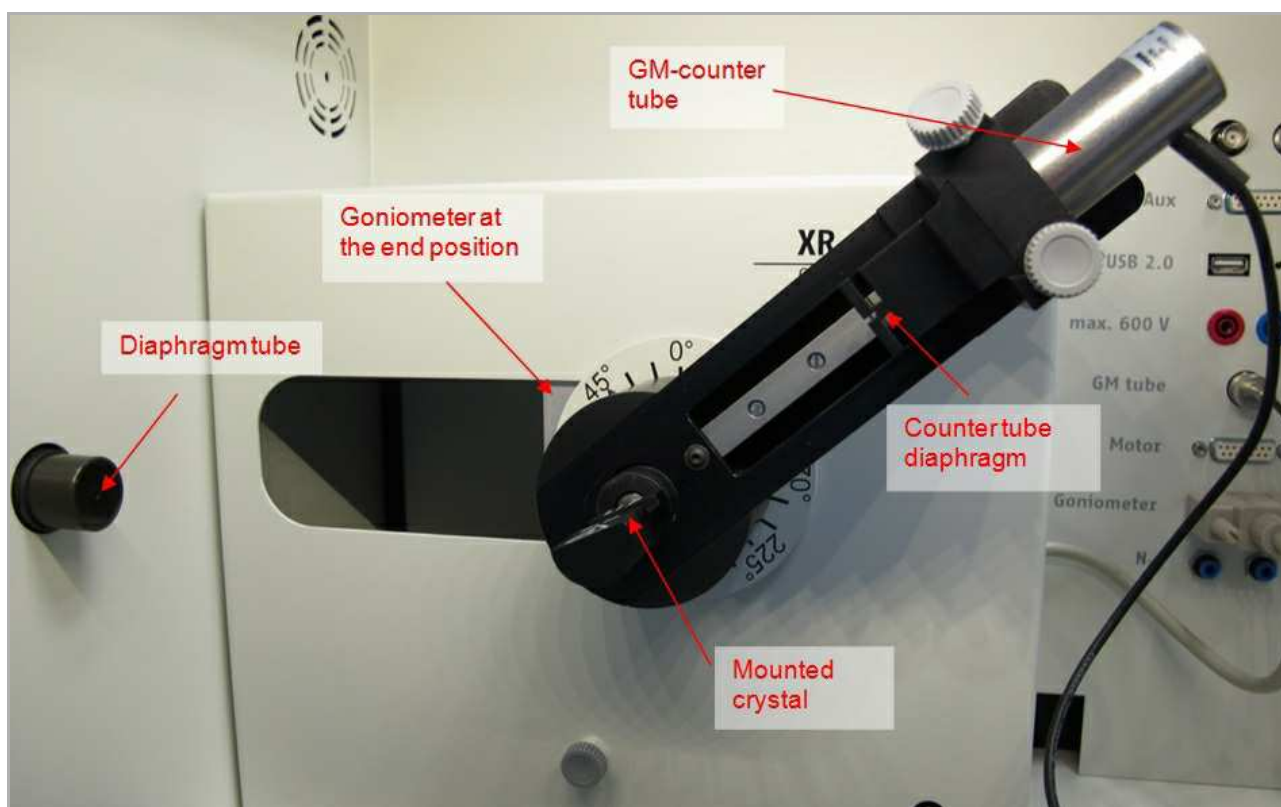


Fig. 3: Set-up of the goniometer

Note

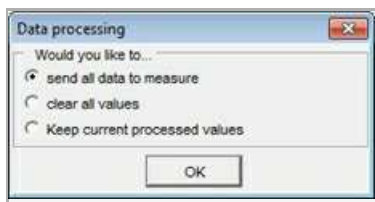
Details concerning the operation of the X-ray unit and goniometer as well as information on how to handle the monocrystals can be found in the respective operating instructions.

Procedure

- 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 $10^\circ - 45^\circ$
- 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 30 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 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 :

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

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:

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

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, $\frac{1}{2}\frac{1}{2}0$, $\frac{1}{2}0\frac{1}{2}$ and $0\frac{1}{2}\frac{1}{2}$. The unit cell of a cubic body-centered lattice has in comparison only 2 atoms at 000 and $\frac{1}{2}\frac{1}{2}\frac{1}{2}$.

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

$$\begin{array}{ll} \text{fcc Lattice} & \\ |F|^2 = 16 f^2 & \text{with } hkl \text{ only even or only odd} \\ |F|^2 = 0 & \text{with } hkl \text{ mixed} \end{array}$$

(4)

$$\begin{array}{ll} \text{bcc Lattice} & \\ |F|^2 = 4 f^2 & \text{with } (h + k + l) \text{ even} \\ |F|^2 = 0 & \text{with } (h + k + l) \text{ odd} \end{array}$$

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, $\frac{1}{2}\frac{1}{2}0$, $\frac{1}{2}0\frac{1}{2}$ and $0\frac{1}{2}\frac{1}{2}$, and the B atoms at $\frac{1}{2}\frac{1}{2}\frac{1}{2}$, $00\frac{1}{2}$, $0\frac{1}{2}0$ and $\frac{1}{2}00$, then the following conditions are given for structure factor F :

$$\begin{array}{ll} \text{fcc Lattice with atoms } A \text{ and } B: & \\ |F|^2 = 16 (f_A + f_B)^2 & \text{with } (h + k + l) \text{ even} \\ |F|^2 = 16 (f_A - f_B)^2 & \text{with } (h + k + l) \text{ odd} \end{array} \quad (5)$$

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 (hkl) is obtained from the quadratic form:

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

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

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

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

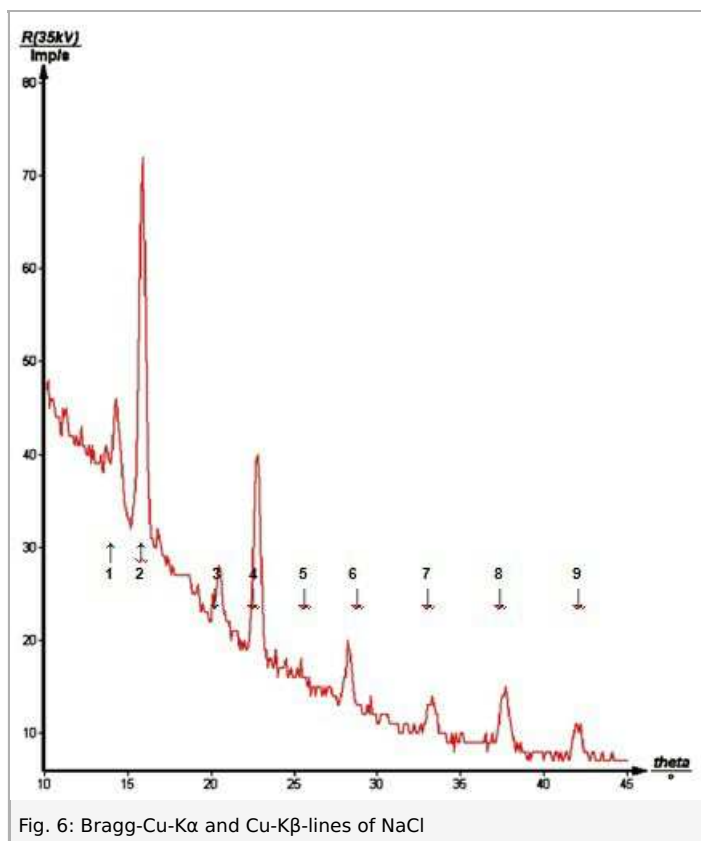
equation (7):

$$1g\alpha = 1g\left(\frac{1}{2}\lambda\right) + 1g\left(\sqrt{h^2 + k^2 + l^2}\right) - 1g(\sin\vartheta) \quad (8)$$

Plot the experimentally determined values for $1g(\sin\vartheta)$ 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.

$$1g = 1g\left(\frac{1}{2}\lambda\right) + 1g\left(\sqrt{h^2 + k^2 + l^2}\right) \quad (9)$$

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 $1g(\alpha)$: Taking anti-logs gives the lattice constant a of the cubic system.



Task 1

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

Fig. 6 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 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 $\lambda(K_\alpha) = 154.18 \text{ pm}$ and $\lambda(K_\beta) = 139.22 \text{ pm}$ that:

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

These values correspond with the quotients of the $\sin \vartheta$ values (Fig. 6) 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. 7). 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.

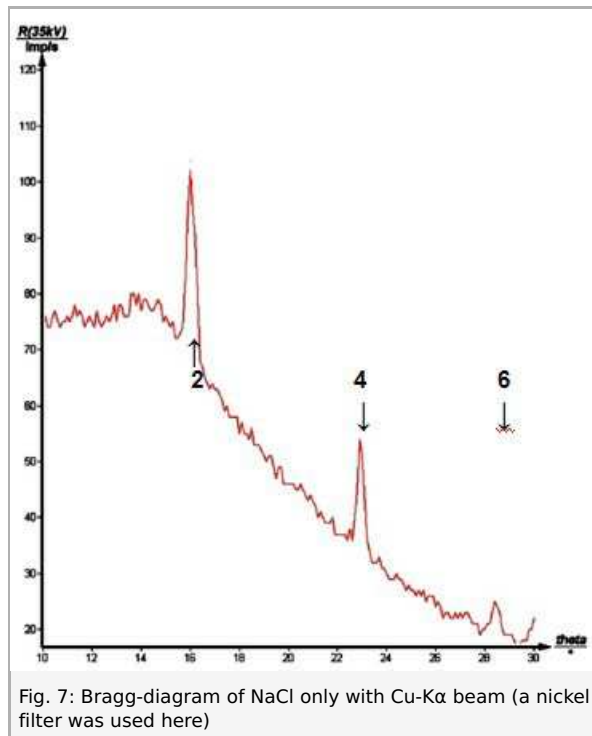


Fig. 7: Bragg-diagram of NaCl only with Cu-K α beam (a nickel filter was used here)

Task 2

Assign the Bragg reflexes to the respective lattice planes. Determine which Bravais lattice type it has.

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 $\lambda(K_\alpha) = 154.18 \text{ pm}$ was used to calculate values from equation (9).

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

hkl	$h^2 + k^2 + l^2$	$1g\sqrt{h^2 + k^2 + l^2} + 1g\frac{1}{2}\lambda$	hkl	$h^2 + k^2 + l^2$	$1g\sqrt{h^2 + k^2 + l^2} + 1g\frac{1}{2}\lambda$
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

For the determination of the reflex angle from Fig. 6, 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. 6, as well as the corresponding sin values and lg(sin) values.

Table 2: Glancing angles of the NaCl reflexes from Fig. 6.

Line	$\vartheta/^\circ$	$\sin\vartheta$	$\lg(\sin\vartheta)$
2	15,89	0,2738	-0,5626
4	22,79	0,3874	-0,4119
6	28,30	0,4741	-0,3241
7	33,25	0,5483	-0,2610
8	37,70	0,6115	-0,2136
9	42,05	0,6698	-0,1741

To obtain satisfactory accuracy from the graphical evaluation, the two scales should preferably be prepared as shown in Fig.8, equal but expanded.

The coincidence of the two scales shows that no mixed indexed triplets occur, but only even numbered h,k,l values.

Lattice constant a is determined from the logarithm of the difference in the zero points of the two scales. As Fig. 8 shows, the two scales coincide at the values 2.30 and -0.45, i.e. the difference is 2.75. Taking the anti-log of 2.75, $\alpha = 562.3$ pm is obtained for the lattice constant (literature value; $\alpha = 563.0$ 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. 6.

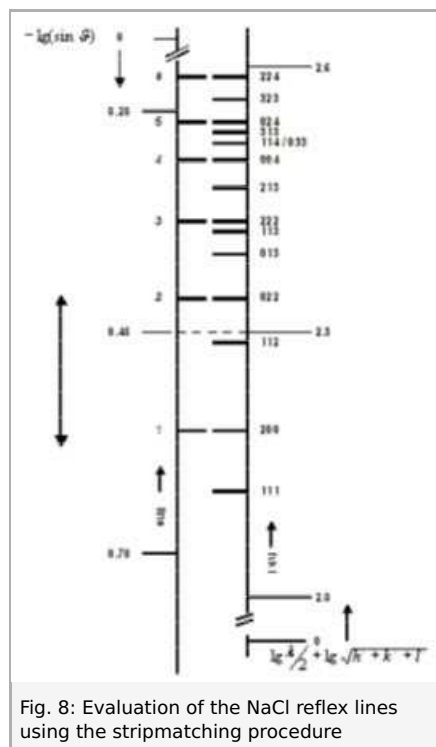


Fig. 8: Evaluation of the NaCl reflex lines using the stripmatching procedure

Task 3

Calculate the number of atoms in the unit cell.

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:

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

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 ($\rho = 2.164 \text{ g} \cdot \text{cm}^{-3}$ and $m_A = 58.44 \text{ g}$) 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.