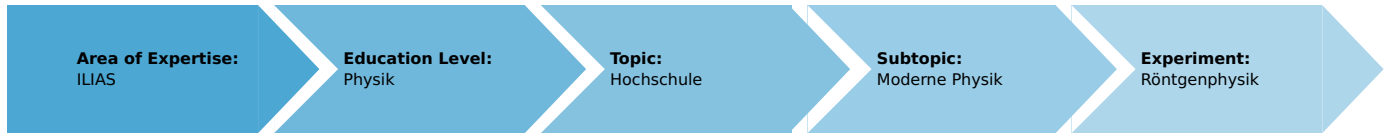# Examination of the structure of NaCl monocrystals with different orientations (Item No.: P2541301)

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:

Characteristic X-radiation, energy levels, crystal structures, reciprocal lattices, Miller indices, atomic form factor, structure factor, Bragg scattering

Overview

Short description

Principle

The spectra of the X-rays that are reflected with various different orientations by NaCl monocrystals are analysed. The associated interplanar spacings are determined based on the Bragg angles of the characteristic lines.

This experiment is included in the "XRS 4.0 X-ray structural analysis".

Fig. 1: P2541301

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 Universal crystal holder for X-ray unit	09058-02	1
6	XR 4.0 X-ray NaCl-monocrystals, set of 3	09058-01	1
7	XR 4.0 Software measure X-ray	14414-61	1
8	Data cable USB, plug type A/B, 1.8 m	14608-00	1
9	XR 4.0 X-ray Diaphragm tube d = 2 mm	09057-02	1

Tasks

1. Determine the intensity of the X-rays that are reflected by the NaCl monocrystals with the orientations [100], [110], and [111] as a function of the Bragg angle.

2. Assign the reflections to the corresponding lattice planes that are given by way of their respective Miller indices.

3. Determine the lattice constant and calculate the interplanar spacing.

4. Determine the mass of a cell and the number of atoms in the 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 (see Fig. 3a).
Insert a diaphragm tube with a diameter of 2 mm into the beam outlet of the tube plug-in unit for the collimation of the X-ray beam.

Fig. 2: Connectors in the experiment chamber

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.

Calibration

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 $\pm 1/10°$ 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".
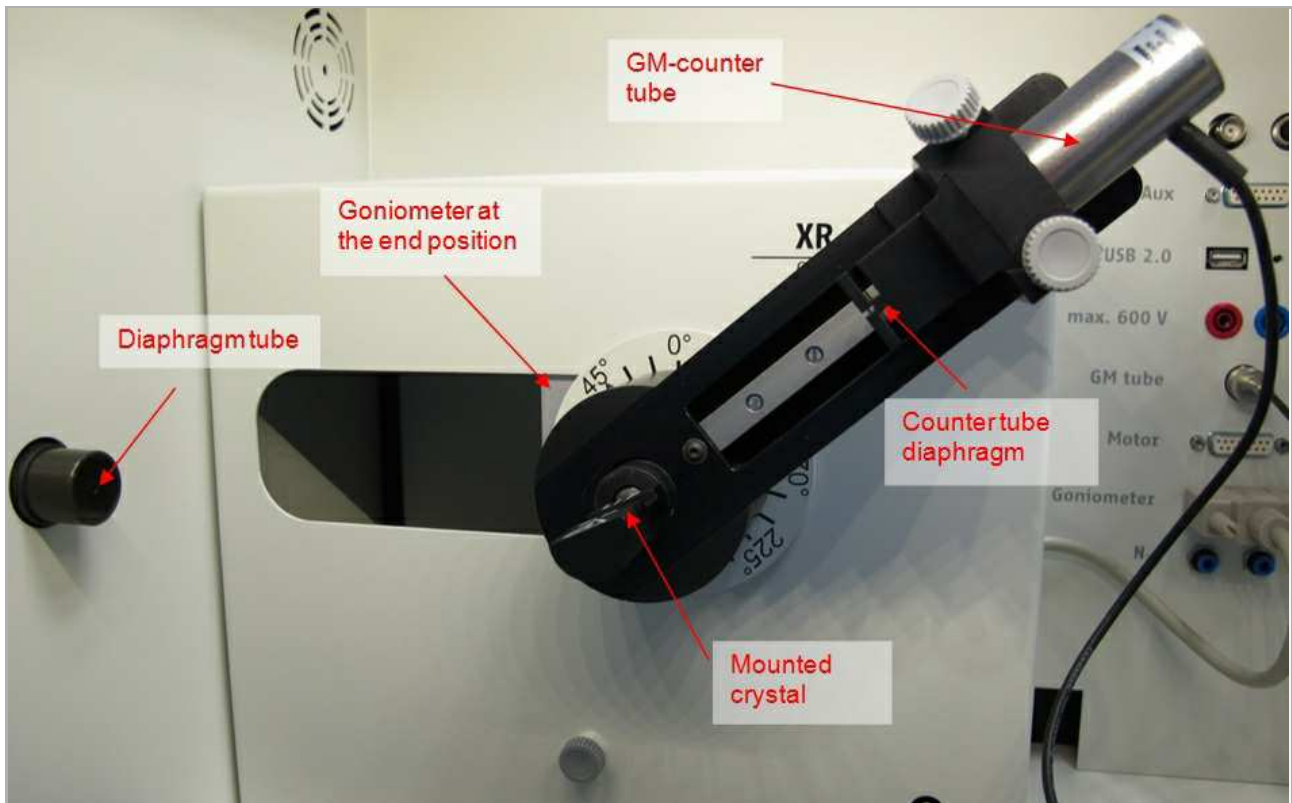
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Fig. 3: NaCl crystal in its holder

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Procedure

- Connect the X-ray unit via the USB cable to the USB port of your computer.

- 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 to change the parameters for the experiment. Select the parameters as shown in Figure 6.

- If you click the X-ray tube, you can change the voltage and current of the X-ray tube. Select the following: anode voltage $U_A = 35kV$; anode current $I_A = 1mA$.

- Mount one of the crystals in the universal crystal holder and attach it to the goniometer (Fig. 3).

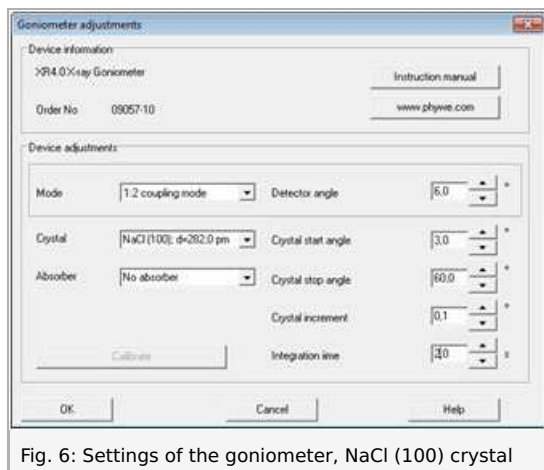- Start the measurement by clicking the red circle:

Fig. 6: Settings of the goniometer, NaCl (100) crystal

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:

- 2:1 coupling mode
- Gate time 2 s; angle step width 0.1°
- Scanning range 3°-60°
- Anode voltage $U_A = 35kV$; anode current $I_A = 1mA$

Note

Never expose the Geiger-Müller counter tube to the primary X-radiation for an extended period of time.

Theory and Evaluation

Theory

If X-rays hit a parallel lattice plane family with the interplanar distance d under the glancing angle ϑ, the radiation will be reflected in a constructive manner provided that the so-called Bragg condition (2) is fulfilled (see Figure 7).

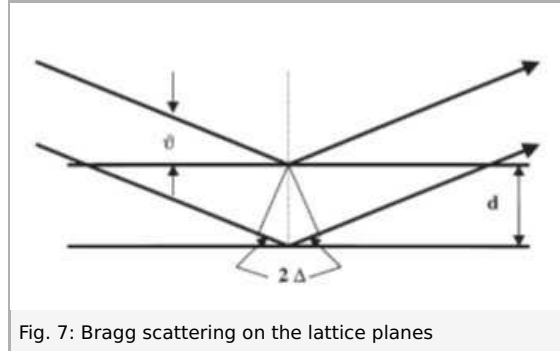$$2dsin\vartheta = n\lambda \ (n = 1, 2, 3,...) \qquad\qquad (1)$$

Fig. 7: Bragg scattering on the lattice planes

In the context of crystal structure analyses, n is often integrated into the distance between the lattice planes.

$$2dsin\vartheta = \lambda \qquad\qquad\qquad (1b)$$

The reflections of the nth order are directly assigned to the diffraction on the various planes.
The Miller indices are a method for naming the various planes in a crystal.
They basically indicate the points of intersection of an imaginary section through the three-dimensional unit cell of the crystal.
The symmetrical fundamental unit of a crystal is the unit cell. In a cubic crystal lattice, like in the case of NaCl, all of the sides of this cell are of the same length. The side length of such a cell is referred to as the lattice constant a.
As shown in Figures 8a to 8c, NaCl monocrystals have a face-centred cubic lattice (fcc). In the primitive cell, an Na+ ion has the coordinates (0,0,0) and a Cl- ion has the coordinates $\left(\frac{12}{,}\frac{1}{2},\frac{1}{2}\right)$. For a cubic crystal with a lattice constant a, the lattice planes that are characterised by the miller indices (h,k,l) have the following interplanar spacing d:

$$d = \frac{a}{\sqrt{h^2+k^2+l^2}} \qquad\qquad (2)$$

Putting (2) into (1b) results in the following connection:

$$sin\vartheta_h kl = \sqrt{h^2 + k^2 + l^2} \cdot \frac{\lambda}{2a} \qquad\qquad (2b)$$
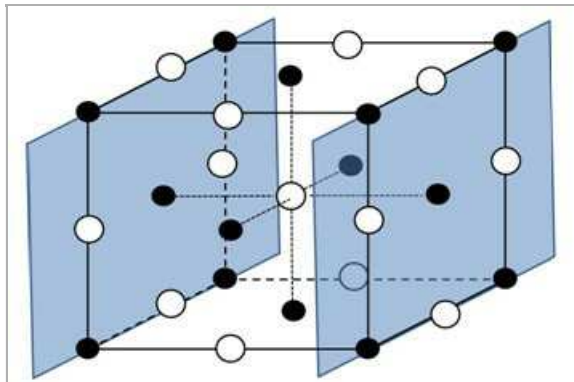
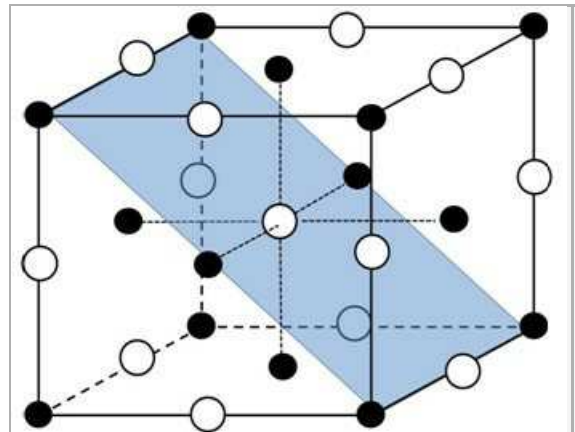Fig. 8a: NaCl crystal with a drawn-in (100) lattice planes

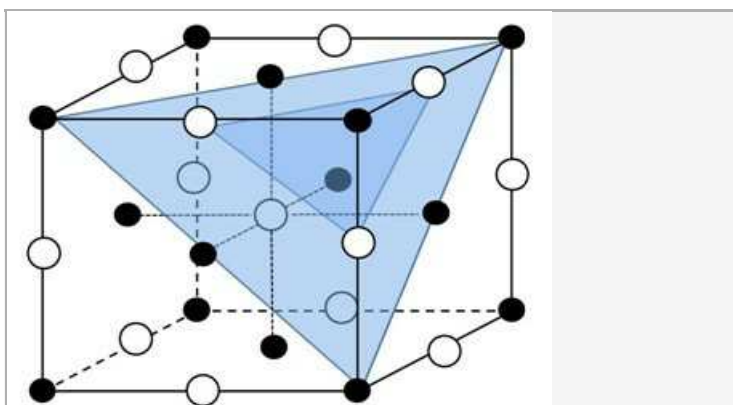Fig. 8b: NaCl crystal with a drawn-in (110) lattice plane

Fig. 8c: NaCl crystal with drawn-in (111) and (222) lattice planes. Na+ ions = ●; Cl- ions = O.

The relative intensity of the reflected radiation is determined by the scattering power and position of the individual atoms in the unit cell of the crystal. It is described by the so-called structure factor $F(h,k,l)$:

$$F(h,k,l) = \sum_n f_n \cdot exp[-2\pi i(hu_n + kv_n + lw_n)] \quad (3)$$

In this equation (3), f_n = the atomic form factor (atomic scattering factor), and $u_n, v_n, and w_n$ = the coordinates of the $n_t h$ atom in the unit cell. The total backscattered beam intensity I is:

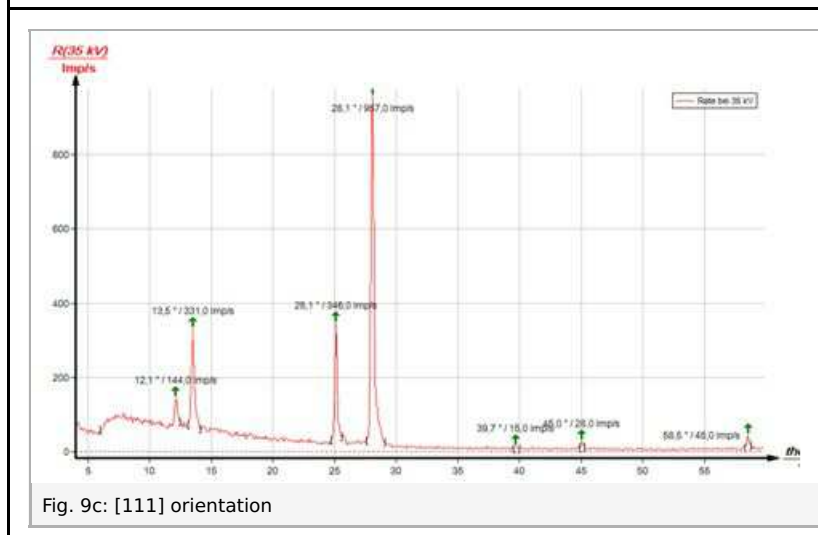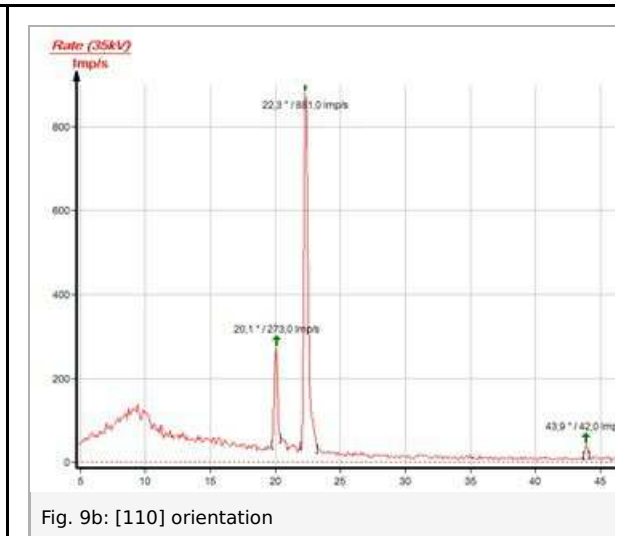$$I = F * F = |F(h,k,l)|^2 \quad\quad\quad (4)$$

With the $000; 0\tfrac{1}{2}\tfrac{1}{2}; \tfrac{1}{2}0\tfrac{1}{2}; and \tfrac{1}{2}\tfrac{1}{2}$ 0 of the basis atoms in the unit cell of an fcc crystal, it follows from (3) that $F = 0$ when the h, k, l triplet contains even and odd numbers, and $F = 4f$ when all of the indices are either even or odd. In addition, in face-centred cubic crystal structures and in the case of the 100 and 110 lattice planes, the reflections of the planes with odd values for $h, k, and l$ are eliminated by systematic extinction. Please refer to the corresponding specialised textbooks.

Task 1

Determine the intensity of the X-rays that are reflected by the NaCl monocrystals with the orientations [100], [110], and [111] as a function of the Bragg angle.

Figure 9a to 9c show the spectra of various NaCl crystals.

Fig. 9a: Intensity of the X-ray spectrum of copper as a function of the glancing angle ϑ: NaCl monocrystals with different orientations as Bragg analysers: [100] crystal orientation

Fig. 9b: [110] orientation

Fig. 9c: [111] orientation
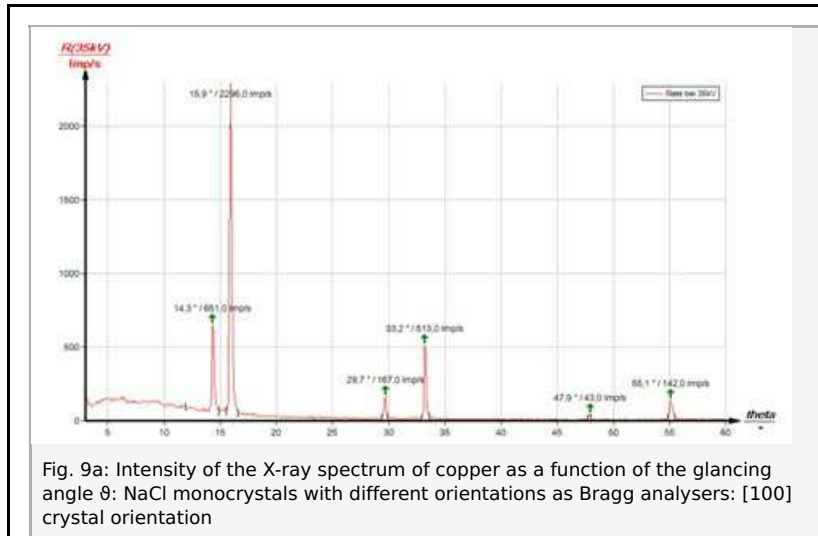
Compared to the other spectra, the spectrum of the [111] crystal (Fig. 9c) shows a noticeable feature. While in the case of the other spectra, the intensity of the characteristic lines is always the highest for the first order ($n = 1$) reflections. This is the case with $n = 2$ in Figure 9c.

In the [111] crystal, the parallel lattice planes are occupied either only by Na+ ions or by Cl- ions. As these two ions have different scattering factors, the intensities also differ from each other. If f_Na and f_Cl are the scattering factors, the following results from (3) for lattice planes with solely odd (h, k, l) indices:

$$F = 4(f_Na + f_Cl) \text{ and } I\infty F^2 = 16(f_Na + f_Cl)^2$$

Accordingly, the following is true for the intensity that is reflected by latticed planes with solely even indices:

$$F = 4(f_Na + f_Cl) \text{ and } I\infty F^2 = 16(f_Na + f_Cl)^2$$

Task 2

Assignment of the Miller indices

In Table 1, the glancing angles ϑ that were determined with the aid of Figures 6a to 6c are assigned to their respective Miller indices. Based on (3), we know that for the 100 and 110 lattice planes only even or only odd values are possible for the h, k, l triplet and that there are in fact no reflections for odd values of $h, k, and\, l$ at 100 and 110. These considerations resulted in the assignments shown in Table 1.

Table 1

(100) crystal				
	15.9	14.3	200	4
	33.2	29.7	400	16
	55.1	47.9	600	36
(110) crystal				
	22.3	20.1	220	8
	50.2	43.9	440	32
(111) crystal				
	13.5	12.1	111	3
	28.1	25.1	222	12
	45.0	39.7	333	27
	-	58.5	444	48

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Task 3

Determine the lattice constant and calculate the interplanar spacing.

If one solves equation (2b) for a, one obtains the lattice constant a for the various reflections based on the hkl triplets that were determined in Task 1 as well as based on the glancing angle ϑ and the wavelength of the characteristic X-radiation of copper ($\lambda K\alpha$ = 154.4 pm; $\lambda K\beta$ = 139.2 pm). Table 2 shows the corresponding values. A comparison of the average value with the literature value of a = 564 pm shows good correspondence.
Equation (2) can now be used to calculate the interplanar spacing for the first plane since the lattice constant a refers to a unit cell with only two planes.
With this value and in accordance with equation (1), the distances between the individual lattice planes are as follows: $d(200)$ = 282.0 pm, $d(220)$ = 201.9 pm, and $d(111)$ = 330.2 pm.
Literature values: $d(200)$ = 282.0 pm, $d(220)$ = 199.4 pm, and $d(111)$ = 325.6 pm.

The very good agreement between the value for the distance between the (100) lattice planes that was determined experimentally and the literature value is due to the fact that ionic crystals can be split very exactly in parallel to this plane. The deviations of the other crystals are due to a slight misorientation.

Table 2

(100) crystal				
K_α	15.9	200	4	567
	33.2	400	16	564
	55.1	600	36	565
K_β	14.3	200	4	564
	29.7	400	16	562
	47.9	600	36	563
			Mean value	564
(110) crystal				
K_α	22.3	220	8	575
	50.2	440	32	568
K_β	20.1	220	8	573
	43.9	440	32	568
			Mean value	571
(111) crystal				
K_α	13.5	111	3	573
	28.1	222	12	586
	45.0	333	27	567
K_β	12.1	111	3	575
	25.1	222	12	568
	39.7	333	27	566
	58.5	444	48	566
			Mean value	572

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Task 4

Determine the mass of a cell and the number of atoms in the cell.

If one calculates the volume of the unit cell of sodium chloride
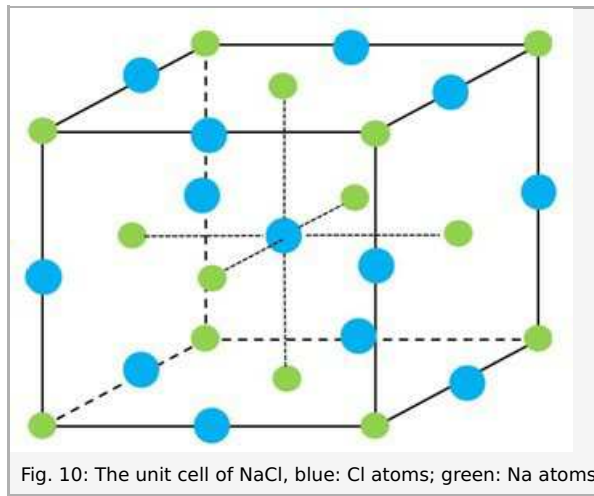
$$a^3 = 1.79 \times 10^{-28} m^3$$

the density of sodium chloride of ρ = 2.163 g/cm^3 leads to the weight of a unit cell as

$$m = \rho.V = 2.163 g/cm^3.1.79 \times 10^{-28} m^3$$
3.87.10^{-25}kg =233u

with the atomic mass unit 1 u = 1.661 . 10^{-27} kg.
Since the number of Na atoms in NaCl equals the number of Cl atoms, the molar masses $M_{(Na)}$ = 22.990g/mol and $M_{(Cl)}$ = 35.453g/mol lead to a number of 3.99 = 4 atoms each in the Bravais lattice, which could also be expected for an fcc lattice based on the following considerations (see also Fig. 10):

Fig. 10: The unit cell of NaCl, blue: Cl atoms; green: Na atoms

Every unit cell includes 4 (green) cations:	
Each of the cations at the 8 corners of the unit cell counts as only $\frac{1}{8}$ to the unit cell since only $\frac{1}{8}$ of the volume actually lies within the unit cell.	8 "corner cations" . $\frac{1}{8}$ = 1 cation
The cations on the surfaces count as only $\frac{1}{2}$:	6 "surface cations" . $\frac{1}{2}$ = 3 cations
	Resulting total number: 4 cations

Every unit cell includes 4 (blue) anions:	
Each of the anions at the 12 edges counts as only $\frac{1}{4}$ to the unit cell:	12 "edge anions" . $\frac{1}{4}$ = 3 anions
The anion in the centre belongs completely to the unit cell:	1 "centre anion" . $\frac{1}{1}$ = 1 anion
	Resulting total number: 4 anions