

# Introduction to X-ray analysis using the diffraction method

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## 1. Introduction

A scientific discipline, which investigates crystal structures by means of the X-ray diffraction method, is called X-ray crystallography or simply crystallography. It originated in a discovery of the phenomena that X-rays are diffracted by crystals, and it has a history of more than one hundred years. Various analytical techniques based on X-ray diffraction have been developed along with the developments of X-ray sources, beam-collimating optics, detectors, mathematical algorithms and computers. X-ray diffraction techniques are used to determine the positions of atoms in a crystal with an accuracy in the order of  $10^{-4}$  nm ( $1 \text{ nm} = 10^{-6} \text{ mm}$ ). They are also used for the identification of crystalline phases of various materials and the quantitative phase analysis subsequent to the identification. X-ray diffraction techniques are superior in elucidating the three-dimensional atomic structure of crystalline solids. The properties and functions of materials largely depend on the crystal structures. X-ray diffraction techniques have, therefore, been widely used as indispensable means in materials research, development and production.

This article has been written for the people who are beginning X-ray analysis of crystalline powder samples using the diffraction method. In X-ray powder diffraction measurements, so-called an X-ray diffraction pattern is recorded, in which many peaks called diffraction lines queue on the abscissa calibrating the diffraction angle. We often hear that it is much more difficult to understand what this diffraction pattern means when the pattern is compared, for examples, with infra-red spectra or the TG-DTA curve in thermal analysis. If we can understand how this diffraction pattern is generated when X-rays irradiate a crystal, it will become much easier to understand the relationship between the X-ray diffraction pattern and the crystal structural information. One purpose of this article is to elucidate the mechanism of X-ray diffraction by the crystal. The knowledge required in reading this article is limited to the mathematics of trigonometric function and the physical principle of the superposition of waves. Imagination and inference by readers will suffice to understand this article.

## 2. What is a crystal?

Most readers of this article will know what a crystal is. Nevertheless, this question is repeated here again for a better understanding for further discussion.

An important feature, which distinguishes crystalline solids from non-crystalline solids, is the periodicity of the crystal structure, in which a structural unit of atomic arrangement is periodically repeated in three-dimensions. Figure 1 shows (a) a structural model of NaCl (halite), in which Na and Cl atoms are arranged regularly in three-dimensions, and (b) the structural unit. We call this structural unit the “unit cell”, its eight corners the “lattice points”, and the periodic arrangement of these lattice points in space the “crystal-lattice”, the “space-lattice” or merely the “lattice”. Real crystals have much more complex features such as lattice defects consisting of atomic vacancy or dislocation, or irregular displacement of atoms of different kinds in solid solution etc. In the following section, the ideal crystal having the periodic arrangement of atoms is discussed.

## 3. Unit-cell parameters

The crystal lattice gives a three-dimensional framework in space. The most general form of the crystal lattice is a parallelepiped, and its size and shape can be expressed with lengths of three axes,  $a$ ,  $b$ ,  $c$  and angles between them,  $\alpha$ ,  $\beta$ ,  $\gamma$  (Fig. 2). These six parameters are called “lattice constants”, “lattice parameters” or “unit-cell parameters”. There are special

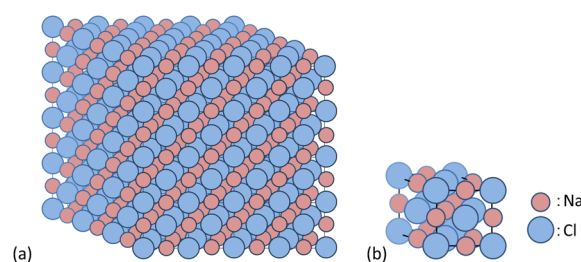


Fig. 1. (a) Structural model of NaCl crystal and (b) the structural unit.

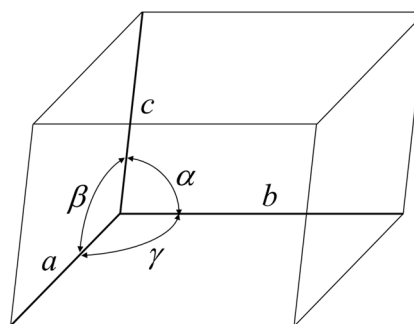
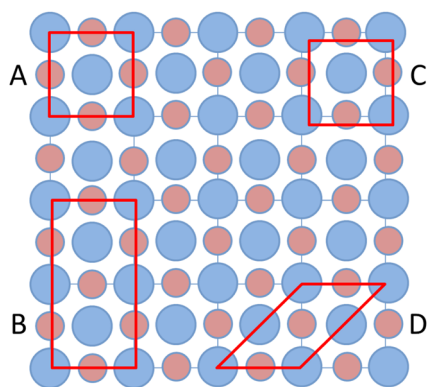


Fig. 2. Crystal lattice and unit-cell parameters.

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**Table 1.** Crystal systems and relationships of unit-cell parameters.

Crystal system	Restrictions on unit-cell parameters	Parameters to be determined
Triclinic	None	$a, b, c, \alpha, \beta, \gamma$
Monoclinic	$b$ -unique setting: $\alpha = \gamma = 90^\circ$	$a, b, c, \beta$
	$c$ -unique setting: $\alpha = \beta = 90^\circ$	$a, b, c, \gamma$
Orthorhombic	$\alpha = \beta = \gamma = 90^\circ$	$a, b, c$
Tetragonal	$a = b, \alpha = \beta = \gamma = 90^\circ$	$a, c$
Trigonal	Hexagonal axes: $a = b, \alpha = \beta = 90^\circ, \gamma = 120^\circ$	$a, c$
	Rhombohedral axes: $a = b = c, \alpha = \beta = \gamma$	$a, \alpha$
Hexagonal	$a = b, \alpha = \beta = 90^\circ, \gamma = 120^\circ$	$a, c$
Cubic	$a = b = c, \alpha = \beta = \gamma = 90^\circ$	$a$

**Fig. 3.** Two-dimensional structure of NaCl and various ways of finding structural units.

relationships among the unit-cell parameters owing to the shape and symmetry of the crystal lattice, and the number of parameters also changes. Crystal lattices can also be classified into the so-called seven “crystal systems” as given in Table 1. Any crystal belongs to one of the seven crystal systems, and, for example, the NaCl crystal belongs to the cubic system.

Figure 3 shows a projection of the crystal structure of NaCl onto the page. Four red frames A to D represent two-dimensional unit cells, all of which satisfies the criterion that the entire crystal is the repetition of these structural units, in this case, in the two-dimension. You shall immediately notice that the structural unit B is twice as large as the unit A, lattice points of the unit C intentionally avoid central positions of atoms, and an oblique coordinate system is necessary for the unit D. All three cases B to D make more complex the description of the crystal structure compared to the unit A. We prefer a simple way of thinking, and so, in determining the unit-cell, we apply two additional criterions that the unit-cell should have 1) the smallest volume and 2) the highest symmetry. These criterions can be rephrased as 1) shorter axis lengths of the unit-cell and 2) less number of unit-cell parameters. Although we are not going into further details here about the crystal system and the symmetry, the symmetry is predominantly important in describing a crystal structure in terms of X-ray crystallography.

**Fig. 4.** Ripples observed on water surface.

#### 4. Properties of X-rays

Visible light, which is visible to human eyes, is the electromagnetic radiation having wavelengths (symbol  $\lambda$  is used throughout) in the range of approximately 400 to 800 nm. X-rays are also electromagnetic radiation. X-rays used in X-ray laboratories have wavelengths in the range of 0.05 to 0.23 nm. Readers who are interested in physics will know that light has a wave-particle duality. X-rays also have a wave-particle duality, and therefore, X-rays can be counted one by one with the photon-counting type detector by utilizing their particle nature. On the other hand, X-ray diffraction is the phenomena that exhibit the wave nature of X-rays.

#### 5. Ripple

We use a word “ripple” in our everyday life. It may be unnecessary to explain the meaning of the “ripple” in that sense. We see a real ripple when we throw a stone onto the water surface of the pond. Figure 4 shows a ripple having a form of the waves in concentric circles and propagating from a source at the center. It is characterized by alternating propagation of crests and troughs.

#### 6. Diffraction of light waves

We learn about the diffraction (or interference) of light waves in high-school physics. Figure 5 is an idealized diagram representing the propagation of light waves. Plane waves coming from a subjacent source far in the distance are incident to the opaque barrier with

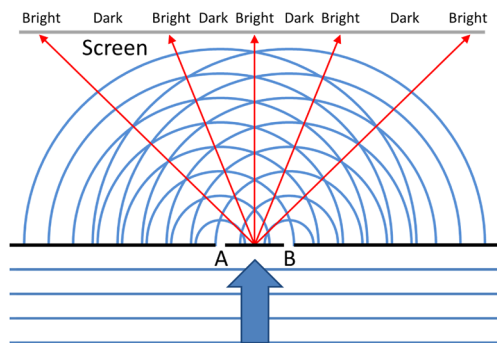


Fig. 5. Diffraction of light waves by two slits.

two narrow slits A and B. Semicircular waves from the two slits as second sources are subsequently propagating upward. In the diagram, semicircles represent the crests of the waves, and the troughs of waves are just in between the two neighboring crests.

The Superposition Principle of waves states that, when two or more waves are superposed, the amplitude of the total wave at each point is given by simply adding the amplitudes of individual waves. As a result, the amplitude at a point becomes large when the crest of the wave meets the crest of the other wave. On the other hand, it becomes small or null by cancelling with each other when the crest of a wave meets the trough of wave. In Fig. 5, red lines are drawn by connecting the points where the crest meets the crest of another wave. If we place a screen in front of the waves, positions where red lines hit the screen will be bright while other positions will be dark. If we shorten the distance between the two slits, intervals between the bright and the dark will be widened. You can imagine the movements of bright and dark positions by shifting whole concentric waves (semicircles) from the slit B toward the slit A in your eyes. This is the phenomena observed in the diffraction (or interference) of light waves. The same phenomena occur in the diffraction of X-rays.

## 7. Diffraction of X-rays

We consider the diffraction of X-rays by replacing Fig. 5 with Fig. 6, in which two slits shown in Fig. 5 are replaced with two atoms of the same kind. In real crystal, electrons revolving around the nucleus of an atom are concerned with X-ray scattering. But we continue with the story by assuming that two atoms are present at points A and B as secondary sources of X-ray scattering. In this regard, it may be noted that the concept of a “point atom” is used in X-ray crystallography. In Fig. 5, light waves are perpendicularly incident to the opaque barrier. In Fig. 6, X-rays in phase<sup>Note 1)</sup> are obliquely incident to the line

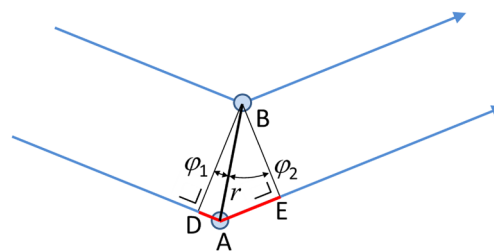


Fig. 6. Diffraction of X-rays scattered by two atoms at points A and B.

$\overline{AB}$  connecting two points A and B as a general case. What we would like to know are 1) the mathematical condition that the diffraction occurs and 2) the direction in which the X-rays are diffracted. Regarding the diffraction condition, the scheme representing the diffraction of light waves in Fig. 5 gives us a hint. We should find the condition that two X-rays, scattered from two atoms at points A and B, are in phase. Regarding the second question, we should find the direction that corresponds to those of red lines in Fig. 5. X-rays are scattered from an atom in all directions just like circular waves in Fig. 5. In Fig. 6, a wave front of scattered X-rays is perpendicular to the blue lines, which represent the direction of the propagating wave.

In Fig. 6, D and E represent foots of perpendiculars, which are drawn from the point B to the beam incident to A and the beam radiated from A, respectively. Angles  $\angle ABD$  and  $\angle ABE$  are represented by symbols  $\phi_1$  and  $\phi_2$ , respectively. The path length of the X-rays, which are scattered from the point A and propagating along the blue line, is longer by  $\overline{DA} + \overline{AE}$  compared to that of the X-rays from the point B. In this article, the difference in path lengths between the two waves is represented by a symbol  $\Delta$ , and it can be calculated by

$$\Delta = r \sin \phi_1 + r \sin \phi_2$$

where  $r$  represents the distance AB. By utilizing the formula for trigonometric function, the above equation is converted to

$$\Delta = 2r \sin \frac{\phi_1 + \phi_2}{2} \cdot \cos \frac{\phi_1 - \phi_2}{2} \quad (1)$$

When the  $\Delta$  is an integral multiple of the wavelength  $\lambda$  of incident X-rays, that is,  $\Delta = n\lambda$  ( $n$ : integer), X-rays scattered from two atoms at points A and B are again in phase, and they reinforce with each other.

## 8. Bragg equation

You often hear about the “Bragg equation” when you study X-ray crystallography or you are occupied with X-ray analysis in materials characterization. The Bragg equation is one of the keystones in understanding X-ray crystallography, and you are encouraged to surmount this big mountain. In deriving the Bragg equation, Fig. 6 is revised by adding two red lines, individuals of which pass through points A and B and, furthermore, have the equal angle  $\theta$  against the

Note 1) Vibration of a wave is generally expressed by a sine function ( $\sin \omega$ ), and  $\omega$  is the phase. “Waves are in phase” means that  $\omega$  is synchronized. For example, the crest of one wave coincides with the crest of another wave.

incident and radiated beams (Fig. 7). A point F is a foot of a perpendicular to the lower red line from the point B. Then  $\angle DBF = \angle EBF = \theta$  and  $\varphi_1 + \varphi_2 = 2\theta$ . By representing the angle  $\angle ABF$  by symbol  $\varphi_3$ ,  $\varphi_1 = \theta - \varphi_3$  and  $\varphi_2 = \theta + \varphi_3$ . Therefore,  $\varphi_1 - \varphi_2 = -2\varphi_3$ . Representing the length  $\overline{BF}$  by symbol  $d$ ,  $r \cos(-\varphi_3) = r \cos\varphi_3 = d$ , and the equation (1) can be rewritten in a form.

$$\Delta = 2d \sin \theta \quad (2)$$

Just as in the case of equation (1), when  $\Delta = n\lambda$ ,

$$2d \sin \theta_B = n\lambda \quad (3)$$

When equation (3) holds, then X-rays scattered from points A and B are again in phase, and the diffraction occurs in the direction defined by the angle  $\theta_B$ . This is called “Bragg’s law”, and the equation (3) is the “Bragg equation”. The angle  $\theta_B$  is the “Bragg angle”, and the symbol  $\theta_B$  (or  $\theta_0$ ) is often used in order to distinguish it from an arbitrary angle by  $\theta$ . Parameter values of  $r$ ,  $\varphi_1$  and  $\varphi_2$  in equation (1) will arbitrarily be varied owing to where points A and B are placed on the red lines. On the other hand, as will be discussed later, the parameter  $d$  is an intrinsic value of the crystal, and the  $\theta_B$  can uniquely be determined if X-rays with a constant wavelength are used for diffraction experiment. Now we can say that the diffraction occurs when the Bragg’s law holds and the direction is given by the  $\theta_B$ .

## 9. Bragg’s law holds throughout the entire crystal

We have discussed the diffraction of X-rays scattered from two atoms at points A and B. How can we extend this picture to the entire crystal? Since the crystal

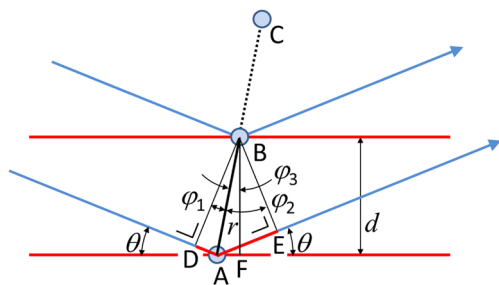


Fig. 7. A scheme with two additional red lines.

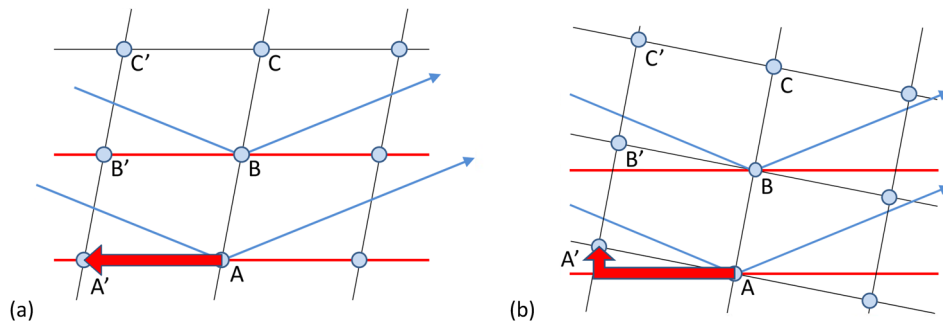


Fig. 8. (a) One-dimensional crystals are translated only in the horizontal direction, and (b) they are translated vertically in addition to horizontal shifts.

structure has the periodic nature, we can expect the presence of the atom of the same kind at point C, which is away from the point B by the distance  $r$  (Fig. 7). If the Bragg’s law holds between the two atoms at points A and B, it should also hold between the atoms at points B and C. Furthermore, it should hold between the atoms at points C and a next neighbor and so on. However, this is just one-dimensional crystal. How does the Bragg’s law hold in two-dimension?

In Fig. 8, the one-dimensional crystal in Fig. 7 is extended to two-dimensions in two ways (a) and (b). In the case (a), copies of the one-dimensional crystal are repeatedly translated toward the horizontal direction on the page while the incident and radiated beams are kept in the same directions. In the case (b), they are translated not only horizontally but also vertically. The periodic nature of the crystal structure is retained in both cases. If X-rays radiated from the one-dimensional crystal are in phase, should they also be in phase for both two-dimensional crystals of (a) and (b)?

We first consider the case (a). In Fig. 9, we focus on the X-ray scattering not from the two atoms at points A’ and B’ but from those at points A’ and B, which are apart by the distance of  $r'$ . In order to find the difference in path lengths  $\Delta$ , we add some lines to the diagram and define angles  $\varphi_4, \varphi_5, \varphi_6$  just as was done in Fig. 7. The  $\Delta$  is given by  $\Delta = \overline{HA'} - \overline{BG} = -\overline{BG} + \overline{HA'}$ , and thus

$$\Delta = -r' \sin \varphi_4 + r' \sin \varphi_5$$

It will be converted in the same manner as before to

$$\Delta = 2r' \sin \frac{-\varphi_4 + \varphi_5}{2} \cdot \cos \frac{\varphi_4 + \varphi_5}{2}$$

It will be found that  $-\varphi_4 + \varphi_5 = 2\theta$ . Since  $\varphi_4 = \varphi_6 - \theta$  and  $\varphi_5 = \varphi_6 + \theta$ , then  $\varphi_4 + \varphi_5 = 2\varphi_6$ . Since  $r' \cos \varphi_6 = d$ , we can derive  $\Delta = 2d \sin \theta$ , which is the same as the equation (2). This result means that if scattered X-rays from the atoms at points A and B are in phase, X-rays from the atoms at points A’ and B are also in phase simultaneously.

Now you shall notice that angle settings between the line  $\overline{AB}$  and additional lines in Fig. 7 and those between the line  $\overline{A'B}$  and additional lines in Fig. 9 are essentially the same. The angles  $\varphi_1$  and  $\varphi_4$  have opposite signs because these angles are set on the

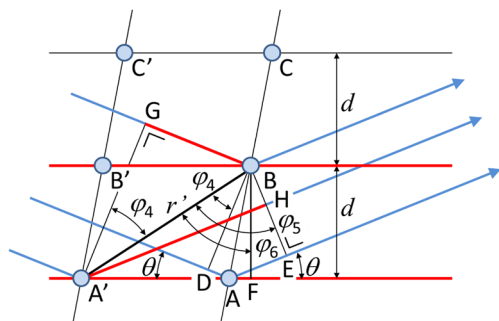


Fig. 9. Diffraction of X-rays in the two-dimensional crystal.

opposite sides of  $\overline{AB/A'B}$ . Yet you can easily see the one-to-one correspondences of  $\varphi_1 \rightarrow \varphi_4$ ,  $\varphi_2 \rightarrow \varphi_5$ ,  $\varphi_3 \rightarrow \varphi_6$ . By imagining the presence of the point  $A''$  on the left-hand side of the point  $A'$  on the same red line, you will be able to easily derive the equation  $\Delta = 2d \sin \theta$  for the two atoms at points  $A'$  and  $B$ . These considerations will be extended to the atoms at points  $C$  and  $B$  and also for the atoms at points  $C$  and  $B'$  so on. Therefore, if the Bragg's law holds for the atoms at two points on the two adjacent lines by the distance  $d$  apart, the Bragg's law will hold for all atoms in this two-dimensional crystal. Although the verification is not given here, the relationship holding in the case (a) does not hold in the case (b). You can easily imagine that the Bragg's law will hold in the three-dimensional crystal by stacking the diagram in Fig. 9 perpendicularly to the page at regular intervals. In this case, red lines become planes perpendicular to the page.

## 10. Lattice plane

Figure 10 shows a crystal structure of NaCl projected onto the page. As was mentioned, NaCl belongs to the cubic system, and its unit-cell parameters have the relationship of  $a=b=c$ . In crystallography, axis-lengths in the three directions, mutually at right angles in the cubic system, are represented by just one parameter  $a$ . It is the same since you cannot distinguish which edge is a particular direction of a monochrome cubic box on your palm. Three parameters  $a$ ,  $b$ ,  $c$  are, however, used in Fig. 10 for better understanding of the directional relationship in the following discussion.

In Fig. 10, four red lines passing through pairs of two points  $O$  and  $A$  and so on represent the planes perpendicular to the page. In this diagram, the point  $O$  was chosen as an origin of the four planes. But any lattice point can be chosen instead because the same structural unit is infinitely repeated in the crystal. For example, if there is a plane passing through the points  $O$  and  $B$ , the plane with the same direction, passing through the points  $E$  and  $C$ , will be present (Fig. 11). In the crystal, a number of planes in the same direction are infinitely repeated at a regular spacing. These planes are called "lattice planes", and the distance between a lattice plane and an adjacent plane is called the " $d$ -spacing".

If we slice the crystal with regularly spaced lattice planes as in Fig. 11, we can see that a structural unit,

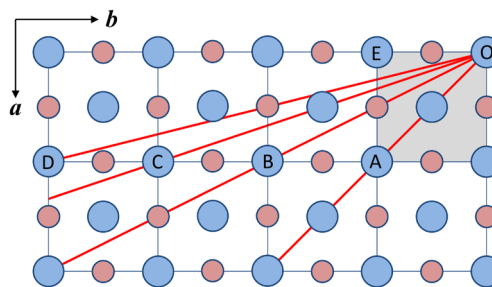


Fig. 10. Four lattice planes (red lines) in the different directions.

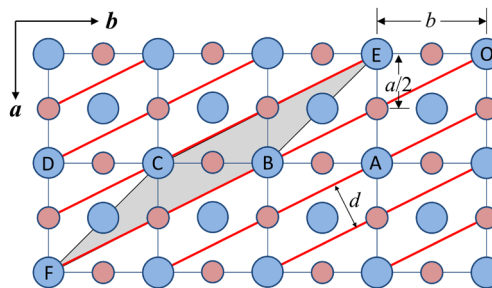


Fig. 11. Infinitely repeated lattice planes in the same direction.

for example,  $BFCE$  is also regularly repeated in the directions both parallel and perpendicular to these planes. The structural unit with the same area in this two-dimensional crystal can be chosen by selecting another set of four points. In any case, the entire crystal will be re-built by tiling these structural units. The same idea will be applied to the remaining three lattice planes in Fig. 10. In these cases, structural units with edge length of  $\overline{OA}$ ,  $\overline{OC}$  or  $\overline{OD}$  will be repeated and the  $d$ -spacing will be narrowed accordingly.

## 11. Plane indices

In Fig. 11, all lattice planes in the same direction pass through the points positioned at regular intervals, which are integral multiples of the period  $a/2$  in the  $a$ -axis direction and the period  $b$  in the  $b$ -axis direction. We can see that the same scheme holds for the remaining three planes in Fig. 10: the corresponding periods for these planes are  $a/1$ ,  $a/3$  and  $a/4$  in the  $a$ -axis direction. Now we can define the lattice plane in three-dimensional crystal space. As shown in Fig. 12, the lattice plane can be defined as a plane that intersects the three axes  $a$ ,  $b$ ,  $c$  at three points  $(a/h, b/k, c/l)$ , where  $hkl$  are integers. Inversely, a set of the integers  $hkl$  is used to uniquely define the lattice plane and consequently its direction. By enclosing the  $hkl$  in parentheses, we call  $(hkl)$  the "plane indices" or the "Miller indices". In this connection, the four lattice planes in Fig. 10 are expressed as  $(110)$ ,  $(210)$ ,  $(310)$  and  $(410)$ . In these cases,  $l=0$  corresponds to  $c/l=\infty$ , and it means that these lattice planes are parallel to the  $c$ -axis and they will never intersect with the  $c$ -axis. In Fig. 12, just one quadrant is presented. The crystal has eight quadrants, and thus it has eight lattice planes having the indices

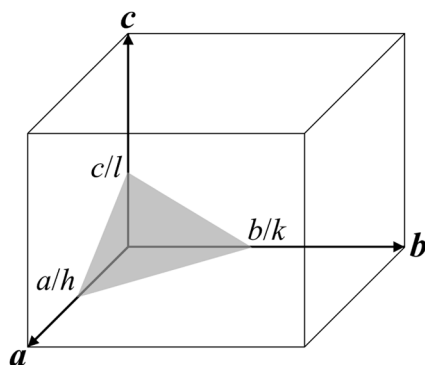


Fig. 12. Definition of the lattice plane in crystal space.

$(hkl)$ ,  $(\bar{h}kl)$ ,  $(h\bar{k}l)$ ,  $(hk\bar{l})$ ,  $(h\bar{k}\bar{l})$ ,  $(\bar{h}k\bar{l})$ ,  $(\bar{h}\bar{k}l)$ ,  $(\bar{h}\bar{k}\bar{l})$  with the same absolute magnitudes  $|h|$ ,  $|k|$ ,  $|l|$ . Here,  $\bar{h}$  means  $-h$ .

It is important to point out again that the plane indices are all integers. As seen in Fig. 11, if a lattice point is present on a certain lattice plane, a next lattice point will also be present on the  $h^{\text{th}}$  lattice plane. Therefore, the periodicity of the crystal structure is retained along the lattice planes. Inverse numbers of the plane indices,  $1/h$ ,  $1/k$  and  $1/l$  are all rational numbers. If they are irrational numbers, for example  $1/\sqrt{2}$  instead of  $1/2$ , you shall see that the periodicity of the structure does not hold anymore along the lattice plane.

## 12. Lattice planes and Bragg's law

We have discussed the lattice plane and the plane indices. Now we will discuss the relationship between the lattice plane and the Bragg's law and, furthermore, how the lattice planes are related to diffraction of X-rays by a crystal.

If we rotate the diagram in Fig. 11 clockwise by approximately  $30^\circ$  and compare it with the diagram in Fig. 9, we will notice that the two diagrams look very similar. Red lines became planes when the diagram in Fig. 9 was extended imaginarily to the three-dimension. These planes are nothing but the lattice planes discussed in sections 10 and 11, and the distance  $d$  in the Bragg equation is simply the  $d$ -spacing between the two adjacent lattice planes. As was discussed in the previous section, the periodicity of the structural unit along the lattice plane will be lost if the definition of the lattice plane is invalidated. It is just the same as that in the case of (b) in Fig. 8, and diffracted X-rays are out of phase. Now you shall understand that the Bragg's law holds when X-rays are incident and radiated at the equal angle against the lattice plane.

In Fig. 11, atoms, for example, at points BFCE are all on the lattice planes  $(210)$ , and they give the same scheme as that in Fig. 9. You might question, however, whether X-rays from these atoms are out of phase with those from atoms which are positioned between the lattice planes and/or atoms between the points C and E. Figure 13 shows a composite lattice, consisting of two lattices I and II with the same shape and size in the two-dimension. All atoms are positioned at lattice points, and therefore on the lattice planes of either lattice I or II.

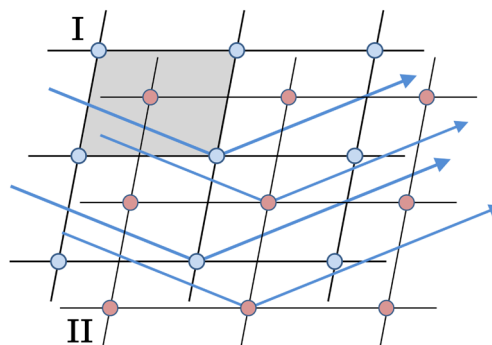


Fig. 13. Diffraction of X-rays from a composite crystal consisting of lattices I and II.

The periodic structure is still retained. As was verified in section 9, if the Bragg's law holds for the atoms positioned at lattice points of the lattice I, it should also hold for the atoms on lattice II. For better understanding, we first considered the Bragg's law for atoms on lattice planes. Figure 13 indicates that the atoms are not necessary to be present on the lattice planes. You shall understand this by erasing the frame of the lattice II in Fig. 13.

## 13. Intensity of diffracted beam

Even though the Bragg's law holds separately for atoms belonging either to the lattice I or the lattice II, X-rays diffracted from atoms belonging to the lattice I and those from the lattice II are not in phase, and they interfere with each other, giving an influence on the amplitude of the total diffracted X-rays. This is exactly a reason why the diffracted intensities differ for different diffraction lines.

The amplitude of superposed X-rays diffracted from all atoms in the unit-cell is called the "Structure Factor". The amplitude of scattered X-rays from an atom increases with the atomic number. As was stated in the beginning, the electrons are concerned with X-ray scattering, and heavy atoms, having more electrons than light atoms, scatter X-rays of higher amplitude. As inferred from Fig. 13, phase differences of X-rays diffracted from individual atoms depend on relative positions of the atoms in the unit-cell. They will also depend on the directions of incident and diffracted X-ray beams. This means that the phase differences also depend on which lattice plane  $(hkl)$  is involved in the diffraction process. Therefore, the structure factor is a function not only of the positions and the kinds of atoms but also of the plane indices  $hkl$ . Thus the structure factor is expressed by using a symbol  $F(hkl)$ . It may be noted that, strictly speaking,  $F(hkl)$  is also dependent on the thermal vibrations of atoms in the crystal. The Bragg equation gives the condition that X-ray diffraction occurs and the direction of diffracted X-rays. The structure factor gives the amplitude of the diffracted X-rays when Bragg's law holds. Intensity of diffracted X-rays is obtained by squaring the amplitude.

#### 14. Single crystal diffraction and powder diffraction

As was stated, the diffraction of X-rays is always concerned with the lattice plane. X-rays are incident and diffracted at an equal angle against the lattice plane, and Bragg's law must hold simultaneously. In the diffraction experiment using a single crystal, the condition of holding the Bragg's law is satisfied by rotating or oscillating the crystal. The rotation of a lattice plane associated with the rotation of the crystal induces an instant at which the Bragg's law does hold. It is just like a revolving mirror ball reflecting irradiated light beam. In the case of the powder diffraction experiment, we use an aggregate of fine crystalline particles, which are supposed to be oriented randomly. If crystalline particles are oriented in all directions, so are the lattice planes without any rotation or oscillation. It is just like an aggregate of micro mirror balls. If the powder sample is irradiated with X-rays, the Bragg's law will always hold for some lattice planes in a statistical sense.

#### 15. Powder diffraction experiment

Figure 14 shows a simplified scheme of the powder diffraction experiment. X-rays coming from the X-ray source located on the left-hand side are incident to the powder specimen at the center of the diagram, in which the lattice planes (red lines) are drawn in an exaggerated scale. The direction of the lattice plane ( $hkl$ ) can be represented with the plane normal, where a symbol  $\mathbf{n}_{hkl}$  is used. The lattice planes are oriented at random associated with the random orientation of crystalline particles in the powder specimen, and their plane normals are also oriented at random. If we rotate the diagram in Fig. 14 around the axis  $\overline{AB}$  by  $360^\circ$ , two cones C and D with the cone angles of  $\pi/2 - \theta_B$  and  $2\theta_B$  are formed (Fig. 15). The plane normals of the lattice planes ( $hkl$ ) that contribute to the diffraction are distributed on the cone C, and the X-rays are diffracted along the cone D. If we place a two-dimensional detector on the right-hand side of the diagram perpendicularly to the axis  $\overline{AB}$ , diffraction rings called "Debye-Scherrer rings" will be observed at the intersection of the cones and the sensor. If we scan the diffracted intensities by using zero- or one-dimensional counter along the circular arc, we will observe a familiar powder diffraction pattern which was mentioned at the beginning of this article. Here  $2\theta_B$  is called "diffraction angle".

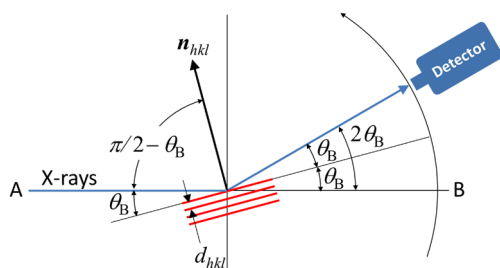


Fig. 14. Scheme of powder diffraction experiment.

#### 16. Peak positions of diffraction lines

Finally we will discuss the peak positions of diffraction lines in the powder diffraction pattern. The diffraction occurs as represented in Fig. 14. The peak positions of the diffraction lines, represented by the diffraction angle  $2\theta_B$ , can be calculated from the Bragg equation [equation (3)] if the  $d$ -spacing  $d_{hkl}$  for the lattice plane ( $hkl$ ) is provided. On the other hand, the  $d$ -spacing  $d_{hkl}$  can be calculated from the unit-cell parameters.

In the case of the orthorhombic system (Table 1), the  $d_{hkl}$  can be calculated from the following equation (see Appendix).

$$d_{hkl} = \left( \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \right)^{-1/2}$$

Monoclinic and triclinic systems have lower symmetry than orthorhombic systems, and the equation becomes much more complex. In the case of the cubic system with the highest symmetry, it becomes a simple form.

$$d_{hkl} = a(h^2 + k^2 + l^2)^{-1/2} \quad (4)$$

Table 2 gives numerical values of the  $d_{hkl}$  and the  $2\theta_B$ , calculated for NaCl ( $a=0.5628\text{nm}$ ) by using equations (3) and (4). In equation (3), we used the  $\lambda$  of  $0.154059290\text{nm}$  for the characteristic X-rays from X-ray source with a Cu target, which is usually used in laboratory powder diffraction experiments. Figure 16 shows an observed diffraction pattern of NaCl. By combining numbers of the indices  $hkl$ , 15 diffraction lines were calculated in the angular range of  $2\theta \leq 70^\circ$  (Table 2). In reality, however, 6 diffraction lines, marked by yellow in Table 2, were observed. A reason why the remaining diffraction lines were not observed is that X-rays scattered from individual atoms at specially related positions interfere with each other resulting in making the total amplitude of diffracted X-rays null. In the case of NaCl crystal (Fig. 1), equivalent atoms are present not only at the corners of crystal lattice but also at the centers of individual faces of the lattice. We call a lattice of this kind "face-centered lattice". In this case, the diffraction will occur when numerical values of  $h+k$ ,  $k+l$ ,  $l+h$  are all even. When they are

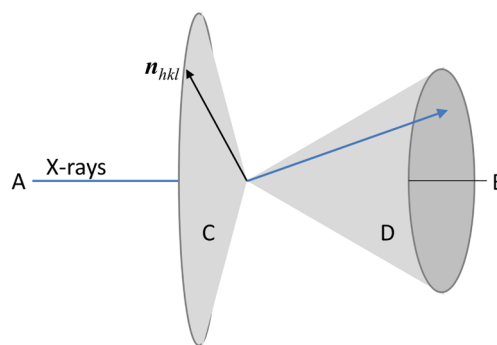


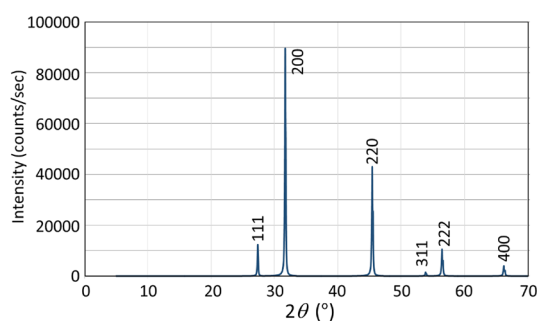
Fig. 15. Cones C and D generated by rotating the diagram in Fig. 14 around the axis  $\overline{AB}$  by  $360^\circ$ .

**Table 2.** Calculated results of the  $d_{hkl}$  and the  $2\theta_B$  for some combinations of  $hkl$ .

$hkl$	100	110	111	200	120	121	220	300/221
$h^2 + k^2 + l^2$	1	2	3	4	5	6	8	9
$d_{hkl}$ (nm)	0.5628	0.3980	0.3249	0.2814	0.2517	0.2298	0.1990	0.1876
$2\theta_B$ (°)	15.73	22.32	27.43	31.77	35.64	39.17	45.54	48.48

$hkl$	301	311	222	230	231	400	232
$h^2 + k^2 + l^2$	10	11	12	13	14	16	17
$d_{hkl}$ (nm)	0.1780	0.1697	0.1625	0.1561	0.1504	0.1407	0.1365
$2\theta_B$ (°)	51.28	53.99	56.59	59.14	61.61	66.39	68.71

**Fig. 16.** X-ray powder diffraction pattern of NaCl.

odd, the structure factor, and therefore, the amplitude of X-rays, becomes zero, and the diffracted intensity is not observed although the Bragg's law holds. You can confirm this from numbers of  $hkl$  in Table 2 and the observed diffraction pattern in Fig. 16. The regularity with which the diffraction occurs or does not occur depending on whether the numerical values of indices or combined indices are even or odd is called "Extinction Rule".

There is one-to-one correspondence between the lattice plane and the diffraction from that plane. So the same numbers as those of the plane indices are given to individual diffraction lines but without enclosing with the parentheses: the diffraction line from the lattice plane ( $hkl$ ) has indices of  $hkl$ . It should also be noted that the crystal lattice has the eight quadrants as was stated in section 11. In the case of NaCl crystal, the lattice plane (200) is equivalent to those with indices ( $\bar{2}00$ ), (020), ( $0\bar{2}0$ ), (002), (00 $\bar{2}$ ), and all these planes gives the diffraction lines with the same intensity at the same diffraction angle. In Fig. 16, the diffraction line at  $2\theta_B = 33.77^\circ$  is observed as if a single peak and indices of only 200 are given as well as in Table 2. In reality, however, the remaining five diffraction lines with indices of  $\bar{2}00$ , 020,  $0\bar{2}0$ , 002, 00 $\bar{2}$  are overlapping at the same  $2\theta_B$ .

You might remember that the intervals of dark and bright are widened if we narrow the distance between the two slits in the diffraction of light waves (Fig. 5). In the case of the diffraction of X-rays by crystals, narrowing the slit distance corresponds to decreasing the size of the unit-cell and there is an associated decrease

of the  $d$ -spacing [equation (4)]. Then the diffraction lines will be observed toward the higher angles as the Bragg equation indicates [equation (3)]. After all, the diffraction of X-rays is based on the same optical principle that the diffraction of light wave obeys.

## 17. Information from the powder diffraction pattern

Some representative examples of materials analysis using powder diffraction techniques are described in this section.

**Crystalline phase identification:** As shown in a real example (Table 2), the angular positions of diffraction lines in the observed powder diffraction pattern are a function of the unit-cell parameters. Furthermore, as was briefly mentioned in section 13, diffracted intensities are a function of chemical elements and their spacial arrangement in the unit-cell. These two things mean that the powder diffraction pattern differ from material to material just as fingerprints do so. By comparing the observed powder diffraction pattern of a target material with those of known materials stored in a database, we can identify the crystalline phase of the target material just as in the fingerprint verification. Chemical analysis cannot distinguish the difference between diamond and graphite, both of which consist of carbon atoms. But X-ray analysis can elucidate the difference. This analysis technique is also called "qualitative analysis", and widely used as a first step in materials characterization.

**Quantitative phase analysis:** When a weight fraction of a crystalline phase in a multi-component sample is increased, the volume fraction will also be increased, and as a result, diffracted intensity will proportionally be increased. Weight fractions of individual phases in a multi-component material can be derived by measuring the relative intensities of relevant crystalline phases. Various techniques are available.

**Measurement of unit-cell parameters:** The diffraction angles are a function of the unit-cell parameters. Inversely, the unit-cell parameters of a material under investigation can be calculated by using observed peak positions of diffraction lines as input data. The unit-cell parameters are intrinsic physical parameters of the material. They also vary with partial

substitution of composing atoms in solid solution and/or variation of environmental conditions such as of temperature and pressure. By pursuing the variation of the unit-cell parameters, we can elucidate the structural variation associated with the change of environmental conditions.

**Measurement of crystallite size:** Here we suppose a single crystal that belongs to the cubic system and has the unit-cell parameter of 1 nm. When a specimen of this crystal has the edge length of  $100\mu\text{m}$ , 100,000 unit-cells are aligned along the edge. The diffracted intensity from this crystal will steeply decrease when the diffracted X-rays are deflected by a small angle of say  $0.001^\circ$  from the  $2\theta_B$ . On the other hand, the diffracted intensity from a nano-crystal with the edge length of 100 nm, and therefore just 100 unit-cells on the edge, will moderately decrease when deflected from the  $2\theta_B$ . In this case, the broadened peak profile will be observed. Angular width of the diffraction profile is used to measure the crystallite size when the size is below  $\sim 200\text{ nm}$ .

**Crystal structure determination and refinement:**

In section 16, the peak positions of diffraction lines have been derived from the unit-cell parameters. Crystal structure determination is a reverse process. The unit-cell parameters are first determined from observed peak-positions. Then the positions of atoms in the unit-cell can be derived from the observed intensities of diffraction lines. In structure refinement, the powder diffraction pattern is calculated from both structural parameters (atomic coordinates etc.) and profile parameters (profile width parameters etc.). Then these parameters are refined by least-squares fitting of the calculated pattern to the observed pattern. A model of the crystal structure can finally be derived.

## 18. Summary

The crystal is characterized by its periodic structure consisting of regularly arranged structural units called the unit-cell. We also see the regular arrangement of atoms when the crystal structure is viewed along the lattice plane. The diffraction of X-rays occurs when Bragg's law holds for the X-rays incident and diffracted at an equal angle against the lattice plane. In the case of single crystal diffraction, the diffraction condition is satisfied for specific lattice planes by rotating or oscillating the crystal specimen against the incident X-ray beam. In the case of powder diffraction, the diffraction condition is satisfied by randomizing the orientation of fine crystalline particles and, therefore, the associated random orientation of the lattice planes with various plane indices. The powder diffraction pattern as shown in Fig. 16 will be obtained by scanning the diffracted intensities from the low angle side. Applications of powder diffraction techniques will be described elsewhere.

## Appendix

Figure 17 shows a lattice plane ( $hkl$ ) and  $d$ -spacing  $d_{hkl}$  in the orthorhombic system.  $\overline{OE}$  is perpendicular to both the lattice plane ( $hkl$ ) and  $\overline{CD}$ , and  $\overline{OD}$  is perpendicular to  $\overline{AB}$ . Lengths of  $\overline{OD}$  and  $\overline{CD}$  are expressed by symbols  $e$  and  $f$ , respectively. Three edges of  $\triangle OCD$  has the relation of  $f^2 = (c/l)^2 + e^2$  by the Pythagoras' theorem. Then we will obtain the following equation by dividing both terms of the equation by  $(c/l)^2 \cdot e^2$ .

$$\frac{f^2}{(c/l)^2 \cdot e^2} = \frac{1}{e^2} + \frac{l^2}{c^2} \quad (\text{A1})$$

Since  $\triangle OCD$  and  $\triangle ODE$  are similar,  $f/(c/l) = e/d_{hkl}$ . Thus,

$$\frac{f^2}{(c/l)^2 \cdot e^2} = \frac{1}{d_{hkl}^2} \quad (\text{A2})$$

In Fig. 17,  $\cos\phi = e/(a/h)$  and  $\sin\phi = e/(b/k)$ . Substituting these terms into  $\cos^2\phi + \sin^2\phi = 1$ , we obtain

$$\frac{h^2}{a^2} + \frac{k^2}{b^2} = \frac{1}{e^2} \quad (\text{A3})$$

From equations (A1), (A2) and (A3), we finally obtain the following equation.

$$d_{hkl} = \left( \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \right)^{-1/2}$$

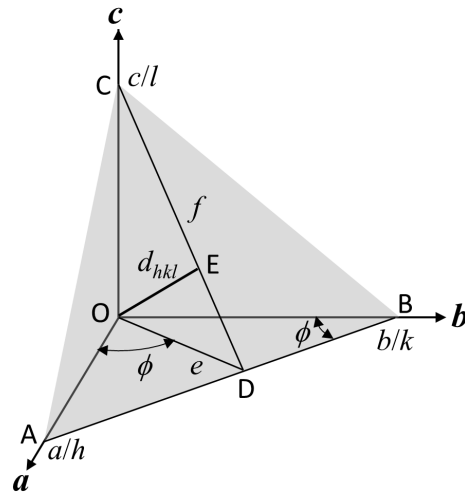


Fig. 17. Lattice plane ( $hkl$ ) and  $d$ -spacing  $d_{hkl}$  in the orthorhombic system.