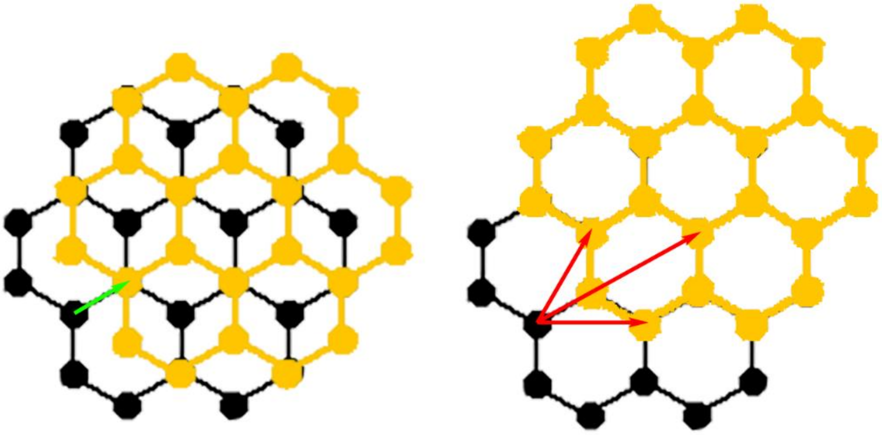
Д.А. Кириленко

PHYSICAL CRYSTALLOGRAPHY



Санкт-Петербург
2022

МИНИСТЕРСТВО НАУКИ И ВЫСШЕГО ОБРАЗОВАНИЯ РОССИЙСКОЙ ФЕДЕРАЦИИ

УНИВЕРСИТЕТ ИТМО

Д.А. Кириленко

PHYSICAL CRYSTALLOGRAPHY

УЧЕБНО-МЕТОДИЧЕСКОЕ ПОСОБИЕ

РЕКОМЕНДОВАНО К ИСПОЛЬЗОВАНИЮ В УНИВЕРСИТЕТЕ ИТМО
по направлению подготовки 16.04.01 Техническая физика
в качестве Учебно-методическое пособие для реализации основных
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Учебное пособие разработано при поддержке Министерства науки и высшего образования Российской Федерации (соглашение № 075-15-2021-1349) и предназначено для использования в качестве учебно-методического пособия в рамках реализуемых дисциплин образовательной программы «Лазерные и синхротронные технологии магесайенс/Megascience laser and synchrotron technologies». В пособии приведены теоретические справки по разделам курса и задания для практических занятий.

Содержание

1. Crystal

A crystal is a body with a crystalline structure, that is, a structure characterized by a periodic arrangement of atoms, as opposed to an amorphous structure with a much more chaotic arrangement of atoms (Figure 1.1). Many substances acquire a crystalline structure at not very high temperatures, that is *crystallize*, as, if a certain distance between any two atoms provides a certain minimum of energy, then we can expect the formation of a phase within which the distances between neighboring atoms are equal to the given optimal and, thus, they are the same, which determines the periodicity of the structure.

The key feature of crystals is the *anisotropy* of physical properties. Anisotropy (from the Greek ἄνισος - unequal and τρόπος - direction) - unevenness of properties in different directions - is a direct consequence of the ordered arrangement of atoms. Indeed, in an amorphous structure there are no geometrically distinguished directions, therefore, physical properties at the macroscopic level will be isotropic, and, at the same time, in a crystal different directions are not equivalent, which not only obviously follows from the images of the crystal structure, but also has many visual manifestations.

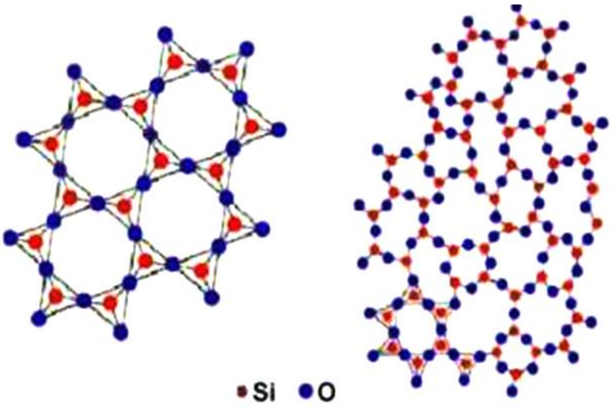

Figure 1.1 - Schematic representation of the structure of quartz (crystalline) and glass (amorphous).

The word "crystal" itself comes from the Greek κρύσταλλος (literally "frozen", "ice"), the word related to Greek κρύος "cold, frost". *Rock crystal* (Figure 1.2), a transparent variety of quartz, was called so in ancient times and is called so nowadays. Colorless crystals found high in the mountains, as previously assumed, are ice, petrified as a result of exposure to sub-zero temperatures for centuries. This point of view is well illustrated by the following lines of the Roman poet Claudian (c. 390 AD):

At furious Alpine winter, ice turns to stone.
The sun is then unable to melt such a stone.

Figure 1.2 - Druse of rock crystal.

A notable feature of rock crystal is the correct shape of individual parts, which significantly distinguishes them from ordinary stones. In particular, for this reason various magical properties were attributed to it, which were also subsequently attributed to other findings of a similar type. This fact led to the use of the word *crystal* in relation to various natural objects that have the shape of a polyhedron, since it was assumed that they all had some common magical feature of their nature. The development of this assumption in the course of natural science evolution turned out to be very fruitful, which led to the emergence of *crystallography* - the science of crystals, their structure, and properties.

The faceting of natural crystals is a visual manifestation of the anisotropy peculiar to their physical properties, that is, a direct consequence of their specific structure. At the same time, *amorphous* bodies (Greek ἀ “non-” + μορφή “form”), which have *an amorphous* structure, are formed shapeless under similar conditions. For this reason, the term "crystal", which was used to designate minerals of the correct form, began to be used to designate bodies with an ordered, "crystalline" structure.

In the context of the terminology established in modern physics, it must be taken into account that, for example, glass, which has been mechanically shaped into a polyhedron, does not become a crystal, since its shape in this case does not reflect its internal properties and is not due to its structure. At the same time, the crystals used in modern technology often have the shape of thin plates, acquired as a result of mechanical cutting and grinding, which is why they do not cease to be crystals, since the shape of the plate arises as a result of highly anisotropic external influences and is also not a reflection of the internal structure that preserves its strict periodicity.

The authorship of the ordered structure theory for natural crystals, as the reason for their regular shape, is attributed to Girolamo Cardano (XVI century), but only in the XX century this assumption received direct experimental confirmation, first in 1912 in the form of X-ray diffraction patterns, then in the second half of the 20th century in the form of direct images of the crystal structure in an electron microscope (Figure 1.3).

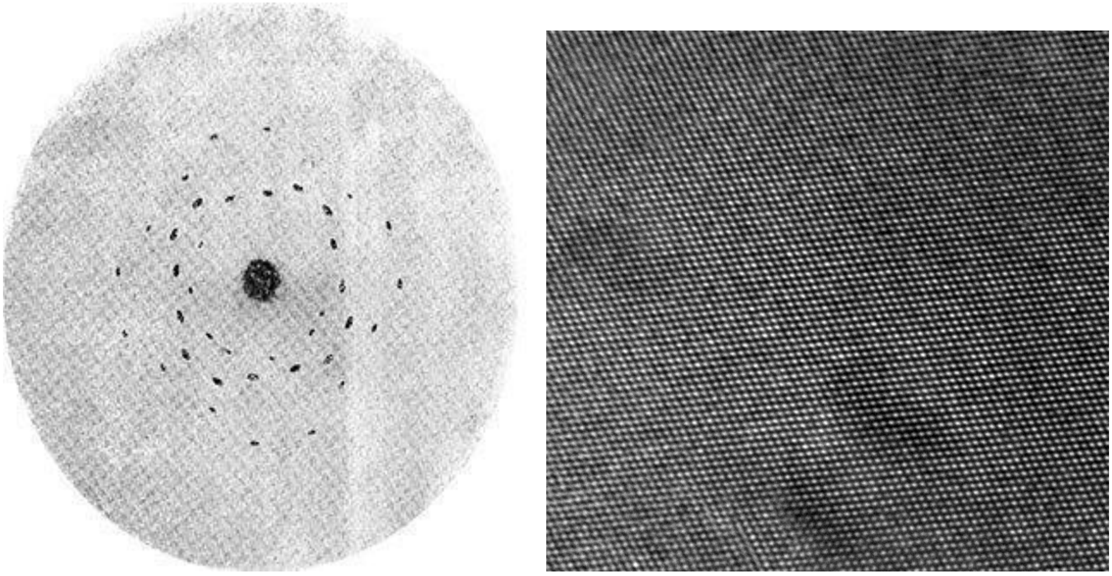

Figure 1.3 - X-ray diffraction pattern and electron microscopic image of the crystal structure.

It is noteworthy that by this time a powerful theory of periodic three-dimensional structures had already been formed, which had gone through a centuries-old path in its development from Johannes Kepler's treatise "On Hexagonal Snowflakes" (1612), where he developed Cardano's hypothesis, to the conclusion about 230 space symmetry groups made by E.S. Fedorov (1890), which underlies modern crystallography.

2. Spatial lattice

A crystal is characterized by a periodic arrangement of atoms. Periodicity in the mathematical sense of the word is the property of an object to coincide with itself with some displacement. For example, by definition, the function f of the argument t is periodic with period T if $f(t+T)=f(t)$ for any t, that is, the graph of the function will completely coincide with itself when it moves along the abscissa axis by the amount T. It is useful to pay attention to an important property that follows directly from the definition, which is that $f(t+2T)= f(t)$ (because $f(t+2T)= f(t+T)$ as well as $f(t+T)= f(t)$), and $f(t-T)= f(t)$, and in general $f(t+nT)= f(t)$ for any *integer* n. That is, the original definition of periodicity automatically implies an infinite cyclicity of function values.

The spatial periodicity of the crystal structure means that when it is moved, in other words, when it is *translated* to some vector, the structure will coincide with itself (Figure 2.1). It is obvious that such *translation vectors* must connect similar points of the structure. The set of all translation vectors or the set of equivalent points of the structure, that is, interconnected by translation vectors, form a three-dimensional lattice is *the spatial lattice of* a given crystal structure.

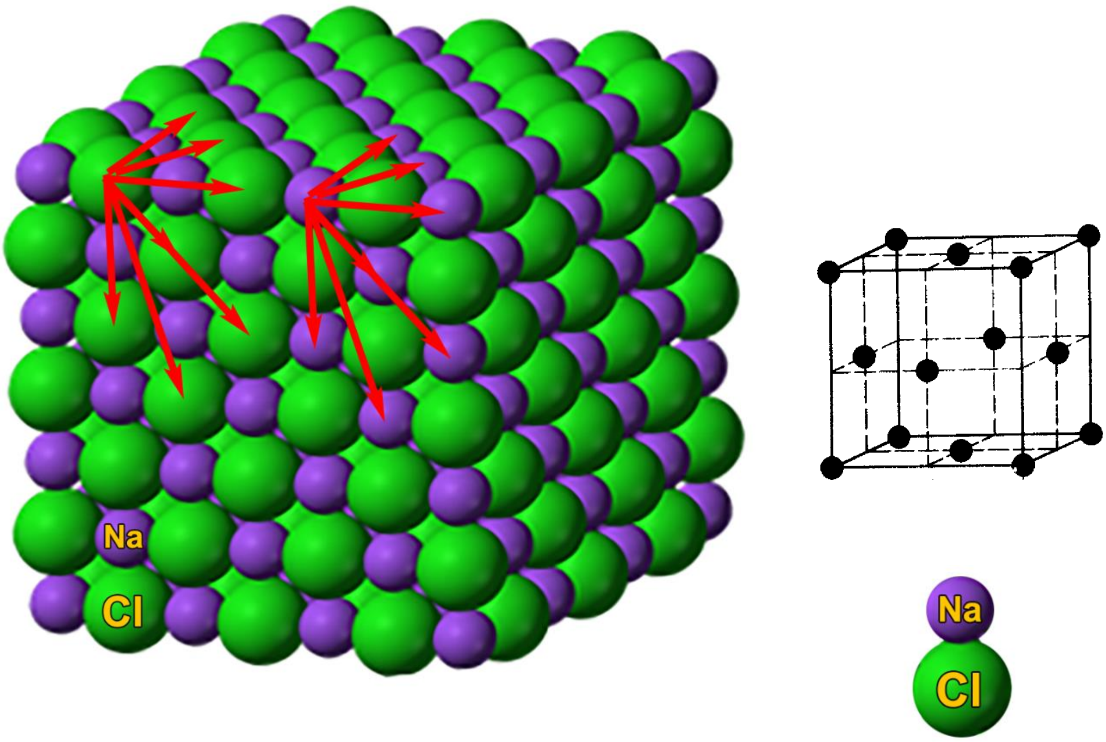

Figure 2.1 - Crystal structure of NaCl and some of the translation vectors. A fragment of the spatial lattice of the structure and its atomic motif.

If a certain geometric operation transforms an object into itself, then one speaks of the presence of a *symmetry* (Greek συμμετρία = “proportionality”; from συν- “together” + μετρέω “measure”), and this transformation is called a symmetry operation. Thus, a crystal structure is a structure that has *translational symmetry*, that is, symmetry with respect to translations.

A spatial lattice is a mapping of a set of translation operations, an auxiliary geometric construction that describes what is included in the concept of “structure periodicity”. Note, that crystals of different structure may well have identical lattices. The very same crystal structure can be represented as a spatial lattice, in each node of which a group of non-equivalent atoms, the so-called *atomic motif*, is located.

For simple substances, the image of the crystal structure can be essentially identical to the image of the spatial lattice, if all atoms are in equivalent positions, as, for example, in the case of the structure of copper (Figure 2.2). In this case, the atomic motif consists of only one atom.

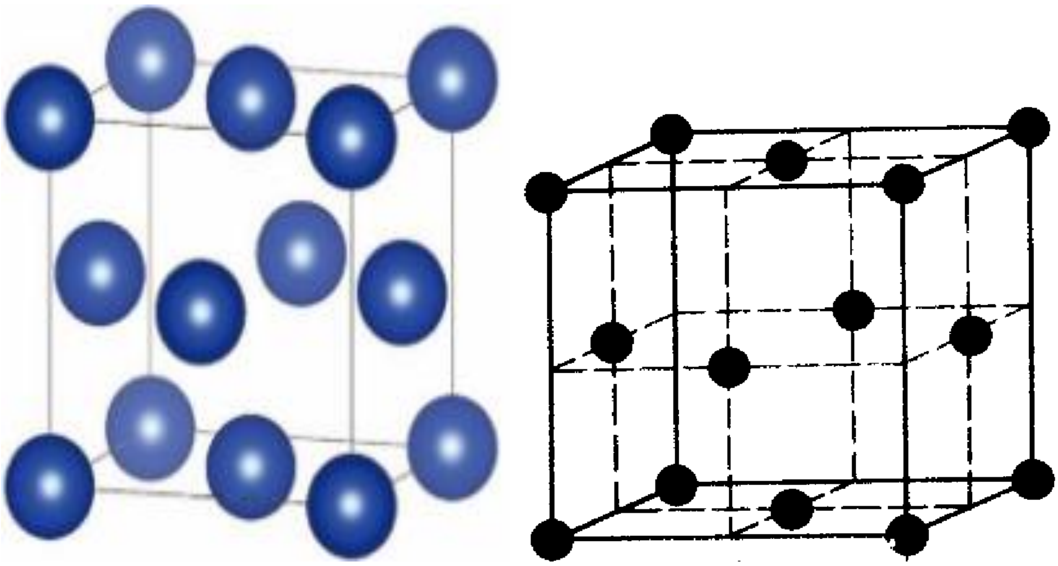

Figure 2.2 - Image of the crystal structure of copper and its spatial lattice.

But even in the case of simple substances, the relationship between structure and lattice can be somewhat more complicated. For example, in the structure of graphite, the vector connecting two nearest atoms is not a translation vector, since with such a displacement the structure does not coincide with itself (Figure 2.3). In other words, two neighboring atoms are in nonequivalent positions in this case. Translation vectors in such a structure, for example, will be a vector connecting an atom with the next closest neighbor, or a vector equal to three times the vector connecting two nearest atoms.

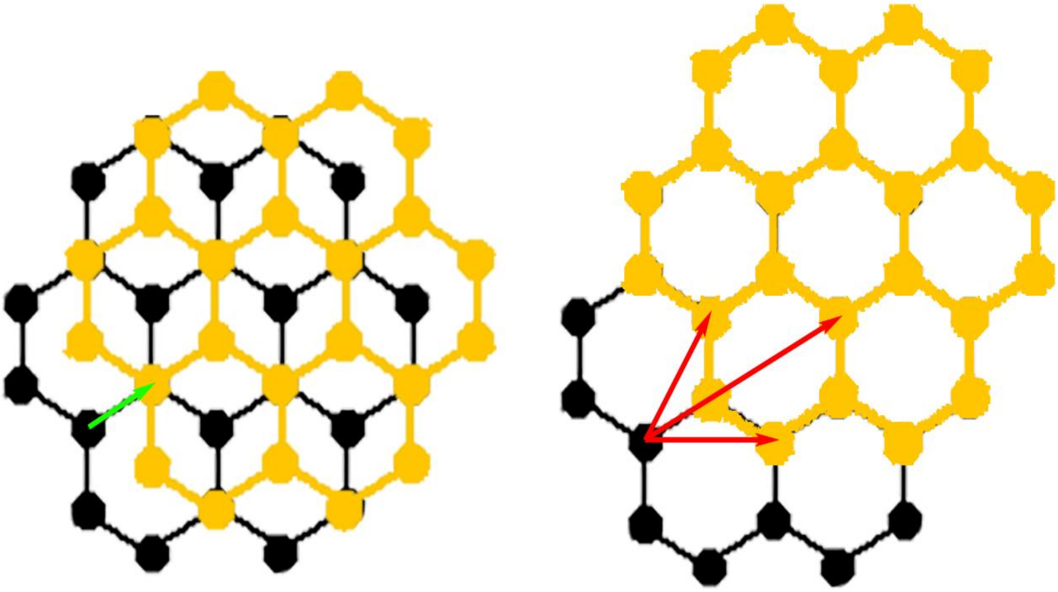

Figure 2.3 - The displacement of the structure by a vector connecting two identical atoms is not always a valid translation, so, for example, in the basal plane of graphite there are two non-equivalent positions of atoms.

In addition, when translating vertically to a vector connecting two adjacent layers, there will be an incomplete coincidence for the positions of the atoms due to the displacement between layers in the structure of graphite (Figure 2.4). For this reason, the spatial lattice of graphite, that is, the set of points corresponding to the equivalent positions of atoms, will differ significantly in appearance from the image of the crystal structure. In this case, the atomic motif will contain four carbon atoms.

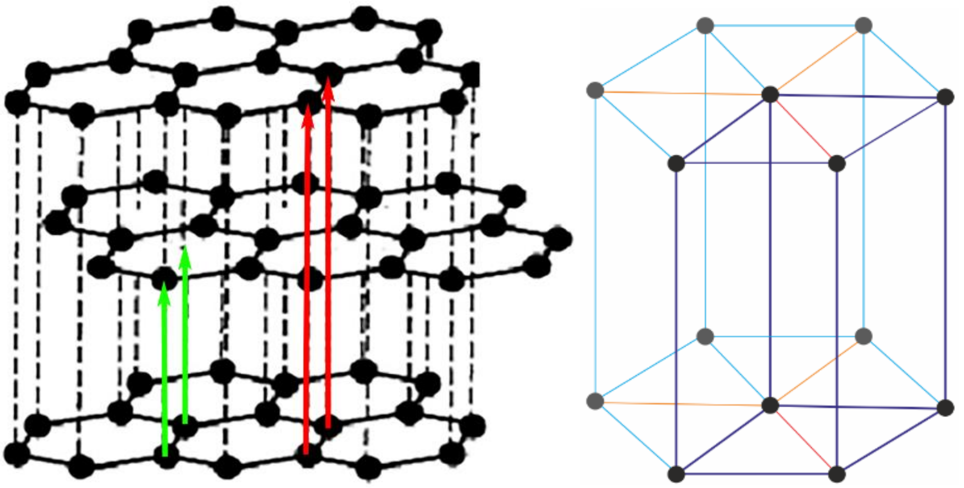

Figure 2.4 - Graphite structure and spatial lattice of graphite.

It is important to note that the term *crystal lattice* is widely used, which is a synonym for *spatial lattice* in crystallography. However, due to the fact that the lattices of some simple structures are indistinguishable from the images of the latter, this term partially merges with the concept of *crystal structure* and is sometimes used in this sense, including scientific literature, which we will consider as an incorrect identification.

3. Elementary cell

A spatial lattice, due to the nature of translational symmetry, can be represented as a dense packing of parallelepipeds. At the same time, the choice of an elementary parallelepiped from which a spatial lattice can be made is fundamentally ambiguous (Figure 3.1), which is even better illustrated on a flat grid.

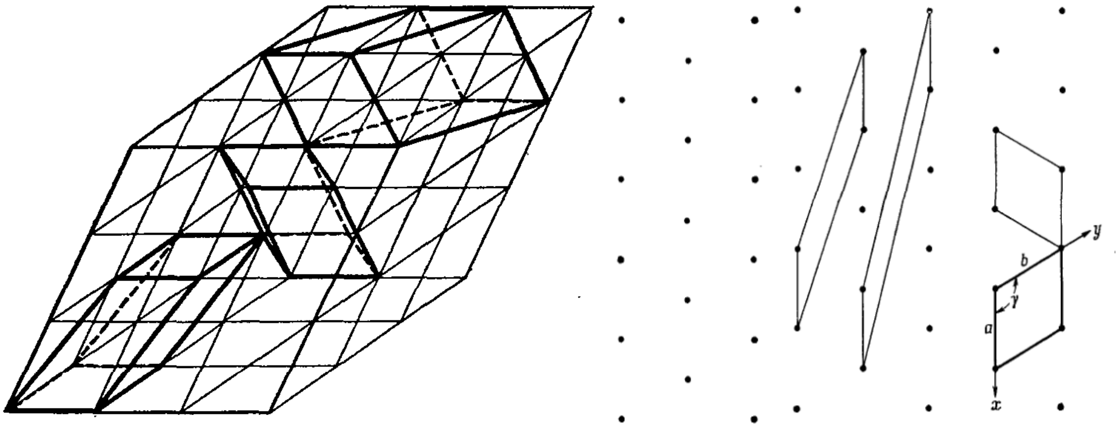

Figure 3.1 - The ambiguity of the choice of an elementary cell in a spatial lattice or a flat grid.

The selected elementary box is called *the elementary cell*. The edges of the elementary cell, since they connect the nodes of the lattice, are translation vectors. The elementary cell is determined by three vectors - *the main translation vectors* ($\mathbf{a}, \mathbf{b}, \mathbf{c}$). The cell is characterized by the lengths of these vectors and the angles between them. There are 6 values in total: $a, b, c, \alpha, \beta, \gamma$ are the *parameters of the cell* (Figure 3.2).

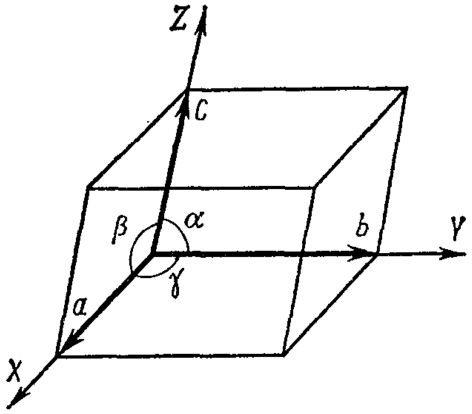

Figure 3.2 - Elementary cell.

An elementary cell is called *primitive* if each cell contains one lattice node. Usually, the smallest possible cell is chosen, but at the same time it should reflect the symmetry of the lattice as much as possible and have as many right angles as possible. For some structures *non-primitive cells* are more suitable, as it is the case for *face-centered cubic lattice*, when primitive elementary cells do not have the symmetry of a cube, in contrast to a correctly chosen non-primitive one (Figure 3.3).

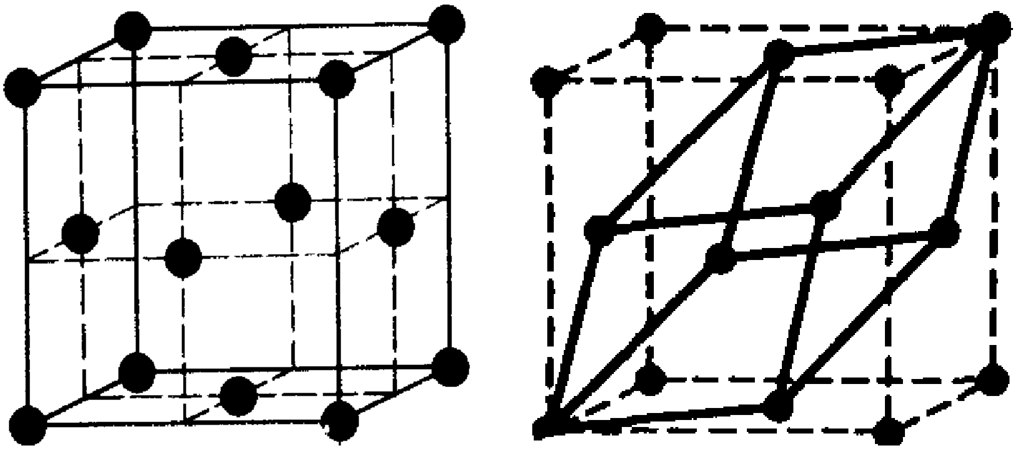

Figure 3.3 - The choice of a non-primitive elementary cell in a face-centered cubic lattice is more preferable.

Regardless of whether a primitive or non-primitive cell is chosen, their dense packing constitutes the original spatial lattice.

4. Crystallographic indexing

The main translation vectors define *the crystallographic coordinate system*. Thus, the choice of an elementary cell determines the coordinate system in which the positions of the lattice nodes or atoms of the structure will be indicated, therefore, it is a very important aspect. In general, $a \neq b \neq c$ and $\alpha \neq \beta \neq \gamma$, and the coordinate system is oblique. However, in many structures it is possible to select a unit cell, at least some of whose angles are straight and/or some edges are equal in length, which is a more preferable option. This is what determines the rules for selecting elementary cells.

4.1. Node indexing

Let us choose one of the lattice nodes as the origin of the crystallographic coordinate system. Any other lattice node is determined by the radius vector $\vec{\boldsymbol{R}} = m\boldsymbol{a} + n\boldsymbol{b} + p\boldsymbol{c}$. In this case, the vertices of various cells of the lattice will be characterized by integers *m*, *n*, *p*, which is the convenience of such a coordinate system. The numbers *m*, *n*, *p* are *node indices*, together with the elementary cell they determine its physical coordinates in space. Node indices are usually written without commas in double square brackets, with a minus sign placed above the digit to shorten the entry, for example: $[\![100]\!], [\![111]\!], [\![112]\!], [\![10\bar{1}]\!], [\![11\bar{2}]\!]$.

The vertices of the elementary cell closest to the reference point correspond to the indices $[\![100]\!], [\![010]\!], [\![001]\!]$. In this case, the node at the origin has indices $[\![000]\!]$. For example, the third index of all nodes lying in the ab plane is 0 (Figure 4.1).

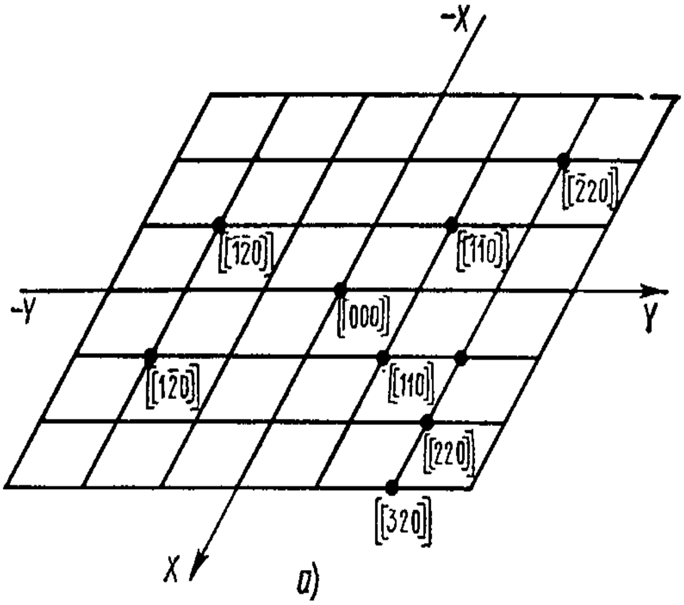

Figure 4.1 - An example of lattice nodes indexing.

If the cell is non-primitive, that is, it contains nodes inside itself, their indices will be, respectively, fractional (Figure 4.2). The coordinates of atoms inside the cell can also be expressed as fractional indices.

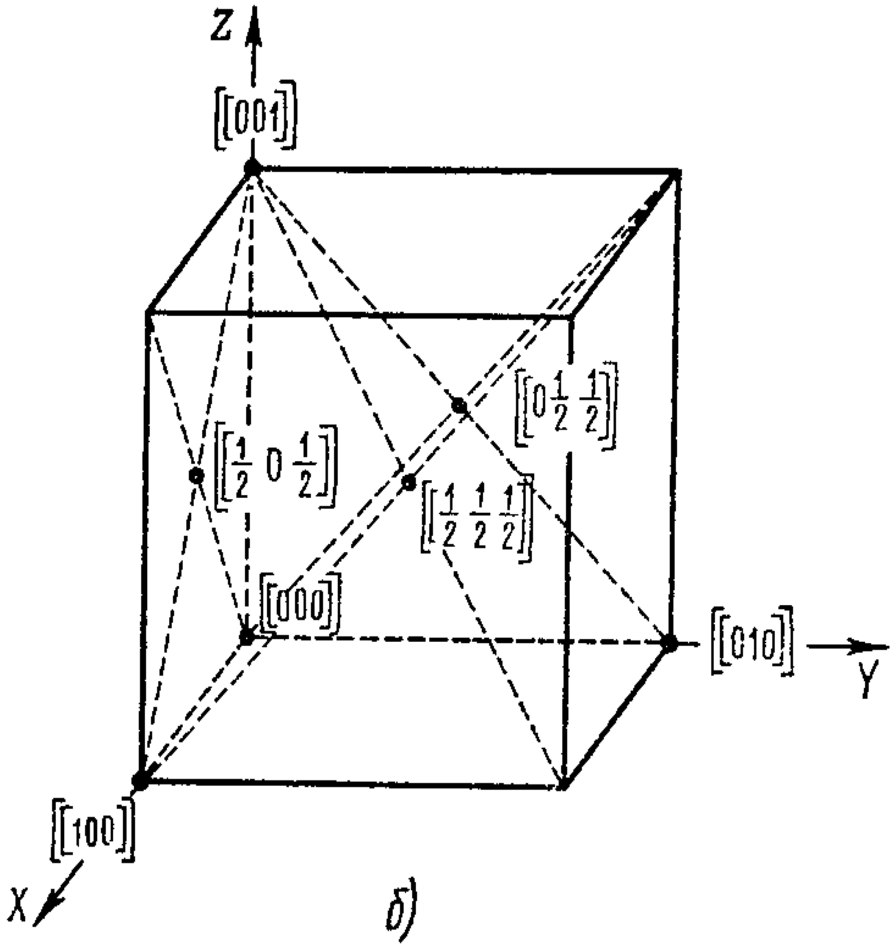

Figure 4.2 - An example of indicating nodes within a non-primitive cell.

4.2. Direction indication

Nodal rows in the lattice correspond to atomic rows in the structure, which appear, for example, as edges of crystalline polyhedra. Since the various nodal rows of the same direction in the lattice are identical, the characteristic of the row is precisely its direction.

Raw direction indices $[uvw]$ are the coordinates of the vector connecting two nodes in this raw, expressed in the crystallographic system: $\boldsymbol{R_2} - \boldsymbol{R_1} = u\boldsymbol{a} + v\boldsymbol{b} + w\boldsymbol{c}$, are written in single square brackets (Figure 4.3). In this case, the indices are reduced by a common divisor and converted to an integer form if necessary. Note, for example, that the indices $[100], [010], [001]$ correspond to the main translations $\boldsymbol{a}, \boldsymbol{b}, \boldsymbol{c}$ and, consequently, to the directions of the coordinate axes.

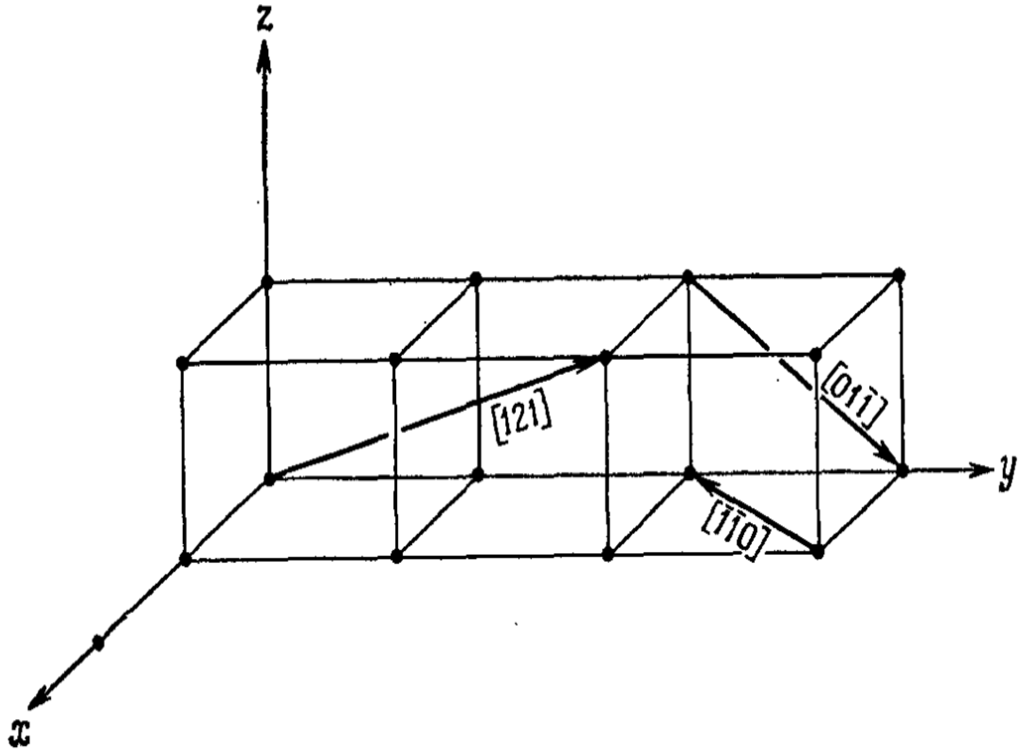

Figure 4.3 - Examples of direction indices in the lattice.

It is useful to note that many different directions belong to each plane of the lattice. For example, in the plane parallel to the lower face of the elementary cell, that is, to the vectors $\boldsymbol{a}$ and $\boldsymbol{b}$, lie all directions in which the third index is equal to zero (Figure 4.4).

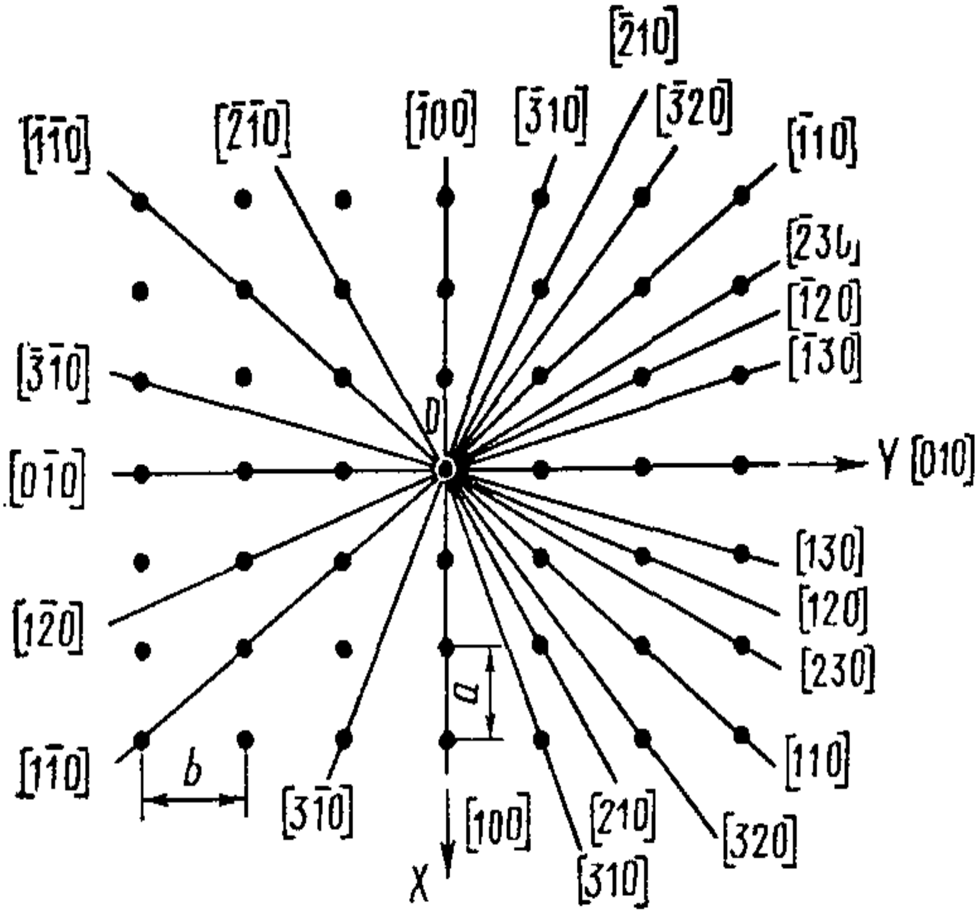

Figure 4.4 - Directions belonging to the plane *ab* lattice, parallel to the lower face of the unit cell.

4.3. Plane Indices

Nodal planes, which appear, for example, as faces of a crystalline polyhedron, are also characterized mainly by their orientation, since all planes of the same inclination in the lattice are identical.

At the end of the 18th century, René Just Haüy derived the "law of rational relations" (*Hauy's law*), which states that the double ratio of the lengths of the segments cut off on the axes by the continuations of the two faces of the crystal is equal to the ratio of small integers. It was this law that allowed Haüy to suggest that crystals are composed of "integrating molecules" in the form of a parallelepiped, long before direct observation of the structure of crystals.

The ratio of the segments cut off on the axes by planes belonging to the same *system of planes*, that is, parallel to each other, is the same for the entire system, but different for different systems (Figure 4.5). In the case of a spatial lattice, this ratio for the pair of axes depicted in the figure will be the number *ma/nb*, where *m* and *n* are integers, *a* and *b* are lattice parameters, with *m/n* most likely being the ratio of small integers (1 :1 and 1:2 in the above example). On a macroscopic scale, the lattice parameters are imperceptible and the numbers *m* and *n* cannot be determined, but nevertheless, *the double ratios* of the segments lengths of the axes, that is, (m_1a / n_1b): $(m_2a / n_2b) = (m_1/n_1)$: (m_2/n_2), will still be treated as small integers, since the lattice parameters *a* and *b* in this expression will cancel out.

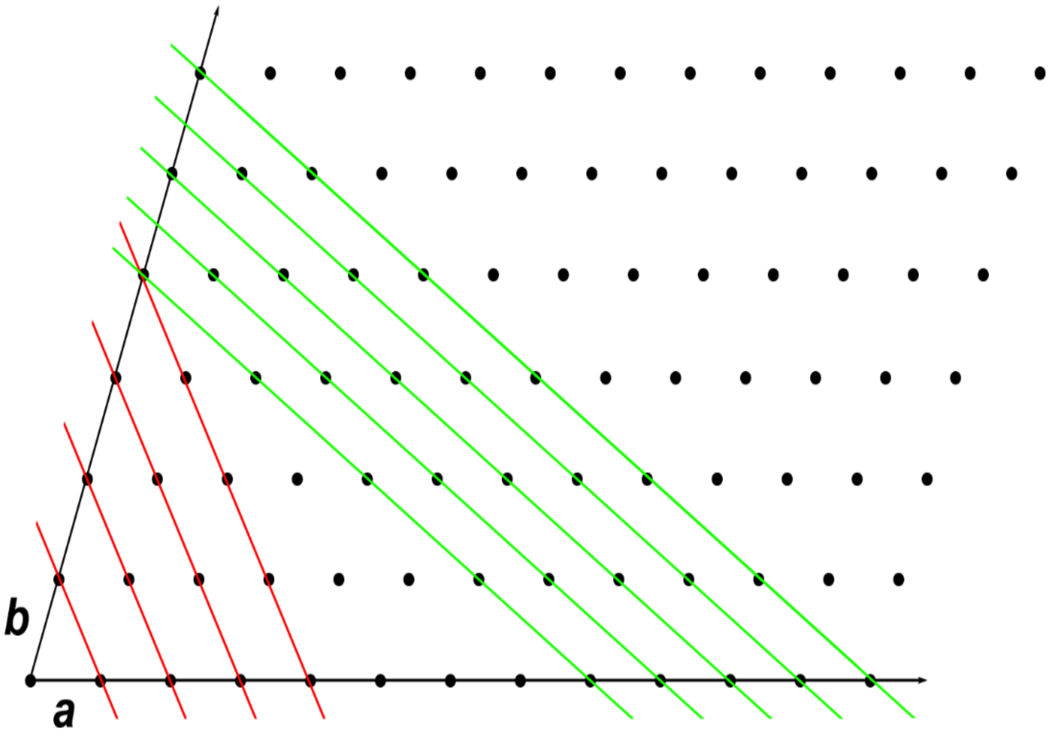

Figure 4.5 - An explanation of Haüy's law.

In modern crystallography, the slope of the plane is characterized by the lengths of the segments cut off by the plane on the coordinate axes, measured in the units of the corresponding lattice parameters (Figure 4.6), that is, a set of three numbers *m, n, p* (in this figure, for example, $\frac{1}{2}:\frac{1}{2}:1$, $1:1:2$, $\frac{3}{2}:\frac{3}{2}:3$, $2:2:4$ etc.). If we bring the numbers *mnp* to an integer form, reducing also by a common divisor, then we get a set of indices *qrs* (112 in the above example) common to the entire system of planes. Indices *qrs* are the so-called *Weiss parameters*.

The Weiss parameters correspond to what is obtained when using the Haüy approach, if we take as a basic plane - the plane with indices (111) (the so-called "unity plane").

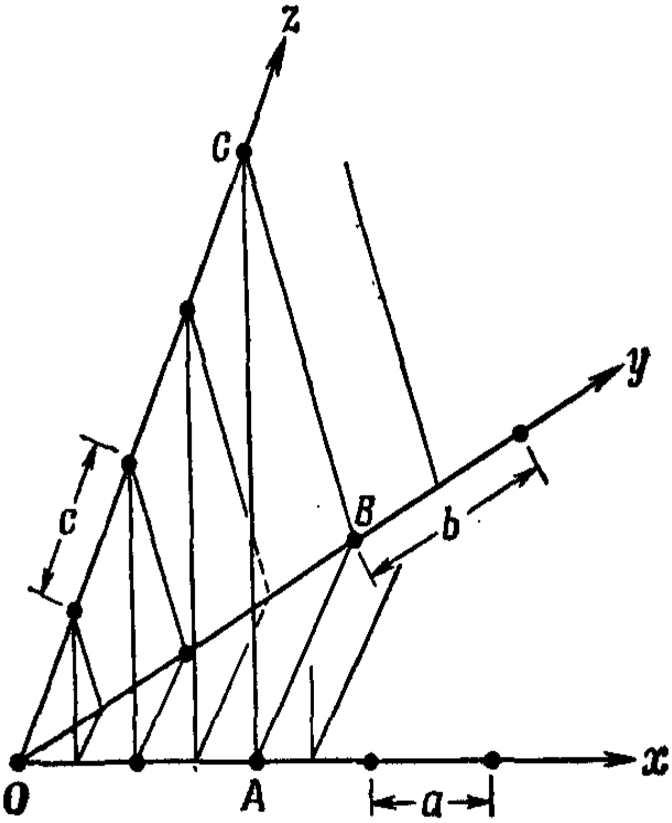

Figure 4.6 - Determining the indices for the system of planes.

In crystallography *Miller indices* are more widely used , which are the reciprocals of the Weiss parameters, also reduced to an integer form:

$$h:k:l = \frac{1}{q}:\frac{1}{r}:\frac{1}{s} \qquad (4.1)$$

In our example, we get $\frac{1}{1}:\frac{1}{1}:\frac{1}{2} \rightarrow 2:2:1$; Miller indices are written in parentheses - (221). Such indexes have a number of advantages. For example, the Weiss parameters of the planes parallel to the faces of the unit cell are equal to 1∞∞, ∞1∞, ∞∞1, respectively, since such planes are parallel to the corresponding crystallographic axes and do not intersect with them. The Miller indices of such planes will be (100), (010), (001), respectively, which is a somewhat more descriptive expression (Figure 4.7).

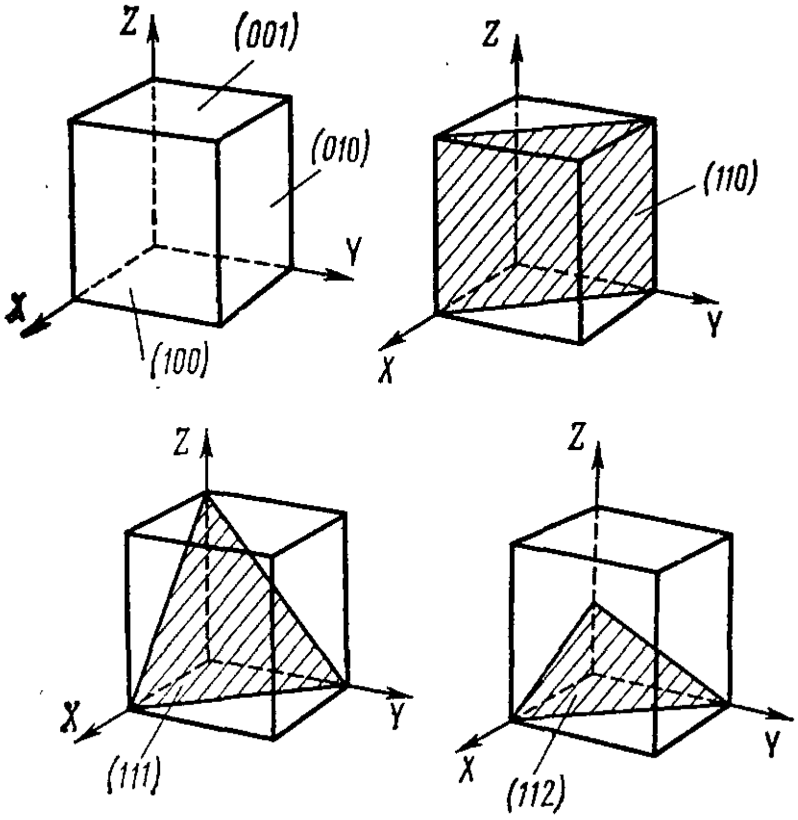

Figure 4.7 - Examples of indexing planes on the example of a cubic cell.

Different directions can be parallel to the same plane, and different planes can be parallel to the same direction. It can be seen in the figure that, for example, the planes (010), (100), (110) are all parallel to the direction [001], that is, the vertical edge of the cell. The set of planes parallel to one direction is called *the zone*, and the direction $[uvw]$ to which these planes are parallel is called *the zone axis*. In particular, the planes (010), (100), (110) belong to the same zone, the axis of this zone is [001]. The zone appears on crystalline polyhedra as a set of mutually parallel faces, a typical example is the side faces of hexagonal prisms of rock crystal or crystals similar in structure (Figure 4.8).

Figure 4.8 - Faces that have a common direction make up the zone.

The main advantage of the Miller indices, defined through the inverse ratios of the lengths of the segments cut off by the plane on the crystallographic axes, is the following. Let us try to find out whether some direction $[uvw]$ belongs to some plane with Miller indices (hkl). The latter implies that this plane intersects the crystallographic axes at the points $\frac{1}{h}\boldsymbol{a}, \frac{1}{k}\boldsymbol{b}, \frac{1}{l}\boldsymbol{c}$, or is parallel to such a plane ($\boldsymbol{a}, \boldsymbol{b}, \boldsymbol{c}$ are the main translations, the basis of the crystallographic coordinate system). The direction [uvw], defined by the vector $u\boldsymbol{a} + v\boldsymbol{b} + w\boldsymbol{c}$, is parallel to the plane (hkl) if it is perpendicular to the normal to it. The normal to the plane can be obtained by the cross product of two vectors lying in our plane, for example, $\left(\frac{1}{h}\boldsymbol{a} - \frac{1}{k}\boldsymbol{b}\right)$ and $\left(\frac{1}{h}\boldsymbol{a} - \frac{1}{l}\boldsymbol{c}\right)$. Then the condition of direction [uvw] being parallel to the plane (hkl) takes the form $(u\boldsymbol{a} + v\boldsymbol{b} + w\boldsymbol{c}) \cdot \left(\frac{1}{h}\boldsymbol{a} - \frac{1}{k}\boldsymbol{b}\right) \times \left(\frac{1}{h}\boldsymbol{a} - \frac{1}{l}\boldsymbol{c}\right) = 0$, which, as it is easy to show, reduces to a simple expression:

$$uh + vk + wl = 0 \tag{4.2}$$

This expression - *the rule of zones*, allows one to easily determine both the indices of planes parallel to one direction, that is, belonging to the same zone, and the indices of directions lying in a certain plane. Thus, the Miller indices, determined in a very non-obvious way, have a significant analytical advantage.

4.4. Reciprocal lattice

This simplicity of the zone rule is not accidental. It can be noted that the expression $uh + vk + wl = 0$ resembles the condition of orthogonality of two vectors in a rectangular coordinate system.

In the Cartesian coordinate system, the plane, generally defined by the relation $\boldsymbol{r} \cdot \boldsymbol{n} = C$ (r is the radius vector, n is the normal to the plane, C is a constant), cuts off the segments X, Y, Z on the axes that satisfy the equation of the plane:

$$X\boldsymbol{e}_x \cdot n = C \;\rightarrow\; \frac{C}{X} = \boldsymbol{e}_x \cdot \boldsymbol{n} = n_x$$

$$Y\boldsymbol{e}_y \cdot n = C \;\rightarrow\; \frac{C}{Y} = \boldsymbol{e}_y \cdot \boldsymbol{n} = n_y \qquad (4.3)$$

$$Z\boldsymbol{e}_z \cdot n = C \;\rightarrow\; \frac{C}{Z} = \boldsymbol{e}_z \cdot \boldsymbol{n} = n_z$$

Thus, it directly follows that the reciprocals of the lengths of the segments of the axes are equal to the coordinates of the vector parallel to the normal of the given plane.

However, the zone rule is also applicable in the case of oblique crystallographic coordinate systems. We should determine a kind of a system in which the numbers *h*, *k*, *l* are the coordinates of the normal to the planes (hkl). Let us find its basis, which we denote as $\boldsymbol{a}^*, \boldsymbol{b}^*, \boldsymbol{c}^*$.

According to our condition, the vector $h\boldsymbol{a}^* + k\boldsymbol{b}^* + l\boldsymbol{c}^*$ must be perpendicular to the vectors lying in the plane (hkl), for example, $\left(\frac{1}{h}\boldsymbol{a} - \frac{1}{k}\boldsymbol{b}\right)$ and $\left(\frac{1}{h}\boldsymbol{a} - \frac{1}{l}\boldsymbol{c}\right)$, and this must be true for any *h*, *k*, *l*, which leads to the following table of scalar products for the vectors of the desired basis and the original one:

*	$\boldsymbol{a}^*$	$\boldsymbol{b}^*$	$\boldsymbol{c}^*$
$\boldsymbol{a}$	1	0	0
$\boldsymbol{b}$	0	1	0
$\boldsymbol{c}$	0	0	1

(4.4)

Thus, for example, the vector $\boldsymbol{a}^*$ must be perpendicular to vectors $\boldsymbol{b}$ and $\boldsymbol{c}$, that is, be parallel to their vector product $\boldsymbol{b} \times \boldsymbol{c}$. The length of the vector $\boldsymbol{a}^*$ is determined from the condition $\boldsymbol{a}^{*}\boldsymbol{a} = \mathbf{1}$, which leads to the expression $\boldsymbol{a}^{*} = \frac{\boldsymbol{b}\times\boldsymbol{c}}{\boldsymbol{a}\cdot\boldsymbol{b}\times\boldsymbol{c}}$. Note that $\boldsymbol{a}\cdot\boldsymbol{b}\times\boldsymbol{c}$ is equal to the unit cell volume *V*. Thus, we get:

$$\boldsymbol{a}^{*} = \frac{\boldsymbol{b}\times\boldsymbol{c}}{\boldsymbol{a}\cdot\boldsymbol{b}\times\boldsymbol{c}};\ \boldsymbol{b}^{*} = \frac{\boldsymbol{c}\times\boldsymbol{a}}{\boldsymbol{a}\cdot\boldsymbol{b}\times\boldsymbol{c}};\ \boldsymbol{c}^{*} = \frac{\boldsymbol{a}\times\boldsymbol{b}}{\boldsymbol{a}\cdot\boldsymbol{b}\times\boldsymbol{c}} \tag{4.5}$$

The vectors $\boldsymbol{a}^{*}, \boldsymbol{b}^{*},$ and $\boldsymbol{c}^{*}$ define a new crystallographic coordinate system and a new lattice - *the reciprocal lattice*. The dimension of the reciprocal lattice is inverse to the dimension of the original lattice - $[m] \rightarrow [\frac{1}{m}]$.

Integer indices *h*, *k*, *l* define the coordinates of the reciprocal lattice nodes, thus, the reciprocal lattice nodes correspond to the planes of the spatial lattice.

Basic properties of the reciprocal lattice:

1. The reciprocal lattice vector $\boldsymbol{H_{hkl}} = h\boldsymbol{a}^{*} + k\boldsymbol{b}^{*} + l\boldsymbol{c}^{*}$ is as perpendicular to the plane (*hkl*) of the direct lattice.
2. The modulus of the reciprocal lattice vector is equal to the reciprocal of the interplanar distance: $|\boldsymbol{H_{hkl}}| = \frac{1}{d_{hkl}}$.
3. The volume of the unit cell of the reciprocal lattice is the reciprocal of the unit cell of the direct lattice: $V^{*} = \frac{1}{V}$.
4. The reciprocal lattice to the reciprocal lattice is the original direct lattice. In other words, the basis inverse to the inverse basis $\boldsymbol{a}^{*}, \boldsymbol{b}^{*}, \boldsymbol{c}^{*}$ is the original basis $\boldsymbol{a}, \boldsymbol{b}, \boldsymbol{c}$.

The second property is of particular importance in structural crystallography. In particular, it shows that if the unit cell decreases (under the action of mechanical stresses or for other reasons), then the reciprocal lattice, on the contrary, expands. It also follows that systems of planes with large indices are characterized by smaller interplanar distances (Figure 4.9).

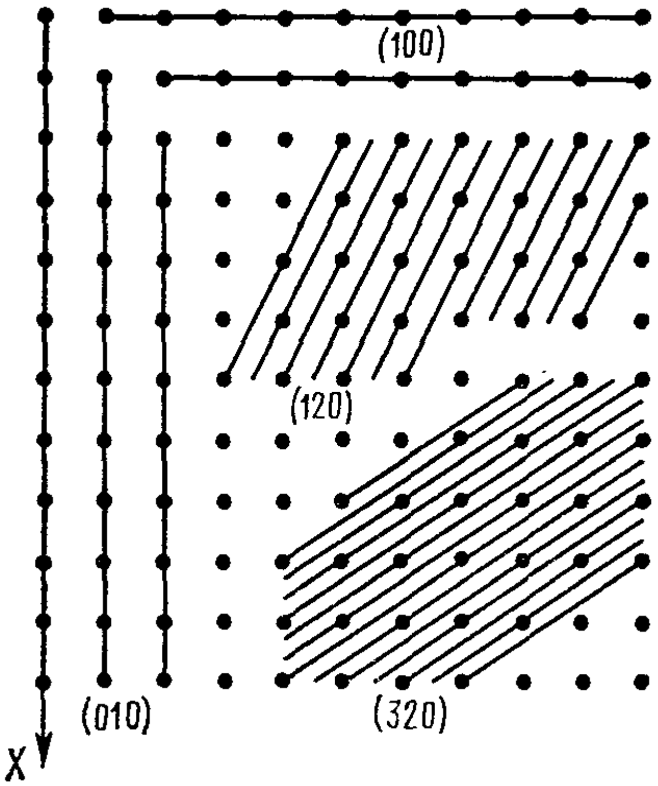

Figure 4.9 - Reducing the interplanar distance with increasing indices.

The reciprocal lattice is a fundamental characteristic of a crystal, just like the spatial lattice. The reciprocal lattice is of great importance for the analysis of diffraction on crystal structures of X-rays, electrons and neutrons, since such diffraction patterns are images of the reciprocal lattice. This is explained quite simply, as the reciprocal lattice is actually the Fourier image of the spatial lattice, which is not surprising, because some properties of the reciprocal lattice correspond to the properties of the Fourier transform. At the same time, in practice, the diffraction of quanta with a small wavelength is Fraunhofer diffraction, that is, the Fourier image of the object on which the radiation is scattered, and, thus, are images of the reciprocal lattice. For the same reason, the reciprocal lattice is also important for the analysis of the movement of various particles and quasiparticles in crystals, since it is simply a representation of the crystal in *the reciprocal space*, that is, in *the momentum space*.

5. Basic formulas of structural crystallography

Knowing the indices of the vector, for example, $[uvw]$, and the lattice parameters *a, b, c, α, β, γ,* we can calculate its length as the length of the vector $ua + vb + wc$:

$$R = \sqrt{(u\boldsymbol{a} + v\boldsymbol{b} + w\boldsymbol{c})^2} = \sqrt{u^2a^2 + v^2b^2 + w^2c^2 + 2uvabcos\,\gamma\ + 2vwbccos\,\alpha\ + 2uwaccos\,\beta} \qquad (5.1)$$

The formula is greatly simplified if, for example, the unit cell is a rectangular parallelepiped, that is, *α=β=γ*=90°, therefore, $cos\,\alpha\ = cos\,\beta\ = cos\,\gamma\ = 0$. The length of the vector $[uvw]$ is then:

$$R = \sqrt{u^2a^2 + v^2b^2 + w^2c^2} \qquad (5.2)$$

The expression becomes even simpler if the unit cell has the shape of a cube, that is, *a=b=c* and *α=β=γ =90*°

$$R = \sqrt{u^2 + v^2 + w^2}\,a \qquad (5.3)$$

The angle between two directions can be calculated as the angle between corresponding vectors $\boldsymbol{R_1} = u_1\boldsymbol{a} + v_1\boldsymbol{b} + w_1\boldsymbol{c}$ and $\boldsymbol{R_2} = u_2\boldsymbol{a} + v_2\boldsymbol{b} + w_2\boldsymbol{c}$:

$$cos\,\varphi\ = \frac{\boldsymbol{R_1}\cdot\boldsymbol{R_2}}{|\boldsymbol{R_1}||\boldsymbol{R_2}|} = \frac{(u_1\boldsymbol{a} + v_1\boldsymbol{b} + w_1\boldsymbol{c})(u_2\boldsymbol{a} + v_2\boldsymbol{b} + w_2\boldsymbol{c})}{\sqrt{(u_1\boldsymbol{a} + v_1\boldsymbol{b} + w_1\boldsymbol{c})^2}\sqrt{(u_2\boldsymbol{a} + v_2\boldsymbol{b} + w_2\boldsymbol{c})^2}} = \qquad (5.4)$$

$$= \frac{u_1u_2a^2 + v_1v_2b^2 + w_1w_2c^2 + (u_1v_2 + u_2v_1)abcos\,\gamma\ + (v_1w_2 + v_2w_1)bccos\,\alpha\ + (u_1w_2 + u_2w_1)accos\,\beta}{\sqrt{u_1^2a^2 + v_1^2b^2 + w_1^2c^2 + 2u_1v_1abcos\,\gamma\ + 2v_1w_1bccos\,\alpha\ + 2u_1w_1accos\,\beta}\ \sqrt{u_2^2a^2 + v_2^2b^2 + w_2^2c^2 + 2u_2v_2abcos\,\gamma\ + 2v_2w_2bc\,cos\,\alpha\ + 2u_2w_2ac\,cos\,\beta}}$$

This expression is also simplified in the case of *α=β=γ*=90° to:

$$cos\,\varphi\ = \frac{u_1u_2a^2 + v_1v_2b^2 + w_1w_2c^2}{\sqrt{u_1^2a^2 + v_1^2b^2 + w_1^2c^2}\sqrt{u_2^2a^2 + v_2^2b^2 + w_2^2c^2}} \qquad (5.5)$$

and for a cubic elementary cell – up to:

$$cos\,\varphi\ = \frac{u_1u_2a^2 + v_1v_2b^2 + w_1w_2c^2}{\sqrt{u_1^2a^2 + v_1^2b^2 + w_1^2c^2}\sqrt{u_2^2a^2 + v_2^2b^2 + w_2^2c^2}} \qquad (5.6)$$

A similar approach is applicable for planes. For example, the period of the system of planes (hkl) is equal to the inverse modulus of the corresponding reciprocal lattice vector $\boldsymbol{H}_{hkl} = h\boldsymbol{a}^* + k\boldsymbol{b}^* + l\boldsymbol{c}^*$, thus:

$$d_{hkl} = \frac{1}{\sqrt{(h\boldsymbol{a}^* + k\boldsymbol{b}^* + l\boldsymbol{c}^*)^2}} \tag{5.7}$$

In general case, this also implies extremely cumbersome expressions, which are simplified at $\alpha=\beta=\gamma=90°$ to:

$$d_{hkl} = \frac{1}{\sqrt{\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}}}$$

In the case of a cubic unit cell, the interplanar distance d_{hkl} is:

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \tag{5.8}$$

The angle between two planes $(h_1k_1l_1)$ and $(h_2k_2l_2)$ can be defined as the angle between the two corresponding reciprocal lattice vectors:

$$cos\varphi = \frac{\boldsymbol{H}_{h_1k_1l_1} \cdot \boldsymbol{H}_{h_2k_2l_2}}{|\boldsymbol{H}_{h_1k_1l_1}||\boldsymbol{H}_{h_2k_2l_2}|} \tag{5.9}$$

Which for $\alpha=\beta=\gamma=90°$ simplifies to:

$$cos\ \varphi = \frac{\frac{h_1h_2}{a^2} + \frac{k_1k_2}{b^2} + \frac{l_1l_2}{c^2}}{\sqrt{\frac{h_1^2}{a^2} + \frac{k_1^2}{b^2} + \frac{l_1^2}{c^2}}\sqrt{\frac{h_2^2}{a^2} + \frac{k_2^2}{b^2} + \frac{l_2^2}{c^2}}} \tag{5.10}$$

and for a cell in the form of a cube:

$$cos\ \varphi = \frac{h_1h_2 + k_1k_2 + l_1l_2}{\sqrt{h_1^2 + k_1^2 + l_1^2}\sqrt{h_2^2 + k_2^2 + l_2^2}} \tag{5.11}$$

Condition of orthogonality for two directions or two planes is $cos\ \varphi = 0$, that is, the numerator in the corresponding expressions must be equal to zero. Obviously, in general case of an oblique cell, it is practically impossible to find two directions or two systems of planes perpendicular to each other, since the cell parameters are relatively arbitrary values. Even in the case of $\alpha=\beta=\gamma=90°$, only vectors parallel to different faces of the elementary cell can be perpendicular, when most of the indices are equal to zero. Only in a structure characterized by a cubic cell, this is quite common, since finding two triples of integers, for example, $[u_1v_1w_1]$ and , satisfying the condition $u_1u_2+v_1v_2+w_1w_2=0$, is quite possible (for example, the directions $[1\bar{1}0]$ and $[110]$ or [112] and $[11\bar{1}]$).

The possibility of calculating the angle between some direction $[uvw]$ and the plane (hkl) is also of interest. The angle between the vector $\boldsymbol{R}=u\boldsymbol{a}+v\boldsymbol{b}+w\boldsymbol{c}$ and the normal to the plane $\boldsymbol{H}_{\boldsymbol{hkl}}=h\boldsymbol{a}^*+k\boldsymbol{b}^*+l\boldsymbol{c}^*$, taking into account the matrix of ratios for the vectors $\boldsymbol{a},\boldsymbol{b},\boldsymbol{c}$ and $\boldsymbol{a}^*,\boldsymbol{b}^*,\boldsymbol{c}^*$, equals:

$$\cos\varphi=\frac{uh+vk+wl}{|\boldsymbol{R}||\boldsymbol{H}_{\boldsymbol{hkl}}|} \tag{5.12}$$

In general case, moduli of vectors are calculated using rather cumbersome expressions, but it is essential that $\cos\varphi=0$ for $uh+vk+wl=0$. This is the aforementioned zone rule, since the cosine is zero if the $[uvw]$ perpendicular to the normal of the plane, that is, parallel to the plane itself. In this case, if the condition of orthogonality for the direction is $[uvw]$ to the plane (hkl) will have the form $\cos\varphi=1$. Naturally, there are practically no nodal rows perpendicular to the planes in an arbitrary lattice, and only with a cubic elementary cell this equation will have a solution in integers. It is easy to show that in a cubic lattice $[uvw]\perp(hkl)$ only if $u=h$, $v=k$, $w=l$ or they differ by a common factor, i.e. $uvw\propto hkl$. That is, in a cubic lattice, for example, the direction $[111]$ is perpendicular to the plane (111).

6. Miller-Brave Indices

Lattices of many crystals have rather high symmetry. If one can choose a cubic elementary cell, then the planes with indices (100), (010), (001) will correspond to different faces of the cube. For example, indexes (110), $(1\bar{1}0)$, (011), $(01\bar{1})$ etc. correspond to the diagonal planes of the cube, which are also similar to each other, and the indices $[111]$, $[11\bar{1}]$, $[1\bar{1}1]$, $[\bar{1}11]$ correspond the directions along the main diagonals of the cube. Thus, similar directions and planes, including similar crystal faces, will be described by similar sets of indices. It does not always make sense to distinguish such planes or faces from each other, therefore, a simplified generalized notation of indices in curly brackets is used to designate them. For example, $\{100\}$ means the faces of a cube, and $\{110\}$ means its diagonal planes. It is true also for directions, but the notation in angle brackets is used – $\langle 100 \rangle$ edges of the cube, $\langle 111 \rangle$ its main diagonals, etc.

In hexagonal lattices, like those of graphite, the unit cell, which must be parallelepiped, is chosen as a rhombic prism with an angle of 120° at the base (Figure 6.1).

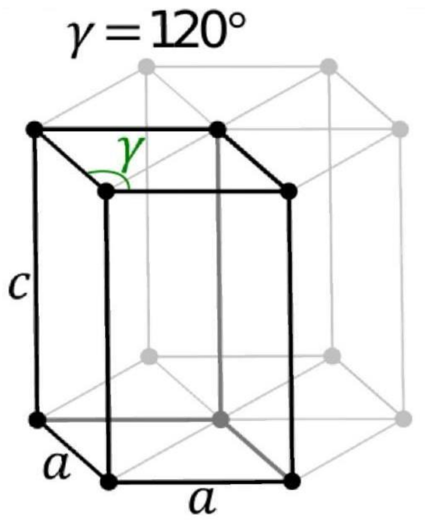

Figure 6.1 - Unit cell of a hexagonal lattice.

The Miller indices of the faces of a hexagonal prism, which is easy to distinguish in such lattices, will be (100), (010) and $(1\bar{1}0)$. That is, not exactly similar sets of indices correspond to similar faces. Moreover, the indices of three similar planes cutting rhombic prisms along the major diagonal are (110), $(2\bar{1}0)$, $(\bar{1}20)$. That is, in hexagonal lattices, the indices $(1\bar{1}0)$ and (110) correspond to planes of a completely different type, which significantly distinguishes them from the case of cubic lattices and creates prerequisites for errors.

In order to correct this peculiarity of indexing in hexagonal lattices, the following trick is used. The fourth coordinate axis is introduced along the translation vector ***e*** at an angle of 120° to the vectors ***a*** and ***b*** (Figure 6.2). Another index *i* is determined along with this axis, like the others, according to the rules of Miller indices, that is, by the length of the segment cut off by the plane on it. Such sets of four indices - $(hkil)$ - are called *Miller-Bravais indices*.

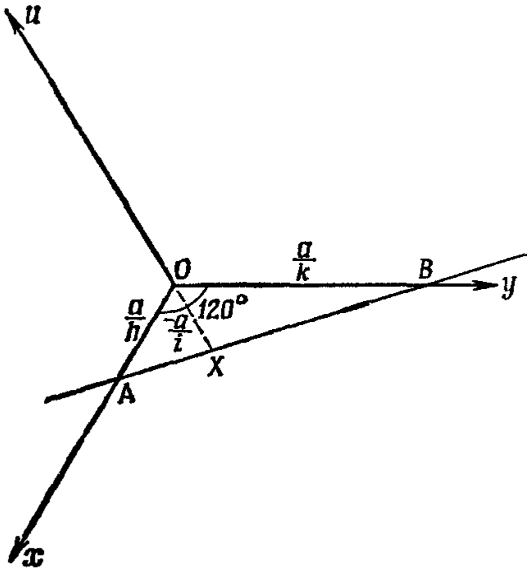

Figure 6.2 - The principle of determining the Miller-Bravais indices by adding the fourth coordinate axis.

Since the complementary axis is the bisector of the ***a*** and ***b***, it is easy to show (since $sin\,\frac{120°}{2} = sin\,120°$) that the Miller-Bravais indices $(hkil)$ obey the following rule:

$$h + k + i = 0 \quad \text{or} \quad i = -h - k \qquad (6.1)$$

Moreover, the indices *h*, *k* and *l* remain the same as in conventional indexing. For example, the plane of the hexagonal grid itself (001) will acquire indices (0001). Thus, the plane indices in the three-index Miller system and the four-index Miller-Bravais system have a transparent relationship:

Miller	**Miller-Bravais**	**Miller**	**Miller-Bravais**
(100)	$(10\bar{1}0)$	$(2\bar{1}0)$	$(2\bar{1}\bar{1}0)$
(010)	$(01\bar{1}0)$	$(\bar{1}20)$	$(\bar{1}2\bar{1}0)$
$(1\bar{1}0)$	$(1\bar{1}00)$	(110)	$(\bar{1}\bar{1}20)$

Moreover, in the new system, similar planes are denoted by similar sets of indices, and essentially different planes - by essentially different indices. This allows using the generalized expressions $\{10\bar{1}0\}$, $\{11\bar{2}1\}$, etc. (Figure 6.3).

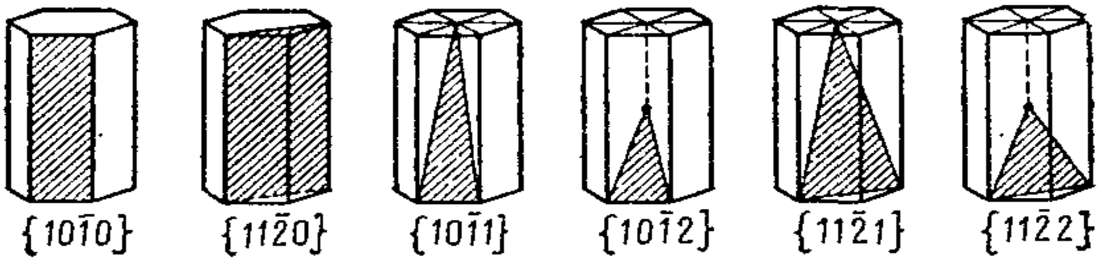

Figure 6.3 - Examples of indexing planes with Miller-Brave indices.

Thus, in order to obtain the Miller-Bravais indices of any plane, we should add one more index $i = -h - k$. To return to the three-index system, simply remove the third index from the record.

This is not the case with the Miller-Bravais indices of vectors and *directions*. The direction indices are determined in the same four-axis coordinate system, but since the decomposition of a vector in a basis of four vectors is not unique, we require that the resulting four indices $[uvtw]$ satisfy the condition $u + v + t = 0$, like the indices of the planes. Thus, the indices of the vector $\boldsymbol{R}$ are determined by the following pair of conditions:

$$\boldsymbol{R} = u\boldsymbol{a} + v\boldsymbol{b} + t\boldsymbol{e} + w\boldsymbol{c} \quad u + v + t = 0 \tag{6.2}$$

From equation (6.2) it follows a non-trivial relationship between the indices of directions $[u'v'w']$ in the three-index system and the new indices $[uvtw]$:

$$u = \frac{1}{3}(2u' - v') \quad v = \frac{1}{3}(2v' - u') \quad t = -\frac{1}{3}(u' + v') \quad w = w' \qquad 6.3$$

Thus, the basic translations $\boldsymbol{a}$, $\boldsymbol{b}$, $\boldsymbol{e}$ having originally indices $[100]$, $[010]$, and $[\overline{11}0]$ respectively, will be written as $\frac{1}{3}[2\overline{11}0]$, $\frac{1}{3}[\bar{1}2\bar{1}0]$, $\frac{1}{3}[\overline{11}20]$. In addition, the long diagonals of rhombuses $[1\bar{1}0]$, $[120]$, $[\overline{21}0]$ turn into $[1\bar{1}00]$, $[01\bar{1}0]$, $[\bar{1}010]$ respectively. In the case of indicating exactly the direction, and not a specific vector, the multipliers are omitted (Figure 6.4).

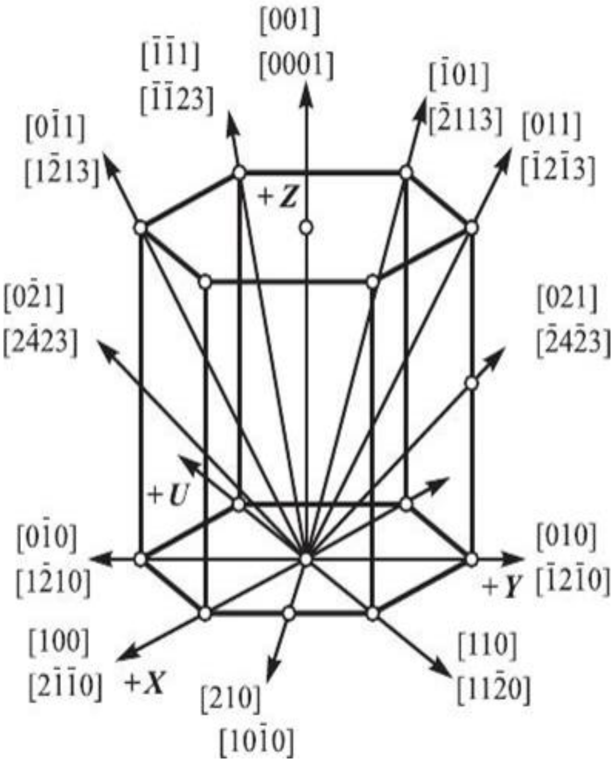

Figure 6.4 - Examples of matching direction indices.

It is important that in the case of directions, the Miller-Brave indices possess their main advantage - similar directions are characterized by similar sets of indices. It also makes easier to use generalized notation for directions, such as $\langle 11\bar{2}0 \rangle$ for axes in the basal plane. Axis *c* has no analogues due to the symmetry of the structure, the indices of this direction are written only in the standard way – $[0001]$ (Figure 6.5).

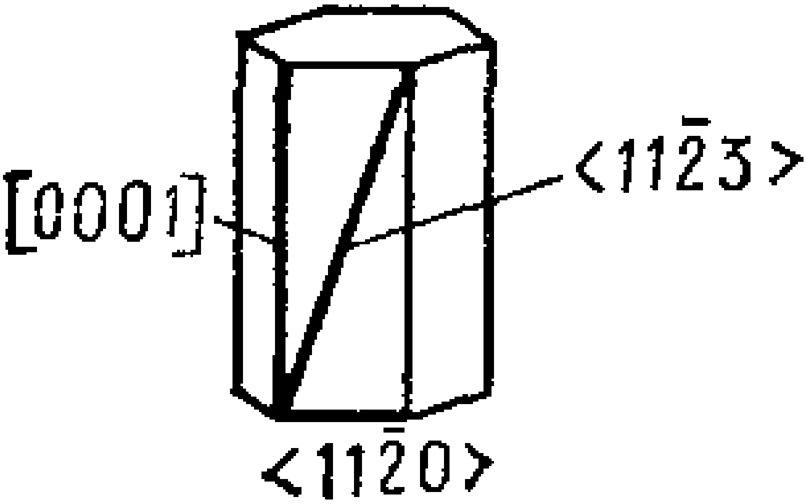

Figure 6.5 - Examples of recording direction indices.

In addition, it can be shown that the four-index system ensures the implementation of the zone rule:

$$uh + vk + it + wl = 0 \tag{6.4}$$

At the same time, for directions lying in the base plane and for planes perpendicular to it, that is, if the last index is 0 , a number of relations similar to those in the cubic lattice are satisfied. Condition of orthogonality for two directions of the type $\langle uvt0\rangle$ is:

$$u_1u_2 + v_1v_2 + t_1t_2 = 0 \tag{6.5}$$

Condition of orthogonality of two planes of type $\{hki0\}$ is:

$$h_1h_2 + k_1k_2 + i_1i_2 = 0 \tag{6.6}$$

The plane $(hki0)$ will also be perpendicular to the direction with the same indices $[hki0]$.

The combination of advantages of the Miller-Brave index system determines their wide application for describing crystals with such lattices.

7. Tasks

1. A vector $\boldsymbol{R}=\frac{a}{4}+\frac{b}{3}+\frac{c}{2}\ is\ given$, where $\boldsymbol{a}, \boldsymbol{b},$ and $\boldsymbol{c}$ are the main translations. Find the indices of the nodal raw parallel to the given vector.
2. Find the indices of the nodal row passing through two lattice nodes with indices $[\![111]\!]$ and $[\![1\bar{1}0]\!]$.
3. The plane cuts along the crystallographic axes segments equal to $2a$, $3b$, c. Find its Miller indices.
4. Find the indices of the plane passing through three lattices $[\![110]\!]$, $[\![101]\!]$, and $[\![011]\!]$.
5. A new basis was chosen in the lattice: the vectors $[110]$, $[011]$, and $[101]$. Find new indices of direction $[111]$ and plane (111).
6. Find the indices $[uvw]$ of the axis for the zone containing the planes (111) and (132). Formula for calculating the zone axis is:

   $$u=k_1l_2-k_2l_1;\ v=l_1h_2-l_2h_1; w=h_1k_2-h_2k_1$$

7. Find the indices of the plane containing the rows $[110]$ and $[111]$.
8. Are planes (111), (120) and $(01\bar{1})$ of the same zone?
9. Find the angle between the directions $[110]$ and $[1\bar{1}0]$ in the cubic lattice.
10. Find the angle between directions $[110]$ and $[10\bar{1}]$ in the cubic lattice.
11. Find the angle between directions $[110]$ and $[100]$ in the cubic lattice.
12. Find the cosine of the angle between directions $[111]$ and $[11\bar{1}]$ in the cubic lattice.
13. Silicon has a crystalline structure with a cubic cell, cell parameter a= 5.43 Å. Determine the interplanar spacing for planes (111) and (112).

14. Derive a formula for the interplanar distance d_{hkil} in a hexagonal lattice with parameters *a* and *c*.
15. Prove that the zone rule holds for the Miller-Brave indices.

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Physical crystallography

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