

0 Geometry of Crystal Lattice

0.1 Translational Symmetry

The crystalline state of substances is different from other states (gaseous, liquid, amorphous) in that the atoms are in an ordered and symmetrical arrangement called the crystal lattice. The lattice is characterized by space periodicity or *translational symmetry*. In an unbounded crystal we can define three noncoplanar vectors $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$, such that displacement of the crystal by the length of any of these vectors brings it back on itself. The *unit vectors* $\mathbf{a}_\alpha, \alpha = 1, 2, 3$ are the shortest vectors by which a crystal can be displaced and be brought back into itself.

The crystal lattice is thus a simple three-dimensional network of straight lines whose points of intersection are called the crystal lattice¹. If the origin of the coordinate system coincides with a site the position vector of any other site is written as

$$\mathbf{R} = \mathbf{R}_n = \mathbf{R}(\mathbf{n}) = \sum_{\alpha=1}^3 n_\alpha \mathbf{a}_\alpha, \quad \mathbf{n} = (n_1, n_2, n_3), \quad (0.1.1)$$

where n_α are integers. The vector \mathbf{R} is said to be a *translational vector* or a *translational period* of the lattice. According to the definition of translational symmetry, the lattice is brought back onto itself when it is translated along the vector \mathbf{R} .

We can assign a translation operator to the translation vector $\mathbf{R}(\mathbf{n})$. A set of all possible translations with the given vectors \mathbf{a}_α forms a *discrete group of translations*. Since sequential translations can be carried out arbitrarily, a group of transformations is commutative (Abelian). A group of symmetry transformations can be used to explain a number of qualitative physical properties of crystals independently of their specific structure.

Now consider the geometry of the crystal lattice. The parallelepiped constructed from the vectors corresponding to the translational periods is called a *unit cell*. It is

¹ The lattice sites are not necessarily associated with the positions of the atoms.

clear that the unit vectors, and thus the unit cell, may be chosen in different ways. A possible choice of unit cell in a planar lattice is shown in Fig. 0.1. As a rule, the unit cell is chosen so that its vertex coincides with one of the atoms of the crystal. The lattice sites are then occupied by atoms, and vectors \mathbf{a}_α connect the nearest equivalent atoms.

By arranging the vectors $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ in the correct sequence, it is easy to see that the unit cell volume $V_0 = \mathbf{a}_1 \cdot [\mathbf{a}_2, \mathbf{a}_3]$. Although the main translation periods are chosen arbitrarily, the unit cell volume still remains the same for any choice of the unit vectors.

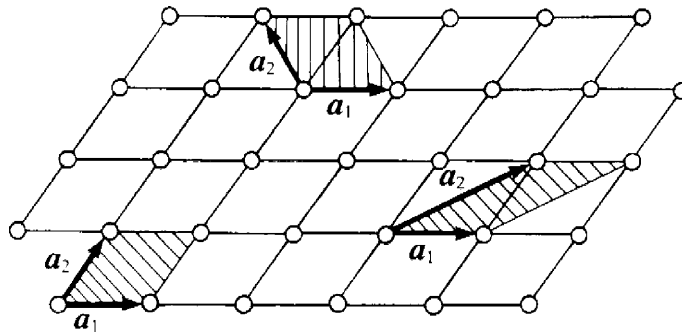


Fig. 0.1 Choice of unit cells (dashed) in a two-dimensional lattice.

The unit cell contains at least one atom of each of the types that compose the crystal². Since the atoms of different type are distinguished not only by their chemical properties but also by their arrangement in the cell, even in a crystal of a pure element there can be more than one type of atom. If the unit cell consists of only one type of atom it is called *monatomic*, otherwise it is *polyatomic*. A monatomic lattice is also often called *simple* and a polyatomic lattice *composite*. Table salt (NaCl) containing atoms of two types is an example of a polyatomic crystal lattice (Fig. 0.2), and 2D lattice composed of atoms of two types is presented also in Fig. 0.3a. A polyatomic crystal lattice may also consist of atoms of the same chemical type. Figure 0.3b shows a highly symmetrical diatomic planar lattice whose atoms are located at the vertices of a hexagon.

The differences between simple and composite lattices lead to different physical properties. For example, the vibrations of a diatomic lattice have some features that distinguish them from the vibrations of a monatomic lattice.

We would like to emphasize that the unit cell of a crystal involves, by definition, all the elements of the translation symmetry of the crystal. By drawing the unit cell one can construct the whole crystal. However, the unit cell may not necessarily be symmetrical with respect to rotations and reflections as the crystal can be. This is clearly seen in Fig. 0.3 where the lattices have a six-fold symmetry axis, while the unit cells do not.

²) We note that the contribution to a cell of an atom positioned in a cell vertex equals 1/8, on an edge 1/4 and on a face 1/2.

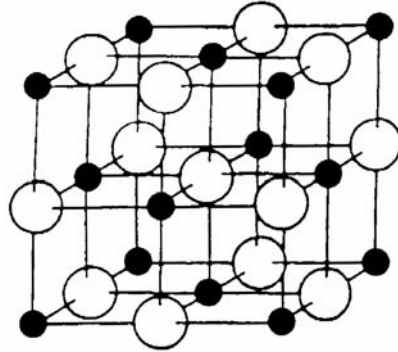


Fig. 0.2 NaCl crystal structure (○ - Na, ● - Cl).

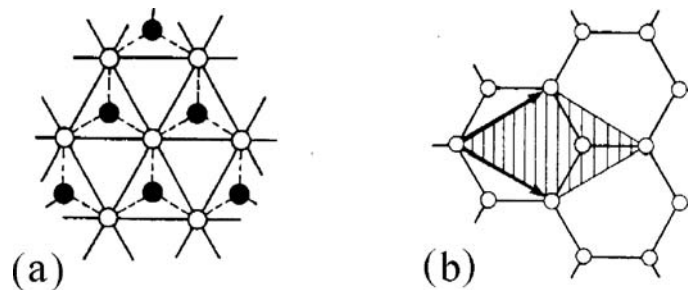


Fig. 0.3 Hexagonal 2D diatomic lattice composed of atoms (a) of different types and (b) of the same type. The unit cell is hatched.

0.2

Bravais Lattice

The Bravais lattice is the set of all equivalent atoms in a crystal that are brought back onto themselves when they are displaced by the length of a unit vector in a direction parallel to a unit vector. Bravais and monatomic lattices are usually coincident. A polyatomic lattice, however, consists of several geometrically identical interposed Bravais lattices.

The Bravais lattice of a polyatomic crystal is often more symmetrical than the crystal lattice itself. It contains all the elements of the crystal symmetry and may also have additional symmetry elements. For example, a planar crystal may have three-fold symmetry (Fig. 0.3a) whereas its Bravais lattice may have six-fold symmetry. The Bravais lattice has inversion centers at all of the sites, whereas the crystal lattices (necessarily polyatomic) do not necessarily have such a symmetry element.

The Bravais lattices are classified according to the symmetry of rotations and reflections. Seven *symmetry groups* or *space groups* are defined. Each of the lattices of a given group has an inversion center, a unique set of axes and symmetry planes. Each space group is associated with a polyhedron whose vertices correspond to the nearest

sites of the corresponding Bravais lattice and that has all the symmetry elements of the space group. The polyhedron is either a parallelepiped or a prism.

In the most symmetrical Bravais lattice, the cube is used as the symmetry “carrier”, and the lattice is called *cubic*. A *hexagonal lattice* is characterized completely by a regular hexahedral prism, the Bravais rhombohedron lattice by a rhombohedron, (i. e., the figure resulting when a cube is stretched along one of its diagonals), etc. A rectangular prism with at least one square face has *tetragonal* symmetry.

Within a given space group an additional subdivision into several types of Bravais lattices can be made. The type of Bravais lattice depends on where the lattice sites are located: either only at the vertices of the polyhedrons or also on the faces or at the center. We distinguish between the following types of Bravais lattice: primitive (P), base-centered (BC), face-centered (FC) and body-centered (BC) lattices.

The lattice of NaCl in Fig. 0.2 gives an example of a cubic lattice. A plane diatomic lattice with the 3-fold symmetry axes is shown in Fig. 0.3a, however, its Bravais lattice has 6-fold symmetry axes; a hexagonal lattice with the 6-fold symmetry axes is presented in Fig. 0.3b.

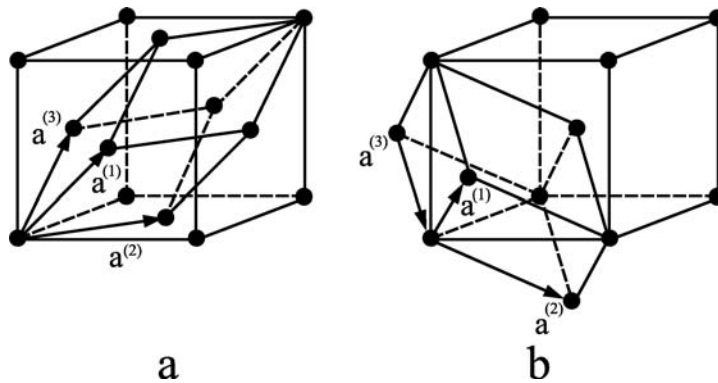


Fig. 0.4 Unit cells with translation vectors inside the cubic unit cells (a) of the FCC lattice and (b) of the BCC lattice.

It should be noted that the unit cell is not a principal geometrical figure being the “carrier” of all rotation elements of symmetry in the case of *centered* lattices. In order to demonstrate this fact a situation of the atoms in the single cube of BC-cubic and FC-cubic lattices is shown in Fig. 0.4a and 0.4b where the unit cells of these lattices are presented as well.

Naming the cubic, hexagonal and tetragonal lattices we have thereby counted the lattices possessing axes of 2-, 3-, 4- and 6-fold symmetry. Naturally, the question arises what types of the symmetry axes are compatible with the translational symmetry of a spatial lattice. It appears that the symmetry axes of the 2-, 3-, 4- and 6-fold only can exist in the unbounded spatial lattice (see *Problems* at the end of the chapter).

0.3

The Reciprocal Lattice

In order to describe physical processes in crystals more easily, in particular wave phenomena, the crystal lattice constructed with unit vectors \mathbf{a}_α in real space is associated with some periodic structure called the *reciprocal lattice*. The reciprocal lattice is constructed from the vectors \mathbf{b}_β , $\beta = 1, 2, 3$, related to \mathbf{a}_α through

$$\mathbf{a}_\alpha \mathbf{b}_\beta = 2\pi \delta_{\alpha\beta}, \quad \alpha, \beta = 1, 2, 3,$$

where $\delta_{\alpha\beta}$ is the Kronecker delta. The vectors \mathbf{b}_β can be simply expressed through the initial translational vectors \mathbf{a}_α :

$$\mathbf{b}_1 = \frac{2\pi}{V_0} [\mathbf{a}_2, \mathbf{a}_3], \quad \mathbf{b}_2 = \frac{2\pi}{V_0} [\mathbf{a}_3, \mathbf{a}_1], \quad \mathbf{b}_3 = \frac{2\pi}{V_0} [\mathbf{a}_1, \mathbf{a}_2].$$

The parallelepiped constructed from \mathbf{b}_β is called the unit cell of a reciprocal lattice. It is easy to verify that the unit cell volume in the reciprocal lattice is equal to the inverse value of the unit cell volume of the regular lattice:

$$\Omega_0 = \mathbf{b}_1 [\mathbf{b}_2, \mathbf{b}_3] = \frac{(2\pi)^3}{V_0}.$$

Note that the reciprocal lattice vectors have dimensions of inverse length. The space where the reciprocal lattice exists is called *reciprocal space*. The question arises: what are the points that make a reciprocal space? Or in other words: what vector connects two arbitrary points of reciprocal space?

Consider a wave process associated with the propagation of some field (e. g., electromagnetic) to be observed in the crystal. Any spatial distribution of the field is, generally, represented by the superposition of plane waves such as

$$\psi_{\mathbf{q}} = e^{i\mathbf{q}\mathbf{r}},$$

where \mathbf{q} is the wave vector whose values are determined by the boundary conditions.

However, in principle the vector \mathbf{q} takes arbitrary values. The dimension of the wave vector coincides with the dimension of inverse length, and the continuum of all possible wave vectors forms the reciprocal space. Thus, the reciprocal space is the three-dimensional space of wave vectors.

By analogy to the translation vectors of the regular lattice (0.1.1), we can also define translation vectors in reciprocal space:

$$\mathbf{G} \equiv \mathbf{G}(\mathbf{m}) = \sum_{\alpha=1}^3 m_\alpha \mathbf{b}_\alpha, \quad \mathbf{m} = (m_1, m_2, m_3), \quad (0.3.1)$$

where m_α are integers. The vector \mathbf{G} is called a *reciprocal lattice vector*.

It can be seen that simple lattices in reciprocal space correspond to simple lattices in real space for a given Bravais space group. The reciprocal lattice of FC Bravais

lattices (rhombic, tetragonal and cubic) is a body-centered lattice and vice versa. A lattice with a point at the center of the base has a corresponding reciprocal lattice also with a point at the center of the base.

In addition to the unit cell of a reciprocal lattice, one frequently constructs a “symmetry” cell. This cell is called the *Brillouin zone*. We choose a reciprocal lattice site as origin and draw from it all the vectors \mathbf{G} that connect it to all reciprocal lattice sites. We then draw planes that are perpendicular to these vectors and that bisect them. If \mathbf{q} is a vector in a reciprocal space, these planes are given by

$$q\mathbf{G} = \frac{1}{2}G^2. \quad (0.3.2)$$

The planes (0.3.2) divide all of reciprocal space into a set of regions of different shapes (Fig. 0.5a).

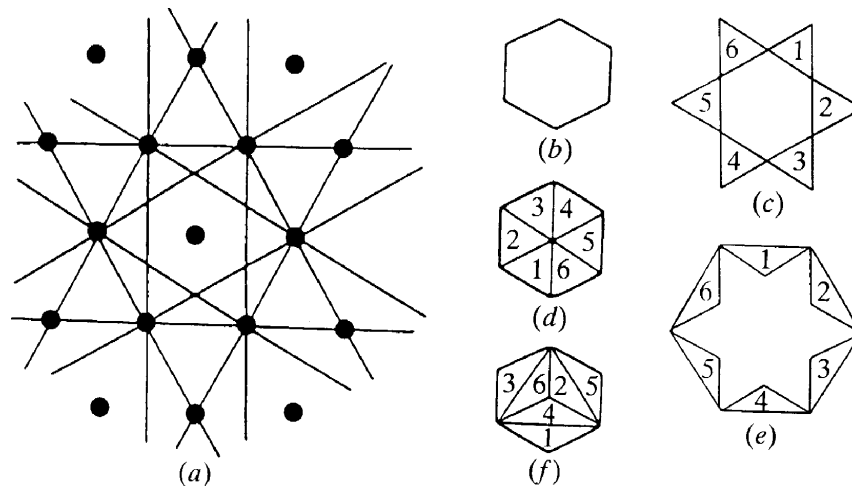


Fig. 0.5 Brillouin zones of hexagonal crystal: (a) construction of zones; the point in the middle is the origin, the lines drawn are the planes perpendicular to and bisecting the vectors connecting the origin with all other lattice sites (not shown); (b) the first zone; (c) the six parts of the second zone; (d) reduction of the second zone to the first; (e) the six parts of the third zone; (f) reduction of the third zone to the first.

The region containing the origin is called the first Brillouin zone. The regions of the reciprocal space that directly adjoin it make up the second zone and the regions bordering that are the third Brillouin zone, etc. The planes given by (0.3.2) are the *boundaries of the Brillouin zones*.

The regions of higher Brillouin zones can be combined into a single figure, identical to the first zone (Fig. 0.5d, f). Thus, any zone can be reduced to the first one. The concept of a reduced zone is convenient because it requires knowledge of the geometry of the first Brillouin zone only.

Mathematical relations between quantities in real and reciprocal space are entirely symmetrical with respect to these spaces and, formally, the lattices constructed with two sets of three vectors \mathbf{a}_α and \mathbf{b}_β are reciprocal to one another. That is, if one is defined as the lattice in real space, the other is its reciprocal. It should be noted, however, that the physical meaning of these spaces is different. For a crystal, one initially defines the crystal lattice as the lattice in real space.

The concept of a reciprocal lattice is used because all physical properties of an ideal crystal are described by functions whose periodicity is the same as that of this lattice. If $\phi(\mathbf{r})$ is such a function (the charge density, the electric potential, etc.), then obviously,

$$\phi(\mathbf{r} + \mathbf{R}) = \phi(\mathbf{r}), \quad (0.3.3)$$

where \mathbf{R} is a lattice translation vector (0.1.1). We expand the function $\phi(\mathbf{r})$ as a three-dimensional Fourier series

$$\phi(\mathbf{r}) = \sum_{\mathbf{q}} \phi_{\mathbf{q}} e^{i\mathbf{q}\mathbf{r}}, \quad (0.3.4)$$

where it is summed over all possible values of the vector \mathbf{q} determined by the periodicity requirement (0.3.3)

$$\sum_{\mathbf{q}} \phi_{\mathbf{q}} e^{i\mathbf{q}\mathbf{r}} e^{i\mathbf{q}\mathbf{R}} = \sum_{\mathbf{q}} \phi_{\mathbf{q}} e^{i\mathbf{q}\mathbf{r}}. \quad (0.3.5)$$

Equation (0.3.5) can be satisfied if

$$e^{i\mathbf{q}\mathbf{R}} = 1, \quad \mathbf{q}\mathbf{R} = 2\pi\mathbf{p}, \quad (0.3.6)$$

where \mathbf{p} is an integer. To satisfy (0.3.6) it is necessary that

$$\mathbf{q}\mathbf{a}_\alpha = 2\pi p_\alpha, \quad \alpha = 1, 2, 3, \quad (0.3.7)$$

where p_α are the integers.

The solution to (0.3.7) for the vector \mathbf{q} has the form

$$\mathbf{q} = m_1\mathbf{b}_1 + m_2\mathbf{b}_2 + m_3\mathbf{b}_3. \quad (0.3.8)$$

It follows from (0.3.8) that the vector \mathbf{q} is the same as that of the reciprocal lattice: $\mathbf{q} = \mathbf{G}$ where \mathbf{G} is determined by (0.3.1).

Thus, any function describing a physical property of an ideal crystal can be expanded as a Fourier series (0.3.4) where the vector \mathbf{q} runs over all points of the reciprocal lattice

$$\phi(\mathbf{r}) = \sum_{\mathbf{G}} \phi_{\mathbf{G}} e^{i\mathbf{G}\mathbf{r}}. \quad (0.3.9)$$

Since there is a simple correspondence between the real and reciprocal lattices there should also be a simple correspondence between geometrical transformations in real

and reciprocal space. We illustrate this correspondence with an example widely used in structural analysis. Consider the vector \mathbf{r} such that

$$\mathbf{G}\mathbf{r} = 2\pi p, \quad (0.3.10)$$

where p is the integer and \mathbf{G} is a reciprocal lattice vector. Equation (0.3.10) describes a certain plane in the crystal. It is readily seen that this is a crystal plane, i. e., the plane running through an infinite set of Bravais lattice sites. Since the constant p may take any value, (0.3.10) describes a family of parallel planes. Thus, each vector of a reciprocal lattice $\mathbf{G} = \mathbf{G}(\mathbf{m})$ corresponds to a family of parallel crystal planes (0.3.10) rather than to a single plane. The distance between adjacent planes of the family is $d_B = 2\pi/G$, where G is the length of a corresponding vector of a reciprocal lattice. Three quantities m_1, m_2, m_3 in these relations can always be represented as a triplet of prime numbers p_1, p_2, p_3 (i. e., assume that p_1, p_2, p_3 have no common divisor except unity). These three numbers (p_1, p_2, p_3) are called the *Miller indices*.

0.4

Use of Penetrating Radiation to Determine Crystal Structure

We consider the transmission of a field (X-rays, beams of fast electrons or slow neutrons) through a crystal. We assume the distribution of the field in space to be described by a scalar function ψ that in vacuo obeys the equation

$$\epsilon\psi + c^2\Delta\psi = 0,$$

where for electromagnetic waves ϵ is the frequency squared ($\epsilon = \omega^2$) and c the light velocity, or in the case of electrons and neutrons they are the energy and the inverse mass ($c = \hbar^2/2m$). The crystal atoms interact with the wave, generating a perturbation. This perturbation is taken into account in the above equation by an additional potential

$$\epsilon\psi + c^2\Delta\psi + U(\mathbf{r})\psi = 0. \quad (0.4.1)$$

The potential $U(\mathbf{r})$ has the same periodicity as the crystal (for example, it may be proportional to the electric charge density in a crystal).

We now consider how the periodic potential can affect the free wave

$$\psi_{\mathbf{k}} = e^{i\mathbf{k}\mathbf{r}}, \quad c^2k^2 = \epsilon. \quad (0.4.2)$$

We assume that U is weak, i. e., we can use perturbation theory (this is a reasonable assumption in many real systems). Let the wave (0.4.2) be incident on a crystal and scattered under the effect of the potential U . In the Born approximation, the amplitude of the elastically scattered wave with wave vector \mathbf{k}' is proportional to the integral

$$U(\mathbf{k}', \mathbf{k}) = \int U(\mathbf{r})e^{-i(\mathbf{k}'-\mathbf{k})\mathbf{r}} dV, \quad (0.4.3)$$

which is the matrix element of the potential U . The scattering probability, i. e., the probability for the wave (0.4.2) to be transformed to a wave

$$\psi_{k'} = Ae^{ik'r}, \quad A = \text{constant}, \quad c^2k'^2 = \epsilon, \quad (0.4.4)$$

is proportional to the squared matrix element (0.4.3).

To calculate the integral (0.4.3) we use an expansion such as (0.3.9) for the periodic function $U(\mathbf{r})$:

$$U(\mathbf{k}', \mathbf{k}) = \sum_{\mathbf{G}} U_{\mathbf{G}} \int e^{i(\mathbf{G}-\mathbf{k}'+\mathbf{k})\mathbf{r}} dV. \quad (0.4.5)$$

In an unbounded crystal (0.4.5) is reduced to

$$U(\mathbf{k}', \mathbf{k}) = (2\pi)^3 \sum_{\mathbf{G}} U_{\mathbf{G}} \delta(\mathbf{k}' - \mathbf{k} - \mathbf{G}). \quad (0.4.6)$$

It is clear that the incident wave (0.4.2) with the wave vector \mathbf{k} can be transformed only into the waves whose wave vector is

$$\mathbf{k}' = \mathbf{k} + \mathbf{G}, \quad (0.4.7)$$

where \mathbf{G} is any reciprocal lattice vector.

In elastic scattering the wave frequency (or the scattered particle energy) does not change, so that

$$k'^2 = k^2. \quad (0.4.8)$$

The relations (0.4.7), (0.4.8) are called the *Laue equations* and are used in the analysis of X-ray diffraction and the electron and neutron elastic scattering spectra in crystallography. By fixing the direction of the incident beam and measuring the directions of the scattered waves, one can determine the vectors \mathbf{G} , i. e., the reciprocal lattice. From these it may be possible to reproduce the crystal structure.

To simplify (0.4.7), (0.4.8) further, we first establish their relation to the reciprocal lattice. We take the scalar product of (0.4.7) and take into account (0.4.8):

$$\mathbf{k}'\mathbf{G} = -\mathbf{k}\mathbf{G} = \frac{1}{2}G^2. \quad (0.4.9)$$

Comparing (0.4.9) and (0.3.2), it can be seen that only those beams whose wave-vector ends lie on the Brillouin zone boundaries (the origin of the waves vectors is at the center of the Brillouin zones) are reflected from the crystal.

We denote the angle between the vectors \mathbf{k} and \mathbf{k}' by 2θ . Then from (0.4.8) we obtain the relation

$$G = 2k \sin \theta. \quad (0.4.10)$$

As was shown above, the length of the vector \mathbf{G} is inversely proportional to the distance d between the nearest planes of atoms to which this vector is perpendicular

$$G = \frac{2\pi n}{d}, \quad (0.4.11)$$

where n is the integer. Substituting (0.4.11) into (0.4.10) and introducing the wavelength of the incident radiation $\lambda = 2\pi/k$ we obtain

$$n\lambda = 2d \sin \theta. \quad (0.4.12)$$

This relation is known as the *Bragg reflection law*. The diffraction described by (0.4.12) is sometimes referred to as “reflection” from crystal planes.

It should be noted that this simplest *geometrical* (or *kinematic*) *theory* of diffraction in crystals is applicable only to scattering in thin crystal samples. It does not include the interaction of the incident and diffracted beams with deeper atomic layers in thick samples.

0.4.1

Problems

1. Prove that if \mathbf{r} is the radius-vector of an arbitrary site in the crystal the following equation is valid

$$\sum_{\mathbf{G}} e^{i\mathbf{G}\mathbf{r}} = V_0 \sum_{\mathbf{R}} \delta(\mathbf{r} - \mathbf{R}), \quad (0.4.13)$$

where the summation on the r.h.s. is carried out over all lattice sites and on the l.h.s. over all reciprocal lattice sites.

2. Derive from (0.4.13) the equation

$$\sum_{\mathbf{R}} e^{-i\mathbf{k}\mathbf{R}} = \Omega_0 \sum_{\mathbf{G}} \delta(\mathbf{k} - \mathbf{G}), \quad (0.4.14)$$

where \mathbf{k} is the position vector of an arbitrary point in the reciprocal space.

3. Elucidate which symmetry axes can be inherent elements of the symmetry of a lattice.

Hint. Consider two neighboring sites A and B in the plane perpendicular to the symmetry axis (see Fig. 0.6). Perform a rotation by the angle $\phi=2\pi/n$ about the axis C_n through the point A ; after that B occupies position B' . Analogous rotation about B transfers A to A' . Since the sites B' and A' belong to the same lattice the length $B'A'$ should be divisible by the length AB .

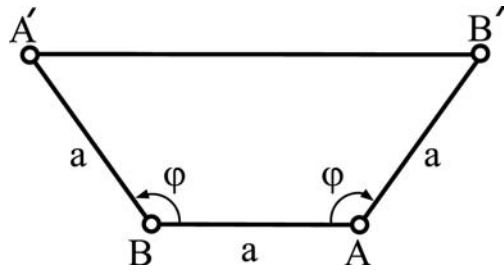


Fig. 0.6 Graphical solution of Problem 3.

Solution. $n = 2, 3, 4, 6$.

