

mental laboratory, where one learns about ultra-high-vacuum systems, their operation and main components, as well as about some general procedures used for sample preparation. Chapters 4–7 are devoted to the experimental methods of surface analysis, including, diffraction techniques, electron spectroscopy, ion-scattering spectroscopy and microscopy, respectively. Within each chapter a set of particular methods are considered. The scheme of the presentation of the technique is as follows: First, the physical phenomena, which constitute the basis of the technique, are introduced. Then, the experimental set-up is described. Finally, information which can be gained by the technique is specified. The purpose of Chap. 8 is to give an impression of what perfect atomically clean surfaces of a crystal constitute on the atomic scale. Chapter 9 illustrates the structure of clean crystal surfaces, on which submonolayer films (i.e., those with thickness below one atomic monolayer) have been adsorbed. Here, the formation of two-dimensional ordered surface phases, phase transitions and phase diagrams are discussed. The defect-free crystal is an apparent idealization. In practice, the crystal surface always contains a certain number of defects (for example, adatoms, vacancies, steps, etc.), which are discussed in Chap. 10. Among other defects, atomic steps are given especial attention, as their discussion involves such important topics as surface stability, surface morphology and equilibrium crystal shape. Surface electronic structure and properties are addressed in Chap. 11. Chapters 12 and 13 are devoted to elementary atomic processes on the surface, namely, adsorption, desorption and surface diffusion. In Chap. 14, the surface phenomena involved in the growth of thin films (with thickness exceeding the monolayer range) and their effect on the growth mode, as well as on the structure and morphology of the grown films, are discussed. Chapter 15 reflects very recent trends in surface science and deals with so-called nanostructures fabricated using atomic manipulations and self-organization processes.

2. Basics of Two-Dimensional Crystallography

In this chapter, the nomenclature used to describe surface structures is developed. An understanding of this nomenclature is very important, as it will be used continuously throughout all the following chapters of the textbook. It should be noted, however, that here only the formal definitions and concepts are given.

2.1 Two-Dimensional Lattices

2.1.1 Lattice, Basis, and Crystal Structure (3D Case)

Recall, first, the main concepts accepted in bulk crystallography. The structure of an ideal crystal is described conventionally in terms of a *lattice*. For the bulk three-dimensional (3D) crystal, the lattice is defined by three *fundamental translation vectors* \mathbf{a} , \mathbf{b} , \mathbf{c} such that the atomic arrangement of the crystal looks absolutely the same when viewed from point \mathbf{r} as when viewed from the point

$$\mathbf{r}' = \mathbf{r} + n\mathbf{a} + m\mathbf{b} + k\mathbf{c}, \quad (2.1)$$

where n, m, k are integers $(0, \pm 1, \pm 2, \dots)$. Hence, a lattice can be visualized as a set of points \mathbf{r}' that fit (2.1). A lattice is a geometrical abstraction. The *crystal structure* (a physical object) is formed when an atom or a group of atoms called a *basis* is attached to every lattice point, with every basis being identical in composition, arrangement and orientation (Fig. 2.1). Thus, it can be written

$$\text{lattice} + \text{basis} = \text{crystal structure}. \quad (2.2)$$

2.1.2 Concept of a 2D Lattice

As for crystalline surfaces and interfaces, these are essentially two-dimensional (2D) objects. Although the surface (or interface) region is, in principle, a 3D entity having a certain thickness, all symmetry properties of the surface are two-dimensional, i.e., the surface structure is periodic only in two directions.

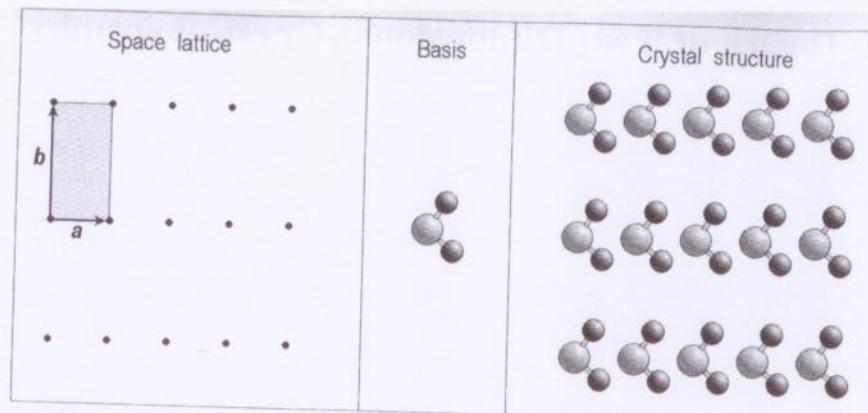


Fig. 2.1. The crystal structure is formed by the addition of the basis to every point of the space lattice

Thus, surface crystallography is two-dimensional and for describing the surface lattice only two translation vectors a and b are used and (2.1) is rewritten as

$$\mathbf{r}' = \mathbf{r} + n\mathbf{a} + m\mathbf{b}. \quad (2.3)$$

Sometimes a surface lattice is called a *net*. The parallelogram with sides a and b is called a *unit cell* or a *mesh*. The unit cell with the minimum area is called a *primitive cell*.

Another possible type of primitive cell is represented by a *Wigner–Seitz cell*, which is constructed according to the following procedure (see Fig. 2.2):

- The chosen arbitrary lattice point is connected by straight lines with all neighboring lattice points.
- Through the midpoints of these lines, perpendicular lines are drawn (planes in the 3D case).
- The smallest area (volume in the 3D case) enclosed in this way comprises the Wigner–Seitz primitive cell.

To describe completely the structure of a given surface, one should define its 2D lattice and its basis (i.e., the arrangement of the surface atoms within a unit cell). This is similar to the concept introduced by logic (2.2) for the bulk crystal. Moreover, one may notice that the schematic example shown in Fig. 2.1 actually corresponds to the 2D case.

2.1.3 2D Bravais Lattices

All the great variety of surface lattices are organized into five main types, called two-dimensional *Bravais lattices* (recall that there are 14 Bravais lat-

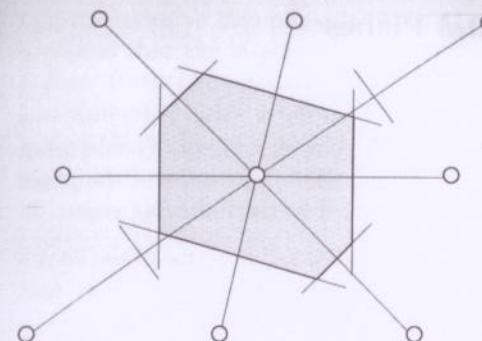


Fig. 2.2. Schematic diagram illustrating the construction of the Wigner–Seitz primitive cell

tices in three dimensions). The 2D Bravais lattices are shown in Fig. 2.3. They are

- oblique lattice $|\mathbf{a}| \neq |\mathbf{b}|, \gamma \neq 90^\circ$,
- rectangular lattice $|\mathbf{a}| \neq |\mathbf{b}|, \gamma = 90^\circ$,
- centered rectangular lattice $|\mathbf{a}| \neq |\mathbf{b}|, \gamma = 90^\circ$,
- square lattice $|\mathbf{a}| = |\mathbf{b}|, \gamma = 90^\circ$,
- hexagonal lattice $|\mathbf{a}| = |\mathbf{b}|, \gamma = 120^\circ$.

Note that in Fig. 2.3 two types of unit cell are shown for the centered rectangular lattice. The primitive unit cell is non-rectangular, while the rectangular cell is non-primitive. Nevertheless, in practice, one often uses it for convenience of description.

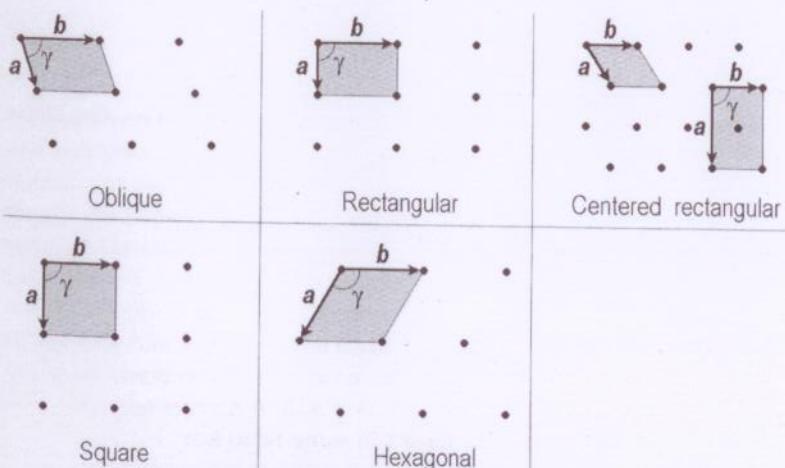


Fig. 2.3. Five two-dimensional Bravais lattices. Translation vectors \mathbf{a} and \mathbf{b} are shown, unit cells (meshes) are hatched

2.2 Miller Indices for Crystal Planes

2.2.1 Definition of Miller Indices

Before describing a particular surface structure one should specify first what the plane of the crystal is under consideration. The orientation of the plane is denoted by Miller indices which are determined in the following way:

- First, the intercepts of the plane on the axes are found in terms of the lattice constants a, b, c , which may be those of a primitive or non-primitive unit cell.
- Then, the reciprocals of the obtained numbers are taken.
- Finally, they are reduced to three integers having the same ratio, usually the smallest three integers.

The result enclosed in parentheses (hkl) constitutes the *Miller index* of the crystal plane.

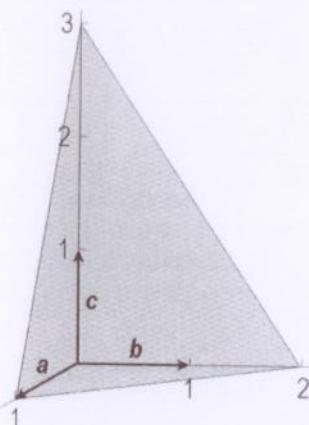


Fig. 2.4. This plane intercepts the a, b, c axes at $1a, 2b, 3c$. Thus, the Miller indices of the plane are (632) (see text)

For example, if the intercepts of the plane are

$1, 2, 3$

(Fig. 2.4), then the reciprocals are

$1, \frac{1}{2}, \frac{1}{3}$

and the smallest three integers that have the same ratio are

$6, 3, 2$,

i.e., the index of this plane is (632) . If the plane is parallel to the axis, it is accepted that the intercept is at infinity and the corresponding Miller index is zero. If the plane intercepts the axis on the negative side of the origin, the corresponding index is negative. To indicate this, a minus is placed above the index: $(\bar{h}kl)$. As an example, Fig. 2.5 illustrates the Miller indices of some important planes in a cubic crystal. The set of planes that are equivalent by symmetry are denoted by braces around the Miller indices (for example, $\{100\}$ for the cube faces).

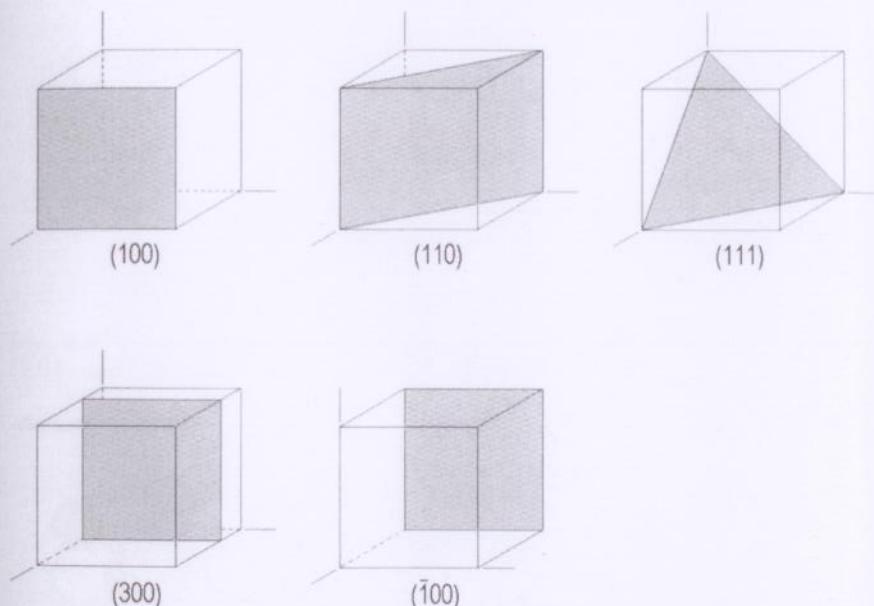


Fig. 2.5. Miller indices of some important planes in a cubic crystal

For the description of the hcp (hexagonal close-packed) lattice, four axes are conventionally introduced, three of equal length a in the basal plane inclined at 120° to each other and one axis of length c normal to this plane. Hence, four-index notation is employed for planes in the hcp crystal. One can see that the three-index notation (hkl) corresponds to the four-index notation $(h, k, -h - k, l)$, i.e., the three-index notation is obtained from the four-index one by simply omitting the third index. Note that the necessary requirement to use this rule is that, in the three-index notation, the axes in the basal plane make an angle of 120° . If the axes are chosen so that they make an angle of 60° , then the corresponding four-index notation is $(h, k - h, -k, l)$.

2.2.2 Low-Miller-Index Planes of Some Important Crystals

Figures 2.6, 2.7, 2.8, and 2.9 show the atomic arrangement of the principal low-index planes of fcc (face-centered cubic), bcc (body-centered cubic), hcp (hexagonal closed-packed) and diamond crystals, respectively. The topmost atoms are shown by white circles, the atoms in the deeper layers by gray circles. The layer numbers, counted from the topmost one, are indicated. The surface unit cells are outlined.

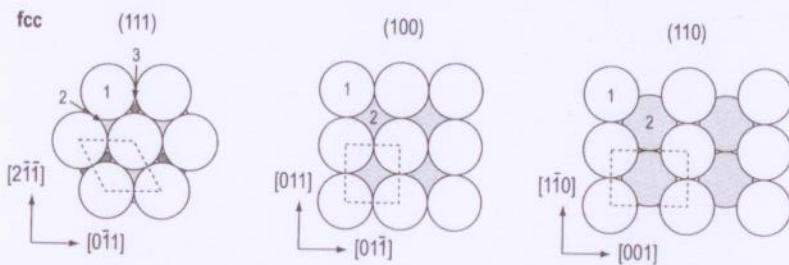


Fig. 2.6. Main low-index planes of a fcc (face-centered cubic) crystal

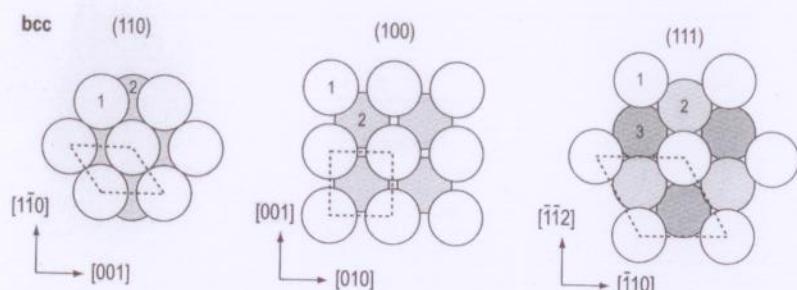


Fig. 2.7. Main low-index planes of a bcc (body-centered cubic) crystal

2.2.3 High-Miller-Index Stepped Surfaces

If the crystal surface is misoriented from the low-index plane by a small angle, it can be described by the combination of three parameters: *tilt angle*, *tilt azimuth*, and *tilt zone*. The tilt zone specifies the axis, around which the rotation from the basal low-index plane to the tilted plane is conducted, the azimuth specifies the direction of the rotation, and the tilt angle specifies the angle of rotation (see Fig. 2.10).

On the atomic scale, such a surface, called *a stepped* or *vicinal* surface, is composed conventionally of terraces separated by steps of monatomic height,

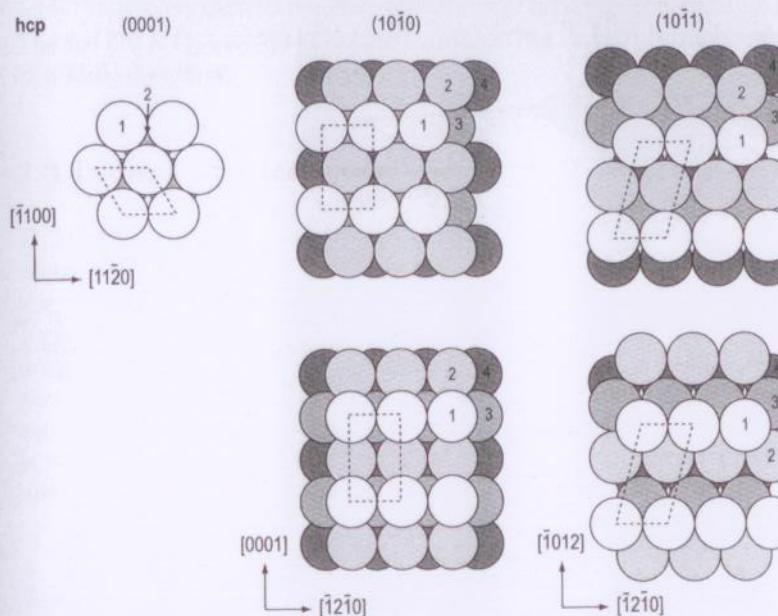


Fig. 2.8. Main low-index planes of a hcp (hexagonal close-packed) crystal. For the (1010) and (1011) planes, two possible types of surface termination are shown

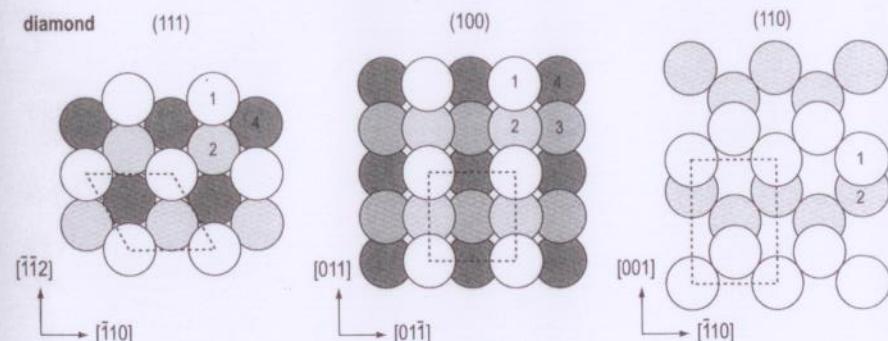


Fig. 2.9. Main low-index planes of a diamond crystal

which may also have kinks in them (Fig. 2.11). Although this surface can be designated by its corresponding Miller indices, for example, (755) for Fig. 2.11a, this notation does not indicate, at a glance, the geometric structure of the surface. A more vivid notation, devised by Lang, Joyner, and Somorjai [2.1], gives the structure in the form of

$$n(h_t k_t l_t) \times (h_s k_s l_s).$$

Here $(h_t k_t l_t)$ and $(h_s k_s l_s)$ are the Miller indices of the terrace plane and step plane, respectively, and n gives the number of atomic rows in the terrace

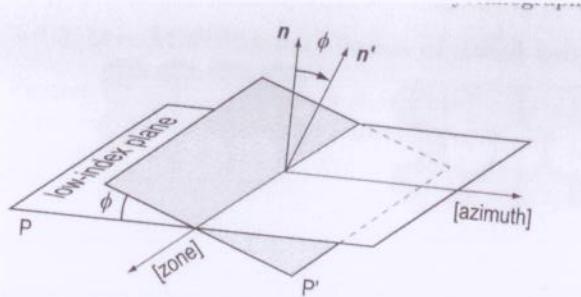
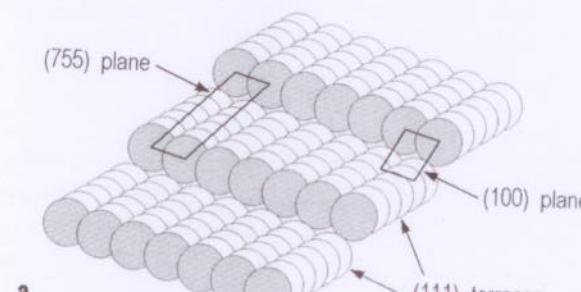


Fig. 2.10. The misoriented plane P' is obtained from the low-index plane P by rotation around the [zone] axis towards the [azimuth] direction by the tilt angle ϕ . The vectors n and n' denote the normals to the planes P and P' , respectively

fcc [6(111)×(100)] or fcc (755)



fcc [7(111)×(310)] or fcc (10,8,7)

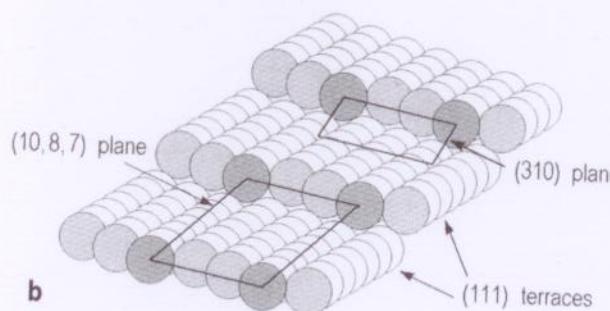


Fig. 2.11. (a) Stepped (755) and (b) kinked (10,8,7) fcc crystal faces

parallel to the step edge. Thus, the (755) surface of the fcc crystal is denoted $6(111) \times (100)$, as it consists of (111) terraces, 6 atoms wide, separated by monatomic steps of (100) orientation (Fig. 2.11a). A stepped surface with steps that are themselves high-Miller-index surfaces is called a *kinked surface*.

2.3 Indices of Directions

To specify a certain direction in a crystal or in its surface, the direction vector is expressed by indices in square brackets, $[hkl]$. The values h, k, l are the set of the smallest integers that have the ratio of the components of a vector, referred to the axes of the crystal. Thus, the directions of the axes are designated as [100], [010] and [001]. The negative component of the direction vector is indicated by a minus placed above the index, $[\bar{h}kl]$. The full set of equivalent directions is denoted as $\langle hkl \rangle$. In cubic crystals, the direction $[hkl]$ is normal to the plane (hkl) with the same indices; however, this does not hold generally for other crystal types.

2.4 Notation for Surface Structures

The structure of the surface layer is not necessarily the same as that of the underlying bulk planes even for clean surfaces (i.e., adsorbate-free). The term *superstructure* is used conventionally to outline the specific structure of the top atomic layer (or a few layers). The notation used to describe a superstructure ties its 2D lattice to that of the underlying substrate plane. This is done conventionally in one of two ways.

2.4.1 Matrix Notation

The notation proposed by Park and Madden [2.2] resides in the determination of the matrix which establishes a relation between the basic translation vectors of the surface under consideration and those of the ideal substrate plane. That is, if \mathbf{a}_s , \mathbf{b}_s and \mathbf{a} , \mathbf{b} are the basic translation vectors of the superstructure and substrate planes, respectively, then they can be linked by the equations

$$\begin{aligned}\mathbf{a}_s &= G_{11}\mathbf{a} + G_{12}\mathbf{b} \\ \mathbf{b}_s &= G_{21}\mathbf{a} + G_{22}\mathbf{b}\end{aligned}\quad (2.4)$$

and the superstructure is specified by the matrix:

$$G = \begin{pmatrix} G_{11} & G_{12} \\ G_{21} & G_{22} \end{pmatrix} \quad (2.5)$$

The values of the matrix elements G_{ij} determine whether the structure of the surface is *commensurate* or *incommensurate* with respect to the substrate.

Commensurability means that a rational relationship between the vectors \mathbf{a}_s , \mathbf{b}_s and \mathbf{a} , \mathbf{b} can be established. If there is no rational relationship between the unit vectors of the surface superstructure and the substrate, the superstructure is incommensurate. In other words, the incommensurate superstructure is registered in-plane incoherently with the underlying substrate lattice.

2.4.2 Wood's Notation

A more vivid but less versatile notation for surface superstructures was proposed by Wood [2.3]. In this notation, the ratio of the lengths of the basic translation vectors of the superstructure and those of the substrate plane is specified. In addition, one indicates the angle of rotation (if any) which makes the unit mesh of the surface to be aligned with the basic translation vectors of the substrate. That is, if on a certain substrate surface $X(hkl)$ a superstructure is formed with the basic translation vectors of

$$|\mathbf{a}_s| = m|\mathbf{a}|, \quad |\mathbf{b}_s| = n|\mathbf{b}| \quad (2.6)$$

and with the rotation angle of φ° , then this surface structure is labeled as

$$X(hkl)m \times n \cdot R \varphi^\circ. \quad (2.7)$$

If the unit mesh of the superstructure is aligned along the axes of the substrate net, i.e., $\varphi = 0$, than the notation does not specify this zero angle (for example, Si(111)7×7). A possible centering is expressed by the character c (for example, Si(100)c(4×2)). If the superstructure is induced by the adsorbate, this adsorbate is specified by its chemical symbol at the end of the notation (for example, Si(111)4×1-In). Sometimes, the number of adsorbate atoms per unit cell is indicated (for example, Si(111)√3×√3-R30°-3Bi).

Note that Wood's notation is applicable only for the cases where the included angles of the superstructure and substrate meshes are the same. This requirement is matched when both meshes have the same Bravais lattice or when one is rectangular and the other is square. But, in general, it does not provide an adequate description for mixed symmetry meshes, in which case the matrix notation should be used. Sometimes, however, the Wood's-type notation is used in the literature even for the cases where strictly speaking it is not applicable. In these instances, the notation is included in quotes, which indicates that it does not provide an exactly true relationship. The clean Si(110) surface can serve as an example. The structure of this surface is properly described in matrix notation as Si(110) $\begin{pmatrix} 2 & 2 \\ 1 & 7 \end{pmatrix}$. However, it is often labeled as Si(110) "2 × 16" with quotes indicating that the unit mesh of the "2×16" structure is non-rectangular in contrast to the rectangular (1×1) mesh of the ideal Si(110) plane.

2.4.3 Some Examples

In conclusion of this section, let us consider some simple examples of using the above nomenclature. Figures 2.12 and 2.13 display several superlattices on hexagonal and square lattices, respectively. The 2D lattice of the substrate is shown by black dots and the lattice of the superstructure is shown by empty circles. Note that we deal here with lattices only, not structures (see Sect. 2.1).

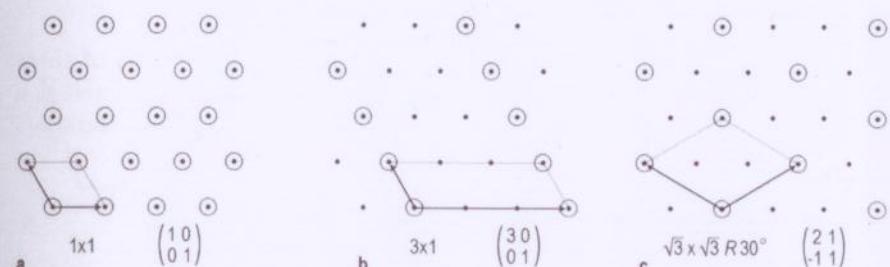


Fig. 2.12. Wood's and matrix notation for some superlattices on a hexagonal 2D lattice

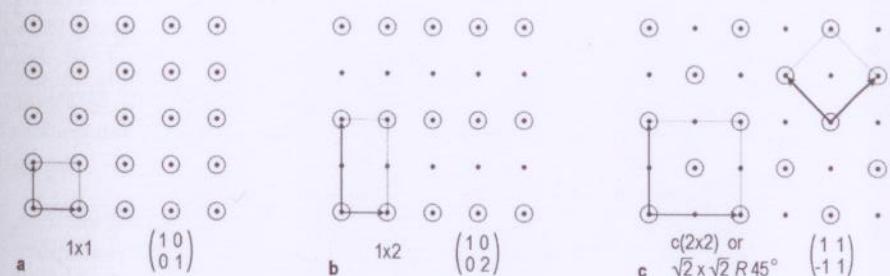


Fig. 2.13. Wood's and matrix notation for some superlattices on a square 2D lattice

When the superstructure has a unit cell of the same size as the substrate unit cell and parallel to it, i.e., the two lattices coincide (Fig. 2.12a and Fig. 2.13a), then the superstructure is designated as

$$1 \times 1 \text{ or } \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}.$$

If the unit cell of the superstructure is three times as long as the substrate unit cell along one major crystallographic axis and has the same length along the other (Fig. 2.12b), the superstructure is designated as

$$3 \times 1 \text{ or } \begin{pmatrix} 3 & 0 \\ 0 & 1 \end{pmatrix}.$$

The qualitatively similar case with the 1×2 or $\begin{pmatrix} 1 & 0 \\ 0 & 2 \end{pmatrix}$ superstructure is shown in Fig. 2.13b.

Figure 2.12c represents the $\sqrt{3} \times \sqrt{3}$ -R30° superlattice, in which the basic vectors are $\sqrt{3}$ times as long as those of the substrate, and the superstructure unit cell is rotated by 30° with respect to the substrate unit cell. The superstructure can be designated in matrix notation as $\begin{pmatrix} 2 & 1 \\ -1 & 1 \end{pmatrix}$.

The superlattice shown in Fig. 2.13c can be designated in one of three possible ways. First, it can be denoted as $c(2 \times 2)$, since it may be viewed as a (2×2) surface lattice with an extra lattice point in its center. If one considers the primitive unit cell, the superstructure can be designated as

$$\sqrt{2} \times \sqrt{2} \text{-} R45^\circ \text{ or } \begin{pmatrix} 1 & 1 \\ -1 & 1 \end{pmatrix}.$$

2.5 2D Reciprocal Lattice

The concept of the reciprocal lattice is very useful when one deals with structural investigations by means of diffraction techniques. This point will be addressed in Chap. 4 devoted to diffraction methods of surface analysis. Here only the basic definitions are introduced.

The 2D reciprocal lattice is a set of points whose coordinates are given by the vectors

$$\mathbf{G}_{hk} = h\mathbf{a}^* + k\mathbf{b}^*, \quad (2.8)$$

where h, k are integers ($0, \pm 1, \pm 2, \dots$) and the primitive translation vectors, \mathbf{a}^* and \mathbf{b}^* , are related to the primitive translation vectors of the real-space lattice, \mathbf{a} and \mathbf{b} , as

$$\mathbf{a}^* = 2\pi \cdot \frac{\mathbf{b} \times \mathbf{n}}{|\mathbf{a} \times \mathbf{b}|}, \quad \mathbf{b}^* = 2\pi \cdot \frac{\mathbf{n} \times \mathbf{a}}{|\mathbf{a} \times \mathbf{b}|}, \quad (2.9)$$

where \mathbf{n} is a unit vector normal to the surface.

From (2.9), one can easily distinguish the following properties of the vectors \mathbf{a}^* , \mathbf{b}^* :

- The vectors \mathbf{a}^* , \mathbf{b}^* lie in the same surface plane as the real-space vectors \mathbf{a} , \mathbf{b} .
- The vector \mathbf{a}^* is perpendicular to vector \mathbf{b} ; \mathbf{b}^* is perpendicular to vector \mathbf{a} .

- The lengths of vectors \mathbf{a}^* , \mathbf{b}^* are

$$|\mathbf{a}^*| = \frac{2\pi}{a \cdot \sin \angle(\mathbf{a}, \mathbf{b})},$$

$$|\mathbf{b}^*| = \frac{2\pi}{b \cdot \sin \angle(\mathbf{a}, \mathbf{b})}.$$

Note that while the real-space vectors \mathbf{a} , \mathbf{b} have the dimensions of [length], the reciprocal lattice vectors \mathbf{a}^* , \mathbf{b}^* have the dimensions of [1/length].

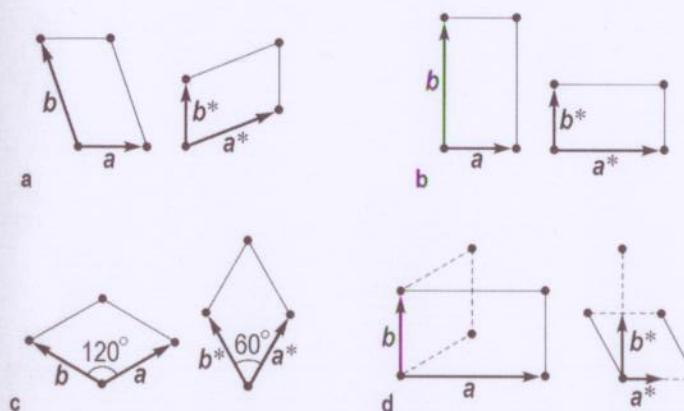


Fig. 2.14. Translation vectors and unit meshes of the real-space and corresponding reciprocal 2D Bravais lattices: (a) oblique lattice; (b) rectangular lattice (the square lattice is essentially the same with $|\mathbf{a}| = |\mathbf{b}|$); (c) hexagonal lattice, (d) centered rectangular lattice

Figure 2.14 shows the reciprocal lattices for the real-space 2D Bravais lattices. Here only the square lattice is omitted as it can be considered as a simple specific case of a rectangular lattice with $|\mathbf{a}| = |\mathbf{b}|$. With reference to Fig. 2.14 two general features can be seen:

- Each pair consisting of a real-space lattice and the corresponding reciprocal lattice belong to the same type of Bravais lattice, i.e., if the real-space lattice is, say, hexagonal, than the reciprocal lattice is also hexagonal; if the real-space lattice is centered rectangular, the corresponding reciprocal lattice is also centered rectangular, etc.
- The angle between the reciprocal unit vectors $\angle(\mathbf{a}^*, \mathbf{b}^*)$ is related to that between the real-space unit vectors (\mathbf{a}, \mathbf{b}) by

$$\angle(\mathbf{a}^*, \mathbf{b}^*) = 180^\circ - \angle(\mathbf{a}, \mathbf{b}). \quad (2.10)$$

Thus, for rectangular and square lattices these angles are the same, 90°, but for the real-space and reciprocal hexagonal lattices the angle is 120° and 60°, respectively.

2.6 Brillouin Zone

A Wigner–Seitz primitive cell (see Fig. 2.2) in the reciprocal lattice is referred to as the first *Brillouin zone*. The concept of the Brillouin zone is of prime importance for the analysis of the electronic energy-band structure of crystals. As an example, Figures 2.15, 2.16, and 2.17 show the 2D Brillouin zones of the main planes of the fcc, bcc and hcp crystals, respectively, in relation to the respective bulk Brillouin zones. Symmetry points and directions are indicated using BSW (Bouckaert–Smoluchowski–Wigner) notation [2.4].

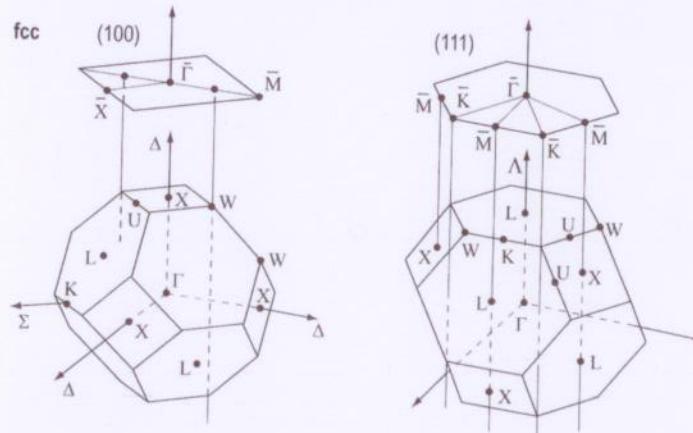


Fig. 2.15. Relation between the 2D Brillouin zones of the (100) and (111) planes of the fcc crystal and the bulk Brillouin zone. Note that the reciprocal lattice of the fcc lattice is the bcc lattice

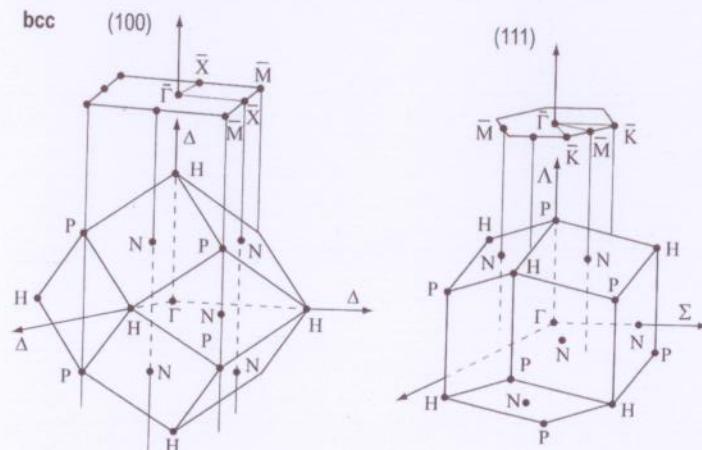


Fig. 2.16. Relation between the 2D Brillouin zones of the (100) and (111) planes of the bcc crystal and the bulk Brillouin zone. Note that the reciprocal lattice of the bcc lattice is the fcc lattice

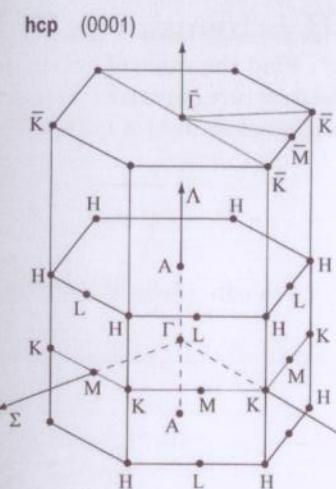


Fig. 2.17. Relation between the 2D Brillouin zone of the (0001) plane of the hcp crystal and the bulk Brillouin zone

Problems

2.1 Do the points shown in the following figure form a 2D lattice? If “yes”, show its primitive translation vectors. If “no”, provide the arguments.



2.2 Show the (133), (331), and (113) planes in the simple cubic crystal. Are they equivalent planes?

2.3 Specify the type of the 2D Bravais lattice of the (111) plane of the fcc (face-centered cubic) crystal. What is the period of this 2D lattice, if the edge of the fcc cell is a ?

2.4 Prove that the matrix notation for the $\sqrt{3} \times \sqrt{3} - R30^\circ$ superstructure on the 2D hexagonal lattice is $\begin{pmatrix} 2 & 1 \\ -1 & 1 \end{pmatrix}$, when the basic translation vectors make an angle of 120° . How will the matrix notation change, if one chooses basic vectors which make an angle of 60° ?

2.5 Nickel adsorption on the Si(111) surface (hexagonal lattice) induces a commensurate superstructure $\sqrt{7} \times \sqrt{7}-R\varphi^\circ$. Find the value of the angle φ° and construct the 2D lattice of this superstructure superposed on the 1×1 lattice. How is this superstructure designated in matrix notation?

Further Reading

1. C. Kittel: *Introduction to Solid State Physics*, 7th edn. (John Wiley, New York 1996) Chapter 1
2. G.A. Somorjai: *Introduction to Surface Chemistry and Catalysis* (John Wiley, New York 1994) Chapter 2

3. Experimental Background

The purpose of this chapter is to familiarize the reader with the experimental background of surface science. First, the necessity for usage of UHV is justified. Then, vacuum concepts are briefly considered before introducing UHV technology. Finally, the main experimental techniques for the preparation of atomically clean surfaces and the deposition of materials are discussed.

3.1 Why Ultra-High Vacuum?

The characterization of a solid surface on an atomic level implies unambiguously that the surface composition remains essentially unchanged over the duration of an experiment. This means that the rate of arrival of reaction species from the gas environment should be low, or, in other words, the experiments should be conducted in vacuum. The concept of vacuum is normally understood in terms of *molecular density*, *mean free path* and the *time constant to form a monolayer*. According to the kinetic theory of gases, the flux I of molecules impinging on the surface from the environment is given by the expression

$$I = \frac{p}{\sqrt{2\pi mk_B T}}. \quad (3.1)$$

Here p is the pressure, m is the mass of the molecule, k_B is Boltzmann's constant, and T is the temperature. Then, one can easily obtain

$$n = \frac{p}{k_B T}, \text{ molecular density}, \quad (3.2)$$

$$\lambda = \frac{f}{n\sigma^2}, \text{ mean free path}, \quad (3.3)$$

$$\tau = \frac{n_0}{I} = \frac{n_0 \sqrt{2\pi mk_B T}}{p}, \text{ time constant to form a monolayer}, \quad (3.4)$$

where σ^2 is the molecular cross-section, and n_0 is the number of atoms in a monolayer.

Table 3.1 illustrates how these values vary with the pressure. What can be learned from the table concerning the vacuum requirements for surface