

# Rudiments of

## 3. Rudiments of Crystallography

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Crystallography deals basically with the question *Where are the atoms in solids?* The purpose of this chapter is to briefly introduce the basics of modern crystallography. The focus is on the description of periodic solids, which represent the major proportion of condensed matter. A coherent introduction to the formalism required to do this is given, and the basic concepts and technical terms are briefly explained. Paying attention to recent developments in materials research, we also discuss aperiodic, disordered, and amorphous matter. Consequently, besides the conventional three-dimensional (3-D) descriptions, the higher dimensional crystallographic approach is outlined, as well as the atomic pair distribution function used to describe local phenomena. The chapter then touches on the basics of diffraction methods, the most powerful tool kit used by experimentalists dealing with structure in solid-state research. Finally, the reader will be apprised of new developments in our understanding of order in condensed matter.

<b>3.1 Crystalline Matter</b> .....	26
3.1.1 Periodic Materials .....	26
3.1.2 Aperiodic Materials .....	31
<b>3.2 Disorder</b> .....	35
3.2.1 Chemical Disorder .....	35
3.2.2 Displacive Disorder .....	36
<b>3.3 Amorphous Matter</b> .....	36
<b>3.4 Methods for Investigating Crystallographic Structure</b> .....	36
3.4.1 X-rays .....	37
3.4.2 Neutron Diffraction .....	38
3.4.3 Electron Diffraction .....	38
<b>3.5 Recent Novel Topics in Crystallography</b> ..	38
3.5.1 Quasicrystals .....	38
3.5.2 Diffraction Analysis Based on Total Scattering .....	38
<b>References</b> .....	39

The structure of solid matter is very important because physical properties are closely related to structure. In most cases solids are crystalline: they may consist of one single crystal, or be polycrystalline, consisting of many tiny single crystals in different orientations. All periodic crystals have a perfect translational symmetry. This leads to selection rules, which are very useful for the understanding of the physical properties of solids. Therefore, most textbooks on solid-state physics begin with a few chapters on symmetry and structure. Today we know that other solids, that have no translational symmetry, also exist. These are amorphous materials, which have little order (in most cases restricted to the short-range arrangement of the atoms), and aperiodic crystals, which show perfect long-range order, but no periodicity – at least in 3-D space. In this chapter, the basic concepts of crystallography – how the space of a solid can be filled with atoms – are briefly discussed.

Readers seeking greater detail about crystallography are referred to the classic textbooks [3.1–5], which, among others, can be found on the website of the International Union of Crystallography (IUCr) [3.6].

Many crystalline materials, especially minerals and gems, were described more than 2000 years ago. The regular form of crystals and the existence of facets, which have fixed angles between them, gave rise to a belief that crystals were formed by a regular repetition of tiny, identical building blocks. After the discovery of X-rays by Röntgen, Laue investigated crystals in 1912 using these X-rays and detected interference effects caused by the periodic array of atoms. One year later, Bragg determined the crystal structures of alkali halides by X-ray diffraction.

Today we know that a crystal is a 3-D array of atoms or molecules, with various types of long-range order. A more modern definition is that all materials that show

**Table 3.1** Classification of solids

Condensed matter (solids)			
Crystalline matter			Amorphous matter
Periodic structures		Aperiodic structures	
	Modulated structures	Composite structures	Quasicrystals

sharp diffraction peaks are crystalline. In this sense, aperiodic or quasicrystalline materials, as well as periodic materials, are crystals. A real crystal is never a perfect arrangement. Defects in the form of vacancies, dislocations, impurities, and other imperfections are often very important for the physical properties of a crystal. This aspect has largely been neglected in classical crystallog-

raphy but is becoming a topic in more and more modern crystallographic investigations [3.6, 7].

As indicated in Table 3.1, condensed matter can be classified as either crystalline or amorphous. Both of these states and their formal subdivisions will be discussed below. The terms *matter*, *structure*, and *material* always refer to single-phase solids.

## 3.1 Crystalline Matter

### 3.1.1 Periodic Materials

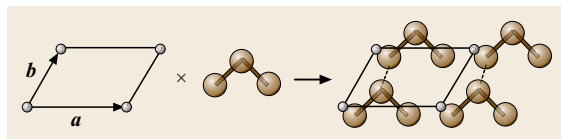
#### Lattice Concept

A periodic crystal is described by two entities, the *lattice* and the *basis*. The (translational) lattice is a perfect geometrical array of points. All lattice points are equivalent and have identical surroundings. This lattice is defined by three fundamental translation vectors  $\mathbf{a}$ ,  $\mathbf{b}$ ,  $\mathbf{c}$ . Starting from an arbitrarily chosen origin of the lattice, any other lattice point can be reached by a translation vector  $\mathbf{r}$  that satisfies

$$\mathbf{r} = u\mathbf{a} + v\mathbf{b} + w\mathbf{c},$$

where  $u$ ,  $v$ , and  $w$  are arbitrary integers. The lattice is an abstract mathematical construction; the description of the crystal is completed by attaching a set of atoms – the *basis* – to each lattice point. Therefore, the crystal structure is formed by a lattice and a basis (Fig. 3.1).

The parallelepiped that is defined by the axes  $\mathbf{a}$ ,  $\mathbf{b}$ ,  $\mathbf{c}$  is called a *primitive cell* if this cell has the smallest volume out of all possible cells. It contains one lattice point per cell only (Fig. 3.2a). This cell is a type of unit cell that fills the space of the crystal completely under the application of the translation operations of the lattice, i. e., movements along the vectors  $\mathbf{r}$ .



**Fig. 3.1** A periodic crystal can be described as a convolution of a mathematical point lattice with a basis (set of atoms). *Gray*: mathematical points; *brown*: atoms

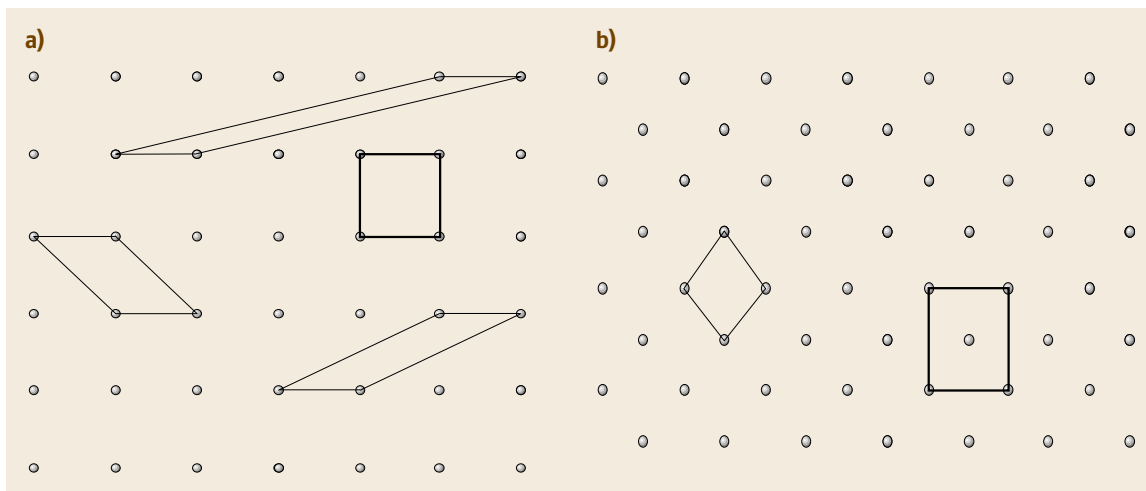
Conventionally, the smallest cell with the highest symmetry is chosen. Crystal lattices can be transformed into themselves by translation along the fundamental vectors  $\mathbf{a}$ ,  $\mathbf{b}$ ,  $\mathbf{c}$ , but also by other symmetry operations. It can be shown that only one-fold (rotation angle  $\varphi = 2\pi/1$ ), twofold ( $2\pi/2$ ), threefold ( $2\pi/3$ ), fourfold ( $2\pi/4$ ), and sixfold ( $2\pi/6$ ) rotation axes are permissible. Other rotational axes cannot exist in a lattice, because they would violate the translational symmetry. For example, it is not possible to fill the space completely with a fivefold ( $2\pi/5$ ) array of regular pentagons. Additionally, mirror planes and centers of inversion may exist. The restriction to high-symmetry cells may also lead to what is known as centering. Figure 3.2b illustrates a 2-D case. The centering types in 3-D are listed in Table 3.2.

#### Planes and Directions in Lattices

If one peers through a 3-D lattice from various angles, an infinity of equidistant planes can be seen. The

**Table 3.2** Centering types for 3-D crystallographic unit cells

Symbol	Description	Points per unit cell
$P$	No centering (primitive)	1
$I$	Body-centered ( <i>innenzentriert</i> )	2
$F$	All-face-centered	4
$S$ ; $A$ , $B$ , $C$ in specific cases	One-face-centered ( <i>seitenzentriert</i> ); ( $\mathbf{b}$ , $\mathbf{c}$ ), ( $\mathbf{a}$ , $\mathbf{c}$ ), and ( $\mathbf{a}$ , $\mathbf{b}$ ), respectively, in specific cases	2
$R$	Hexagonal cell, rhombohedrally centered	3



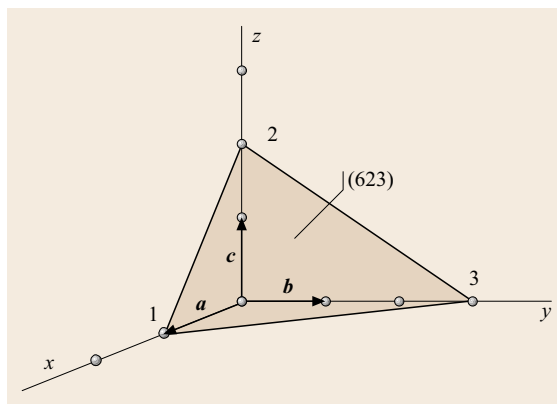
**Fig. 3.2a,b** Possible primitive and centered cells in 2-D lattices. *Open circles* denote mathematical points. **(a)** In this lattice, the conventional cell is the *bold square cell* because of its highest symmetry,  $4mm$ . **(b)** Here, convention prefers  $90^\circ$  angles: a centered cell of symmetry  $2mm$  is chosen. It contains two lattice points and is twice the area of the primitive cell

position and orientation of such a crystal plane are determined by three points. It is easy to describe a plane if all three points lie on crystal axes (i. e., the directions of unit cell vectors); in this case only the intercepts need to be used. It is common to use *Miller indices* to describe lattice planes. These indices are determined as follows:

1. For the plane of interest, determine the intercepts  $x, y, z$  of the crystal axes  $\mathbf{a}, \mathbf{b}, \mathbf{c}$ .
2. Express the intercepts in terms of the basic vectors  $\mathbf{a}, \mathbf{b}, \mathbf{c}$  of the unit cell, i. e., as  $x/a, y/b, z/c$  (where  $a = |\mathbf{a}|, \dots$ ).
3. Form the reciprocals  $a/x, b/y, c/z$ .
4. Reduce this set to the smallest integers  $h, k, l$ . The result is written  $(hkl)$ .

The distance from the origin to the plane  $(hkl)$  inside the unit cell is the interplanar spacing  $d_{hkl}$ . Negative intercepts, leading to negative Miller indices, are written as  $\bar{h}$ . Figure 3.3 shows a  $(623)$  plane and its construction.

A direction in a crystal is given as a set of three integers in square brackets  $[uvw]$ ;  $u, v,$  and  $w$  correspond to the above definition of the translation vector  $\mathbf{r}$ . A direction in a cubic crystal can be described also by Miller indices, as a plane can be defined by its normal. The indices of a direction are expressed as the smallest integers which have the same ratio as the components of a vector (expressed in terms of the axis vectors  $\mathbf{a}, \mathbf{b}, \mathbf{c}$ ) in that direction. Thus, the sets of integers 1, 1, 1 and 3, 3, 3 represent the same direction in a crystal, but



**Fig. 3.3** Miller indices: the intercepts of the  $(623)$  plane with the coordinate axes

the indices of the direction are  $[111]$  and not  $[333]$ . To give another example, the  $x$  axis of an orthogonal  $x, y, z$  coordinate system has Miller indices  $[100]$ ; the plane perpendicular to this direction has indices  $(100)$ .

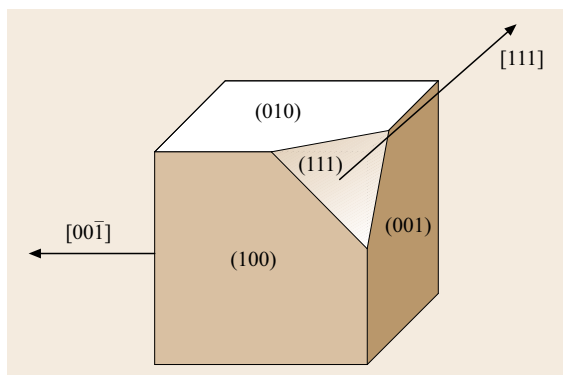
For all crystals, except for the hexagonal system, the Miller indices are given in a three-digit system in the form  $(hkl)$ . However, for the hexagonal system, it is common to use four digits  $(hkil)$ . The four-digit hexagonal indices are based on a coordinate system containing four axes. Three axes lie in the basal plane of the hexagon, crossing at angles of  $120^\circ$ :  $\mathbf{a}, \mathbf{b},$  and  $-(\mathbf{a} + \mathbf{b})$ . As the third vector in the basal plane can be expressed in terms of  $\mathbf{a}$  and  $\mathbf{b}$ , the index can be expressed in terms of  $h$  and  $k$ :  $i = -(h + k)$ . The fourth axis is the  $\mathbf{c}$  axis normal to the basal plane.

### Crystal Morphology

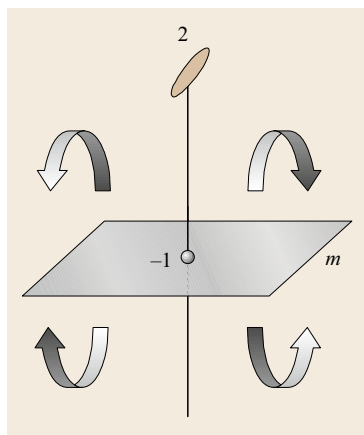
The regular facets of a crystal are planes of the type described above. Here, the lattice architecture of the crystal is visible macroscopically at the surface. Figure 3.4 shows some surfaces of a cubic crystal. If the crystal had the shape or morphology of a cube, this would be described by the set of facets  $\{(100), (010), (001), (\bar{1}00), (0\bar{1}0), (00\bar{1})\}$ . An octahedron would be described by  $\{(111), (\bar{1}\bar{1}\bar{1}), (1\bar{1}\bar{1}), (\bar{1}1\bar{1}), (\bar{1}\bar{1}1), (1\bar{1}1), (\bar{1}11), (\bar{1}\bar{1}1)\}$ . The morphology of a crystalline material may be of technological interest (in relation to the bulk density, flow properties, etc.) and can be influenced in various ways, for example by additives during the crystallization process.

### The 32 Crystallographic Point Groups

The symmetry of the space surrounding a lattice point can be described by the point group, which is a set of symmetry elements acting on the lattice. The crystallographic symbols for the symmetry elements of point groups compatible with a translational lattice are the rotation axes 1, 2, 3, 4, and 6, mirror planes  $m$ , and the



**Fig. 3.4** Some crystal planes and directions in a cubic crystal, and their Miller indices



**Fig. 3.5** The point group  $2/m$  ( $C_{2h}$ ). Any object in space can be rotated by  $\varphi = 2\pi/2$  around the twofold rotational axis 2 and reflected by the perpendicular mirror plane  $m$ , generating identical copies. The inversion center  $\bar{1}$  is implied by the coupling of 2 and  $m$

center of inversion  $\bar{1}$ . Figure 3.5 illustrates, as an example, the point group  $2/m$ . The 2 denotes a twofold axis perpendicular ( $\perp$ ) to a mirror plane  $m$ . Note that this combination of 2 and  $m$  implies, or generates automatically, an inversion center  $\bar{1}$ . We have used the Hermann–Mauguin notation here. However, point groups of isolated molecules are more often denoted by the Schoenflies symbols. For a translation list, see Table 3.3.

No crystal can have a higher point group symmetry than the point group of its lattice, called the *holohedry*. In accordance with the various rotational symmetries, there are seven crystal systems (Table 3.3), and the seven holohedries are  $\bar{1}$ ,  $2/m$ ,  $mmm$ ,  $4/mmm$ ,  $\bar{3}m$ ,  $6/mmm$ , and  $m\bar{3}m$ . Other, less symmetric, point groups are also compatible with these lattices, leading to a total number of 32 crystallographic point groups (Table 3.4). A lower symmetry than the holohedry can

**Table 3.3** The 32 crystallographic point groups: translation list from the Hermann–Mauguin to the Schoenflies notation

Crystal system	Hermann–Mauguin symbol	Schoenflies symbol
Triclinic	1	$C_1$
	$\bar{1}$	$C_i$
Monoclinic	2	$C_2$
	$m$	$C_s$
	$2/m$	$C_{2h}$
Orthorhombic	222	$D_2$
	$mm2$	$C_{2v}$
	$mmm$	$D_{2h}$
Tetragonal	4	$C_4$
	$\bar{4}$	$S_4$
	$4/m$	$C_{4h}$
	422	$D_4$
	$4mm$	$C_{4v}$
	$\bar{4}2m$	$D_{2d}$
	$4/mmm$	$D_{4h}$
Trigonal	3	$C_3$
	$\bar{3}$	$C_{3i}$
	32	$D_3$
	$3m$	$C_{3v}$
	$\bar{3}m$	$D_{3d}$
Hexagonal	6	$C_6$
	$\bar{6}$	$C_{3h}$
	$6/m$	$C_{6h}$
	622	$D_6$
	$6mm$	$C_{6v}$
	$\bar{6}2m$	$D_{3h}$
	$6/mmm$	$D_{6h}$
Cubic	23	$T$
	$m\bar{3}$	$T_h$
	432	$O$
	$\bar{4}3m$	$T_d$
	$m\bar{3}m$	$O_h$

**Table 3.4** Crystal families, crystal systems, crystallographic point groups, conventional coordinate systems, and Bravais lattices in three dimensions. Lattice point symmetries (holohedries) are given in *bold*

Crystal family	Symbol	Crystal system	Crystallographic point groups	No. of space groups	Conventional coordinate system		Bravais lattice (Pearson symbol)
					Restrictions on cell parameters	Parameters to be determined	
Triclinic (Anorthic)	<i>a</i>	Triclinic	$1, \bar{1}$	2	None	<i>a, b, c, α, β, γ</i>	aP
Monoclinic	<i>m</i>	Monoclinic	$2, m, 2/m$	13	Setting with <i>b</i> unique: $\alpha = \gamma = 90^\circ$ Setting with <i>c</i> unique: $\alpha = \beta = 90^\circ$	<i>a, b, c, β, a, b, c, γ</i>	mP, mS (mC, mA, mI) mP, mS (mA, mB, mI)
Orthorhombic	<i>o</i>	Orthorhombic	$222, mm2, mmm$	59	$\alpha = \beta = \gamma = 90^\circ$	<i>a, b, c</i>	oP, oS, (oC, oA, oB) oI, oF
Tetragonal	<i>t</i>	Tetragonal	$4, \bar{4}, 4/m, 422, 4mm, \bar{4}2m, 4/mmm$	68	$a = b, \alpha = \beta = \gamma = 90^\circ$	<i>a, c</i>	tP, tI
Hexagonal	<i>h</i>	Trigonal	$3, \bar{3}, 32, 3m, \bar{3}m$	18	$a = b, \alpha = \beta = 90^\circ, \gamma = 120^\circ$ (hexagonal axes)	<i>a, c</i>	hP
				7	$a = b = c, \alpha = \beta = \gamma \neq 90^\circ$ (rhombohedral axes)	<i>a, α</i>	hR
		Hexagonal	$6, \bar{6}, 6/m, 622, 6mm, \bar{6}2m, 6/mmm$	27	$a = b, \alpha = \beta = 90^\circ, \gamma = 120^\circ$	<i>a, c</i>	hP
Cubic	<i>c</i>	Cubic	$23, m\bar{3}, 432, \bar{4}3m, m\bar{3}$	36	$a = b = c, \alpha = \beta = \gamma = 90^\circ$	<i>a</i>	cP, cI, cF

be introduced by a less symmetric basis in the unit cell.

Since  $\bar{3}m$  and  $6/mmm$  are included in the same point lattice, they are sometimes subsumed into the hexagonal crystal family. So there are seven crystal systems but six crystal families. Note further that rhombohedral symmetry is a special case of centering (*R*-centering) of the trigonal crystal system and offers two equivalent possibilities for selecting the cell parameters: hexagonal or rhombohedral axes (Table 3.4).

It can be shown that in 3-D there are 14 different periodic ways of arranging identical points. These 14 3-D periodic point lattices are called the (translational) Bravais lattices and are shown in Fig. 3.6. Table 3.4 presents data related to some of the crystallographic terms used here. The 1-D and 2-D space groups can be classified analogously but are omitted here.

### The 230 Crystallographic Space Groups

Owing to the 3-D translational periodicity, additional symmetry operations other than point group operations are possible: these are *glide planes* and *screw axes*. A glide plane couples a mirror operation and a translational shift. The symbols for glide planes are *a, b, and c* for translations along the lattice vectors *a, b, and c*, respectively, and *n* and *d* for some special lattice vector combinations. A screw axis is always parallel to a rotational axis. The symbols are  $2_1, 3_1, 3_2, 4_1, 4_2, 4_3, 6_1, 6_2, 6_3, 6_4,$  and  $6_5$ , where, for example,  $6_3$  means a rotation through an angle  $\varphi = 2\pi/6$  followed by a translation of  $3/6 (= 1/2)$  of a full translational period along the sixfold axis.

Thus, the combination of 3-D translational and point symmetry operations leads to an infinite number of sets of symmetry operations. Mathematically, each

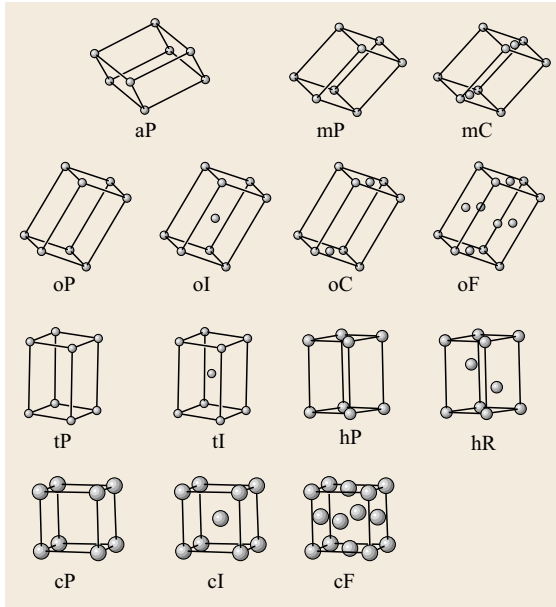


Fig. 3.6 The 14 Bravais lattices

of these sets forms a group, and they are called *space groups*. It can be shown that all possible periodic crystals can be described by only 230 space groups. These 230 space groups are described in tables, for example the *International Tables for Crystallography* [3.8].

In this formalism, a conventional space group symbol reflects the symmetry elements, arranged in the order of standardized *blickrichtungen* (symmetry directions). We shall confine ourselves here to explaining one instructive example:  $P4_2/mcm$ , space group number 132 [3.8]. The full space group symbol is  $P4_2/m2/c2/m$ . The meaning of the symbols is the following:  $P$  denotes a primitive Bravais lattice. It belongs to the tetragonal crystal system indicated by 4. Along the first standard *blickrichtung* [001] there is a  $4_2$  screw axis with a perpendicular mirror plane  $m$ . Along [100] there is a twofold rotation axis, named 2, with a perpendicular glide plane  $c$  parallel to  $c$ . Third, along [110] there is a twofold rotation axis 2, with a perpendicular mirror plane  $m$ .

#### Decoration of the Lattice with the Basis

At this point we should recall that in a real crystal structure we have not only the lattice, but also the basis. In [3.8], there are standardized sets of general and special positions (i. e., coordinates  $x, y, z$ ) within the unit cell (Wyckoff positions). An atom placed in a general position is transformed into more than one atom by the action of all symmetry operators of the respective space group. Special positions are located on special points that are mapped onto themselves

by one or more symmetry operations – for example a position in a mirror plane or exactly on a rotational axis. Reference [3.8] also provides information about symmetry relations between individual space groups (group–subgroup relations). These are often useful for describing relationships between crystal structures and for describing phase transitions of materials.

The use of the space group allows us to further reduce the basis to the *asymmetric unit*: this is the minimal set of atoms that needs to be given so that the whole crystal structure can be generated via the symmetry of the space group. This represents the main power of a crystallographically correct description of a material: just some ten parameters are sufficient to describe an ensemble of some  $10^{23}$  atoms.

Thus, a crystallographic periodic structure of a material is unambiguously characterized by:

- The cell parameters
- The space group
- The coordinates of the atoms (and their chemical type) in the asymmetric unit
- The occupation and thermal displacement factors of the atoms in the asymmetric unit.

For an example, the reader is referred to the crystallographic description of the spinel structure of  $MgAl_2O_4$  given below under the heading *Structure Types*.

To complete the information on space group symmetries given here, periodic magnetic materials should also be mentioned. Magnetic materials contain magnetic moments carried by atoms in certain positions in the unit cell. If we take into account the magnetic moments in the description of the structure, the classification by space groups (the 230 *gray* groups, described above) has to be extended to 1651 *black and white*, or Shubnikov, groups [3.9]. A magnetic periodic structure is then characterized by:

- The crystallographic structure
- The Shubnikov group
- The cell parameters of the magnetic unit cell
- The coordinates of the atoms carrying magnetic moments (the asymmetric unit in the magnetic unit cell)
- The magnitude and direction of the magnetic moments on these atoms.

#### Structure Types

It is useful to classify the crystal structures of materials by the assignment of *structure types*. The structure type is based on a representative crystal structure, the parameters of which describe the essential crystallographic

**Table 3.5** Complete crystallographic parameter set for  $\text{MgAl}_2\text{O}_4$ , spinel structure type

Material	$\text{MgAl}_2\text{O}_4$				
Structure type	$\text{MgAl}_2\text{O}_4$ , spinel				
Pearson symbol	cF56				
Space group	$Fd\bar{3}m$ (No. 227)				
$a$ (Å)	8.174(1)				
Atom	Wyckoff position	$x$	$y$	$z$	Occupancy
Mg	8a	0	0	0	1.0
Al	16d	5/8	5/8	5/8	1.0
O	32e	0.3863(2)	$x$	$x$	1.0

features of other materials of the same type. As an example, we consider the structure of the spinel oxides  $AB_2O_4$ . The generic structure type is  $\text{MgAl}_2\text{O}_4$ , cF56. The *Pearson symbol*, here cF56, denotes the cubic crystal family and a face-centered Bravais lattice with 56 atoms per unit cell (Table 3.5 and also the last column in Table 3.4).

Regarding the free parameters, for example  $a$ , the notation 8.174(1) in Table 3.5 means  $8.174 \pm 0.001$ . The chemical formula and the unit cell contents can easily be calculated from the site multiplicities (given by the Wyckoff positions) and the occupancies; so can the (crystallographic) density, using the appropriate atomic masses.

A huge variety of other materials belong to the same structure type as in this example. The only parameters that differ (slightly) are the numerical value of  $a$ , the types of atoms in the positions, the numerical value of the parameter  $x$  for Wyckoff position 32e, and the occupancies. Thus, for example, the crystal structure of the iron sulfide  $\text{Fe}_3\text{S}_4$  can be characterized in its essential features via the information that it belongs to the same structure type.

### 3.1.2 Aperiodic Materials

In addition to the crystalline periodic state of matter, a class of materials exists that lacks 3-D translational symmetry and is called *aperiodic* [3.10]. Aperiodic ma-

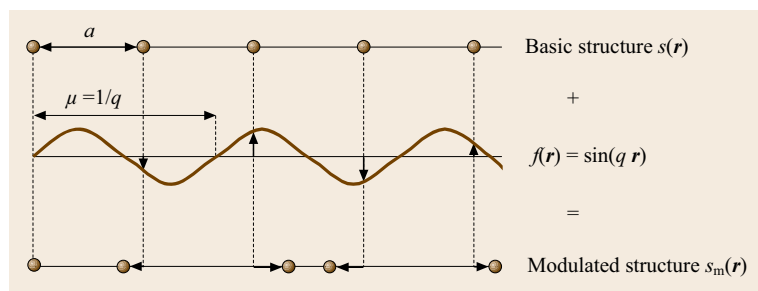
terials cannot be described by any of the 230 space groups mentioned above. Nevertheless, they show another type of long-range order and are therefore included in the term *crystal*. This notion of long-range order is the major feature that distinguishes crystals from amorphous materials. Three types of aperiodic order may be distinguished, namely modulated structures, composite structures, and quasicrystals. All aperiodic solids exhibit an essentially discrete diffraction pattern and can be described as atomic structures obtained from a 3-D section of an  $n$ -dimensional ( $n$ -D) ( $n > 3$ ) periodic structure.

#### Modulated Structures

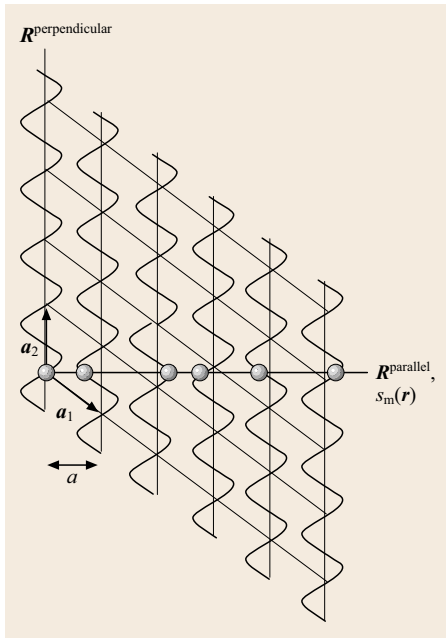
In a modulated structure, periodic deviations of the atomic parameters from a reference or basic structure are present. The basic structure can be understood as a periodic structure as described above. Periodic deviations of one or several of the following atomic parameters are superimposed on this basic structure:

- Atomic coordinates
- Occupancy factors
- Thermal displacement factors
- Orientations of magnetic moments.

Let the period of the basic structure be  $a$  and the modulation wavelength be  $\lambda$ ; the ratio  $a/\lambda$  may be (1) a rational or (2) an irrational number (Fig. 3.7). In case (1), the structure is commensurately modulated; we observe a  $qa$  superstructure, where  $q = 1/\lambda$ . This superstructure is periodic. In case (2), the structure is incommensurately modulated. Of course, the experimental distinction between the two cases is limited by the finite experimental resolution.  $q$  may be a function of external variables such as temperature, pressure, or chemical composition, i. e.,  $q = f(T, p, X)$ , and may adopt a rational value to result in a commensurate *lock-in* structure. Conversely, an incommensurate charge-density wave may exist; this can be moved through a basic crystal without changing the internal energy  $U$  of the crystal.



**Fig. 3.7** A 1-D modulated structure  $s_m(\mathbf{r})$  can be described as a sum of a basic structure  $s(\mathbf{r})$  and a modulation function  $f(\mathbf{r})$  of its atomic coordinates. If  $a/\lambda$  is irrational, the structure is incommensurately modulated. *Circles* denote atoms

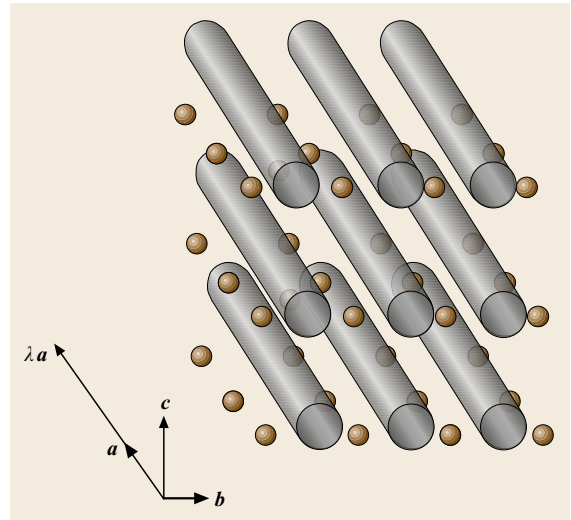


**Fig. 3.8** 2-D hyperspace description of the example shown in Fig. 3.7. The basis of the hyperspace  $\mathbf{R} = \mathbf{R}^{\text{parallel}} \oplus \mathbf{R}^{\text{perpendicular}}$  is  $(\mathbf{a}_1, \mathbf{a}_2)$ ; the slope of  $\mathbf{a}_1$  with respect to  $\mathbf{R}^{\text{parallel}}$  is proportional to  $\lambda$ . Atoms of the modulated structure  $s_m(\mathbf{r})$  occur in the physical space  $\mathbf{R}^{\text{parallel}}$  and are represented by circles

When a 1-D basic structure and its modulation function are combined in a 2-D hyperspace  $\mathbf{R} = \mathbf{R}^{\text{parallel}} \oplus \mathbf{R}^{\text{perpendicular}}$ , periodicity on a 2-D lattice results. The real atoms are generated by the intersection of the 1-D physical (external, parallel) space  $\mathbf{R}^{\text{parallel}}$  with the hyperatoms in the complementary 1-D internal space  $\mathbf{R}^{\text{perpendicular}}$ . In the case of a modulated structure, the hyperatoms have the shape of the sinusoidal modulation function in  $\mathbf{R}^{\text{perpendicular}}$ .

Figure 3.8 illustrates this construction. We have to choose a basis  $(\mathbf{a}_1, \mathbf{a}_2)$  in  $\mathbf{R}$  where the slope of  $\mathbf{a}_1$  with respect to  $\mathbf{R}^{\text{parallel}}$  corresponds to the length of the modulation  $\lambda$ .

It is clear that real atomic structures are always manifestations of matter in 3-D real, physical space. The cutting of the 2-D hyperspace to obtain real 1-D atoms illustrated in Fig. 3.8 may serve as an instructive basic example of the concept of higher dimensional ( $n$ -D,  $n > 3$ ) crystallography. The concept is also called a superspace description; it applies to all aperiodic structures and provides a convenient finite set of variables that can be used to compute the positions of all atoms in the real 3-D structure.



**Fig. 3.9** Host-guest channel structure. The guest atoms reside in channels parallel to  $\mathbf{a}$ , with a periodicity  $\lambda \mathbf{a}$

The modulation may occur in one, two, or three directions of the basic structure, yielding 1-D, 2-D, or 3-D modulated structures. If we introduce one additional dimension per modulation vector (the direction  $\mathbf{r}$  that the modulation corresponding to  $\lambda$  runs along), these structures can be described as periodic in 4-D, 5-D, or 6-D superspace, respectively.

### Composite Structures

Composite crystals are crystalline structures that consist of two or more periodic substructures, each one having its own 3-D periodicity to a first approximation. The symmetry of each of these subsystems is characterized by one of the 230 space groups. However, owing to their mutual interaction, the true structure consists of a collection of incommensurately modulated subsystems. All known composite structures to date have at least one lattice direction in common and consist of a maximum of three substructures. There are three main classes:

- Channel structures
- Columnar packings
- Layer packings.

These composite structures are also known as intergrowth or host-guest structures. Figure 3.9 illustrates an example of a host with channels along  $\mathbf{a}$ , in which atoms of the substructure with a periodicity  $\lambda \mathbf{a}$  reside as a guest.

The higher dimensional  $n$ -D formalism ( $n > 3$ ) used to describe composite structures is essentially the same as that which applies to modulated structures.



### Quasicrystals

Quasicrystals represent the third type of aperiodic materials. Quasiperiodicity may occur in one, two, or three dimensions of physical space and is associated with special irrational numbers such as the golden mean

$$\tau = \frac{1 + \sqrt{5}}{2},$$

and

$$\xi = 2 + \sqrt{3}.$$

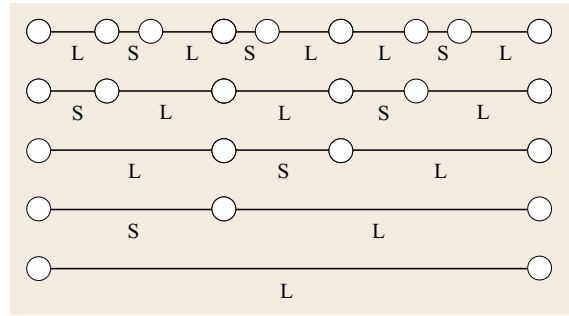
The most remarkable feature of quasicrystals is the appearance of noncrystallographic point group symmetries in their diffraction patterns, such as  $8/mmm$ ,  $10/mmm$ ,  $12/mmm$ , and  $2/m\bar{3}5$ . The golden mean is related to fivefold symmetry via the relation  $\tau = 2\cos(\pi/5)$ ;  $\tau$  can be considered as the *most irrational* number, since it is the irrational number that has the worst approximation by a truncated continued fraction,

$$\tau = 1 + \frac{1}{1 + \frac{1}{1 + \frac{1}{1 + \frac{1}{1 + \dots}}}}.$$

This might be a reason for the stability of quasiperiodic systems where  $\tau$  plays a role. A prominent 1-D example is the Fibonacci sequence, an aperiodic chain of short and long segments S and L with lengths  $S$  and  $L$ , where the relations  $L/S = \tau$  and  $L + S = \tau L$  hold. A Fibonacci chain can be constructed by the simple substitution or inflation rule  $L \rightarrow LS$  and  $S \rightarrow L$  (Table 3.6, Fig. 3.10). Materials quasiperiodically modulated in 1-D along one direction may occur. Again, their structures are

**Table 3.6** Generation of the Fibonacci sequence using the inflation rule  $L \rightarrow LS$  and  $S \rightarrow L$ . The ratio  $F_{n+1}/F_n$  tends towards  $\tau$  for  $n \rightarrow \infty$ .  $F_n$  is a Fibonacci number;  $F_{n+1} = F_n + F_{n-1}$ . The sequence starts with  $F_0 = 0$ ,  $F_1 = 1$

Sequence	$n$	$F_{n+1}/F_n$
L	1	$1/1 = 1$
LS	2	$2/1 = 2$
LSL	3	$3/2 = 1.5$
LSLLS	4	$5/3 = 1.66666\dots$
LSLLSLSL	5	$8/5 = 1.6$
...		
...LSLLSLSLS...	$\infty$	$\tau = 1.61803\dots$



**Fig. 3.10** 1-D Fibonacci sequence. Moving downwards corresponds to an inflation of the self-similar chains, and moving upwards corresponds to a deflation

readily described using the superspace formalism as above.

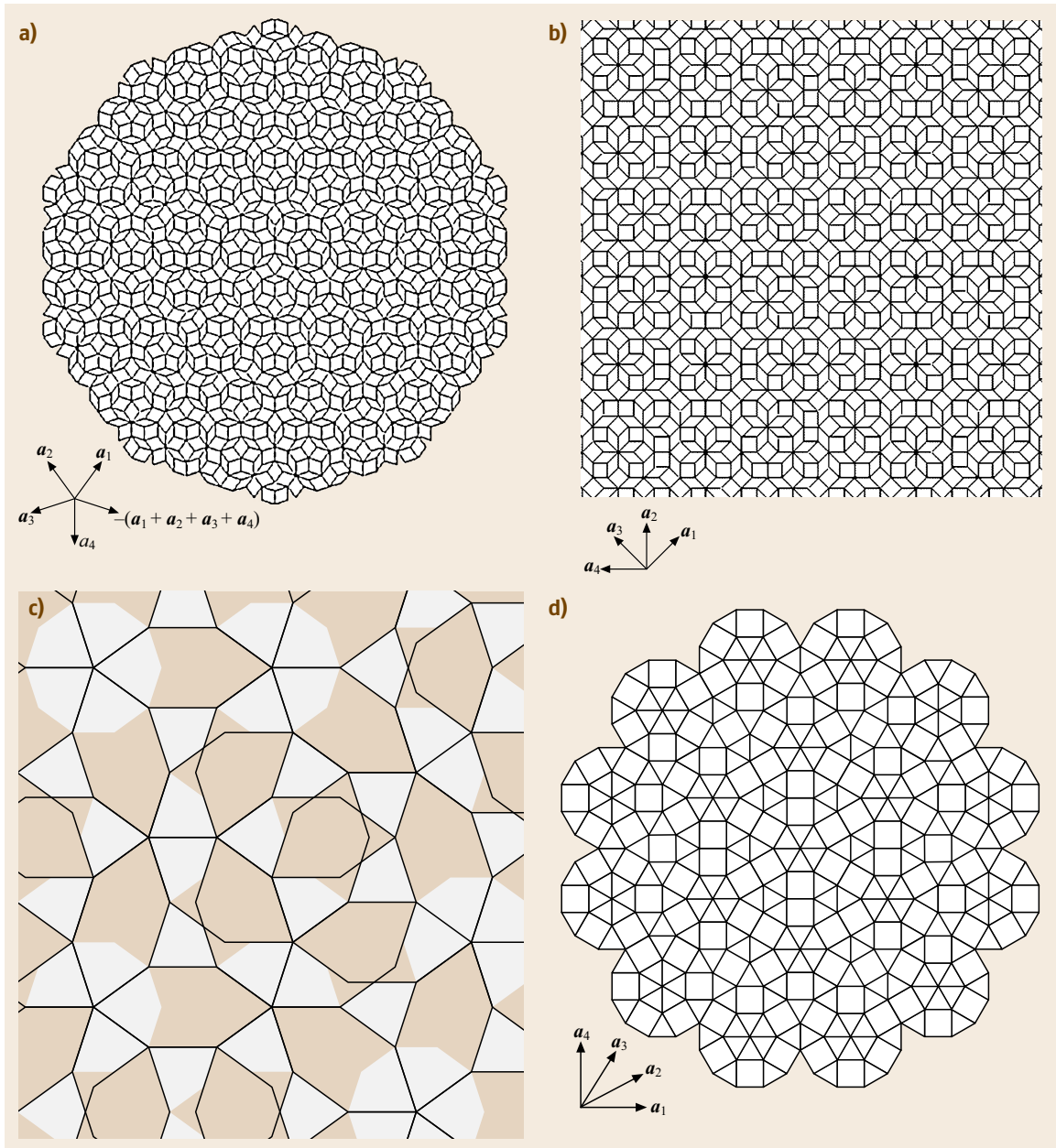
The Fibonacci sequence can be used to explain the idea of a periodic rational approximant. If the sequence  $\dots LSLLSLSLS \dots$  represents a quasicrystal, then the periodic sequence  $\dots LSLSLSLSLS \dots$ , consisting only of the word LS, is its  $2/1$  approximant (Table 3.6). In real systems, such approximants often exist as large-unit-cell (periodic!) structures with atomic arrangements locally very similar to those in the corresponding quasicrystal. When described in terms of superspace, they would result via cutting with a rational slope, in the above example  $2/1 = 2$ , instead of  $\tau = 1.6180\dots$

To date, all known 2-D quasiperiodic materials exhibit noncrystallographic diffraction symmetries of  $8/mmm$ ,  $10/mmm$ , or  $12/mmm$ . The structures of these materials are called octagonal, decagonal, and dodecagonal structures, respectively. Quasiperiodicity is present only in planes stacked along a perpendicular periodic direction. To index the lattice points in a plane, four basis vectors  $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3, \mathbf{a}_4$  are needed; a fifth one,  $\mathbf{a}_5$ , describes the periodic direction. Thus, a 5-D hypercrystal is appropriate for describing the solid periodically. In an analogous way to the 230 3-D space groups, the 5-D superspace groups (e.g.,  $P10_5/mmc$ ) provide:

- The multiplicity and Wyckoff positions
- The site symmetry
- The coordinates of the hyperatoms.

Again, the quasiperiodic structure in 3-D can be obtained from an intersection with the external space [3.10].

On the atomic scale, these intermetallic (*hard*) quasicrystals consist of units of some 100 atoms, are called clusters. These clusters, of point symmetry  $8/mmm$ ,  $10/mmm$ , or  $12/mmm$  (or less), are fused, may

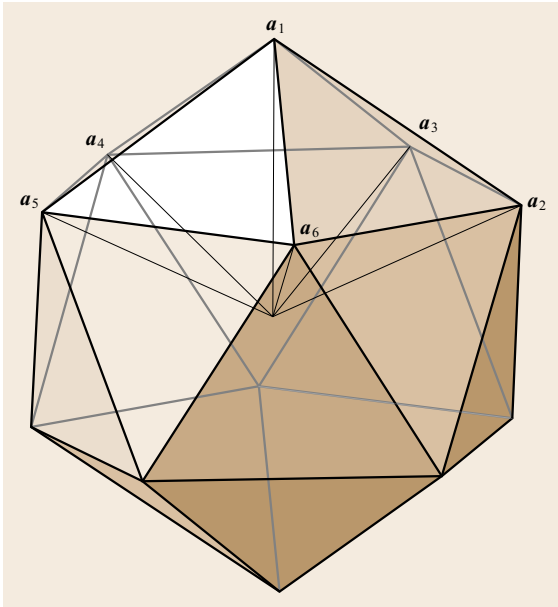


**Fig. 3.11a–d** Some 2-D quasiperiodic tilings; the corresponding four basis vectors  $\mathbf{a}_1, \dots, \mathbf{a}_4$  are shown. Linear combinations of  $\mathbf{r} = \sum_i u_i \mathbf{a}_i$  reach all lattice points. **(a)** Penrose tiling with local symmetry  $5mm$  and diffraction symmetry  $10mm$ , **(b)** octagonal tiling with diffraction symmetry  $8mm$ , **(c)** Gummelt tiling with diffraction symmetry  $10mm$ , and **(d)** dodecagonal Stampfli-type tiling with diffraction symmetry  $12mm$

interpenetrate partially, and can be considered to decorate quasiperiodic tilings. In a diffraction experiment, their superposition leads to an overall noncrystallographic symmetry. More recently, mesoscopic organic structures exhibiting 12-fold diffraction symmetry (*soft* quasicrystals) have been found. There are a number

of different tilings that show such noncrystallographic symmetries. Figure 3.11 depicts four of them, as examples of the octagonal, decagonal, and dodecagonal cases.

*Icosahedral quasicrystals* are also known. In 3-D, the icosahedral diffraction symmetry  $2/m\bar{3}5$  can be ob-



**Fig. 3.12** Unit vectors  $a_1, \dots, a_6$  of an icosahedral lattice

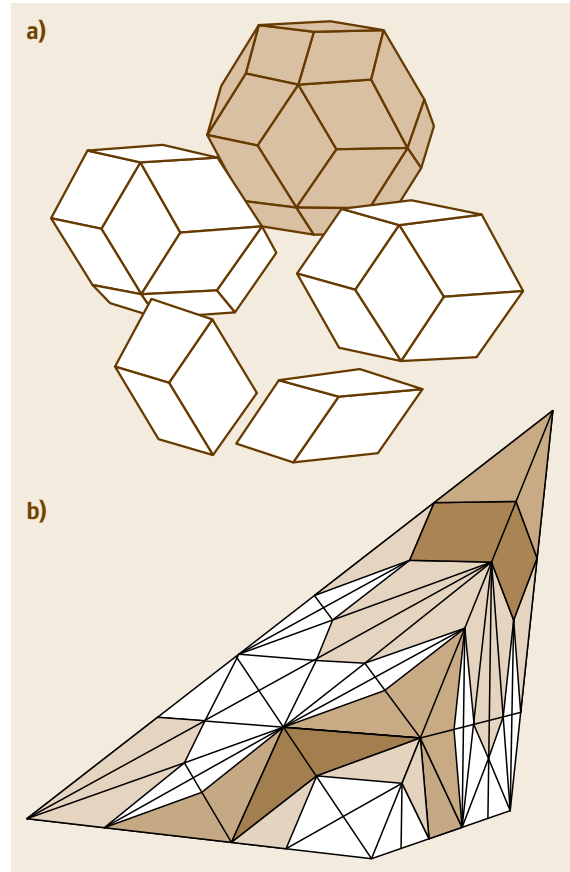
served for these quasicrystals. Their diffraction patterns can be indexed using six integers, leading to a 6-D superspace description (Fig. 3.12). On the atomic scale in 3-D, in physical space, clusters of some 100 atoms are arranged on the nodes of 3-D icosahedral tilings; the clusters have an icosahedral point group symmetry or less, partially interpenetrate, and generate an overall symmetry  $2/m\bar{3}5$ . Many of their structures are still waiting to be determined completely. Figure 3.13 shows the two golden rhombohedra and the four Danzer tetrahedra that can be used to tile 3-D space icosahedrally.

## 3.2 Disorder

In between the ideal crystalline and the purely amorphous states, most real crystals contain degrees of disorder. Since too many types of possible disorder exist, they cannot be discussed in this short overview. Two types of statistical disorder have to be distinguished: chemical disorder and displacive disorder (Fig. 3.14). Statistical disorder contributes to the entropy  $S$  of the solid and is manifested by diffuse scattering in diffraction experiments. It may occur in both periodic and aperiodic materials.

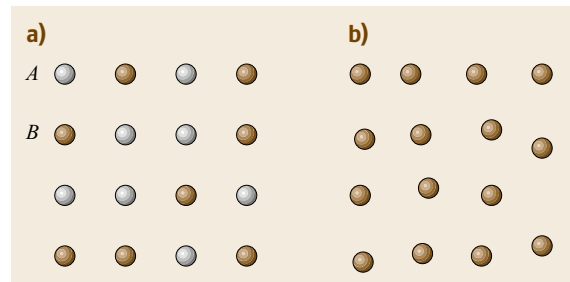
### 3.2.1 Chemical Disorder

Chemical disorder is observed, for example, in the case of solid solutions, say of  $B$  in  $A$ , or  $A_{1-x}B_x$  for short.



**Fig. 3.13a,b** Icosahedral tilings. (a) The two *white* rhombohedra (*bottom*) can be used to form icosahedral objects (the rhombic triacontahedron with point symmetry  $m\bar{3}5$  shown in *brown*). (b) Danzer's  $\{ABCK\}$  tiling: three inflation steps for prototile A

Here, an average crystal structure exists. On the crystallographic atomic positions, different atomic species



**Fig. 3.14a,b** Schematic sketch of (a) chemical and (b) displacive disorder

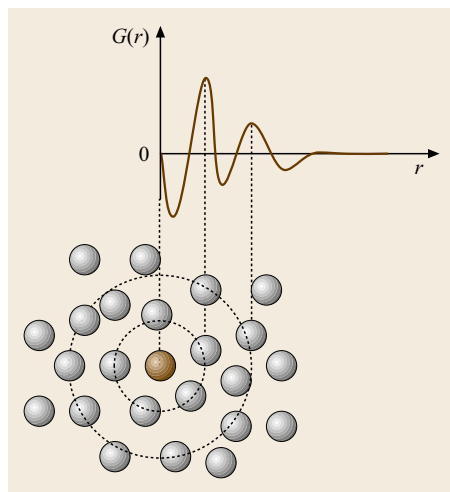
(the chemical elements  $A$  and  $B$ ) are distributed randomly. Generally, the cell parameter  $a$  varies with  $x$ . For  $x = 0$  or  $1$ , the pure end member is present. A linear variation of  $a(x)$  is predicted by Vegard's law. On the atomic scale, however, differences in the local structure are present owing to the different contacts  $A-A$ ,  $B-B$ , and  $A-B$ . These differences are usually represented by enlarged displacement factors, but can be investigated by analyzing the pair distribution function  $G(r)$ .  $G(r)$  represents the probability of finding any atom at a distance  $r$  from any other atom relative to an average density. Chemical disorder can also occur on only

one or a few of the crystallographically different atomic positions (e.g.,  $A(X_{1-x}Y_x)_2$ ). This type of disorder is often intrinsic to a material and may be temperature-dependent.

### 3.2.2 Displacive Disorder

The displacive type of disorder can be introduced by the presence of voids or vacancies in the structure or may exist for other reasons. Vacancies can be an important feature of a material: for example, they may lead to ionic conductivity or influence the mechanical properties.

## 3.3 Amorphous Matter



**Fig. 3.15** Radial atomic pair distribution function  $G(r)$  of an amorphous material. Its shape can be deduced from diffuse scattering

The second large group of condensed matter is classified as the amorphous or glassy state. No long-range order is observed. The atoms are more or less statistically distributed in space, but a certain short-range order is present.

This short-range order is reflected in certain average coordination numbers or average coordination geometries. If there are strong (covalent) interactions between neighboring atoms, similar basic units may occur, which are in turn oriented randomly with respect to each other. The  $\text{SiO}_4$  tetrahedron in silicate glasses is a well-known example. In an X-ray diffraction experiment on an amorphous solid, only isotropic diffuse scattering is observed. From this information, the radial atomic pair distribution function (Fig. 3.15) can be obtained. This function  $G(r)$  can be interpreted as the probability of finding any atom at a distance  $r$  from any other atom relative to an average density.

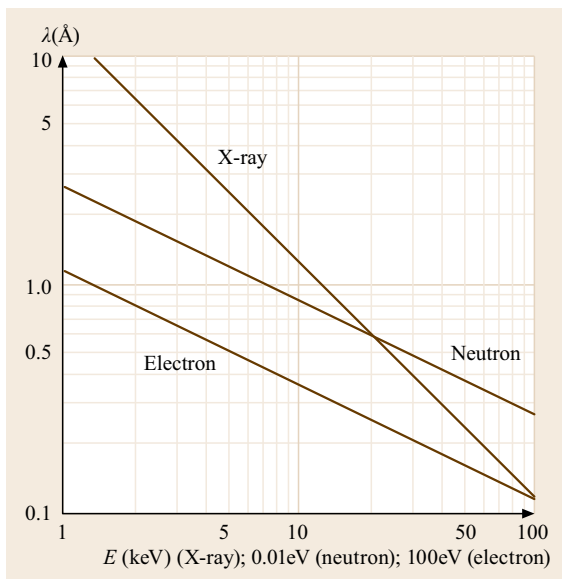
## 3.4 Methods for Investigating Crystallographic Structure

So far, we have been dealing with the formal description of solids. To conclude this chapter, the tool kit that an experimentalist needs to obtain structural information about a material in front of him/her will be briefly described.

The major technique used to derive the atomic structure of solids is the diffraction method. To obtain the most comprehensive information about a solid, other techniques may be used in addition to complement a model based on diffraction data. These techniques include scanning electron microscopy (SEM), atomic force microscopy (AFM), wavelength-dispersive analysis of X-rays (WDX),

energy-dispersive analysis of X-rays (EDX), extended X-ray atomic fine-structure analysis (EXAFS), transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), differential thermal analysis (DTA), and a number of other methods.

For diffraction experiments, three types of radiation with a wavelength  $\lambda$  of the order of magnitude of interatomic distances are used: X-rays, electrons, and neutrons. The shortest interatomic distances in solids are a few times  $10^{-10}$  m. Therefore, a non-SI unit, the angstrom ( $1 \text{ \AA} = 10^{-10} \text{ m}$ ) is often used in crystallography. In the case of electrons and neutrons, their energies



**Fig. 3.16** Wavelengths  $\lambda$  in Å and particle energies  $E$  for X-ray photons (energies in keV), neutrons (energies in 0.01 eV), and electrons (energies in 100 eV)

have to be converted to de Broglie wavelengths

$$\lambda = \frac{h}{mv},$$

$$\lambda(\text{Å}) = \frac{0.28}{\sqrt{E(\text{eV})}}.$$

Figure 3.16 compares the energies and wavelengths of the three types of radiation.

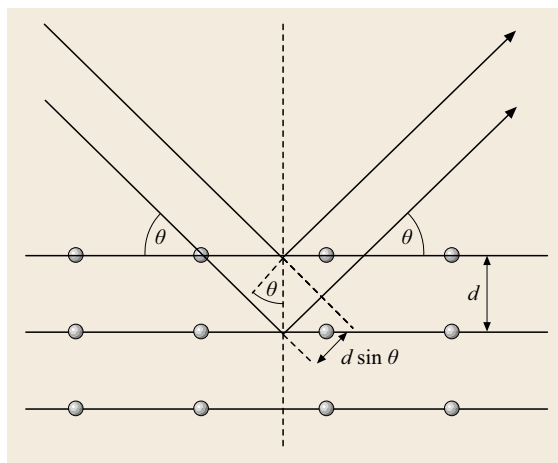
From wave optics, it is known that radiation of wavelength  $\lambda$  is diffracted by a grid of spacing  $d$ . If we take a 3-D crystal lattice as such a grid, we expect diffraction maxima to occur at angles  $2\theta$ , given by the Bragg equation (Fig. 3.17)

$$\lambda = 2d_{hkl} \sin \theta_{hkl}.$$

For the aperiodic ( $n$ -D periodic crystal) case,  $d_{hkl}$  has to be replaced by  $d_{h_1 h_2 \dots h_i \dots h_n}$ . To give a simple 3-D example, for the determination of the cell parameter  $a$  in the cubic case, the Bragg equation can be rewritten in the form

$$\left(\frac{Q}{2\pi}\right)^2 = \frac{4 \sin^2 \theta_{hkl}}{\lambda^2} = \frac{(h^2 + k^2 + l^2)}{a^2}.$$

Thus, the crystal lattice is determined by a set of  $\theta_{hkl}$ . In the case of X-rays and neutrons, information about the atomic structure is contained in the set of diffraction intensities  $I_{hkl}$ . Here we have  $I_{hkl} = F_{hkl}^2$  where  $F_{hkl}$  are the structure factors.



**Fig. 3.17** Geometrical derivation of the Bragg equation  $n\lambda = 2d \sin \theta$ .  $n$  can be set to 1 when it is included in a higher order  $hkl$

To reconstruct the matter distribution  $\rho(xyz)$  inside a unit cell of volume  $V$ , the crystallographic phase problem has to be solved. Once the phase factor  $\phi$  for each  $hkl$  is known, the crystal structure is solved.

$$\rho(xyz) = \frac{1}{V} \times \sum \sum \sum_{\text{all } h,k,l} |F| \cos[2\pi(hx + ky + lz) - \phi].$$

Non-Bragg diffraction intensities  $I(Q)$  and therefore a normalized structure function  $S(Q)$  can be obtained, for example, from an X-ray or neutron powder diffractogram. The sine Fourier transform of  $S(Q)$  yields a normalized radial atomic pair distribution function  $G(r)$

$$G(r) = \left(\frac{2}{\pi}\right) \int_0^{\infty} Q[S(Q) - 1] \sin(Qr) dQ.$$

For measurements at high  $Q$ , the 1-D function  $G(r)$  contains detailed information about the local structure. This function therefore resolves, for example, disorder or vacancy distributions in a material. The method can be applied to 3-D diffuse scattering distributions as well and thus can include angular information with respect to  $r$ .

### 3.4.1 X-rays

X-rays can be produced in the laboratory using a conventional X-ray tube. Depending on the anode material, wavelengths  $\lambda$  from 0.56 Å (Ag  $K\alpha$ ) to 2.29 Å (Cr  $K\alpha$ ) can be generated. Filtered or monochromatized radiation is usually used to collect diffraction data, from either single crystals or polycrystalline fine powders.

A continuous X-ray spectrum, obtained from a tungsten anode, for example, is used to obtain Laue images to check the quality, orientation, and symmetry of single crystals.

X-rays with a higher intensity, a tunable energy, more narrow intensity distribution, and higher brilliance are provided by synchrotron radiation facilities.

X-rays interact with the electrons in a structure and therefore provide information about the electron density distribution – mainly about the electrons near the atomic cores.

### 3.4.2 Neutron Diffraction

Neutrons, generated in a nuclear reactor, are useful for complementing X-ray diffraction information. They interact with the atomic nuclei, and with the magnetic moments of unpaired electrons if they are present in a structure. Hydrogen atoms, which are difficult to locate using X-rays (they contain one electron, if at all, near the proton), give a far better contrast in neutron diffraction experiments. The exact positions of atomic nuclei permit *X minus N* structure determinations, so that the location of valence electrons can be made observable. Furthermore, the magnetic structure of a material can be determined.

### 3.4.3 Electron Diffraction

The third type of radiation that can be used for diffraction purposes is an electron beam; this is usually done

in combination with TEM or HRTEM. Because electrons have only a short penetration distance – electrons, being charged particles, interact strongly with the material – electron diffraction is mainly used for thin crystallites, surfaces, and thin films. In the TEM mode, domains and other features on the nanometer scale are visible. Nevertheless, crystallographic parameters such as unit cell dimensions, and symmetry and space group information can be obtained from selected areas.

In some cases, information about, for example, stacking faults or superstructures obtained from an electron diffraction experiment may lead to a revised, detailed crystal structure model that is *true* than the model which was originally deduced from X-ray diffraction data. If only small crystals of a material are available, crystallographic models obtained from unit cell and symmetry information can be simulated and then adapted to fit HRTEM results.

The descriptions above provide the equipment needed to understand the structure of solid matter on the atomic scale. The concepts of crystallography, the technical terms, and the language used in this framework have been presented. The complementarities of the various experimental methods used to extract coherent, comprehensive information from a sample of material have been outlined. The *rudiments* presented here, however, should be understood only as a first step into the fascinating field of the atomic structure of condensed matter.

## 3.5 Recent Novel Topics in Crystallography

Currently, we are witnessing a major change in crystallographic science. *Normal* crystallographic science, in the sense of the philosopher *Thomas S. Kuhn* [3.10], is an extremely powerful technique for 3-D atomic-structure determination in almost any (crystalline!) material. The basics for this technique were discovered by Max von Laue, who won the Nobel Prize in Physics as early as 1914 for his contribution. The current paradigm shift, however sluggish, may be attributed to a scientific *revolution* [3.11] in crystallography which is twofold.

### 3.5.1 Quasicrystals

The existence of quasicrystals was not accepted for a long time. The reason for, e.g., 5-fold symmetry was controversially discussed. With the Nobel-Prize the existence was accepted. The discovery of inter-

metallic (*hard*) quasicrystals was followed by both that of photonic metacrystals – which are macroscopic man-made arrays – and the discovery of organic *soft* aperiodic supramolecular phases in colloidal systems. The latter, often exhibiting 12-fold symmetry, have been much more likely to be discovered since materials researchers have become aware that they may look beyond the old paradigm of only seven crystal systems, 14 Bravais lattices, and 230 space groups to describe order.

### 3.5.2 Diffraction Analysis Based on Total Scattering

Secondly, this similarly holds for the recent idea of using total scattering [3.7] to analyze Bragg *and* diffuse scattering in order to derive information about local atomic structure. Often, local structure influences

the properties of a material in a decisive way, particularly when dealing with nanostructures. Interestingly, in William Henry Bragg's lab journal [3.12, 13], he notes down – but does not discover, however – diffuse scattering on page 5, and it takes 6 more pages before he notes, and this time discovers Bragg peaks on page 11 in 1913 (Nobel Prize in Physics 1915). Here, more than 90 years later, T.S. Kuhn's statement is very apt [3.10]:

[...] during [scientific] revolutions scientists see new and different things when looking with familiar instruments in places they have looked before. It is rather as if the professional community had been suddenly transported to another planet [...]

In this very sense, a paradigm shift can be declared today in our investigation and understanding of order in condensed matter by diffraction methods.

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