

# Chapter 1

## Basic Crystallography and Other Properties Linked with Symmetry

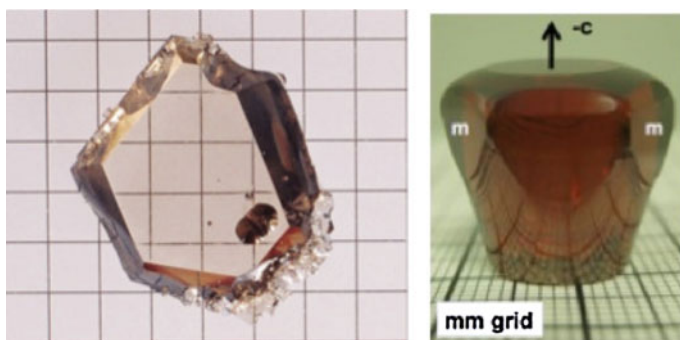
This chapter treats of crystallography, basic physical properties linked to the crystal structure. It also gives a few elements of basic group theory.

### 1.1 The Hexagonal Point Symmetry Deduced from the Shape of Natural Wurtzitic Crystals

Atomic organisation of wurtzitic semi-conductors follows the crystallographic structure named "zincite", that was, to the author's knowledge, first described as red oxide of zinc by American mineralogist Archibald [1] at the dawn on the nineteenth century. Some sulfide minerals also crystallize according to this atomic organisation, among which are greenockite (CdS), first observed in 1840 in Bishopton, Scotland, and named after the landowner Lord Greenock. The term "wurtzite" is correlated with the description of the hexagonal form of zinc sulfide crystals in 1861 and named after French chemist Charles-Adolphe Wurtz. The wurtzite group also includes, rambergite (MnS) discovered in sediments and named at the end of the twentieth century after the Norwegian-Swedish mineralogist, Hans Ramberg. We also wish to indicate that cadmoselite CdSe (artificially synthesized before it was identified as a mineral stone) was discovered in 1957. In the language of semi-conductorists, these materials belong to the group of II–VI compounds: the cation (resp. anion) is a group II (resp. VI) element of Mendeleev's table. Apart from the II–VI family, III-nitrides (III-N's) are also important semi-conductors the cation is a group-III element generally boron, aluminium, gallium or indium. The most energetically favourable atomic organisation for boron nitride is not wurtzite; BN is a layered compound like graphite. The most stable crystalline structure of AlN, GaN and InN semi-conductors is wurtzitic. These materials are not extracted from mines as binary compounds probably due to the high stability of the nitrogen molecule (9.3 eV per bond) or to the chemical reactivity of ammoniac.  $\text{NH}_3$  is a very stable molecule: nitrogen single atoms are highly reactive and donot live long without binding to the most abundant



**Fig. 1.1** Photograph of a natural wurtzitic crystal. Note the needle-like shape and the existence of many facets with different orientations illustrating the hexagonal symmetry



**Fig. 1.2** *Left* Photograph of an artificial crystal of bulk gallium nitride (courtesy Dr. I. Grzegory, Polish Academy of Sciences). *Right* Photograph of an aluminum nitride bulk artificial single crystal (courtesy Prof. Zlatko Sitar, North Carolina State University)

elements in nature: H, O, etc. Therefore, the necessary conditions to associate nitrogen and group III element in order to form pure III-Ns are never met in nature, to the best of our knowledge. The existence of AlN was demonstrated in 1862 by Briegleb and Geuther [2] and Mallet synthesized it in 1876 [3] with metallic aluminum and sodium carbonate reactant at high temperatures. The growth of GaN was achieved in 1932 by Johnson et al. [4] later achieved, in 1938, the growth of indium nitride was later achieved, in 1938 [5]. The hexagonal symmetry of wurtzite crystals was quantitatively calibrated during the nineteenth century from the orientation of the directions orthogonal to the facets of crystals found in mines. Crystals are most generally found as small needles, exhibiting specific shapes as shown in Fig. 1.1.

Artificially grown bulk semi-conductors like gallium nitride (Fig. 1.2-left) or aluminum nitride (Fig. 1.2-right) are also obtained under faceted crystalline shapes. Although the shape of the crystals presented in Fig. 1.2 (left) and 1.2 (right) are

**Fig. 1.3** Photograph of wooden tutorial object designed such as to show a typical repeat of basic building blocks which at the end to form the whole crystal shape

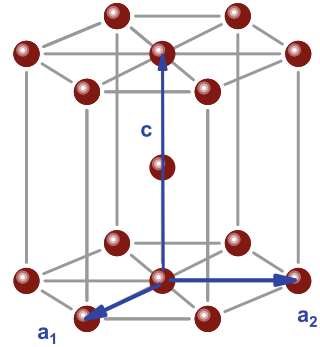


fairly different, they share a common property. The shape of the bunch of directions orthogonal to the crystal facets constitutes some kind of figure of merit.

The figure obtained after the stereographic projection of the ensemble of the directions that are orthogonal to the facets of these crystals is compatible with the symmetry of a regular hexagonal polygon. This figure is a constant quantity typical of the crystalline structure according to the first law of crystallography. It is known as “the law of constant angles between crystal facets”, early initiated by Danish Nicolas Steno’s seminal work in 1669 and later formulated by French mineralogist Jean-Baptiste Romé de l’Isle in 1772. For wurtzitic semi-conductors, this figure permits to reveal a six-fold symmetry along a given direction, the existence of a three-fold and two-fold symmetries collinear to the six fold one and six symmetry planes parallel to the six-fold symmetry axis. These symmetry elements are generic of the crystalline form named di-hexagonal pyramidal by mineralogists. In terms of modern group theory language, from the shape of these needles, one establishes that the orientation (or point symmetry) of wurtzite crystals is a subgroup (labelled  $C_{6v}$  in Schoenflies notation or  $P_6mm$  in the Hermann-Mauguin one) of the full hexagonal symmetry (labelled  $D_{6h}$  in Schoenflies notations or  $P_6/mmm$  in the Hermann-Mauguin one). French abbot René-Just Haüy in 1774 carefully observed facets of minerals and proposed the second law of crystallography: crystals consist of three-dimensional stacking at a macroscopic scale of a given microscopic basic building block as tentatively illustrated in Fig. 1.3. This kind of wooden crystal were still used as tutorial examples to teach students in the middle of the twentieth century.

In 1849, French scientist Auguste Bravais postulated the principle of specific three-dimensional translational invariance (existence of translational symmetry operations on the basic building block imagined by Haüy). From this postulate results the notion of three-dimensional periodic crystalline lattice which is the basic principle used to determine the crystallographic structure of materials using radio-crystallography. Before discussing this very recent technique since X-rays were discovered by German physicist Wilhelm Conrad Röntgen in 1895, it is worthwhile allocating some time to simple mathematical analysis of crystal properties in line with their symmetries. We will restrict ourselves to wurtzite and, in particular, catch the opportunity to show how powerful the first laws of crystallography are. From the bunch of angles made by the directions normal to the crystal’s facet, we can determine the ratio  $c/a$  or  $a/c$  of the basic hexagonal building block parameter—along the six-fold symmetry axis—to the one orthogonal to it.

**Fig. 1.4** Representation of the crystallographic axes  $\vec{a}_1$ ,  $\vec{a}_2$  and  $\vec{c}$  that generate the unit hexagonal cell (blue lines). The full hexagonal cell is shown for the completeness



## 1.2 The Hexagonal Lattice, Its Reticular Planes and Their Description Using Simple Euclidian Geometry

The hexagonal crystallographic system is based on two vectors  $\vec{a}_1$  and  $\vec{a}_2$  of identical length  $a$  at  $120^\circ$  from each other, and a third one, of length  $c$  orthogonal to the plane generated by the preceding two, as described by French scientist Auguste Bravais in 1849 and as illustrated in Fig. 1.4.

Lengths  $a$  and  $c$  being the dimensions of the lattice vectors of the hexagonal cell, we associate them to unit vectors  $\vec{i}$ ,  $\vec{j}$  and  $\vec{k}$ .

This gives:

$$\vec{i} \cdot \vec{k} = \vec{j} \cdot \vec{k} = 0$$

and

$$\vec{i} \cdot \vec{j} = \cos(120^\circ) = -1/2$$

We now consider the  $(hk\ell)$  reticular plane in terms of its so-called Miller indices. This notation was proposed by British mineralogist William Hallows Miller in 1839.

By definition, the  $(hk\ell)$  plane intersects the reticular axes at lengths  $\frac{a}{h}$ ,  $\frac{a}{k}$  and  $\frac{c}{\ell}$  from the origin as shown in Fig. 1.5.

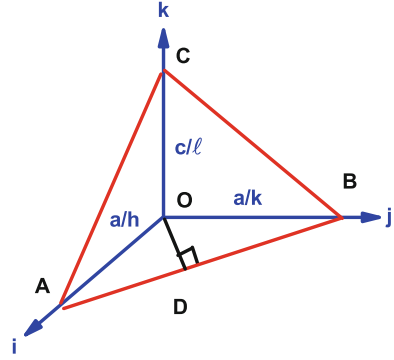
Letters  $h$ ,  $k$  and  $\ell$  are algebraic integer numbers. There are some specific simple orientations for such planes:

- Miller indices  $(100)$  represent a plane parallel to the  $(\vec{j}, \vec{k})$  plane,
- Miller indices  $(010)$  represent a plane parallel to the  $(\vec{i}, \vec{k})$  plane,
- Miller indices  $(001)$  represent a plane parallel to the  $(\vec{i}, \vec{j})$  plane.

The notation  $\{hk\ell\}$  is traditionally used to identify all the planes equivalent to  $(hk\ell)$  by the symmetry of the lattice. As an example,  $(100)$  and  $(010)$  planes belong to the  $\{100\}$  family.

Thanks to hexagonal symmetry, and in contrast to the cubic case,  $\{100\} \neq \{001\}$ .

**Fig. 1.5** Orientation of the reticular plane  $(hkl)$  with respect to the crystallographic axes of the hexagonal lattice



Let  $[hkl]$ —with square brackets—represent a direction in the basis of the direct lattice vectors:  $[hkl]$  is equivalent to  $h\vec{a}_1 + k\vec{a}_2 + l\vec{c}$ . The notation  $\langle hkl \rangle$  is used for all the directions that are equivalent to  $[hkl]$  by symmetry operations of the crystal.

In the most general case, and for non-cubic crystals, direction  $[hkl]$  is **NOT** orthogonal to plane  $(hkl)$ .

Given an  $(hkl)$  plane, we define three unit vectors  $(\vec{U}, \vec{V}, \vec{W})$  orthogonal to each other, two of them ( $\vec{U}$  and  $\vec{V}$ ) being vectors of the  $(hkl)$  plane, whilst the third one ( $\vec{W}$ ) is orthogonal to it.

The  $\vec{U}$  direction ( $\vec{U}$  is parallel to vector  $\vec{AB}$  in Fig. 1.5) is chosen as  $[-kh0]$ , and thus lies in the  $(\vec{i}, \vec{j})$  plane.  $\vec{U}$  satisfies the sonal equation and corresponds to a crystal direction.

The  $[-\ell 0h]$  direction (vector  $\vec{AC}$  in Fig. 1.5) connects intersections of the  $(hkl)$  plane with crystallographic directions  $\vec{a}_1$  and  $\vec{c}$  at lengths  $\frac{a}{h}$  and  $\frac{c}{\ell}$  from the origin. It forms with  $\vec{U}$  a basis of the  $(hkl)$  plane. This direction is not orthogonal to  $\vec{U}$ , which is not the best choice for mathematical calculations. Thus, it is more appropriate to determine, using an orthonormalization procedure a vector  $\vec{V}$  lying in the  $(hkl)$  plane and perpendicular to  $\vec{U}$ . This vector is parallel to vector  $\vec{DO} + \vec{OC}$  with

$$\|\vec{DO}\| = \frac{a\sqrt{3}}{2\sqrt{h^2 + hk + k^2}}$$

and  $\|\vec{OC}\| = \frac{c}{\ell}$  as indicated in Fig. 1.5.

*It also satisfies the zone equation for the  $(hkl)$  plane, demonstrating that it corresponds to a crystal direction.*

To this couple of vectors  $(\vec{U}, \vec{V})$ , we add  $\vec{W}$ , also obtained after an orthonormalization procedure.

In the hexagonal  $(\vec{i}, \vec{j}, \vec{k})$  basis, the coordinates of these unit vectors are:

$$\begin{bmatrix} \vec{U} \\ \vec{V} \\ \vec{W} \end{bmatrix} = \begin{bmatrix} -Ak & Ah & 0 \\ -AalB_{ac}(2h+k) & -AalB_{ac}(2k+h) & 2c\frac{B_{ac}}{A} \\ \frac{2}{\sqrt{3}}cB_{ac}(2h+k) & \frac{2}{\sqrt{3}}cB_{ac}(2k+h) & \sqrt{3}\ell aB_{ac} \end{bmatrix} \begin{bmatrix} \vec{i} \\ \vec{j} \\ \vec{k} \end{bmatrix} \quad (1.1)$$

**Table 1.1** Values of the ratio  $c/a$  for various wurtzitic semi-conductors

Material	BN	GaN	InN	AlN	ZnS	ZnSe	CdS	CdSe	ZnO
$c/a$	1.64	1.62	1.61	1.6	1.64	1.63	1.62	1.63	1.60

The number of digits is compatible with the determination method

where

$$A = \frac{1}{\sqrt{h^2 + hk + k^2}}$$

and

$$B_{ac} = \frac{1}{\sqrt{3\ell^2 a^2 + 4c^2(h^2 + hk + k^2)}}$$

The angle between the  $[001]$  direction and  $\vec{W}$  is given as:

$$\Theta = \arccos \left[ \frac{1}{\sqrt{1 + \frac{4c^2}{3a^2} \frac{(h^2 + hk + k^2)}{\ell^2}}} \right]$$

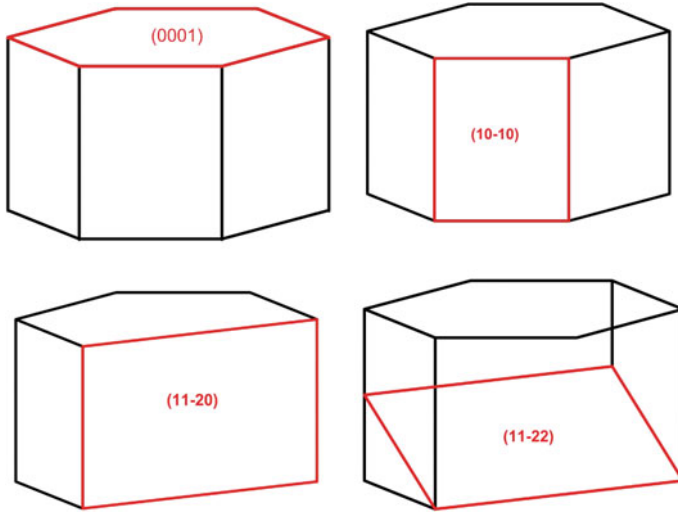
that depends on the value of the three Miller indices and on the ratio  $c/a$ .

At this stage, elementary Euclidian algebraic calculations demonstrate the possibility to determine the  $c/a$  ratio in wurtzitic crystals from the orientation of the directions of the crystal facets. The only issue is to have crystals with a large enough number of facets. Thus, we gain access to a well documented set of experimental values of  $\Theta$ , so that their associated  $h$ ,  $k$  and  $\ell$  numbers can be determined simultaneously with the value of  $c/a$ . Table 1.1 summarizes the results of  $c/a$  ratio typical of the most common wurtzitic semi-conductors.

### 1.3 The Four-Index Bravais-Miller Representation of the Orientation of Reticular Planes in Hexagonal Crystals

In the case of the hexagonal (and rhomboidal) lattice systems, one alternative convention is to use a 4-numbers representation ( $h \ k \ i \ \ell$ ) for reticular planes, where  $i = -(h + k)$ . In this case,  $h$ ,  $k$  and  $\ell$  are identical to the Miller indices, and  $i$  is redundant: four independent vectors cannot generate a three-dimensional space. Figure 1.6 illustrates some typical orientations of  $(hk\ell)$  planes that are found in natural crystals.

This four-indices scheme for labelling planes in a hexagonal lattice is very convenient to illustrate the identical nature of reticular planes by permutation of the indices. For example, we better spot the similarity between planes  $(11\bar{2}0)$  and  $(\bar{1}210)$  than when they are written as  $(110)$  and  $(\bar{1}20)$ .



**Fig. 1.6** Sketches of typical orientations of reticular planes of interest for wurtzitic semi-conductors. The four-indices Miller-Bravais indexing system is used to represent the orientations

## 1.4 Representation of Hexagonal Crystal Directions Using Four Indices

In some books of mineralogy, we find another four-indices system for the directions in hexagonal crystals.

Let:

$$\vec{D} = h\vec{a}_1 + k\vec{a}_2 + \ell\vec{c}$$

This direction may be also noted as  $[hk.\ell]$  and is fully determined with respect to the hexagonal cell.

The corresponding Weber four indices are defined as:  $[hk.\ell] \rightarrow [h'k't\ell']$  and the relationships are:

$$\begin{aligned} h' &= \frac{n(2h - k)}{3} \\ k' &= \frac{n(2k - h)}{3} \\ t &= -(h' + k') \\ \ell' &= n\ell \end{aligned}$$

where  $n$  is a factor used to transform the new indices into smaller integers. To avoid confusion, we will not use this notation.

## 1.5 The Reciprocal Lattice

The reciprocal lattice is not necessary for geometric crystallography. However, it facilitates some calculations, and its utilization is mandatory when studying X-ray diffraction by periodical structures or, out of the context of crystallography, to treat band structure phenomena, or light propagation. The reciprocal lattice is the Fourier transform of the direct lattice. It generates a three-dimensional (3D) space via basis vectors  $\vec{a}_1^*$ ,  $\vec{a}_2^*$  and  $\vec{c}^*$  that are defined from the basis vectors  $\vec{a}_1$ ,  $\vec{a}_2$  and  $\vec{c}$  of the direct lattice:

$$\begin{aligned}\vec{a}_i \cdot \vec{a}_j^* &= \delta_{ij} \\ \vec{c} \cdot \vec{c}^* &= 1 \\ \vec{a}_i^* \cdot \vec{c}^* &= 0\end{aligned}$$

One deduces then, that  $\vec{a}_1^*$  is orthogonal to both  $\vec{a}_2$  and  $\vec{c}$ , which dictates that:

$$\begin{aligned}\vec{a}_1^* &= \alpha(\vec{a}_2 \wedge \vec{c}) \\ \vec{a}_1 \cdot \vec{a}_1^* &= \alpha \vec{a}_1 \cdot (\vec{a}_2 \wedge \vec{c}) = \alpha \cdot V_{ol} = 1\end{aligned}$$

$V_{ol}$  is the volume  $(\vec{a}_1 \wedge \vec{a}_2) \cdot \vec{c} = \vec{a}_1 \cdot (\vec{a}_2 \wedge \vec{c})$

$$\alpha = \frac{1}{V_{ol}}$$

then

$$\vec{a}_1^* = \frac{\vec{a}_2 \wedge \vec{c}}{V_{ol}}$$

Similarly, one obtains  $\vec{a}_2^*$  and  $\vec{c}^*$ :

$$\vec{a}_2^* = \frac{\vec{c} \wedge \vec{a}_1}{V_{ol}}$$

and

$$\vec{c}^* = \frac{\vec{a}_1 \wedge \vec{a}_2}{V_{ol}}$$

In line with the definitions of the direct and reciprocal lattices, it is possible to generate operations like scalar or vectorial products, using vectors from both spaces:

Let:

$$\vec{R} = r_1 \vec{a}_1 + r_2 \vec{a}_2 + r_3 \vec{c}$$



and

$$\vec{N}^* = n_1 \vec{a}_1^* + n_2 \vec{a}_2^* + n_3 \vec{c}^*$$

Scalar product:

$$\vec{R} \cdot \vec{N}^* = r_1 n_1 + r_2 n_2 + r_3 n_3$$

Let us consider a series of reticular planes  $(hkl)$  and choose the closest to the origin  $O$ .

Let A, B and C be the intersections of this plane with the three axes (see Fig. 1.5).

Vectors  $\vec{AB}$  and  $\vec{AC}$  both belong to that plane, their directions are respectively  $[-k \ h \ 0]$  and  $[-\ell \ 0 \ h]$ .

$$\begin{aligned}\vec{AB} &= \vec{AO} + \vec{OB} = -\vec{a}_1 \frac{1}{h} + \vec{a}_2 \frac{1}{k} \\ \vec{AC} &= -\vec{a}_1 \frac{1}{h} + \vec{c} \frac{1}{\ell}\end{aligned}$$

Let  $\vec{N}_{hkl}^*$  be a vector of the reciprocal lattice:

$$\vec{N}_{hkl}^* = h\vec{a}_1^* + k\vec{a}_2^* + \ell\vec{c}^*$$

This vector defines the  $[hkl]^*$  family in the reciprocal lattice.

The three integer numbers  $(h, k, \ell)$  being primes between each other, the extremity of  $\vec{N}_{hkl}^*$  is the first node of the reciprocal lattice from the origin along the  $\vec{N}_{hkl}^*$  direction.

$$\begin{aligned}\vec{AB} \cdot \vec{N}_{hkl}^* &= \left(-\vec{a}_1 \frac{1}{h} + \vec{a}_2 \frac{1}{k}\right) \cdot (h\vec{a}_1^* + k\vec{a}_2^* + \ell\vec{c}^*) = -\vec{a}_1 \cdot \vec{a}_1^* + \vec{a}_2 \cdot \vec{a}_2^* = 0 \\ \vec{AC} \cdot \vec{N}_{hkl}^* &= \left(-\vec{a}_1 \frac{1}{h} + \vec{c} \frac{1}{\ell}\right) \cdot (h\vec{a}_1^* + k\vec{a}_2^* + \ell\vec{c}^*) = -\vec{a}_1 \cdot \vec{a}_1^* + \vec{c} \cdot \vec{c}^* = 0\end{aligned}$$

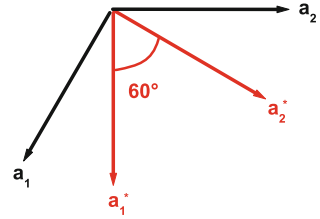
The two vectors  $\vec{AB}$  and  $\vec{AC}$  of the  $(hkl)$  plane are orthogonal to the vector  $\vec{N}_{hkl}^*$  of the reciprocal lattice, which gives birth to the very important statement below:

*The direction  $[hkl]^*$  of the reciprocal lattice is orthogonal to the reticular plane  $(hkl)$  of the direct lattice.*

After some simple geometrical calculation, one could also demonstrate that the length of  $\vec{N}_{hkl}^*$  is connected with the distance  $d_{hkl}$  between adjacent reticular  $(hkl)$  planes of the direct lattice by:

$$\begin{aligned}\vec{N}_{hkl}^* \cdot \vec{d}_{hkl} &= 1 \\ d_{hkl} &= \frac{ac\sqrt{3}}{\sqrt{4c^2(h^2 + hk + k^2) + 3a^2\ell^2}}\end{aligned}$$

**Fig. 1.7** Relative orientations of the vectors of the reciprocal (starred symbols) and direct (unstarred letters) lattice of the hexagon in the (0001) plane. Vectors  $c$  and  $c^*$  are both orthogonal to that plane



We wish to outline that, in the most general way, direction  $[hkl]$  in the basis of the direct lattice vectors IS NOT orthogonal to  $(hkl)$  plane expressed in the basis of the direct lattice vectors, since they do not form an orthogonal basis.

On Fig. 1.7 are represented the direct and reciprocal lattices basis vectors for the hexagon in the (0001) plane.

Relatively to the crystallographic basis set, the vectors of the reciprocal lattice express as:

$$\begin{bmatrix} \vec{a}_1^* \\ \vec{a}_2^* \\ \vec{c}^* \end{bmatrix} = \begin{bmatrix} \frac{4}{3a} & \frac{2}{3a} & 0 \\ \frac{2}{3a} & \frac{4}{3a} & 0 \\ 0 & 0 & \frac{1}{c} \end{bmatrix} \cdot \begin{bmatrix} \vec{i} \\ \vec{j} \\ \vec{k} \end{bmatrix} \quad (1.2)$$

We note that mathematical calculations can be made using any of these two bases.

$$\vec{N}_{hkl}^* = h\vec{a}_1^* + k\vec{a}_2^* + \ell\vec{c}^*$$

may be expressed in terms of direct-lattice basis-vectors  $\vec{a}_1$ ,  $\vec{a}_2$  and  $\vec{c}$  as:

$$\vec{N}_{hkl}^* = h\vec{a}_1^* + k\vec{a}_2^* + \ell\vec{c}^* = \frac{2}{3a^2}(2h+k)\vec{a}_1 + \frac{2}{3a^2}(2k+h)\vec{a}_2 + \frac{\ell}{c^2}\vec{c}$$

that we rewrite versus  $(\vec{i}, \vec{j}, \vec{k})$ :

$$\vec{N}_{hkl}^* = \frac{2}{3a}(2h+k)\vec{i} + \frac{2}{3a}(2k+h)\vec{j} + \frac{\ell}{c}\vec{k}$$

After renormalisation of  $\vec{N}_{hkl}^*$  with its length, one obtains a unit vector  $\frac{\vec{N}_{hkl}^*}{\|\vec{N}_{hkl}^*\|}$  identical to  $\vec{W}$ .

Hence, zone indices of the direction perpendicular to plane  $(hkl)$  are, in suitably normalized triplet form, simply:

$$\left[ 2h+k, h+2k, \frac{3a^2}{2c^2}\ell \right],$$

that are not, in general, three integer numbers.

## 1.6 The Orthogonal Basis Set

In order to express tensors and matrices, that represent physical properties of crystals, it is recommended to use a new set of axes:  $(\vec{x}, \vec{y}, \vec{z})$  which are always mutually perpendicular. Starting from now, the calculations will be made in the international orthogonal  $(\vec{x}, \vec{y}, \vec{z})$  basis. The relationship between the unit vectors of the international basis and those of the hexagonal one are:

$$\begin{bmatrix} \vec{x} \\ \vec{y} \\ \vec{z} \end{bmatrix} = \begin{bmatrix} \frac{2}{\sqrt{3}} & \frac{1}{\sqrt{3}} & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \cdot \begin{bmatrix} \vec{i} \\ \vec{j} \\ \vec{k} \end{bmatrix} \quad (1.3)$$

Vector  $\vec{x}$  is orthogonal to  $\vec{j}$ —and, therefore,  $\vec{y}$ —and makes a  $30^\circ$  angle with  $\vec{i}$ .

This basis change leads to the following expressions relating  $(\vec{U}, \vec{V}, \vec{W})$  and  $(\vec{x}, \vec{y}, \vec{z})$ :

$$\begin{bmatrix} \vec{U} \\ \vec{V} \\ \vec{W} \end{bmatrix} = \begin{bmatrix} -\frac{\sqrt{3}}{2}Ak & \frac{1}{2}A(2h+k) & 0 \\ -\frac{\sqrt{3}}{2}Aa\ell B_{ac}(2h+k) & -\frac{3}{2}Aa\ell B_{ack} & 2c\frac{B_{ac}}{A} \\ AcB_{ac}(2h+k) & \sqrt{3}AcB_{ack} & \sqrt{3}\ell aB_{ac} \end{bmatrix} \begin{bmatrix} \vec{x} \\ \vec{y} \\ \vec{z} \end{bmatrix} \quad (1.4)$$

The unit vectors of the crystallographic basis and the vectors of the reciprocal lattice express as follow in terms of the unity vectors of the international basis set:

$$\begin{bmatrix} \vec{i} \\ \vec{j} \\ \vec{k} \end{bmatrix} = \begin{bmatrix} \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \cdot \begin{bmatrix} \vec{x} \\ \vec{y} \\ \vec{z} \end{bmatrix} \quad (1.5)$$

and

$$\begin{bmatrix} \vec{a}_1^* \\ \vec{a}_2^* \\ \vec{c}^* \end{bmatrix} = \begin{bmatrix} \frac{2}{a\sqrt{3}} & 0 & 0 \\ \frac{1}{a\sqrt{3}} & \frac{1}{a} & 0 \\ 0 & 0 & \frac{1}{c} \end{bmatrix} \cdot \begin{bmatrix} \vec{x} \\ \vec{y} \\ \vec{z} \end{bmatrix} \quad (1.6)$$

respectively.

## 1.7 The Determination of the Lattice Parameters by X-ray Diffraction

Soon after the discovery of the X-rays by Wilhelm Conrad Röntgen in 1895, people were hesitating regarding their nature. It was, however, believed that they had very short wavelengths ( $10^{-9}$  m). After some measurements, German physicist Arnold

Johannes Wilhelm Sommerfeld had determined the ratio between the wavelengths of visible light and X-rays was close to 10,000. Italian chemist Amedeo Avogadro had claimed in 1811 that two equal volumes of different gases, in identical temperature and pressure conditions contained identical numbers of atoms. One century later, this inspired in 1912 Max von Laüe to suggest from the values of Avogadro's number and molar weights of species, the sizes of atoms and molecules. He then proposed that crystals could be used as diffraction gratings for X-rays. He determined theoretically the way to observe such a diffraction and, in addition, proposed diffraction patterns. The experiment was carried out by German scientists Walter Friedrich and Paul Knipping. After a few initial failures, they met with success on April 23, 1912. X-rays when travelling through the crystal formed the pattern of bright spots that proved Laüe's hypothesis was correct. The explanation of the phenomenon is the following and ruled by two different mechanisms: first, each atom scatters the impinging beam in all directions of the three dimensional space. Then, the scattered propagating waves interfere, thus creating the observed diffraction patterns. British physicist George Paget Thompson (the son of Scottish physicist Joseph John Thompson who discovered the electron in 1897) has produced a theory, treating the scattering of X-rays by an atom with  $Z$  electrons like  $Z$  scatterings independent of each other. This model, which neglects the influence of the nucleus of this atom, predicts the scattered intensity to be proportional to  $Z$ . X-rays poorly detect a light atom, like H or Li, whilst a heavy one like gold for instance is easily spotted, thus explaining its use in contemporary medicine.

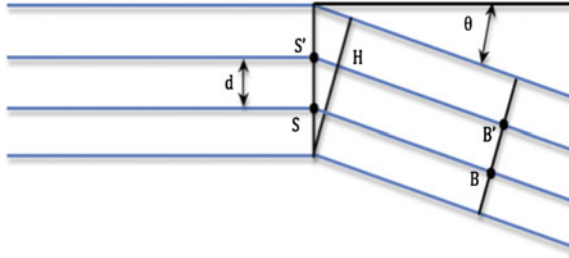
### 1.7.1 Diffraction by a Linear Grating

Regarding the interference pattern, let us consider a reticular plane. In this plane, atoms are by definition regularly arranged according to a two-dimensional lattice. There exists a family of identical planes parallel to the considered one. They are regularly spaced by a quantity we call  $d$  here. Each atom behaves like a point source and diffuses X-rays in all dimensions of the 3D space. The scattered beams interfere. The phenomenon is identical to the diffraction of light by a linear grating but it is much more difficult to address because it occurs at three dimensions.

Let us consider a network of parallel slits  $\{ \dots, S, S', \dots \}$  separated by a constant distance  $d$ . An incident beam, normal to the plane of the slits—so that, all slits are excited in phase and emit accordingly—is diffracted by the series of slits in a direction making the angle  $\theta$  with the incident direction.

Figure 1.8 illustrates the geometrical aspects of the diffraction phenomenon in a plane orthogonal to the plane of slits. The plane of the figure then contains both incident and transmitted (or diffracted) beams. The condition for having light in the  $BB'$  plane is that the difference in optical paths between all beams be an integer number times the wavelength, which writes:

$$S'B' - SB = n\lambda$$



**Fig. 1.8** Geometrical aspects of the diffraction phenomenon in a plane orthogonal to the plane of slits

This quantity equals  $SH$  may be identified to  $d \sin \theta$ .  
Therefore, we get:

$$d \sin \theta = n\lambda$$

or, alternatively

$$\theta = \arcsin(n\lambda/d)$$

In case the incident beam makes an angle  $i$  with the plane's normal, this equation becomes:

$$d(\sin \theta - \sin i) = n\lambda$$

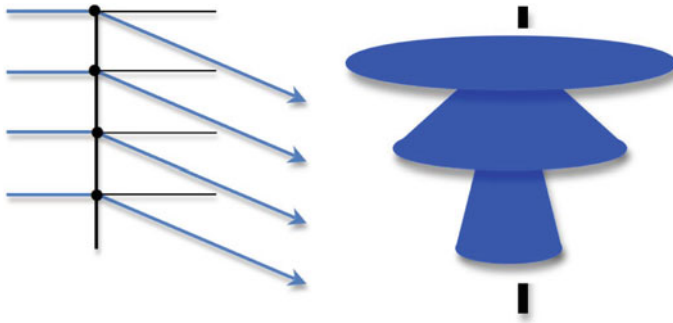
or, alternatively:

$$\theta = \arcsin(n\lambda/d + \sin i)$$

The angle  $\theta$  varies with the diffraction order  $n$ .

### 1.7.2 Diffraction by a Linear Lattice, and by a Planar One

Let us now consider a linear chain of equidistant atoms shined by a monochromatic beam of X-rays. Such a situation is encountered when rotating a crystal around a given crystallographic direction. This configuration is called the rotating-crystal diffraction method. The X-ray detector can be either a cylinder photographic sheet (detector of the old days) or a linear/bi-dimensional array of X-ray detectors (a smarter detection system but more expensive too...). Now, the elementary scattering sources are individual points. In contrast to the linear slits, the scattering is now isotropic around each source. The scattering occurs in the 3D space, and the diffracted beams of different orders  $n$  form a series of cones parallel to the linear chain, each one having an apex angle  $\phi = \pi/2 - \theta$  forming diffraction surfaces. See Fig. 1.9 (left) and (right).



**Fig. 1.9** *Left* Geometrical representation of the X-ray diffraction in a plane that contains the linear chain, the incoming beams and the reflected ones. *Right* Geometrical representation of the X-ray diffraction surfaces plane that is parallel to the linear chain. Note the cones have different angles when  $n$  changes

Let us now consider a planar two-dimensional periodic arrangement of atoms. One can demonstrate that each plane reflects the incident beam as if it was reflected by a plane mirror whatever the incidence angle, similarly with the laws of light reflection. To avoid confusion, we emphasize here that the origin of this behaviour is correlated to interferences whereas the reflexion of light by a mirror has to be interpreted using Maxwell's equations.

### 1.7.3 Diffraction by a Three-Dimensional Lattice

Let us consider a family of reticular planes ( $hkl$ ) with interplane reticular distance  $d$ . Each plane reflects the X-rays, as mentioned above, whatever the incident angle. The beams reflected by all planes interfere, with extinctions at specific angles. A global reflexion occurs for specific angles, what is called selective reflectivity. Let us consider in Fig. 1.10, the optical paths  $A'B'C'$  and  $ABC$  of X rays impinging two adjacent planes under an angle  $\theta$ .

$AA'$  and  $CC'$  are orthogonal to  $AB$  and  $BC$  respectively. The incidence and reflexion angles are equal.

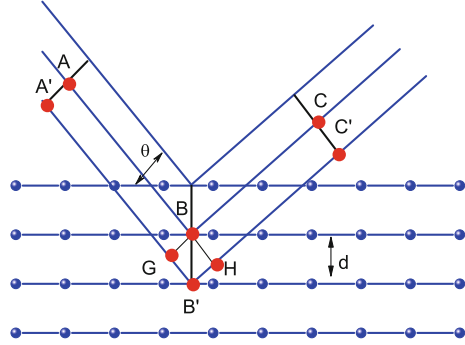
The necessary condition to observe a diffracted radiation in the plane orthogonal to  $BC$  and  $B'C'$  is:

$$A'B'C' - ABC = n\lambda.$$

Let  $G$  (resp.  $H$ ) be the projection of  $BC$  (resp.  $AB$ ) on  $A'B'$  (resp.  $B'C'$ ). We remark that:

$$HB = GB' = d \sin \theta$$

**Fig. 1.10** Geometrical sketch showing the orientation of incident and relected beams on a family of reticular planes



Then:

$$A'B'C' - ABC = 2d \sin \theta$$

Then, the so-called “Bragg relation” is obtained:

$$n\lambda = 2d \sin \theta$$

which is of paramount importance in radio-crystallography. It indicates that, when an X-ray beam encounters a family of reticular planes, it is diffracted under an angle:

$$\theta = \arcsin \frac{n\lambda}{2d}$$

Back to the hexagonal lattice, keeping in mind that the distance  $d_{hkl}$  between adjacent reticular  $(hkl)$  planes of the direct lattice is correlated with the norm of the reciprocal lattice vector  $N_{hkl}^*$  by:

$$\vec{N}_{hkl}^* \cdot \vec{d}_{hkl} = 1$$

For any lattice, a simple calculation leads us to express analytically the Bragg relation:

$$\theta_{hkl} = \arcsin \left[ \frac{n\lambda}{2} \sqrt{\frac{4}{3a^2}(h^2 + hk + k^2) + \frac{\ell^2}{c^2}} \right]$$

*X-ray diffraction angles lead to the determination of  $a$  and  $c$ .*

Table 1.2 summarizes the values of  $c$  and  $a$  measured for wurtzite semi-conductors as well as values of the  $c/a$  ratio that should be compared with optical values. We have also included information regarding hexagonal boron nitride and graphite. For these two cases, one notices large values of  $c$  with respect to  $a$ , due to the loose chemical bound along the six-fold symmetry axis. These compounds are layered compounds. For boron nitride, the wurtzitic phase is metastable.

**Table 1.2** Values of the lattice parameters  $c$  and  $a$  together with the ratio  $c/a$  for various wurtzitic semi-conductors

Material	BN	GaN	InN	AlN	ZnS	CdS	ZnO	hex-BN	hex-C
$c$ ( $10^{-10}$ m)	4.170	5.185	5.708	4.980	6.260	6.714	5.213	6.661	6.708
$a$ ( $10^{-10}$ m)	2.550	3.188	3.539	3.110	3.822	4.136	3.253	2.504	2.461
$c/a$ (X-ray)	1.635	1.627	1.613	1.610	1.638	1.623	1.602	2.66	2.725
$c/a$ (optics)	1.64	1.62	1.61	1.6	1.64	1.62	1.60	–	–

The two right-hand columns correspond to layer compounds, which are found under the crystalline-layered compound hexagonal system; which differ from wurtzite. Values of  $c/a$  obtained using both X-rays and optics are given. The number of digits is compatible with the determination method

## 1.8 The Determination of Space Symmetry by X-ray Analysis

### 1.8.1 The First Brillouin Zone

German physicist Max Von Laüe has proposed to compute, at a recording distance much larger than the size of the studied crystal, the amplitude of a wave elastically scattered from  $\vec{k}$  to  $\vec{k}'$ :

$$A = \sum_{uvw} \exp \left[ -i2\pi \vec{\rho}_{uvw} \cdot \Delta \vec{k} \right]$$

The summation is extended over all the sites of the lattice generated by vectors  $\vec{a}_1$ ,  $\vec{a}_2$  and  $\vec{c}$ :

$$\vec{\rho}_{uvw} = u\vec{a}_1 + v\vec{a}_2 + w\vec{c}$$

This summation reaches a maximum when all scattering centres are in phase, i.e. when

$$\vec{\rho}_{uvw} \cdot \Delta \vec{k} = n (\text{with } n \in N)$$

This requires to simultaneously fulfill three equations:

$$\vec{a}_1 \cdot \Delta \vec{k} = p$$

$$\vec{a}_2 \cdot \Delta \vec{k} = q$$

and

$$\vec{c} \cdot \Delta \vec{k} = r$$

with

$$(p, q, r) \in N^3$$

These three identities are the Laüe equations: they indicate that  $\Delta \vec{k}$  is by definition a vector of the reciprocal lattice.



We now write:

$$\Delta \vec{k}^2 = (\vec{k}' - \vec{k})^2 = (\vec{k} - \vec{G})^2 - \vec{k}^2$$

by introducing a vector of the reciprocal lattice  $\vec{G}$ .

Thanks to energy conservation in case of elastic scattering:  $\Delta \vec{k}^2 = 0$  which leads us to rewrite:

$$\Delta \vec{k}^2 = (\vec{k}' - \vec{k})^2 = (\vec{k} - \vec{G})^2 - \vec{k}^2 = \vec{k}^2 - 2\vec{k}\vec{G} + \vec{G}^2 - \vec{k}^2$$

This gives the important relation:

$$2\vec{k} \cdot \vec{G} - \vec{G}^2 = 0$$

We rewrite this equation:

$$2\vec{k} \cdot \vec{G} = \vec{G}^2$$

can be rearranged into:

$$\vec{k} \cdot (\vec{G}/2) = (\vec{G}/2)^2$$

It means that  $\vec{k}$  is a half-vector of the reciprocal lattice:

$$\vec{k} = \vec{G}/2$$

*The locus of these  $\vec{k}$ 's is called the Wigner-Seitz cell or the first Brillouin zone of the reciprocal lattice.*

### 1.8.2 The Structure Factor

In the preceding sections, we have considered the interferences made by atoms forming families of reticular planes. From the interferences patterns made by the atomic arrangement and these atoms, a simple geometrical analysis led us to obtain the Bragg relation, correlating a diffraction angle to the wavelength of the X-rays and to the separation between adjacent reticular planes. The pattern obtained by intercepting the diffracted beam with a recording system gives an accurate description of the reciprocal lattice, which basic building block is interpreted in terms of the Wigner-Seitz cell of the reciprocal lattice, often called the first Brillouin zone. Typical diffraction angles being measured for different reticular planes, one can, at the end, reach the value of the lattice parameters. In the case of simple structures, an extended version of the equation is:

$$A = \sum_{uvw} \exp \left[ -i2\pi \vec{\rho}_{uvw} \cdot \Delta \vec{k} \right]$$

can be alternatively written:

$$A = \int n(\rho) \exp \left[ -i2\pi \vec{\rho} \cdot \Delta \vec{k} \right] dV$$

where  $n(\vec{\rho})$  is the local electronic density.

Let us suppose that each cell contains several atoms (s for example); the nucleus of the  $j$ th atom located at position:

$$\vec{\rho}_j = x_j \vec{a}_1 + y_j \vec{a}_2 + z_j \vec{c}$$

relatively to the position of the node:

$$\vec{\rho}_{uvw} = u \vec{a}_1 + v \vec{a}_2 + w \vec{c}$$

$$(x_i, y_i, z_i) \in [0, 1]^3$$

Let the origin be  $\rho_{000}$  so that we can write the total electronic density in the crystal  $n(\vec{\rho})$  as a double summation over all atomic positions in one cell, and through all cells:

$$n(\vec{\rho}) = \sum_{uvw} \sum_{j=1,s} c_j (\vec{\rho} - \vec{\rho}_j - \vec{\rho}_{uvw})$$

where  $c_j$  is the electronic density associated with atom  $j$ . Then:

$$\begin{aligned} A_{\Delta \vec{k}} &= \sum_{uvw} \sum_{j=1,s} \int c_j (\vec{\rho} - \vec{\rho}_j - \vec{\rho}_{uvw}) \exp \left[ -i2\pi \vec{\rho} \cdot \Delta \vec{k} \right] dV \\ A_{\Delta \vec{k}} &= \sum_{uvw} \sum_{j=1,s} \int c_j (\vec{\rho} - \vec{\rho}_j - \vec{\rho}_{uvw}) \exp \left[ -i2\pi (\vec{\rho} - \vec{\rho}_j - \vec{\rho}_{uvw}) \Delta \vec{k} \right] \\ &\quad \exp \left[ -i2\pi (\vec{\rho}_j + \vec{\rho}_{uvw}) \Delta \vec{k} \right] dV \end{aligned}$$

This equation becomes:

$$A_{\Delta \vec{k}} = \sum_{uvw} \sum_{j=1,s} F_j \exp \left[ -i2\pi (\vec{\rho}_j + \vec{\rho}_{uvw}) \cdot \Delta \vec{k} \right] dV$$

where quantities  $F_j$  are defined as:

$$F_j = \int c_j(\vec{x}) \exp \left[ -i2\pi \vec{x} \cdot \Delta \vec{k} \right]$$

$$A_{\Delta \vec{k}} = \sum_{uvw} \exp \left[ -i2\pi \vec{\rho}_{uvw} \cdot \Delta \vec{k} \right] \sum_{j=1,s} F_j \exp \left[ -i2\pi \vec{\rho}_j \cdot \Delta \vec{k} \right]$$

We know, from above, that  $\sum_{uvw} \exp \left[ -i2\pi \vec{\rho}_{uvw} \cdot \Delta \vec{k} \right]$  does not vanish—if and only if— $\Delta \vec{k}$  is a vector  $\vec{G}$  of the reciprocal lattice.

Then, the quantity:

$$S_{\vec{G}} = \sum_{j=1,s} F_j \exp \left[ -i2\pi \vec{\rho}_j \cdot \vec{G} \right]$$

is called structure factor.

Let

$$\vec{G}_{hkl} = h\vec{a}_1^* + k\vec{a}_2^* + \ell\vec{c}^*,$$

then:

$$S_{hkl} = \sum_j F_j \exp \left[ -i2\pi (hx_j + ky_j + \ell z_j) \right]$$

This equation leads to selection rules on (h, k and  $\ell$ ), depending on the relative positions of atoms within the cell, when the argument of the complex exponential vanishes. Beyond the scope of point group symmetry, from the relative positions of similar atoms in the cell, are defined complementary symmetry operations within the cell that give access to the space group of the crystal. There are 32 point groups and 230 space groups. Studying them is beyond the scope of this monography.

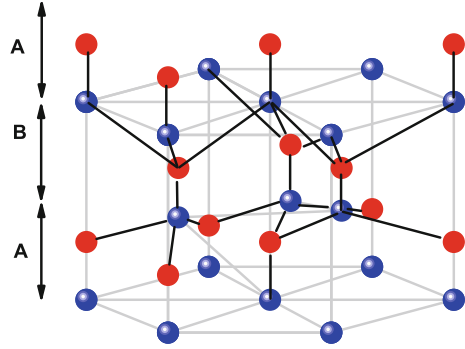
### 1.8.3 The Perfect Wurtzite Structure

The wurtzite structure is more complex than this: as demonstrated by W.L. Bragg in 1914, it consists of two interpenetrating Hexagonal Closed Packed sub-lattices, one for each atomic species, offset along the  $c$  axis by  $5/8$  of the cell height. The atomic positions in the unit cell are (0, 0, 0) and (2/3, 1/3, 1/2) for the anions, and (0, 0, 3/8) and (2/3, 1/3, 7/8) for the cations and the positions of the atoms in a hexagonal cell are indicated in Fig. 1.11.

It is worthwhile noticing that the structure factor is the sum of contributions from the cations and from the anions:

$$S_{hkl} = \left( 1 + \exp \left[ -i\pi \frac{2h + 4k + 3\ell}{3} \right] \right) \left( F_{cation} + F_{anion} \exp \left[ -i\frac{3\pi\ell}{4} \right] \right)$$

**Fig. 1.11** Plot of the positions of the atoms in a hexagonal cell of a wurtzite crystal



We know from the properties of the exponential function that:

$$\begin{aligned}
 & 1 + \exp \left[ -i\pi \frac{2h + 4k + 3\ell}{3} \right] \\
 &= 2 \cos \pi \frac{2h + 4k + 3\ell}{6} \left( \cos \pi \frac{2h + 4k + 3\ell}{6} - i \sin \pi \frac{2h + 4k + 3\ell}{6} \right) \\
 &\cos \pi \frac{2h + 4k + 3\ell}{6} = 0
 \end{aligned}$$

when

$$\pi \frac{2h + 4k + 3\ell}{6} = p \frac{\pi}{2} \quad \text{with } p \in \mathbf{Z}$$

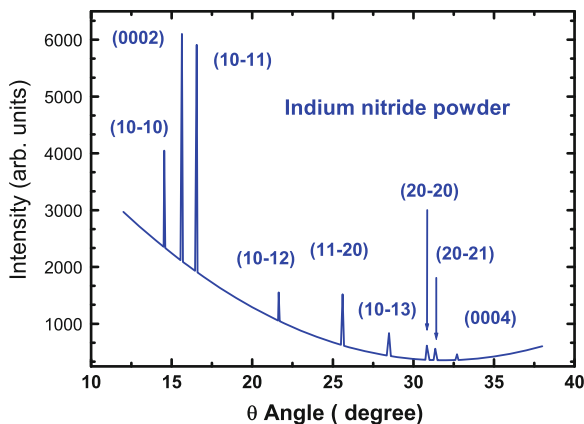
This equation indicates that extinguished radiations correspond to  $(h, k, -(h + k), \ell)$  reticular planes for which  $2h + 4k + 3\ell = 3p$ , with  $p \in \mathbf{Z}$

*This equation is called a selection rule.*

On Fig. 1.12 is reported the diffraction pattern recorded by shining a powder of indium nitride with the  $\text{CuK}_\alpha$  X-ray radiation ( $\lambda = 0.15 \text{ nm}$ ). The powder is constituted with micro-crystals randomly oriented so that artefact selection rules due to specific configuration of the crystals in the context of the geometry of the diffraction experiment can be disregarded.

The intensity of the diffraction pattern corresponding to a given set of Miller indices  $\{h, k, \ell\}$  is given by the square of the diffraction amplitude,  $\|A_{hkl}\|^2$ .

Identification of the  $(hkl)$  sets that lead to a given peak in the context of an overall consistency is a tricky problem. Signatures of specific planes are at last identified, indicating the existence of selection rules. The cell parameters are  $a_0 = 3.5390 \text{ \AA}$  and  $c_0 = 5.7083 \text{ \AA}$ . We note that these values are given with a large number of digits, this is not systematic, and have to be correlated with the experiment's temperature (here room temperature), and with doping since the presence of foreign atoms modifies the lattice constants. The corresponding space group indicating the site symmetry for the wurtzite is No. 186 (in International Union of Crystallography classification) or  $P_{63mc}$  in Hermann-Mauguin notation or  $C_{6V}^3$  in Schoenflies notation.



**Fig. 1.12** Powder diffraction pattern of indium nitride recorded at room temperature using the  $\text{CuK}\alpha$  radiation ( $\lambda = 0.15 \text{ nm}$ )

### 1.8.4 The Internal Displacement Parameter

The internal displacement parameter  $u$  is defined as the anion-cation bond length that is also the nearest-neighbour distance in the crystal divided by the  $c$  lattice parameter. The interatomic distances are expressed versus this parameter.

In an ideal wurtzite structure represented by four touching hard spheres, the values of the axial ratio and the internal parameter are  $c/a = \sqrt{\frac{8}{3}} = 1.633$  and  $u = 3/8 = 0.375$ , respectively. In the hexagonal basis, the atomic positions in the unit cell are  $(0, 0, 0)$  and  $(2/3, 1/3, 1/2)$  for the anions,  $(0, 0, u)$  and  $(2/3, 1/3, (u+1/2))$  for the cations.

In *Cartesian coordinates*, the crystallographic vectors of wurtzite are:

$$\begin{bmatrix} \vec{a}_1 \\ \vec{a}_2 \\ \vec{c} \end{bmatrix} = a \begin{bmatrix} \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 1 & 0 \\ 0 & 0 & \frac{c}{a} \end{bmatrix} \cdot \begin{bmatrix} \vec{x} \\ \vec{y} \\ \vec{z} \end{bmatrix} \quad (1.7)$$

The atomic positions are  $(0, 0, 0)$ , and  $a(\frac{1}{\sqrt{3}}, 0, \frac{c}{2a})$  for anions.

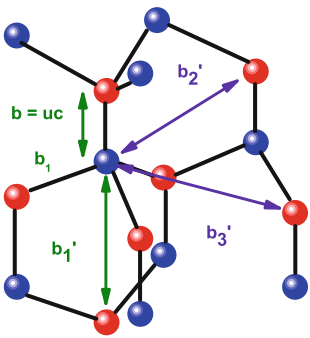
For cations, positions are  $a(\frac{1}{\sqrt{3}}, 0, (\frac{1}{2} - u)\frac{c}{a})$ , and  $a(0, 0, (1 - u)\frac{c}{a})$ .

The nearest-neighbour bond length along the  $c$  direction is:

$$b = cu$$

and off-axis nearest-neighbour bond length is, as indicated in Fig. 1.13:

**Fig. 1.13** Relative positions of the atoms in the wurtzite structure, directions to nearest neighbours. The  $c$  axis is vertical



**Table 1.3** The evolution of  $a$ ,  $c/a$  and  $u$  for wurtzitic III-nitrides

Material	GaN	InN	AlN
$a$ ( $10^{-10}$ m)	3.1879	3.5390	3.110
$c/a$	1.626	1.613	1.610
$u$	0.377	0.379	0.382

$$b_1 = \sqrt{\frac{a^2}{3} + (1 - u^2)c^2}$$

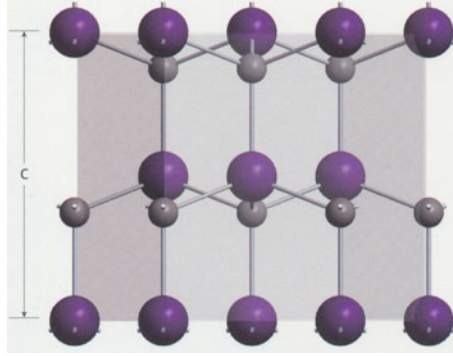
*The four nearest neighbours of each atom form a trigonal pyramid.*  
We remark that there are three types of second-nearest neighbours designated as:

$$\begin{aligned} b'_1 &= (1 - u)c \\ b'_2 &= \sqrt{a^2 + u^2c^2} \end{aligned}$$

and

$$b'_3 = \sqrt{\frac{a^2}{3} + (\frac{1}{2} - u)^2c^2}$$

In many wurtzitic semi-conductors such as nitrides, experimentally observed  $c/a$  ratios and values of internal displacement parameter  $u$  differ from the ideal values. These discrepancies are due to atoms being real quantum objects, departing more or less from the hard sphere description, either in vacuum or when chemically bonded to other atoms. It should be pointed out that a strong correlation exists between the  $c/a$  ratio and the  $u$  parameter so that when  $c/a$  decreases,  $u$  increases in a manner to keep the four tetrahedral distances nearly constant through a distortion of tetrahedral angles. Table 1.3 illustrates the evolution of  $c/a$  and  $u$  for wurtzitic III-nitrides.



**Fig. 1.14** Relative ordering of the atomic planes in the wurtzite structure along the  $c$  direction

**Table 1.4** The evolution of spontaneous polarization  $P_{sp}$ , ratio  $c/a$  and internal displacement parameter  $u$  for wurtzitic semi-conductors

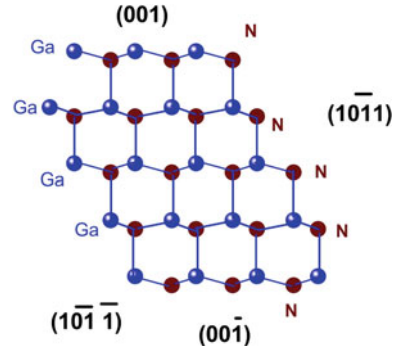
Material	GaN	InN	AlN	ZnO	BeO
$P_{sp}$ (Cm <sup>-2</sup> )	-0.0339	-0.0413	-0.0898	-0.057	-0.045
$c/a$	1.626	1.613	1.610	1.60	1.622
$u$	0.377	0.379	0.382	0.382	0.378

## 1.9 The Spontaneous Polarization Along the $c$ Axis

In Fig. 1.14, we present a sketch of the atomic planes along the six-fold symmetry axis, which consists of successive stacking of planes that only contain cations or anions, the so-called ABAB stacking.

The important point to outline from the figure is the non-overlap of the center of gravity of reticular planes of cations (positive charges) and anions (negative charges) that produces an electronic dipole along the  $c$  direction of the crystal. There is a spontaneous polarization internal to the wurtzitic crystal. This quantity is not easy to measure in bulk crystals, due to the polar nature of the surface. This surface easily traps impurities so that the total polarization drop through the crystal vanishes. Impurities, topological defects may create electric fields and compensate this quantity too. This quantity has been computed by several group of theorists, using very sophisticated approaches in the context of the quantum mechanics description of the chemical bonds. These so-called ab-initio calculations have furnished some numerical values for these quantities. It can be seen in Table 1.4 that the spontaneous polarization  $P_{sp}$  in III-Ns (resp. II-Os) has a negative value. The conventional [0001] direction taken as positive goes from the group III- (respectively group II-) element atom to the group V- (respectively group VI-) element and opposes to  $P_{sp}$ . In nitrides for instance, the negative value indicates that the electric dipole is oriented from the N atom towards the group III-element (Al, Ga, or In) one.

**Fig. 1.15** relative orientation of the atomic stackings and non equivalence of the (0001) and (000 $\bar{1}$ ) surface. By convention, the (0001) plane only contains metallic atoms



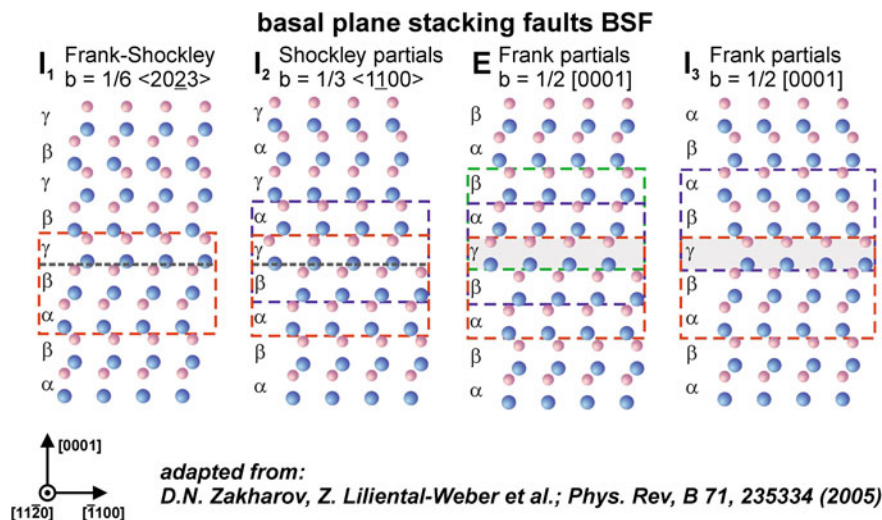
It is worthwhile noticing, from Fig. 1.15, that when cutting the [0001] bonds above a group III- (respectively group II-) element, we define the (0001) surface only composed with metallic atoms. If cutting the [0001] bonds below the reticular plane of group V- (respectively group VI-) element, the (0, 0, 0,  $\bar{1}$ ) surface contains now non metallic atoms. The chemical composition of the (0, 0, 0, 1) surface differs from that of the (0, 0, 0,  $\bar{1}$ ) surface. These two surfaces are not equivalent. One can anticipate that they will behave very differently, when studying, for instance, their responses to chemical aggressions. Let's define the metallic surface as the (0001). One can easily demonstrate that the (3, 0,  $\bar{3}$ ,  $\bar{1}$ ) surface only contains metallic atoms whereas (3, 0,  $\bar{3}$ , 1) does not contain any. In contrast, some surfaces such as (1, 1,  $\bar{2}$ , 2) contain both kinds of atoms.

There are no real correlations between the values of  $P_{sp}$  and the  $c/a$  ratio, the internal displacement parameter. This indicates that  $P_{sp}$  is a real effect, deriving from the quantum nature of the chemical bonds, that depends on the specific stacking of the different atoms. The important point to outline here is that, thanks to the quantum origin of the value spontaneous polarization, its value in an alloy like  $In_{1-x}Ga_xN$  is not obtained by averaging the spontaneous polarization in both binaries, since local modifications of the crystal composition due to chemical disorder in the cation lattice may lead to significant departure of the real value from the predicted one.

In the case of nitride reticular planes having arbitrary ( $hkl$ ) orientations, according to the relation that connects the ( $\vec{U}$ ,  $\vec{V}$ ,  $\vec{W}$ ) vectors and the international basis set, the spontaneous polarization has components in the  $\vec{V}$  and  $\vec{W}$  directions only. These components are obtained by simple matrix algebra as follows:

$$\begin{bmatrix} (P_{sp})_U \\ (P_{sp})_V \\ (P_{sp})_W \end{bmatrix} = \begin{bmatrix} -\frac{\sqrt{3}}{2}Ak & \frac{1}{2}A(2h+k) & 0 \\ -\frac{\sqrt{3}}{2}AalB_{ac}(2h+k) & -\frac{3}{2}AalB_{ack} & 2c\frac{B_{ac}}{A} \\ AcB_{ac}(2h+k) & \sqrt{3}AcB_{ack} & \sqrt{3}\ell aB_{ac} \end{bmatrix} \begin{bmatrix} 0 \\ 0 \\ P_{sp} \end{bmatrix} \quad (1.8)$$





**Fig. 1.16** Basal stacking faults along the  $[0001]$  direction. Courtesy Gordon Schmidt, Frank Bertram and Juergen Christen, University Otto von Guericke of Magdeburg

## 1.10 Defects in the Lattice

There are sometimes some departures from the perfect crystal arrangements. Such departures constitutes defects which may have deleterious influence on optical and transport properties. Among such defects are basal stacking faults. In Fig. 1.16 are represented basal stacking faults which are some of the possible lattice defects. Studying defects is out of the scope of this book.

## 1.11 Piezoelectric Effects in Wurtzitic Semi-conductors

As discussed in the preceding section, the non-overlap of positive and negative atomic charges produces a polarization field along the six-fold symmetry axis of wurtzitic semi-conductors. This effect is sometimes called the pyroelectric effect because its magnitude may change when temperature of the crystal changes, leading to change of the  $c/a$  ratio for instance. Among the thirty-two possible point groups required to describe the orientational symmetries for bulk crystals, only ten are pyro-electric crystals, i.e. they exhibit a spontaneous polarisation field of given orientation with respect to the crystallographic axes. These point groups are in general moderate symmetry sub-groups of the seven groups that describe the full symmetry of the seven crystallographic systems. Among the twenty-one non centro-symmetric groups, ten do not exhibit inversion symmetry with respect to a center point of the cell. In addition, they also possess a complementary property that does not exist in the eleven

**Table 1.5** Piezoelectric and pyroelectric properties of the 32 point groups

32 symmetry classes	
12 non piezo-electric classes	20 piezo-electric classes
O and the 11 centro-symmetric classes:	10 non pyroelectric or non polar classes:
$O, C_i, C_{2h}, D_{2h}, D_{4h}, C_{3i}, D_{3d}, C_{6h},$	$D_2, D_{2d}, D_3, D_4, S_4, D_6, C_{3h}, D_{3h}, T, T_d$
$D_{6h}, T_h, O_h$	10 pyroelectric or polar classes:
	$C_1, C_2, C_3, C_4, C_6, C_s, C_{2v}, C_{3v}, C_{4v}, C_{6v}$

centro-symmetric groups and group O—this one, due to redounding symmetry effects: upon application of a strain field, a complementary polarization may be induced in the crystal. This strain-induced polarization is called piezo-electric polarization and a crystal behaving accordingly is named piezo-electric. Symmetry considerations and utilization of group representations have enabled researchers to determine whether a crystal is piezo-electric, pyro-electric, both or none. The results are compiled in Table 1.5. Some cubic crystals like the zinc-blende semi-conductors ( $T_d$  symmetry) are piezo-electric crystals like rhomboedral quartz ( $D_3$  symmetry). Quartz is not pyro-electric whilst the most symmetrical wurtzite ( $C_{6v}$  symmetry) exhibits spontaneous and may be piezo-electrically polarized. The impossibility to tune the spontaneous polarization in wurtzite crystals—we remind that it is oriented along the six-fold symmetry axis—is a rigid situation, compensated by a flexible situation regarding the piezo electric one. The orientation, magnitude and sign of the latter can be tuned almost at will (Table 1.6).

Given a strain field described by a two-dimensional strain tensor which components are  $\epsilon_{xx}, \epsilon_{yy}, \epsilon_{zz}, \epsilon_{xz}, \epsilon_{yz}$  and  $\epsilon_{xy}$  the components of the piezo electric polarization are given by:

$$\begin{bmatrix} P_x \\ P_y \\ P_z \end{bmatrix} = \begin{bmatrix} 0 & 0 & 0 & 0 & 2e_{15} & 0 \\ 0 & 0 & 0 & 2e_{15} & 0 & 0 \\ e_{13} & e_{13} & e_{33} & 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} \epsilon_{xx} \\ \epsilon_{yy} \\ \epsilon_{zz} \\ \epsilon_{yz} \\ \epsilon_{xz} \\ \epsilon_{xy} \end{bmatrix} \quad (1.9)$$

where quantities  $e_{ij}$  are the components of the piezo-electric tensor.

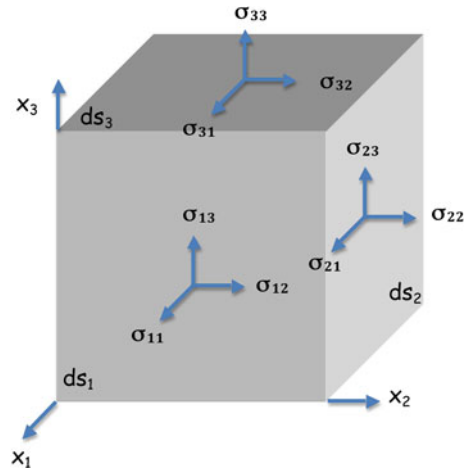
In the case of nitride reticular planes having arbitrary ( $h, k, \ell$ ) orientations, according to the relation that connects the ( $\vec{U}, \vec{V}, \vec{W}$ ) vectors and the international basis set, the piezo-electric polarization has components in the  $\vec{U}, \vec{V}$  and  $\vec{W}$  directions.

These components are obtained by simple matrix algebra as follows:

$$\begin{bmatrix} (P_{pz})_U \\ (P_{pz})_V \\ (P_{pz})_W \end{bmatrix} = \begin{bmatrix} -\frac{\sqrt{3}}{2}Ak & \frac{1}{2}A(2h+k) & 0 \\ -\frac{\sqrt{3}}{2}Aa\ell B_{ac}(2h+k) & -\frac{3}{2}Aa\ell B_{ack} & 2c\frac{B_{ac}}{A} \\ AcB_{ac}(2h+k) & \sqrt{3}AcB_{ack} & \sqrt{3}\ell aB_{ac} \end{bmatrix} \begin{bmatrix} P_x \\ P_y \\ P_z \end{bmatrix} \quad (1.10)$$

**Table 1.6** The components of the piezo electric tensor for wurtzitic semi-conductors

Material	GaN	InN	AlN
$e_{13} \text{ (Cm}^{-2}\text{)}$	-0.338	-0.413	-0.533
$e_{33} \text{ (Cm}^{-2}\text{)}$	-0.372	-0.454	-0.623
$e_{15} \text{ (Cm}^{-2}\text{)}$	-0.167	-0.112	-0.351

**Fig. 1.17** relative orientation of the components of the stress tensor

## 1.12 Stresses and Strains

### 1.12.1 The Stress Tensor

Let us consider an elastic solid at the equilibrium with the directions orthogonal to its facets parallel to the  $\vec{x}$ ,  $\vec{y}$  and  $\vec{z}$  directions that we propose to represent as  $\vec{x}_1$ ,  $\vec{x}_2$  and  $\vec{x}_3$  respectively. It is well known from continuous media mechanics that side  $i$  of facets located at the origin  $O$ , which elementary surface is  $ds_i = dx_j dx_k$  experiences an elastic force:

$$d\vec{F}_i = \vec{\sigma}_i ds_i = \vec{\sigma}_i dx_j dx_k$$

Here, the  $(i, j, k)$  triplet designs a circular permutation through triplet  $(1, 2, 3)$ . The components of such a force along the  $\ell$  direction is:

$$dF_{i\ell} = \sigma_{i\ell} dx_j dx_k$$

as shown on Fig. 1.17.

We obtain 3 equations  $d\vec{F}_i = \vec{\sigma}_i ds_i = \vec{\sigma}_i dx_j dx_k$  and 9 equations  $dF_{i\ell} = \sigma_{i\ell} dx_j dx_k$ .

The scalar quantities  $\sigma_{i\ell}$  are the components of the stress at the origin  $O$ .

$$|\sigma_{i\ell}| \simeq |\sigma_{i\ell}^0| + \frac{|\partial\sigma_{i\ell}^0|}{\partial x_i} dx_i$$

In the context of homogeneous stress:

$$|\sigma_{i\ell}| \simeq |\sigma_{i\ell}^0| + \frac{|\partial\sigma_{i\ell}^0|}{\partial x_i} dx_i = |\sigma_{i\ell}^0|$$

One can further demonstrate that the scalar quantities  $\sigma_{i\ell}$  are the components of a rank-two symmetric tensor called the stress tensor that we write as follows:

$$\begin{bmatrix} \vec{\sigma} \\ \vec{\sigma} \end{bmatrix} = \begin{bmatrix} \sigma_{11} & \sigma_{12} & \sigma_{13} \\ \sigma_{12} & \sigma_{22} & \sigma_{23} \\ \sigma_{13} & \sigma_{23} & \sigma_{33} \end{bmatrix} \quad (1.11)$$

From the technical point of view, it is very convenient to write the stress tensor:

$$\begin{bmatrix} \vec{\sigma} \\ \vec{\sigma} \end{bmatrix} = \begin{bmatrix} \sigma_{11} & \sigma_{12} & \sigma_{13} \\ \sigma_{12} & \sigma_{22} & \sigma_{23} \\ \sigma_{13} & \sigma_{23} & \sigma_{33} \end{bmatrix} = \begin{bmatrix} \sigma_1 & \sigma_6 & \sigma_5 \\ \sigma_6 & \sigma_2 & \sigma_4 \\ \sigma_5 & \sigma_4 & \sigma_3 \end{bmatrix} \quad (1.12)$$

where couples of indices 11, 22, 33, 23, 13, and 12 are one by one represented by one index running from 1 to 6.

Alternatively, the stress tensor may be written under the useful form below:

$$\begin{bmatrix} \vec{\sigma} \\ \vec{\sigma} \end{bmatrix} = \begin{bmatrix} \sigma_1 & \sigma_6 & \sigma_5 \\ \sigma_6 & \sigma_2 & \sigma_4 \\ \sigma_5 & \sigma_4 & \sigma_3 \end{bmatrix} = \begin{bmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \\ \sigma_4 \\ \sigma_5 \\ \sigma_6 \end{bmatrix}. \quad (1.13)$$

### 1.12.2 The Strain Tensor

Let us consider two close points  $A$  and  $B$  of a solid at the equilibrium in the absence of any mechanical perturbation. We write their coordinates relatively to the origin  $O$ , in terms of the orthogonal vectors  $\vec{x}$ ,  $\vec{y}$  and  $\vec{z}$  as follows:

$$\begin{bmatrix} \vec{OA} \end{bmatrix} = \begin{bmatrix} x_1 \\ x_2 \\ x_3 \end{bmatrix} \text{ and } \begin{bmatrix} \vec{OB} \end{bmatrix} = \begin{bmatrix} x_1 + dx_1 \\ x_2 + dx_2 \\ x_3 + dx_3 \end{bmatrix} \quad (1.14)$$

That gives:

$$[\vec{AB}] = [\vec{ds}] = \begin{bmatrix} dx_1 \\ dx_2 \\ dx_3 \end{bmatrix} \quad (1.15)$$

Under the influence of the stress,  $A$  shifts to  $A'$  and  $B$  shifts to  $B'$  as follows

$$[\vec{AA'}] = [\vec{u}] = \begin{bmatrix} u_1 \\ u_2 \\ u_3 \end{bmatrix} \text{ and } [\vec{BB'}] = [\vec{u} + d\vec{u}] = \begin{bmatrix} u_1 + du_1 \\ u_2 + du_2 \\ u_3 + du_3 \end{bmatrix} \quad (1.16)$$

The coordinates of  $A'$  and  $B'$  are:

$$[\vec{OA'}] = \begin{bmatrix} x_1 + u_1 \\ x_2 + u_2 \\ x_3 + u_3 \end{bmatrix} \quad (1.17)$$

and

$$[\vec{OB'}] = \begin{bmatrix} u_1 + du_1 + x_1 + dx_1 \\ u_2 + du_2 + x_2 + dx_2 \\ u_3 + du_3 + x_3 + dx_3 \end{bmatrix} \quad (1.18)$$

Then  $\vec{ds}$  is transformed into  $\vec{ds'}$

$$[\vec{A'B'}] = [\vec{ds'}] = \begin{bmatrix} du_1 + dx_1 \\ du_2 + dx_2 \\ du_3 + dx_3 \end{bmatrix} \quad (1.19)$$

We now write for every component  $i$ :

$$du_i = \frac{\partial u_i}{\partial x_1} dx_1 + \frac{\partial u_i}{\partial x_2} dx_2 + \frac{\partial u_i}{\partial x_3} dx_3$$

or, by introducing a  $(3 \times 3)$  matrix  $[\beta]$  which components are  $\beta_{ij} = \frac{\partial u_i}{\partial x_j}$ :

$$[\vec{du}] = [\beta] \cdot [\vec{dx}] \quad (1.20)$$

Here,  $[\beta]$  is the matrix representation of the strain tensor  $\vec{\beta}$ .

$[\beta]$  is the sum of an antisymmetric matrix  $[\varpi]$  plus a symmetric one  $[\epsilon]$ .

$$\begin{bmatrix} \beta_{11} & \beta_{12} & \beta_{13} \\ \beta_{21} & \beta_{22} & \beta_{23} \\ \beta_{31} & \beta_{32} & \beta_{33} \end{bmatrix} = \begin{bmatrix} 0 & \varpi_{12} & \varpi_{13} \\ -\varpi_{12} & 0 & \varpi_{23} \\ -\varpi_{13} & -\varpi_{23} & 0 \end{bmatrix} + \begin{bmatrix} \epsilon_{11} & \epsilon_{12} & \epsilon_{13} \\ \epsilon_{21} & \epsilon_{22} & \epsilon_{23} \\ \epsilon_{31} & \epsilon_{32} & \epsilon_{33} \end{bmatrix} \quad (1.21)$$



**Fig. 1.18** Sketch of a stretching under the effect of the diagonal components of the strain tensor



**Fig. 1.19** Sketch of a shear (*right*) acting on an unstrained sample (*left*) under the effect of the off-diagonal components of the strain tensor

where

$$\varpi_{ij} = \frac{1}{2} \left( \frac{\partial u_i}{\partial x_j} - \frac{\partial u_j}{\partial x_i} \right)$$

and

$$\epsilon_{ij} = \frac{1}{2} \left( \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right)$$

One can demonstrate that the antisymmetric tensor has the symmetry of a pseudo-vector which can be represented by a three-component axial vector of components  $\varpi_{23}$ ,  $\varpi_{31}$ , and  $\varpi_{12}$ . This contribution shall be disregarded here.

The symmetric tensor represents the variation of the lengths between the different points of the solid.

The diagonal elements  $\epsilon_{ii}$  are the stretching components of the strain field.

On Fig. 1.18 is illustrated a typical stretching of a barrel: the length is increased along one direction, reduced along the remaining two. On Fig. 1.19 is illustrated a typical shear of a barrel:

The off-diagonal elements  $\epsilon_{ij}$  with  $i \neq j$  are the shear components of the strain field. The symmetric tensor represents the variation of the lengths between the different points of the solid.

One may have to represent the symmetrical strain tensor as a six-component vector:

$$\begin{bmatrix} \epsilon_1 \\ \epsilon_2 \\ \epsilon_3 \\ \epsilon_4 \\ \epsilon_5 \\ \epsilon_6 \end{bmatrix} = \begin{bmatrix} \epsilon_{11} \\ \epsilon_{22} \\ \epsilon_{33} \\ 2\epsilon_{23} \\ 2\epsilon_{31} \\ 2\epsilon_{12} \end{bmatrix}. \quad (1.22)$$

### 1.12.3 The Stiffness and Compliance Tensors

Hooke's law is a well known proportionality relation that correlates the deformation experienced by a solid with the stress it is submitted to. In our case, a tensorial relation connects the rank-two strain tensor with the rank-two stress one. It writes:

$$\begin{bmatrix} \vec{\epsilon} \end{bmatrix} = \begin{bmatrix} \vec{S} \end{bmatrix} \cdot \begin{bmatrix} \vec{\sigma} \end{bmatrix} \quad (1.23)$$

where  $\vec{S}$  is the *compliance tensor*, a rank-four tensor.

Reversely, one can write:

$$\begin{bmatrix} \vec{\sigma} \end{bmatrix} = \begin{bmatrix} \vec{C} \end{bmatrix} = \begin{bmatrix} \vec{\epsilon} \end{bmatrix} \quad (1.24)$$

where  $\vec{C}$  is the *stiffness tensor*, a rank-four tensor.

Both  $\vec{S}$  and  $\vec{C}$  have  $3^4 = 81$  independent components—all are scalar numbers—that are represented by  $S_{ijkl}$  or  $C_{ijkl}$  with each of the four indices running from 1 to 3.

Fortunately, the number of these components can be reduced to 36, thanks to symmetry considerations.

Components of both  $\vec{S}$  and  $\vec{C}$  are governed by the same symmetry rules.

Let us here take  $\vec{C}$  for the sake of the illustration.

One can demonstrate that  $C_{ijkl} = C_{jikl} = C_{ijlk} = C_{klij}$ .

Then, it is possible to represent any of these rank-four tensors using a  $(6 \times 6)$  matrix.

We remind the reader that both the stress and strain tensors can be represented by 6-component vectors.

The relationships between the indices of the six-component vectors and those of the  $(3 \times 3)$  symmetrical tensors are the following: the indices of the six-component vectors run from 1 to 6 when where couples of indices are 11, 22, 33, 23, 13, and 12 respectively.

The components of the stress tensor are:  $\sigma_m = \sigma_{ij}$ .

The components of the strain tensor and of its representative vector are, in addition, connected by a complementary relation:

$$\epsilon_m = f(m)\epsilon_{ij}$$

with:

$$f(m) = 1 \quad \text{when } m \in \{1, 2, 3\}$$

$$f(m) = 2 \quad \text{when } m \in \{4, 5, 6\}$$

Here, we have to write the following relationships:

$$C_{mn} = g(m, n)C_{ijkl}$$

with:

$$g(m, n) = 1 \quad \text{when } (m, n) \in (\{1, 2, 3\}, \{1, 2, 3\})$$

$$g(m, n) = 2 \quad \text{when } (m, n) \in (\{1, 2, 3\}, \{4, 5, 6\}) \quad \text{or when } (m, n) \in (\{4, 5, 6\}, \{1, 2, 3\})$$

$$g(m, n) = 4 \quad \text{when } (m, n) \in (\{4, 5, 6\}, \{4, 5, 6\})$$

Then, the compliance and stiffness rank-four tensors can be represented using  $(6 \times 6)$  matrices of the kind below:

$$\begin{bmatrix} \vec{S} \end{bmatrix} = \begin{bmatrix} S_{11} & S_{12} & S_{13} & S_{14} & S_{15} & S_{16} \\ S_{12} & S_{22} & S_{23} & S_{24} & S_{25} & S_{26} \\ S_{13} & S_{23} & S_{33} & S_{34} & S_{35} & S_{36} \\ S_{14} & S_{24} & S_{34} & S_{44} & S_{45} & S_{46} \\ S_{15} & S_{25} & S_{35} & S_{45} & S_{55} & S_{56} \\ S_{16} & S_{26} & S_{36} & S_{46} & S_{56} & S_{66} \end{bmatrix}; \quad \begin{bmatrix} \vec{C} \end{bmatrix} = \begin{bmatrix} C_{11} & SC_{12} & C_{13} & C_{14} & C_{15} & C_{16} \\ C_{12} & C_{22} & C_{23} & C_{24} & C_{25} & C_{26} \\ C_{13} & C_{23} & C_{33} & C_{34} & C_{35} & C_{36} \\ C_{14} & C_{24} & C_{34} & C_{44} & C_{45} & C_{46} \\ C_{15} & C_{25} & C_{35} & C_{45} & C_{55} & C_{56} \\ C_{16} & C_{26} & C_{36} & C_{46} & C_{56} & C_{66} \end{bmatrix} \quad (1.25)$$

The relations between the strain and the stress now write:

$$[\vec{\epsilon}] = \begin{bmatrix} \vec{S} \end{bmatrix} \cdot [\vec{\sigma}] \quad \text{and} \quad [\vec{\sigma}] = \begin{bmatrix} \vec{C} \end{bmatrix} \cdot [\vec{\epsilon}] \quad (1.26)$$

*We wish here to insist on the fact that these objects are representations in the Voigt's notation of tensors of the three-dimensional space and that we can not apply to them classical algebraic calculations, typical of Euclidian spaces like matrix equations for rotation of axes. In such cases, one has to use relations for tensors.*

#### ***1.12.4 The Stiffness and Compliance Tensors in Wurtzitic Semi-conductors***

It may be demonstrated that, in line with the six-fold symmetry along the  $\vec{z}$  ( $\vec{x}_3$  axis), directions  $\vec{x}_1$  and  $\vec{x}_3$  are equivalent. Then, the compliance and stiffness tensors take



the simplified forms given below:

$$\begin{bmatrix} \bar{\bar{S}} \end{bmatrix} = \begin{bmatrix} S_{11} & S_{12} & S_{13} & 0 & 0 & 0 \\ S_{12} & S_{11} & S_{13} & 0 & 0 & 0 \\ S_{13} & S_{13} & S_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & S_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & S_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & S_{66} \end{bmatrix}; \quad \begin{bmatrix} \bar{\bar{C}} \end{bmatrix} = \begin{bmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{13} & 0 & 0 & 0 \\ C_{13} & C_{13} & C_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{66} \end{bmatrix} \quad (1.27)$$

Adding the complementary equation:

$$S_{66} = 2(S_{11} - S_{12})$$

$$C_{66} = \frac{1}{2}(C_{11} - C_{12})$$

Then, the wurtzite symmetry prescripts five components to be different and independent for stiffness and compliance tensors.

We would like to indicate that:

$$[\bar{\epsilon}] = [\bar{\bar{S}}] \cdot [\bar{\bar{C}}] \cdot [\bar{\epsilon}] \quad (1.28)$$

The matrix product of the compliance and stiffness tensors gives the identity (6 × 6) matrix:

$$[\bar{\bar{S}}] \cdot [\bar{\bar{C}}] = [1] \quad (1.29)$$

The  $C_{ij}$ s can be expressed as functions of the  $S_{ij}$ s and vice versa:

$$\begin{aligned} S_{11} &= \frac{C_{33}C_{11} - C_{13}^2}{(C_{11} - C_{12})[C_{33}(C_{11} + C_{12}) - 2C_{13}^2]} \\ S_{12} &= \frac{C_{13}^2}{(C_{11} - C_{12})[C_{33}(C_{11} + C_{12}) - 2C_{13}^2]} \\ S_{13} &= -\frac{C_{13}}{C_{33}(C_{11} + C_{12}) - 2C_{13}^2} \\ S_{33} &= \frac{C_{11} + C_{12}}{C_{33}(C_{11} + C_{12}) - 2C_{13}^2} \\ S_{44} &= \frac{1}{C_{44}} \end{aligned}$$

The recommended values of the stiffness coefficients of nitride semi-conductors are given in Table 1.7.

**Table 1.7** Values of the stiffness coefficients of nitride semi-conductors (at room temperature)

Material	GaN	InN	AlN
$C_{11}$ (GPa)	$390 \pm 15$	190	$410 \pm 10$
$C_{12}$ (GPa)	$145 \pm 20$	104	$149 \pm 10$
$C_{13}$ (GPa)	$106 \pm 20$	121	$99 \pm 4$
$C_{33}$ (GPa)	$398 \pm 20$	182	$389 \pm 10$
$C_{44}$ (GPa)	$105 \pm 10$	100	$125 \pm 5$

### 1.12.5 The Energy of a Strained Crystal

Let us consider an unstrained crystal, initially shaped as a unit cube, experiencing a small homogeneous strain field of components represented by  $\epsilon_i$  in the context of matrix notation.

When the strain changes from  $\epsilon_i$  to  $\epsilon_i + d\epsilon_i$ , one can demonstrate that the work due to the stress components  $\sigma_i$  acting on the cube faces is:

$$dW = \sum_i \sigma_i d\epsilon_i$$

that we re-write, using Einstein's notation to get rid of the summation symbol on index repeated twice:

$$dW = \sigma_i d\epsilon_i$$

This can be rearranged into:

$$dW = C_{ij} \epsilon_j d\epsilon_i$$

still using Einstein's notation.

After integration, taking into account  $C_{ji} = C_{ij}$ , one arrives at:

$$W = \frac{1}{2} C_{ij} \epsilon_j \epsilon_i$$

$W$  has the dimension of a pressure (GPa) and represents the strain energy per unit volume of the crystal.

## 1.13 Basic Elements of Group Theory

### 1.13.1 The Concept of Algebraic Groups

- A group  $G$  is a collection of elements  $\{A, B, C, \dots\}$  which are inter-related according to certain rules.

**Table 1.8** Multiplication table of group  $G$ 

$G$	$E$	$A$	$B$	$\dots$	$U$	$V$
$E$	$E$	$A$	$B$	$\dots$	$U$	$V$
$A$	$A$	$AA$	$AB$	$\dots$	$AU$	$AV$
$B$	$B$	$BA$	$BB$	$\dots$	$BU$	$BV$
$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\ddots$	$\vdots$	$\vdots$
$U$	$U$	$UA$	$UB$	$\dots$	$UU$	$UV$
$V$	$V$	$VA$	$VB$	$\dots$	$VU$	$VV$

- The product of two elements of the group must be an element of the group:  $\forall(A, B) \in G \times G; AB = C$ , with  $C \in G$ . When  $AB = BA$  the group is called Abelian.

There exists one identity element  $E$ :

$E \in G$  and  $\forall(A) \in G; AE = EA = A$ .  $E$ —comes from German word *Einheit*—is called identity element.

- The associative law of multiplication must hold:

$$\forall(A, B, C) \in G \times G \times G; (AB)C = A(BC)$$

- Any element  $A$  of a group must have a reciprocal element. This reciprocal element may be noted  $A^{-1}$ .

$$\forall(A) \in G, \exists B \in G \text{ so that } AB = BA = E.$$

- The reciprocal of a product of two or more elements is equal to the product of the reciprocals in reverse order.

$$(ABC\dots XY)^{-1} = Y^{-1}X^{-1}B^{-1}A^{-1}$$

Groups may have a finite number of elements (they are called finite groups) or unlimited numbers of elements (infinite groups). The number of elements of a group, generally represented  $G$  is called the order of the group.

- The multiplication table of the symmetry elements (Table 1.8) is a table of  $h$  rows and  $h$  columns. At the intersection of column  $X$  and row  $Y$  is the product  $XY$ . Each row and each column in the group multiplication table lists each of the group elements once and only once: this is the rearrangement theorem. Two rows may not be identical, nor may be two columns. Thus, each row and each column is a rearranged list of the group elements.

When groups are Abelian, the multiplication table is symmetric:  $AB = BA$ .

- A group has subgroups, labelled  $H$ , which are collections of elements of  $G$  that are themselves forming a group.  $E$  belongs to all subgroups of  $G$ .  $E$  alone is a

subgroup of  $G$ . Let  $h$  be the order of  $H$ . Then, as prescribed by the theorem of Lagrange,  $g/h$  is an integer number.

- A group may be separated into various smaller sets of elements called classes. Let  $A$  and  $X$  be two elements of a group  $G$  and  $B$  a third element of  $G$ , so that  $B = X^{-1}AX$ .  $B$ , the similarity transform of  $A$  by  $X$ , is the conjugate of  $A$ . Three important properties may be derived from this definition: each element is self-conjugate; and if  $A$  is conjugate of  $B$ , then  $B$  is conjugate of  $A$ ; and if  $A$  is conjugated of  $B$  and  $C$ , then  $B$  and  $C$  are conjugate with each other. *A complete set of elements conjugate one to another is called a class of the group.*

The orders of classes must be integral factors of the order of the group. The identity constitutes a class. In an Abelian group, each element constitutes its own class. Classes are symmetry operations of the same kind.

- Two groups  $G$  and  $G'$  are isomorphic if there exists a function that sets up a one-to-one correspondence between the elements of the groups in a way that respects the given group operations. Such a function is called an isomorphism. From the standpoint of group theory, isomorphic groups have the same properties (same order, same multiplication table,...) and need not be distinguished.

An isomorphism from a group  $(G, \cdot)$  to itself is called an automorphism of this group. Thus, it is a bijection  $f : G \rightarrow G$  such that  $f(A) \cdot f(B) = f(A \cdot B)$ ,  $\forall (A, B) \in G \times G$ .

An automorphism always maps the identity to itself. The image under an automorphism of a conjugacy class is always a conjugacy class (the same or another). The image of an element has the same order as that element.

- Besides the one-to-one correspondence between two groups, many-to-one correspondence may exist. The groups are said to be homomorphic. The isomorphism preserves the structure of the original group, but a homomorphism causes some of the structure of the original group to be lost. Both properties are reflected in the behaviour of multiplication tables. The orders of the two homomorphic groups may be different.
- The **direct product** of groups  $G$  and  $H$  which orders are  $g$  and  $h$  respectively is a group of order  $g \cdot h$ , noted  $G \times H$ . Its elements are, by construction, the products of all the elements of  $G$  by all the elements of  $H$ . If  $G$  has  $p$  classes and  $H$  has  $p'$  classes, then  $G \times H$  has  $p \cdot p'$  classes. A condition for a group to be a direct product of two groups is that neither its order nor its number of classes are prime numbers.

### 1.13.2 Representations of Finite Groups by Matrices

Let us consider a  $n$ -dimensional vectorial space  $E_n$  with its eigenvectors  $\{\vec{e}_n\}$ .

Let  $X = \sum_j X_j \vec{e}_j \equiv X_j \vec{e}_j$  (with Einstein's notation for summation) a vector of  $E_n$ .

Let the operator  $\mathbf{A}$  so that  $Y = \mathbf{A}X$ .

This may be written  $Y_k = A_{kj} X_j$ .

The  $(n \times n)$  matrix with elements  $A_{kj}$  is a representation of operator  $\mathbf{A}$  in the basis  $\{\vec{e}_n\}$ .  $k$  (resp.  $j$ ) is the column (resp. row) index.

The trace of the matrix representative of operator  $\mathbf{A} = \sum_k A_{kk}$ —is an invariant under any basis transformation. *It is called the character of matrix A.*

The full set of the matrices representating in the basis  $\{\vec{e}_n\}$  all the operators  $\mathbf{A}$  of a  $n$ -dimensional group  $G$  forms a group and forms a  $n$ -dimensional representation of the operators  $\mathbf{A}$  of the  $n$ -dimensional group  $G$ . Any representation of a finite group  $G$  is equivalent to a unitary representation of this group (all matrices are unitary matrices).

**Note:** When two operators  $\mathbf{A}$  and  $\mathbf{B}$  are represented by matrices  $M_A$  and  $M_B$  respectively:  $\mathbf{A} \neq \mathbf{B} \nrightarrow M_A \neq M_B$ . Isomorphisms and homomorphisms may exist between  $G$  and the group of matrices  $M$  representing the operators of  $G$ . Homomorphisms often occurs: several operators of  $G$  are represented by the same matrix.

The abstract **basis of irreducible representations** is of paramount importance for representing symmetries. Let  $\Gamma_\nu(A)$  and  $\Gamma_\mu(A)$  be two matrix representations of a group  $G$ . These representations are of dimensions  $\nu$  and  $\mu$  respectively. If for each element of the group we define a matrix of dimension  $\nu + \mu$  as:

$$\Gamma(A) = \begin{array}{|c|c|} \hline \Gamma_\nu(A) & 0 \\ \hline 0 & \Gamma_\mu(A) \\ \hline \end{array} = \Gamma_\nu(A) \oplus \Gamma_\mu(A)$$

The matrices  $\Gamma$  form a representation of  $G$ . This representation leads to block-diagonal matrices. It is said to be reducible; it is the direct sum of representations  $\Gamma_\nu$  and  $\Gamma_\mu$ . The summation differs from a classical summation; it is a summation over two different vectorial spaces  $\epsilon_\nu$  and  $\epsilon_\mu$ .

$$\Gamma = \Gamma_\nu \bigoplus \Gamma_\mu \quad \text{and} \quad \epsilon = \epsilon_\nu \bigcup \epsilon_\mu.$$

A representation with a block-diagonal shape is a **reducible representation**. Once the ultimate sizes of the blocks are reached, i.e. when no similarity operation is susceptible to reduce the sizes of such blocks, the representation is named **irreducible**.

There is an infinite number of possible representations for a group, just like an idea may be formulated using as many languages as one can invent. The number of irreducible representations of a group is limited: it is equal to the number of classes of the group. The number of irreducible representations of an Abelian group is equal to the number of its elements.

Let us compare the full set of irreducible representations to the finite number of Chinese ideograms. Any language spoken by a person can be written with these Chinese ideograms. An assembly of people speaking different tongues can hardly communicate. But writing their sayings using the Chinese ideograms allows anyone knowing Chinese ideograms to understand every word. Since it is possible to associate many sounds to a Chinese ideogram, each of the irreducible representations has an infinite number of possible basis vectors. Any representation can be expanded along the set of irreducible representations by manipulating with an ad-hoc algebra the representation characters to reduce with the characters of the irreducible rep-

**Table 1.9** Table of characters of group G

$G$	$C_1$	$C_2$	$C_3$	$C_4$
$\Gamma_1$	$\chi_{11}$	$\chi_{12}$	$\chi_{13}$	$\chi_{14}$
$\Gamma_2$	$\chi_{21}$	$\chi_{22}$	$\chi_{23}$	$\chi_{24}$
$\Gamma_3$	$\chi_{31}$	$\chi_{32}$	$\chi_{33}$	$\chi_{34}$
$\Gamma_4$	$\chi_{41}$	$\chi_{42}$	$\chi_{43}$	$\chi_{44}$

representations. We will develop this quantitatively. To achieve that, it is necessary to construct the table of character of the group.

### 1.13.3 Character Tables and Irreducible Representations

The **table of characters** is a table with as many rows as irreducible representations ( $\Gamma_i$ s), and as many columns as classes ( $C_j$ s). Let  $n$  be this number, it is a  $n \times n$  table sketched in Table 1.9 when  $n = 4$ .

Quantity  $\chi_{ij}$  is the character of matrices representing elements of class  $C_j$  in irreducible representation  $\Gamma_i$ . these quantities may be complex numbers.

**Trick:** a quick method to calculate the character of a matrix representing an operator  $\mathbf{A}$  in a given representation is to consider the number of basis vectors unchanged under  $\mathbf{A}$  (character 1) diminished from the number of basis vectors transformed into their opposite under  $\mathbf{A}$  (character  $-1$ ). The vectors transformed differently under  $\mathbf{A}$  have a vanishing contribution to the characters of the representation.

There are a few orthogonality relations that help to construct the table of irreducible representations:

$$\sum_{\mathbf{A}} \chi_j(\mathbf{A}) \chi_i^*(\mathbf{A}) = g \delta_{ij}$$

Let class  $C_A$  of  $\mathbf{A}$  have  $N_A$  elements. Then, the equation above becomes:

$$\sum_{C_A} N_A \chi_j(C_A) \chi_i^*(C_A) = g \delta_{ij}$$

$$\sum_{C_A} N_A \chi_j(C_A) \chi_i^*(C_B) = g \delta_{AB}$$

- Given an irreducible representation, the sum of the squared moduli of characters through all operators  $\mathbf{A}$  is the order of the group:

$$\sum_{\mathbf{A}} |\chi_j(\mathbf{A})|^2 = g$$

- The sum of the squared moduli of characters of the identity through all irreducible representations ( $\Gamma$ 's) is the order of the group:

$$\sum_{\Gamma} |\chi_{j1}|^2 = g$$

Since  $\chi_{j1}$  is the dimension  $n_j$  of irreducible representation  $\Gamma_j$ , the sum of the squared dimensions of the irreducible representations is the order of the group.

$$\sum_{\Gamma} |n_j|^2 = g$$

This permits us to decompose a reducible representation  $\Gamma$  into irreducible representations. Starting from:

$$\Gamma = \sum_i a_i \Gamma_i$$

and

$$\chi(\Gamma) = \sum_i a_i \chi(\Gamma_i)$$

The number of times  $a_i$  the representation  $\Gamma_i$  appears in the decomposition of  $\Gamma$  is:

$$a_i = 1/g \sum_{\mathbf{A}} \chi_{\Gamma(\mathbf{A})} \chi_{i(\mathbf{A})}^*$$

$$a_i = 1/g \sum_{C_A} N_A \chi_{\Gamma}(C_A) \chi_i^*(C_A)$$

The direct product of two representations is a representation which has for each class and each irreducible representation a character with value the product of the characters for this class and this irreducible representation. It is sometimes an irreducible representation but not always. The notation is:  $\Gamma = \Gamma_1 \otimes \Gamma_2$ . The multiplication table is a  $(n \times n)$  table with  $n$  rows and  $n$  columns. At the intersection of  $i$ th row and  $j$ th column is the product  $\Gamma_i \otimes \Gamma_j$  expressed as an expansion of irreducible representations. An example is sketched below (Table 1.10) in case of four irreducible representations.

It is important to note there are relationships between wave functions of the Schrödinger equation and irreducible representations.

One can demonstrate that the non-degenerate solutions of the Schrödinger equation are basis functions of unidimensional irreducible representations of the group that describe the system under examination.

A  $k$ -degenerate wave function generates a representation of dimension  $k$  which can be irreducible or reducible.

**Table 1.10** Multiplication table of the irreducible representations of group G

Multiplication table	$\Gamma_1$	$\Gamma_2$	$\Gamma_3$	$\Gamma_4$
$\Gamma_1$	$\Gamma_1$	$\Gamma_2$	$\Gamma_3$	$\Gamma_4$
$\Gamma_2$	$\Gamma_2$	$\Gamma_2 \otimes \Gamma_2$	$\Gamma_2 \otimes \Gamma_3$	$\Gamma_2 \otimes \Gamma_4$
$\Gamma_3$	$\Gamma_3$	$\Gamma_3 \otimes \Gamma_2$	$\Gamma_3 \otimes \Gamma_3$	$\Gamma_3 \otimes \Gamma_4$
$\Gamma_4$	$\Gamma_4$	$\Gamma_4 \otimes \Gamma_2$	$\Gamma_4 \otimes \Gamma_3$	$\Gamma_4 \otimes \Gamma_4$

Any wave function can be decomposed as a linear combination of irreducible representations of the group of the Schrödinger equation:

$$\Psi(\vec{r}) = \sum_P \sum_{n=1, n_p} \Psi_n^P(\vec{r})$$

where  $\Psi_n^P(\vec{r})$  is the  $n$ th basis function of state P of irreducible representation  $\Gamma_P$ , of degeneracy  $n_p$ . To go further, if the calculation of symetrized wave functions is necessary, one has to determine the matrix that represents the action of each symmetry operator in the basis set chosen to treat the problem one wants to solve. Then, one applies **projection operators** to the basis set in order to obtain a new basis which basis functions are those of the irreducible representations.

A projector is an operator which applied to an arbitrary function  $f$  transforms it specifically. To each irreducible representation  $\Gamma_\mu$  of dimension  $n_\mu$  can be associated a projector  $P^\mu$  which is built as an appropriate linear combination of the symmetry operations  $\mathbf{A}$ . Group theory permits to demonstrate that operator  $P^\mu$  is defined as a summation through all symmetry operations weighted by the character of the class this operation has in irreducible representation  $\Gamma_\mu$ :

$$P^\mu = \sum_{\mathbf{A}} \chi^\mu(\mathbf{A}) \mathbf{A}$$

Then:

$$P^\mu f_i^\nu = 0 \quad \text{when } \mu \neq \nu, \forall i, i = 1, \dots, n_\nu$$

and

$$P^\mu f_i^\mu = g/n_\mu f_i^\mu \quad \text{when } \mu = \nu.$$

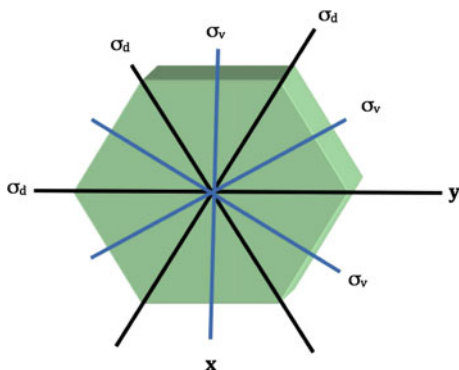
### 1.13.4 The Point Group $C_{6v}$

Each of the following are symmetry elements of group  $C_{6v}$  and constitute a class:

- The identity.
- Two six-fold symmetry axis parallel to the [001] direction: one corresponds to a rotation of  $2\pi/6$  and the second to a rotation of  $-2\pi/6$  (or  $10\pi/6$ ).



**Fig. 1.20** Geometrical representation of some of the reflection planes of  $C_{6v}$  relatively to the hexagon



- A rotation of  $2\pi/3$  around the  $[001]$  direction rotation of  $-2\pi/3$  (or  $4\pi/3$ ) around the  $[001]$  direction.
- A rotation of  $\pi$  around the  $[001]$  direction rotation.
- Three reflection planes making  $\pi/3$  with each other. These planes are generated by  $(\vec{y}, \vec{z})$  and are noted  $\sigma_d$ .
- Three reflection planes making  $\pi/3$  with each other, orthogonal to the precedent three. These planes are generated by  $(\vec{x}, \vec{z})$  and are noted  $\sigma_v$ . The geometrical representation of these reflection planes relatively to the hexagon is shown in Fig. 1.20.

### 1.13.5 Application of Group Theory to the Calculation of Integrals

Let integral:

$$\int \Psi_{\alpha}^* F_{\beta} \Psi_{\gamma} d\tau$$

where  $\Psi_{\alpha}$  and  $\Psi_{\gamma}$  are wave vectors corresponding to eigenvalues  $E_{\alpha}$  and  $E_{\gamma}$  of a quantum problem. The quantity  $F_{\beta}$  is an operator, the elementary volume of the integration space is  $d\tau$ .

Let us suppose that the relationship between the quantifies  $(\Psi_{\alpha}, \Psi_{\gamma}, F_{\beta})$  and irreducible representations  $(\Gamma_{\alpha}^*, \Gamma_{\gamma}, \Gamma_{\beta})$  has been established.

The product  $\Psi_{\alpha}^* F_{\beta} \Psi_{\gamma}$  transforms like  $\Gamma_{\alpha}^* \otimes \Gamma_{\gamma} \otimes \Gamma_{\beta}$

If, using an appropriate basis transformation, we are able to reduce the product representation into:

$$\Gamma_{\alpha}^* \otimes \Gamma_{\gamma} \otimes \Gamma_{\beta} = \Gamma_{\delta} \oplus \Gamma_{\mu} \oplus \Gamma_{\nu} \oplus \dots$$

Then, the product  $\Psi_\alpha^* F_\beta \Psi_\gamma = \varphi_\delta + \varphi_\mu + \varphi_\nu + \dots$  where  $\varphi_\delta$  is a function belonging to the functional space which basis generates irreducible representation  $\Gamma_\delta$ .

The use of projectors permits us to establish that, if  $\Gamma_\delta$  does not appear in the decomposition of  $\Gamma_\alpha^* \otimes \Gamma_\gamma \otimes \Gamma_\beta$ , there is no term  $\varphi_\delta$  in the above expansion. Then:

$$P^\delta \Gamma_\alpha^* \otimes \Gamma_\gamma \otimes \Gamma_\beta = 0$$

In particular, if  $\Gamma_\alpha^* \otimes \Gamma_\gamma \otimes \Gamma_\beta \notin \Gamma_1$  then  $\int \Psi_\alpha^* F_\beta \Psi_\gamma d\tau P^1 \Gamma_\alpha^* \otimes \Gamma_\gamma \otimes \Gamma_\beta = 0$  or

$$P^1 \Psi_\alpha^* \otimes \Psi_\gamma \otimes \Psi_\beta = 0$$

that may also be written after introducing the expression of  $P^1$ :

$$\sum_A \Psi_\alpha^* \otimes \Psi_\gamma \otimes F_\beta = 0$$

Conclusion:

$$\text{if } \Gamma_\alpha^* \otimes \Gamma_\gamma \otimes \Gamma_\beta \notin \Gamma_1 \text{ then } \int \Psi_\alpha^* F_\beta \Psi_\gamma d\tau = 0$$

This identity constitutes the conditions for matrix elements to vanish.

### 1.13.5.1 Selection Rules for Optical Transitions

Time-dependent perturbation theory and Fermi Golden rule permit to calculate the radiative recombination rate  $\omega$  for a transition between an initial level  $|i\rangle$  and a final level  $|f\rangle$  as proportional to the square of the matrix element between levels  $|i\rangle$  and  $|f\rangle$  under the action of operator  $H$ . This writes:

$$\omega \sim |\langle i|H|f\rangle|^2$$

In the frame-work of the dipolar interaction,  $H$  transforms like a vector of the three-dimensional space. It will transform like  $\Gamma_1$  or  $\Gamma_5$  depending on the photon polarization field, as indicated by the tables of  $C_{6v}$ . Then, straightforward application of multiplication table permits to calculate the selection rules between any initial level  $|i\rangle$  and any final level  $|f\rangle$  for both polarizations of the electric field of the photon.

### 1.13.6 Group Theory and Perturbations

We consider a crystal with initial Hamiltonian  $H_0$  under an external perturbation  $V$ .

$$H = H_0 + V.$$

The Hamiltonian  $H_0$  (resp. external perturbation  $V$ ) has symmetry  $G_0$  (resp.  $G_1$ ).  $G_1$  symmetry is in general lower than  $G_0$  one.

We will consider two possible situations here.

- *Case a:*  $G_0 = G_1$ , the perturbation does not change the symmetry of the crystal.

The eigen-values of the Schrödinger equations are already classified, according to the irreducible representations of  $G_0$ . The classification and degeneracies of energy levels in  $H$  are identical to those of  $H_0$ , the eigenvalues are shifted by  $V^\mu = \langle f^\mu | V f^\mu \rangle$ . The perturbation does not lead to a dissociation of the degenerated levels except in case of accidental degeneracy when the wave functions of the un-perturbed problem transform like a reducible representation of  $G_0$ .

We now consider two wave functions  $|i\rangle$  and  $|j\rangle$ , both transforming like an irreducible representation  $\Gamma_\mu$  of  $G_0$ . In addition, let:  $E_i = \langle f_i | H_0 | f_i \rangle$  and  $V_{ij} = \langle f_i | V | f_j \rangle$ .

$H_0$  and  $V$  transform like  $\Gamma_1$  of  $G_0$ . Then, matrix element  $\langle f_i | \Gamma_1 | f_j \rangle$  transforms like  $\Gamma_\mu \otimes \Gamma_\mu = \Gamma_1 \oplus \dots$ . Then, both  $E_i \neq 0$  and  $V_{ij} \neq 0$ .

#### 1.13.6.1 Levels of Identical Symmetry are Coupled by a Non-symmetry-Breaking Perturbation

Eigenstates are obtained as the solution of the  $(2 \times 2)$  Hamiltonian:

$$\begin{vmatrix} E_1 + V_{11} - E & V_{12} \\ V_{12}^* & E_2 + V_{22} - E \end{vmatrix}$$

when  $E_1 = E_2$ , the degeneracy is lifted except if, simultaneously,  $E_1 + E_2 + V_{11} + V_{22} = 0$  and  $V_{12} = 0$ , a possible but very restrictive situation.

If  $E_1 = E_2$  and wave functions  $(|i\rangle, |j\rangle)$  belong to different irreducible representations of  $G_0$ ,  $V_{12} = 0$ ; then, the degeneracy of the two levels is lifted via  $V_{11}$  and  $V_{22}$ .

- *Case b:*  $G_0 > G_1$ , the perturbation reduces the symmetry of the crystal.

In that case,  $G_1$  is a sub-group of  $G_0$ ; the eigen values of  $H$  have to be classified, according to the irreducible representations of  $G_1$ . Each irreducible representation  $\Gamma$  of  $G_0$  is a representation  $\gamma$  of  $G_1$ . That representation  $\gamma$  may be reducible or irreducible in  $G_1$ .

$$\Gamma = \sum_i a_i \gamma_i$$

Irreducible representation  $\Gamma$  of  $G_0$  must be equivalent to  $\gamma$  of  $G_1$  for all symmetry operations  $g$  belonging to both  $G_0$  and  $G_1$ . The characters of representations are in the following relationship:

$$\chi[\Gamma(g)] = \sum_i a_i \chi[\gamma_i(g)]$$

The relationships between the  $\Gamma$ s of  $G_0$  and the  $\gamma$ s of all possible  $G_1$ s are given in the compatibility table.

### 1.13.7 Angular Momenta and Group Theory: Simple and Double Groups

When an atom is located in the free space, the group of symetrie of the Schrödinger equation belongs to the group of rotations, and its wave functions are the spherical harmonics  $Y_{m_\ell}^\ell$ . The ensemble of the rotations in the three-dimensional space formq an infinite group, with an infinite number of classes (all the rotations of any angle around an axis of arbitrary orientation). A rotation of the function of an angle  $\alpha$  around  $z$ —equivalent to rotating the axes of  $-\alpha$  on the  $Y_{m_\ell}^\ell$ —writes:

$$\begin{pmatrix} e^{-i\ell\alpha} & 0 & & & & \\ 0 & e^{-i(\ell-1)\alpha} & 0 & & & \\ & 0 & \ddots & & & \\ & & & \ddots & 0 & \\ & & & & \ddots & 0 \\ & & & & 0 & e^{i(\ell-1)\alpha} & 0 \\ & & & & & 0 & e^{i\ell\alpha} \end{pmatrix}$$

The character is:

$$\chi^\ell(\alpha) = \frac{\sin[(\ell + \frac{1}{2})\alpha]}{\sin[\alpha/2]}$$

Angular momentum algebra indicates this equation holds for any value of the total angular momentum  $\vec{J} = \vec{L} + \vec{S}$ , where  $\vec{S}$  is the spin operator.

We remark that:

$$\begin{aligned} \chi^J(\alpha + 2\pi) &= \chi^J(\alpha)(-1)^{2J} \\ \chi^J(\alpha + 4\pi) &= \chi^J(\alpha) \end{aligned}$$

We remark that, if  $J$  is half-integer, we will have to consider for identity a rotation of  $4\pi$ . In this specific case, a supplementary operation occurs, as well as supplementary irreducible representations. These  $4\pi$  and  $2\pi$  symmetries double the number

of elements and add complementary irreducible representations. **The double group represents the symmetries of Fermions** ( $J$  is half-integer) while **the simple group represents the symmetries of Bosons** ( $J$  is integer).

For the simple group, we had the relation:  $\sum_{\Gamma} |n_j|^2 = g$ .

For the double group, we now have:  $\sum_{\Gamma} |n_j|^2 = 2g$ .

In the specific case of  $C_{6v}$ , we have a simple group twelve-fold with six classes and six irreducible representations:  $12 = 1 + 1 + 1 + 1 + 2^2 + 2^2$ .

The double group  $C_{6v}$  is twenty-four-fold with 9 classes and 9 irreducible representations:  $24 = 1 + 1 + 1 + 1 + 1 + 2^2 + 2^2 + 2^2 + 2^2 + 2^2$ .

**Note 1:** The symmetry operations are not always rotations. When the point group of the crystal contains a symmetry plane, or other symmetry operations like reverse rotations, we use the isomorphism between this point group and the holoaxial group of the same singony.

**Note 2:** Identical values of total angular momenta can be obtained in very different conditions. For example,  $J = 1$  is obtained either from a spherical harmonics  $Y_{m\ell}^{\ell}$  with  $\ell = 1$ , odd function in real space or by coupling two  $J = 1/2$  spins giving an even function in real space. It is, then, mandatory to take the partial parity of the wave function into account. The symmetry of an angular momentum with even spatial parity is noted  $D_J^+$  whilst the symmetry of an angular momentum with even spatial parity is noted  $D_J^-$  in the compatibility tables with the full rotation group.

### 1.13.8 Character Tables, Compatibility Table and Multiplication Tables

In this section, we give the tables required to handle group theory when dealing with  $C_{6v}$  and its subgroups. The notations are the following ones:

- $E$  represents the identity,
- $C_n$  represent rotations of  $2\pi/n$  around the six-fold axis,  $\sigma_v$  and  $\sigma_d$ ,
- Operations of the double group are over-lined.—Some wave functions of angular moment  $J = +3/2$  and  $+1/2$  are represented as  $|J, m_J\rangle$  in the columns of the wave functions.

**Character table and basis functions for  $C_{6v}$**

$C_{6v}$	$E$	$\bar{E}$	$(C_2, \bar{C}_2)$	$2C_3$	$2\bar{C}_3$	$2C_6$	$2\bar{C}_6$	$(3\sigma_d, 3\bar{\sigma}_d)$	$(3\sigma_v, 3\bar{\sigma}_v)$	basis functions
$\Gamma_1$	1	1	1	1	1	1	1	1	1	$z$
$\Gamma_2$	1	1	1	1	1	1	1	-1	-1	
$\Gamma_3$	1	1	-1	1	1	-1	-1	1	-1	$x^3 - 3xy^2$
$\Gamma_4$	1	1	-1	1	1	-1	-1	-1	1	$y^3 - 3yx^2$
$\Gamma_5$	2	2	-2	-1	-1	1	1	0	0	$(x, y)$
$\Gamma_6$	2	2	2	-1	-1	-1	-1	0	0	$\Gamma_3 \otimes \Gamma_5$
$\Gamma_7$	2	-2	0	1	-1	$\sqrt{3}$	$-\sqrt{3}$	0	0	$ 1/2, \pm 1/2\rangle$
$\Gamma_8$	2	-2	0	1	-1	$-\sqrt{3}$	$\sqrt{3}$	0	0	$\Gamma_3 \otimes \Gamma_7$
$\Gamma_9$	2	-2	0	-2	2	0	0	0	0	$ 3/2, \pm 3/2\rangle$

### Multiplication table for $C_{6v}$

	$\Gamma_1$	$\Gamma_2$	$\Gamma_3$	$\Gamma_4$	$\Gamma_5$	$\Gamma_6$	$\Gamma_7$	$\Gamma_8$	$\Gamma_9$
$\Gamma_1$	$\Gamma_1$	$\Gamma_2$	$\Gamma_3$	$\Gamma_4$	$\Gamma_5$	$\Gamma_6$	$\Gamma_7$	$\Gamma_8$	$\Gamma_9$
$\Gamma_2$		$\Gamma_1$	$\Gamma_4$	$\Gamma_3$	$\Gamma_5$	$\Gamma_6$	$\Gamma_7$	$\Gamma_8$	$\Gamma_9$
$\Gamma_3$			$\Gamma_1$	$\Gamma_2$	$\Gamma_6$	$\Gamma_5$	$\Gamma_8$	$\Gamma_7$	$\Gamma_9$
$\Gamma_4$				$\Gamma_1$	$\Gamma_6$	$\Gamma_5$	$\Gamma_8$	$\Gamma_7$	$\Gamma_9$
$\Gamma_5$					$\Gamma_1 + \Gamma_2 + \Gamma_6$	$\Gamma_3 + \Gamma_4 + \Gamma_5$	$\Gamma_7 + \Gamma_9$	$\Gamma_8 + \Gamma_9$	$\Gamma_7 + \Gamma_8$
$\Gamma_6$						$\Gamma_1 + \Gamma_2 + \Gamma_6$	$\Gamma_8 + \Gamma_9$	$\Gamma_7 + \Gamma_8$	$\Gamma_7 + \Gamma_8$
$\Gamma_7$							$\Gamma_1 + \Gamma_2 + \Gamma_5$	$\Gamma_3 + \Gamma_4 + \Gamma_6$	$\Gamma_5 + \Gamma_6$
$\Gamma_8$								$\Gamma_1 + \Gamma_2 + \Gamma_5$	$\Gamma_5 + \Gamma_6$
$\Gamma_9$									$\Gamma_1 + \Gamma_2 + \Gamma_3 + \Gamma_4$

### Full rotation compatibility table for $C_{6v}$

$D_0^+$	$\Gamma_1$	$D_0^-$	$\Gamma_2$
$D_1^+$	$\Gamma_2 + \Gamma_5$	$D_1^-$	$\Gamma_1 + \Gamma_5$
$D_2^+$	$\Gamma_1 + \Gamma_5 + \Gamma_6$	$D_2^-$	$\Gamma_2 + \Gamma_5 + \Gamma_6$
$D_3^+$	$\Gamma_2 + \Gamma_3 + \Gamma_4 + \Gamma_5 + \Gamma_6$	$D_3^-$	$\Gamma_1 + \Gamma_3 + \Gamma_4 + \Gamma_5 + \Gamma_6$
$D_{1/2}^+$	$\Gamma_7$	$D_{1/2}^-$	$\Gamma_7$
$D_{3/2}^+$	$\Gamma_7 + \Gamma_9$	$D_{3/2}^-$	$\Gamma_7 + \Gamma_9$
$D_{5/2}^+$	$\Gamma_7 + \Gamma_8 + \Gamma_9$	$D_{5/2}^-$	$\Gamma_7 + \Gamma_8 + \Gamma_9$

### Compatibility table for $C_{6v}$ and some of its subgroups

$C_{6v}$	$\Gamma_1$	$\Gamma_2$	$\Gamma_3$	$\Gamma_4$	$\Gamma_5$	$\Gamma_6$	$\Gamma_7$	$\Gamma_8$	$\Gamma_9$
$C_{2v}$	$\Gamma_1$	$\Gamma_3$	$\Gamma_2$	$\Gamma_4$	$\Gamma_2 + \Gamma_4$	$\Gamma_1 + \Gamma_3$	$\Gamma_5$	$\Gamma_5$	$\Gamma_5$
$C_s(E = x)$	$\Gamma_1$	$\Gamma_2$	$\Gamma_1$	$\Gamma_2$	$\Gamma_1 + \Gamma_2$	$\Gamma_1 + \Gamma_2$	$\Gamma_3 + \Gamma_4$	$\Gamma_3 + \Gamma_4$	$\Gamma_3 + \Gamma_4$
$C_s(E = y)$	$\Gamma_1$	$\Gamma_2$	$\Gamma_2$	$\Gamma_1$	$\Gamma_1 + \Gamma_2$	$\Gamma_1 + \Gamma_2$	$\Gamma_3 + \Gamma_4$	$\Gamma_3 + \Gamma_4$	$\Gamma_3 + \Gamma_4$

### 1.13.9 The Translation Group

The properties of crystals are unchanged under translations  $\vec{\tau}_n = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$  where the  $n_i$ 's are integers and the  $\vec{a}_i$ 's are the primitive translation vectors. This may be written as  $\{E|\vec{\tau}_n\}$  using the symbol of Seitz.

Obviously, from the definition above,  $\{E|\vec{\tau}_n + \vec{\tau}_{n'}\} = \{E|\vec{\tau}_{n+n'}\}$  and as  $(\mathbb{Z}, +)$  form an Abelian group, the ensemble of translations  $\{E|\vec{\tau}_n\}$  constitutes an Abelian finite translation group with  $N_1N_2N_3$  elements.

The cyclic boundary conditions for crystals of finite dimensions  $N_1\vec{a}_1$ ,  $N_2\vec{a}_2$  and  $N_3\vec{a}_3$  write

$$\{E|\vec{\tau}_{N_1,0,0}\} = \{E|\vec{\tau}_{0,N_2,0}\} = \{E|\vec{\tau}_{0,0,N_3}\} = \{E|\vec{0}\}$$

Further defining a vector of the reciprocal lattice  $N_{hkl}^* = h\vec{a}_1^* + k\vec{a}_2^* + l\vec{a}_3^*$ , and using cyclic boundary conditions leads to:

$$\vec{k} = (h/N_1)\vec{a}_1^* + (k/N_2)\vec{a}_2^* + (l/N_3)\vec{a}_3^*$$

$$\{E|\vec{\tau}_n\} \text{ may be represented by } e^{-i\vec{k} \cdot \vec{\tau}_n}.$$

### 1.13.10 The Space Group

Let  $\vec{t}_1, \vec{t}_2, \dots, \vec{t}_j$  be the positions of identical atoms in the unit cell.

For the wurtzite  $C_{6v}$  structure,  $\vec{t}_1 = \vec{0}$ , and  $\vec{t}_2 = 2/3\vec{a}_1 + 1/3\vec{a}_2 + \vec{c}/2$  for the anions; and  $\vec{t}_3 = 3/8\vec{c}$  and  $\vec{t}_4 = 2/3\vec{a}_1 + 1/3\vec{a}_2 + 7/8\vec{c}$  for the cations.

The elements of the space group write  $\{\mathbf{A}|\vec{\alpha}\}$  where  $\mathbf{A}$  is a symmetry operator of the point group and  $\vec{\alpha} = \vec{\tau}_n + \vec{t}$ . In this notation,  $\vec{t}$  is a fractional translation operator. Let

$$\{\mathbf{A}|\vec{\alpha}\} \cdot t_j = \vec{\tau}_{n'} + \vec{t}_{j'}$$

where  $\vec{t}_{j'}$  represents the position of an atom in the unit cell— $\vec{t}_{j'}$  may coincide with  $\vec{t}_j$ —and  $\vec{\tau}_{n'}$  is a suitable translation vector. Since  $\{\mathbf{A}|\vec{\alpha}\}$  is a symmetry operation of the crystal,  $\vec{t}_{j'}$  and  $\vec{t}_j$  correspond to similar atoms.

In summary, operator  $\{\mathbf{A}|\vec{\alpha}\}$  contains the operators of the point group  $A$ , and accounts for the translational symmetry at the scale of the crystal via  $\vec{\alpha}$ . The translational symmetry operator  $\vec{\alpha}$  has two contributions: an intra-elementary cell contribution— $\vec{t}$ —and an inter-elementary cell— $\vec{\tau}$ .

It can be easily verified that

$$\{\mathbf{A}|\vec{\alpha}\} \cdot \{\mathbf{B}|\vec{\beta}\} = \{\mathbf{AB}|S\vec{\beta} + \vec{\alpha}\}$$

and that:

$$\{\mathbf{A}|\vec{\alpha}\}^{-1} = \{\mathbf{A}^{-1} | -\mathbf{A}^{-1}\vec{\alpha}\}.$$

### 1.13.10.1 The Ensemble of Operators $\{A|\bar{\alpha}\}$ Constitutes the Space Group of the Crystal

The wurtzite space group is identified as  $P6_3mc$  or  $C_{6v}^4$  in the international tables.

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