layers in the slab can be written as $A\beta\beta A$ or $A\gamma\gamma A$. There are thus six possible sequences for the unit slab. These unit slabs can be stacked in the manner described for equal spheres. Thus, for example, the 2*H* structure can have three different layer stackings: $/A\beta\beta A\,B\gamma\gamma B/\ldots$, $/A\beta\beta A\,B\alpha\alpha B/\ldots$ and $/A\beta\beta A\,C\beta\beta C/$. Periodicities containing up to 21 unit slabs have been reported for GaSe (see Terhell, 1983). The bonding between the layers of a slab is predominantly covalent while that between two adjacent slabs is of the van der Waals type, which imparts cleavage characteristics to this material.

9.2.1.3. *Symmetry of close-packed layer stackings of equal spheres*

It can be seen from Fig. 9.2.1.2(*a*) that a stacking of two or more layers in the close-packed manner still possesses all three symmetry planes but the twofold axes disappear while the sixfold axes coincide with the threefold axes (Verma & Krishna, 1966). The lowest symmetry of a completely arbitrary periodic stacking sequence of close-packed layers is shown in Fig. 9.2.1.2(*b*). Structures resulting from such stackings therefore belong to the trigonal system. Even though a pure sixfold axis of rotation is not possible, close-packed structures belonging to the hexagonal system can result by virtue of at least one of the three symmetry axes parallel to [00.1] being a 6_3 axis (Verma & Krishna, 1966). This is possible if the layers in the unit cell are stacked in special ways. For example, a 6*H* stacking sequence $/ABCACB/\ldots$ has a 6_3 axis through 0, 0. It follows that, for an *nH* structure belonging to the hexagonal system, *n* must be even. A packing *nH*/*nR* with *n* odd will therefore necessarily belong to the trigonal system and can have either a hexagonal or a rhombohedral lattice (Verma & Krishna, 1966).

Other symmetries that can arise by restricting the arbitrariness of the stacking sequence in the identity period are: (i) a centre of symmetry at the centre of either the spheres or the octahedral voids; and (ii) a mirror plane perpendicular to [00.1]. Since there must be two centres of symmetry in the unit cell, the centrosymmetric arrangements may possess both centres either at sphere centres/octahedral void centres or one centre each at the centres of spheres and octahedral voids (Patterson & Kasper, 1959).

9.2.1.4. *Possible lattice types*

Close packings of equal spheres can belong to the trigonal, hexagonal, or cubic crystal systems. Structures belonging to the hexagonal system necessarily have a hexagonal lattice, *i.e.* a lattice in which we can choose a primitive unit cell with $a = b \neq c$, $\alpha = \beta = 90^\circ$, and $\gamma = 120^\circ$. In the primitive unit cell of the hexagonal close-packed structure $/AB/\ldots$ shown in Fig. 9.2.1.6, there are two spheres associated with each lattice point, one at 0, 0, 0 and the other at $\frac{1}{3}, \frac{2}{3}, \frac{1}{2}$. Structures belonging to the trigonal system can have either a hexagonal or a rhombohedral lattice. By a rhombohedral lattice is meant a lattice in which we can choose a primitive unit cell with $a = b = c$, $\alpha = \beta = \gamma \neq 90^\circ$. Both types of lattice can be referred to either hexagonal or rhombohedral axes, the unit cell being non-primitive when a hexagonal lattice is referred to rhombohedral axes and *vice versa* (Buerger, 1953). In close-packed structures, it is generally convenient to refer both hexagonal and rhombohedral lattices to hexagonal axes. Fig. 9.2.1.7 shows a rhombohedral lattice in which the primitive cell is defined by the rhombohedral axes a_1, a_2, a_3; but a non-primitive hexagonal unit cell can be chosen by adopting the axes A_1, A_2, C. The latter has lattice points at $0, 0, 0$; $\frac{2}{3}, \frac{1}{3}, \frac{1}{3}$; and $\frac{1}{3}, \frac{2}{3}, \frac{2}{3}$. If this rhombohedral lattice is rotated through 60° around [00.1], the hexagonal unit cell will then be centred at $\frac{1}{3}, \frac{2}{3}, \frac{1}{3}$ and $\frac{2}{3}, \frac{1}{3}, \frac{2}{3}$. These two settings are crystallographically equivalent for close packing of equal spheres. They represent twin arrangements when both occur in the same crystal. The hexagonal unit cell of an *nR* structure is made up of three elementary stacking sequences of $n/3$ layers that are related to each other either by an anticyclic shift of layers $A \rightarrow C \rightarrow B \rightarrow A$ (obverse setting) or by a cyclic shift of layers $A \rightarrow B \rightarrow C \rightarrow A$ (reverse setting) in the direction of z increasing (Verma & Krishna, 1966). Evidently, *n* must be a multiple of 3 for *nR* structures.

In the special case of the close packing $/ABC/\ldots$ [with the ideal axial ratio of $\sqrt{(2/3)}$], the primitive rhombohedral unit cell has $\alpha = \beta = \gamma = 60^\circ$, which enhances the symmetry and enables the choice of a face-centred cubic unit cell. The relationship between the face-centred cubic and the rhombohedral unit cell is shown in Fig. 9.2.1.8. The threefold axis of the rhombohedral unit cell coincides with one of the ⟨111⟩ directions of the cubic unit cell. The close-packed layers are thus parallel to the {111} planes in the cubic close packing.

9.2.1.5. *Possible space groups*

It was shown by Belov (1947) that consistent combinations of the possible symmetry elements in close packing of equal spheres can give rise to eight possible space groups: $P3m1$, $P\bar{3}m1$,

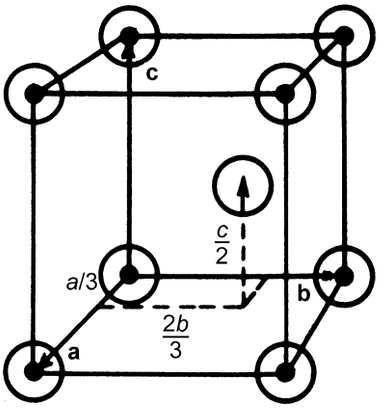

Fig. 9.2.1.6. The primitive unit cell of the 2*H* close packing.

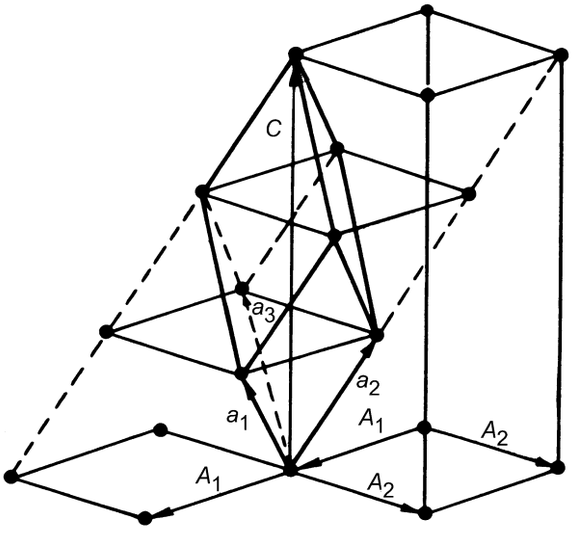

Fig. 9.2.1.7. A rhombohedral lattice (a_1, a_2, a_3) referred to hexagonal axes (A_1, A_2, C) (after Buerger, 1953).

$P\bar{6}m2$, $P6_3mc$, $P6_3/mmc$, $R3m$, $R\bar{3}m$, and $Fm3m$. The last space group corresponds to the special case of cubic close packing $/ABC/\ldots$. The tetrahedral arrangement of Si and C in SiC does not permit either a centre of symmetry ($\bar{1}$) or a plane of symmetry (m) perpendicular to [00.1]. SiC structures can therefore have only four possible space groups $P3m1$, $R3m1$, $P6_3mc$, and $F\bar{4}3m$. CdI_2 structures can have a centre of symmetry on octahedral voids, but cannot have a symmetry plane perpendicular to [00.1]. CdI_2 can therefore have five possible space groups: $P3m1$, $P\bar{3}m$, $R3m$, $R\bar{3}m$, and $P6_3mc$. Cubic symmetry is not possible in CdI_2 on account of the presence of Cd atoms, the sequence $/A\gamma BC\beta AB\alpha C/$ representing a 6R structure.

9.2.1.6. *Crystallographic uses of Zhdanov symbols*

From the Zhdanov symbols of a close-packed structure, it is possible to derive information about the symmetry and lattice type (Verma & Krishna, 1966). Let n_+ and n_- be the number of positive and negative numerals in the Zhdanov sequence of a given structure. The lattice is rhombohedral if $n_+ - n_- = \pm 1 \bmod 3$, otherwise it is hexagonal. The + sign corresponds to the reverse setting and − to the obverse setting of the rhombohedral lattice. Since this criterion is sufficient for the identification of a rhombohedral structure, the practice of writing three units of identical Zhdanov symbols has been abandoned in recent years (Pandey & Krishna, 1982*a*). Thus the 15R polytype of SiC is written as (23) rather than $(23)_3$.

As described in detail by Verma & Krishna (1966), if the Zhdanov symbol consists of an odd set of numbers repeated twice, *e.g.* (22), (33), (221221) *etc.*, the structure can be shown to possess a 6_3 axis. For the centre of symmetry at the centre of a sphere or an octahedral void, the Zhdanov symbol will consist of a symmetrical arrangement of numbers of like signs surrounding a single even or odd Zhdanov number, respectively. Thus, the structures (2)32(4)23 and (3)32(5)23 have centres of symmetry of the two types in the numbers within parentheses. For structures with a symmetry plane perpendicular to [00.1], the Zhdanov symbols consist of a symmetrical arrangement of a set of numbers of opposite signs about the space between two succession numbers. Thus, a stacking |522|225| has mirror planes at positions indicated by the vertical lines.

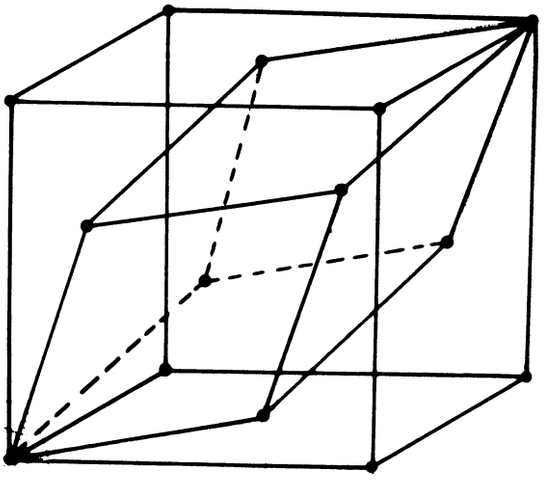

Fig. 9.2.1.8. The relationship between the f.c.c. and the primitive rhombohedral unit cell of the c.c.p. structure.

The use of abridged symbols to describe crystal structures has sometimes led to confusion in deciding the crystallographic equivalence of two polytype structures. For example, the structures (13) and (31) are identical for SiC but not for CdI_2 (Jain & Trigunayat, 1977*a*,*b*).

9.2.1.7. *Structure determination of close-packed layer stackings*

9.2.1.7.1. *General considerations*

The different layer stackings (polytypes) of the same material have identical a and b parameters of the direct lattice. The a^*b^* reciprocal-lattice net is therefore also the same and is shown in Fig. 9.2.1.9. The reciprocal lattices of these polytypes differ only along the c^* axis, which is perpendicular to the layers. It is evident from Fig. 9.2.1.9 that for each reciprocal-lattice row parallel to $\mathbf{c}^*$ there are five others with the same value of the radial coordinate ξ. For example, the rows 10.l, 01.l, $\bar{1}1.l$, $\bar{1}0.l$, $0\bar{1}.l$, and $1\bar{1}.l$ all have $\xi = |\mathbf{a}^*|$. Owing to symmetry considerations, it is sufficient to record any one of them on X-ray diffraction photographs. The reciprocal-lattice rows $hk.l$ can be classified into two categories according as $h - k = 0 \bmod 3$ or $\pm 1 \bmod 3$. Since the atoms in an nH or nR structure lie on three symmetry axes $A : [00.1]_{00}$, $B : [00.1]_{\frac{1}{3},-\frac{1}{3}}$, and $C : [00.1]_{-\frac{1}{3},\frac{1}{3}}$, the structure factor F_{hkl} can be split into three parts:

$$F_{hkl} = P + Q\exp[2\pi i(h-k)/3] + R\exp[-2\pi i(h-k)/3],$$

where $P = \sum_{z_A} \exp(2\pi i l z_A/n)$, $Q = \sum_{z_B} \exp(2\pi i l z_B/n)$, $R = \sum_{z_C} \exp(2\pi i l z_C/n)$, and z_A/n, z_B/n, z_C/n are the z coordinates of atoms at A, B, and C sites, respectively. For $h - k = 0 \bmod 3$,

$$F_{hkl} = P + Q + R = \sum_{z=0}^{n=-1} \exp(2\pi i l z/n),$$

which is zero except when $l = 0, n, 2n, \ldots$. Hence, the reflections 00.l, 11.l, 30.l, *etc.*, for which $h - k = 0 \bmod 3$, will be extinguished except when $l = 0, n, 2n, \ldots$. Thus, only those $hk.l$ reciprocal-lattice rows for which $h - k \neq 0 \bmod 3$ carry information about the stacking sequence and contain in general reflections with $l = 0, 1, 2, \ldots, n-1$, *etc.* It is sufficient to record any one such row, usually the 10.l row with $\xi = |\mathbf{a}^*|$, on an oscillation, Weissenberg, or precession photograph to obtain information about the lattice type, identity period, space group, and hence the complete structure (Verma & Krishna, 1966).

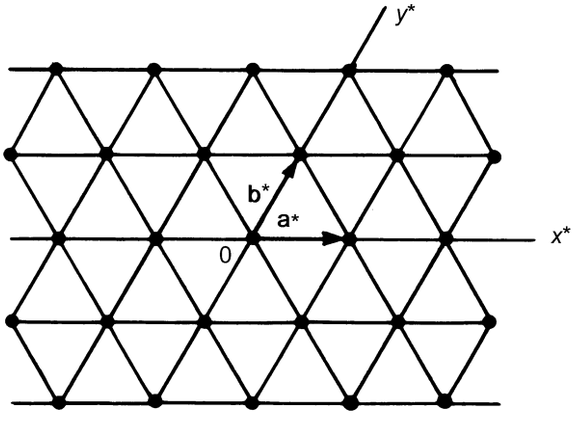

Fig. 9.2.1.9. The $\mathbf{a}^*$–$\mathbf{b}^*$ reciprocal-lattice net for close-packed layer stackings.

references