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Table 9.2.1.2. *List of SiC polytypes with known structures in order of increasing periodicity (after Pandey & Krishna, 1982a)*

Polytype	Structure (Zhdanov sequence)	Polytype	Structure (Zhdanov sequence)
$2H$	11	$57H$	$(23)_9 3333$
$3C$	∞	$57R$	$(33)_2 34$
$4H$	22	$69R_1$	$(33)_3 32$
$6H$	33	$69R_2$	33322334
$8H$	44	$75R_2$	$(32)_3(23)_2$
$10H$	3322	$81H$	$(33)_5 35(33)_6 34$
$14H$	$(22)_2 33$	$84R$	$(33)_3(32)_2$
$15R$	23	$87R$	$(33)_4 32$
$16H_1$	$(33)_2 22$	$90R$	$(23)_4 3322$
$18H$	$(22)_3 33$	$93R$	$(33)_4 34$
$19H$	$(23)_3 22$	$96R_1$	$(33)_3 3434$
$20H$	$(22)_3 44$	$99R$	$(33)_4 3222$
$21H$	333534	$105R$	$(33)_5 32$
$21H_2$	$(33)_2 63$	$111R$	$(33)_5 34$
$21R$	34	$120R$	$(22)_5 23222333$
$24R$	35	$123R$	$(33)_6 32$
$27H$	$(33)_2(23)_3$	$126R$	$(33)_2 2353433223$
$27R$	2223	$129R$	$(33)_6 34$
$33R$	3332	$125R$	$32(33)_2 23(33)_3 23$
$33H$	$(33)_2 353334$	$141R$	$(33)_7 32$
$34H$	$(33)_4 2332$	$147R$	$(3332)_4 32$
$36H_1$	$(33)_2 32(33)_2 34$	$150R_1$	$(23)_3 32(23)_3 322332$
$36H_2$	$(33)_4 3234$	$150R_2$	$(23)_2(3223)_4$
$39H$	$(33)_2 32(33)_3(32)_2$	$159R$	$(33)_8 32$
$39R$	3334	$168R$	$(23)_{10} 33$
$40H$	$(33)_5 2332$	$174R$	$(33)_6 6(33)_5 4$
$45R$	$(23)_2 32$	$189R$	$(34)_8 43$
$51R_1$	$(33)_2 32$	$267R$	$(23)_{17} 22$
$51R_2$	$(22)_3 23$	$273R$	$(23)_{17} 33$
$54H$	$(33)_6 323334$	$393R$	$(33)_{21} 32$

A large number of crystallographically different modifications of SiC, called polytypes, has been discovered in commercial crystals grown above 2273 K (Verma & Krishna, 1966; Pandey & Krishna, 1982*a*). Table 9.2.1.2 lists those polytypes whose structures have been worked out. All these polytypes have $a = b = 3.078$ Å and $c = n \times 2.518$ Å, where n is the number of Si–C double layers in the hexagonal cell. The $3C$ and $2H$ modifications, which normally result below 2273 K, are known to undergo solid-state structural transformation to $6H$ (Jagodzinski, 1972; Krishna & Marshall, 1971*a*,*b*) through a non-random insertion of stacking faults (Pandey, Lele & Krishna, 1980*a*,*b*,*c*; Kabra, Pandey & Lele, 1986). The lattice parameters and the average thickness of the Si–C double layers vary slightly with the structure, as is evident from the h/a ratios of 0.8205 (Adamsky & Merz, 1959), 0.8179, and 0.8165 (Taylor & Jones, 1960) for the $2H$, $6H$, and $3C$ structures, respectively. Even in the same structure, crystal-structure refinement has revealed variation in the thickness of Si–C double layers depending on their environment (de Mesquita, 1967).

The structure of ZnS is analogous to that of SiC. Like the latter, ZnS crystals grown from the vapour phase also display a large variety of polytype structures (Steinberger, 1983). ZnS crystals that occur as minerals usually correspond to the wurtzite ($/AB/\ldots$) and the sphalerite ($/ABC/\ldots$) modifications. The structural transformation between the $2H$ and $3C$ structures of ZnS is known to be martensitic in nature (Sebastian, Pandey & Krishna, 1982; Pandey & Lele, 1986*b*). The h/a ratio for ZnS-$2H$ is 0.818, which is somewhat different from the ideal value (Verma & Krishna, 1966). The structure of the stackings in polytypic AgI is analogous to those in SiC and ZnS (Prager, 1983).

9.2.1.2.3. *Structure of CdI_2*

The structure of cadmium iodide consists of a close packing of the I ions with the Cd ions distributed amongst half the octahedral voids. Thus, the Cd and I layers are not stacked alternately; there is one Cd layer after every two I layers as shown in Fig. 9.2.1.5. The structure actually consists of molecular sheets (called minimal sandwiches) with a layer of Cd ions sandwiched between two close-packed layers of I ions. The bonding within the minimal sandwich is ionic in character and is much stronger than the bonding between successive sandwiches, which is of van der Waals type. The importance of polarization energy for the stability of such structures has recently been emphasized by Bertaut (1978). It is because of the weak van der Waals bonding between the successive minimal sandwiches that the material possesses the easy cleavage characteristic of a layer structure. In describing the layer stackings in the CdI_2 structure, it is customary to use Roman letters to denote the I positions and Greek letters for the Cd positions. The two most common modifications of CdI_2 are $4H$ and $2H$ with layer stackings $A\gamma B C\alpha B\ldots$ and $A\gamma B A\gamma B$, respectively. In addition, this material also displays a number of polytype modifications of large repeat periods (Trigunayat & Verma, 1976; Pandey & Krishna, 1982*a*). From the structure of CdI_2, it follows that the identity period of all such modifications must consist of an even number of I layers. The h/a ratio in all these modifications of CdI_2 is 0.805, which is very different from the ideal value (Verma & Krishna, 1966). The structure of PbI_2, which also displays a large number of polytypes, is analogous to CdI_2 with one important difference. Here, the distances between two I layers with and without an intervening Pb layer are quite different (Trigunayat & Verma, 1976).

9.2.1.2.4. *Structure of GaSe*

The crystal structure of GaSe consists of four-layered slabs, each of which contains two close-packed layers of Ga (denoted by symbols A, B, C) and Se (denoted by symbols α, β, γ) each in the sequence Se–Ga–Ga–Se (Terhell, 1983). The Se atoms sit on the corners of a trigonal prism while each Ga atom is tetrahedrally coordinated by three Se and one Ga atoms. If the Se layers are of A type, then the stacking sequence of the four

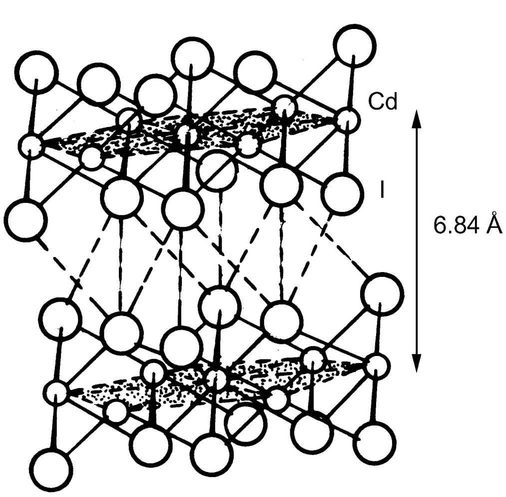

Fig. 9.2.1.5. The layer structure of CdI_2: small circles represent Cd ions and larger ones I ions (after Wells, 1945).

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 $2H$ 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 $6H$ 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 $A \to C \to B \to A$ (obverse setting) or by a cyclic shift of layers $A \to B \to C \to A$ (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 $\langle 111 \rangle$ 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: $P3m1$, $P\bar{3}m1$,

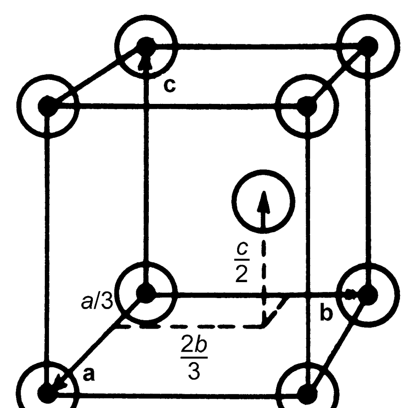

Fig. 9.2.1.6. The primitive unit cell of the $2H$ close packing.

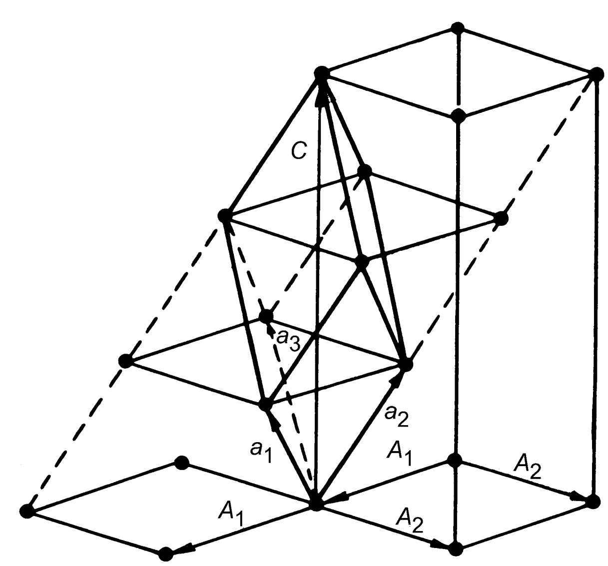

Fig. 9.2.1.7. A rhombohedral lattice (a_1, a_2, a_3) referred to hexagonal axes (A_1, A_2, C) (after Buerger, 1953).

references