

9.2. LAYER STACKING

Table 9.2.1.1. Common close-packed metallic structures

Stacking sequence	Identity period	Ramsdell notation	Zhdanov notation	Jagodzinski notation	Prototype
$AB, A \dots$	2	$2H$	11	h	Mg
$ABC, A \dots$	3	$3C$	∞	c	Cu
$ABCB, A \dots$	4	$4H$	22	hc	La
$ABCBCACAB, A \dots$	9	$9R$	21	hhc	Sm

cyclic ($A \rightarrow B \rightarrow C \rightarrow A$) or anticyclic ($A \rightarrow C \rightarrow B \rightarrow A$) shift of layers in the same plane. The vector s can be either $(1/3)[1\bar{1}00]$, $(1/3)[01\bar{1}0]$, or $(1/3)[\bar{1}010]$. Zhdanov (1945) suggested summing the number of consecutive offsets of each kind and designating them by numeral figures. Successive numbers in the Zhdanov symbol have opposite signs. The rhombohedral stackings have three identical sets of Zhdanov symbols in an identity period. It is usually sufficient to write only one set.

Yet another notation advanced, amongst others, by Jagodzinski (1949a) makes use of configurational symbols for each layer. A layer is designated by the symbol h or c according as its neighbouring layers are alike or different. Letter ' k ' in place of ' c ' is also used in the literature.

Some of the common close-packed structures observed in metals are listed in Table 9.2.1.1 in terms of all the notations.

9.2.1.2. Structure of compounds based on close-packed layer stackings

Frequently, the positions of one kind of atom or ion in inorganic compounds, such as SiC, ZnS, CdI₂, and GaSe, correspond approximately to those of equal spheres in a close packing, with the other atoms being distributed in the voids. All such structures will also be referred to as close-packed structures though they may not be ideally close packed. In the close-packed compounds, the size and coordination number of the smaller atom/ion may require that its close-packed neighbours in the neighbouring layers do not touch each other.

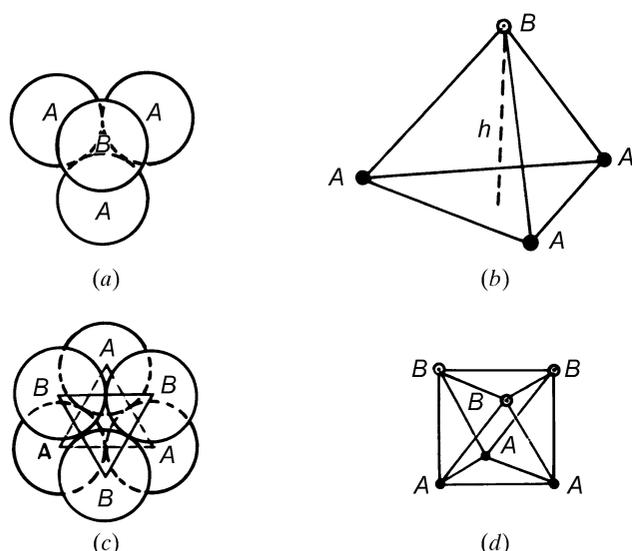


Fig. 9.2.1.3. Voids in a close packing: (a) tetrahedral void; (b) tetrahedron formed by the centres of spheres; (c) octahedral void; (d) octahedron formed by the centres of spheres.

9.2.1.2.1. Voids in close packing

Three-dimensional close packings of spheres have two kinds of voids (Azaroff, 1960):

(i) If the triangular interstices in a close-packed layer have spheres directly over them, the resulting voids are called tetrahedral voids because the four spheres surrounding the void are arranged at the corners of a regular tetrahedron (Figs. 9.2.1.3a,b). If R denotes the radius of the four spheres surrounding a tetrahedral void, the radius of the sphere that would just fit into this void is given by $0.225R$ (Verma & Krishna, 1966). The centre of the tetrahedral void is located at a distance $3h/4$ from the centre of the sphere on top of it.

(ii) If the triangular interstices pointing up in one close-packed layer are covered by triangular interstices pointing down in the adjacent layer, the resulting voids are called octahedral voids (Figs. 9.2.1.3c,d) since the six spheres surrounding each such void lie at the corners of a regular octahedron. The radius of the sphere that would just fit into an octahedral void is given by $0.414R$ (Verma & Krishna, 1966). The centre of this void is located half way between the two layers of spheres.

While there are twice as many tetrahedral voids as the spheres in close packing, the number of octahedral voids is equal to the number of spheres (Krishna & Pandey, 1981).

9.2.1.2.2. Structures of SiC and ZnS

SiC has a binary tetrahedral structure in which Si and C layers are stacked alternately, each carbon layer occupying half the tetrahedral voids between successive close-packed silicon layers. One can regard the structure as consisting of two identical interpenetrating close packings, one of Si and the other of C, with the latter displaced relative to the former along the stacking axis through one fourth of the layer spacing. Since the positions of C atoms are fixed relative to the positions of layers of Si atoms, it is customary to use the letters A , B , and C as representing Si–C double layers in the close packing. To be more exact, the three kinds of layers need to be written as $A\alpha$, $B\beta$, and $C\gamma$ where Roman and Greek letters denote the positions of Si and C atoms, respectively. Fig. 9.2.1.4 depicts the structure of SiC-6H, which is the most common modification.

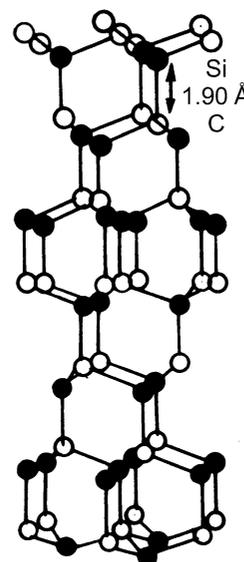


Fig. 9.2.1.4. Tetrahedral arrangement of Si and C atoms in the SiC-6H structure.

9. BASIC STRUCTURAL FEATURES

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) ₃ 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) ₃ 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, 1982a). Table 9.2.1.2 lists those polytypes whose structures have been worked out. All these polytypes have $a = b = 3.078 \text{ \AA}$ and $c = n \times 2.518 \text{ \AA}$, 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, 1971a,b) through a non-random insertion of stacking faults (Pandey, Lele & Krishna, 1980a,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 ($/AB/...$) and the sphalerite ($/ABC/...$) 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, 1986b). 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 CdI₂

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 CdI₂ 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 CdI₂ are 4H and 2H with layer stackings $A\gamma B C\alpha B...$ 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, 1982a). From the structure of CdI₂, 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 CdI₂ is 0.805, which is very different from the ideal value (Verma & Krishna, 1966). The structure of PbI₂, which also displays a large number of polytypes, is analogous to CdI₂ 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

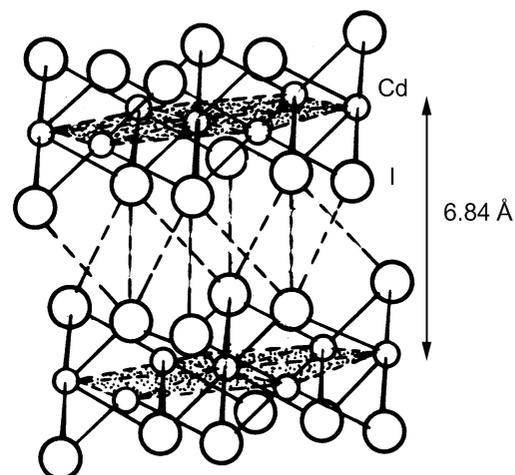


Fig. 9.2.1.5. The layer structure of CdI₂: small circles represent Cd ions and larger ones I ions (after Wells, 1945).