9.2. Layer stacking

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9.2.1. Layer stacking in close-packed structures (By D. Pandey and P. Krishna)

The crystal structures of a large number of materials can be described in terms of stacking of layers of atoms. This chapter provides a brief account of layer stacking in materials with structures based on the geometrical principle of close packing of equal spheres.

9.2.1.1. *Close packing of equal spheres*

9.2.1.1.1. *Close-packed layer*

In a close-packed layer of spheres, each sphere is in contact with six other spheres as shown in Fig. 9.2.1.1. This is the highest number of nearest neighbours for a layer of identical spheres and therefore yields the highest packing density. A single close-packed layer of spheres has two-, three- and sixfold axes of rotation normal to its plane. This is depicted in Fig. 9.2.1.2(*a*), where the size of the spheres is reduced for clarity. There are three symmetry planes with indices $(1\bar{2}.0)$, $(\bar{2}1.0)$, and (11.0) defined with respect to the smallest two-dimensional hexagonal unit cell shown in Fig. 9.2.1.2(*b*). The point-group symmetry of this layer is 6*mm* and it has a hexagonal lattice. As such, a layer with such an arrangement of spheres is often called a hexagonal close-packed layer. We shall designate the positions of spheres in the layer shown in Fig. 9.2.1.1 by the letter '*A*'. This *A* layer has two types of triangular interstices, one with the apex angle up ($\triangle$) and the other with the apex angle down ($\triangledown$). All interstices of one kind are related by the same hexagonal lattice as that for the *A* layer. Let the positions of layers with centres of spheres above the centres of the $\triangle$ and $\triangledown$ interstices be designated as '*B*' and '*C*', respectively. In the cell of the *A* layer shown in Fig. 9.2.1.1 ($a = b$ = diameter of the sphere and $\gamma = 120°$), the three positions *A*, *B*, and *C* on projection have coordinates $(0, 0)$, $(\frac{1}{3}, \frac{2}{3})$, and $(\frac{2}{3}, \frac{1}{3})$, respectively.

9.2.1.1.2. *Close-packed structures*

A three-dimensional close-packed structure results from stacking the hexagonal close-packed layers in the *A*, *B*, or *C* position with the restriction that no two successive layers are in identical positions. Thus, any sequence of the letters *A*, *B*, and *C*, with no two successive letters alike, represents a possible manner of stacking the hexagonal close-packed layers. There are thus infinite possi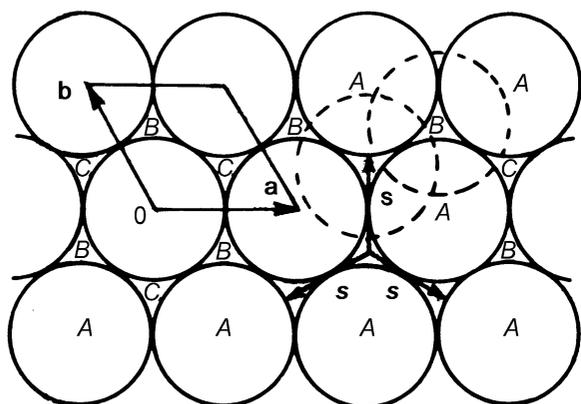bilities for close-packed layer stackings. The identity period *n* of these layer stackings is determined by the number of layers after which the stacking sequence starts repeating itself. Since there are two possible positions for a new layer on the top of the preceding layer, the total number of possible layer stackings with a repeat period of *n* is 2^{n-1}.

In all the close-packed layer stackings, each sphere is surrounded by 12 other spheres. However, it is touched by all 12 spheres only if the axial ratio h/a is $\sqrt{2/3}$, where *h* is the separation between two close-packed layers and *a* is the diameter of the spheres (Verma & Krishna, 1966). Deviations from the ideal value of the axial ratio are common, especially in hexagonal metals (Cottrell, 1967). The arrangement of spheres described above provides the highest packing density of 0.7405 in the ideal case for an infinite lattice (Azaroff, 1960). There are, however, other arrangements of a finite number of equal spheres that have a higher packing density (Boerdijk, 1952).

9.2.1.1.3. *Notations for close-packed structures*

In the Ramsdell notation, close-packed structures are designated as *nX*, where *n* is the identity period and *X* stands for the lattice type, which, as shown later, can be hexagonal (*H*), rhombohedral (*R*), or in one special case cubic (*C*) (Ramsdell, 1947).

In the Zhdanov notation, use is made of the stacking offset vector **s** and its opposite −**s**, which cause, respectively, a
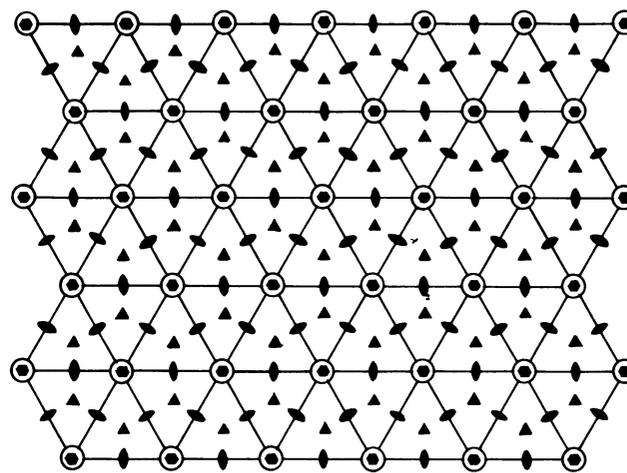
(*a*)
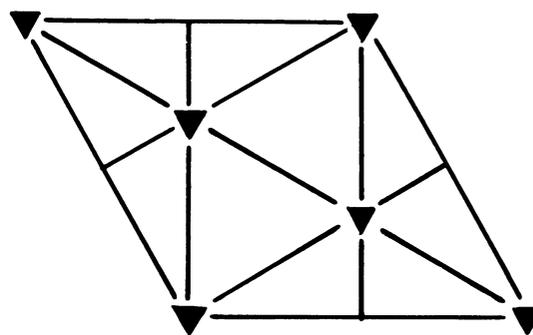
(*b*)

Fig. 9.2.1.2. (*a*) Symmetry axes of a single close-packed layer of spheres and (*b*) the minimum symmetry of a three-dimensional close packing of spheres.

Fig. 9.2.1.1. The close packing of equal spheres in a plane.

Table 9.2.1.1. *Common close-packed metallic structures*

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

cyclic ($A \to B \to C \to A$) or anticyclic ($A \to C \to B \to A$) 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 (1949*a*) 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, CdI_2, 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.
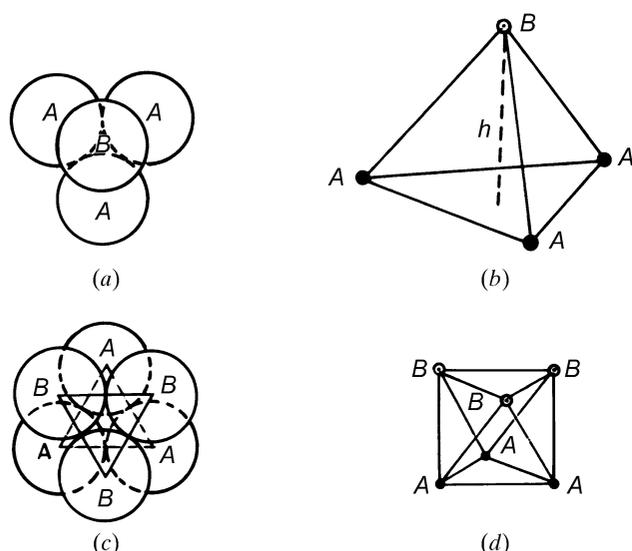
9.2.1.2.1. *Voids in close packing*

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. 9.2.1.3*a*,*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. 9.2.1.3*c*,*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-6*H*, which is the most common modification.
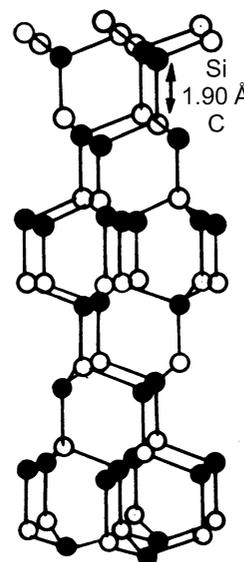

Fig. 9.2.1.3. Voids in a close packing: (*a*) tetrahedral void; (*b*) tetrahedron formed by the centres of spheres; (*c*) octahedral void; (*d*) octahedron formed by the centres of spheres.

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

references