SIMPLE CRYSTAL STRUCTURES

Sodium Chloride Structure

The sodium chloride, NaCl, structure is shown in Figs. 17 and 18. The lattice is face-centered cubic; the basis consists of one Na atom and one Cl atom separated by one-half the body diagonal of a unit cube. There are four units of NaCl in each unit cube, with atoms in the positions

Cl:	000 ;	$\frac{1}{2}\frac{1}{2}0$;	$\frac{1}{2}0\frac{1}{2}$;	$0\frac{1}{2}\frac{1}{2}$.
Na:	$\frac{1}{2}\frac{1}{2}\frac{1}{2}$;	$00\frac{1}{2}$;	$0\frac{1}{2}0$;	$\frac{1}{2}00$.

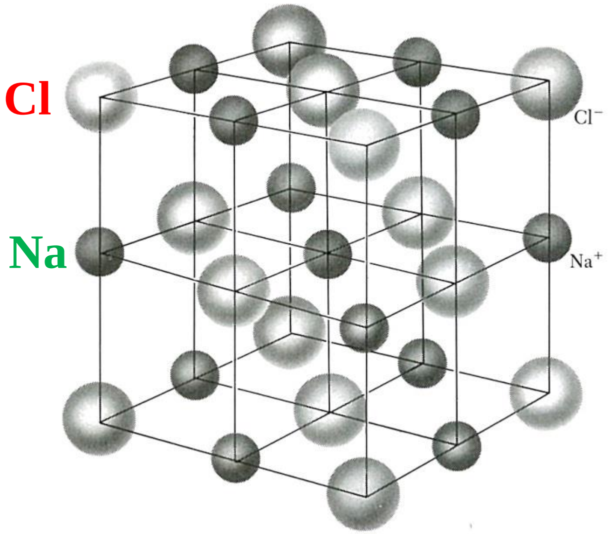


Figure 17 We may construct the sodium chloride crystal structure by arranging Na^+ and Cl^- ions alternately at the lattice points of a simple cubic lattice. In the crystal each ion is surrounded by six nearest neighbors of the opposite charge. The space lattice is fcc, and the basis has one Cl^- ion at 000 and one Na^+ ion at $\frac{1}{2}\frac{1}{2}\frac{1}{2}$. The figure shows one conventional cubic cell. The ionic diameters here are reduced in relation to the cell in order to clarify the spatial arrangement.

Each atom has as nearest neighbors six atoms of the opposite kind. Representative crystals having the NaCl arrangement include those in the following table. The cube edge *a* is given in angstroms; $1\ \text{Å} \equiv 10^{-8}\ \text{cm} \equiv 10^{-10}\ \text{m} \equiv 0.1\ \text{nm}$.

Cesium Chloride Structure

The cesium chloride structure is shown in Fig. 20. There is one molecule per primitive cell, with atoms at the corners 000 and body-centered positions $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ of the simple cubic space lattice. Each atom may be viewed as at the center of a cube of atoms of the opposite kind, so that the number of nearest neighbors or coordination number is eight.

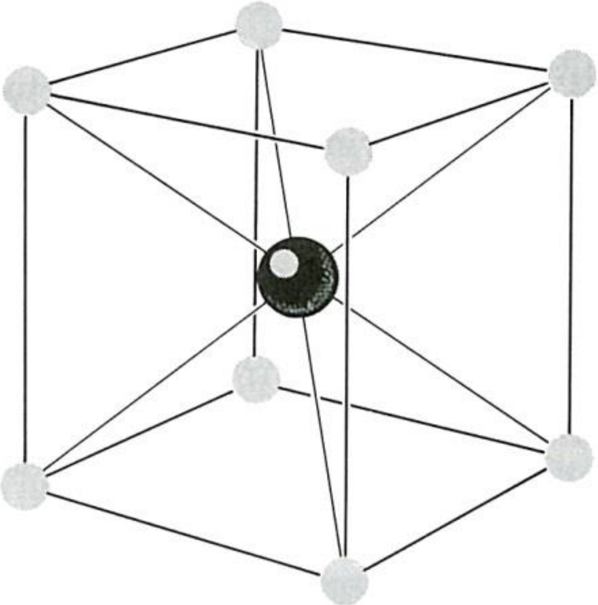
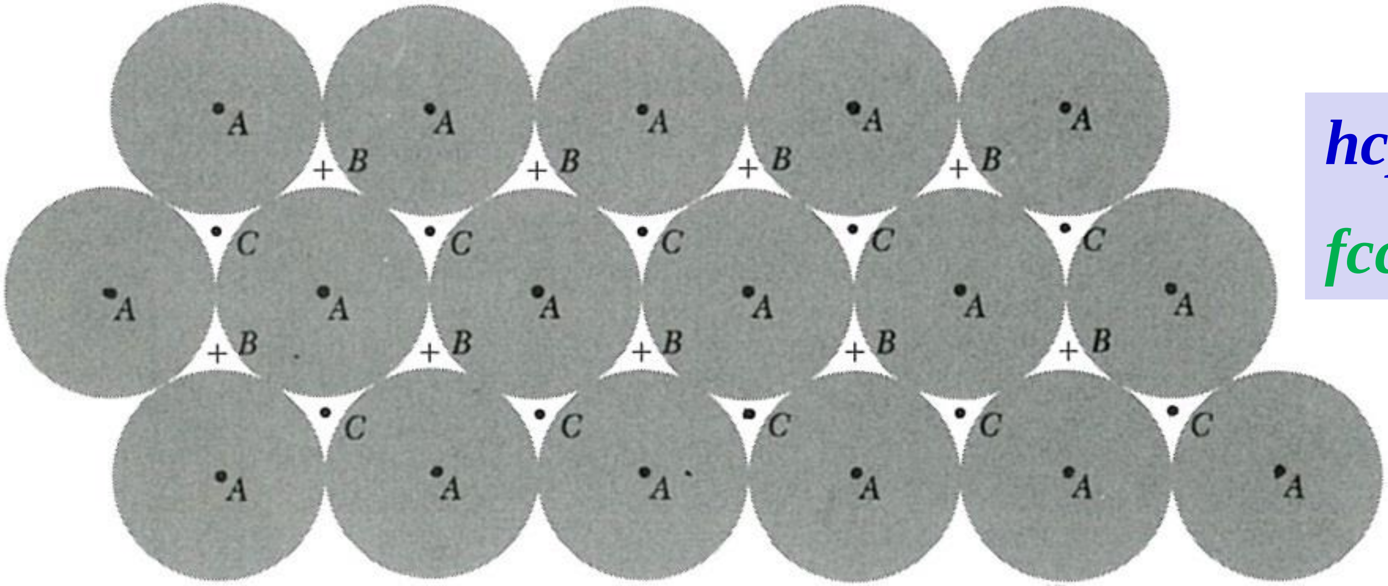


Figure 20 The cesium chloride crystal structure. The space lattice is simple cubic, and the basis has one Cs^+ ion at 000 and one Cl^- ion at $\frac{1}{2}\frac{1}{2}\frac{1}{2}$.

Hexagonal Close-packed Structure (hcp)

There are an infinite number of ways of arranging identical spheres in a regular array that maximizes the packing fraction (Fig. 21). One is the face-centered cubic structure; another is the hexagonal close-packed structure (Fig. 22). The fraction of the total volume occupied by the spheres is 0.74 for both structures.



hcp: **ABABAB**

fcc: **ABCABC**

Figure 21 A close-packed layer of spheres is shown, with centers at points marked *A*. A second and identical layer of spheres can be placed on top of this, above and parallel to the plane of the drawing, with centers over the points marked *B*. There are two choices for a third layer. It can go in over *A* or over *C*. If it goes in over *A* the sequence is *ABABAB*. . . and the structure is hexagonal close-packed. If the third layer goes in over *C* the sequence is *ABCABCABC*. . . and the structure is face-centered cubic.

The hcp structure has the primitive cell of the hexagonal lattice, but with a basis of two atoms (Fig. 23).

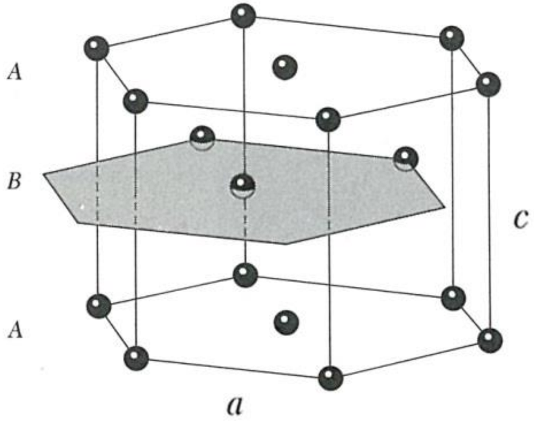


Figure 22 The hexagonal close-packed structure. The atom positions in this structure do not constitute a space lattice. The space lattice is simple hexagonal with a basis of two identical atoms associated with each lattice point. The lattice parameters a and c are indicated, where a is in the basal plane and c is the magnitude of the axis $\mathbf{a}_3$ of Fig. 14.

The ratio c/a (or a_3/a_1) for hexagonal closest-packing of spheres has the value $(\frac{8}{3})^{1/2} = 1.633$.

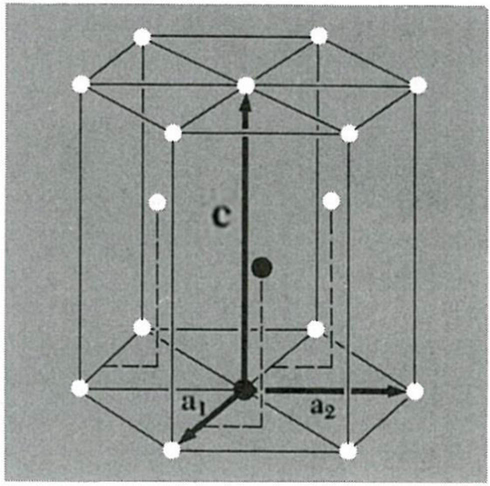


Figure 23 The primitive cell has $a_1 = a_2$, with an included angle of 120°. The c axis (or $\mathbf{a}_3$) is normal to the plane of $\mathbf{a}_1$ and $\mathbf{a}_2$. The ideal hcp structure has $c = 1.633\ a$. The two atoms of one basis are shown as solid circles. One atom of the basis is at the origin; the other atom is at $\frac{2}{3}\frac{1}{3}\frac{1}{2}$, which means at the position $\mathbf{r} = \frac{2}{3}\mathbf{a}_1 + \frac{1}{3}\mathbf{a}_2 + \frac{1}{2}\mathbf{a}_3$.

The number of nearest-neighbor atoms is 12 for both hcp and fcc structures.

Diamond Structure

The space lattice of diamond is fcc. The primitive basis has two identical atoms at 000; $\frac{1}{4}\frac{1}{4}\frac{1}{4}$ associated with each point of the fcc lattice, as in Fig. 24. Thus the conventional unit cube contains eight atoms. There is no way to choose the primitive cell such that the basis of diamond contains only one atom.

The tetrahedral bonding characteristic of the diamond structure is shown in Fig. 25. Each atom has 4 nearest neighbors and 12 next nearest neighbors. The diamond structure is relatively empty: the maximum proportion of the available volume which may be filled by hard spheres is only 0.34.

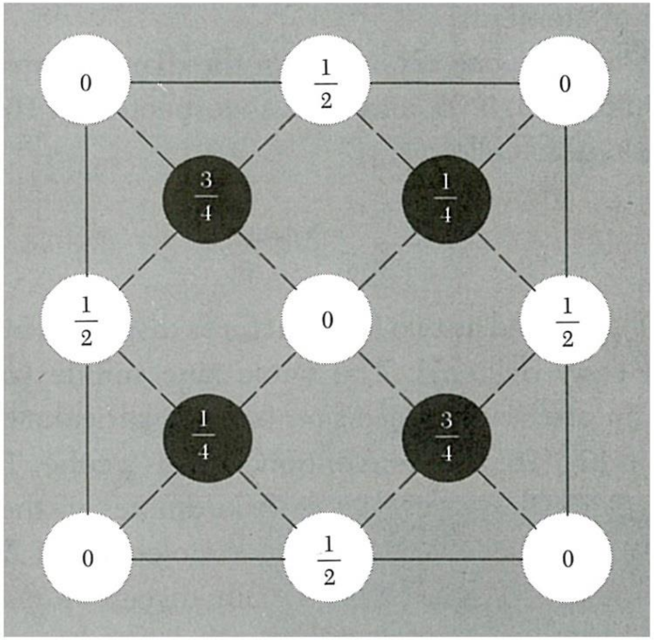


Figure 24 Atomic positions in the cubic cell of the diamond structure projected on a cube face; fractions denote height above the base in units of a cube edge. The points at 0 and $\frac{1}{2}$ are on the fcc lattice; those at $\frac{1}{4}$ and $\frac{3}{4}$ are on a similar lattice displaced along the body diagonal by one-fourth of its length. With a fcc space lattice, the basis consists of two identical atoms at 000; $\frac{1}{4}\frac{1}{4}\frac{1}{4}$.

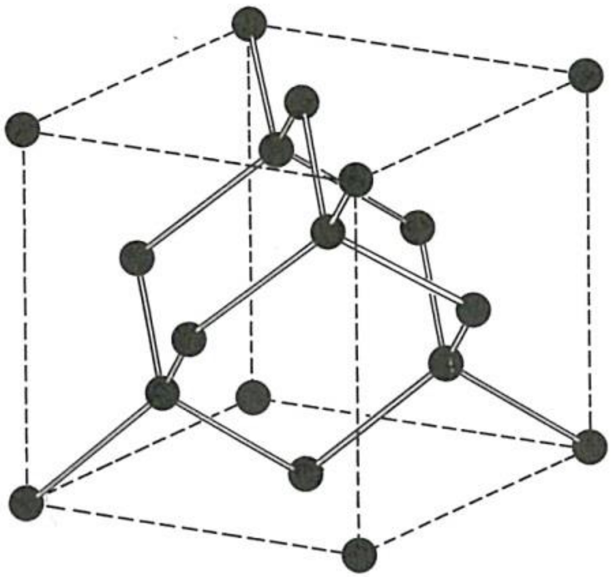


Figure 25 Crystal structure of diamond, showing the tetrahedral bond arrangement.

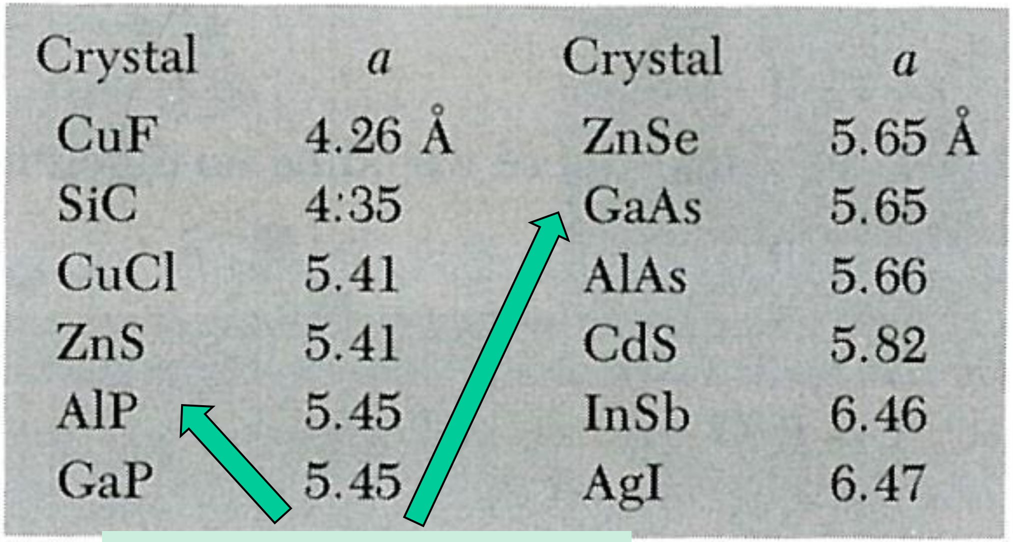
diamond structure is an example of the directional covalent bonding found in column IV of the periodic table of elements.

Carbon, silicon, germanium, and tin can crystallize in the diamond structure, with lattice constants $a = 3.56$, 5.43, 5.65, and 6.46 Å.

Cubic Zinc Sulfide Structure

The diamond structure may be viewed as two fcc structures displaced from each other by one-quarter of a body diagonal. The cubic zinc sulfide (zinc blende) structure results when Zn atoms are placed on one fcc lattice and S atoms on the other fcc lattice, as in Fig. 26. The conventional cell is a cube. The coordinates of the Zn atoms are 000; $0\frac{1}{2}\frac{1}{2}$; $\frac{1}{2}0\frac{1}{2}$; $\frac{1}{2}\frac{1}{2}0$; the coordinates of the S atoms are $\frac{1}{4}\frac{1}{4}\frac{1}{4}$; $\frac{1}{4}\frac{3}{4}\frac{3}{4}$; $\frac{3}{4}\frac{1}{4}\frac{3}{4}$; $\frac{3}{4}\frac{3}{4}\frac{1}{4}$. The lattice is fcc. There are four molecules of ZnS per conventional cell. About each atom there are four equally distant atoms of the opposite kind arranged at the corners of a regular tetrahedron.

The cubic ZnS structure does not have inversion symmetry.



Crystal	*a*	Crystal	*a*
CuF	4.26 Å	ZnSe	5.65 Å
SiC	4.35	GaAs	5.65
CuCl	5.41	AlAs	5.66
ZnS	5.41	CdS	5.82
AlP	5.45	InSb	6.46
GaP	5.45	AgI	6.47

III-V semiconductors

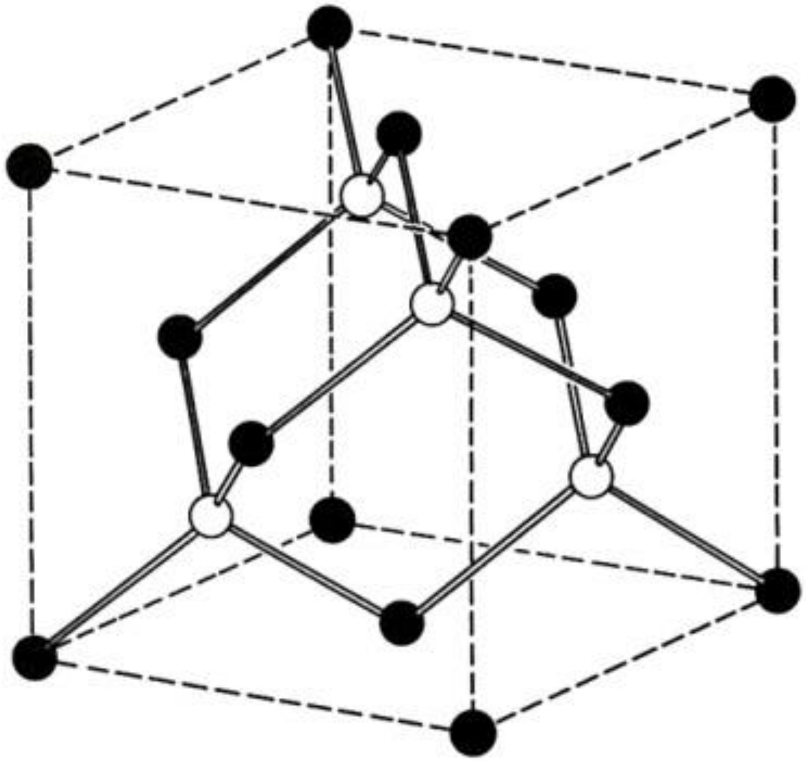


Figure 26 Crystal structure of cubic zinc sulfide.

Fundamental Types of Lattices

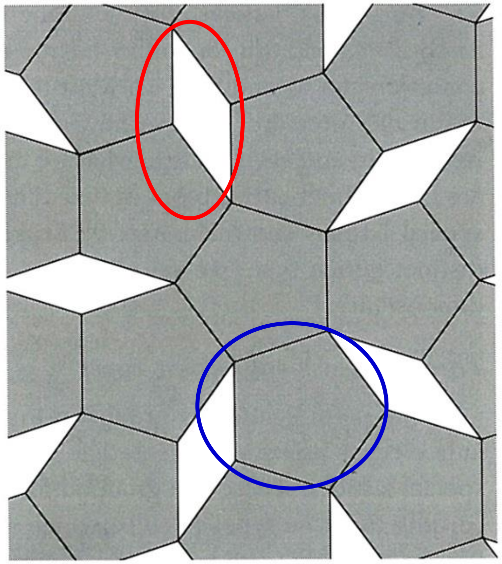
A typical symmetry operation is that of rotation about an axis that passes through a lattice point. Lattices can be found such that one-, two-, three-, four-, and sixfold rotation axes carry the lattice into itself, corresponding to rotations by 2π, $2\pi/2$, $2\pi/3$, $2\pi/4$, and $2\pi/6$ radians and by integral multiples of these rotations.

A single molecule properly designed can have any degree of rotational symmetry, but an infinite periodic lattice cannot. We can make a crystal from molecules that individually have a fivefold rotation axis, but we should not expect the lattice to have a fivefold rotation axis.

Five fold symmetry ?

Quasi-crystal !

Figure 7 A fivefold axis of symmetry cannot exist in a periodic lattice because it is not possible to fill the area of a plane with a connected array of pentagons. We can, however, fill all the area of a plane with just two distinct designs of "tiles" or elementary polygons. A quasicrystal is a quasiperiodic nonrandom assembly of two types of figures. Quasicrystals are discussed at the end of Chapter 2.



We can have mirror reflections m about a plane through a lattice point. The inversion operation is composed of a rotation of π followed by reflection in a plane normal to the rotation axis; the total effect is to replace $\mathbf{r}$ by $-\mathbf{r}$.

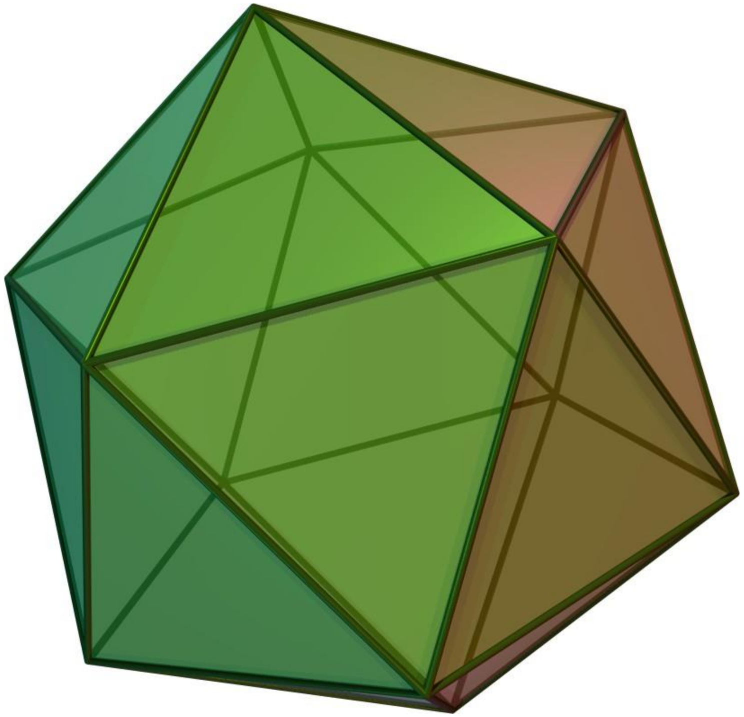
Quasicrystals

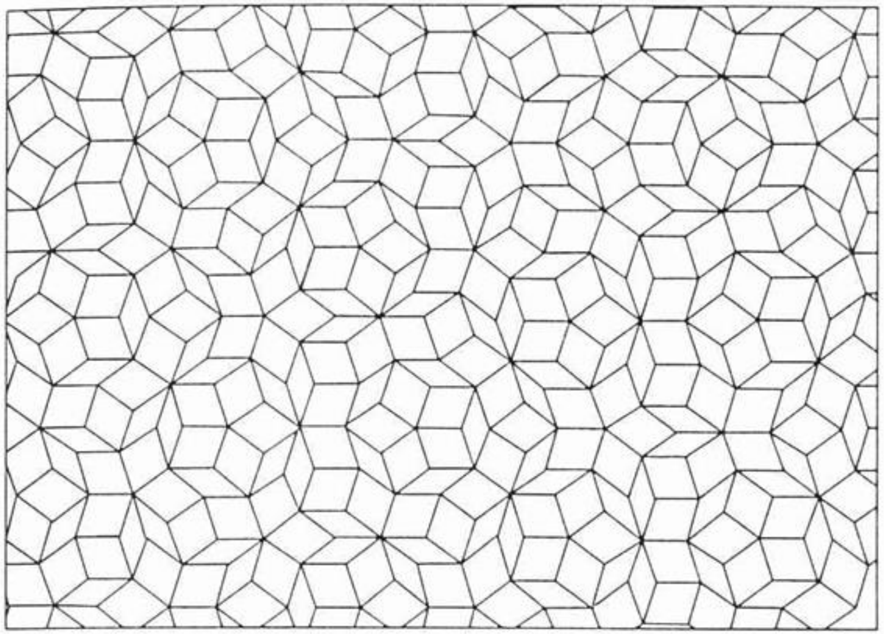
$Al_{0.86}Mn_{0.14}$

In 1984 quasicrystals were first observed; these are structures which cannot be indexed to any Bravais lattice and “which have symmetries intermediate between a crystal and a liquid.” They were first observed in grains of size 2 μm in an alloy of Al with 14 at.% Mn. The smaller Mn atoms are each surrounded by 12 Al atoms arranged at the corners of an icosahedron. The structure is made up of parallel icosahedra attached at their edges. **Crystals cannot exhibit the fivefold symmetry of an icosahedron**, but a crystal can be constructed by nucleation at a center cell, followed by outward growth from there. All of the space of a nodule cannot be filled by repeating the basic unit (see Figures 19 and 7 for the picture in two dimensions), although the “parallel” part of the specification does give a long-range orientational order to the structure. It is perhaps surprising that the x-ray diffraction pattern of such a structure can have fivefold symmetry; that is how they were first observed.

The known quasicrystals are intermetallic alloys and are very poor electrical conductors; they are **nearly insulators** with a somewhat well-defined band gap (Chapter 7) at the Fermi level. They are of great interest intellectually in expanding the definition of crystal lattice.

在幾何學中，**二十面體**（icosahedron）是指具有二十個面的多面體。



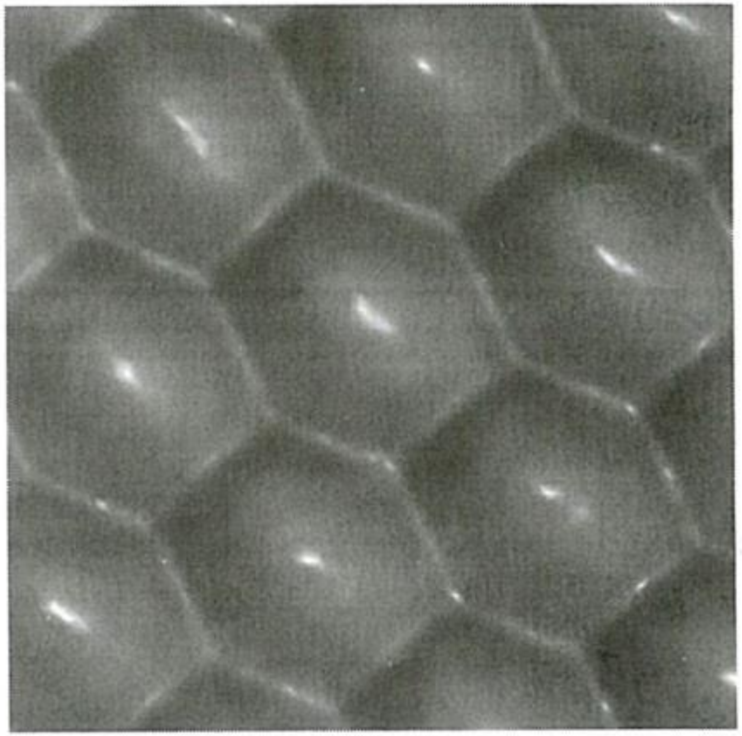


Penrose tiling

Figure 19 A quasicrystal tiling in two dimensions, after the work of Penrose. The long-range orientational order and the long-range non-periodic order are shown.

DIRECT IMAGING OF ATOMIC STRUCTURE

Direct images of crystal structure have been produced by transmission electron microscopy. Perhaps the most beautiful images are produced by scanning tunneling microscopy; in STM (Chapter 19) one exploits the large variations in quantum tunneling as a function of the height of a fine metal tip above the surface of a crystal.



STM image

Figure 27 A scanning tunneling microscope image of atoms on a (111) surface of platinum at 4 K. The nearest neighbor spacing is 2.78 Å. (Photo courtesy of D. M. Eigler, IBM Research Division.)

Scanning Tunneling Microscope (STM)

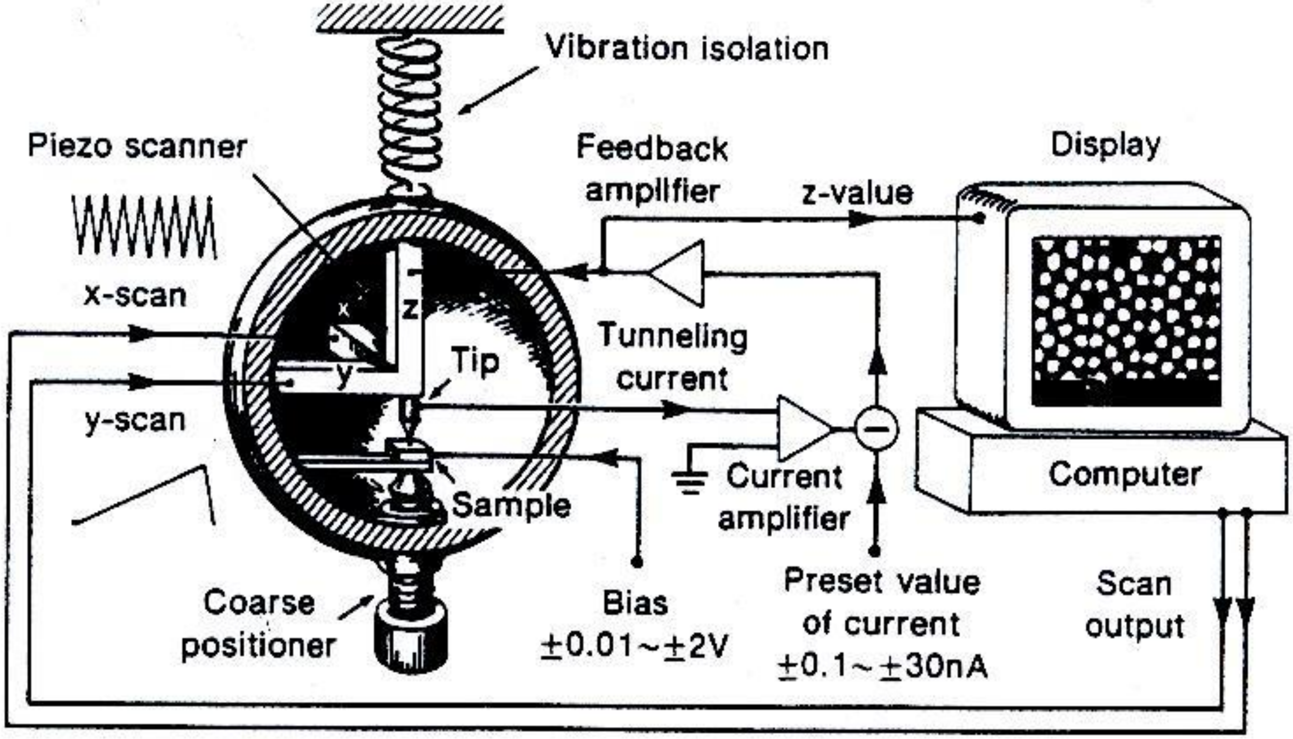


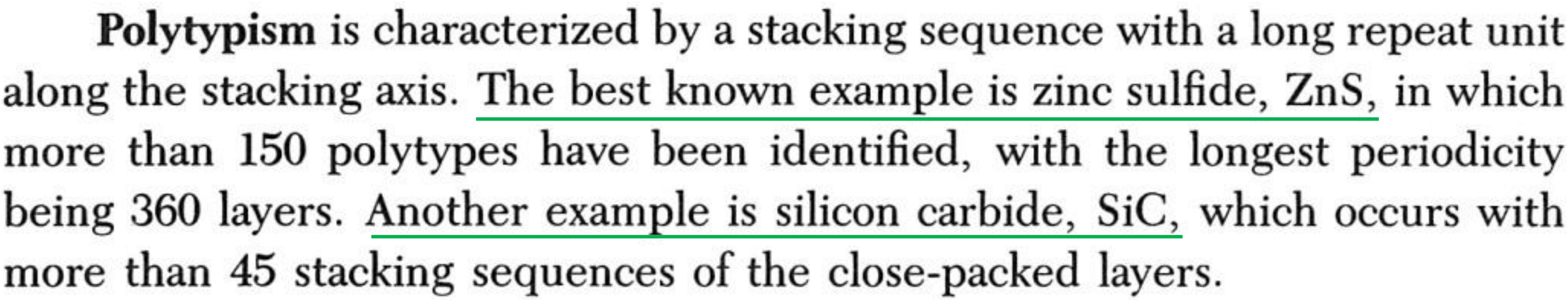
Figure 1.10 Scanning tunneling microscope. (From C. Julian Chen, *Introduction to Scanning Tunneling Microscopy*, Oxford: Oxford University Press, 1993.)

NONIDEAL CRYSTAL STRUCTURES

But no general proof has been given that the ideal crystal is the state of minimum energy of identical atoms at absolute zero. At finite temperatures this is not likely to be true. Many structures that occur in nature are not entirely periodic; see the quasicrystals treated at the end of Chapter 2.

Random Stacking and Polytypism

Structures are known in which the stacking sequence of close-packed planes is random. This is known as random stacking and may be thought of as crystalline in two dimensions, and noncrystalline or glasslike in the third.



Polytypism is characterized by a stacking sequence with a long repeat unit along the stacking axis. The best known example is zinc sulfide, ZnS, in which more than 150 polytypes have been identified, with the longest periodicity being 360 layers. Another example is silicon carbide, SiC, which occurs with more than 45 stacking sequences of the close-packed layers.

The mechanism that induces such long range crystallographic order is not a long range force as such, but is associated with the presence of spiral steps due to dislocations in the growth nucleus (Chapter 21).

Chapter 21, Spiral crystal growth from dislocation line

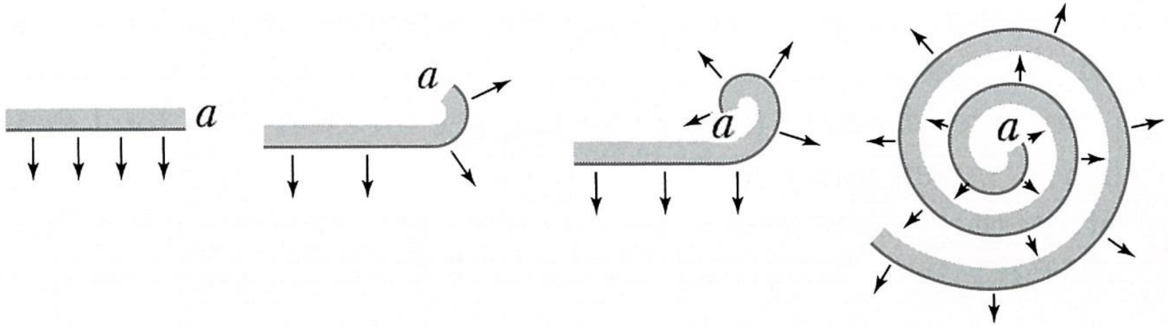


Figure 20 Development of a spiral step produced by intersection of a screw dislocation with the surface of a crystal as in Fig. 8. (F. C. Frank.)

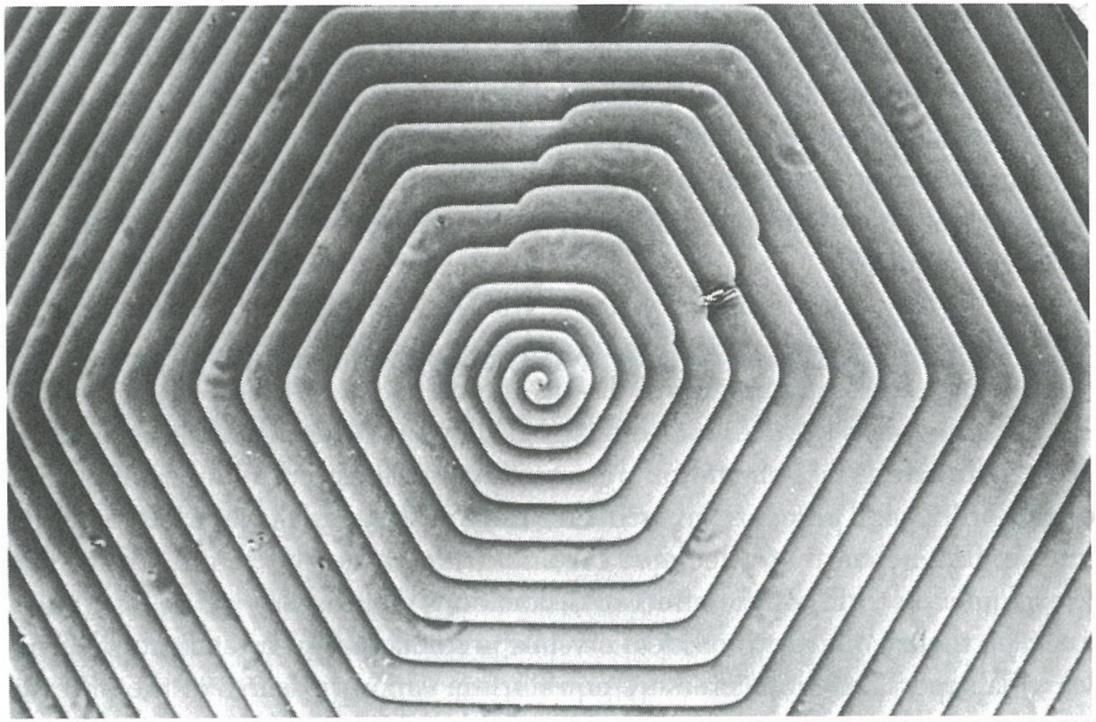
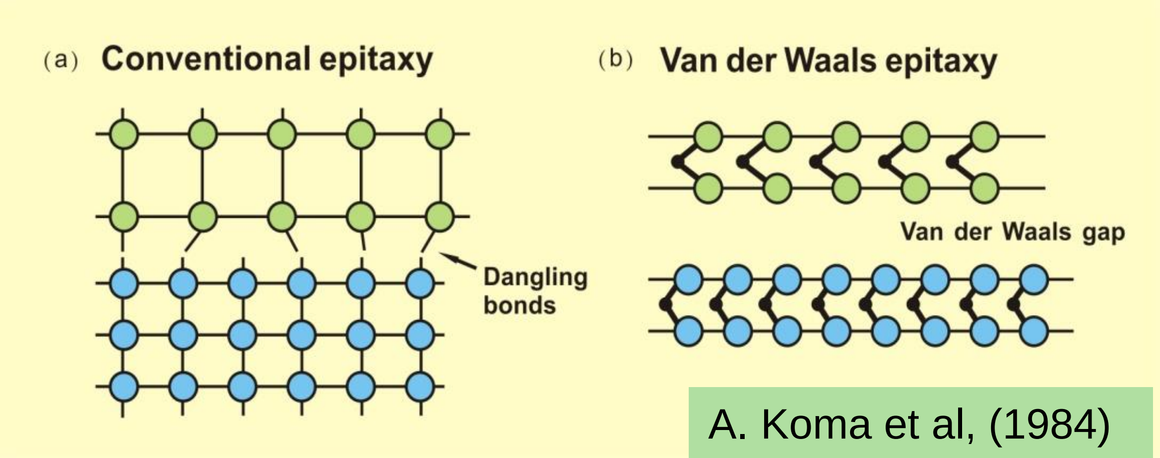


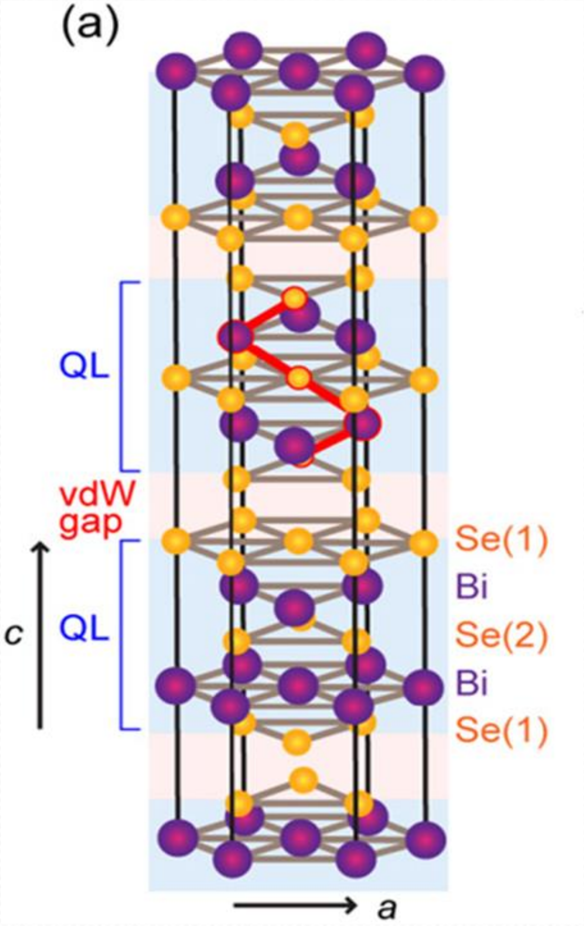
Figure 21 Phase contrast micrograph of a hexagonal spiral growth pattern on a SiC crystal. The step height is 165 Å. (A. R. Verma.)

Thin Film Growth for 3D-TIs

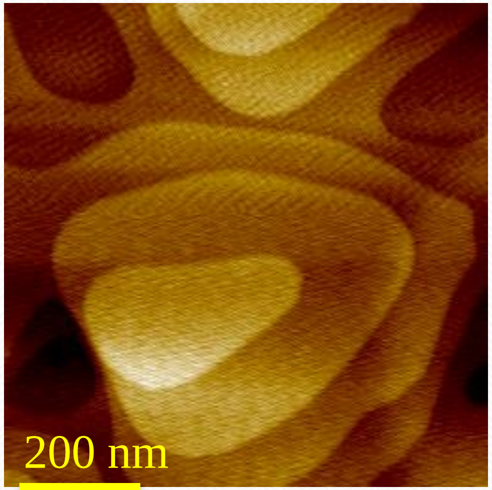
3D TI films of the tetradymite family like Bi_2Se_3 by van der Waals epitaxy, ideally suited for transition metal chalcogenide layered structures

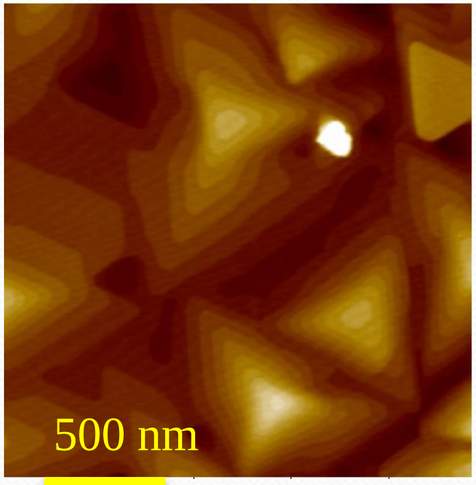


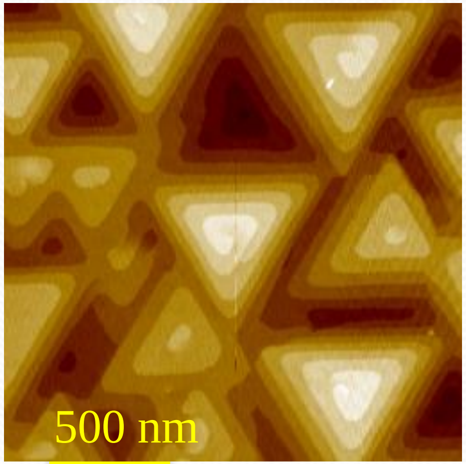
A. Koma et al, (1984)



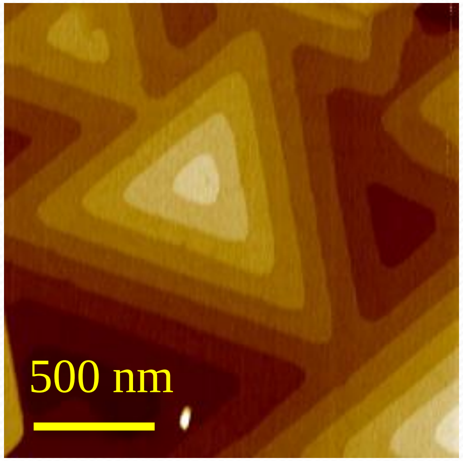
Bi_2Te_3 Surface Morphology Examined by AFM

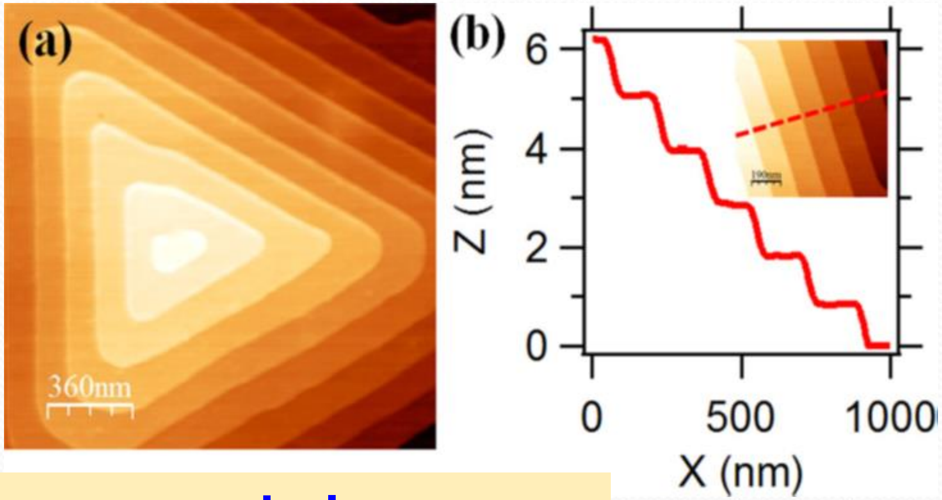

Ts=275 ℃


Ts=300 ℃


Ts=320℃

- The size of triangular shaped domain increases with growth temperature


Ts=340℃



- The size of domains is approaching to 2μm at Ts = 340℃

Typical hillock terrace morphology,

Calls for micro-ARPES, or nano-ARPES !

Appl. Phys. Lett. **102**, 171906 (2013).
by Jim Harris et al (Stanford)

CRYSTAL STRUCTURE DATA

In Table 3 we list the more common crystal structures and lattice structures of the elements. Values of the atomic concentration and the density are given in Table 4.

Problems

1. **Show for the hcp structure, the basis has two atoms: (1) one is at the origin, and (2) the other is at the position of $2/3\ \mathbf{a}_1 + 1/3\ \mathbf{a}_2 + 1/2\ \mathbf{a}_3$**

2. ***Hcp structure.*** Show that the c/a ratio for an ideal hexagonal close-packed structure is $(\frac{8}{3})^{1/2} = 1.633$. If c/a is significantly larger than this value, the crystal structure may be thought of as composed of planes of closely packed atoms, the planes being loosely stacked.