Structures of metals

Concept of close packing

The structure of many solids can be described as stacking of hard spheres representing the atoms or ions. The close packing concept is ideal for metals, because all atoms are equal. Furthermore, there are no directional covalent bonds and the atoms are electrically neutral. The outcome of this is a close packing in which the spheres occupy 74% of the available space. The coordination number of close- packed structures is 12, which means that each sphere has 12 neighbors, the greatest number that geometry allows.

How is the close packing of spheres built on?

The close- packed structures of equal spheres results from close- packed two- dimensional layers on top of each other.

a) The first layer is composed of adjoining spheres and each sphere has 6 nearest neighbors in the plane.

b) The second layer is constructed by placing spheres in the dips of the first layer. The second layer covers only half of the holes in the first layer

c) The arrangement of the third layer decides about two polytypes (polytypes are structures that are same in two dimensions (in this case in the planes) but different in the third.).

- If the spheres lie directly above the spheres of the first layer, than a structure with a hexagonal unit cell results. This ABAB arrangement is called hexagonally- close- packed **hcp**.
- In the other polytype the spheres of the third layer are placed above the gaps in the first layer. This ABCABC pattern gives a structure with a cubic unit cell, which is called cubic close- packed **ccp** or face- centered cubic **fcc.**

The hcp- type is also known as **Mg- type**. The space filling is 74 %. Metals which crystallize in hcp are Be, Cd, Co, Mg, Ti, Zn.

The cubic close- packing is known as **Cu- type**. The space filling is 74 %. Ag, Al, Au, Ca, Cu, Ni, Pb and Pt crystallize in ccp.

Holes in close packed structures

In close packed structures are two different types of holes.

An octahedral hole is formed by two oppositely directed planar triangles between spheres in adjoining layers. In the close packed structure there are N octahedral holes (N= number of atoms). Each octahedral hole can accommodate another hard sphere with a radius not larger than 0.414 r.

A tetrahedral hole results from a planar triangle between neighboring spheres capped by a single sphere lying in the dip they form. In this case there are two different tetrahedral holes, in one the apex of the tetrahedron is directed up and in the other the apex is directed down. In the close packed- structure are 2N tetrahedral holes. A tetrahedral hole can accommodate another hard sphere with a radius not larger than 0.225 r.

Coordination polyhedra

The coordination polyhedra depend on the coordination number:

CN= 3: triangle, CN= 4: tetrahedron, CN= 6: octahedron, CN= 8: cube, CN= 12: anticuboctahedron or cuboctahedron

The coordination polyhedra of hcp is an anti- cuboctahedron with CN=12.

The coordination polyhedra of ccp is a cuboctahedron with CN=12.

Structures that are not close packed

The W- type is a non close- packed structure. Tungsten crystallize in the body- centered cubic structure. That means that there is a sphere at the center of a cube with spheres at each corner. The

coordination number is 8. The space filling is 68 %. Other metals which crystallize in bcc are Ba, Cr, Fe and the alkali metals.
Another structure of metals is the primitive cubic (cubic- P) . In this case the spheres are located at the corners of a cube. The coordination number is 6 and the space filling is 52%. This structure type is only known for alpha-Po under normal conditions.

Literature

[1] P. Atkins, T. Overton, J. Rourke, M. Weller, F. Armstrong, *Shriver & Atkins` Inorganic Chemistry*, 3th edition, 1999, Oxford University Press, Oxford

[2] lecture notes, Prof. Dr. Deiseroth, *Advanced inorganic chemistry*, University Siegen, 2010

Exercises

1) Calculate the space filling for a primitive packing of spheres.
2) Calculate the size of a tetrahedral hole.