02. Constructing a Nanoparticle

So lets see what could be the easiest way to visualize the construction of a nanoparticle. I assume that most of us have had some basic course in crystallography. If not, I urge you at this point of time to read a couple of chapters related to the structure of solids. In any case you can still go on to read this portion without fear of losing out much.

We will start with the close-packed structures. Well I guess I have chosen it as it is quite easy to visualize. Moreover, I would use the cubic close-packed structures as they are far simpler to work with compared to the hexagonal close-packed ones. One could easily distinguish the two fairly easily. Start with spheres; all of the same size. Think of a sphere that is surrounded by spheres in the same plane; spheres in close contact to each other. No matter what you can place only six more spheres around the central one as you can see in Figure 2.1a. Now try placing a few spheres on top of this layer. These can only go into the depressions between the central sphere and the surrounding spheres as seen in Figure 2.1b. Lets call this an AB arrangement. The third layer on top would have two possibilities: (i) one sphere goes exactly on top of the red sphere that is the void created in the centre as shown in Figure 2.1b or (ii) it goes in the alternate voids as shown in Figure 2.1c. The former would correspond to an ABC type of an arrangement, in other words the cubic close-packed structure whereas the latter would be an ABAB type, also called the hexagonal close-packed structure. One could definitely construct a variety of other close-packed structures other than these two with the smallest unit-cell. For example, a possibility could be ABABCAB… and so on.

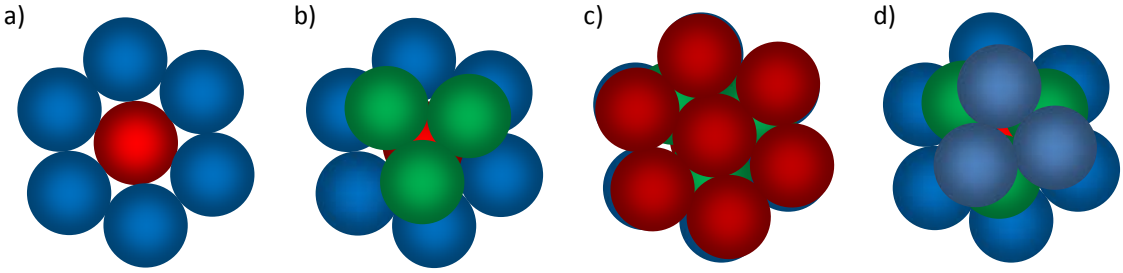
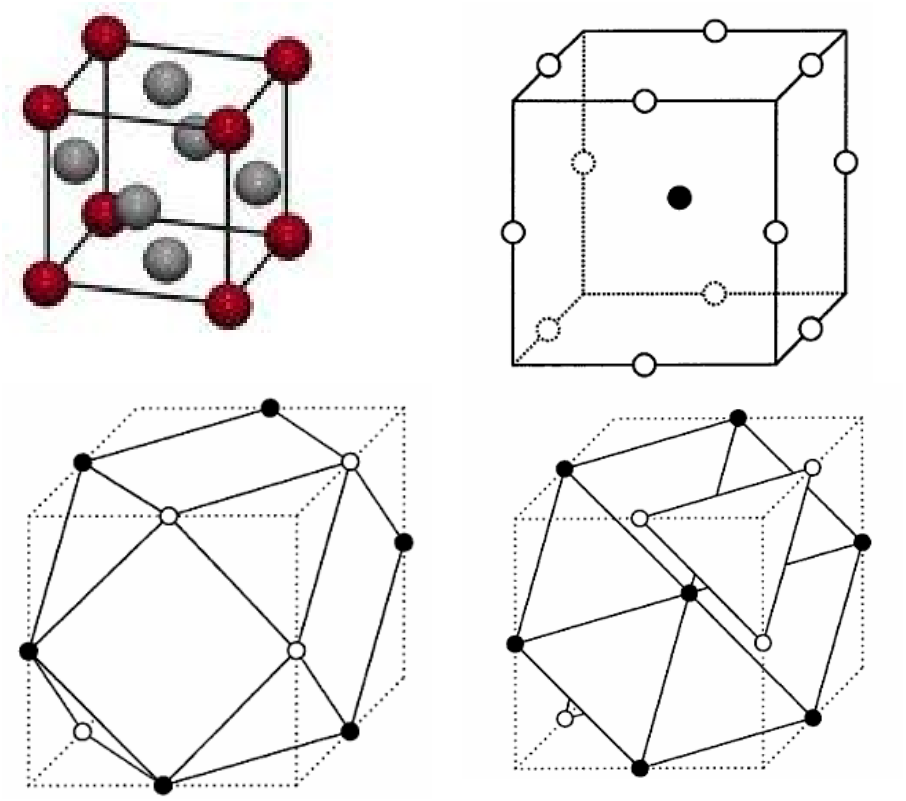


Figure 2.1: Close-packed arrangement for a) plane b) two-planes c) ABAB d) ABCABC

Now, if you look at the metals in their native state the close-packing is by far the most favoured among them. What we are then aiming at is a structural description of most of the metal nanoparticles. Coming back to the cubic close packed structures, another way to visualize them is to use the concept of a unit cell. The conventional unit cell, named the face-centered cubic (FCC) unit cell is depicted in Figure 2.2a. One could easily correlate this with the ABCABC structure described above. You need to look at the two sets of the three atoms on the face centres and imagine them as planes. Then if the lower front left corner atom belongs to plane A, the set of grey atoms would be in plane B and the next set would constitute plane C. The top back right corner atom would lie exactly on top of the lower front left corner atom, if we view the crystal along a direction perpendicular to these planes.

Now, we would need to worry about the number of nearest neighbours that each atom has. Do note that each atom is very much identical. With the structure shown in Figure 2.2a, its not very

convenient to calculate the number of nearest neighbours. Well, its not convenient since none of the atoms shown is completely surrounded by all of its neighbours. We need to do a little bit of jugglery and bring one of the atoms to a position that it is now completely surrounded by its nearest neighbours. The easiest way would be to translate the unit cell by ½ the cell edge length along an edge as is done in Figure 2.2b. Now anyone could just easily count all the atoms surrounding the central atom and shout out – 12! (Actually one could have counted from the constructions in Figure 2.1 – 6 in the plane, 3 above and 3 below. However, we use these cube figures to understand the shapes of the nanoparticles with the symmetry they possess.)



Perspective along the [111] direction

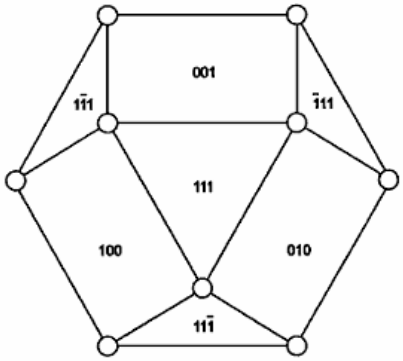


Figure 2.2: The FCC unit cell

What we have arrived at is the smallest nanocluster, crystallizing in the FCC structure that has a central atom surrounded by nearest neighbours. In total 13 atoms.

Magic Numbers

From here we come to the concept of magic numbers in nanoclusters. Lets introduce some nomenclature. The central atom belongs to the first shell and all its nearest neighbours to the second shell. What about the third shell. Evaluate the number of nearest neighbours of all the 12 atoms that belong to the second shell. This would definitely be a tedious task; the result is 42. If we count the total number of atoms in the nanocluster, it comes out to be 55. These nanoclusters are structurally closed in a sense that all the inner atoms have completely satisfied valencies. Of course the surface atoms will not be bonded in all directions. Due to this completeness these nanoclusters are termed as magic sized particles. The series continues as 1, 13, 55, 147, 309… and can be represented by the equation

$$N = \frac{1}{3}\,(10n^3 - 15n^2 + 11n - 3)$$

where, *N* is the number of atoms in a magic sized cluster containing *n* shells. However, one must note that these are *structural magic numbers*. Another type of magic numbers is the electronic magic numbers which we discuss shortly.



I would urge you to calculate the first few magic numbers for the bcc and the zinc blende structures. Zinc blende is the most important structure for the known semiconductors.

The structural magic numbers are arrived from spherical, minimum volume, maximum density nanoclusters. The electronic structure is, however, governed by other factors and not just the geometrical packing of atoms and this could be the dominating factor in deciding the size of the nanoparticle. According to this picture, the interactions would lead to an electronically stable configuration. Closed shell configurations are known to be more stable. In a sense these are hierarchical analogs of atoms or molecules where an octet is needed to stabilize the electronic configuration.

Experiments suggest small-sized nanoclusters prefer electronic stabilization whereas the larger sized nanoparticles are happier off with structural stabilization. Figure 2.3 shows the mass spectra of particles different sizes of sodium. The first 15 magic numbers observed are the electronic magic numbers (*n'* = 15) corresponding to N = 1220, whereas structural magic numbers take over from N = 1415 (*n* = 8) Na units.

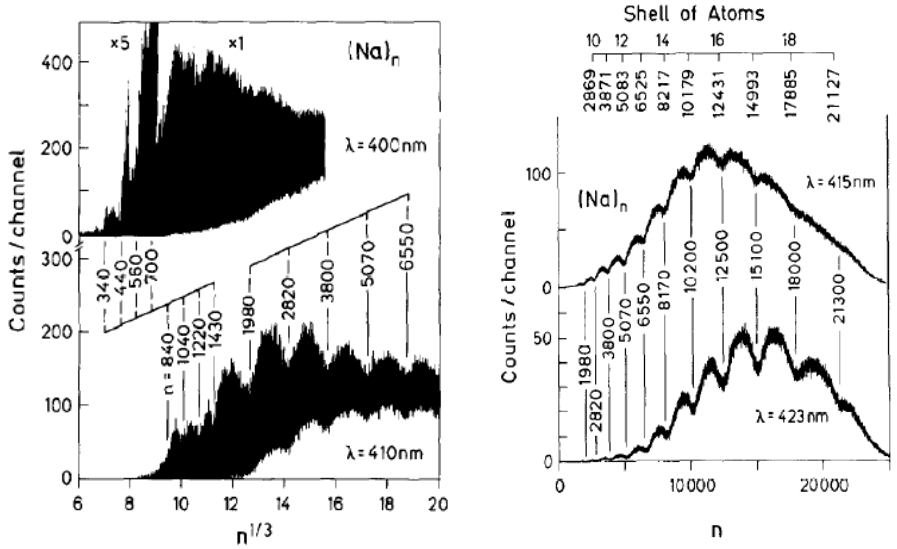


*Figure 2.3: Na nanoparticles – the changeover from electronic to structural magic numbers. [Adapted from T. P. Martin, T. Bergmann, H. Gohlich, T. Lange, Chem. Phys. Lett. **172**, 209 (1990).*

TABLE 1.1. Diameter, Total Number of Atoms, Number on Surface, and Percentage on Surface of Rare Gas or Metallic Nanoparticles with FCC Close-Packed Structures and a Structural Magic Number of Atoms[a]

Shell	Diameter	Total Number	Number on Surface	Percentage on Surface
1	d	1	1	100
2	$3d$	13	12	92.3
3	$5d$	55	42	76.4
4	$7d$	147	92	62.6
5	$9d$	309	162	52.4
6	$11d$	561	252	44.9
7	$13d$	923	362	39.2
8	$13d$	1415	492	34.8
9	$17d$	2057	642	31.2
10	$19d$	2869	812	28.3
11	$21d$	3871	1002	25.9
12	$23d$	5083	1212	23.8
25	$49d$	4.90×10^4	5.76×10^3	11.7
50	$99d$	4.04×10^5	2.40×10^4	5.9
75	$149d$	1.38×10^6	5.48×10^4	4.0
100	$199d$	3.28×10^6	9.80×10^4	3.0

[a]The diameters d in nanometers for some representative fcc atoms are Ag 0.289, Al 0.286, Ar 0.372, Au 0.288, Cu 0.256, Fe 0.254, Kr 0.404, Pb 0.350, and Pd 0.275.

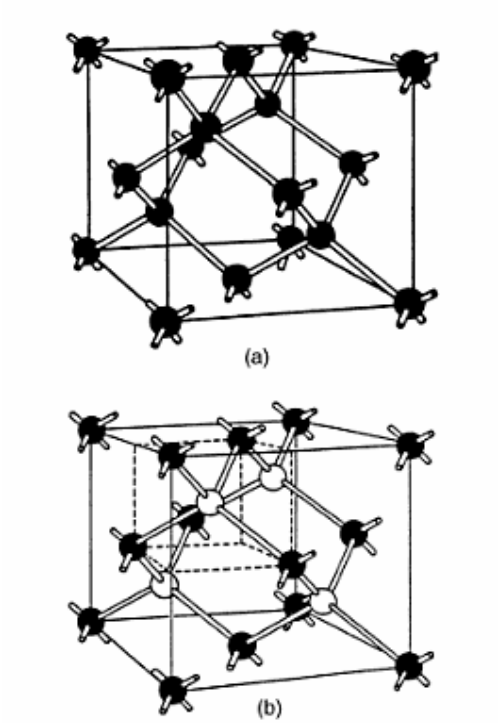


Figure 2.4: Diamond and zinc blende lattice