Nanomaterials and their Properties
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Lecture – 08
Nanomaterials: Magic Numbers

Dear students, hope we have enjoyed the last few lectures on surface energy. This is lecture number 8 and we are going to continue our discussion on the surface energy related aspects.

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Discussion of surface energy and related aspect continue

Lattice parameter
Magic numbers
Vapour pressure

Recap..

M. F. Ashby, P.J. Ferreira and D. L. Schodek; **Nanomaterials, Nanotechnologies and Design**

So, first let me tell you that we have been discussing about very interesting things about surface energy of nanomaterials and their properties right. In last lecture, few important aspects which I have discussed is one is the lattice parameter, how it is dependent on the surface energy and the size of particle. Then, I talked about very interesting concept called magic numbers right, how unique numbers like 13, 55, 147, 306, 561 numbers appear as the number of atoms sitting on the cluster for the FCCs nanoparticles.

I hope you have understood it, it is very difficult concept, but important to know the origin of this magic numbers. Then, I talked about vapour pressure, how the vapour pressure of different nanoparticles are significantly dependent on the surface energy as well as the particle size obviously, particle size and surface energy are related right. So, these are all aspects which I discussed. So, today again, I am going to have some recap on these things and then, I will go forward with something new right.

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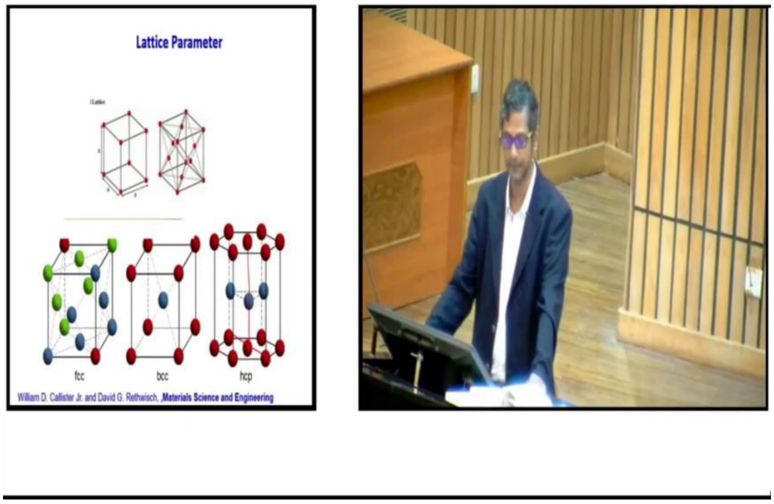

Lattice Parameter

William D. Callister Jr. and David G. Rethwisch, Materials Science and Engineering

So, what are the things we are going to recap? First is the lattice parameter right. Lattice parameter as we know is a very important characteristics of any crystalline material. And we metallurgist or material scientists, mostly deal with metals and ceramics where cubic and hexagonal structures are predominant. And their lattice parameters are basically kind of dependent on what kind of crystal system it is in fcc, bcc or simple cubic, there is only one lattice parameter.

On the other hand, hexagonal crystal structure there are two lattice parameter a and c, c is this vertical one, a is the horizontal one as you know right. So, they are dependent on the size and the surface energy.

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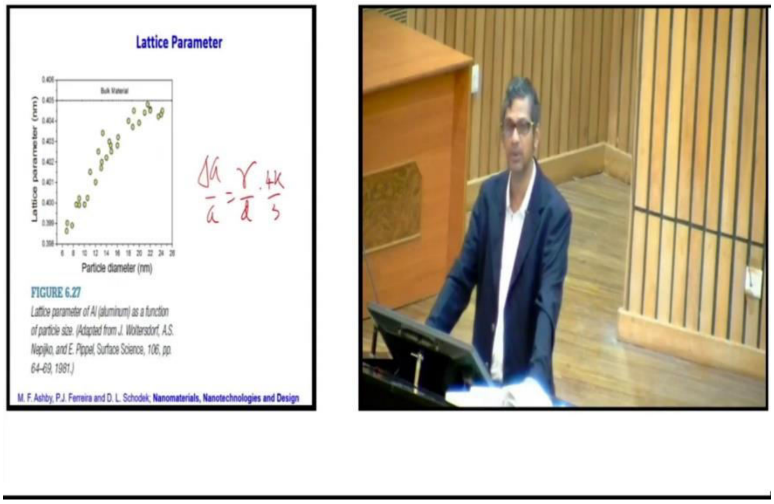

Lattice Parameter

FIGURE 6.27

Lattice parameter of Al (aluminum) as a function of particle size. (Adapted from J. Woltersdorf, A.S. Nepijko, and E. Pippel, Surface Science, 106, pp. 64–69, 1981.)

$$\frac{\Delta a}{a} = \frac{\gamma}{d} \cdot \frac{4k}{3}$$

M. F. Ashby, P.J. Ferreira and D. L. Schodek; **Nanomaterials, Nanotechnologies and Design**

And in fact, they are related to that with the relationships, I have discussed about it ok $\frac{\Delta a}{a}$ is inverse is proportional to the size and directly proportional to γ right that we have discussed right, $\frac{\Delta a}{a} = \frac{\gamma}{d} \times \frac{4k}{3}$ ok I remember that. So, now the question is k is the compressibility right and therefore, and in case of pure experimental basis, lattice parameter do undergo decrease as the size decreases.

Significantly, lattice parameter can be decreased quite a bit about 1 Angstrom for pure aluminum when the particle size goes down to 6 or 7 nanometers. That is something which is very very high when you talk about lattice parameter decreasing such a level well.

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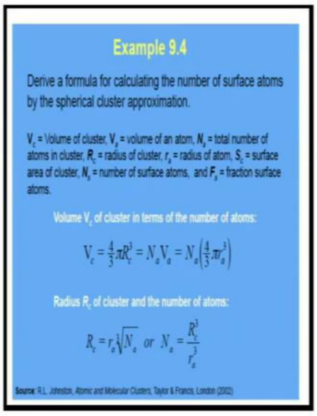

Example 9.4

Derive a formula for calculating the number of surface atoms by the spherical cluster approximation.

V_c = Volume of cluster, V_a = volume of an atom, N_a = total number of atoms in cluster, R_c = radius of cluster, r_a = radius of atom, S_c = surface area of cluster, N_s = number of surface atoms, and F_s = fraction surface atoms.

Volume V_c of cluster in terms of the number of atoms:

$$V_c = \frac{4}{3}\pi R_c^3 = N_a V_a = N_a\left(\frac{4}{3}\pi r_a^3\right)$$

Radius R_c of cluster and the number of atoms:

$$R_c = r_a\sqrt[3]{N_a} \quad or \quad N_a = \frac{R_c^3}{r_a^3}$$

Source: R.L. Johnston, Atomic and Molecular Clusters, Taylor & Francis, London (2002)

Then, I talked about something called magic numbers and in magic numbers, basic aspect is the relationship between the surface atoms by the bulk atoms, how many atoms are sitting in the surface versus bulk. And, first important aspect is the spherical cluster approximation which we dealt with. If you assume a spherical nanoparticle, then you can calculate what is the fraction of the atom sitting on the surface for the particular diameter of the atom as well as the, you know number density right.

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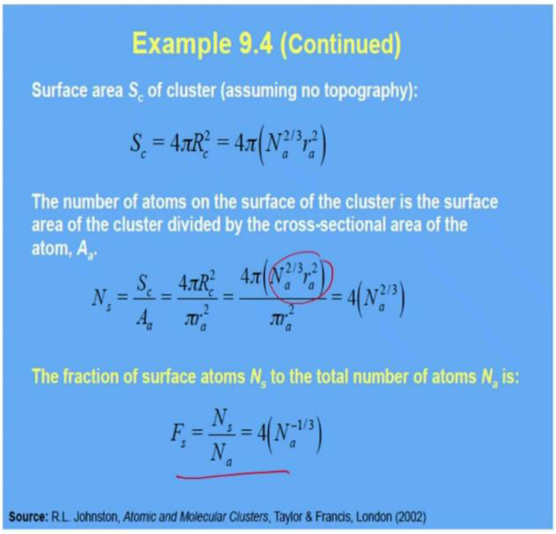

Example 9.4 (Continued)

Surface area S_c of cluster (assuming no topography):

$$S_c = 4\pi R_c^2 = 4\pi\left(N_a^{2/3} r_a^2\right)$$

The number of atoms on the surface of the cluster is the surface area of the cluster divided by the cross-sectional area of the atom, A_a.

$$N_s = \frac{S_c}{A_a} = \frac{4\pi R_c^2}{\pi r_a^2} = \frac{4\pi\left(N_a^{2/3} r_a^2\right)}{\pi r_a^2} = 4\left(N_a^{2/3}\right)$$

The fraction of surface atoms N_s to the total number of atoms N_a is:

$$\underline{F_s = \frac{N_s}{N_a} = 4\left(N_a^{-1/3}\right)}$$

Source: R.L. Johnston, Atomic and Molecular Clusters, Taylor & Francis, London (2002)

So, that is done here, you can see that $F_s = \frac{N_s}{N_a} = 4(N_a)^{-\frac{1}{3}}$ where N_a is the number of atoms sitting in the spherical cluster correct. That is something which is mathematically derived in the last lecture, and you probably have understood it right. In case you have not understood it, please do yourself, this is a very easy thing to do in perfect spherical cluster ok.

That is basically comes from these number of atoms or the number of sitting on the surface area divide by the surface divide by the cross-sectional area of the atom right. $\frac{S_c}{Aa}$ as you can see this $4\pi R_c^2$ that is equal to this parameter divided by πr_a^2, the surface that is the area of the atom, r_a is the radius of the atom. We are assuming several things here, we are assuming the spherical cluster, hard sphere model of atoms.

And the spherical cluster is packed such nicely that the free space is very minimal, we are ignoring even the free space ok that is not 100 percent correct.

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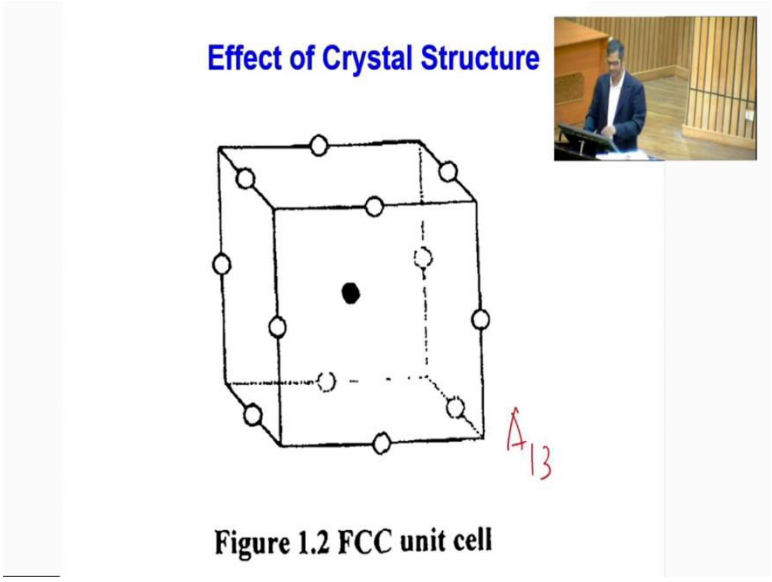

Effect of Crystal Structure

Figure 1.2 FCC unit cell

So, by doing that, we can actually arrive something formally, but then, you know most of the crystals does not form spherical type of structures, they have a different shape other than sphere, and which is dictated by the underlying crystal structure. So, the crystal structure actually affects significantly, these shape or the in fact, these number of surface atoms or the fractional surface atoms that is obvious. Because if you consider an FCC structure, you know that this is the structure of FCC which is shown on your screen, as you see here, there is a central atom if I put it around which there are 12 FCC atoms.

So, that is a 13-atom cluster, A 13 ok in which one of the atom is a bulk atom is all bond satisfied, but other 12 atoms are surface atoms right. So, that is our first cluster, first layer consisting of 12 atoms, if we consider FCC lattice correct.

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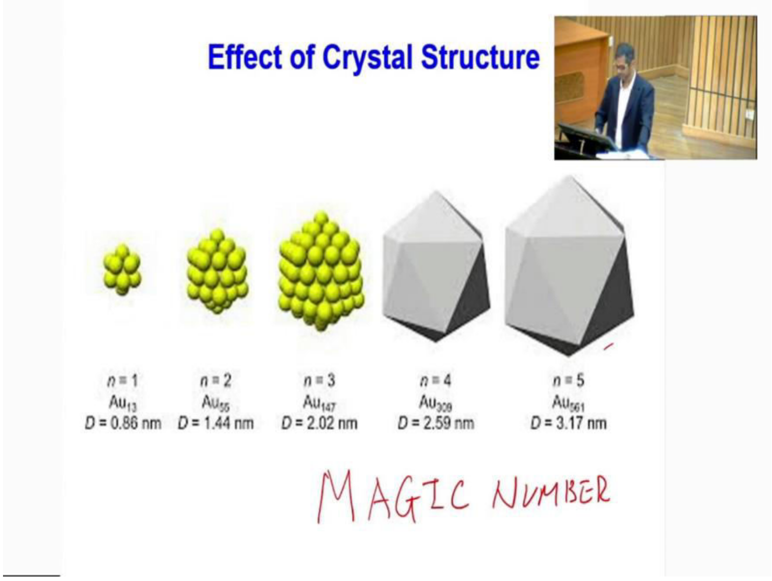

Effect of Crystal Structure

MAGIC NUMBER

So, you can have put around the second clusters if you do that, you need about 22 ok, you need about 55 atoms. So, that means, in the second layer we will have about 40 new atoms right that is possible. But you know FCC crystals does not form cuboid or cubic structure, they actually form what is known as a cuboctahedral structure, it is a 14 phase solid ok, this is what is shown here. In fact, some of these we will discuss today.

This cuboctahedral cluster or the things actually is what is predominantly observed because that is the surface energy minimized structure. And if you keep on adding those kind of class shape of layer of atoms, then you grow these clusters from single layer to double layer to triple layer to 5 layer structures. And in that case, your peculiar numbers come into picture: 13, 55, 147, 308, 308 or 306 308, 561 and they are called magic numbers, these numbers are called magic numbers.

This is very important concept, it is present in chemistry, physics even for electronic structure also right.

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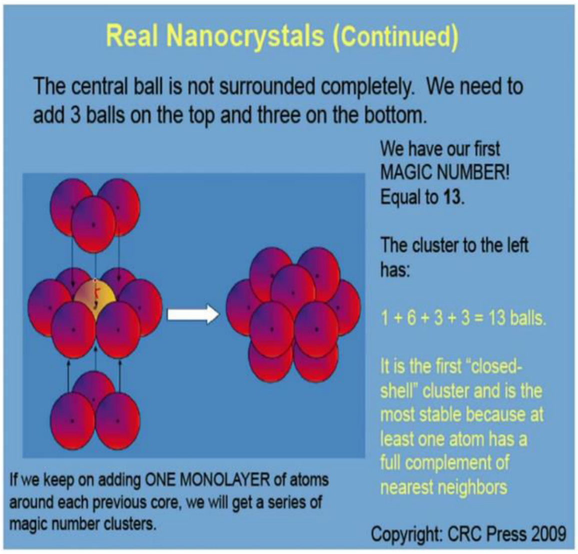

Real Nanocrystals (Continued)

The central ball is not surrounded completely. We need to add 3 balls on the top and three on the bottom.

We have our first MAGIC NUMBER! Equal to **13**.

The cluster to the left has:

1 + 6 + 3 + 3 = 13 balls.

It is the first "closed-shell" cluster and is the most stable because at least one atom has a full complement of nearest neighbors

If we keep on adding ONE MONOLAYER of atoms around each previous core, we will get a series of magic number clusters.

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And that is something to explain it I told you how it is possible. If you call it a single layer that is one atom in the pink ball or the central ball here ok, the yellow color ball is surrounded by 6 pink color atoms. And then, you can put on the top 3 layer, 3 atoms in the bottom 3 atoms that is from fcc structure a, b, c. So, you have basically 1+6+6+3=13 balls.

So, it is the first closest shell cluster, it is more stable because at least one atom is full compensation of the nearest neighbors, one atom is the bulk atom rest is. So, if you keep on adding one, one monolayers atoms around the previous core, we will get a series of magic numbers that is what I discussed about it and this you should understand and remember very well.

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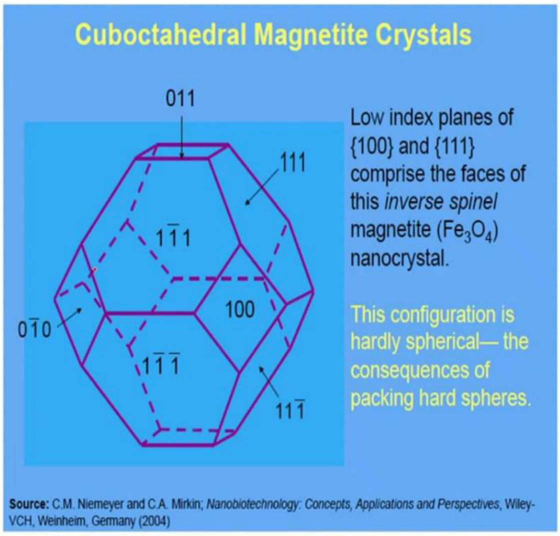

Cuboctahedral Magnetite Crystals

Low index planes of {100} and {111} comprise the faces of this *inverse spinel* magnetite (Fe_3O_4) nanocrystal.

This configuration is hardly spherical— the consequences of packing hard spheres.

Source: C.M. Niemeyer and C.A. Mirkin; *Nanobiotechnology: Concepts, Applications and Perspectives*, Wiley-VCH, Weinheim, Germany (2004)

So, in a cuboctahedral shaped crystals, you have 111 facets, 110 facets and 10 facets right so, that is how actually the configuration is formed. But, why this cuboctahedral kind of shapes form at all? that is because of surface energy minimization ok which is we are going to discuss today.

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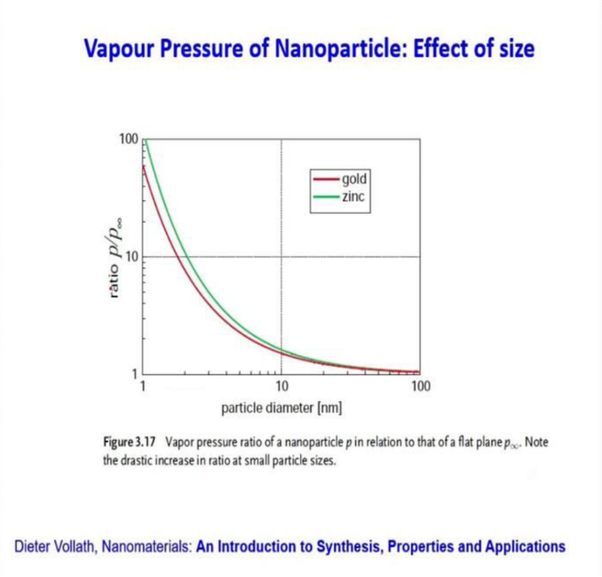

Vapour Pressure of Nanoparticle: Effect of size

Figure 3.17 Vapor pressure ratio of a nanoparticle p in relation to that of a flat plane p_∞. Note the drastic increase in ratio at small particle sizes.

Dieter Vollath, Nanomaterials: **An Introduction to Synthesis, Properties and Applications**

Well, so, let us start with that, then I talked about vapour pressure effect, vapour pressure is dependent on the size for the gold and zinc I have shown as the particle size decreases, vapour pressure ratio $p\backslash p_{\infty}$ increases very rapidly, goes up to about 50 to 100 times ok, that is the very important aspects of the things.

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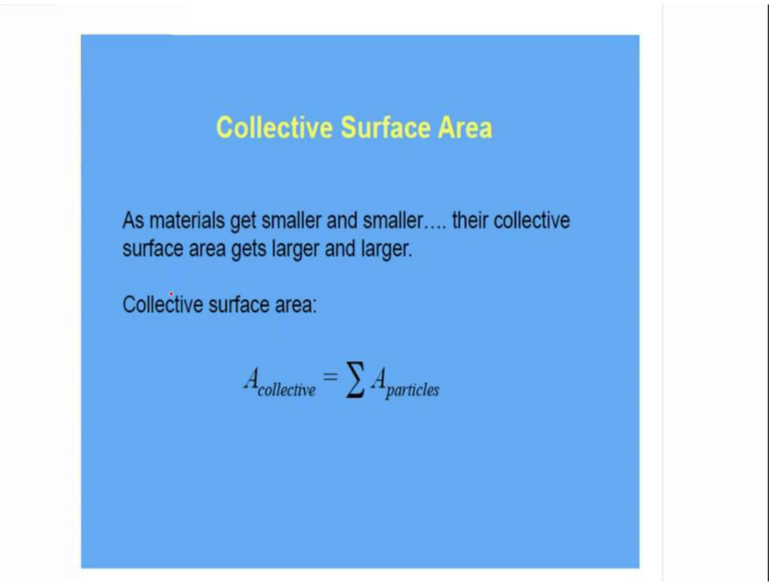

Collective Surface Area

As materials get smaller and smaller…. their collective surface area gets larger and larger.

Collective surface area:

$$A_{collective} = \sum A_{particles}$$

Well, let us now start the lectures today that is almost about 10 minutes or 8 minutes we discussed. Now, as the material goes smaller, their collective surface area becomes larger and larger or the surface to volume increases right. So, it is this collective surface area what dictates the total surface energy. When you multiply the specific substance with the collective surface area, you get total surface energy and that is what actually is important having important role in dictating the shape of the nanoparticles ok. You may be thinking how? Let us discuss a little bit about it.

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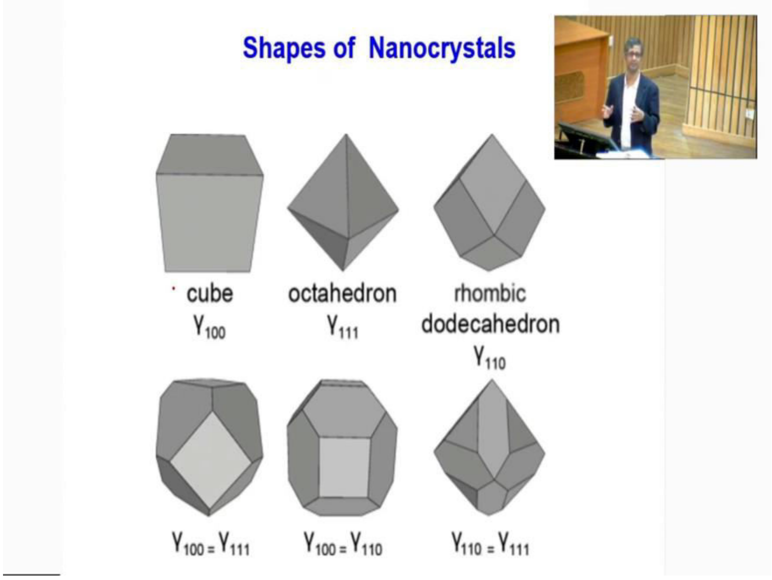

Shapes of Nanocrystals

You know crystals have many shapes, you can have initial crystals of a cuboid shapes, the facets of the initial crystals is bounded by 11, 10 type of surfaces. You can have octahedron ok, there are few crystals which is from zinc sulfide actually all this forms octahedron type of things. Octahedron is nothing, but a 8 equilateral triangles connected together. You can have rhombic dodecahedron ok, you can have even other kind of structures possible ok.

So, why this kind of things forms? Something is written at the bottom of each figure. For the cubic, the surface energy of 110, 100 surface is the least that is why it forms a cuboid. In octahedron, 111 facets of the least surface energy that is why all the surface are bound by 111. The rhombic dodecahedron it is 110 surfaces has the least energy. On the other hand, you have complex shapes like cube many many of them are shown at the bottom ok, I do not remember all of the shapes.

But for each of these surface energies will obey such a kind of rules and regulations, these are all nicely documented.

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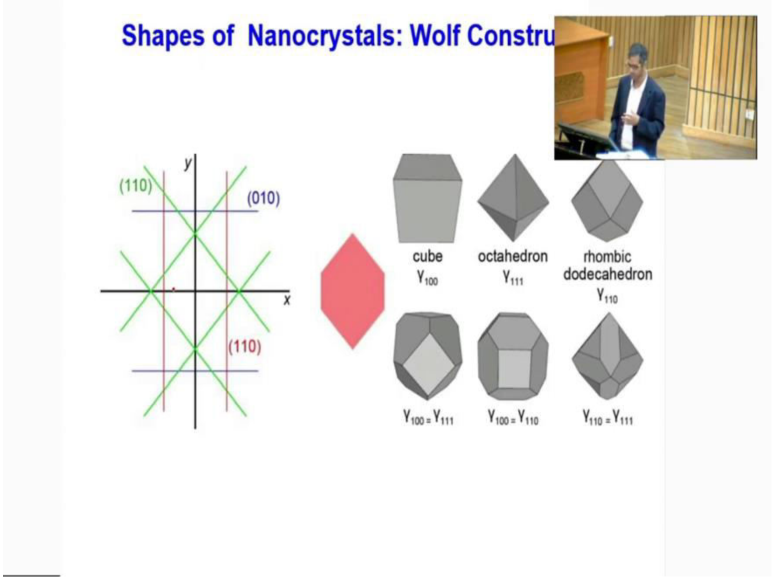

Shapes of Nanocrystals: Wolf Constru

Now, why it happens so? That is something which bugs everyone right. Well, to understand that we should discuss about something known as Wulff constructions. Long back in 1901, Wulff actually first time discussed about this and that is why it is name known by Wulff constructions ok that is something which you should know ok.

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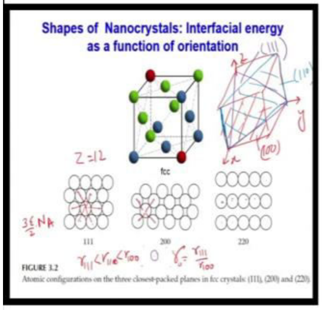

Shapes of Nanocrystals: Interfacial energy as a function of orientation

FIGURE 3.2

Atomic configurations on the three closest-packed planes in fcc crystals: (111), (200) and (220).

Before I discuss about it, let us talk about how this aspect is important for a cubic crystals. Well, you know in a cubic crystal, there are three important planes. First one is 10 or 20 ok, here it is written 20 because to make a similarity, but let us consider its 10 and then, you have 11o, o corresponding to 0 actually in my language please remember that, basically it helps you to remember that is why so, 100 to 110 and 111 planes and if you forgotten, let me again draw and show you so that you remember it ok, this is the cubic crystal, I am drawing it a little bit at an angle so that you can see it nicely.

So, this is x axis ok let us erase it out, it does not look good x, y and z right. So, for me 111 plane is the 11 sorry 100 plane is this right. Now, I use different color to use to make the other planes. So, I am making 110 plane which is this correct right that is my 110 plane right. You must know the Miller indices concept ok. Now, I will use another color to paint 111 plane right that is my 111 plane.

Now, you have the corresponding fcc crystal structure with atoms there. So, if you look at the atomic configuration on 111 plane, this is basically closed pack, 1 atom surrounded by 6 atoms. But if you look at 110 plane that is my this plane so, you can see there are 4 atoms, this 4 atom and there is a central that is a face centered atom ok that is obvious which is this or this that is this one right correct. So, there are two atoms, so it will sit on each other because they are taking a position right.

So, that is nothing, but this atom and there are 4 atom like this correct and this there are two atoms here that is what I am drawing a dot and a circle. Then, on the other hand, this 10 facets is this like this right. You can see that there are 1, 2, 3, 4 atoms and then, there is a central atom right which is missing here, not shown. So, therefore, it will be like this correct ok oh wrong, this is wrong basically, there will be no such atoms situating there, it will be like this ok. Now, let us consider this kind of structures.

So, this is the atomic configurations of the three closest pack or three planes actually, I will not take closest pack in fcc crystal 111, 200 or 1, 100 and 220 ok. So, now, as you can clearly see if these are my surfaces, suppose, suppose 111 is my surface, let us consider for the sake of understanding. So, as you can see that for each atom, three bonds are missing, how may you thinking how?

Obviously, if I consider this atom, if I consider this atom central atom, it is bonded with 1, 2, 3, 4, 5, 6, at the bottom also is bounded with 3 and fcc has a coordination number of 12. So, that means, how many atoms are missing? 3 right, 3 atoms are missing, 3 top atoms are missing. So, 3 bonds are missing ok, am I clear for each atom. So, as you know very clearly right if the bond energy says epsilon so, this basically $\frac{3\epsilon}{2}$.

Now, if I 1 mole, I can write down N_a, that is my surface energy of 111 facets. What about this? If you clearly see each atom is having 4 nearest neighbors, but in fcc unit cells will be more required because z is 12. So, that obviously, then surface energy if number of bonds broken everything and it is higher, same thing is true for these atoms also correct. So, that is why γ_{111} is least and this is how this relationship holds to any cubic structure.

So, depending on the crystallographic plane surface energies are going to be varying, this is a well-known fact ok. In fact, surface energies are anisotropic that means, surface energy of these planes are not same, had it been same we could have told this is told that this is isotropic. But because it is they are not same, this is a case of anisotropic surface energy correct.

So, always you define anisotropic things like ok a parameter kind of this ratio between surface energy of 111 plane by 100 plane that is obviously, less than 1, it is a fraction, there is 111 plane is the least surface energy plane having least surface energy they compared to 1o plane.

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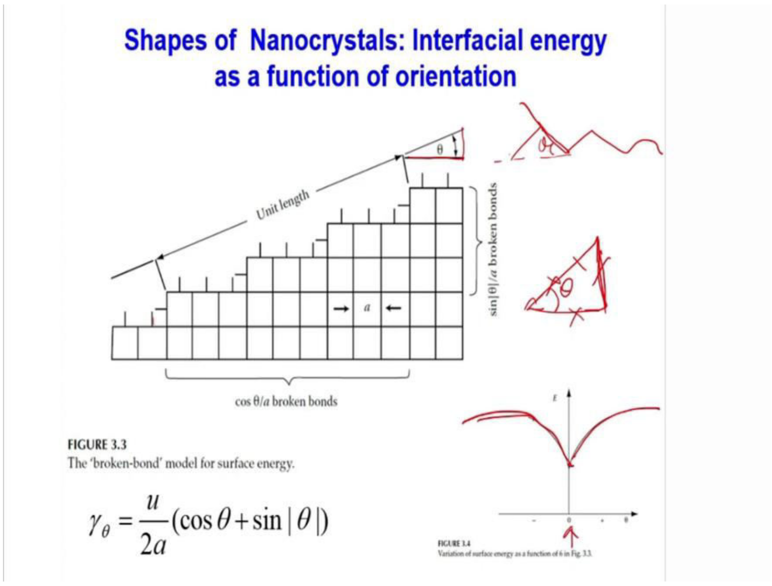

Shapes of Nanocrystals: Interfacial energy as a function of orientation

FIGURE 3.3
The 'broken-bond' model for surface energy.

$$\gamma_\theta = \frac{u}{2a}(\cos\theta + \sin|\theta|)$$

FIGURE 3.4
Variation of surface energy as a function of θ in Fig. 3.3.

So, upon knowing these facts so, that means, so, interfacial energy is in a crystalline structure is a function of its orientation of the plane so, how can we put it into picture? Well, let us say suppose that this is a plane which is at an angle theta with respect to one of the closest packed planes, you are not able to understand. Surfaces will be like this right so, I am talking about this surface.

Let us suppose this surface is making an angle theta that is what is shown there theta with respect to one of the closest packed plane, close pack plane can be 111, 11 bar 1 so, many there are two planes are there one, one type right. So, now, if you look at if you want to measure the surface energies of this two-dimensional plane, what you need to know is the number of broken bonds. So, what are the number of broken bonds on these horizontal thing? That is $\frac{cos\theta}{a}$, a is the spacing between the two planes and what is the number of broken bonds on the horizontal vertical things?

See you are, you may be thinking what is horizontal, vertical, why sir is talking like this ok? Horizontal things are this ok, which are lying like that, and vertical things are this right. So, this is I am talking about sin is this, cos is this right because this is the length. So, with respect to this length, sin, cos you can easily understand right. Sin is this length divided by this length; cos is this length by this length. So, finally, this becomes a common length.

So, therefore, this is equal to sin mod theta by a number of broken bonds will be broken. So, you can add them together, it is become $\frac{u}{2a}(cos\theta + \sin|\theta|)$ where a is used in the number of bonds is a bond energy its basically. So, now, because it is orientation dependent, it is theta dependent so, I can plot surface energy correct and this we will looking like this, surface energy will be small or minimum for the closest packed plane.

So, you have, you have drawn these things as a function of theta which is nothing, but angle this plane is making with one of the closest packed plane. So, if that is my reference point, surface energy will minimum on the closest packed plane and slowly it will increase and taper out. This is what has been observed, this is what has been measured, this has been calculated. So, two things you could connect right, first is that crystallographic planes so, we have fcc crystal have different number of broken bonds per unit area, so they have different surface energies, different value of gamma.

Here, gamma is the specific surface energy per unit area right, we are talking about that, please remember this I should not come again and again on the same concept. And this is now connected with a generalized concept. Why you will be talking about only fcc or something? It can be true for any crystalline structures, generalized conceptually it will look like this I am sorry we are not discussing with 3D, because the equation will looks a little bit complex and explaining that may take more time and you may need to study also more. So, 2D is very easy to understand.

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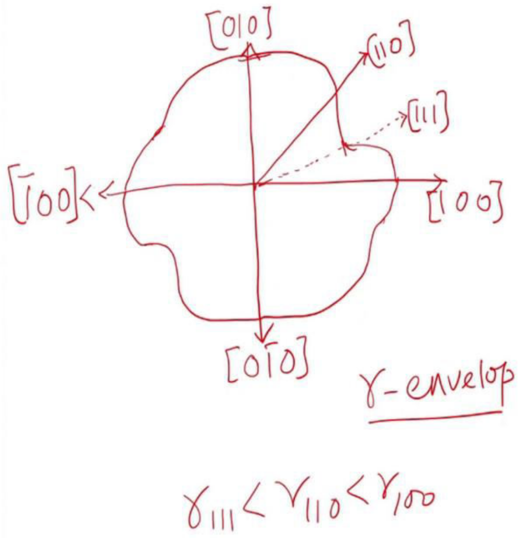

Now, do this very simple thing, let us suppose make us make it 2D things. As you know in a cubic crystals, directional planes are perpendicular to each other. So, let us suppose this is my 100 direction and this is my 010 direction right so, this will be my $0\bar{1}0$ direction and this will be $\bar{1}00$ direction. I think I should draw it much better way so that you do not forget right ok.

So, now, knowing this, what is my 110 direction? That is basically these are the two vectors 010, 100 so, addition of that that will be lying at a 45 degree am I clear. So, what is then 111 direction? Where it will lie? Ok so, that is between this and the z axis because this axis is my 001 direction this one right, this is my perpendicular this is my 01 10 directions.

So, this will lie somewhere there vertically this plus this so, if I project it, it will be lying here not clear. Well, that is not difficult. Why it is not difficult? Because, my 01 direction is vertical with respect to this plane of the screen. So, if I want to have 111 direction, so I must have a vector addition of 110 and 001. So, this vector addition will lie on the vertical plane. So, I am projecting here right that is all.

So, now, this is my one quadrant, you can do other quadrant also, easily you can do yourself, I think it is you should better do that. So, now, I know the surface energy is maximum along these directions, minimum along this direction like 111. And intermediately, it will be along 110 right, you know that, $\gamma_{111} < \gamma_{110} < \gamma_{100}$ so, I do it.

So, I make a plot like that right I can do it for everything, I can do it here also right. So, that is my gamma envelope on a 2D for an fcc crystal. This is gamma envelope, what does it indicate? It shows how gamma is varying as a function of orientation theta and this is known, this is known to us, long back this is known to us. Oops! this is not correct, it is something like this, it will look like ok. So, even you can do better on this side.

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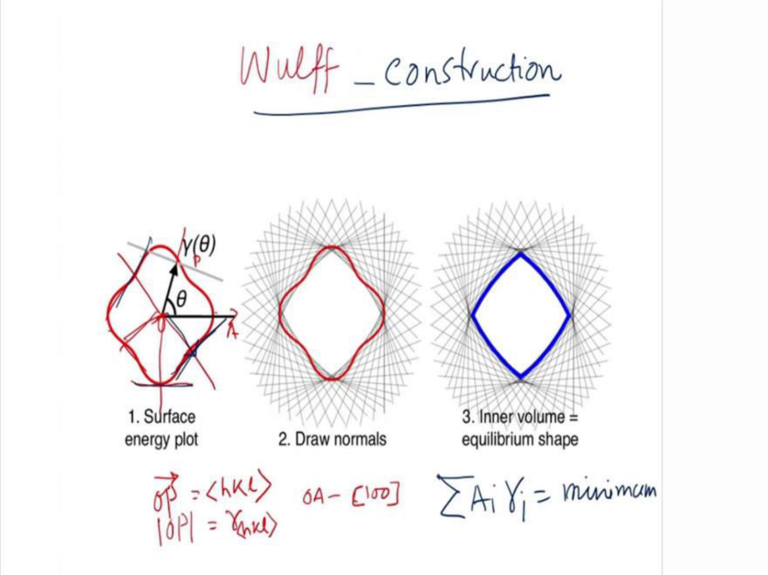
Wulff _ construction

1. Surface energy plot

2. Draw normals

3. Inner volume = equilibrium shape

$\vec{OP} = \langle hkl \rangle$

$|OP| = \gamma_{\langle hkl \rangle}$

OA – [100]

$\sum A_i \gamma_i$ = minimum

So, this is what is my gamma envelope; this is what is my gamma envelope, what I can do, ok? So, in order to create the structure inside it, what is done is very simple that is what is known as Wulff construction. So, now, what is done? So, this is one such plot NOD ok what I have drawn, this is one better way I have drawn ok. These are your 1110 directions ok, this one, this one. So, to have a Wulff construction, what you do is very simple.

You draw a vector, this is a vector suppose lied at a point P, this is O so, OP is a vector and now, |OP| is telling me one of the direction crystallography, it can be any directions, any odd direction. Obviously, if you draw this way, this is this direction suppose this is OA, OA is for me is 100 direction right. For OP is in general direction, which is <hkl>, hkl can be anything, hkl is <hkl> are each of these are actually Miller indices.

So, now, what I do? I and the magnitude of this vector is basically $\gamma_{<hkl>}$ as cubic crystal planes and directions are normal so, this is $\gamma_{<hkl>}$ plane only ok. So, now, then, what I do? Then I take a tangent at the point p on this curve right ok, I can do that, you can see that. So, if I do that and if I do for every points on this curve like that I draw another normal, another normal sorry another normal here, another one here, another one there, like this and you can do this like that ok.

Or let me use a different chalk color that is what is done in the next these normal sorry, it is not tangent, normal ok. You are drawing a normal at this point with respect to this vector. If this is the vector, you are drawing a normal. So many normal are drawn. Now, if you connect them, what is the thing you get is the equilibrium shape and this is known as a Wulff construction. This is very easy right, this is not difficult to do, provided you know the surface energy as a function of theta orientation.

The moment you know that, then it is very easy to do, it is not difficult at all. So, that means, first and foremost thing is these aspects. Now, once you do that, then you can get this equilibrium shapes, the shapes which will be having the lowest minimum. Remember the conditions which you are using in doing that is this, that means, we are minimizing this $\sum A_i\gamma_i$ where A is the surface area, γ is the surface specific surface energy.

So, total surface energy of the system is minimized, the moment you do this construction, this can be mathematically proved, theoretically sorry, can be proved by even construction wise. But let us not get into all these difficulties, just try to understand what is the Wulff construction? how this construction can give you such a kind of important equilibrium shape of a crystal correct.

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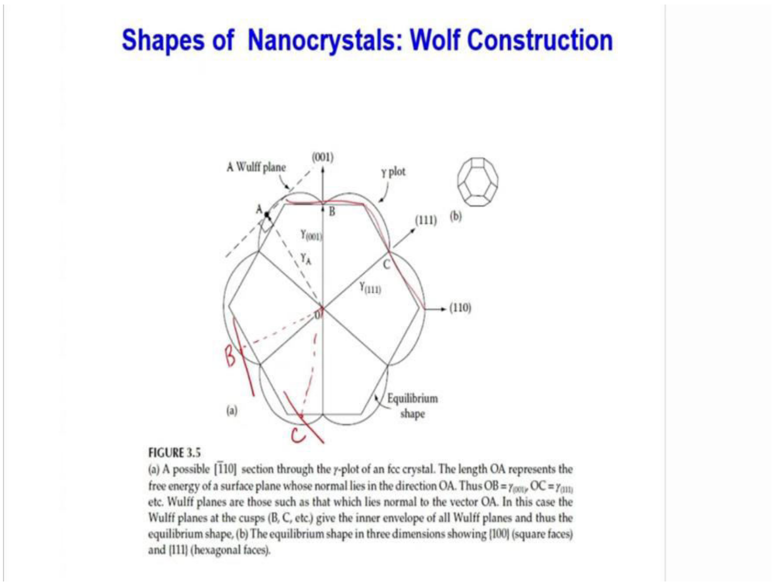

Shapes of Nanocrystals: Wolf Construction

FIGURE 3.5

(a) A possible $[\bar{1}10]$ section through the γ-plot of an fcc crystal. The length OA represents the free energy of a surface plane whose normal lies in the direction OA. Thus $OB = \gamma_{(001)}$, $OC = \gamma_{(111)}$ etc. Wulff planes are those such as that which lies normal to the vector OA. In this case the Wulff planes at the cusps (B, C, etc.) give the inner envelope of all Wulff planes and thus the equilibrium shape, (b) The equilibrium shape in three dimensions showing {100} (square faces) and {111} (hexagonal faces).

This again shown here very nicely, what you can see here is that this outer envelope, the curved one is basically a surface energy isotropic, sorry surface energy plot as function of theta correct. Now, if I draw one of these vectors from this origin to this and this vector is corresponding to a atomic or the planar direction right and then, I take a normal to that thing on that point a correct, you can see that this is a normal drawn, the dotted line is a normal drawn that is what is known as a Wulff plane.

I am sorry I am making all this mistake on Wulff ok, I should correct it ok, here I made a mistake I am sorry about it this should be ok please correct it that is what is done. So, you can do it right for any such plane. Suppose if I draw it here at this point, then I draw a normal, this is my OB, you can draw it anywhere, you can draw it here, you can draw a normal, this is OC like that. Then, the inner envelope which you join is basically the equilibrium shift.

You can clearly see this is in cuboctahedral shape terminal in 2D correct and equilibrium shifts in the crystal is showing 100 ok or 11 hexagonal faces. So, that is few thing actually you can see that 111 facets, these are 111 facets and 100 facets, there is no 110 facets, 110 is this direction so, there is no facet perpendicular to that. So, this has only two facets ok. I hope it is clearly understood to you, we can discuss further.

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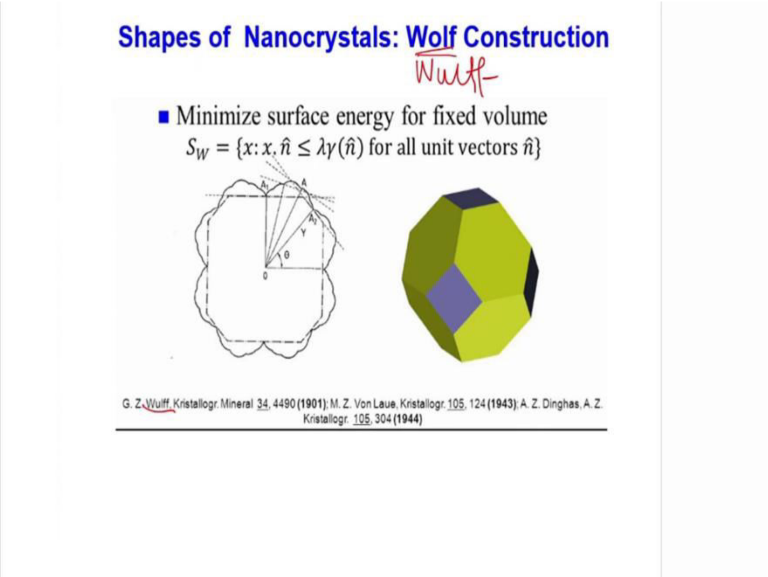

Shapes of Nanocrystals: Wolf Construction

Wulff

- Minimize surface energy for fixed volume

$S_W = \{x : x.\hat{n} \le \lambda\gamma(\hat{n}) \text{ for all unit vectors } \hat{n}\}$

G. Z. Wulff, Kristallogr. Mineral 34, 4490 (1901); M. Z. Von Laue, Kristallogr. 105, 124 (1943); A. Z. Dinghas, A. Z. Kristallogr. 105, 304 (1944)

So, shapes of nanocrystals is I see some people use Wolf, but basically in German terms, it is Wulff's ok, this is what it is, but people write it Wolf ok. So, let us talk about that exactly same thing shown here. Even you have arbitrarily surface energy and then, you can draw these normal and do this, I am doing it again that this is a cuboctahedral shape. So, this is the reason why fcc crystals or fcc structures, they show such a kind of a cuboctahedral shapes.

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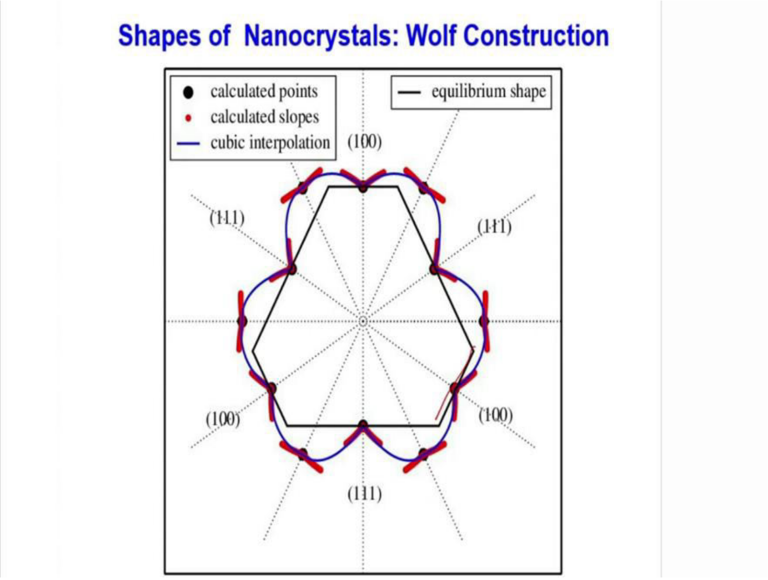

Shapes of Nanocrystals: Wolf Construction

Again, I am showing you some arbitrary shapes, you can see here it is very peculiar shape, actually ok. Here, you have 110 facets and 111 facets right. So, this is the surface energy envelope and each one is shown by such a kind of nice points, you see here, this, these points are shown. So, you can generate the shapes right if you know this, it is not difficult at all for you now ok.

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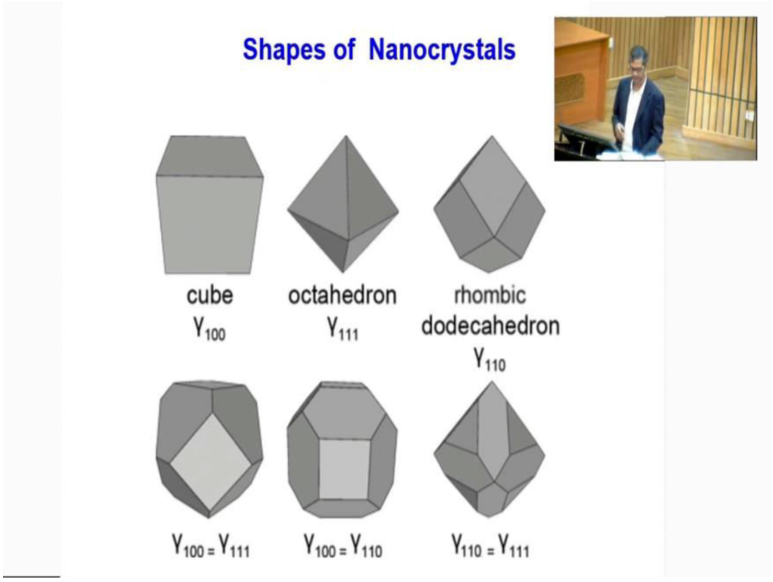

Shapes of Nanocrystals

So, I will just go back and to my this crystallographic shapes here. So, all these shapes are basically because of this aspect because of the Wulff constructions. When you have different kinds of surface energy comes into picture, comes into play, this kind of shapes will be generated that is a cubic, octahedron or a rhombic dodecahedron or such a kind of peculiar shapes only when these conditions will be satisfied.

So, therefore, actually in the real world, different shapes form because of minimization of the surface energy, I just discussed about it and this is manifested by the Wulff construction, the manifestation by Wulff construction. So, Wulff's original paper came in 1900 almost like 120 years ago, this is a classic paper. So, that is basically that shows how we can understand the shape evolution of the crystals. Remember in 1901, people even did not know nanocrystals, but people have seen natural crystals, different kinds of natural crystal available in the real world.

So, those natural crystals actually have different shapes like ice crystals or maybe diamonds or some other crystals from there, people are intrigued by the shapes and other things. And that is how actually these concepts of this shape business came into picture. Well, so, that is something which you need to understand very well ah. So, on the basis of this calculating surface energy, equilibrium crystal shapes can be created ok.

And mostly, cubic shapes, crystal structures have a cuboctahedral shapes always observe in the real life and that is something we should you should always remember that ok. So, I think with this, I will stop the today’s lecture, because this is a big concepts which I thought I should discuss with you in detailed manner. And, that is the reason actually I started with a very simple thing and then, I went on it. So, let me just summarize these lectures.

So, after I talked about some recap of the previous lecture, lecture number 7 on different things mostly magic numbers. Then I went ahead talked about why different shapes of nanocrystals are possible and to discuss that, I talked about examples of fcc. And fcc has three important planes; 111, 110 and 100 and their relative surface energies are discussed.

From there, I draw on the 2D surface energy, landscape as a function of orientations and then, I discussed with the Wulff constructions, how we can arrive at equilibrium shapes. This is something which you would remember always, because these questions will keep on coming to your mind or coming to you may be asking to this various instructor, why this crystal have this kind of shapes that is mainly because of these particular aspects. So, virtually, it tells you the surface energy to minimize that is $\sum A_i \gamma_i$ should be minimized that is what it tells you.

So, in next lecture, we will talk something else about surface energy related things mostly some fundamental concepts, then we will wind up and move ahead with thermodynamics aspects of that ok.