Nanostructures and Nano Materials: Characterization and Properties

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Lecture - 12
Surface Effects and Physical Properties of Nano Materials

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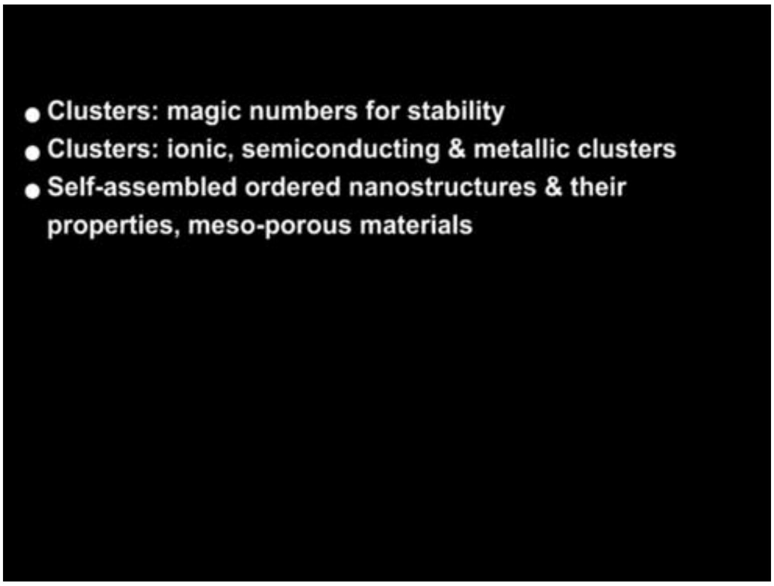

- Clusters: magic numbers for stability
- Clusters: ionic, semiconducting & metallic clusters
- Self-assembled ordered nanostructures & their properties, meso-porous materials

Let us consider a few more points about clusters, and importantly about what we call the magic numbers associated with some of these clusters.

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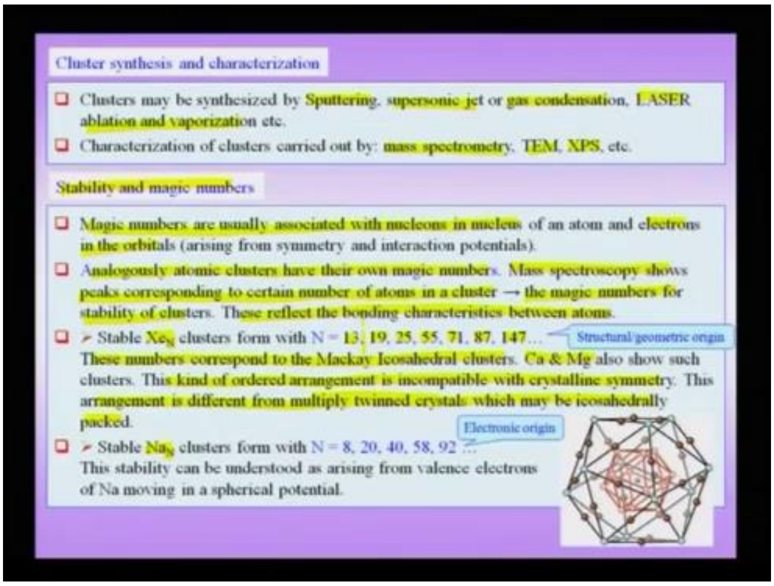

Cluster synthesis and characterization

- Clusters may be synthesized by Sputtering, supersonic jet or gas condensation, LASER ablation and vaporization etc.
- Characterization of clusters carried out by: mass spectrometry, TEM, XPS, etc.

Stability and magic numbers

- Magic numbers are usually associated with nucleons in nucleus of an atom and electrons in the orbitals (arising from symmetry and interaction potentials).
- Analogously atomic clusters have their own magic numbers. Mass spectroscopy shows peaks corresponding to certain number of atoms in a cluster → the magic numbers for stability of clusters. These reflect the bonding characteristics between atoms.
- ➢ Stable Xe_N clusters form with N = 13, 19, 25, 55, 71, 87, 147… These numbers correspond to the Mackay Icosahedral clusters. Ca & Mg also show such clusters. This kind of ordered arrangement is incompatible with crystalline symmetry. This arrangement is different from multiply twinned crystals which may be icosahedrally packed.
- ➢ Stable Na_N clusters form with N = 8, 20, 40, 58, 92 … This stability can be understood as arising from valence electrons of Na moving in a spherical potential.

Structural/geometric origin

Electronic origin

Clusters can be synthesized by various techniques like spattering, supersonic jet or gas condensation, laser ablation, vaporization, etcetera. Some of these clusters are very suitable for ceramic materials or others very may be good for carbon and other specific kind of compounds, which might be, whose clusters we want to construct.

Characterization of clusters requires important techniques like mass spectrometry which not only does us the mass of the various a species which are produced during a certain process, but also helps a separate out the various clusters which may be produced as the mixture in the original process. Transmission electron microscopy can give us the local structure of these clusters and also the defect structure within these clusters, except photoemission, spectroscopy, etcetera; other techniques which can add to our information that we gain about the clusters. We had been mentioning about the stability of certain number of atoms ions or molecules in a cluster.

So, let us see what is the origin of the stability, and what kind of numbers they are going to encounter when we talking about these magic numbers. We typically encounter magic numbers though it is not often stated that in that language, that magic numbers are usually associated with nucleons in the nucleus of an atom and the electrons in the orbitals. You already know that person, suppose I have a S orbital, then I know that only two electrons can sit there. The orbital can accommodate 6 of them, and I also have the formula, something like 2n square, which could open the particular shell.

Therefore, though we do not often say this, it is obvious that given Pauli's exclusion principle and the Hund's rule, we know that only a certain specific number of electrons can be accommodated in an particular electronic configuration. And these can constitute what may call magic numbers at the level of the atom when we are talking about the electronic contributions.

Similarly, nucleons also have their own magic numbers that means, not at any set nucleons are allowed within the nucleus. But the term magic number is not often used to refer to these kind of numbers which come out of such an, what you me to call in filling rule, or such an kind of an electronic configuration. But in the case of these clusters this is of more often than not a term which is used. Analogous to these terms which we are using for electronic or nucleonic configuration, are atomic clusters having their own magic numbers. Mass spectroscopy shows peaks corresponding to certain number of atoms in a cluster.

The magic numbers for stability of clusters, these are the magic numbers we are talking about. These reflect the bonding characteristics between the atoms therefore, what we are saying here is that, when I make up have a process in hand where in clusters of various sizes can be produced simultaneously, then I would find that not all clusters are equally abundant. In other words, there are peaks corresponding in the mass spectrograph to certain number of atoms in a cluster.

And the reason behind this is obvious that, these clusters are more stable than the others, and that is why they are produced in higher abundance in corresponding to other clusters, which may not be that stable. Couple of examples we see here first, we can talk about xenon, which is a noble gas, and sodium clusters. The subscript here and refers to the number of atoms in a cluster. So, suppose I am talking about the stability of xenon clusters, then we find that those clusters with 13, 19, 25, 55, 71, 87, 147, etcetera atoms are more stable, then say for instance a cluster with something in between like a 15 atom, a 16 atom, or a 17 atom cluster.

Now, these numbers, why are these the automatic question arises, why are certain number of atoms in a cluster more stable than the others. And there two reason as we shall see in the next slide, but one of the reasons is that, these numbers correspond to the Mackay icosahedral kind of a cluster. And xenon is of course, not the only example, couple of more common examples are calcium and magnesium, and they also show these exact precise kind of a wood mead called magic numbers. This kind of an ordered arrangement is in-compatible with this crystalline symmetry. This arrangement is different from multiply twinned crystals which may be icosahedral packed.

So, in the case of xenon, we noticed that certain magic number of clusters are more frequent than the others. And this is similar to the case for calcium and magnesium also. And when we talking about the 19 atom cluster or a 25 atom cluster, this is not a crystalline packing, it is a packing with icosahedral symmetry, which is different from what you might call a crystalline kind an order which is a long-range order. And it is also different from multiply twinned crystals, which may also makes some of this symmetry.

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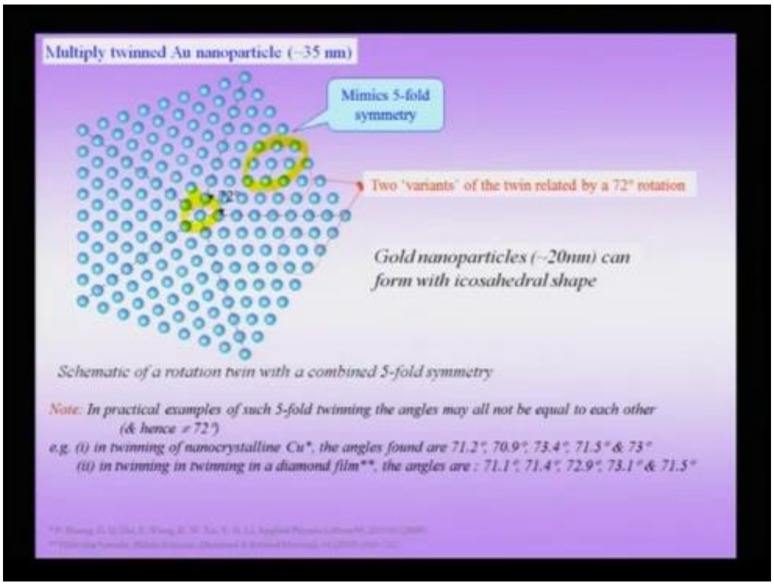

Multiply twinned Au nanoparticle (~35 nm)

Mimics 5-fold symmetry

Two 'variants' of the twin related by a 72° rotation

Gold nanoparticles (~20nm) can form with icosahedral shape

Schematic of a rotation twin with a combined 5-fold symmetry

Note: In practical examples of such 5-fold twinning the angles may all not be equal to each other (& hence ≠ 72°)

e.g. (i) in twinning of nanocrystalline Cu, the angles found are 71.2°, 70.9°, 73.4°, 71.5° & 73°*

*(ii) in twinning in twinning in a diamond film**, the angles are : 71.1°, 71.4°, 72.9°, 73.1° & 71.5°*

And in a few slides back, we had all in fact, talked about some such example of a multiply twinned crystal and we have pointed out that, often this kind of a system would mimic a symmetry higher than that present actually in any one of the crystalline variants.

When this is a crystalline variants and with also pointed out that, in the case of nano crystals or a nano particle, this kind of tuning may be more feasible because of the lack of constraints of bulk as compared to, as compared to the bulk crystal, wherein such kind of a tuning may not be that easy.

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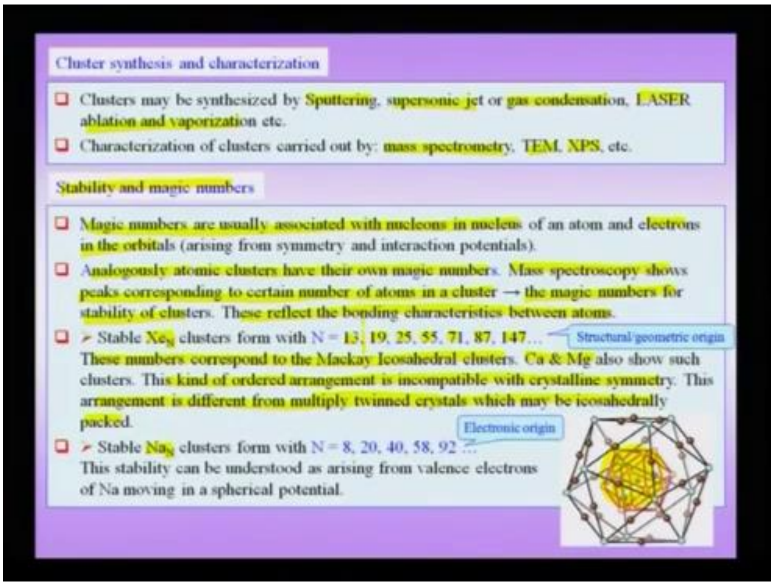

Cluster synthesis and characterization

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Structural/geometric origin

Electronic origin

Therefore, the stable xenon clusters have certain numbers which stabilize them, and these are the magic numbers. And these clusters can have what you might call in, they are coming from the geometrical origin of packing around with a symmetry which is like the icosahedral symmetry. On the other hand, if we took at a sodium N cluster, a different set of magic numbers emerge. In other words, the first thing we notice that, there is no universal set of magic numbers.

And depending on the kind of effect we are taking to account, and the kind of system you are talking about there are a set of magic number which evolve. In the case of sodium, we note that not again, not all the numbers are equally probable, numbers like 8, 20, 40 58, and 92 atom clusters are more stable than the other ones for instance at 12 atom cluster or 14 atom cluster.

So, this stability can be understood as arising from balance electrons of sodium moving in a spherical potential. We will have a little more to say about this in the coming slides, and also a lot more to say perhaps later, but essentially we see that, to summarize the slide two import ((Refer Time: 07:32)) come out, number one that not all clusters are equally stable, number two there are magic numbers associated with the stability of clusters.

These number three, these magic numbers are system depended and the reason behind this magic numbers is also not the same. So, suppose I want to understand this magic numbers.

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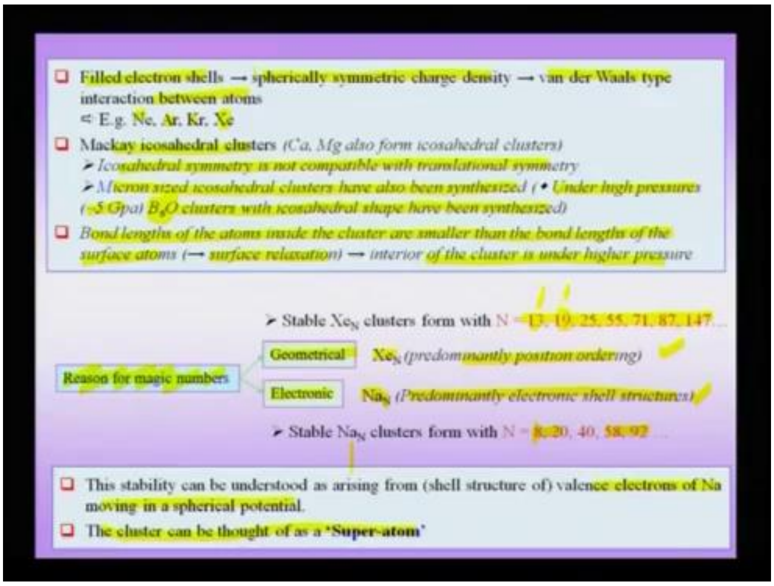

- ☐ Filled electron shells → spherically symmetric charge density → van der Waals type interaction between atoms
  - E.g. Ne, Ar, Kr, Xe
- ☐ Mackay icosahedral clusters *(Ca, Mg also form icosahedral clusters)*
  - *Icosahedral symmetry is not compatible with translational symmetry*
  - *Micron sized icosahedral clusters have also been synthesized (• Under high pressures (~5 Gpa) B_6O clusters with icosahedral shape have been synthesized)*
- ☐ *Bond lengths of the atoms inside the cluster are smaller than the bond lengths of the surface atoms (→ surface relaxation) → interior of the cluster is under higher pressure*

- Stable Xe_N clusters form with N = 13, 19, 25, 55, 71, 87, 147...

Reason for magic numbers

Geometrical Xe_N *(predominantly position ordering)*

Electronic Na_N *(Predominantly electronic shell structures)*

- Stable Na_N clusters form with N = 8, 20, 40, 58, 92 ...

- ☐ This stability can be understood as arising from (shell structure of) valence electrons of Na moving in a spherical potential.
- ☐ The cluster can be thought of as a '**Super-atom**'

I can think of that in two ways, one is geometrical reason, another is an electronic kind of a reason. Now, these filled shells of electron shells leading to a spherically symmetric charge density, lead to Van Der Waals kind of a interaction between atoms, which is, what is stabilizing. The kind of xenon clusters which is in no different in behavior from say the other inert glasses, like neon, argon, krypton. Because these filled electrons themselves do not have a propensity for bonding, like for instance an unfilled electron shell.

And therefore, the bonding between two atoms in a cluster is more of Van Der Waals type, and even when larger congregation of these atoms gives rise to crystalline array, even in that case, the bonding at the fundamental level between the atoms remains of the Van Der Waals stype. That means, that these obviously will have a very low melting point and also a very low perhaps a sublimation or vaporization point, vaporization point as compared to something which is covalently or ionically bonded.

In the case of the Mackay icosahedral clusters, we know that the icosahedral symmetry is incompatible with translational symmetry because this is the symmetry typically found in quasi crystals. Micron size icosahedral clusters also have been synthesized. Not only do we have small clusters which have icosahedral symmetry which is what we saw in the case of these numbers which are coming for instance 13, 19, 25, 55, etcetera. These are can be considered as small clusters because we have very small finite number of atoms, but much larger clusters.

And now we are talking about micron size crystals, I not crystals micron size icosahedral clusters have been synthesized and this can be thought of as in a massive achievement that means, it even in the micron sized clusters, we have manage to avoid crystallization, and we have maintained this what you might call in growing order from a point outward to get this kind of micron sized clusters.

So this is a very interesting kind of icosahedral cluster. We are talking about whose scale is not in the clue atom level, whose scale is not even in the nanometer level, but whose scale is now micron level. Under high pressures and we are talking about 5 giga pascals, B 6 O clusters with icosahedral shape have also been synthesized. So, these are couple of beautiful examples of not only of inert gas kind of an element which interacts with Van Der Waals type, but also even compounds which have been synthesized in icosahedral shape.

So, these are very interesting examples. Another important point to note in the case of these clusters, and again we are talking about small clusters here. Bond lengths of the atoms inside the cluster are smaller than the bond lengths of these surface atoms. That means, now we have already seen this that, surfaces is an important part of nano crystal or a cluster, may be small or big. And this is clearly seen in this example wherein the bond lengths are not uniform, the atoms inside the cluster are better bonded. I have a smaller lattice parameter or we can called it as lattice parameter inter atom distance, as compared to the atoms of the surface, which faces surface relaxation.

And hence, the interior of the cluster is under higher pressure. So, these are some important points we need to note here. Number one that though there is a tendency for larger clusters to not exist clusters, but become actually crystalline, but there have examples, specific examples wherein, larger size clusters have been synthesized. Second thing that the inner cluster, not all atoms are equivalent, not all bond lengths are equivalent and as expected, the surface atoms have a certain bond length, which is different from the atoms in the interior of the cluster.

So, we had said that there are two reasons, why we can have a magic number of atoms in a cluster. And we took to a typical examples for this, the xenon N, which is predominantly position ordering kind of a system, and the sodium N system, which is predominantly an electronic shell kind of a structure. In other words, here the stability is coming from geometrical reasons, and here it is coming from the electronic structure reasons.

So, there are two different reasons and we also seen the numbers like for instance, the numbers for the electronically stabilize structure is like we have seen is 8, 20, 40, 58 etcetera. While in the case of this icosahedral, what you might call close pack configuration because icosahedral kind of a confirmation gives us a close packing, but only in the short range. Because in the long range, we typically prefer have a crystalline kind of an order.

So, they have the a different kind of a magic numbers. Now, and we had already seen that, this stability in the case is sodium can be thought of a arising from the shell structure of valance electrons of sodium moving in a spherical potential. The important and the crust of the whole, this slide is that, this whole cluster can be thought of as an super atom. In other words, now we have the concept of an atom with, we know that whose stability depends on a certain kind of an electronic configuration that means, a filled shell would actually given atom is stability and electronic stability.

Similarly, here we are not taking about individual atoms constituting the basic building block, but the entire cluster behaving like a super atom. In other words now that is the reason that when I add a single atom to, for instance and 8 atom cluster or atom to a 13 atom cluster, I do not have a same as stable configuration. You require to add say from 13, 6 more atoms to about a 19 atoms before you have a stable cluster.

Because now, this is akin or very similar to our case of electronic configuration wherein, you have a filled or a half filled orbital which gives us a certain stability. And the origin of the stability to some to reiterate is coming, can coming from purely geometrical or structural factors or it can come from electronic reasons, in other words, electronic shell structures. And this whole cluster now can be thought of as a super atom, and if they have these magic numbers, then they are stable and this super atom can itself function as a building block in some kind of an hierarchical or a higher order assembly. And we will take up a few of these higher order assemblies as we go along in what we call an hierarchical construction.

So, I will summarize these two important slides, this in summary. There are some stable magic numbers available, these stable magic numbers of clusters have a structure which is very different from that of a long range crystalline order or some kind of defected crystal like a twinned crystal. These magic numbers can arise from geometrical or electronic stabilization, geometrical civilization implies that I am getting a close pack structure.

And in these kind of, sometime these clusters can be grown to larger sizes, and this whole cluster can behave like what you might call a super atom which itself can be the fundamental building block in a larger assembly. So, having made a cluster, we may want to ask some of the questions right here, and we need to utter a some issues. The answers for some of these questions will be perhaps I am not yet fully way understood, some of these questions may be answered later, but these are important questions before we go from the level of an atom to a cluster which you have already achieved, to a much larger unit like a crystal. And we have already asked some of these questions, like what is bulk, what is a bulk like property, etcetera.

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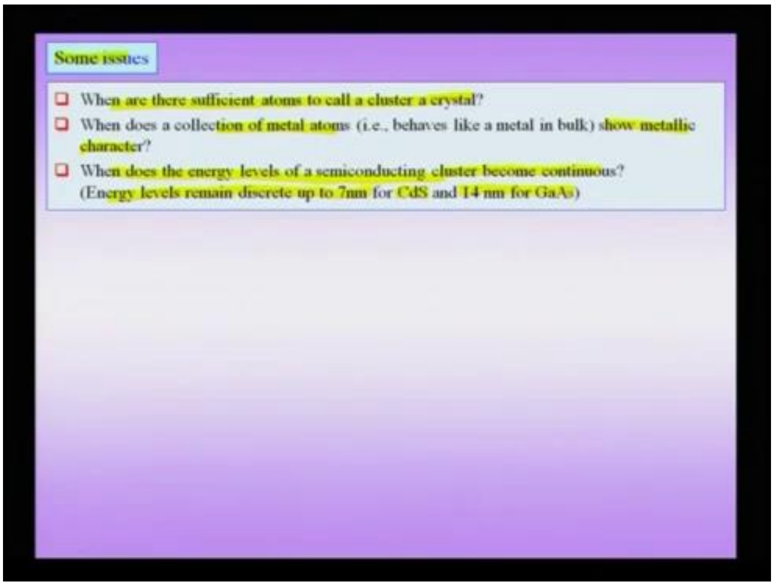

Some issues

- ☐ When are there sufficient atoms to call a cluster a crystal?
- ☐ When does a collection of metal atoms (i.e., behaves like a metal in bulk) show metallic character?
- ☐ When does the energy levels of a semiconducting cluster become continuous? (Energy levels remain discrete up to 7nm for CdS and 14 nm for GaAs)

So, the issues are, when are their sufficient atoms to call a cluster a crystal. So, and we will precisely address these issues in some of the coming slides, but is it enough that I have a few units cells, or 10 units cells, or 3 unit cells, or a 3 by 3 by 3 unit cell. Can I call it a crystal? When does a collection of metal atoms show metallic character? That means, now I am talking about metal atoms, I am talking about the bulk structure being a metal, rather than an individual atom in is no point talking about individual atom to be a metallic or nonmetallic.

Therefore, when does my now atoms which would be metallic in the bulk, start to behave like a bulk metals? This is second question I can ask myself. When does the energy levels of the semi conducting cluster become continuous? That means, that we know that semiconductor have bands, and these bands do not overlap. For instance, the valance and conduction bands do not do overlap.

And if you have only a few atoms in the cluster, then obviously you have discrete energy levels. There is not enough sufficient atoms to give us the semi continuous levels, which you observe in the case of a complete large crystal consisting of say a mole of atoms. If you notice, then you will notice that, energy level that means discrete up to 7 nano meter clusters in the case of cadmium sulphide, and even up to 14 nanometers for galeo mars. Of course, the exact transition in many of these cases as you would appreciate is going to be to blurred.

There might be states intermediate to what you might call a bulk metal and those which you may have to call individual clusters. But it nevertheless these are interesting questions, which we need to keep in mind, when we are trying to study the properties of clusters and growing larger and larger clusters with some point of time merged into the bulk level. Now, let us take up some individual examples of clusters, and we will consider clusters…

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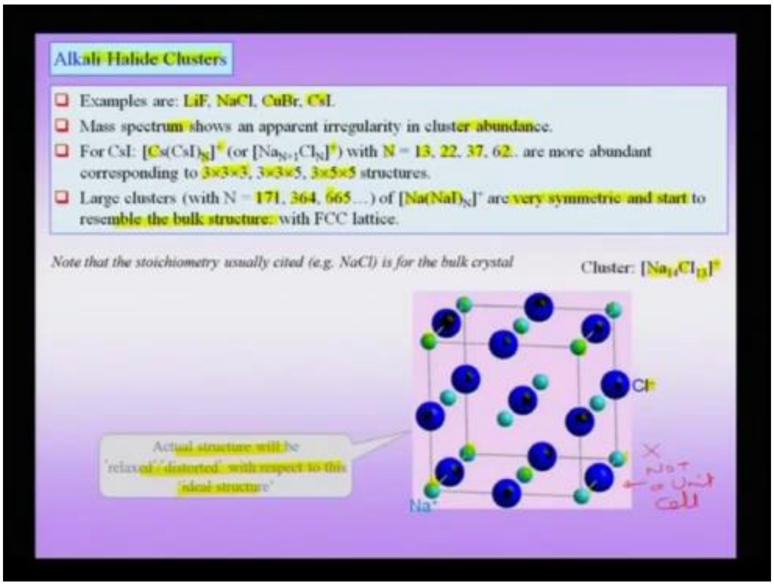

Alkali Halide Clusters

- Examples are: LiF, NaCl, CuBr, CsI.
- Mass spectrum shows an apparent irregularity in cluster abundance.
- For CsI: $[Cs(CsI)_N]^+$ (or $[Na_{N+1}Cl_N]^+$) with N = 13, 22, 37, 62.. are more abundant corresponding to 3×3×3, 3×3×5, 3×5×5 structures.
- Large clusters (with N = 171, 364, 665…) of $[Na(NaI)_N]^+$ are very symmetric and start to resemble the bulk structure: with FCC lattice.

Note that the stoichiometry usually cited (e.g. NaCl) is for the bulk crystal

Cluster: $[Na_{14}Cl_{13}]^+$

Actual structure will be 'relaxed'/'distorted' with respect to this 'ideal structure'

which are like alkali halide clusters, we will also take up some semiconducting clusters, will also consider metallic clusters, and we will scale our selves ups to consider semiconductor nano particles. So, we will consider a few type of clusters to understand, again the aspect of what you might the magic number, and also to understand, how a cluster even though locally might resemble, what you might call the bulk kind of a structure, it is definitely different from the bulk structures.

So, these couple of things have to kept in mind. Of course, we already seen those other examples where the cluster level structure is totally different from the bulk level structure. So, this is has to be kept in mind. So, examples of alkali halide clusters are, and we know that a alkali halide clusters can be ionic in nature. Lithium fluoride, sodium chloride, copper bromide, cesium iodide, etcetera. And again like in the case of the other clusters we saw that, there is an irregularity in cluster abundance, when we look at the mass spectrograph.

In other words, certain number of atoms in the cluster are more stable than certain other number N. And when we are talking about N in these cases, we are talking about for instance Cs CsI N kind of a cluster, which has a net positive charge. And when we look at the cluster like this, it will become obvious, and here we are seeing for instance, a sodium chloride kind of a cluster. And here an important point has to be kept in mind that, we are actually, though this diagram resembles or is showing something we might actually see for the unit cell of a sodium chloride kind of a structure, we should know, this is not a unit cell.

So, this should not be constitute as unit cell. What we are talking about here is a cluster of course, a real cluster would not look like this, the actual structure of a cluster. The actual structure will be relaxed distorted with respect to this idea structure, as expected because this of course, a just geometrical presentation. In ideality, this can function as units cell in a much largest, what you might call structure wherein, you have may be a few million atoms, but when we are talking about small size clusters, and this obviously is not going to be there. What you call the ideal geometric configuration is not a stable structure.

Now, we have seen that this formula for instance Cs CsI N plus, let us see what is the origin of this kind of a formula. Now, suppose I take a cluster like this, and now I calculate the number of atoms in a, if this were a unit cell in an infinite or large crystal, then each one of these corner ions would actually be contributing one-fourth, one-eighth to this unit cell. Similarly, and blue ion, which is chlorine in this example consider, would actually be contributing one-fourth to this unit cell, but in a cluster, we make a calculation based on net number of atoms that means, there is a complete contribution to this structure.

And therefore, there are 5 of these here, 5 of these here, and 4, so that makes it 14 sodium ions in this cluster. But similarly, when you count the number of chlorine here, it is 1, 2, 3, 4 in the mid plane plus 1 phi plus 4. So, that makes it 12 plus 1, 13 chlorine, and that leaves me with a net charge of plus 1 for the entire cluster. Now, if I look at the stability of such kind of clusters, I would notice that, there is some nice geometrical patterns which evolve here, like a 3 by 3 by 3 cluster is found to be more abundant.

And similarly, a 3 by 3 by 5, a 3 by 5 by 5 etcetera clusters are found. And these clusters have number of atoms going as 13, 22, 37, 62. So, this not number of atoms, for this is N, which would go into this formulae here N, wherein the number of chlorine atoms is what is N, and a number of sodium atoms is 1 more than the number of chlorine atoms, giving rise to a net positive charge to the entire complex of the cluster. If you talk about larger clusters with N equal to 171, 364, 665, etcetera and we are purposely taking an example of sodium iodide here, are very symmetric and start to resemble the bulk structure with an FCC lattice.

hat means, that again there is a transition from cluster like behavior wherein, in some sense it resembles the larger unit to some extent, unlike the previous cases where it start taking icosahedron form like the example we saw here. Here there was no resemblance between the short range cluster shown in the right bottom, and the real crystal structure which the system would adopt. But here there is some resemblance, though not a complete resemblance between the unit cell of a larger cluster or larger crystal, and a cluster which is observed for small number N.

Therefore, at some point of time, for instance with any number of number N starts to touch 665 or 1000 or more, then you try to observe that it has a bulk kind of a behavior, and this unit which we are seeing tends to go to a more, what it might call geometrically perfect configuration. So, when we consider alkali halide clusters, we see that there is a market difference on the clusters we saw for the sake of xenon etcetera. And here, there are other kind of magic numbers coming, but these magic numbers can be easily understood in terms the geometric of the cluster which we are seeing here as for the example of sodium chloride.

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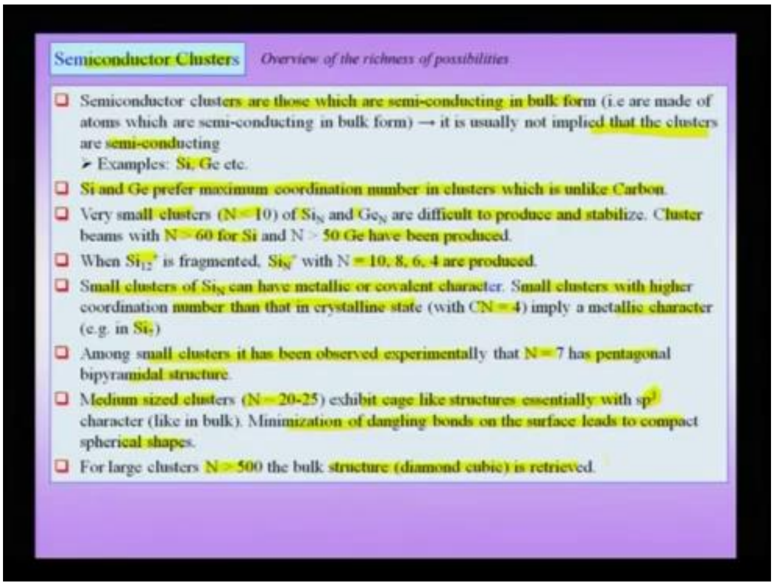

Semiconductor Clusters *Overview of the richness of possibilities*

- ❑ Semiconductor clusters are those which are semi-conducting in bulk form (i.e are made of atoms which are semi-conducting in bulk form) → it is usually not implied that the clusters are semi-conducting
  - ➢ Examples: Si, Ge etc.
- ❑ Si and Ge prefer maximum coordination number in clusters which is unlike Carbon.
- ❑ Very small clusters ($N < 10$) of Si_N and Ge_N are difficult to produce and stabilize. Cluster beams with $N > 60$ for Si and $N > 50$ Ge have been produced.
- ❑ When Si_{12}^+ is fragmented, Si_N^+ with $N = 10, 8, 6, 4$ are produced.
- ❑ Small clusters of Si_N can have metallic or covalent character. Small clusters with higher coordination number than that in crystalline state (with $CN = 4$) imply a metallic character (e.g. in Si_7)
- ❑ Among small clusters it has been observed experimentally that $N = 7$ has pentagonal bipyramidal structure.
- ❑ Medium sized clusters ($N \sim 20\text{-}25$) exhibit cage like structures essentially with sp^3 character (like in bulk). Minimization of dangling bonds on the surface leads to compact spherical shapes.
- ❑ For large clusters $N > 500$ the bulk structure (diamond cubic) is retrieved.

Now, if you go to semiconducting clusters we again see a richness of possibilities. At this point of time of course, we will not going to the details of all these possibilities, but it is important to note that, there is a lot of richness, there is a lot of variety, there is a lot of physics which can come out of studying these kind of semiconducting clusters. And when I am using the word semiconducting clusters, what this typically implied here, that these are semiconducting in bulk form.

So, we are referring to something like silicon, germanium etcetera, which are semiconductors in the bulk form. And we are not implying that, the clusters themselves are semiconducting, this is not implication. So, we being using terms for instance, later on like metallic clusters. Again here, we would actually imply that, the bulk form is actually metallic, or the bulk form is semiconducting and not the cluster itself, which is actually comprising of a small number of atoms.

And we have already seen there are market differences in the electronic structure, and the physical structure between the clusters and that of the bulk form. Silicon and germanium preferred maximum coordination numbers in cluster, which is unlike carbon. So, there is a difference between for instance, carbon, germanium, silicon, which all adopt diamond cubic structure, and which are all we might call between semiconducting and insulating because carbon has a larger band gap as compared to silicon and germanium. But they all have this diamond cubic structure and with a 4 coordination around each one of those silicon or germanium atom. Very small clusters, when you are talking about very small, we are talking about N less than 10 of silicon and germanium are difficult to produce and stabilize.

So, while we are seeing for the case of some of these earlier, what you might call noble gases. We could easily synthesize some of the larger clusters which were stable. But here even though there is a possibility of synthesis of small clusters, they are usually difficult to produce especially for silicon and germanium. Cluster beans with N greater than 60 for silicon and N greater than 50 for germanium have easily been produced.

So, it is in the small scale regime, or the small size of regime for clusters that is difficult to produce, but larger clusters have been easily synthesized for silicon and germanium. When silicon 12 plus is fragmented, silicon N plus with N is equal to 10, 8, 6, 4 are produced. So, there are techniques by which actually you can produce these smaller clusters, that is by actually fragmentation of larger clusters and hence you can produce some small clusters as well.

Small clusters of silicon can have metallic or covalent character that means, that they can be different from what the bulk form is. Small clusters with higher coordination number, then the crystalline state, cause the crystalline state we know have a coordination number 4 imply a metallic character for instance, Si 7 has some kind of a metallic character as compared to say something like Si 4. Among small clusters it has been observed experimentally that, N equal to 7 has pentagonal bipyramidal structure that means, that again we are noting that it is not the bulk structure, which is stable for the small cluster.

And there are certain specific geometrics which come out, when you are talking about the structure of these small clusters. And again we have already noted that, in a case of small clusters that, two neighboring Ns for instance N equal to 4 or N equal to 5 need not have either similarity in structure or similarity in property. So, it is now case by case, that I need to take up, these small clusters N equal to 7, N equal to 8, etcetera are very different in their structure and properties.

Medium size clusters, when we, when I am referring to medium sized, I mean 20 to 25 atoms exhibit cage like structures essentially with a sp 3 kind of a character. Minimization of the dangling bonds on the surface to a compact spherical shapes. So, for larger clusters, you get this cage like structures, and the bonding characteristic, we cannot call it exactly sp 3, but gets close to sp 3.

For instance, we know in the C 60 cluster, we know that which is, which is much larger and of course, this N equal to 20 to 25. We know that the bonding characteristic is somewhere between sp 2 and sp 3. For large clusters, N greater than equal to 500, the bulk structure which is the diamond cubic structure is retrieved. So, to summarize this slide about semiconducting clusters, there is a richness of possibilities, number 1 of course, we know that it is actually difficult to produce some of these small clusters as compared to some of the larger clusters, and could very large clusters as we expect take up the bulk structure, which is the diamond cubic structures.

When I am taking about, talking about these small clusters, each one of these clusters could have a different property. For instance the N equal to 7 cluster has a pentagonal bipyramindal structure, and also shows metallic character which is unlike the large silicon crystal which we know is exactly semi conductive. Having produce some of these clusters, their stability could be very different and therefore, stabilizing some of these clusters is more easy as compared to some of the other clusters. And it is specially so for these smaller size clusters, like be 4 atoms cluster, or the 6 atom cluster, or the 8 atom, or 10 atom cluster.

Therefore, when I am talking about semiconducting clusters, which is now we are talking about semiconducting in the bulk form. Then, there is actually a vast richness of possibilities. And this richness of possibilities helps us actually in tailoring clusters to a given kind of a property which, then as we noted before can be used in a kind of a construction at a larger scale.

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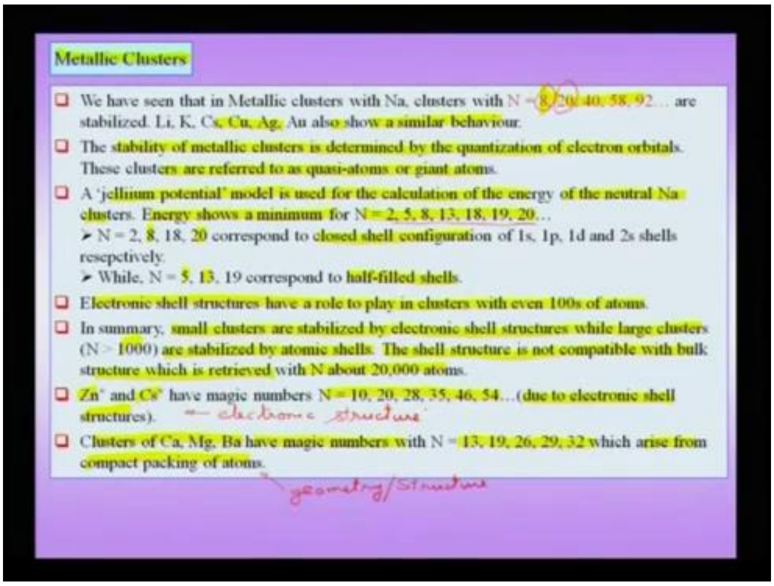

Metallic Clusters

- ☐ We have seen that in Metallic clusters with Na, clusters with N = 8, 20, 40, 58, 92… are stabilized. Li, K, Cs, Cu, Ag, Au also show a similar behaviour.
- ☐ The stability of metallic clusters is determined by the quantization of electron orbitals. These clusters are referred to as quasi-atoms or giant atoms.
- ☐ A 'jellium potential' model is used for the calculation of the energy of the neutral Na clusters. Energy shows a minimum for N = 2, 5, 8, 13, 18, 19, 20…
  - ➢ N = 2, 8, 18, 20 correspond to closed shell configuration of 1s, 1p, 1d and 2s shells resepctively.
  - ➢ While, N = 5, 13, 19 correspond to half-filled shells.
- ☐ Electronic shell structures have a role to play in clusters with even 100s of atoms.
- ☐ In summary, small clusters are stabilized by electronic shell structures while large clusters (N > 1000) are stabilized by atomic shells. The shell structure is not compatible with bulk structure which is retrieved with N about 20,000 atoms.
- ☐ Zn^+ and Cs^+ have magic numbers N = 10, 20, 28, 35, 46, 54…(due to electronic shell structures). ← electronic structure
- ☐ Clusters of Ca, Mg, Ba have magic numbers with N = 13, 19, 26, 29, 32 which arise from compact packing of atoms.

geometry/structure

Next we take up metallic clusters, and here we are talking, we already seen one class of metallic clusters in our example, or a few class of metallic clusters in our examples before, which was the sodium main kind of a cluster. And we noted that, we also have calcium magnesium kind of a clusters, and we have also seen that some of these clusters like the sodium, and shows us certain magic numbers, which we are again noting down here. So, the magic numbers with sodium clusters exhibit we have noted is 8, 20, 40, 58, etcetera.

And similarly, lithium, potassium, cesium, etcetera also seem to show a similar kind of a behavior. And again to reiterate, we are talking about metallic clusters implying that the bulk form is metallic. The stability of metallic clusters is determined by the quantization of electronic orbital's, these clusters are referred to a quasi atoms or giant atoms or super atoms, as the case we have see before. So, this entire cluster is now starting to behave like a single quantum mechanical system and therefore, I have to talk about not the electronic configuration of the individual atoms alone, but of the entire cluster.

And now, this cluster is like a quasi atom, and it can be treated like this. A jelliium model is used for the calculation of the energy of the neutral sodium clusters, energy shows minimum for N equal to 2, 5, 8, 13, 18, 19, 20, etcetera. So, there are been theoretical advances in this area, and people have tried to calculate that where are these stability regimes for a cluster consisting of sodium atoms. Now, we already seen that by doing experiments we come up these numbers which is shown on the right hand side, which is numbers like 8, 20, etcetera.

So, when you do a theoretical calculation, it is seen that this, there is a larger set of numbers which emerge, and we can understand this kind of a larger set of numbers by considering that. Now, we are talking about two kinds of electronic or shell kind of a electronic configuration. One those corresponding to a complete close shell configuration, and the other corresponding to a half filled configuration. So, obviously the closed shell configuration will have a higher stability as compared to the half filled configuration.

And these numbers as you can see here 8, 20, etcetera which correspond experimental results are coming from a close shell configuration. While others which may be included in this list like a 5, 13, etcetera are coming from a half filled configuration. Therefore, again similar to what we normally play for a single atom is being play out at a larger scale consisting of a larger number of atoms, but it is basically the same principles of electronic filling of shells, or and we note already that a full filled shell or which is called a close shell, or half filled shell can give us certain kind of a stability.

The surprise thinking of course, that you would expect that only that very small clusters which are about say, 10 atoms, 20 atoms, etcetera would having this dominance of this, what you might call long range electronic interactions. But electronic shell structures seem to play a dominant role even when the cluster is consisting of a few 100s of atoms. So, this is something very interesting and therefore, we had noted previously in the case of the semi conducting clusters that, we actually had to go to something like 500 atoms or more before we actually retrieve, what you might call the total bulk kind of a structure.

So, if you want to summarize, small clusters are stabilized by electronic shell structures, where large clusters are stabilized by atomic shells. And in atomic shells we know that the general rules of you know, electronic configuration and also the pair wise interaction into the crystal orbit. The shell structure is not compatible with the bulk structure, which is retried for about N equal to 20000 atoms. That means, these are all some theoretical calculation, which tell us that this the two rules, one local rule which is giving us these clusters, and one is the rule for bulk wherein you are worried about a different set of parameters controlling the structure.

But there is a transition which we can see typically occurring at about say, for instance more than 1000 atoms. And when you go to say something at cluster 20000 atoms, then we see that it is clearly the bulk structure we are talking about. Zinc plus and cesium plus have magic numbers, which are different from that observed, for instance our case of sodium, and these magic numbers at 10, 20, 28, 35, 46, 54. And this is again due to electronic shell structures. Though the numbers are different, the basic physics giving rise to these numbers is no different.

Clusters of calcium, magnesium, barium have magic numbers with N equal to 13, 19, 26, 27 which arise from compact parting of atoms that means, again we have the two kinds of rules coming in, one we may say this is coming from geometry of structure, and here we talk about physical structure, the other coming from what you might call the electronic structure. So, even within the case of metals we have both the examples which we are cited before…

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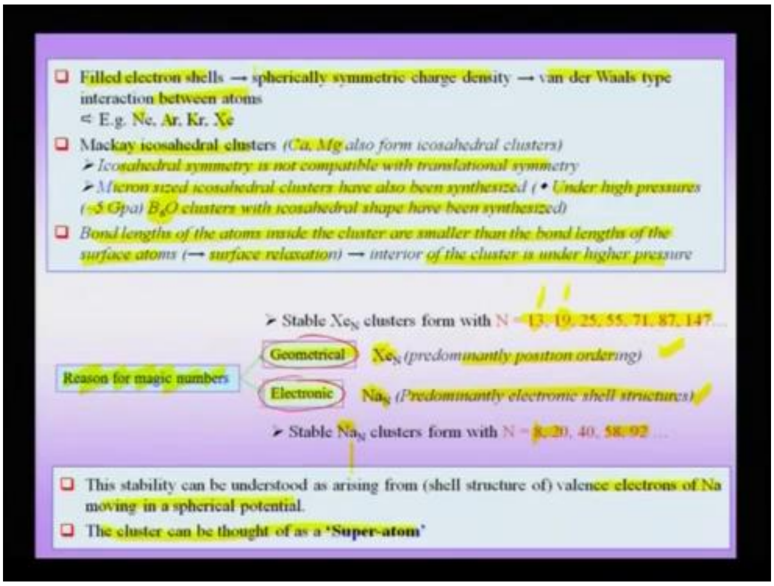

- ❑ Filled electron shells → spherically symmetric charge density → van der Waals type interaction between atoms
  - E.g. Ne, Ar, Kr, Xe
- ❑ Mackay icosahedral clusters *(Ca, Mg also form icosahedral clusters)*
  - ➢ *Icosahedral symmetry is not compatible with translational symmetry*
  - ➢ *Micron sized icosahedral clusters have also been synthesized (• Under high pressures (~5 Gpa) B_6O clusters with icosahedral shape have been synthesized)*
- ❑ *Bond lengths of the atoms inside the cluster are smaller than the bond lengths of the surface atoms (→ surface relaxation) → interior of the cluster is under higher pressure*

➢ Stable Xe_N clusters form with N = 13, 19, 25, 55, 71, 87, 147 …

Reason for magic numbers

Geometrical: Xe_N *(predominantly position ordering)*

Electronic: Na_N *(Predominantly electronic shell structures)*

➢ Stable Na_N clusters form with N = 8, 20, 40, 58, 92 …

- ❑ This stability can be understood as arising from (shell structure of) valence electrons of Na moving in a spherical potential.
- ❑ The cluster can be thought of as a '**Super-atom**'

which we had, when we classified. We said that the reason for these magic numbers can come from geometrical aspects, or from electronic aspects and in the case of metallic clusters. We see that both these kind of stabilities come into play and some of them are dominated by in the case of calcium, magnesium are dominated by the geometrical aspects while, others are dominated by electronic shell structure aspect. The next scale is the scale of the one may call semiconducting nano particles.

So, these are and many of these nano particles, we are going, we are talking about here are actually compound nano particles. These include cadmium sulphide, cadmium selenide, cadmium telluride, zinc sulphide and zinc sulphide which is doped with manganese etcetera.

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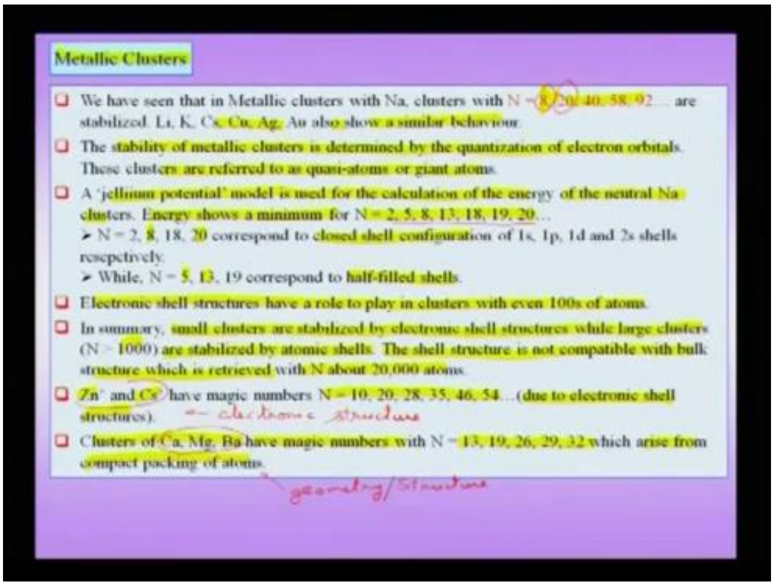

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- Clusters of Ca, Mg, Ba have magic numbers with N = 13, 19, 26, 29, 32 which arise from compact packing of atoms.

geometry/Structure

And these are obviously very different than in terms of the synthesis difficulty in terms of maintaining what you might call stoichiometry etcetera, very different from these pure elemental clusters which we talked about, like the case of the xenon or sodium.

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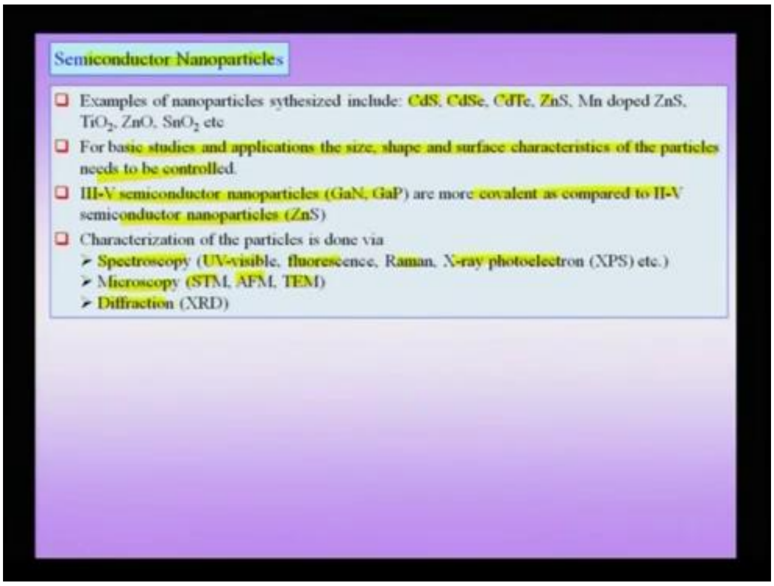

Semiconductor Nanoparticles

- Examples of nanoparticles sythesized include: CdS, CdSe, CdTe, ZnS, Mn doped ZnS, TiO_2, ZnO, SnO_2 etc
- For basic studies and applications the size, shape and surface characteristics of the particles needs to be controlled.
- III-V semiconductor nanoparticles (GaN, GaP) are more covalent as compared to II-V semiconductor nanoparticles (ZnS)
- Characterization of the particles is done via
  - ➢ Spectroscopy (UV-visible, fluorescence, Raman, X-ray photoelectron (XPS) etc.)
  - ➢ Microscopy (STM, AFM, TEM)
  - ➢ Diffraction (XRD)

So, and we know that some of these compound semiconductors actually are technologically very important, and they have been studied in diverse context intensely and nano particles are many of these have been synthesized and they show very-very interesting properties.

Here we are of course, briefly introducing the concept of these semiconducting to nano particles, and we are not really taking up it in any detail. But we will return to some of these important particles, like cadmium telluride, cadmium sulphite, and cadmium selenide, which are important from even the optical property aspects and many other semiconducting properties. For basic studies and applications psi shape and surface characteristics of these particles need to be contour sob.

This is obvious that now we are talking about nano particles there are additional parameters that I need to control, which include not only the size of these particles, but what you might call the shape and also the surface characteristics which I want to perhaps maintain pure III-V semiconductor nano particles, like gallium nitride and gallium phosphide are more covalent as compared to II-V semiconductor nano particles like zinc sulphide. Therefore, when it go to nano particle size, then the what you are given the bonding characteristics can change depending on the kind of compound, we are talking about.

And typically we may want to characterize some of these properties and these bonding characteristics. And we use various kind of techniques which includes various spectroscopic techniques like UV visible, fluorescence, raman, x ray photo electron etcetera. We also use of course, microscopic techniques to determine the particle shapes etcetera, and local defect structure which includes transmission electron microscopy, atomic force microscopy, scanning tunneling microscopy, etcetera.

And of course, we use various kind of diffraction studies which can give us not only the particle size, but the strain in this particles which include x ray diffraction and electron diffraction. So, after this what you might call a very-very brief introduction to semi conductor nano particles. We will return to some of these other these compounds, when we actual talk about electronic properties of these particles. But nevertheless here we have stress to emphasize that, we have this semiconducting clusters and also, which is now made up pure elemental things like silicon and germanium. But we can also have semiconducting compound clusters and also semiconducting nano particles, which are made of compounds.

So, this makes a large gamete of materials, which we can study and use them for our benefits. When we had, next we move on to the topic of what is known as self assembled ordered nano structures. When we dealt with the topic of nano manufacturing, we came across a concept called nano manipulation. We said that, suppose I want to make an useful assembled structure, which is coming using these clusters and particles, then I may want to take and position these, what I might call clusters and nano crystals in a very precise fashion, may be on a sub strait, may be in a 3 dimensional array.

And I had pointed out that though this is a beautiful technique, and beautiful techniques are available for this kind of a manipulation using nano tweezers. But this is not only a cumbersome, but definitely not available to mass manufacturing or even scaling up. But there are certain other classes which we had pointed out, that there are systems which assemble themselves, and these are very beautiful systems because here we do not have to actually put the system into a given order.

For instance, I may want to assemble a 2 dimensional crystal out of nanoparticles or I may want to even assemble it in a 3 dimensional form, I do not have to do it myself. This system actually organizes given a certain kind of a process conditions, which I would use for, to get a certain kind of assembly.

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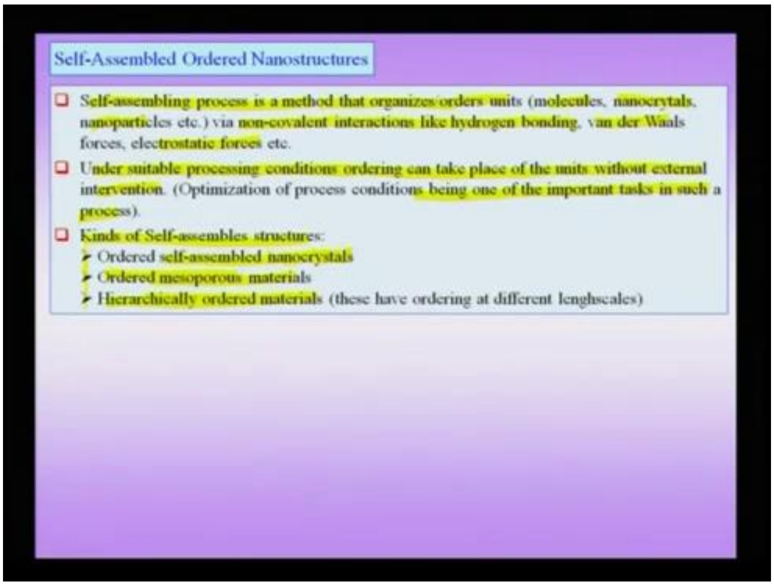

Self-Assembled Ordered Nanostructures

- ❑ Self-assembling process is a method that organizes/orders units (molecules, nanocrytals, nanoparticles etc.) via non-covalent interactions like hydrogen bonding, van der Waals forces, electrostatic forces etc.
- ❑ Under suitable processing conditions ordering can take place of the units without external intervention. (Optimization of process conditions being one of the important tasks in such a process).
- ❑ Kinds of Self-assembles structures:
  - ➢ Ordered self-assembled nanocrystals
  - ➢ Ordered mesoporous materials
  - ➢ Hierarchically ordered materials (these have ordering at different lenghscales)

Self assembling processes a method that organizes and orders units. And I am talking about units, there could be very small units like molecules, there could be nano crystals or there could be nano particles and of course, they can also be nanostructures of various kinds. And the interactions leading to this kind of self assembly is non covalent interactions like hydrogen bonding, Van Der Waals bonding forces, electro static forces, etcetera.

So, in this process we can do only the process parameter and the system organizes your orders its units, and these units could be of course, are starting from the very small at the molecules to somewhat larger unit like nano crystals and even larger particles. And the interactions leading to this kind of an ordering is the weak interactions typically like hydrogen bonding or Van Der Waals bonding. And if any of these particles are charged, in that charged itself electrostatic charge would help it in the ordering process.

Under a suitable crossing conditions, ordering can take place of these units which we were talking about with all without external intervention. And I am meaning external intervention, I mean what it might call a control at the cluster or at the level of the nano crystal. Of course, I am going to intervene this innocent of controlling. Under suitable crossing conditions, ordering can take place and the ordering we are talking about is the ordering of the units, without external intervention. When I mean external intervention is I am referring to intervention at the level of the nano crystal or the individual nano particle, but I will definitely be controlling the process parameters, which include temperature, pressure, the amount of solvent, etcetera.

And this optimization of process conditions being is an important in actually achieving this process. The kind of order I obtain, the kind of units, the size to which they pack, etcetera is depend on the crossing conditions, which I am going to optimize. Various kind of self assembly I can visualize are, ordered self assemble nano crystals, ordered mesoporous materials, and hierarchically ordered materials. So, in all these cases I have of course, the basic structural unit, and this structural unit is somehow organized in a fashion, which we call us as a self assemble way of organization.

And of course, we already seen the example of the nano crystals being self assemble. In materials where pores is the main focus of the material, then we can actually have ordered mesoporous materials, and we will see even examples of this. And finally, we can also hierarchically order materials that means, ordering is not a just a one length scale, but at multiple length scales. So, we can, to summarize this slide, self assembled or those kind of a nanostructures, which assembled themselves are in some sense, a good solution for the making what you might call a mass production of these kind of a crystals or nanostructures.

Because if we are going to manipulate it unit by unit, then actually this kind of a process is definitely not amenable to scale up, or not amenable to large scale production. And when we are talking about self assembled nanostructures, the process parameters are very important, and there are classes of the self assembled nanostructures which include a self assembled nano crystals, mesoporous materials, and hierarchically ordered materials.

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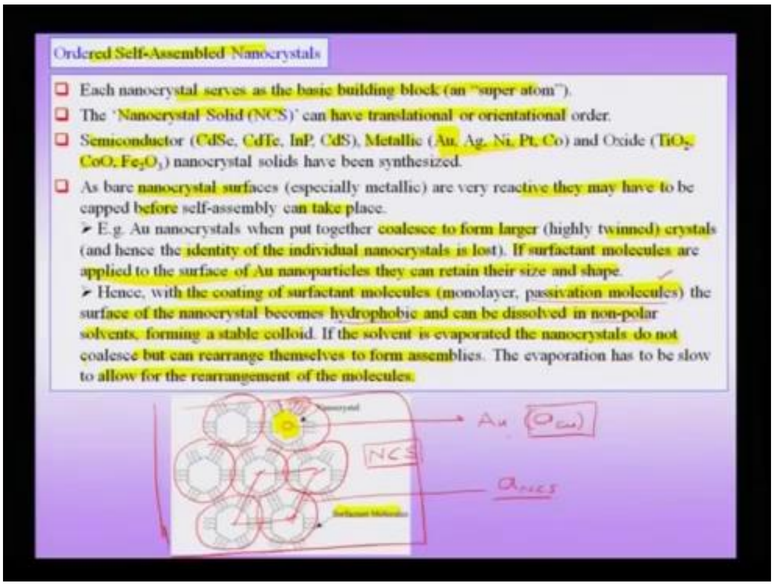

Ordered Self-Assembled Nanocrystals

- Each nanocrystal serves as the basic building block (an "super atom").
- The 'Nanocrystal Solid (NCS)' can have translational or orientational order.
- Semiconductor (CdSe, CdTe, InP, CdS), Metallic (Au, Ag, Ni, Pt, Co) and Oxide (TiO_2, CoO, Fe_2O_3) nanocrystal solids have been synthesized.
- As bare nanocrystal surfaces (especially metallic) are very reactive they may have to be capped before self-assembly can take place.
  - E.g. Au nanocrystals when put together coalesce to form larger (highly twinned) crystals (and hence the identity of the individual nanocrystals is lost). If surfactant molecules are applied to the surface of Au nanoparticles they can retain their size and shape.
  - Hence, with the coating of surfactant molecules (monolayer, passivation molecules) the surface of the nanocrystal becomes hydrophobic and can be dissolved in non-polar solvents, forming a stable colloid. If the solvent is evaporated the nanocrystals do not coalesce but can rearrange themselves to form assemblies. The evaporation has to be slow to allow for the rearrangement of the molecules.

So, let us take of some examples of these ordered self assemble nanostructures, and in this each nano crystal serves as a basic building block or a super atom.

So, now I am not building a crystal starting from atoms, I am building a crystal starting from a nano crystal itself. And the end product is referred to as a nano crystalline solid, and we will also note there are alternate terms used in literature sometimes for this nano crystalline solid, like one such example, one such term is often used as what is known as a super lattice. And we will point out that it is better to avoid the term super lattice in this context because it can actually be confusing.

So, in this set of lectures, we will typically use the term nanocrystalline solid or nano crystalline solid, and this nanocrystalline solid can have translational, orientational or both translational and orientational kind of an order. The starting point for my building up of this nanocrystalline solid could be a semiconductor crystal, like cadmium selenide, cadmium telluride, indium phosphide, cadmium sulphide, etcetera. Could be a metallic nano particle or nano crystal, like gold, silver, nickel, platinum, cobalt, etcetera. Could even be an outside like titanium oxide, cobalt oxide or if Fe 2 O 3..

So, I am starting with some kind of a crystalline material, a crystalline nano particle, and I am making a larger unit crystal. And if I am talking about a metallic for instance a system and I say starting with a gold as a nice typical example. Because many kind of nano crystalline solids have been synthesized using gold, then the bare nano crystal surface are very reactive and they have to be cap before the self assembly takes place.

So, in some sense when I am dealing with metallic nano particles, I am not truly talking about what we will call a monolithic kind of nano crystalline solid, but it is a composite now of a gold nano particle which is being coated with some second layer, which is now helping me to avoid coalescence to form larger, which is usually a highly twinned crystal.

And hence the individual entity of individual nano crystal is lost. Suppose I do not do this coating, then what would happen? Then this because now these nano particles have a tendency to melt at low temperature, the surface diffusivity high, and they can get into those kind of configuration which are not allowed for bulk, which include distant configuration. So, they would coalesce, they would get twinned. And therefore, my individual nano particle lose its identity.

Therefore, if I want to preserve the identity of a individual nano particle, or a nano crystal to actually synthesis a nano crystalline solid, then I typically have two capital the capping layer. In other words, now my unit in the assembly is not a what it might call a bare metallic gold nano particle, but is actually a gold nano particle coated with some kind of a surfactant molecule, as in the schematic shown below. And this surfactant molecule is now the region by which one unit is going to interact with another unit. If surfactant molecules are applied to the surface the Gold nano particle, they can retain their size and shape.

Now, I do not have the fear of this gold nano particles you know coalescing, or you know adsorbing certain other species which may actually spoil my structure. But nevertheless, this system which definitely not a pure system, it is actually now a composite of gold and a surfactant molecules which is now helping me isolate these molecules. Hence, with coating of surfactant molecules which sometime are called a passivation molecules. The surface of nano crystals become hydrophobic and can be dissolved in an nonpolar solvent, forming a stable collide.

So, one successes in method to form this are organized self assembled nano crystal is actually coating it with a hydrophobic passivation molecule in the surface and which can be dissolved to form a stable collide. If the solvent is operated in the nano crystals do not coalesce, but arrange themselves in the form of assemblies. And that is why, this is called a self assembled system because here all you doing is controlling the process parameter, which includes the, you know the kind of solvent, which you added initially, they have operation on the rate of the solvent.

And if the operation rate is slow enough, then this we have these molecules or these units, which are nano crystals coated with this affected molecules of sufficient you know, time to slowly adding themselves into an ordered structure which can be a nano crystalline solid. So, let us look at the schematic, where we have this say for instance, a gold kind of a nano particle, and these gold nano particles now are having coated with these molecules, which are schematically shown by this wiggly arrows. And typically in some synthetic methods, this wiggly arrows represent, what you might call a non polar, represent a passivation molecule which is hydrophobic.

And therefore, helps us this can be dissolve in a nonpolar solvent and later on when the evaporation, this gives rise to an structure, where the fundamental unit is of course, a gold nano particle with this cover layer, but now these have been arranged in a crystalline array which we call an nano crystalline solid. Of course, this is a crude symmetric wherein we are representing a 2-dimensional crystal here, which is now a nano crystalline solid. The kind of arrangement which I can get from a single, what it might call a passivation molecule, a single solvent, etcetera is dependent on the process parameters.

That means, I may use different conditions to obtain different kind of ordering. But nevertheless, all of these would be come would all of these come under the, what it might call self assembled structures. And specifically here we are referring to a crystalline solid obtain which is a nano crystalline solid. And this should not be confused with a nano crystal, which is what each of one these, so each one of these is a nano crystal, but this whole assembly here is a nano crystalline solid.

So, this distinction has to be kept in mind, and now we have what you means in ordering a two length scales. One length scale being the lattice parameter of this gold for instance, suppose this is my gold, and I am talking about the length scale which is the lattice parameter of gold which is ACU, but the second length scale is the lattice parameter of this crystal itself, which can be thought of as this. So, there are two distinct length scale in this problem, of course, instead of starting with a gold which is a crystalline material, I could have started with an amorphous glassy kind of a beat and done this kind of an assembly, in which case of course, I may or may not obtain of course, a same kind of structure.

But for simplicity, assuming that we are getting a same kind of a structure, then we do not have this underlying crystalline order which is in the case of gold. Therefore, this is what you might call a very-very interesting, a beautiful example of a 2 level hierarchical crystal. In other word, there is ordering a two length scale one length scale this is of the order of arm storms and one which is of the order of nanometers or 10s of nanometers or actually could be even larger. Therefore, this what we are talking about here is a new kind of a crystal altogether, which is to be very clearly has to be distinguished from the kind of crystals, which are the typically, we talk about when you talk about atomic or molecular crystals.

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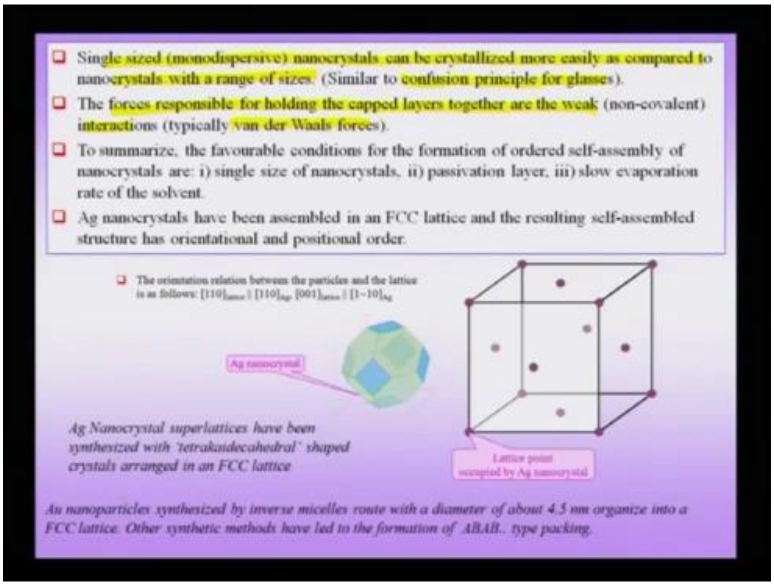

- Single sized (monodispersive) nanocrystals can be crystallized more easily as compared to nanocrystals with a range of sizes. (Similar to confusion principle for glasses).
- The forces responsible for holding the capped layers together are the weak (non-covalent) interactions (typically van der Waals forces).
- To summarize, the favourable conditions for the formation of ordered self-assembly of nanocrystals are: i) single size of nanocrystals, ii) passivation layer, iii) slow evaporation rate of the solvent.
- Ag nanocrystals have been assembled in an FCC lattice and the resulting self-assembled structure has orientational and positional order.

- The orientation relation between the particles and the lattice is as follows: $[110]_{lattice} \| [110]_{Ag}$, $[001]_{lattice} \| [1\text{-}10]_{Ag}$

Ag Nanocrystal superlattices have been synthesized with 'tetrakaidecahedral' shaped crystals arranged in an FCC lattice

Au nanoparticles synthesized by inverse micelles route with a diameter of about 4.5 nm organize into a FCC lattice. Other synthetic methods have led to the formation of ABAB.. type packing.

If you more points in this regard are to be noted. Single sized mono dispersive nano crystals can be crystallized more easily as compared to nano crystals with a range of sizes, this is in some sense is obvious. Suppose, I have, I did not start with a single size for this unit. I started with the multiple size for this unit, then it is unlikely or it is difficult to crystallize that structure because obviously there will be mismatch in the way in the backing takes place. This is in some sense, the opposite of what it might call the confusion principle of a glasses wherein, it deserted suppose I want to make a glassy or amorphous material, then I would put in very many different kind of elements with very many different sizes.

Now, this implies that now when the crystal is trying to grow from xenon melt, then atoms have to precisely arranged in without actually reading too much strain in the lattice. And this is not possible because now the atoms are all of different type and in the end up, end up arranging themselves typically in an amorphous fashion. Of course, this is depend on passing parameters suppose I have a multi ((Refer Time: 52:37)) alloy and I cool faster, then the chance of actually making it a amorphous is much larger then come, say for instance suppose I took a pure elemental aluminum and I cooled it to produce, to try to produce a glass.

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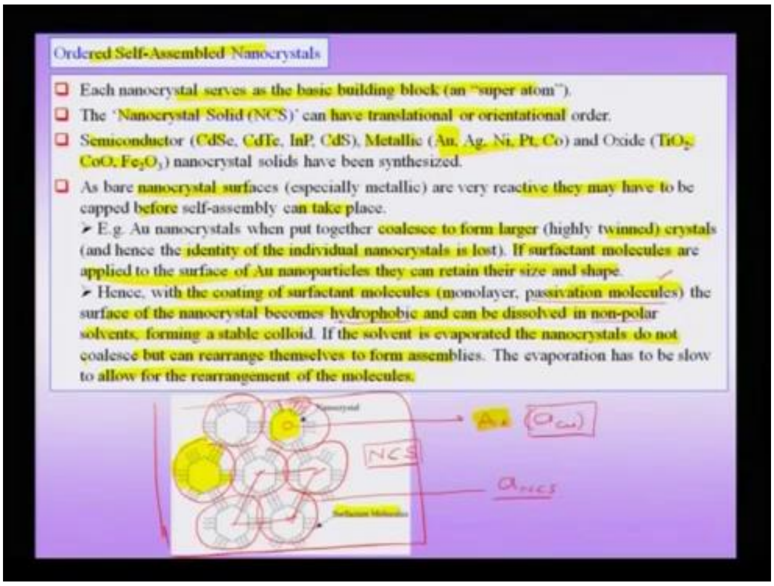

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- Each nanocrystal serves as the basic building block (an "super atom").
- The 'Nanocrystal Solid (NCS)' can have translational or orientational order.
- Semiconductor (CdSe, CdTe, InP, CdS), Metallic (Au, Ag, Ni, Pt, Co) and Oxide (TiO_2, CoO, Fe_2O_3) nanocrystal solids have been synthesized.
- As bare nanocrystal surfaces (especially metallic) are very reactive they may have to be capped before self-assembly can take place.
  - E.g. Au nanocrystals when put together coalesce to form larger (highly twinned) crystals (and hence the identity of the individual nanocrystals is lost). If surfactant molecules are applied to the surface of Au nanoparticles they can retain their size and shape.
  - Hence, with the coating of surfactant molecules (monolayer, passivation molecules) the surface of the nanocrystal becomes hydrophobic and can be dissolved in non-polar solvents, forming a stable colloid. If the solvent is evaporated the nanocrystals do not coalesce but can rearrange themselves to form assemblies. The evaporation has to be slow to allow for the rearrangement of the molecules.

Therefore, a single size for these units is preferred if I am trying to produce a crystal, and if I am trying to produce a crystal by for instance, a slow evaporation rate. The forces responsible for holding the cap layers together are the week interactions typically Van Der Waals forces. So, the bonding at the level of the individual nanocrystal which is the gold nano crystal is obviously metallic type, but the bonding leading to the formation of the nano crystalline solid is not any one of the strong forces.

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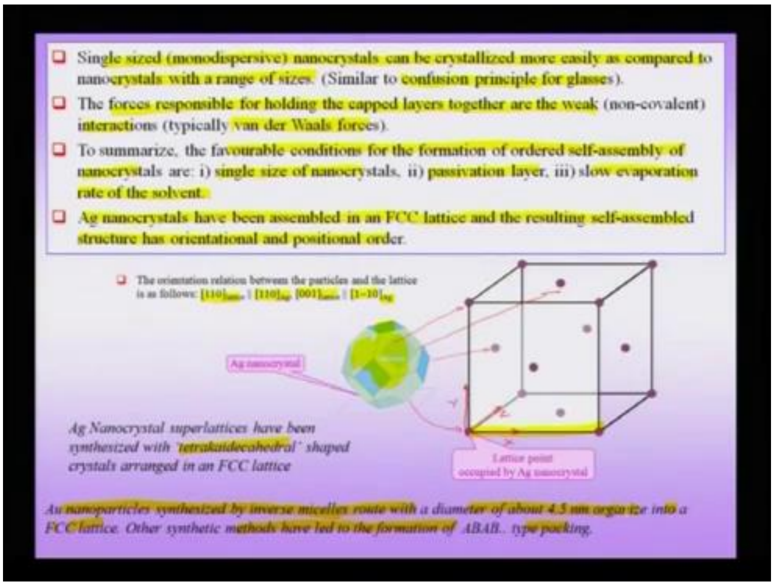

- Single sized (monodispersive) nanocrystals can be crystallized more easily as compared to nanocrystals with a range of sizes. (Similar to confusion principle for glasses).
- The forces responsible for holding the capped layers together are the weak (non-covalent) interactions (typically van der Waals forces).
- To summarize, the favourable conditions for the formation of ordered self-assembly of nanocrystals are: i) single size of nanocrystals, ii) passivation layer, iii) slow evaporation rate of the solvent.
- Ag nanocrystals have been assembled in an FCC lattice and the resulting self-assembled structure has orientational and positional order.

- The orientation relation between the particles and the lattice is as follows: $[110]_{lattice} \| [110]_{Ag}$, $[001]_{lattice} \| [1\text{-}10]_{Ag}$

Ag Nanocrystal superlattices have been synthesized with 'tetrakaidecahedral' shaped crystals arranged in an FCC lattice

Au nanoparticles synthesized by inverse micelles route with a diameter of about 4.5 nm organize into a FCC lattice. Other synthetic methods have led to the formation of ABAB.. type packing.

But is actually of the weak kind, which could typically be the Van Der Waals kind of forces. Because the interaction is now mediated by these, what I might call surfactant molecules. So, these surfactant molecules are actually talking to each other. Whenever there are two units in contact and therefore, this interaction between these molecules is not of the strong type, and it is a non covalent interaction which is responsible for it.

And therefore, even though gold might melt at higher temperature, but this solid itself where it are can be dissolved at a lower temperature. Therefore, the favorable conditions for the formation of a self ordered assembly of nano crystals are, single size for the nano crystals along with of course, now we are not only talking about nano crystal itself we are talking about it along with the passivation layer the passivation layer itself, which is actually giving rise to the interaction between these units and slower operations rate of the solvent.

So, the slower operation rate as I pointed out is very similar to that the rules which are applicable for a even normal crystals growing from the melt if I cool faster. Then, the chance of producing amorphous material is larger as compared to cooling slowly. Wherein, there is sufficient time for the atoms to arrange in a precise crystalline order. Silver nano crystals have been assembled in an FCC lattice and resulting the self assemble structure has orientational and positioning order.

So, one beautiful example of this kind of, what it might call self organized nanocrystal or nano crystalline solid is the example of gold nano crystals, and these gold nano crystals have a beautiful shape, which is the shape of the tetrakaidecahedral. So, we know that there are two semi regular space filling solids, one of them is the tetrakaidecahedran, others is of the rhombic dodecahedron. And this tetrakaidecahedran shown here has is a semi regular solid because it is got square and a hexagonal faces. All vertices of course, are identical because they are consist of a four face joining with two 6 faces, so these radical and this beautiful space filling solid has been often used as a model for grain structure.

And this now, this polyhedral crystal of silver itself is an unit in the assembly leading to a larger crystal which itself as an FCC lattice. So, now again we have a two levels of ordering we are talking about here, one within the silver particle just now has a very specific shape which is a shape of tetrakaidecahedran, and the the next level is this silver particle of silver crystal organizing itself into an FCC lattice, and now we have a larger lattice parameter for this FCC lattice. And at each one of these lattice points I am going to put one of these silver tetrakaidecahedran.

And therefore, this a nice example of what you might call in a nano crystalline solid having to length scales, and an important point to note is that this kind of an ordered crystal has both positional and orientational order. In other words, when I am putting this nanocrystal as a motive in this FCC crystal, its orientation is maintained precisely with respect to now my basis vectors, which are now my three basis vectors for this nano crystalline solid.

So, I maintain my orientation with respect to my the x y z coordinate axis, and the typical orientation relationship which has been synthesized so far is that the 110 of the lattice is parallel to the 110 direction of the silver. And the 001 direction of the lattice is parallel to the 11 bar 0 direction of the silver crystal. Therefore, I have now synthesized us crystal, which is both positionally and orientation in order having two length scales. So, this is a very what you might call a different kind of a crystal, from what we encounter which had made of just of atoms ((Refer Time: 58:05)). Gold nano particles synthesized by inverse myself root, have a diameter of about 4.5 nano meters organized into an FCC lattice.

Other synthetic methods are led to the formation of ABAB kind of packing. In other words, as I pointed out that, actually I can change my processing parameters to obtain, for instances an ABCABC kind of a packing of these units, and in the case of a specific example being considered. We are talking about the gold nano particle, then I can get both an FCC kind of a lattice or any synthetic kind of a structure wherein in ABAB kind of packing.

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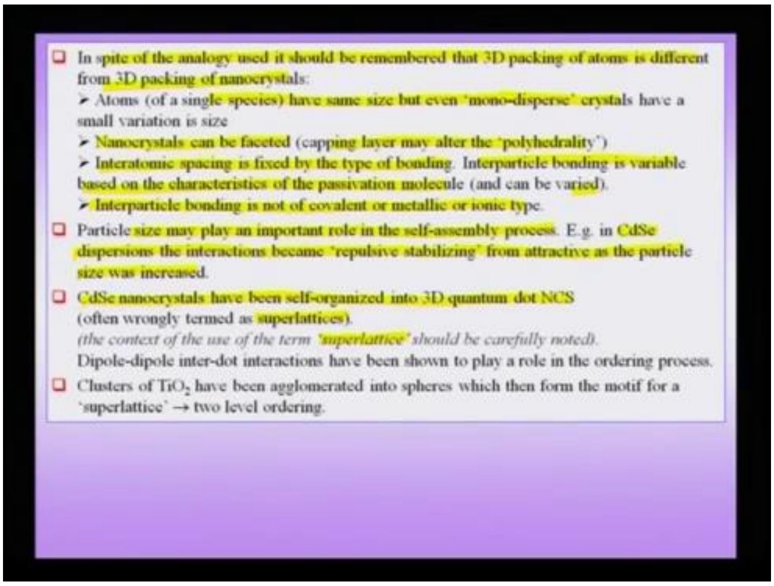

- ❑ In spite of the analogy used it should be remembered that 3D packing of atoms is different from 3D packing of nanocrystals:
  - ➢ Atoms (of a single species) have same size but even 'mono-disperse' crystals have a small variation is size
  - ➢ Nanocrystals can be faceted (capping layer may alter the 'polyhedrality')
  - ➢ Interatomic spacing is fixed by the type of bonding. Interparticle bonding is variable based on the characteristics of the passivation molecule (and can be varied).
  - ➢ Interparticle bonding is not of covalent or metallic or ionic type.
- ❑ Particle size may play an important role in the self-assembly process. E.g. in CdSe dispersions the interactions became 'repulsive stabilizing' from attractive as the particle size was increased.
- ❑ CdSe nanocrystals have been self-organized into 3D quantum dot NCS (often wrongly termed as superlattices).
  (the context of the use of the term 'superlattice' should be carefully noted).
  Dipole-dipole inter-dot interactions have been shown to play a role in the ordering process.
- ❑ Clusters of TiO_2 have been agglomerated into spheres which then form the motif for a 'superlattice' → two level ordering.

Therefore, multiple options are possible here, and this definitely is a new class of what you might call crystals and new class of an ordered solid, which is very-very different from any other class which we you normally will talk about. A few important points again have to be stressed in this context, in spite of the knowledge we used, it should be remembered that 3D packing of atoms is different from 3D packing of nano crystals.

So, there are very distinct reasons for us to differentiate these crystals compared to the atomic crystal, which could be a building block in this kind of an structure. Atoms of a single species have the same size, but even what we call mono disperse crystal have a small variation in size. So, when I am talking about a mono disperse size, I typically mean. And here we are not in the cluster regime, where very only certain number of atoms in certain geometry very-very stable, but we are talking about nano crystals. That means, that here even the term mono disperse does not imply exactly the same size, in exactly the same number of atoms for, or exactly the same shape for each one of those building crystals.

Therefore, there is a small variation in size and therefore, what I mean to to say is that, we have to differentiate these from what you might call the 3D packing of nano crystals. Nano crystals can be faced at, while we know that atoms are not, and this capping, we talked about that means, we are capping this or putting on outer shell of these molecules.

This capping layer can actually alter the shape, this passivation layer itself contributes a shape.

And therefore, even though the starting crystal may be polyhedral, the nano crystal which are the unit which we are starting off to make this nano crystalline solid, may actually, may not be polyhedral. And any case, this assembly is definitely different from the case of the 3D packing of what it might call atoms. Inter atomic spacing is fixed by the type of bonding, inter particle bonding is variable based on the characteristics of the passivation molecule, and can be varied. In the case of a normal crystal there is only typically a fixed bonding of course, it could be a measure of covalent dynamic, it could just be pure metallic, etcetera, etcetera.

But whatever the case may be, for a given set of atoms of compounds I am talking about the atomic spacing is fixed, and that cannot be changed. But in the case of the nano crystalline solid, I am putting in a passivation layer, and that implies that, based on the type of passivation molecule I am using, based on the thickness of this passivation molecule, or if I am putting it in a configuration like this, the length of the passivation molecule, my bonding characteristics may change. And its interaction with the neighboring units in the assembly also can be vary.

That means, I have a certain degree of freedom when it comes to, when it comes to the kind of assembly I want, the kind of crystal I can manufacture using these kind of what it might call nanocrystals and passivative nano crystals. Inter particle bonding is not of covalent metallic type or ironic type. In the case of normal crystals, we note that typically, and we are talking about normal crystals, and talking about non molecular crystals. We know that typically, the bonding is covalent metallic or ironic, but in this case it is usually the weak interactions.

So, there are reasons which make this 3D a crystalline, nano crystalline solids, very interesting, and very similar to our usual atomic crystals or molecular crystals. But we have to differentiate them based on these parameters, which I have just now stated. The particle size also may play an important role in the self assembling process for example, the CdSe dispersions, the interaction become repulsively stabilizing from attractive as the particle size is increased. That means, at one size regime of the CdSe particles, I have an attractive kind of interaction, and other size regime, I may have a repulsive kind of a stabilization.

That means, that the bonding or the inter particle interactions may change character, as I am varying my particle size, which is not the case as you know for the a simple atomic or molecular crystals. Wherein, you do expect that because the, now the size of the atom is fixed, and therefore the interaction is not going to change with the in other kind of crystalline making. CdSe nano crystals have been self organized into 3D quantum dot nano crystaline solids.

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And many times in this context, the term super lattice is used which in my view should be avoided because the term super lattice refers as we know to the case where an a structure is composed of two sub lattices. So, when I am using this term super lattice I imply as in these cases, it is clear that this system is not actually comprising of the sub lattices, the system actually has an order at the lower lengths scale, and also an order at the higher lengths scale.

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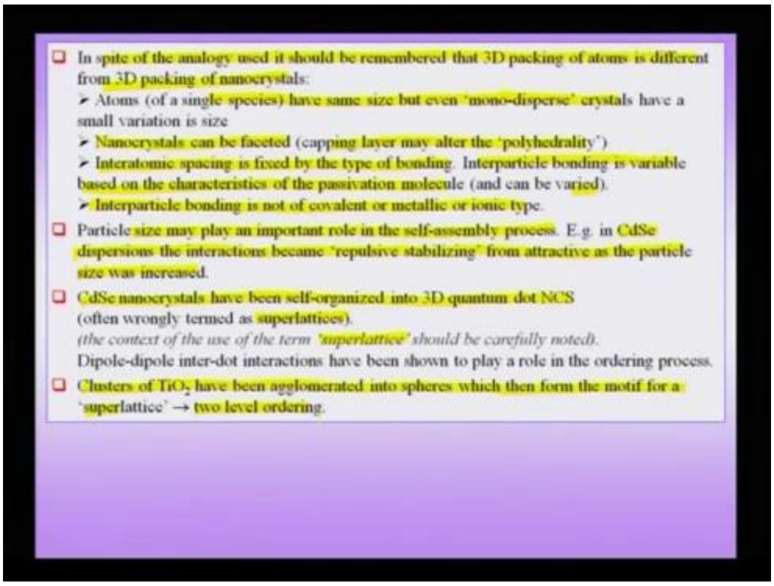

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- ☐ Clusters of TiO_2 have been agglomerated into spheres which then form the motif for a 'superlattice' → two level ordering.

Therefore, I cannot call this a super lattice, but whenever somebody is reading literature and this kind of term is called a super lattice you should understand that. What one is referring to, is not the usual super lattice, but a different kind of super lattice or what you might call a nano crystalline solid. Clusters of TiO 2 have been agglomerated into spheres, which then form a motive for the super lattice in a two level ordering.

So, there are other examples like the case of TiO 2 wherein, you first assemble these clusters into a sphere, and this sphere themselves becomes a motive for a crystalline ordering. Therefore, there is a two level of ordering I am talking about, one level wherein you have the individual clusters of TiO 2 forming a sphere, and a sphere itself forming a crystalline order. Of course, the first level is not a crystalline packing, but put together the first and second level consist of a two level ordering, which is again a very, very interesting.