Nanostructures and Nanomaterials: Characterization and Properties

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Lecture - 15
Surface Effects and Physical properties of nanomaterials
(C2) Defect Structure
Mechanical Behaviour of Nanomaterials (C3)

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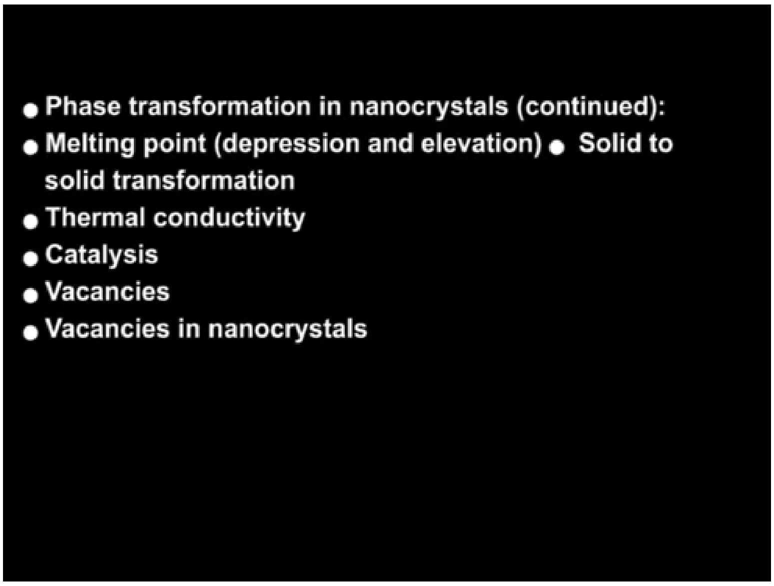

- Phase transformation in nanocrystals (continued):
- Melting point (depression and elevation) ● Solid to solid transformation
- Thermal conductivity
- Catalysis
- Vacancies
- Vacancies in nanocrystals

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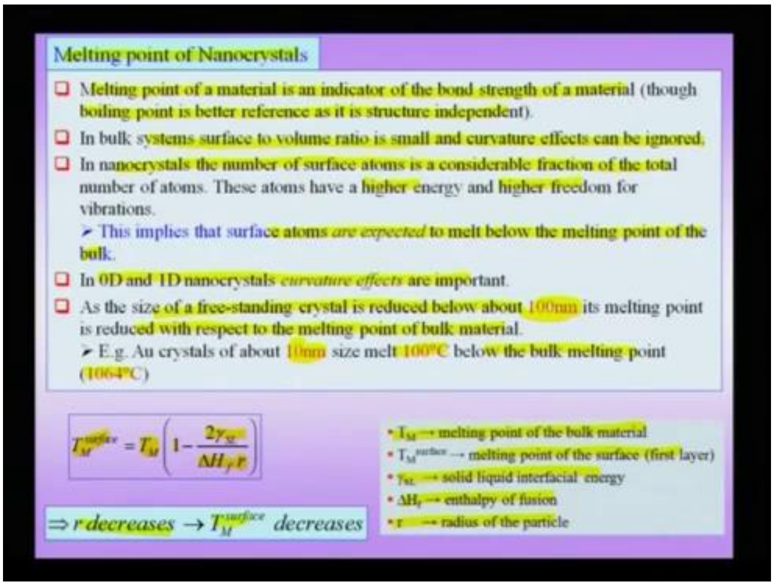

Melting point of Nanocrystals

❑ Melting point of a material is an indicator of the bond strength of a material (though boiling point is better reference as it is structure independent).

❑ In bulk systems surface to volume ratio is small and curvature effects can be ignored.

❑ In nanocrystals the number of surface atoms is a considerable fraction of the total number of atoms. These atoms have a higher energy and higher freedom for vibrations.
➢ This implies that surface atoms *are expected* to melt below the melting point of the bulk.

❑ In 0D and 1D nanocrystals *curvature effects* are important.

❑ As the size of a free-standing crystal is reduced below about 100nm its melting point is reduced with respect to the melting point of bulk material.
➢ E.g. Au crystals of about 10nm size melt 100°C below the bulk melting point (1064°C)

$$T_M^{surface} = T_M\left(1 - \frac{2\gamma_{sl}}{\Delta H_f r}\right)$$

$\Rightarrow r\ decreases \rightarrow T_M^{surface}\ decreases$

- T_M → melting point of the bulk material
- $T_M^{surface}$ → melting point of the surface (first layer)
- γ_{SL} → solid liquid interfacial energy
- ΔH_f → enthalpy of fusion
- r → radius of the particle

After having a broad overview on phase transformation, and the important concept of a critical radius for phase transformations, let us look at melting of Nanocrystals. We had noted that, we have a well-defined melting point T M at which the entire lattice breaks, and therefore you have a molten state. And this is unlike the freezing, which we had talked about. On the other hand, when we talked about the melting point, it was the melting point of what is known as a bulk crystal or a large crystal.

The melting point of a material is an indicator of the bond strength of the material. Though the boiling point is better reference as it is structure independent, in the solid state for instances you have various kinds of phases possible like the BCC crystal or the FCC crystal, and this would affect the melting point, but boiling point is from the liquid state to the gaseous state and that is the better indicator of the bond strength.

But never the less, melting point also gives you a some kind of indication, of what is the bond strength in a material. In bulk systems surface to volume ratio is small, and curvature effects can be ignored, that essentially implies, we can talk about a single number known as the bulk melting point. In Nanocrystals, the number of surface atoms is a considerable fraction of the total number of atoms, and these atoms as we know, have got a higher energy, and a higher degree of freedom, which means they have freedom of more vibrations as compared to the atoms in the bulk. This implies as a first intuitive guess, that surface atoms are expected to melt below the melting point of the bulk.

So, now this is a how much is it true, how much it does it stand to experimental result we will call scrutiny, we will see in a moment. But, as a first intuitive guess, we would expect, that surface atoms because of the higher energy they have got, and the higher freedom they enjoy, they would tend to melt before the bulk atoms. And we have already noted that in 0 d and 1 d Nanocrystals curvature effects are important and cannot be ignored.

Now, as the size of a free standing Nanocrystal is reduced below about say for instance say about 100 nanometre, and I am talking about single crystals, which are free standing. It is noticed that, it is melting point is reduced with respect to the bulk melting point. In fact experiments have shown that gold crystals of about 10 nanometres in size, melt about 100 degrees below the melting point of the bulk. So, there is considerable depression in the melting point when you go to nano scale. And for that we really have to go really go to small sizes like 10 nanometres, and the bulk melting point of the gold happens to be 1064 degree Celsius.

Now, there is a continuum formula which exists, and we will though how correct is the formula, or how accurate it is. We will ignore for now and we will consider, a formula in which the melting point of the surface is given with respect to the melting point of the bulk material, the formula goes as T surface melting is T M into 1 minus 2 gamma solid liquid, by delta H f into r, where T M is, as we noted is the bulk melting point, T surface melting point, that means as if we are assuming now that the surface atoms are melting first.

The gamma solid liquid is the solid liquid interfacial energy, and delta H f is the enthalpy of fusion of the bulk material. And r is the radius of the particle. The important take home message from this formula is that, if I reduce my size, that means if r decreases then, the surface T M surface would decrease, that means that there will be because this is 1 minus this fraction and therefore, you would notice that if I decrease my radius of the particle, which means also the curvature is going to increase, then I would note that, the T M surface would actually decrease. That means the surface atoms would show a depression in the melting point with respect to the bulk melting point.

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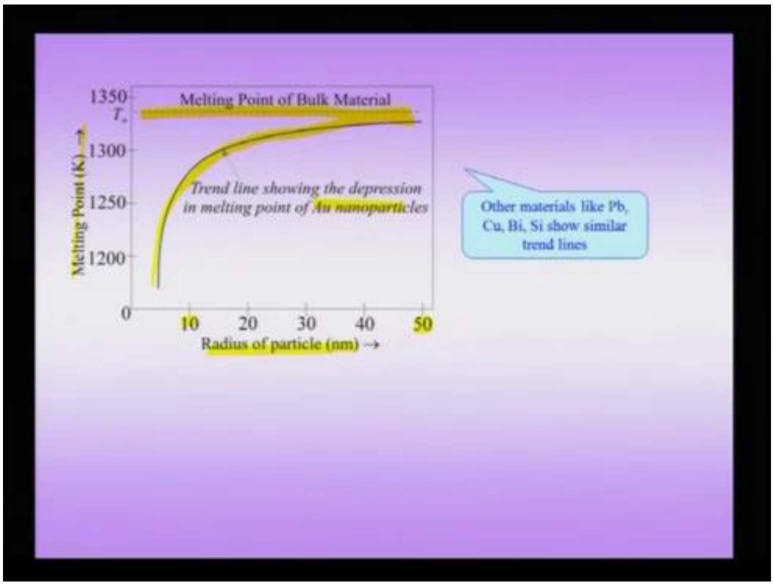

Other materials like Pb, Cu, Bi, Si show similar trend lines

Now, if I now track my melting point, with visa v the radius of the particle, then of course, you have the bulk melting, and this is some kind of schematic drawn, schematic trend line, which is drawn for gold nanoparticles, then we notice that there is a severe depression in melting point as you reduce the size, and this starts to play the considerable role, when the size of the particle is below about 50 nanometres. And we already noted that when the size is 10 nanometres, there is almost a 100 degrees depression in the melting point.

Now, this implies there are two points we have talked about, and these two points need to be resolved, and the first point we mentioned is that, surface would tend to melt below the melting point of the bulk, this is point number one. And we have a few more things to say regarding that, how true is it or how true it is not. Second thing we are noticing an experimental result, where in you are noticing, that actually the melting point of a Nanocrystal.

And now, I am not differentiating the surface from the interior, I am assuming that the entire Nanocrystal is melting, and this we are seeing there is a depression in the melting point of the Nanocrystals. And this trend line which is seen for gold, can also be observed for other materials like lead, copper, bismuth, silicon and the trend lines are very similar. In other words, if you go below about 50 nanometre size, there is a depression in the melting point.

Now, the question, obvious question which arises is that, is the surface melting first. And therefore, the next layer becomes the surface then the next layer becomes the surface or the next layer becomes then therefore there is a continuous melting from outward to inward. There are two possibilities. So, let me write down the scenario of melting.

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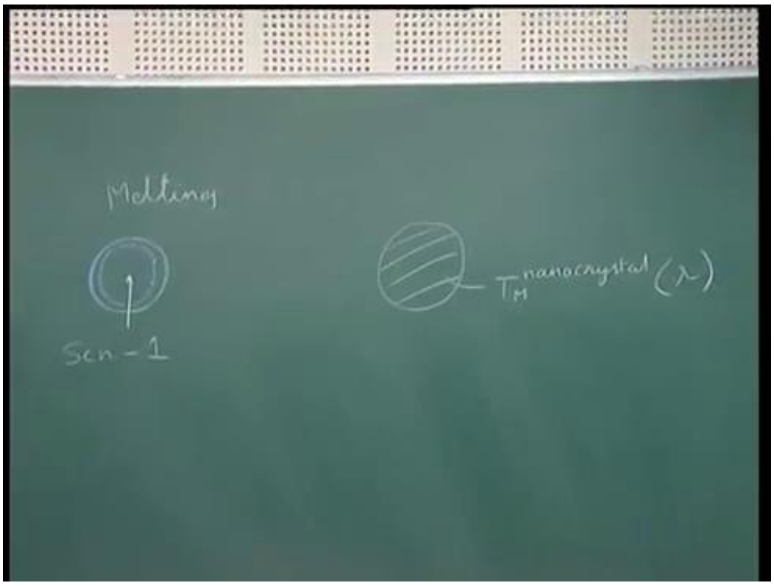

So, there is one possibility that the surface actually melts first, so this layer gets molten, which means now the effective surface has moved inward and this is the new surface, and which is even smaller in size. And since the temperature is already above the melting point of the surface, this crystal, it is definitely this is going to be above the melting point of this crystal and therefore, my melting would progress inward, this is scenario 1.

The other possibility is that the entire crystal melts at a single temperature, and now I call it of course, the T M of the Nanocrystal, which is now obviously a function of radius r. Now which of these two is true is a important question, is it that the melting actually happens at the surface and it progresses inward, or does the whole nanoparticle melt at the single temperature?

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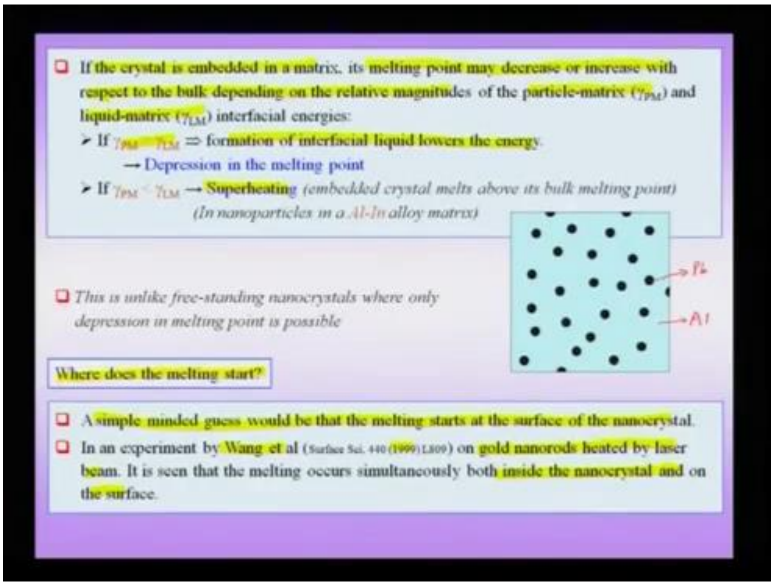

- If the crystal is embedded in a matrix, its melting point may decrease or increase with respect to the bulk depending on the relative magnitudes of the particle-matrix (γ_{PM}) and liquid-matrix (γ_{LM}) interfacial energies:
  - If $\gamma_{PM} > \gamma_{LM}$ ⇒ formation of interfacial liquid lowers the energy.
    → Depression in the melting point
  - If $\gamma_{PM} < \gamma_{LM}$ → Superheating *(embedded crystal melts above its bulk melting point)*
    (In nanoparticles in a Al-In alloy matrix)
- *This is unlike free-standing nanocrystals where only depression in melting point is possible*

Where does the melting start?

- A simple minded guess would be that the melting starts at the surface of the nanocrystal.
- In an experiment by Wang et al (Surface Sci. 440 (1999) L809) on gold nanorods heated by laser beam. It is seen that the melting occurs simultaneously both inside the nanocrystal and on the surface.

And let us answer this question that where does melting start first. A simple minded guess would be that the melting starts at the surface of the nanocrystal, as the formula I pointed out in the previous slide. But in actual experiments and the one which I would like to cite now is the Wang et al which is goes back to 1999, which they did on gold nano rods heated by laser beam, they found that they could not differentiate the melting of the surface from the interior, and both the inside and of the nanocrystal and the surface seem to actually melt as a whole.

Though more work has to be done on various systems and more careful experimentation has to reveal really does actually the surface melt before the interior, but as it stands today. The understanding seems to be, that it is not a scenario one which is operative, but a scenario two, wherein actually the whole nanocrystal melts at a single temperature, which is what you expect for a bulk crystal, in a bulk crystal you define a melting point, which is not surface, interior etcetera dependent. So, you expect that it is melting at a single temperature, though as I pointed out more work has to be actually done to understand this phenomenon.

Now, it is not always necessary that this nanocrystal need be a free standing nanocrystal. Often, this nanocrystal, it could be embedded in a matrix, like for instance the way to produce lead nanocrystal is to actually melt spin. Melt spinning is a technique in which you actually take, you melt your lead and aluminium together and spin it in the form of a ribbon, and often you will get lead nanoparticles which are embedded in a matrix, and a schematic of such a system is shown here. Wherein for instance, this lead is the, this lead could be this phase, which is the black phase or and this could be the matrix, which could be aluminium.

So, another in this system, the nanoparticles or nanocrystals are not free standing, but they are embedded in a matrix. In such a scenario, there is an extension of the concept we just now saw about melting, that it is now not purely, we cannot say that there is going to be a depression or an elevation in the melting point, both of them which are possible, we will have to take it system by system. So, if the crystal is embedded in a matrix, it is melting point may decrease or increase with respect to the bulk, depending on the relative magnitudes of the particle matrix, that means a crystal matrix, and liquid matrix interfacial energies.

So, now if I know the relative magnitudes of these two, the crystal matrix and the liquid matrix interfacial energies, I can predict, will I have a depression in the melting point, or will there be something known as superheating, which is means an elevation in the melting point. Now, if gamma particle matrix, is greater than the gamma liquid matrix, in other words the gamma liquid matrix is the lower of the two interfacial energies then, formation of interfacial liquid lowers the energy it is obvious.

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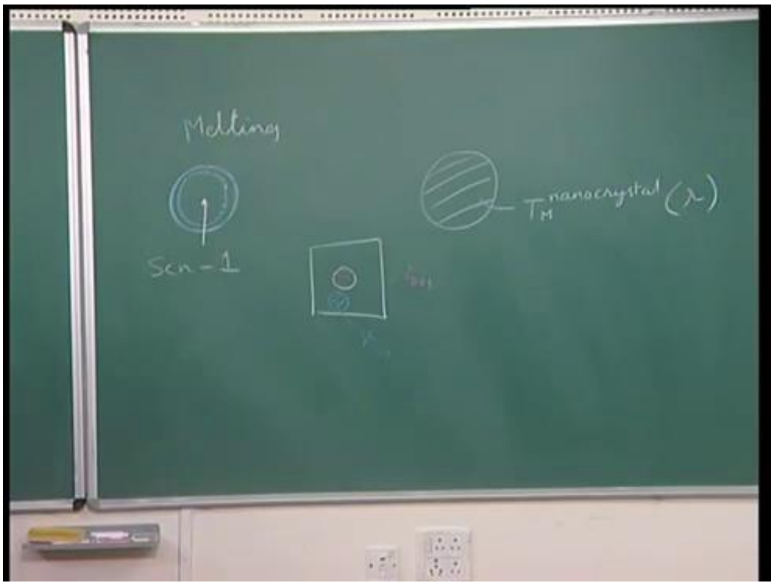

Therefore, now suppose originally there was an unmolten state in which case, I had this particle in a matrix, and now the interfacial relevant interfacial energy, is for the solid with the liquid which is gamma solid or particle matrix. Now, if instead of this thing melts, this region of space melts, then I will have to replace it with this quantity, which is now my or this a molten state, in which case I can replace this by gamma liquid matrix. And since gamma liquid matrix is lower in energy, it would rather melt at a lower, so overall reduce an energy of the system and that means there would be a depression in the melting point.

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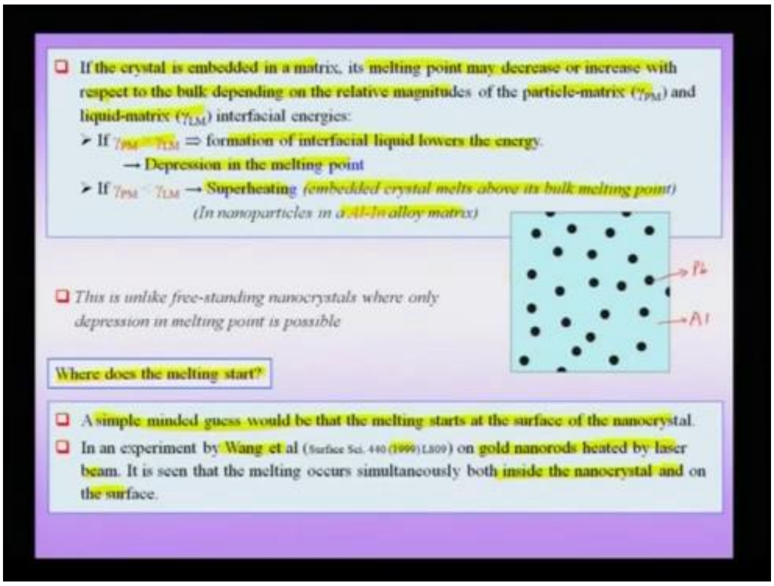

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The opposite would be true, if the gamma particle matrix is lower than the gamma liquid matrix. In such a case, you would observe an elevation in melting point which is called superheating and embedded crystal will melt above its bulk melting point. And this is observed in example of aluminium indium alloy matrix. So, suppose you had aluminium indium particles in an aluminium alloy matrix, then you would actually observe an elevation in melting point which is called superheating.

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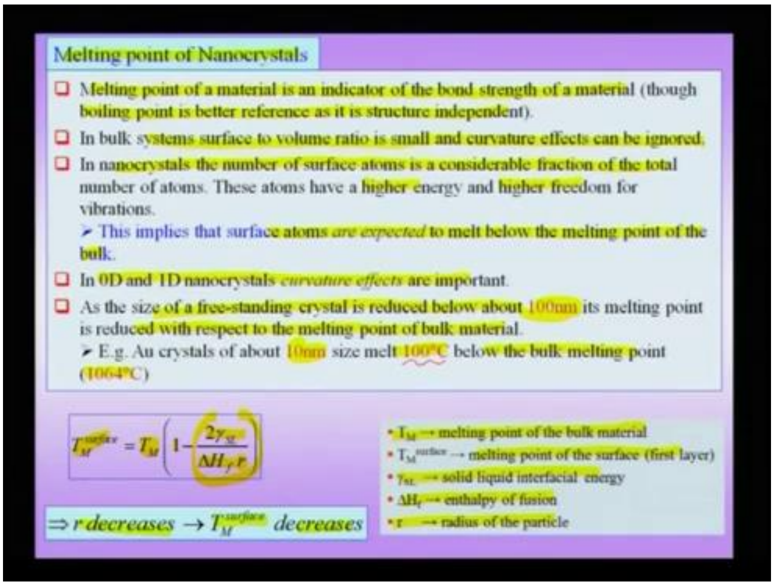

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So, just to summarize the slides related to melting, we observe that if you have free standing nanocrystals, then there is a depression in the melting point which could be a large fraction of the overall melting point for instance, if this is 100 degrees depression would imply, that there is about 10 percent reduction in melting point, if we reduce the crystal size to about ten nanometre.

Second thing we noticed is that as the understanding stands today, the entire nano particle melts at a single temperature, rather than the surface inward melting, which could also be a possibility which needs to be explored. Now, and the third thing we noticed was that, if I have this nanocrystal not as a free nanocrystal, but as embedded in a matrix, then there could be a elevation in the melting point or there could be a depression in the melting point, that depends on the relative interfacial energies between the solid and the liquid or the crystal and the matrix.

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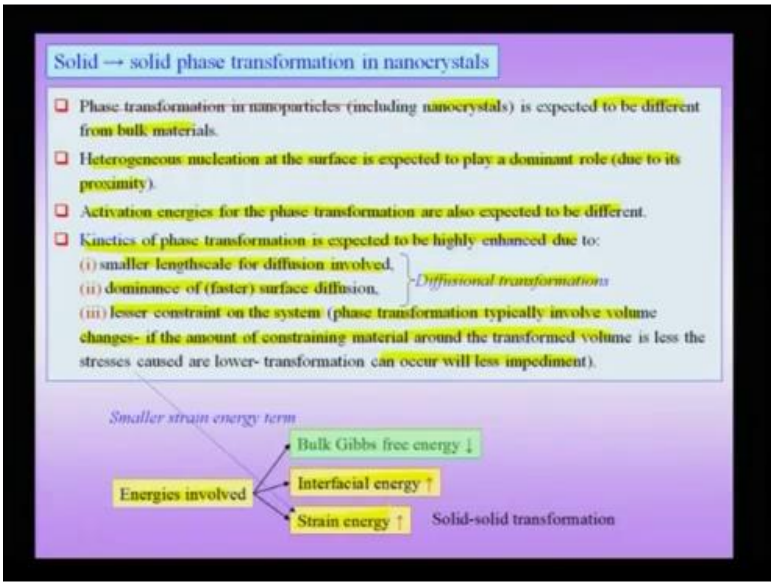

Solid → solid phase transformation in nanocrystals

- ☐ Phase transformation in nanoparticles (including nanocrystals) is expected to be different from bulk materials.
- ☐ Heterogeneous nucleation at the surface is expected to play a dominant role (due to its proximity).
- ☐ Activation energies for the phase transformation are also expected to be different.
- ☐ Kinetics of phase transformation is expected to be highly enhanced due to:
  (i) smaller lengthscale for diffusion involved,
  (ii) dominance of (faster) surface diffusion,
  (iii) lesser constraint on the system (phase transformation typically involve volume changes- if the amount of constraining material around the transformed volume is less the stresses caused are lower- transformation can occur will less impediment).

Now, let us take up the example of solid to solid phase transformation in nanocrystals and we already noticed that in when you talking about for instance liquid to solid, or a solid to liquid phase transformation. Then I can ignore something known as the strain energy, but when you talk about solid to solid phase transformation, still the concept of r star is valid. But in the calculation of r star, I need to invoke the strain energy term as well, that is what we had noted before phase transformations in nanocrystals is expected to be different from bulk materials, so this is very obvious and we will see why it is obvious very soon. Heterogeneous nucleation at the surface is expected to play a dominant role due its proximity.

So far we said that suppose I am doing a melt solidification experiment, and suppose I do this experiment for instance in a container less method that means, I have no container, there is no wall. Then I can reasonably expect that homogenous nucleation is going to take place, but in a solid, to solid face transformation, it is heterogeneous nucleation which is going to be a dominant form of nucleation because, you cannot avoid defects in the material. Like there are going to be grain boundaries, there are going to be stacking faults, there are going to be dislocations, and the even enriched regions of vacancies have known to be playing, are known to play a role in heterogeneous nucleation.

So, heterogeneous nucleation and in the case of nanoparticles, there is one defect which is very close to the bulk of the material, which is the surface and therefore, surface is expected to play an important role, in heterogeneous nucleations in nanocrystals, or heterogeneous nucleation leading to a phase transformation in nanocrystals. Additionally we also expect that the activation energies for the phase transformation is expected to be different from the bulk, which is not an unreasonable expectation.

Additionally apart from the thermodynamic aspects, we also would notice, that the kinetics of phase transformation is expected to be highly enhanced with respect to the bulk. And the reason obvious, we list the three reasons, the important reasons, that smaller length scale for diffusion involved. And suppose I am talking about a diffusional transformation for now, like we have been doing so far the first order diffusional transformations, which produce the nucleation, which progress by nucleation and growth. Then I would notice that since overall particle size is very-very small, the overall length scale for diffusion for phase transformation to be completed is going to be small, it is about of the order of nano scale.

Then there are going to be other effects like surface diffusion, which are going to play a prominent role because now, the entire material is dominated by the surface. Then the third important point is that there is going to be lesser constraint on the system. We had noted that previously by drawing some schematics, that how if I take a region out of the material and it transforms to a different volume, then I have to refit that material into the bulk of the material, which is going to give rise to strain energy.

But suppose the system is very small, then the free surfaces can actually relax and therefore, the system is less constraint that implies that phase transformation typically involve volume changes and there since the amount of constraining material is less, the transformed volume stress is caused by the transformation are lower. That means that there is going to be less impediment to the phase transformation, and we noted earlier that actually the out of the three terms energies involved in a phase transformation, it the interfacial energy and the strain energy term tends to oppose the phase transformation.

And since now the system is less constrained, that means if there is a volume change or a shape change, this can easily be accommodated, because there is a free surface in proximity and that implies that typically the strain energy term is going to be a lower term in a nanocrystal transformation as compared to a bulk transformation. So, let us understand this.

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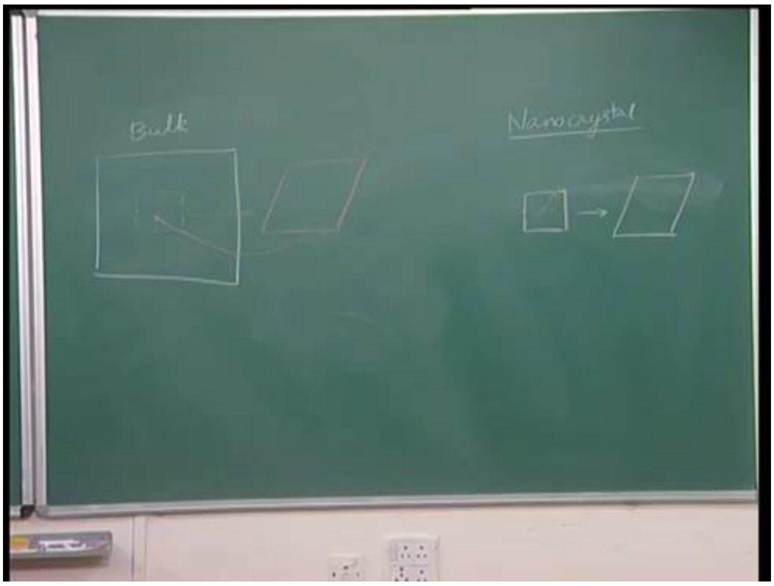

Now, suppose I have a bulk crystal, and I have a certain region which is transforming, and assume that after transformation, this volume becomes like this, that means there is a shape change, and there is a volume change. Now, in the case of the bulk this transformed volume has to be re-inserted into this volume and therefore, there is going to be lot of strain energy term. In the case of a nanocrystal, there is no surrounding medium therefore this transformation can proceed with lesser constraint.

And therefore, and additionally we have already noted that suppose there can be surface diffusion dominance. There can also be overall length scale for diffusion for this would be small, and therefore if even if it is a diffusional transformation or a diffusion less sheer transformation, the overall expectation is that, the strain energy term is going to be small term, and many a, many a times you, we may like to ignore this strain energy term with the phase transformation.

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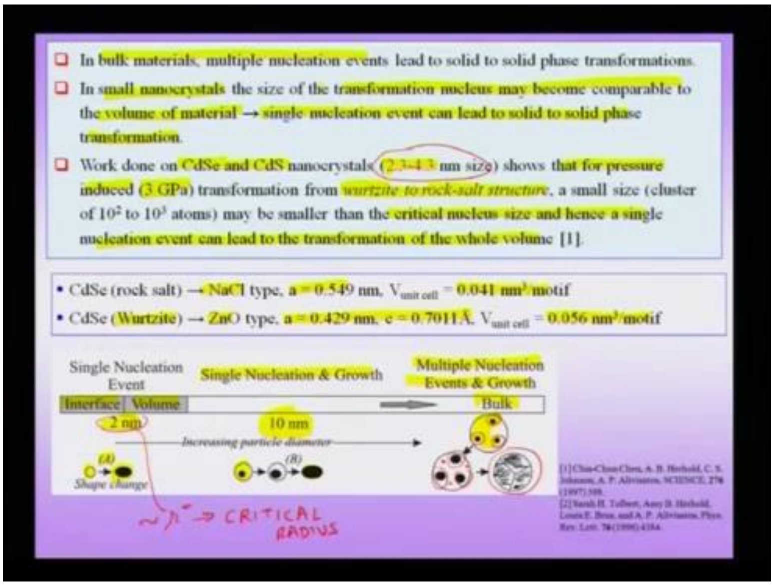

- ☐ In bulk materials, multiple nucleation events lead to solid to solid phase transformations.
- ☐ In small nanocrystals the size of the transformation nucleus may become comparable to the volume of material → single nucleation event can lead to solid to solid phase transformation.
- ☐ Work done on CdSe and CdS nanocrystals (2.3-4.3 nm size) shows that for pressure induced (3 GPa) transformation from *wurtzite to rock-salt structure*, a small size (cluster of 10^2 to 10^3 atoms) may be smaller than the critical nucleus size and hence a single nucleation event can lead to the transformation of the whole volume [1].

- CdSe (rock salt) → NaCl type, a = 0.549 nm, $V_{unit\ cell}$ = 0.041 nm³/motif
- CdSe (Wurtzite) → ZnO type, a = 0.429 nm, c = 0.7011 Å, $V_{unit\ cell}$ = 0.056 nm³/motif

[1] Chia-Chun Chen, A. B. Herhold, C. S. Johnson, A. P. Alivisatos, SCIENCE, 276 (1997) 388.
[2] Sarah H. Tolbert, Amy B. Herhold, Louis E. Brus, and A. P. Alivisatos, Phys. Rev. Lett. 76 (1996) 4384.

Now, we already noted many times before that in bulk materials multiple nucleation events are necessary and we all characterize nucleation as nucleation rate, that means number of nuclei forming per unit time, per unit volume, and that is what leads to phase transformation. So, suppose and schematic is shown here for that, so you have a region of material, wherein there is certain nuclei which form the black dots and with time these nuclei grow. And as these nuclei grow, fresh nuclei are formed in different regions, and finally the entire volume is transformed.

So, you, when you have transformed volume, so it is actually should be shaded black. So, maybe it is a good idea to shade the whole region black, because now this is the transformed volume which is now the black material. Now, in the case of nanocrystals, the size of the transformation nucleus may become comparable to the volume of material. And when we talked about this r star, the critical size for nucleation nucleus, we noted that it is of the order of nanometres 1 to 10 nanometres it is of the order of the nano scale.

And therefore, a single nucleation event may lead to a solid to solid phase transformation in a nanocrystals, which is very-very different from the case of a bulk crystal. And schematic is shown here that you have a nanocrystal at the bottom, which is shown by A and I assume that the nanocrystal is of the order of nanometres, then a single nucleation event is as good as transforming the material, entire material. Therefore, the transformed material is shown on the right. There have been some good research work, and this is typically done on materials like CdSe and CdS which are semiconductors. And the particle size range of 2.3 to 4.3 nanometres, shows that for pressure induced transformation.

Now, this is not that usual heating transformation, but pressure induced transformation. It is seen that for a transformation from a wurtzite to a rock salt structure wurtzite happens to be a ZnO type of a structure, which is an hexical kind of a structure, which has an A and C parameters as given here.

On the other hand, the rock salt structure is a familiar Natl, NaCl type structure, which is cubic, and you can notice here, that the wurtzite structure has a higher volume per motive, as compared to the rock salt structure that means if I increase the pressure, the tendency would be to actually convert this wurtzite to rock salt. And this pressure typically is of the order of giga pascals, and if you apply 3 giga pascal, it is seen that a, that the single nucleation event can lead to the transformation of the whole volume. And that implies that this situation is very different from that of a bulk crystal, wherein nucleation alone does not lead to transformation, there has to be nucleation followed by growth.

Now of course, there is has to be transition, from the nucleation event to a single nucleation event to a bulk system wherein there is multiple nucleation events, and the transition occurs via, what is known as a single nucleation followed by growth regime. So, now I can divide my size regimes into three parts.

One is the very small regime, of the order of 2 nanometres, one a intermediate size regime of 10 nanometres, or maybe 10 to 15 of course, these depend on system to system. And in this case of course, I am taking the example of CdSe or CdS crystals and therefore, if I change the system, these numbers would be different. And the third is the bulk which is now when I am talking about bulk it could be more than about 100 nanometres or 500 nanometres, which I call a bulk system. In the small Nano scale regime, I noticed that this 2 nanometre is of the same order of magnitude as the r star, my critical nucleus nucleation radius.

So, this of the order of critical nucleation radius and therefore, a single nucleation event can lead to phase transformation. In this intermediate size particles like about 10 nanometre particles, we noticed that, single nucleation can lead to a phase transformation, but there needs to be certain growth because the nucleus size as you can see here, as indicated by this black is actually smaller than the particle. But then there is not sufficient region around it for a second nucleus to form, with that means given a small size and therefore, this nucleus grows leading to complete phase transformation.

And finally, of course, you have the bulk wherein, which is as I told you could be of 100 nanometres or more multiple nucleation events followed by growth which is the usual mechanism for bulk crystals. Now, further if you look at closely at the 2 nanometre size crystals, which is frequency region, or in the same region as the experimental study which is from 2.3 to 4.3 nanometres. You notice that you can subdivide this region into very small sizes which wherein they, the nucleation event is interface controlled, that is surface controlled, and you can talk about what you might call a volume controlled regime which is slightly bigger than those very small volumes.

So, let me summarize this very important slide, since r star, which is a critical nucleation radius, is of the order of nanometres especially typically 1 nanometre or 2 say may be 10 nanometres. In some systems, not assume system like CdSe or CdS, wherein it is of the order of 1 nanometre then, a single nucleation event can lead to a phase transformation, which is unlike the bulk crystals.

Now, the important work on CdSe has been done on this pressure induced transformation and the pressure for transformation is pretty high of the order of giga pascals and we was talking about the phase transformation from the wurtzite structure to the rock salt structure. That means from an hexagonal structure, it is going to a cubic structure, and that it since it is pressure induced transformation, we expect that there is going to be a reduction in volume of the unit cell, which is what is seen here from thevolume of the unit cells. And in such a system, we see that in small scales a single nucleation event is enough to cause the entire transformation of the volume.

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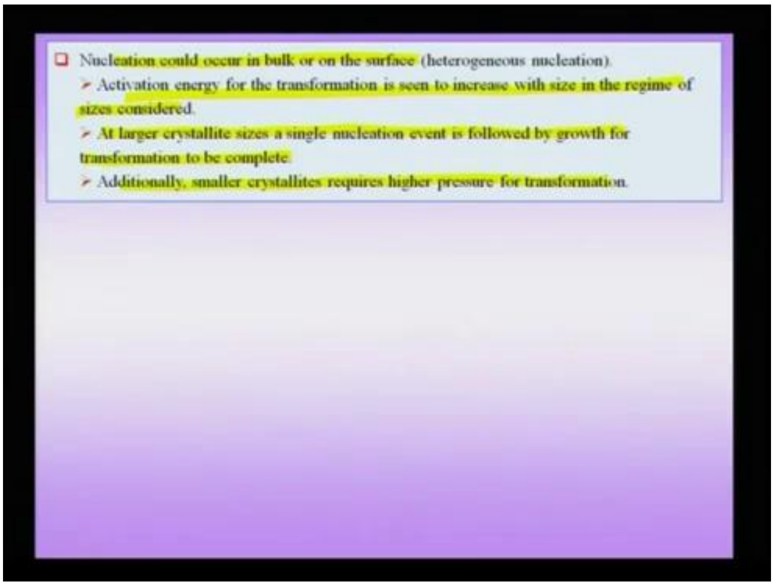

- ☐ Nucleation could occur in bulk or on the surface (heterogeneous nucleation).
  - ➢ Activation energy for the transformation is seen to increase with size in the regime of sizes considered.
  - ➢ At larger crystallite sizes a single nucleation event is followed by growth for transformation to be complete.
  - ➢ Additionally, smaller crystallites requires higher pressure for transformation.

Now, nucleation could occur in the bulk or on the surface, and the activation energy for the transformation is seen to increase with size regime size considered. So, if you are talking about experiments conducted in a CdSe and CdS and you are talking about these Nano scale particles, then the activation energy for the transformation is seen to increase with size. At larger crystallite sizes, single nucleation event is followed by growth of transformation to be complete which we noted before additionally we note that smaller crystallites require higher pressure for transformation. And this for this particular case we will see more examples, and we will actually, we will see one more example wherein we will actually note the pressure at which smaller crystals transform as compared to bulk larger crystals both being in the nano scale.

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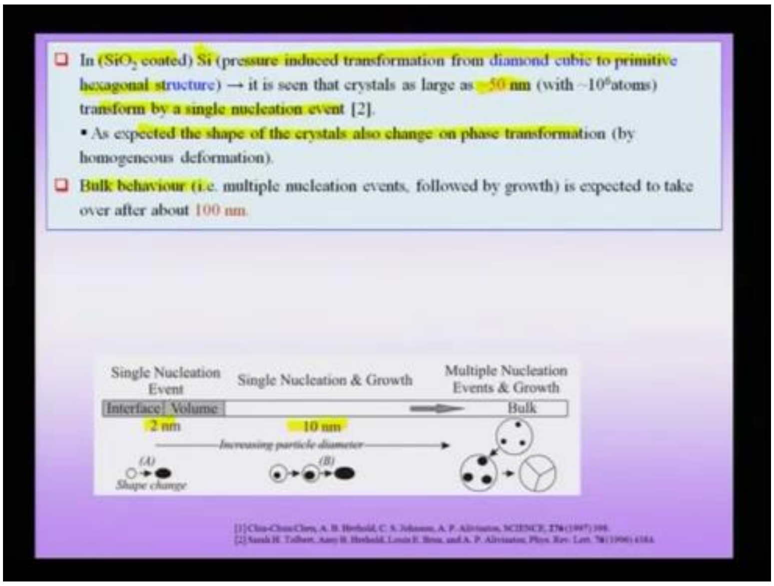

- ❑ In (SiO_2 coated) Si (pressure induced transformation from diamond cubic to primitive hexagonal structure) → it is seen that crystals as large as ~50 nm (with ~10^6atoms) transform by a single nucleation event [2].
  - As expected the shape of the crystals also change on phase transformation (by homogeneous deformation).
- ❑ Bulk behaviour (i.e. multiple nucleation events, followed by growth) is expected to take over after about 100 nm.

[1] Chia-Chun Chen, A. B. Herhold, C. S. Johnson, A. P. Alivisatos, SCIENCE, 276 (1997) 398.
[2] Sarah H. Tolbert, Amy B. Herhold, Louis E. Brus, and A. P. Alivisatos, Phys. Rev. Lett. 76 (1996) 4384.

In other example, we consider here, and here we are taking some illustrative examples, but much of these, the concepts can be applied across many, very many systems, including metallic systems and other systems. In silicon, and now we are talking about SiO 2 coated silicon. Pressure induced transformation from diamond cubic to primitive hexagonal structure, we it is seen that crystals as large as 50 nanometres, transform by a single nucleation event.

So, here we noted that for instance, that it is about of the order of 2 nanometres that we single, about 10 nanometres, sorry, of the order of 10 nanometres that a single nucleation event is responsible. But in other systems, this size can as be as long as 50 nanometres, and this also tells us that the concept is applicable to broader class of systems, and in this case we have to especially note that it is not a free standing silicon crystal, but it is some kind of a ((Refer Time: 24:23)) structure, where silicon is coated with SiO 2.

And this is a natural, can be also thought of as a natural consequence oxidation of the silicon crystal. And as expected the shape of the crystals change on phase transformation, and this is of course, a homogeneous deformation we are talking about, and bulk behaviour in this case of the silicon is expected to take over after about 100 nanometres.

So, it is clear that, when you study more than one size system, that up to about 50 nanometres seems to be the regime, where you can actually have a single nucleation event. Of course, it could be nucleation followed by growth, but the single nucleation event is responsible for the entire phase transformation, and when you go to, for an instance about 100 nanometre or more, we can assume that, it is bulk like behaviour with respect to what you might call them phase transformation by nucleation and growth.

So, now we are taking more and more examples, we are seeing more and more examples, and we had asked and very early in the course, we had asked a question that, what is bulk? So, now with respect to nucleation and phase transformation, we can see that a 100 nanometre crystal can be called bulk, even though we know it is a nano scale crystal, because in terms of the mechanisms for phase transformation, it is no different from a bulk crystal or it is not very different from bulk crystal, because now you have multiple nucleation events followed by growth. So, I can call it bulk like even though it is still in the nano scale.

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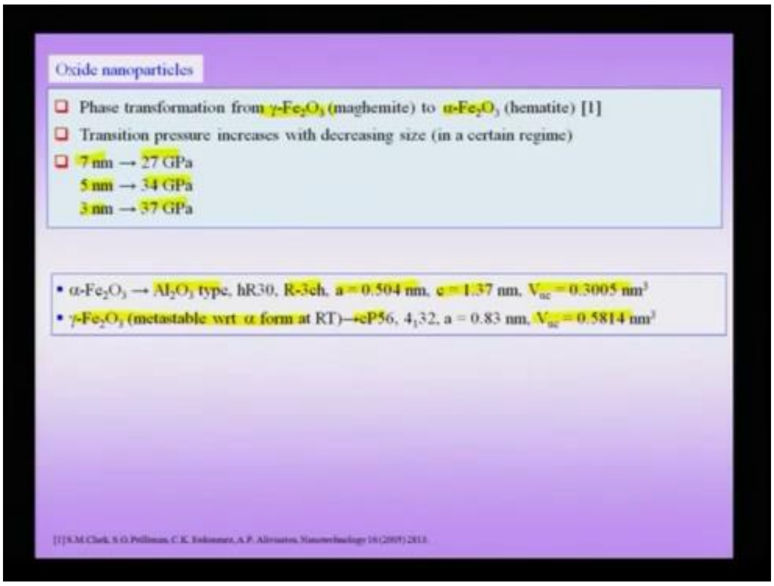

Oxide nanoparticles

☐ Phase transformation from γ-Fe_2O_3 (maghemite) to α-Fe_2O_3 (hematite) [1]

☐ Transition pressure increases with decreasing size (in a certain regime)

☐ 7 nm → 27 GPa
5 nm → 34 GPa
3 nm → 37 GPa

- α-Fe_2O_3 → Al_2O_3 type, hR30, R-3ch, a = 0.504 nm, c = 1.37 nm, V_{uc} = 0.3005 nm^3
- γ-Fe_2O_3 (metastable wrt α form at RT)→cP56, 4_132, a = 0.83 nm, V_{uc} = 0.5814 nm^3

[1] S.M.Clark, S.G.Prilliman, C.K. Erdonmez, A.P. Alivisatos, Nanotechnology 16 (2005) 2813

Another example of a solid to solid phase transformation which is studied is the transformation from gamma Fe 2 O 3 to alpha Fe 2 O 3. Again this is pressure induced phase transformation, and this gamma Fe 2 O 3 is actually a meta stable form at room temperature, with respect to the alpha form. This is a cubic form, and its volume of unit cell is about 0.58. The alpha form and which is a smaller unit cell, is actually a rhombohedra crystal, and it has got A and C parameters as an equal to 0.504 and C is 1.37, is an alumina form of a crystal.

So, you have two forms, one with a larger unit cell, one with a smaller unit cell, and this transformation as you can as perhaps you can guess, that can be driven by pressure. And important thing to note is that as you decrease the size, and now we are really in the very small size regime, 7 nanometre to 5 nanometre to 3 nanometre, you can see that the transformation pressure actually increases. That means for smaller and smaller particles, actually you need larger and larger pressures for phase transformation to take place. And of course, these pressures are employed by using a diamond ((Refer Time: 27:01)) and so there are inherent complications and actually studying the in situ phase transformations, and getting the signal of how the transformation has taken place.

So, these are very careful experiments, which have to be conducted, but the general trend line seems to be that as you reduce the crystallite size, you need to apply more and more pressure for phase transformation to take place. Next we take up couple of more physical properties, and both of these are actually vast areas of research, where in lot of work has been done, but we will take a small sample of results, to understand that how nano materials can actually be different from bulk materials, and as usual we take up those examples where the demarcation is very clear cut.

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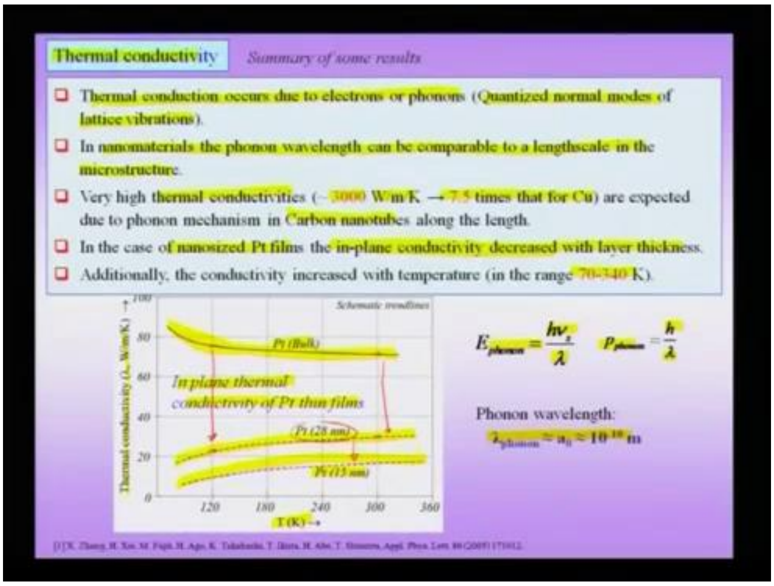

Thermal conductivity *Summary of some results*

- ❑ Thermal conduction occurs due to electrons or phonons (Quantized normal modes of lattice vibrations).
- ❑ In nanomaterials the phonon wavelength can be comparable to a lengthscale in the microstructure.
- ❑ Very high thermal conductivities (~3000 W/m/K → 7.5 times that for Cu) are expected due to phonon mechanism in Carbon nanotubes along the length.
- ❑ In the case of nanosized Pt films the in-plane conductivity decreased with layer thickness.
- ❑ Additionally, the conductivity increased with temperature (in the range 70-340 K).

$$E_{phonon} = \frac{hv_s}{\lambda} \quad P_{phonon} = \frac{h}{\lambda}$$

Phonon wavelength:

$$\lambda_{phonon} \approx a_0 \approx 10^{-10}\,\text{m}$$

[1] K. Zhang, H. Xie, M. Fujii, H. Ago, K. Takahashi, T. Ikuta, H. Abe, T. Shimizu, Appl. Phys. Lett. 86 (2005) 171912.

And often there is a startling or a very different kind of variation as compared to the bulk. So, that we can understand that at the Nano scale there are some very interesting effects, which we do not observe in the bulk materials. So, let us take one of those physical properties we talk about now next is that thermal conductivity.

We know that thermal conduction occurs due to electrons and phonons. In normal metallic materials electrons are the dominant form of conduction, but suppose I am talking about a diamond, we know that diamond has no free electrons, and therefore, or very little free electrons at room temperature. Therefore, it is phonons which are responsible for thermal conduction, actually diamond happens to be a very good thermal conductor. In fact, if one holds a diamond blade and actually cuts through ice, the heat of the hand can actually conduct it very nicely through the diamond and it will actually cut ice very nicely. And this phononic mode of conduction, as you know phonons are quantized normal modes of lattice vibrations.

And later on we will talk about plasmons in the context of optical properties, plasmons are collective oscillations of electrons while phonons are collective oscillations of quantized oscillations of elastic oscillations of atoms or we may call lattice vibrations. In nano materials, the phonon wavelength can be comparable to the length scale of the microstructure or in the case a nano particle itself.

So, this is an important point, that means phonons can get confined in the material, because now it cannot travel through the medium. So, that is an important point to note. And therefore, we do expect that when phononic conduction is dominant form of conduction, that in nano scale materials, things are going to be very different. Even in cases where electronic conduction is the important mechanism, you do expect that it is going to be different from the normal materials.

Now, if you talk about phonon wavelength, you can write down E phonon is hv by lambda, v is the velocity of sound. And the momentum of photon h by lambda, putting together we can see the lambda phonon, is of the order of 10 power minus 10, or in some cases, you can talk about it being in the nano scale. Now, in experiments, there are two at least, two experiments, we will take up, and or two results we will summarize here, and both of these results are you might say opposite sides of the whole spectrum. One is the case of carbon nanotube, where you see a highly enhanced thermal conductivity, which is occurring because of phonons.

And in fact you observe something like, about 3000 watt per metre per Kelvin which is seven times or more than that of copper, and this is observed in carbon nano tubes along the length. And this is expected to be because of the phononic mechanism. Now, we later on when we talk about conduction, electrical conduction, we will also notice that in carbon nanotubes, you can actually have electrical transport which is ballistic. Again that means, un-imperial transport of electrons across the length of the carbon nanotube, which means that you cannot have ballistic conduction.

So, you can see that thermal conductivities and electronic conductivities, along carbon nano tubes is very high. And the result which is contrary to that which we are also talking about which we will take up now, is the case of nano sized platinum films, and we are talking about in plane conductivity, and its dependence on thickness. So, we have two examples in front of us, one is the case of the carbon nano tube, where in phononic conductivity is giving us very high conductivity as compared to even that of copper, along the length of the tube. The other case is a case of platinum, where you expect free electrons to be present, and we notice that the in plane conductivity of these thin films, these are platinum thin films, actually decreased with size.

Now, suppose I am talking about thermal conductivity and it is plot with temperature then, you notice that for platinum bulk that the thermal conductivity actually decreases with temperature, which is the normal behaviour you would observe, because now you going to have more and more collisions of electrons with phonons. Therefore, you actually will have a decreased mean free path and therefore, you expect that the resistance of the material is going to actually decrease, increase which is case of electrical conductivity. And similarly, you would also notice that the thermal conductivity is actually going to degrade with temperature.

So, the thermal conductivity and electrical conductivity, both you expect to degrade with temperature and which is what you see in the case of platinum bulk. Now, if you take about, talk about in plane thermal conductivity of platinum thin films, there are two important things to be noticed, which are both of which are unexpected and startling in some sense. Number one is that the overall conductivity value for any given temperature actually is much-much lower.

So, you can see that a 28 nanometre film, the conductivity for instance you take at temperature like 120 Kelvin, you notice that it is about 20, and this is slightly less than 80. So, there is a considerable reduction in the thermal conductivity at any given temperature, and here when it higher temperature 300 kelvin, you notice this is about 30, and this is about 70.

So, it is more than double or 2 and a half times reduced with respect to the bulk value. Further you also noticed, if the film size is made thinner, then the thermal conductivity actually decreases even more, that means a 15 nanometre film, is actually having a lower thermal conductivity as compared to a 28 nanometre film, which is having a lower thermal conductivity as compared to the bulk. So, therefore we keep on increasing the thickness at some point of time, I would perhaps have a transition from what you might call a nano scale regime to bulk regime.

Now, there is another important effect, which we see from the curve, which is very different from that of the bulk, and this is seen in the regime of 70 to about 340 Kelvin, which in, which is the regime in which the experiment was done in the platinum films. And you can notice that, in this regime actually the thermal conductivity increases with temperature. In the case of bulk semiconductor you already noticed that the thermal conductivity decreases with temperature, but unlike the bulk for the nano size films, the thermal conductivity actually increased with temperature.

So, the through startling effects in the case of materials having electronic conductivity number 1 is that, the thermal conductivity actually increased with temperature in a nano scale materials and number 2. The thermal conductivity of a nano scale materials and I am talking about in plane conductivity of films, and this is not nano particles, this is not nano tubes, but actually films, and these films is much lower than the bulk counterparts. And this is in contrast with a nanostructure like a carbon nano tube, wherein you actually observe much higher or highly enhanced thermal conductivity along the length of a carbon nanotube.

So, though we have only considered a very little part of the whole story of the thermal conductivity, but this I hope can convey the, what you call an important message that the thermal conductivity of nanomaterial is going to be very different from that of the bulk materials. And this may have important consequences when you are actually designing devices, and you are worried about the cooling of these devices because there is a lot of heat generated, because of and you may want to put design various strategies for the cooling purposes. And you will notice, that the cooling rate or the dissipation of heat through the some of these. For instance nanostructure is going to be very different from that of bulk, and therefore that aspect has to be kept in mind when devices are designed.

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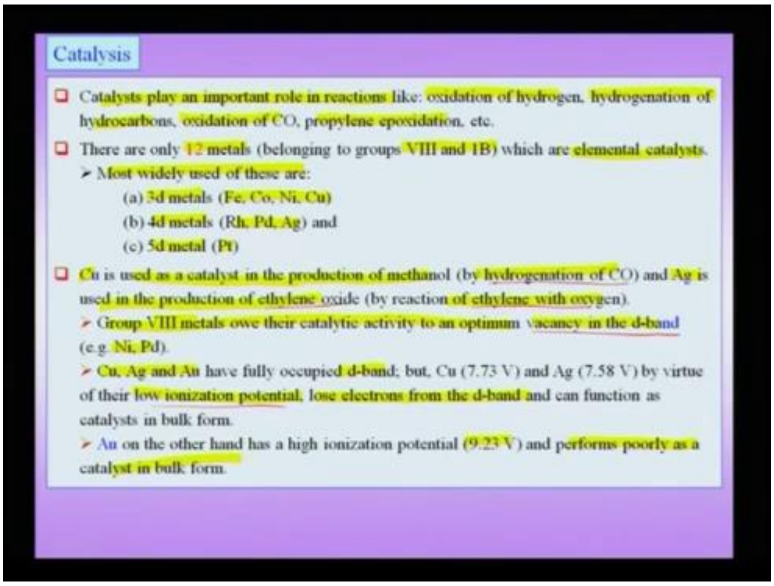

Catalysis

- ☐ Catalysts play an important role in reactions like: oxidation of hydrogen, hydrogenation of hydrocarbons, oxidation of CO, propylene epoxidation, etc.
- ☐ There are only 12 metals (belonging to groups VIII and 1B) which are elemental catalysts.
  - ➢ Most widely used of these are:
    - (a) 3d metals (Fe, Co, Ni, Cu)
    - (b) 4d metals (Rh, Pd, Ag) and
    - (c) 5d metal (Pt)
- ☐ Cu is used as a catalyst in the production of methanol (by hydrogenation of CO) and Ag is used in the production of ethylene oxide (by reaction of ethylene with oxygen).
  - ➢ Group VIII metals owe their catalytic activity to an optimum vacancy in the d-band (e.g. Ni, Pd).
  - ➢ Cu, Ag and Au have fully occupied d-band; but, Cu (7.73 V) and Ag (7.58 V) by virtue of their low ionization potential, lose electrons from the d-band and can function as catalysts in bulk form.
  - ➢ Au on the other hand has a high ionization potential (9.23 V) and performs poorly as a catalyst in bulk form.

The next property, which perhaps is in some sense is very much related to the other properties we have been seeing before, which is related to the surface property. Because in some sense the conduction, we were talking about is more dominant by the bulk rather than the surface. But in catalysis it is clear, that it is the surface effect which is very-very important, and we know what is a catalyst, a catalyst is something which enhances the rate of the reaction, but it itself does not get consumed by the reaction.

So, that is an important thing about catalyst, that it itself does not get consumed, and you know a lot of industries rely upon good catalyst for industrial production. Catalysts are known to play an important role in reactions like oxidation of hydrogen, hydrogenation of hydrocarbons, oxidation of carbon monoxide, polypropylene peroxidation, etcetera.

Again, like before we will view this from a slightly classical viewpoint, and also we will take up only couple of examples which are startling, while literature on this area is again extremely vast and it as because of the industrial application, this is also very useful to study catalysis, an especially role of nanoparticles and nano crystals in catalysis. If you look at the history of the materials, only about 12 metals, they and these typically belong to groups VIII and 1b, which are elemental catalysts.

So, there are very small representation of the whole element periodic table which are naturally catalysts. Most widely used ones of those are 3d metals like iron, cobalt, nickel, copper, 4d metals like rhenium, palladium, silver and 5d metals like platinum. So, these are some of the usually used catalysts for these some of the reactions which we have seen before. Copper is used in the catalysis of methanol production, by hydrogenation of carbon monoxide, and silver is used in the production of ethylene oxide by the reaction of ethylene with oxygen.

So, there are some examples, now how does this catalytic activity come in? So, again we go back a little back in time and perhaps take a classical viewpoint and try to understand this, that group VIII metals owe their catalytic activity to an optimum vacancy in the d band, like nickel and palladium, they have some kind of optimum vacancy in the d b. And therefore, these group VIII metals, have you expect them to be having some catalytic activity. On the other hand, if you look at copper, silver and gold, they have a completely filled d band, but by the virtue that they have a low ionization potential, and they can lose electrons from the d band these can also function as catalysts is bulk form.

So, therefore either you need to have an vacancy in the d band or if you have a low ionization potential, then you expect that such a material would be able to perform the role of the catalyst. And this reaction we could be talking about is an example of ethylene reaction, ethylene oxygen produce, ethylene oxide or hydrogenation of carbon monoxide etcetera. Gold, if you look at, gold does not satisfy any of these criteria, and it has a high ionization potential like 9.23, and therefore you expect gold to perform poorly as a catalyst in bulk form. So, the classically in bulk form if you see gold, then you would say a gold is not going to be a catalyst, and therefore I would discard it in the bulk form to play the role of the catalyst.

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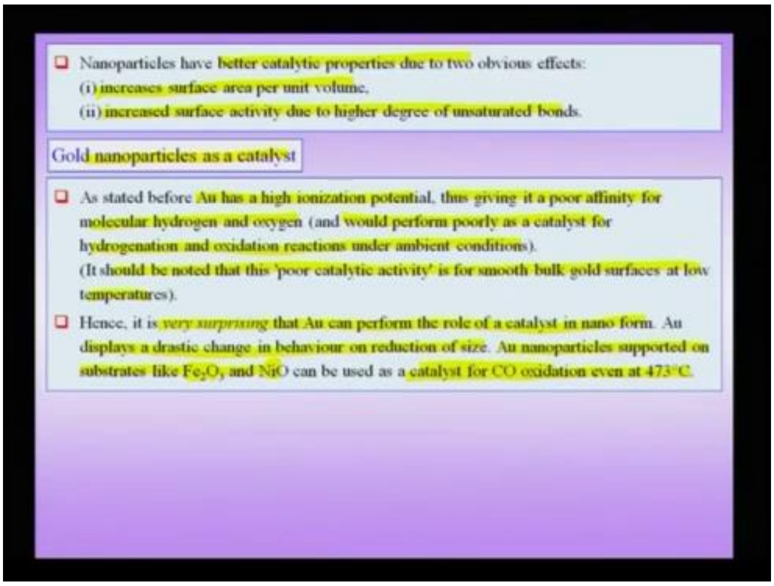

- Nanoparticles have better catalytic properties due to two obvious effects:
  (i) increases surface area per unit volume,
  (ii) increased surface activity due to higher degree of unsaturated bonds.

Gold nanoparticles as a catalyst

- As stated before Au has a high ionization potential, thus giving it a poor affinity for molecular hydrogen and oxygen (and would perform poorly as a catalyst for hydrogenation and oxidation reactions under ambient conditions).
  (It should be noted that this 'poor catalytic activity' is for smooth bulk gold surfaces at low temperatures).
- Hence, it is *very surprising* that Au can perform the role of a catalyst in nano form. Au displays a drastic change in behaviour on reduction of size. Au nanoparticles supported on substrates like Fe_2O_3 and NiO can be used as a catalyst for CO oxidation even at 473°C.

Instead of talking about bulk crystals, suppose I am talking about nanoparticles, then it is obvious that nano particles are expected to have certain better catalytic property as compared to bulk materials, and these comes from two obvious effects, one is the increase in surface area per unit volume, and the increase in surface activity to high degree of unsaturated bonds. So, we do expect already, that when you go to the nano scale, there will be a certain benefit in using of a catalyst in the nano crystalline or nano form.

Now, we just noted that gold actually does not perform good, when you are talking about a bulk gold, but then it has been found that gold can actually be used as a catalyst in the nano form. So, gold has a high ionization potential. Thus, giving it poor affinity for molecular hydrogen and oxygen, and expected to perform poorly as a catalyst for hydrogenation and oxidation reactions, under ambient conditions. Of course, it should be noted that, the poor catalytic activity is for smooth gold surfaces at low temperatures.

So, this is what we are referring to, and the expectation is that gold is not a very good catalyst. And it is very surprising that gold can perform the role of catalyst in nano form. Gold displays a drastic change in behaviour on reduction of size, gold nano particles supported on substrates like Fe 2 O 3 and NiO can be used a catalyst for CO oxidation, even at low temperatures like 473 degree Celsius.

So, the observation is that, now gold which is not a bulk catalyst, can actually be used as a catalyst in nano form. And needless to say that we have already noted before that these gold nano particles cannot be kept in touch with each other, then they will tend to coagulate therefore, they are typically embedded in a substrate, and these substrates have been noted to be Fe 2 O 3 and NiO.

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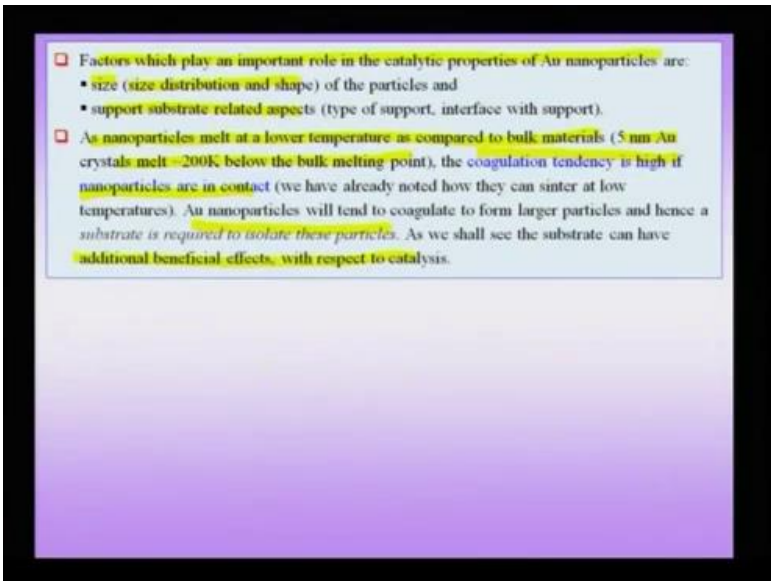

- ☐ Factors which play an important role in the catalytic properties of Au nanoparticles are:
  - size (size distribution and shape) of the particles and
  - support substrate related aspects (type of support, interface with support).
- ☐ As nanoparticles melt at a lower temperature as compared to bulk materials (5 nm Au crystals melt ~200K below the bulk melting point), the coagulation tendency is high if nanoparticles are in contact (we have already noted how they can sinter at low temperatures). Au nanoparticles will tend to coagulate to form larger particles and hence a *substrate is required to isolate these particles*. As we shall see the substrate can have additional beneficial effects, with respect to catalysis.

And we will note shortly the relevance and the importance of substrate in the whole process, but the important thing to note is that the gold now in nano form can be used as a catalyst, and this is a very startling expectation or startling behaviour. Factors which play an important role in catalytic properties of gold are, first of course we are talking about gold nano particles, size. That means size and size distribution and shape of the gold nanoparticle, and additionally which is a important point is the substrate. That means what is the type of the support, what is interface with the support, substrate which is having, all this plays an important role in final outcome of the gold nanoparticles catalytic behaviour.

We already noted that gold nanoparticles melts at lower temperature as compared to bulk materials, for instance we have noted that 5 nanometre gold actually melts 200 degrees below the melting point. And this enhances the coagulation tendency and nano particles are left in contact.

And we have also noted that actually nano particles can sinter at temperatures much lower than, and we have noted the role of vacancies in the process sintering. Therefore, we cannot leave these gold nano particles in touch with each other, they have to be isolated and substrate therefore, performs the first important role of isolating these gold nanoparticles. And, but the important thing which comes out of this study, with the experimental study is that, there are additional benefits with respect to catalysis of using the substrate, and we have noticed the two substrates we noted before Fe 2 O 3 and NiO.

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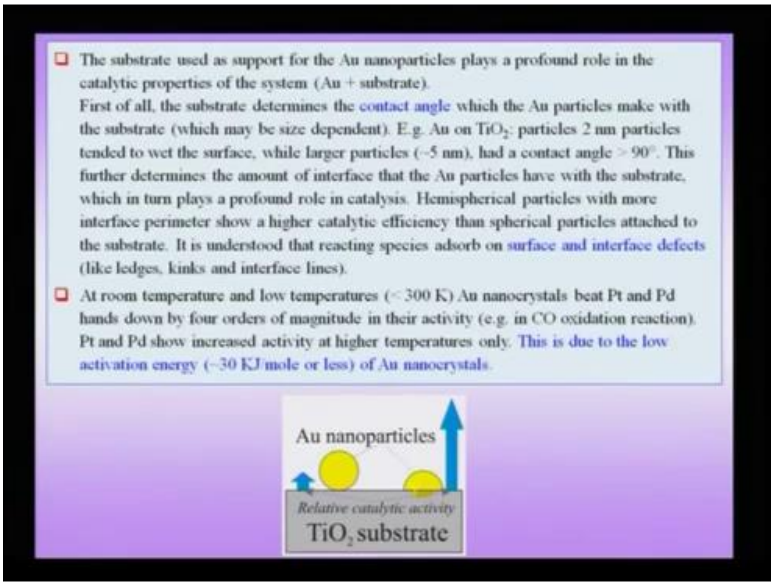

- ☐ The substrate used as support for the Au nanoparticles plays a profound role in the catalytic properties of the system (Au + substrate).
  First of all, the substrate determines the contact angle which the Au particles make with the substrate (which may be size dependent). E.g. Au on TiO_2: particles 2 nm particles tended to wet the surface, while larger particles (~5 nm), had a contact angle > 90°. This further determines the amount of interface that the Au particles have with the substrate, which in turn plays a profound role in catalysis. Hemispherical particles with more interface perimeter show a higher catalytic efficiency than spherical particles attached to the substrate. It is understood that reacting species adsorb on surface and interface defects (like ledges, kinks and interface lines).
- ☐ At room temperature and low temperatures (< 300 K) Au nanocrystals beat Pt and Pd hands down by four orders of magnitude in their activity (e.g. in CO oxidation reaction). Pt and Pd show increased activity at higher temperatures only. This is due to the low activation energy (~30 KJ/mole or less) of Au nanocrystals.

Now, when I embedded, embedded gold nano particle in a substrate, there are important parameters which automatically come about, what is suppose the shape of the gold nano particle? Is the embedding partial like this picture on the right or is it more to, more like this wherein the particle is not embedded deep into the substrate? So, we could have a range of embeddings.

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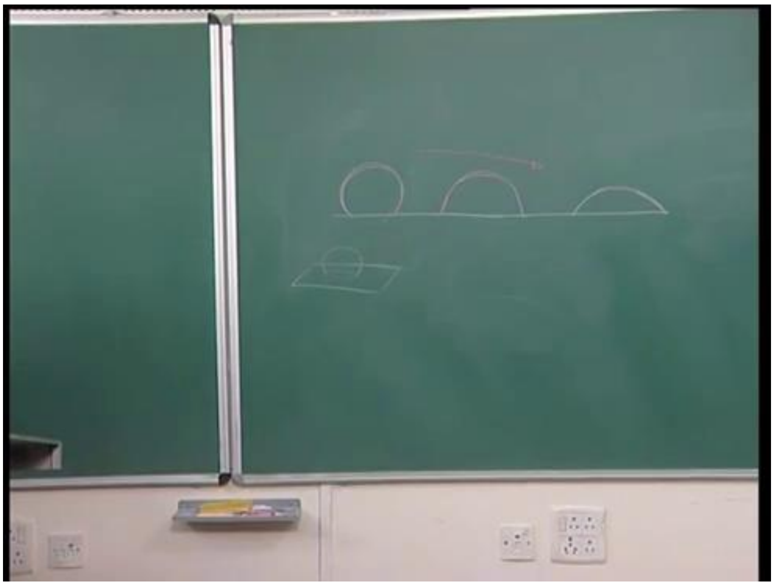

So, if I have a substrate, so my gold nano particle could be embedded such that only a small part of it is embedded, it could be such that it is almost like a semicircle, or it could be even deeper embedded. And what is the difference between all these of course it is of course, the surface area of gold which is exposed, which is going to be this number, this area. And you can see that the surface area of gold is actually decreasing as you go from small embedding to a large embedding.

Additionally there is one more parameter to be noted in this embedding, and that is the interface. Suppose, I look at the three dimensional figure of this, I can actually notice that, when I have a particle which is embedded, then I would have actually a circular interface which is the line of contact between the particle and the substrate. So, this area, interface or a triple point line, which is the interface between the gold nano particle the substrate and air, and that length would change depending on the embedding.

So, in this case the length is small, in this case it is maximum possible, and in this case there is somewhat intermediate length of embedding. That means, now the triple line which is passing as an interface between the three phases, that is also changing depending on the embedding.

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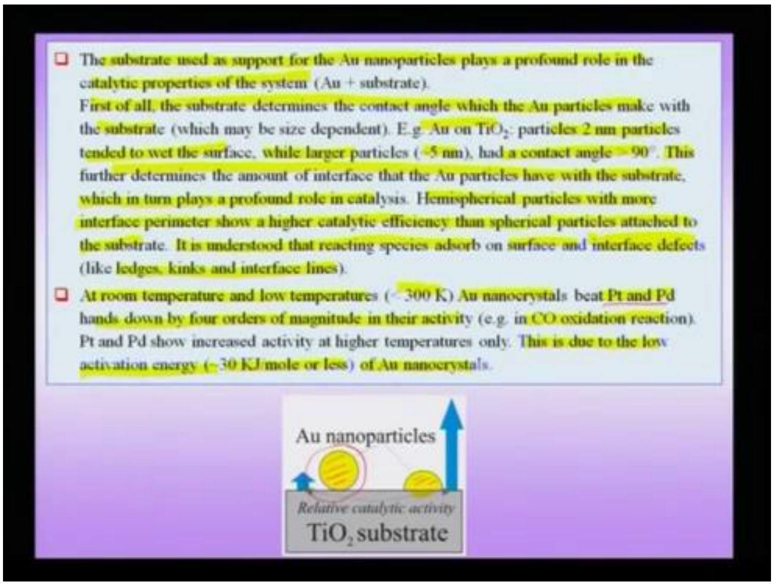

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Now, this has important consequence on the catalysis, and we will note that by reading this phrase here. The substrate used in as support for gold nano particle plays a profound role in the catalytic properties of the system. First of all, the substrate determines the contact angle with which the gold nano particles make with the substrate, and which is of course, size dependent. Gold and titanium 2 nanometre particles tended to wet the surfaces, while larger particles 5 nanometre have a contact angle of 90 degrees, that means 90 degrees mean partial wetting. And in the case of 2 nanometre particles, which is extremely small particles, they tend to form a uniform coverage, that means there is a wetting tendency.

So, the wetting tendency itself is a function of the size of the nano particle. This wetting also is going to tell you, what is the amount of interface that the gold nano particles will have with the substrate, which in turn performs a profound role in the catalysis. Hemispherical particles with more interface perimeter show higher catalytic efficiency than spherical particles attached to the substrate.

So, if you compare the two pictures, which are drawn here schematically below, one is the case of the non wetting kind of a situation, where the particle is sitting virtually outside, versus a case of a 90 degree contact angle with wherein the perimeter area is large. Then you notice that the one which is embedded nicely is the one or a hemispherical cap kind of an embedding is actually giving you higher catalytic activity as compared to the one which is not wetting the surface.

It is understood that the reacting species adsorb on the surface and interface defects, like ledges, kinks and interface lines. So, interface lines play an important role apart from ledges and kinks which anyhow exist on the gold surface, in determining the catalytic activity. At room temperature and low temperatures about less than 300 Kelvin, gold nano particles beat platinum palladium, hands down by 4 orders of magnetic magnitude in their catalytic activity. If you go back and look at this slide, where we have talked about a catalysts, we have noted that platinum and gold are well known catalysts, platinum and palladium are well known catalysts, but gold we said in bulk form is not a catalyst.

But when you go to nano scale, it looks like the roles are reversed and you can actually note that, gold can outperform platinum palladium. Of course, in a certain regime of temperature certain regime of embedding, that it can actually go and beat platinum and palladium with respect to the catalytic activity. And here we are talking about of course, as I said a limit of regime where the cobalt carbon monoxide oxidation reaction has been studied, and this is understood due to the low activation energy of about 30 kilo joule per mole for, by using gold nanocrystals. Therefore, we see that when you go to nano scale, there are behaviours which are highly unexpected, and this is this continues to be...

So, in case of catalysis, where in spite of gold not being in the list of usual known catalyst like, the 3d metals, like and the 4d metals and 5d metals like platinum, palladium, silver, cobalt. But you find that when you go the nano scale, and especially when we are trying to track catalytic activity of gold nano particles in the low temperature regime, and for a particular reaction like carbon monoxide, you can actually go ahead and beat some of the well known catalysts.

And the important parameters of course, in the whole thing is the shape of the nano particles, the size of the gold nano particles, the substrate medium is it titanium, or is it nickel oxide, or is it one of the other materials which can be chosen as substrate materials. The contact angle that the gold nano particle makes with the substrate and all this put together it can be seen that there is an effective role that gold in nano scale can actually perform in the case of catalysis. And this is again one of the startling effects, which you see only when you go to the Nano scale.

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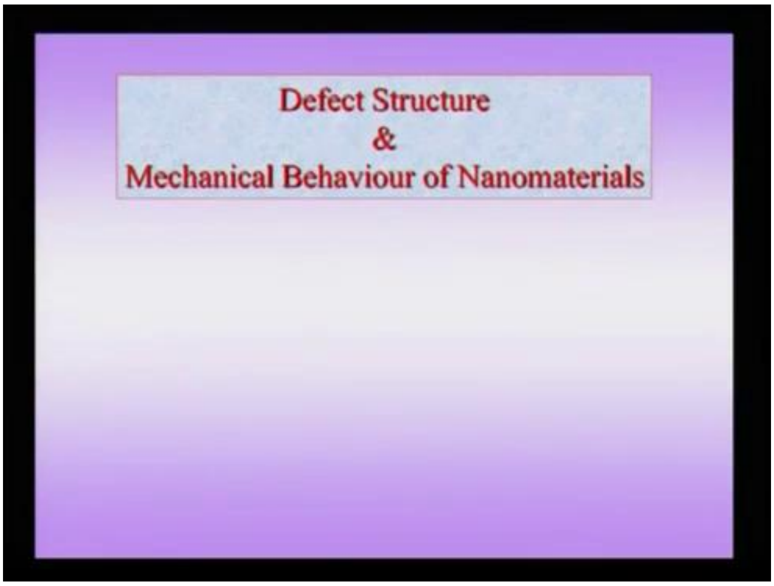

Defect Structure
&
Mechanical Behaviour of Nanomaterials

The next chapter we take up is related to the mechanical behaviour of nano materials. And since defect structure plays a very important role in the mechanical behaviour, we first talk about the defect structure followed by the mechanical behaviour of the nano materials.

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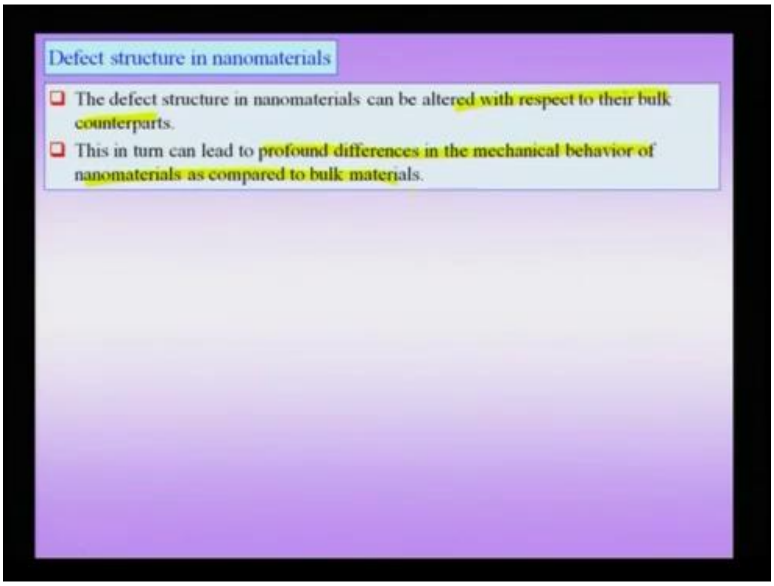

Defect structure in nanomaterials

- ☐ The defect structure in nanomaterials can be altered with respect to their bulk counterparts.
- ☐ This in turn can lead to profound differences in the mechanical behavior of nanomaterials as compared to bulk materials.

The defect structure in nano materials can be highly altered with respect to bulk materials, and this actually plays a direct role in terms of the properties. And these properties could be conductivity, diffusion, could be we could be even talking about compressive strength, or fracture toughness, any one of those properties. And therefore, I need to know the defect structure of nano-materials, and we have already previously defined what is it, what is it term defect structure means?

It terms it include as we have noted before, entities like distribution of defects, its size, its overall volume fraction, etcetera or length per unit volume etcetera. So, we need to know the defect structure in a material, so that I understand the profound differences in the mechanical behaviour of nano materials as compared to bulk materials. So, the first of these defects I take up is vacancies.

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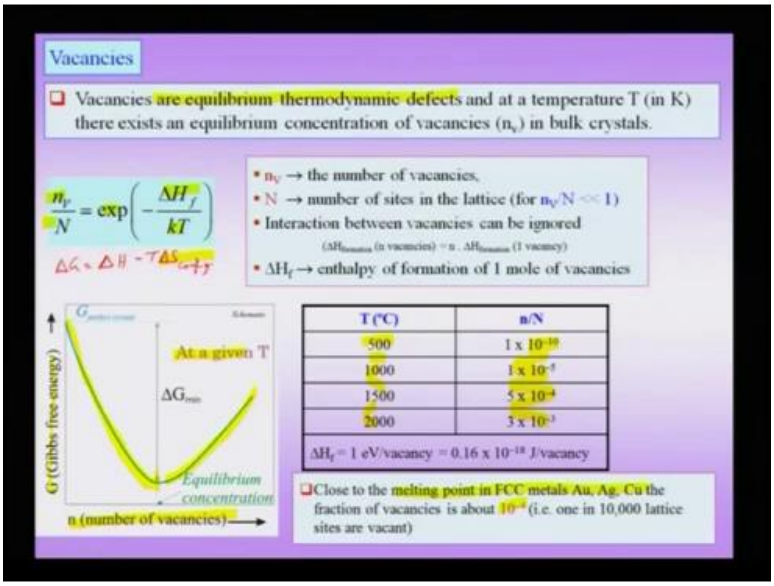

Vacancies

❑ Vacancies are equilibrium thermodynamic defects and at a temperature T (in K) there exists an equilibrium concentration of vacancies (n_v) in bulk crystals.

$$\frac{n_v}{N} = \exp\left(-\frac{\Delta H_f}{kT}\right)$$

$\Delta G = \Delta H - T\Delta S_{c+T}$

- n_v → the number of vacancies,
- N → number of sites in the lattice (for $n_v/N << 1$)
- Interaction between vacancies can be ignored
  ($\Delta H_{formation}$ (n vacancies) = n . $\Delta H_{formation}$ (1 vacancy))
- ΔH_f → enthalpy of formation of 1 mole of vacancies

T (°C)	n/N
500	1×10^{-10}
1000	1×10^{-5}
1500	5×10^{-4}
2000	3×10^{-3}
ΔH_f = 1 eV/vacancy = 0.16×10^{-18} J/vacancy	

❑ Close to the melting point in FCC metals Au, Ag, Cu the fraction of vacancies is about 10^{-4} (i.e. one in 10,000 lattice sites are vacant)

We have already talked about vacancies in the context of diffusion, in the context of sintering of nanoparticles, and we have noted that depending on the curvature of the nano particle, is it going to be convex or concave. We have noted that there can actually an enhancement in the vacancies or there can be a depression in the equilibrium concentration of vacancies.

And we have noted this, we will briefly revise what we mean by equilibrium concentration of vacancies. We have noted that they are equilibrium thermodynamic defects, and suppose I am, for now I will restrict myself to metals wherein there is no charge involved and the arguments can be simplistic made.

We know that it cause enthalpy for you for because there are broken bonds when you have a vacancy in a crystal, there it cause enthalpy in terms of putting a vacancy. But we also know that there is a configurational benefit when you have vacancy. That means that when you try to minimize Gibbs free energy, which is given by delta G is equal to delta H minus T delta S.

And for now I am restricting myself to configurational entropy, then I can note that there will be an offset because of this configurational entropy, at certain temperature, at each temperature, there will be an equilibrium concentration of vacancies. That means that, if I am talking about the Gibbs free energy versus vacancy concentration, then I would notice that there initially will be a depression when I increase my temperature. But there will be an at a given temperature of course, there will be an when increase the number of vacancies, then there will be a depression in the Gibbs free energy, but after the equilibrium concentration. Then there will be an increase of the Gibbs free energy, that means the energy minima appears for a, only a certain number of vacancies.

Now of course, when increase the temperature, then you will have a increased concentration of vacancies, and you go even further high temperature, there will be increased concentration of vacancies and close to the melting points in FCC metals like gold, silver and copper. The fraction of vacancies which is given by this formula n v by N is, which is depends as goes exponential of minus delta H f by kT, is about 10 power minus 4, one in 10000 of the lattice sites go missing close to the melting point in these metals. And as I pointed out, there is you increase the temperature, the fraction of vacancies keeps on increasing. And therefore, if I take any bulk material and I am talking about any finite temperature, like about 300 Kelvin, then I expect an equilibrium concentration of vacancies.

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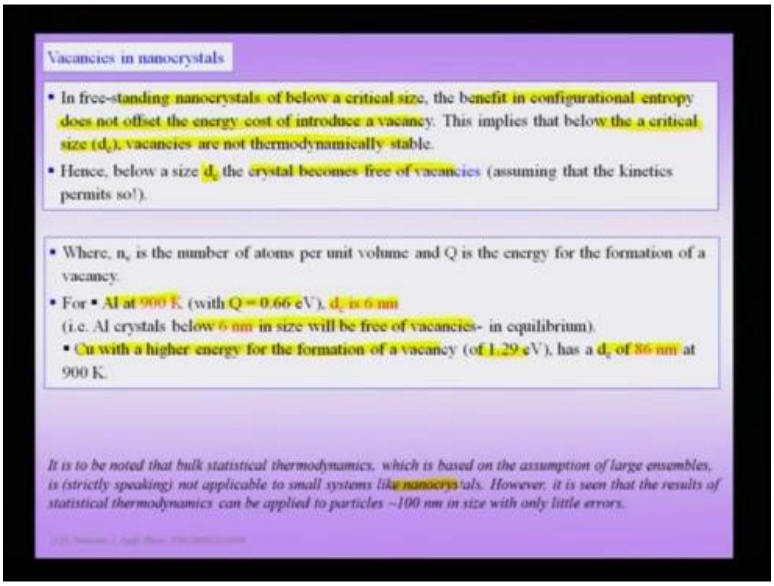

Vacancies in nanocrystals

- In free-standing nanocrystals of below a critical size, the benefit in configurational entropy does not offset the energy cost of introduce a vacancy. This implies that below the a critical size (d_c), vacancies are not thermodynamically stable.
- Hence, below a size d_c the crystal becomes free of vacancies (assuming that the kinetics permits so!).

- Where, n_v is the number of atoms per unit volume and Q is the energy for the formation of a vacancy.
- For ▪ Al at 900 K (with Q = 0.66 eV), d_c is 6 nm
  (i.e. Al crystals below 6 nm in size will be free of vacancies- in equilibrium).
  - Cu with a higher energy for the formation of a vacancy (of 1.29 eV), has a d_c of 86 nm at 900 K.

It is to be noted that bulk statistical thermodynamics, which is based on the assumption of large ensembles, is (strictly speaking) not applicable to small systems like nanocrystals. However, it is seen that the results of statistical thermodynamics can be applied to particles ~100 nm in size with only little errors.

Now, what happens in nanocrystals? That is a question we are asking, in free standing nanocrystals below a critical size, the benefit in configurational entropy does not offset the energy cost of introduction of vacancy. Because now it is a nano crystals, the number of sites over which these vacancies can configure are smaller and this implies below a critical size, you expect that vacancies may become thermodynamically unstable.

Though, this critical size we call d c, the crystal can become free of vacancies of course, if you start from a high temperature and go to low temperature, the kinetics have to permit for these vacancies to escape. Now, for aluminium at 900 degree Celsius, with an activation energy of 0.66 eV, the critical size of the order of about 6 nanometres. That means aluminium crystals below 6 nanometres will be free of vacancies, that means such a crystal, will have no equilibrium concentration or thermal vacancies will not be in thermodynamic equilibrium if put in such a crystal. Copper with higher energy for formation of vacancy of about 1.29 electron volts, the critical size happens to be higher of about 86 nanometres.

Now, the important point to note in this whole argument is that, normally when you talking about configurational entropy, you are talking about Gibbs free energy, we are talking about what is known as bulk thermodynamics. That means, and these configurational entropy comes from statistical physics, which implies that I am talking about a large ensemble, which means about a mole of atoms or more, which are being sites, which are being configured.

But in nano crystals, obviously then size of the system is limited, and the important question which arises, can I use bulk thermodynamics for calculation of quantities in these nano crystals? The answer is obviously no, but it has been found that if you apply bulk statistical thermodynamics to even 100 nanometre crystals, so it is found approximately true that the results are reliable, but if you go down to very small sizes like about 6 nanometres, then the classical formulae cannot be used and they need to be modified for nanocrystals.

Since, we are not dealing in detail about the thermodynamics of nano scale systems, but this important effect, thought the calculation based on this may be 6 nanometre could be erroneous, but the important thing is that, when you go down to small scale system, we do expect that the system will become spontaneously free of vacancies. In other words, the system will not support vacancies as a thermal, stable thermodynamic effect, which is what is the case for the case of bulk crystals.

Later on we will see when we talk about dislocations also that when you go to nano scale, the system can actually become spontaneously free of dislocations. But in the case the important difference between a dislocation and vacancy being that in the case of vacancy, a vacancy can be a thermodynamic defect in bulk, which or is a thermodynamic defect in bulk. That means is thermodynamically stable defect, but dislocation is not a thermodynamic effect, that means it is not stable in bulk, but in nano scale, the kinetics becomes such that it can actually move out of the crystal. So, there are important differences when you are talking about nano crystals visa v bulk crystal when it comes to defects.