

Advanced Ceramics for Strategic Applications
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Lecture - 11
Electrical Conduction in Ceramics

Today, we are going to start a new chapter and a very important chapter so far, the ceramics materials are concerned; this is on Electrical Conduction in Ceramics. Earlier we have mentioned that ceramics as a group, as a very void spectrum of electrical properties and therefore, not only even to discuss those properties, but at the same time, we like to understand, what is the how the phenomena can the explained in not only in different kind of oxides, different kinds of ceramics, but in different materials as such starting from metals to oxides to other compounds.

So, our topic today is electrical conduction in ceramics but initially, we discuss about the theories of electrical conduction or electrical phenomena as such, in metals semiconductors and finally, we come to ceramics. As you know, some of the ceramics are actually semiconductors, others are insulators and many of them also have metallic or super conducting properties. So, it is necessary for us to understand, what is the basic phenomenon involved in electrical conduction or how the materials respond to an external electrical field, so that is the topic electrical conduction in ceramics.

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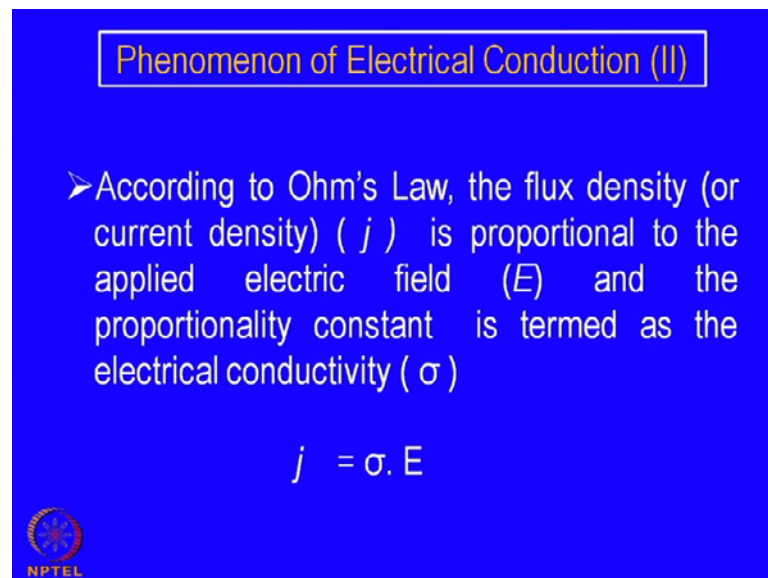
Phenomenon of Electrical Conduction (I)

- Electrical conduction is the result of charge transport through a medium – solid, liquid or gas.
- Two basic parameters, which characterize this transport phenomenon are: the quantity of charge (q) and the velocity of its movement (v_d)
- The conduction is normally induced by an externally applied electric field (E).



And the very first thing we like to discuss is the basic phenomena, the phenomena of electrical conduction as such I think say very basic property of the material, many materials. And we just say, the electrical conduction is the result of charge transport through a medium, either solid, liquid or gas, but our concern is primarily on solid today. Two basic parameters, which characterize this particular transport phenomenon, the charge transport phenomena is the quantity of charge, which is getting transported and the velocity with which it is moving, so q and v , v is the velocity, q is the charge. The conduction is normally induced by an, by an external applied electric field. So, obviously it is the response of the material to the external applied electrical field that is, the property of electrical conduction and what happens, when this field is applied.


(Refer Slide Time: 03:24)



Phenomenon of Electrical Conduction (II)

➤ According to Ohm's Law, the flux density (or current density) (j) is proportional to the applied electric field (E) and the proportionality constant is termed as the electrical conductivity (σ)

$$j = \sigma \cdot E$$


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To continue with that, according to Ohm's law, which is a basic law governing the electrical phenomena, the flux density what in another words the current density j , is proportional to the applied electric field and the proportionality constant is termed as the electrical conductivity σ . So, you can simply write very simply question j equal to σ into E , so σ is the electrical conductivity. And as you know, the inverse of this 1 by σ is ρ , the electrical resistivity. So, will be using these two terms very often, either in terms of conductivity or inverse of that is the resistivity.

(Refer Slide Time: 04:25)

Phenomenon of Electrical Conduction (III)

If z is the number of electronic charge (e) with each of the mobile species and n is the number of charge carriers per unit volume or in other words the concentration of the charge carrier, the current flowing per unit cross section i.e. the current density (j) may be expressed as

$$j = n \cdot z \cdot e \cdot v_d$$


Let us go little, atomistic nature or the microscopic nature of this particular phenomena, if you assume that j be the number of electronic charge that is, e with each of the mobile species. We are considering that there is a charge carrying species, which is moving under the application of the external field. And it need not be an electron may be something else, also some other species will come to that in a minute.

So, although electron has only one electronic charge j equal to 1, but there are maybe other species in which the j may not be 1. So, to generalize, z is the number of the electronic charge e with each of the mobile species and n is the number of charge carrier per unit volume. That means, is the concentration with concentration of recharge carriers per unit volume, the number per unit volume, the current flowing per cross, per unit cross section of the solid, that is the current density j , may be expressed as j equal to $n z e v_d$, once again the velocity comes on and the concentration, and $j d$ is the charge, total charge per species and n is the concentration of that particular species. So, the total number, total cross density or the current density in this case are unit area equal to $n z e v_d$, v_d is the velocity with which it is moving, we have applying in electric field.

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Phenomenon of Electrical Conduction (IV)

where, v_d is known as the drift velocity, which is the net velocity of the charged species in the direction of the applied field. Under certain considerations, it is also the average drift velocity between two consecutive collisions of the electronic charge with some barrier/obstacles coming in the way of the movement of the species.

Applying Ohm's law $\sigma E = n z e v_d$

So, $\sigma = (n z e) (v_d/E) = n z e \mu$

where, μ is the mobility of the charged species. $= v_d / E$




v_d is known as sometimes known as the drift velocity, which is the net velocity of the charge species in the direction of the applied field, or in the reverse direction depending on the charge either be negative or the positive. If it is negative it will move in the reverse direction, if the positive in same direction. Under certain conditions, it is also the average drift velocity between two consecutive collisions, if you are assume that there are certain collisions taking place again, that phenomena will be discuss in a few minutes.

If there are number of collisions in during the moment of the charge species, which some obstacles some barrier. The electronic charge with some barrier and obstacles some upcoming in the way of the moment of the species that is, that is hold by a talking about the collision; it is colliding with some other barrier or obstacles diving it is moment, then the drift velocity is the average velocity between the two consecutive collisions.

Applying Ohm's law once again σ into E they are that is a nothing but, j so $n z e v_d$. So, σ equal to $n z e$ multiplied by v_d over E , so v_d by over E we separate out $n z e \mu$'s another co component of the this expression and so, we write $n z e \mu$, μ is the defined as the v_d by E . So, v_d by E is the another term, we introduced is the mobility called it mobility and this is the be velocity per unit electric field. So, that is the definition of mobility and will come across this particular term mobility very often in our expression of conductivity.

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Units of different parameters:	
E :	Volts / cm
J :	Amps / cm ²
n :	number / cm ³
z :	Number (Integer)
e :	Electronic Charge (1.602×10^{-19} coulombs)
μ :	cm ² / Volt. Sec
σ :	Ohm ⁻¹ . cm ⁻¹ or Siemens per meter (S. m ⁻¹)



Now, we have introduced few parameters and let us like, like to have the idea of the units. E the electric field, it is volt per centimeter. J it can be written as small j also, here it written capital J , but it is same thing ampere per centimeter square. Number, that is the actually in is the concentration for the number per centimeter cube, that is or meter cube different systems.

Z is the number only the integer, total number of electrons in may be small numbers obviously because then may be small electronic charges either 1, 2, 3, 4 like that, is the electronic charge and which is a constant 1.602 into 10 power minus 19 coulombs. μ an important parameter for conductivity of many solids are charge carriers, basically the mobility of the charge carriers centimeter square per volt second. And σ their conductivity Ohm inverse centimeter inverse or Siemens or meter inverse.

So, Ohm inverse becomes actually Siemens and if you talk about resistivity inverse of which is not listed here, resistivity that is one by one oval σ that is ρ , ρ is Ohm centimeter or Ohm meter.

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Transference Number


Particularly in ceramics, there may be more than one type of mobile charged species, which may contribute to the transport process under an applied electric field and therefore the general expression of conductivity is:

$$\sigma_T = \sum_{i=1}^n \sigma_i = \sigma_1 + \sigma_2 + \sigma_3 + \dots + \sigma_n$$

In this context transference number (t) refers to the fraction of total current carried by the specific charge carrier (i).

$$t_i = \sigma_i / \sigma_T$$

Ceramic materials, ideally, may have four different kinds of charge carriers e.g. "free electron", "electronic hole", "cation" and "anion".

$$t = t_1 + t_2 + t_3 + t_4 = 1$$


We also like to introduce another per important parameter, which is may be relevant for ceramics or ionic solids. Particular in ceramics there are maybe more than one type of mobile charge species, which may contribute to the transport process, basically we are talking about a moment of charge in different forms. And there may be more than one charge carrier and in which case, the moment of the charge actually give rise to the current so, that is the as per definition.

So, if there are more than one charge carriers, all of them will contribute to the current, all they will carry part of the current, total current. And they will correspondingly give rise to second conductivities. So, the general expression of sigma t then, t stands for total, the overall conductivity is actually is summation of different conductivities arising from different species. The higher species, i varies from 1 to n so, it becomes sigma 1 plus sigma 2 plus sigma 3 up to sigma n.

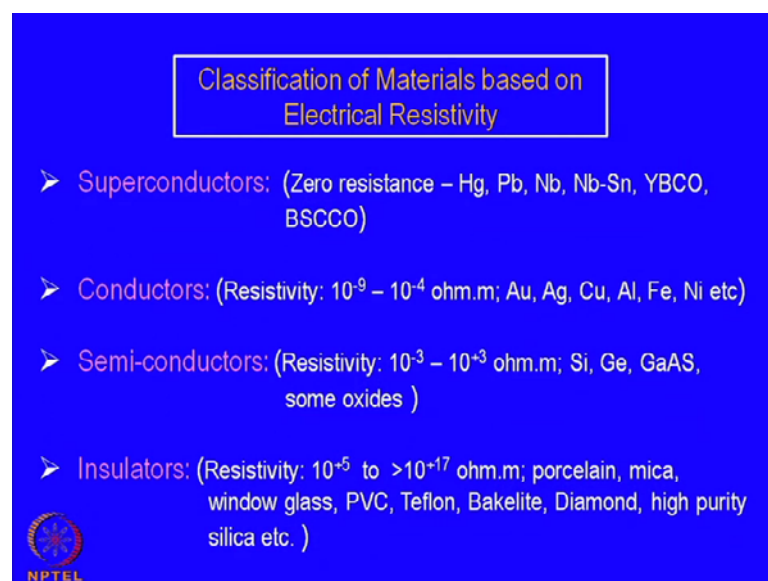
For in this context, transference number refers to the fraction of total current carried by the specific charge charge carrier i by the total current. Or the fraction of the total current, which is being carried by the particular species, that is higher species. So that fraction, that is t i the transparent number equal to sigma i by sigma t that is, sigma i is the current carried by the or the fraction of the current carried by the higher species or the total current i t.

Or in the case, if you write in term form of conductivity, it becomes σ_i by σ_t so, it is basically a ratio or sometimes expressed in percentage also. Ceramic materials ideally may have four different kinds of charge carriers normally, that is the most reliable try, or one can have because it has electrons. Obviously the free electrons will be there some form of free electrons may not be completely free, but it may be polar an some so on, we will come to back later.

It may be cations, it may be anions and whenever there is a free electron there may be a possibility of holes as well, the absent of election or the vacancy of an electron and so, The concept of hole is also there, it is very similar to the vacancy to concept of vacancy in point in defects, so there are in general. Four types of charge carriers one can anticipate and these are free electron, free hole cation and anion, so particularly ionic solids or ceramics general.


T the total t is t_1 plus t_2 plus t_3 plus t_4 , which will be equal to 1 provided there are only four charge carriers. In this will be very important, when will be talking about the ionic conductivity in some of the solids, some of the ceramic materials are known for their high ionic conductivity, in which electronic conduction is negligible. It is either cation or the anion is is the primary charge carrying species and there one has to understand and particularly, we look we will take it of sound the applications, the transparent number is becomes quite important.

(Refer Slide Time: 14:58)



Classification of Materials based on Electrical Resistivity

- Superconductors: (Zero resistance – Hg, Pb, Nb, Nb-Sn, YBCO, BSCCO)
- Conductors: (Resistivity: 10^{-9} – 10^{-4} ohm.m; Au, Ag, Cu, Al, Fe, Ni etc)
- Semi-conductors: (Resistivity: 10^{-3} – 10^3 ohm.m; Si, Ge, GaAS, some oxides)
- Insulators: (Resistivity: 10^{+5} to $>10^{+17}$ ohm.m; porcelain, mica, window glass, PVC, Teflon, Bakelite, Diamond, high purity silica etc.)

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Now, these are some sub classification of the hole gamete of different materials. There are four varieties of material based on electrical resistivity and electrical parameter and electrical conductivity. And is your anybody know about that, we just for completeness take up completeness, we once again repeat it. It is super conductors, which is suppose to the highest conductive materials available. In fact there are suppose to have zero resistance so, theoretically they will have a infinite conductivity.

There are elements an also some ceramics, also some ceramics are known for their super conducting property, particularly at a related below temperature. In fact, super conductors are suppose to high t c super conductors, then the high temperature super conductors compare to many of the metals analyze, which is been listed here. (()) And then y b c o, it is actually a complex oxide of yttrium barium copper. So, y b c o that is that is of the name came.

And this is b s c c o, this much terms in calcium copper oxide so, there very complex oxides. We look in to it at a later stage, what are doing materials, what do the structure and why there conductor super conductor. So, this is the very specific group of material, which are called super conductor having the highest possible conductivity or near zero resistivity. For all practical purpose resistance is a, then in the scale of higher resistivity comes the conductors, the resisting resistivity is of the order of 10 to the power of minus 9 to 10 to the power of minus 4 ohm meters.

And most of the metals most of the metals are good conductors, (()) that there are super conductors but, most of the metals are really good conductors and their fall in this particular resistivity range. Examples of obviously copper, gold, silver, aluminum, iron nickel and so on. Then, comes semiconductors resistivity is still higher, this is in the order of 10 to the minus 3 (()) the plus 3 ohm cent ohm meter.

And there are very important group up of materials, some of their elements, some of their compounds, some of their oxides and there are whole range of oxa materials available under the semi conductor group. Of course, the semi conductivity you are originally discovered primarily in silicon in germanium and you possible aware, that silicon is one of the most important material today, for the micro electronics industry.

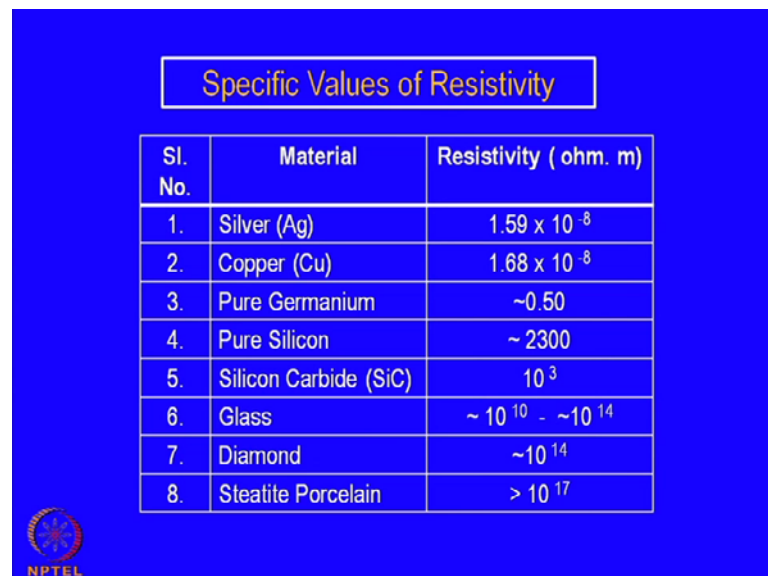
So, it is the advancement the micro electronics actually came up would the develop would the discovered of silicon as super con semiconducting material and then, very

important topic is, which is utilized in the technological area. So, without silicon, we cannot think of a microelectronics index today computer industry controlling in telecommunication and everything.

Then the highest range of resistivity, those are called insulators. The resistivity range value is between 10 to the power of 5 to 10 to the power of 17 once again, a very wide range of resistance, it is almost 12 resistance all these materials fall in this category. And they have different exact value of resistance, but the important materials which are known to be good insulators many of them are actually ceramics.

First think counts porcelain, you know porcelain has been used in electrical industry or electrical power industry for a long, long time, because they have a good insulating material and it insulates one conductor from the other. Mica, window glass, PVC, polymer, Teflon is also another polymer, Bakelite, diamond and high purity silica all of them have very good electrical resistivity, very high electrical resistivity and a good insulating property. So, they have been categories there are insulators. So, you have four major categories under which all the different materials can be classified starting from zero resistance to very high resistance.

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Sl. No.	Material	Resistivity (ohm. m)
1.	Silver (Ag)	1.59×10^{-8}
2.	Copper (Cu)	1.68×10^{-8}
3.	Pure Germanium	~ 0.50
4.	Pure Silicon	~ 2300
5.	Silicon Carbide (SiC)	10^3
6.	Glass	$\sim 10^{10} - \sim 10^{14}$
7.	Diamond	$\sim 10^{14}$
8.	Steatite Porcelain	$> 10^{17}$

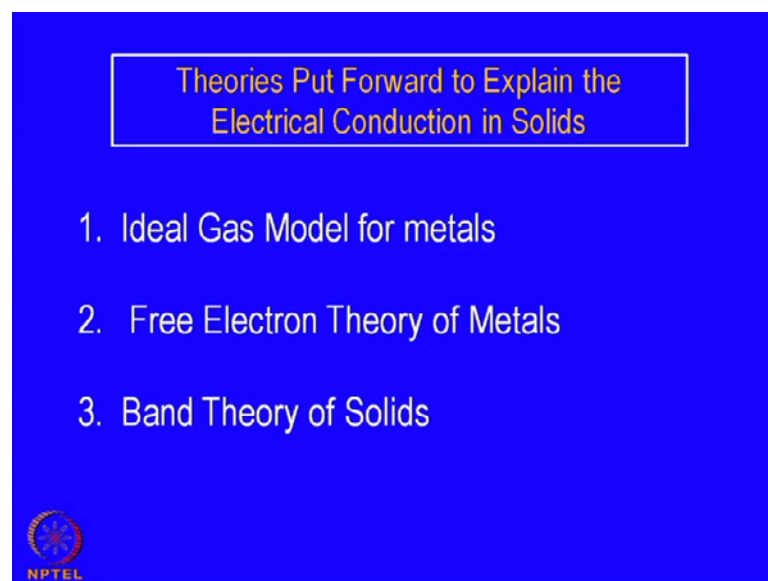
This is just to give you an idea of the resistance values of some of the materials, which will be mentioned just now. Silver is one of the very good conductors, one of the best conductors available, next gold, silver is better passively silver is better than gold, but

there more com morel more values comparable, 1.59 into 10 to the power of minus 8 ohm meter. Copper next wizard 1.68 into 10 to the minus 8 ohm meter, it is very close, but it is look lately higher resistivity.

Pure germanium, which is semiconductor insolently silver and copperier conductors, pure germanium is 0.5 ohm meter and pure silicon is little high higher 2300 ohm meter. Silicon carbide ceramics, but it good high temperature semiconductor, these days silicon carbide is one of the instant materials, for the sera metric industry, for second application of course, it is about 10 to the power 3 that is means 1000.

Glass, normal glass is a insulator 10 to the power 10 to 10 to the 14 ohm the ohm meter. Diamond 10 to the power of 14 more and Steatite porcelain, basically Steatite is in magnesium silicate, so it magnesium silicate porcelain is more than 10 to the power of 17 ohms an ohm meter. Show once again, we have conductors, semiconductors and insulators.

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Theories Put Forward to Explain the Electrical Conduction in Solids

1. Ideal Gas Model for metals
2. Free Electron Theory of Metals
3. Band Theory of Solids

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All having understood that, there are a huge range of conductivities available in different materials, different groups of materials, there bonding are different. chemical bonds nature of chemical bonds are different and but, super as resistivity is concerned. They can fall in particular scale so, we have the understand, why some materials are highly conducting some others not so conducting, others some insulators and another group of materials are highly conducting in the super conducting.

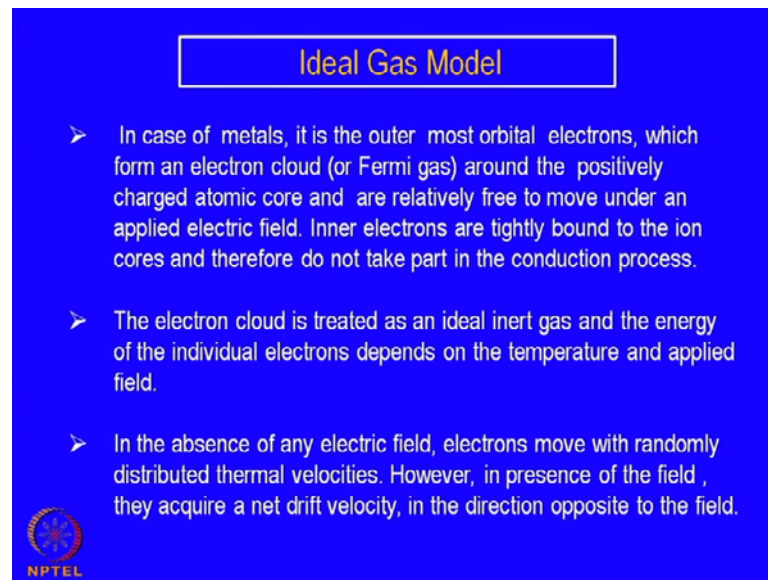
So, there is a need to understand, what is the basic mechanism of conduction, why different materials behave in a different way? And so, there are various theory is from very beginning of the understanding of the electrical behavior. (()) would forward different theories not all theories are acceptable at the stage, but you like to discuss of the history behind it, how exactly would have develops on the current understanding had been developed and what are the basic concept in that.

So, these are the three different models are theories had been band width to understand the phenomena electrical conduction. First two are particularly or metals, because metal highly at that leading those days, when this theories will be in develop. Metal was the one of the best conducting material and there electrical there temperature dependence was one kind, where it others have a different kind of temperature dependence of conductivity.

So, we will start discussing or understanding basically, the conductivity behavior of metals to start with. So, the first theory, which have been it follows ideal gas model for metals and then, came the free level almost micron logical manner. It is not that all of them came simultaneously, but it came in electron logical manner.


First the ideal gas model of metals, then it was not really quite sufficient to explain all the property, then come the freely electron theory of metals, that also had some limitations. And then finally, the current model model less applicable to most of the materials or band theory of solids so, in discuss one by one.

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Ideal Gas Model

- In case of metals, it is the outer most orbital electrons, which form an electron cloud (or Fermi gas) around the positively charged atomic core and are relatively free to move under an applied electric field. Inner electrons are tightly bound to the ion cores and therefore do not take part in the conduction process.
- The electron cloud is treated as an ideal inert gas and the energy of the individual electrons depends on the temperature and applied field.
- In the absence of any electric field, electrons move with randomly distributed thermal velocities. However, in presence of the field, they acquire a net drift velocity, in the direction opposite to the field.

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And what are the different assumptions. So, let us first of the top the ideal gas model to explain the conduction behavior of metals in particular. Because, most of the theory has been developed with metals, then semiconductors and once you understand the basic phenomena or the basic concept. It will be applicable to ceramic materials as well, a little will be easiest for us to understand, what really happens in case of ceramics. In case of metals, it is the outer most orbital electrons, which form an electron cloud that is known from the principal of chemical bonding metallic bond.

We will not talking about metallic bond, it is the, we have the electron cloud. Electron cloud are sometimes it is call the Fermi gas, around the positively charged atomic core and are relatively free to move under an applied electric field. Inner electrons are tightly bound to the ion cores and therefore, do not take part in the conduction process, i think that is basic assumption not only the assumption, it is a true.

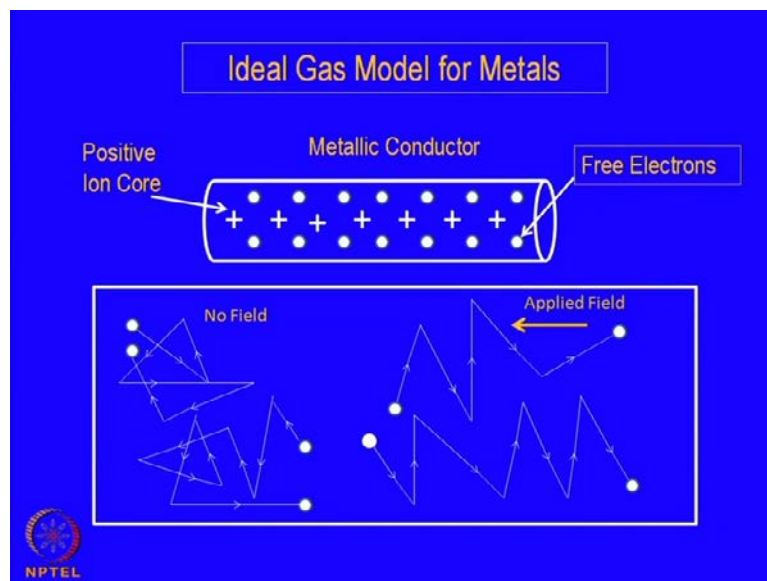
Experimentally verified also, that only the outer most electrons take part in the both in the bonding look a chemical bonding mechanism, metallic bond we can metallic bonds as well as, those are the electrons, which take part in the conduction process. We have apply electric field actually those at the electrons, which gets effected for as the inner electrons really remains and part of it. The other the assumption is the electron cloud is treat as with ideal inert gas, that is why it call the ideal gas module.

So, we are talking about a cloud that means a electron gas, that is why it is also call the gas so, it is as if a gas is there, where the particles at basically electrons. So, it is very difficult to distinguish one gas from one electron form the other, but it is a combined effect of all the electron put together. And energy of the individual electron depends on the temperature and applied field so, when we apply in electric field energy changes, the kinetic energy changes and also increase temperature or change the temperature, the kinetic energy changes.

So, it is assume to be a gas and, so many of the basic concepts of gas dynamics, the molecular moments of the gas is applicable here, that is what the assumption means. In the absence of electric fields electrons move with randomly distributed thermal velocities. However, in presence of the field they acquired in net drift velocity, in the direction opposite to the field, because these are electron negative be charge so, they will be moved in opposite direction.

Now, the basic idea is as the name suggest of the title suggest, that it is a as if we have a gas, ideal gas and whatever the concept of theory is of molecular moment in gas, they may be applied here. And that is why, it has been assumed z gal ideal gas and one as try to explain how this moment can take place and the influence of new electric field.

(Refer Slide Time: 29:52)



Well, this is a pictorial view of what can be happening, what is happening there provided, we assumed that it is a gas. So, in case of, this is (()) conductor, where you

have ion cores, the positive ion cores and dots are electrons. So, these are the moving species, the ion cores are fixed have their own site only the electron cloud, which is moving are getting this started and they application the electric field.

So, if you look at the particular electron, they are moving in a random fashion; that is a part taking followed by the electron, because of the thermal energy. There is always a movement of the gas molecules as also the electrons here so there is a random motion. There is a moving, but there is no net movement spatial distribution. So for, as the volume of the solid is an saw so, they may be moving in a random version, but the late movement is not there.

So, that is because of the thermal energy that moving, but if you have a electric field. Then, this random motion is to some extend gets order, although they random motion is not completely avoid it, because of the thermal energy. So, there will be movement of this nature some kind of this nature and there is drift velocity so, with the application of the electric field, which some time. This electron has actually moved to the system, but it is not gone through a linear distance, but straight line manner, it has gone through a zigzag manner.

So, it is moving in much larger distance than actually, we are absorbing from the outside so, these they are two electrons has been given, this is the kind of random motion, which the gas molecules also have and here, it has been assume for the electrons as well.

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Concept of Drift Velocity (v_d)

- The velocity of a charge carrier (normally free electron) increases in presence of an external field. This incremental velocity is normally termed as "Drift Velocity". (v_d)
- During their movement the charge carriers normally collide with some barriers / obstacles resulting in loss of the drift velocity, however, it regains the same if the field continues. So the drift velocity varies with time following a saw tooth profile:

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The velocity of a charge carrier in this case, electron increases in the presence of external field. This incremental velocity is normally termed as drift velocity that means, that is the net velocity in addition to its random motion that is the net movement of the electrons in the particular detection, depending on the application of the detection of the application of the field. So, did not their movement, the charge carries normally collide so, that is a because of the random motion.

If the possibility of the collision between the electrons also, with the different kind of other barriers or obstacles and that results in the loss of drift velocity. So, once the collision is there, they come is stand still and however, up to sometime it is again regain it is velocity and goes to add value. Once again, there is a possibility of collision and then, it this is the way we goes on.

So, the velocity of this electrons actually, it is not constant, it goes through a kind of saw tooth profile and this is, what one can except, it goes to re high values. Suddenly, there is a collision and talk and then, comes back and this show the collision takes place, so that is the this in sometimes drift velocity has been defined as the average velocity between the two conjugative collisions. So, there are large number of collisions taking place, either if the electron themselves or with the ion core. So, it is moving, but the ion core is also there, possible charge ion core so this is, how it happens.

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Estimation of Drift Velocity

While the intrinsic velocity of a free electron is very high , their drift velocity is quite low due to the chaotic motion.


$$j = n e v_d ; \text{ So } v_d = j / n e$$

$$n \approx 10^{23} / \text{cm}^3 = 10^{29} / \text{m}^3 ; e = 1.6 \times 10^{-19} \text{ C}$$

Assuming i (current) = 1.6 Amp amp, A (area) = 1mm^2

$$j = i / A = 1.6 \times 10^6 \text{ A/m}^2$$

Therefore, $v_d = i / enA = 10^{-4} \text{ m/s} \ll v_{rms} (10^5 \text{ m/s})$



Now we have introduced terms called drift velocity so, while the intrinsic velocity of a free electron is very high, because of the thermal vibration, a thermal motion. A their drift velocity is quite low due to the chaotic motion, that is the random motion of the chaotic motion and collision of course. It is the collision, which holders their moment and the average velocity is much lower and so, there is a order of magnitude calculations here.

One can go through, the once again the definition of current density so, the v_d is j by $n e$, where is a value to 10 to the power around (()) digit number and then it the constant here 29 meter cube and this is the electronic charge so assuming, i about 1.6 amp per meter. There are two amps one is extra and change this note 1.6 has been just used have been taken, because this value is 1.6 so, where taken the attempt regular figure.

It can be in that scale area is 1 meter square so by this one can get the v_d the drift velocity becomes about 10 to the power of minus 4 meter per second. This is much much less than another term will come across, that is the velocity, that is root mean square velocity any kind taken energy term thermal, because of the thermal vibration there is velocity and that velocity, they root mean square velocity is about the 10 to the power minus four in minus five meter per second.

Choose is much much high. So, whatever thermal velocity acquire, they with the thermal vibration thermal energy is much larger compared to the net velocity, because of the applied electric field. So, it is moment to the much smaller of the velocity is much slower.

(Refer Slide Time: 37:12)

Ideal Gas Model for Electrical Conduction in Metals


For an ideal gas the velocity depends on temperature (T).
So the kinetic energy is written as:

$$\frac{1}{2} m_e v^2 = \frac{3}{2} kT$$
$$v_{rms} = \sqrt{\frac{3kT}{m_e}} \approx 10^6 \text{ m/s at Room Temp (T = 300K)}$$

AS

$$\sigma \propto v_{rms}$$
$$\sigma \propto \sqrt{T}$$

However, Experimental observation is

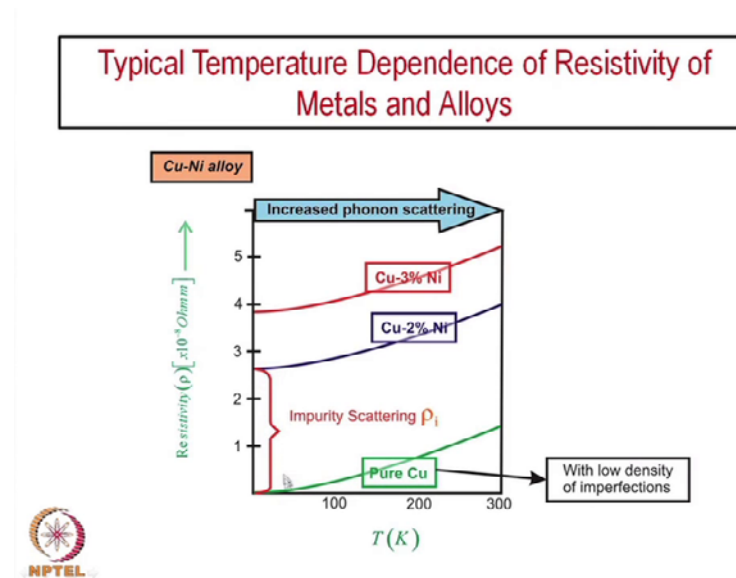
$$\sigma \propto \frac{1}{T}$$


Well, this is, what you are talking about the rms velocity, the ideal gas model for in an ideal gas for an ideal gas velocity depends on the temperature that has been mentioned. So, the kinetic energy is it can be written as half m e v square, these the velocity because of the thermal energy and then, this is the temperature term 3 by 2 k t. So, this is an expression for the effect of temperature on the velocity of the gas molecules this same thing has been written here for the electrons m e is the electronic mass.

So, from this actually the v rms is nothing but, a root 3 k t by m e. And this is approximately equal to 10 to the power of 6 meter per seconds, which has been written 10 to the power of 5, but in that order. At room temperature so taking t equal to 300 k so, this becomes the v rms. As sigma is proportional to v rms that is, one kind of velocity of course, and sigma becomes also proportional to root t. However, the experimental observation is sigma equal to is proportional to 1 by t.

The resistance actually increases, resistance increases root temperature that has been the observation, show from the gas ideal gas module one expects, that the sigma is proportional to root t, Whereas the observation is just opposite and that is the limitations of this and that is problem with this model. So, this cannot really explain the temperature dependence of the conductivity in metals. So, although it one talks about a family gas, but this gas is completely different, than the normal in an gas molecule.

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So, that is one observation and just show that, ideal gas model is not really suitable or applicable for to explain the temperature dependence of conductivity, electrical conductivity. This was the experimental parameter, i will just mentioning that, the resistivity is here of the not conductivity. Resistivity has been plotted as a function of temperature the degree kelvin and if you talk about pure copper, which is one of the good conductor.

One can see the resistance is increasing as a function of temperature, i need almost linearly. Linear relationship slightly above 0 degree kelvin very close to are 100 degree kelvin, this is not exactly linear. There is slightly deviation from linearity and although it shows that, it goes to 0 at absolute 0. Their resistivity is should absolute 0, but it is not once, we discuss about the super conductivity in find there is (()) serial resistance. It is not zero so, only in a very few elements are compounds.

We have seen that the conductivity really goes to 0 and they are those have been classified super conductor, but metals do not resistivity or resistance. If the metal really do not go to the 0 at absolute 0, there is always some amount of the schedule a resistance, but the more important for us for the time being is the temperature dependence. The temperature dependence is resistance increases of the conductivity decreases as we increase the temperature, when there are some more data here, you will discuss that later.

This is the effect of impurity atoms. This is pure copper, if you add some quantum nichol. Either 2 percent nichol or 3 percent nichol over and above the temperature effect, there is an effect of impurity as well. So, in fact, that is a common phenomenon for almost all metals, that whenever you add some impurity to the system, to the pure material is resistivity increases. In addition to the temperature effects so that is, what give many have this is the temperature, what we called impurities scatter, we come to that later.

So, we having discuss that ideal gas model, next clearing than next concept, which has been to explain the temperature dependence of conductivity or electrical conductivity of different metals or the free electron theory. Their of course, two wise of looking at a classical model of free electron theory and quantum mechanical concept of free electron theory. But will discuss them modules in a the combined fashion.

(Refer Slide Time: 42:58)

Free Electron Theory of Metals

- The electrons are assumed to have a constant but negative potential throughout the volume of the solid. However, the potential is very high at the edges of the solid and therefore the free electrons are normally bound within the volume of the solid.
- The kinetic energy of the electrons is much less than that of the bound electrons.

The diagram shows a horizontal line at a constant negative potential level between two vertical lines at $-L/2$ and $L/2$. At the ends of these lines, the potential rises sharply to a high positive value, representing the binding potential at the edges of the solid.

The basic assumption here, that the electron once again, the electrons of the free electrons or the outer most arbitrary electrons, those are the electrons taking part in the conduction process. But they assumed to have a constant, but negative potential through out of the following of this solid. So, you are talking about not just the thermal energy, but there is an electrical potential, because there at charge particles, the electron charge particles and also moving a environment of positive charges of the and course are the nuclear of which of the atoms.

So, it is just not thermal energy only, but it is also the electrical potential, which is of concern and that was introduced later, after the gas molecule the ideal gas model failed. However, the potential is very high at the edges of the solid and therefore, the free electrons are normally bound within the volume of the solid. And this is the kind of potential barrier, one has assumed, this is the volume of the solid. They are free electrons, which are moving in the solid within the volume of the solid, but it is not going out, it is not living in the solid.

So, therefore, they assume there is way high energy barrier. So, there is a high potential energy barrier, this is actually negative potential but flat potential so, throughout this solid, throughout the volume of the solid. It has a constant potential that is, one of the basic assumptions of the free electron theory and so, the electrons with this kind of a well energy well.

In which the electrons are moving in this, but it is not able to go out the system, which is obvious the electrons are really within the solid and that is out assuming that, this kind of potential model has been considered. So, the kinetic energy of the electron is much less than that of the bound electrons. The kinetic energy free electron, which is much less, than that of the bound electrons that is than of the assumptions, which has been made here.

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Wave – Particle Duality : de-Broglie Hypothesis

Electrons are considered to have both particle and wave characteristics as per de-Broglie hypothesis. The relationship is as follows:

$$\lambda = \frac{h}{mv}$$

λ is the de-Broglie wavelength

h is the Planck's Constant

m is the mass of the electron

and v is the velocity of the free electron.



Other most important of the aspect free electron theory, this for the first time actually, the free electrons are considered, as have both characters. This was called the particle

character and the wave character that was the concept of the mechanical of the quantum mechanical approach. And electrons are considered to have both particle and wave characteristics as per the de-Broglie hypothesis.

And the relationship between then since, they have a wave characteristics, they have a wave length, which is taken as lambda and than that lambda is related to the planks constant h. The mass of the electron also the velocity with each it more it; so, h is the de-Broglie wave length and h of the planks constant, m is mass of the electron and v is the velocity of the free electron. So, if we had that, so you can considered wave nature of the electrons particle are it has both the particle characteristics and the wave characteristics and that is relationship between them. So, when we are talking about particle, it has a mass and we have talking about a wave, it has a wave length.


(Refer Slide Time: 47:21)

Energy of a free electron

Based on classical mechanics the kinetic energy of a free electron may be expressed as:

$$E = \frac{1}{2}mv^2 = \frac{h^2k^2}{8\pi^2m}$$

$$\vec{k} = \frac{2\pi}{\lambda} \Rightarrow \lambda = \frac{2\pi}{k}$$

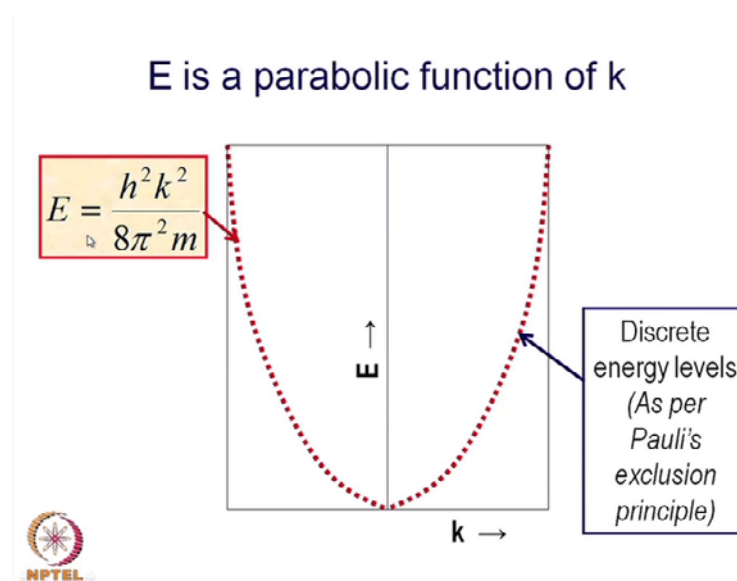
$$\lambda = \frac{h}{mv} \Rightarrow v = \frac{h}{m\lambda} = \frac{hk}{2\pi m}$$


Under this condition, we can without going to the details of the calculation, one can find out what will be the energy of the free electron. If we introduce this de Broglie concept and best and also, we have constant potential, in which the moving and it is a energy barrier at the end of the solid. In which it is there, they based on the classical mechanics the kinetic theory of free electron may be expressed as, e equal to that is the energy, energy of each electron is half m v square the kinetic energy and v replaced v by the de Broglie expression so, you will get h square k square 8 pi square m.

Now k is another term, which has been introduced to here. In addition to h , h is the plank constant of course, k is a vector and it is the magnitude of the vector is 2π by λ . Once again, λ is the de Broglie wave length so, the λ equal to 2π by k . So, this is a vector, which is called wave vector and that is, defined either is so, the wave length inverse of the wave length actually, it is inverse of the wave length multiplied by 2π or in other words, the λ is 2π by k .

So, one get λ equal to h by $m v$ and therefore, velocity with which the left can move, which is h by $m \lambda$. So, once again, the λ is the wave length and aim is the mass of the electron. So, we have $h k$ by $2\pi m$ replacing λ by this.. So, we get the velocity and the kinetic energy is like this and in fact ultimately, if you replace v although this expression (()) already been given initially, but this is how one gets it.

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So, the expression of the energy is not talking about the velocity now. Velocity terms has been replaced and we have a k term. So, k is the mentioned it is a wave vector and is the reciprocal of the wave length and so. So, this is energy equation, which has been plotted with respect to k vector and this is the parabolic equation, e is a parabolic function of k . This is the energy of the free electrons, energy of the not all the electrons, but the only free electrons and it has k increases the energy also increases.

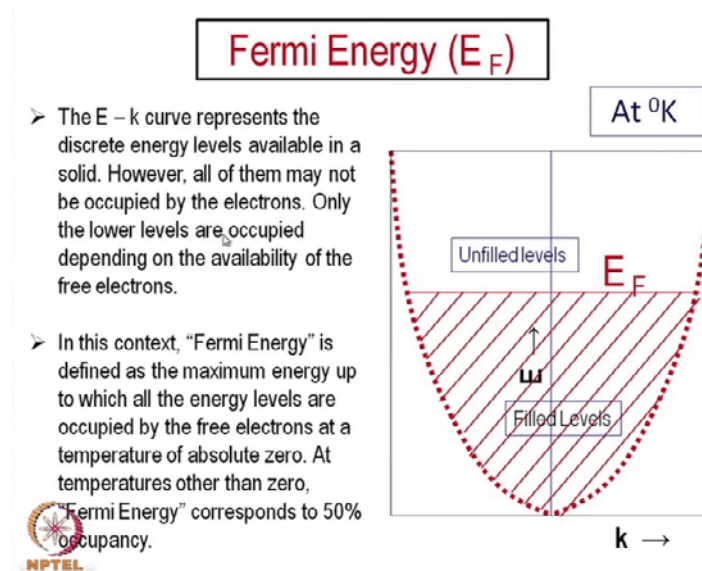
Now, this k can be related to the position, particular position of the electron within the solid. It is actually related to the reciprocal lattice space of the crystal and it is related to

that kind of a position of the particular electron within the volume of this holly wood material. So, at different places, but it basically means and different (()) places are different histro graphic positions or crystal lattice sites. The electron whenever, it is deciding their at different energy levels.

So, and that will determine at what velocity, they will move and what will be its mobility and so on. So, this is the $e k$ curve, which is the one of the most important findings of this free electron theory and this explains many of the properties of the metals, as well as the solids. Now, these are all although this is the suppose to be continuous curve, as a function of k , e is a proportional to k square. So, it is a parabolic function, but this curve is really not a continuous curve.

It is a quasi one can call a quasi continuous curve, it is discrete curves and discrete energy levels as per pauli exclusion principle. We have plus of minus of expense and they slightly different energy levels. So, each of this electrons depending on their quantum mechanical numbers, you have discrete energy levels. They are not a continuous energy line. So, that is another important aspect of this curve the $e k$ curve.

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Now, if this concept, we also introduce another important energy term, which is called Fermi energy. Now, $e k$ curve represent the discrete energy levels available in a solid. However, all of them may not be occupied by the electrons, only the lower levels are

occupied depending on the availability of the free electrons. So, in a solid theoretically, we can have many such levels.

Energy levels possible, possible energy states and all of them did not the occupied by the electrons and that, how many of them will be occupied by the electrons. It depends on the availability of the total electrons, depending on the total number free electrons available in that system, that also depends on the the valence of the particular element some of them are mono valiant, some of them are bi valiant, some of them are tri valiant.

So, if you mono valiant metal is there is will be released, the number of electrons will be less whereas, bi valiant metal, a di valiant metal, more number of electrons in the same mono valiant are available and so on, so for. So, depending on the availability of the free electrons outer most arbitrary electrons, the electron availability will be different, but the theoretical curve, which has been computed.

So, if you depending on the number of the available electrons, the lower almost energy levels should be first occupied and waste of the energy levels although they exist. They theoretically, they can have, the electrons can have this kind of energy levels, but they will be no electrons to occupied them. So, it is the occupational situation that means, the filling half of the energy levels will be from the lower level and more and more depending on the more and more energy levels available.

Sorry, the more and more electrons available, more and more energy states will be occupied. So, in this context, Fermi energy the defined has the maximum energy up to which, all the energy levels are occupied by the free electrons at a temperature of a absolute zero. So, Fermi level of course, of this energy levels, energy levels will be their, but the occupancy will change with temperature, but you will see in a few minutes are of sometime.

So but, we have a defining particular energy level, Fermi energy level is only for absolute zero. So, at absolute zero, whatever the maximum energy level up to which, the electronic states of the energy states are filled by the electrons that is, what we called the Fermi energy. And it has once again, very important conversation as will seen (()). So, this is in this diagram, this is the Fermi level are e_f below, which all the energy states available are actually filled up although one thing, we must also remember or i must point out.

This is a two dimensional curve and this is two dimensional plot, but actually this is a three dimensional figure. It is a three dimensional figure in both x and y z detections, it is available its volume. So, it is actually a parabola. So, it is a actually parabola so, it is not a line actually, it is a surface. So, it is like a container so, in which as you put more and more electrons and lower states are getting filled up and it has been as if the container has been filled up with water up to certain level.

So, the highest level up to which, the container has been filled up is actually call the Fermi energy and that is at absolute zero. However, you will see after words, that this energy is a kind of constant and higher temperatures the occupancy changes, but the energy level (()) and of that kind will see. Another way to defined, this particular energy is the occupancy level will correspond to 50 percent about occupancy.

So, at temperatures other than zero, the Fermi energy corresponds to 50 percent occupancy and that will see later. Some electrons will jumped to the higher and there will be some vacancy so, but the occupancy level will not 100 percent, it will be up to 50 percent so, but the e f the energy level is a constant for particular system. So, with this come to the end of this particular lecture will continue, this discussion on the electrical phenomenon in ceramic or in metals i solid in general in our next class.

Thank you, Thank you for your attention.