Non - Metallic Materials
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Module - 05
Electrical, Magnetic and Thermal Properties of Non - Metallic Materials
Lecture - 28
Thermoelectric effect and magnetocaloric effect

Welcome to my course Non Metallic Materials and this is module number 5, Electrical, magnetic and thermal properties of nonmetallic materials. And this is lecture number 28, where I will be talking about Thermoelectric effect and magnetocaloric effect in solid materials.

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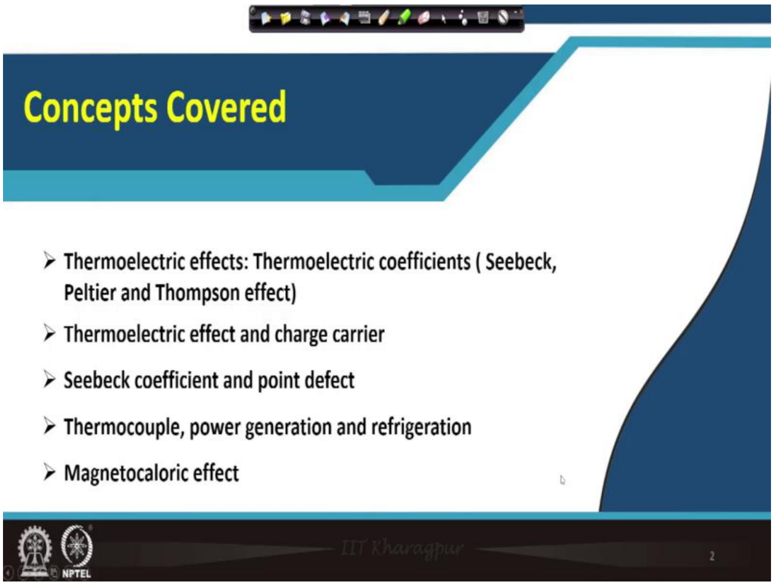

Concepts Covered

- Thermoelectric effects: Thermoelectric coefficients (Seebeck, Peltier and Thompson effect)
- Thermoelectric effect and charge carrier
- Seebeck coefficient and point defect
- Thermocouple, power generation and refrigeration
- Magnetocaloric effect

So, part of this thermoelectric effect, many of you are familiar with this; we will be talking about various thermoelectric coefficients, illustrate the Seebeck coefficient, Peltier coefficient and also Thompson coefficient we will be talking about. How the thermoelectric effect is related to the normal charge carriers and also how it is related.

Particularly the Seebeck coefficient is related to the point defects we will talk about it. And the use of this material, various used like thermocouple, power generation using thermoelectric material, refrigeration, magnetic refrigeration we talked about and finally, magnetocaloric effect will be introduced, which is a quite new topic.

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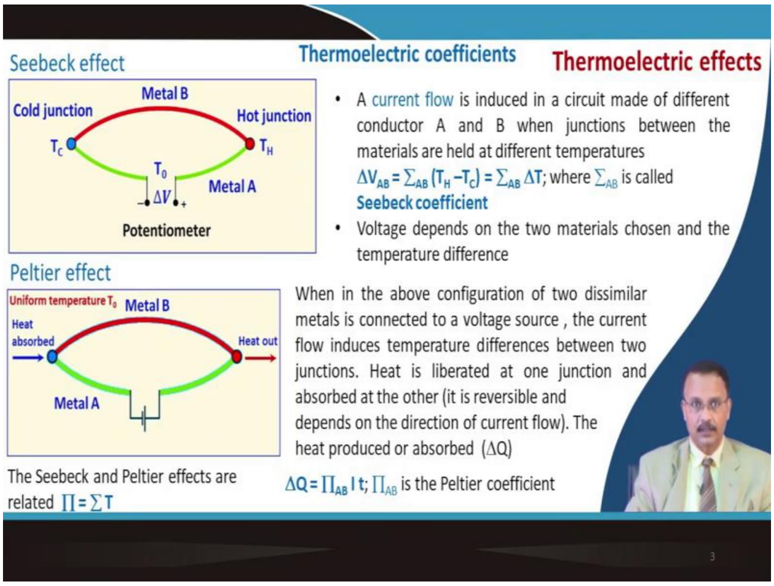

Thermoelectric coefficients

Thermoelectric effects

- A current flow is induced in a circuit made of different conductor A and B when junctions between the materials are held at different temperatures $\Delta V_{AB} = \sum_{AB} (T_H - T_C) = \sum_{AB} \Delta T$; where $\sum_{AB}$ is called Seebeck coefficient
- Voltage depends on the two materials chosen and the temperature difference

When in the above configuration of two dissimilar metals is connected to a voltage source , the current flow induces temperature differences between two junctions. Heat is liberated at one junction and absorbed at the other (it is reversible and depends on the direction of current flow). The heat produced or absorbed (ΔQ)

$\Delta Q = \prod_{AB} I\, t$; $\prod_{AB}$ is the Peltier coefficient

The Seebeck and Peltier effects are related $\prod = \sum T$

So, many of us we are familiar with this Seebeck and Peltier effect. So, you have two metallic couple and the current flow is induced in the circuit that is made out of this A and B and the junction is made here. So, if you put the junction and keep it at different temperatures; then you will see that you will generate voltage, right.

So, the voltage generation between A and B that is given by the so called Seebeck coefficient and this is the change in temperature across this to two different junctions, which is kept one is hot and one is cold. So, it is related to the temperature difference and this is the actual Seebeck coefficient.

And voltage generation depends on the true material that you are using and also the temperature difference of course. So, when the above configuration of two dissimilar metal is connected to a voltage source, then you see a reverse phenomena. The current flow induce the temperature difference between these two junction. So, heat is liberated at one junction and absorbed in the other junction.

So, it is reversible in nature and in fact, depends on which direction you are passing the current. So, the heat produce if you take it as delta Q, then delta Q is related to your Seebeck coefficient; the current that is flowing and the temperature. So, sorry this pi is your Peltier coefficient, not Seebeck coefficient. In fact, this Peltier and Seebeck coefficient they are related by this relation.

So, this is your Peltier coefficient, this is your Seebeck coefficient and temperature is involved in it. So, it is a well-known fact known for many years.

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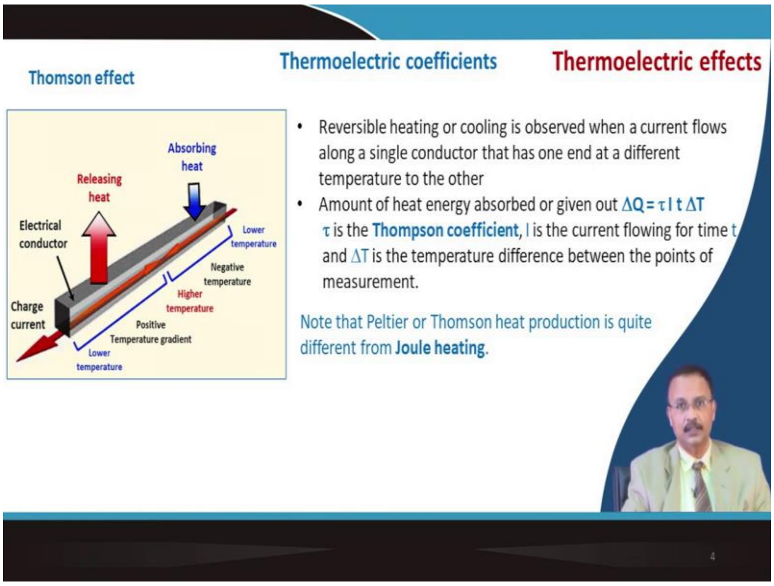

Thermoelectric coefficients

Thermoelectric effects

Thomson effect

- Reversible heating or cooling is observed when a current flows along a single conductor that has one end at a different temperature to the other
- Amount of heat energy absorbed or given out $\Delta Q = \tau I t \Delta T$ τ is the **Thompson coefficient**, I is the current flowing for time t and ΔT is the temperature difference between the points of measurement.

Note that Peltier or Thomson heat production is quite different from **Joule heating**.

Another effect which is quite interesting which is called a Thompson effect and here it is found that reversible heating or cooling, you can observe when a current flow along a single conductor. So, there is no by metal; single conductor and one end is at a different temperature with respect to other.

So, here in a whole big rod; if I put a Bunsen burner here, so it will be hot, this will be a cold region, this will also be a cold region. So, in some place and current is flowing in this direction. So, some place you will see the heat will absorb here and other place the heat will be releasing.

So, this heat absorption or given out; so this delta Q amount is the current flow and time involved and the temperature difference. So, this tau the constant involved that is known as Thompson coefficient and as you can see I is the current which is flowing for a time t and delta T is the temperature difference between the point of measurement.

So, the Peltier or Thompson heat production is quite different than the normal Joule heating which we all know that, when you pass current through a conductor due to I square into r into t theta heat is generated. So, this heat generation is definitely different than this.

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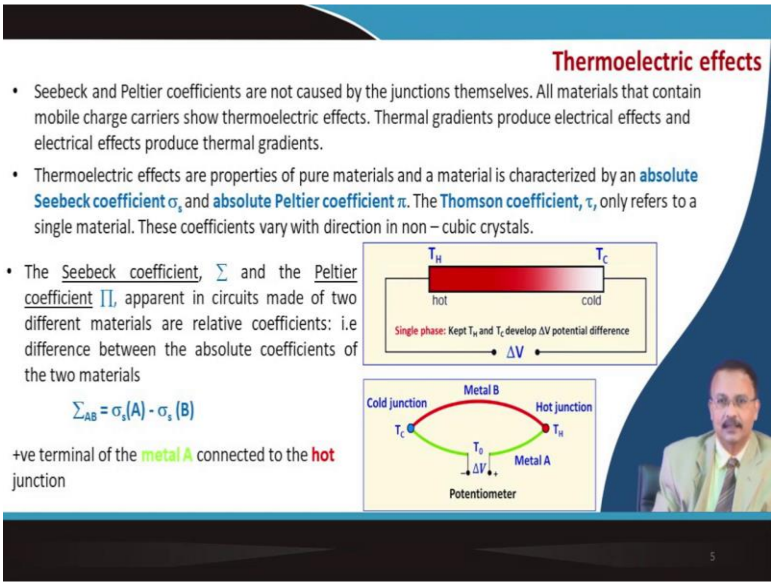

Thermoelectric effects

- Seebeck and Peltier coefficients are not caused by the junctions themselves. All materials that contain mobile charge carriers show thermoelectric effects. Thermal gradients produce electrical effects and electrical effects produce thermal gradients.
- Thermoelectric effects are properties of pure materials and a material is characterized by an **absolute Seebeck coefficient** σ_s and **absolute Peltier coefficient** π. The **Thomson coefficient,** τ, only refers to a single material. These coefficients vary with direction in non – cubic crystals.
- The Seebeck coefficient, Σ and the Peltier coefficient Π, apparent in circuits made of two different materials are relative coefficients: i.e difference between the absolute coefficients of the two materials

$$\Sigma_{AB} = \sigma_s(A) - \sigma_s(B)$$

+ve terminal of the metal A connected to the **hot** junction

Now, the Seebeck or Peltier coefficient which I have talked about that is not caused only by the junction themselves; all materials that contain a mobile charge carriers, they can show thermoelectric effect in fact. So, thermal gradient is important and that can produce a electrical effect, which I have seen in case of the Seebeck effect.

And electrical effect when you pass current, electric current; then it can also produce a thermal gradient. So, it is not any junction is involved; but it is also possible for you to get in a single material. So, this thermoelectric effect are the properties of pure material and material is characterized by absolute Seebeck coefficient, which I have defined it as sigma s or absolute Peltier coefficient.

Of course, the Thompson effect the tau that is for the single metal of course. But in case of Seebeck and Peltier also, you can define the absolute Seebeck and Peltier coefficient. Now, the actual Seebeck coefficient the large sigma, which I have talked about or the Peltier coefficient large pi in the circuit that I showed earlier, made out of two different types of material.

They are all relative coefficients, that means the difference between the absolute coefficient of the two material. So, likewise this large sigma, you can define by individual sigma of A minus individual sigma of B. So, the positive terminal of the metal A is connected to the hot junction as you can see. So, that is worth to be mentioned.

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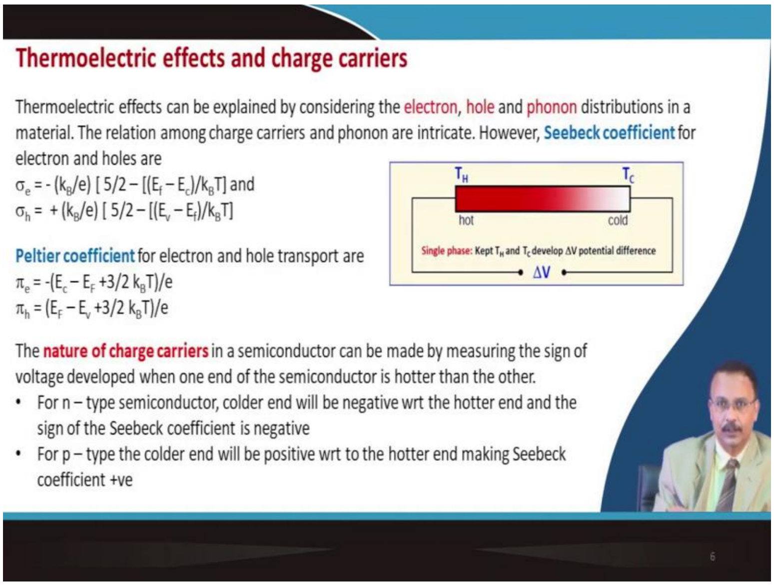

Thermoelectric effects and charge carriers

Thermoelectric effects can be explained by considering the electron, hole and phonon distributions in a material. The relation among charge carriers and phonon are intricate. However, **Seebeck coefficient** for electron and holes are

$\sigma_e = -(k_B/e)\,[\,5/2 - [(E_f - E_c)/k_BT]$ and

$\sigma_h = +(k_B/e)\,[\,5/2 - [(E_v - E_f)/k_BT]$

Peltier coefficient for electron and hole transport are

$\pi_e = -(E_c - E_F + 3/2\,k_BT)/e$

$\pi_h = (E_F - E_v + 3/2\,k_BT)/e$

The **nature of charge carriers** in a semiconductor can be made by measuring the sign of voltage developed when one end of the semiconductor is hotter than the other.

- For n – type semiconductor, colder end will be negative wrt the hotter end and the sign of the Seebeck coefficient is negative
- For p – type the colder end will be positive wrt to the hotter end making Seebeck coefficient +ve

Now, this thermoelectric effect is certainly related to the charge carriers. And thermoelectric effect in fact, can be explained by considering that the solid is having electron; it can have holes, it can have defect also, the phonons are also involved. So, it is a complicated phenomena in order to model the individual thermoelectric effect.

So, if you consider the relation among the charge carriers and phonon, they are indeed quite in integrate; but if you consider only the charge carrier itself, then the problem you can solve with a relatively in a easier fashion. So, individual Seebeck coefficient for electron and hole, they are given by this relation. As you can see it is related to the Boltzmann constant and also it is related to the Fermi energy, bottom of the conduction band E c and top of the valence band.

So, for hole and sorry for electron and hole, the Seebeck coefficient, individual Seebeck coefficient that can be approximated by this relation. Similarly, for Peltier coefficient also; if you only consider the electron and hole transport, then this two simplified equations they are valid. And note the charges this signs are different in case of the different charge carriers; for electron it is negative and for hole it is positive.

So, the nature of the charge carrier in a semiconductor can be made that, what is the nature of the charge carrier by measuring the sign of the voltage which is developed; when one end of the semiconductor is hotter than the other end, the cooler end in case of the Seebeck effect.

So, for a negative type of semiconductor, the colder end will be negative with respect to the hotter end and the sign of the Seebeck coefficient is negative. And the reverse is true for p type, the colder end will be positive with respect to the hotter end making the Seebeck coefficient is positive. So, this is another way to know the prominent charge carrier of a extrinsic semiconducting material.

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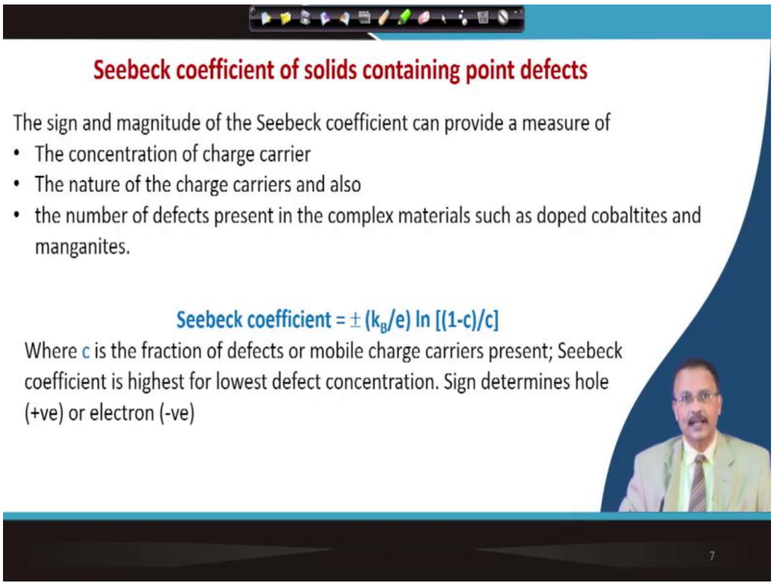

Seebeck coefficient of solids containing point defects

The sign and magnitude of the Seebeck coefficient can provide a measure of

- The concentration of charge carrier
- The nature of the charge carriers and also
- the number of defects present in the complex materials such as doped cobaltites and manganites.

Seebeck coefficient = $\pm (k_B/e) \ln[(1-c)/c]$

Where c is the fraction of defects or mobile charge carriers present; Seebeck coefficient is highest for lowest defect concentration. Sign determines hole (+ve) or electron (-ve)

Now, interestingly the Seebeck coefficient of solids which are having defects, that also can be treated in a interesting way. The sign and magnitude of the Seebeck coefficients as I have told, can also provide a measure of the concentration of the charge carrier. So, what is the concentration of the effective charge carrier that you can estimate? Nature of the charge carriers from the voltage sign and also number of defect that is present in a complex material; like we already introduced this cobaltite’s and manganite’s.

So, in those kinds of material, what are the number of defects that is present which otherwise is very difficult to estimate. So, that also you can do. So, the Seebeck coefficient as you can see, you can approximate it by k B by e l n of 1 minus c by c, where c is the defect concentration. So, if you have a normal site; I will just show in a typical example. So, that is basically the site which does not have a defect, that is 1 minus c and c is the concentration of the defect.

So, c is actually the fraction of defects of mobile charge carrier present. So, Seebeck coefficient of course will be highest for the lowest defect concentration; that is from the relation. And as I told, the sign determines the hole whether it is hole that is positive or electron.

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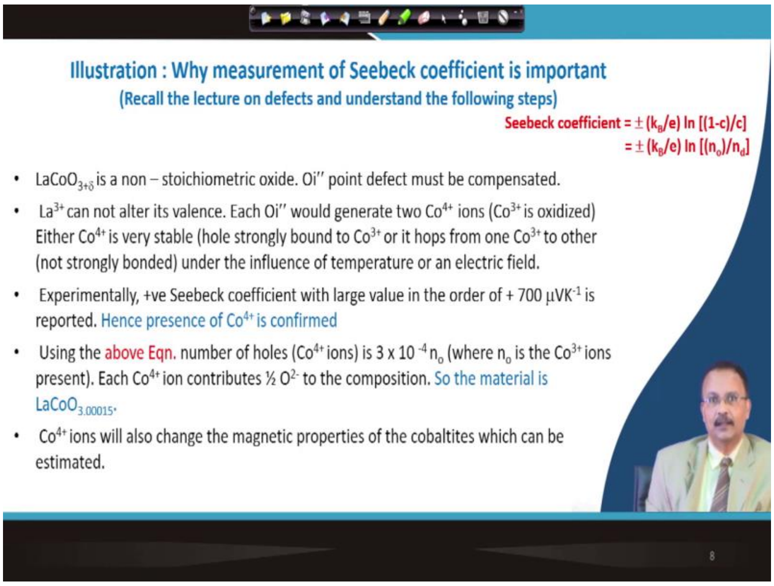

Illustration : Why measurement of Seebeck coefficient is important

(Recall the lecture on defects and understand the following steps)

Seebeck coefficient = $\pm (k_B/e) \ln [(1-c)/c]$

$= \pm (k_B/e) \ln [(n_o)/n_d]$

- $LaCoO_{3+\delta}$ is a non – stoichiometric oxide. O_i'' point defect must be compensated.
- La^{3+} can not alter its valence. Each O_i'' would generate two Co^{4+} ions (Co^{3+} is oxidized) Either Co^{4+} is very stable (hole strongly bound to Co^{3+} or it hops from one Co^{3+} to other (not strongly bonded) under the influence of temperature or an electric field.
- Experimentally, +ve Seebeck coefficient with large value in the order of + 700 μVK^{-1} is reported. Hence presence of Co^{4+} is confirmed
- Using the above Eqn. number of holes (Co^{4+} ions) is $3 \times 10^{-4} n_o$ (where n_o is the Co^{3+} ions present). Each Co^{4+} ion contributes ½ O^{2-} to the composition. So the material is $LaCoO_{3.00015}$.
- Co^{4+} ions will also change the magnetic properties of the cobaltites which can be estimated.

Let us cite an example to clarify this thing and let us understand that why this measurement of Seebeck coefficient is important. So, let us see this cobaltite you know; because part of my other lecture already we have introduced this material. Let us have that this is having a effluence in oxygen. So, oxygen is in the interstitial position, it is coming during heat treatment.

So, that will bring two negative charge and as you know that the charge will have to be balanced. So, while we talked about the defect, you understood that, charge neutrality will have to be maintained. So, lanthanum cannot change it valence state, so it will remain in plus 3 state. And each oxygen interstitial will generate two cobalt 4 plus ions; because lanthanum cobaltite's, it is cobalt is in plus 3 valence state.

So, in order to maintain the charge neutrality, so you are bringing extra negative charge. So, some positive charge will have to be there to balance this. So, let us assume that cobalt 3 plus ion in cobaltite lanthanum cobalt oxide that is getting oxidized to cobalt 4 plus.

Now, the hole which is generated during the process, that can be either weekly absorbed or very strongly absorbed with the this cobalt 3 plus. So, making this defect either very strong or it is possible that the generated hole hops from one cobalt 3 plus to another cobalt 3 plus. So, progressively oxidizing in both is possible.

So, if you do a experiment to estimate the Seebeck coefficient, the value is typically found in the order of plus. So, sign of the voltage is plus and you know that where from this sign is coming; it depends on which one is a hot end which one is the cold end. So, if it is positive; that means the hole is contributing more. So, you are seeing that the measurement tells you that, it is coming around 700 micro volt per Kelvin.

So, you know the relation of the Seebeck coefficient, which I introduced earlier and then you can say that cobalt is getting oxidized. So, hole is the contributing charge carrier. Now, if you use this relation, which I already introduced k B by e l n of n 0 by n d, where n d is the defect concentration and put the value of the Seebeck coefficient all the other terms are known.

So, in terms of n 0, you can calculate that it is given 3 into 10 to the power minus 4 n 0. So, n 0 is now here in case of this particular case is cobalt 3 plus. So, you can estimate that how many cobalt 4 plus you are getting. Now, you know that each cobalt 4 plus ion contributes to half oxygen ion. So, you basically know what is the composition of oxygen; so you put that value, this is half of it.

So, it will be indeed oxygen plus. So, it is a superoxide it is forming and that is the formula that you are getting. So, how many things you know that, what kind of charge carrier is there that you can understand. What is the defect concentration with respect to the original cobalt 3 plus ion that you can get, and what is the composition of oxygen; because oxygen is creating this defect that also you can estimate.

And finally, cobalt 4 plus ion will also change the magnetic property and you know that how to calculate the magnetic property. You remember in one of the classes, we talked about it is mostly spin quantum number; because orbital quantum number is quenched. So, you can estimate its magnetic moment. So, these many things you can do out of this simple measurement of a Seebeck coefficient.

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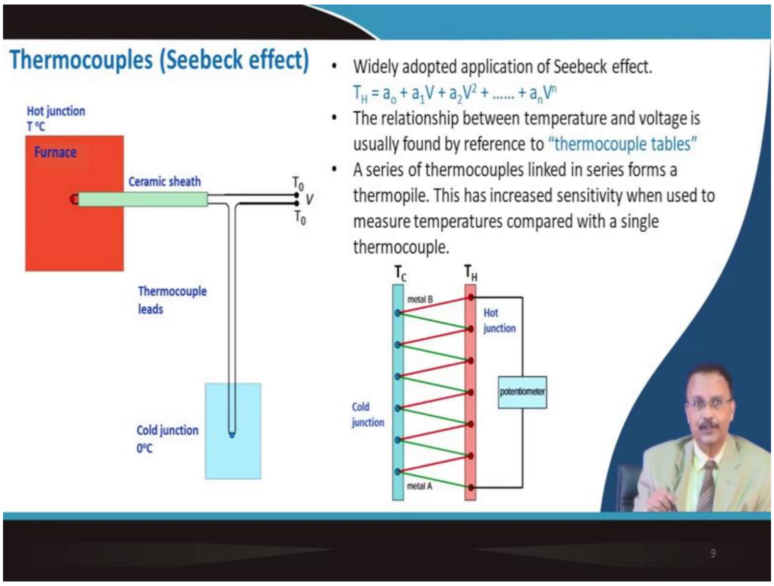

Thermocouples (Seebeck effect)

- Widely adopted application of Seebeck effect.
  $T_H = a_o + a_1V + a_2V^2 + \ldots\ldots + a_nV^n$
- The relationship between temperature and voltage is usually found by reference to "thermocouple tables"
- A series of thermocouples linked in series forms a thermopile. This has increased sensitivity when used to measure temperatures compared with a single thermocouple.

This part all of you more or less you know that this Seebeck effect can be used for the thermocouple. So, it is widely applied adopted application, the temperature T H is related to the voltage that is generated and this is a typical polynomial equation to fit the voltage versus temperature data in the hot end.

So, the hot end is, the hot junction is inside a furnace and the cold junction you put under 0 degree Celsius and you measure the voltage and then calibrate it with the temperature, the measured voltage and temperature. Calibration charts are already available in various sources and handbooks; we know that is called thermocouple table.

And if you want to make a very precise measurement; then instead of one junction as you can see this cold junction and hot junction. You have multiple points here and you collect the data collectively here as one can show. So, this is much more reliable. So, this is one of the example of thermocouple that we all are familiar with.

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T/C Type	Conductor		T/C Junction Continuous Temperature range °C	INTERNATIONAL	FORMER UNITED KINGDOM	FRANCE	GERMANY	JAPAN	USA	Cable code
	+	-								
E	Ni-CR	Cu-Ni	0 to +800							EX
J	Fe	Cu-Ni	0 to +750							JX
K	Ni-Cr	Ni-Al	0 to +1100							KX
N	Ni-Cr-Si	Ni-Si-Mg	0 to +1100							NX NC
R	Pt-13Rh	Pt	0 to +1600							RCA
S	Pt-10Rh	Pt	0 to +1600							SCA
T	Cu	Cu-Ni	-185 to +300							TX
B	Pt-30Rh	Pt-6Rh	+200 to +1700							BX

And here this is just an example, different types of conductor you can use and accordingly the temperature range you can decide. So, some of the examples are given. So, right from 0 to 800 degrees Celsius the first one up to 1700 degrees Celsius you can measure the temperature using this thermocouple. And the voltage chart, the temperature versus voltage is well available in the literature or various handbooks.

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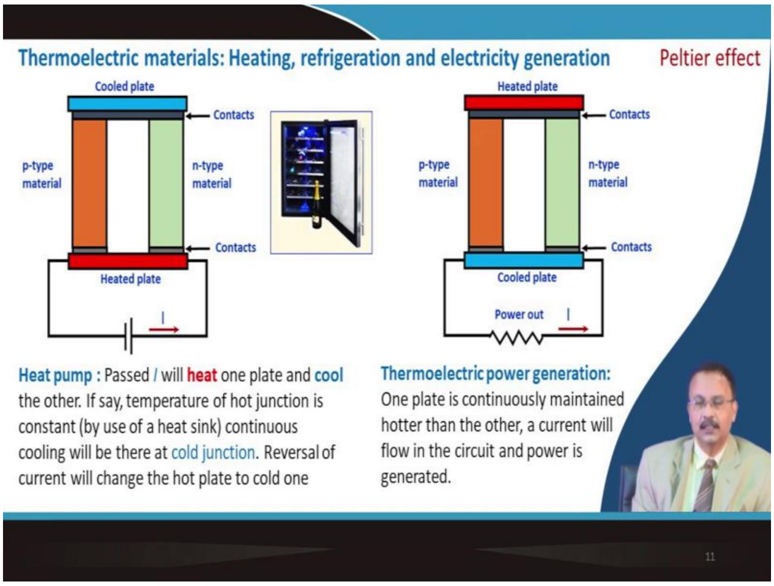

Thermoelectric materials: Heating, refrigeration and electricity generation

Peltier effect

Heat pump : Passed I will **heat** one plate and **cool** the other. If say, temperature of hot junction is constant (by use of a heat sink) continuous cooling will be there at cold junction. Reversal of current will change the hot plate to cold one

Thermoelectric power generation: One plate is continuously maintained hotter than the other, a current will flow in the circuit and power is generated.

So, this thermoelectric materials that can be used as a heat pump, that can be used as a refrigeration system and also that can be used for electricity generation. And this is already we have described in a different form it is presented. So, you know that this is a p type of semiconductor, this is n type of semiconductor and this is a one plate connected with this.

So, this is one of the junctions and this is another junction. So, as a heat pump you just connected with a small car battery and this kind of couple you make and this is used for small refrigerator as the figure shows and this is very popular nowadays. So, this is used as a heat pump. So, when current is passed, one plate will be hotted and other plate will be cooled.

So, the temperature of the hot junction is constant, if you can make it by a heat sink. So, another heat sink is added here. So, that will not raise this temperature. And also the thermal conductivity of this materials are relatively low, so that the cold end will not be affected. So, continuously you pass on current and a with heat sink you absorb this heat, then this will be colder.

So, that is the principle of making refrigeration. And if you change the current direction, then this hot plate and cold plate this will change its site. So, you can use it as a thermoelectric power generator also; one plate is continuously maintained hotter than the other. So, you have a waste heat source. So, one end you put it in the hot zone and then eventually you will find the current is passing through the other end.

So, though very small kind of a power you can generate out of it. We are using this thermoelectric material; this is a good way to generate power from the waste heat source; that is shown in the next photograph, on the right hand side photograph.

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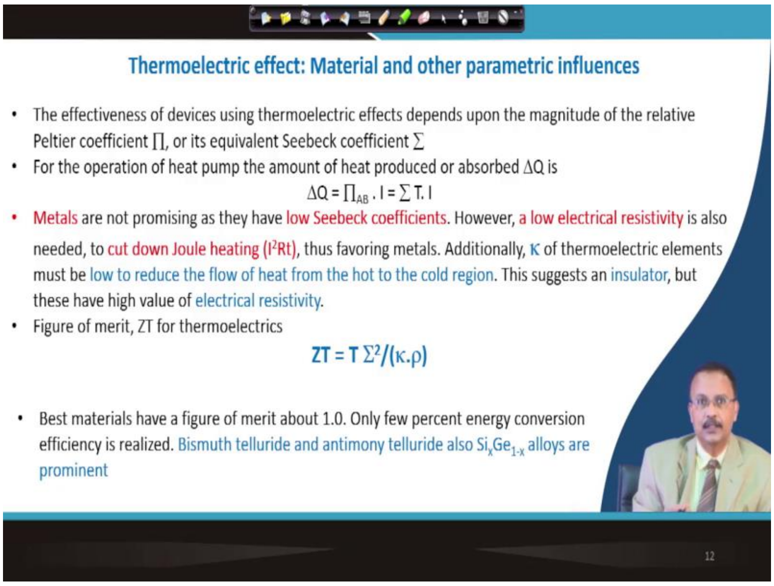

Thermoelectric effect: Material and other parametric influences

- The effectiveness of devices using thermoelectric effects depends upon the magnitude of the relative Peltier coefficient $\prod$, or its equivalent Seebeck coefficient $\sum$
- For the operation of heat pump the amount of heat produced or absorbed ΔQ is

$$\Delta Q = \prod_{AB} . I = \sum T. I$$

- Metals are not promising as they have low Seebeck coefficients. However, a low electrical resistivity is also needed, to cut down Joule heating (I^2Rt), thus favoring metals. Additionally, κ of thermoelectric elements must be low to reduce the flow of heat from the hot to the cold region. This suggests an insulator, but these have high value of electrical resistivity.
- Figure of merit, ZT for thermoelectrics

$$ZT = T \Sigma^2/(\kappa.\rho)$$

- Best materials have a figure of merit about 1.0. Only few percent energy conversion efficiency is realized. Bismuth telluride and antimony telluride also Si_xGe_{1-x} alloys are prominent

But these things are not that simple, I mean thermoelectric effect, the other parameteric influence also we will have to take into consideration. So, the of course, the primarily concern is the Peltier coefficient or equivalent Seebeck coefficient. But for the operation of the heat pump, as you can see that this del Q is related to your Peltier coefficient into current and that is also related with the Seebeck coefficient.

So, that is ok, but metals are not very promising; because they have relatively low Seebeck coefficient. But it is important to have metal, because it has low electric resistivity; this is also required. Otherwise due to Joule heating I square R T your heat generation will be jeopardized. So, that factor favors metal, but poor Seebeck coefficient that is not good for metal to have.

Additionally thermal conductivity of the thermoelectric element must also be low; I just explained it, because hot end and cold end they will there will be heat transfer. So, you will have to reduce the flow of heat from hot to cold region. So, that basically talks about the insulator; but once you have a insulator, they have a high value of electrical resistivity. So, it is problematic to, I mean optimize all these parameter.

So, for thermoelectric material, the figure of merit is defined by Z into T, which is given by this relation. Temperature and Seebeck coefficient square divided by its individual thermal conductivity and the density of the material. So, the best possible thermoelectric material so far whatever is available is having the Z T value is 1.

So, that indicates only a few percent of energy conversion, but still it is good; because you are anyway utilizing the waste heat, you are doing something useful product. Bismuth telluride is the material of choice; antimony telluride is another material and nowadays silicon germanium alloys they are also prominent thermoelectric material.

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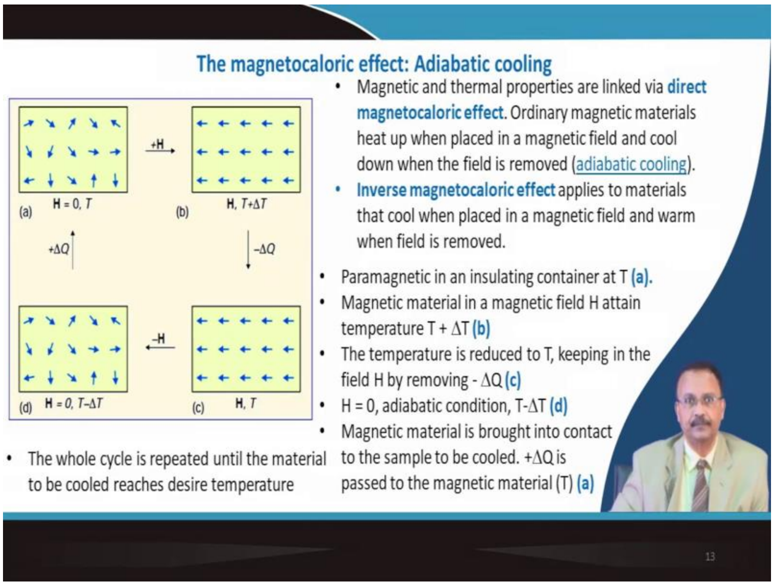

The magnetocaloric effect: Adiabatic cooling

- Magnetic and thermal properties are linked via **direct magnetocaloric effect**. Ordinary magnetic materials heat up when placed in a magnetic field and cool down when the field is removed (adiabatic cooling).
- **Inverse magnetocaloric effect** applies to materials that cool when placed in a magnetic field and warm when field is removed.

- Paramagnetic in an insulating container at T **(a)**.
- Magnetic material in a magnetic field H attain temperature T + ΔT **(b)**
- The temperature is reduced to T, keeping in the field H by removing - ΔQ **(c)**
- H = 0, adiabatic condition, T-ΔT **(d)**
- Magnetic material is brought into contact to the sample to be cooled. +ΔQ is passed to the magnetic material (T) **(a)**

- The whole cycle is repeated until the material to be cooled reaches desire temperature

Now, the final effect which is quite interesting is called magneto caloric effect. And people have used it for adiabatic cooling and this relation is interesting and it is still for research purpose it is important no such device so far has come into the market. So, the basic principle is that, magnetic and thermal properties are linked via direct magneto caloric effect.

So, what is that magnetocaloric effect? That ordinary magnetic materials heat up when you place in a magnetic field and cooled down when the field is removed. So, that is a adiabatic cooling, the principle of adiabatic cooling. And the inverse effect is that, materials that cooled when placed in a magnetic field and reverse is true, it will warm when the field is removed. So, let us consider a paramagnetic material here.

So, in paramagnetic material escaped in a insulating container. So, adiabatic condition is maintained. So, temperature is say T and your heat is 0, sorry the magnetic field is 0. So, magnetic field is 0 here and temperature is a certain temperature it is maintained. Now, when you apply the heat, this confusing; it is not heat, when you are applying a magnetic field, then this paramagnetic, this magnetic domain will orient along with the magnetic field and as a result your temperature will get heated.

So, here with the application of magnetic field, your temperature is increased T plus delta T, right. So, this is the figure number b. Now, this temperature is reduced again to T. So, you absorb a little bit of heat to keep the temperature T. So, you will have to move, remove little bit of heat, right. So, here you maintain the field.

So, field is maintained. So, H is there and temperature is reduced from T plus delta T to T, right. So, this is this figure. Now, the magnetic material you keep in contact with the sample to be cooled. So, you put it in a cold sample and once you put it in a cold sample, then from the sample del Q heat it will take. So, in between I just missed this point; in between what is happening that, in this case your temperature is dropped down to T and slowly you take this magnetic field out.

So, once you take the magnetic field out, again this will transform into a paramagnetic state. And this temperature will be cooled down right; because as I have told that when it orders. So disorder to order phase transition takes place, then it gets temperature increased and when it is again disordered, then it will cool down.

So, once it is cool down, then you the material which you want to cool; you just put in close contact. So, it will take heat from that material and again go back to its original position. So, you just keep on doing this cycle and then due to this adiabatic cooling, your temperature will drop down to a very low level. I mean this is actually the concept, but maintain the through adiabatic condition is really challenging.

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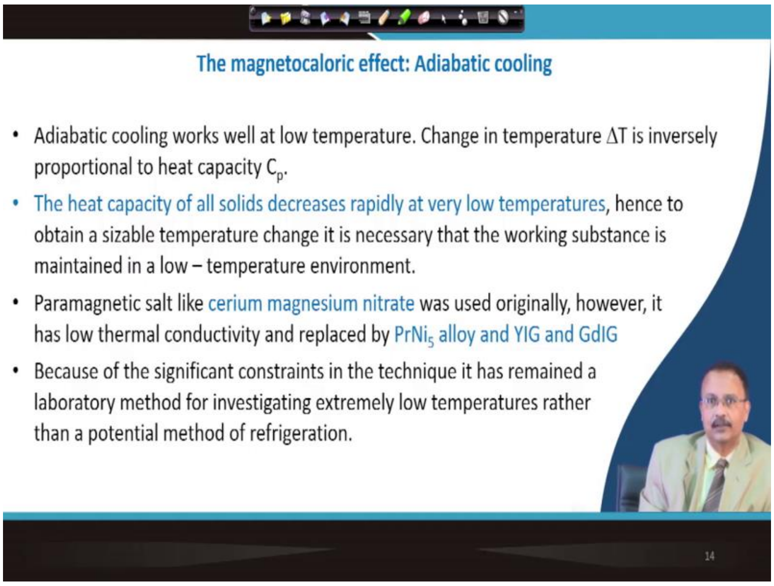

The magnetocaloric effect: Adiabatic cooling

- Adiabatic cooling works well at low temperature. Change in temperature ΔT is inversely proportional to heat capacity C_p.
- The heat capacity of all solids decreases rapidly at very low temperatures, hence to obtain a sizable temperature change it is necessary that the working substance is maintained in a low – temperature environment.
- Paramagnetic salt like cerium magnesium nitrate was used originally, however, it has low thermal conductivity and replaced by $PrNi_5$ alloy and YIG and GdIG
- Because of the significant constraints in the technique it has remained a laboratory method for investigating extremely low temperatures rather than a potential method of refrigeration.

Now, this adiabatic cooling works well at low temperature; because from the curve that I have shown, a change in temperature is inversely proportional to the heat capacity. The heat capacity of the solid decrease very rapidly at low temperature; to obtain a sizable temperature change it is necessary that the working substance maintain at very low temperature. So, at very low temperature indeed it works well.

Typical paramagnetic salts like cerium magnesium nitrate is one material; but now a days PrNi 5 alloy and yttrium iron garnet or gadolinium iron garnet they are also good material. You know about this material part of magnetic material, we already talked about it. And significant constraint is there for this material. So, still this is laboratory material for refrigeration.

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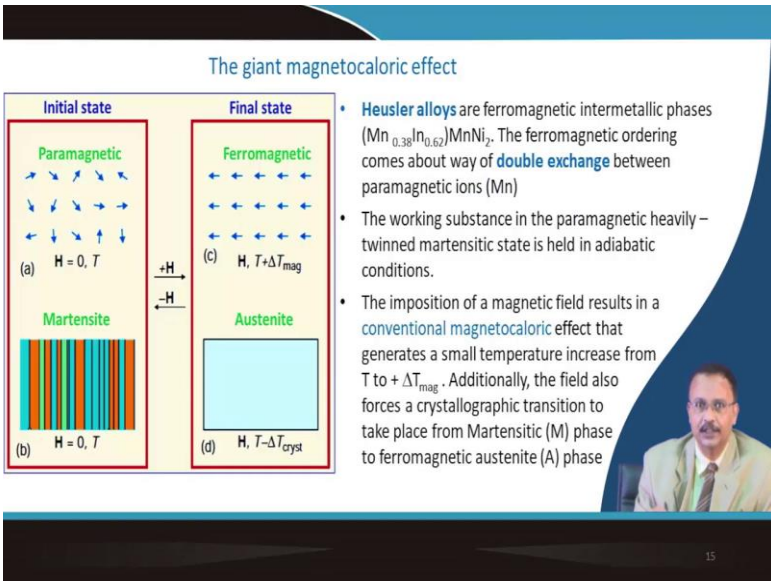

The giant magnetocaloric effect

- **Heusler alloys** are ferromagnetic intermetallic phases $(Mn_{0.38}In_{0.62})MnNi_2$. The ferromagnetic ordering comes about way of **double exchange** between paramagnetic ions (Mn)
- The working substance in the paramagnetic heavily – twinned martensitic state is held in adiabatic conditions.
- The imposition of a magnetic field results in a conventional magnetocaloric effect that generates a small temperature increase from T to + ΔT_{mag} . Additionally, the field also forces a crystallographic transition to take place from Martensitic (M) phase to ferromagnetic austenite (A) phase

Another thing is quite important it is coming up is giant magnetocaloric effect. So, here the same principle, whatever I have described that is valid; but in addition to that, there is a paramagnetic to ferromagnetic phase transformation takes place, which is a first order phase transition and due to that it basically pulls down.

So, it is perfectly applicable for Heusler alloy and this is the formula of the Heusler alloy, manganese indium and manganese in this side as well in this site with nickel too. So, this alloy ferromagnetic ordering takes place through double exchange phenomena which already I described. So, the working substance in the paramagnetic is heavily twinned martensitic state, that is held in a adiabatic condition.

Now, impose of a magnetic field result the conventional magnetocaloric effect; whatever I told about that once you have the field applied, then the temperature increases. But in addition there is a transition, the additionally the field also forces the crystallographic transition from martensitic phase to austenitic phase. So, that is new in this type of material.

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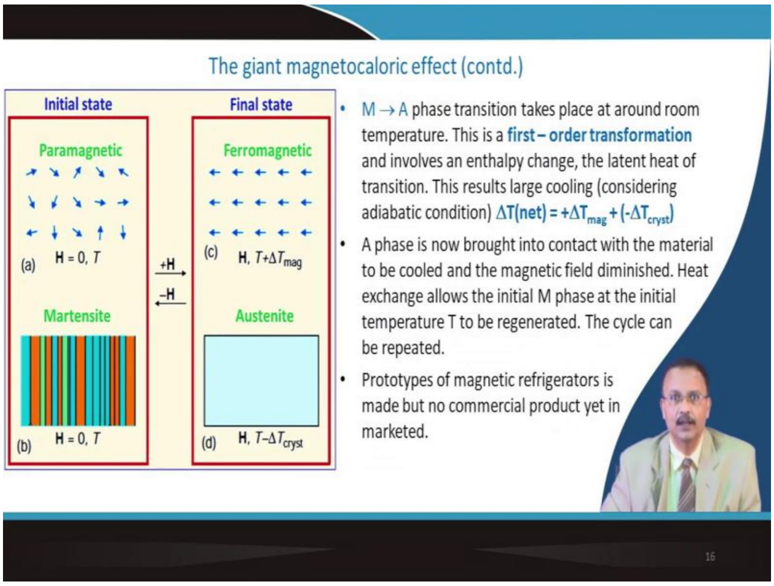

The giant magnetocaloric effect (contd.)

- M → A phase transition takes place at around room temperature. This is a **first – order transformation** and involves an enthalpy change, the latent heat of transition. This results large cooling (considering adiabatic condition) $\Delta T(net) = +\Delta T_{mag} + (-\Delta T_{cryst})$
- A phase is now brought into contact with the material to be cooled and the magnetic field diminished. Heat exchange allows the initial M phase at the initial temperature T to be regenerated. The cycle can be repeated.
- Prototypes of magnetic refrigerators is made but no commercial product yet in marketed.

And what is happening when this phase transition takes place, it is a first order phase transition and it involves enthalpy change. So, the latent heat of transition is involved and that actually results a large cooling; as you can see the net del T value is for your magnetic effect which already I have talked about plus this crystallographic change. So, there is a huge kind of cooling that is available and the same cycle is maintained as I have explained in the earlier case for adiabatic cooling.

So, this phase you know brought into contact with a material to be cooled and the magnetic field is diminished. So, H is turned to be 0. So, heat exchange allows the initial martensitic phase at the initial temperature T to be regenerated. So, again it will go back to its original position and this cycle can be repeated.

So, using this because this is a prominent phenomena of magnetocaloric effect and using this refrigerators prototype that has been built, which works quite well; but no such commercial giant magneto caloric effect prototype is available, but the actual thing is yet to come into the market.

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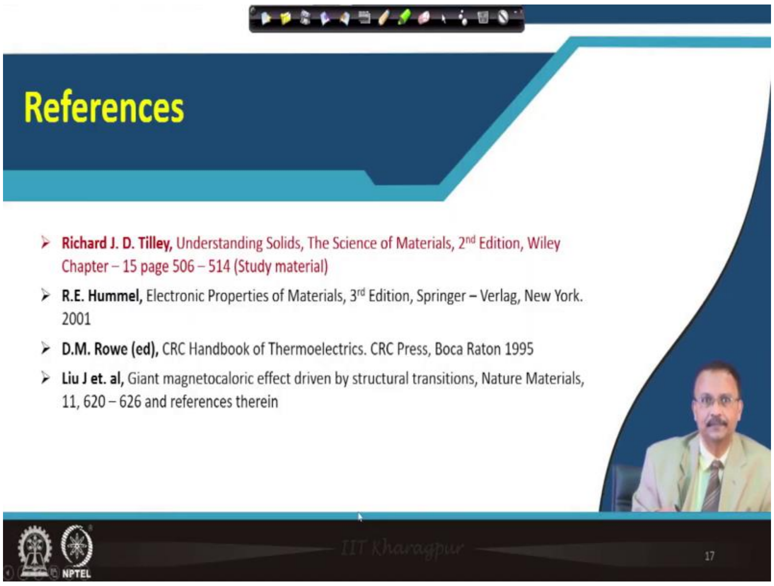

References

- **Richard J. D. Tilley,** Understanding Solids, The Science of Materials, 2nd Edition, Wiley Chapter – 15 page 506 – 514 (Study material)
- **R.E. Hummel,** Electronic Properties of Materials, 3rd Edition, Springer – Verlag, New York. 2001
- **D.M. Rowe (ed),** CRC Handbook of Thermoelectrics. CRC Press, Boca Raton 1995
- **Liu J et. al,** Giant magnetocaloric effect driven by structural transitions, Nature Materials, 11, 620 – 626 and references therein

So, the reference is again the book by Tilly, chapter number 15; the book by Hummel is also a good book and there is an exclusive book by Rowe, it is a edited book that can be considered.

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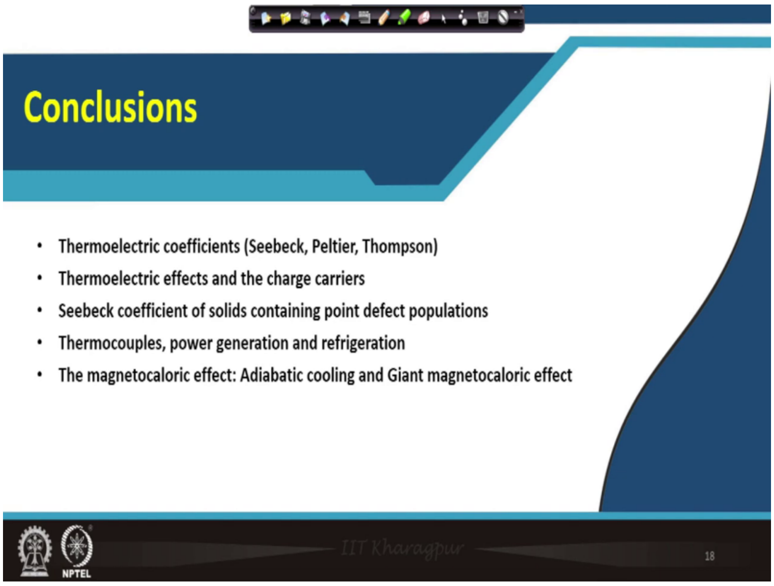

Conclusions

- Thermoelectric coefficients (Seebeck, Peltier, Thompson)
- Thermoelectric effects and the charge carriers
- Seebeck coefficient of solids containing point defect populations
- Thermocouples, power generation and refrigeration
- The magnetocaloric effect: Adiabatic cooling and Giant magnetocaloric effect

And in this lecture, we talked about thermoelectric coefficient, especially Seebeck, Peltier and Thompson coefficients. Then thermoelectric effect, how it is related to the charge carrier that has been illustrated; Seebeck coefficient of solids containing point defect population that also estimated.

And how you can use the Seebeck coefficient in estimating the concentration of the defect, type of the defect; then composition of the non-stoichiometric oxide that has illustrated through an example. Then we talked about thermocouple principle, power generation and refrigeration and finally, magnetocaloric effect, that is adiabatic cooling and giant magnetocaloric effect has been introduced.

Thank you for your attention.