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GANG CHEN: --not a question, I will continue. So, again, I think what you're saying is exactly-- that we start-- so it's a very steep dive. We start from very basic thinking. And then we're trying to understand the materials-- what determines the material properties.

And this lecture-- after I told some of you this is topic of thermal conductivity, what I'm hoping is to real [INAUDIBLE] from here, what people are thinking in making materials better.

But let me start with a very brief review of last lecture. We showed what is a simple-- remember, my picture is always simple. It goes from left to right and right to left. And the difference gives you the flux.

So from there, we show the general relation. The current flux is related to electrostatic potential. So that's the charged driving force for charge flow. And then we will have a temperature gradient that is comparable to the [INAUDIBLE] gradient. So now you see the electricity to heat properly.

And then this one shows the peak current. So really, now, electron is carrying the heat, and the heat current is the electric current. Heat current is, again, coupled, in this case, not just to parameter gradient, but also to the actual potential gradient.

And this is a very general [INAUDIBLE] relation. If I have written-- really, this gradient in terms of generalized force, and this coefficient-- across coefficients are equal. And this is what the [INAUDIBLE] before.

And then I gave some-- we use some of the concept we learned before-- for example, density of states and the-we have expression for this coefficient. So one is the electric conductivity. And this other coefficient from this other coefficient, called the Seebeck coefficient, and the [INAUDIBLE] equations.

Let me just make one remark that those expressions are not the most general. You can have different transport regimes. This is the regime that most people do-- the most common transport regime. So those expression-- you can-- rather than [INAUDIBLE] derivation, you can access from Boltzmann equation to derive those coefficients.

And I show examples. One thing that I want to emphasize is that the properties depends on temperature. So different temperature-- you can see the property [? attribute. ?]

For electric conductivity, if you follow these simple Boltzmann statistics, you actually get the electric conductivity. In semiconductor, we know typical microelectronics type of doping. The electric conductivity increases with temperature.

But for thermoelectric material-- so this is not quite right for thermoelectric materials. You can see the thermal conductivity, electric conductivity increases with temperature. And that's because of the doping, very heavily-- metals like this. Metal-- the electric conductivity decreases because when you get hot, they are not more photons. The atoms are vibrating more violently, and that's scattered electron. And that's why the electric conductivity will decrease.

And they see that this typically will have a peak. And if you just talk simply, one-band transport. So one-band means if I have a conduction band and each electron only go one to one conduction band, then the series say it should increase with temperature because as the temperature increases, the separation of the chemical potential from the bottom-- so the [INAUDIBLE] chemical potential [? from ?] the center of the band.

But in almost all materials, the behavior is you will pick some temperature and start to decrease. And the reason is, as the temperature increase, you excite-- intrinsically, you leave the thermal energy and the electron from the valence band through the hole behind the electron conduction band.

So in this case, now, you have both electron and hole. So when you flow current-- electron current energy in one direction, flow current energy in the opposite direction-- so they cancel each other. In this case, you actually could get a higher electric conductivity, but the Seebecks cancel each other.

So this is-- when you look at experimental data, it turns out that [INAUDIBLE] we do that and say, we cannot calculate exactly. So we look at experiments, and this is what happened. This is why it died. And this is where--OK, how you can move this to higher temperature?

If you have more electron, you dope it more heavily-- you will go to higher temperature. And if you have larger bandgap, it's more difficult to generate the thermal electron-hole pairs, and then you can move this to higher. So that's how you look at the different configurations with different materials.

So that's where we were in the last lecture, and those were mainly discussion on electrons. And we also talked about the whole concept of lattice vibration. And we gave a very simple expression, before, on the phonon thermal conductivity.

And again, my picture is left to right, right to left. So when I want to find out the heat flux going through any band, I say, how much heat is going in from one side to the other without scattering? So this is one relaxation time. And how much from left to right? [INAUDIBLE] one relaxation time. So difference gave me the heat flux.

And what I want to do is a little bit more-- better [INAUDIBLE] meaning before-- I will just say this is the number density n per unit volume. Now, I'm going to do modes, so I'm going to sum up-- so this-- it's the same as what I drew here. But here is more rigorous.

So this is the energy of one Coulomb lattice vibration-- [INAUDIBLE] of lattice vibration, so one phonon. And then this is-- per Coulomb mechanical modes, the Boltzmann-Einstein distribution Per state, quantum state, how many phonon you have? And this is the velocity.

So this is really telling me, for quantum mechanical modes, how many phonons is moving to the forward, positive x direction? The one path gives me path-- random motion. So the idea is the same, but now I'm trying to do a better job counting-- better counting job.

And here, what do we have-- this is-- remember, in the second lecture, I was doing blackbody counting-blackbody radiation. So this is counting all the quantum mechanical allowed modes, kx wave vector. It's a [? phonon ?] wave. kx, ky, kz. So I'm summing up all those modes. And that's from left to right, minus from right to left, giving me the left flux. So that's what I showed before in simpler form. But if I do this-- and I will get the integral-- no longer just a simple one third of cv gamma. That's what we had before. And now it's the integration of all the frequency, each frequency. Remember, [? phonon-- ?] so the acoustic wave-- for example, low-frequency acoustic wave-- that's what you hear. And they have the different mean-free path, different group velocity, the higher frequency ones.

So this can all change as a function of frequency. So what we're writing now is a more rigorous form for the thermal conductivity carrying heat conduction by the last waves. That's really important.

So this is a typical [INAUDIBLE] bulk material. And people have measured the thermal conductivity. And this is a typical curve of thermal conductivity, of material versus temperature. And this is specific example of gallium arsenide. And you can say there is a peak.

So there's a-- in bulk material, its peak is typically between 10 to 20 kelvin. And then after the peak [INAUDIBLE] it drops below, it increases. And this actually reflects different physics.

So at a very high temperature, each mode is carrying energy kt. So the number of phonons is also proportional to t, temperature. And in this case, what happens-- because as the temperature increases, you excite more phonons, and they scatter each other. They scatter each other, and they drop the thermal conductivity. So that's why the thermal conductivity is dropping.

And in fact, if you follow the [INAUDIBLE] same, the number is proportional to t, the thermal conductivity is typically inversely proportional to [INAUDIBLE] temperature. But see, that's a simple picture. And then in reality, this exponent is not 1. It's typically, depending on the material, between 1 and 1.5. People still are trying to figure out why it's not exactly 1.

So this is a higher temperature range. And as you go to lower temperature, the phonon-phonon scattering-- the lattice wave interaction with itself-- becomes weaker. So in this case-- so the thermal conductivity will increase, even though-- if you go to check specific heat-- specific heat of-- which, in this dielectric is due to phonons.

Specifically, this is typically this curve. I forgot to show one. And it's not a constant. It increases from low temperature to the high temperature. But thermal conductivity-- so even though there are less energy-- specifically the measure of phonon energy-- less energy in this region compared to this region-- but because less scattering, the phonon goes longer. So the thermal conductivity actually increases.

So in this region it's typically phonon-phonon scattering-- no longer dominant [INAUDIBLE] you've got an [INAUDIBLE] atoms. So for example, in silicon, if you have a phosphor or boron, you dope it, they are lighter. So you think about that-- you have a string. Again, phonon is the lattice vibration.

You have the same mass [INAUDIBLE] And suddenly, you put a different mass that created some scattering of the waves. And so this is the region where the limit-- the peak here is very much limited by these impurities in the material.

And then when you go to very low temperature-- so the mean-free path becomes very long. In fact, even you can measure-- make a fault material, the mean-free path is longer than your sample size. So in this case, the boundary scattering becomes dominant. And the mean-free path is no longer dependent on the frequency, but dependent on-- is limited by the sample size. So in this region, the thermal conductivity is exactly due to the specific heat. So the behavior-- just specific heat and sample size. So-- yes.

AUDIENCE: No question because I just think-- because of [INAUDIBLE] the power. That's why t--

GANG CHEN: That's exactly the reason. So, by the way, this is why blackbody radiation to the fourth power. Specifically, the third power-- the energy is dU dt. So if you integrate, the energy is the temperature fourth power. And the [? phonon-phonon-- ?] this is a regime. Unfortunately, it's a very low-temperature regime. But this regime, phonon behave almost identically to photon.

Now, scatter-- very weak scatter. So you can see the temperature-- the power is the same.

So that's a typical behavior of lattice thermal conductivity in crystals. And just give one example. The highest thermal conductivity material is diamond. And if you purify the diamond, you can change this peak by-- from this peak. Diamond-- [INAUDIBLE] temperature is about 2,000. And that peak go very high.

And if you purify it-- just to say even isotopes-- carbon 12 versus carbon 13-- you can significantly limit this peak. [INAUDIBLE] room temperature, the thermal conductivity will be influenced by the [INAUDIBLE] of isotopes.

So now if I combine the thermal conductivity, it turns out lattice has a contribution. The electron also carry heat. So if I have an electron and I have four-- four [INAUDIBLE] So I have electron hole.

And then I mentioned-- when they move-- when the electron hole or diffuse, the higher temperature region-- you may get more electron hole. When you go to lower temperature region, they have less electron hole.

What happens? The electron hole will combine each with each other and give off heat. So in that case, they carry the potential energy from one place to other. And this is the bipolar contribution, which is a really bad for thermoelectric.

So this is an example of-- most people who do thermoelectrics don't pay attention to this, and that's wrong. For example, the electronic contribution-- you can calculate it from Wiedemann-Franz law, The electric conductivity divided by thermal conductivity is proportional to temperature [INAUDIBLE] constant mentioned in Wiedemann-Franz law.

So many people will do this. They will calculate this term and this term, and they measure this term, and they subtract the difference, gives you the lattice. But they don't calculate this term. And this is actually difficult to calculate, and that's the reason.

But you can see that the thermal conductivity at a higher temperature goes up. The lattice thermal conductivity always goes down. And the reason for this goes up is due to this term-- a very strong signature of bipolar thermal conductivity from electrons and the holes.

And correspondingly, the Seebeck goes down-- the Seebeck-- because the electron hole cancel that. But the thermal conductivity is still getting both terms, [INAUDIBLE].

So now let's go back. I've talked a long time on this [INAUDIBLE] which parameters-- electrical, Seebeck, thermal conductivity. And we see that the thermal conductivity in the electronic part and phonon part. And now if I divide it by the electric conductivity-- so here, I have Lorenz number. And here, I have phonon divided by [INAUDIBLE], so sigma t. That's just the simple manipulation.

And the Lorenz number in metal-- that's the exact number. But when you go to semiconductor, this depends on doping. So that's why I read it out as a function of n. But see, if you look at it, in metal Seebeck cancel each other. The electron above the Fermi level, electron below the Fermi level cancel each other. You will get a Seebeck [INAUDIBLE].

So you plug in those letters, and the best you get-- the most metal is about 0.01. When I first got into the thermoelectric proposal, I didn't know whether metal was good or bad, or semiconductor.

Well, now you take a good thermal [INAUDIBLE]-- Bismuth telluride-- that's a typical example. And Seebeck is about 200 microwatt per kelvin. And [? phonon ?] thermal conductivity is about 1. Electrical conductivity is essentially 57 per meter. So Seebeck is just the inverse of [INAUDIBLE]. So that's the unit of electric conductivity. And you plug all those numbers, and then you find that's of the order of 1.

So from 1950s to 1990s, the best thermoelectric materials have a figure of about 1. People have-- because experimentally, you can't get better. So people are reading a lot of papers on why we can't break-- this is the absolute maximum. So they're questioning whether their theory-- trying to say, why this is the maximum.

So this is the-- really the theoretical foundation. We've talked-- and the last slide on this is a mature-- I said sometimes, you can get a really good one, or you throw away because the doping isn't right. You can say that-say, because the doping determine where is the chemical potential,

So the properties are so intertwined with each other-- Seebeck coefficient as a function of doping. Here is a bipolar effect. In fact, this one-- why it goes down? I have to check. The electric conductivity-- this looks better. The electric conductivity increases, and the thermal conductivity-- and you pick your zt at a certain value,

So this is clearly-- so you have to really increase your doping. That's adding other materials or creating-- there are different ways, creating doping carriers. So this is the difficulty with thermoelectric optimization. A lot of work one has to do. Now we're going to really just say, what are the materials? Yes.

- AUDIENCE: That graph was actually measured experimentally?
- GANG CHEN: These curves?

AUDIENCE: Yeah.

GANG CHEN: These curves were calculated.

AUDIENCE: So they're calculated,

GANG CHEN: Yeah. Typically, when you see, like, two dots, that's mostly experimental. OK. Those are experimental-- what are you seeing here in this frame. So this is the summary. Not always updated, and people always are reporting progresses most days. So here is a summary of zt of different materials.

And what people have traditionally been using-- this one's tenorite. That's in all the modules-- commercial module-- [INAUDIBLE]. And this is the function of temperature, So this commercial zt takes around room temperature-- 1. And [INAUDIBLE] tenorite is in the intermediate temperature-- 400 degree, 500 degree. And the peak is less than 1-- 0.8, 0.9.

And the silicon-germanium-- this is what NASA has been using. NASA used it for space missions. They use nuclear as a heat source. But they build their system so they operate at a very high temperature. So silicon-germanium is what NASA used in the past.

And remember, if you want to build a device, you have to have both n-type and p-type materials. So it's not all shown whether it's p-type or n-type. But for each type, you build a device-- you need both n and p.

And also, ideally, if we go back to look at the notes in the device section, when we talk about device, you want these two materials closed-- properties closed. Otherwise, it's not the material that determine your efficiency.

So you look at-- let's say the same temperature range-- what materials are available? And like I said, zt has been 1 most of the time, and there are some recent progress. We'll discuss these progresses.

This is a more traditional material. Like I said, bismuth telluride, then tenorite, silicon-germanium, n-type and ptype materials. And skutterudite is a newer material.

So the commercialized bismuth telluride-- bismuth telluride-- go to periodic table. I can't remember all those positions, every time I'm in my office I look at the periodic table. But those are heavy. So bismuth, [INAUDIBLE] are heavy elements. And why we want heavy elements in this case? Why is it good?

So you look at it-- as it becomes heavier, the bandgap decreases here. This is the bandgap. The bandgap decrease is typically about-- you need-- for the bandgap versus temperature range-- around 10 kg. 10 times kdt-- kt.

So at room temperature, the kt is 26 million electron volts. So 10 is the 0.26. Turns out the bismuth telluride-- the bandgap is about 0.15 range.

So you go to, say, heavier material-- your band gap decreases. And now you think about thermal conductivity. Recall that when I say the vibrational frequency, vibrational frequency is the spring constant divided mass square root.

So we have our mass-- you got the lower vibrational frequency. Lower vibrational frequency-- you look at the group velocity-- it travels slower. So the phonon [INAUDIBLE] to go more slowly than lighter atoms. So that's why the thermal conductivity is lower when you go to a heavier material.

So bismuth telluride has a very complicated unit cell. This is really-- in terms of full periodicity, when you consider a hexagonal unit cell, it's really 30.7 angstrom-- many atoms here.

And it's interesting. This is where you really want to understand the material. So it's a polaron bismuth terms of linear structure, And this is the polaron. This is the bismuth polaron.

And in between the layers-- you got you see here-- this [INAUDIBLE] was bonded. And here is more a mixture of covalent and ionic bonding. And there are a lot of study-- people look at which layer is conducting electron, which layer is conducting hole.

And it's really-- we're still working on bismuth telluride. And it's important to understand those details because people have been working this for many years. You want to do something, you need to look at detail. Where are they? Which are the layers of electrons? Think about something that you can-- example-- still got the electron transport well in this layer, but screw up the phonon, kill the phonon propagation in the materials.

So people calculate the band structure. I'm not going to detail. This is really-- [? obviously, ?] you do this. This band structure calculation is also relative standard. You do a density functional theory calculation.

And this is a pure-- bismuth telluride-- If you just do a pure bismuth telluride, [INAUDIBLE] the best is about 0.6. And how you get the 1 is really by alloying. Alloying-- so you can further reduce thermal conductivity by alloying.

So bismuth telluride is a compound semiconductor. And you look at the same column of the periodic table. When we are thinking alloys, same column, periodic table. And then you substitute, for example, bismuth by antimony. And that way, you could reduce thermal conductivity.

And the best example of alloying reduced thermal connectivity is silicon-germanium. And silicon-germanium-this is not a thermal conductivity unit. The inverse thermal conductivity unit.

So here is the silicon [INAUDIBLE] conducting. The thermal conductivity of silicon is about 150 watt per meter per kelvin. And the germanium is also very conductive-- about 60 watt per meter per kelvin.

Now, you mix a little bit. You can see this is not a linear curve, You mix a little bit of silicon with germanium. Your thermal conductivity drops sharply. And the lowest thermal conductivity here-- your [INAUDIBLE] is about 67 watt per meter kelvin. So you drop from 100 to about 67 by alloying.

And this is because-- again, if you think about it, you have an [INAUDIBLE]. First thing you do-- you can try with pure atoms there. Secondly, you mess up the atom periodicity. The wave becomes frustrated. And so the thermal conductivity will drop.

So this is one way of scattering. And that's-- all thermoelectric materials that are made of alloys. And the typical [INAUDIBLE] of the alloy is in terms of scattering-- the additional scattering. And you can see here, this is a Rayleigh scattering relation.

What is Rayleigh scattering? You go outside on a sunny day. You see blue skies. And the blue sky is-- the blue light gets scattered. And high-frequency blue light compared to red-- solar radiation. The high-frequency scatter more.

So here is the Rayleigh scatter regime. That's the Rayleigh scattering, high-frequency. And the sound wave is the typical-- that's a typical model. High-frequency is the inverse time to scatter time. Relaxation time is shorter. So that's a Rayleigh scatter. And then this depends on the mass contrast, and also it depends on lattice parameter, lattice constant contrast.

Those series were done in the '50s. And in fact, I have a lot of suspicion whether they are truly valid or not. And I say that's what people do. This is just the current status.

The problem is you go to think about thermal conductivity-- I showed k equals one third cv gamma integration. And integration is very forgiving in the sense-- if you make the error in one place, you make up the other place. And when you don't have exact theory there and you got a lot of [INAUDIBLE] parameter, and that integration can help you publish your papers. But the details, very often, are missing.

Like I said, this is-- typically, that's how people make the material-- bismuth in [INAUDIBLE] bismuth, antimony. And this x is about 0.3-- 0.3 to 0.5. And then the impact material, bismuth, antimony, and selenium.

And if any of you, actually, are in front of physics department, you probably went to-- I remember a few weeks ago there was a seminar on topological conductor. Turns out that this material is very hot in the physics-- people are looking at antimony, telluride and its topological conductor. So very hot topic there. But see, we don't know whether that has any implication of thermodynamics or not.

And doping-- you can always add other materials as doping. But say, here, typically, is by defects-- the so-called anti-site. So if you look at it, it's possible that bismuth go to tellurium site. And this is a particularly-- because bismuth and tellurium, their so-called char-- electronegativity is very similar.

So when they exchange positions, the disturbance will increase very small. But the number of charge is different, so that create either holes or electrons.

So that's the traditional material. We're now moving to more current materials people are talking. This is a oxide-- sodium cobalt oxide. And these were originally started in Japan. Terasaki made a lot of contribution to this.

And it turns out people are interested in oxide since 1980s. Why? That's because the high-temperature superconductor was discovered out of oxide. It's a surprising amount [INAUDIBLE] BCO, boron, C, copper, oxygen. And that got lower [INAUDIBLE] So the transitional temperature, now in this high-temperature superconductor, has reached probably around 130 kelvin or 140 kelvin [INAUDIBLE].

But the superconductor itself is not interesting for thermoelectrics. Why? This is because there's only one quantum state. So the entropy is 0. Log of quantum state. That's the Boltzmann relation. Entropy carried by as a-- is a log state.

So superconductor is not interesting. But this one is not a superconductor, and people have achieved about [INAUDIBLE] one. I think this is around 800 degrees Celsius, so it's a high-temperature application.

[INAUDIBLE] I mentioned this material because if you go to Japan-- I talk a lot to Japan thermoelectric guys, and also, from company. Whenever you work on-- you look at the bismuth telluride-- Japan is very sensitive to-because they have limited amount of materials. It's a small country, and the resources are limited.

So they don't want-- they always say, can you make, out of this abundant material-- what are the abundant materials? Silicon and aluminum. So those type of materials. And so this is the one example where the material is called abundant-- nickel, tin, and titanium. And it has reached a reasonable figure of merit.

And this is where-- for example, you look at [INAUDIBLE] this figure [INAUDIBLE] thermal conductivity is still very high. Why it's still very high? Why is it very high? Because you always think of bismuth telluride. That's a good number to remember. Thermal conductivity is about 1 or 1.5. Seebeck is about 200 microwatts per kelvin and electrical [INAUDIBLE].

So if you look at this, the thermal conductivity is in the denominator. And you get this good zt-- that means the electron is really good. x square sigma-- that's the power vector-- it's pretty good.

Do you [? kill ?] this guy? Do you [? kill ?] it? Thermal conductivity, reducing. Particularly, Can you reduce the phonon pump. You don't just want to reduce it-- because the electronics are also part of the thermal conductivity-- this is part of thermal conductivity.

So people are now looking into-- if you look at the pump materials, it's typically a bismuth telluride-- then telluride silicon-germanium. Those are simple structures-- simple compounds-- two atoms, binary.

And now, people are looking-- going more into more complex structures. And why complex structure? From thermal conductivity point of view, there is a good reason there. This is a few lecture back. I was talking about the modes, in terms of optical phonon, acoustic phonons.

Optical phonon is very flat, and acoustic phonon is really the one that carries heat. So when you got a lot of atoms in the unit cell, you have a lot of upper branches. So those upper branches don't carry much heat. So that's-- the more complex the crystal, typically, the lower is their thermal conductivity.

And that's the only very simple hand-waving way of saying it. And of course, you can see some of this material has really low thermal conductivity. Bismuth telluride is here. And it's a particularly [INAUDIBLE] now. This [INAUDIBLE], zinc, pyrithione.

Zinc is abundant. If you can make zinc-- zinc is a good one if you can make it work. And it has a very low thermal conductivity.

And in fact, I think the antimony thermoelectric figure of merit, now has reached-- I think it's about 1.4. Pretty good, except that there are also issues-- material stability. And when you heat up to high temperature, zinc speed up. I have some pictures showing that under temperature gradient, the material grew here. Here are zinc coming out. So you've got a lot of material reliability issues.

But generally, there are a lot of people looking into a lot more complex structures, crystal structures, and the broader-- a much broader range of thermoelectric materials.

I mentioned this already, but now let's look at the ideas. We said that complex structure-- and this is another idea that's really interesting because the alloy-- if you think about silicon-germanium alloy-- and it's really-- germanium go to silicon atomic site.

So you can think of that as a substitution, So silicon-germanium substitute silicon atom. The lattice-- if you think of a cube. Like, let's take a crystal [INAUDIBLE]. Think about cube. And the silicon sits in the corner of the cube. And now you take out the one off the corner, and you put in germanium. And so this is the substitutional type of--I pulled that-- you can think of the impurities. And skutterudite is a simple, interesting material. This is a skutterudite that is cobalt antimonide, or rubidium antimonide, iron antimonide, that type of structure. And what is interesting is that it has a very large unit cell. A lot of atoms there.

And also, in those unit cells-- so here, we got two [INAUDIBLE]. And so you can see this-- each is a square, But in this eight-- How many? We have eight cubes. Six of the square has atoms inside. Two of them don't have anything inside.

So there is an open space there. The open space gives you an opportunity-- let's put another atom there. [INAUDIBLE] Another atom-- this atom has a very different [INAUDIBLE] from the host atom, cobalt antimonide.

So the idea is like a rattlesnake. You put the atom-- the rattler on. And this rattler will disturb the normally periodical lattice strips in the surrounding material surrounding the lattice itself. So that was called phonon rattlers.

And the next one-- is an example of-- you can see cobalt antimonide. And you fill this with other regular lanthanum. And people tried many different ways. This is-- I was in a meeting last week. And people are still putting-- first with one rattler, one atom, one type of atom. Now, people have gone to three rattlers.

Well, the hope is each rattler have its own rattling frequency, and you kill the whole acoustic frequency of the whole lattice waves. So this is clearly a very dramatic decrease in the lattice thermal conductivity. And people have done neutron scattering to actually look at the atomic displacement in this material.

So you can see here, this is a lanthanum cobalt antimonide. So here, you have iron, cobalt-- that's their atomic displacement. So inside, it's doing Brownian motion. And this is measurement that can actually measure what's the amplitude of the-- so the [INAUDIBLE] square is here.

And what's the amplitude of that motion? And the lanthanum-- they put it into the cage there since we have a very large amplitude here, you can see. And the theory is that this scatter deforms, Again, the theory is still evolving. And the explanation-- people came up with different explanations. But you try to do the modeling experiment to really make this material [INAUDIBLE].

Here, I forgot whether this is a-- what type, n-type, but I do want to tell you a story. Many years ago, people reported the p-type skutterudites, cobalt antimonide, figure of merit for 1.4. And now nobody can get 1.4. Everybody-- the best they can get is 0.95.

And the reason-- this will bring up a very important point. Thermoelectric research-- measuring this property is tricky. And you have three properties to measure-- electric conductivity, thermal conductivity, Seebeck. And even if you are very good, each property-- you say, OK, I have about 5% uncertainty, which I think is pretty good. And you go to [INAUDIBLE] and that's about 15%.

And it turns out that many times, your system can take the same sample. So you do thermal conductivity. You take a sample. You go to pick another sample for electric conductivity. And you measure the wrong things.

And sometimes, if you look at the-- telluride-- it's a layered structure. The property is very isotropic. So this will be really dangerous. You measure-- even the same sample. You measure properties-- thermal conductivity in one direction. You measure electrical in the other direction. And you can just get a good zt. That's not true. So this is-- every time you go to a meeting, people will be debating. And most of the time, people are skeptical of any report. It's just difficult because measurements are difficult.

Now I turn to my favorite-- nanostructure. And I said that there are bulk material. People look at the different material, different crystal structures, phonon rattler, all working on crystalline materials.

And there was-- say-- this nanostructure approach was really Millie Dresselhaus in the EE department at the time. And the story-- this is a really good story. Around the 1990-- US navy start to rethink thermoelectrics. So they went around-- asked around and they came to Millie, whether she had any idea on thermoelectrics.

Millie didn't work on thermoelectrics before. And she thought about it. And there was a physics student who walked into her office, wanted to ask her whether she had a topic. So she said, oh, why don't you look at quantum well-- whether it can give better thermoelectric properties?

So the student looked, and-- it's really a homework problem. I'll show you later. But the calculation turns out to be really interesting, and a lot of people started working on that. So sometimes a simple idea really stimulate the research.

And here, this is a slide that I tried to make and seeing the potential of using metal. So you think about the electron and phonon. Electron is what carries the heat around. And of course, the quantum mechanics, they always-- we mentioned this [INAUDIBLE] before, but they have different wavelengths.

And it turns out it's a spread. In real material, it's always a spread. And we need to look into the details. But in general, actually, electron movements can be longer, average speaking, than the phonon-- heat-carrying phonons.

And so that's an order of magnitude that I often use. But again, each material is different, and each country is different. And the other is the mean-free path. That's the average distance in electron-phonon [INAUDIBLE].

So we look at-- one possibility is to look at the wavelength difference because the wavelength difference means-an intuitive picture is if you have a surface, whether it's a smooth or rough-- really depends on the feature, on the surface versus the feature of the wave.

If you have a visible light coming towards a surface like this, it look rough. You scatter light all direction. But if you have, really, a microwave coming in, very long wavelengths, the surface will be smooth. Much-- wavelengths larger than the roughness features.

So while this idea was-- if you recall, the thermal conductivity-- the curve-- at a very low temperature, the thermal conductivity increases with the specific heat because the mean-free path equals the sample size. It's limited by sample size.

So low temperature already have the size effect. And if I make the structure very small, that size effect-- I can shift to the high temperature, as long as it's small enough so that the-- let's take a wire or film-- if the diameter or thickness is comparable to the mean-free path, now, the phonon will no longer-- is a phonon-phonon collision. They will collide with the surface. And another simple intuitive picture is-- OK, what happens at the interface of the material? You have the lattice wave coming in and at the interface, you hear echoes. Well, we hear echoes for the visible-- audible range. But say-- and the peak current is [INAUDIBLE].

So those are high frequency. You still got the same phenomena happening. And the echo means some [INAUDIBLE] don't go forward anymore. So you could use those phenomena to [INAUDIBLE] the thermal conductivity.

And Millie's idea at the time was squeeze electrons. So quantum effect-- which I'll talk more. But-- now, think about the quantum effect. Electron is a wave. Wave function is a function. The s orbital-- wave function is a ball. And let's say this is the size of the ball. Let's say [INAUDIBLE] angstrom.

Now, you see this-- this is electron. You make a film only 10 angstrom or 50 angstrom. What happens? The ball is no longer a ball. I once-- when I was a student with [INAUDIBLE] there was an interesting analogy made by Professor [INAUDIBLE]. But think of this. You put a basketball into a piece of box. You squeeze the ball. You have energy quantization.

So you have this wave, and then when your size is small, you quantize the wave. And ideally, what you want is this wave is-- under ideal quantization, you want this smooth surface, You don't want the interface-scattered electrons.

And this is possible, again, using the wavelength range because whether the surface is smooth or rough depends on wavelength. For the case of electrons, the scatter is electrical potential. Your potential-- whether it's rough or not. And for the case of phonon lattice wave, fundamental or electrostatic-- but it's really-- you can think of mass spring, whether those-- the force is [INAUDIBLE] now.

And so you actually have the potential-- if you think about the phonon and the electron-- your electron-- if you quantize it-- is the smooth. And because the wavelength difference-- you can potentially actually have the same surface will be rough for phonon, the acoustic wave.

So this will be ideal. [INAUDIBLE] You want to screw up the atomic vibration, but electron can go as a waveguide. That will be one scenario.

And the people started a lot-- and in fact, I should say at the same time, maybe go to other places, and people have a similar idea, although Millie did really a good calculation. This superlattice idea was from Rama, [INAUDIBLE]. And what he did is-- the perpendicular direction, the superlattice.

And this is-- you can see-- the experiment-- thermal conductivity and the drop. So the bismuth skutterudite [INAUDIBLE] about 1.2, and they drop to 0.5. Very difficult measurement. And this is where I start getting into thermoelectrics.

So my thesis-- my PhD, I was looking at the superlattice heat conduction. I was worried about lasers, not thermoelectric. I didn't know anything about thermoelectric.

And the electron here decreased a little bit. This is s square sigma. The power factor, s square sigma, decreasing a little bit. And in the case of-- this is a [INAUDIBLE] map. He grew the telluride-- the [INAUDIBLE] on that telluride. And because the lattice constant is very different, the [? strain-- ?] so you grow certain thickness, the strain will break up the film and form dots.

So he grew these multilayer structures. And this picture-- I don't think it is from him. I don't remember. But what he showed was, again, no thermal conductivity. And the power factor [INAUDIBLE].

So at the end, it turns out that, historically, the thermal conductivity alloy-- institutional. And now with this nanostructure, it turns out that the thermal conductivity seems to be a very effective strategy.

But let me, again, caution-- almost now everybody questioned those results. It's a very interesting result-- very intriguing, but it's a very hard measurement.

And [INAUDIBLE] retired. He's a very respected. And I talked to him a lot. [INAUDIBLE] He has a book. If you want to understand thermoelectric, he has a very good book. Not many people read because it's too difficult.

[LAUGHTER]

But very good if you read. And the first-- I remember the first two pages was talking about electrostatic computer. As a mechanical engineer, [INAUDIBLE] always been hard to understand, what's the electrical potential, what's the chemical potential?

And Raman [INAUDIBLE] is from RTI. They have spin-off company trying to do the superlattices for microelectronics [INAUDIBLE]. And if you're interested, you can check the [INAUDIBLE]. They have [INAUDIBLE] start-ups [INAUDIBLE].

And the superlattice-- I guess the challenge is grew very thick, and also reduced the cost. So this is where my story is. I said I would be working on this for a long time. Since my [INAUDIBLE] was really useful leaders.

And so those are experiments. In the along-the-field direction, you can see it's isotropic. This is the [INAUDIBLE]. But see-- the superlattice structure [INAUDIBLE]. So this is perpendicular to the [INAUDIBLE] plane direction-parallel to the [INAUDIBLE] plane direction.

And the problem is, if you think about this superlattice, basically, superlattice was invented by [INAUDIBLE] and Esaki. Esaki got the Nobel Prize for his work in resonant diode. That's before, even, the superlattice concept.

And the name of superlattice means you have a super crystal. And so you see-- I say this is one layer. There's another layer. Now, you look at-- a unit cell is no longer cube, but the tetrahedral that cover from here to here. One period of a crystal.

So that's what the name implies. According to the name, this is a new crystal. You can calculate a new energy phonon spectrum. You calculate group velocity. You have [INAUDIBLE] states. You do all this calculation.

And then you do one third of cv gamma. I don't know gamma. But I know I can-- from that calculation. I know c, and I know v, from this state. [INAUDIBLE] That's the curve. You get as a function of thickness. Just-- it's not correct. So basically, the picture is not about forming a coherent structure. People are still debating, so I don't want to prejudice you. You should read literature. And that's my own prejudice because I've been doing research on that. But when you get into it and say, oh, [INAUDIBLE] look into the literature. Look at the different sides of the argument.

And so when I go to look into the other picture, I just say, OK, now I got a surface. I only just consider not this supercell-- just two layers. And of course, periodic structure. We consider all that.

And then we got an interface roughness. And that roughness scatter phonon diffusely. And that can cause the thermal conductivity reduction. And here, I got a fudging parameter. Yes.

- AUDIENCE: When you say, roughness, are you talking about just like obstacle spacing, like an electron diffraction or [INAUDIBLE] diffraction experiment, or you expect something to be scattered by something with spacing [INAUDIBLE] wavelength?
- **GANG CHEN:** Right. And so that's a very good question. And what's the mechanism of that roughness? And it turns out that when you grew superlattice, molecular beam epitaxy, and then you find out that they're in the 80s. There are a lot of-- gallium arsenide is the best studied system. And there are diffusion of atoms between the layers, about the one to three monoatomic layer. And they said the phonon weakness is very short.

So my picture is really the atom-- if it's a perfect periodic, you see the atomic spacing is all periodic, the same atom. Then you should not have that. But now if you just have one atom [INAUDIBLE] and the random distance, later, another atom [INAUDIBLE], and that's the surface-- whether is rough or smooth-- is about 1/10 of the wavelength.

So if you go to optics-- so here, again, we don't know exactly. So you go to optics. When people say whether surface is smooth or not-- it's about a 1/10 weakness. 1/10-- you look at the phase of the wave. So here-- because the wavelengths are falling, is about 1 nanometer to 10 nanometer range. So a little bit of atomic diffusion can cause that.

But there are a lot of puzzles at this stage. You should read [INAUDIBLE] paper from UIUC, and they have done constant diselenide and some newer material system. And they found that they can have thermal conductivity really, really [INAUDIBLE]. The noise they have is twice [INAUDIBLE], solid, fully solid.

Anyway-- so I say this is the picture I have, but I think there are probably more things that need to be done. So what I see from this picture-- what I conclude is, OK, we do need a periodic structure because if it's not a unit cell type of picture, then I don't need a periodicity. So that's why I need us to do this random composite structures, because that way, I can do [INAUDIBLE] lower cost.

So we try this, and it works in some materials. This is [INAUDIBLE] telluride. This is about [INAUDIBLE] telluride. And this is-- this is skutterudite. This is skutterudite [INAUDIBLE] and nano. And [INAUDIBLE] I say what we do is just a [INAUDIBLE] material, and we contact them in nano form.

Bismuth skutterudite works on [INAUDIBLE] geometric also. Didn't quite work on that telluride. That telluride grid growth. And skutterudite didn't work out either because of grid growth. So we're still trying to figure out how we can prevent-- stop that growth of the grid, and we drop the thermal connectivity. Yes.

AUDIENCE: What about the quasicrystals? Is that [INAUDIBLE]

GANG CHEN: That's a very good suggestion. And I didn't look at quasicrystals. But there are people looking for [INAUDIBLE]. Clustering is a very complicated-- like, you can have silicon [INAUDIBLE] germanium [INAUDIBLE]. So it's a-- it has a-- say, it has holes inside, and they have a little similar [INAUDIBLE].

> But further crystal decay-- [INAUDIBLE] decay is whether you can make the electrons in your [INAUDIBLE]. Remember, you can kill a phonon if you just want to kill a phonon [INAUDIBLE]. But you also want to keep the electron moving.

> So the idea-- very good terminology came from Glen Slack. And he said, what you want is an electron crystal phonon glass in one material because the phonon in glass-- this glass here-- amorphous random atomic arrangement. So the phonon thermal conductivity is very poor.

But this superlattice is different. It's still crystal. So you are-- where we can-- for example, we're looking into whether a randomized wave-- localized [INAUDIBLE] and localized wave. Very difficult, I think, but it's worth trying because you need this crystal structure to get the electron propagating.

Very difficult because the short wavelengths. You can do photonic crystal, all that, for electromagnetic wave because the wavelength is pretty long. But it's very hard to do this for phonon because wavelengths are short, and they don't propagate very long. You need a long coherence to have the waves [? disrupt ?] each other. So those are the difficulties.

So here are more detailed example. You can see the thermal conductivity dropped. So when I started this, everybody was saying, electron-- what are you going to do with the electron? I said, I don't know. I wish it would work out. But when I think back, you actually have good reason-- the general idea is, OK, let's don't get too much electrical potential offset at the interface, That's what the scatter electron [INAUDIBLE].

But see, it turns out in bismuth skutterudite, you can see the electron is better. When I first look at this, I couldn't believe it. And the reason is, of course, it's a semiconductor. The electric conductivity depends on the carrier concentration, It's the mobility times n, the carrier concentration, times charge.

So turns out the bismuth telluride-- when you warm [INAUDIBLE], you generate defects that generate more electron. Or in this case, it's more holes because it's a positive Seebeck in the positive poles. Again, you can see that's the typical behavior.

So at the end, if I plot the s square here-- so higher electron density, lower Seebeck. Higher electron density. Fermi level is closer to the [INAUDIBLE] edge, or you can get into the band. The Seebeck is the average distance thermal energy of electron [INAUDIBLE]

So higher electric conductivity, lower sigma-- that's [INAUDIBLE]. But because you have higher carrier concentration, the bipolar decreases [INAUDIBLE] later, you can see here. It goes to higher temperature.

And then-- so if you plot s square sigma, this is actually better than this. We try that very hard in superlattice. We didn't get a s square sigma. Both equally thermal conductivity increase [INAUDIBLE] factor, and this actually work. But we still don't know how exactly the model [INAUDIBLE] very difficult to model in random structure. We're doing that.

And we're not the only one. In fact, [INAUDIBLE] has been working in this material system, which they call [INAUDIBLE]. And so [INAUDIBLE] telluride-- and the single crystal-- he grew single crystal. He spent several days growing single crystals, pulling heat in, and got the very good properties.

And again, let me caution you-- you can't believe at this point because they extrapolate it. No, he doesn't show this anymore. And measurement is always a hard problem. One has to realize-- sometimes I scare people away by saying that, but that's reality of this.

And what they found later on is that this material actually-- even though it's a single crystal, but a lot of precipitates out of nanodots. And with that, the thermal conductivity is also quite low. So we got a good figure of merit.

This is a really interesting system. I've been talking to [INAUDIBLE] And I still can't really give you a very simple picture. Basically, I was asked give a very simple picture so I can explain to my students. And I don't think that I got a simple picture yet.

But the idea it's looking at is-- here, is a silver [INAUDIBLE] It's a cubic structure. Silver antimony telluride [INAUDIBLE] similar. And what it's saying is the electron clouds between the atoms have overlap. And when one set of atoms moving that squeeze this flow of clouds, it's very significant.

So the electron clouds are very significant. Squeezing cause the force anharmonicity. And this anharmonicity gives a very low-- so what you want is-- you want to make the atoms strongly scatter each other.

High thermal conductivity-- if you just have a pure spring harmonic oscillator, you have infinite thermal conductivity. And the finite thermal conductivity really comes from the third term of the potential. It's not a f equals kx. For f equals kx plus a perturbation, kx squared. That square makes the two different frequency wave interact with each other.

That's so hard for optical wave. It's much easier for phonon. But when you want to push to very low, very small limit, you got to [INAUDIBLE] get this anharmonicity very large. And one way to gauge that is this recent parameter, which is related to thermal expansion. And thermal expansion--- so higher [INAUDIBLE] thermal expansion material typically is more anharmonic.

And what is showing is this minimum thermal conductivity theory. That's also another thing I never believe-minimum thermal connectivity. The idea is one third-- k equals one third cv gamma. That's the kinetic theory. Anc the minimum thermal conductivity is replacing the mean-free path by the wavelength.

So that's the minimum mean-free path you could have. And this was a Glen Slack original theory. And then David Cahill and Bobby Powell from Cornell said, oh, it should not be just a mean-free path wavelength. It should be mean free path equals plus wavelength. Einstein-- based on Einstein's argument. So that reduced thermal conductivity minimum by another half.

And so very often, people will draw this thermal conductivity against the minimum. So this is the one example we say, OK, you've reached the minimum. You can't reduce anymore. But in fact, I said David Cahill because he measured layer structure. His thermal conductivity is twice the error. It's an order of magnitude smaller than the minimum. So his own minimum theory. There is a minimum-- his experiment, is an order of magnitude smaller.

So that's why I say I don't believe in it because you should go look at their better formulation. When you have an [INAUDIBLE] you don't have one [INAUDIBLE] mean-free path. And if you're interested in this, I'll point you more to literature.

This is something that I really want. [INAUDIBLE] OK, I bring you from the basics to, really, the forefront. Just a few months ago, there was a paper, indium [INAUDIBLE]. And what it's saying-- this is a charged density wave. And the [INAUDIBLE] instability. And this got really--

So what happens is this direction [INAUDIBLE] this is more like a layer structure. And then into the z-axis, that's the covalent bonding. But because the charge distortion-- so in the z-axis, actually, charge a strongly distorted and create a very large anharmonicity for the last wave scatter.

So the thermal conductivity is really strange because when the [INAUDIBLE] direction, force weak force typically means low thermal conductivity. But in this case, what you have-- this is the z-axis for one direction. You have lower thermal conductivity in the [INAUDIBLE] direction. And very interesting, and definitely worth more study here.

Now let me go to [INAUDIBLE]. This is the quantization I mentioned and the pizza box problem-- the possible [INAUDIBLE] in the box. So you have a simple-- this is a simple homework. I said before this is the z direction. Energy is quantized. And you can do the same standing wave argument I did before and see what's the wavelength and what's the corresponding energy.

And so xy direction, is called the continuous wave vector. So now, for different n, we have the sub bands. So this energy quantized different energy levels in the-- due to the thickness in the z direction. So that's the basic [INAUDIBLE] idea.

And now you go to do this. You calculate the density of states. I don't want to go through this math. But you can say this is the same thing we did before, except in the z direction. Now. I don't do-- I do not convert this summation into integration in the z direction. I convert the xy direction because the z direction-- that separation is too large, and the summation into integration-- that conversion is not a rigorous-- not mathematically accurate. So I still keep this summation here.

And at the end, what you show is the density of states now is a staircase, or in typical parabolic band approximation, we got this 3D. This is 2D.

And now, with that, there is advantage. Where is the advantage? Let's go back to the picture I showed before. Seebeck is a measure of the average energy of the electron relative to chemical potential. Electrical activity is really proportional to the number of electrons.

So when I have this-- if you look at it, this [INAUDIBLE] says this is df Fermi-Dirac derivative. Now this is very small. This type of state-- that's the region where it's contributing to electrons.

Because of the parabolic, this is a small number times small number. So the electric conduction-- the number of charges that carry the Seebeck-- most of them-- it's very low energy. The average energy is here. Those are low-energy electrons. They carry more electrical charge. So that's a problem with the [INAUDIBLE] band, with the density-- the [INAUDIBLE] density of states.

OK, now you do the [INAUDIBLE] You have a sharp staircase. And you can put it-- and you see here-- you can put it in more charge or still have the same Seebeck. Or if you have similarity [INAUDIBLE], then you can increase your Seebeck At the end of what you want is for sigma to be larger,

So that's why those quantum structures-- like, in the quantum wells, it can give you larger s square sigma. And then you look at the other quantum structures. The density of states-- this is the staircase for the twodimensional.

And then wires is a sharp peak here. And dots are just discrete lines. So progressively, going from 3D, 2D, to 1D, 0D, progressively better.

So that's what the theory says. And at the time, Millie and [INAUDIBLE] in Lincoln Lab did the experiment. And they showed that-- I want, first, to show the trend is all right, except there is one caveat. You see there? This is not s square sigma. This is s square n. Electric conductivity is n times mobility times the carrier charge-- electron charge.

And the reason is that the superlattice was not-- the quantum well was not very good-- interface scattered electrons. The electric conductivity-- if you plot-- I don't know the detail, but let's say there are still questions here because this is s square sigma and s squared n, not s square sigma. But the trend is there, and that generate a lot of interest.

And this is just a more calculation I got from a book that [INAUDIBLE] and myself are writing and never have finished. I did not finish this. If anyone wants to read their draft. 3D, 2D, 1D, progressively, is better. That's a theory. And if you do an experiment, like I said, you can't scatter electrons. You have to be very careful.

And there's another problem. So of course, superlattice-- the quantum well is just the [? film ?] that's conducting electron. And the problem is you have to sandwich this. Or you can use the air or vacuum or quantum wire in vacuum. Then there's no leakage.

But normally, when you use another material to create a barrier to confine electron in the field, then you've got the phonons in the barrier. The phonons in this barrier will kill your conduction. So they'll kill your-- create a more [INAUDIBLE] leakage here.

And there are solutions on this, theoretically. I've worked with Millie on this before. Just as a caveat, one has to pay attention. For example, there are also study by [INAUDIBLE] and others say if you reduce the thickness-- you want to reduce barrier [INAUDIBLE], you reduce thickness.

And then you have another problem where these two [INAUDIBLE] will start talking to each other-- colony. And that colony, actually, is not good. The [INAUDIBLE] becomes less sharper than the pure quantum well. There are potential solutions. I encourage you to read the literature and work on this.

But it turns out this general idea of [INAUDIBLE] featuring density of states is a universal, not only in thin films but in bulk materials. And there was one paper by [INAUDIBLE]. And he wrote a paper around '97. And he's a very good theoretician. He just took a simple math problem. He said, I'm going to optimize the density of states. Just write the expression I wrote before. Treat it as a function that d [INAUDIBLE] states as a function of mathematics. What's the function that will give you maximum s square sigma or give you maximum zt? And at the end, he concluded it's the delta function. So delta function is the best.

And if you go back to what I showed here, quantum dot is best. Except the electron model-- how are you going to move quantum dots-- the electron going to [INAUDIBLE] delta t or quantum dots. So wire is also good. So this is a general principle.

Another interesting comment I want to make is you go to check the Lorentz number. And that's what I suspected-- the Lorentz number in quantum dot can be 0. Very strange. Nobody demonstrated that. Very interesting experiment. Electrical activity is not 0, but the electronic thermal conductivity is 0. Very easy to check.

Let me go here. So this is really the reason [INAUDIBLE] and he said-- we talk a lot, but very smart guy, and would say-- He worked on nanowires-- bismuth nanowires. Worked with Millie and-- And he say, I'm going to turn to bulk material.

So one day-- he read Russian literature, and this is all, actually, in Russian literature. It turns out there is some doping. Particularly when we think about doping-- we think about doping-- the energy level is inside the band, in the bandgap. But there are some other atoms. The doping level is within the conduction of valence band.

And in this case, is in the valence band. And this valence band-- the doping form additional energy states that create a sharp feature in the density of states. And this [INAUDIBLE] feature led to very good Seebeck coefficient and very high [INAUDIBLE]. Very nice idea.

The question is whether you can replicate it in different materials because [INAUDIBLE] nobody wants to touch it because it's very poisonous because-- it's not that terrible. I have a friend. And he said, I focused on it for more than 50 years, superconductor, and nothing happened. But the person-- be careful.

Now, this is another idea I think, again, come back to-- you can interpret the same intensity of state. This is Seebeck coefficient. If [INAUDIBLE] position is here in the band, this [INAUDIBLE] is a positive. So they cancel each other. Of course, this is larger. So you still have-- the cancellation is small.

But if you put a potential-- so you have a particle, or you have an interface, that just happen to have this potential height, then those electrons are scattered. So that's for the energy field or thermionic emission. I'll talk about thermionic emission in the next lecture. We'll talk about thermionic engines. That's a different way. But this is a solid.

So you scatter this low-energy electron, and then you only have high-energy electrons [INAUDIBLE]. And if I draw the [INAUDIBLE] state picture is-- although there [? are high ?] electrons in this region, but I scatter them-- they do not move. So now, in terms of this state, what's really moving is-- you still have a sharp picture. So that's my interpretation of this picture-- this different idea. So you can always think about the different states, features for electron.

But really, the one that has win so far is-- the only successful example I know is this one. Truly work in materials. So most other approach that's successful is important. So with that, I [INAUDIBLE] will from the very simple things I don't know. And you can figure out.