

The following content is provided by MIT OpenCourseWare, under a Creative Commons license. Additional information about our license and MIT OpenCourseWare in general is available at [ocw.mit.edu](http://ocw.mit.edu)

**PROFESSOR:** The final quiz is scheduled for a week from today, on December 8. Following that weekend, we'll have one class on the 13th. And the last days of classes are Monday, Tuesday, and Wednesday, the 12th, 13th, and 14th.

So I know a number of you spoke up last time and said that you have a conflict on Thursday, the eighth, with a quiz in another class. So could I see a show of hands again of how many of you have this conflict? So three, six people, seven people, you're going to enroll in the other course just so you can put off taking the quiz. That's unfortunate, I don't think anybody should have to take two quizzes in one day.

We can't move it up. We'll have to move it back. So I don't know if I am violating any Institute rule, but I know that it is strictly illegal to give assignments that are due after the last day of classes, let alone have a quiz after the last day of classes, which has not been previously scheduled as a final examination. So we can't give it after Wednesday, the 14th, the last day of classes. So, do any of the six impacted people have a strong preference for when we should schedule the quiz?

**AUDIENCE:** Monday?

**PROFESSOR:** Due it Monday? It doesn't have to be that soon. Monday?

**AUDIENCE:** Why not Tuesday?

**PROFESSOR:** Because Tuesday we have a class.

**AUDIENCE:** Or Wednesday? Well we would have a Thursday class instead. Correct?

**PROFESSOR:** No. If we're doing it after the quiz next week, there's a class. We have a last meeting here on the 13th. And I'm not going to shift it for other people, just for the

impacted. So of the six who are entitled to vote, how many would prefer to have it Monday, the 12th? Three and I know how it's going to turn out. And for Wednesday, the 14th? Three.

**AUDIENCE:** I can't take the test because-- not because of another test-- I'm out of town. And I might come back Saturday. And Monday is just a little quick to take it after we get back.

**PROFESSOR:** I think I'm going to have to make an executive-- yes

**AUDIENCE:** Professor, when you mean by conflict, do you mean having an exam at the exact time?

**PROFESSOR:** No, it's on the exact same day. Considering this is a two hour examination, to have another examination exactly the same day, if you're not brain dead after an hour or two, you will be pretty close to it. So I think that is an unfair penalty to pay.

I think, to keep it as close as possible to the quiz that the rest of the people will be taking, why don't we make it-- since it's a tie vote-- on Monday, the 12th. Do it sooner, rather than later. And I'll let you know next time of where we will hold it. I'll have to arrange a room for it. So that will not be a make-up quiz. It would be a made-up-- invented-- quiz.

And, as I say on Monday, I should have all of the homework and the previous quiz to return to you. Reason you don't have it now is all the little crabbed handwriting that you see before you in the form of these notes, which takes forever.

All right, so since we've satisfied the unpleasant aspects of the end of the term, let's get back to discussing some of the other piezoelectric effects that we have defined. And then also ask the question rhetorically, is there anything like a representation surface for a third-ranked tensor property? And it doesn't look promising. But there are some things that we can do to discuss variation of properties with direction, and we'll see directly what those are.

But first let's look at the converse piezoelectric effect. And this again is a third-

ranked tensor property, but what we do is to have the elements of strain,  $\epsilon_{ij}$ , a second-ranked tensor. And to take advantage of this curious relation between the directed converse effects, we define the converse piezoelectric effect as giving you nine elements of strain in terms of a third-ranked tensor  $d_{ijk}$  times  $e_{sub i}$ .

So what is not standard is our convention for the order of the subscripts on the moduli. And we make up the rules, we can do it any way we like. And the advantage of defining it this way, in nonstandard tensor notation, is that we can use the same coefficients for both the direct and the converse effects.

So let me-- to illustrate what these equations look like-- write out a few examples.  $\epsilon_{11}$  would be  $d_{1jk}$  times  $e_{sub 1}$ . I'm writing it in simple fashion, and not expanding fully, just to save space and time.  $\epsilon_{22}$  would be  $d_{2jk}$  times  $e_2$ .  $\epsilon_{33}$  will be  $d_{3jk}$  times  $\epsilon_{sub 3}$ .

And let me stop after these six terms, and write, at least for these, an expansion. Because this gives us some interesting information. I'm not doing the equal signs in here. So this would say that the element of strain  $\epsilon_{11}$  is  $d_{111}$  times  $e_1$  plus  $d_{112}$  times  $e_2$  plus  $d_{113}$  times  $e_3$ . And I want to say this is  $11k$ . And I want to say that this is  $22k$ . The next term would be  $\epsilon_{22}$ , and that would be  $d_{122}$  times  $\epsilon_{sub 2}$  plus  $d_{212}$ .

**AUDIENCE:** Wouldn't the 2's be balanced?

**PROFESSOR:** Hm?

**AUDIENCE:** Wouldn't that be  $d_2$ 's?

**PROFESSOR:** Yeah, you're right. This should be  $\epsilon_{jk}$  equals  $d_{ijk}$  times  $e_{sub i}$ . So this is all  $e_1$ . This is  $e_1$ . And this one goes with this one. This 2 goes with this one. You're right.  $d_2$  and this is the  $d_{311}$  times  $e_{11}$ . This would be  $122$  times  $e_1$  plus  $222$  times  $e_2$  plus  $d_{322}$  times  $e_3$ . And the fourth one would be  $e_{33}$  equals  $d_{133}$  times  $e_1$  plus  $d_{233}$  times  $e_2$  plus  $d_{333}$  times  $e_3$ .

OK, these elements here are the three that appear in the box that I had indicated

for the terms  $d_{jk}$ . When we write the direct piezoelectric effect, this would be the box of coefficients. When we write the converse effect, this is the box of coefficients.

And now what I wanted to point out is that  $\Delta v / v$  is equal to  $\epsilon_{11} + \epsilon_{22} + \epsilon_{33}$ , which is the trace of the strain tensor. And we're going to get one set of terms which depends on the  $x_1$  component of the field, another set of three terms that depend on the  $x_2$  component of the field, and another one on the  $x_3$  component. If these expressions sum to 0, then there would be no volume change.

So this first set of 3-- 3 of the first 6 equations-- give you an indication of when the application of a field will result in no volume change in the sample. And that again, I remind you, can be for two reasons. It could be because all of these six of the nine piezoelectric moduli are 0.

Or alternatively, if you examined the form of the piezoelectric moduli matrices that is required by symmetry constraints, you'll find that there are a substantial number of point groups for which some terms are 0. But then there is, in addition, an equality between some of the other terms, which make the volume change zero. Even though, not all of the elements within this 1/2 box of moduli are zero. So that is an interesting effect.

And it turns out that the majority of the non-centrosymmetric point groups do not have a volume change, when you apply in a field in any way you choose. A few do, but it's a minority. Alright, but this is not the main point of writing this. I want to-- at this point-- point out that this tells you about the volume change.

And then we would have additional terms, we would have a term of the form  $e_1$  something like  $e_{123}$  or  $e_{132}$ . And this would be  $e_{14}$ . This would also be  $e_{14}$  since we replace both of those subscripts by a single subscript.

And the tensor elements that would go in here would be  $d_{123}$ . We just want one of the them.  $d_{123}$  times  $e_1$ , and then we want  $d_{223}$  times  $e_2$ , and then  $d_{323}$  times  $e_3$ . We're writing one of the specific equations for the shear strings. If we write the

expression for  $d_{132}$ , this is going to be  $d_{132}$  times  $e_1$  plus  $d_{232}$  times  $e_2$  plus  $d_{332}$  times  $e_3$ .

There are two interesting consequences of this. The strain tensor is symmetric. And this element of strain-- why have I got three subscripts in here? Don't want that one in there.

These two strains are equal. And therefore, if we would apply just an  $e_1$  for example, let  $e$  be equal to just a component of field along  $x_1$ . The strains have to be equal. But we have two different tensor elements here. And the only way that strain can be symmetric, and it's defined as such, is that  $d_{123}$  be identical to  $d_{132}$ . And that resolves the issue that came up in connection with the direct case electric effect.

We said the direct piezoelectric effect depends just on the sum of the elements  $d_{ijk}$  and  $d_{ikj}$ . And since they're lumped together, all we can measure is the sum. And, so, we'll just have to call that a single matrix element.

The converse piezoelectric effect tells us these tensor elements have to be equal, if the strain tensor is to be symmetric. So that says that, since we defined  $d_{16}$  as the sum of  $d_{123}$  plus  $d_{132}$ , this says that  $d_{132}$  is equal to  $d_{123}$  is equal to  $1/2$  of  $d_{16}$ , just making the equality in the reverse direction. The converse effect let's us say that  $123$  has to be  $132$ , that any  $ijk$  has to be equal to a  $d_{ijk}$ .

So if I tried now to write this first expression in the reduced subscript notation,  $e_{23}$  is what we let  $e_5$  be. And now we have this equal to and in our reduced subscripts, we have this as  $1/2$  of  $d_{16}$ . And the field that's multiplying this is piezoelectric modulus is  $e_1$ .

And that messy factor of 2 has come back to haunt us again. It's like trying to stuff a jack-in-the box back in the box. It keeps popping up. We ate the factor of 2 in defining the matrix representation of the piezoelectric electric modulus. And now when we try to go to a reduced subscript notation for the converse piezoelectric effect, we've got a  $1/2$  in there. And similarly, the second equation would be  $e_5$ --

same result  $\epsilon_{5--}$  and it's 132, but 132 is  $1/2$  of  $d_{16}$  times  $e_1$ .

And we have a similar mess for the other coefficients here. So what do we do? Do we say that the relation between strain  $\epsilon_j$  equals  $d_{ij} e_{sub j}$  has  $1/2$  in front of several of the coefficients and not in others? Well, we can't really absorb the factor of 2 in the definition of the piezoelectric moduli, because we've already done that. So the only thing we can do is to say that we will have to take the off diagonal strains, and define them as having a  $1/2$  in front, and we add these up.

So we will have to write matrix strain in this reduced subscript notation. We'll have to take  $\epsilon_{11}$ ,  $\epsilon_{12}$ ,  $\epsilon_{13}$ ,  $\epsilon_{21}$ ,  $\epsilon_{22}$ ,  $\epsilon_{23}$ ,  $\epsilon_{31}$ ,  $\epsilon_{32}$ , and  $\epsilon_{33}$ . And in converting this to matrix form, we'll call this  $\epsilon_1$ , analogous to what we did for the tensile stresses. We'll call this  $\epsilon_2$  and this  $\epsilon_3$ .

And then for all of the off-diagonal elements of strain, in order to avoid the factor of 2 popping up in front of the matrix representation of the piezoelectric moduli, we're going to have to put in here  $1/2$  of  $\epsilon_4$ ,  $1/2$  of  $\epsilon_5$ , and  $1/2$  of  $\epsilon_6$ , and same for the off diagonal terms  $1/2$  of  $\epsilon_5$ ,  $1/2$  of  $\epsilon_4$ , and  $1/2$  of  $\epsilon_6$ . So the moral of this story is that you can't win, but if you play it right, you can come out even. So only if we define the reduced subscript strains in this fashion, can we write an expression of this form.

So this algebra is carried through for you for the other elements in the notes. But this is the way we are forced, unless we want to have a factor of 2 in some terms, and not in others, is the way we have to define matrix strain. All this is formalism and definition, but I'd like to now do two things. First of all, give you some examples of real numbers for piezoelectric moduli, and then ask the question about representation surfaces. Once again, these numbers are in the handout for you, so you don't have to make note of them.

But one of the very important piezoelectric materials is the quartz form of  $\text{SiO}_2$ .  $\text{SiO}_2$  has many polymorphic forms. Quartz is the form that's stable at room temperature, and it has point group 32 asymmetric. And there are higher

temperature polymorphs of SiO<sub>2</sub>. There's a phase transition in quartz to a more symmetric form, and then there are cubic forms at the highest temperatures.

Now, quartz is not the material that displays the largest piezoelectric moduli. But it has the following advantages. One is it is a naturally occurring material that is very inexpensive. So it's not an exotic expensive material. Very stable. It's not water soluble. Extremely tough. You can take a thin wafer of quartz, for example, if you want to make a monochromator for a diffraction experiment.

You can take a thin wafer of quartz, and bend it like this, and it does not break, very elastic. And if you want a material that's going to earn its living by being squished, you want something that doesn't plastically deform and something that is very hard and resistant to stress. So quartz, even though the moduli are not the largest, is a very attractive material, and is used in a variety of devices.

There was a time when CB radios were very, very popular. Everybody had to have one in their car. I guess so they could pretend that they were truck drivers. But anyway, you don't have them anymore now that cellphones have come in in existence.

But for your CB radio, you needed something called a crystal. And they were fairly expensive. And the number of channels on which you could communicate dependent on the number of crystals that you could plug into your CB radio.

The so-called crystal was exactly that. It was a little black box that looked almost like a transistor. And there were two leads coming out of it. If you ever got curious and broke this thing open, what you found was a nice wafer of quartz. And on the wafer of quartz-- brazed onto it-- were two wires. And that's all there was in the box. The crystal really was a crystal. And the crystals had been very precisely ground to thicknesses such that when a field caused these wafers to hit a resonance, that resonance would be at exactly a particular frequency. And that was the frequency of that channel.

One of the crises, during the Second World War, is that the highest quality natural

crystals of quartz come from Brazil, and during the conflict the sea channels were essentially blocked. And so, people-- in order to make all these communication devices-- had to learn how to synthesize crystals of quartz synthetically. And there are a number of companies, such as Sylvania up on the North Shore, that developed entire buildings devoted to growing single crystals of quartz.

And they're big tanks like something out of the aquarium. And in the center of the tank is a rod, and seeds of quartz are placed on the rod. And the thing very slowly rotates around in this solution. And on the rod, eventually, are single crystals of quartz that are this size. And its a very spectacular thing to see.

In any case, symmetry 3 2, and the moduli that are 0 and non-zero. If we refer the reference axes to a set of coordinates with  $x_1$  in this direction, and  $x_2$ -- since it has to be orthogonal to  $x_1$ -- in between the two-fold axes, and  $x_3$ . And for all materials of commerce that are anisotropic, there has to be some standard for defining the choice of axes. For example, crystallographers would say the unique axis should be along the  $z$  direction, the  $x_3$  direction. But why isn't  $x_1$  and  $x_2$  in between the two-fold axis?

There's some professional society that is responsible for giving standards for representing property measurements in some mutually agreed upon form. And this is the standard set of axes for the quartz and symmetry 3, 2. The moduli,  $d_{ij}$ , not  $d_{ijk}$ , but  $d_{ij}$ , these two are constrained to be equal. This one is 0. This is minus 0.67, 0, 0, 0, 0, 0, 0, 0, 0.67, 4.6, 0, 0, 0, 0, 0, 0, 0. One of the strange materials for which no field can create a strain-- field along  $x_3$  cannot create a strain. And these are all in units of  $10$  to the minus 12 coulombs per Newton.

An example they give you here, if you apply a field of 100 volts per centimeter, which is not terribly large, but would be comparable to what you have in some electronic device, perhaps. So this, since our units are MKS, this would correspond to  $10$  to the 4 volts per meter. The strain  $\epsilon_{11}$ , which is  $d_{11}$  times  $e_1$ . It turns out to be minus 2.3, which means it contracts. That's the significance of the negative times  $10$  to the 4. And that turns out to be  $10$  to the minus 12 times  $10$  to

the fourth. That turns out to be a strain of minus 2.3 times 10 to the minus eighth.

10 to the minus eighth is not exactly a large point strain. You're not going to see the crystal wafer twitch and jump, if you apply a field of 100 volts on it. But yet, even a strain of this sort is more than enough to be useful. But this is just to illustrate that quartz is not the most sensitive of piezoelectric materials.

Another one that I give you data for is so-called ADP. And this is a widely used material. This is ammonium dihydrogen phosphate. And this is one of the family of salts that have very large piezoelectric responses. The nice part about it is that it's water soluble, so you can grow very, very large crystals easily from solution. The nasty part about it is that it is water soluble, so you have to be careful to protect this material from moisture if you're going to use it in any sort of device.

But if we look at the moduli, relative to the standard axes, and this has point group 4-bar 2m. So x3 is taken along the 4-bar axis. Then there are two-fold axes and orientations like this. And since they are orthogonal, you can take both x1 and x2 along the two-fold axes. And the numbers here for dij, are 0, 0, 0, 1.7, 0, 0, 0, 0, 0, 0, 1.7, 0. This is one of the interesting tensors where there's a diagonal row of non-zero terms off on the right hand side. And finally, the big surprise is the third modulus this is 51.7.

So you can see this has a very strong effect. This is over 10 times the maximum piezoelectric modulus in quartz. So this is a material that's very commonly used in transducers. This is again times ten to the minus 12 coulombs per Newton.

One of the very, very exciting developments in recent years is a class of materials that are perovskites. And they are very, very new. I gave you the reference to the first one that was reported, and that was just in the spring of 2000. And these are perovskites.

Perovskites are materials that in the type form are cubic. But depending on composition and temperature, they can transform to a distorted version of this very simple cubic structure that is tetragonal. And this material can exhibit piezoelectric

effects. And whether it distorts or not depends on the relative sizes of what goes into the perovskite.

Perovskite has a composition  $ABO_3$  like barium titanate is one example. And the material has two different cations. And they have different valences so they have different sizes. And I won't bother to describe the structure, but it is only a very restricted locus in the field  $RA$  versus  $RB$ , where both the  $A$  and the  $B$  can remain in contact with the oxygen without distortion. And it turns out to be a line that does something like that.

Any other perovskite-- and there are lots of them in this field of radii-- has to have one of the ion sort of flopping around. And if that gets too serious, the structure distorts so that all these ions can remain in contact with the oxygen. OK in order to do that, many of them distort to tetragonal forms. Others distort to super structures, which have very, very large unit cells.

But in any case, when you're right at the phase boundary between the distorted structure and the true perovskite structure, these materials sometimes have very, very complicated  $x$  solutions of the two phases, on a very sort of fine scale. And it's not known exactly why they have this property. But they have absolutely enormous piezoelectric moduli, very close to this phase boundary.

And the references that I give you-- here-- is a compound that is a lead titanium zinc niobate. And the complicated composition is to get you close to this phase boundary. This has a  $d_{333}$  that is greater than 2,000 picocuries per Newton. And pico is  $10$  to the minus  $12$ .

So this is a piezoelectric electric modulus that is  $10$  to the  $3$  times  $d_{11}$  for quartz. So  $3$  orders of magnitude stronger than this very commonly used piezoelectric material. Some of these materials have strains getting close to  $1\%$ .

So this is something that will actually twitch on the lab bench, when you apply a field to it. So these are entirely new. People still don't know the origin of this behavior. And it's still under considerable study. So this is a new family of materials. It's very

exciting, and undergoing a lot of investigation and development work at the moment.

Alright, we are almost out of time. Time goes fast when you're having fun. Let me raise the question that we'll consider next time, which will be one of our last lectures. And that is, is it possible to create representation surfaces that tell you how the piezoelectric properties of a particular material will vary with direction? Well, vary with what?

Well, we talk about the direct piezoelectric effect. This gives us components of-- well let's look at the simpler one, in terms of what we apply. We have the converse piezoelectric effect that says that  $\epsilon_{ijk}$  is going to be  $d_{ijk}$  times  $e_{sub\ i}$ . So we've got a piece of material, and we apply a field,  $e_{sub\ i}$ . So we can vary this in space relative to a coordinate system  $x_1, x_2, x_3$ . But how in the world are we going to show what happens? So I always do an extra thing in here.

There are 9 components to the strain tensor, which is symmetric. So they're really six responses that are unique. So yes, we can define the direction of the applied field. But they're going to be 6 different strains. So we're going to need six representation surfaces. One for each of the three tensile strains, and one for each of the three shear strains. So you can't do it with a single surface. So you can't do much other than say, there are certain responses which are intended to emphasize one particular sort of strain or one particular sort of polarization.

So one of the things we might do is to cut a very thin plate of something like quartz, and subject it to a uniaxial stress. So let's say  $\sigma$  along the  $x_3$  axis. So we're looking at a very restricted strain tensor. That's 0, 0, 0, 0, 0, 0, 0, 0,  $\sigma_3$ . And in response to that strain, there are going to be three different components of the polarization.

Polarization is manifested as a charge per unit area. So if we make a very thin plate-- to be sure there will be charges induced on these thin edges-- but if it's got a surface area that's a large compared to the area of these thin edges, we are going to be measuring primarily  $p_3$ -- the component of polarization that's normal to this

surface-- and that might have a charge per unit area that is comparable to these other two charged surfaces. But because the area by design of our specimen is so large, the response that would be most easy to detect, and which would be the largest response, by design, would be  $p_3$ , which is the charge per unit area on this surface. So this is an effect we can define for a particular sample, and for a particular special form of the generalized force.

And we then can ask, what is the value of the single modulus that relates  $p_3$  to  $\sigma_3$ ? And that's a question we can ask. And we can plot that response as a function of direction of a plate that we consider as being cut out of a single crystal, and different orientations, and then ask how this modulus-- which connects the two-- changes with the orientation of  $x_3$ . So that is a question we can ask.

And these surfaces are absolutely wild, highly anisotropic, can be identically zero in certain special directions, and they are very interesting, and a lot of fun to look at. So we'll take a quick look at a couple of those, which won't come as a surprise because they're already worked out for you in the notes. So we'll take a look at one of those. And in the problem set, I invite you to amuse yourself by looking at such representation surfaces for two other point groups. And with that, having kept you til five after the hour I will quit.