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# PHONONS, RUS, AND NEUTRON SCATTERING

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## ABSTRACT

Simple but very precise acoustical probes such as RUS can be combined with very sophisticated but less accurate probes such as inelastic neutron scattering and diffuse neutron scattering to provide a powerful picture of the vibrational spectrum of a solid. Such a picture can be used to extract information about fine-scale microstructure, phase transformations and more. We describe here recent work applicable to martensites and Pu.

## TRANSCRIPT

DR. MIGLIORI: I am going to talk about recent work at Los Alamos National Laboratory or, as it has become more recently known, the Chinese Takeout Place. (Laughter)

After this Kosovo thing the Chinese have decided to give us back our military secrets. (Laughter)

[Transparency]

I am going to talk about our work on plutonium today. I want to use it primarily as a vehicle to show you how important the measurement of elastic properties is and, of course, the work that we have done has all been done using resonant ultrasound, partly because there is an absolutely stupendous administrative overhead in attempting to make a measurement on plutonium.

At this point we estimate that some of the samples we have measured recently are worth on the order of \$2-5 million on the black market just because of the plutonium content. All of these measurements are really the very first ultrasound measurements on plutonium since 1975, when Hassel Ledbetter and Roger Moment published their single-crystal work. I think that was the last one, Hassel, for this.

Plutonium is interesting -- I will show you why in a minute. This has nothing to do with its only known practical application, but it is interesting. We are going to use resonances, because, number one, we will be able to see very small changes in elastic properties with temperature, time, and so on. In fact, I will show you in a second just how good that can be.

Plutonium has a very complicated phase diagram, and because of the very strong dependence of things like interatomic potentials on elastic moduli, studies of elastic properties can eke out some of the details of this complicated phase diagram and make it seem a lot less complicated, and I will touch on that, also -- I am not going to explain anything completely today.

Finally, there are completely thermodynamic quantities, so they are good.

[Transparency]

Okay, plutonium: Plutonium sits right here. For example, these are a bunch of actinides. You can see very few of them have more than an fcc and a bcc in a liquid phase, but as you get to this particular electronic configuration the whole thing turns into a complete mess. That provides a wonderful test bed for doing solid-state physics of various sorts.

[Transparency]

These are the phases that plutonium exhibits between room temperature and 640 C, so it is monoclinic, body-centered monoclinic, face-centered orthorhombic, face-centered cubic -- I do not think this is a phase -- and then body-centered cubic. It undergoes a huge number of phase transitions as you warm it up.

[Transparency]

It also has other strange properties. For example, as I begin to warm it up and I look at the length as a function of temperature of a plutonium sample (this is thermal expansion), monoclinic phase, monoclinic, orthorhombic. When it becomes fcc, the volume thermal expansion coefficient goes negative.

Then, as you warm it up, it goes to body-centered cubic and the volume drops 3%, a very large amount. In fact, I am going to concentrate on this region here and try to convince you that it is not really mysterious at all.

[Transparency]

Just to complete the introduction, there are the crystal structures of plutonium, and I think we are going to make some headway in understanding them. Just remember that Willie

Zacharias had figured this thing out in 1961, I think. He had to be a complete mad man to get that crystal structure out of his x-ray data.

[Transparency]

I am going to start by showing you some of the hardware. This is one of the resonant ultrasound cells that is installed in an argon glove box in the plutonium facility at Los Alamos. That is not a piece of plutonium, however.

This is about a half-inch across here, to give you an idea of size. We have used that apparatus so far to make room-temperature measurements, although we have cryogenic and higher-temperature stuff in the works. It takes roughly six months to get any change in your experiment approved for operation in these facilities.

Plutonium turns out, even in the polycrystal alloys we have right now, to be a superb mechanical resonator; the Q's are easily  $10^4$ . Here is a typical mechanical resonance of a plutonium 4% gallium sample. Gallium is often put in plutonium to stabilize the fcc phase at room temperature.

The little arrows here give you an idea of what would change. For example, from here to here is roughly a half-Kelvin change in temperature, so with these kinds of Q's we have extreme precision for following elastic constant shifts. Remember, we can fit this Lorentzian resonance to about 1% of its width, so we can see very small changes.

[Transparency]

I am going to show you data and then talk about what it all means. With nice sharp resonances, here are typical

-- and this, really, by the way, is typical (not like Jay's)

-- errors, measured frequencies, we are looking at RMS errors like this, we get values of elastic constants. Just to get these data is absolutely amazing.

DR. SACHSE: What are  $\nu_{\text{ex}}$  and  $\nu_{\text{fr}}$ ?

DR. MIGLIORI: That is all explained in this book I wrote, but I will tell you anyway.  
(Laughter)

These are the measured frequencies and these are a Levenberg-Marquat [phonetic] best fit, adjusting, in this particular case, only two elastic moduli,  $C_{11}$  and  $C_{44}$ , because it is an isotropic polycrystal. It turns out these alloys are very well prepared and they are very isotropic and very amenable to elastic constant fit.

[Transparency]

Here is how well we do. These are Hassel's and Roger Moment's elastic constant measurements of a 3.3-atomic percent gallium-stabilized fcc plutonium crystal at room temperature,  $C_{11}$ , bulk modulus, shear modulus.

Here is our measurement of a polycrystal sample, same composition, so Hassel did pretty well. We also have now, for the first time, different gallium concentrations, and you can see a fairly strong variation in elastic properties with gallium.

For comparison, this is a 1963 measurement of pure plutonium without gallium, and here is our measurement; again, very good correspondence with the pulse echo and the torsional oscillator work.

What is interesting here is that up until recently it has been assumed that when you put gallium in plutonium to stabilize this face-centered cubic phase against monoclinic, the properties are essentially exactly the same as if you did not put it in, and we are starting to see substantial differences in compressional properties with the gallium, which is a little surprising at those concentrations.

DR. ISAAK: You do not have a monotonic change.

DR. MIGLIORI: That is right, it is not a monotonic change, and that is the first surprise for the people funding this work.

[Transparency]

Just to show you the next stage here, this is a thermoelectrically cooled system, because it is very difficult to get cryogen in the secure environments in the plutonium glove box because of both security and safety considerations, so we have a thermoelectric cooler, and here is your resonant ultrasound stage with a sample in it.

This should go -- well, maybe not quite this far, but we should be able to get a reasonable temperature derivative and, therefore, the temperature derivatives of these alloys.

Why do we care about all of this stuff? There are some very strange things about plutonium and we are going to talk about some of them.

[Transparency]

Pure plutonium has a negative in the fcc phase. It has a negative volume thermal-expansion coefficient. As you add gallium it becomes ordinary. The atomic structure guys, who claim they can calculate ab initio the structure of every single element, wind up doing the

following calculation, in which they find that the bcc phase that is observed for plutonium, and the fcc phase that is observed for plutonium are not minima in the free energy, according to their calculations, they are maxima and, therefore, they are maximally unstable, so they have got problems.

[Transparency]

However, all of these guys ignore thermodynamics and entropy when they do these calculations. In plutonium especially -- here are Hassel Ledbetter's data and, of course, you can all read this after lunch and, if you cannot, it is okay, because I am going to tell you what is going on, or at least the important things -- entropy is really important in plutonium.

The reason it is especially important is that the shear wave speeds vary very strongly with direction in the single crystal. In fact, the shear stiffness varies by 7 to 1, which is the highest for any fcc metal. What that does is bring down the entire phonon dispersion curve. This was computed by our co-workers at Los Alamos from the diffuse scattering piece of an elastic scattering spectrum on plutonium that was not great, but these are estimates in which the force constants are computed and then the entire dispersion curve.

[Transparency]

The soft modes are reflected in these little slopes here. What this does is it brings the entire phonon dispersion curve down and it brings it down substantially, so that the following goes on.

[Transparency]

We are trying to understand negative thermal expansion coefficient and the volume collapse as we warm fcc plutonium up to the bcc phase. I can be really dumb and just compute the bulk modulus, or at least compute the change in energy if I compress plutonium when it is fcc. That energy, if I know the volume change, which is about 3%, and I know the bulk modulus, which has been measured by resonant ultrasound, then I can estimate an energy change.

I can also estimate an entropy shift, noting that basically the TS term and the free energy is  $3 kT \log$ . All these things are phonon-dominated. Plutonium is really a bunch of mechanical vibrators and every one of them has a certain number of quanta in its simple harmonic oscillator normal mode.

The log of the quantum number, averaged over the entire phonon dispersion curve, is intrinsically the entropy with a few constants on it. So we take  $kT$ , the temperature, times

Boltzmann's constant, and some average phonon frequency, this number is sort of the quantum number of the harmonic oscillator and, therefore, the entropy.

Remember, plutonium has a very soft elastic constant in one direction, so this number is extremely large for plutonium, meaning the following: In most metals the bulk modulus is very, very large, like iron, and in plutonium it is very small. In plutonium the average phonon frequencies are very small; therefore, the harmonic oscillator entropies are very large.

Therefore, in plutonium, if I can make tiny changes in the phonon distribution, I can stabilize against almost any energy shift, because I have so much entropy to do it. More precisely, when plutonium goes from fcc to bcc, the bcc phase has a smaller volume, but all bcc materials have even softer shear modes than fcc phases, so they have a lower average phonon frequency and higher entropy. In plutonium that effect is stronger than for almost, I think, any element (I am not sure if it is exactly that) and, therefore, entropy will take you to places that look energetically unfavorable, which is why the electronic structure guys get plutonium as unstable. It is, in fact, entropy-stabilized.

[Transparency]

As you put numbers in, we are looking for this to be true, that is, the change in  $TS$  over the change in energy when we go from fcc to bcc, we want that to be true, and it turns out that using unfavorable numbers, that is, the worst that we can find, the energy differences are sort of 2 mV per unit cell in going from fcc to bcc, but that would require only a change of about 1% in the average phonon frequency, a drop of 1% to stabilize.

In plutonium, because of these very soft elastic properties, it is clear that these odd phases with smaller volumes are being stabilized simply because they are more probable via the entropy.

[Transparency]

The thermal expansion is also related to the anisotropies, which are then related to an interesting thing called the Bain route, which goes like this. Here is an fcc crystal.

[Transparency]

I have put on it a body-centered tetragonal set of lines. This is the same crystal structure, but I am drawing here a body-centered tetragonal. Face-centered cubic is the same as body-centered tetragonal, where  $c$  (which is this), over  $b$  (which is that), is the square to 2. I am just waving my hands now.

But look, if I start to squeeze this way, that is, compress the fcc structure, eventually this will equal this and it will become bcc, so I can continuously deform fcc to become bcc. That is called the Bain route and it has the stunningly weird property that goes like this.

As I start to squeeze it -- I am squeezing fcc here

-- the initial stress-versus-strain slope is Young's modulus. As I continue to squeeze it, I move it all the way over to bcc. Now, look, I have squeezed something, its crystal structure between my hands is now body-centered cubic and I have free surface boundary conditions here and here, because I am squeezing it on only these faces.

Therefore, by symmetry, this is a symmetry argument, the force goes to zero. That is, as I squeeze it from fcc to bcc, it is stiff, stiff, stiff, and then boom, and there is no longer any force holding it. It is an unstable thermodynamic equilibrium point, but there is no force that is required to hold that there.

This, by the way, is the energy surface for that process, which we have just calculated recently. We have taken very simple, radially symmetric Leonard Jones-like potentials and put together an fcc lattice and squeezed it, and you can see here an fcc and a bcc minimum in the energy surface.

[Transparency]

For parameters that are very similar -- that is, if the potentials that we use for plutonium are taken as the same sort of phenomenological ones we would use for iron, then we find that the bcc phase that we compute has smaller volume and higher energy (just like plutonium). In fact, now, if you think about the thermal expansion process, usually you think of thermal expansion as moving along the fcc line.

This line here that is very faint is the locus of points in which the crystal structure is face-centered cubic. This line is for body-centered cubic. When I put thermal energy into this thing, people usually think it stays here, but, in fact, things do not do that, they run around all over the place and average out to fcc.

[Transparency]

When you do that, you find that this Bain route between fcc and bcc is also a volume-decreasing route and so when you do the averaging you find out that the volume thermal expansion coefficient is negative and it is absolutely a result of this shear anisotropy that is a result of this very soft Bain route in the crystal structure, so you do not need to invoke any



strange electronic structure or anything else to explain this negative thermal expansion coefficient and volume decrease in plutonium.

The whole point here is to touch on the things that you can really do well with elastic constant measurements and how much you can really learn about phase stability in the structure of solids.

Thanks.

DR. ANDERSON: This Bain route, you say it is for iron?

DR. MIGLIORI: Iron has a Bain route between fcc and bcc as well and I believe it takes that route, which you can tell by looking at the crystallograph. You take an x-ray pattern of a single crystal and if it rotates 45 degrees when it goes bcc, then it has taken that Bain route to get from fcc to bcc.

By the way, it is a first-order phase transition, but that route has the minimum atomic displacement, so often it is very easy.

DR. ANDERSON: I have got to learn more about this, that is news to me, and I thought I had worked in iron.

DR. MIGLIORI: Isn't that interesting, the whole symmetry argument? There are other Bain routes, for example, between cubic and rhombohedral.

DR. LEDBETTER: And there are many, many systems beside iron that go fcc to bcc via Bain.

DR. MIGLIORI: Lots and lots. It is a very common way of going and it is entropy-driven, in some sense, because usually the bcc mode has softer elastic constants and, therefore, more phonon entropy, so the system can head in that direction regardless of what the energy or the volume of the bcc phase is.

DR. ANDERSON: What is interesting to me is the fact that --

DR. MIGLIORI: Hassel is the real expert on this, by the way.

DR. ANDERSON: -- four or five years ago there was a belief that there was a bcc phase in iron up at 200 GPa and 4000°, and there was good reason to believe that.

Then the first-principle calculators got busy and said, hey, the Helmholtz energy of bcc will not allow that transition in this domain, so the idea kind of lost its momentum, but now I am wondering if we know anything about that.

DR. MIGLIORI: You know, it would be easy to mistake the thermodynamic free energy for the internal energy, which is what the electronic and band structure people typically do. Those are always zero temperature calculations and they usually say, oh, well --

PARTICIPANT: It has nothing to do with temperature.

DR. MIGLIORI: They are athermal, because they do not include --

DR. ANDERSON: The bcc phase in iron that was disposed of is first on top of fcc.

DR. MIGLIORI: Which is where you would expect it to be, because bcc systems always have -- well, roughly always -- a soft shear modulus in the 110 direction and, therefore, they always have higher entropy than the nearby fcc phase (I mean, you know, "always" within reason, but it is pretty much true).

You can get to a bcc phase that is energetically distinctly unfavorable merely because it is so much more probable because its entropy is so high.

DR. ANDERSON: And you say the reason you can do that is because the entropy has to be large?

DR. MIGLIORI: Yes, and it does not care what the energy is, it can be plus or minus. It does not care what the volume is. If it can head for that spot with lots of entropy, it is going to just drag everything along. Yes, the linear augmented-plane-wave sort of calculation is really a zero temperature -- well, they put in a certain model for the electronic structure. They compute the energy and then they say this is the free energy, having never computed the properties of any of the competing structures.

They put it in fcc, then they compute the energy. They put it in bcc, they compute the energy. If fcc energy is lower than bcc energy, they say fcc is a stable structure. They do not compute the full elastic tensor or the entropy at finite temperature.

DR. ANDERSON: They say it is reasonable to take the entropy [inaudible].

DR. MIGLIORI: Right. I think we have seen that it fails, that the plutonium experts at Los Alamos fail because they do not bother computing the entropy and, in fact, they are probably pretty close to having the right answers if they did.

Thanks