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TITLE: Elasticity of Leucite Through High-Temperature Phase Transitions

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ELASTICITY OF LEUCITE THROUGH HIGH-TEMPERATURE PHASE TRANSITIONS

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ABSTRACT

A mean-field Landau-type model predicts that in some crystals certain elastic moduli experience significant softening in the neighborhood of phase transitions. Experimental verification of the influence of structural phase transitions on elastic moduli are needed to build a complete physical model and to predict the elastic behavior of minerals that undergo structural phase transitions.

At ambient pressure and temperature, leucite ($KAlSi_6O_6$) is tetragonal, but undergoes two structural transitions at about 870 and 900 K to a high-temperature cubic phase. We used resonant ultrasound spectroscopy (RUS) to monitor the resonant modes of leucite ($KAlSi_6O_6$) from room temperature to 1500 K. In the stability field of cubic leucite, the five lowest resonant modes were measured from 900 to 1500 K. These five modes are predominantly shear vibrations, thus constrain the the shear moduli, but not the compressional moduli. We find that C_{44} increases gradually from 19.3(3) GPa to 26.5(7) as temperature increases from 950 K to 1500 K. This behavior in C_{44} demonstrates the influence that phase transitions have on elastic properties at temperatures well removed from the transition temperature.

TRANSCRIPT

DR. ISAAK: My name is Don Isaak and I am from UCLA. The work I will discuss was done at the UCLA lab with Orson Anderson, J.D. Carnes, and Steve Moser. Moser is an undergraduate at Azusa Pacific University.

The abstract focuses on phase transitions in leucite. In my presentation, however, I will show results from our leucite work and from two other major areas of study during the past year.

[Transparency 1]

The first item represents work we have done in the last year on phase transitions at high temperature. The second item refers to information we obtained from rutile data. Specifically, I wish to show inferences we made on the pressure derivatives of elasticity at high temperature based on our high-temperature RUS work and systematics. The third item is included to correct some conclusions I presented in a talk two years ago. Many of you were present at that talk; it is appropriate to update you on the results of our work regarding the pressure derivatives of the shear modulus using the RUS technique.

[Transparency 2]

Let us turn to the leucite work. When I submitted my abstract, I received an e-mail suggesting I misspelled the mineral. I remind you (or inform you) that we studied this white, gray mineral, described on the left side, which is leucite -- not this plastic-like material over here on the right. That material is lucite.

[Transparency 3]

Leucite exists in a tetragonal form at ambient temperature. When heated, it goes through a ferroelastic transition at 918 K and then a small volume-changing transition near 940 K. A tetragonal-to-cubic change in crystal symmetry also occurs at the high temperature transition. We wanted to look at the elastic properties associated with this change in crystal structure.

DR. MIGLIORI: So as you heat this, it goes tetragonal to cubic?

DR. ISAAK: Yes, that is exactly right, the high-temperature phase is cubic, it goes to a higher symmetry form. The elastic constants of that high-temperature cubic phase are unknown and are the subject of our study.

[Transparency 4]

Here is a brief look at the sample description that we used. The density is a little more than 2. The specimen size is between 1 and 2 mm on a side. We used a right-rectangular parallelepiped. The assumed starting C_{ij} for the cubic phase are also shown.

DR. LEDBETTER: How did you get the starting moduli?

DR. ISAAK: I will come back to that in detail shortly, but it would be worth mentioning something now on that. The C_{11} and C_{12} values are actually calculations from Martin Dove at Cambridge, England. This leucite work was a collaboration between the UCLA lab and the Cambridge group: Michael Carpenter; Martin Dove; and Andy Shen. Dove gave us the C_{11} and

C_{12} values and suggested a value for the C_{44} modulus that was different from the 20 GPa shown here. I will come back to that point shortly.

[Transparency 5]

These are the five modes we looked at. We could see only these five modes - presumably they are the five lowest modes. We could not make an analysis of the six C_{ij} of the low-temperature tetragonal phase using only five modes.

Furthermore, the low-temperature phase is highly twinned; it is very difficult to make meaningful interpretations in terms of the low-temperature C_{ij}. The modes are very clear below 900 K but, it is not apparent how to interpret them as the C_{ij} of the low-temperature phase.

We wanted to see what happens after the high-temperature transition to the cubic phase.

[Transparency 6]

Here is another diagram of the frequencies as a function of temperature. These thin, solid lines show the calculated frequencies made using C_{44}=20GPa and the C_{11} and C_{12} values provided to by the Cambridge group. The seven lowest modes calculated this way are labeled along the right edge of the plot.

The point of all this is that with a C_{44} value of 20 GPa the calculated modes intersect the measured modes at about the same temperature, 950 K. This answers the question of how, in principle, we arrived at the starting modulus for C_{44}. We just used those values of C_{44} that match the first five calculated modes with the five measured modes.

You can see how sensitive the calculated frequencies are to changes in the C_{44} modulus by changing C_{44} and recalculating the modes. We changed C_{44} by 10%, making it 22 GPa instead of 20 GPa. The ensuing changes in calculated frequencies are shown by the red dashed lines. Thus, we have some idea of the sensitivity of this method of estimating C_{44} at each temperature. By carrying out this analysis of fitting the five lowest calculated frequencies to the measured frequencies at each temperature, we are able to estimate the C_{44} modulus as a function of temperature for cubic leucite.

DR. MIGLIORI: I did not quite get that. You changed C_{44} by 10%, so that is a 5% change -- okay.

DR. SACHSE: But you are using the computed C_{11} and C_{12} and then you are playing around with the C_{44}. I know the computed ones are for the --

DR. ISAAK: Yes, that is what I will now show. As it turns out, those five measured modes are very insensitive to C_{11} and C_{12}. It happens that the modes we were able to see only constrain C_{44} - that is the bottom line - so we have a limited amount of information. At the same time, we can be quite certain that the information we do extract is not obscured by other uncertainties.

[Transparency 7]

This illustrates the point I just made. It shows computed frequencies (thin solid line) using the value of C_{12} given to us originally by Dove and cited earlier in this talk. The frequencies are recalculated (thick dashed line) after changing C_{12} by 10%. There is virtually no change in the computed frequencies. A similar case occurs with C_{11}. So, uncertainty about the values of C_{11} and C_{12} does not obscure our determination of the value of C_{44}.

[Transparency 8]

The story here is that we are able to measure the C_{44} modulus as a function of temperature after this phase transition. This plot shows $C_{44}(T)$ with the uncertainties as determined from the five measured modes discussed earlier. The fact that C_{44} increases over such a wide temperature range is very unusual. It appears that this soft-mode behavior extends over a temperature range of more than 500°C. That is a bit puzzling to me; it does not seem to follow a Landau-type explanation of a transition.

[Transparency 9]

That is almost the end of the story. We wish, however, to make some interpretation in terms of the Landau theory of phase changes. That is the reason the Cambridge group involved us in this study that is still in progress. From our understanding of Landau theory, for the type of transition we are looking at, the C_{44} modulus should not deviate substantially from the normal C_{44} (referred to as C_{44}^{o} in the diagram) after the transition to the cubic phase.

That, however, is not what our results with leucite show. Again, the C_{44} modulus should be equal to the undisturbed C_{44} modulus. This undisturbed modulus is the C_{44} without the influence from the transition.

Let us conclude this part of the talk with an observation. In geophysical studies, one must consider the effect of phase transitions on mineral elasticity over much broader temperature ranges than is generally appreciated. When modeling properties of the deep Earth, the effects of phase transitions hundreds and hundreds of degrees from the transition must be accounted for.

I compared this to Migliori, et. al (1993) where the C_{44} modulus in that tetragonal-to-cubic transition for strontium titanate was limited to about 15 or 20°C from the phase transition. The C_{11} and C_{12} moduli were affected over a much broader temperature range.

DR. MIGLIORI: In our lanthanum-two copper-four measurements, we got a similar range of variation of the transition that you did; that is, there is a structural phase transition.

DR. ISAAK: I have not reviewed that.

DR. MIGLIORI: We did that around 500 K and it has an amazingly broad range over which the C_{44} increases as you heat it.

DR. ISAAK: As we are seeing here with leucite - interesting.

DR. MIGLIORI: I think basically the entire Landau business does not work on these systems.

DR. ISAAK: I am not that knowledgeable, but my data also seems to say there is a discrepancy.

DR. MIGLIORI: To make the comment precise, if you take the Ginzberg-Landau model for a structural phase transition, you pick anything you want for an order parameter, you have freedom of choice, then you attempt to compute the temperature dependence of that order parameter through the phase transition. That will make very specific predictions about what all the elastic moduli are going to do.

What you have done, really, is simply say the order parameters are linearly or quadratically coupled to the elastic moduli. We found in lanthanum-two copper-four that no functional form of a simple Ginzberg-Landau phase-transition theory would reproduce the behavior of all the elastic moduli, but we had a critical exponent of exactly one for the shear modes. We do not understand it.

DR. ISAAK: Well, I am glad at least what I am saying is similar to that.

DR. LEDBETTER: It seems to me that this condition of the C_{44} as not being equal could be due to factors other than lattice softening. I think there are a lot of examples of this. These ferroelectric materials with phase transitions have normal temperature dependence on both sides. So there is a splitting of the C_{44} term.

DR. ISAAK: Okay, I will just take that as a comment at this point.

What I would like to do now is move on to the second general subject of this talk in which I will show inferences we made about what is called the mixed pressure-temperature derivative of the bulk modulus from high-temperature work on rutile.

[Transparency 10]

Very quickly, rutile is titanium oxide, $Ti0_2$. Here are a couple of spectra of five modes - one is at room temperature, one is at 1500 K.

[Transparency 11]

Very quickly, this is for those who want to see what the high-temperature data look like. Our maximum temperature was 1800 K. The reason the signals are deteriorating at 1800 K is that the polycrystalline alumina buffer rods are losing their integrity. Higher temperatures are possible with single-crystal corundum rods.

[Transparency 12]

We measured the temperature dependences of about 30 modes. Here we show five such modes.

[Transparency 13]

Here is an example of what often happens in high-temperature work. Some modes are not orthogonal to each other, and when they try to cross you get complicated interactions. Modes that coupled like this were not used in our data reduction; we used only modes that were clean all the way through.

[Transparency 14]

One reason we did this experiment was to measure the high-temperature properties of mineral. If you take the previous data that go to about 400 K, they extrapolate to high temperature as shown by the dashed lines. The actual high-temperature data, however, can show significant deviations from the extrapolations.

[Transparency 15]

An interesting result from rutile work is seen in this figure. We looked at systematic relationships between the pressure derivative and the parameter which is the bulk modulus times the cube root of the mean molecular weight divided by the density, which we can measure to high temperature.

Here we see the systematic relationship between these parameters for three isostructural minerals, SiO_2, GeO_2, and TiO_2, at room temperature and show the linear fit by the dashed line.

This relationship is the Law of Corresponding States proposed by Orson Anderson in 1966. There are reasons why SnO_2 deviates from the trend, but we will not have time to discuss that. The Law of Corresponding States suggests that materials with the same structure obey the same type of behavior in their relationship between $K_S(M/\rho)^{1/3}$ and $(\partial K_S/\partial P)_T$.

We make high-temperature placements of TiO_2 on the dashed line by their high-temperature values of $K_S(M/\rho)^{1/3}$. Then we read over to the $(\partial K_S/\partial P)_T$ axis to infer the $(\partial K_S/\partial P)_T$ value at high temperature.

By this process, we obtain the value of the mixed derivative, $\partial[(\partial K_S/\partial P)_T]/\partial T$. For rutile, we find $\partial[(\partial K_S/\partial P)_T]/\partial T$ is $70x10^{-5}$ K^{-1} which seems high when compared with estimates of other materials.

[Transparency 16]

We find, however, further justification for this high value in work I recently did with Frank Stacey. Using thermodynamic arguments, we found that this mixed derivative, i.e., how the pressure derivative changes with temperature, varies with the pressure derivative of the bulk modulus.

Even though we got a high value for $\partial[(\partial K_S/\partial P)_T]/\partial T$, it seems to make sense because the pressure derivative of the bulk modulus is also somewhat large. The ambient value of $(\partial K_S/\partial P)_T$ (written as K_S' on the plot) would be out to the right at around 7, implying a large value of $\partial[(\partial K_S/\partial P)_T]/\partial T$. Most materials have values of $(\partial K_S/\partial P)_T$ around four or five.

My conclusion is that we have estimated the mixed T,P derivative of the bulk modulus for rutile. We obtain what seems to be a high value of about $70x10^{-5}$ K^{-1}, but this value corresponds to what is obtained from the thermodynamic scheme developed recently by Frank Stacy.

We now move on to the third and final section of the presentation. We will relook at work done with the pressure derivative of elasticity of fused silica spheres. This revisits what was reported at the Asilomar meeting a year ago. We present here, however, a different conclusion than what was given at the Asilomar meeting.

[Transparency 17]

We took fused silica spheres and measured certain resonance peaks as a function of pressure. Data on sphere at ambient pressure, 60 bar, and 120 bar for the T_{02} torsional mode are shown here.

[Transparency 18]

This plot shows the data more completely on one pressure run. Going up in pressure is represented by triangles pointing up; going down in pressure is represented by triangles pointing down. The open triangles represent the primary data; the closed triangles represent the data with temperature corrections applied. The temperature-corrected data are very precise and repeatable.

[Transparency 19]

At the Asilomar meeting, I reported how we used argon, nitrogen, and helium as pressurizing gases to determine the effective pressure derivative, $(\partial G/\partial T)_P$, of the shear modulus, G. The idea was to then extrapolate to zero gas mass loading conditions as shown in the plot. The result for zero-mass conditions resulted in the magnitude of $(\partial G/\partial T)_P$ being 3.7 (This actually is negative because fused silica has a negative pressure derivative of elasticity). Earlier ultrasonic plane-wave methods showed that $(\partial G/\partial T)_P$ for fused silica is around 3.4 or 3.5.

This arrow in the plot shows a change of 5%. The difference between our value and the average of the plane-wave was about 8%. Some will recall my suggestion that this 8% difference could be due to effects of bonding between specimen and transducers in the plane-wave experiments.

A couple of people took issue with that suggestion at the Asilomar meeting, and they were correct to do so.

[Transparency 20]

As it turns out, my earlier analysis was incomplete. It ignored this second term on the right-hand side that allows for the effect of sphere radius on resonant modes. As pressure increases the resonant modes will change because of changes in elastic moduli and changes in sphere radius. By ignoring this effect we essentially ignore the second term in the numerator of the expression for dG/dP. This ignored term accounts for about 8% of the whole. So I was wrong.

[Transparency 21]

We now see that the line comes down a little and intersects the axis right between the earlier plane-wave data.

DR. MIGLIORI: So the pulse-echo guys did not blow it?

DR. ISAAK: Well, one guy is a little high and one guy is a little low. (Laughter)

But you are exactly right. The size of that 'X' is basically the standard deviation of a weighted fit to the three data points.

Let us look at one more issue before closing this discussion. We have recently done a more rigorous analysis of the expected effect of gas on the torsional mode. We attempted to remove, using theory, the effect of the viscosity of the gas. This is reasonable since we are looking only at shear torsional modes, not dilatational modes, in this work.

[Transparency 22]

It may not be polite to end a talk with a slide full of math, but please bear with me. When gas viscosity is considered, we obtain a third term in the differential expression for changes in frequencies. We assume the penetration depth of the torsional vibrations into the surrounding gas effectively increases the mass of the specimen and we obtain the third term in the right-hand side of the differential expression. The resulting expression for dG/dP requires another term - the third term in the numerator. We apply this correction to the equations for each of the 3 gases. The added corrective term is opposite in sign from the main term, df/dP, in the denominator. Thus, the magnitude of dG/dP decreases for each gas.

[return to Transparency 21]

When the correction is applied, each effective dG/dP value drops (see diamond shapes) and the values from the three gases line up as shown by the horizontal solid line - a result that is somewhat pleasing.

What is not so pleasing is that the 'answer' for dG/dP found this way is slightly higher (by about 3%) than found by simply extrapolating empirically to zero-mass.

If you want to see the details, I refer you to our JASA publication and have copies here with me. Thank you very much.

DR. DARLING: What is the melting point of leucite? How close did you come on those experiments? I assume it is quite high.

DR. ISAAK: We did not melt it. (Laughter)

DR. DARLING: I think the shear modulus might have diminished a little, had you done that.

DR. ISAAK: Yes. I did that once before with garnet. I pushed it too high. I had the melting temperature in my mind in degrees Kelvin, and I was measuring degrees Celsius. So I misjudged by about 300 degrees the temperature I could go to. I lost my signal and later found the specimen partially melted and fused to the buffer rods. What I mean to say is that I now always check when going up in temperature. I cannot, however, remember off the top of my head the exact melting point of leucite.

DR. MARSTON: This mass shift effect that you introduced at the very end, did you check your modeling of that by just varying the pressure at a given temperature for one of the denser gases?

DR. ISAAK: Yes, I did that for every experiment. I think the real test of this theory would be that when you make the correction, you make it different for each gas. When all the gases are corrected, do they line up at the same value for dG/dP? Each gas has a different correction because of differences in viscosity and especially density.

DR. MARSTON: The point is you checked the scaling with that form by --

DR. ISAAK: Well, I applied this correction to each of the pressure runs for each of the gases. If that is correct, you would expect this gas dependence to be no gas dependence, or you would get the same answer. I think that is what you are getting at. That is exactly what we got, fairly close to each other.

I also have some ideas as to why the two solid lines on the plot do not converge at the same point.

DR. LEVY: Have you checked that with -- what you have done here seems slightly different. Have you tried the other one?

DR. ISAAK: No, because the other one was radiating energy into the gas. It is basically a different consideration. In the Sorbello paper he was focusing more of his attention on the dilatational energies.

DR. LEVY: No, no, he also did shear at the very end.

DR. ISAAK: I do not know the answer to that. I have some questions about that. That paper is on review and we actually need to discuss some things about that. This assumes a completely different starting point. I am not saying it is contradictory, of course, but it is just a different --

DR. LEDBETTER: I think you said you had only 5 resonance peaks.

DR. ISAAK: That I could see with that leucite, yes.

DR. LEDBETTER: And you spread that to twins. But since this is a natural material, could it also have been due to the voids and cracks? What percentage of theoretical density was it?

DR. ISAAK: That I do not know. I did not analyze that specimen that way. I do not want to dodge the question; I just do not know and the reason I do not know is because Andy Shen came to our lab from Cambridge. He brought the specimen and the work is not complete yet. How much is due to the problems due to voids I do not know at this point.

I am trying to recall - we did actually measure the bulk density, we came very close to the actual density. We did a density measurement and are okay with that, but there were problems with twins. The signal to noise was fairly poor. What we are doing now is looking at another specimen. We have not heated it yet but we just made some room temperature runs on it. We see very nice signals.

That previous specimen, we saw 5 signals. They were clear but the signal to noise was not that crisp.

DR. MCCALL: Did you happen to bring a diagram of your experimental setup?

DR. ISAAK: No, and the reason is because at every talk I show those and I did not want to bore people with that. (Laughter)

I will be glad to send you those.

DR. MARSTON: Returning to the torsional mode situation, again, could you say something about how the Q varies with pressure?

DR. ISAAK: Yes, with those torsional modes that we are looking at, the 2 lowest torsional modes, we saw almost no effect with pressure on Q, and that is why we were confident of our analysis.

[return to Transparency 17]

Quickly, this illustrates the situation qualitatively. With applied pressure, the modes they are all the same.

Thanks very much.