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STUDIES OF METAL-HYDROGEN SYSTEMS

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ABSTRACT

Many metals absorb significant amounts of hydrogen. The hydrogen frequently alters the material properties of the host metal with resulting effects that are sometimes beneficial and sometime deleterious, but generally interesting. Resonant Ultrasound Spectroscopy (RUS) has been found useful for the study of these materials. The absorption of hydrogen affects the elastic constants, usually, but not always, causing a softening of the lattice. The diffusive/hopping motion of the hydrogen gives rise to ultrasonic attenuation if the hopping rate is comparable to the ultrasonic frequency. RUS measurements on hydrogen in Laves phase compounds, rare-earth metals, and quasicrystals will be discussed.

TRANSCRIPT

[Transparency 1]

DR. LEISURE: I would like to tell you about some work we have been doing at Colorado State studying metal-hydrogen systems using the technique of resonant ultrasound. Various people have contributed to this work, both in terms of carrying out the measurements (Foster, Shaklee), supplying us with interesting samples (Kelton, Kim, Skripov) and, in the case of a couple of people in the audience, just generally helping us with resonant ultrasound.

[Transparency 2]

This transparency is a road map of where we are going with the talk today. I will give a little background information on metal-hydrogen systems. I will try to make the connection between hydrogen motion in these materials and ultrasonic attenuation. Then I will discuss measurements on two different metal-hydrogen systems: first I will discuss a Laves-phase material which came from Alexander Scripov in Russia; and second, I will discuss a quasicrystal and a crystalline approximate which came from Ken Kelton's group at Washington University.
The background: There are really quite a lot of metals that absorb hydrogen and retain their metallic character. Among these are transition metals, rare earths, and actinides. If we include various intermetallic compounds and alloys, there is really a whole host of materials that can take up substantial amounts of hydrogen.

In the typical situation the hydrogen sits on some interstitial site. This transparency illustrates the situation for a face-centered cubic lattice. The black circles indicate interstitial sites and the open circles indicate lattice points. Two types of sites are indicated here, octahedral and tetrahedral. Those are the two common types of sites for hydrogen in metal-hydrogen systems. Metal-hydrogen systems are typically non-stoichiometric. A wide range of hydrogen concentrations is possible. At lower concentrations the site occupancy is random and one has a solid solution. At higher hydrogen concentrations one often finds ordered phases that may be precipitated as hydrides.

The hydrogen usually moves very rapidly because of its light mass. The mobility can be 10 to even 15 orders of magnitude greater than for a heavy interstitial such as carbon. This means that we can see effects due to the interstitial motion in metal-hydrogen systems that, in principle, might be present in other systems, but would not normally be seen (they would be too slow). Also, it means that there are going to be more quantum effects because of the light mass.

These materials exhibit a lot of interesting physical effects and they find a lot of practical application. There is a whole community of people who study these materials: physicists, metallurgists, chemists, and electrochemists. People have discussed for many years using hydrogen as a fuel. One problem is how to store the hydrogen? One possibility is to store it in a metal-hydride system. There has been a lot of work on such storage, although I doubt that that is really going to be practical solution in the end except for special applications. If you have a cellular phone, there is a high probability that it has a metal-hydride battery in it. Batteries are probably the biggest commercial application of these materials at the moment.

In the past few years people have found for some of these systems, particularly in the form of films, that you can pump hydrogen in and out and switch these things from a metal to an insulator. The corresponding switch in the optical properties has been described as a switchable mirror. Then there is a long-standing problem of hydrogen embrittlement of metals. Just last
night in talking with Dipen Sinha I learned that there are current problems in that area of which I was not aware.

For all of these useful applications or for the problems, hydrogen has to get into the material and diffuse. It many applications it is necessary to get the hydrogen back out again. Thus the mobility of the hydrogen is a key parameter.

[Transparency 4]

The hydrogen mobility leads into the kind of thing I want to talk about now, the motion of the hydrogen and how to study it. It is typically studied by quite a few different techniques. Three common ones are quasi-elastic neutron scattering, nuclear magnetic resonance, and mechanical spectroscopy.

This transparency indicates typical frequency ranges for these different techniques. I do not mean this to be definitive, but just an illustration. The quasi-elastic neutron scattering typically takes care of the very high-frequency motion. NMR takes care of some mid-point range. Toward the lower frequencies there is mechanical spectroscopy, including, of course, resonant ultrasound spectroscopy.

As we all know, these meetings are important for informal exchanges. At breakfast this morning I was speaking with Tim Darling and he pointed out that there is a whole host of interesting materials effects that lie down in this low-frequency range. The mechanical techniques are very sensitive in this low-frequency range. Some of the other techniques, which are very sensitive and highly touted, do not work so well for very low frequencies.

I think, though, at least for the case of hydrogen in metals, these three techniques are really complementary; it is really nice to have information over a wide frequency scan if you want to make sense of what is going on.

We will focus now on the mechanical aspects, or ultrasonic attenuation. How does the hydrogen motion lead to attenuation? It leads to attenuation because when an ultrasonic stress is applied the hydrogen tends to redistribute itself on the interstitial sites; it will go from high-energy sites to low-energy sites, but that redistribution occurs only if the ultrasound affects the different sites differently.

In other words, the ultrasound has to make some distinction among the sites. For that to occur the site symmetry (defect symmetry) must be lower than the crystal symmetry. The book by Nowick and Berry states this as “the selection rule for anelasticity.”
This transparency gives a diagram to illustrate how that selection occurs. This diagram is just for illustration, it does not represent any real physical system of which I am aware, but a real physical system gets too complicated to actually draw.

Let's consider some simple cubic material and look at a (100) face. We will consider the interstitial sites indicated and imagine that they are randomly occupied by hydrogen. In the absence of any external influence, obviously, the energies of all those sites are the same. However if we apply some stress (and I have indicated here a uniaxial stress), then it is clear not all the interstitial sites are affected in the same way.

Looking at the bottom part of the transparency we see that some of the sites clearly get "squeezed" when we apply the uniaxial stress and some of the sites do not get "squeezed." The hydrogen will undergo some redistribution on those sites to reach the lower energy sites. Of course, the hydrogen is moving rapidly back and forth at all times and the transitions indicated on the bottom diagram represent some net flow from one type of site to the other.

This is only a symmetry argument. We do not know which direction that flow goes, because that would depend on which sites become lower in energy and which become high, and that depends on the details of the bonding. However, it is easy to see that the stress breaks the symmetry of these interstitial sites.

The basic idea is we apply a stress and there is an immediate strain. However, during the "relaxation time" the hydrogen adjusts itself to that stress and this adjustment leads to additional strain. As a result, the stress and strain are out of phase. If the stress and strain are out of phase we get ultrasonic attenuation.

The resulting relaxation attenuation is given by a simple Debye-type expression. In the experiments I am going to talk about we measured the Q. Typically we determined the loss, 1/Q, as a function of temperature. The objective, then, is to determine the relaxation time as a function of temperature and hence infer something about the hydrogen motion.

PARTICIPANT: What is C?

DR. LEISURE: C is actually the elastic constant and delta C is its change. Delta C/C is just the coupling strength.
For the case of hydrogen, because of its light mass, there are a variety of effects that can occur. What I have tried to illustrate here is some double-well potential describing hydrogen in two adjacent interstitial sites. The double-well potential, of course, is produced by the surrounding metal atoms. At high enough temperature the hydrogen may go from one site to the next by classical barrier hopping (I). Another possibility is that the hydrogen is excited to some vibrational level in the well and then tunnels through (II) or maybe it just tunnels through from the ground state (III).

This diagram itself is somewhat oversimplified, because there are other effects that can occur as well. There may be some self-trapping, so these two wells are probably not, in fact, of quite equal depth. As a result, some thermal excitation energy may be required to overcome the self-trapping. Because of the light mass, quantum effects are usually very important. It is probably not very common that the purely classical description works. However, even for the quantum effects where there is thermal excitation then tunneling, the equations describing the motion often have some Arrhenius-looking form, although the actual parameters will not be those of classical barrier hopping.

Unlike Don, I do not mind using the same diagram over and over at different meetings. Since we have all of the parents and grandparents of RUS here, I probably should not show such a simple diagram, but here is a schematic of how we do the experiment. I know this is familiar to most people in the audience. We place some parallelepiped corner to corner between the transducers, excite one corner and detect at the other. For our work, the samples are typically 1 - 2 mm on an edge.

The first system I want to discuss is Laves-phase $\text{TaV}_2$. These materials were prepared in Ekaterinberg, Russia, at the Metals Institute there. Many Laves-phase materials absorb hydrogen readily. One reason for the high absorption is that the Laves-phase structure has a high number of interstitial sites. A second reason is that the chemistry is often favorable. Elements such as tantalum and vanadium tend to absorb a lot of hydrogen. The interstitial sites are illustrated at
the top part of the transparency. The large number of tetrahedral sites favors hydrogen absorption. The network of the sites is such, apparently, as to favor mobility, because some of these materials show exceptionally high hydrogen mobility.

There has been previous work on C-15 Laves-phase materials by the two complementary techniques I mentioned earlier, quasi-elastic neutron scattering and NMR. For several of those systems the previous work indicates that there are two types of hydrogen motion, labeled, "fast" and "slow."

The interpretation of that motion has been as outlined in the bottom part of the transparency. The diagram gives a two-dimensional representation of the interstitial sites. As we can see from the diagram, the interstitial sites form a series of linked hexagons. The interpretation of the previous work has been that the fast motion corresponds to hydrogen zipping around within one of the hexagons, while the slow motion corresponds to the occasional hop to an adjacent hexagon. The origin of the difference in rates has to do with the distances between interstitial sites. The distance between interstitial sites is less within a hexagon than the distance between adjacent hexagons.

The previous work did not resolve these two types of motions very cleanly. For example, in NMR relaxation data the fast rate just appears as a shoulder on the slower rate. One objective of our work was to see if the effect is observable with ultrasound, i.e. does this motion couple to the ultrasonic strain. A second objective, assuming the effect is observable, was to better resolve these two motions. We expect that we might be able to achieve the second objective because our measurement frequency is much lower than those of the other techniques so that the effects may occur at well-separated temperatures.

[Transparency 10]

This transparency presents ultrasonic attenuation measurements at several frequencies for two different concentrations of hydrogen in TaV₂; we have TaV₂H₀.₃₄ at the top and TaV₂H₀.₅₃ at the bottom. There is not very much difference in the results for those two different concentrations, so I will not focus on the concentration dependence.

The measurements extend from about 15 K to about 325 K. Although not shown, measurements in the hydrogen-free material did not give a peak, there was just a flat background. Thus, we attribute these attenuation peaks to the motion of the hydrogen. The peaks behave as expected for thermally activated processes; they shift to higher temperatures
with higher frequencies. The solid lines represent fits to the data, and the fit parameters suggest that this is the slow motion that was talked about earlier, not the fast motion.

The conclusion at this point is that there are at least two possibilities why we did not see the fast motion. One reason might be that the fast motion remains much faster than our ultrasonic frequency throughout this entire temperature range in which case we would not see it. The other reason might be that this motion is only weakly coupled to the ultrasound so that the effect is just too small to see.

This transparency shows results of experiments on the deuterated material. The initial experiments, shown on the top part of the viewgraph, extend down to only about 115 K and go up to 325 K. We see similar-looking thermally activated peaks as for the hydrogenated material. The solid lines represent fits to the data, and the fit parameters indicate that these peaks are due to the slow motion. At this point we were about to stop the experiments concluding that we could not see the fast motion. However, we decided to extend the experiments on the deuterated material to lower temperatures. The results are shown on the bottom part of the transparency. Notice that the vertical axis here is quite expanded as compared to the top plot. The green points represent the hydrogen-free material; it is essentially a flat background. The red is the material with hydrogen, which shows the beginning of the high-temperature peak at about 150 K. The deuterated material, represented in blue, shows the high-temperature peak beginning at about 200 K, but in this case the attenuation rises again at low temperatures – below 50 K. We believe that this low-temperature component to the attenuation represents the fast motion for the deuterium. The reason we see this effect for deuterium and not for hydrogen is most likely due to the fact that the deuterium moves more slowly than the hydrogen. This difference would be expected if the motion is due to tunneling. Most likely the hydrogen motion remains fast compared to the ultrasonic frequency throughout the entire temperature range we investigated. We conclude that we have resolved the two types of motion – fast and slow – for the deuterium. We were able to do this because the experiments were done at low frequencies compared to other techniques which meant that everything shifted to lower temperatures. Since the two processes have different temperature dependencies, they split apart.
I am going to skip a discussion of the fitting parameters for the high-temperature peaks for the TaV$_2$ materials and go to the other system we studied, which was a titanium-based quasicrystal and a crystalline approximate.

[Transparency 12]

These materials were prepared by Ken Kelton's group at Washington University. His group has shown that these materials can absorb substantial amounts of hydrogen, up to a hydrogen-to-metal ratio of 1.6. There has not been much study of hydrogen motion in these materials, because it is relatively new to put hydrogen in them (there has been a preliminary NMR experiment). These materials are interesting for several reasons, including the fact that we can look at hydrogen motion in a nonperiodic potential. We studied two different materials, an icosahedral-phase quasicrystal (i phase) and a W-phase crystalline approximant. The W-phase material is a large lattice constant BCC crystal for which it is believed that the local atomic structure is very close to that of the quasicrystal. H enters, apparently, in solid solution in these materials.

[Transparency 13]

This transparency gives ultrasonic loss data for the i-phase material. The hydrogen-free material shows a fairly flat background loss. We also did experiments on samples loaded to a hydrogen-to-metal ratio of 0.79. There are fairly large attenuation peaks with the hydrogen, and these peaks shift to higher temperatures with increasing frequency as in a thermally activated process. The solid lines are to guide the eye, they are not a fit to any theoretical model. The general shape of the curve, however, suggests that it will not be possible to fit those data with a single activation energy. Most likely several, or a distribution of, activation energies will be needed.

[Transparency 14]

We also did measurements on the crystalline approximate phase, the W phase. The hydrogen-free material shows a relatively flat background loss. The material loaded to a hydrogen to metal ratio of 0.20 gives large ultrasonic loss peaks. In comparing results for the two materials we see that the loss is higher in the i phase than in the W phase, probably reflecting the higher hydrogen concentration (0.79 as compared to 0.20). The hydrogen motion is faster in the i phase (the peaks occur at a lower temperature for a given frequency). Whether this faster
motion is a concentration effect or reflects some basic difference between the \( i \) and \( W \) phases cannot be determined from the present results.

The work on the quasicrystalline materials is of a preliminary nature. Our work is the first to apply ultrasonic methods to the study of Ti-based quasicrystalline alloys. Only recently has it been possible to load these materials with hydrogen in the bulk form needed for the ultrasonic work. We plan to do experiments where we have the same hydrogen concentration in the \( i \)-phase and \( W \)-phase materials. In that way we can use hydrogen as a probe of the local structure. If the ultrasonic attenuation results are different for the two materials when the H concentrations are equal, that will imply that the local structure in the two materials is different.

[Transparency 15]

The final transparency summarizes the results. In the \( \text{TaV}_2\text{D}_{0.17} \) system we find evidence for two types of D motion with two different characteristic frequencies. RUS was able to resolve these two components of the motion.

The present work represents the first ultrasonic, or mechanical spectroscopy, study of hydrogen motion in quasicrystals. The results for the \( i \)-phase and \( W \)-phase materials, loaded to different hydrogen concentrations, are different and suggest future experiments to study this effect.

RUS is a sensitive probe of internal motions in solids. In addition, the RUS experiments occur in a frequency range which is a nice complement to other techniques.

Thank you.

DR. BASS: I will start with the first question. How do you control the amount of hydrogen in these samples and how do you know what it is?

DR. LEISURE: The materials were prepared at Washington University by Ken Kelton's group. They shipped the samples to us. We prepared parallelepipeds and made the RUS measurements on the bare material and then shipped the parallelepipeds back to Washington University to be loaded with hydrogen.

To get the hydrogen to go into these materials they put on a very thin coating of palladium, palladium soaks up hydrogen very readily, and that helps the hydrogen go in. I think they just put the palladium-coated materials in hydrogen gas and raise the temperature.
The hydrogen concentration can be determined quite accurately by measuring the weight gain of the specimen. They are also able to determine how much hydrogen gas is absorbed by monitoring the pressure in a known volume.

In some other hydride materials, where the lattice parameter is well-known as a function of concentration, the concentration can be determined by x-ray measurements of the lattice constant before and after hydrogen absorption.

DR. OGI: How was the activation done?

[Transparency 16]

DR. LEISURE: We determined the activation energy for H and D hopping in TaV$_2$ by fitting the data to an Arrhenius-type expression. In fitting our data, taken at about 1 MHz, we also took into account NMR measurements which were made at around 20 MHz. For H we found it necessary to include two Arrhenius processes to fit results for both types of experiments. The parameters for the two processes are given on this transparency. We "hand-wavingly" attribute these two processes with high activation energy and low activation energy to excitation to some excited state in the well and then tunneling through, and tunneling from the ground state, respectively. For the deuterated material we found that just one single process was sufficient for a description of the data.

Why would the deuterium be different from the hydrogen? If we are right that this second process for H is tunneling through the ground state, then this process might be suppressed for deuterium. Tunneling is highly sensitive to the mass of the tunneling particle and deuterium has twice the mass of hydrogen

DR. MIGLIORI: I just want to make the comment that using transducers very similar to the ones you used we recently saw a Q of 105,000 on [inaudible]. It just tells you that when you are measuring Q's around 1000 to 10,000 you are probably pretty accurate. The instrumental losses are really low compared to the material losses.

DR. LEISURE: Right. Usually we are looking at just changes in Q, not absolute value, and we hope that any instrumental part is just a steady background, but certainly low is better than high in that regard, and it is good to know that that is the case.

DR. DARLING: At the 2 frequencies of lines emitted, did you also determine that they had different mode types, so for instance, on the quasi-crystal was there a difference between
longitudinal mode Q's and transverse mode Q's? With a complex crystal structure you may change the energies of the fast and slow modes differently with different types of motions.

DR. LEISURE: We did determine the modes for the lower frequencies. Some of the results I put up were at about 2 MHz and I do not think we determined the modes to that high a frequency, but for the lower frequency ones -- well, for the first 45 to 50 resonances, we identified the modes, but I do not have that information with.

My general picture, which may be incorrect, is that different modes will usually reflect the same motion, but the coupling constant will almost surely be different. In looking at different modes, the peak height of the attenuation peak may be different due to the different modes and different coupling, but I think, unless there is really something strange going on, that the actual shape of the curve should be the same for the different modes, because I think that is just reflecting the same hydrogen motion.

DR. SACHSE: In your experimental setup you had a source and then the transducers and the parallelepiped and receiver. Did you actually record the original waveforms or did you have a commercial system that mapped out what were the amplitudes of the various modes?

DR. LEISURE: We used the DRS system, which records the in-phase and out-of-phase parts of the signal and computes Q. We did something else for the quasicrystals. These are small samples, and when the attenuation gets very high we have problems with some coherent background feeding through. We modeled that coherent background and then fit each individual scan to a Lorentzian line shape plus some coherent background. We determined the Q from such a fit. We did not do that for the TaV₂ material, but the scatter could probably be improved if we went back and did it that way.

Thank you.