LISTENING TO MATERIALS: FROM AUTO SAFETY TO REDUCING THE NUCLEAR ARSENAL

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Acoustics is an essential tool for 21st century society. From arts to science to business and everyday life, the use of acoustics, beyond the built-in communication tool we all possess, is ubiquitous. In this article, we focus on one aspect of acoustics—the application of acoustic resonances to probe the properties of materials and objects. Such an application has a significant impact on us all as it connects to science, engineering, quality control, public safety and protection (including military applications), and more. For example, the use of acoustic resonances to study the material properties of plutonium has improved the confidence that our military possesses in present-day thermonuclear weapons. This has enabled the US nuclear weapons science-based stockpile stewardship program to support reduction of the nuclear arsenal from more than 36,000 to just above 5,000 today. In another more commonplace example, resonances are used today to inspect the disc brake rotors of automobiles in a production environment with very high throughput. In this application, the acoustic “signature” of an automobile part coming off an assembly line can be used to determine if the part is “good.” The basic idea for this is very old. During the steam-age, one of the more unusual jobs found at railway stations was that of the carriage and wagon inspector, or wheel-tapper as they were affectionately known—when a train paused for any period at the station, the wheel-tapper would walk the length of the train, checking the wheels for signs of stress or fracture. He would do this by striking each wheel with a special long handled hammer and listen to its “ring.” Because cracked wheels, like cracked bells, do not sound the same as their intact counterparts, a good wheel-tapper could identify a defect by the sound his strike made. If a problem was found, the wheel-tapper would report it, the train would be delayed and the defective vehicle removed.

Modern maintenance procedures have mostly eliminated the need for the wheel-tapper, but the “tap-and-ring” approach to determine a material’s properties and/or quality has become a vital tool in a material scientist’s laboratory. With the material to be measured held lightly between a drive transducer (the “tap”) and detecting transducer (the “ring”), the frequency of the drive is swept and a sequence of resonance peaks can be recorded which, when processed along with the shape and mass, will yield all the elastic constants for the material. Or, in another application of resonances, changes in the resonance pattern or deviations in the spectrum from “known good” spectra are useful, nondestructive tests for quality control. This contemporary adaptation of the wheel-tapper’s technique is known as Resonant Ultrasound Spectroscopy (RUS), and its precise measurements of elastic constants have furnished valuable information about materials.

Basic principles of RUS

The idea of using resonances to study the elastic response of a material goes back to the 1960’s, when Schreiber, Anderson, Soga, and Warren and Demarest developed computational procedures to find the elastic moduli for millimeter-sized mineral samples. RUS, in its present form, was developed in 1988 by Migliori and Visscher, who—with the advantage of modern computing power—developed sophisticated codes and turned RUS into a powerful method for measuring elastic constants of materials with a variety of shapes and symmetry. Mechanical resonances can be calculated for a sample with known dimensions, density, and elastic tensor, laying the basis for the reverse process—going from resonances to material properties. In a RUS experiment, the frequencies of mechanical resonances of a freely vibrating solid of known shape are measured, and an iterative procedure is used to adjust elastic constants until the calculated spectrum corresponds to the measured frequencies. In this way, all elastic constants are determined from a single frequency scan, a clear advantage of RUS. There is no need for separate measurements to measure different moduli, and multiple sample remounts and temperature sweeps are avoided. Figure 1 shows the original RUS set-up, where the sample was lightly held at opposite corners between two transducers, eliminating bonding agents that can be particularly bothersome at low temperatures. Another advantage lies in the abil-
ity of RUS to work with small samples. Whereas conventional techniques can demand a sample dimension up to a centimeter, RUS measurements can be made on samples a fraction of a millimeter in size.

Since its development, RUS has proven to be a valuable technique for materials research. Not only can the magnitude of the elastic constants—and sound velocity—be measured at room temperature with high accuracy (the shear modulus is usually determined with a precision of 0.05% or better), RUS can easily be performed as a function of temperature. Such measurements are very useful for studying thermodynamically-driven changes in the free energy such as phase transitions and local modes. In such cases, RUS has established itself as a very powerful tool.

Figure 2 shows a low-temperature probe and transducers set for RUS in high magnetic fields. This allows RUS measurements to be taken as a function of temperature between 300 mK and 350 K and in magnetic fields up to 15 Tesla. The magnetic forces exerted by the field on ferromagnetic samples tend to launch such specimens into the surrounding exchange-gas space, because the samples are typically only loosely held between the transducers, as illustrated in Fig. 1. The newly designed transducers use a “flat-mount” approach, making it possible to keep the sample in place even when high magnetic fields are applied.

For samples with irregular shape or symmetry lower than orthorhombic, the procedure for calculating the elastic moduli from the resonances becomes more involved, but RUS measurements can give important information even without an absolute value for the elastic constants. Any deviation from “normal” thermodynamic behavior will be reflected in the temperature-dependence of the resonant frequencies, and these can be measured and interpreted without long computation.

Extensions of RUS that were motivated by interesting samples

Typically, RUS samples are polished into rectangular parallelepipeds, cylinders or spheres, a few millimeters or larger in size, and these shapes and sizes are readily handled with the conventional RUS technique. However, very new materials may pose some problems that require modification of the conventional method. For example, single-crystal samples of very new materials often are available only in small sizes—crystalline samples of new exotic materials may have dimensions of only a few hundred microns, and the sample masses may be less than 100 µg (one sample measured with RUS was only 70 µg). Such small samples virtually appear as
specks of dust. The major difficulty for such small samples arises from the notion that for resonance, “the part that is being measured is the part that is storing the energy.” Thus a small sample requires small transducers—if one is to measure the properties (e.g., temperature dependence) of the sample, rather than those of the transducers, then the transducers must be sufficiently smaller than the sample. In a similar fashion, reducing the transducer loading of a small sample requires small transducers. Another requirement for the transducers occurs because the small samples have high natural frequencies, and this necessitates that the transducers be broadband. These restrictions led to the use of transducers made of thin piezoelectric film, polyvinylidene fluoride (PVDF), with dimensions of only 500 x 500 x 9 microns (Fig. 3).

A second potential problem is that some new materials are intended for applications for which the material must be in the form of a thin film on a substrate. The lattice mismatch between the substrate and the film produces strain and a shifted potential energy field for the new material. This results in modified (and presumably improved) properties for the new material. The strain mechanism causing the altered properties is readily probed by measuring the elastic properties of the film. The difficulty is that to measure the elastic constants of a film on a substrate, the film must occupy a sufficient fraction of the whole sample. Roughly, if one can measure resonant frequencies to about ten parts per million, then the sample should be about 1/1000 of the whole sample. A film of a few hundred nanometers should be on a substrate with a thickness of a few hundred microns. Such samples are readily measured with the small sample RUS described above.

A third problem that may occur with new materials is that samples may be fragile or chemically reactive so that polishing into a suitable shape for RUS is too risky. Such samples must be used “as is,” and the RUS’s theory must be modified to apply to an arbitrary shape. For such samples the Visscher RUS analysis is replaced with a finite element method. For the analysis, the shape of the sample as well as the acoustic field inside is fit with “isoparametric shape functions,” and a sophisticated computer code is used to find the eigenvalues and eigenfunctions of a matrix with a size as large as 20,000 x 20,000 elements.

**Thermoelectric rattlers**

Anybody regularly filling the gas tank of a car has most likely wondered how to increase the number of miles the car travels on a gallon of gas. Realizing that two-thirds of a car’s fuel is emitted unused in the form of heat, makes one wonder if a significant portion of this waste-heat could be recovered and improve the car’s mileage. A generator using thermoelectric materials could, in principle, accomplish this feat. Thermoelectric materials, that are also found in the portable cooler that is powered from your car battery, generate electric currents when heat is applied and induce a change in temperature when an electric current passes through them. Not only could these materials lead to a noticeable reduction in fuel consumption, they could also replace today’s refrigerator-compressors with systems that have no moving parts and are ozone-layer friendly. So why is not every car and kitchen equipped with thermoelectric generators and refrigerators? There is a catch-22—the greatest thermoelectric efficiency comes from materials that have very good electrical conductivity, but poor heat conductivity. Unfortunately, only a handful of materials fit in this category, and thermoelectric research is focusing on increasingly complex materials that can reconcile these requirements. One set of materials that have promising thermoelectric properties are semiconductor structures (hosts) that contain large, open voids. The ability to populate these voids with other atoms (guests) makes them useful thermoelectrics. The guests tend to “rattle” in the oversized structure, which leads to a dramatic decrease in the thermal conductivity, while good electronic conductivity is maintained by the host.

Before looking into the elastic properties of these novel thermoelectric materials, it might be useful to briefly display “normal” elastic behavior. Such “normal” behavior is typified in Fig. 4—the elastic moduli gradually increase with decreasing temperature, and level off at low temperatures. The rattling guest atoms in the structures discussed in this section provide an elastic system of slightly more complex behavior, and the
rattlers leave a distinct fingerprint on the elastic response of the material. This is shown in Fig. 5 where the temperature-dependence of the shear modulus $c_{44}$ is plotted for $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$, $\text{Sr}_8\text{Ga}_{16}\text{Ge}_{30}$, and $\text{Eu}_8\text{Ga}_{16}\text{Ge}_{30}$, compounds known as clathrates. Ga and Ge form the host structure, while Ba, Ga, and Eu are the rattlers, residing in the oversized cage. The data were taken on single crystals, using RUS in a temperature region from 3 K to 300 K. The figures illustrate that these three materials— with very similar structure—behave quite differently. The Ba-clathrate shows an almost normal behavior, the Sr-clathrate shows a small but relevant “dip” at low temperatures, and the Eu-clathrate displays a very unusual temperature-dependence, reaching a maximum at about 100 K, before plunging down.

The difference in behavior between the three compounds can be related to the size of the rattler and its position in the cage. The insets in Fig. 5 show what is known as the nuclear density, i.e., the probability of finding the Ba, Sr, or Eu nucleus at different positions near the center of the cage. For Ba, a relatively large atom, the probability is clearly centered at the center of the cage, but somewhat smeared, consistent with the picture of an atom that is rattling around its equilibrium position. The Sr nuclear density is even broader than that for the Ba atoms and indicates a substantial probability for the Sr atom—which is smaller than the Ba atom—to move off the site center to one of four crystallographically equivalent positions. The Eu nuclear density distribution unmistakably shows the tendency of the Eu atoms to move away from the site center. Four separate peaks are resolved in the nuclear density maps, indicating four equivalent positions for the tiny Eu atom to reside inside its oversized cage. Instead of being a simple rattler, moving around its central position, the rattling Eu atom is more adequately described as traveling between the four equivalent positions in the cage, resulting in a dramatic decrease in the elastic constants at low temperatures.

**Unusual thermal response**

Resonances can also help to unravel puzzling behavior of solids with strange thermal behavior that are of increasing importance as micro-scale silicon-based devices come into use. Historically, solids with negative thermal expansion coefficients and elastic stiffnesses with a temperature-dependence that is opposite to “regular behavior” have been essential in solving the “longitude problem,”i.e., the problem of determining one’s longitude while at sea for many months. Noting that most solids expand and soften on warming, new materials with zero thermal expansion or zero change in stiffness on warming were needed to construct well-temperature-compensated mechanical clocks. In 1897, Guillaume discovered an amazing alloy of Fe containing 35% Ni. That alloy—now known as Invar—exhibited the remarkable property of zero thermal expansion and was of such great technological importance that its discoverer received the 1920 Nobel Prize in physics. Poorly understood, the effect’s origins became especially puzzling when Grüneisen in 1912 proposed a way of understanding the general problem of thermal expansion by relating the variation of elastic stiffness with pressure to variation in the volume with temperature in an elegant general way. His theory worked for a remarkable variety of materials but not for $\text{Fe}_{65}\text{Ni}_{35}$.

Today, the promise of micro-scale devices for applications where a precise temperature-independent mechanical response is needed requires that the mainstay-semiconductors of lithographically produced micro machines have mechanical responses compensated by materials with “backward” thermal properties. From liquid helium temperatures to just above room temperature, $\text{ZrWO}_8$ has a negative thermal expansion coefficient. That is, this cubic-structure...
material shrinks as it is warmed. But what does its elastic stiffness do on warming? To put it in perspective, Invar, when warmed, has no volume change. It acts as if it “tries” to expand but internal forces “compress” it at the same time. This “compression” makes Invar stiffen as it heats, just the way most materials stiffen when compressed. ZrW$_2$O$_8$, shrinking with temperature, behaves as if it is strongly compressed on warming. But measurements using RUS of the bulk modulus, the parameter that describes the resistance to hydrostatic compression, show that it decreases with increasing temperature. Thus, this solid material softens as it is compressed. How can this be? And what would happen if the temperature were held constant and ZrW$_2$O$_8$ were put under pressure? Using pulse-echo ultrasound measurements in a SiC pressure cell, it was found that ZrW$_2$O$_8$ softens when compressed, completing the puzzling picture of this strange solid. The root of this behavior, revealed by ultrasound, can be visualized with the cartoon in Fig. 6.

**Listening to plutonium**

Plutonium (Pu), a fuel for nuclear energy production, and a fuel for the triggers of thermonuclear weapons, is of essential importance to the security of the United States. With the Nuclear Non-proliferation Treaty of 1968 and the Comprehensive Test Ban Treaty of 1996, the safety of our nuclear arsenal, now down to just over 5000 warheads, falls upon science-based predictive capabilities for understanding essential physical properties of Pu such as compressibility, chemistry, and radiation-induced effects on aging. With six allotropes (crystal structures) and irregular melting behavior, plutonium presents a perplexing array of physical properties, still much studied, both experimentally and theoretically.

The simplest of the six crystal structures, δ-plutonium, displays the most puzzling properties. Besides having the highest atomic volume of all Pu-structures, it displays extreme elastic anisotropy, negative thermal expansion, a strong response to alloying, and large volume changes during transformations to adjacent phases. It also shows strong elastic softening with increasing temperature, an extreme behavior among densely-packed elements. Much of the strange behavior of Pu, perhaps the second most interesting element after He, is often ascribed to the outer electron shell (containing the so-called f-electrons) of Pu introducing instabilities into the fundamental electronic properties that control all of the non-nuclear oddities. That is, these outer electrons cannot decide whether to be “localized,” making Pu less metal-like, or “itinerant,” making it more metallic. This vacillation turns out to be sensitive to temperature and volume. Using many techniques, the structure of δ-Pu has been found to shrink on warming. Adding about 2.4 atomic % Ga to Pu changes the thermal expansion coefficient to zero above
about 350K. Thus nature has provided us with a special alloy of Pu that behaves in most ways the same as pure Pu, but with the powerful benefit of not changing volume with temperature. How can we use this to improve our understanding of this still-mysterious metal? Using RUS, the bulk modulus of Pu has been measured recently over the full temperature range of the first three phases of pure Pu,19-21 and moduli of the gallium-stabilized fourth phase as well.22 The findings are remarkable. Unlike ZrW₂O₈, Pu is an elemental metal and so has no complex structures to assist with an understanding of the zero thermal expansion alloy. But invar, which experiences a gradual change from one phase to another over a temperature range around room temperature, provides a clue. The high temperature phase has a smaller volume than the low temperature phase, so by adjusting composition, as temperature rises, just enough high temperature phase grows to keep the volume constant. Can the same thing happen with Pu? Maybe, and ultrasound certainly can help with understanding, if not providing the still unknown answer. From RUS measurements of the compressibility of δ-Pu-2.4 at. % Ga, we find that this alloy, now stable to well below room temperature, exhibits stunningly large (near 30%, compared to 3.5% for Cu) softening of its compressibility in a smooth way from 10⁰K to above 400⁰K. Figure 7 shows this softening. The measurements are exceedingly difficult because of the safety and security issues involved, and the simplicity of RUS, with its lack of a transducer bond requirement (glue doesn’t last long on highly radioactive materials) has made accurate and comprehensive studies possible for the first time. However, the results are both tantalizing and important. What we find is that even though the spacing between the constituent atoms is not changing at all, the electronic structure, which is a key component of the compressibility, varies wildly. How can this be? A second clue, provided by RUS, is the absolute value of the elastic moduli. These are very low, even lower than Pb, making the amplitude of thermally-induced atomic vibrations very large for a given temperature. Can this be the answer? That is, electron localization occurs because for a fraction of the time the vibrating Pu are close together, and for a fraction of the time they are far apart, a consequence of the elastic softness of the material. Thus acoustics suggests a dynamically-induced effect, something beyond the capability of current models.

A final word

The examples above have barely begun to unveil the many aspects of Resonant Ultrasound Spectroscopy for the study of materials. Many other accounts of RUS are available in literature. And many other applications of sound to various solid state problems have been reported. Acoustics has provided an important tool in materials research, and is expected to remain a useful instrument for understanding and testing new materials. After all, it is mainly through listening that we learn.

References


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