Resonant Ultrasound Spectroscopy

With a means of measuring a sample's natural resonance frequencies and a desktop computer, one can use resonant ultrasound spectroscopy to determine the elastic constants of a broad range of crystalline and noncrystalline materials.

Julian Maynard

When a new crystalline material is discovered, one of the first fundamental properties to be determined is the atomic structure, defined by the minimum in the free energy with respect to the positions of the atoms. Another fundamental characteristic of interest is the curvature of the free energy in the vicinity of the minimum, and this would be manifest in the elastic constants for the material. As derivatives of the free energy, elastic constants are closely connected to thermodynamic properties of the material. They can be related to the specific heat, the Debye temperature and the Gruneisen parameter (which relates the thermal expansion coefficient to the specific heat at constant volume), and they can be used to check theoretical models. Extensive quantitative connections among thermodynamic properties can be made if the elastic constants are known as functions of temperature and pressure. The damping of elastic waves provides information on anharmonicity and on coupling with electrons and other relaxation mechanisms. The elastic properties are perhaps most valuable as probes of phase transitions, such as superconductivity transitions. Clearly precise and accurate measurements of elastic constants furnish significant information about materials.

Elastic constants, like spring constants, can be determined by means of a static technique that measures a displacement as a linear response to a small applied force. However, it was learned long ago that a better method is to measure an elastic vibration, as found, for example, in a propagating sound wave. Most existing complete sets of elastic constants for materials have been determined by measuring the time of flight of sound pulses.

More recent determinations of elastic constants have used a technique called resonant ultrasound spectroscopy (RUS), in which one measures the natural frequencies of elastic vibration for a number of a sample's normal modes, and processes these, along with the shape and mass of the sample, in a computer. With a proper configuration, a single measurement yields enough frequencies to determine all of the elastic constants for the material (as many as 21 for a crystal with low symmetry). Samples may be prepared in rectangular, spherical and a wide variety of other shapes, and crystalline samples need not be oriented with respect to their crystallographic axes. Samples may be as small as a few hundred microns, with masses less than 100 micrograms, or they may have dimensions of several centimeters and masses of several kilograms. (See figure 1.) The largest sample yet tested with an acoustic resonance method was a bridge spanning the Rio Grande River. RUS shifts the emphasis from experimental technique to digital data analysis. In the data analysis, one must first solve the problem of calculating the natural frequencies in terms of elastic constants and sample shape and mass (this is known as the forward problem), and then apply a nonlinear inversion algorithm to find the elastic constants from the measured natural frequencies (the inverse problem). While the methods used in RUS are not new, it is only with the recent increasing availability of powerful microcomputers that RUS has experienced a rapid growth in popularity.

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History of RUS

Interest in elastic properties dates back to studies of the static equilibrium of bending beams by Galileo and other 17th-century philosophers. With the basic physics introduced by Hooke in 1660, the development of the theory of elasticity followed the development of the necessary mathematics, with contributions from Leonhard Euler, Joseph Lagrange, Siméon-Denis Poisson, George Green and others. The resulting theory was summarized in the treatise by Augustus Love in 1927.[1]

The theory of elasticity indicated that the elastic constants of a material could be obtained by measuring sound velocities in that material. This led to the conventional time-of-flight measurements with ultrasonic pulses. Natural frequency measurements were used at least by 1935,[2] but the early methods could find only approximate solutions to the forward and inverse problems.

Around 1880 Gabriel Lamé and Horace Lamb found analytic solutions to the forward problem for some special shapes (cubes and spheres) for isotropic, noncrystalline, materials. In 1964 D. B. Frasier and R. C. LeCraw used the solution for a sphere of isotropic material, inverted graphically, in what may be the first RUS measurement.[3] The problem of crystalline materials was considerably more difficult. Although some perturbative methods were developed for crystalline materials, it was not until after 1956 that the power of digital computers made the more general forward problem soluble.[4,5]

Much of the impetus for solving the inverse problem came from the geophysics community, where solutions were needed to use seismic data (particularly Earth's free-oscillation modes) to determine Earth's interior structure, and to measure accurately the elastic moduli of materials believed to be Earth's constituents. The studies

Vol. 49

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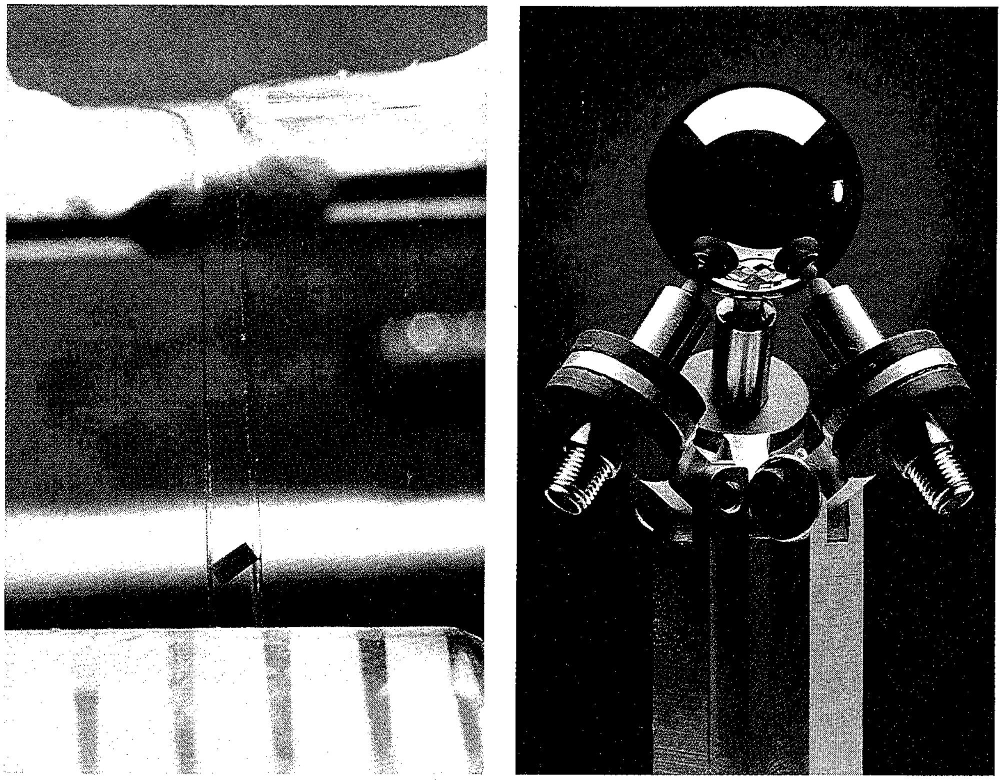


RUS MEASUREMENTS can be taken for a variety of samples and with a variety of apparatus. **a:** A device using thin piezoelectric films has been used to measure samples with masses down to 70 micrograms. In this photo, the space between divisions on the scale is 1 millimeter. (From ref. 17.) **b:** RUS has also been used to detect defects in ball bearings several centimeters in diameter. (Courtesy of Quatro Corporation, Albuquerque, New Mexico.) FIGURE 1

of elastic moduli led to further use and development of RUS, in particular by geophysicists Orson Anderson, Naohiro Soga, and Edward Schreiber, who collaborated at Columbia University to improve the method of Frasier and LeCraw and introduced the term resonant sphere technique (RST). Anderson and Schreiber generated excitement when they used RST to measure spherical lunar samples in 1970. In their paper they quoted Erasmus—"With this pleasant merry toy, he . . . made his friends believe the moon to be made of green cheese"—and they compared the low sound speed in lunar rock to sound speeds in various cheeses. Although the velocities were comparable, the cheeses were of much lower mass density. However, Anderson noted that the difference "may readily be accounted for when one considers how much better aged the lunar materials are."[6]

Encouraged by the excitement the lunar measurements had generated, Anderson gave his Columbia University student Harold Demarest the problem of extending the method for use with a cubic sample. Demarest found that the problem could be solved numerically for a rectangular parallelepiped of an anisotropic, crystalline material as well as for spheres of isotropic materials. Demarest's method, verified with experiments, was published in 1971,[5] and was later referred to as the rectangular parallelepiped resonance (RPR) method.

A postdoc at Columbia University, Mineo Kumazawa, learned Demarest's method, and upon joining the faculty at Nagoya University, pursued the technique with graduate student Ichiro Ohno. In 1976 Ohno published a paper[7] with some significant extensions to Demarest's work. Together, the papers of Ohno and Demarest cover nearly all of the important aspects of RUS. Researchers in geophysics have used RST and RPR extensively since 1976.

In 1988 Albert Migliori and I were collaborating on an attempt to measure sound velocities in very small crystals of high-T_c superconductor material then available, using small piezoelectric film transducers.[8] When the problem of what to do with measured resonance frequencies had to be faced, Migliori tracked down the references describing RPR in the geophysics literature (confirming his wry observation that, "six months in the lab can save you a day in the library"), and the RPR technique was introduced into the general physics community. Migliori immediately extended the limits of the technique with regard to loading (the shifts in a sample's natural frequency resulting from attaching transducers) and low-level electronic measurement, and with William Visscher brought the computer algorithms to their current state. I applied the technique to even smaller samples (70 micrograms is the current record) using piezoelectric films. Promoting the technique in the physics community, Migliori introduced the term *resonant ultrasound spectroscopy* to encompass all techniques in which ultrasonic resonance frequencies are used to determine elastic moduli. For the current state of RUS theory and apparatus, see references 9–11.

Finding elastic constants

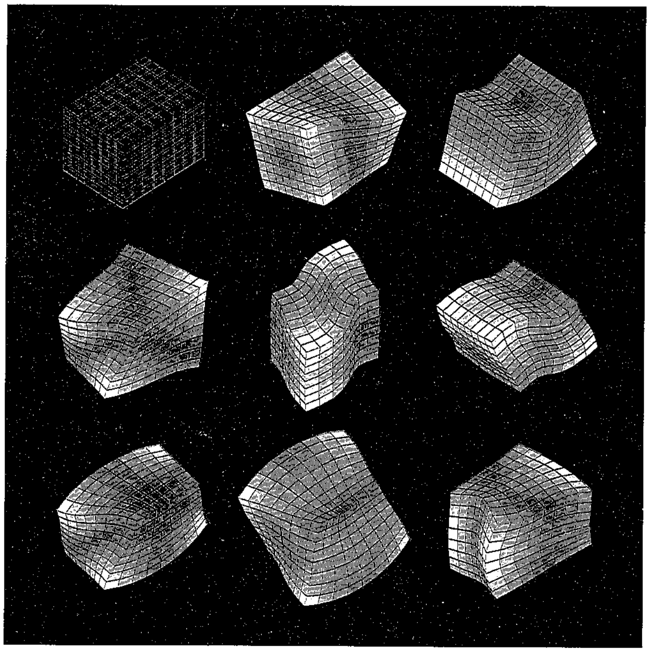
If a spring under an initial tension is subjected to an additional stress σ, two points at positions x and $x + dx$ will be displaced by $\psi(x)$ and $\psi(x + dx)$, respectively. The strain ε is then equal to $d\psi/dx$, and Hooke's law is $\sigma = c\varepsilon$, where c is a one-dimensional elastic constant. For a three-dimensional elastic solid, the displacement becomes a three-dimensional vector $\boldsymbol{\psi}$. The strain is defined as $\varepsilon_{ij} = \partial\psi_i/\partial x_j + \partial\psi_j/\partial x_i$. Hooke's law becomes

$$\sigma_{ij} = \sum_{k=1}^{3}\sum_{l=1}^{3} c_{ijkl}\varepsilon_{kl} \tag{1}$$

and Newton's second law for a small volume element with mass density ρ is

$$\sum_{j=1}^{3} \frac{\partial\sigma_{ij}}{\partial x_j} = \rho\frac{\partial^2\psi_i}{\partial t^2} \tag{2}$$

The symmetry of the definitions and the assumption



COMPUTER-GENERATED ILLUSTRATIONS of some normal modes of vibration for a rectangular parallelepiped of anisotropic crystalline material. The mode displacements depend non-trivially on all of the elastic constants, and a powerful computer is required to sort out the relationships. Animated illustrations are available at http://www.phys.psu.edu/MAYNARD/maynard.html on the World Wide Web. FIGURE 2

that the elastic energy must be quadratic in the strains reduce the number of independent elements of c_{ijkl} from 81 to 21. Additional symmetries of a particular crystal group further reduce the number of independent constants. For example, cubic crystals have three independent elastic constants, while orthorhombic crystals have nine.

To determine the modes of vibration, one solves equations 1 and 2 assuming stress-free boundary conditions at the surface of the sample:

$$\sum_{j=1}^{3} \sigma_{ij} n_j = 0 \qquad (3)$$

where the n_j are the components of the unit vector normal to the surface. Because of the tensor nature of the equations, the relation between particle displacement and the direction of wave propagation is quite complicated. One uses a computer first to solve numerically the forward problem for the natural frequencies in terms of the elastic constants for a solid with a given shape and stress-free boundary conditions and then to invert the resulting complicated matrix equations. Assuming a time dependence proportional to $\cos(2\pi ft)$, solutions to equations 1–3 exist only for those values of f that are natural frequencies. Examples of computer-generated normal modes of vibration found by solving the forward problem for a typical anisotropic sample are illustrated in figure 2.

The boundary value problem described by equations 1–3 can be replaced by a single variational problem. It is interesting to note that the variational problem yields not only the differential equation for ψ, but also the stress-free boundary conditions. To quote Visscher, getting both equations from the basic Lagrangian is "a mathematical fortuity that may have occurred during a lapse in Murphy's vigilance."

One can find approximate solutions to the variational problem using the Rayleigh–Ritz method, in which one approximates ψ_i as a linear combination of N basis functions Φ_p:

$$\psi_i = \sum_{p=1}^{N} a_{pi} \Phi_p \qquad (4)$$

Minimizing the resulting Lagrangian with respect to the coefficients a_{pi}, one obtains a $3N \times 3N$ matrix eigenvalue problem that can be solved with a computer algorithm, yielding the resonance frequencies of the system and the expansion coefficients from equation 4. The expansion coefficients can be substituted into equation 4 to construct normal modes like those shown in figure 2.

The basis functions should be selected to give well-conditioned matrices and to permit analytic evaluation of the integrals involved. Early work on uniform rectangular parallelepipeds used Legendre polynomials. Because these were orthogonal, the matrix problem was considerably simplified and could be solved with a faster computer algorithm. However, Visscher pointed out that using basis functions of the simple form $x^l y^m z^n$ allowed analytic evaluation of the integrals involved for a large number of shapes, including prisms, spheroids, ellipsoids, shells, bells, eggs, potatoes, sandwiches and others. The great versatility of this basis set more than compensates for the slight increase in time required to compute the solution.

To obtain a good approximation to the correct solutions and natural frequencies, it may be necessary to use as many as 400 basis functions. However, for most crystal types it is not necessary to solve the eigenvalue problem for a full 1200×1200 matrix—because of the symmetry of the elastic tensor, a proper arrangement of basis functions will put the matrix into block diagonal form. The eigenvalue problem for each block can be solved independently, with significant savings in computation time. For example, for orthorhombic or higher symmetry, the matrices may be reduced to eight blocks, resulting in a nearly eightfold reduction in computation time. The details of the manipulation of the basis functions are in the paper by Ohno.[7]

For RUS, one must invert this forward problem to obtain the elastic constants c_{ijkl} in terms of the resonance frequencies f_n. In most cases, there will be more measured frequencies than independent elastic constants, so one seeks the set of independent elastic constants that best fits the measured frequencies, usually in a least squares sense. In both the forward and the inverse problems, it is advisable to manipulate the matrices with singular value decomposition[12] because this technique allows one to monitor the conditioning of the matrices. In the inverse problem, the appearance of small singular values in such a decomposition indicates elastic constants that were not well determined from the measured frequencies, perhaps because the sample had a pathological shape. One can also define linear combinations of elastic constants which are best determined by the measured frequencies.

To solve the inverse problem, one may start with a "guessed" set of elastic constants in the forward problem and then use an iteration procedure to find the set of constants that best fits the measured frequencies. Provided that the "guessed" elastic constants used to start the iteration procedure are close to the actual values and that the forward-problem normal modes are correctly assigned to the measured resonance frequencies, the inversion should typically converge to the elastic constants after a fraction of an hour of desktop computer time. These points are discussed below in the description of the measurement methods.

Because a typical RUS measurement will usually provide many more frequencies than the number of independent elastic constants, the measured frequencies can also be used to give a best fit to other parameters, such as the sample's shape and dimensions (although one known length is necessary) and the orientation of its crystallographic axes relative to its faces. In any case, one need not orient the crystallographic axes with respect to the sample faces, although this does greatly simplify computations. For RST, the orientation of crystallographic axes is irrelevant for determining the elastic constants.

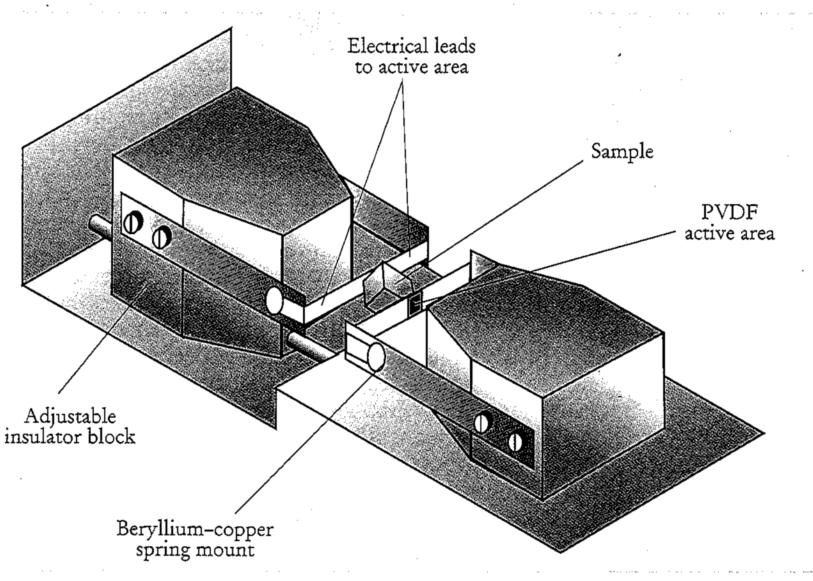
Measurement methods for RUS

A general RUS measurement[10,11] determines the natural frequencies of a sample with stress-free boundary conditions by measuring the resonance frequencies of the sample when it is held lightly, with no bonding agents, at two positions on the sample surface between two transducers. One transducer drives vibrations in the sample at a tunable frequency; the second measures the amplitude (and possibly the phase) of the sample's response. As the frequency of the drive is swept, a sequence of resonance peaks is recorded. The positions of the peaks occur at the natural frequencies f_n (from which the elastic constants are determined), and the quality factor (Q, given by f_n divided by the full width of a peak at its half-power points) for each resonance provides information about the dissipation of elastic energy.

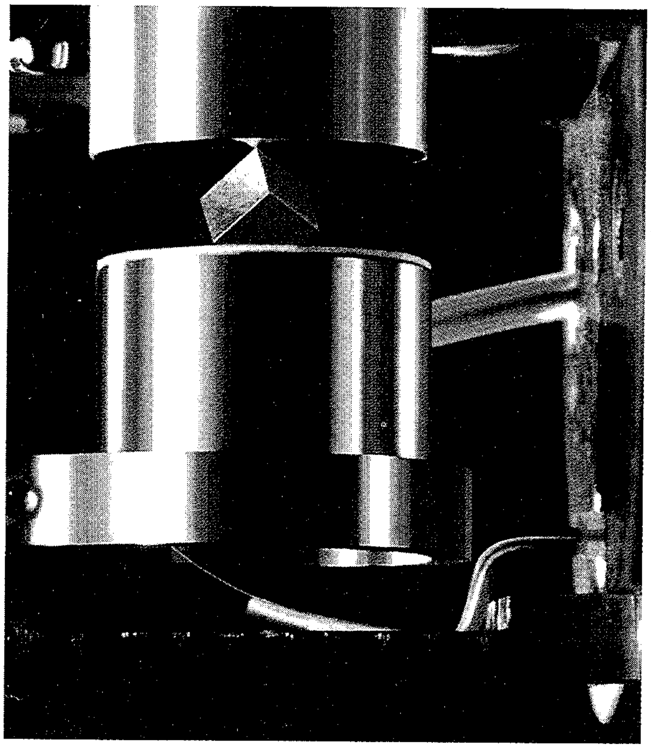
In order for the resonance frequencies to equal the natural frequencies with sufficient accuracy, one must minimize the loading of the sample by the transducers. Samples can be measured with loadings only slightly greater than their weight, resulting in a measurement accuracy on the order of a tenth of a percent. This is generally no worse than the accuracy to which the sample's size and shape are known. Independent of the accuracy, the precision of the measurement is usually on the order of a few parts per million, and this helps when investigating small changes as a function of temperature or pressure and when probing phase transitions and related phenomena.

It is worth noting that in a conventional ultrasonic pulse measurement, great pains are taken to maximize the coupling between the transducer and the sample, so that the resonating transducer can deliver the largest possible amplitude to the non-resonating sample.[10] In a method that resonates the sample, strong coupling is not necessary, because at resonance, the sample acts as a natural amplifier with a gain equal to the Q (typically 1000 to 10 000), and readily measured sample amplitudes are generated. An additional advantage of resonating the sample is that when measurements change as a function of temperature, pressure and other variables, one can be confident of measuring changes due to the sample, rather than to the transducer or transducer bonding agent. Yet another benefit of a resonance method is that it uses continuous wave excitation, allowing one to employ phase-sensitive detection methods to extract signals from noise. This feature, along with the large gain at the sample resonance, permits RUS measurements in the presence of thermal noise at high temperatures.[13]

A simple apparatus for making RUS measurements is shown in figure 3.[10] In the illustration, a rectangular parallelepiped sample is supported by transducers at diametrically opposite corners. Corners are used for contact because they provide elastically weak coupling to the transducers, greatly reducing loading, and because they are always elastically active (that is, they are never nodes) and thus couple to all of the normal modes of vibration. The two transducers in this apparatus consist of 9-μm thick polyvinylidene fluoride (PVDF) piezoelectric film,[10] cut into strips about 500 μm wide. The strips are partially metallized on each side, so that conducting portions overlap in the central part of the strip, forming a capacitor sandwiching the piezoelectric film. Electrical contact is made by means of the metal film on the strip to metal spring mounts, which maintain a small tension in the strips. One adjustable transducer block is brought toward the other until the sample is just supported by its corners at the centers of the strips; no bonding or ultrasonic coupling agent is required. As in the general RUS measurement, one transducer drives the sample and the other



SIMPLE RUS APPARATUS holds a rectangular parallelepiped sample lightly at its corners between two 9-μm-thick piezoelectric-film (PVDF) transducers One transducer excites the vibration of the sample; the other monitors the sample response and detects resonance frequencies. Samples may be as small as a few hundred microns. (Adapted from ref. 10.) FIGURE 3



SOPHISTICATED RUS APPARATUS supporting a sample at its corners. The operation is similar to that of the apparatus in figure 3, but the transducers are piezoelectric disks backed by diamond cylinders. With this apparatus, the orientation of the sample between the transducers can be varied, allowing better determination of the mode to which a measured frequency belongs. (Photograph courtesy of Albert Migliori, Los Alamos National Laboratory.) FIGURE 4

monitors the sample resonances. Because the thin piezoelectric film has a low value of Q, its resonances do not interfere with the sample resonances. This simple apparatus can be used for samples as small as a few hundred microns.

A more sophisticated RUS apparatus is illustrated in figure 4. As in the apparatus just discussed, the transducers contact a rectangular parallelepiped sample at its corners. Constant loading is maintained (even if the temperature is varied) with a balanced, pivoted lever like the tone arm of a phonograph. The transducers are conventional piezoelectric disks bonded to diamond cylinders to increase the resonance frequencies of the transducers so that they do not interfere with those of the sample. In this apparatus, the lower transducer may be moved laterally while measurements are being taken, yielding additional information that can be used to identify the normal modes.

As mentioned in the theory section, an important consideration for the convergence of the RUS data analysis procedure is that the normal modes excited in the measurement be correctly identified, in order that the measured frequencies may be matched with the corresponding frequencies determined in the forward problem. A number of clever techniques for identifying the modes are discussed in the RUS literature.[5,7,10,11] These include (1) using good values for the initial elastic constants (possibly theoretically predicted or obtained from incomplete pulse measurements) and assigning each experimental frequency to the closest estimated frequency; (2) varying the size of the sample and using the rates of change of the frequencies for identification; (3) switching assignments for frequencies most likely to cross during the iterations and searching for the best fit;[10] and (4) varying the orientation of the sample relative to the transducers and monitoring changes in the signal amplitude,[11] as mentioned in the description of the second apparatus above. For different normal modes, the sample corner vibrates in different directions; hence, changing the sample's orientation relative to the transducer varies the transducer signal amplitude in different patterns. These patterns can be used to identify the normal mode.

An important application of RUS is the determination of elastic constants for a material at temperatures significantly higher than its Debye temperature. At such high temperatures, however, the performance of ultrasonic transducers is severely degraded and bonding agents for conventional pulse measurements fare even worse. In 1988 Anderson[13] solved this problem with a variation of the RUS method, illustrated in figure 5a. In this variation, the sample was supported between the ends of long, thin alumina buffer rods which extended outside a high-temperature oven, allowing the transducers to be mounted at the outer ends of the rods at a safe temperature. One might suspect that the long rods would have many resonances which would obscure the resonances of the sample, but it turns out that the resonances of the rods are so dense and highly damped that they overlap into a smooth background. The resonances of the sample, with high Qs even at high temperatures, are easily observed above the background. An example of data from this RUS apparatus is shown in figure 5b.

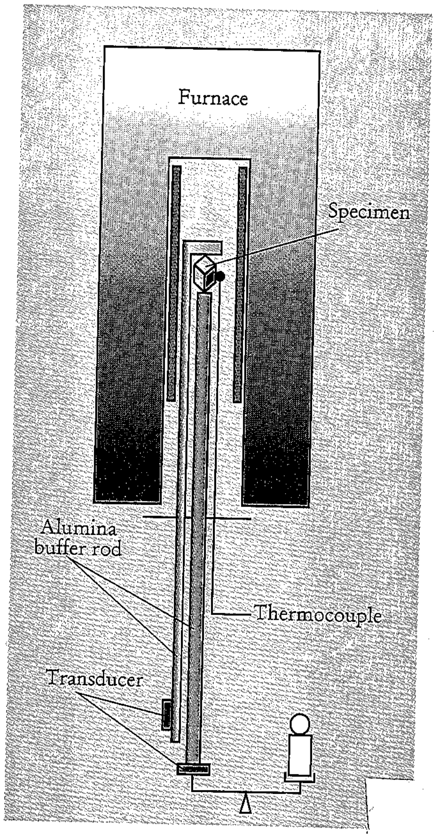
Ricardo Schwarz introduced another noteworthy variation of RUS.[14] In this case, a sample of magnetostrictive material or a nonmagnetic sample coated with a magnetostrictive film is excited with an alternating magnetic field from a drive coil. A second coil measures the effective permeability of the sample, detecting elastic-resonance shifts in the inductive coupling. The technique is interesting in that no contact with the sample is required.

Further details of RUS apparatus and measurement are available in the literature.[10,11,13,14] RUS apparatus may vary considerably in sophistication. One can avoid fabrication and development altogether by purchasing a commercial unit, like that shown in figure 1b. A complete unit includes the components for holding the sample, automated data acquisition and computer processing. By simply placing a sample in the holder, one can determine all of the elastic constants in a fraction of an hour.

RUS applications

RUS has been most extensively applied in geophysics, where the measurement of the thermodynamic properties and anharmonic effects of materials at temperatures exceeding twice the Debye temperature is a high priority. Such elastic data can be used to check theoretical models and their extension to high temperature and pressure, where some asymptotic behavior may be convenient for other geophysical calculations and extrapolations. Anharmonic effects are evident in the Gruneisen relation and in the departure of heat capacity from the Law of Dulong and Petit. Many geophysicists have used RUS, most notably Anderson and the Japanese.

Measurements of elastic constants have proved to be excellent probes of phase transitions. At a second-order phase transition, while many thermodynamic quantities show no obvious evidence of the transition, the elastic constants may show discontinuities. One may use the discontinuity to learn about the physics driving the phase transition. A particularly noteworthy application has been for high-temperature superconducting phase transitions, a



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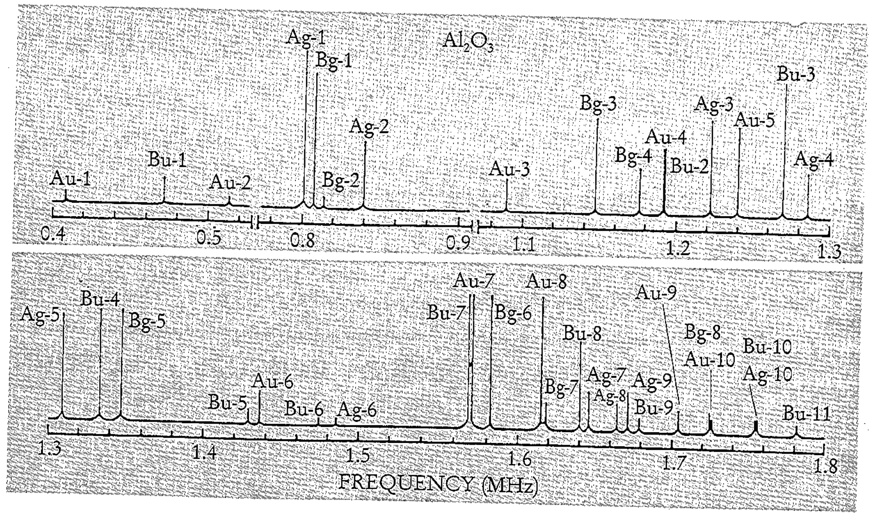

HIGH-TEMPERATURE RUS measurements can be made using a modified apparatus which holds the sample between two alumina buffer rods in a furnace. **a:** The piezoelectric disks are attached to the buffer rods outside the furnace and couple to the sample through the rods. Measurements can be made at temperatures up to 1825 kelvins. **b:** Because the resonances of the rods are dense and highly damped, they form a continuous background against which the sample resonances stand out as sharp peaks. This permits high-precision determinations of elastic constants even at high temperatures. The peaks are labeled using the mode classification scheme from ref. 7. (Adapted from ref. 13.) FIGURE 5

since elastic constants are sensitive probes of the environment in which the electrons pair. Superconducting transitions are often accompanied by structural phase transitions, and elastic constants can yield information about the thermodynamics of the phase transitions. Even if the structural transition is arrested by the superconducting transition, the elastic constants may still indicate structural instability. Migliori and collaborators have used RUS to study phase transitions, including those for high-temperature superconductors, with great success.[15] A good deal of physics may be studied by means of high-precision (a few parts per million) measurements of frequencies or quality factors as functions of variables such as temperature, pressure and isotopic content, without having to absolutely determine the elastic constants. The quality factors for different modes, governed for the most part by different lattice motions, can shed light on various aspects of the physics involved. Some complex systems may involve diffusive motion of constituents on a time scale close to that of the period of the ultrasound wave, and such dynamics may be studied as relaxation effects. Robert Leisure has demonstrated the utility of RUS in this area.[16]

The high accuracy and precision of RUS are evident in studies of quasicrystals.[17] Unlike conventional crystals, quasicrystals are elastically isotropic. While many physical properties of highly symmetric conventional crystals (for example, cubic crystals) are very nearly isotropic, the property of linear elasticity is fundamentally anisotropic; that is, the velocity of sound is different in different directions. Thus, it is interesting that icosahedral quasicrystals, while having long-range order like conventional crystals, must be isotropic in sound propagation. Experimentally measuring elastic anisotropy has proved challenging because while conventional crystals are fundamentally anisotropic, their elastic constants may be numerically very close to isotropic values, making it difficult to distinguish between intrinsically isotropic and anisotropic behavior in a measurement. RUS has been used to obtain high-precision measurements of the elastic constants of both quasicrystalline and closely related periodic phases. These measurements have shown the quasicrystal to be isotropic with an unprecedented confidence level of ten standard deviations.

Because of the ease of use of RUS and the widespread availability of powerful microcomputers, it is expected that the measurement of elastic constants will become readily accessible for many more research applications.

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