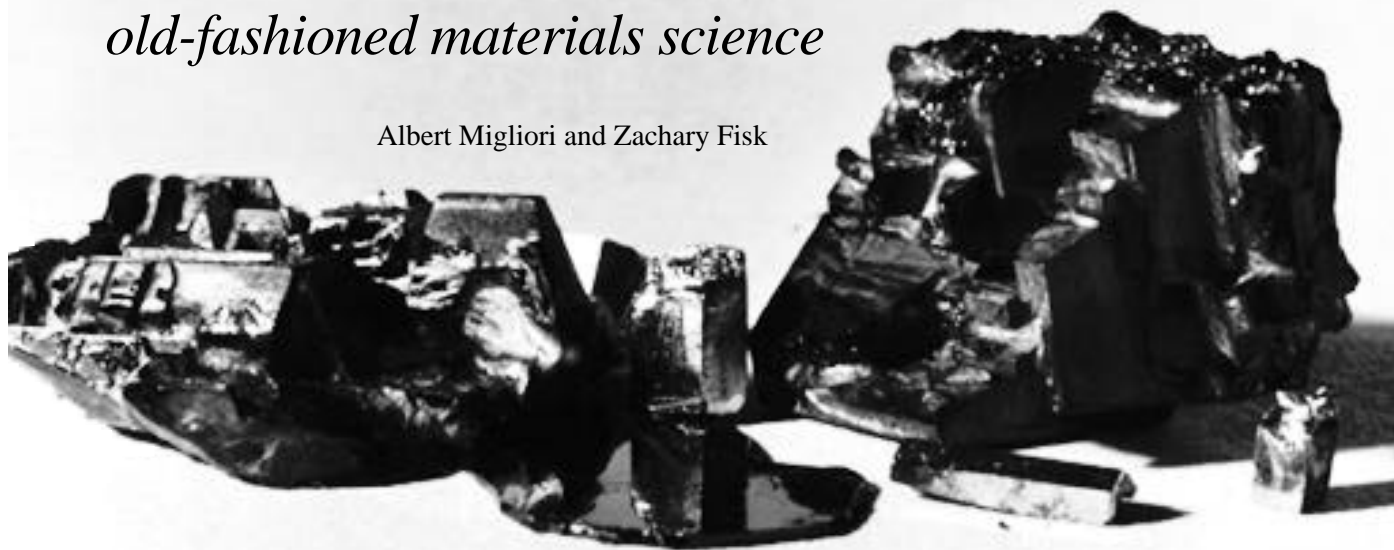


# Crystals and Ultrasound

*old-fashioned materials science*

Albert Migliori and Zachary Fisk



Stone Age, Bronze Age, Iron Age, the age of exploration and the search for gold, the industrial revolution and the steel that made it possible, and, of course, the present age of electronics—totally dependent on tiny chunks of ultrapure, single-crystal silicon—it seems that entire chapters in human history are strongly connected to certain special materials that enabled massive bursts of what has come to be called progress.

But the pursuit of human progress is not the driving force behind physicists studying new materials today. We have much simpler motivations, more akin to the curiosity of the scientist who four thousand years ago first noticed the brilliant luster revealed by scratching the surface of the glob of bronze pulled from a state-of-the-art, charcoal-driven, high-temperature, controlled-atmosphere furnace. That scientist had, by serendipity, produced some sort of very imperfect alloy. The appearance and the properties of even that poor excuse

for bronze were so remarkable that many, many others spent lifetimes advancing available technology to improve that material to the point where the fully developed and vastly improved copper alloys were to the first bronze nugget as that nugget was to the stone it replaced.

Just as important as the production of high-performance bronzes were the parallel developments necessary to understand completely the properties of such alloys. And so goes the story for many other materials. The entire business of materials science, from the first discovery of a new substance to the full development of its properties, is a tremendously attractive intellectual puzzle of sufficient complexity to interest almost anyone. Moreover, the incredible importance of new materials, the qualitative changes in human life that they produce, their intrinsic physical attractiveness, their appeal to the intellect, and our total inability to foresee how important their impact will be

make the study of new materials exciting, risky, difficult, and what seems best described as fun.

Essential to the richness of the field is an understanding of the laws of physics and chemistry that enable detection and realization of new properties of matter. But despite having its roots in basic science, condensed-matter physics is viewed as a kind of applied science: After all, we know all of the fundamental physical laws that describe the individual atoms in solids. The interesting fact, however, is that the collective properties of many atoms assembled together are too complex to be predicted from first principles. For example, the sharp transition from non-magnetic to magnetic behavior in iron at 1043 kelvins cannot be predicted from a calculation of the properties of an assemblage of a few or even a few hundred iron atoms. Such calculations indicate no abrupt transition to ferromagnetism but only a gradual change from weakly magnetic to more strongly

magnetic. Nobel laureate P. W. Anderson has most clearly laid out this idea in his article "More is Different": He makes the point that phenomena arising as more and more particles interact are not simple extrapolations of the behavior of a few particles. Further, we cannot, nor do we want to, solve the most basic equations for the many-atom system because those equations are too complex and provide too much information. No one cares where a particular atom is at a particular time in the magnetic powder of a cassette tape. What is important is the overall magnetization of millions of atoms. Thus most of the useful theoretical descriptions of solids rely on statistical averages to predict measurable quantities. There is, then, a theoretical gap between our knowledge of the basic laws for each atom and our ability to predict what large numbers of interacting atoms do.

In the last few years some attempts have been made to control macroscopic material properties by constructing artificial materials through the deposition of sequential layers of carefully controlled composition and thickness. Attempts are being made also to produce nanostructures, materials assembled atom by atom through such processes as molecular-beam epitaxy and chemical or vapor deposition. Both approaches produce very small, but not quite microscopic, building blocks, or repeated units. Such designed materials are applicable to the production of practical devices as well as the study of quantum physics, and they have properties that are roughly predictable from theory. Still, the theoretical tools needed to predict their material properties necessarily include statistics and macroscopic approximations.

Recent work on "materials by design" contrasts strongly with the work of what one could call "old-fashioned" materials scientists, who work semi-

empirically and produce structures that are largely only what nature allows; that is, the materials are microscopically homogeneous and theoretically intractable. The payoff from this old-fashioned work is the discovery of completely new phenomena, which often arise when the number of atoms is large (on the order of  $10^{18}$ ).

A particular innovation that arose from the "large-number effect" coupled with "old-fashioned" intuition was the inadvertent discovery by K. Mueller in 1987 that certain cuprates (namely, those copper-oxide compounds that are doped with transition-metal and other impurities) are high-temperature superconductors, that is, they become superconducting at temperatures well above absolute zero (above 30 kelvins). Mueller knew that those cuprates are quite unusual solids. He also knew that in many materials, if a smaller atom is deliberately substituted for a larger atom at the center of each unit cell in the crystal lattice, then when the solid cools the smaller atom and its cloud of electrons would not have a stable resting spot in the center of its symmetric cage. As a result it must move to some other position in the unit cell and spontaneously break the crystal symmetry. The effect (called a Jahn-Teller instability) is driven by large symmetric arrays of atoms and is only poorly understood in detail ("large numbers" + "intuition" = "mysterious phenomena"). Mueller's brilliant conjecture was that, in electrical conductors, the distortion of the crystal lattice resulting from the Jahn-Teller instability would produce new material properties provided the energy associated with the lattice distortion is comparable to one of the energy scales of the conduction electrons. As it turned out, the marvelous superconducting properties of the cuprates were not attributable to Mueller's conjecture, but nevertheless his very cre-

ative idea led to their discovery.

The unpredictable effects found when large numbers of various atoms are assembled thus provide both motivation and justification for the empirically based search for new physics and chemistry through the study of new materials. Fortunately, the production of any single new material is often accomplished by a very few scientists working with a small budget and a limited collection of inexpensive equipment. The demonstration of superconductivity in heavy-fermion compounds by F. Steglich at Universität zu Köln, and the discovery of the high-temperature superconductors by K. Müller at IBM Zurich are typical examples of small, successful efforts. However, underlying all of the apparently small efforts is a powerful information and technology base easily accessible to those working within the umbrella of a large research laboratory or university. That access is crucial; without it small groups of scientists, driven by whatever odd notions motivate them, could not succeed.

### The Remarkable Effects of Impurities

Also important to success is a clear focus on some particular set of material properties. Many groups today are focused on modifying the electronic and magnetic properties of solids by doping them with impurities and studying the effects of those impurities as the solids are cooled to low temperatures. Often the presence of impurities causes the solids to undergo a drastic change in some physical property as they cool, from conducting to superconducting, from non-magnetic to magnetic, from paraelectric to ferroelectric, and so on. These drastic changes are called phase transitions.

It is a curious finding that some seemingly intrinsic properties of solids

owe their existence to small amounts of impurities. For example, off-the-shelf tungsten metal is typically hard and brittle. When pains are taken to remove the various trace impurities dissolved in nominally pure tungsten, it becomes quite soft. The change in hardness is so pronounced that the purity of a tungsten sample can be reliably estimated with an ordinary Dremel grinding tool. The very pure metal is softer than annealed copper, and its x-ray pattern becomes blurred, no doubt because of the large deformations that easily occur in its soft condition. Perhaps a more surprising case is that of salt (NaCl). Usual NaCl contains a small amount of hydroxyl,  $\text{OH}^-$ . When great care is taken to prepare  $\text{OH}^-$ -free NaCl, the resulting solid can be spread like butter on bread.

The most important example ever in which the effects of impurities were understood and then exploited was in the development of transistors. In the early decades of this century, work by Thompson, Drude, Pauli, Fermi, Dirac, and Sommerfeld led from the discovery of the electron to an understanding of the special quantum physics governing conduction processes in pure and impure (doped) semiconductors.

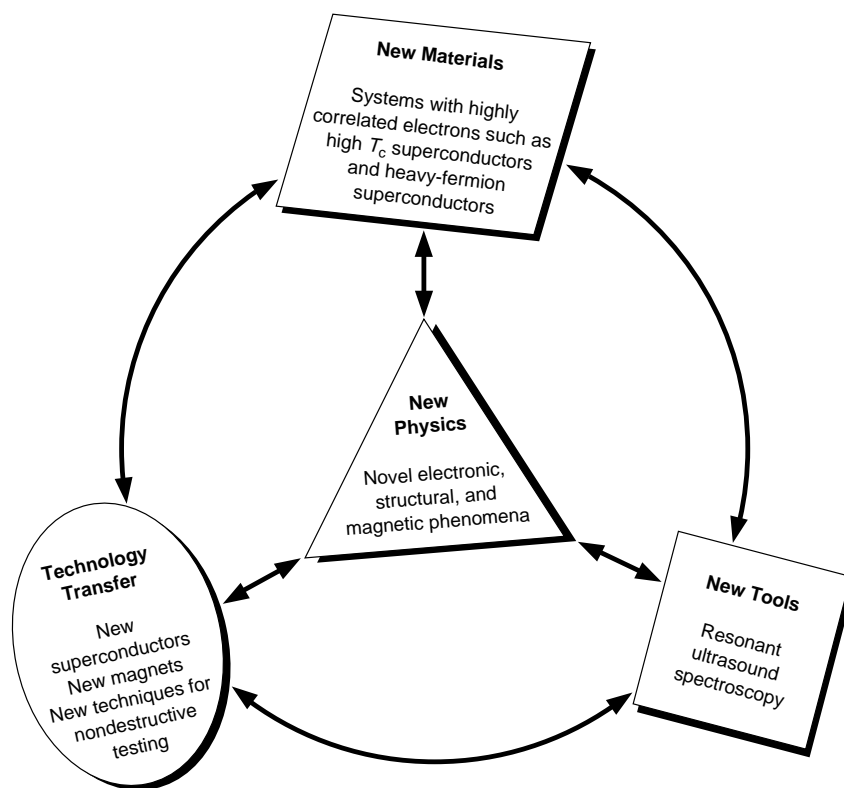
This revolution in understanding the electronic properties of solids had, by

the late 1930s and early 1940s, germinated into an idea in the minds of John Bardeen, William Shockley, and Walter Brattain at AT&T Bell Laboratories. They realized that the intrinsic properties of very pure (but still doped) semiconductors would allow the electrical conductivities of these materials to be controlled and varied by externally applied voltage, just as the flow of electrons is in a vacuum tube. Therefore such materials might serve as replacements for the reed relays in telephone switchboards. In order to obtain this effect, they knew they needed to pro-

duce single crystals of germanium and silicon with the impurity content kept to the unprecedented low level of 1 part per million—and they used every piece of technology available to reach their goal.

Along the way, when state-of-the-art was inadequate, their team developed new methods of growing and characterizing crystals, such as zone-refinement, a simple method for removing impurities while a crystal is growing. In the end they were able to make the first transistors. In the process of succeeding, they significantly advanced the theory and methods of solid-state physics. Not only did they predict the need for purity so

high as to seem unnecessary, unachievable, and up until then unmeasurable, they also developed methods to produce crystals of the desired purity, developed characterization schemes, grew the crystals, and then produced practical devices whose function was totally reliant on the remaining and carefully controlled impurities. Their odyssey from the purest of basic research to the stupendous discovery of one of the most important practical devices ever was one of the greatest achievements of twentieth century physics.



**Figure 1. Materials Science at Work**

**The production of new materials with exotic properties leads to the development of new tools to study them, the use of those tools to advance the understanding of the new materials and the application of the new materials, the new tools, and the new science in the commercial sector. Here we elaborate on this paradigm with examples from our own work.**

## Second-Order Phase Transitions and the Measurement of Elastic Properties

We have been interested in producing and understanding materials that undergo second-order phase transitions. In some metals the transition from the normal conducting phase to the superconducting phase is second order, as are many other structural, magnetic, and electric phase transitions. In this type of phase transition, the symmetry and material properties of the solid change gradually rather than abruptly (as in first-order phase transitions), but the changes nevertheless begin at a very distinct temperature called the critical temperature,  $T_c$ . The solid is in a more symmetric phase above  $T_c$  than below.

In a crudely parallel way the introduction of various amounts of impurities can also break the symmetry of a solid, at least locally. The combination of changes in temperature and control of impurity levels can thus be used to tune, in more or less continuous ways, important physical properties in metastable materials. Therefore, the study of such systems is widespread in materials science. It involves many tools, requires science, intuition, and luck, and it produces returns in both fundamental physics and very practical applications.

The tale we are about to tell concerns the development of a very old technique into a powerful and essentially new one for determining the changes in the elastic stiffness of crystals, particularly as they undergo second-order phase transitions. This now mature technique, called resonant ultrasound spectroscopy, has led to a simple procedure for making what once was a very difficult measurement. Our work illustrates the synergism among the production of new materials, the invention of

### Discontinuities at Second-Order Phase Transitions

Three thermodynamic quantities, the specific heat  $C_p$ , the thermal-expansion coefficient  $f_i$ , and the elastic-stiffness tensor  $c_{ij}$ , can be discontinuous at the critical temperature  $T_c$  of a second-order phase transition. Each is proportional to a second derivative of  $\phi G$ , the change in the Gibbs free energy per unit mass across the boundary separating two phases. Although  $\phi G$  is always zero in any phase transition, in a second-order phase transition the first derivatives of  $\phi G$  are always continuous and the first sign of any discontinuities occurs in the second derivative of  $\phi G$ .

The relationships between  $\phi G$  and  $C_p$ ,  $f_i$ , and  $c_{ij}$  are particularly simple to write down for a liquid because the elastic-stiffness tensor has only one component, namely, the bulk modulus,  $B$ .

In terms of temperature  $T$ , pressure  $P$ , and volume  $V$ , the thermodynamic relations are

$$\frac{\partial^2 \phi G}{\partial P^2} = \frac{\partial \phi V}{\partial P} = f_i \frac{1}{B}; \quad B = \text{bulk modulus}$$

$$\frac{\partial^2 \phi G}{\partial T^2} = f_i \frac{\partial \phi S}{\partial T} = f_i \frac{C_p}{T}; \quad C_p = \text{specific heat}$$

$$\frac{\partial^2 \phi G}{\partial P \partial T} = \frac{\partial \phi V}{\partial T} = f_i; \quad f_i = \text{thermal-expansion coefficient}$$

$\phi V$  is the change in volume per unit mass across the phase boundary and  $\phi S$  is the change in entropy per unit mass across the phase boundary. Although  $\phi G$ ,  $\phi V$ , and  $\phi S$  are zero and the phase transition is continuous,  $B$ ,  $C_p$ , and  $f_i$  can exhibit discontinuities at the critical temperature  $T_c$ .

The relationships for a solid are more complicated and are usually written in terms of the stress tensor  $\sigma_{ij}$  and the strain tensor  $\epsilon_{kl}$  instead of  $P$  and  $V$ . Further, the bulk modulus  $B$  becomes the elastic-stiffness tensor  $c_{ijkl}$ , which relates the stress to the strain in terms of the fundamental relation

$$\sigma_{ij} = \sum_{kl} c_{ijkl} \epsilon_{kl}$$

new tools to study them, the subsequent use of those tools to advance the physics of other materials, and the application of the tools, the science, and the materials to industrial applications. In other words, our story illustrates a

paradigm of how materials science actually works (Figure 1).

Measuring the elastic stiffness, or elasticity, of a solid as a function of temperature has been a traditional and very important technique for studying

second-order phase transitions in materials doped with impurities. Nature helps us with the measurement because the elasticity of a solid is discontinuous at  $T_c$ ; that is, it jumps to a different value when that solid begins to undergo a second-order phase transition. The jump is perhaps surprising because, as we mentioned above, the solid exhibits no obvious microscopic changes at the critical temperature. The atoms do not suddenly change position, magnetism and ferroelectricity do not suddenly appear, and a conductor is not suddenly able to carry super-large currents. However, three thermodynamic quantities—the elastic stiffness, the specific heat, and the thermal-expansion coefficient—do exhibit discontinuities at  $T_c$  and those abrupt changes can be measured. The accompanying box defines these three quantities in terms of variations with respect to temperature and pressure of the change in the Gibbs free energy per unit mass across the boundary between the two phases.

Discontinuities are a boon to the experimentalist because they are often the most unambiguous of measured quantities. Of the three discontinuous quantities mentioned, elastic stiffness is particularly informative because in a solid this quantity is a fourth-rank tensor,  $c_{ijkl}$ , with 81 components. The elastic-stiffness tensor relates the stresses (forces) to the strains (displacements) in the solid through the fundamental relation

$$\sigma_{ij} = \sum_{kl} c_{ijkl} \epsilon_{kl}$$

where  $\sigma_{ij}$  is the stress tensor and  $\epsilon_{kl}$  is the strain tensor. This relation between stress and strain is simply the generalization of Hooke's law,  $F = -kx$ , where  $F$  is the force developed in a spring if it is stretched a distance  $x$ . Thus the elastic-stiffness tensor  $c_{ijkl}$ , in analogy with the spring constant  $k$ , describes the

stiffness of the bonds holding the solid together. Although  $c_{ijkl}$  has 81 components (or moduli), in crystalline structures that do not produce external magnetic fields, the tensor has at most 21 independent components. Consequently the elastic stiffness tensor is commonly written as  $c_{ij}$ , where  $i$  and  $j$  run from 1 to 6, for pragmatic rather than mathematical reasons.

It is also important to realize that the stiffness of a metallic solid comes not only from the chemical bonds that hold the ions together but also from the degeneracy pressure of the Fermi sea of electrons. Thus a great deal of information about the crystal is contained in a complete description of its elasticity. Because of this wealth of information, if one knows the crystal structure and can measure the changes in the elastic-stiffness tensor as a function of temperature through a phase transition, then it is possible to infer the detailed changes in the crystal lattice or in the electronic structures that are driving the phase transition. Few other measurements can reveal as much of the physics of phase transitions. Consequently we would like to be able to make this measurement in high- $T_c$  superconductors, heavy-fermion superconductors, and other exotic materials exhibiting second-order phase transitions.

### The Need for a New Measurement Technique

Unfortunately, nature, while permitting us to produce single crystals of high-temperature superconductors, heavy-fermion superconductors, and other materials in variously doped versions, has often restricted the dimensions of the crystals that can be easily grown to the millimeter range. That size is entirely adequate for many measurements. But for the crucial determi-

nation of elastic stiffness, a thermodynamic measurement that provided the first verification of the BCS theory of ordinary low-temperature superconductivity, millimeter-sized crystals are a disaster.

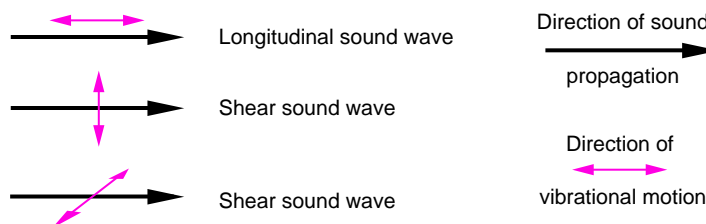
What we describe below is a solution to this measurement problem. It involves measuring the resonances (or natural frequencies of vibration) of a crystal and often makes measurement of the elastic-stiffness tensor more trivial than measurement of the resistivity tensor.

Prior to development of this the new resonance approach, elastic moduli were determined mostly from measurements of the speeds of longitudinal and shear sound waves along different directions in a sample. Figure 2 shows the simple relationships among these sound speeds and the elastic moduli for a cubic crystal. For a large chunk of isotropic material such as ordinary glass, there are only two independent sound speeds, one for longitudinal waves in which the atoms vibrate along the direction of the sound wave (these are the waves we hear), and shear waves, in which the atoms vibrate in a direction perpendicular to the direction of the sound waves. A simple measurement of the pulse-echo time of each type of sound is easy to do and yields sound speeds for glass accurately and completely. As shown in Figure 2, the pulse-echo time is the time for a short sound pulse to travel the distance from one face of the sample to the opposite face and back again.

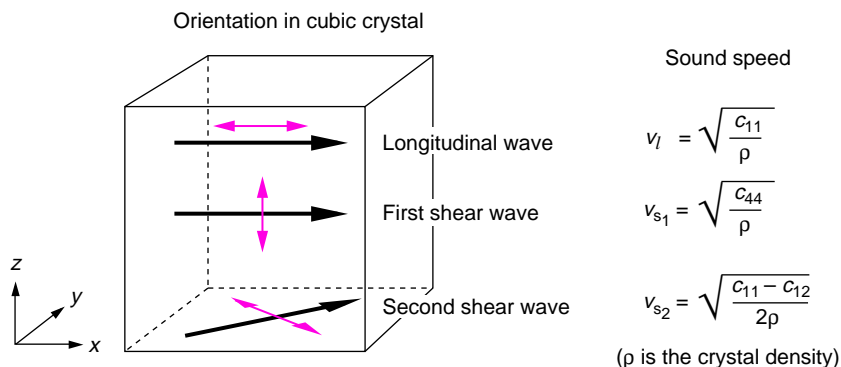
In applying the pulse-echo technique to single crystals of more exotic materials, the first catch is that the speed of sound in nearly every solid that interests us is a blazing 5 millimeters per microsecond or so (Mach 15 in jet fighter units). The second catch is that we need to use very-high-frequency ultrasound (several hundred megahertz or

**Figure 2. Sound Speeds, Elastic Moduli, and Pulse-Echo Measurements****(a) Longitudinal and Shear Sound Waves**

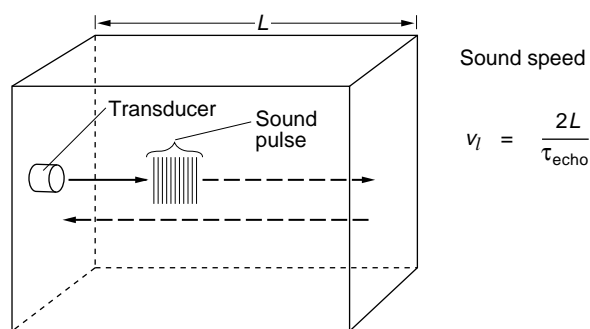
In longitudinal sound waves atoms vibrate along the direction of wave propagation. In shear sound waves atoms vibrate perpendicularly to the direction of wave propagation.

**(b) Sound Speeds and Elastic Moduli**

The elastic-stiffness tensor of a cubic crystal has three independent elastic moduli ( $c_{11}$ ,  $c_{12}$ , and  $c_{44}$ ) and therefore there are three sound speeds in a cubic crystal. The elastic modulus  $c_{11}$  is determined from the speed  $v_l$  of the longitudinal sound wave shown at right. The two shear moduli  $c_{12}$  and  $c_{44}$  are determined from two speeds  $v_{s1}$  and  $v_{s2}$  of the two shear waves shown at right.

**(c) Pulse-Echo Measurements of Sound Speed**

Conventional measurements of the elastic stiffness tensor  $c_{ij}$  are made by measuring the sound speeds of longitudinal and shear sound waves along various directions in a large crystal. In the example shown here a short pulse of longitudinal sound is generated by a transducer on one crystal face; the sound pulse travels as a narrow beam through the crystal and bounces back from the opposite face to produce an echo that is picked up by the transducer. The measured time between the initiation of the pulse and the echo (called the pulse-echo time,  $\tau_{\text{echo}}$ ) is equal to  $2L/v_l$ , where  $L$  is the distance between the two crystal faces and  $v_l$  is the longitudinal sound speed. Thus the sound speed can be calculated directly from  $\tau_{\text{echo}}$ . Further, if the density of the crystal,  $\rho$ , is known, the measurement also provides a direct determination of  $c_{11}$ , one component of the elastic-stiffness tensor. By placing the transducer at various locations on the crystal and using both longitudinal and shear sound waves, all the components of the elastic-stiffness tensor can be determined.



higher) to measure the sound speed in samples whose largest dimension is about a millimeter. But often ultrasonic attenuation increases to prohibitive levels at such frequencies.

Let's say that we want to measure the speed of sound in a 1-centimeter cube (big!) of  $\text{La}_2\text{CuO}_4$ . Above 530 kelvins this cuprate has a tetragonal

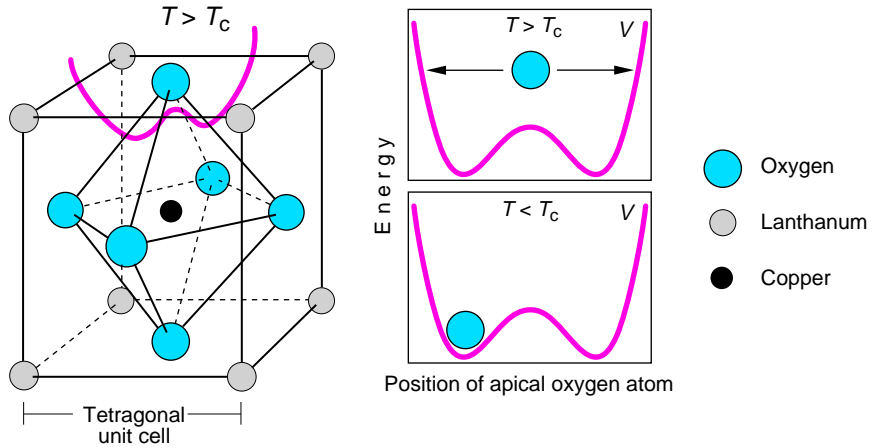
structure (all three crystal axes of the unit cell are at right angles, two axes are equal in length, and one is longer or shorter).  $\text{La}_2\text{CuO}_4$  is an interesting material because when doped with strontium it becomes a high-temperature superconductor and its doped versions undergo a structural phase transition as they cool, from a tetragonal to

an orthorhombic structure (see Figure 3). Therefore, we're interested in the variation in sound speed (or equivalently, elastic-stiffness tensor) as a function of temperature through the structural phase transition. In our 1-centimeter sample, a single cycle (wavelength) of 50-megahertz sound is 0.1 millimeter long. To obtain a good signal-to-noise

**Figure 3. Structural Phase Transition of  $\text{La}_2\text{CuO}_4$**

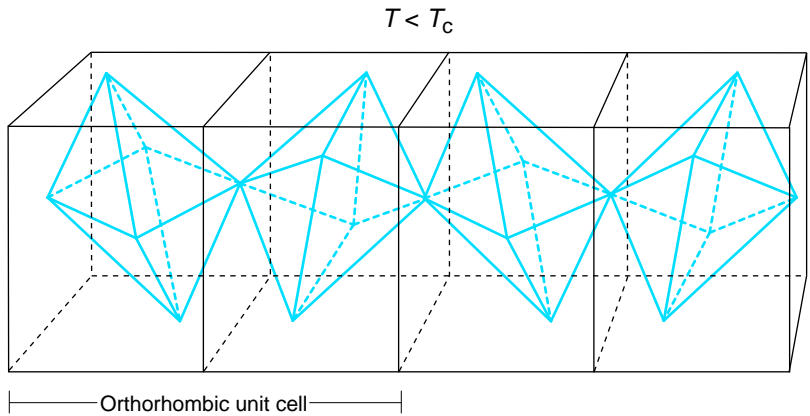
(a) Tetragonal Structure of  $\text{La}_2\text{CuO}_4$  above  $T_c$

The unit cell of  $\text{La}_2\text{CuO}_4$  above the critical temperature,  $T_c = 525$  kelvins, is tetragonal; that is, the axes are at right angles, the  $x$  and  $y$  axes are of equal length, and the  $z$  axis is longer. Note that the oxygen atoms form an octahedron. Each oxygen atom at the apex of the octahedron sits in a double-well potential,  $V$  (shown here in red). Thermal motions of the apical oxygen atoms are sufficiently large that the equilibrium position of each is at the center of its potential well.



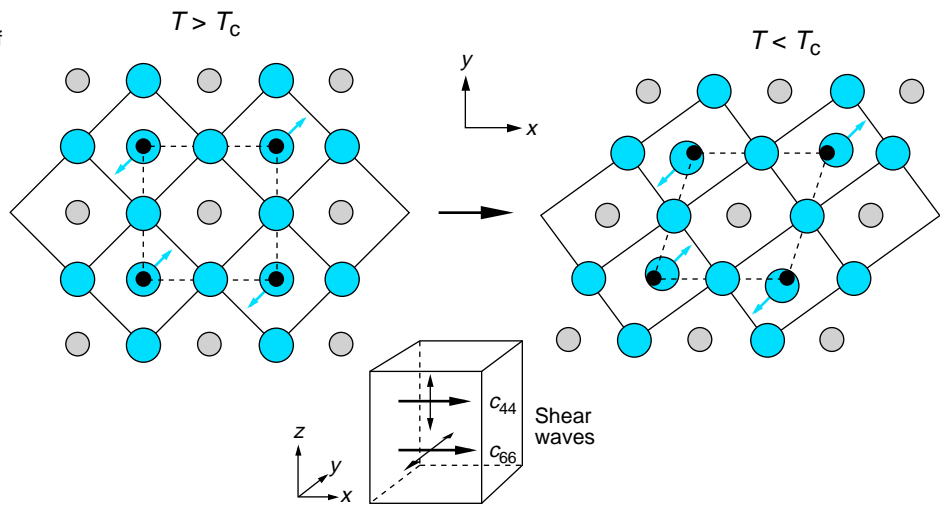
(b) Orthorhombic Structure of  $\text{La}_2\text{CuO}_4$  below  $T_c$

At temperatures below the critical temperature, each apical oxygen atom falls into one or the other minima of its double-well potential so that the octahedron of oxygen atoms in each unit cell has a static tilt. Since octahedra in adjacent cells tilt in opposite directions, two of the old unit cells form the unit cell of the new structure. Thus the crystal now has an orthorhombic structure (all three axes of the unit cell are unequal in length).



(c) Top View of Phase Transition from Tetragonal to Orthorhombic Structures of  $\text{La}_2\text{CuO}_4$

As the temperature decreases below  $T_c$  and oxygen octahedra develop permanent tilts, shear forces develop and change the square array of copper atoms to a rhombus. Here the distortion is exaggerated for the purposes of illustration. Theory predicts that the shear modulus  $c_{66}$ , which characterizes shear forces in the  $x$ - $y$  plane, will shift abruptly during the phase transition whereas the shear modulus  $c_{44}$ , which characterizes shear forces in the  $z$ - $y$  and  $z$ - $x$  planes, will remain unaffected by the phase transition.

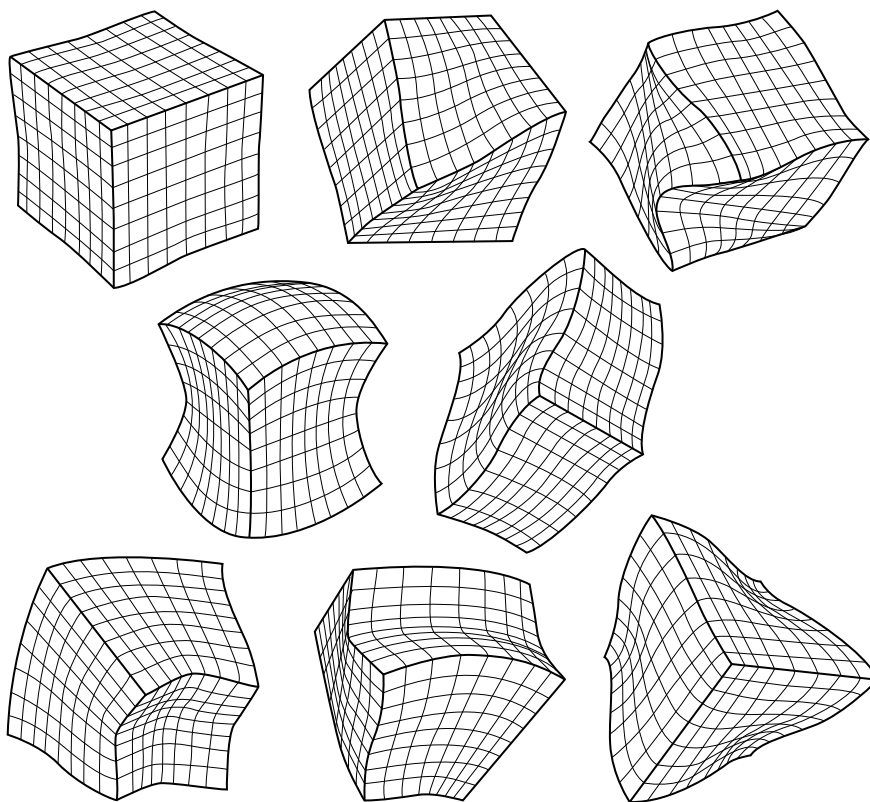


ratio, we send in a pulse consisting of many cycles of sound and bounce the pulse from the inside walls of the crystal. Such a pulse might last, then, 0.2 microseconds and be 1 millimeter long, 10 percent of the width of the sample.

To determine the relative change in sound speed to 1 part per million, a not unreasonable goal, we would need to time the pulse echo to an accuracy of 2 picoseconds, corresponding to about 1/1000 of a wavelength of sound. All of this is not wildly difficult to do for the frequencies appropriate to big samples. But for a 1-millimeter crystal we must increase the frequency, and therefore the timing accuracy, by a factor of 10. At 500 megahertz and 0.2-picosecond timing accuracy, things get tough. Even worse, the orthorhombic phase of  $\text{La}_2\text{CuO}_4$ , whether pure or doped, has nine independent elastic moduli and therefore nine different sound speeds, each requiring a separate measurement. And each measurement requires that a small transducer be glued to the sample and that it not fall off as we cool the sample from room temperature down to a temperature well below the critical temperature. The pulse echo is an intermittent signal, and the signal can easily become so greatly attenuated that barely one echo can be detected.

### The Development of Resonant Ultrasound Spectroscopy

Direct measurement of the pulse-echo time (or sound speed) to determine elastic stiffness would seem to be nearly hopeless for small crystals. But usually, when nature makes the measurement of time tough, the measurement of frequency is much easier. In fact, if we apply continuous sound to a solid sample, the solid will resonate, or ring just like a bell, provided the applied sound frequency is one of the



**Figure 4. Distortions of a Cube-Shaped Sample on Resonance**

Each figure above is an example of the distortions that a cubical object undergoes when it is driven at a natural (resonant) vibrational frequency. At each resonant frequency the vibrational motion is dependent on complicated linear combinations of all the elastic moduli as well as the exact shape of the object. Because of this complexity, Rayleigh, Love, and others were unable to compute the resonances of such short, fat objects from their elastic moduli. With the advent of big computers and some clever algorithms, such computations are now easily done.

solid's natural vibrational frequencies. (Application of this technique to long, thin rods is perhaps hundreds of years old!) Because the resonant frequencies are related to the pulse-echo times, we can measure resonant frequencies instead of pulse-echo times to determine elastic-stiffness tensors.

We measure the frequency of a resonance by driving the sample continuously with ultrasound and slowly changing the frequency of the sound until the sample suddenly starts to resonate (1-millimeter samples resonate at

1 megahertz or so, a wonderfully low frequency). The resonating sample acts like a natural amplifier, greatly increasing the amplitude of the vibrations (a factor of 10,000 is not uncommon). We now need only measure frequency. We can take as long as we like to do it, and the naturally amplified signal is present during the entire time we are doing the measurement. Therefore, a resonance measurement can easily have a signal-to-noise ratio that is a million times higher than a measurement of the echo time of short pulses of sound.



You might, at this point, wonder why anyone would have used echoes rather than resonant frequencies to determine the components of the elastic-stiffness tensor. The catch is that the resonant frequencies are hard to interpret because they have a somewhat complicated relationship to the elastic moduli.

Over a hundred years ago John William Strutt, Baron Rayleigh, attempted to calculate the resonant frequencies of cubes, short cylinders, and other short fat objects from known elastic moduli. Unlike the corresponding calculation for thin rods and plates, this wonderfully tantalizing and seemingly simple problem stymied the brilliant Rayleigh, who finally concluded that “the problem . . . has for the most part, resisted attack”. Figure 4 illustrates the origin of the complexity: When a cube resonates, it exhibits significant distortion typically involving all the elastic moduli in complicated linear combinations. A. E. H. Love, Willis Lamb, and others were also stymied by this problem. But in the 1960s Orson Anderson of Columbia University and his postdoc, Harold Demarest, hit on a fast, accurate numerical algorithm for obtaining the solution. The algorithm requires computations only at the surface of the object and achieves an accuracy much greater than the relatively crude “finite-element” techniques, which compute throughout the volume of a sample and are the only alternate method. With this fast, accurate algorithm Anderson and his coworkers were able to make the first fully interpreted resonant ultrasound measurements on large, high quality mineral crystals. That is, they were able to match measured resonance frequencies to predicted ones, but they had big crystals, big signals, and almost perfectly known answers for the elastic moduli before they started. In contrast,

our small and completely uncharacterized samples could not be so easily attacked, so we had to develop new hardware and refined analysis procedures.

To measure the resonant frequencies of a 1-millimeter object, we had better (1) not disturb the sample’s resonances with the measuring device and (2) not generate resonances in the measuring system that might confuse the issue. To not change what we wish to measure in the process of measuring it requires that our transducers make extremely weak contact with the sample. So if our sample is approximately cubical, we lightly contact its corners with transducers, using no glue or any other coupling medium, and apply just a gram or so of force (pardon the unit).

With that light contact we lose a factor of 1000 in our signal-to-noise ratio. We must also drive the sample lightly so as not to destroy it. Fortunately, the natural amplification at resonance recovers most of what is lost with a gentle drive. The resonances generated in the measurement apparatus are another matter. We are not ourselves small enough to make transducers much smaller than 1 millimeter or so; therefore, most transducers would ring in just the same frequency range as the sample and spoil the signal. The way around this problem is to make the transducers of a composite structure consisting mostly of single-crystal diamond. Diamond, with a sound velocity of 17 millimeters per microsecond (Mach 50!) has such a high sound speed that its resonance frequencies are much higher than those of the crystals of comparable size that we wish to measure.

When we hooked all the pieces together and connected them to electronics specially designed (with the help of Thomas Bell) to maximize the signal-to-noise ratio, John Sarrad, a student working with us on his thesis research,

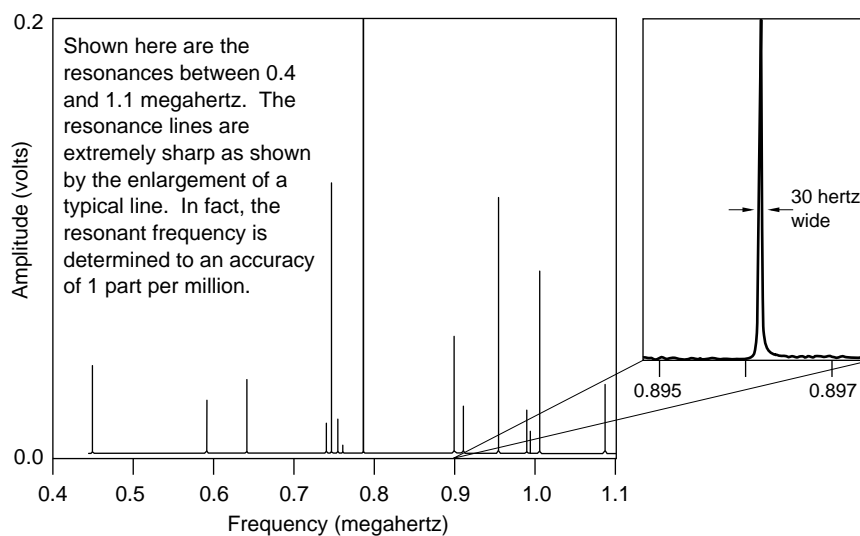
was able to measure all of the lower fifty or so resonant frequencies of a crystal with a largest dimension of 1 millimeter or so. The entire experiment fits on the top of a desk and costs less than a car. Figure 5 shows the measurement apparatus and a typical resonance spectrum.

### Analysis of Resonant Ultrasound Data

To our surprise, the algorithm to compute resonant frequencies from elastic moduli and our simple technique to measure accurately the resonances of a useful sample were not quite enough to produce a robust technique for determining elastic moduli from measured resonances. (Note that this is the inverse of the problem solved by Orson Anderson.) In real life the measured resonant frequencies have some errors relative to the resonant frequencies of a perfect sample. The errors arise from many sources including anomalies in the geometry of the sample (such as chips and rounded edges) and transducer loading effects. Typically, the resonances of the mathematical model of the solid and those measured for the real object differ in frequency by 0.1 percent, more or less. Further, one or two resonances out of the thirty or forty that exist in a given frequency range may be missing from our data because some resonances, by accident, may have no component of vibrational motion along the driving direction of the transducer. The experimental data are fed into a computer program that tries to find a set of elastic moduli consistent with the measured resonances, the sample dimensions, and the symmetry of the sample’s crystal lattice. If one or two resonances are missing from the measured resonance spectrum, the computer will invent an answer that is “not even wrong.”

**Figure 5. Ultrasound Measurements of  $\text{La}_{1.86}\text{Sr}_{0.14}\text{CuO}_4$** **(a) Measurement Technique**

The photograph shows a sample of  $\text{La}_{1.86}\text{Sr}_{0.14}\text{CuO}_4$  held between two transducers, one of which drives the sample over a continuous range of frequencies in the megahertz range. The apparatus is placed in a cryostat, which can cool the sample to the desired temperatures. While the temperature is held fixed, the frequency of the driver is gradually and automatically changed by an electronic signal generator until the sample resonates and thereby amplifies the applied signal. The amplified signal is picked up by the second transducer and recorded automatically by a specially designed electronic detector. The frequency of the driver then continues to change again until another resonant frequency is reached. All the resonant frequencies of the sample are thus recorded during a single experimental run. The entire resonance spectrum is measured in several seconds. To study a second-order phase transition in the sample, the experiment is repeated at various temperatures between room temperature and the critical temperature of the phase transition.

**(b) Resonance Spectrum of  $\text{La}_{1.86}\text{Sr}_{0.14}\text{CuO}_4$  at  $T = 297.2$  kelvins**

We have not yet developed a computer program for guessing at the absence of a resonance; however, those guesses can be made by looking at the data and relying on the intuition that comes from experience. After several iterations and applications of William M. Visscher's pioneering computer algorithms, we usually do guess which resonance is missing, and then the computer instantly determines the elastic moduli of the sample to an accuracy of 0.05 percent or better. The algorithms also determine the true dimensions of the sample to an accuracy as high as 0.01 micron. The results are the most accurate and complete measurements to date of the elastic-stiffness tensor, and the many elastic moduli are obtained simultaneously from a single measurement of the resonance spectrum.

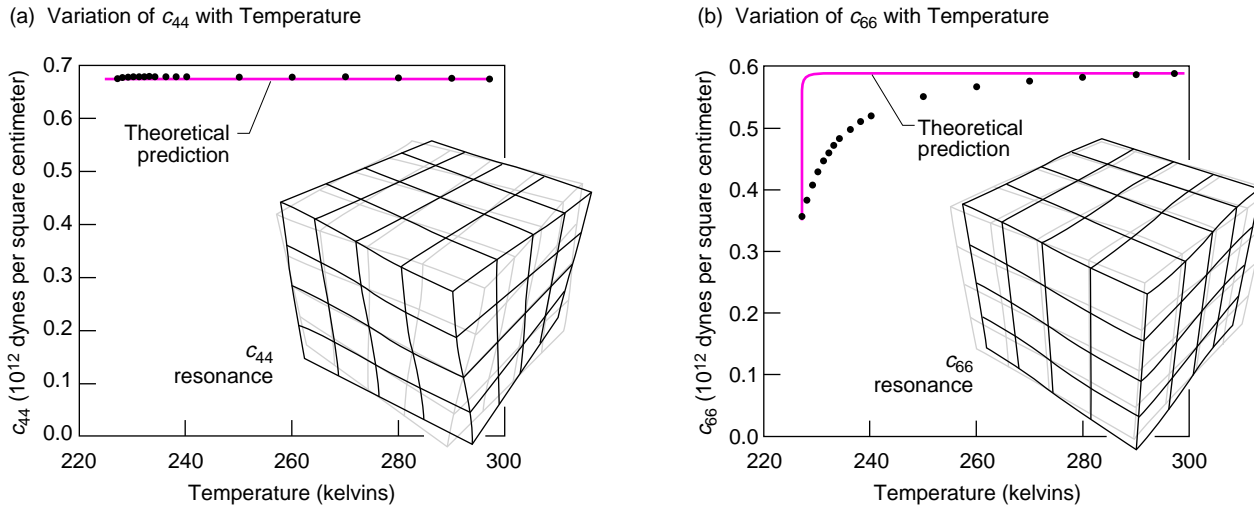
Our ability to infer the existence of missing resonances in our data was critically dependent on our being able to produce some samples that were perfect small single crystals and then using their known perfection to refine our experiment for less perfect crystals. This McLuhanesque bootstrapping of the development of a measurement technique by using known properties of near-perfect materials is not uncommon and is often the only safe route. Without the collaboration among crystal growers, instrument developers, and theorists, the resonant ultrasound spectrometer could not have been developed to its full potential. Without the instrument our perfect small single crystals would have remained strangers to the ultrasound and their elastic properties would still be a mystery. Although the project has involved many types of expertise, the size of the overall effort has remained small. The required components of the effort, however, were not predictable when we began developing the instrument. Thus the work really needed to be done at a national laboratory, which could serve

as a technology supermarket with a large and available stock from which to select just the right things.

### Applications of the Resonant Ultrasound Spectrometer

With our resonant ultrasound spectrometer and a wonderful collection of

crystals doped with various impurities, we, our postdoc, and our students have been able to make steady progress in expanding our knowledge of second-order phase transitions. Our resonant ultrasound measurements on pure and doped  $\text{La}_2\text{CuO}_4$  single crystals near their structural phase transition from tetragonal to orthorhombic are particularly interesting.



**Figure 6. Surprising Results from Resonant Ultrasound Measurements**

To study the transition of the superconducting cuprate  $\text{La}_{1.86}\text{Sr}_{0.14}\text{CuO}_4$  from a tetragonal structure to an orthorhombic structure, we measured the elastic moduli of an approximately cubical, strontium-doped sample as a function of temperature using the resonant ultrasound technique. Resonance spectra were taken at various temperatures from room temperature down to the critical temperature of the sample, 223 kelvins. The values of the elastic moduli at the various temperatures were determined from the resonance spectra by using a computer program discussed in the main text. As explained in Figure 4 and the main text, theory predicts that the shear modulus  $c_{44}$  should remain constant through the transition, whereas the shear modulus  $c_{66}$  should remain constant but then undergo an abrupt change at (or slightly above)  $T_c$ . Above are shown the results from the resonant ultrasound measurements. (a) shows that the value of  $c_{44}$  remains constant, as expected, and (b) shows that the value of  $c_{66}$  begins decreasing at a temperature roughly 80 kelvins above  $T_c$  and continues to decrease as the temperature decreases to  $T_c$ . The departure from theoretical predictions (shown in red) indicates that this second-order phase transition is less well understood than was thought. The dotted and dashed lines of the cube inset in each graph indicate peak distortions at opposite ends of the vibrational cycle for each resonance.

When we started the measurement, the structural phase transition was thought to be well understood. As shown in Figure 3a, at high temperatures each apical oxygen atom in the unit cell sits in the center of a double-well potential (a potential with two minima). More precisely, fast thermal motions cause each oxygen atom to vibrate so that it appears to fill the available space symmetrically. Near the critical temperature of the structural phase transition, the energy of thermal vibrations is just about equal to the height of the bump (local maximum) in the center of the potential well. Thus the thermal motion is now too weak to keep the atom buzzing in the center

(the atom can no longer make it over the bump of the potential well). As the solid cools further, the atom gradually drops into one of the two small wells at the bottom of the potential. Thus the arrangement of atoms is altered; that is, the solid experiences a structural phase transition.

Figure 3b shows the rearrangement. Each oxygen atom in the unit cell undergoes a displacement such that the octahedron formed by the oxygen atoms develops a permanent tilt. Because the octahedra in neighboring unit cells develop tilts in alternate directions, the two neighboring unit cells are no longer identical. In fact, the unit cell of the new structure is now com-

posed of two of the old unit cells and has orthorhombic symmetry.

In Figure 3c, a projection of the crystal lattice onto the  $x$ - $y$  plane shows that as the oxygen octahedra develop alternating tilts during the phase transition, they pull apart the corners of the unit cells and shear the square array of atoms into a rhombus (or diamond shape). Thus, according to theory, the shear modulus  $c_{66}$  should drop abruptly as the temperature drops below the critical temperature, whereas the shear modulus  $c_{44}$  should remain unaffected. In fact, very general symmetry arguments can be used to predict exactly how each of the six independent elastic moduli of the tetragonal structure

should change as a function of temperature near the critical temperature.

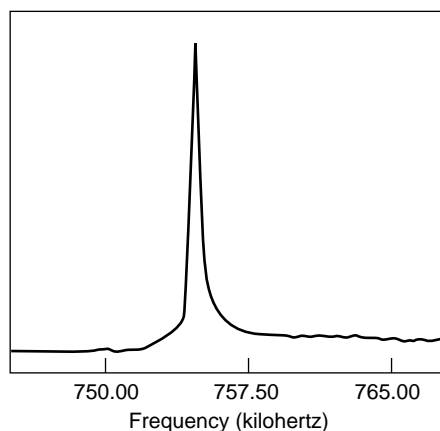
Much to our surprise, the behavior of the elastic moduli as a function of temperature determined from our resonant ultrasound measurements differed markedly from theoretical predictions. Rather than changing abruptly at the critical temperature, the shear modulus  $c_{66}$  changes smoothly over a temperature drop of 80 kelvins or so (Figure 6). Because our simultaneous measurements of the six elastic moduli are extremely precise, there can be no doubt as to the validity of our results. What we are left with is a clear indication that this structural phase transition is not as well understood theoretically as was thought. Moreover, measurements on pure  $\text{La}_2\text{CuO}_4$  as well as samples doped with oxygen, barium, and strontium showed similar results. Whether these results are related to the mysteries of high-temperature cuprate superconductors remains to be seen.

Our results for the  $\text{La}_2\text{CuO}_4$  system are typical of the surprises we find with resonant ultrasound measurements. The surprises provide motivation for improving our understanding of the basic physics, which in turn enables us to see the way to make new materials that have desirable structural, magnetic, or other properties. Thus, the physics we uncover has the promise that it will eventually apply directly to the real engineering aspects of materials.

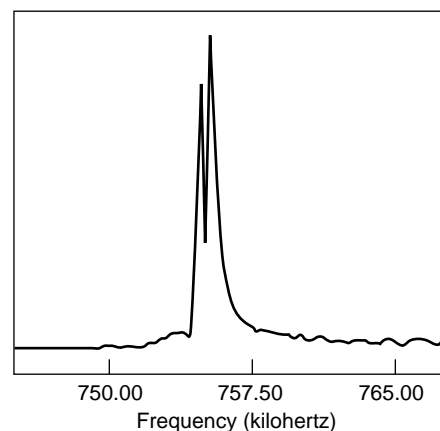
### A Breakthrough in Nondestructive Testing

Because of our justifiable confidence in the accuracy and precision of resonant ultrasound measurements, when the measured resonance spectrum of a sample of known structure cannot be made to fit the mathematical model to within 1 percent or so, as happened

(a) Resonance Line in Spectrum of Perfect Ball Bearing



(b) Split Resonance Line in Spectrum of Scratched Ball Bearing



**Figure 7. Fast, Accurate Detection of Flaws in Ball Bearings**

The resonant ultrasound technique is accurate enough to detect tiny flaws in high-precision objects. The figure compares two resonance lines, one from a perfect silicon nitride ball bearing and the other from a similar ball bearing with a tiny surface scratch. The flaw causes the single line to split into two lines separated in frequency by 824 parts per million. The resonant ultrasound measurement can detect errors in sphericity as small as 0.005 microns in seconds, whereas commonly used optical inspections typically require one hour. The resonant ultrasound spectrometer is now being readied to test these newly developed ceramic ball bearings, which can withstand very high temperatures and acidic environments and are compatible with dry lubricants. A resonant ultrasound spectrometer specifically designed to test ball bearings is now available from Quatro Corporation as a result of a collaborative technology-transfer effort between that company and Los Alamos National Laboratory (see Figure 8).

with a few brittle samples we attempted to study, we were able to conclude that the samples were not the perfect cube-like chunks that the microscope revealed but were, in fact, cracked. The cracks altered the resonance spectrum, and therefore, the data could not be fit to any object shaped like the sample. From this simple effect, discovered accidentally during our research on single-crystal samples, we developed new nondestructive testing approaches that subsequently received a 1991 RD100 award and a 1993 Federal Laboratory Consortium Award for Excellence in Technology Transfer. In particular, together with Raymond D. Dixon and

others we have shown how certain anomalies in the resonance spectrum can be used to detect cracks and other flaws in small, precision objects including aluminum plates, ball bearings, high-strength permanent magnets for lightweight motors, and more.

One test for cracks involves identifying the presence of second harmonics in the resonance spectrum under dry conditions and the absence of those second harmonics under wet conditions. We, together with George W. Rhodes, discovered that a crack produces second harmonics when dry but not when filled with fluid because the fluid prevents the crack from banging



**Figure 8. Resonant Ultrasound Spectrometers on the Market**

The photograph shows a commercial resonant ultrasound spectrometer complete with computer, receiver, transducers, and sample. This system, produced by Quatro Corporation, is designed to perform nondestructive testing of ball bearings and other small objects. After having devised applications of resonant ultrasound technology to the detection of flaws in precision objects, we sought through a public advertisement a commercial company that could develop the technology for a wide variety of applications. Quatro came to us in 1991 and in 1992 obtained a license to develop, manufacture, and market systems for nondestructive testing based on our resonant ultrasound measurement techniques and computer software. The systems under development by Quatro will perform nondestructive inspections of metal, ceramic, composite, and rigid plastic parts in a high-volume manufacturing environment. Quatro is presently working with numerous clients to design custom-engineered systems that meet the particular needs of each application. The Quatro system for testing ball bearings is being adapted to handle thousands of ball bearings per hour and is sensitive to geometry errors as small as 2 parts per million. Another system tests the integrity of oxygen sensors. The commercial production of research electronics, hardware, and software by Quatro has, in turn, assisted us in expanding research efforts and government applications of resonant ultrasound spectroscopy.

shut when mechanically excited on resonance. Ceramic ( $\text{Si}_3\text{N}_4$ ) ball bearings, which can withstand very high temperatures, are being developed for use in naval and military aircraft operations. Accurate resonance measurements of these precision objects can reveal tiny internal and surface flaws. As shown

in Figure 7, these flaws shift and break the symmetry of the resonances of the ball bearings. As a result, 0.005-micron errors in sphericity of a ball bearing can be detected in seconds, instead of the hour needed with present optical studies. These nondestructive testing techniques, fathered by basic research

in materials science at the Laboratory, have been transferred to private industry (Figure 8). Thus new jobs are now being created in Albuquerque as a direct result of the technology we developed here. ■

### Further Reading

William M. Visscher, Albert Migliori, Thomas M. Bell, and Robert A. Reinert. 1991. On the normal modes of free vibration of inhomogeneous and anisotropic elastic objects. *Journal of the Acoustical Society of America* 90: 2154.

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**Albert Migliori** (left) received his B.S. in physics from Carnegie-Mellon University and his M.S. and Ph.D. in physics from the University of Illinois. He came to Los Alamos as a Laboratory Postdoctoral Fellow, remained as a National Science Foundation Postdoctoral Fellow, and then accepted his current position as a Staff Member in the Condensed Matter and Thermal Physics Group. He was honored by the Laboratory in 1989 with a Distinguished Performance Award. He has authored numerous publications and been awarded fourteen patents.

**Zachery Fisk** was educated at Harvard University and the University of California, Dan Diego. He received his Ph.D. in physics at the latter in 1969. A postdoctoral year at Imperial College, London, was followed by a year as Assistant Professor of Physics at the University of Chicago. He returned to UCSD, becoming Research Physicist and Adjunct Professor of Physics before joining the Laboratory in 1981 as a staff member in the Physical Metallurgy Group of what is now the Materials Science and Technology Division. His research interests include the low-temperature electrical and magnetic properties of metals and the growth of single crystals of these materials. Fisk is a Laboratory Fellow.